

International Winter School

Molecules @ Surfaces

Surfaces: structure, electronic states, defects

Molecules @ surfaces: foundations

Molecules & Surfaces at work

Molecules @ surfaces and quality of life

RESEARCH SUMMARIES AND POSTERS

Book of Abstracts - Section 2

Edited by

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Department of Chemistry
University of Torino

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Welcome to the "Molecules @ Surfaces" winter school!

Surfaces define the boundary of all kind of objects, made of both soft and hard matter, from the macro- to the nanoscale. Their "talking" with molecules from the surrounding environment often rules relevant functional properties. These functions are as diverse as in the case of devices for air and water purification, heterogeneous catalysts for the sustainable production of energy and chemicals, implanted biomaterials or injected nanocarriers of signals and drugs, or the origin of biomolecules in space. On such a basis, the importance of surfaces and of their interaction with molecules has been recognized since a long time as a central topic in many fields of chemistry and material science. The actual possibility to achieve new breakthroughs in many fields strategic to mankind, like food&water, health or sustainable growth, is based on advances in our knowledge and engineering of surface-molecule physical and chemical interactions.

This is the field targeted by the "Molecules@Surfaces" school, the 2016 winter edition of the series of courses organized by the Physical Chemistry Division of the Italian Society of Chemistry, this time featured also with an international character, including the auspices of the Physical Chemistry Division of the European Association for Chemical and Molecular Sciences (EuCheMS). The school will take place from January 31 to February 5 in Bardonecchia, near Torino (North-West Italy), one of the ski resorts of the 2006 Winter Olympic Games.

"Molecules@Surfaces" offers to PhD students and Post-Docs updated "tools" for acting as relevant scientific players in surface-related materials science and technology. Participants will be actively involved in lectures given by established experts, covering a comprehensive path from fundamental aspects to cutting-edge applications, based on both experimental and modeling approaches (with lab activities). Details can be found in the "Topics" section. The program includes the presence of industrial researchers, the possibility for participants to present their on-going research activities (also in an ISBN coded Abstract Book), an overview of relevant H2020 and complementary EC research funding actions, ...and specific sessions on the surfaces of the Bardonecchia ski-slopes!

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GRAPHICAL ABSTRACTS

and

POSTER ABSTRACTS

The following section collects for each student a short description of his/her research interests and the abstract of their posters presented at the School.

Poster sessions:

SESSION 1 – Monday Feb. 1, 20:30-22:30
SESSION 2 – Tuesday Feb. 2, 20:30-22:30
SESSION 3 – Wednesday Feb. 3, 20:30-22:30

GA-1

APPLICATION OF ATOMIC FORCE MICROSCOPY TO NANOBIOLOGY

Abimbola Feyisara Adedeji

Supervisor: Prof. Giacinto Scoles, Tutor: Dr. Matteo Castronovo

Affiliation: University of Trieste & University of Udine

Project Summary

Nanobiology is a research area that involves novel physical approaches to accurately address challenges in biology, including quantitatively characterizing complex biochemical reaction within the highly compartmentalized, living cell. In our approach we exploit the ability of biomolecules to self-assemble over solid support, which serve as reaction environment where DNA-protein interactions and protein-peptide interactions (PPI) are structurally and label-free investigated by atomic force microscopy (AFM). Hitherto, we have been able to study quantitatively the effect of crowding and confinement on the reactivity of DNA and DNA-restriction enzyme recognition. Presently, we are focusing on the AFM-based quantitative approach for characterising the binding affinity of several, computationally designed decapeptides for protein recognition. Our studies will enable novel biosensing applications, such as biomarkers detection with multiplex, surface-based nanodevices.

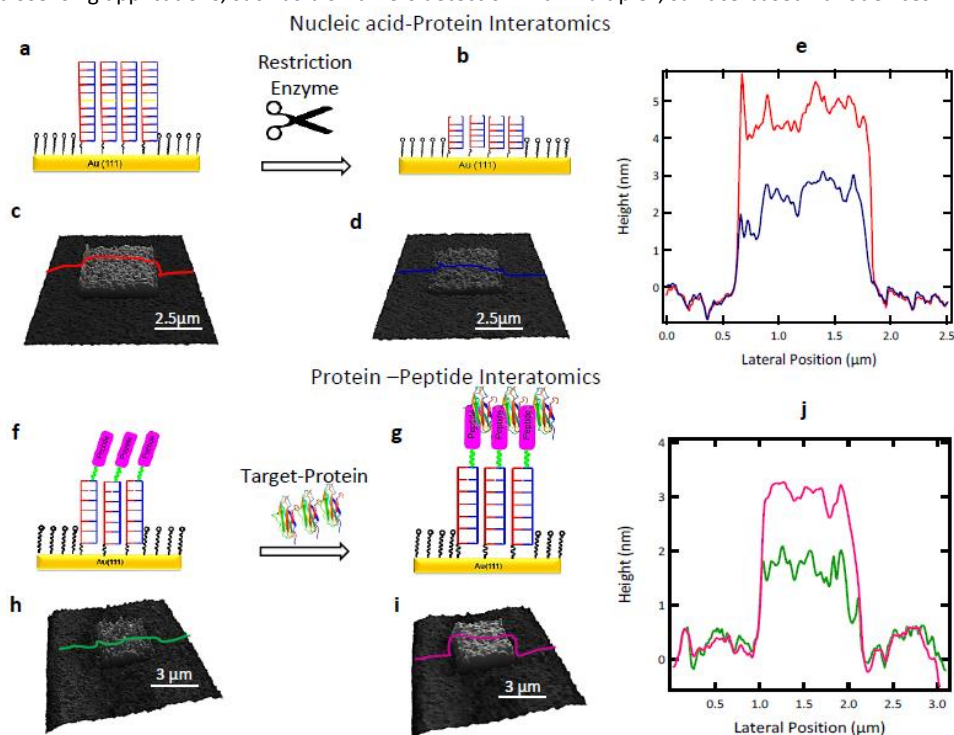


Fig 1: **(a)** Depicts the result of a tip-induced self-assembly process (nanografting) of short dsDNA molecules (with inherent restriction site at the middle) within bio-inert alkanethiol passivated ultra-flat gold surface. **(b)** Depicts the product of dsDNA after a restriction enzymatic reaction (RER). **(c)** AFM micrograph of a DNA assemblage before RER. **(d)** AFM micrograph of the same DNA assemblage after RER. **(e)** AFM height profiles, showing decrease in height of the DNA assemblage after RER. **(f)** Depicts the result of nanografting of peptide-DNA conjugates within a bio-inert alkanethiol passivated Au(111). **(g)** Depicts the peptide-protein complex upon protein recognition. **(h)** AFM micrograph of peptide-DNA assemblage before PPI. **(i)** AFM micrograph of the same peptide-DNA conjugates assemblage after PPI. **(j)** AFM height profiles that shows an increase in assemblage height demonstrating successful PPI.

P-1

DIGITAL BEHAVIOURS OF ENDONUCLEASE RECOGNITION IN HIGHLY DENSE DNA NANOREACTORS

Abimbola Adedeji^{a,b,§}, Dianne Choi^{c,§}, Vincent Inverso^{d,§}, Shiv K. Redhu^d, Marco Vidonis^{b,e}, Luca Crevatin^f, Allen W. Nicholson^{c,d}, Giacinto Scoles^{a,b,c}, Matteo Castronovo^{a,b,c}

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ABSTRACT

The inherent capacity of nucleic acids to self-assemble with Watson-Crick base pairing into programmable nanostructures allows their application as promising biomaterials in different research areas. DNA nanotechnology for example has spurred the development of a molecular approach to information technology termed DNA computing, which has however led to implications for synthetic biology and nanomedicine. In our work, we focus on DNA nanotechnology applied to the study of nucleic acid-protein interactions within highly dense and crowded nanosystems. Our goal is to elucidate the biomolecular reactions in conditions that are more similar to the cell interior in terms of macromolecular crowding and compartmentalization, which cannot be accurately reproduced in solution due to solubilisation limits of crowding agents [1].

In our work, we study the behaviour of protein-nucleic acid interactions in opportunely designed, self-assembled nucleic acid-based nanostructures that serve as nanoreactors. In this poster, I will present the results of our study on the BamHI restriction enzyme reactions in nanoreactors consisting of self-assembled monolayers (SAMs) of short, double stranded (ds) DNA molecules of varying DNA density that are confined laterally by the presence of adjacent and biologically inert, ethylene glycol-terminated alkythiol SAMs over ultra-flat gold surfaces. We generate such SAM-based nanoreactors (SAM-NR) by means of an atomic force microscopy (AFM)-based nanolithography technique termed nanografting [2,3]. Due to self-assembly inhomogeneity, the DNA density in each SAM-NR varies on the surface, and typically a SAM-NR is comprised of several different domains. We designed three distinct, 44-bp-long DNA molecules with recognition sites located in the middle. One is provided with the correct BamHI restriction site that ensures specificity for the enzyme (5'-GGATCC-3', termed **DNA-1**), while the other two are provided with sequences that only partially match such restriction site (i.e. 5'-AGATCA-3' and 5'-CGATCA-3', termed **DNA-2** and **DNA-3** respectively).

With such tools we studied BamHI action as a function of DNA density and sequence by measuring the height of the DNA monolayer before and after their reaction with BamHI in standard catalytic conditions. Height measurements are carried out using side-by-side AFM topographic profiling, followed by correlation analysis of the individual height profiles to detect the enzyme behaviour in all the different density domains of each SAM-NR. In fact, the height of a DNA monolayer is directly related to the inherent DNA density or, at any fixed density, to the length the inherent DNA molecules [2,3].

Our results show that DNA density is a crucial determinant for the action of BamHI. As confirmed by previous published results from our group [2,3], BamHI cleaves the canonical site (DNA-1) in SAM-NR with height lower than 14 nm. This height value corresponds to a critical DNA density, above which the dsDNA accessibility is negligible due to steric hindrance. In addition, we observed three distinct and unprecedented behaviours for DNA-2 and DNA-3. For each DNA, we demonstrated three distinct regimes. At very low densities, BamHI cleaves none of the two. This is in agreement with its known high specificity for the canonical site (DNA-1) in dilute systems. For SAM-NR with thickness profiles higher than 6 nm, BamHI unexpectedly digests both non-canonical sites (DNA-2 and DNA-3). In such SAM-NR, however, the reaction reaches completion only within the lower-density domains. Finally, the enzymatic

reaction is fully inhibited for SAM-NR with thicknesses higher than 12 nm for DNA-2, and 14 nm for DNA-3.

Our interpretation is that the restriction enzyme is physically trapped within SAM-NR with thicknesses higher than 6 nm, as substantiated by previous published work of our group [3]. Thus, the enzyme diffuses two-dimensionally in the SAM-NR and the non-canonical reactivity of DNA-2 and DNA-3 is likely an effect of nano-crowding. Previous studies of crowding on biochemical reactions suggest that the DNA molecular density is 1) directly related to enzyme and DNA activities, and 2) inversely related to enzyme mobility within the highly dense DNA phase (diffusion-limited regime) [1]. I.e. high activities and affinities favour the successful reaction, whereas low diffusivity inhibits the enzyme-DNA collisions and thus complex formation. Our results therefore, show that under nanoscale confinement the strength of the enzyme-DNA binding (that varies with the different restriction sites) strongly contributes to balance of such factors, and underlies novel enzyme behaviours that are not observable in solution.

In conclusion, the use of nanoreactors allows studying unprecedented modes of protein-DNA recognition. Our results open the door to the possibility of using DNA self-assemblages as nanofluidic devices for understanding biomolecular interactions in complex systems.

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- [2] M. Castronovo et al., *Nature Communication*, 2011, 2, 1-10
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Notes

GA-2

CYCLODEXTRINS NANOSPONGES AS PRECURSOR FOR POROUS CARBON MATERIALS

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Summary

Porous carbon materials have received a great attention due to their many applications. Porous carbon has been synthesized using various methods. In this way, thermal degradation of polysaccharides has been studied. In particular, the thermal degradation of nanosponge derived from β -cyclodextrins in an inert atmosphere has been investigated. It is found that in an inert atmosphere it could leave a residue (char). This char is quite thermally stable. The object of my ph.D work is hence to provide a carbon material having specific physical features such as narrow pore size and high and constant specific surface area.

In this ph.D the production of carbon materials will proceed via direct pyrolysis of different types of nanospunges.

The evaluation of gases adsorption and the properties of the surface will be carried out through a microcalorimeter.

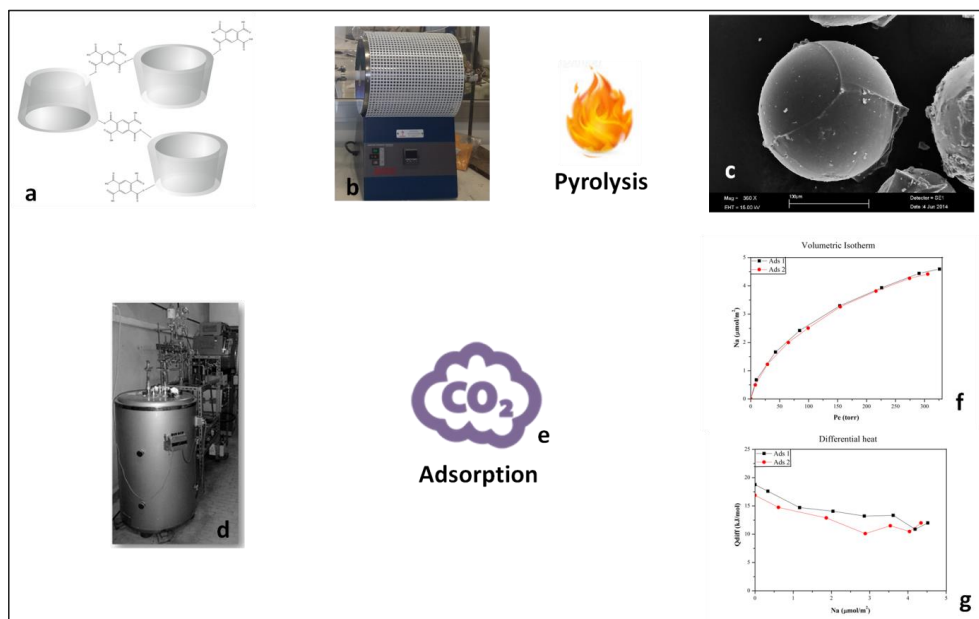


Figure 1. a) Images of a nanosponge derived from β -cyclodextrins cross-linked with pyromellitic dianhydride. b) Tubular furnace for the pyrolysis of nanospunges c) Sem imagine of the carbon obtained after the pyrolysis process d) Microcalorimeter e) Study of CO_2 adsorption f) Volumetric Isotherms obtained for CO_2 adsorption on carbon g) Differential heat of adsorption obtained for CO_2 adsorption on carbon.

P-2

CYCLODEXTRINS NANOSPONGES AS PRECURSOR FOR POROUS CARBON MATERIALS

A. Anceschi^a, M. Zanetti^a, G. Magnacca^a, A. Tiseo^b, G. Rosi^b, F. Caldera^a, F. Trotta^a.

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ABSTRACT

Porous carbon materials are promising products in the fields of catalysis and energy as they can behave as supercapacitors. They are also used in the adsorption and storage of carbon dioxide and in the removal of pollutants such as arsenic from water. Such porous materials are generally produced by pyrolysis of biomasses [1].

Recently the synthesis of porous carbon using cyclodextrins in form of nanospunges was investigated [2]. The nanosponge was prepared crosslinking β -cyclodextrin with pyromellitic dianhydride.

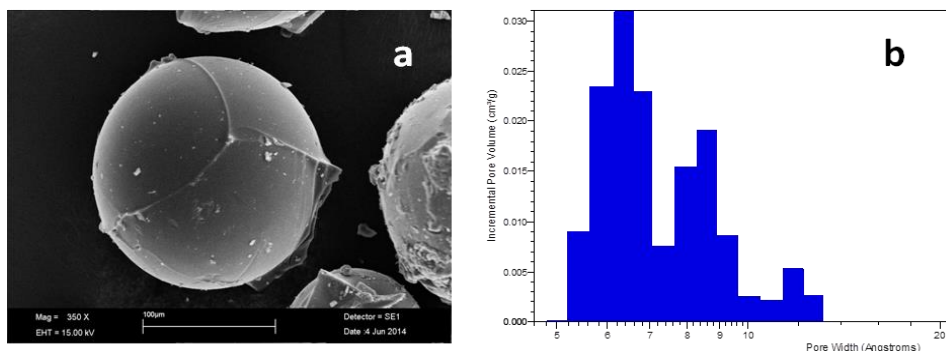


Figure 1: a) SEM picture of the carbon particle obtained by nanosponge pyrolysis; b) DFT pore size distribution plot obtained by N₂ gas-volumetric adsorption at 77K.[3]

Figure 1a reports a SEM image of the material obtained heating the nanosponge under nitrogen flow in a tubular furnace. The carbon obtained was mainly composed of spherical particles. Using a semiautomatic instrument (ASAP 2020 by Micromeritics) the specific surface area and the pore size of the material were determined. The N₂ adsorption isotherm obtained was of type 1 (IUPAC classification) typical of microporous materials, so Langmuir model was used for determining the specific surface area of the samples. Pore volume and pore size distribution was determined applying DFT method. The surface area was about 560 m²/g and the pore size distribution was in the range 5-16 Å, as shown in figure 1b, confirming that material is microporous.

The material was tested in the adsorption of gases through an adsorption microcalorimeter (Tian-Calvet type by Setaram) allowing to assess adsorbed amounts and heats of adsorption. Different gases were used, such as CO₂, CO, N₂ and O₂ keeping the sample at 30°C after a preliminary outgassing in vacuo at 30°C. Surprisingly, the carbon produced from cyclodextrin nanosponge was able to adsorb only CO₂. Figure 2a reports the relative gas-volumetric isotherms obtained. The adsorption experiment was repeated twice in order to evaluate the presence of irreversible adsorption, namely CO₂ not removed after an overnight outgassing at 30°C, evidenced by a difference between the first and the second adsorption runs. In this case, the first isotherm and the second one were overlapped, hence the adsorption of CO₂ seems completely reversible.

Figure 2b reports the adsorption heat vs. CO₂ coverage. This plot allows to determinate the site energy distribution. The initial heat value q_0 , corresponding to the highest energy of interaction of CO₂ with the surface, was evaluated by extrapolating the heat vs. coverage plot at zero coverage. A slight difference is

observed, since 19 kJ/mol is obtained for the primary adsorption run whereas 16 kJ/mol is for the secondary run. The secondary curve remains always lower than the first one but in both cases the interaction energy at high coverage is around 12 kJ/mol. Summarizing, a very limited surface heterogeneity was evidenced by CO₂ adsorption.

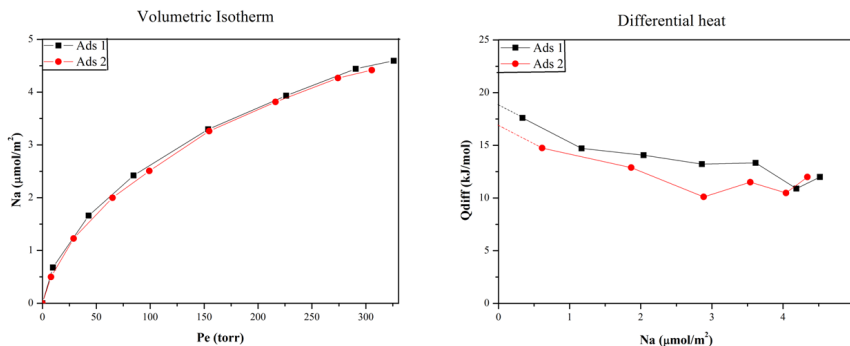


Figure 2: a) Volumetric Isotherm obtained by CO₂ adsorption; b) Qdiff vs Na plot for CO₂

In order to understand the nature of carbon-CO₂ interaction, H₂O adsorption was studied. The results obtained are shown in figure 3.

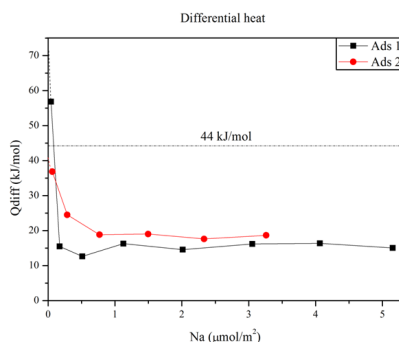


Figure 3: Adsorption of water on carbon obtained by nanospunges

The differential heat of adsorption measured can be compared with the latent heat of liquefaction of water (44 kJ/mol) to identify polar (heat higher than 44 kJ/mol) or apolar (heat lower than 44 kJ/mol) surfaces. In this case, the surface is almost apolar (except for a very limited amount of defective sites evidenced by the q° value obtained in the first adsorption run). This suggests that the interaction with CO₂ is not due to affinity (polar molecule with a polar surface) but the lack of interaction with other molecules (CO, N₂ and O₂) allows to exclude that the adsorption is merely due to physical interactions with material pores. Other studies will be carried out to clarify this point.

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Notes

GA-3

MOFS FOR FUNCTIONAL APPLICATIONS

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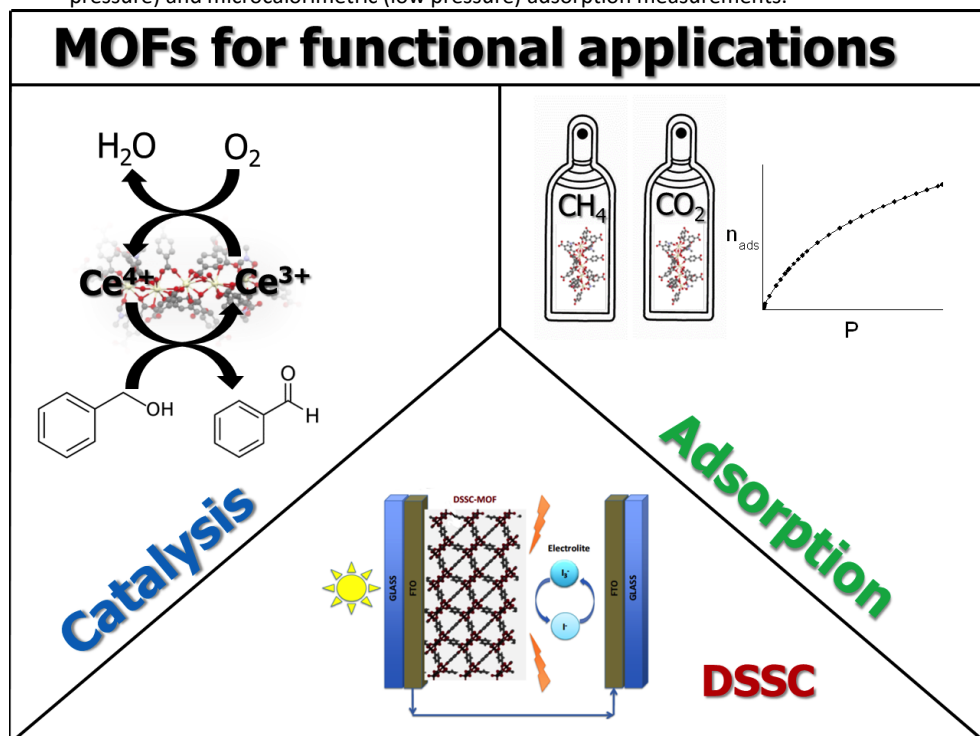
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Summary

My PhD project can be divided mainly in three parts: 1) Synthesis and characterization of innovative MOFs engineered for CO₂, CH₄ and other light gases capture and storage, and for catalysis in fine chemistry applications; 2) Design of MOFs to be used as light harvesters in innovative DSSCs (Dye-sensitized solar cells); 3) Advanced characterization of continuous-synthesized MOFs from industrial international partners by means of high-pressure volumetric adsorption.

Main skills that will be developed during my PhD activity are related to:

- Advanced synthesis procedures (i.e. air-free techniques) that I will try to learn during a three months stay in Prof. Stock group in Kiel (Germany).
- High competence in all the characterization techniques mainly involving spectroscopies (FTIR, Raman, XAS, UV-Vis) both *in situ* and *in operando* conditions, PXRD, volumetric (low and high pressure) and microcalorimetric (low pressure) adsorption measurements.



P-3

Ce³⁺/Ce⁴⁺-BASED MOFS: FROM SYNTHESIS TO CO₂ CAPTURE AND REDOX APPLICATIONS.

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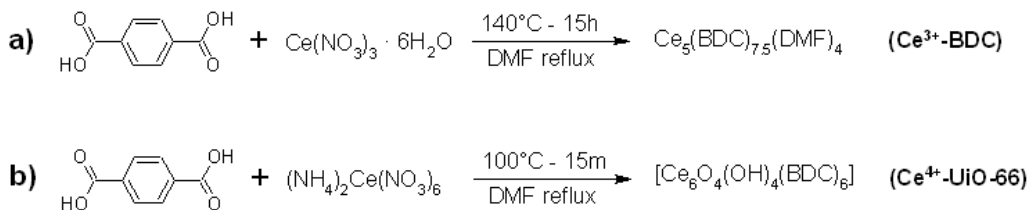
ABSTRACT**Introduction:**

MOFs^[1] (Metal-Organic Frameworks) are porous crystalline materials built from organic linkers and inorganic metal (or metal-containing clusters) nodes. Being partly organic and partly inorganic they are also called hybrid solids. Traditional porous materials, zeolites and activated carbons, are widely used in many industrial processes especially in the petrochemical field, which reflect the importance of such materials in our economy. Being MOFs candidates for similar applications they have an unmatched tunability and design freedom made possible by the huge number of organic and inorganic units that can be used, also exploiting the power of organic chemical synthesis. For this reason MOFs are being regarded as advanced porous materials capable to surpass the performances of the currently used materials and technologies. These materials can be exploited in many industrial processes like heterogeneous catalysis and gas adsorption and capture, i.e. CO₂ capture and sequestration^[2] (where they reveal very high performances for carbon dioxide uptake capacities and separation selectivities) and redox catalysis^[3] (where electron transfer from metal centers can be exploited).

In this work a synthesis of a very recently prepared^[4] Ce³⁺-based MOF made from terephthalic acid ligand (H₂BDC) and Ce³⁺ cations is reported by a solvothermal method together with a preliminary characterization (by means of PXRD, TGA, SEM, FTIR, Raman, XAS), followed by a surface area (by means of N₂ adsorption at 77K), active sites (by means of in-situ FTIR CO adsorption) and a volumetric and calorimetric CO₂ adsorption characterization. More recently, also a Ce⁴⁺-based MOF has been synthesized in a similar manner^[3], obtaining a material isostructural with the UiO-66^[5] MOF; the characterization of this material is still going on.

Results and discussion

Both materials have been prepared by means of a solvothermal technique, where the organic ligand (H₂BDC) and a metal precursor are added to the solvent (DMF) and upon mild heating the product precipitates out.



Scheme 1) – Synthesis reactions and conditions for a) Ce³⁺-BDC MOF, b) Ce⁴⁺-UiO-66.

(Ce³⁺-BDC) The solvothermal synthesis gives rise to a MOF with high purity and acceptable yield (about 85%). The crystal structure is very complex, with five Ce atoms different by symmetry in the unit cell, and shows 2D channels filled with DMF^[4].

(Ce⁴⁺-UiO-66) The synthesis gives rise to the material with good yields and purity. The MOF is iso-structural with UiO-66 and shows octahedral Ce₆O₄(OH)₄ clusters surrounded by ligands, resulting in a highly packed fcc structure^[3,5].

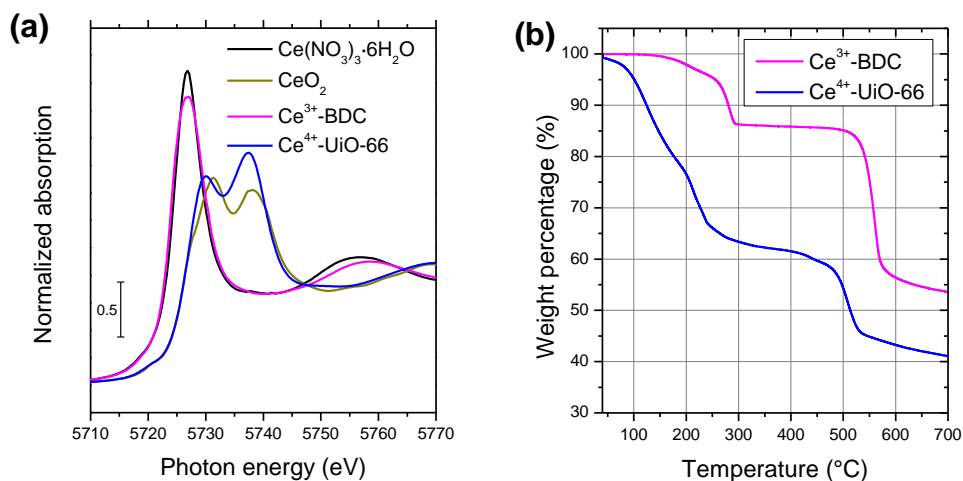


Figure 1) – a) XANES spectra of Ce^{3+} -BDC and Ce^{4+} -UiO-66 with Ce^{3+} and Ce^{4+} standards.
b) Thermogravimetric data for both materials, in N_2 flow.

The oxidation state of the metal cations in the two materials has been confirmed by XANES measurements (see Figure 1a).

Upon thermal activation, Ce^{3+} -BDC (DMF molecules are lost with a rearrangement of the crystal structure, as shown by PXRD) maintains the crystallinity up to 450°C (see figure 1b) and it reveals Ce^{3+} open-metal sites accessible to CO probe at low temperatures (FTIR measurements). Contemporarily Ce^{3+} -BDC shows an increase of the accessible surface area, up to $230 \text{ m}^2/\text{g}$, a value that is quite low for a MOF^[1]. This MOF has been tested for CO_2 capture, giving the results summarized in Table 1. The general low uptake can be explained by the observed low surface area.

Ce^{4+} -UiO-66 showed a lower thermal stability (see Figure 1d) than both Ce^{3+} -BDC and Zr^{4+} -UiO-66^[5]. Nevertheless it revealed to have a promising redox catalyst activity^[3]. This activity is still under progress.

Treatment <i>in vacuo</i>	N_2 adsorption at 77 K		CO_2 uptake at RT (1 atm)	
	$S_{\text{Langmuir}} [\text{m}^2/\text{g}]$	$S_{\text{BET}} [\text{m}^2/\text{g}]$	$[\text{mol}/\text{kg}]$	% by weight
$150^\circ\text{C} - 3\text{h}$	6.0 ± 0.2	3.630 ± 0.087	0.1281	0.52%
$200^\circ\text{C} - 3\text{h}$	16.11 ± 0.24	11.572 ± 0.059	0.2728	1.11%
$250^\circ\text{C} - 3\text{h}$	217.31 ± 0.22	160.4 ± 2.4	0.7954	3.24%
$350^\circ\text{C} - 3\text{h}$	232.9 ± 0.5	176.1 ± 2.8	0.8352	3.40%
$450^\circ\text{C} - 3\text{h}$	231.5 ± 0.37	175.3 ± 2.9	0.8301	3.38%

Table 1) - Summary of N_2 and CO_2 volumetric adsorption results on Ce^{3+} -BDC MOF.

Conclusions

$\text{Ce}^{3+}/\text{Ce}^{4+}$ -terephthalate MOFs have been synthesized, characterized by means of advanced techniques and tested for adsorption and catalysis.

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Notes

GA-4

CO₂ METHANATION OVER LAYERED NiAl-HYDROTALCITE PRECURSOR CATALYSTS

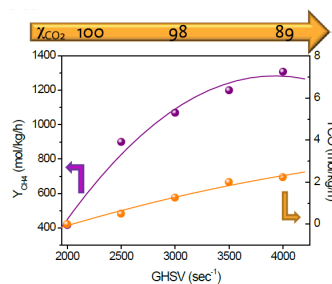
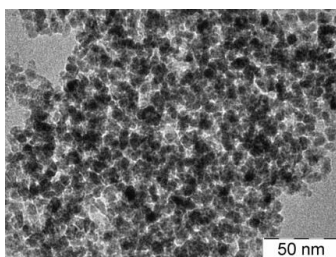
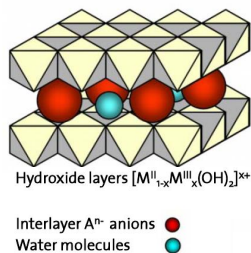
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Summary

Nickel based catalysts are often used for industrial hydrogenation reactions because they are cheap, selective, and less sensitive to sulphur poisoning than other metals. Nevertheless, it is crucial to avoid sintering phenomena and, at the same time, to increase the amount of active metal centers. Methane formation from CO₂ hydrogenation is related to the surface area of metallic Nickel obtained when the catalyst is reduced. The highest surface area of metal and the highest activities are obtained when the nickel is produced as very small crystallites, (<100 Å). A good methanation catalyst is one which is physically strong, reducible at 300°C, and has a high activity, and in order to provide a long life, it must retain these properties during use. Commonly lives of 3-5 years are achieved, depending on the temperature of operation and the presence of poisons in the synthesis gas. Hydrotalcite materials have been demonstrated to be good candidates because they offer the possibility to have higher Ni loading (75 wt%) without compromise metal dispersion, and long life-time performance in reaction of industrial interest, such as methane synthesis from CO₂ and renewable hydrogen, with respect to other catalysts prepared with different methods (i.e. impregnation) over mesoporous supports.



P-4

INFLUENCE OF SITING AND STRENGTH OF CATALYTIC ACTIVE CENTERS IN MICROPOROUS MATERIALS ON HMF ETHERIFICATION REACTION

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ABSTRACT

The activity of acid catalysts in the conversion reaction of biomass derivatives to employable diesel-range products has been widely explored, evidencing how the nature and strength of active sites influence the catalytic performance [1-2]. In case of 5-hydroxymethyl-2-furfural (HMF), the main product in the acid-catalyzed conversion of ligno-cellulosic biowastes, the selectivity in the etherification with ethanol to biodiesel components, i.e. 5-(ethoxymethyl)furan-2-carbaldehyde (EMF), and ethyl-4-oxopentanoate (EOP), is strongly depending on the relative amount of Lewis and Brønsted acid sites (Figure 1).

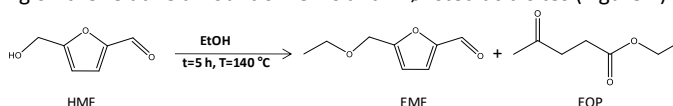


Figure 1. Scheme of HMF etherification reaction

However, a low selectivity due to competition reaction, such as acetalization, dimerization and furan ring fragmentation reactions, is often observed. For this reason the aim of this work is to investigate the role played by the siting, and hence the local environment effect, of the acidic catalytic centers. This aspect results of note not only for the applicative interest of the products as biodiesel additives but also for its fundamental character.

In this study we have probed the surface acidity of three different microporous ordered materials, Beta and ZSM-5 zeolites (Si/Al=12.5), and Silicalite-1 (as Al-free reference), both in ammonium and protonic forms, and related the physical-chemical properties with their catalytic performance in the above cited reaction (Table 1), observing an higher catalytic activity for the NH₄-Beta and NH₄-Sil samples in respect to their protonic counterparts, despite of their well-know metastable condition. Whereas an inverse behavior is observed for NH₄-ZSM-5.

<i>Samples</i>	<i>HMF Conversion%</i>	<i>STY EMF</i> <i>mmol/h/g_{cat}</i>	<i>STY EOP</i> <i>mmol/h/g_{cat}</i>
NH ₄ -Beta	100	3.518	0.438
H-Beta	100	3.110	0.623
NH ₄ -ZSM-5	60	1.291	0.437
H-ZSM-5	100	2.285	0.626
NH ₄ -Sil	55	0.916	0.154
H-Sil	51	0.819	0.129

Table 1. Catalytic activity of all the samples under study

Therefore, an extensive spectroscopic analysis was carried out over NH₄-form zeolites, by use of basic probe molecules having significative different pK_a, i.e. pyridine (pK_a=5.2), D₂O (pK_a=16.6), CH₃CN and d₃-CN (pK_a=25), evidencing how the superior performance in HMF etherification could be related to the different strength and nature of NH₄ bonds to the acidic Brønsted sites present on the surface of zeolite. Figure 2 shows the comparison of probe molecules interaction over NH₄-Beta zeolite as example.

In the weak acidic hydroxyl group range (3800–2800 cm⁻¹) the interaction with base (full line) vapor

pressure, results always in a strong reduction in all hydroxyl bands, but further desorption at room temperature and 150 °C (dotted and dashed lines, respectively), some irreversible interactions can be observed in case of pyridine and D₂O dosages, but not for acetonitriles. In parallel, in the region between 1800-1350 cm⁻¹, it is possible to observe some significant changes in the NH₄⁺ bending frequencies. Starting from the pure zeolite, five IR- modes fall in two distinct ranges: 1700-1600 cm⁻¹, and 1550-1350 cm⁻¹, with the first being associated to a tridentate- and bidentate- NH₄⁺ coordination to OH groups of zeolite, respectively [3]. Upon interaction with bases, the relative intensities undergo to a significant change. Different behaviors were observed for NH₄-MFI (not shown here), which present a higher mobility of ammonium ion even in presence of weaker base molecules.

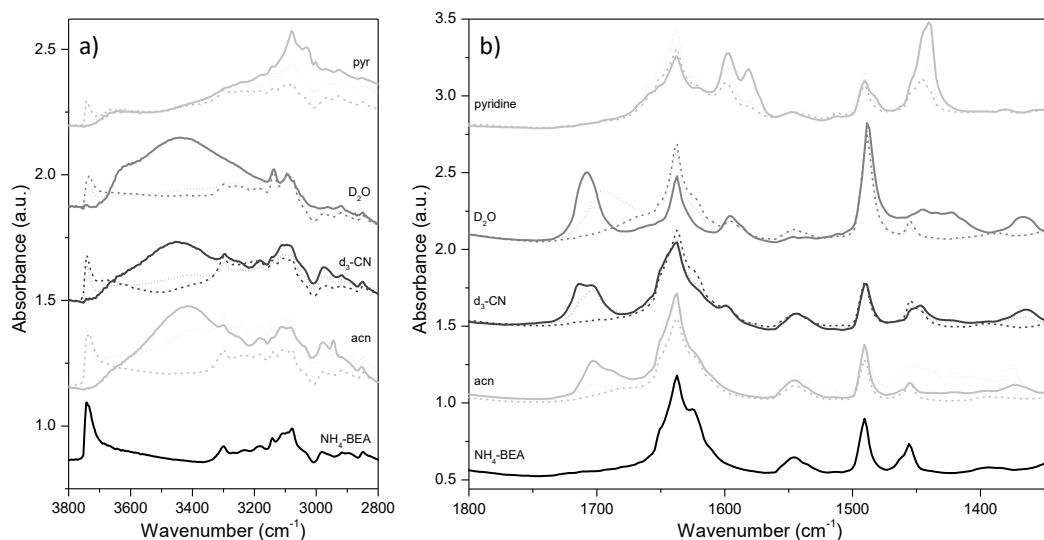


Figure 2. FT-IR spectra of NH₄-Beta after interaction with different basic probe molecules. a) hydroxyl region, b) irreversible portion of different bases interacting with the zeolite in the region of NH₄⁺ bending frequencies.

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Notes

GA-5

SMART MATERIALS FOR ON DEMAND DRUG DELIVERY

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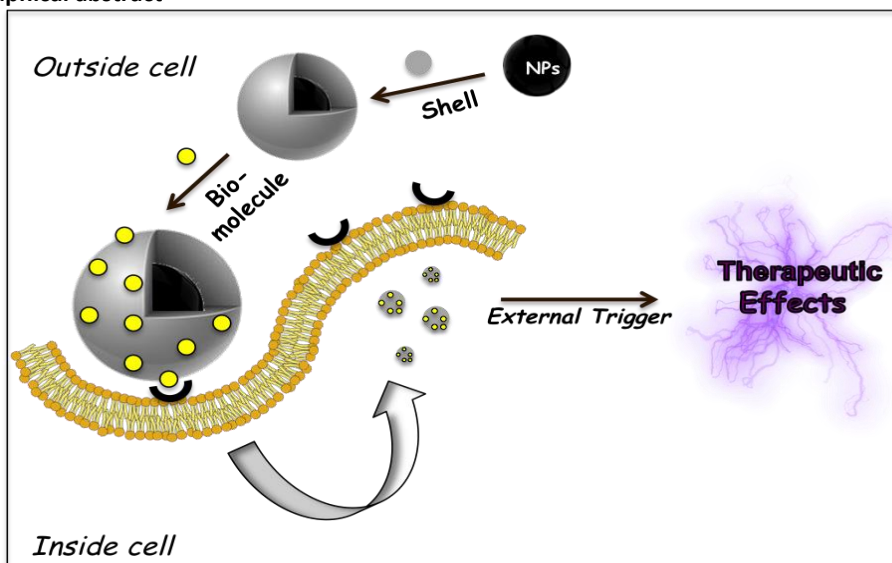
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Summary

The PhD project is focused on the realization of both nano-scaled and 3D systems for the delivery of active biomolecules. The possibility to obtain systems able to vehicular and to release active ingredients or drugs on demand represents a very fascinating goal in biomedical field. Nanomaterials, including in the size range of the 100 nm, are very suitable for the drug delivery. One of the main aims of this research project is to point out simple protocols to synthesize metallic nanoparticles (NPs), such as iron oxide NPs, and to grow different kind of surface shell. The shell (typically correspondent to an inorganic capping) can be exploited to stabilize the metallic core as well as to confer particular superficial feature, as the capability to bind molecules of interest. For instance, the conjugation of targeting moieties can enhance receptor-mediated delivery mechanism. Drug targeting can enable the delivery of chemotherapeutics selectively into cancer cells, reducing systemic side effects. In parallel, the PhD project envisages the fabrication of "smart" biocompatible 3D matrices for drug delivery and tissue engineering applications. The idea is to create hybrid materials, composed by biopolymer, such as collagen, and nanoparticles, such as iron oxide nanoparticles, to confer to the system a sensitivity to an external trigger, the application of an external magnetic field. If a compound is loaded in a "smart" matrix, its release could be controlled on demand. It is a very intriguing scenario, since many treatments and therapies need a precise space and time controlled release.

Graphical abstract



P-5

FOLIC ACID CONJUGATED HYPERTHERMIC IRON OXIDE NANOPARTICLES FOR CANCER TREATMENT

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ABSTRACT

The possibility to specifically target a drug into a diseased cell is a paramount goal to avoid involvement of healthy tissues in therapies. In particular, most of the cancer therapies are not selective and very invasive. A wide range of nanomaterials of dimensions smaller than 100 nm is used in bio-medical applications.^[1] One of the crucial advantages of such class of compounds resides in the possibility to manage and to change the physical and chemical properties by means of constructed and targeted surface functionalization. Paramagnetic nanoparticles were employed as diagnostic tool as well as therapeutic compounds. More in particular, in the hyperthermia therapy superparamagnetic crystal suspensions can absorb the energy of an oscillating magnetic field and convert it into heat.^[2] High temperature can kill cancer cells because if the temperature increases above 42°C the cellular death is induced; on the contrary healthy cells appear more robust than the tumor ones.^[3] Besides this, a very specific approach is proposed: super paramagnetic iron oxide nanoparticles (IONPs) have been synthesized and their hyperthermal properties have been evaluated.

The NPs were synthesized by means of a co-precipitation method and then were capped by a SiO₂ shell by an easy and fast sol-gel method.^[4] In order to improve the specificity of nanoparticles targeted into diseased cells, paramagnetic iron oxide nanostructures were further functionalized by folic acid (FA). Nanoparticles functionalized by folic acid terminations can interact with the folate receptors (FR) on the membranes cells. FRs are overexpressed in many kind of human cancer cells.^[5] The adduct iron oxide nanoparticles_silica shell_folate functionalization (IO@SiO₂@FA) was characterized by means of UV-Vis and FTIR spectroscopy. The supramolecular adduct formation presumably induces a rearrangement of the whole FA molecule. In particular, C=O band of folate is very affected by the interaction with IO@SiO₂ nanoparticles. It suggests that carboxyl groups of glutamic acid, of the FA molecule, behave as binding sites, allowing the IO@SiO₂@FA generation. XRD and SAED experiments disclose the magnetite crystal structure of the iron oxide core. Size and morphology of the nanoparticles and nanoadducts were revealed by TEM analysis. The naked IO nanoparticles were characterized by almost spherical particles with an average diameter ranging from 5–10 nm (Figure 1a). The IO@SiO₂ nanoparticles became larger than the pure Fe₃O₄ because of the surface coating (Figure 1b). The silica surface reduced the agglomeration phenomena of the nanoparticles inducing also a stabilization of the colloidal suspension. Instead, the conjugated FA in the IO@SiO₂@FA adducts appears as smaller aggregates on the silica surface as well as embedded in this matrix (Figure 1c). The presence of the folate functionalization does not increase nanoparticles diameter, if compared with the IO@SiO₂, and preserves the stabilizing effect of the inorganic coating. When a colloidal suspension of IO@SiO₂@FA is exposed to an oscillating magnetic field of 18 mT (operating frequency 100 kHz), an abrupt increase of the temperature is recorded, reaching an asymptotic value of about 42°C. It can be supposed that such nanoadducts can be internalized in cancer cells and exposed to a non-invasive magnetic field. The IO@SiO₂@FA uptake in cancer cells has been monitored by ellipsometry and by optical microscopy. Such nanoadducts have been demonstrated to be not cytotoxic even after 72 hours treatment. More in particular, ellipsometric analysis evidences the behavior of FR as accumulating point for micrometric aggregates of the hyperthermic nanoadducts across the cell membrane, permitting the internalization via potocytosis, a

caveolin-coated endocytosis pathway. This internalization is not verified when a fibroblast cells line, 3T3 cells, known to not overexpress the FRs, was uploaded with FA functionalized nanoadduct.

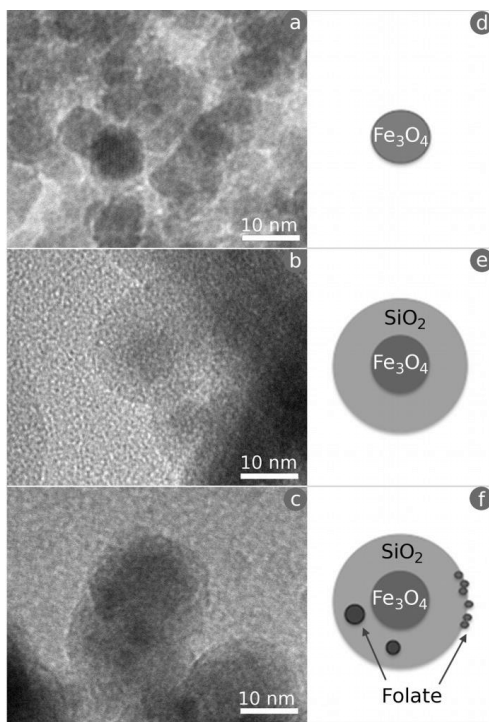


Figure 1. TEM micrographs of a) IO NPs, b) IO@SiO₂, c) IO@SiO₂@FA and schematization of the surface morphology of d) IO NPs, e) IO@SiO₂, f) IO@SiO₂@FA

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Notes

GA-6

HETEROGENEOUS CATALYSTS AND MATERIALS FOR HYDROGEN PRODUCTION

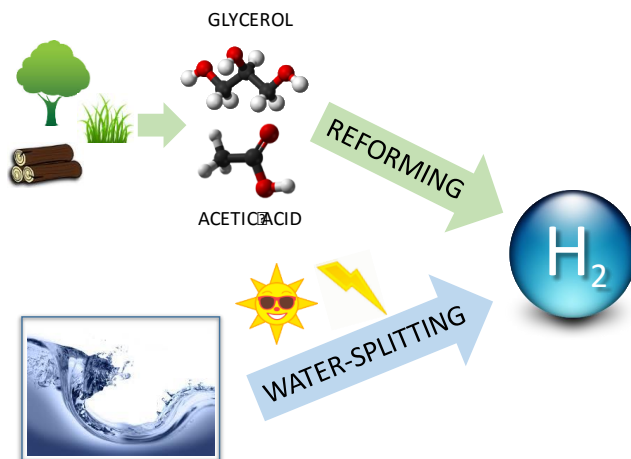
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Summary

The research project of the PhD is inserted in the broad world of renewable raw materials, like biomass and water, and sustainable production of hydrogen, which is considered to be one of the possible future energy vectors. In particular, the work is focused on the preparation, characterization and testing of heterogeneous catalysts and materials for hydrogen production via steam and aqueous phase reforming of light oxygenates, such as acetic acid and glycerol, and photo-electrochemical water splitting. As far as the first two reactions, the research is devoted on the preparation and characterization of mono- and bimetallic based catalysts, coupling noble metals (Ru and Pt) with cheaper metals (Ni and Mn), via colloidal synthesis or more classical impregnation techniques. A novel plasma-enhanced chemical vapor deposition technique is under development for the preparation of nanostructured hematite ($\alpha\text{-Fe}_2\text{O}_3$) and Si-doped hematite photo-electrodes for water-splitting under simulated sunlight. A third part included the FT-IR characterization with pyridine as probe molecule of modified niobium phosphate catalysts used in the direct conversion of cellobiose in 5-(hydroxymethyl)furfural, with particular focus on the investigation of the lively acidic properties of this material in presence of water.



P-6

INVESTIGATION OF THE PROMOTING EFFECT OF MN IN THE STEAM AND AQUEOUS REFORMING OF GLYCEROL OVER Pt/C CATALYST.

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ABSTRACT

New and sustainable energy vectors, as well as production of fuels from biomass, are considered to be among the main energy-related issues of this century [1]. In this scenario, hydrogen plays an important role as one of the most promising energy vectors, coupling high efficiency and low greenhouse gas emission [2]. Nowadays, hydrogen is mainly produced by reforming of fossil fuels [1], thus making of primary importance the development of new and environmentally friendly processes wherein only biomass-derived raw materials are used. Steam reforming of light oxygenates, in particular short-chain alcohols and simple hydrocarbons, is an interesting route since combines a well-known industrial process with sustainable feedstock. Among many others, as a byproduct of the emerging biodiesel industry, glycerol is one of the most important organic compounds, and its use as feedstock has been widely reviewed [3,4]. However, cheap and active catalysts, both in terms of stability and hydrogen production, are currently lacking.

One of the most studied transition metals active in reforming reaction is platinum, because of its high C–C bond cleavage activity and stability against coking. However, its high cost, as well as for any other noble metal, is one of the main reasons why the modern scientific effort is focused on the development of bimetallic catalysts, wherein the noble metal is generally paired with a non-noble metal [5,6]. One of the most famous example of promoter for Pt-based catalysts in real industrial applications is Re, which provides CO spillover center when oxidized by water (*i. e.* ReO_x), boosting the catalytic activity [7]. As mentioned before, since Re is noble metal, a proper substitute must be found.

Manganese is a cheap transition metal with very interesting properties that has already been reported to enhance the catalytic activity of a good range of reactions, including CO oxidation reaction, Fischer-Tropsch and aqueous phase reforming of oxygenates [8–10]. However, in the literature, an investigation of the actual promoting mechanism, in particular on the impact of Mn on the surface properties, is currently lacking, especially in reforming reactions. The aim of this work is therefore the investigation of the impact of Mn on the catalytic properties of a Pt/C catalyst in the steam (SR) and aqueous phase reforming (APR) reactions of glycerol.

Pt/C and Pt-Mn/C catalysts were prepared by incipient wetness impregnation using activated carbon as support (TA60, PICATAL). The metal precursors for Pt and Mn were tetraammineplatinum nitrate hexahydrate (Sigma-Aldrich) and manganese nitrate tetrahydrate (Sigma-Aldrich), respectively. In this work the Pt metal loading was 3 wt.% and the molar ratio between Pt and Mn was 1. The samples were characterized by BET, H₂-TPR, CO-pulse chemisorption and XRPD. The two catalytic reactions were carried out at 225 °C with a solution 10 wt.% glycerol aqueous solution, and before each reaction the catalysts were reduced in 10% H₂ flow (50 sccm) at 280 °C. Steam reforming was performed in a fixed-bed reactor, which basically consisted of a vaporizer, a quartz tube and a condenser, whereas the APR reactions were performed in a bench Parr reactor, with an initial nitrogen pressure of 30 bar. The gas products were analyzed with an Agilent 490 micro GC, while the condensed liquid products with a Agilent7890A GC. The gas hourly space velocity in the SR reactions was adjusted in order to achieve similar conversion levels (~20%).

The Pt-Mn catalyst showed comparable dispersion and only a slight increase in the reduction temperature compared to the Pt-based catalyst, suggesting that the two metals are in close contact. In the XRPD diffraction patterns of both samples, the peak assigned to the Pt were at 37.9, 46.2 and 67.5°,

which correspond to the (111), (200) and (220) facets for polycrystalline Pt face centered cubic phase, respectively (Figure 1 – Left). Due to the contraction of the unit cell of Pt alloyed with other metals, the position of the (111) diffraction peak is shifted to a higher angle ($2\theta = 40.3^\circ$) [10]. Since no shift was observed in the XRPD pattern of the Pt-Mn sample, and no peaks assigned to Mn were observed as well, the promoter is probably highly dispersed on the surface of the catalyst.

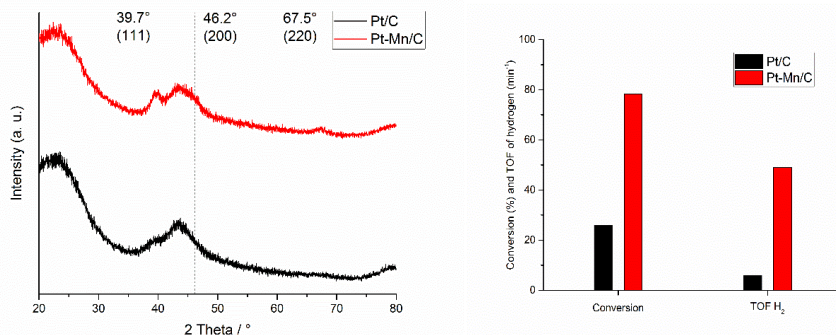


Figure 2. (Left) Diffractograms of Pt/C and Pt-Mn/C and (Right) conversion and TOF of hydrogen in SR of glycerol.

The major impact of Mn on the catalysts reactivity was on the steam reforming of glycerol, where the Pt-Mn/C showed conversion and turnover frequency (TOF) of hydrogen increased of a factor around 7 and 4, respectively. On the other hand, the same catalyst had a minor impact on the aqueous phase reforming, with factors of 1.6 and 1.4, respectively (Figure 1 - Right). Noteworthy, in the steam reforming the selectivity toward CO and hydrogen, as well as ethylene glycol, decreased, while acetol selectivity almost tripled. In the APR reactions, no major differences were found.

These preliminary findings suggest that in the steam reforming the Mn, which is likely present as unreduced MnO_x due to the low reduction temperature, promotes a dehydration pathway. The first step of the reaction then involves an activation of the glycerol on the surface of Pt, followed by a weakening of the C–O bonds on the MnO_x sites, leading to either the cleavage of the bond or to an increase in the CO oxidation. The latter conclusion is supported by the fact that also the selectivity toward CO₂ increased with the addition of Mn. On the contrary, in the APR reaction, the liquid water is probably too tightly bond to the promoting sites, suppressing any promoting effect. Further investigation on the acidity and on the CO adsorption will provide more detailed insights on the promoting mechanism of Mn.

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Notes

GA-7

FUNCTIONALIZATION OF POROUS MATERIALS WITH NANOPARTICLES

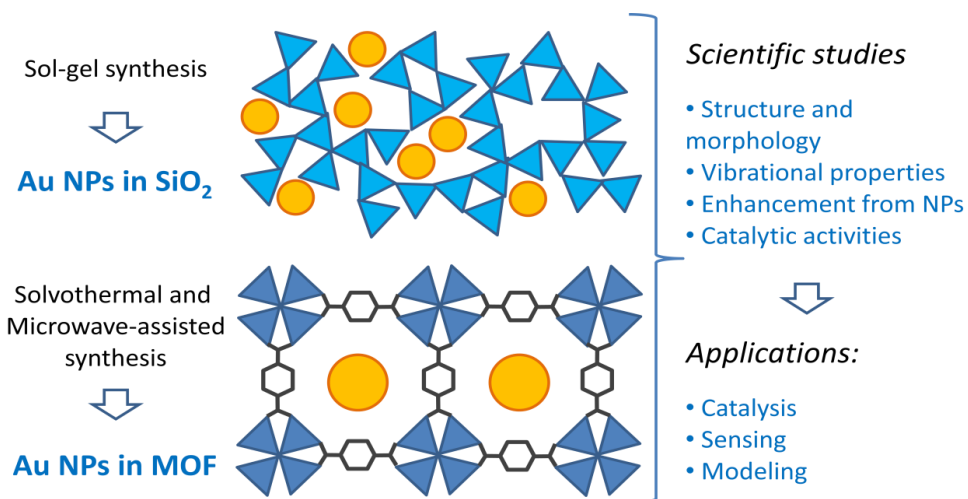
Andriy Budnyk

(Vera Butova, Alexander Guda, Kirill Lomachenko, Alexander Soldatov, Alessandro Damin, Carlo Lamberti, Silvia Bordiga, Adriano Zecchina)

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Summary

The use of porous materials as supports for nanoparticles (NPs) allows to generate composites possessing unique properties deserved in fields of heterogeneous catalysis and enhanced sensing. The resulting NPs size and shape can be controlled as well. The amorphous porous systems can be obtained via sol-gel synthesis, providing optical transparency as an additional benefit for spectroscopy studies. We have been optimizing synthesis procedure to immobilize gold NPs inside a mesoporous silica monolith. There are already successful examples of formation of guest metal oxide NPs in silica matrix. Metal-Organic Frameworks (MOFs) are porous hybrid polymeric materials with a crystalline structure. The different solvothermal techniques (in reactor and microwave-assisted) have been adopted to produce various MOFs (HKUST-1, ZIF-8, UiO-66) and further functionalize them with gold NPs. The obtained materials are passing a complex characterization with spectroscopy techniques towards application in fields of catalysis and sensing.



P-7

FUNCTIONALIZATION OF HKUST-1 AND ZIF-8 MOFS WITH GOLD NANOPARTICLES

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ABSTRACT

The use of porous materials as supports for nanoparticles (NPs) allows the generation of specific adsorption sites. It is also should be possible to control the size and shape of the resulting NPs [1]. Metal-Organic Frameworks (MOFs) are coordination networks of metal ions and organic ligands [2] with wide range of potential applications in gas storage, in bio-medical studies, and in catalysis [3-5]. MOFs are commonly produced by solvothermal methods. Gold NPs of 3-10 nm range have shown a remarkable catalytic activity [6], and being hosted in porous material form a promising heterogeneous catalyst [7]. For this reason MOF can be treated with gold precursor during the synthesis or in post-processing, looking for formation of metal NPs on external surfaces of crystallites or in pores of the framework [8]. This work presents the results of functionalization of MOFs HKUST-1 [9] and ZIF-8 [10] with gold NPs by using microwave-assistant solvothermal synthesis.

The HKUST-1 MOF samples were produced by solvothermal technique [11] or by using microwave (MW) irradiation [12], starting from copper(II) acetate and H₃BTC (BTC – benzene-1,3,5-tricarboxylic acid) in ethanol/water solutions. The commercially available analogous Basolite C300 (Cu₃(BTC)₂) was also used for functionalization. The ZIF-8 MOF was produced in a MW oven from zinc nitrate and 2-methylimidazole in DMF. Before functionalization samples were activated by heating in dynamic vacuum at 200 °C for 6 hours and then refluxing with dry air at room temperature.

For functionalization with gold two methods were used. According to Method 1, aqueous NaAuCl₄ taken in different molar ratio to MOF (from 1:0.25 to 1:660) was poured on MOF powder. The mixture has been kept under magnetic stirring for various periods of time (from 2 min to 2 days). After that, water solution of 16 mg/ml sodium citrate was added and the mixture was placed into a MW oven to react at 100 °C for 16 minutes. After centrifugation the resulting powder was dried at 50 °C in air. Following Method 2, MOF powder was dispersed in hexane (40 ml) with help of ultrasound bath for 20 min. The 160 µl of aqueous NaAuCl₄ were added dropwise and the mixture has been kept under magnetic stirring for 3 h. After centrifugation and redispersion in hexane, a water solution of Na₂C₆H₅O₇ was added dropwise. Finally, the mixture was placed into a MW oven to react at 100 °C for 16 minutes.

The structures of synthesized MOFs were analyzed with XRD measurements. Applying Method 1 to HKUST-1 MOF it was found that in case of low gold loading and short stirring time the resulting Cu₃(BTC)₂ transforms into the phase with 1D open channels – Cu₂(OH)(BTC)(H₂O). Further increase in gold amount and time of stirring did not lead to appreciable improvements, resulting in materials without traceable gold residuals or having significant degradation of MOF framework. Instead, this method allowed to functionalize well the ZIF-8 MOF (at 1:12.2 molar ratio and 30 min of stirring), with XRD data showing ZIF-8 phase with additional reflections from gold. Method 2 was applied to HKUST-1 and resulted in its successful functionalization of MOF with gold NPs without appreciable degeneration of the framework.

The representative TEM images of functionalized MOFs HKUST-1 and ZIF-8 MOFs are presented in Figure 1. In the case of adoption of Method 1 for HKUST-1, the AuNPs of 6-8 nm are observed most probably decorating the crystals of MOF (Fig. 1A). Instead, for ZIF-8 the gold NPs of 5-13 nm are embedded in the matrix (Fig. 1B). Method 2 results in functionalization of HKUST-1 with ~4 nm Au NPs (Fig. 1C).

By changing the synthesis parameters, the dependence of penetration depth of gold NPs inside the MOF framework with time of stirring was also noticed. Diffusion constrains due to small pore size of MOFs, interplay between the gold precursor and a reducing agent, concentration of gold atoms to form NPs - all influences the process of functionalization. It was also found that AuNPs cannot be grown in MOF's pores without thermal treatment. Gold NPs supported on or embedded in MOF crystals are preserved against

aggregation and rather stable in time.

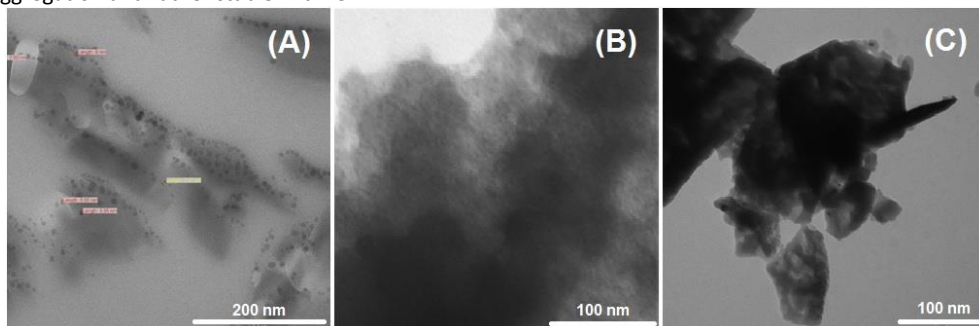


Fig. 1. TEM images of MOF samples functionalized with gold NPs: (A) HKUST-1 and (B) ZIF-8 prepared by Method 1, and (C) HKUST-1 obtained by Method 2.

In conclusion, we have developed two methods for functionalization of MOFs with gold NPs in 5-13 nm range. Both methods are based on MW-assistant solvothermal synthesis, but different solvent (water of hexane) is involved. Variations in time of mixing of the reagents allowed for optimization of gold penetration into the MOF framework. Method 1 resulted in functionalization of HKUST-1 (although with partial structural degradation) and ZIF-8 MOFs, while Method 2 allowed for functionalization of HKUST-1 without causing harm to the framework. Low loading of gold leads to formation of NPs in 6-8 nm range, preferentially on the surface of MOF crystallites; molar ratio Au:MOF = 1:110 results in growths of smaller (4 nm) NPs inside the bulk and bigger ones (20 nm) on the surface of MOF crystals; further increase in gold loading augments average size of gold NPs to 8-10 nm, being accompanied by formation of big crystals. Short time of stirring (about few min) is not enough to ensure total entrance of gold precursor into the porous matrix. Extension of stirring time in aqueous media with gold salt affects mostly HKUST-1 MOF, causing its destruction.

Obtained materials have good stability and may be applied for catalytic tests. Currently, a complex characterization of successful samples is under run with results to be reported elsewhere. The financial support from Mega-grant No. 14.Y26.31.0001 of the Russian Federation Government is acknowledged.

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Notes

GA-8

DETERMINATION OF THE STRUCTURE AND ELECTRONIC PROPERTIES OF SUPPORTED METAL NANOPARTICLES WITH X-RAY BASED TECHNIQUES

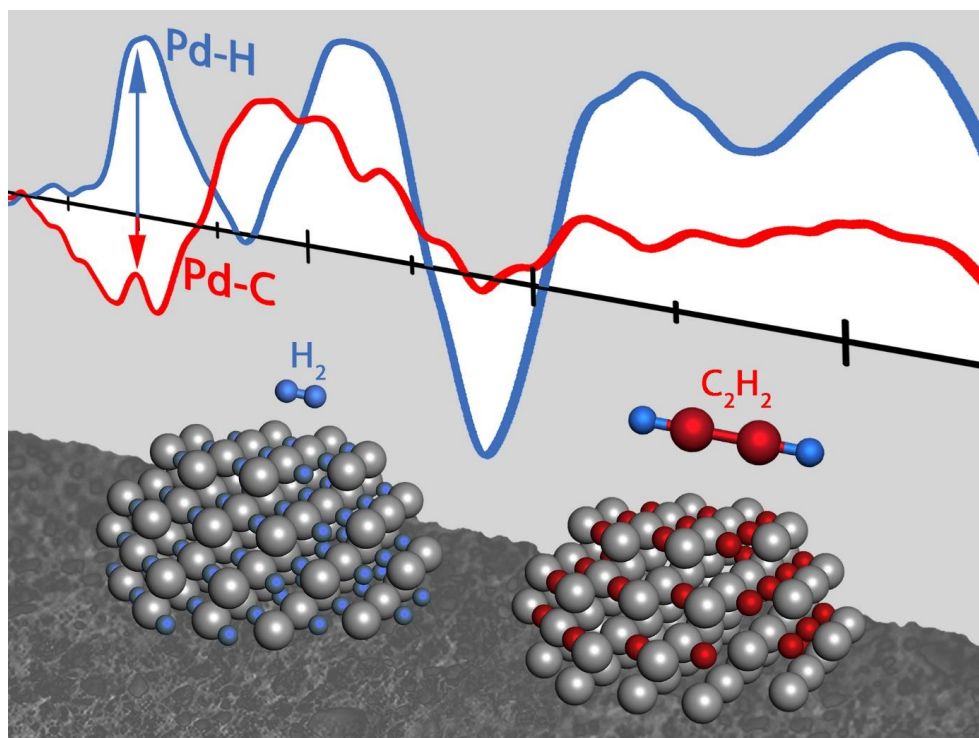
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Summary

In a number of hydrogenation reactions, palladium nanoparticles may undergo a transition to the hydride or the carbide phase, which affects the catalytic properties. The aim of current project is to determine structural evolution of an industrial Pd/C catalysts under reaction conditions by in situ and operando X-ray based techniques. Combination of synchrotron X-ray absorption spectroscopy and X-ray powder diffraction provides detailed information on the atomic structure of the nanoparticles during formation of hydrides and carbides. At the same time, theoretical simulation of near-edge structure of the absorption spectra (XANES) allows to discriminate between Pd-C and Pd-H species and quantify the amount of x and y in PdH_x and PdC_y, respectively. It is shown that the presence of hydrogen and carbon atoms have a direct effect on the near-edge region. For the first time these effect is reproduced by theoretical simulations performed in the Monte-Carlo approach.



P-8

HYDRIDE AND CARBIDE PHASE FORMATION IN PALLADIUM NANOPARTICLES UNDER REACTION CONDITIONS

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ABSTRACT

Metal nanoparticles play an important role in catalysis. For hydrogenation of hydrocarbons, such as alkynes and alkenes, palladium is recognized as the preferred catalyst. In reaction conditions, palladium nanoparticles may undergo phase changes to hydride and carbide phases, whose natures affect the catalytic properties [1]. Therefore, determining the hydride and carbide formation during a catalytic process becomes an important problem, also relevant to industry. Being a subject of numerous theoretical and experimental studies, palladium hydride is one of the most-studied metal hydrides. In contrast to the hydride, the structure and properties of the carbide phase are still under discussion [1, 2]. The aim of the current work is to present a systematic approach for *in situ* and *operando* investigation of the formation of hydride and carbide phases in an industrial palladium-based catalyst under realistic working conditions.

The formation of both hydride and carbide phases is accompanied with an expansion of the palladium lattice, which can be followed by X-ray powder diffraction (XRPD) [3, 4] and extended X-ray absorption fine structure (EXAFS) [2, 5-7]. EXAFS is an element-selective technique and demonstrates high sensitivity to the local structure changes, such as bond distances and coordination numbers of the absorbing atom. In the case of the palladium containing material, whose K- absorption edge is 24357 eV, hard X-rays can be easily applied to perform *in situ* and *operando* experiments. One should take into consideration that both EXAFS and XRPD are least sensitive to light atoms, such as carbon and especially hydrogen, due to their low scattering amplitudes compared to palladium. Thus, palladium hydride and carbide phases are observed by these techniques only indirectly, via Pd-Pd distance elongation or lattice expansion.

X-ray absorption near-edge structure (XANES) include a part of the absorption spectrum up to 30 – 50 eV above the absorption edge. It was shown [2, 6, 8-10] that the formation of palladium hydride directly affects the shape X-ray absorption near edge structure due to mixing of unoccupied states of hydrogen and palladium. This makes XANES a promising tool for *in situ* investigation of palladium hydride and carbide formation, because unlike EXAFS and XRPD this method is sensitive to the presence of light atoms. For the first time, we have reproduced the changes in XANES by theoretical simulations applying Monte-Carlo approach.

Figure 3a shows that in the presence of hydrogen (violet curve) the first near-edge peak at 24369 eV becomes narrower and is shifted by 1 eV to lower energy. Formation of palladium carbide (orange curve) leads to a broadening of the same peak and shifts it by 1 eV to higher energy. This opposite behavior of XANES spectra during hydride and carbide formation is more pronounced in the difference spectra and provides us a method to discriminate between the two phases under hydrogenation reaction conditions. To test this thesis we investigated the system sending at 100 °C a mixture of 650 mbar of hydrogen and 350 mbar of acetylene, see red curve in Figure 3b. Comparing the XANES spectrum collected under hydrogenation reaction conditions with those obtained sending at 100 °C the pure reagents separately (100 and 600 mbar of H₂ or 1000 mbar of C₂H₂) we can conclude that hydride phase is formed, having a similar composition to that obtained sending 600 mbar of pure hydrogen at the same temperature.

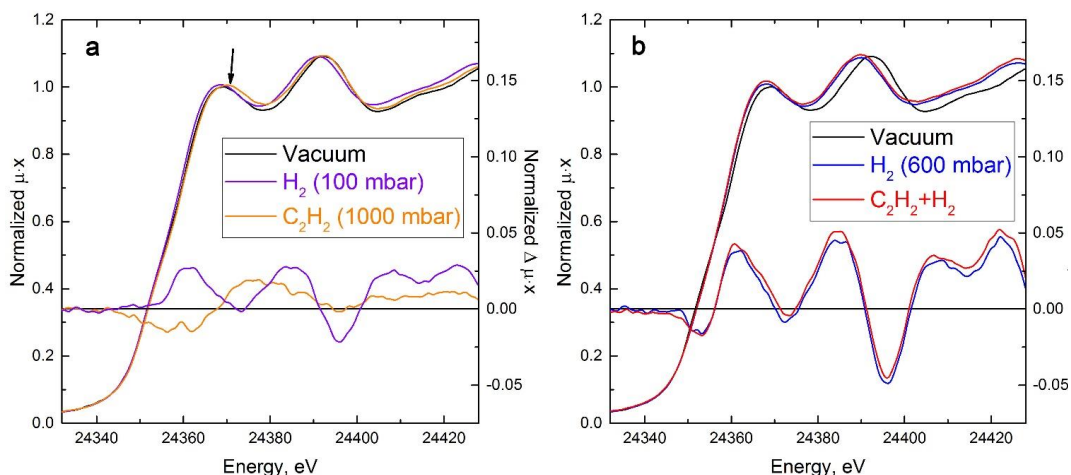


Figure 1. Part (a): Experimental Pd K-edge XANES spectra (left ordinate axis) and difference XANES (right ordinate axis) spectra collected at 100 °C on the palladium nanoparticles in vacuum (black), in 100 mbar (violet) and 600 mbar (blue) of hydrogen, in 1000 mbar of acetylene (orange). Part (b), as part (a) for a mixture of 650 mbar of hydrogen and 350 mbar of acetylene (red). The corresponding spectra of pure metal and hydrate phase are also reported for comparison.

In summary, we have demonstrated a scheme to obtain structural information on supported palladium nanoparticle relevant in catalysts by applying *in situ* and *operando* X-ray absorption and powder diffraction techniques. Analysis of XANES spectra allows determining whether hydride or carbide phase is formed in the nanoparticles. Possibility to extract this information from XANES becomes extremely important in the cases, when the catalyst is exposed to a mixture of gasses, and the type of the phase (carbide or hydride) cannot be predicted in advance. In addition to the type of the phase determined from XANES, and interatomic distance obtained from EXAFS, XRPD analysis gives quantitative information on the phase concentrations.

The described scheme of experimental measurements and analysis may be applied to investigate the structural evolution of supported metal nanoparticle catalyst during catalytic processes in *operando* conditions, such as hydrogenation of hydrocarbons and will allow correlating catalytic properties of the nanoparticles with their structure and phasing content.

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Notes

GA-9

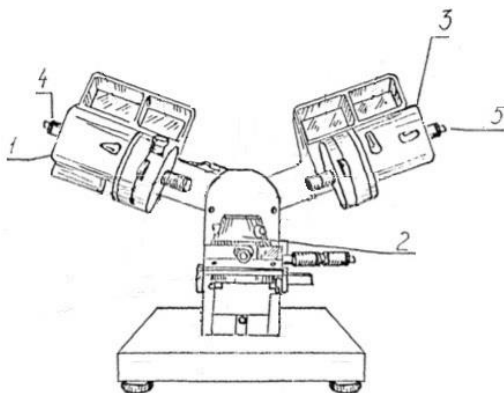
DEVELOPMENT OF A SYSTEM FOR INVESTIGATIONS OF SURFACE ENHANCED PHOTOLUMINESCENCE KINETICS

Fedor Bystrov

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Summary

The main subject of my master work is investigation of photosensitizer's luminescence enhancement by surface plasmon resonance and analysis of the surface plasmon enhanced luminescence intensity decay. I have developed a system for luminescence enhancement based on the Kretschmann configuration. Laser radiation from the source transmits by optical fiber and enters the polarizer shoulder, which consists of Glan prism and system of mirrors, and then polarized light is focused on the prism with the sample. In the next step enhanced luminescence from the sample collects by the analyzer shoulder and then transmits by optical fiber to the streak camera.



1 – Polarizer shoulder; 2 – stage; 3 – analyzer shoulder; 4 and 5 – fiber connectors.

P-9

FLUORESCENCE KINETICS OF ALUMINUM PHTHALOCYANINE NANOPARTICLES IN THE BIOLOGICAL ENVIRONMENT

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ABSTRACT

Nanoparticles of aluminum phthalocyanine (nan-ALPc) are one of the most promising type of nanophotosensitizers due to their unique properties. Fluorescence and photodynamic activity of injected in biological tissue nan-ALPc appears only in pathologically changed areas. It has been shown [1] that nan-ALPc can be used to assess the risks of rejection of skin autografts. It was found that application of colloidal solution of nan-ALPc on autografts leads to the increasing of fluorescence intensity in the case of inflammatory rejection. Furthermore, our studies have shown the decrease of fluorescence intensity after prolonged exposure to laser radiation - so-called photobleaching, that is absent for molecular form of aluminum phthalocyanine. Therefore, the appearance of fluorescence and photodynamic activity of nan-ALPc cannot be explained as process of nanoparticle dissolving.

This work is dedicated to the study of the photoluminescence kinetics of aluminum phthalocyanine nanoparticles applied to skin autografts of mouse, using ultrafast laser spectroscopy methods. For measurements we used a registration system based on Hamamatsu streak camera with picosecond temporal resolution, and picosecond laser pumping. Our study consists of two parts: the first one is to analyze the intensity decay of nan-ALPc deposited on autografts in order to identify the number of lifetime components and their distribution, and the second is to expose the experimental mouse to the photodynamic (PD) effect and do the same analysis. In the first stage the presence of three lifetimes was recorded: 6.5 ns (35% of the total number of photons); 2 ns (41% of the total number of photons) and 800 ps (24% of the total number of photons). It should be said that molecular form of aluminum phthalocyanine dissolved in water has only one lifetime component - 5 ns. After photodynamic exposure the intensity distribution of nan-ALPc in streak image has changed and it can be seen by distribution of lifetimes after mathematical treatment. Analysis of nan-ALPc fluorescence decay from skin autograft after PD showed: 6.5 ns (23% of the total number of photons); 800 ps (30% of the total number of photons) and 200 ps (47% of the total number of photons).

Based on the fact that fluorescence of nan-ALPc is susceptible to the photobleaching effect, that is absent for molecular form of aluminum phthalocyanine, it can be assumed that the appearance of nan-ALPc fluorescence in the diseased tissue is not only due to the normal dissolution, but also due to the transitions of surface molecules of nanoparticle to the different states. The appearance of several fluorescence lifetime components each of which corresponds to particular state of the molecule on the surface might be the evidence of these transitions.

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Notes

GA-10

CHEMICAL CHARACTERIZATION OF MATERIALS USED IN CONTEMPORARY ARTWORKS

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Summary

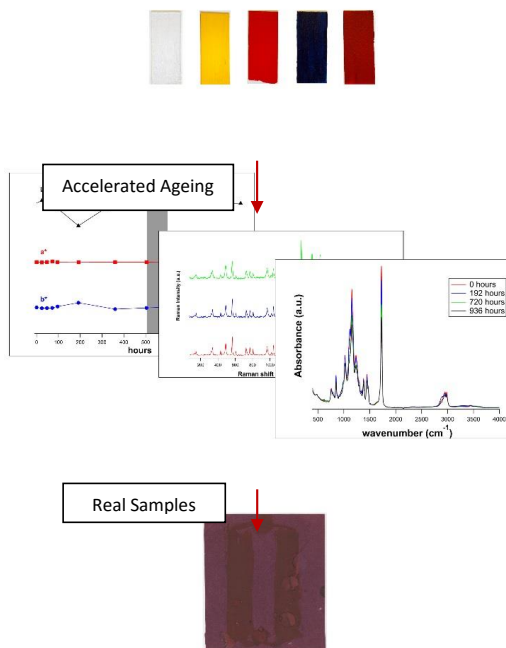
The PhD project is aimed to the characterization of artistic synthetic pigments, typical of XXth century, and particularly it is focused on the identification of degradation products from accelerated ageing processes, which can simulate natural one.

Aim of the study is the prediction of degradation processes which can involve pictorial layers in Modern and Contemporary paintings; furthermore, it can provide new information to select and optimize analytical techniques for art diagnostics.

First step of the project involves selection of several synthetic pigments –azo-pigments, quinacridones, phtalocyanines, DPP- to cover most classes of material used in contemporary paintings. Samples of pigment powders and pictorial film obtained mixing the pigments with artistic binder media are aged through several methods to induce formation of degradation products.

These will be analyzed through several techniques: NMR and Mass spectrometries and UV-Vis spectroscopy will provide chemical characterization of degradation species, while other techniques commonly used in cultural heritage analysis –colorimetry, FTIR and Raman- will be a reference to correlate degradation mechanism hypotheses with artworks diagnostics.

After these results, analysis will be extended to other materials used in contemporary art –different binders, pigments in tube or mixed with extenders; finally, identification of degradation products will be done on samples from contemporary art objects or original artists' palette, to confirm degradation hypotheses from reference samples.



P-10

MULTIANALYTICAL CHARACTERIZATION STUDY OF DEGRADATION PRODUCTS FROM SYNTHETIC MATERIALS USED IN CONTEMPORARY ART

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ABSTRACT

During 19th and 20th centuries, the industrial revolution and synthetic chemistry development provided artists new materials, characterized by different properties in comparison to traditional art's materials: in fact, synthetic organic pigments present vibrant shades and they are easier to use and less expensive than ancient ones[1], while synthetic polymeric art binders are characterized by short drying-time and good esthetic properties.

However, because their recent origin and industrial nature, it is not possible to know their behavior in a pictorial film during natural ageing and it is hard to predict their stability in exposition environment, that is a combination of several factors –UV and visible light components, temperature, Relative Humidity.

This study –part of a PhD project- is focused on chemical characterization of degradation products from synthetic organic pigments and polymeric binders used in contemporary paintings: degradation process is realized through artificial ageing in photochemical stress conditions (UVB lamp with high Lux level) and monitoring environmental parameters (temperature, Relative Humidity). Artificial ageing is conducted on pigment powders and on pictorial films samples obtained mixing pigments with polymeric art binder: from comparison of these two set it will be possible to identify degradation products which derive from pigments molecules and those which originate from interaction with binder.

The characterization of degradations products is studied through some spectroscopic techniques commonly used in cultural heritage studies: particularly, ATR-IR[2] and Raman[3] spectroscopies can provide important information on variations of chemical bonds during accelerated ageing. These spectra can also represent a direct reference for cultural heritage diagnostics on contemporary artworks.

To confirm spectroscopic measurements, other techniques are used, as UV-Vis spectroscopy, NMR[4] and Mass Spectrometry: combinations of all these techniques can provide a complete structural characterization of painting degradation products and it can result useful to understand ageing processes than involve a pictorial film in contemporary artworks. Obtained data will be even useful to identify possible analytical markers for contemporary art materials and to project new artistic materials with better conservation characteristics.

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Notes

GA-11

NANOSTRUCTURATION OF MAGNETIC MOLECULES FOR SPINTRONICS AND QUANTUM COMPUTATION

Irene Cimatti

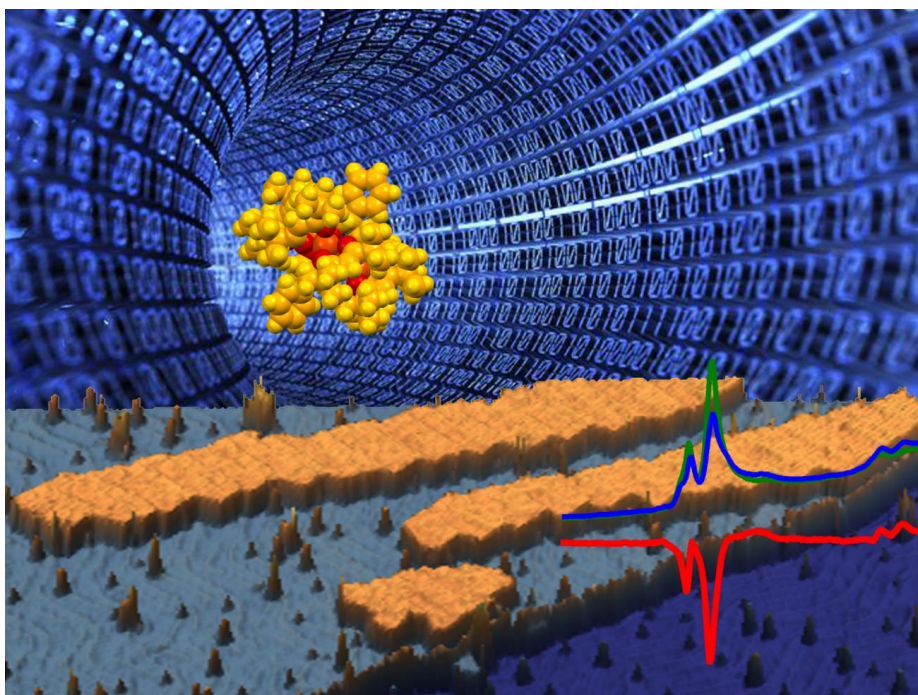
Lorenzo Poggini, Brunetto Cortigiani, Matteo Mannini, Roberta Sessoli

Department of Chemistry, University of Florence

My PhD is focused on the deposition on metallic surfaces of magnetic molecules *via* sublimation in Ultra High Vacuum. The final aim of this research is the exploration of nanoscale properties of magnetic molecules suitable for spintronics or quantum computation purposes. The three classes of molecular candidates I am investigating contain β -diketonate ligands that promote their volatility. Sublimation is chosen in order to achieve ultra-pure and highly ordered deposits that can be investigated *in situ* with morphological and spectroscopic tools. Additionally X-Rays Magnetic Circular Dichroism investigation, carried out using synchrotron light sources, allows probing the magnetic properties of these ultra-thin films.

The first two complexes I'm studying are single molecule magnets (SMM): molecules exhibiting magnetic hysteresis, that are the target of intense research as they represent the ultimate miniaturization limit of magnetic memories and the starting point to develop molecular spintronic devices profiting of the richness of quantum effects governing the dynamics of the magnetization of SMM.

The third project concerns a small molecule that can be used as a qubit, the base unit of quantum computation. A qubit is a system on two levels that has to be isolable and well defined, to be able to interact with other qubits and it must possess decoherence times longer than the time required for the basic computation action. Also in this case the realization of arrays of these molecules will be the starting point for the local addressing of the molecular properties and then for the development of molecular-spin qubit.



P-11

NANOSTRUCTURATION OF SUBLIMABLE MAGNETIC MOLECULES CONTAINING BETA-DIKETONATE LIGANDS

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ABSTRACT

Magnetic molecules can have different applications in the new frontiers of nanoelectronics. Their peculiar properties can be exploited for spintronics and quantum computing.

Molecular spintronics (spin + electronics)[1] exploits the spin degree of freedom as an information carrier through molecules inserted in a device. One of the most interesting candidates for this purpose are Single Molecule Magnets (SMMs). This class of magnetic molecules presents low temperature magnetic bistability of molecular origin.[2] Their intriguing quantum and classical properties would be exploited for spintronics and quantum computing applications.[3][4] The development of spintronics is focused on solving problems related to injecting, manipulating and detecting spin in a solid state system[1] but also deals with stability of molecular systems at the surface that must retain the SMM behaviour after the grafting.[5] More recently molecular systems have been introduced as qubit for quantum computation.[6] [7] This research field is focused on the exploitation of quantum interference and entanglement to create a faster way to perform calculations. The basic unit of computation is the qubit that must be a quantum system. A classical bit can be in two states 0 or 1, a qubit can be 0, 1 or a superposition of the two states. Following the DiVincenzo rules,[8] a qubit must be a two level system, isolable and well defined, it must interact with other qubits and have a coherence time 10^4 times bigger than the computation time for the basic computational action.

One of the advantage of molecular systems for these two applications is the exploitation of the versatility of chemical approaches for the fine tuning of the functionality of the system that can be nanostructured in thin film with techniques such as molecular beam epitaxy.

Several studies demonstrated that molecular systems, when sublimated on surface, can interact with the substrate and loose some of the intriguing properties of the systems.[9][10] It is therefore crucial to carefully control the growth of the films at a monolayer level. To deal with this requirement we perform the sublimation *in situ* in a platform gathering together spectroscopic (XPS, UPS, LEIS) and morphologic (STM, AFM) characterisation techniques.

The first presented system is part of the family of Fe_4 , that is among the most promising SMM that has been found to retain its dynamic magnetic properties after the grafting via self-assembling from solution.[11] More recently our group demonstrated that by modifying the molecular structure of Fe_4 is possible also to assemble these SMM sublimation in Ultra High Vacuum (UHV).[10] In particular, we have chosen $[Fe_4(L)_2(dpm)_6]$ (see Fig. 1.a.), hereafter Fe_4Ph , a molecule that sublimate in UHV at around 480K. The magnetic core of the molecule is constituted by four Fe^{3+} , where the central one is antiferromagnetically coupled with the three peripheral ones. Each one of these is bonded to two dipivaloylmethane ligands (Hdpm), and to complete the structure, there are two tripodal ligands (L = 2-hydroxymethyl-2-phenylpropane-1,3-diol) containing the phenyl ring, peculiarity that makes this analogue sublimable.

The STM characterisation of a monolayer coverage (see Fig. 1.b.) shows an ordered layer-by-layer growth

of the film. The dimensions of the objects observed are in good agreement to what we expected for a Fe_4Ph intact molecule. A more complex scenario appears studying the submonolayer deposition where two species are presents.[10], [12] The extended research to unravel the interaction of this molecule with the substrate gives us the opportunity to build up a protocol for the characterisation of complex molecule deposited on metallic surfaces. The support and the comparison with the theoretical models are important instruments to confirm our hypothesis.

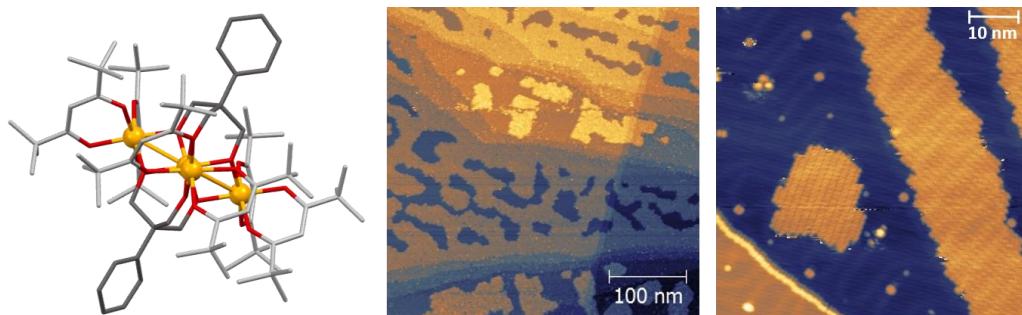


Figure 1. a. Fe_4Ph structure. b. and c. STM images performed at 30K on a substrate of Au (111). b. a monolayer coverage of Fe_4Ph . c. A submonolayer deposition of $\text{VO}(\text{dpm})_2$.

The protocol developed with Fe_4Ph was then applied to another magnetic molecule containing a β -diketonate ligand: $\text{VO}(\text{dpm})_2$. The small paramagnetic complex presents interestingly low decoherence times that makes the molecule a possible candidate as a qubit for quantum computation. One of the DiVincenzo rules[8] states that a qubit must be a two level system well defined and isolable. For a molecular system, in order to obey to the last indication, a possibility is to deposit the system on a surface. Therefore we deposited the $\text{VO}(\text{dpm})_2$ and we performed a spectroscopic and morphological (see Fig. 1.c.) characterisation to test its robustness. [13]

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Notes

GA-12

**PULSED LASER DEPOSITION OF THIN FILMS OF NEW GENERATION
BIOCOMPATIBLE MATERIALS**

Mariangela Curcio

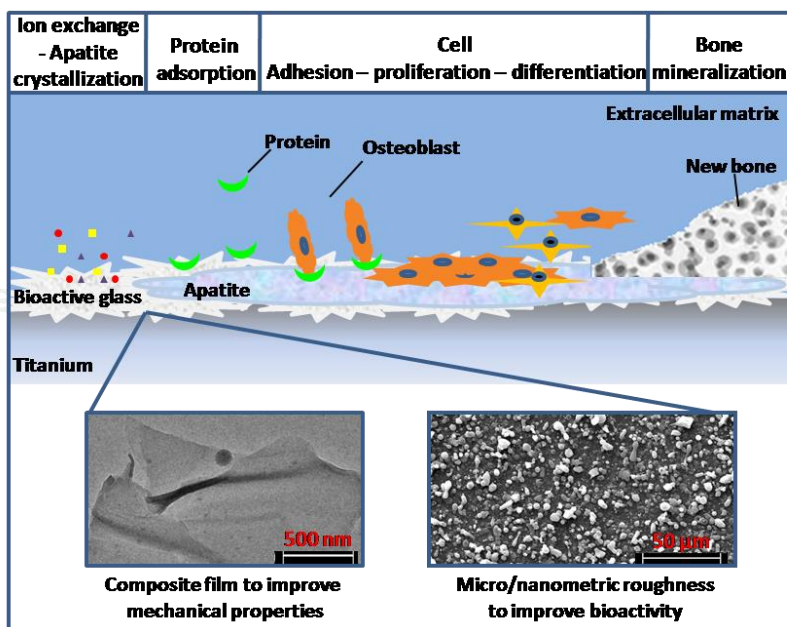
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Summary

Biomaterials are synthetic or natural materials that have an appropriate function into the biological environment. The fundamental property of these materials is biocompatibility, which mainly depends on surface characteristics, such as topography, roughness and chemistry. To this class of materials special glass and glass-ceramics belong. These materials exhibit bioactivity and mechanical resistance suitable to coat bone-related implants. The coating is used to provide a surface composition different from the substrate, to ensure the osseointegration. When bioinert substrate are used (usually titanium or alumina and zirconia), the coating is important to give bioactivity to the implant. On the other hand, when the substrate is a biodegradable material (such as Mg-Ca alloys), the coating is necessary to control the kinetic of degradation. In this contest, Pulsed Laser Deposition (PLD) is an appropriate technique for thin film production. PLD ensures the congruent transfer of the target composition to the film, the control of film’s growth kinetics, thickness and roughness, the possibility of producing nanocrystalline and composite films. Therefore, the goal of this project is to optimize PLD experimental parameters and the composition of starting target materials with the purpose to obtain thin films based on bioactive glass and glass-ceramic on different substrate, for a real use in tissue engineering and implantology. The chemical-physical films properties will be tested with several spectroscopical and microscopical techniques, mechanical characteristic with Vickers microhardness tests. Bioactivity evaluation will be conducted in SBF (simulated body fluid), to prove the formation of hydroxyapatite layer, and by testing various cell lines.



P-12

COMPOSITE THIN FILMS OF RKKP GLASS WITH IMPROVED MECHANICAL PROPERTIES AND SURFACE ROUGHNESS FOR BONE-RELATED IMPLANTS

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ABSTRACT

The biomaterial/host tissue interface largely determine the success of a biomedical implant: when in contact with the body fluid or tissue.

Bioactive glasses and glass-ceramics are an important class of biomaterials used to bone tissues repair and regeneration, in the form of scaffolds, cements and film-coatings for bone-related implants.

Surface modification is the promising strategy to improve biocompatibility, bioactivity and mechanical properties of implants. Therefore, the main object of this work is to improve the mechanical properties and surface roughness. In fact, an increased mechanical resistance, comparable to that of the host tissue, favors the success of the implant, subjected at stresses within the organism. On the other hand, a micro-and/or nanoscale surface roughness promotes the protein absorption and the osteoblast adhesion and growth.

RKKP, a bioactive glass of innovative composition, has been used in this work to coat Titanium substrate. The chemical-physical properties and bioactivity of film have already been reported in our previous works [1,2]. In order to improve mechanical its properties and biological performances carbon-based materials, such as reduced graphene oxide (rGO) and fullerene (C₆₀) have been added to RKKP glass.

For the film preparation, Pulsed Laser Deposition (PLD) technique has been applied. PLD presents several advantages with respect to the other deposition procedures, such as the congruent transfer of target composition to films, the possibility to control adherence, crystallinity and surface roughness.

PLD experiment has been performed in a vacuum chamber with a frequency doubled Nd:YAG laser source (532 nm emission wavelength, 10 Hz repetition rate, 7 ns pulse duration). The experimental parameters have been optimized to prepare film with physical, chemical and biological properties suitable to coat the bone-related implant.

The surface characteristics of target materials and deposited coating have been investigated by microscopical and spectroscopical techniques. Moreover, Vickers microhardness measurements on the deposited films have been carried out.

Pulsed Laser Deposition of the mixed RKKP-rGO target has produced a composite film of glass particles in a carbon matrix, as shown in TEM and SEM images (Fig.1(a) and (b), respectively). TEM image, referred to the early steps of the film's growth, is reported in Fig.1(a). The presence of two structures - sheet-like structure of rGO and RKKP nanoparticles - is evident. Similar information has been obtained by the SEM analysis of the film surface; in the micrograph reported in Fig.1(b), RKKP particles have been found anchored on the rGO structure. Micro-Raman investigation (Fig.1(c)) has confirmed the presence of both components. Moreover, the results of the Vickers microhardness measurements testify the improvement of mechanical characteristics with respect to RKKP films reported previously [1].

Similar investigations have been conducted on RKKP-C₆₀ composite films, obtained at different deposition temperatures. SEM micrograph of the film deposited at 500°C (Fig.2) reveals that higher deposition temperatures benefits on the homogeneity and surface roughness of the coating.

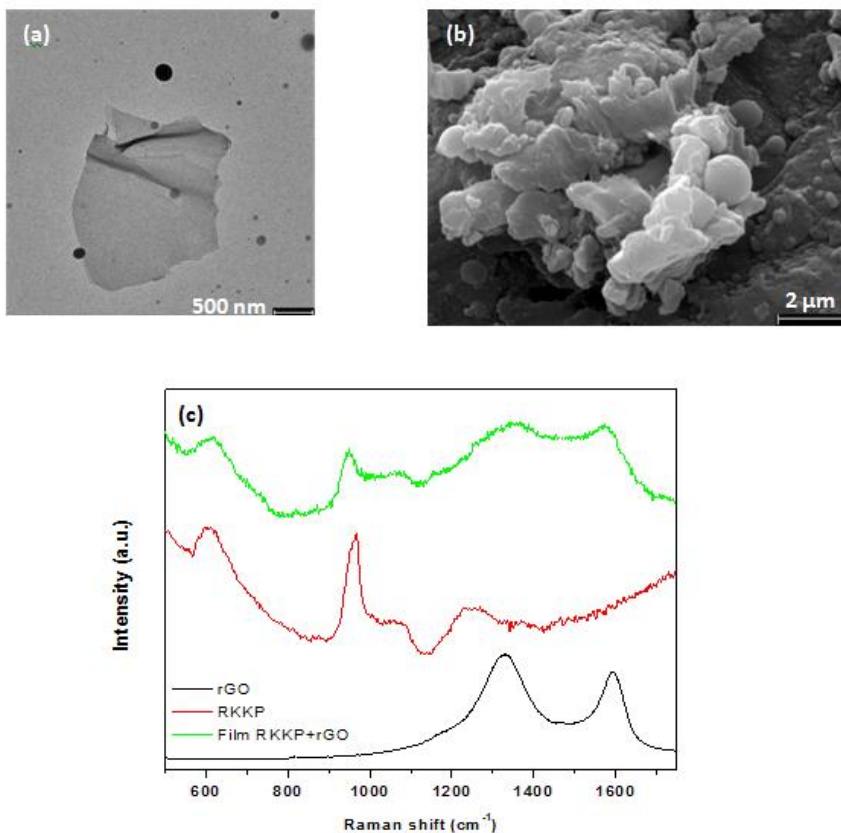


Fig.1. RKKP-rGO film's characterization: (a) TEM image, (b) SEM image, (c) micro-Raman spectra of RKKP-rGO film compared with target materials.

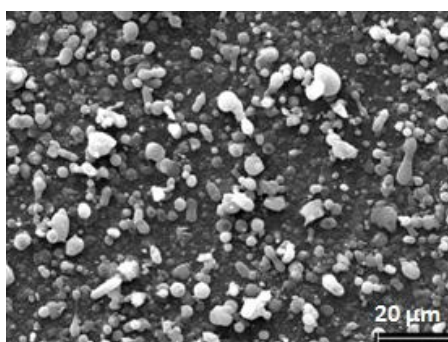


Fig.2. SEM image of RKKP-C₆₀ film deposited at 500°C.

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Notes

GA-13

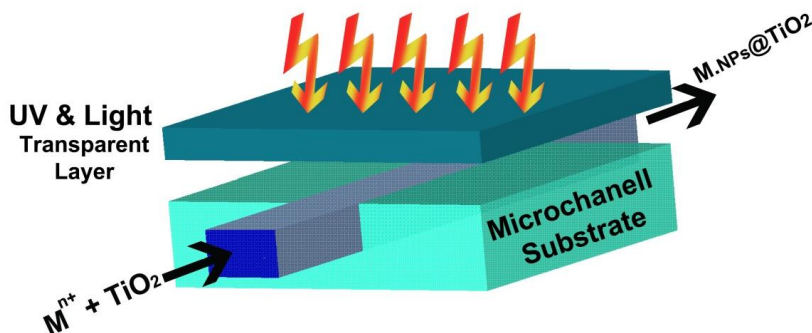
PHOTOCATALYTIC DEPOSITION OF Pd ON TiO₂ NANOPARTICLES BY CHANNEL TYPE REACTOR

Samira Dadsetan
(Saeid Baqshahi)

Imam Khomeini International University

Summary

Photocatalytic properties of TiO₂ can be improved by surface deposition of noble metal nanoparticles. Such particles can play an important role on electron trapping and chemical reactivity improvement. Pd@TiO₂ can be synthesized by photocatalytic deposition under UV irradiation. Using micro channel reactor for synthesizing Pd@TiO₂, can be a useful way to decrease and control the metallic Pd nanoparticle size which is deposited on TiO₂ nanoparticles and hence improving its activity. Studying the effect of flow condition of particles and other parameters such as type and shape of TiO₂ nanoparticles on the photocatalytic deposition of Pd on TiO₂ nanoparticles is going to be done using microchannel reactors during UV irradiation.



Notes

GA-14

IMPROVED CATALYST PERFORMANCE FOR UNIDIRECTIONAL ZSM-22 AND ZSM-23 ZEOLITE CATALYST

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Summary

The overall objective of the PhD project is to improve the catalyst performance of unidirectional zeolite catalysts ZSM-22 and ZSM-23 in the conversion of methanol to hydrocarbons with particular focus on catalyst lifetime, while maintaining the high selectivity towards the aromatics free C₅₊ fraction. These materials show an interesting aromatic-free gasoline product, but the stability towards deactivation is lower than the commercially used zeolite catalysts for the conversion of methanol into hydrocarbons.

To accomplish the goal, additional network of mesopores are introduced in the material using post-synthesis treatments based on surfactant aided desilication in alkaline solution and sequential acid washes. Improvements in the diffusion properties by created mesoporosity might lead to improved catalyst performance.

The parent and treated materials are characterized by means of elemental analysis to evaluate the loss of silicon atoms, textural properties using adsorption isotherms and microscope techniques to study the surface porosity and morphology. Also, the internal and external surfaces as well as the acidity of these materials are evaluated using FT-IR combined with sterically demanding probe molecules.

The parent and treated materials were tested in the Methanol-to-Hydrocarbons reaction in order to study the differences in terms of selectivity and lifetime.

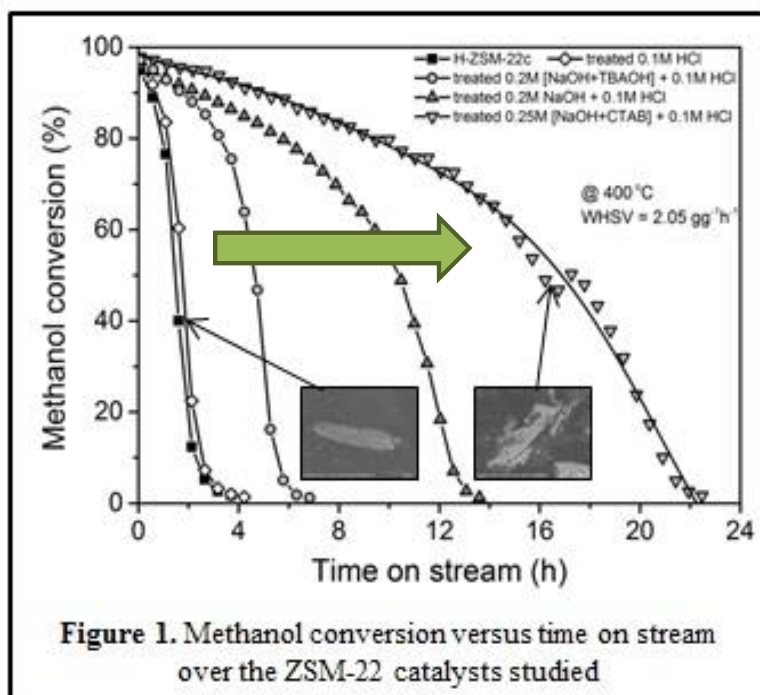


Figure 1. Methanol conversion versus time on stream over the ZSM-22 catalysts studied

P-14

INFLUENCE OF POST-SYNTHETIC TREATMENTS ON UNIDIRECTIONAL ZSM-22 ZEOLITE CATALYST: TOWARDS IMPROVED CLEAN GASOLINE CATALYTIC PROCESS

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ABSTRACT

Production of clean fuels from alternative sources stands for the challenge of replacing the current oil-based energy carriers and meeting new environmental requirements¹. The methanol-to-gasoline (MTG) process over acidic one-dimensional H-ZSM-22 zeolite represents a technology where a high-octane gasoline virtually without aromatics can be obtained directly from methanol². Despite the exceptional aromatic-free branched C₅₊ product spectrum, the primary drawback associated with this catalyst is the rapid deactivation. Improvements in catalyst lifetime may be achieved by increasing the diffusion paths for reacting molecules and coke precursors within the zeolitic crystals and this can be addressed by creation of a secondary network of pores via post-synthetic desilication methods³⁻⁵.

The effect of different base-acid treatments employing alkaline and surfactant aided approaches and sequential HCl washing over the parent ZSM-22 material on the MTG process is examined in this work. A striking improvement in lifetime for the base-acid treated catalysts was successfully achieved (Figure 1). The high selectivity to the branched hydrocarbon alkenes was maintained after the treatments.

The Si/Al was effectively reduced after desilication, but the ratio returned to the parent value after washing, suggesting that the acid wash lead to remove extra-framework Al species from the crystal surface. SEM micrographs and nitrogen adsorption experiments showed that the zeolite agglomerates were fragmented or eroded and the external surface area and pore volume increased as a consequence of the base-acid process, attributed to the presence of intra- and inter-crystalline mesopores. Surprisingly, the Brønsted acid sites were almost unaffected, whereas Lewis sites were increased as observed by FT-IR with CO and pyridine.

This work demonstrates a remarkable enhancement of the catalytic lifetime of the promising ZSM-22 zeolite catalyst for an optimal clean gasoline production via MTG. Extensive characterization using standard molecules spectroscopy and diffusion measurements are in progress to elucidate the causes of the enhanced catalytic performance.

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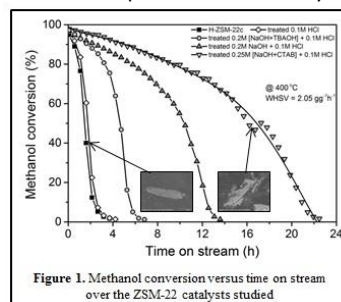


Figure 1. Methanol conversion versus time on stream over the ZSM-22 catalysts studied

Notes

GA-15

A COMPREHENSIVE ASSESSMENT OF THE SURFACE ACIDIC PROPERTIES OF HETEROGENEOUS CATALYSTS BY THE AMMONIA TEMPERATURE PROGRAMMED DESORPTION TECHNIQUE

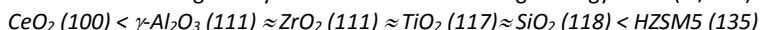
R. Di Chio

(F. Arena, G. Trunfio)

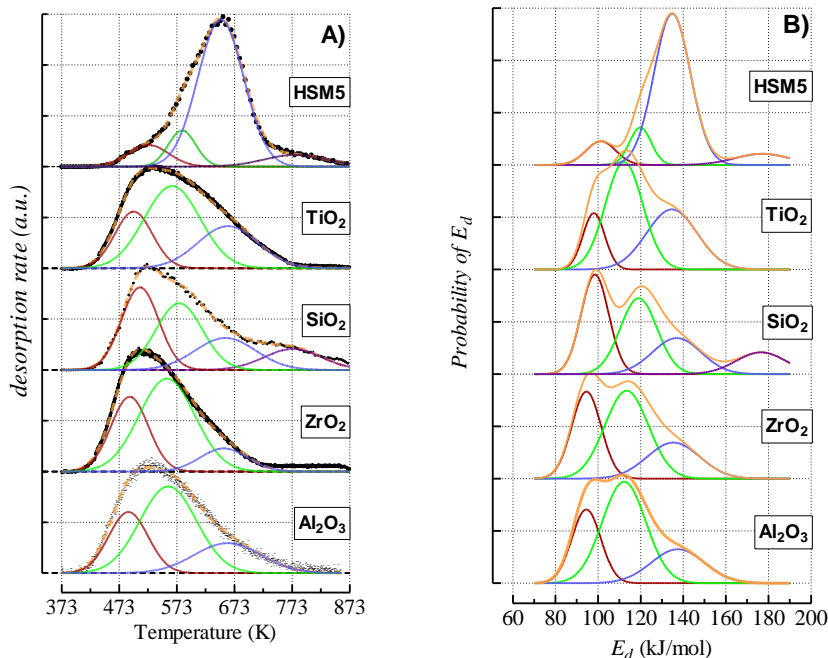
Dipartimento di Ingegneria Elettronica, Chimica e Ingegneria Industriale, Università degli Studi di Messina, Viale F. Stagno D'Alcontres 31, I-98166 Messina, ITALY

Summary

The TPD of ammonia (ATPD) is a very popular characterization technique of the surface acidity of solid catalysts because of the method and apparatus simplicity. The aim of this study was to use it as tool for comparative study of the surface acidity of several catalytic oxide materials (γ - Al_2O_3 , CeO_2 , ZrO_2 , SiO_2 , TiO_2 , HZSM5 zeolite). Using the ceria sample as a model system for weak-type acidity and modelling its profile as a *Gaussian* function with satisfactory accuracy, we could be able to state that the profiles of all the studied systems can be described as a linear combinations of three/four Gaussian curves spanned in the range of 423–873K. This corresponds to a general energy distribution pattern including four populations (e.g., *weak, medium, strong, very strong*) of surface acid sites obtained using two different distribution models in good agreement with each other. The cumulative distributions of ammonia adsorptions indicate the following acidity scale based on the average energy value (kJ/mol):



Moreover, the dehydration of iso-propyl alcohol to propylene, indicated as "probe reaction", has been used to characterize type (Brønsted or Lewis) and strength of catalyst acid centers. The results obtained match the acidity scale provided by the modelling analysis of ATPD profiles.



P-15

A COMPREHENSIVE ASSESSMENT OF THE SURFACE ACIDIC PROPERTIES OF HETEROGENEOUS CATALYSTS BY THE AMMONIA TEMPERATURE PROGRAMMED DESORPTION TECHNIQUE

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ABSTRACT

Under the guidelines of Green Chemistry, the discovery of new and clean catalytic synthesis routes has become a topic of major concern in the last years. Indeed, many of the industrial processes developed in the past century were mostly aimed at maximizing the product yield with a poor consideration for the environmental impacts of the manufacture cycle, often making use of dangerous reagents, solvents, catalysts, etc. In this respect, heterogeneous catalysis can ensure higher efficiency and environmental compatibility to many chemical processes, by a substantial reduction of waste production in addition to several intrinsic advantages like ease of product separation and catalyst re-use, elimination of purification steps and utilities (e.g., solvents, reagents, etc.), multifunctionality; and continuous reactor operations, concurring to remarkable improvements of the atom economy, E-factor, and process economics [1]. In particular, a high relevance of acid-catalysed reactions to current technologies like isomerisation, acylation, alkylation, dehydration, esterification, amidation, oxidative dehydrogenation, hydrolysis, transesterification, etc., stimulates a strong scientific concern on synthesis of solid acid and superacid catalysts and tuning of their physico-chemical properties. Then, apart from the conventional time-consuming titration measurements, the most common characterization methods of solid acid catalysts relies on the study of the interaction pattern of more or less basic probe molecules with the catalyst surface by temperature programmed, spectroscopic and calorimetric techniques [2-4].

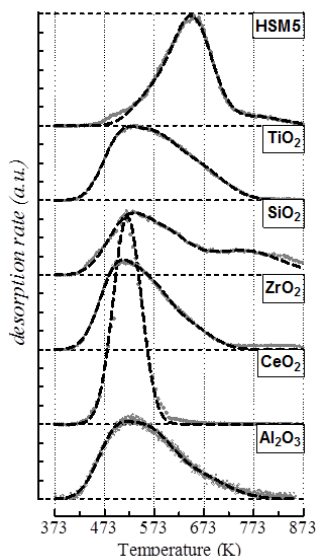


Figure 1. Normalized ammonia TPD

Although the TPD of ammonia (ATPD) has become a very popular characterization tool of the surface acidity of solid catalysts, because of the simplicity of the method and apparatus, yet, several experimental issues are critical for the reliability of ATPD data; first, a high reactivity of ammonia responsible of the interaction with non-acidic species like Ca or Na ions, and the choice of improper experimental parameters, like flow and heating rate, catalyst particle size and bed length which can deeply affect the desorption pattern. As a consequence, the reliability of ATPD analysis to get energy data is still matter of debate. Then, after assessing accuracy and reliability of ATPD data using a QMS as analytical tool [5], this work reports a comprehensive study of the surface acidic properties of some commercial catalytic oxides like γ -Al₂O₃, CeO₂, ZrO₂, SiO₂, TiO₂, HZSM5 zeolite by ATPD measurements in the range of 373–873K. The ATPD profiles of the studied materials are shown in Figure 1, while their main physico-chemical properties are summarized in Table 1. Qualitative and quantitative data signal marked differences in the surface acidic properties reflecting the main physico-chemical characteristics of the various systems. In particular, γ -Al₂O₃ and SiO₂ show the maximum and minimum specific adsorption capacity respectively (Table 1), although referred to surface area, TiO₂ has the maximum surface uptake (4.7 $\mu\text{mol}/\text{m}^2$) almost two orders of magnitude larger than silica (0.07 $\mu\text{mol}/\text{m}^2$). Intermediate surface uptake of ZrO₂ (3.4 $\mu\text{mol}/\text{m}^2$), γ -Al₂O₃ (1.7 $\mu\text{mol}/\text{m}^2$), CeO₂ (0.6 $\mu\text{mol}/\text{m}^2$) and HZSM5 zeolite (0.5 $\mu\text{mol}/\text{m}^2$) are still more than one order of magnitude larger, according to the poorest surface reactivity of silica materials [5].

Table 1. List of the studied materials.

Sample	Supplier	Comm. Code	NH ₃ uptake		
			S _{ABET} (m ² /g)	(μmol/g)	(μmol/m ²)
γ-Al ₂ O ₃	Akzo Nobel	000-1.5E	260	430±30	1.7±0.1
CeO ₂	Strem Chemicals	58-1400	75	45±2	0.6±0.1
ZrO ₂	Aldrich	544760	35	120±10	3.4±0.3
SiO ₂	Akzo Nobel	Si 4-5P	380	30±3	0.07±0.01
TiO ₂	Evonik (ex Degussa)	P25	55	260±20	4.7±0.3
HZSM5	Zeolyst Int.	M80	430	230±20	0.50±0.03

In addition, considering the ceria sample as a "model system" of weak-type acidity and the evidence that its ATPD profile can be satisfactorily described by a *Gaussian* function (**Fig. 1**), we attempted to get also energy data by modelling the experimental ATPD profiles of the studied systems as linear combinations of 3 (γ-Al₂O₃, TiO₂, ZrO₂) or 4 (HZSM5, SiO₂) analogous *Gaussian* curves (**Fig. 2A**), corresponding to the energy distribution functions shown in **Figure 2B** [5,6]. The derived cumulative distributions of ammonia adsorption indicate the following acidity scale based on the average energy value (kJ/mol):

$$\text{CeO}_2 (100) < \gamma\text{-Al}_2\text{O}_3 (111) \approx \text{ZrO}_2 (111) \approx \text{TiO}_2 (117) \approx \text{SiO}_2 (118) < \text{HZSM5} (135)$$

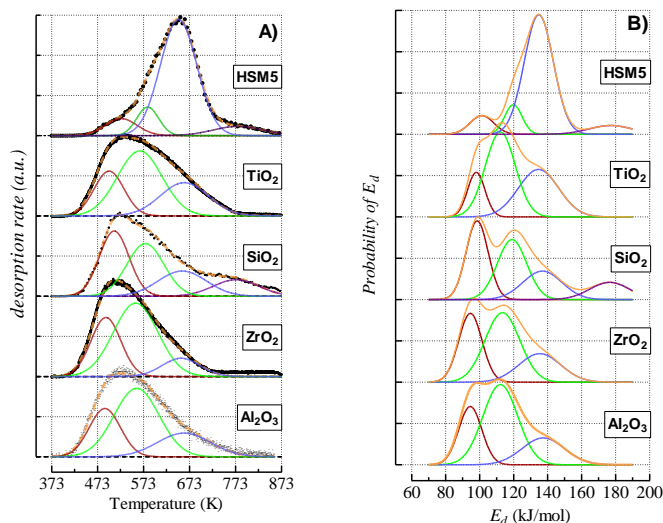


Figure 2. Deconvolution analysis of ATPD profiles (A) and energy distributions (B) of the studied materials. Dotted yellow lines depict the generated profiles as sum of the 3-4 Gaussian components, while black points are the experimental data.

Furthermore, beside matching the above acidity scale obtained by the modelling of ATPD profiles, experimental data in the dehydration reaction of iso-propyl alcohol to propylene shed lights onto the nature of surface acidic sites of the studied materials [5].

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Notes

GA-16

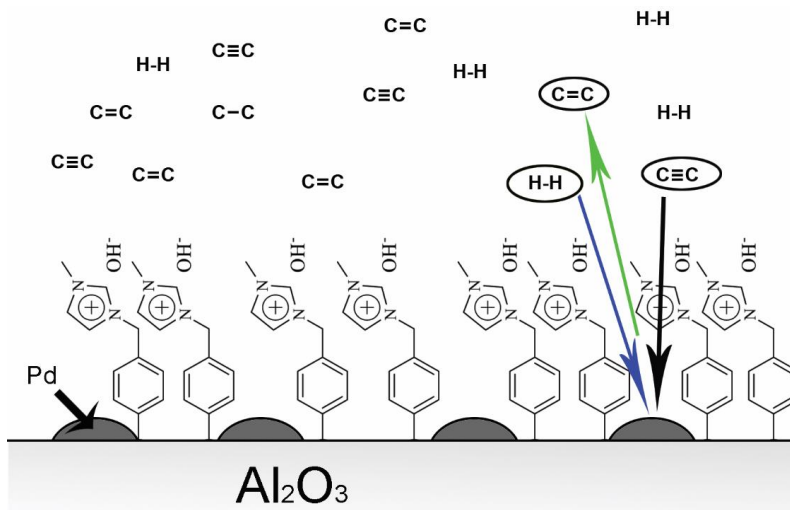
THEORETICAL AND EXPERIMENTAL INVESTIGATION OF IONIC LIQUIDS AND PD NANO PARTICLES COMPOSITE COATING EFFECT ON SELECTIVITY IMPROVEMENT OF ALUMINA BASED ACETYLENE HYDROGENATION CATALYST

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Summary

Polymerization grade ethylene is obtained by endothermic cracking, but traces amounts of acetylene, especially at low pressure process using Ziegler-Natta catalyst, influences the ethylene polymerization by poisoning the catalyst. Then, reduction of acetylene to less than 1 ppm, which is done by catalytic hydrogenation of acetylene, is an important step in polymerization of ethylene. Since the hydrogenation of ethylene is not preferred economically because of the product reduction, this process should be highly selective to partial hydrogenation of acetylene. Palladium based catalysts are capable to accomplish mentioned demands. Feeding CO or adding some metals like Ag or Ga to the catalyst can improve the selectivity.

Nowadays ionic liquids (IL) with surprising characteristics are introduced into chemical and catalytic reactions. Basically, they are low melting point and very low vapor pressure organic salts. Many transition metal complexes dissolve readily in ionic liquids, which enable their use as solvents for transition metal catalysis. This system has beneficial of high selectivity of homogenous catalyst with large interaction areas and ease of product separation. This is due to the difference between polarities of the IL and the product especially nonpolar or low polarity hydrogenated one. In summary, at the end we have a solid catalyst with the behavior of homogenous catalyst and the ability of facile decantation of the product.



P-16

ROLE OF 1-BUTYL-3-METHYLIMIDAZOLIUM-HYDROXIDE IN PREVENTING SELECTIVITY LOSS OF ACETYLENE PARTIAL HYDROGENATION OVER PALLADIUM CATALYST

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ABSTRACT

Acetylene acts as a poison in high density grade polyethylene production by Ziegler-Natta catalyst and its removal from ethylene is an essential process. Industrially, the acetylene content can be decreased to less than 5 ppm by hydrogenation which is usually carried out in adiabatic packed bed reactors. Alumina supported catalysts with 0.01-0.1% by weight palladium are mostly used for the selective partial hydrogenation of acetylene in excess ethylene feed [1, 2]. One of the important features of palladium catalyst is dissociative chemisorption of the reactants and migration of formed atomic hydrogen and carbon towards the bulk of palladium nanoparticles. Hydrogen absorption in presence of acetylene shows PdH_xC_n which can be assumed as two distinguishable phases of PdH_x and PdC_n . The ratio of these two phases alters acetylene hydrogenation rate and selectivity. As the result of subsurface phases formation, the acetylene hydrogenation activity and selectivity over palladium catalysts changes by aging towards higher activity and lower selectivity. Different promoters and additives are investigated to maintain selectivity of commercial catalysts over aging under constant stream and temperature [3-6].

By introducing ionic liquids (ILs) into catalytic reactions, new approaches towards selective partial hydrogenation of unsaturated hydrocarbons have been achieved [7]. Here BMIm[OH] is used to evaluate the effect of ionic liquid on aging phenomenon of Pd/ γ -Al₂O₃ based acetylene hydrogenation catalyst. The Catalyst has 0.05 wt.% Pd. The content of the Ionic liquid was chosen 0.5 wt.% in the prepared catalyst.

The catalytic performance was evaluated in a quartz fixed bed reactor under atmospheric pressure. The gaseous feed stream with a volumetric composition of 5% C₂H₂, 68% C₂H₄, 17% C₂H₆ and 10% H₂ was introduced into the reactor. The gas hourly space velocity (GHSV) was chosen 4500 hr⁻¹ in all reaction tests. Catalytic performances of the fresh IL free and IL impregnated Pd/ γ -Al₂O₃ is illustrated in Figure 1. As shown in this figure, addition of ionic liquid to the catalyst decreases the catalyst activity and conversion rate

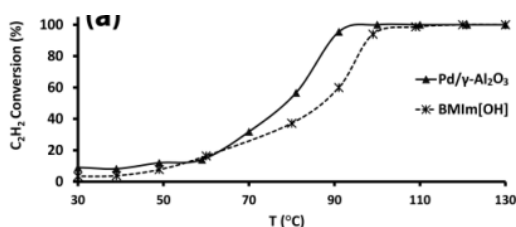


Figure 1. Acetylene Conversion of IL free and 0.5 wt.% BMIm[OH] impregnated Pd/ γ -

The catalytic performance changes by time at a constant temperature of 50% acetylene conversion, which is 80°C for ionic liquid free and 90°C for BMIm[OH] impregnated Pd/ γ -Al₂O₃ one, are shown in Figure 2. For both catalysts, acetylene conversion increases by time until a steady conversion is achieved, which is 92% for Pd/ γ -Al₂O₃ and 87.75% for BMIm[OH] impregnated Pd/ γ -Al₂O₃. But Ethylene selectivity of ionic liquid loaded catalyst is almost higher than ionic liquid free Pd/ γ -Al₂O₃.

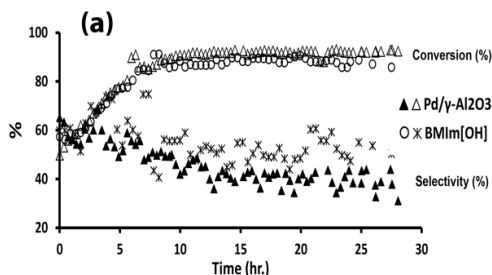


Figure 3. Conversion and activity improvement of aged catalysts after 30 hr. at steady state of temperature and feed composition

As shown in figure 3, The ethylene selectivity of the aged Pd/γ-Al₂O₃ is dropped to 57% at 80°C, 53.5% at 100°C and is improved to 60% at 100°C compared to fresh one. However, the ethylene selectivity of the aged Pd/γ-Al₂O₃ is almost lower than those observed for the aged BMIm[OH] impregnated catalyst which is shown in figure 3(down-right chart).

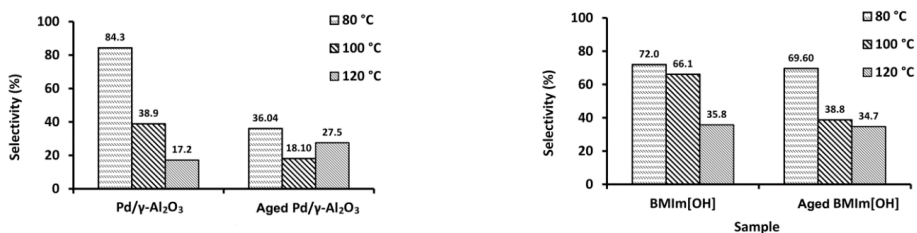


Figure 3. Ethylene selectivity of fresh and aged Pd/γ-Al₂O₃ (left) and IL impregnated Pd/γ-Al₂O₃ (right)

Activation Energy of partial and complete hydrogenation of acetylene on ionic free and ionic liquid loaded Pd/γ-Al₂O₃ catalysts is given in Table 1. Catalytic activity improvement of ionic liquid free Pd/γ-Al₂O₃ by aging is contemporaneous with degradation of complete hydrogenation activation energy which results to ethylene selectivity drop. Ionic liquid loading improves the activation energy of complete hydrogenation by aging which leads to maintain higher selectivity.

Table 1 Activation Energy (Kj/mol) of partial and complete hydrogenation of acetylene on IL free and IL impregnated Pd/γ-Al₂O₃ catalysts for fresh and aged samples

		C ₂ H ₂ +H ₂ →C ₂ H ₄		C ₂ H ₂ +2H ₂ →C ₂ H ₆	
		fresh	aged	fresh	aged
Pd/γ-Al ₂ O ₃	IL free	20.97	54.04	112.5	48.2
	IL loaded	39.5	27.7	61.71	75.46

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Notes

GA-17

BIO-WASTES VALORISATION FOR THE PRODUCTION OF PLASTICS AND CHEMICALS

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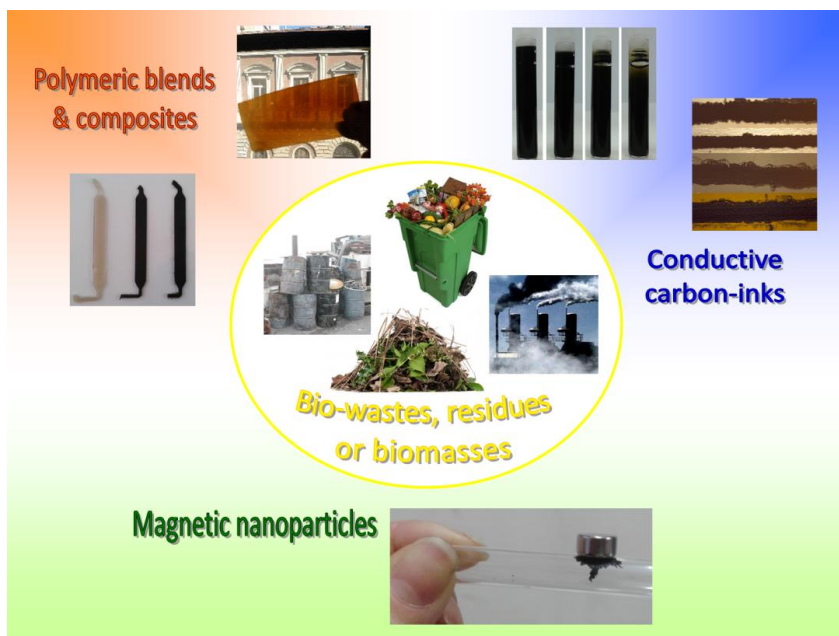
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Summary

Enormous amounts of organic waste are generated in the harvesting, processing and use of agricultural products, including food and beverages. In developed countries, additional waste is generated when food is discarded. The second generation bio-based economy is founded on the full utilisation of agricultural biomass and wastes for the production of fuels and chemicals by employing green and sustainable chemistry. Biomass is essentially a rich mixture of chemicals and materials that can be extracted for use or that can be converted into other useful products including high value chemicals. The aim of the project is the valorisation of different, common and easily available biomasses and bio-wastes in order to develop chemicals suitable for application in various fields with high technological interest.

Chemicals obtained after basic hydrolysis of bio-wastes, processed in a pilot plant, are used to produce plastic materials, obtained as blend or composites using two different synthetic co-polymer and various waste-derived organic substances. Two methods for the production of these materials are investigated and studied: casting films and extrusions process.

Furthemore, the magnetic and electric properties of materials prepared using different wastes and residues is studied along with (i) the preparation of magnetic iron oxides nanoparticles, functionalized with bio-wastes chemicals, tested in wastewater treatments, and (ii) the preparation and characterisation of conductive inks based on a carbon obtained as by-product of an innovative method to convert not-purified natural gas into hydrogen.



P-17

URBAN COMPOSTED BIOWASTE-BASED MAGNETIC MATERIALS FOR ENVIRONMENTAL APPLICATIONS

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ABSTRACT

In recent years, the synthesis of magnetic nanoparticles has been intensively developed not only for their unique magnetic properties, but also for widespread applications in several technologic fields including biosensing, catalysis, drug delivery systems or waste-water treatments (i.e. remediation of (in)organic contaminants and disinfection of groundwater) [1]. In this context, magnetic materials consisting of iron oxide particles (typically magnetite and maghemite) dispersed in and/or stabilized by a polymeric matrix, have received great attention as a new generation of magnetic stimuli-responsive materials that combine the advantages of both components [2-4].

The preparation method of these magnetic nanomaterials plays a key role in determining the particle size and shape, size distribution and surface chemistry as fundamental characteristics in some application fields [5]. In addition, the preparation method also determines the degree and distribution of structural defects or impurities present in the particles [6].

Numerous chemical methods can be used to synthesize magnetic nanoparticles as microemulsions, sol-gel syntheses, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow injection syntheses, and electrospray syntheses. The first main chemical challenge consists of defining experimental conditions, leading to a monodisperse population of magnetic grains of suitable size. The second critical point is to select a reproducible process that can be industrialized without any complex purification procedure [7]. Therefore, the simplest and most efficient chemical pathway to obtain magnetic nanoparticles is the chemical coprecipitation technique of iron salts [8,9].

The main advantage of the coprecipitation process is that a large amount of nanoparticles can be synthesized, but the control of particle size distribution is limited. In general, the addition of chelating organic anions (i.e. carboxylate or hydroxyl-carboxylate species) or polymeric complexing agents (such as chitosan, dextran, starch, or polyvinyl alcohol) during the formation/precipitation of magnetite can both favor the nanoparticles size-control as well as enhance the magnetite stability, preventing the iron oxides-based magnetic nanoparticles (m-NPs) aggregation and their oxidation into the non-magnetic hematite.

As widely discussed in the literature, the valorization of urban and/or agricultural biowastes into chemicals (re-entering them into the economic cycle) is becoming an increasingly important issue which catch the attention of worldwide experts [10]. In this context, Bio-Based Substances (BBS) isolated from urban biowastes [11] and Chitosans (biopolymers derived from fish industry wastes) [12] are considered an interesting green alternative to standard stabilizing agents for the production of magnetic composites. The morphology of such hybrid nanoparticles was evaluated by transmission electron

microscopy (TEM), by scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS) and by atomic force microscopy in the intermittent-contact mode (AFM-IC), whereas gas-volumetric N₂ adsorption/desorption experiments were performed for estimating the surface area and materials porosity. Vibrational properties of the particles were investigated by means of FTIR spectroscopy, whereas the identification of the crystalline phases produced were carried out by X-rays diffraction (XRD). Thermo-gravimetric analysis on-line coupled with FTIR detector (TGA-FTIR) was performed in order to evaluate the magnetite/coating ratio. Finally, surface and bulk magnetic properties were assessed by means of magnetic force microscopy (MFM) and by magnetization measurements, respectively.

The application was investigated in heterogeneous Fenton and photo-Fenton degradation processes for wastewater treatments. Experiments were performed taking caffeine as reference of the new class of emerging pollutants (EPs) in order to verify the wastewater purification capacity of nanoparticles containing BBS (MB). The pyrolysis of the hybrid magnet-sensitive nanoparticles containing both BBS (MB) and Chitosan (MC) permitted to obtain carbon coated magnetic nanoparticles able to adsorb non polar contaminants (such as anthracene and naftalene) from aqueous media. Promising results were reached, suggesting their industrial feasibility.

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Notes

GA-18

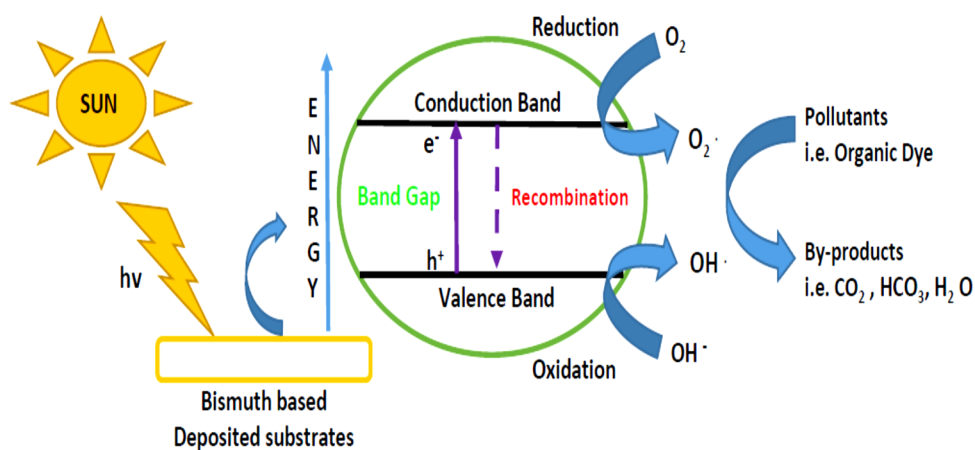
BISMUTH BASED PHOTOCATALYTIC NANOMATERIALS FOR WATER TREATMENT

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Summary

The research activity concerns the modification of bismuth based photocatalysts for improved activation in visible/solar light as well as the evaluation of photocatalytic process under varying parameters that have a high relevance from the industrial and environmental point of view. In particular medium of photocatalyst in interaction, treatment of mixed pollutants with varying chemical behaviors, loaded quantities and most importantly final composition of treated water and photocatalyst after photocatalysis are targeted and investigated. Considering all this, tests will focus on the investigation of photocatalytic performance by selecting textile dyes of different chemical compositions, to be degraded separately and in combine, with different pH and concentration. For a thorough investigation, post analysis of the treated water and photocatalyst is performed, that help in understanding the mineralization of pollutants, stability and reuse of photocatalyst. Besides evaluation with bulk material, a new method is developed by introducing bismuth nanoparticles into sintered silica filter, for the comparison in all manner i.e. interaction with pollutants, photocatalytic effect, material cyclic stability, recovery or reuse.



P-18

DEPOSITED Bi_2O_3 THIN FILMS ON SINTERED SILICA SURFACE FOR PHOTOCATALYTIC WATER TREATMENT

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ABSTRACT

Bismuth oxide (Bi_2O_3) thin films were deposited on sintered silica surface by the spray pyrolysis method using bismuth acetate as the precursor salt. Spray pyrolysis enables uniform film distribution on sintered silica. The films were characterized by X-ray diffraction (XRD) to investigate the obtained Bi_2O_3 phase, UV-vis diffuse reflectance spectroscopy (DRS) to obtain the energy band gap, and Field Emission Scanning Electron Microscopy (FESEM) to study the morphological structure. XRD pattern revealed that obtained phase of films is tetragonal β - Bi_2O_3 , by using DRS results the calculated energy band gap is 2.4eV and FESEM images show porous flowery structures. Furthermore the heterogeneous photocatalytic activity of the films was investigated by introducing the deposited silica filters into organic dyes solution and irradiating in UV and visible light for photocatalyst activation. Bi_2O_3 thin films shown good photocatalytic activity showing that (i) spray pyrolysis is a promising deposition method and that (ii) deposited silica filters are suitable support to promote effective interaction of photocatalyst with dye molecules while avoiding the problem of photocatalyst powders suspension in dye solution. Improved photocatalytic activity in visible light proves Bi_2O_3 thin films for sustainable water treatment and related applications.

Notes

GA-19

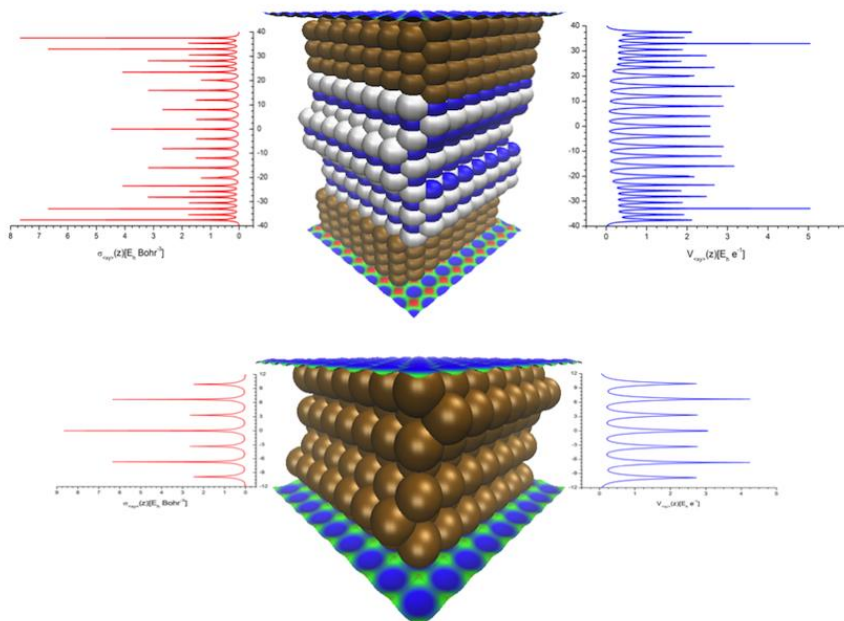
PROPERTIES OF NICKEL (100) SURFACE SUPPORTED BY TITANIUM NITRIDE: A DFT INVESTIGATION WITH LCAO APPROACH

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Summary

The PostDoc project involves several topics about the study of the crystalline structures with DFT methods, using the linear combination of atomic orbitals LCAO approach. Particular attention is dedicated to research of structured materials (slab, rod and nanocrystal surfaces) of transition metal oxides, nitrides and carbides, investigating their physical properties. These materials are modelled as periodic and molecular systems and different methods to calculate and analyse the wave function are developed. The atomic structures, the optical and electronic properties are computed comparing the simulation with experimental results. The atomic layer deposition processes, atom absorptions and material adhesions are taken into account and energetic estimates of these reactions are calculated. In this way a Nickel catalyst is studied in presence of different supports: Titanium Nitride, Titanium Carbide and TiO2 Anatase. In fact the simulations are able to calculate the electronic structures of these materials, varying the nature of chemical substrates. A vibrational analysis is doing in order to compare the simulations with spectroscopic data. Moreover the Electron Localized Function (ELF) and the Maximum Probability Domains (MPD) are computed. These last two methods are well consolidated in a large class of materials like the inorganic oxides, or biological molecules, giving wide information about the chemical nature of bond in terms to correlate these calculations with catalytic behaviour of different supports.



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PROPERTIES OF NICKEL (100) SURFACE SUPPORTED BY TITANIUM NITRIDE: A DFT INVESTIGATION WITH LCAO APPROACH

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ABSTRACT

Lignin, after the cellulose, is the second abundant available biopolymer in nature. Lignin from biomass, after depolymerization process, can become a sustainable source of aromatic compounds in a perspective of a "green chemistry". The strategy to realize catalysts, based on cheap and readily available metals, represents one of more suitable ways for the optimization of the hydrogenolysis reaction. A sustainable composite of Nickel (Ni) supported by the Titanium Nitride (TiN) is employed as catalyst for the hydrogenolysis of aryl ethers, a model for lignin. The catalytic activity of the new material during hydrogenation reactions is proven to be superior to that of either component alone; indeed, in presence of the TiN support, different aryl ethers could be more efficiently converted into aromatic compounds and cycloalkanes[1].

The role of the support in these catalytic processes is still not completely clarified and the theoretical investigations are helpful, highlighting the chemical and physical properties of the surfaces; indeed both cases, Ni and TiN-Ni, have been studied by ab-initio calculations using density functional theory (DFT) with LCAO approach in the attempt to understand the electronic description of the two systems and the possible correlation with the enhanced catalytic activity dues to the support presence.

The surfaces of the catalyst Ni (100) and of the support TiN (100) have been modelled as 2D periodic slabs using respectively the own cell parameter. The supported catalyst TiN-Ni (100) surface is also modelled as 2D periodic slab but the cell parameter used has been imposed from the crystal structure of the support TiN. In effect the TiN-Ni structure is resulted as an epitaxial growth of the metallic Ni deposited over a TiN substrate. The deposition occurs layer by layer, relaxing the whole system after each new Nickel layer has been deposited.

The experimental evidences in literature, performed using the Pulsed Laser Deposition technique, have corroborated the crystal orientation index chosen in epitaxial system. The orientation relationship of Ni (100) over TiN (100), so-called "cube-on-cube" relationship, is favourite, nevertheless the remarkable mismatches in the cell parameters of catalyst and support [2].

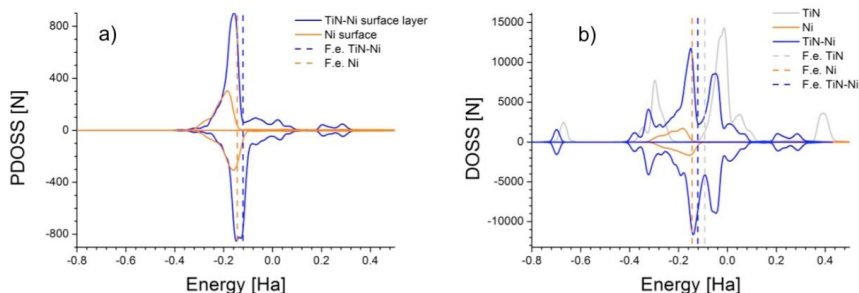


Fig.1 a) Density of states of TiN, Ni and TiN-Ni. b) The surface Nickel projected DOSS of TiN_Ni and Ni systems.

All simulations were performed with the CRYSTAL14 package. A pure GGA (PBE) functional has been adopted for an all electron calculations together with a triple ζ quality basis set.[3]

The wave functions calculated for all systems have been used to get some physical properties, e.g. charge density, potential, density of states and band structure.

The results have been analysed in the perspective to compare the supported and unsupported catalyst properties. The band structures DOSS and PDOSS (Fig.1), projected in a region near to the surface layer of Ni, show a difference between the two cases.

The variations of the isosurface values (Fig.2) of the charge densities and the potential surface, at fixed z-distance from the Ni nuclei coordinates, in the surface layer are observed.

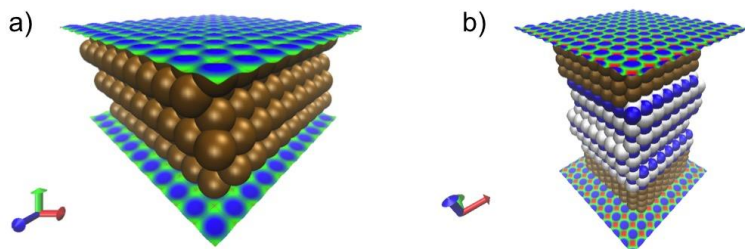


Fig.2 The Ni a) and TiN-Ni b) slabs and the relative charge isosurfaces calculated at z-fixed distance. The different colours surfaces represent the potentials (blue positive, green neutral and red negative).

The trends of the integrated charge density and potential over xy plane along z-direction (Fig.3) have been computed for all systems in order to characterize the catalytic exposed surfaces.[4]

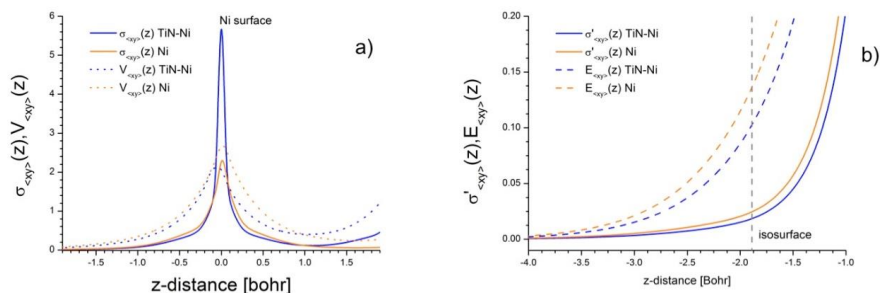


Fig.3 a) The charge densities [e/Bohr³] and potentials [E_h e⁻¹], with the relative first derivatives (b), for the Nickel surface atoms in supported and unsupported catalysts.

Moreover the largest components of the selected eigenvectors, corresponding to the AO of the Nickel, are evaluated to extract the relative eigenvalues of energy. They represent the orbital energies of the core level in attempt to calculate a shift between the supported and unsupported case. This last analysis, applying the Koopmans theorem, will provide a direct comparison with the XPS experiments, helping in the interpretation. The XPS experimental result performed on real sample are ongoing.

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Notes

GA-20

DESIGN OF LI-O₂ CELLS AND INVESTIGATION ON THEIR INTERFACIAL CHEMICAL REACTIONS BY MEANS OF A MULTI-TECHNIQUE CHARACTERIZATION APPROACH

Daniela Giacco^a

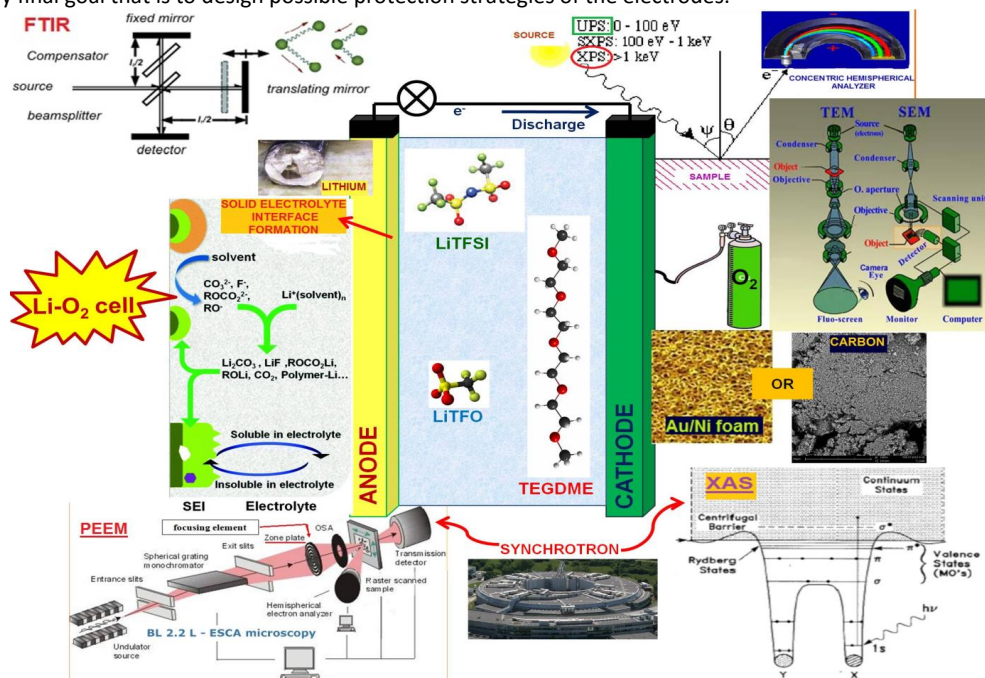
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Summary

My project involves the study of Li-O₂ cells with a lithium anode, an aprotic electrolyte and a porous cathode. A metal foam, electrochemically and chemically inert, replaces the usual carbon paper that is known to deteriorate upon cycling. Electroactive catalysts, deposited onto the metal foam, are used to promote the ORR or OER reactions. Cell performances are tested by galvanostatic cycling and voltammetry to evaluate the activity of the catalysts, the role of the metal foam and the stability of the electrolyte. My research strategy is based on the elimination of any carbon-source besides the electrolyte components in order to monitor the degradation of the solvent and distinguish its products from those of the carbon paper referring to previous data collected for "traditional" cells.

Post mortem analyses of the electrodes are carried out by various techniques taking advantage from their different selectivity, sensibility and resolution. In particular the S.E.I. grown on the anode and the composition of the cathode surface are studied by means of XPS and UPS whereas the core regions via FTIR or XRD. TEM and SEM imaging are used to investigate the growth and the decomposition of lithium oxides, organic by-products and the morphological changes of the electrodes. XAS (NEXAFS and EXAFS) and PEEM measurements are planned in synchrotron facilities to confirm XPS results, to probe the local order of the metallic cathodes and to map the degradation sites on the electrodes. The latest results are functional to my final goal that is to design possible protection strategies of the electrodes.



P-20

CHARACTERIZATION OF CATHODES FOR APROTIC LI-O₂ CELLS BY MEANS OF XPS, FTIR AND ELECTRON MICROSCOPYDaniela Giacco,^a Andrea Giacomo Marrani,^a Sergio Brutti,^b Marco Carboni,^a Robertino Zanonì^a

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ABSTRACT

Li-O₂ cells are at the cutting edge among the devices for energy accumulation. Due to their especially high theoretical specific energy^[1,2,3] they could profitably be applied in those areas where the common Li-ion batteries are at the present less likely to succeed (e.g. electric transport). Moreover, they prove competitive thanks to the lightness of the electrode materials and to the possibility of utilizing oxygen, the reactant reduced at the cathode during discharge, directly from the environment.

The cathode is usually a carbon paper which has various useful qualities, except its low inertness to chemical oxidative attacks from reduced forms of oxygen originating during discharge (O₂⁻, O₂²⁻, LiO₂, Li₂O₂)^[1,2].

Lithium is usually adopted at the anode and it also causes operational issues. However it has been rarely replaced because of its unequalled lightness^[1,2].

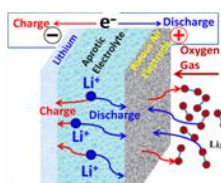


Figure 1. Diagram of operation of an aprotic Li-O₂ cell.

The electrode reactions occur at the interface between the cathode and an aprotic solvent (e.g. an ether) in presence of a lithium salt.

The reduction of oxygen to lithium peroxide (Li₂O₂) and the decomposition of the latter releasing oxygen take place during discharge and charge, respectively. These processes are called ORR (Oxygen Reduction Reaction) and OER (Oxygen Evolution Reaction) and their mechanisms are still uncertain^[1,4,5,6,7,8].

During operation of the cell, it is desirable to promote Li₂O₂ nucleation and growth in the pores of the cathode, limiting that of lithium oxide (Li₂O), which is unwanted due to its only partial dissolution upon charge. Chemical oxidation of carbon paper and solvent to lithium carbonate, lithium alkylcarbonates, organic carbonates and alkylcarbonates, carboxylates etc. must be limited.

The recent experimental effort of my research group has been focused on the assembly of two sets of batteries working with LiTFO (i.e. *lithium trifluoromethanesulfonate*) and LiTFSI (i.e. *lithium bis(trifluoromethane sulfonyl) imide*) dissolved in TEGDME (tetraethylene glycol dimethyl ether) as electrolytes, on their controlled-potential galvanostatic cycling and on the characterization of the cathode materials by means of X-ray Photoemission Spectroscopy (XPS), Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM).

Sensitivity to samples surface has been guaranteed by XPS. Transmission FTIR measurements allowed both to confirm the results provided by photoemission spectroscopy and to identify compounds grown in the pores of the cathodes. Furthermore, the morphological changes of the electrodes during galvanostatic cycling have been monitored by means of electron microscopies.

Our work on the systems with LiTFO^[9] was aimed at obtaining information on the interactions between the carbon paper, the solvent and the lithium salt, on their possible degradation and on the reversible formation of lithium oxides. In this context we wanted to define the most suitable working potential range. A too low-voltage discharge is

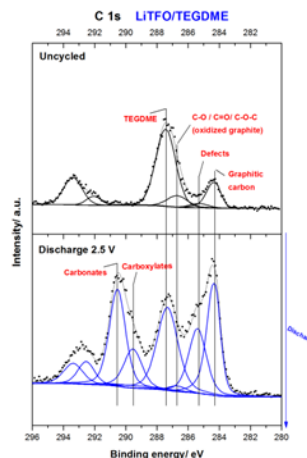


Figure 2. Examples of curve fitting of C 1s regions of XPS spectra. Samples to which they refer are a cathode uncycled and the same after discharge to 2.5 V in a cell with LiTFO/TEGDME as electrolyte.

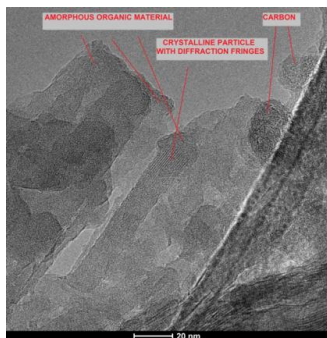


Figure 3. Example of TEM image. We can observe the materials at the cathode of a cell discharged to 2.5 V with LiTFO/TEGDME as electrolyte.

likely to extend the conversion of Li_2O_2 to Li_2O and to promote the oxidative attacks to the carbon paper and the solvent. The most desirable charge cut off potential allows an efficient reconversion of Li_2O_2 while at the same time limiting energy losses.

Afterwards, we planned to assess whether LiTFSI can be more or less compatible than LiTFO with the carbon paper and the solvent in terms of recorded discharge capacity and reversibility.

As to the batteries working with LiTFO/TEGDME, 2.5 V has resulted the best discharge cut off potential because it allowed to obtain a favorable $\text{Li}_2\text{O}_2/\text{Li}_2\text{O}$ ratio, to limit the degradation of the carbon paper and the solvent and to avoid irreversible structural damage to the cathode.

We also found that charging the cell up to 4.6 V maximizes the oxygen evolution while allowing a full compositional and morphological recovery of the cathode material due to oxidation of the degradation products to CO_2 .

The batteries working with LiTFSI/TEGDME proved less efficient. Their discharge capacities at the same voltages were approximately 25-30 % lower than those recorded with LiTFO. The low capacities during discharge and charge can be associated to a poor formation of lithium oxides and a limited O_2 evolution. This latter phenomenon is then associated to a scarce reversibility and high overvoltages.

We speculated the OER is possibly limited by a layer of organic carbonates and alkylcarbonates, originated from the degradation of TEGDME, thicker and more resistant to oxidation than that formed on the cathode surface with LiTFO. We believe that this layer was grown at the interface between Li_2O_2 particles and the electrolyte solution and could contribute to the rise of the overvoltage hindering the oxygen release from Li_2O_2 . According to these results, TEGDME seems less compatible with LiTFSI than with LiTFO.

Nevertheless, we are still interested in the use of LiTFSI salt coupled to TEGDME because our FTIR results did not show the presence of Li_2CO_3 often reported in the literature^[3,6,10,11,12] as a degradation product grown at the interface between carbon and Li_2O_2 .

Therefore, we concluded that LiTFSI could be more compatible with the carbon paper than LiTFO.

For these reason the use of LiTFSI will still be one of the objects of the investigations in my Ph.D. studies.

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Notes

GA-21

SHELL-ISOLATED NANOPARTICLE-ENHANCED RAMAN SPECTROSCOPY FOR STUDYING FISCHER-TROPSCH

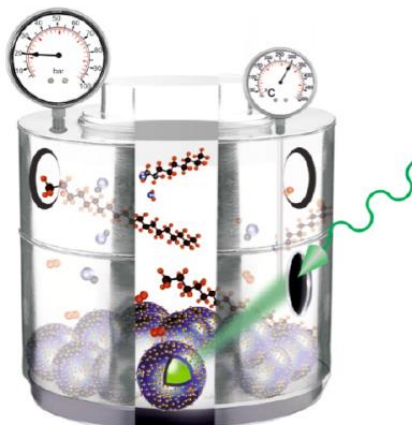
Thomas Hartman
(Bert M. Weckhuysen)
Utrecht University

Summary

Heterogeneously catalyzed reactions typically take place at the solid/gas or solid/liquid interface. To characterize the binding and reaction of surface adsorbates, in situ techniques are needed that can identify surface species. Surface enhanced Raman spectroscopy (SERS) is a surface sensitive technique and is therefore a valuable method to study adsorbed species on a catalyst. For this technique, Au and Ag nanoparticles can be used to significantly enhance the electromagnetic field in the vicinity of the particle.[1]

Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) is a relatively new SERS-based technique that makes use of gold or silver nanoparticles coated by a thin (<5 nm) oxide layer.[2] This thin oxide layer prevents the sintering of the noble metal nanoparticle and blocks the direct chemical interaction of it with analytes. The electromagnetic enhancement is only slightly reduced by the coating.

Shell-isolated nanoparticles (SHINs) will be implemented to increase our understanding of the effect of size, shape and structure of cobalt nanoparticles on their performance in the Fischer-Tropsch reaction (FTR). Various sizes and shapes of gold nanoparticles with different oxide coatings will be synthesized and subsequently tested for their enhancing properties in SHINERS. Pre-synthesized cobalt nanoparticles will then be deposited onto these SHINs. These Co/oxide/Au systems will be investigated as a function of temperature, time and pressure to study the types of adsorbates and intermediates during the FTR.



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Notes

GA-22

CHARACTERIZATION OF ACIDIC SITES IN ZEOLITES USING SOLID-STATE NMR SPECTROSCOPY

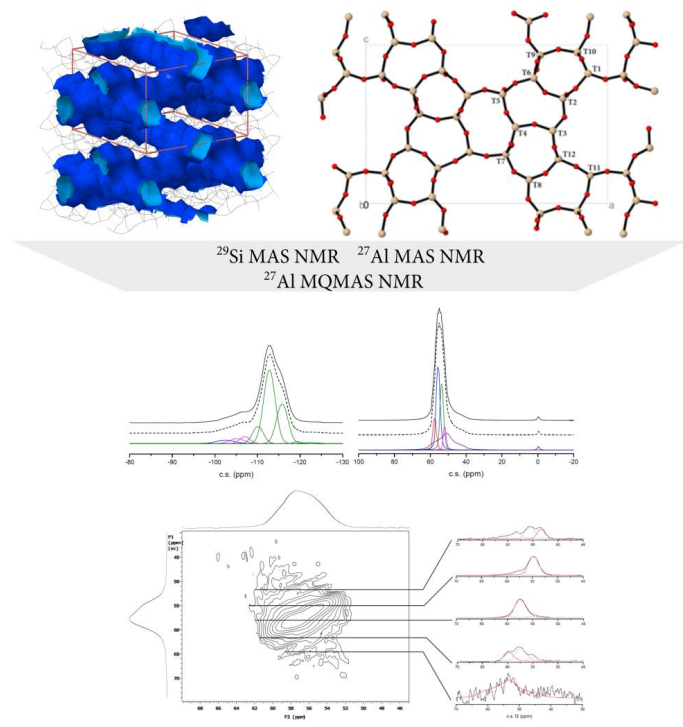
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Summary

Having regularly shaped channels or pores of molecular dimensions that run through the material and catalytically active sites within them, makes zeolites to widespread industrially used shape-selective, solid-acid catalysts, for example in the field of methanol-to-hydrocarbon conversion. Despite being used for several decades and produced on a million tons scale per year, not all the aspects and properties are yet well understood. For example, recently, the localization and distribution of aluminium atoms in the framework structure have been recognized as a substantial factor for activity and selectivity. To get a deeper understanding and insight into these fundamental characteristics, solid-state NMR spectroscopy is a powerful tool for investigating structural properties of zeolites. This is mainly due to the ability of NMR to investigate different geometries and local orderings and to probe specific elements (e.g. ¹H, ¹³C, ²⁹Si, ²⁷Al) and their mutual connectivities on a short-range scale.



In this PhD project the focus is on the identification, characterization and assignment of catalytic active sites of different ZSM zeolites. In different subprojects the location and alteration of these sites and the distribution of the aluminium in the zeolite structure of differently synthesized, degraded, regenerated, and transition metal modified zeolites are investigated. For this purpose modern solid-state NMR techniques are employed.

Figure: Characterization of Al sites in a ZSM-5 zeolite via solid-state NMR techniques.

P-22

LOCALIZATION OF ALUMINIUM SITES IN ZSM-5 ZEOLITES FOR MTH CONVERSION

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ABSTRACT

With having a high energy density and a quite easy transportability, liquid hydrocarbon fuels are still one of the most important energy resources. For the production of consumer goods, olefins play a similar role. Due to the fact that the oil reserves are getting smaller and for being independent from oil suppliers and volatile oil prices, alternative carbon sources, such as biomass, coal, natural gases and CO₂ have to be considered for a future fuel and olefin production. One possible process for this purpose is the methanol-to-hydrocarbons (MTH) process which can be differentiated due to the preferential product to the methanol-to-gasoline (MTG) and methanol-to-olefins (MTO), depending on the choice of catalyst and reaction conditions. One type of catalyst employed for these processes are the zeolites. Those are crystalline aluminosilicates built from corner-sharing SiO₄ and AlO₄ tetrahedra. Exclusively constructed with SiO₄ the result is a neutral structure, whereas partially replacing Si by Al will create a charge deficit that must be balanced by cations. When these charge-balancing cations are H⁺, a material with Brønsted-acid properties is obtained.

The zeolite ZSM-5 which was discovered in 1972 [1] is one catalyst of choice when it comes to MTH conversion. It is present in the MFI structure which has 12 crystallographically distinct T-sites and consists of parallel and straight 10-MR channels (diameter ca. 5.5 Å) building up a 3D network with sinusoidal ten-membered rings channels. At the intersections there are large spherical spaces with a diameter of 10 Å [2].

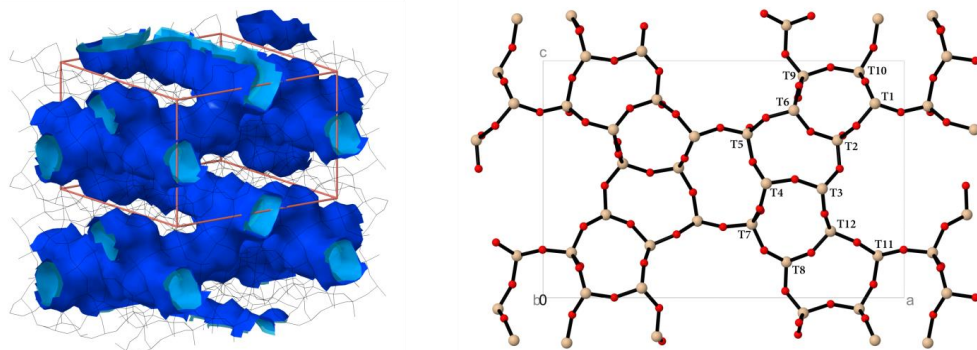


Figure 4: Framework structure and coloured channel system (left), and a view on the (010) plane and the 12 crystallographically distinct T-sites (right) of the MFI structure.

ZSM-5 is for instance used in a fluid-bed version process with temperatures around 400°C and a pressure around 20bar [3]. During the industrial operation of a ZSM-5 catalyst, the material degrades as a result of deposition of unwanted hydrocarbons and coke inside the porous structure [4, 5]. Therefore, in the process section parallel reactors are built in allowing for intermittent regeneration. In order to do this reactivation of the zeolite's active sites, the formed coke has to be burned off or the zeolite is treated with steam, for example at 500°C. However, after such a steam treatment the activity cannot be restored completely [6].

For ascertaining the reason for this loss of activity and to understand the process during the steam treatment nuclear magnetic resonance (NMR) spectroscopy is one method of choice. NMR is a powerful tool when it comes to investigating structures and dynamics of solid state and especially amorphous materials. It is not only element selective, but also offers the possibility to analyse distinct structural elements and their near field due to different electronic and magnetic interactions of the nuclear spins with their surroundings. By employing modern solid-state NMR methods like for example MAS, CP MAS and MQMAS NMR it is possible to get a deeper insight into the species, location and distribution of Al atoms in the zeolite framework structure. This is of certain interest since not only the pore structure, acid strength and acid amounts of the zeolite affect the catalytic properties but also, the location and distribution of Al atoms have been recognized as an important factor for activity, selectivity and lifetime. Because of this there are some points of particular interest: In which way are the Al atoms distributed on the distinct T-sites? Which effect has this distribution on the catalytic behavior? Can the distribution be affected by different synthesis methods and how do the Al-sites alter during a regeneration treatment like steaming?

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Notes

GA-23

UNDERSTANDING REACTIONS MECHANISMS

Giada Innocenti
(Fabrizio Cavani)

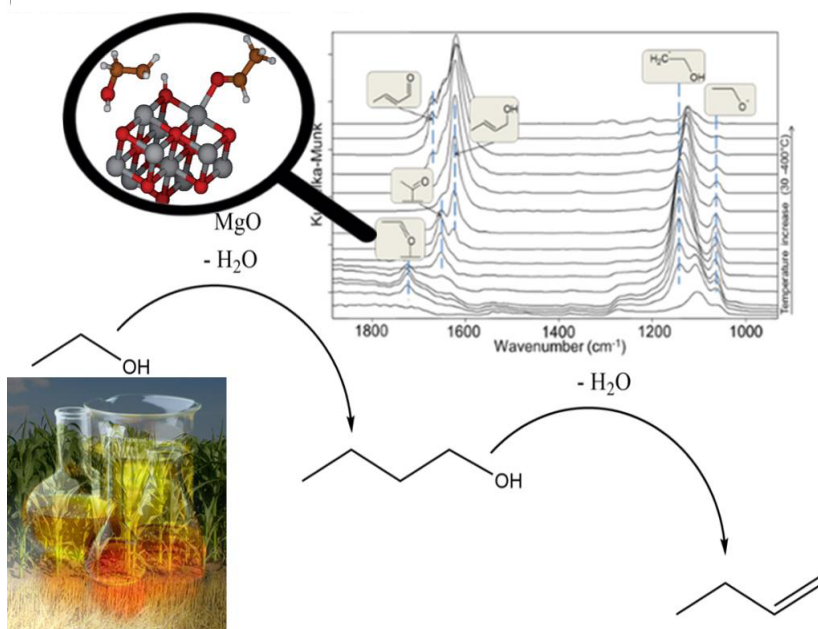
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Summary

The research activity will be aimed at studying the interaction between catalyst surface and reactants under reaction conditions for selected reaction types. More specifically, the research project is aimed at investigating the reaction mechanism for gas-phase catalytic reactions by combining in-situ spectroscopic methods (Diffuse Reflectance Infrared Spectroscopy and Raman Spectroscopy), ex-situ structural, morphology and surface characterization of catalysts, and reactivity experiments; also DFT calculations will be eventually used.

Classes of reactions which will be investigated include:

- (a) The Guerbet reaction carried out in the gas-phase, which allows to upgrade short-chain alcohols into higher alcohols. Classes of catalysts which catalyze this reaction in the gas-phase are based on mixed metal oxides with bifunctional characteristics, such as catalysts based on alkaline earth oxides doped with transition metal ions.
- (b) The dehydration of bio-alcohols to olefins. Dehydration may occur in the gas-phase either under basic-catalyzed conditions, or with acid systems, or even by means of radicalic reactions. The type of mechanism occurring on different catalysts will be investigated, with the aim of understanding under which conditions one mechanism may become preferred over another one.



P-23

ETHANOL TO CHEMICALS: A BETTER UNDERSTANDING OF THE LEBEDEV REACTION

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ABSTRACT**Introduction**

Transformation of (Bio) alcohols into chemicals is an undoubted protagonist on the sustainable chemistry scenario [1]. Nevertheless, an important reaction such as the conversion of ethanol over basic oxides to obtain butadiene is still carried out based on empirical conclusions since the proposed mechanism has not yet been definitely proven. In this study we discerned the different route leading to 1-butanol, butadiene or ethylene when ethanol reacts on MgO.

The industrial catalysts for the Lebedev reaction are based on MgO and SiO₂ and their preparation mode and composition are considered to be crucial factors for their performance. To date a Mg/Si ratio equal to or higher than unity is thought to be essential to achieve high butadiene selectivity. [2]

By the way with the previous tests about the mechanism we saw that the Lebedev reaction might be carried out (with low efficiency) even with a purely basic catalyst. Because of this the sol-gel was chosen as synthesis method in order to obtain a material where synergic effects between the two metal cations are promoted while the influence of the Mg/Si ratio was studied. We discovered that a very small amount of Si can significantly improve the performance according to acidic/basic catalyst requirements.

Materials and Methods

For the mechanism study purpose, MgO catalyst was prepared by precipitation from an aqueous solution of Mg(NO₃)₂·6H₂O. The solid was calcined at 450 °C for 8 h in air. For the catalysts optimization materials with various Mg/Si ratio ranging from 1 to 30 were prepared by the sol-gel method from an aqueous solution of Mg(NO₃)₂·6H₂O. The obtained gels were dried at 120 °C overnight and calcined at 600 °C for 5 h. Catalysts synthesized by sol-gel method shows a lower surface area than the ones synthesized by

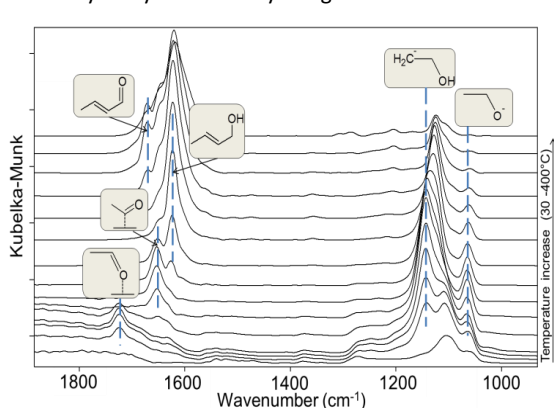


Figure 4 In situ diffuse reflectance infrared spectra of ethanol transformation over MgO from 30 to 400 °C.

precipitation. Reactivity experiments were carried out using a continuous flow glass reactor. Inlet feed molar ratio was constant. Downstream products were monitored by on-line gas-chromatography analysis.

DRIFTS-MS: In all cases the sample was pre-treated at 450 °C in a He flow and then cooled down to room temperature. Ethanol was fed at 0.6 ml·min⁻¹ until saturation. After the evacuation of physically adsorbed ethanol, different temperature programs were run. Selected mass spectrometry signals (*m/z*) were monitored continuously in time and temperature. In order to understand the differences among the catalysts some pyridine adsorption experiments were carried out. After the samples pre-treatment, pyridine pulse was injected at 50 °C, then temperature was raised.

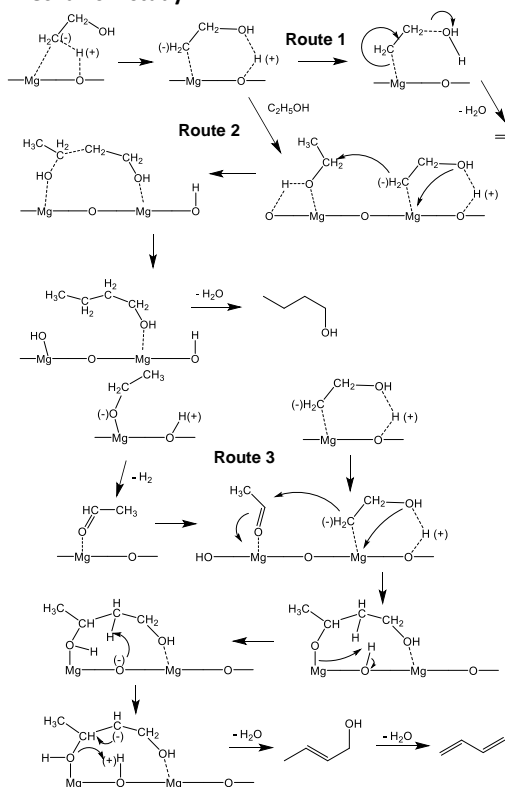
Mechanism study:

Figure 5 Suggested mechanism for the transformation of ethanol on catalysts with basic properties

The mechanism explains the formation of dehydration compounds even on purely basic materials [3].

Catalysts optimization:

The catalytic performance of mixed Mg-Si oxides is highly dependent on the synthesis method, Mg/Si ratio and experimental conditions. In general, during the characterization tests, we noticed that an increased Mg/Si atomic ratio led to a decreased surface area value. The number of acid sites per unit surface area increased up to Mg/Si = 9. A further increase in Mg/Si ratio led to a slight decrease in acid sites. From pyridine adsorption test we deduced that the acidic sites are Lewis type.

The reactivity tests showed that catalysts with a low Mg/Si ratio are more active (higher conversion) but the maximum selectivity to butadiene was seen at Mg/Si = 15. So increasing Mg content improved the selectivity to butadiene and, although the conversion decreased, the butadiene yield was slightly higher. DRIFTS experiments showed that ethanol is strongly interacting with catalysts having a low Mg/Si ratio, which induced the preferred dehydration to ethylene. Both crotyl alcohol and the carbanion were identified also with MgO-SiO₂ catalysts. This confirms that the mechanism previously proposed for ethanol to C₄ compounds is still valid with these bifunctional catalysts. Spectroscopic measurements also validated that catalysts having higher Mg/Si atomic ratio lead preferentially to butadiene [4].

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The reactivity tests, performed varying the residence time, showed that 1-butanol, acetaldehyde, ethylene and crotyl alcohol were primary products. C₄ aldehydes and C₄ olefins (butenes and butadiene) were only detected as secondary products at high temperature. In situ DRIFTS showed the evolution of the surface species with temperature (see Figure 1). In this way, it was possible to detect some surface intermediates of the ethanol transformation; these included an activated form of the ethanol (a carbanion) and an adsorbed form of crotyl alcohol. These results showed that the formation of crotonaldehyde by aldolic condensation, was not the key reaction to explain the products distribution. We proposed that crotonaldehyde is formed after crotyl alcohol; in fact, the tests carried out by feeding some of the possible intermediates showed that the alkenol has a similar product distribution to the one obtained with ethanol. This mechanism discards the key role of both acetaldol and crotonaldehyde as reaction intermediates. We have found that crotyl alcohol (see route 3 in Figure 5) is the key intermediate of the Lebedev process and precursors for butadiene formation. On the other hand, the reaction between ethanol and its activated form might explain the formation of the alcohol as a kinetically primary product (route 2).

Notes

GA-24

INTERFACIAL MOLECULAR RECOGNITION IN COMPLEX SYSTEMS: THE INTERACTION OF NANOSTRUCTURED SILICA CRYSTALS AND CELL MEMBRANE

Riccardo Leinardi

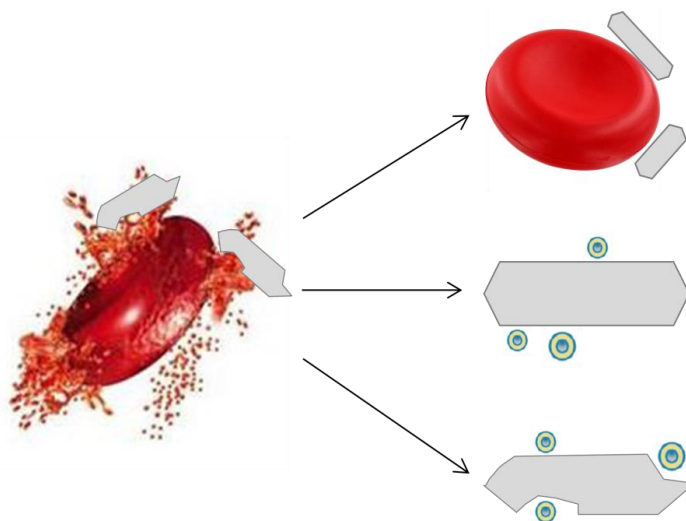
(Prof. Bice Fubini – Dott. Francesco Turci)

Toxicity and Biocompatibility of Materials – Department of Chemistry – University of Turin

The pathogenicity of crystalline silica is known from ancient times. Prolonged exposition to respirable crystalline silica dusts may lead to the development of silicosis, lung cancer and autoimmune diseases. Nevertheless, biological responses to crystalline silica dusts are extremely variable, and it is generally agreed that quartz, which is the most common crystalline polymorph, is a “variable entity” as far as its pathogenic activity is concerned.

Because of the extreme complexity of the interaction inorganic-biological systems, simple models are required to achieve fundamental insights into the molecular mechanisms involved. Recent results, obtained using red blood cells to simulate the interaction between biomembrane and respirable quartz crystals, highlighted a strong correlation between membrane lysis and the onset of an inflammatory response. Therefore, the main aim of this PhD project is advancing in the understanding of the molecular mechanisms involved in crystalline silica particle and cell membrane interaction, which are still unclear. To reduce the complexity of the system, synthetic quartz crystals with designed surface and liposomes will be used to model surface and cell membrane. This will result in four specific objectives:

1. develop a method to grow perfect quartz crystals in respirable size (both nano and micro);
2. develop protocols for obtaining membrane-models, including liposomes, red blood cell and membrane fragments, with specific and tunable properties;
3. evaluate the interaction of real crystals faces with membrane models;
4. evaluate the interaction of selected quartz crystals with cultured cell lines (e.g. A459 cells and Raw 267.4 macrophages, both involved in silica-related pathologies).



P-24

INVESTIGATION OF THE INTERACTION BETWEEN NANOSTRUCTURED QUARTZ CRYSTALS AND PHOSPHOLIPID MEMBRANES

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ABSTRACT

A large body of experimental work in the past 20 years, reported in recent reviews and books [1–6], has evidenced two main points: the crucial role played by the particle surface in triggering the adverse biological response and the extreme variability in the pathogenic potential among different sources of particulate silica [7,8]. Variability is not only the consequence of the various existing forms of crystalline silica, but is also due to (i) surface properties determined by the history of the dust, (ii) several kinds of surface features implicated in the mechanism of action, and (iii) multiple particle/biological matter interactions taking place in subsequent stages of the body reaction to silica. While amorphous silica is generally considered safe, the prolonged exposure to fine and ultrafine crystalline silica dust, particularly quartz, is known to induce severe diseases, including cancer. The main paradigm for quartz toxicity, relies on its crystal structure, that imparts to the solid a spike-shaped morphology, which may mechanically perturb bio-membranes; moreover, freshly ground quartz dust is known to exhibit surface reactivity due to the formation of surface radical species generated by the homolytic rupture of the Si-O bond in silica tetrahedrals [9, 10].

An investigation on the interaction between crystalline silica particles and red blood cells as bio-membrane model [11], has recently showed different lytic potential among several silica samples, highlighting that a specific biological answer is strongly related to the physico-chemical properties of the particles.

To overcome the intrinsic complexity of the inorganic-biological system interaction, and to achieve fundamental insights into the molecular mechanisms involved, it is pivotal the need for particle and cell membrane simple models. Therefore, we have developed an innovative approach for the synthesis of quartz crystals of respirable size (<4 μm), crystalline down to the extreme edge, as shown in fig. 1. The method employs an amorphous silica gel, obtained from 25% Na-metasilicate solution, polymerized through the use of mineral acids (HNO_3 and H_2CO_3) chosen to reduce the chemical complexity of the gel as starting phase. The advantage of using a gel during the crystallization of large crystals of sparingly soluble salts, mainly resides in the low supersaturation reached into the reaction porous medium even in the presence of high concentrated solutions. This limits the number of nuclei reaching the critical size and decreases the crystal growth rate, allowing to control the surface reaction rate [12,13]. A full characterization of the synthetic α -quartz crystals obtained (n-Qz-syn and μ -Qz-syn) was carried out. Crystal structure (XRPD), surface area (Kr-BET), surface charge (ELS), crystal morphology (SEM, TEM) and particle size (DLS) were evaluated and compared to the characteristics of a natural quartz dust, previously used in many toxicological studies.

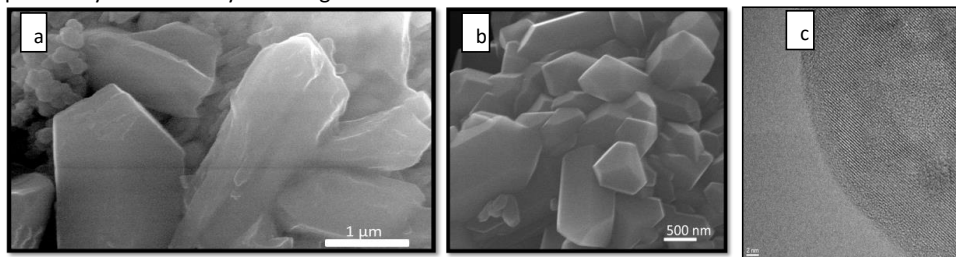


Figure 1 – Morphological characterization of synthetic quartz crystals

This method allows control on particle dispersion in biological solutions, and on the biophysico-chemical interactions that occur at the solid-bio interface.

To mimic the natural phospholipidic double-layer, we have set up a protocol for obtaining liposomes

with detailed properties (nanometric size, uni-lamellarity), used as simple membrane model. Lipid vesicles are convenient models to reduce complexity of the system, due to specific properties. Their lamellar structure resembles that of at least one model of natural membranes. Moreover, liposomes are capable of ion discrimination as cations diffuse poorly from membranes, which are permeable to monovalent anions and water. Furthermore, they swell osmotically, as do natural membrane-bound structures. The interaction between vesicles and α -quartz crystals have been investigated through a liposome leakage assay [14], in which a self-quenching fluorescent probe (calcein) is used to quantify liposomes rupture by evaluating the fluorescence increase in solution.

Results (fig. 2) highlighted that the interaction between liposomes and two as-grown quartz crystals of sub-micro (n-Qz-syn) and micrometric (μ -Qz-syn) size showed a negligible lytic activity, as previously shown using red blood cells. As for red blood cells, lytic activity significantly increased when a grinding treatment was applied to as-grown quartz crystals (μ -Qz-syn-f), and became comparable to what observed for natural pure quartz dust (Qz-f), used as positive control.

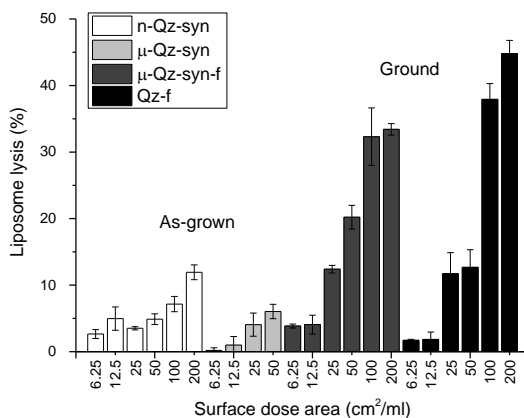


Figure 2 – Liposome lytic activity of synthetic integer or ground quartz particles.

These results indicate that surface chemistry is crucial in the interaction with bio-membrane. In fact, as is well known from the literature, the mechanical grinding of quartz crystals causes the creation of radicals at the surface, by homolytic cleavage of siloxane bridges (Si-O-Si), namely Si[•] and SiO[•]. Such this highly-reactive species are involved, at some stages, in the toxicity of crystalline silica.

The present research will proceed by the addressing the role of size and surface decoration of liposome to better understand the effect of curvature and electrostatic interactions with the quartz surface.

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Notes

GA-25

DEVELOPMENT OF NANOSTRUCTURED MATRICES FOR DRUG DELIVERY IN DERMATOLOGICAL APPLICATION

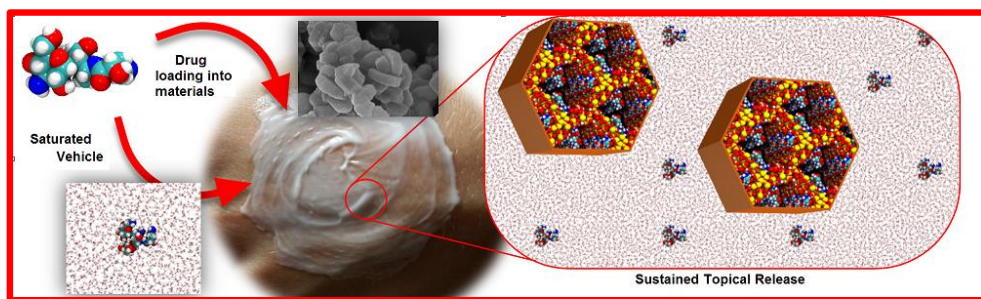
Federica Leone

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Summary

The main purpose of mine PhD research work is the development of nanostructured porous materials able to act as skin surface drug reservoir to control drug delivery in dermatological applications. Two oxidic materials were selected for this purpose. ZnO-based matrices, because ZnO can play a key role in dermatological applications both due to its intrinsic biological properties and the possibility to deliver a drug, tailoring the porosity of its structure. Mesoporous silica was also selected, since it is widely used in different administration routes as controlled drug delivery system. The research project is structured in different phases. Firstly, the porous materials are synthesized and characterized in order to elucidate their morphological and physico-chemical properties. Secondly, porous materials are loaded with drugs, using different loading techniques, such as supercritical CO₂ technique, incipient wetness method and adsorption. Drug-loaded materials are characterized in order to study the drug-material interactions and the material properties after the drug-loading treatment. Moreover, *in vitro* dissolution studies are performed in order to define the drug release kinetics from the nanostructured matrices. Finally, the last part of the project will concern the development of a semisolid pharmaceutical formulation containing the drug-loaded nanostructured materials for dermatological applications. *In vitro* permeation studies using vertical diffusion cells (Franz's cells) will be performed in order to evaluate the drug release from the pharmaceutical formulation and to assess the role of nanostructured materials as skin surface reservoir in order to obtain a control drug release over time.



P-25

DEVELOPMENT OF NANOSTRUCTURED ZINC OXIDE-BASED MATERIALS WITH TAILORED POROSITY FOR DRUG DELIVERY IN DERMATOLOGICAL APPLICATION

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ABSTRACT

Controlled drug delivery systems are one of the most promising applications in biomedical materials science. In particular, the development of nanostructured materials with tailored porosity is attracting much interest for the possibility to use them as potential drug carriers, allowing a fine control of the drug load and release kinetics [1].

Among all the several oxidic porous materials, the possibility to obtain nanostructured ZnO-based materials (NsZnO) having high surface areas have attracted increasing interest because of ZnO unique physical and chemical properties. In fact, ZnO is a multifunctional material with abundant morphologies and wide applications, from the ceramics industry to biomedicine [2]. It is a matter of fact that zinc, elemental or in its various forms (salts), has been used as a therapeutic modality for centuries, due to its biological properties, such as low toxicity, biocompatibility and biodegradability. In particular, topical preparations containing zinc oxide have been in use in several dermatological conditions, for instance in infections, inflammatory dermatoses, and as photoprotecting and/or soothing agents [3].

The general purpose of this research work is the development of innovative nanostructured ZnO-based materials acting as skin surface drug reservoir to control drug delivery in dermatological applications. ZnO was selected as suitable material for this purposes because it can play a key role in dermatological applications due to both its intrinsic biological properties and the possibility to deliver a drug.

The research activity is structured in different phases. First, three different nanostructured ZnO-based materials were synthesized and characterized in order to elucidate their morphological and physico-chemical properties. In a second phase, the nanostructured ZnO-based materials have been used to incorporate Clotrimazole (CTZ), an antifungal active pharmaceutical ingredients (API), using a supercritical CO₂ technique [4]. Drug-loaded materials were characterized in order to study the drug-material interactions and the material properties after the treatment with supercritical CO₂. Moreover, *in vitro* dissolution studies were performed in order to define the CTZ release kinetics. The last part of the activity will concern the development of a semisolid pharmaceutical formulation, tailored to deliver the CTZ-loaded nanostructured ZnO-based materials to the skin for dermatological applications. *In vitro* permeation studies using vertical diffusion cells (Franz's cells) will be performed in order to evaluate the CTZ release from the pharmaceutical formulation and to assess the role of nanostructured ZnO-based materials as skin surface reservoir controlling drug release over time.

As described earlier, three different nanostructured ZnO-based materials were synthesized using different wet chemistry strategies, such as chemical bath deposition approach (NsZnO_1)(modified from [5]), sol gel method using a template (NsZnO_2) and nanocasting technique (NsZnO_3).

Supercritical CO₂ (scCO₂) procedure was used in order to incorporate CTZ into NsZnO. The NsZnO materials were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), thermogravimetric analysis (TGA), Infrared Spectroscopy (IR), Differential Scanning Calorimetry (DSC) and nitrogen adsorption before and after CTZ incorporation.

NsZnO_1 was obtained by chemical bath deposition approach starting from ZnCl₂ and urea as precursors. FESEM analysis of NsZnO_1 revealed that the morphology of the material consists in micrometric platforms composed by several nanosheets (about 15 nm-thickness), formed by the aggregation of ovoid nanoparticles (around 15-20 nm).

In another preparation, a sol gel method was also tuned up in order to synthesized a nanostructured porous ZnO with high surface area, using Pluronic F127 as template agent and Zn(COOCH₃)₂ as zinc precursor. The synthesized material, named NsZnO_2, showed agglomerated ovoid-shaped nanoparticles

(about 20 nm), organized in micrometric platforms (about 20 μm).

A third ZnO-based material, NsZnO-3, was obtained using a hard templating approach (nanocasting) selecting porous silica, with a cubic symmetry, as hard template and $\text{Zn}(\text{NO}_3)_2$ as zinc precursor. The resulting material possessed a hybrid composition, silica (80%) and ZnO (20%) due to the partial removal of silica obtained by wet treatments. The morphology of the hybrid material is approximately the replication of a typical porous silica. All ZnO-based materials were characterized before and after the incorporation of CTZ by scCO₂ treatment.

XRD analyses showed no modifications of the materials structure after scCO₂ treatment, confirming the peculiar hexagonal wurtzite structure for the sample NsZnO-1 and NsZnO-2 and the amorphous structure for the hybrid material NsZnO-3. XRD and DSC analyses confirmed the amorphous state of CTZ inside the ZnO-based materials after incorporation by scCO₂ treatment. The drug loading percentages were assessed by TGA analyses, showing about the 25% for NsZnO-1 and for NsZnO-3 and the 15% for NsZnO-2. Nitrogen adsorption analyses before drug incorporation revealed that NsZnO-1 is a mesoporous material with pore dimension of 27,3 nm, Specific Surface Area (SSA) 67,13 m^2/g and pore volume of 0,23 cm^3/g , while NsZnO-2 has a pore dimension of 5,2 nm, SSA 19,23 m^2/g and pore volume of 0,05 cm^3/g . NsZnO-3 showed the higher SSA, with 95,10 m^2/g , with a pore dimension of 9,7 nm and a pore volume of 0,23 cm^3/g . After CTZ incorporation by scCO₂ treatment, nitrogen adsorption analyses confirmed the drug loading inside the porous structure of all the ZnO-based materials.

In vitro release studies were performed using a rotating disk, fitted with semi-permeable membrane. The kinetic release profiles emphasized the ability of the CTZ-loaded ZnO-based materials to release the drug over time.

In conclusion, three different nanostructured ZnO-based materials were synthesized, in order to obtain drug delivery platforms for the topical administration of CTZ in dermatological applications. From these preliminary results the all the three materials seem to be promising for this purpose and the development of a semisolid pharmaceutical formulation is in progress.

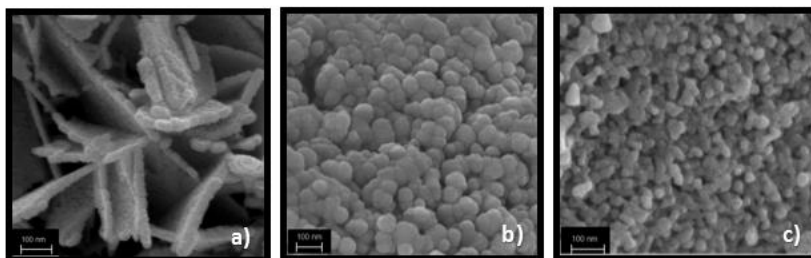


Figure 5 FESEM images of the three NsZnO based-materials: panel a) NsZnO-1, panel b) NsZnO-2, panel c) NsZnO-3

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Notes

GA-26

OPTIMIZING THE CRYSTALLIZATION OF ZEOLITES USING ORGANIC ADDITIVES

Katarzyna Lukaszuk

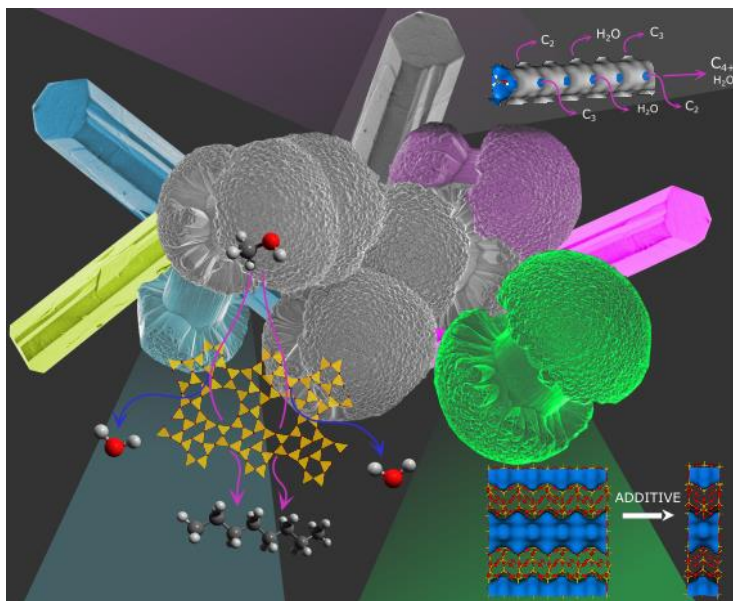
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Summary

An important challenge of crystallization science is providing a high quality crystalline product that is not only pure but also has desired size and shape of the particles. Gaining control over the crystallization process in the zeolite synthesis would allow us to obtain materials tuned with respect to their morphology. As an implication, the number of pores exposed to the surface of a crystal, as well as the length of pore channels is tailored greatly influencing a catalytic performance.

The main goal of my PhD thesis is to understand how an introduction of foreign substances (growth modifiers) affects the gel chemistry, thus altering the crystal size and morphology of zeolites. The influence of organic additives on the crystal morphology of offretite (OFF) and ZSM-22 (TON) has been investigated providing crystals with different shape and size. It has been also shown that addition of organic co-solvents may accelerate the crystallization process of offretite and improve the purity of the final product. In order to improve an experimental investigation High Throughput Synthesis (HTS) has been applied as a promising extension for the screening of different crystal additives. The synthesized samples are tested in the Methanol -To -Hydrocarbons (MTH) reaction as shape selective catalysts in order to investigate correlation between their catalytic performance and morphology.



P-26

THE IMPORTANCE OF CRYSTAL MORPHOLOGY IN THE METHANOL-TO-HYDROCARBONS REACTION

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Summary

For many conversion processes in heterogeneous catalysis the reaction products are determined by how the reactants and products are transported through the space offered by the catalyst i.e shape selectivity. Shape selective catalysis is the domain of zeolite materials which can be tuned to a variety of applications due to a large number of available framework topologies. Another factor influencing the product distribution for a particular choice of zeolite framework and reaction is the length of the channels in zeolites that is to a large extent controlled by the size and shape of their crystals. Moreover crystal morphology can be directly tied to the diffusion and coking of the catalyst therefore greatly influencing its performance. Offretite (OFF) is a zeolite that has a topology consisting of interconnected straight 12-ring and sinusoidal 8-ring channels. As offretite is commonly intergrown with erionite (ERI), care needs to be taken when addressing the shape-selective properties of pure offretite [1, 2]. It is known that offretite is not an efficient catalyst in the MTH process due to fast deactivation via coking [3]. However, due to the high shape-selectivity of the MTH reaction, we have chosen this zeolite topology as a model to study the recently developed morphology-induced shape-selectivity concept [4].

In this contribution we synthesized 3 different morphologies of offretite using the established approach by changing parameters such as silica and aluminum sources, water content, temperature and crystallization time. The second strategy involved addition of so called “growth modifiers”. The samples were characterized by powder X-ray diffraction (XRD), single crystal X-ray diffraction (SC-XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The offretite samples were tested as acid catalysts in the Methanol to Hydrocarbons reaction (MTH) at 400°C using an U-shaped fix bed quartz reactor.

SEM was used to ascertain the morphology and size of the synthesized erionite-free offretite crystals. We distinguished 3 different morphologies: hexagonal, broccoli-like and spherical (Figure 1) and investigated them in the MTH reaction.

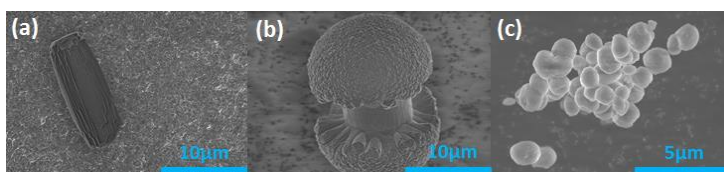


Figure 6. Scanning electron micrographs of offretite samples: (a) hexagonal shape crystals of reference sample (OFF-R), (b) broccoli-like morphology (OFF-B), (c) spherical morphology (OFF-S).

The influence of crystal morphology on product selectivity of offretite is shown in Figure 2. The results for samples with crystals possessing comparable aspect ratios (OFF-R and OFF-B) are very similar. The highest selectivity towards the light fractions (C2 and C3) indicates that the product distribution is dominated by the 8-ring channels, rather than 12 ring channels located at the ends of the crystal. In contrast, the spherical crystals (OFF-S) with the lowest aspect ratio, revealed the highest product selectivity towards the heavier fractions (C5+). This showed a significant contribution of the bigger 12MR openings to the product distribution.

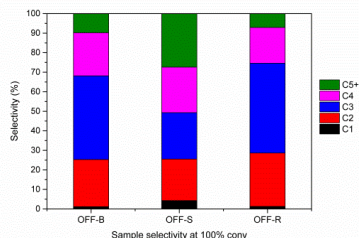


Figure 7. Product selectivity of the different offretite samples at 100% MeOH conversion.

The important point to emphasize in this study is also the fact that lifetime is highly influenced by the catalyst morphology and size (Figure 3). We observed the longest life time for the smallest crystals, whereas the OFF-R with almost 3 times higher aspect ratio deactivated as first. The broccoli-like crystals (OFF-B) revealed an intermediate behavior. We hypothesize that the small branched hexagonal needles deactivate as the last, thus extend the catalytic life time of the crystal in comparison to OFF-R.

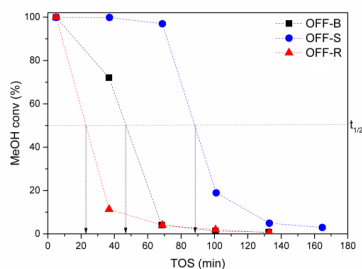


Figure 8. Methanol conversion as a function of time on stream of offretite samples with different morphology.

The SC-XRD measurement of the reference sample (OFF-R) revealed twinning. We proposed two mechanisms of twinning that are energetically likely to occur. One of them provides material with structure that does not consist of intergrowths within 12MR channels (Figure 4a). However, the presence of C layer in the second mechanism (Figure 4b) effectively blocks continuous access down the 12-membered ring pores, altering the adsorption, diffusion and potential catalytic properties.

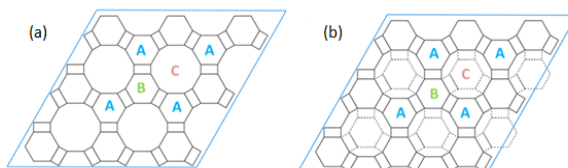


Figure 9. [001] projection on offretite framework. (a) Unblocked 12MR channels in the layer sequence ABB, (b) The 12 MR channels are blocked as a result of rotating layers of cancrinite cages by 60° in the AAC sequence.

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Notes

GA-27

SYNGAS TO CLEAN-BURNING FUEL VIA OXYGENATES: EFFECT OF EFFLUENT RECYCLING

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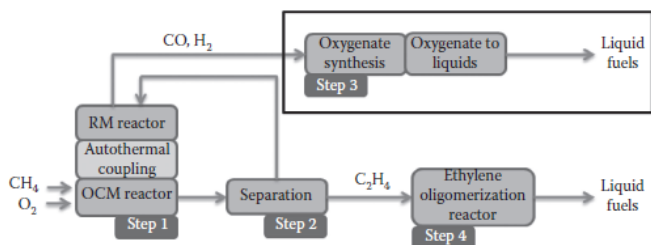
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Summary

The OCMOL (Oxidative Coupling of Methane followed by Oligomerization to Liquids) partnership brought together 17 universities, research institutions and companies. As the global energy demand and crude oil price rise, alternative production routes for the same hydrocarbon products are becoming more and more economically attractive. In this respect, synthetic fuels created from natural gas offer now an alternative to the traditional fuel supply mix.

The OCMOL project aims at developing an innovative chemical route adapted to the exploitation of small gas reservoirs from both a technical and an economic point of view. The process is based on oxidative coupling of methane followed by oligomerization to liquids on one side, and the reforming of methane followed by oxygenates synthesis and gasoline synthesis on the other side. Our work on the project focused on the integration of a unit combining the oxygenates synthesis from syngas (STO) and the clean-burning gasoline synthesis (OTL).

Commercial routes already exist for the conversion of synthesis gas to gasoline via methanol. However, the OCMOL project introduced two additional challenges: first, the STO-OTL unit would need to be integrated in the OCMOL process, which implies that the feed for the STO reactor would consist of a blend of unconverted methane, various products and inert gas, and that the pressure of the STO reactor was mainly defined by the preceding steps. Second, the target for the OTL reactor was set to 75% yield of non-aromatic C₅+ hydrocarbons, a hydrocarbon blend that had not yet been achieved in an OTL process.



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SYNGAS TO CLEAN-BURN FUEL VIA OXYGENATES: EFFECT OF EFFLUENT RECYCLING

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ABSTRACT

This work is set within the frame of the OCMOL (Oxidative Coupling of Methane followed by Oligomerization to Liquids) project. The global aim of OCMOL is to develop an integrated process for production of liquid fuels from relatively small natural gas wells in a sustainable way. The integrated process, simplified in Figure 1, is characterized by extensive recycling of by-products, including CO₂. The focus of this Abstract will be on Step 3, where syngas from the methane reforming unit will be converted into a clean-burning gasoline with a low content in aromatics. This target is achieved by combining the processes of Syngas conversion To Oxygenates (STO) and Oxygenates conversion To Liquids (OTL).[1]

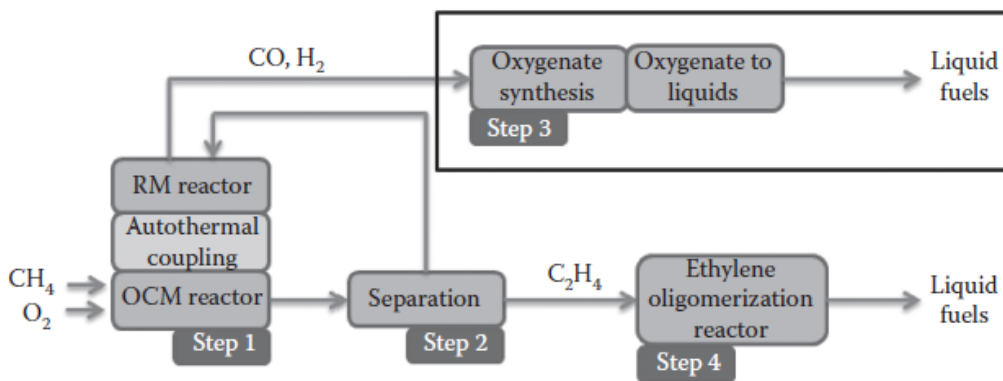


Figure 1. Block diagram of OCMOL. OCM (Oxidative Coupling of Methane), RM (Reforming of Methane).

The STO study focused on the optimization of the conversion of syngas into oxygenates. The received feed gas composition from the methane reforming unit was converted into oxygenates at moderate pressure and temperature (50 atm, 240°C) with a 95% efficiency and a modest recycle to makeup ratio of 1. The by-product CO₂ improved the separation of the products due to the high solubility of dimethyl ether (DME) in CO₂. The OTL study focused on the research of zeolite catalysts for production of aromatics-free gasoline. Zeolites H-ZSM-22 and H-ZSM-23, characterized by a unidimensional pore framework with medium-size pores, were the most attractive materials. Both catalysts gave an optimum 55% per pass yield in aromatics-free gasoline, which was substantially increased by co-feeding C₂-C₄ olefins (Figure 2-left), simulating a by-product recycle.[2] On the materials side, the activity and methanol conversion capacity need to be further optimized in order to compete with conventional H-ZSM-5 (Figure 2-right).

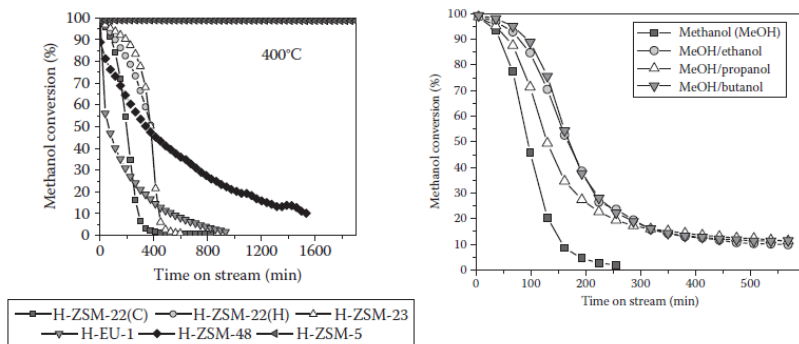


Figure 2. Left: Methanol conversion as a function of TOS at 400°C over different zeolitic materials. WHSV = 2 g/g_{cat}*h. Right: Methanol conversion as a function of TOS at 400°C when co-feeding ethanol, propanol and butanol. WHSV = 2 g/g_{cat}*h (methanol) over H-ZSM-22.

The integration of the STO-OTL units allowed us to simulate and experimentally test the process with a industrially-relevant feed. The lifetime of the zeolitic catalyst operating in the OTL unit was extended dramatically due to the positive effect of the by-products recycling (alkenes and alkanes mainly). Additionally, significant amounts of the “undesired” recycled light olefins (ethene, propene, butenes) were converted into the final gasoline fraction (C5+), leading to a process with >80 wt% gasoline yield with extremely small amounts of aromatics. Even though the lifetime of the catalyst (reaching 50% oxygenates conversion) was extended by a factor of 10 due the effect of the recycle, further optimization in catalyst is needed to make this process industrially competitive.

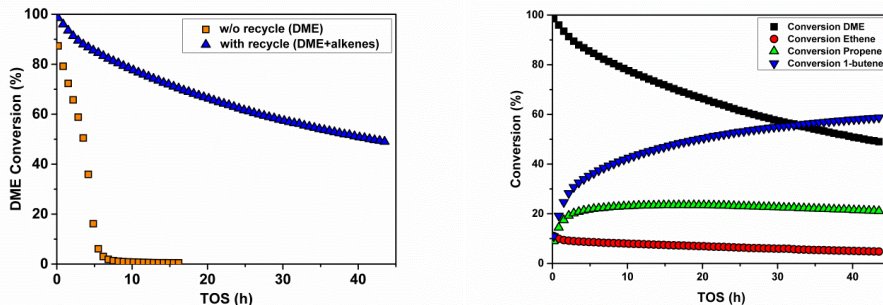


Figure 3. Left: Oxygenates conversion as a function of TOS at 400°C, with and without recycling of alkenes over H-ZSM-22. WHSV = 2,32 g/g_{cat}*h (DME), 3,56 g/g_{cat}*h (alkenes). Right: Oxygenates light alkenes conversion as a function of TOS at 400°C over H-ZSM-22. WHSV = 2,32 g/g_{cat}*h (DME), 3,56 g/g_{cat}*h (alkenes).

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Notes

GA-28

RATIONAL DESIGN OF HETEROGENEOUS CATALYSTS

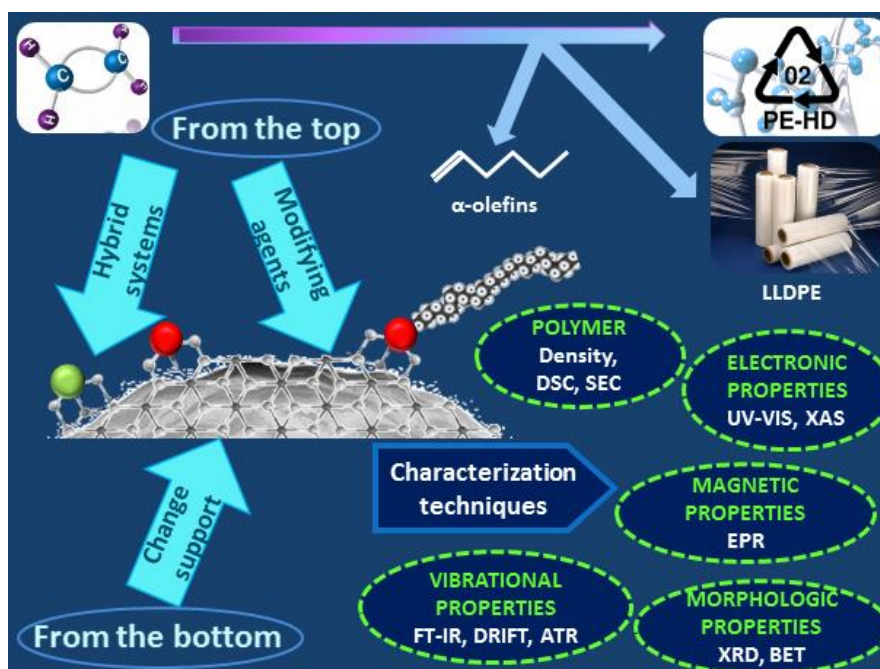
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Summary

My PhD project is focused on the rational modification of heterogeneous catalysts, in particular of those employed for ethylene polymerization and oligomerization. In this field, the most famous heterogeneous catalysts used are the Phillips catalysts, composed of chromium sites grafted on amorphous metal-oxides), and the Ziegler-Natta catalysts, based on $Ti-Cl_x$ precursors supported on crystalline $MgCl_2$. For both catalysts a detailed understanding of the structure of the active sites and of the ethylene activation is still subject of intense research. The purpose of this PhD project is to clarify these two points in order to perform an engineering of the catalyst's active sites, leading to a higher performances or polyolefins having a tailored architecture. A rational modification of a catalyst can be done following two different approaches. The first one is "starting from the top": i) using modifying agents that act on the surface of the system or ii) adding an additional metal center to obtain a bimetallic catalyst. The second approach is "starting from the bottom", which means changing the support (for example using crystalline supports instead of amorphous ones). To understand the modifications introduced all the investigated samples will be characterized by means of several techniques, in particular: IR techniques (FT-IR, ATR, DRIFT), electronic techniques (UV-Vis, XAS), magnetic techniques (EPR), X-Ray Diffraction and adsorption of nitrogen (BET). Moreover, the products of ethylene conversion will be studied with Differential Scanning Calorimetry, Size Exclusion Chromatography and density measurements.



P-28

ALUMINA AS SUPPORT FOR Cr-BASED PHILLIPS CATALYST COMPARED TO SILICA

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INTRODUCTION

The Phillips catalyst is among the most important heterogeneous catalysts for ethylene polymerization. It accounts for about 50% of the high density polyethylene (HDPE) world's demand and it has also a large share of linear low density polyethylene (LLDPE) production. The active phase is constituted by a highly dispersed chromium oxide supported on a high surface area material, mainly porous SiO_2 [1].

In this contribution, we present the role of the support in affecting the catalytic performances of the Cr-based Phillips catalyst, and in particular we compare Al_2O_3 to SiO_2 . In respect to silica, alumina is a crystalline support presenting weakly acidic Al-OH surface groups and exhibiting a larger population of surface OH groups in the same activation conditions. Moreover, for activation temperatures above 600 °C, it exhibits also exposed Lewis acidic Al^{3+} sites at the surface [2]. All these factors might influence the properties of the grafted chromium sites. Indeed, according to the specialized literature, Al_2O_3 -supported Phillips catalysts provides only about 10-20% of the polymerization activity of Cr/silica, but it exhibits a faster kinetics profile and produces a polyethylene with an extremely high molecular weight, even reaching the ultrahigh (UHMWPE) classification [1].

EXPERIMENTAL

Two Cr/ SiO_2 and two Cr/ Al_2O_3 samples having a Cr loading of 0.5 and 1.0 wt% were prepared by wet-impregnation with a water solution of CrO_3 of a silica-aerosil (specific surface area about 380 m^2/g) and a commercial δ - Al_2O_3 (Halon C, Degussa, specific surface area about 100 m^2/g), respectively. The samples were activated at 650 °C under dynamic vacuum and calcined in pure oxygen at the same temperature. Two different reduction steps were followed: a) in CO at 350 °C, providing the samples named CO-reduced samples; b) in H_2 at 350 °C resulting in the H_2 -reduced samples.

RESULTS AND DISCUSSION

All of the catalysts were tested in the gaseous ethylene polymerization, by monitoring the ethylene consumption as a function of time. Figure 1 compares the ethylene consumption for the CO-reduced Cr/ SiO_2 and Cr/ Al_2O_3 catalysts. These data demonstrate that Cr/ Al_2O_3 has a faster kinetics profile with respect to Cr/ SiO_2 , in agreement with literature reports. Hence, the support should have an influence on the properties of the Cr sites.

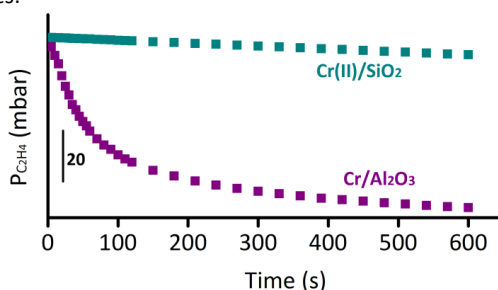


Figure 1: Kinetics of ethylene polymerization on the CO-reduced Cr/ SiO_2 and Cr/ Al_2O_3 catalysts.

In the attempt to understand the origin of the different catalytic behaviour of Cr/alumina vs. Cr/silica catalysts, Diffuse Reflectance UV-Vis spectroscopy (DR UV-Vis) and transmission FT-IR spectroscopy have been mainly employed. DR UV-Vis spectroscopy provides information on the oxidation and coordination states of the supported Cr sites [2]. Indeed, the electronic configuration of the metal centre is strongly

influenced by its coordination environment (number and type of ligands, geometry and others). Whereas FT-IR spectroscopy (also coupled with probe molecules) gives direct information on the surface properties and on the structure of the chromium sites.

Figure 2 shows the DR UV-Vis (part a) and FT-IR spectra (part b) of the CO-reduced Cr/SiO₂ catalyst (dark cyan), in comparison with those of the CO-reduced Cr/Al₂O₃ ones (purple). Important differences are observed in both cases, suggesting that the support strongly influences the structure of the reduced Cr sites. UV-Vis spectra indicate that different types of reduced sites may be formed. The spectrum of CO-reduced Cr/SiO₂ shows two well defined d-d bands (at 7500 and 12000 cm⁻¹) characteristic of isolated Cr²⁺ sites in pseudo-tetrahedral coordination [3]; whereas the spectrum of CO-reduced Cr/Al₂O₃ catalyst displays a multitude of d-d bands, assigned to three types of chromium sites, namely Cr^{3+_{6c}} (17500 and 25100 cm⁻¹), Cr^{2+_{6c}} (14000 cm⁻¹), and Cr^{2+_{4c}} (9000 and 11500 cm⁻¹), differing in the oxidation state (3+ or 2+), and in the coordination geometry (6-fold or 4-fold). Transmission FT-IR spectra (Figure 2b) indicate a difference in the amount and type of surface species in the two CO-reduced systems. The spectrum of Cr/SiO₂ catalyst is mainly characterized by the fingerprints of highly dehydroxylated silica. The spectrum of Cr/Al₂O₃ catalyst shows, in addition to the fingerprints of highly dehydroxylated alumina, a multitude of bands in the 1850-1100 cm⁻¹ region, ascribed to pseudo-carbonates originated from the reaction of the CO₂ formed during the reduction of the catalyst in CO with the alumina surface. The presence of these pseudo-carbonate species might influence the type and reactivity of the reduced chromium sites.

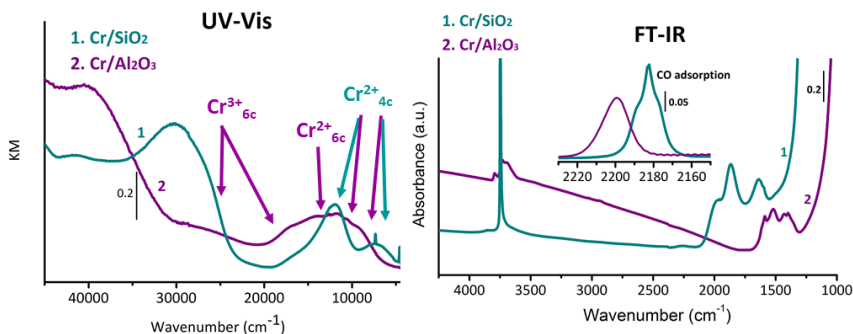


Figure 2. UV-VIS (part a) and FT-IR (part b) spectra of the CO-reduced Cr/SiO₂ (dark cyan) and Cr/Al₂O₃ (purple) catalysts. The inset in part b shows the FT-IR spectra in the $\nu(\text{CO})$ region, of CO adsorbed at room temperature on the two catalysts.

To gain information on the structure of the reduced Cr species, carbon monoxide was used as probe molecule (inset in Figure 2b) at room temperature. The spectrum of CO adsorbed on Cr/SiO₂ is characterized by a triplet of bands centred at 2184 cm⁻¹ and ascribed to dicarbonyl and monocarbonyl species formed at two different Cr²⁺ pseudo-tetrahedral sites [3]. Contrarily, the spectrum of CO adsorbed on Cr/Al₂O₃ shows a single broad band at 2199 cm⁻¹ assigned to monocarbonyl species on a heterogeneity of Cr²⁺ pseudo-tetrahedral sites, testifying the presence of coordination vacancies able to coordinate ethylene only on the Cr^{2+_{4c}} sites. The difference in the $\nu(\text{CO})$ frequencies is attributed to the higher ionicity of the alumina support with respect to silica.

The data collected on the two Cr-based systems allow to figure out the active species in ethylene polymerization (Cr^{2+_{4c}} sites) and the role of Al₂O₃ in affecting the structural and electronic properties of the grafted Cr sites. In particular the higher ionicity of the support and the presence of different surface species formed upon reduction (pseudo-carbonates species) are the main reasons behind the different behavior in ethylene polymerization reaction on the Al₂O₃ supported Phillips catalyst.

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Notes

GA-29

ADVANCED CHARACTERIZATION OF NANOSTRUCTURED ZEOLITE CATALYST BY ELECTRON MICROSCOPY

Andrea Molino

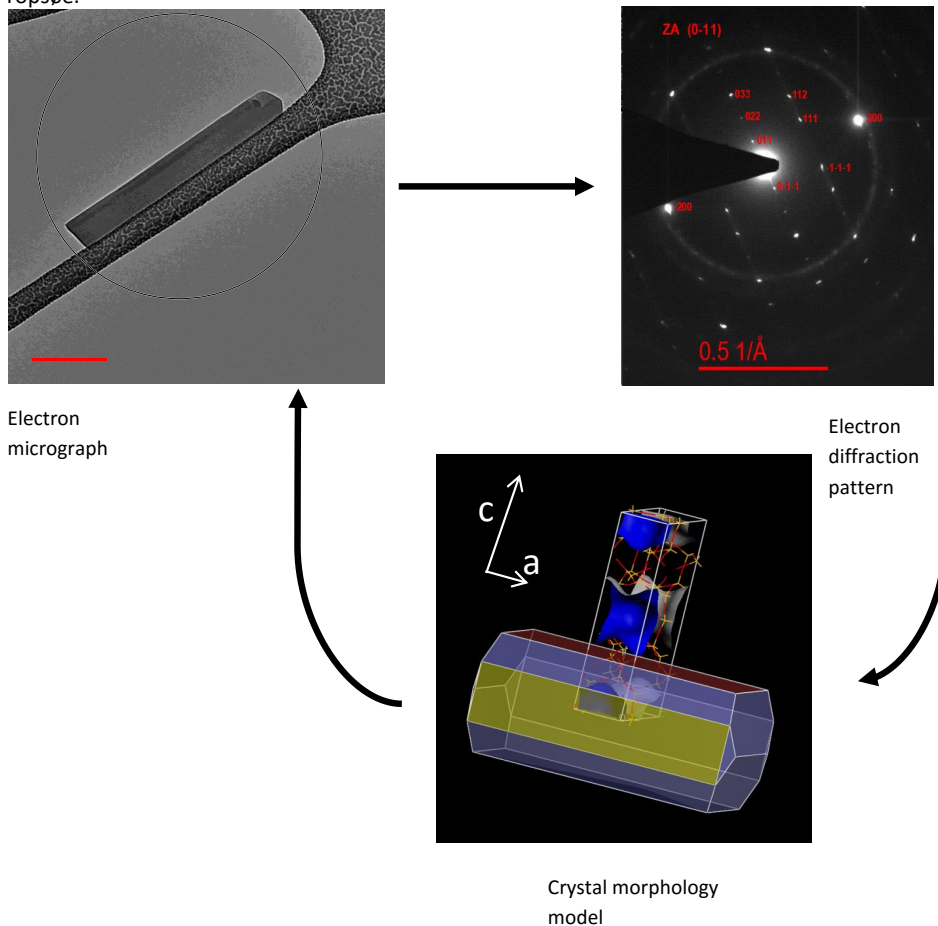
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Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark

Summary

The overall objective of this project is to carry out an advanced characterization of nanostructured zeolite catalyst used for the methanol to hydrocarbons reaction (MTH). Transmission electron microscopy will be employed to determine the morphology and nanostructure of the zeolite catalysts and to investigate the build-up of coke precursors and surface rearrangements and degradation during reaction on spent catalyst samples. A final objective will be to perform in situ reaction studies using transmission electron microscopy.

This project is part of the EU-ITN Zeomorph project, an on-going collaboration between the catalysis group at the Department of Chemistry, University of Oslo and the Danish catalyst company Haldor Topsøe.



P-29

STRUCTURE ANALYSIS OF NANOMETRIC-SIZED ZEOLITES BY TRANSMISSION ELECTRON IMAGING AND DIFFRACTION

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ABSTRACT

The zeolite catalysts possess strong Brønsted acid sites distributed within regular pores of molecular dimensions. The confined chemical environment around the active sites and the restricted access to and exit from the internal surface gives rise to the widespread use of zeolites as shape-selective catalysts in the petrochemical industry. In this work, we use the transmission electron microscope to determine how the particle morphology may influence the access to the zeolite internal surface and thus become a tunable parameter to influence lifetime and selectivity in zeolite catalysis.

The effects of preferential exposure of certain crystal facets are well documented within other areas of catalysis, such as nanoparticle-based catalysis, but only few work are present on zeolite catalysis, the first by Choi and co-workers [1] on few unit cell thick 2-dimensional nanosheets of ZSM-5 (Figure 10).

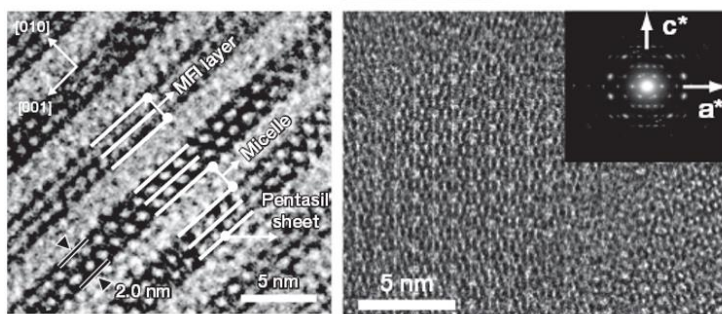


Figure 10 TEM micrograph of ZSM-5 nanosheets (left) a thickness of the sheet of 2 nm, corresponding to two unit cells along the crystallographic axis b. The electron diffraction pattern (right) along the zone axis (010) shows the details of the microporous straight channels along b. Adapted from [1]

A more recent work on a peculiar morphology of pentagonal-shaped sheets of ZSM-57 (Figure 11) and needle-like shaped of SUZ-4 (Figure 12) of Teketel et al, [2].

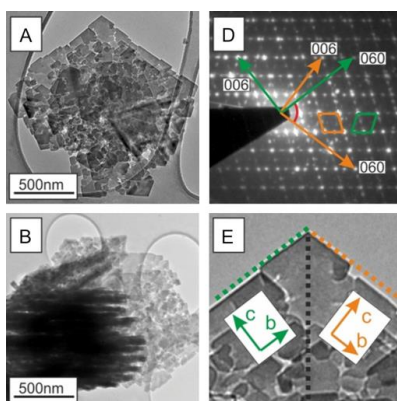


Figure 11 TEM images (A,B,E) and electron diffraction (D) of pentagonal-shaped crystals of ZSM-57. The electron diffraction shows as the unusual shape is caused by a twinning of the crystal (detail in E). Adapted from [2].

In case of SUZ-4, an 8- and 10-membered ring channel zeolite, a new concept in zeolite catalysis has been proposed: a morphology-induced product selectivity; the exposure of only one set of crystal facets allow the diffusion of reactants and products through one set of channels among the other, a concept different than the previous work based only on the length of the diffusion pathways.

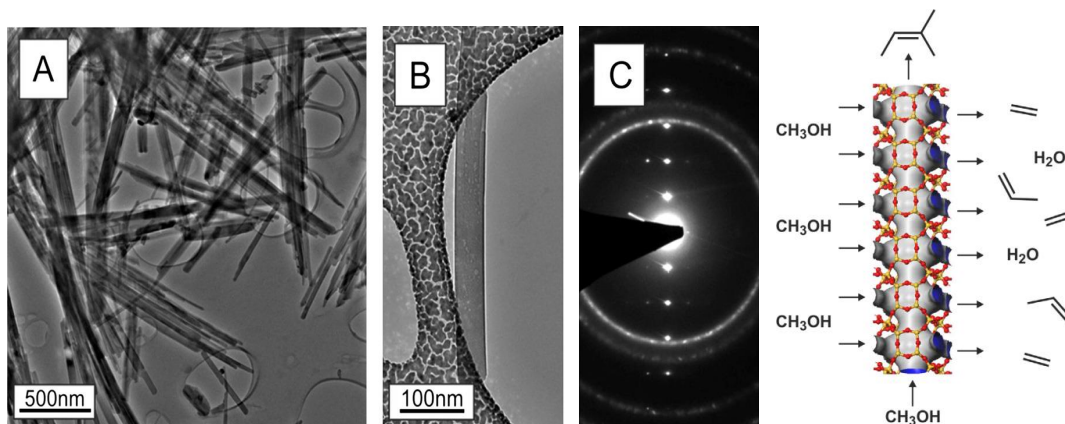


Figure 12 TEM images (A,B) and Electron diffraction (C) of needle-like shaped crystals of SUZ-4. The electron diffraction on a single crystal shows as the needle has the 10-membered ring channels parallel to the longest dimension of the crystallite, resulting in an external surface of mainly 8-membered ring pore openings, allowing only small molecules to diffuse out. Adapted from [2]

As part of the Zeomorph project, the aim of this work is to extend the structural characterization on other zeolite structures, used as catalysts for the methanol to hydrocarbon (MTH) reaction, an important catalytic process for the production of synthetic fuels.

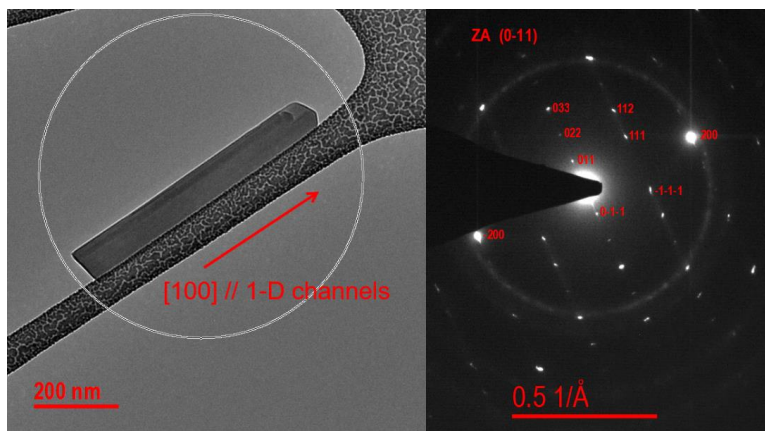


Figure 13 Unpublished TEM micrograph and the corresponding selected area electron diffraction pattern of a single needle-like shaped crystal of zeolite ZSM-23. The electron diffraction shows as the 1-dimensional channel system is running parallel to the longest direction of the needle, giving rise to a diffusion limitation for the reactants and products

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Notes

GA-30

THE GOLDEN CATALYST FOR THE OXIDATION OF ETHANOL TO ACETIC ACID

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Prof. Dr. Jeroen A. Van Bokhoven

ETH Zurich

SUMMARY

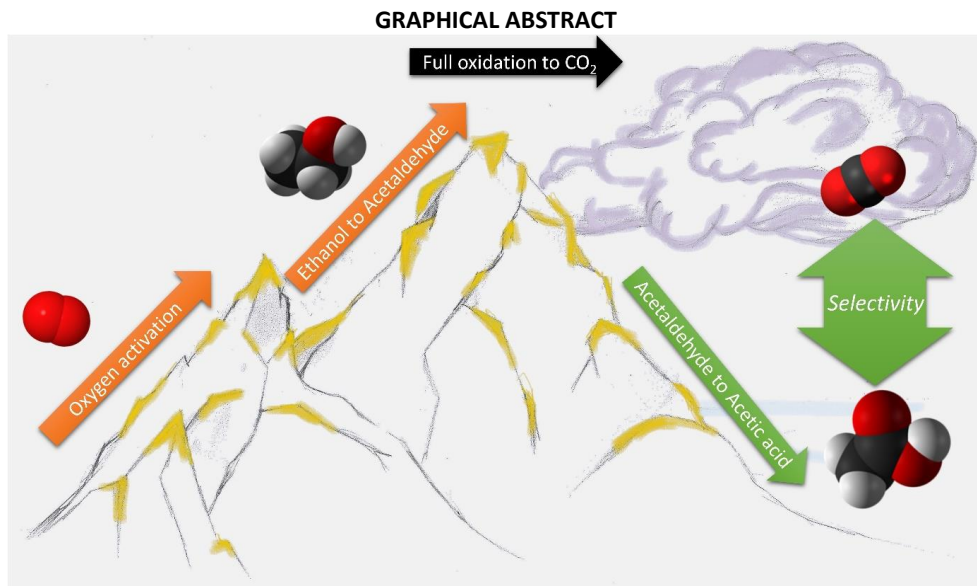
Gold has been considered as a chemically inactive metal until the late 1980s, when Haruta et al.^[1] showed that supported gold nanoparticles (3-5 nm) catalyse the CO oxidation even below 200 K. Since then, research on gold catalysis expanded also to oxidation of alcohols^[2] and diols.^[3] Herein, we focus on the liquid phase selective oxidation of ethanol with molecular oxygen over gold systems. We aim to comprehend the reaction mechanism that leads to acetic acid, a more environmentally friendly process than the traditional carbonilation of methanol to acetic acid,^[4] and to implement this understanding to improve the acetic acid yield.^[5]

Activation of oxygen is an essential step and probably takes place on the perimeter of the gold-support interface.^[6-7] Hence, the nature of the support and its interaction with gold will be investigated, by testing different supports (reducible, non-reducible oxides, and metals); in-situ X-ray spectroscopic techniques could reveal information about the site that activates oxygen.^[8]

In addition to enhanced oxygen activation, the hydrogen elimination to form the intermediate acetaldehyde should be facilitated, as it is the rate determining step of the liquid phase oxidation of ethanol.^[9] Therefore, combination of highly active oxidation or hydrogenation catalysts with the remarkably selective gold, i.e. alloys^[10] and bi-metallic catalysts^[11], shows potential to increase the catalytic activity, while retain high selectivity. The key to an optimized catalyst is a deeper knowledge of how structural, electronic, and surface properties alter by the addition of one or more components and how these properties translate into activity and selectivity.

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Representation of the two energy demanding steps i) activation of oxygen and ii) elimination of hydrogen to form acetaldehyde. The formation of acetic acid from acetaldehyde is facile and selectivity prevents full oxidation to CO_2 .

Notes

GA-31

STRUCTURE AND REACTIVITY OF Cu IONS IN Cu-SSZ-13 ZEOLITE FOLLOWED BY OPERANDO UV-Vis SPECTROSCOPY

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Summary

In the past years the increase in pollution was paralleled by an increasing interest in catalysts with environmental applications. Among them, a variety of Cu-exchanged zeolites have been investigated, as they are active for the selective catalytic reduction by NH_3 (NH_3 -SCR) of nitrogen oxides (NO_x) from the exhaust of lean-burn engines. Currently, Cu-SSZ-13 – characterized by a small pore CHA structure – is attracting increasing attention due to its higher activity and selectivity in SCR conditions. In this contest, aiming to understand the structure and the role of the Cu ions in the SCR cycle, in this PhD project the study of the active sites will be performed coupling different *operando* techniques, such as FT-IR, XAS and UV-Vis-NIR DR spectroscopies. These techniques will be employed to evaluate the expected differences both in structure and in catalytic behavior while changing the Si/Al ratio and the Cu loading in the zeolite.

The information obtained by this detailed investigation, combined with accurate DFT calculations, could lead to a better comprehension of the complex processes occurring on Cu-SSZ-13 catalyst during NH_3 -SCR reaction.

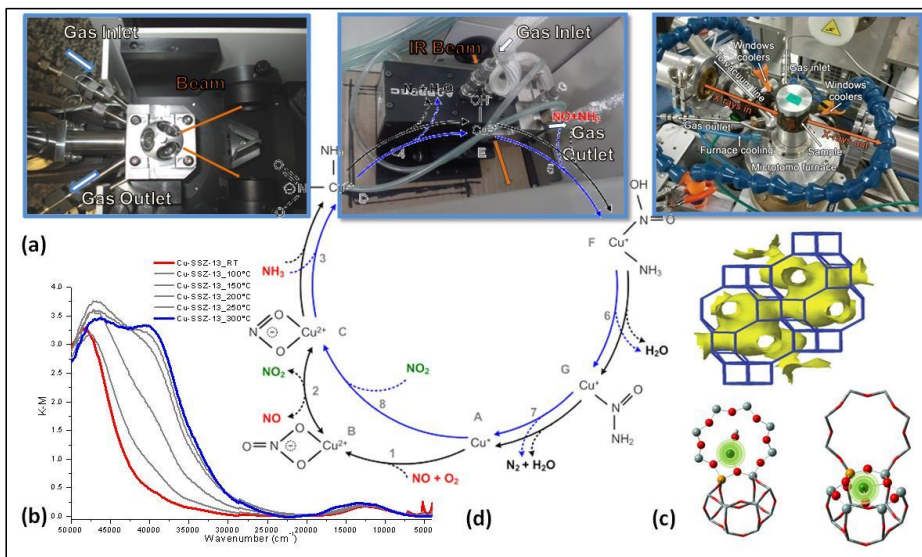


Figure 14. a) Images of the *operando* setup developed for UV-Vis-NIR diffuse reflectance, FT-IR and XAS spectroscopy (from left to right). b) UV-Vis-NIR DR spectra of Cu-SSZ-13 activated under O_2 flux. c) Cu-SSZ-13 site structure, developed with periodic DFT calculations (reproduced from ref. [1]). This information, combined with the accurate investigation of the structure of the active sites using suitable spectroscopic techniques, will lead to a better comprehension of the complex processes (see pictorial representation in part d - reproduced from ref. [1]-) occurring on Cu-SSZ-13 catalyst during NH_3 -SCR reaction.

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P-31

STRUCTURE AND REACTIVITY OF CU IONS IN CU-SSZ-13 ZEOLITE FOLLOWED BY *OPERANDO* UV-VIS SPECTROSCOPY

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ABSTRACT

In the past years the increase in environmental pollution has led to an increasing interest in catalysts and catalytic processes that are able to abate climate change and improve the air quality. Among the catalysts, a variety of Cu-exchanged zeolites have been investigated, as they are active for the selective catalytic reduction of nitrogen oxides (NO_x) from the exhaust of lean-burn engines by addition of NH₃ (NH₃-SCR). Zeolites with different topologies, such as Cu-ZSM-5 and Cu-beta, have been extensively studied over the past 20 years as they have shown high catalytic activity in different conditions [1]. More recently, Cu-SSZ-13 – a small pore zeolite with CHA topology – has attracted much attention, due to its higher activity, selectivity and in particular stability under SCR conditions [2,3]. In order to further enhance the catalytic properties of Cu-zeolites, it is important to understand in detail the nature of the active sites in these materials.

For this purpose, in-depth characterization studies have been carried out applying different spectroscopic techniques. In our group FTIR, EPR, UV-Vis-NIR DR and XAS were employed to perform comparative analysis on as-prepared and dehydrated Cu-SSZ-13, Cu-ZSM-5 and Cu-beta with the same Si/Al ratio and Cu content [1,4,5]. These studies highlighted the presence of [Cu-OH]⁺ species, likely balanced by one framework Al atom and the presence of [Cu₂(μ-O)]²⁺ dimers, the latter observed in Cu-ZSM-5 and Cu-β, but not in Cu-SSZ-13 [1].

These findings and the significant experimental/interpretative background accumulated, opened up the possibility to establish fundamental structure-activity relationships in Cu-zeolite-based catalysts. However, so far this knowledge was obtained from a limited variety of samples, and it is known that Cu ion locations and redox properties can be systemically tuned by varying Si/Al and Cu/Al ratios zeolite catalysts [3]. Therefore a series of Cu-CHA samples with controlled composition (Si/Al and Cu/Al ratios) was in-house synthesized and these samples are being characterized with respect to their catalytic performances and structural properties. Proper *operando* spectroscopy set-ups were further developed, in order to study the chemistry taking place during NH₃-SCR reaction on Cu sites *via* FTIR, XAS and XES techniques.

In this context, we optimized a set-up allowing to acquire DR spectra while having a gas flow at a broad range of temperatures. A Praying Mantis cell (equipped with a low temperature reaction chamber – operating from -130°C to 600°C-) coupled to a gas flow system allow to investigate in great detail the reactive sites and their changes while activating the sample in O₂ or/and N₂ atmosphere and in the presence of small amounts of water, and afterwards under SCR conditions.

This information, combined with complementary spectroscopic techniques, will hopefully lead to a better understanding of the working principles of Cu-zeolite catalyst during NH₃-SCR reaction.

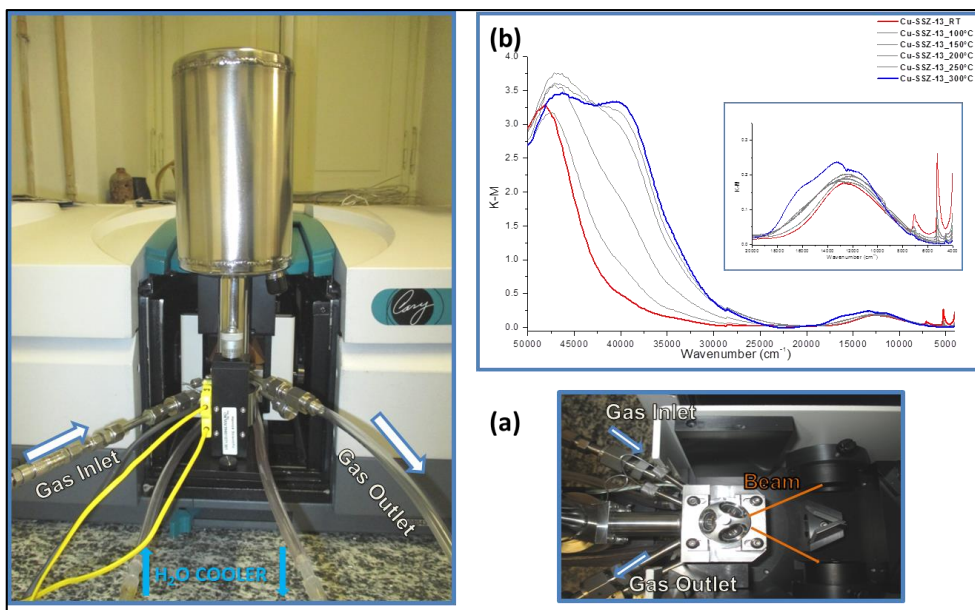


Figure 15. a) The UV-Vis DR spectroscopy *operando* setup. b) UV-Vis DR spectra of Cu-SSZ-13, activated at 300°C under O₂ flux (spectra measured in temperature).

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Notes

GA-32

SINGLE PARTICLE DIAGNOSTICS: INTEGRATING BIOMASS AND SOLAR CATALYSIS WITH OPTICAL SPECTROSCOPY WITHIN A MICROREACTOR DEVICE

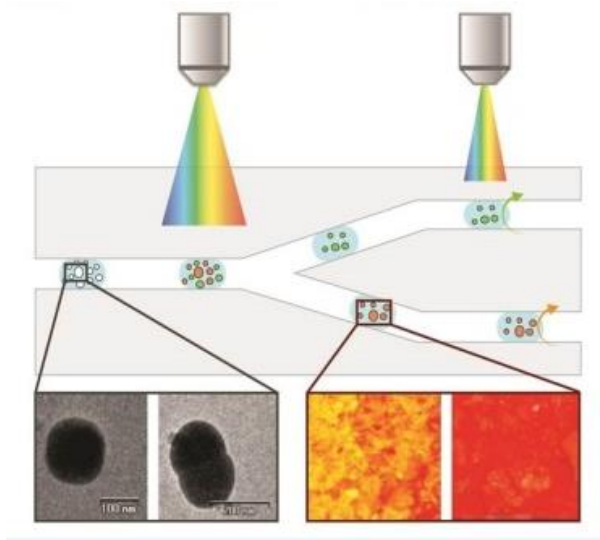
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Summary

The search for more effective materials for e.g. biomass and solar catalysis is hampered by the wide variety of variables, such as temperature, pressure as well as catalyst composition and structure, all of which naturally lead to the exploration of a large experimental space. One way to perform so many catalytic testing experiments is to develop high-throughput tools. This approach has been developed over the past two decades. Giving the fact that catalytic solids are very heterogeneous in nature, and inter-particle heterogeneities are more the rule than the exception, it would be very advantageous if we could bring the high-throughput experimentation approach one step further. This can be done by studying the activity of single catalyst particles. This requires the integration of microreactor technology, single particle separation and analysis, as well as the integration of various analytical methods within microreactors. This is the goal of this project in which we will develop optical methods, more specifically electronic and vibrational spectroscopies, which allow characterizing inline the activity and properties of single catalyst particles for relevant reactions in the field of biomass catalysis, photo-catalysis and solar catalysis. This approach will add to the general strategy of single catalyst diagnostic platform, as will be developed by Utrecht and Twente University researchers within the MCEC program.



Notes

GA-33

USE OF NATURAL SUBSTANCES FOR OBTAINING USEFUL MATERIALS FOR ENVIRONMENTAL APPLICATIONS

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Summary

Despite the highly-technologic level reached by our society, still nowadays the majority of the processes require the use of several expensive synthetic intermediates, typically derived from fossil sources. Recently, one of the most promising solutions explored is the valorization of green bio-based synthetic sources as more eco-friendly alternatives to standard processes. In particular, aim of my post-doctoral project is the valorization of natural- and biowaste-derived substances for the production of functional materials with enhanced capacities for environmental applications.

During this project, I am focusing my research on the use of two categories of substances: i) chitosans (amino-polysaccharides derived from crab/shrimp shells), and ii) lignin-like biosurfactants obtained from composted biowaste (BBS). The reactivity of both macromolecules is given by their peculiar functionalities (i.e. amino and carboxylic acids groups, respectively), which can be exploited for the production of several interesting and useful materials. The main relevant application is their action as stabilizers for the production of shape- and size-controlled nanoparticles (NPs). For instance biosurfactants were used to prepare antibacterial metallic silver NPs (AgNPs) for the surface functionalization of natural fibers (wool and cotton) to produce technical textiles usable in health-care and sport activities. Moreover, both chitosan and BBS are also investigated as stabilizers/dispersant-matrix for the production of hybrid organic/inorganic magnet-sensitive materials (with a magnetite core and an organic coating), which can be used as adsorbents/reactive species for the wastewater purification. Finally, these macromolecules can be used as building blocks for the production of highly-porous materials (for instance carbons and/or organic aerogels).



P-33

PLASMA-INDUCED ADHESIVE SURFACE FUNCTIONALIZATION OF POLYPROPYLENE
HERNIOPLASTY DEVICES

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ABSTRACT

Polypropylene (PP) is one of the most commonly used non-absorbable polymeric materials which find application in hernioplasty in the shape of meshes, alone or coupled with other biocompatible materials [1]. Even if hernia-repair interventions (mainly inguinal and abdominal) are extensively performed worldwide, still nowadays there is a significant risk of post-surgery complications, which can cause the failure of such surgical intervention [2]. In particular, hernioplasty failure can be provoked by several factors, but the main relevant ones are at least two: i) surgical infections due to implantation of biomaterials which can bring bacteria in the surgical site (i.e. micro-organisms proliferation), and ii) post-intervention displacement of the prostheses due to meshes shrinking and collapse of the anchoring sutures [3-6].

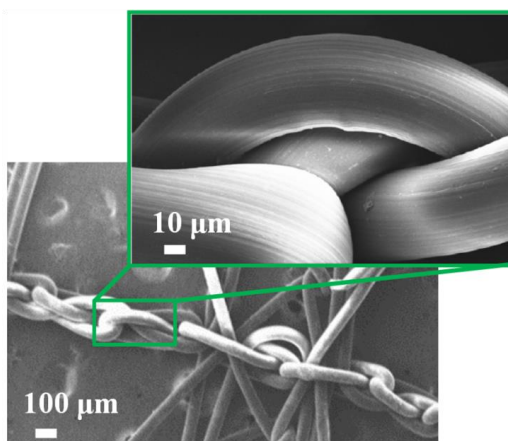


Figure 1. SEM micrographs of PP hernia-repair meshes collected at low and high (green zoomed area on top) magnifications.

To solve these issues, thus reducing the risks related to hernioplasty failure, the surface modification of standard polymeric meshes seems to be a promising route to follow. Among the different procedures, plasma treatments have recently gained much attention, thanks to their ability to induce modifications only at the surface level without altering the bulky properties of the starting biomaterials [7].

In order to confer adhesive properties to commercial polypropylene (PP) meshes, and therefore limiting the possibility of post-intervention displacement, the plasma-induced deposition of poly-(acrylic acid) (PPAA) is performed in a lab-scale pulsed plasma RF-discharge CVD reactor. This technique allows transformation reactions between low molecular weight chemical species (monomers or organic

precursors) into high molecular weight ones (macromolecules or polymeric coatings), taking advantage of the extremely highly reactive environment induced by the plasma phase [8]. Activated molecules in the plasma phase collide toward the material surface, leading to both etching of the fibers surface with formation of activated, reactive sites, and chemical reactions between such surface active sites and reactive species present in the plasma phase [9].

Surface adhesion properties induced by the deposition of such plasma-polymerized poly-(acrylic acid) (PPAA) coating onto the PP meshes were evaluated by means of AFM force/distance measurements. Once biomaterials were functionalized, in order to optimize the adhesion properties and test the storing conditions, different post-deposition treatments (i.e. water washing and/or thermal treatments) were investigated by monitoring the adhesive coating degradation (and therefore the loss of adhesion) after 3 months of aging in both humid/oxidant (air) and inert (nitrogen) atmospheres [10].

Results obtained confirmed that the adhesion forces exerted by PPAA-functionalized meshes toward the silicon probe tip are significantly higher (namely twice or even more) than the reference standard PP material. Additionally, no significant change of the adhesive properties is observed after aging, whatever the storage atmosphere applied. This way, plasma-polymerization confirmed itself to be a convenient procedure for the production of surface modified polymeric biomaterials with a stable coating, durable in time.

Promising results were obtained encouraging further *in vitro* and *in vivo* tests, in order to make these functional devices really industrially-applicable.

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Notes

GA-34

PREPARATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF MATERIALS WITH CONTROLLED POROSITY FOR ENVIRONMENTAL APPLICATIONS

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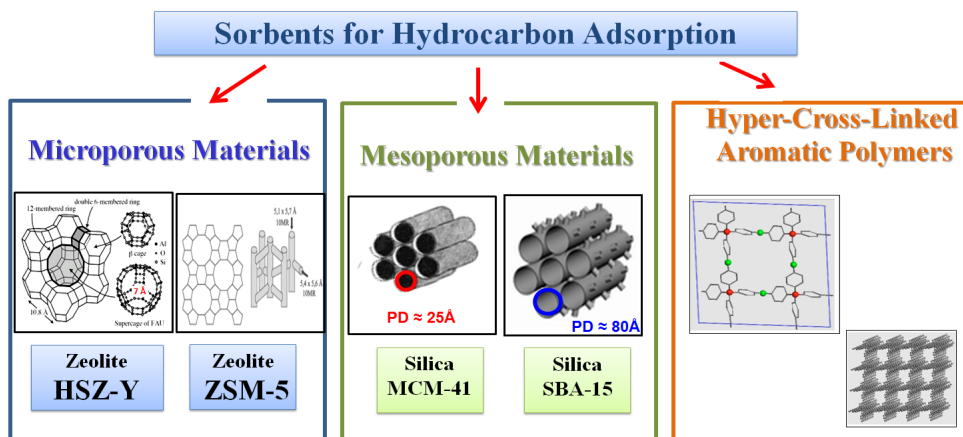
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Summary

In the frame of my thesis work, special attention is devoted to the development of solids with controlled porosity for potential application in groundwater depollution. Solids with different structure, pore dimensions and architecture, particle size and textural properties will be selected and tested as sorbents for hydrocarbon adsorption. The sorption properties of different types of zeolites will be studied in order to monitor the type and strength of interactions originating between the different solids and the pollutants molecules. Besides microporous solids, mesoporous materials characterized by larger pores with respect to zeolites and specific surface areas will be studied. In this specific case, taking into account that in real conditions solids have to be used for water decontamination, particular attention will be also devoted to the determination of hydrothermal stability of mesoporous materials.

The possibility to increase the affinity between the guest pollutants and host solids will be also investigated. To this aim, the functionalization of silica surface with different organic groups (i.e. aliphatic or aromatic species) and the final performances of functionalized materials towards pollutants adsorption will be monitored. Finally, the adsorption properties of Hyper-Cross-Linked Aromatic Polymers (HCPs), characterized by different pore dimensions, high specific surface area, thermal stability and hydrophobic surface, will be monitored.



P-34

ON THE HOST-GUEST INTERACTIONS OF TOLUENE AND *N*-HEXANE ADSORPTION ON HIGH SILICA ZEOLITES

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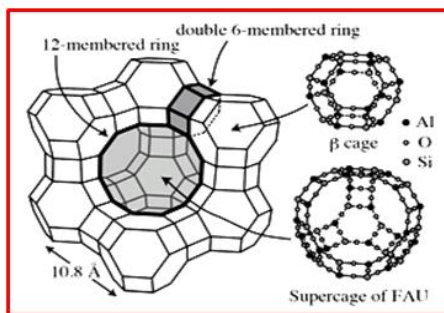
ABSTRACT

The knowledge of host-guest interactions occurring in confined space between porous solids and embedded molecules of different origin is an important task to improve adsorption properties of materials, thus extending their application fields. We present here a study of the interactions at the interface between silica surfaces and hydrocarbons selected as models of organic pollutants coming from industrial waste of oil refineries and gas stations^[1-2]. The sorption capability of silicas, with different nature and number of surface OH sites and pore size architecture, were studied. High silica ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=280$), and Y zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 200)^[3] were indeed chosen as sorbents for their physico-chemical properties (Fig 1). The interactions of toluene and *n*-hexane on selected solids were studied by means of both experimental and computational approaches.

Different toluene adsorption regimes were observed for both zeolites by gravimetric analysis: at low pressure (up to 1 mbar), toluene uptake on HSZ-Y zeolite is ca. 17 wt %, whereas the overall toluene adsorption at 27 mbar is ca. 22 wt %. Although the shape of the gravimetric isotherm collected on ZSM-5 sample is similar to that observed for HSZ-Y sample, the overall toluene uptake on MFI zeolite is considerably lower (8.8 wt %) (Fig. 2).

FTIR and SS-NMR of adsorbed toluene allowed monitoring different types of interactions between the zeolites and the pollutants. The admission of small doses of toluene on HSZ-Y sample results in a progressive interaction of the toluene with isolated silanols, whereas for pressure higher than 2 mbar the adsorption is likely driven by van der Waals interactions (host-guest) and between toluene molecules (guest-guest). Upon toluene adsorption on ZSM-5 zeolite, π -hydrogen bonding interactions between toluene molecules and isolated SiOH species and residual acid protons were monitored. Host-guest and guest-guest interactions were also enlightened for ZSM-5 zeolite. ^1H solid state MAS and ^{13}C CPMAS NMR experiments were carried out to get more insights on the local environment that the pollutants experience inside the zeolites pores. Although toluene adsorbed on HSZ-Y shows sharp resonances with narrow line widths, relatively broad resonances are observed in the case of ZSM-5 because of the restricted motion of

HSZ-Y



ZSM-5

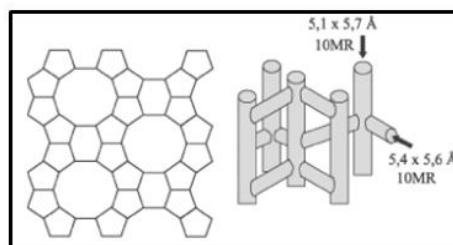


Fig.1: Y zeolite supercage (above) and the sinusoidal and intersecting straight channels of ZSM-5 (down).

the pollutant molecules inside the MFI channels. Computational approaches were used to estimate the energies of interaction between the pollutant and zeolite surfaces. For both zeolites the interaction of toluene with isolated silanols is fairly weak and the adsorption process is mainly driven by dispersion forces (even more evident for ZSM-5 zeolite). As for the case of toluene, due to the difference in textural properties, the overall uptake of *n*-hexane for ZSM-5 zeolite is lower than for HSZ-Y sample. Weak interactions between SiOH species present at the surface of both zeolites and *n*-hexane molecules are found by IR spectroscopy. SS-NMR data indicate that adsorption and diffusion of *n*-hexane in both zeolites are influenced by the pore/channel architecture and volume availabilities in zeolites. Moreover, adsorption of binary mixtures of pollutants (i.e. toluene and *n*-hexane) will be also presented. Finally, the adsorption properties of zeolites will be compared with those of mesoporous materials such as MCM-41 and SBA-15 silicas.

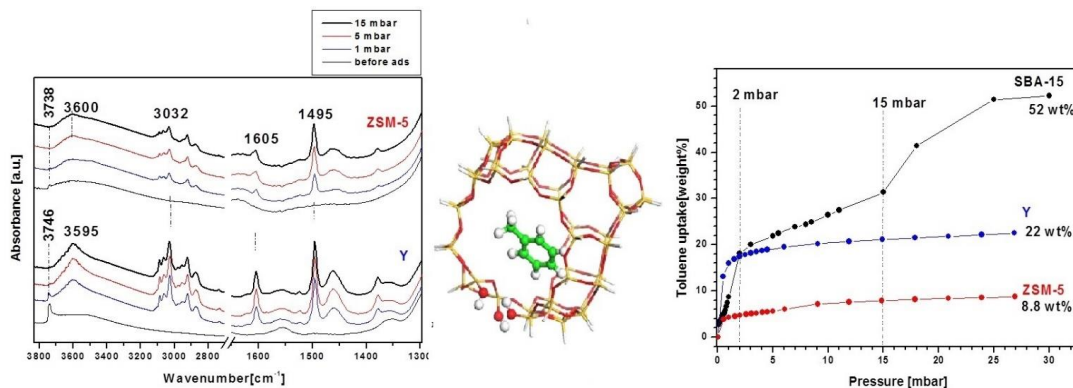


Fig.2: FTIR spectra of increasing doses of toluene on HSZ and ZSM-5 zeolites outgassed at r.t (left) and gravimetric isotherms (right) of toluene adsorbed on different porous materials (i.e. HSZ-Y and ZSM-5 zeolites and mesoporous SBA-15). A model representing a possible location of toluene molecule in HSZ-Y cage is also reported (center).

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Notes

GA-35

DEVELOPMENT OF TITANIA BASED PHOTOCATALYTS FOR CO₂ PHOTOREDUCTION

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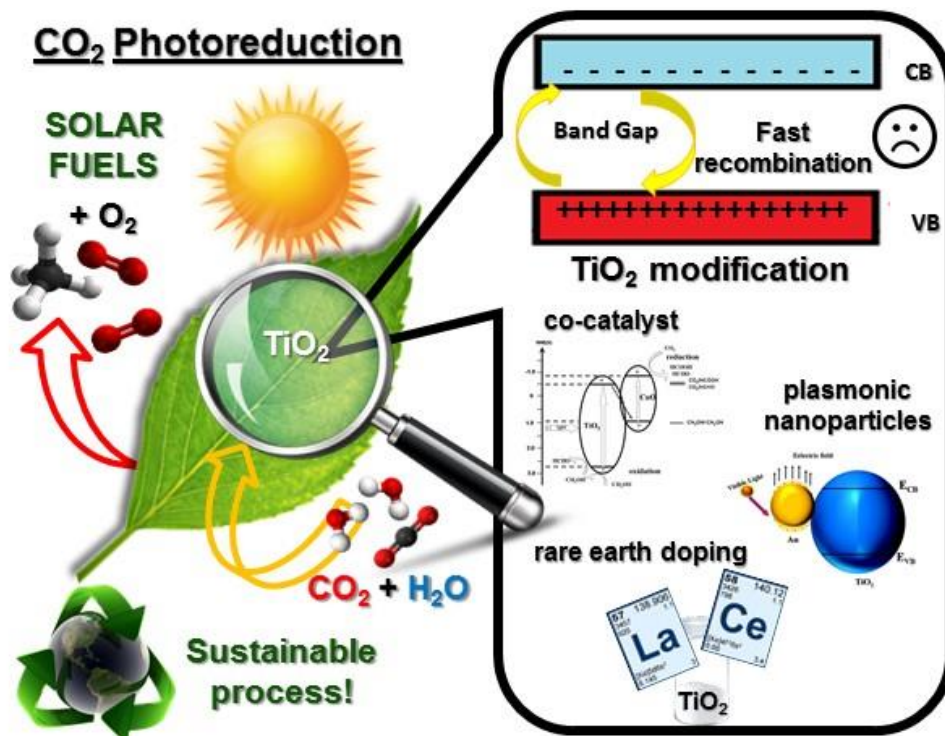
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Summary

Carbon dioxide increasing emissions in atmosphere are a serious challenge for the scientific community: one of most promising technologies to face this problem is carbon dioxide photoreduction to solar fuels due to its great sustainability and usefulness for our society. In fact, light is the primary source of energy, water is employed as a green reductant and titanium dioxide, an abundant and chemically stable semiconductor material, is the perfect photocatalyst. However, electron-hole recombination on TiO₂'s excited surface is the biggest drawback of this technology.

Therefore this Ph.D. research project is aimed at increasing the efficiency of the whole process of carbon dioxide photoreduction, performing this reaction in mild conditions (i.e. room temperature, atmospheric pressure and low irradiance).

To pursue this aim, the focus is centered to the photocatalyst, that is the core of the entire process. Titania optical and electronical properties are modified in order to reduce electron-hole recombination. To do so, several components are introduced in titania, such as metal plasmonic nanostructures, semiconductor co-catalysts and rare earth oxides. Physicochemical characterization of titania based photocatalyst is a key aspect of this investigation to correlate morphological properties to photocatalytic performances in CO₂ photoreduction to solar fuels.



P-35

METAL-MODIFIED TITANIA FOR SUSTAINABLE CARBON DIOXIDE PHOTOREDUCTION

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ABSTRACT

The research for sustainable and readily available energy sources is the most challenging issue of our century. Carbon dioxide, a global threat to the environment deriving from depleting fossil fuels combustion, might be used for chemicals and fuels production. However, the exploitation of CO₂ as green source of carbon is deeply connected to technological breakthrough and market competitiveness of these processes. Photocatalysis is a promising technology since it allows the use of CO₂ to synthesize fuels in the presence of an irradiated semiconductor. This means that the primary source of energy of the entire process is light and water can be used as a reductant instead of other more hazardous and expensive reductants like hydrogen [1].

Titanium dioxide is the perfect candidate as a catalyst for this purpose due to its semiconductor properties, chemical stability, availability and low cost. Moreover, redox potential in valence band (VB) is sufficiently positive for water oxidation, while, differently from most semiconductors, redox potential in conduction band (CB) is negative enough to allow carbon dioxide photoreduction [2]. Unfortunately, electron-hole recombination in photoexcited titania is faster than desired and this factor affects negatively the effectiveness of the process [3].

To overcome this drawback, several strategies have been pursued. Among them, modification of reactor design has been widely studied to increase catalyst exposition to light and the interaction between reactants and the photocatalyst. Also reaction conditions have been pushed in terms of temperature, pressure, irradiance [4] though the sustainability of the process is affected by that.

Besides these aspects, the modification of the catalyst, which is the core of the whole process, is highly desirable to overcome electron-hole recombination. To do so, two paths can be followed: the addition of other semiconductors as a co-catalyst, or the introduction of plasmonic metal nanoparticles. In the former case, the coupling of a semiconductor with a higher Fermi level than TiO₂, allows an electron flow between from the co-catalyst to titania, that causes an excess of charge on titania [5]. Among semiconductors, CuO, ZnO and CdSe are the most studied. In the latter case, irradiated noble metals nanoparticles, like gold and silver, by means of collective oscillation, create trap sites that propagate light within the semiconductor [6]. This means that, for different reasons, both modification lengthen excited electron-hole life.

This study is aimed at comparing the effect these two kinds of promotions on titania photoactivity in CO₂ photoreduction to methane. To do so, CuO has been chosen as a co-catalyst and gold as plasmonic nanoparticles. Both CuO and Au loaded on the same titania in the same amount, namely 0,5 wt. %. Physico-chemical properties have been investigated using several techniques, like nitrogen physisorption, X-ray diffraction, diffuse reflectance spectroscopy, etc.

Samples have been tested in CO₂ photoreduction in a thin film reactor under mild conditions, i.e. room temperature, atmospheric pressure and low irradiance (50 W·cm⁻²). It has been observed that all samples are active in this catalytic system despite mild reaction conditions, but promotion affect not only activity of CO₂ reduction, but also selectivity. In fact, photocatalytic water splitting can happen in the same reaction conditions [7]. From experimental data, CuO presence on titania surfaces increases activity in CO₂ photoreduction to methane while gold nanoparticles enhance hydrogen production. The catalytic behavior is connected to the physicochemical properties of the photocatalysts. This means that selectivity can be guided choosing according to the desired products, that can be either methane or hydrogen according to specific needs.

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Notes

GA-36

SYNTHESIS, FUNCTIONALIZATION AND DEPOSITION OF PIEZOELECTRIC ZINC OXIDE ADDUCT

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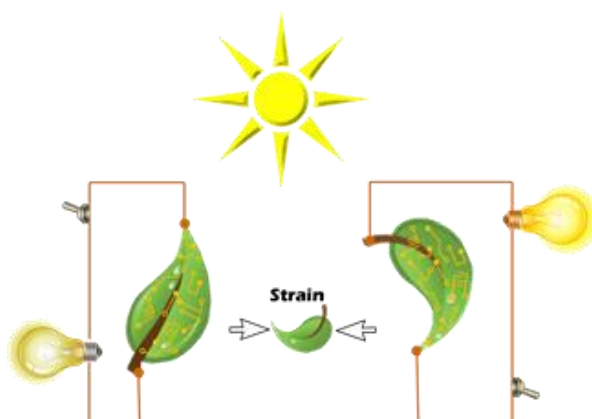
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Summary

The possibility to obtain thin piezoelectric films can represent a very intriguing chance to realize devices on cm square area that can be employed in many applications. In particular, ZnO is very appealing for its biocompatibility and also because it can be easily synthesized, avoiding excessive costs. Nanostructured ZnO functionalized with organic compounds can be used as pressure sensor for touch screen, or as active tactile sensor system for human like skin or as implantable device. Moreover, this material appears very fascinating also for applications in the field of the dye-sensitized solar cells (DSSC). The band gap of such inorganic semiconductor is very close to that one of TiO₂, then it can be used as charge collector when opportunely interfaced with a dye. ZnO is present in three crystalline forms. Only the wurtzite form shows the better piezoelectric response. The PhD project aims to point out a protocol that could permit to obtain zinc oxide functionalized with different organic compounds by means of a simply and fast co-precipitation method. The procedure doesn't require high temperature. This is very important for the possibility to use organic compounds during the synthesis steps in order to supramolecularly functionalize the crystalline ZnO. Another important aim is to deposit the obtained functionalized ZnO adduct on different supports preserving the crystallinity. The obtained hybrid piezoelectric films can be employed for different applications, such as the enhancement of the open circuit voltage of a DSSC based on nanostructured ZnO as semiconductor according to the piezotronic effect.

Graphical abstract



P-36

PIEZOTRONIC EFFECT IN ZNO-BASED DYE SYNTHETIZED SOLAR CELL

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ABSTRACT

ZnO-based day sensitive solar cell (DSSC) technology alternative to TiO₂ is considered as one of the most promising materials for solar cells [1]. Wurtzite form of ZnO suffers of piezoelectricity and possesses energy band structure and physical properties similar to those of TiO₂[2]. In this work, the piezoelectric properties of ZnO were exploited in order to increase the efficiency of DSSC; more in particular, according to the piezotronic effect, the enhancement of the open circuit voltage (V_{oc}) could be achieved. In this study, the synthesis of nanoadduct formed by nanostructured zinc oxide and ditetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) (also known as N719) was promoted. ZnO@N719 nanoadduct was obtained using a simple precipitation method. This method provides some advantages such as, low synthesis temperature, small particle size and simplicity of procedure. The process is divided in two step. In the first step, a sodium hydroxide solution is added dropwise to a zinc sulfate and N719 mixture dissolved in isopropanol, following by the precipitation of the zinc hydroxide from the solution. The obtained precipitate was washed several time with MilliQ grade water by centrifugation. The crystalline form of zinc oxide was obtained only after the second synthesis step that is the thermal treatment. The most common synthesis methods always required very high temperature to obtain the crystalline form. On the contrary the proposed method requires a treatment at 100 °C for 8 hours. The obtained powder was characterized by Raman spectroscopy in order to individuate the presence of wurtzite form of zinc oxide as well as of the N719 dye confirming the ZnO@N719 formation.

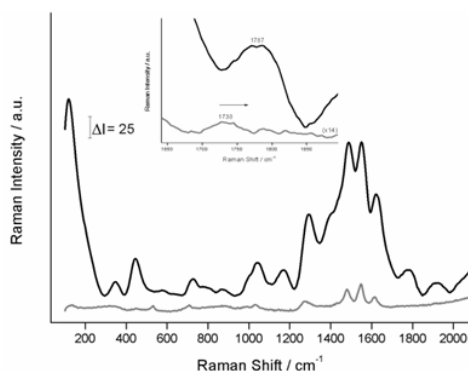


Figure1: Raman spectra of ZnO@N719 nanoadduct (black spectrum) and of N719 powder (grey spectrum). In inset the amplification of the 1650-1900 cm⁻¹ frequency range.

The N719 peaks, characteristic of the spectrum of the adduct (black line, figure 1), appeared shifted if compared to the spectrum of the dye (grey line, figure 1), confirming the interaction between the two species. The obtained inorganic/organic complex preserved the wurtzite form of ZnO, so the piezoelectric properties of the nanoadduct were tested. ZnO@N719 nanoadduct was deposited on a glass/ITO substrate by means of dip coating technique and the film was mechanically stressed applying an oscillating external force. The formation of a piezopotential was measured changing the strain intensity and the time duration of the applied stress. Once demonstrated the piezoelectricity characteristic of the synthesized ZnO, the behavior of the ZnO@N719 adduct was evaluated when the device was simultaneously subjected to an alternate external strain and to illumination. More in detail, piezopotential generated in the material bulk as a consequence of an external stress can work as a driving force to inject the electrons on an external load. According to the piezotronic effect [3], mechanical strain can contribute to enhance the Voc. Open circuit voltage of a dye sensitized solar cell of a piezotronic active material is dependent even on the density of polarization charges and on the width of the region where are distributed the piezoelectric charges, then it can be strongly influenced by the external applied pressure.

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Notes

GA-37

TAILORING THE SURFACE PROPERTIES OF TiO₂: SHAPE CONTROLLED NANOPARTICLES FOR THE OPTIMIZATION OF FUNCTIONAL PROPERTIES.

Pellegrino Francesco

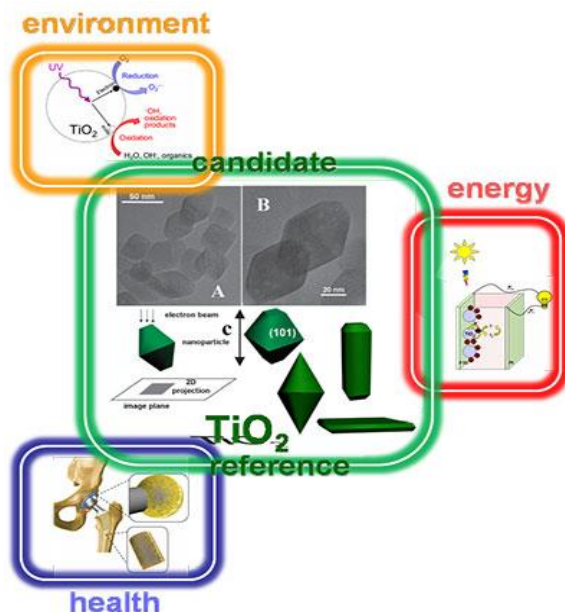
(Maurino Valter, Spoto Giuseppe, Pellutiè Letizia, Deiana Chiara, Mino Lorenzo, Alberto Gabriele)

University of Torino

Summary

The PhD proposal is part of a European project named SETNanoMetro. The project stems from the importance to establish validated methods and instrumentations for detection, characterization and analysis of nanoparticles. Central for this project is the development of new synthetic procedures and paradigms for the production of shape and size controlled sets of TiO₂ NPs. In the framework of the SETNanoMetro project, the use of various measurement techniques for the determination of the NPs properties will allow to move from the currently used "trial and error" approach toward the development of well defined and controlled protocols for the production of TiO₂ NPs. A particular care will be devoted to the establishment of correct metrological traceability chain in order to ensure the reliability of the results. The lack of international measurement standards for calibration is an aspect of particular relevance in nanotechnologies as it is difficult to select a universal calibration artifact to achieve repeatability at nanoscale. The materials produced according to such procedures, will be hence sufficiently characterized and homogeneous in their properties to become candidate Certified Reference Materials to be used in various applications where the lack of metrological traceability is encountered. The project results are expected to lead to fundamental impacts on the following areas:

- **Environment:** improving the photocatalytic properties for the treatment of pollutants;
- **Energy:** improving the traceability of DSSC measurements;
- **Health:** production of prostheses exhibiting optimized interfacial properties for a better and quicker integration of the implants in the hosting bone tissues.



P-37

HYDROTHERMAL SYNTHETIC PROCEDURES AND GROWTH MECHANISM FOR SHAPE AND SIZE CONTROLLED ANATASE NANOPARTICLES

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ABSTRACT

The synthesis of TiO₂ nanoparticles (NPs) with well-defined morphology and size is fundamental for the development of advanced nanomaterials in various application fields: photocatalysis, photovoltaics, sensors, bone-implants with enhanced bone integration [1,2]...

Synthetic routes were developed for bipyramidal TiO₂ facet-controlled anatase NPs with low truncation along the c-axis and acicular morphology, through hydrothermal treatments of aqueous solutions of Ti(IV)(triethanolamine)₂ (Ti(Teoah)₂) [3,4].

The Ti(Teoah)₂ was prepared by dropping Ti(IV) isopropoxide into triethanolamine. The isopropyl alcohol was then distilled off. A preliminary characterization of a methanolic solution of this compound was carried out by Electrospray Ionization – High Resolution Mass Spectrometry (ESI-HRMS).

The formation of anatase (101) surfaces is favoured by the presence of OH ligands, including water. Therefore the shape control agents used were pH and triethanolamine.

Bipyramidal TiO₂ anatase NPs with low truncation along the c-axis (mainly (101) facets exposed) and with dimensional polydispersity in the 5-20% range were produced, along with the procedure and the process parameters (pH, temperature and reagent concentrations) to modulate the NP size along the c-axis in the 20-60 nm range.

The growth mechanism was studied stopping the synthesis at different times: 2, 5, 15, 25, 35 and 50 hours. The other parameters are the same for all the experiments. Observing the evolution of the shape

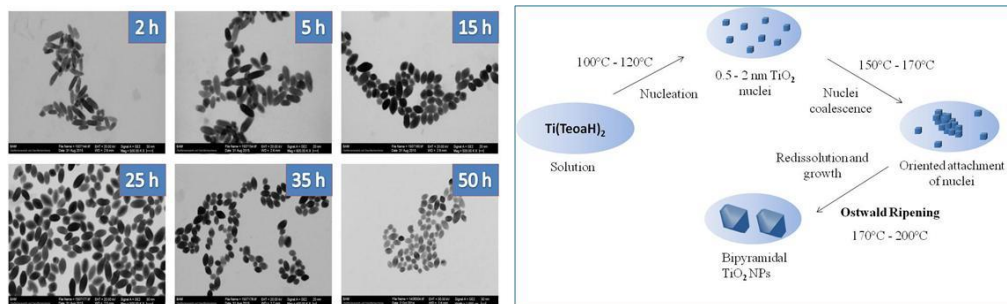


Figure 16. TSEM Micrographs of the six materials produced stopping the hydrothermal synthesis at different time (left) and growth mechanism for bipyramidal nanoparticles (right).

and size as a function of time, it is possible to note the formation of particles with a high shape factor at the early stages. Proceeding with the hydrothermal treatment, the particles grow in volume by expanding along the a-axis. These experimental evidences lead us to conclude that between 100-120 °C the hydrolysis with the formation of TiO₂ cuboidal nuclei with rh between 0.5 - 1 nm occurs, these nanoparticles at 150-170°C coalesce head to head forming high shape factor particles. This is also confirmed by the synthesis performed at 120 °C which led to this type of subnanometer particles. The high shape factor particles, between 170 and 200°C undergo a Ostwald ripening process which provides for a re-dissolution of the smaller particles and an evolution towards the bipyramidal particle.

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Notes

GA-38

SEMICONDUCTOR OXIDES MODIFICATION FOR PHOTOCATALYTIC APPLICATIONS

Valeria Polliotto

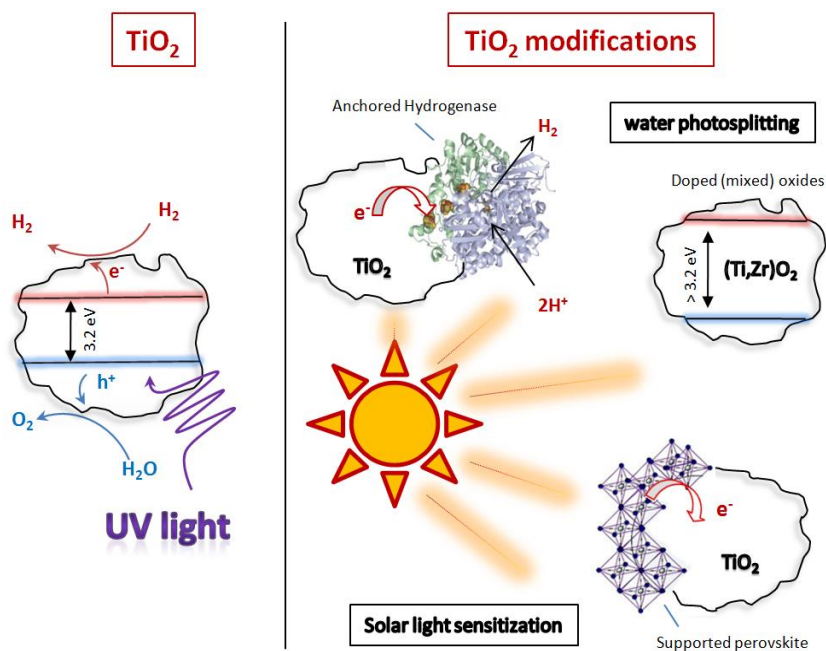
(E. Giamello, M. C. Paganini, M. Chiesa, S. Livraghi, C. Gionco)

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Summary

Aim of this PhD project is the preparation, the characterization and the photocatalytic applications of modified TiO₂ systems. These materials will be properly engineered and combined with other materials in order to favor the photoproduction of hydrogen from water using solar light. This implies to adjust the electronic structure and the photochemical properties of titania extending to the visible range its optical absorption. The systems under investigation are:

- Hydrogenase-modified TiO₂ systems. These devices are, per se, able to reduce H⁺ ions producing hydrogen. Coupling hydrogenase to an efficient photochemical system, the electrons generated by irradiation are transferred from TiO₂ to the active site of the enzyme where the reduction of water protons into hydrogen occurs. Furthermore, using doped-TiO₂ the hydrogen could be produced exploiting also some visible light component of the solar spectrum.
- Organic-inorganic halide perovskites-TiO₂ composites. The organic-inorganic halide perovskites, as CH₃NH₃PbI₃, are semiconductors with interesting optical and electronic properties, and can be used as a TiO₂ visible-light sensitizers. The process occurring upon irradiation of these systems starts with the photoexcitation of perovskite with visible light, followed by electron transfer from perovskite to TiO₂.
- Mixed ZrO₂-TiO₂ systems. These systems will be explored in order to identify new families of semiconductors with optimal electrochemical potentials for the water photosplitting. Since an extension of the band gap values is forecast, we will pay our attention to the modification of the band gap itself in order to create intraband gap levels capable of promoting the photoexcitation under visible light.



P-38

PROTEIN-SUPPORT INTERACTION, ELECTRON TRANSFER AND HYDROGEN EVOLUTION IN [Fe-Fe]HYDROGENASE-TiO₂ HYBRID SYSTEMS PREPARED USING VARIOUS TiO₂ MATERIALS.Valeria Polliotto,^a Simone Morra,^b Francesca Valetti,^b Gianfranco Gilardi,^b Elio Giamello^a

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ABSTRACT

An efficient conversion of solar energy into either electrical power or renewable fuels is one of the most important targets in the last decades. The various strategies aimed at this purpose are based on the use of semiconductors. In particular titanium dioxide, or titania, is one of the most employed semiconductors, since the discovery of the Honda-Fujishima effect in 1972^[1], because of its high photocatalytic reactivity combined with chemical and thermal stability, and non toxicity. In spite of its great advantages titania shows two serious drawbacks hampering its direct use in the process of water photosplitting. The first one is the large value of the band gap (around 3.2 eV for the anatase polymorph) that implicate the use of UV photons to perform the excitation of electrons from the valence band to the conduction band limiting therefore the use of sun light (poor of UV components at the earth surface) in photochemical applications of titanium dioxide. The second drawback is the electrochemical potential of the conduction band electrons which is only slightly more negative than the H⁺/H₂ potential thus limiting the reductive capability of photoexcited electrons. Our aim is therefore to overcome these two limitations of titania. On the one hand, to favor the production of hydrogen, the use of an enzyme called [Fe-Fe] Hydrogenase anchored to the surface of TiO₂ could be a valid alternative to typical noble metal co-catalyst. This TiO₂-hydrogenase system is able to produce hydrogen from water in the presence of a scavenger of the photogenerated holes. However, so far, this system works thanks to the addition of synthetic ruthenium-dyes allowing visible light absorption.^[2] On the other hand, among the methods to adjust the photochemical properties of titania extending to the visible range its optical absorption, a possible approach consists of exploiting TiO₂ powder materials in which the band gap is engineered by means of alio-valent doping. This type of doping generates intra band gap energetic levels allowing the electron excitation under visible light.^[3,4]

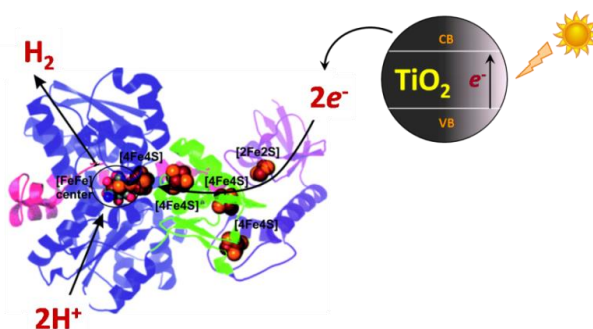


Figure 17. Schematic representation of the mechanism for the H₂ evolution of the TiO₂-Hydrogenase hybrid system.

The purpose of our work is to investigate hybrids systems prepared coupling doped titanias with a hydrogenase enzyme for hydrogen reduction. In particular we employed two kind of materials: i) N-doped anatase, a yellow material, and ii) a substoichiometric reduced anatase which shows a deep blue colour. In N-doped TiO₂ the presence of nitrogen defects in the lattice of the oxide generates intra band

gap energetic levels available to promote the excitation of the electrons of the valence band to the conduction band under visible light. These states cause the yellow colour of the powder.^[5] The substoichiometric TiO₂ is prepared via a particular synthetic route that lead to a partially reduced, blue-colored oxide (TiO_{2-x}) which is stable in air and shows the presence of Ti³⁺ ions. The color in this case is due to the tail of a broad absorption centered in the infrared region and typical of reduced titanias.^[6] Our attention is paid not only to the efficiency of the hydrogenase-TiO₂ materials in hydrogen production but also to the mechanism of interaction of the protein with the solid and to the effect of the irradiation on the hybrid materials. We have followed in particular the electron transfer occurring upon irradiation using Electron Paramagnetic Resonance (EPR).

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Notes

GA-39

UPCONVERSION NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

Pominova Daria

(A.V. Ryabova, S.V. Kuznetsov, J.A. Rozhnova)

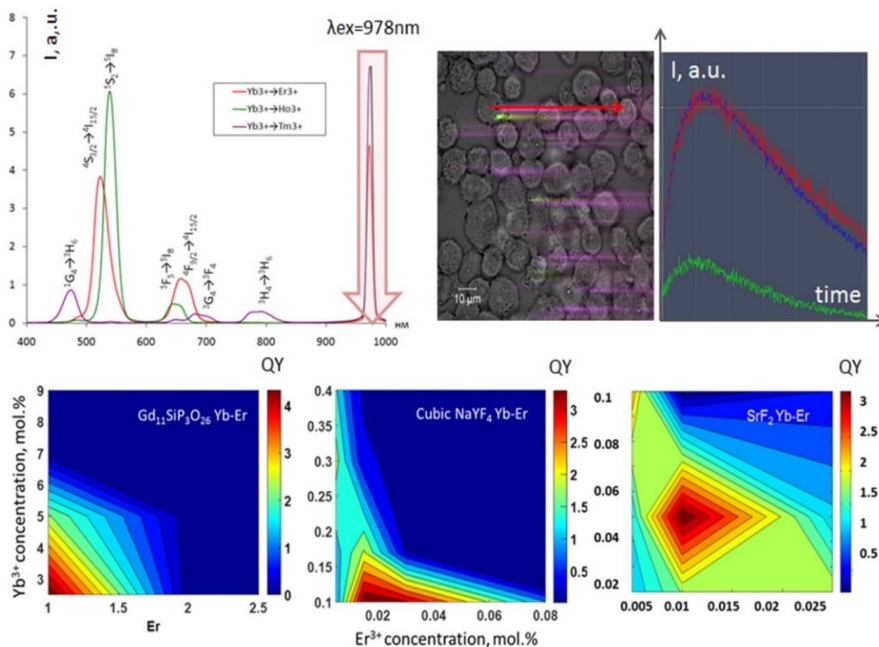
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Summary

The subject of my PhD work are upconversion nanoparticles, which can convert infrared excitation in luminescence in visible region, and their interactions with biological microenvironment. The advantages of these nanoparticles are high photostability, narrow emission peaks and ability to use infrared excitation, which provides increased light penetration depth, low autofluorescence, reduced photobleaching and photo toxicity. The main limitation of use upconversion nanoparticles is low quantum yield(QY), so researchers are trying to find possible ways of its increase.

Due to my work were chosen the best matrices (SrF₂, CaF₂, NaYF₄) and optimal concentrations of the doping ions (Yb-Er, Yb-Tm) to obtain maximum QY (up to 5.5%) and bright luminescence in blue, green and most promising for bioapplications red and infrared spectral ranges. QY of upconversion luminescence has dependence on excitation power density, with areas of quadratic dependence and saturation, where dependence is linear. Therefore, the optimal ranges of pump power for highest QY without tissue damage were chosen. To further upconversion efficiency increase the plasmonic nanoparticles can be used. The multifunctional structures on base of upconversion and gold nanoparticles, allows enlarging light absorption and possibility of radiative transitions. Now I deal with modeling of optimal geometries, which provide maximum upconversion QY enhancement and the upconversion luminescence spectrum tuning, depending on the maximum plasmon resonance in the gold nanoparticle.

For iterations with biological microenvironment study was proposed a new method using a laser scanning microscope LSM-710-NLO, which allows to visualize upconversion nanoparticles accumulation in biological samples with simultaneously luminescence lifetime determination.



P-39

MODELING OF RARE-EARTH IONS LUMINESCENCE PLASMON ENHANCEMENT AND SPECTRAL TUNING

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ABSTRACT

Rare-earth activated materials are receiving a lot of attention for potential applications in bioimaging: for use in microscopy [1], deep biotissue visualization [2], tomography [3], as highly sensitive biosensors [4], for temperature measurement [5], fluorescence diagnostic and photodynamic therapy [6].

Rare-earth ions have unique luminescent properties and emit in a wide range of wavelengths, covering the ultraviolet (UV), visible and near-infrared (NIR) regions. The luminescence of rare-earth ions is attributed to 4f-4f transitions. Because the electrons of the partially filled 4f shell are shielded from interactions with external forces by the overlying 5s² and 5p⁶ shells, the emission spectra demonstrate narrow emission bands and large distances (up to 500 nm) between the individual luminescence peaks and excitation wavelength that allows them to be easily separated. The Er³⁺ ions are especially interesting due to their emission at 1.5 μm and the green upconversion obtained under near infrared excitation. However the absorption and emission cross sections associated with these transitions are very small. This results in relatively long luminescence lifetimes (up to a few ms). In order to improve emission, the sensitization of trivalent erbium luminescence with Yb³⁺ ions may be a good choice because of the efficient energy transfer process from Yb³⁺ to Er³⁺ ions [7]. Materials, doped with rare-earth ions pair Yb³⁺-Er³⁺ (so called upconverters) absorb near infra red excitation and convert it into luminescence in visible spectral region. The use of infrared excitation sources provides increased penetration depth of light, low autofluorescence, reduced photobleaching and phototoxicity. Together with the high photostability, and excellent biocompatibility, such nanoparticles are perfect for *in vivo* and *in vitro* applications.

However, the main limitation of use upconversion nanoparticles is low quantum yield (QY), because even using sensitization, the absorption cross section of rare-earth ions is quite low, and maximum obtained QY reaches up to 5% (the absolute value depends on the composition, shape, size and the pumping power density)[8].

To further upconversion efficiency increase the plasmonic nanoparticles can be used. At a specific wavelength of light, collective oscillation of electrons on the plasmonic nanoparticle surface cause surface plasmon resonance resulting in strong extinction of light (absorption and scattering). Major determinants of the optical properties of plasmonic nanoparticles are their material, shape and size. In this work the influence of gold nanoparticles of different shapes and sizes on rare-earth ions luminescence was investigated. The surface plasmon resonance in gold can easily be tuned to give absorption maxima from around 500nm into the near-infrared part of the spectrum. The multifunctional structures on base of upconversion and gold nanoparticles allow enlarging light absorption and possibility of radiative transitions.

It was performed modeling of optimal plasmonic nanoparticles geometries, which provide maximum rare-earth ions luminescence QY enhancement and spectrum tuning, depending on the wavelength of plasmon resonance in the gold nanoparticle. Two cases: luminescence of trivalent erbium ions and sensitized with Yb³⁺ upconversion luminescence of Er³⁺ ions were compared.

For calculation of extinction cross-section and modeling of field enhancement near gold surface free finite-difference time-domain (FDTD) simulation software package Meep was used. Obtained field enhancement factors were used in rate equation model, which describes population and depopulation dynamics of rare-earth ions levels, and allow to calculate luminescence quantum yield.

It was shown that plasmon enhancement has more influence in case of upconversion mechanism, because of quadratic dependence of quantum yield on pump power. So, in upconversion case, enhancement of luminescence has fourth order dependence on the local field enhancement, in contrast to quadratic dependence of Er³⁺ luminescence enhancement. When maximum of plasmon resonance is tuned to absorption wavelength of upconverter, the strong upconverter absorption enhancement,

resulting in luminescence intensity increase up to 16 times was observed. Tuning of plasmon resonance maxima to the wavelength, corresponding to radiative transition allow to enhance transition rate and to tune the spectral properties of nanoparticles.

This work was supported by a grants RFBR #15-32-21152-mol-a-ved, MES RF, agreement #14.616.21.0064 from 2015 (RFMEFI61615X0064); FP7-PEOPLE-2013-IRSES No.612620.

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Notes

GA-40

LONG TERM ACTIVITY, STABILITY AND PERFORMANCE OF ZEOLITE BASED CATALYSTS IN THE CONVERSION OF METHANOL TO HYDROCARBONS.

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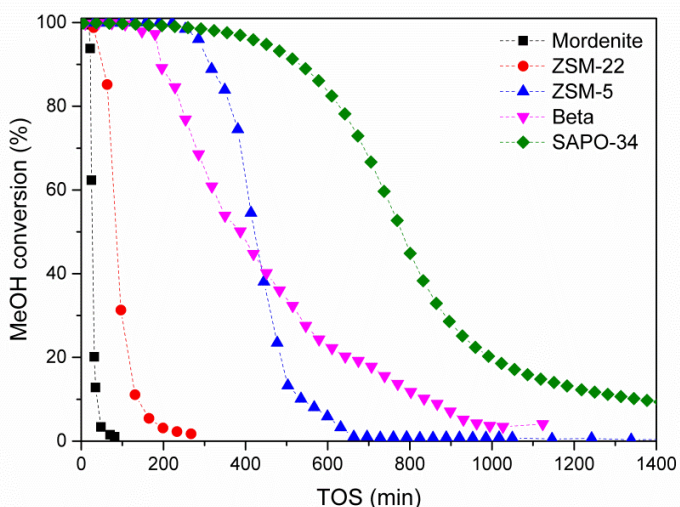
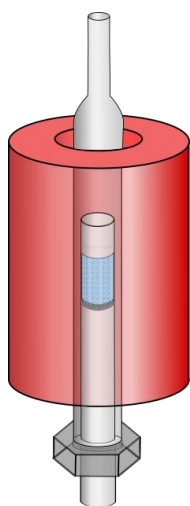
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Summary

Zeolites are a class of aluminosilicates and belong to the wider class of materials known as molecular sieves. More than 200 different zeolite structures are known today. The defining characteristic of the zeolites are their porosity: These materials have pores or channels of molecular dimensions, typically in the range of 4 to 12 Å. Also, for many zeolites it is possible to introduce catalytically active sites within these pores, such as Brønsted acidity. Combined, these two characteristics have led to the successful use of zeolites as shape selective catalysts in many large scale petrochemical/refinery processes. The term shape selectivity is a reference to these materials ability to discriminate reactants, products, and reaction intermediates based on molecular size.

The overall objective of this Industrial PhD Project is to carry out prolonged investigations of the long term catalytic activity and stability of nanostructured catalysts at industrially relevant conditions (elevated pressure, relevant feed rates and reaction temperatures) in reactions with current industrial interest such as the conversion of methanol to hydrocarbons, alkylation/oligomerization, and, tentatively, cracking of model feedstock representing heavy crude oil or pyrolysis oil. There is a special interest in investigating the evolution of the compounds triggering the activity decay in such catalysts with respect to both, time and space. In addition to the previous objectives, the regenerability and hydrothermal stability of these zeolite catalysts will be investigated in depth.



P-40

ZEOLITE DEACTIVATION BY COKING IN THE METHANOL TO HYDROCARBONS PROCESS.

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ABSTRACT

Zeolites are microporous silico-aluminate materials widely used as catalysts in many industrial processes [1]. Their Brønsted acidity, high surface area and their ability to selectively yield certain products that fit into their cavities and channels, known as shape selectivity[2, 3], make them suitable in the methanol into hydrocarbons process (MTH), which transforms a relatively cheap raw material into valuable products that can be blended as gasoline. Even though zeolites are the most suitable catalysts in the mentioned process; they suffer from deactivation, losing its ability to transform reactants into desired products over time [4]. The main cause of deactivation is the formation of coke, heavy hydrocarbon species that either have too low volatility or too a high proton affinity, which cause the irreversible deactivation of zeolites. The objective of this study is two-fold. Firstly, it aims to assess the internal consistency of different experimental techniques to evaluate and quantify the coke; and the second purpose is to investigate the differences in deactivation that can be ascribed to topology variation on 5 different catalysts.

In order to investigate the way zeolites deactivate, the methanol to hydrocarbon reaction was performed in a U-shaped reactor (o.d. 11 mm). The MTH reaction, which was done at 400°C with a P_{MeOH} of 13 kPa, WHSV of 2 $\text{g}_{\text{MeOH}}/\text{g}_{\text{cat}}\cdot\text{h}^{-1}$, and with particle sizes between 250-420 μm . The MTH reaction was quenched at different reaction times to follow the evolution of coke with time. Moreover, partially deactivated catalysts were further characterized by N_2 adsorption, by thermogravimetric experiments to quantify the total amount of coke and finally, catalyst were dissolved with HF and the addition of CH_2Cl_2 allowed the extraction and quantification of soluble coke.

Fresh catalysts were characterized by XRD, FTIR with CO and Py as probe molecules, SEM and N_2 adsorption. Results showed that not only the topology, but also properties such as acid site density, morphology and surface area varied among catalysts. Topology is a key parameter in the deactivation, because in the cases of Mordenite and ZSM-22, both 1 dimensional structure, the catalyst lifetime is much lower than in the case of BETA, ZSM-5 and SAPO-34, materials with a 3 dimensional channel system which facilitates on a larger extent the diffusion of products out of the crystal.

As observed in [1,2], each zeolite shows a different deactivation pattern. In cases A and B, (Mordenite and ZSM-22 respectively), the fact that the channels of these zeolites are 1 dimensional, influences significantly the performance, resulting in a much shorter lifetime (in blue) than in C, D and E, (ZSM-5, BETA and SAPO-34). Another interesting parameter that can be discussed depending on the MeOH conversion curve [4] is that in Mordenite (A) and ZSM-5 (C), MeOH seems to be the responsible for the formation of deactivating species. However, in the case of BETA (D) and SAPO-34 (E), products of the reaction trigger the formation of coke. The long tail observed at lower MeOH conversion values is the indication that products are transformed into deactivating species. Finally, in ZSM-22 (B), both, MeOH and products take part in the formation of heavy hydrocarbon compounds.

The evolution of BET surface area (in green) and micro-pore volume (in purple) is somewhat different in the case of 1 dimensional zeolites, (Mordenite and ZSM-22) and in 3 dimensional structures (ZSM-5, BETA and SAPO-34). As shown in [3] the reduction in these parameters is steeper at shorter reaction times in the former cases, while in the latter; the decrease is more gradual without sharp decreases at shortest reaction time, because the latter materials have better diffusion properties.

In all materials, the evolution of BET surface area and micro-pore volume, obtained by the t-plot method, is similar. Both parameters display a similar decrease with respect the pristine sample. A common

feature that was observed in all catalysts is that coking species are distributed on the external surface first, causing pore blockage and reducing significantly the access of MeOH to the internal surface. Concerning the evolution of coke content displayed in red in [4] the same explanation as with respect the BET surface area is applied. In the case of Mordenite and ZSM-22, the largest amount of coke is detected at relatively high methanol conversion values, close to 80% and since then, the parameter reaches an asymptotic value. However, the accumulation of deactivating species in three dimensional zeolites is gradual, without sharp increases at shortest reaction times. The multidimensionality of the zeolite channels enhances the diffusion of products, which can be transformed into deactivating species, delaying the accumulation of coke. In the case of totally deactivated samples, the amount of coke detected by thermogravimetric analyses showed that in 3 dimensional samples, ZSM-5, BETA and SAPO-34, a larger amount of coke can be accommodated, as it would be expected, than in the case of one dimensional catalysts (Mordenite and ZSM-22). Finally, with respect the relative amount of soluble coke detected in each zeolite, no clear trend was observed in these materials. In the case of BETA, soluble coke content was almost negligible while in the case of ZSM-22 and SAPO-34, the maximum values obtained were 45 and 52% of the total coke content, respectively.

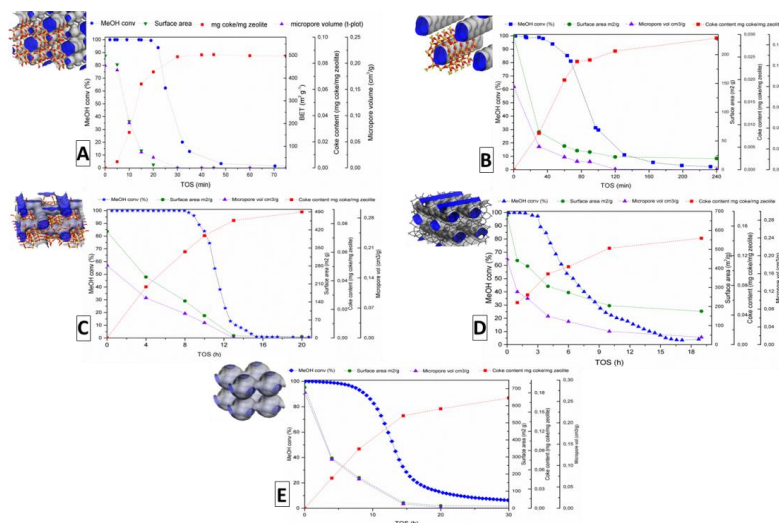


Figure 18. Evolution of MeOH conversion, total coke content, BET surface area and micropore volume in different zeolite topologies. A) Mordenite; B) ZSM-22; C) ZSM-5; E) BETA and F) SAPO-34

To sum up, it can be said that zeolites lose activity as acid catalyst in the Methanol to Hydrocarbon (MTH) reaction over time. In the current study, different MTH reactions have been performed to study the deactivation pattern and to quantify the amount of coke on different catalysts. This study has shown very large differences in their way of deactivation among five zeolite/zeotype topologies.

In 1 dimensional zeolites (Mordenite and ZSM-22), their deactivation pattern is similar but it differs extensively from the deactivation behaviour observed in 3 dimensional materials (ZSM-5, BETA and SAPO-34). The intrinsic diffusion properties, much more limited in unidimensional structures is one of the main causes of the faster deactivation observed in these zeolites. However, the evolution of micropore volume has revealed that in all materials, pore blocking is the mechanism followed to start the deactivation. Finally, it has to be said that there is not yet any single method to describe satisfactorily the origin of deactivation in zeolites in the MTH process.

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Notes

GA-41

COPPER CATALYSTS FOR THE CO₂/HCOOH CYCLE

Nicola Scotti

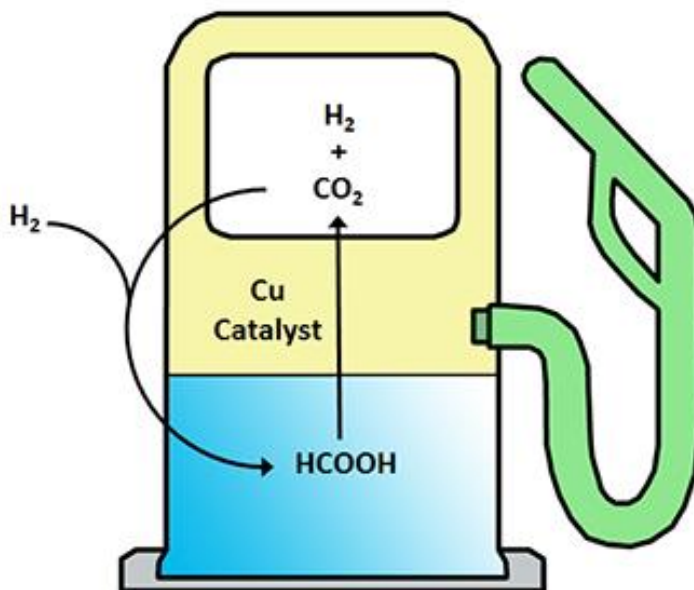
(Nicoletta Ravasio, Federica Zaccheria, Matteo Mariani, Rinaldo Psaro)

ISTM-CNR Milano

Summary

New catalytic systems for the hydrogenation of CO₂ to formic acid followed by its decomposition to give back CO₂ and H₂ are extremely interesting as the combination of the two reactions would allow one to valorize CO₂ by its transformation in a highly useful tool for hydrogen storage. The development of improved technologies for H₂ generation and H₂ storage in a safe and reversible way is a prerequisite for the utilization of hydrogen as fuel. Moreover formic acid is one of the major by-products of levulinic acid production with the Biofine process. Compared to H₂, formic acid is liquid and easy to store, transport and handle. Besides, HCOOH is considered less hazardous than methanol (its first competitor as hydrogen carrier) and therefore a valuable alternative in spite of its lower hydrogen density (43 vs. 125 g kg⁻¹).

The research project is devoted to the development of homogeneous and heterogeneous copper catalysts aimed to the study and optimization of the CO₂/HCOOH cycle.



P-41

UNRAVELING THE ACIDITY OF A METAL NANOPARTICLE: A STEP FORWARDS THE SELECTIVE SYNTHESIS OF NEW GENERATION BIOFUELS

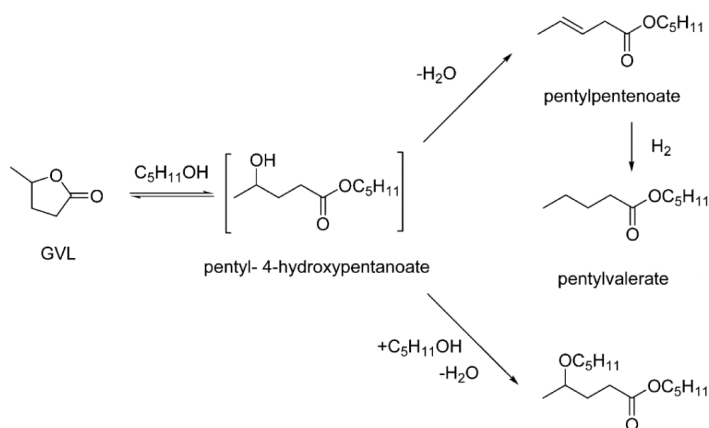
Nicola Scotti^a, Milind Dangate^a, Antonella Gervasini^b, Claudio Evangelisti^a, Nicoletta Ravasio^a, Federica Zaccheria^a

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ABSTRACT

γ -valerolactone (GVL) has been identified as a platform molecule with many applications as a precursor for chemicals, as solvent, fuel additive, and fuels precursor. Among the molecules that can be obtained from GVL, valeric esters showed excellent features as gasoline or diesel fuel depending on the alcoholic residue [1]. In particular, some of us reported a process for the production of ethyl and pentyl valerate directly from GVL and the proper alcohol by using an heterogeneous Cu/SiO₂-ZrO₂ catalyst. The reaction takes place under H₂ through nucleophilic addition of the alcohol to the carboxylic group giving hydroxypentanoate, followed by dehydration to pentenoate and hydrogenation to pentyl valerate (Scheme 1). In this case, the acid-catalyzed reactions were ascribed to the acidic support, whereas hydrogenation activity was linked to the presence of supported copper [2].



Scheme 1. Reaction Mechanism for the Conversion of GVL into Pentyl Valerate

We have long been investigating the relationships between metal oxide dispersion and acidity in supported catalysts and recently reported on a new concept of solid Lewis catalyst. Indeed we could put in light a relationship between the high dispersion of a non acidic oxide such as CuO and its acidic activity. Highly dispersed CuO/SiO₂ supported materials shows an unexpected Lewis acidity that could be properly exploited for different catalytic applications (epoxide ring opening, cellulose deconstruction, and Friedel Craft acylation) [3].

Therefore, we were interested in investigating the acidity of the same CuO/SiO₂ system in the reduced state. If the acidity of the reduced Cu/SiO₂ catalyst was preserved, this would result in a true bifunctional catalyst where both acidic and reduction activity are carried out by the same site. This may allow us to tune the activity and/or selectivity in the one-pot transformation of GVL into pentyl valerate by using a more simple catalyst. It is well-recognized that the type and strength of acidic sites are very important in

designing solid acid catalysts for renewable raw material transformations, solid Lewis acids emerging as a very valuable alternative to Brønsted ones such as zeolites and sulfonated materials.

As a matter of fact Cu/SiO₂ was able to catalyze the transformation of GVL into valeric esters, resulting to be even more selective than the previous Cu/SiO₂-ZrO₂, without losing in activity [4].

The Cu metallic phase highly dispersed on silica was deeply characterized, in particular by means of FT-IR of adsorbed GVL and pyridine, and HR-TEM.

The spectra of adsorbed GVL on Cu/SiO₂ strongly confirm the hypothesis of the relevant role of reduced copper not only in the hydrogenation reaction but also in the activation of the substrate toward nucleophilic addition by virtue of its Lewis acidic properties. These data well agree with pyridine characterization, in which both CuO/SiO₂ and Cu/SiO₂ show the presence of Lewis acid sites, that increase upon CuO reduction. The presence of a unique catalytic site and in particular the absence of catalytically relevant Brønsted acid sites on the support may in fact have a positive effect on product selectivity.

The unexpected acidity is ascribed to the surface defectivity of the highly dispersed Cu phase. HRTEM analysis clearly shows the presence of well dispersed metallic phase with well formed, highly defective metal nanoparticle.

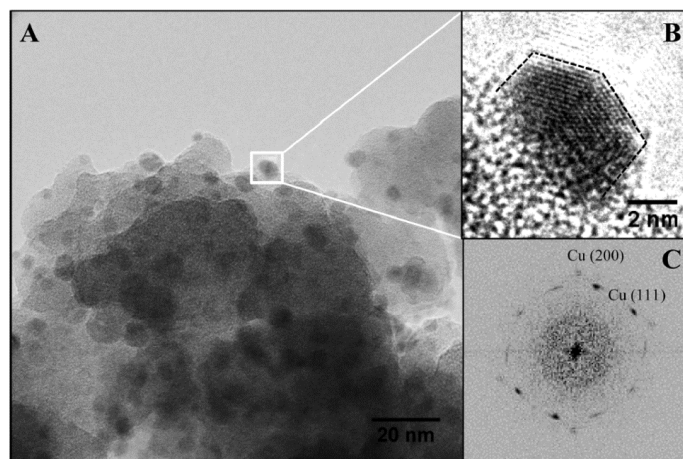


Figure 1. (A) HRTEM micrographs of Cu/SiO₂ catalyst; (B) magnified view of the Cu nanoparticle squared in A; (C) inverted FFT pattern taken from image B.

The influence of the supported metal particle size on the acidic properties of the catalyst has very rarely been investigated. The present work shows that very small metal particles can exhibit catalytically relevant Lewis acidity. This property, joined with a significant hydrogenation activity of the metal, allows one to design new bifunctional catalysts, such as Cu/SiO₂, without the need of an acidic support.

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Notes

GA-42

NATURAL ORGANIC DYES IN TAPESTRIES. NEW METHODOLOGIES FOR THE RECOVERY OF ORGANIC DYES AND THEIR RESTORATION THROUGH NANOMATERIALS IN ARTWORKS

Ilaria Serafini

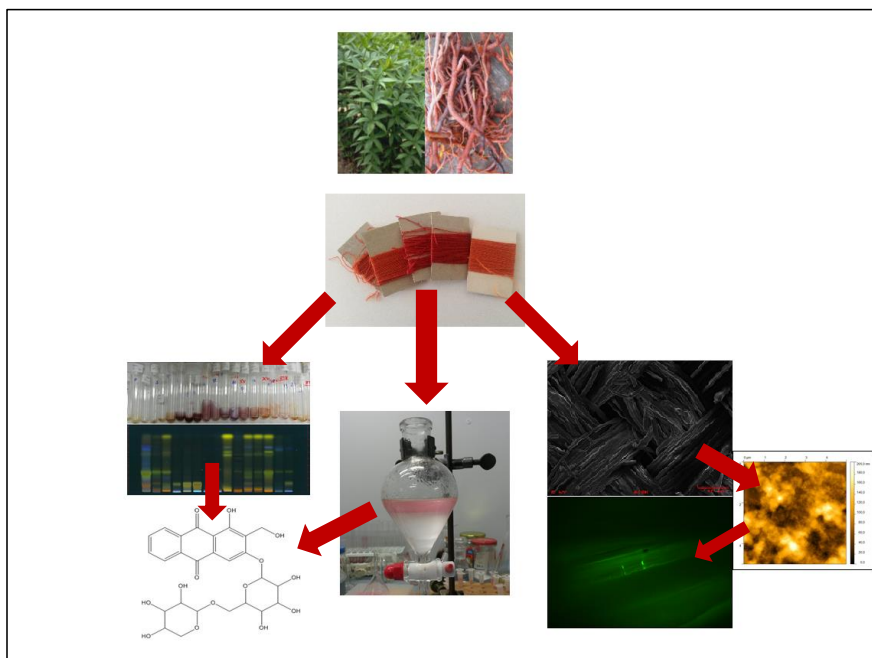
(Livia Lombardi, Fabio Sciubba, Marcella Guiso, Armandodoriano Bianco)

University of Rome "Sapienza", Piazzale Aldo Moro 5, 00185, Rome (Italy)

Summary

The aim of my PhD project is the development of a new method of restoration and conservation for the tapestries and textile works in general. This consolidation would be achieved through a particular class of nanomaterials, never used before in the field of cultural heritage. To achieve this scope, it has been necessary to include in the research the study of natural dyes and textile fibers, in terms of physical and chemical characterization and study of their degradation mechanisms. For these reasons, it has been investigated new ways of extraction of organic dyes from artworks, correlating the non-invasive measurements, carried out with SERS on fiber analysis, with data obtained through $^1\text{H-NMR}$ and ESI-MS and MS^n analyses.

Graphical Abstract



P-42

PRELIMINARY APPROACH FOR THE RESTORATION OF TEXTILE THROUGH NANOPARTICLE MATERIALS

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ABSTRACT

This work is aimed on the use of nanoparticles as consolidation materials for textiles.

Nowadays, we observe a widespread state of decay for many yarns in different tapestries, conserved in different museums in the world. This state of deterioration interests at the first the dyed yarn: organic dyes, in fact, are subjected to chemical alteration, induced by light, and consequent loss of colour. Furthermore, mechanical properties of silk or wool fibers are significantly reduced, due to their chemical degradation for light exposure and tensile stress, resulting in the damage of textiles that lose entire pieces of the works.

Traditionally, the approach in the conservation of tapestries tries to avoid the use of restoration products, generally accepted for other kind of arts, and restorers are used to replace the destroyed fibers with new ones and also put in place dyed yarns with synthetic dyes, in order to return the recompose the figure.

However, this approach can be considered in opposition of traditional idea of restoration, which tries to preserve the artworks from every kind of falsification or excessive manipulation.

For this reason, different researches in the last period, investigated the use of different products as possible restoration materials for textile. Cocca et al. [1] compared water dispersed polymer, not thought directly for textile but recently employed in this field. Pelosi et al. [2] have conducted a trial on panels in silk paintings kept in Palazzo Barberini in Rome, consolidated with the Aquazol 200, a poly-ethylossazol. Other experiments conducted directly on tapestries are reported by Shun-Qing Wu et al., which shows the results of a restoration of a historic Chinese silk through the development of a cellulosic film obtained from bacterial cultures [3]

According to these studies, our group is testing the reliability of nano-fibroin as potential nano-consolidating for tapestries and textiles. Following the protocol already known in the literature [4], starting from silk yarn, we synthesized nanoparticles of fibroin. Nanoparticles characterization was carried out by AFM, fluorescence microscopy and 1D and 2D NMR spectroscopy (TOCSY; DOSY, NOESY, ROESY).

AFM was used to confirm the dimension of nanoparticles, not exceeding 40 nm diameter. 1D and 2D NMR spectroscopy allowed to verify the amino acid composition of the nanoparticles and which residues were exposed.

A solution of nano-fibroin particles, labeled with fluorescein isothiocyanate, was deposited on artificial aged silk textiles. Observing this material through fluorescence microscope, we collected preliminary data concerning a potential interaction with damaged fibers.

The ultimate goal of this process is the creation of a film of nano-fibroin, which could chemically interact with the aged yarns, improving their mechanical properties.

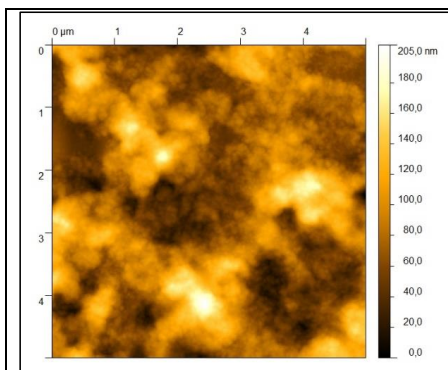


Fig. 1 Image of nanoparticle aggregates at AFM

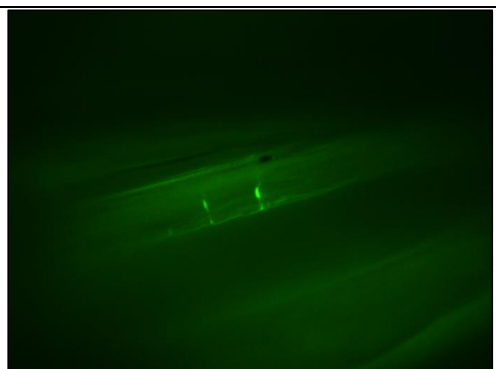


Fig. 2 Nanoparticles labelled with FITC and observed at fluorescence microscope.

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Notes

GA-43

RAMAN SPECTROSCOPY OF ZEOLITES: *IN SITU* AND *OPERANDO* STUDIES

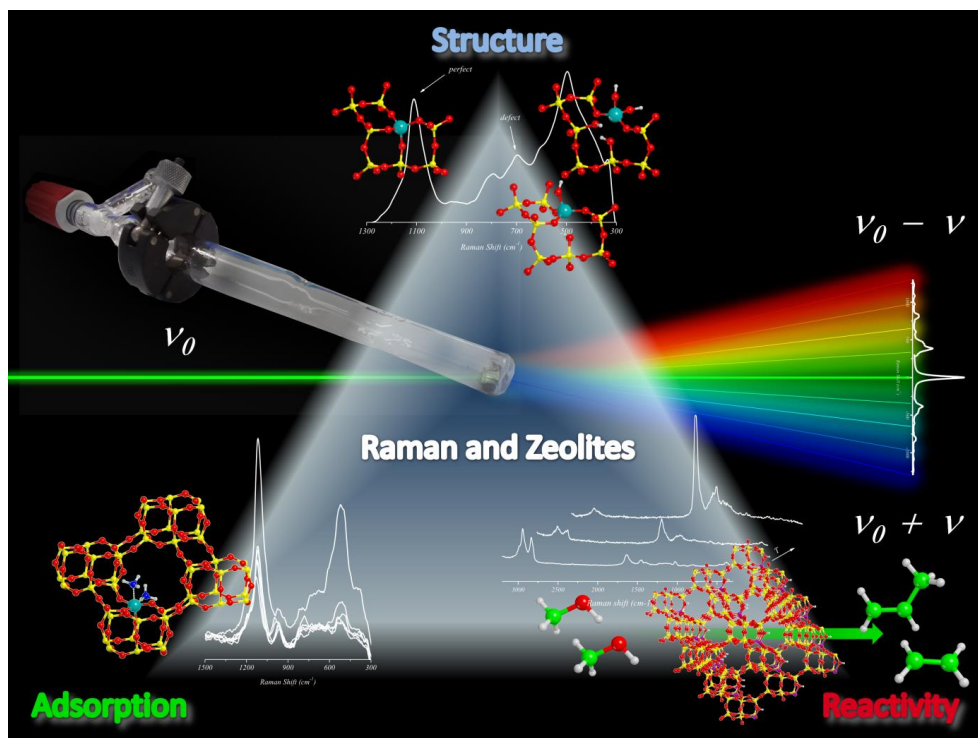
Matteo Signorile

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Summary

Raman spectroscopy is a powerful tool to characterize the bulk vibrational modes of zeolites (i.e. their structure). The application of this technique is often not straight forward: Raman scattering is a low probability effect, often competing with undesired effects (e.g. fluorescence). Moreover the use of laser excitation sources and microscope-focusing could cause the sample degradation consequently to the concentration of high powers in restricted surfaces. All these problems are amplified in zeolites, as: i) the Raman scattering of silicates is poor; ii) the microporous structure of zeolites behaves as a "sponge", trapping species (e.g. hydrocarbons) which are sources of fluorescence; iii) following ii), UV Raman is used to overcome the fluorescence issue, but implying an increased degradation of samples because of the intrinsically high energy of the exciting photons. The goal of my scientific activity is to characterize the structure, the adsorptive properties and the reactivity of zeolites exploiting under *in situ* and *operando* conditions. Several cases have been investigated and among these: i) Ti-zeolites have been analyzed in a combined experimental-computational study on their structure and defectivity, also characterizing them by *in situ* probe molecules adsorption; ii) the deactivation of acid zeolites in the Methanol-To-Hydrocarbons (MTH) process has been studied by comparing *in situ/operando* experiments with a collection of reference compounds, such as Polycyclic Aromatic Hydrocarbons (PAHs). Dedicated methodologies, tools and setups have been developed to allow the such studies, overcoming the intrinsic problems of the Raman spectroscopy applied to zeolites.



P-43

RAMAN AND ZEOLITES: DEVELOPMENT AND TESTING OF DEDICATED INNOVATIVE SETUPS

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ABSTRACT

Raman spectroscopy of zeolites is an helpful tool allowing the characterization of the bulk vibrational modes of these materials, whereas the most common FTIR spectroscopy (at least concerning the transmission mode) fails because of the excessive intensity of such vibrations. In general the Raman characterization of a material is not a trivial task: the Raman scattering is an extremely improbable phenomenon (approximately 1 photon each 10^7 scattered belongs a Raman scattering), so that high power excitation sources (i.e. lasers) are require in order to collect reasonable spectra in acceptable times. Furthermore it is very common to focalize the excitation light onto the sample through a microscope, concentrating the excitation photons in a relatively restricted area. Even if the Raman signal can be largely enhanced by these technical solutions, the samples can undergo a degradation induced by the high power flow concentrated on a small surface. Moreover other side effects can compromise the Raman measurement: typically the sample fluorescence is the worst drawback, where the Raman signal is literary "buried" below the emission profile. The simpler way to avoid the fluorescence is to excite the sample with a wavelength falling outside the typical emission range of most of the molecules (i.e. the visible): IR and deep UV laser have been demonstrated to efficiently allow the Raman measurement, even in presence of highly emissive moieties. However the use of such sources (and in particular UV ones) gives rise to an increase of the degradation problems previously described, not allowing to study easily degradable molecules or probes with small interactions with the support.

All these drawbacks are amplified on zeolites, since: i) silicates are poor Raman scatterer giving an intrinsically low signal; ii) the microporosity and their hydrophobic character makes them "sponges" for hydrocarbons, often cause of strong fluorescence; and iii) according to ii), the use of UV excitation is required, increasing the degradation problems related to the excitation source.

In order to completely exploit the potentialities of our UV Raman ($\lambda = 244$ nm) instrumentation toward zeolites characterization a dedicated setup has been developed. The key concept is to keep the sample under constant movement when it is exposed to the laser. As demonstrated by previous literature,[1-4] this method effectively reduces the sample degradation, allowing to measure it for longer time with higher excitation power. The innovative idea introduced is to produce the sample movement without introducing mechanical parts inside the controlled atmosphere zone of the cell: a rotational movement is transmitted to a specific sample holder through an alternate magnetic field (like in a laboratory magnetic stirrer). This advance represents a big advantage with respect to the past works, as the design of the cell can be extremely simple (even a simple quartz cuvette can be directly applied). A particular effort has been put in the development of a cell for *in situ* studies allowing high vacuum/static atmosphere treatments (Figure 19).

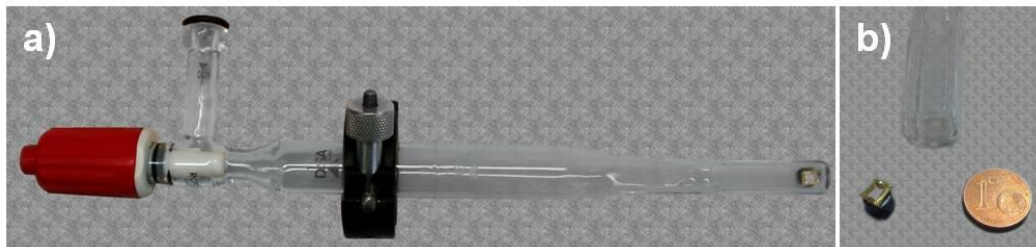


Figure 19. Design of the newly developed *in situ* cell: a) the full mounted cell; b) detail of the rotating sample holder.

Some examples of the application of such cell will be given (see Figure 20): a) highly diluted Polycyclic Aromatic Hydrocarbons (PAHs) have been characterized as adsorbates on high surface area materials [5]; b) the reactivity of low Al content H-ZSM-5 toward the Methanol-To-Hydrocarbons (MTH) reaction has been studied with an *in situ* approach, with particular regard on the deactivation products exploiting the data on PAHs; c) the Ti species and their coordination environment in Ti zeolites have been studied through a combined experimental-computational approach.

Moreover, the construction of cells allowing flow treatments and temperature control (toward *operando* conditions) is under study and will be implemented and further developed in the near future.

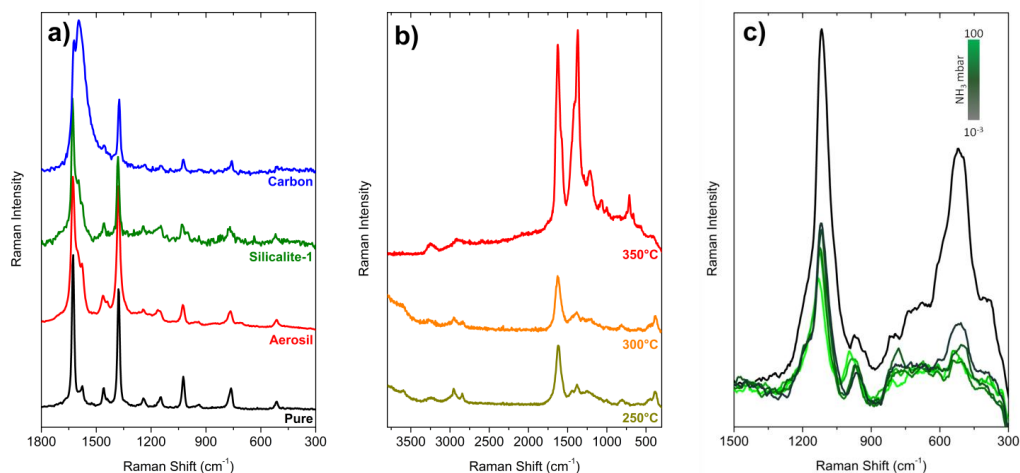


Figure 20. Examples of applications of the new setup: a) gas phase adsorption of naphthalene on Aerosil-300, Silicalite-1 and activated carbon; b) reactivity of H-ZSM-5 (Si/Al = 45) toward MeOH at different temperatures); and c) NH₃ adsorption on TS-1 (2 w% Ti).

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Notes

GA-44

NANOPARTICLES IMPREGNATION OF SILK FIBERS USING SUPERCRITICAL CARBON DIOXIDE

Manish Singh
(**Estera Dey, Cedric Dicko**)

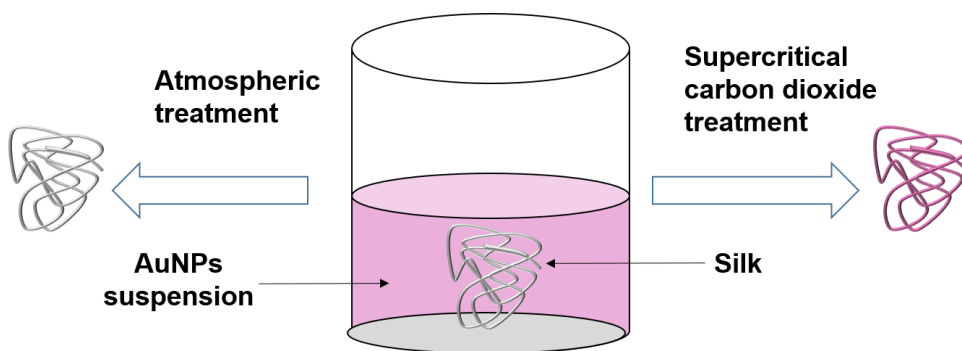
Division of Pure and Applied Biochemistry, Chemical Center, Lund University, Sweden

Summary

It's been more than 15 year, since the discovery of nanoparticles. They are being used in various fields including IT, defense, cosmetic, medicine, security, and textile. Nanoparticle exhibits anti-microbial, UV protection, and self-cleaning properties. Due to the distinct properties, they are being used to add functionalities in textile industry. However, incorporation of nanoparticles in textile have certain drawback such as leakage, the process demands harsh chemical pre-treatment. The leakage as well as the pretreatment step has a negative effect on environment and humans.

The aim of my PhD research is to identify and exploit raw silk using supercritical carbon dioxide (sc-CO₂) to fabricate low cost nanocomposites without leakage of nanoparticles. The work focusses on four types of silks namely Bombyx, Eri, Muga and Tasar and a selection of nanoparticles such as gold, silver, titanium oxide and zinc oxide will be focused.

The critical part of this research is to permanently bind the silk to nanoparticle. With sc-CO₂, permanent interaction can be achieved without sacrificing the texture or other properties of silk. Sc-CO₂ is a fluid state of carbon dioxide above its critical pressure (72.9 atm) and critical temperature (31.1 °C). Non-toxic property of sc-CO₂ make it environmental friendly process. Sc-CO₂ plasticizes and significantly increases the diffusivity of nanoparticles into silk fibers, thus allowing loading. The general aim is to produce sustainable advanced materials using green processes.



P-44

Supercritical carbon dioxide (scCO₂) can open-close Indian silks fibers and permanently load standard size gold nanoparticle

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a) Division of Pure and Applied Biochemistry, Chemical Center, Lund University, Sweden

ABSTRACT

Silk are diverse in form, quality and cost. New properties can be added to silk by its functionalization with nanoparticles. However, bringing additional functionalities is hampered by the silks' inert surface. More generally the application of nanotechnology in textile is limited by the difficulties of loading the textile fibers with nanoparticles, and most importantly, by the uncontrolled leakage of the loaded particles.

In this work, we demonstrate the facile impregnation of Indian silks (Mulberry, Eri, Muga and Tasar) with standard gold nanoparticles of different size (5 nm, 20nm, 50 nm, 100 nm and 150 nm) in water. Comparing the control at atmospheric and the supercritical carbon dioxide conditions (200 bar, 40 °C), we found that supercritical carbon dioxide (sc-CO₂) can plasticize and significantly increase the diffusivity and thus loading of gold nanoparticles into silk fibers.

The evaluation of the robustness of the impregnation process is tested by successive water washes, and evaluation of the wash supernatant by UV absorption. The three different stages in the wash process are: (i) directly after impregnation – "gold loading", (ii) after fiber gentle washing- "wash leakage", and (iii) after harsher wash at 50 °C for 1h – "fastness leakage" (Figure 1).

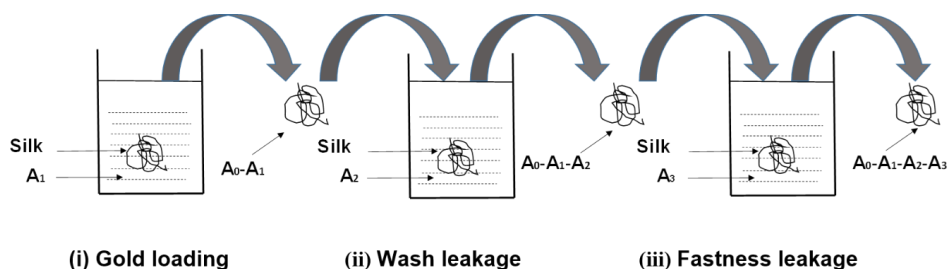


Figure 1. Three different stages in the wash process. Where, A_0 is absorbance of gold suspension before impregnation, while A_1 , A_2 and A_3 are absorbance of liquid supernatant after impregnation, water wash and fastness treatment.

The total efficiency of gold nano-particles in silk fibers is calculated as the cumulative loss of gold through the three wash steps. Figure 2 summarizes the comparison between scCO₂ impregnation and control for all four silks and five sizes of gold nanoparticles.

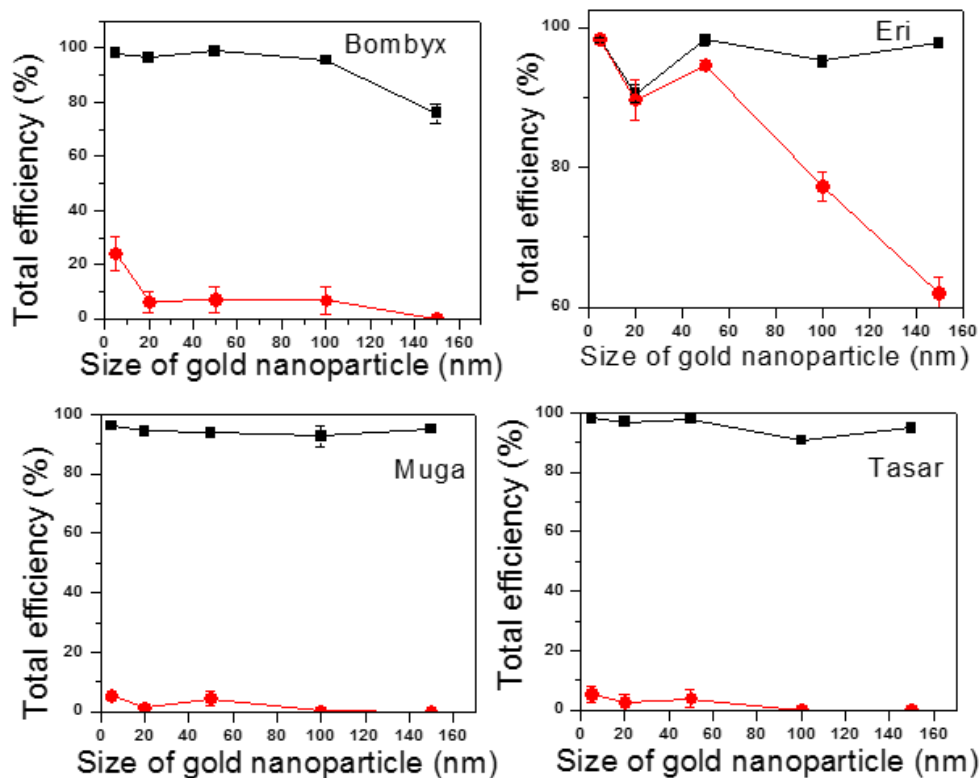


Figure 2. ■ ● Stands for supercritical and control treatment, respectively. Comparison of total efficiency at supercritical and control impregnation, of Indian silks: (a) Bombyx (b) Eri (c) Tasar (d) Muga with different size gold nanoparticle (5 nm, 20 nm, 50 nm, 100 nm and 150 nm).

Structural and morphological characterization of the impregnated fibers using FTIR, XRD and SEM suggest a low impact of the supercritical treatment.

In conclusion, we demonstrated the permanent loading of gold nanoparticle in four types of silk (Bombyx, Eri, Tasar and Muga) using green and scalable technology like supercritical carbon dioxide. This work addresses the existing problem of uncontrolled leakage of the loaded particles from textile fibers, which is great concern for environment and a hurdle in the applications of nanotechnology in textile.

Notes

GA-45

NANOCRYSTALLINE MATERIALS FOR PHOTOCATALYSIS

Alessandra Truppi

A. Agostiano, R. Comparelli, M.L. Curri, M. Striccoli, T. Placido, F. Petronella.

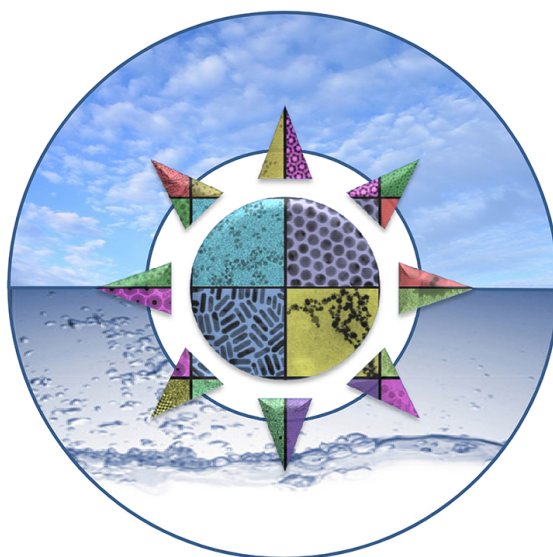
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Summary

The research project is focused on designing, fabrication and processing inorganic semiconductor and metal solids at the nanoscale. In particular, the goal of the project is to set up the synthesis of visible light active metal modified TiO₂-based photocatalysts (TiO₂/Cu_xO, TiO₂/Au NRs, TiO₂/Fe₂O₃/Ag), for application in water and gas phase photocatalysis. This work is carried out in collaboration with CNR-IPCF. The present project aims at studying novel synthetic protocols as colloidal chemistry routes (sol-gel techniques or hot-injection) for synthesizing semiconductor and metal nanocrystals, with a good control on size, shape, crystalline phase in order to finely tune their chemical-physical properties and control their efficiency for catalytic applications. In particular the potential of the prepared materials is investigated for photocatalytic degradation processes of the pollutants in aqueous matrices and in the gas phase induced by both UV light and sunlight. The goal is to achieve stable particles, with a high degree of crystallinity and high surface area. Furthermore, the prepared TiO₂ nanocrystals are modified with metal nanoparticles, narrow band gap semiconductors, or doped with non-metal ions to improve their absorption in the visible range. The obtained nanosized photocatalyst are characterized by XRD, BET, TEM, SEM, EDS, XPS and AFM. In addition, their photocatalytic properties are tested in the photocatalytic degradation of several organic pollutants in comparison with their commercial counterpart. These properties are evaluated in solution, at solid air interface, in a standard mortar, under UV light and sunlight.

Grafical abstract:



P-45

SYNTHESIS AND CHARACTERIZATION OF TiO₂/Au NRS BIFUNCTIONAL CATALYSTS FOR UV AND VISIBLE LIGHT PHOTOCATALYSIS

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ABSTRACT

In recent years, air and water pollution is notoriously a serious problem facing all anthropic activities throughout the world. Photocatalysis is a very promising approach to face relevant questions connected with the increasing environmental pollution. In particular, as one of the most promising solutions for these problems, plasmonic nanostructures of noble metals in combination with semiconductors have been attracting tremendous attention.[1]Photocatalysis takes place when a semiconductor is irradiated with light higher than or equal to its band gap energy, thus generating photo-electrons (e⁻) or photo-holes (h⁺) that, reacting with oxygen molecules or water molecules, give rise to the formation of Reactive Oxygen Species (ROS) able to remove organic pollutants from water or air. TiO₂ has been commonly regarded as the benchmark material for photocatalysis related applications and its role in the relevant area has been substantially studied for decades.[2]In spite of this, the pure TiO₂ possesses a wide band gap which limits its photoabsorption to only the UV region ($\lambda < 390$ nm), namely just a small fraction (4%) of the whole solar energy, thus limiting the possibility to exploit energy from natural sunlight for photocatalysis related applications.[3]To overcome the serious drawbacks of fast charge recombination and the limited visible-light absorption of semiconductor photocatalysts, many strategies have been developed in the past few decades and the most widely used one is to develop plasmonic photocatalysts.[4]Compared with the common semiconductor photocatalysis, plasmonic photocatalysis possesses two distinct features: a Schottky junction and localized surface plasmon resonance (LSPR); each feature benefits photocatalysis differently.[5]Indeed, noble metals are expected to reduce the electron-hole pairs recombination events by trapping electrons and to facilitate the transfer of holes on the TiO₂ surface. In particular, Au NPs have attracted great interest owing to their strong optical absorption in the visible range due to localized surface plasmon resonance, their great stability in a wide range of temperatures and environments, and their chemical activity.[4]However, it must be pointed out that the role played by gold nanoparticles in the overall photoactivation mechanism is different according the photoactivation wavelength. Under UV irradiation titania is activated and photo-generated electrons, sink in NPs of noble metal, hindering the recombination of charge carriers (e⁻/h⁺), which results in an increase of the photocatalytic activity. Under visible light irradiation titania cannot be activated (band-gap: 3–3.2 eV), and thus light must be absorbed by plasmonic NPs. Two possible mechanisms of titania activation by plasmonic NPs under visible light irradiation have been recently proposed, i.e. charge and energy transfer.[4]

The goal of the present work is to set up the gram-scale synthesis of visible light-active Au nanorods modified TiO₂-based photocatalysts, for potential application in water and gas phase photocatalysis. We have investigated synthesis and characterization of nanostructured photocatalysts in three different calcination temperatures for to observe the relative instability of the nanorods. Photocatalytic experiments were performed under UV irradiation in order to test the degradation of a target compound (methylene blue) in aqueous solution using TiO₂ P25 Degussa as a reference material. Moreover, these powders were successfully employed for the degradation, under Visible light of Nalidixid acid, a widely diffused antibacterial agent of environmental relevance known to be non-biodegradable. Absorbance spectroscopy measurements pointed out that TiO₂/Au NRs calcined at 450°C presented a photoactivity

up to 3 times higher than TiO₂ P25 Degussa under UV light. Interestingly, after 15 min of Visible light irradiation the photocatalytic reaction assisted by TiO₂/Au NRs 450°C nanocomposite showed higher percentage of degradation than other TiO₂/Au NRs samples, pristine TiO₂ and TiO₂ P25 Degussa, which exhibited a negligible degradation. The obtained results highlight a strong enhancement in the photocatalytic performance of TiO₂/Au NRs compared to pristine TiO₂, arising from the presence of Au NRs. This points out the possibility to shift their photoactivity in the visible range and their viability for several environmental related applications.

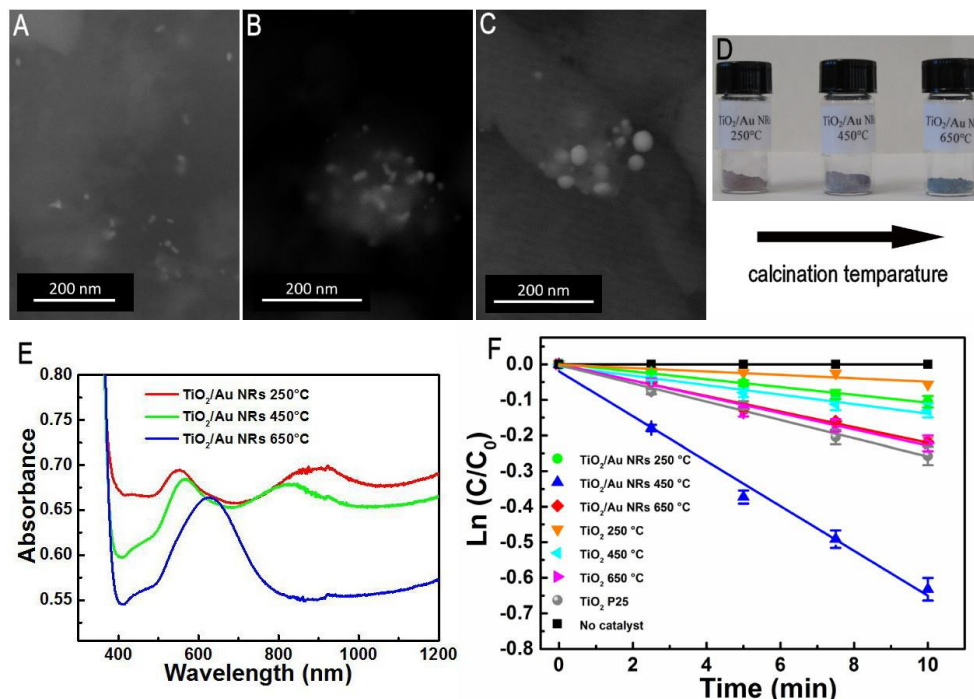


Figure 1. SEM micrograph of the same portion of TiO₂/Au NRs photocatalysts deposited onto silicon slide, obtained by BSE detector: **A)** TiO₂/Au NRs 250 °C; **B)** TiO₂/Au NRs 450 °C; **C)** TiO₂/Au NRs 650 °C. **D)** Photographs of “as prepared” TiO₂/Au NRs nanocomposites at different calcinations temperatures. The image shows that the colour of samples changes from pink, violet to blue by increasing calcination temperature, probably due to small changes in mean aspect ratio. **E)** Reflectance spectra of TiO₂/Au NRs nanocomposites deposited onto quartz slides, recorded in absorption mode. **F)** Comparison of MB decolouration rates in presence of TiO₂/Au NRs 250 °C, TiO₂/Au NRs 450 °C, TiO₂/Au NRs 650 °C, TiO₂ 250 °C, TiO₂ 450 °C, TiO₂ 650 °C and TiO₂ P25. Experiments were carried out at pH 6 under UV light irradiation at 254 nm. MB concentration has been evaluated monitoring the absorbance intensity at 630 nm.

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Notes

GA-46

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF INNOVATIVE MATERIALS FOR ENVIRONMENT AND ENERGY

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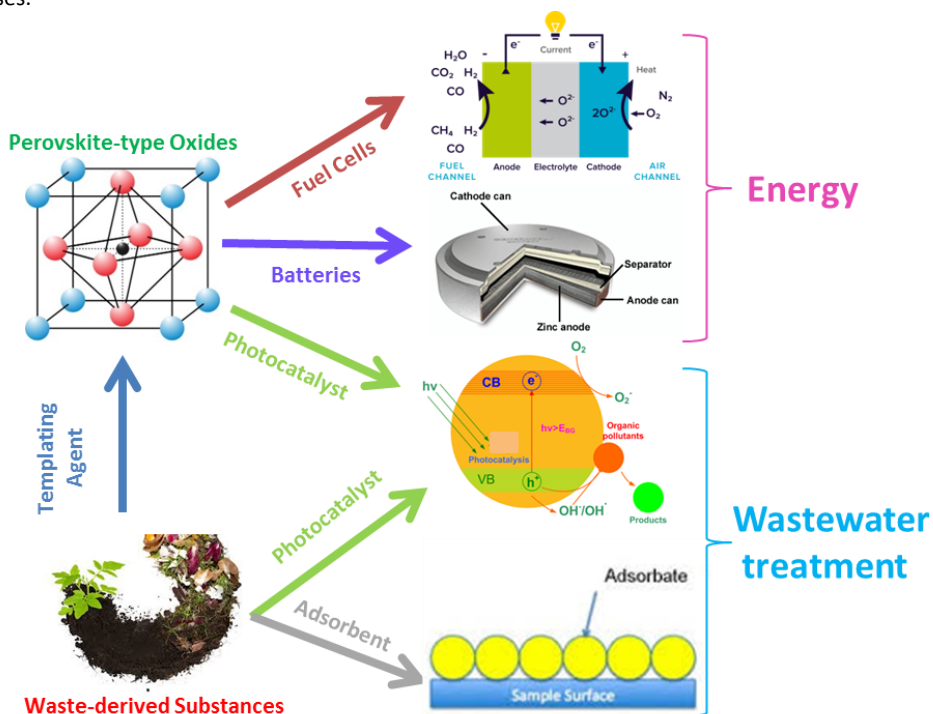
Università degli studi di Torino, Via P. Giuria 7, 10125, Torino, Italy

Summary

My Ph.D project is included in this wide context focusing on green chemistry, with the aim of preparing new materials for abatement of pollutants and "clean" energy production. In particular, this project is divided in two main branches: the study of perovskite-type oxides and of materials obtained from urban wastes.

Perovskite-type oxides (like $\text{Sr}_{0.85}\text{Ce}_{0.15}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.6}\text{Mn}_{0.4}\text{O}_3$ and LaFeO_3) were employed as cathodes for Intermediate Temperature Solid Oxide Fuel Cells and Zn-air batteries (for energy application) and as photocatalysts (for wastewater treatment). In this research, the production of these mixed oxides was based on Solution Combustion Synthesis, which is a versatile method to obtain oxides with different features, thanks to the possibility of changing many synthesis parameters.

On the other side, substances extracted from compost, similar to humic substances, were exploited as surfactants, photosensitizers and adsorbents. The main aim of producing waste-derived materials is the application for water depollution. Moreover, refuses become a valuable resource for environmental purposes.



P-46

ECOFRIENDLY PHOTOSENSITIZING SUBSTANCES @ MODIFIED SILICA SUPPORTS

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ABSTRACT

Functionalization is a surface modification process of a material carried out by chemical and/or physical treatments to change its surface chemistry and add new functions or properties. Herein, soluble waste-derived substances (WDS), with photosensitizing features [1], were immobilized on silica obtaining organic-inorganic hybrid photosensitizers for polluted water cleaning [2].

Silicas of different nature and morphology were used as supports: amorphous, HMS (with tortuous channels) and SBA-15 (with regular hexagonal geometry of the porous network) were modified to be compatible to WDS (the schematic process is reported in Figure 1). WDS could be defined as humic-like substances, bearing chemical similarities with humic acids. WDS involved in this work were isolated from urban public park trimming and home gardening residues aged under aerobic conditions for 230 days and were labelled CVT230. Silicas were functionalized with amino groups in order to covalently bind CVT230 carboxylic groups through activation by *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) [3,4]. The immobilization on silica was a required step to make CVT230 insoluble and this heterogenization process favored the reusability and recyclability of the photosensitizer.

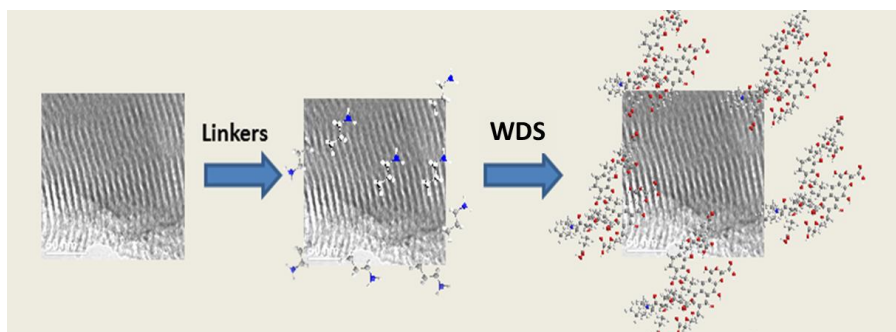


Fig.1: Synthetic steps for production of hybrid photocatalysts. SBA-15 channels are evident in TEM pictures reported in background. The first reaction is related to functionalization of SiO₂ with amino-linkers and the second one is the heterogenization of waste-derived substances.

The hybrids were carefully characterized by several techniques (Small Angle X-ray scattering, Transmission Electron Microscopy, N₂ uptake at 77K, Fourier transform infrared spectroscopy, Thermogravimetric Analysis TGA) to investigate the morphology, the texture and the photoactive moiety loading.

In particular TGA curves allowed to quantify the amount of linker and WDS bonded to the siliceous surface (an example of the procedure carried out for SBA-15-based sample is reported in Figure 2).

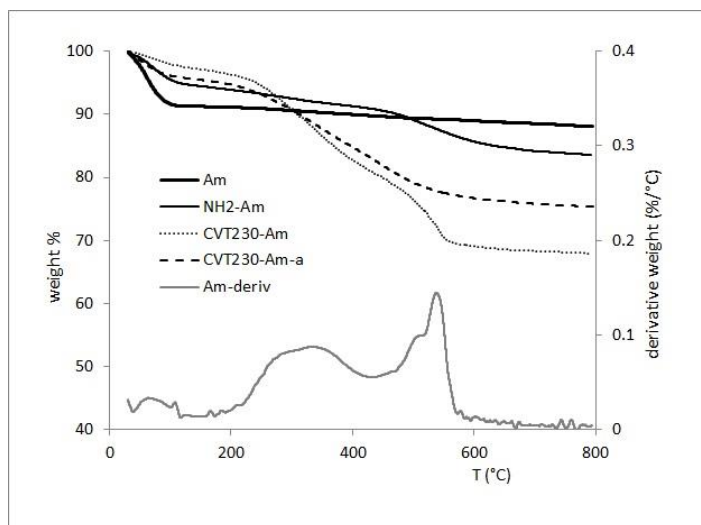


Fig.2: Thermogravimetric analysis profiles of the Amorphous (Am) sample as prepared, after aminopropyl (linker, NH₂-Am) and CVT230 (CVT230-Am) functionalizations, and after the photoactivated reaction (CVT230-Am-a). The grey curve is the derivative of the CVT230-Am profile.

The photosensitizing activity was evaluated by irradiating suspensions of CVT230-Silica hybrid and substrate under simulated solar light irradiation through a Solarbox system equipped with a cut-off filter of 340 nm. A probe molecule, 4-methylphenol, was used as model pollutant: CVT230-Silica materials showed satisfactory results in terms of substrate degradation, stability and reusability. In particular, the hybrid produced from SBA-15 resulted the most promising material, thanks to its stability during irradiation and interaction with the substrate. For this reason, it was also chosen to be tested for adsorption and photoactivated abatement of differently charged dyes, namely Orange II and Rhodamine B.

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Notes

GA-47

PREPARATION AND PHYSICO-CHEMICAL FUNCTIONALIZATION OF POROUS SOLIDS FOR CO₂ ADSORPTION

Chiara Vittoni

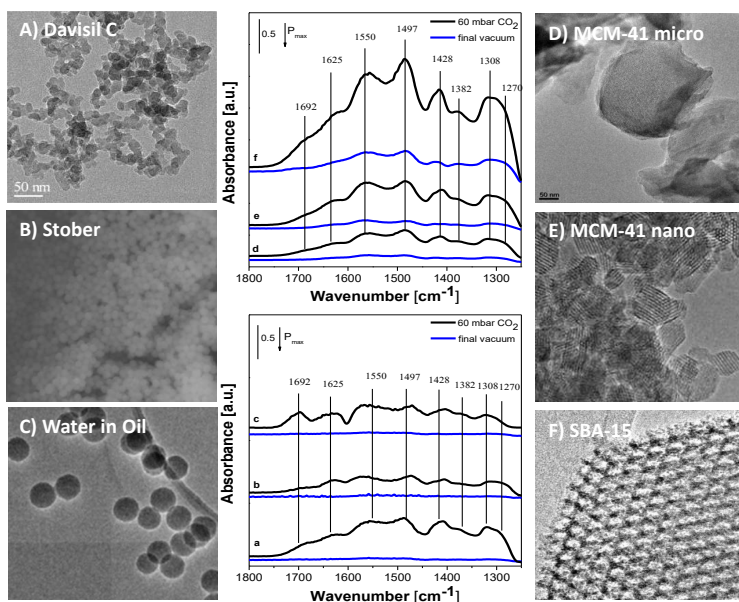
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Summary

My Ph.D research project concerns the synthesis of different inorganic-organic hybrid silicas with different structure and morphology (i.e. pore architecture and particle dimensions) with potential application for CO₂ adsorption. Several silica based materials with different structure, morphology and particle size are selected in order to understand the effect of their physico-chemical properties on the CO₂ adsorption mechanisms. Until now, the following materials are considered: i) commercial mesoporous amorphous silica, ii) non-porous silica particles with micrometric and nanometric size obtained by using Stöber and Water-in-Oil methods, respectively, iii) mesoporous MCM-41 silica with ordered arrays of pores, and iv) a mesoporous SBA-15 material.

In order to make the siliceous materials reactive towards CO₂, basic groups such as NH₂ species on the silica surface are needed on the silica surface. These species can be introduced on the surface by grafting of different organosilanes (for instance: i) 3-aminopropyltriethoxysilane (APTS); ii) 3-(2-aminoethyl) aminopropyltrimethoxysilane (EAPTS) and iii) 3-[2-(2-aminoethyl)aminoethyl] aminopropyltrimethoxysilane (PAPTS)) or by using one-pot preparation method. In addition, amino-groups can also be introduced by impregnating siliceous materials with polyethyleneimine (PEI). Physico-chemical properties of materials are evaluated by using a multidisciplinary approach especially focusing on their structure (evaluated by XRD analysis), morphology (studied by SEM and TEM analysis), textural properties (monitored by N₂ Physisorption) and surface properties (determined by FT-IR analysis). The reactivity of the materials towards carbon dioxide is evaluated by means of SS-NMR and FTIR spectroscopies of adsorbed CO₂, while the amount of CO₂ adsorbed is evaluated by volumetric analysis.



SEM Analysis of amorphous Davisil C silica (A) and Stöber silica (B).

TEM Analysis of Water-in-Oil silica (C), bulky MCM-41 (D), nanosized MCM-41 silica (E) and SBA-15 silica (F).

FT-IR spectra of 60 mbar of CO₂ adsorbed on PAPTS_Davisil C (a), PAPTS_Stöber (b), PAPTS_Water-in-Oil (c), PAPTS_MCM-41 micro (d), PAPTS_MCM-41 nano (e) and PAPTS_SBA-15 (f)

P-47

SYNTHESIS, FUNCTIONALIZATION AND PHYSICO-CHEMICAL CHARACTERIZATION OF ORGANIC-INORGANIC HYBRID MATERIALS FOR CO₂ ADSORPTION

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ABSTRACT

In recent decades, the atmospheric concentration of CO₂ is strongly increasing in relation to anthropogenic causes, contributing to the change of the Earth's average temperature (Greenhouse Effect). In order to prevent the increase in the atmospheric concentration of CO₂ several methods, that include CO₂ sequestration by adsorption and storage processes on different solids, have been proposed in the literature [1]. In this work the adsorption properties of organic-inorganic hybrid mesoporous silica functionalized with different organo-silanes were studied. Particular attention has been given to the preparation and physico-chemical characterization of amino-functionalized SBA-15 mesoporous silica. The materials were prepared following two approaches: i) the organic functionalities were introduced on a previously prepared sample through a surface post-synthesis grafting method; ii) a one-pot co-condensation approach was used in order to prepare organo-modified materials in a single reaction step (Fig. 1). Three different amino-silanes were used for the SBA-15 functionalization: i) 3-aminopropyltriethoxysilane (APTS); ii) 3-(2-aminoethyl) aminopropyltrimethoxysilane (EAPTS) and iii) 3-[2-(2-aminoethyl)aminoethyl] aminopropyltrimethoxysilane (PAPTS).

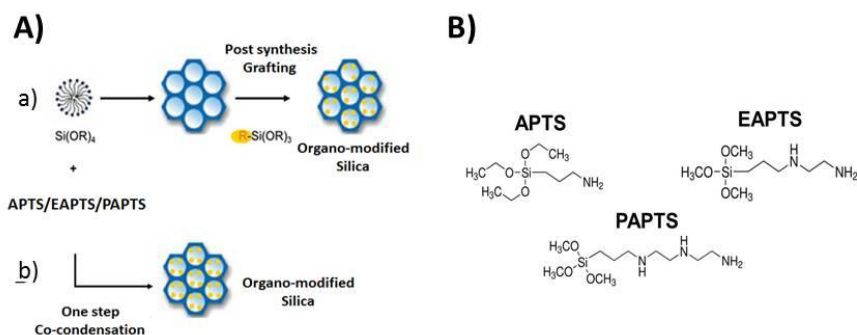


Figure 1. A) Scheme of a) post synthesis grafting and b) one pot co-condensation methods for the preparation organo-modified silica materials. B) Amino-silanes used for the SBA-15 functionalization: 3-aminopropyltriethoxysilane (APTS), 3-(2-aminoethyl) aminopropyltrimethoxysilane (EAPTS) and 3-[2-(2-aminoethyl)aminoethyl] aminopropyltrimethoxysilane (PAPTS).

The structural and textural properties of the obtained materials were strongly influenced by the preparation method. In particular, it was shown that the samples prepared by one-pot method were characterized by a higher structural disorder compared to the grafted-one. The reactivity of the materials towards carbon dioxide was tested using different experimental techniques. CO₂ adsorption properties was studied by means of both SS-NMR and FTIR spectroscopies. The analysis of CO₂ adsorbed in post combustion conditions (35 °C, partial pressure CO₂ = 0.1 bar) indicated that all materials are reactive towards carbon dioxide and that carbamate-type species are formed [2]. However, it was shown that the reactivity is influenced by the synthesis preparation and the type of organosilane used for the functionalization of materials. In particular, samples containing higher amount of amino groups (prepared by post-synthesis methods) are more reactive, following the order SBA-15+APTS < SBA-15+EAPTS < SBA-15+PAPTS. The number of amino groups per nm² was 4.3, 9.4 and 12.3, respectively. Moreover, materials prepared via one-pot method are significantly less reactive than those prepared with post-synthesis grafting, and this is due to the fact that the amino groups are protonated during the one-pot synthesis conditions.

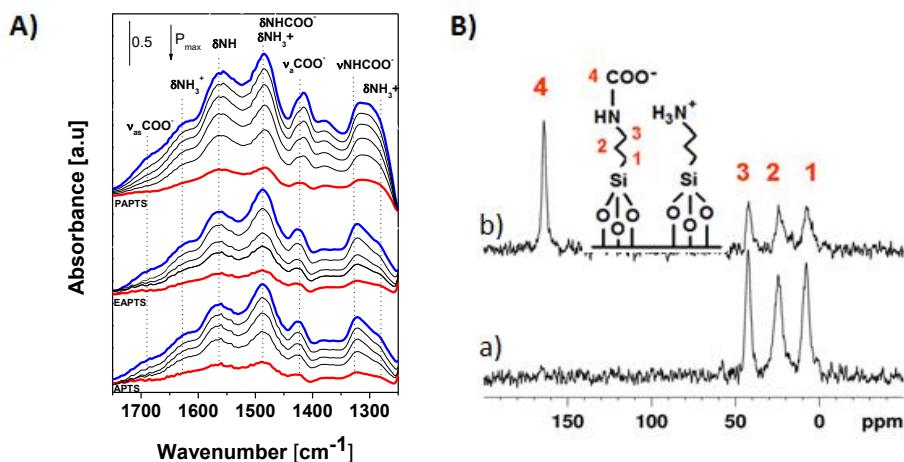


Figure 2. A) FT-IR spectra of 60 mbar of CO₂ adsorbed on SBA-15 sample grafted post synthesis with APTS, EAPTS and PAPTS and B) SS-NMR spectra of SBA-15 grafted post synthesis with APTS a) before and b) after the adsorption of 60 mbar of ¹³CO₂

The CO₂ adsorption properties were also studied by using the "Zero-Length Column" chromatography technique. This analysis showed that the hybrid samples have a different mechanism of interaction with the CO₂. In fact, the SBA-15 + APTS sample weakly adsorbs the CO₂, while SBA-15 + EAPTS and SBA-15 + PAPTS samples are more reactive, probably because of the presence of multiple amino-groups on the same organic chain. These measurements also allowed proposing a mechanism of interaction of CO₂ on samples containing different amount of NH₂ groups.

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Notes

GA-48

STRUCTURE SENSITIVITY OF SUPPORTED NICKEL CATALYSTS IN (DE)HYDROGENATION REACTIONS

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Summary

Catalysts play an important role in chemical industry and have the ability to enable processes that will fuel the future. An example is the conversion of synthesis gas (a mixture of CO and H₂) to a variety of different, more valuable end products. Characteristic for metallic catalysts is their ability to dissociate hydrogen. My research focuses on nickel because it is a cost effective, thus practically relevant, alternative to noble metals for many different (de-) hydrogenation reactions. What is the ideal size of nickel metal particles in catalysis: atoms, clusters or nanoparticles? A rule of thumb in catalysis is, the smaller the (nickel) particles; the more active they are due to a higher surface area to bulk molecule ratio. Metal nanoparticles exhibit particularly interesting catalytic behavior when they become *really* small (<10 nm)[1,2]. It is important to understand the influence of particle size and structure on catalyst activity in order to be able to develop better, more efficient catalysts in the future.

By combining different operando spectroscopic techniques and several catalytic model reactions, we hope to gain a fundamental understanding of different structure sensitivity effects and aspects on supported nickel catalysts. This project is a co-effort between University of Utrecht, TU-Eindhoven, and BASF.

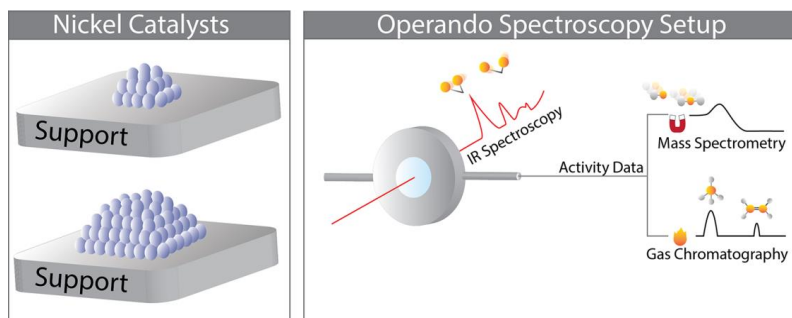


Figure 1: a) Schematic depiction of supported nickel b) operando spectroscopy setup used to examine the activity of nanoparticulate nickel catalysts.

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Notes

GA-49

DEVELOPMENT OF FERRITE SPINEL STRUCTURES FOR PHOTOREDUCTION REACTIONS

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Monica Barroso, Bert M. Weckhuysen

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Summary

The increasing demand of energy by society, rapidly depleting fossil fuels and increasing CO₂ emissions are serious economic and environmental challenges. To decrease the necessity for fossil fuels, but still satisfying the energy demand calls for the need of renewable and alternative energy sources. One of the most promising sources of renewable energy is solar energy. Storing this energy is a challenge however. One possibility is storing this energy chemically, producing solar fuels.[1-2] The most thoroughly studied solar fuel is hydrogen, formed by splitting water. However, most of the fuel-based infrastructure is based on carbon fuels. This is why the generation of carbon-based fuels is more desirable. This is possible by reducing CO₂ to for example CO, CH₃OH or CH₄. [3]

In this research several spinel ferrites in combination with copper alloys will be focused upon as low cost, non-toxic photoactive materials for CO₂ reduction (Figure 1).[4-5] Electronic properties and performance in photoelectrochemical CO₂ reduction are key in this research. Once stable, well-performing photocathodes have been designed by combining ferrites and copper alloys optimization will be done by nanostructuring these electrodes (Figure 1). For example forming nanopillar structures has been shown to increase the quantum yield of materials by significantly increasing the catalytic surface area, decreasing the amount of material and decreasing the path length for charge carriers to travel, effectively lowering charge carrier recombination rates.[1]

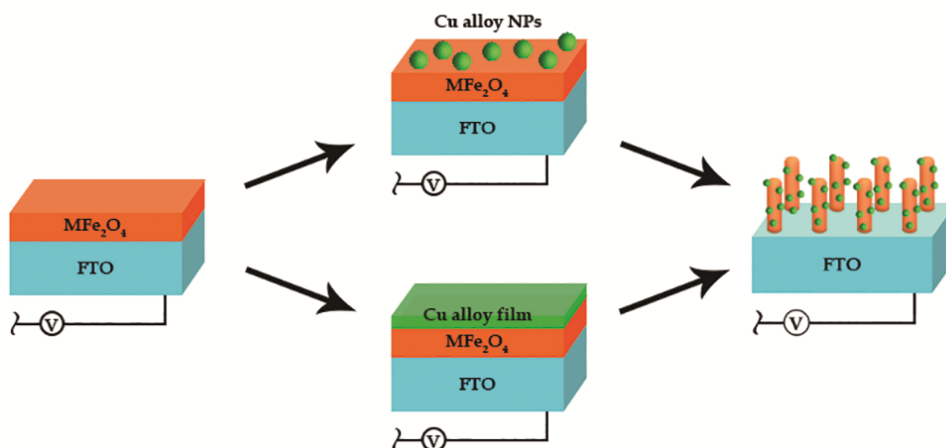


Figure 1: The research path to design nanostructured, ferrite spinel-based photocathodes for CO₂ reduction.

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P-49

DEVELOPMENT OF FERRITE SPINEL STRUCTURES FOR PHOTOREDUCTION REACTIONS

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ABSTRACT

The increasing demand of energy by society, rapidly depleting fossil fuels and increasing CO₂ emissions are serious economic and environmental challenges. To decrease the necessity for fossil fuels, but still satisfying the energy demand calls for the need of renewable and alternative energy sources. One of the most promising sources of renewable energy is solar energy. Storing this energy is a challenge however. One possibility is storing this energy chemically, producing solar fuels.[1-2] The most thoroughly studied solar fuel is hydrogen, formed by splitting water. However, most of the fuel-based infrastructure is based on carbon fuels. This is why the generation of carbon-based fuels is more desirable. This is possible by reducing CO₂ to for example CO, CH₃OH or CH₄. [3]

Recent research in ferrite spinel structures (MFe₂O₄) has picked up in the photocatalysis field since these materials have favorable band gaps around 2 eV, meaning a significant portion of visible light can be absorbed.[4] Also, the conduction bands of ferrites are often positioned such that it is thermodynamically possible for CO₂ to be reduced at the surface of these materials. Finally most ferrites studied are found to be stable in aqueous media under neutral and alkaline conditions.

The synthesis of well dispersed, metal oxide thin films is a challenge. In this research the synthesis of ferrite spinel thin films on transparent conductive oxides (TCOs) has been studied. Several synthesis techniques including spincoating, spray pyrolysis and electrodeposition have been explored. These materials have been studied in terms of chemical character, morphology and photoelectrochemical response to determine the best synthesis method for obtaining these binary metal oxides used for light-driven reactions.

The ferrite spinel structure that has been studied is NiFe₂O₄. With X-ray diffraction (Figure 1) it is shown that indeed the desired spinel structure can be formed with several techniques. A typical image obtained with focused ion beam scanning electron microscopy (FIB-SEM, Figure 2) shows that relatively flat and thin films can be obtained in with nanometer range thicknesses.

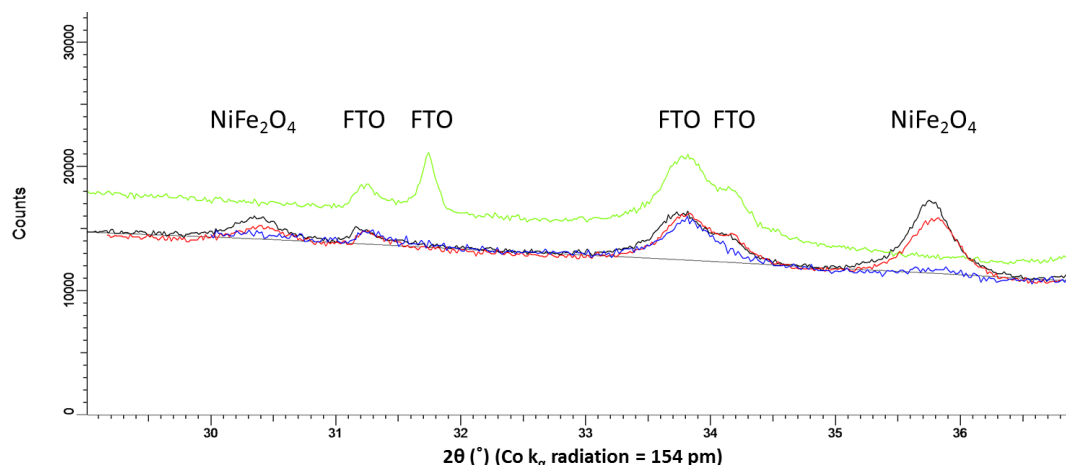


Figure 1: Typical X-ray diffractograms of Spincoated NiFe₂O₄ (Black), spray pyrolyzed NiFe₂O₄ (red), electrodeposited NiFe₂O₄ (Blue) and bare FTO substrate (SnO₂:F) (Green).

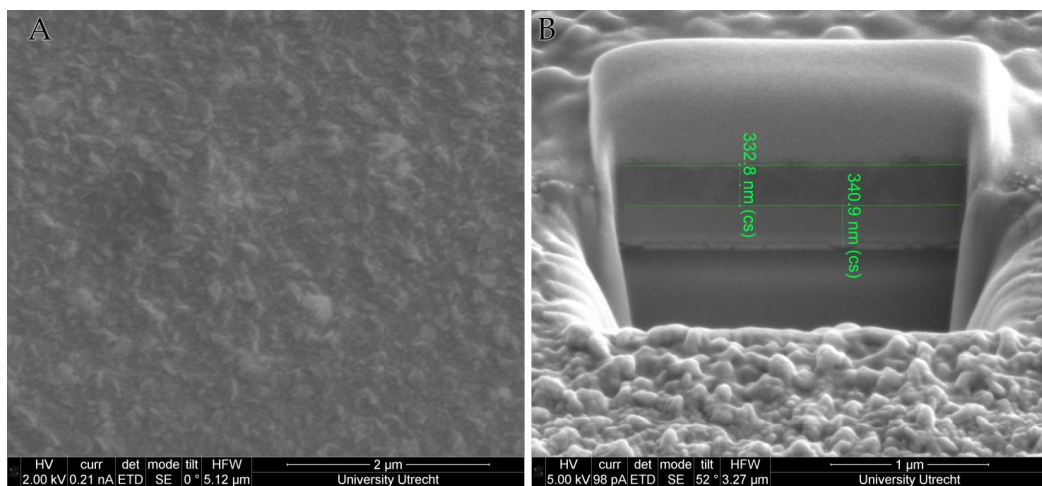


Figure 2: Typical FIB-SEM images obtained for NiFe₂O₄ thin films. A) shows the surface of the sample, B) shows a cross section obtained using the ion beam from top to bottom it shows Pt, NiFe₂O₄, SnO₂:F and glass.

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Notes

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