



**COST Chemistry D36**

**“Molecular Structure-Performance Relationships at the  
Surface of Functional Materials”**

**2<sup>nd</sup> WORKSHOP**

**and 4<sup>th</sup> Management Committee Meeting**

**University College Dublin,  
Belfield,  
Dublin 4,  
Ireland.**

**Thursday, September 4<sup>th</sup> – Friday, September 5<sup>th</sup>, 2008**



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**Meeting Venue:** Room B109/110,  
UCD Health Sciences Centre,  
Belfield,  
Dublin 4,  
Ireland.

**Organiser:** Dr James A Sullivan,  
UCD School of Chemistry and Chemical Biology,  
Science Centre South,  
Belfield,  
Dublin 4,  
Ireland

[james.sullivan@ucd.ie](mailto:james.sullivan@ucd.ie)

## Programme

Thursday, September 4th, 2007

8:45 – 9:10		REGISTRATION
9:10	SESSION 1	Chair: Dr. Maria Rosa INFANTE
9:10 – 9:15	Welcome	James SULLIVAN, Symposium Organizer Miguel A. BAÑARES, Action Chair
9:15 – 9:45	O–1	Anna Maria VENEZIA. PdO catalysts for CH <sub>4</sub> oxidation: attempts to improve the activity and the tolerance to SO <sub>2</sub> .
9.45 – 10:15	O–2	Laszlo GUCZI. Colloidal approach in preparation of interfaces for nanoparticles used as catalyst in the CO oxidation.
10:15 – 11:15	KEY-1	S.C. Edman TSANG. Development of Novel Nano-materials for Catalysis, Sensor and Bio-medical applications.
11:15 – 11:45		Coffee Break
9:10	SESSION 2	Chair: Professor Soghomon BOGHOSIAN
11.35 - 12.05	O–3	Maria G. MONTES de OCA. Electrochemical responses of Te <i>upd</i> layers at Au-Pd core-shell nanostructures
12.05 - 12.35	O–4	Lubomir POSPISIL. Electrochemical Cationic Catalysis of Radical Anion Reduction and Model of Hidden Negative Resistance.
12.35 - 1.05	O–5	Viorica PARVULESCU. Functionalized organic-inorganic hybrid supports for enzyme immobilization.
1:05 – 2:15		LUNCH (Belfield Restaurant)

**2:15 SESSION 3**

Professor Vasile PARVULESCU

**2.15 - 3.15**

KEY-2

Jan KAŠPAR.  
CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides as environmental catalysts: How complex is it to design such a "simple" material?

**3.15 - 3.45**

O-6

Graeme WATSON.  
The interaction of CO and NO<sub>2</sub> with low index surfaces of ceria.

**3.45 - 4.15**

O-7

Anna E. LEWANDOWSKA.  
The effect of alkali additives on the structure and reactivity of the vanadium catalytic system. Combination of theoretical and experimental studies.

**4:15 – 4:45**

Coffee Break

**4:45 – 6:00**

4<sup>th</sup> Management Committee Meeting

**6:15 – 7:30**

Workshop Dinner, Norah Greene Room, Belfield Restaurant.

**Friday, September 5th, 2007**

**9:00 SESSION 4**

Chair: Dr Magali BOUTONNET Chair:

**9:00 – 10:00**

KEY-3

Justin HOLMES.  
The synthesis, characterisation and assembly of nanoscale materials for electronic and magnetic applications.

**10:00 – 10:30**

O-8

M. Olga GUERRERO-PÉREZ.  
New reaction: ammoxidation of glycerol into acrylonitrile.

**10:30 – 11:00**

O-9

Agnieszka M. RUPPERT.  
Novel Space-resolved method of basicity examinations and their application in the catalytic glycerol etherification.

**11:00-11:20**

Coffee Break

**11:20 SESSION 5**

Chair: Professor Jacques FRAISSARD

**11:20 – 11:50** O-10

Maciej TREJDA.  
The radical active species and impurities present in mesoporous silicas as oxidation active centres.

**11:50 – 12.20** O-11

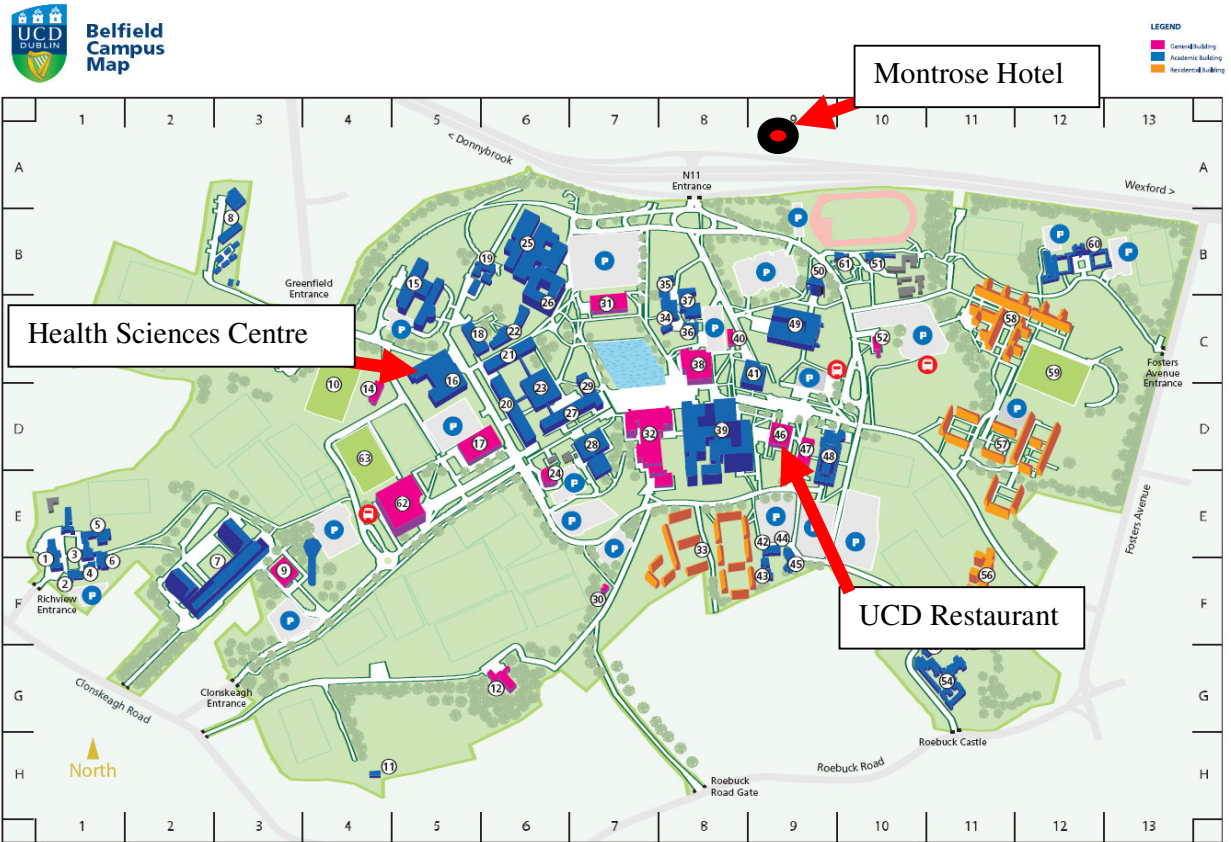
Maria Dolores HERNANDEZ ALONSO.  
Understanding the chemical reactivity of alcohols over catalytic materials: from probe molecules to practical applications.

**12:20 – 12:50** O-12

Lyuba ILIEVA-GENCHEVA.  
NO reduction by CO on gold catalysts supported on ceria, modified by Me<sup>3+</sup>:effect of water in the gas feed.

WORKSHOP END

# Map of UCD Belfield Campus showing Restaurant / Lecture Room and Montrose Hotel.



# **Keynote Presentations**

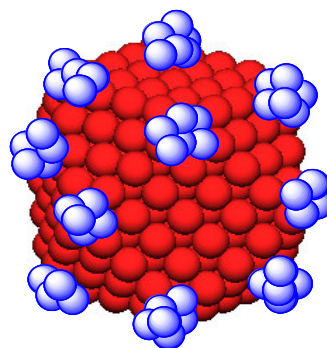
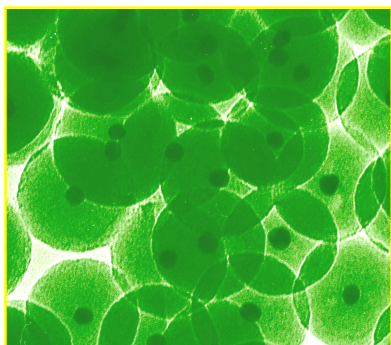
## Development of Novel Nano-materials for Catalysis, Sensor and Bio-medical applications

SC Edman Tsang

Wolfson Catalysis Centre, Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR,  
UK, Email Address: [edman.tsang@chem.ox.ac.uk](mailto:edman.tsang@chem.ox.ac.uk)

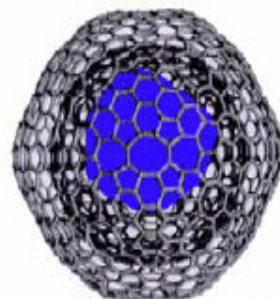
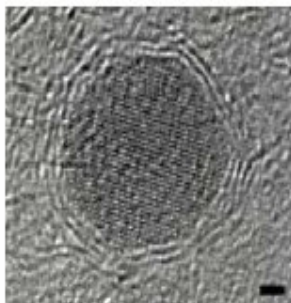
Recent developments in nano-science have opened up new directions in chemistry to allow the synthesis of new nano-materials which could not be obtained by conventional means. The current research shows that they exhibit many fascinating size dependent properties. The use of well-defined, well-characterised pre-formed nanomaterials as building blocks for the synthesis of functional materials is a new direction for many exciting applications.

In this presentation we will report some novel *core-shell* nanoparticles of controllable composition, size and morphology (see diagrams below). Some of them show exceptional catalytic activity and selectivity towards desired products. For example, a new class of silica coated nano-magnet of controlled dimensions to host biocatalysts with the unique advantage of facilitating separation is also described by our group. By using simple nano-chemistry skills, we show that Pt nanocrystals with tailored sizes can be decorated with Co atoms in a controlled manner. The blockage of unselective Pt corner sites by Co and its electronic influence to the Pt surface can dramatically improve the catalytic performance of Pt for the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes.



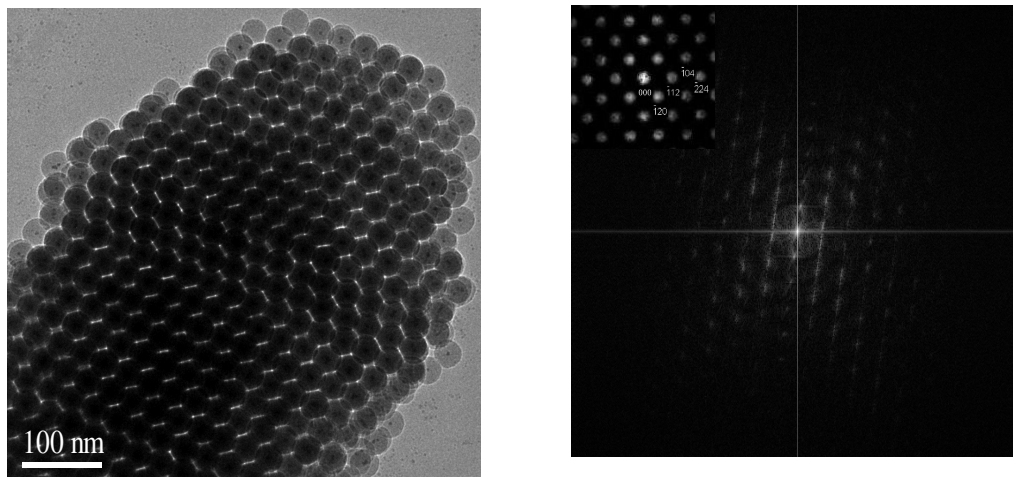
(L) Nanosize magnet (4nm core) in silica coated with catalyst/enzyme as magnetic separable catalysts; (R) A model showing Co atoms decorating on corner sites of Pt nanocrystal as an ultrasensitive nanocatalyst for hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to corresponding alcohols

In sensor and biomedical areas, our interests include using hollow carbon nanotube as nano-scale test tube for catalysis, separation, storage, magnetic, electronic applications. I should present our research on attachment, testing and characterization of enzymes and DNA in opened carbon nanotubes and other porous supports. These studies open up promising lines allowing developments of biosensors or drug or gene-delivery/ storage methods as well as nano-surgical devices. Also, the synthesis of some new encapsulated nano magnetic materials for bio-applications will be presented in this meeting.





(L) Opening and filling of carbon nanotubes; (R) Filling Nano-size Carbon Onions with Radioisotope ( $^{99m}\text{Tc}$ ) as new lungs imaging and medical bio-tracers



(L) A TEM micrograph shows an assembly of 33 nm  $\text{SiO}_2@\text{FePt}$  particles with size distribution  $<5\%$  in form of a high quality colloid crystal as a molecular filter; (R) corresponding electron diffraction patterns (and with simulated patterns-left hand corner) indicative of a hcp packing;

#### Selected Recent Publications

1. Carbon Dioxide Fixation into Chemicals (Methyl Formate) at High Yields By Surface Coupling Over Pd/Cu/ZnO NanoCatalyst, K. M. Kerry Yu, Connie M. Y. Yeung and Shik Chi Tsang, *Journal of the American Chemical Society* (2007), 129(20) 6360 – 6361; ranked the top three most accessed article in JACS in Q2 of 2007.
2. Chemically Immobilized Single Stranded Oligonucleotide On Praseodymium Oxide Nanoparticle As Non-labeled DNA Sensor Probe Using Impedance, S. Shrestha, C.M.Y. Yeung, C.E Mills, J. Lewington, and S.C. Tsang, *Angew. Chem. Int. Ed. Engl.* (2007), 46 (21) 3855-3859.
3. Pressure-dependent product distribution of citral hydrogenation over micelle-hosted Pd and Ru nanoparticles in supercritical carbon dioxide, P. Meric, K.M.K Yu, A.T.S. Kong, S.C. Tsang, *Journal of Catalysis* (2006), 237(2) 330-336.
4. Synthesis and Fabrication of A Thin Film Containing Silica Encapsulated Face-Centered Tetragonal FePt Nanoparticles, Chih Hao Yu, Nick Cailuo, Chester C.H. Lo, Kin Tam, and Shik Chi Tsang, *Advanced Materials*, (2006), [18 \(17\)](#) 2312 - 2314.
5. Engineering Pt in Ceria for a Maximum Metal-Support Interaction in Catalysis, C.M.Y. Yeung, K.M.K. Yu, Q.J. Fu, D. Thompsett, M. I. Petch, S.C. Tsang, *Journal of the American Chemical Society* (2005), 127(51) 18010-18011; highlighted by *Science*, (2005) 310, Issue 5756, 23 Dec.
6. Synthesis and characterization of thiol-capped FePt nanomagnetic porous particles, Gao Xin, K.Y. Tam, K.M.K. Yu, S.C. Tsang, *Small* (2005), 1(10) 949-952.
7. Magnetically Separable Carbon Supported Nano-Catalysts For Fine Chemical Manufacture, S.C. Tsang, V. Caps, I. Paraskevas, D. Chadwick, D. Thompsett, *Angew. Chem. Int. Ed. Engl.* (2004), 43 5643-5645.

# Notes



## **CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides as environmental catalysts: How complex is to design such a "simple" material.**

Jan Kašpar, Roberta Di Monte and Neal Hickey

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CeO<sub>2</sub>- and ZrO<sub>2</sub>-containing materials have attracted much interest in the last years due to their extensive use in very different fields, ranging from catalysis to ceramics, fuel cell technologies, gas sensors, solid state electrolytes, etc. Among others, the most relevant use of CeO<sub>2</sub>-based compounds is in the automotive pollution control, as promoters of the so-called three-way catalyst (TWC), even though there is also high interest in use of these materials as catalyst promoters in H<sub>2</sub> production related processes. Virtually all the vehicles are nowadays equipped with catalytic converters, which invariably contains some CeO<sub>2</sub>-containing oxide as catalyst promoter, mainly doped CeO<sub>2</sub>-ZrO<sub>2</sub> materials. Despite the use of such technology dates back nearly 30 years, there is a renewed interest in this technology in view of the more and more restrictive legislation that will be phased-in in the next few years: higher and higher efficiency, thermal stability and durability are required in comparison to existing materials.

The capability of CeO<sub>2</sub>-based materials to promote the activity of supported noble metals with respect to conventional supports is nowadays well assessed, their redox properties being relevant in this promotion mechanism. The comprehension of these properties is therefore critical for their application.

Whereas CeO<sub>2</sub>-ZrO<sub>2</sub> based materials have been widely used in the field of ceramics since half a century, their use as TWC components dates to mid-90': this prompted a strong interest with regards to these materials in the form of nano-sized – high surface area powders in comparison to their traditional form of sintered micro-dispersed ceramics.

Here we address the issues related to the catalytic use of such nano-materials, discussing the present targets for the synthesis and characterisation in the form of nano-sized particles in order to achieve effective catalysts for a real application. The correlations between textural, structural and chemical properties and their dependency on the nano-dispersed vs. micro-dispersed nature of the mixed oxide will be highlighted. It will be shown that a subtle interplay of these properties exists, *leading to CeO<sub>2</sub>-ZrO<sub>2</sub> containing nano-materials with nominally equal composition but very different textural and redox properties.*

In the second part of the lecture, the nature effects of Al<sub>2</sub>O<sub>3</sub> addition to the CeO<sub>2</sub>-ZrO<sub>2</sub> will be discussed. It must be recalled that close contact between Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> has long been considered as an undesirable factor since on thermal ageing it favours formation of CeAlO<sub>3</sub> that represents a major deactivation route for CeO<sub>2</sub>-based catalysts, due to its invariable Ce(III) redox state.

We will show that the choice of synthesis strategies and sample composition promotes formation of Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposites where CeO<sub>2</sub> is partially protected from the interaction with Al<sub>2</sub>O<sub>3</sub>, thereby minimising the deactivation of the catalyst.

Finally, a self-assembling process for a CeO<sub>2</sub>-ZrO<sub>2</sub>-BaO-Al<sub>2</sub>O<sub>3</sub> systems will be illustrated, leading to nanocomposites where site-specific doping is achieved. This generates a very particular and well-defined catalyst morphology – a “*nano-centipede*” – consisting of large barium hexaaluminate particles that act as anchoring sites for an inter-growing network of barium doped alumina and Ce<sub>0.2</sub>Zr<sub>0.8</sub>O<sub>2</sub> particles.

These materials appear as the highly promising systems for the thermally stable – next generation - catalysts due to their high thermal stability and the site-specificity of the doping that fully protects the ceria redox component from deactivation.

# Notes



## **The Synthesis, Characterisation and Assembly of Nanoscale Materials for Electronic and Magnetic Applications**

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### **Summary**

Many technologies will be enhanced by the ability to control the structure of materials on a nanometre-length scale. For example, the ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilise the unique transport properties associated with these architectures, is expected to lead to future generations of computer processors with device sizes many times smaller and faster than current silicon-based processors. However, both physical constraints and economics are expected to limit continued miniaturisation of electronic devices using current 'top-down' lithography based methods. Consequently, alternative non-lithographic methodologies for constructing the smallest mesoscopic features of an integrated circuit will soon be needed. One promising non-lithographic strategy is the use of solution phase chemistry to promote the self assembly of materials from precursor 'building blocks' into complex hierarchical mesoscopic architectures. In this presentation I will describe how 'chemistry' can be used can be used to generate oriented, high density, high-aspect ratio metal and semiconductor nanowires. For example the growth of single crystal nanowires of Mn-doped Ge nanowires that have potential as materials in the next generation logic and memory devices. Additionally, I will illustrate how mesoporous filaments, with intriguing columnar and circular arrangements of pores, allow for the inclusion of a variety of aligned metallic (Pt, Au and Pd) and semiconductor (Ge) one dimensional nanostructures which have potential applications in future nanoscale electronic devices.

# Notes



# **Oral Presentations**

## **PdO catalysts for CH<sub>4</sub> oxidation: attempts to improve the activity and the tolerance to SO<sub>2</sub>.**

A. .M. Venezia<sup>a</sup>, G. Di Carlo<sup>b</sup>, G. Pantaleo<sup>b</sup>, L. F. Liotta<sup>b</sup>, G. Melaet<sup>c</sup>, N. Kruse<sup>c</sup>

<sup>a</sup>Istituto dei Materiali Nanostrutturati (ISMN-CNR) via Ugo La Malfa, 153, Palermo, I- 90146

<sup>b</sup>Dipartimento di Chimica Inorganica ed Analitica “Stanislao Cannizzaro”, Università di Palermo, Viale delle Scienze, Palermo I-90128;

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Methane or natural gas fuelled engines (NGVs) are presently considered a valid alternative to those fuelled by diesel and gasoline. Indeed they produce lower emission of NO<sub>x</sub>, of CO<sub>2</sub> and of particulates in virtue of the lower combustion temperature of the lean-operated NGV's and of the high H:C ratio. Still a major drawback is represented by the emission of unburned CH<sub>4</sub>, a very effective greenhouse gas which, because of its long lifetime, contributes to global atmosphere warming even more than CO<sub>2</sub>. Therefore, to comply with modern legislation, highly efficient catalysts for the complete abatement of the unburned methane are needed [1-2]. Supported PdO are among the most active catalysts for the methane combustion at low temperatures. However, their catalytic activity depends on several factors such as the nature of the support, the palladium precursors, and the size of the PdO crystallites. Sintering of the active phase and poisoning by sulphur containing compounds represent major drawbacks [2].

In this study, two different approaches to improve the catalytic performance of PdO catalyst, in terms of methane conversion and sulfur tolerance, are investigated. In particular, the use of a mesoporous silica (HMS) with and without addition of Au [3] and the combination of sulfating (TiO<sub>2</sub>) and not sulfating (SiO<sub>2</sub>) supports will be described.

### **References**

- 1) P. Gelin, M. Primet, Appl. Catal. B 39 (2002) 1.
- 2) L.F. Liotta, G. Di Carlo, G. Pantaleo, A. M. Venezia and G. Deganello, Appl. Catal. B 66 (2006) 217.
- 3) A. M. Venezia, R. Murania, G. Pantaleo, G. Deganello, J. Catal. 251 (2007) 94.



# Notes



## Colloidal approach in preparation of interfaces for nanoparticles used as catalyst in the CO oxidation.

László Guzzi<sup>a,b\*</sup>, Andrea Beck<sup>a</sup>, Anita Horváth<sup>a</sup>, Gyula Tolnai<sup>b</sup>, Olga Geszti<sup>c</sup> and György Sáfrán<sup>c</sup>

<sup>a</sup>Institutes of Isotopes, HAS, P. O. Box 77, Budapest, H-1525, Hungary, ([guczi@sunserv.kfki.hu](mailto:guczi@sunserv.kfki.hu), fax: +36-1-392-2703)

<sup>b</sup>Chemical Research Center, HAS, P. O. Box 17, Budapest, H-1525, Hungary

<sup>c</sup>Research Institute for Materials and Technical Physics, P. O. Box, 49, Budapest, H-1525, Hungary

**Abstract:** *The morphology effect of the oxide component in the Au/TiO<sub>2</sub>, Au/CeO<sub>2</sub> systems on the CO oxidation activity has been investigated. Controlled formation of Au/TiO<sub>2</sub>, Au/CeO<sub>2</sub> nanocomposites on inert amorphous SiO<sub>2</sub> or on mesoporous SBA-15 support has been carried out. In order to eliminate the Au particle size effect, Au colloids with well defined particle size and narrow size distribution have been used. Au particle diameter > 5 nm is a less sensitive size range for the CO oxidation activity, while amorphous-like oxide layer on SiO<sub>2</sub> has significantly increased the activity as well as the sintering thereby can be diminished.*

**Keywords:** Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub> nanocomposites, Au particle size and effect of oxide morphology

### 1. Introduction

In the nano size range unique changes including discrete electronic and modified physical structures as well as altered chemical reactivity, may manifest themselves as improved catalytic properties. Nano size gold is a spectacular example possessing exceptional catalytic activity in the CO oxidation if is interfaced with suitable (reducible) oxides. Beside the classical deposition-precipitation (DP) method we have introduced sol deposition techniques<sup>1,2</sup> in order to test the activity of a metallic gold nanoparticles. However, we observed that one of the crucial problems is the active oxide morphology in order to fabricate a well defined catalyst. We aim at reporting how the structure of a nanocomposite system (uniform nanosized Au particles with Au/oxide perimeter) benefits the fabrication of a novel catalyst family.

### 2. Experimental

Gold nanoparticles were fabricated from HAuCl<sub>4</sub> reduced and stabilized by Na-citrate+tannic acid (method 1) to produce Au hydrosol,  $d_{Au}=6-7$  nm or reduced by NaBH<sub>4</sub> and stabilised by polyvinylalcohol (PVA) (method 2)  $d_{Au}=2-3$  nm. SiO<sub>2</sub> was decorated by titanium oxide prepared either from Ti-isopropoxid or Ti(IV) bis(ammoniumlactato)dihydroxide (TALH). The nano size gold catalyst preparation was conducted by adding Au sol to SiO<sub>2</sub> or SBA-15 decorated by Ti-isopropoxide after calcination at 600°C (**I**)<sup>3</sup>. Samples were produced by hydrolysing TALH in Au sol forming (Au-TiO<sub>x</sub>(OH)<sub>y</sub>) that was adsorbed on SiO<sub>2</sub> by PDDA assistance. (**II**)<sup>4</sup>. Finally, Au sol was adsorbed on SiO<sub>2</sub> in the presence of PDDA or on SBA-15, then Au/SiO<sub>2</sub> or Au/SBA-15 was decorated by TALH (**III**)<sup>4</sup>. CeO<sub>2</sub> modified gold samples were prepared by impregnating Au/SiO<sub>2</sub> and Au/SBA-15 by Ce(NO<sub>3</sub>)<sub>2</sub>. All samples were calcined to remove organic residues. The samples were characterized by HRTEM, XPS, XRD and the CO oxidation was employed as test reaction and the conversion vs. temperature was used to compare the activity of the various samples.

### 3. Results and discussion

In comparing the samples prepared in different methods we establish the importance of the amorphous-like  $\text{TiO}_2$  and  $\text{CeO}_2$  covering the  $\text{Au/SiO}_2$  samples. In Fig 1 the HRTEM picture indeed shows the presence of  $\text{CeO}_2$  decorating gold particles. It is clearly indicated that the  $\text{SiO}_2$  supported samples with minute amount of  $\text{TiO}_2$  or  $\text{CeO}_2$  improves the activity as compared with those deposited on pure  $\text{CeO}_2$  and  $\text{TiO}_2$  (anatase) as shown in Fig.2. The same statement is valid for  $\text{Au/CeO}_2/\text{SBA-15}$  sample. The activity depends also on the length of the Au-active oxide perimeter, so its controlled formation has key importance, that is, we also studied how the surface charge and the electrostatic interaction during the colloidal preparation affects the active interface.

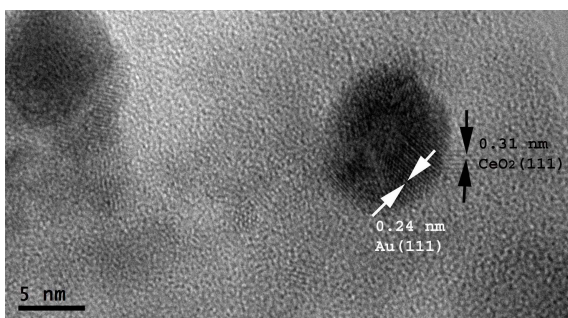


Fig. 1 HRTEM picture of  $\text{Au-CeO}_2/\text{SiO}_2$

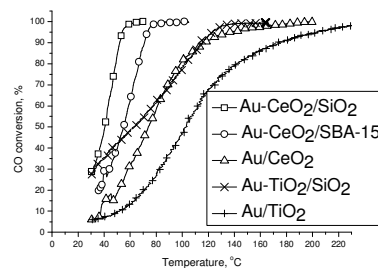


Fig. 2 CO oxidation conversion curves

Two major conclusions can be drawn from the results. For high activity we need nano size gold particles as Norskov and coworkers described<sup>5</sup>. This needs for CO and oxygen activation. However, the active amorphous oxide decoration has two further affects: first, it has an enhanced charge modification and second it may stabilize the small gold particle size.

### 4. Conclusions

In the highly active  $\text{Au/MO}_x/\text{SiO}_2$  catalysts the activity is strongly affected by the length of Au/oxide perimeter, which is regarded as the active phase. The presence of such perimeter can be evidenced by the increased CO oxidation activity.

The activity of the  $\text{Au/MO}_x$  perimeter depends not only on the Au particle size, but the morphology of the oxide component. The active oxides applied as promotors in small size, not well crystallised form and stabilised on an inactive support seems to be more active.

For highly active catalysts the controlled formation of the  $\text{Au/MO}_x$  nanoensembles is desirable. Controlling the electrostatic interactions between the components during the preparation is an important factor.

### References

1. A. Beck, A. Horváth, A. Sárkány and L. Guzzi, Roadmap to new catalyst system: Palladium nanoparticles, Chapter 5. in "Nanotechnology in Catalysis", eds.: G.A. Somorjai, S. Hermans and B. Zhang, Kluwer Publ. Co., Amsterdam 2003
2. László Guzzi, Andrea Beck, Anita Horváth, Antal Sárkány, Györgyi Stefler, Olga Geszti, *Studies Surf. Sci. Catal.*, 172 (2007) 221
3. A. M. Venezia, F. L. Liotta, G. Pantaleo, A. Beck, A. Horváth, O. Geszti, A. Kocsonya and L. Guzzi, *Appl. Catal. A.*, **310** (2006) 114
4. Anita Horváth, Andrea Beck, Antal Sárkány, Györgyi Stefler, Zsolt Varga, Olga Geszti, Lajos Tóth and László Guzzi, *J. Phys. Chem. B.*, **110** (2006) 15417
5. B. Hvolbaek, T. V. W. Janssens, B. S. Clausen, H. Falsig, C. H. Christiansen, J. K. Norskov, *Nano Today*, 2 (2007) 14

# Notes



## Electrochemical responses of Te *upd* layers at Au-Pd core-shell nanostructures

*Maria Montes de Oca\** and David J. Fermín

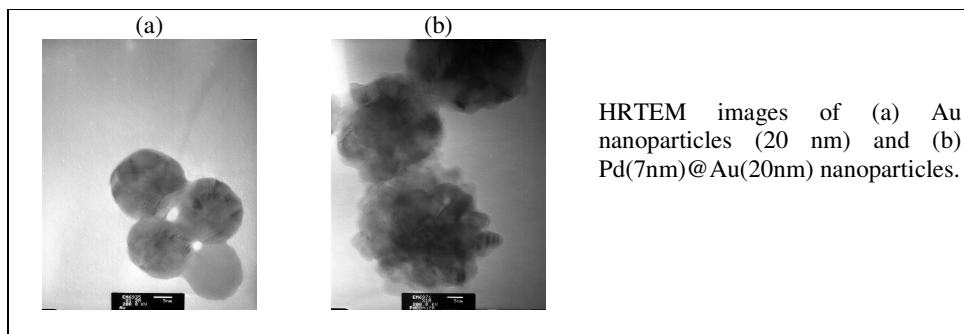
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Colloidal based synthetic methods can provide delicate control over the size, composition and shape of metallic and bi-metallic nanostructures.<sup>1</sup> These developments has allowed unravelling fascinating catalytic properties, particularly in system involving Au and Pd nano-domains.<sup>2,3</sup> The origin of the enhanced reactivity of Pd nanostructures on Au, with respect to single metallic structures, remains a controversial issue.<sup>4,6</sup> In order to gain further understanding on the reactivity of these systems, detailed information on the surface structure and composition of the nanoparticles should be uncovered. These aspects are rather challenging to interrogate by either high resolution electron microscopy or scanning probe microscopy. Feliu and co-workers have approached this problem by examining the voltammetric responses of surface sensitive electrochemical probes, e.g. underpotential deposited (*upd*) layers.<sup>7</sup> In this contribution, we investigate the surface properties of Au-Pd core-shell nanostructures assembled at electrode surfaces by examining the voltammetric responses of Te adatoms in acid solutions.

The Au-Pd nanostructures are synthesised by seeding-growth methods, where PdCl<sub>4</sub><sup>2-</sup> is reduced at the surface of 20 nm Au cores in the presence of ascorbic acid. This method allows adjusting the average shell thickness between 1.6 and 7.0 nm. Transmission electron micrograph of the Au cores and Au-Pd (average shell thickness of 7 nm) are contrasted in the figure. While the citrate stabilised Au particles exhibit a “faceted” surface, Au-Pd is characterised by extensively corrugated surfaces. Furthermore, the narrow size distribution of the bi-metallic nanostructures strongly suggests that the Pd is exclusively nucleated at the surface of the nano-seeds. 3D multilayers of the nanostructures were assembled at In-doped SnO<sub>2</sub> electrodes by alternate electrostatic adsorption steps involving poly-L-lysine and the nanoparticle colloid.<sup>8</sup>

The voltammetric responses of Au nanoparticle multilayers in the presence of TeO<sub>2</sub> in HClO<sub>4</sub> exhibits the characteristic *upd* signals reported for polycrystalline Au surfaces. Estimation of the voltammetric charges indicates that the overwhelming majority of the nanoparticles in the array contribute to the *upd* signal. These responses are used for probing whether portion of the Au cores are exposed to the electrolyte in the various core-shell structures. In addition, we can also interrogate the interaction energy between the Te adatom and the Pd surface as a function of the shell thickness.



### References

1. S.E. Habas, *et al.*, *Nat. Mater.*, **2007**, 6, 692.
2. D.I. Enache, *et al.*, *Science*, **2006**, 311, 362.
3. J. Greeley, *et al.*, *ChemPhysChem*, **2006**, 7, 1032.
4. J. Greeley, *et al.*, *Nat. Mater.*, **2006**, 5, 909.
5. J.K. Norskov, *et al.*, *J. Electrochem. Soc.*, **2005**, 152, J23.
6. W. Schmickler and S. Trasatti, *J. Electrochem Soc.*, **2006**, 152, L31.
7. J. Solla-Gullón, *et al.*, *Phys. Chem. Chem. Phys.*, **2008**, 10, 1359.
8. M. Carrara, *et al.*, *ChemPhysChem*, **2004**, 5, 571

# Notes

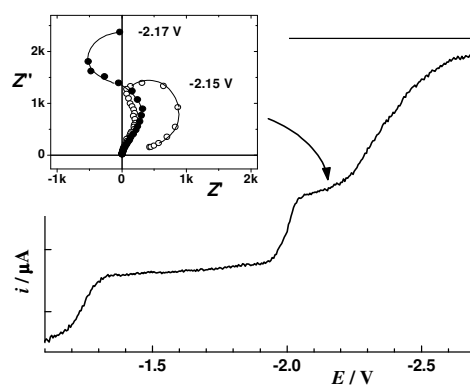


## Electrochemical Cationic Catalysis of Radical Anion Reduction and Model of Hidden Negative Resistance

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Well-known reduction of nitrobenzene in aprotic solvents (acetonitrile) yields an anion radical, which is further reduced at more negative potentials. The further reduction of anion radical is strongly retarded by the electrostatic repulsion of the electrode double layer. This is seen as the dependence of the electron transfer rate on parameters determining the interfacial double layer potential, e.g. the concentration and the nature of supporting electrolytes. Here tetraalkylammonium salts (tetramethyl- to tetraheptylammonium) were used. At very low concentrations of tetrahexylammonium salts the anion radical reduction occurs at extremely negative potential. However, traces of alkali metal cations yield a remarkable acceleration effect. At potentials where alkali metal cations are reduced the acceleration ceases. As a result the current–potential curves show negative or hidden negative resistance. Electrochemical impedance spectroscopy sensitively indicates the presence of the negative differential resistance (NDR) or the hidden negative differential resistance (HNDR). Oscillatory behavior based on this type of cationic catalysis is currently under investigation.



DC polarogram and electrochemical impedance spectra of the Hg drop electrode in 60  $\mu\text{M}$  nitrobenzene, 0.05 M tetrahexyl ammonium  $\text{PF}_6$  and 50  $\mu\text{M}$   $\text{KPF}_6$  in acetonitrile.

L.Pospíšil, M.Hromadová, R. Sokolová, J. Bulíčková, N. Fanelli, *Electrochim. Acta* 53 (2008) 4852.

# Notes





## Functionalized organic-inorganic hybrid supports for enzyme immobilization

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The construction of organic polymer and inorganic hybrid materials on the molecular or nanometer level is an important and evolutionary way to combine the distinct properties of organic polymers and inorganic materials within a single molecular material [1]. Development of new heterogeneous catalysts by immobilization of enzymes is an area of great interest because of their applications in synthesis of fine chemicals. The support for the enzyme plays an important role in the overall yield of the bioconversion reaction because it determines the enzyme activity and the use numbers of the active enzyme. Porous materials of organic, inorganic or organic-inorganic hybrid compounds are usually used as support for the enzyme immobilization. In this study, laccase from *Trametes versicolor* and horseradish peroxidase were immobilized on organic-inorganic hybrid supports. Styrene-divinylbenzene functionalized with benzaldehyde groups were reacted with diisopropylphosphite (dibutylphosphite) and 3-aminopropyl-trimethoxysilane („one-pot” reactions). The obtained polymer materials then underwent hydrolysis and condensation together with TEOS in the presence of aqueous HCl catalyst. The interest on polymer-supported chelating agents focuses the study of molecular structure, porous morphology, physico-chemical nature and functionalization of the supports. The properties of the hybrid materials thus obtained are discussed. The obtained hybrid materials were characterized by FTIR, SEM, N<sub>2</sub> adsorption-desorption and TG. The fraction of the repetitive units functionalised with aminophosphonate groups was determined by using the statistical structure of the repeated unit of the initial (I) and final copolymer (F). Different immobilization conditions in relation to the nature of the support surface, amount of enzyme, pH of the reaction system, temperature and reaction time were tested, aiming at reaching high enzymatic activity with the immobilized enzyme. The ABTES substrate was used for the determination of enzymatic activity. A high enzymatic activity (77-95%) was obtained for all the obtained composite system. The best results were obtained for the supports with -N<sup>+</sup>Oct<sub>3</sub>Cl<sup>-</sup> and -NH-Pr groups. The longer radicals of the function groups increase the porosity of the support, yield of the functionalization and catalytic activity. The degradation efficiencies of these immobilized laccases on oxidation of polycyclic aromatic hydrocarbons (PAHs) were tested. Laccases catalyze the 1-electron oxidation of phenolic substrates or aromatic amines to form quinones or polymerization products.

### References

[1] Liu G., Zhang H., Yang X., Wang Y., *Polymer*, 48 (2007) 5896

### Acknowledgement

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# Notes



## The interaction of CO and NO<sub>2</sub> with low index surfaces of ceria

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An understanding of the interaction between ceria and environmentally sensitive molecules is vital for developing its role in catalysis. We present the structure and energetics of CO and NO<sub>2</sub> adsorbed onto the (111), (110) and (100) surfaces of stoichiometric (CO) and reduced (NO<sub>2</sub>) ceria from first principles density functional theory corrected for on-site Coulomb interactions, DFT+U. DFT+U is applied, as it can describe consistently the properties of both the stoichiometric and reduced surfaces. In both cases we see surface dependence and significant structural and electronic rearrangement.

Upon interaction of CO with the (111) surface, weak binding is found, with little perturbation to the surface or the molecule. For the (110) and (100) surfaces, the most stable adsorbate is that in which the CO molecule bridges two oxygen atoms and pulls these atoms out of their lattice sites, with formation of a (CO<sub>3</sub>) species. This results in a strong modification to the surface structure, consistent with that resulting from reduction. The electronic structure also demonstrates reduction of the ceria surface and consequent localisation of charge on cerium atoms neighbouring the vacancy sites. The surface bound (CO<sub>3</sub>) species is identified as a carbonate, (CO<sub>3</sub>)<sup>2-</sup> group, which is formed along with two reduced surface Ce(III) ions, in good agreement with experimental infra-red data.

The interaction of NO<sub>2</sub> with reduced (111), (110), and (100) surfaces gives an adsorbate-surface structure in which the bond lengths around one Ce(III) ion from the reduced surface shortens, while one N-O bond lengthens. Analysis of the electronic structure and spin density distributions demonstrates that one Ce(III) has been reoxidized to Ce(IV), with the formation of adsorbed NO<sub>2</sub><sup>-</sup>. Finally, we discuss the energetics of the interaction of NO<sub>2</sub> with ceria.

These results provide a detailed investigation of the interactions involved in the adsorption of CO and NO<sub>2</sub> on ceria surfaces, allowing a rationalisation of experimental findings and demonstrate further the applicability of the DFT+U approach to the study of systems in which reduced ceria surfaces play a role.

# Notes



## The effect of alkali additives on the structure and reactivity of the vanadium catalytic system. Combination of theoretical and experimental studies.

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Vanadium supported catalysts are widely applied in selective oxidation reactions [1]. The catalytic properties of the supported vanadium oxide species are strongly affected by the vanadia loading, preparation method, nature of the support and type of the promoter. Among catalysts promoters, alkali metals are of particular interest since they are commonly use as promoters for industrial catalysts.

Titania-supported vanadia catalysts exhibit a noticeable dependence on the preparation method, on the coverage of the support and on the characteristics of the promoter [2]. The effect of alkali additives on the structure and reactivity of the VO<sub>x</sub>/TiO<sub>2</sub> catalytic system is studied by combining theoretical modelling (DFT) and experimental *in situ* Raman spectroscopy and temperature-programmed reduction (TPR) [2,3]. The vanadium loading are adjusted below monolayer coverage since supported species do not form bulk V-alkali-O aggregates. However, both of the techniques

(experimental and theoretical) highlight the strong affinity between vanadium oxide species, alkali ions and titania support. This interaction affects the structure, reactivity and reducibility properties of the catalytic system. There is a clear distinct interaction for each of alkali metal ion. DFT modelling predicts that the reducibility of the VO<sub>x</sub> species decreases in the sequence undoped > Li > Na > K > Rb > Cs. Figure 1 illustrates the excellent agreement between theoretical and experimental results.

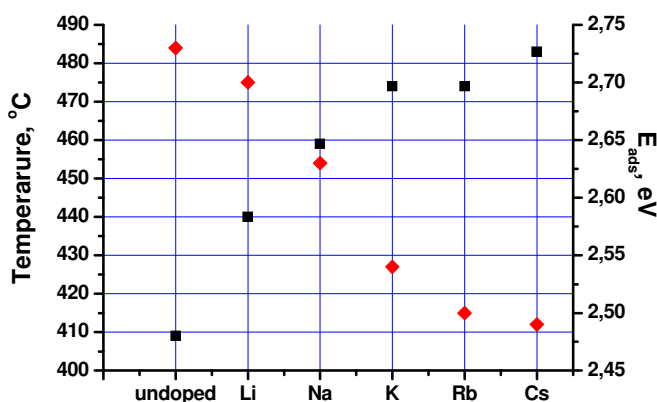


Fig. 1. Reduction temperature of VO<sub>x</sub> species (black); Hydrogen adsorption energy in eV (red) where positive value indicates exothermic process.

**Keywords:** DFT, alkali, vanadia-titania, *in situ* Raman, H<sub>2</sub>-TPR

### References

- [1] M.A. Bañares, Catal. Today 51 (1999) 319
- [2] H. Si-Ahmed, M. Calatayud, C. Minot, E. Lozano Diz, A.E. Lewandowska, M.A. Bañares, Catalysis Today 126 (2007) 96
- [3] M. Calatayud, C. Minot, J. Phys. Chem. C 111 (2007) 6411

# Notes



## New reaction: ammoxidation of glycerol into acrylonitrile

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Glycerol is a major by-product in the methanolysis during biodiesel production; thus, it is an increasingly important molecule in the context of renewable biomass resources to provide energy and chemical intermediates; however, developing selective glycerol-based catalytic processes is a major challenge due to their low selectivity. *In this communication, we propose a reaction with ammonia to nitriles that minimizes side reactions and affords a high value-added product, via the direct ammoxidation of glycerol to acrylonitrile under moderate reaction conditions.* Acrylonitrile is probably the nitrile manufactured on the largest scale since it is used mainly as a [monomer](#) in the manufacture of synthetic [polymers](#), especially [polyacrylonitrile](#) for acrylic fibres.

Catalyst	Conv. [%]	Selectivity to main products [%]											
		CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	propylene	propane	1,2 propanediol	acetonitrile	propanal	acrolein	acrylonitrile
Sb/Al	10.4	0.5	7.7	0.0	-	-	-	-	28.1	19.2	14.4	28.9	1.2
Nb/Al	16.2	0.2	6.8	0.0	-	-	-	-	28.8	1.5	34.7	26.7	1.3
V/Al	87.2	0.6	7.7	0.1	1.5	1.2	0.1	0.1	27.1	1.1	53.5	6.9	-
VSb/Al	71.6	0.7	2.9	0.5	-	-	-	-	5.7	1.0	4.3	28.9	56.0
VSbNb/A	82.6	1.1	4.4	0.2	-	-	-	-	6.9	0.8	2.1	26.2	58.3

Table 1. Glycerol conversion (%) and selectivity to main products (%)

Table 1 shows the conversion and selectivity to main products on alumina-supported catalysts. Samples VSb/Al and VSbNb/Al catalysts produce acrylonitrile. The details of the reaction mechanism are to be determined. It is interesting that acrolein appears as an intermediate in the production of acrylonitrile. Acrolein is produced from glycerol too; therefore, a possible reaction scheme would involve a combination of the glycerol dehydration mechanism followed by a subsequent C-N bond formation. Therefore, the presence of ammonia appears as a critical co-reactant to narrow selectivity trends towards nitriles. VSb catalyst is efficient for this process; the presence of Nb in the VSbNb catalyst would increase acidity, which would enhance ammonia activation.

### References

- M.O. Guerrero-Pérez, M.A. Bañares, ChemSusChem 2008, 1, 511-513 (DOI: 10.1002/cssc.200800023)
- M.A. Bañares, M.O. Guerrero-Pérez, Spanish Patent P200702992

# Notes





## Novel Space-resolved method of basicity examinations and their application in the catalytic glycerol etherification

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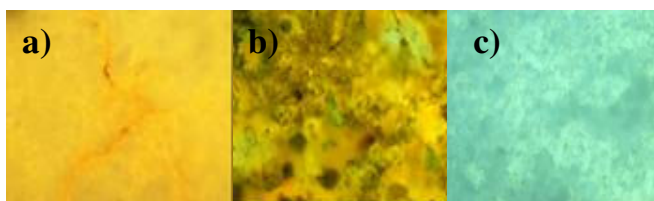
Glycerol has recently attracted considerable attention as a synthetic building block, being a highly functionalized molecule. The supply of glycerol, as a biodiesel by-product, has increased significantly, and its price dropped to low levels. Therefore, new applications of glycerol are being researched, including the production of di- and polyglycerols, which are used e.g. in cosmetic and pharmaceutical industries. Our target is to develop active basic heterogeneous catalysts for the selective etherification of glycerol to di- and triglycerols.

Our work focused on the characterization of different types of CaO materials as catalysts of glycerol etherification. It was found that depending on their method of preparation, catalysts differed not only in their surface areas, numbers of basic sites, but also in their Lewis acid strength. We postulate an alternative reaction mechanism that involves basic but also Lewis acid sites. Based on the above results, a catalyst with the highest activity was prepared, which had the optimum balance of the above physicochemical properties. [1]

The catalyst basicity is one of the crucial factors influencing the glycerol etherification. Therefore, in the second part of our research we focused on the basicity examinations allowing at the same time to develop a new method for surface basicity measurements. The methodology is based on Hammett indicators in a combination with UV-Vis spectroscopy and fluorescence microscopy. Its novelty is that a Hammett indicator is effectively used as a titrating agent, unlike in the traditional method where it is only an indicator *sensu stricto* [2]. Its advantage is that it gives the opportunity of mapping the sites on the material surface in a visible way. It is achievable thanks to the reactions that take place for certain indicator molecules when both forms of the indicator (neutral and deprotonated) can be adsorbed on the surface. In this case a specific choice of the indicator is necessary, so that it has sufficient affinity to the examined surface due to the matching chemical structure of both the indicator and the surface. As our work was concentrated on CaO materials, we focused on Clayton yellow (CY) which is a 'border' indicator for CaO having  $pK_B$  of 13.4. Using UV and fluorescence microscopes we followed the changes occurring on the surface while storing the materials in ambient conditions. We found that the OH and carbonate groups are not equally distributed, which might be related to surface defects.

The CaO material with the highest Lewis acidity (connected with the surface structure defects) indeed had the most visible distribution irregularities. (Fig 1)

The method developed complements the catalytic results of glycerol etherification. Moreover, in itself it creates further opportunities for application in other catalytic reactions.



**Fig.1.** Fluorescence microphotographs of CaO materials after contact with (CY) indicator (a) 'fresh' material; (b) stored in ambient condition. For comparison (c) CaCO<sub>3</sub> material with a contact with CY.

### Literature

[1] A.M. Ruppert, J.D. Meeldijk, B.W.M. Kuipers, B.H. Ern , B.M. Weckhuysen *Chem. Eur. J.* **2008**, 14, 2016.

[2] W. Xie, H.Li, *J. Mol. Catal. A: Chemical* **2006**, 255, 1.

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# Notes



## The radical active species and impurities present in mesoporous silicas as oxidation active centres

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Silica seems to belong to the most frequently used supports for various active species applied in catalytic processes. It is commonly considered as catalytically inactive solid. However, it has been mentioned in the literature that silica sometimes exhibits unexpected oxidizing properties [1]. Since 1992, when the mesoporous molecular sieves of M41S family have been synthesized for the first time [2], the hundreds of papers dealing with these materials have appeared. Among these mesoporous silicas the oxidation activity has been also found. It was proposed that the defects in the mesoporous structure could be involved in the activity of these solids. The explanation of this behaviour has been the aim of this study.

In this work a three different siliceous mesoporous catalysts (MCM-41, SBA-3, SBA-15) were prepared and studied in details using: XRD, N<sub>2</sub> adsorption/desorption measurements, UV/Vis, FTIR, ESR as well as acetylacetone transformation, 2-propanol decomposition and cyclohexene and methanol oxidation processes.

The structure/texture parameters of prepared materials as well as their oxidation activity are given in the table below. All the samples possess a high surface area typical of mesoporous silicates. The XRD patterns as well as N<sub>2</sub> adsorption/desorption isotherms indicated mesoporous character of the solids. The reaction of acetylacetone transformation pointed out on the basic

<i>Catalyst</i>	BET surface area, m <sup>2</sup> g <sup>-1</sup>	Pore volume, cm <sup>3</sup> g <sup>-1</sup>	Pore diameter, nm	Methanol conversion, %	Cyclohexene conversion, %
MCM-41	950	1.09	3.7	0.58	5.1
SBA-3	1170	0.38	2.6	0.35	2.6
SBA-15	700	0.53	5.1	0.19	2.0

character of MCM-41 surface. For this material the highest oxidative activity was observed. The two other catalysts exhibited acid-base properties. The generation of SiO<sup>•</sup> radicals due to the temperature treatment of the solid material and SiOO<sup>•</sup> radicals created as a result of the interaction with oxygen molecules at high temperatures has been correlated with the catalytic activity in the reaction of cyclohexene with hydrogen peroxide in the liquid phase and methanol oxidation in the gas phase. The silicate MCM-41 catalyst showed the highest activity in both processes. For this material the two kinds of radicals (SiO<sup>•</sup>, SiOO<sup>•</sup>) has been found on the surface after the desired pretreatment. The oxidation of methanol led to the formation of formaldehyde, whereas the diol was the main product of cyclohexene oxidation.

The role of impurities, such as chloride ions as well as iron present in the mesoporous catalysts has been also considered. The most active material, i.e. MCM-41, showed the highest amount of iron ions on its surface, as evidenced by ESR measurements and ICP analysis. It has been documented that the sources of siliceous, nature of templates and the preparation conditions (pH) play a crucial role in the formation of active species.

[1] F. Cavani, F. Trifiro, *Catal. Today*, 51 (1999) 561.

[2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.*, 114 (1992) 10834.

# Notes



*Operando Raman and ATR-FT-IR Spectroscopy of Liquid Phase Heterogeneous Catalytic Processes*

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In the first part of this presentation the effect of process parameters on the sensitivity of Raman based probes in the analysis of the activity of catalytic materials in solvents is discussed (Figure 1). Based on trends in the strong intensity of the  $945\text{ cm}^{-1}$  C-O-C vibration of 1,3-dioxolane, a typical solvent used for liquid phase catalysis, the following conclusions were derived: i) above 500 rpm a linear increase in stirring speed induces a linear decrease in Raman intensity; ii) a linear increase in gas pressure also leads to a linear decrease of the Raman signal; iii) linear temperature elevation decreases the Raman intensity exponentially; iv) increasing the catalyst particle concentration results in a steep non-linear decrease of the Raman signal. Light scattering by gas bubbles, or combined scattering and absorption by catalyst particles, reducing the amount of light collected by the optical fiber probe, will be discussed to explain the observed experimental trends. Furthermore, the sensitivity of Raman spectroscopy will be directly compared with ATR-FT-IR spectroscopy, using the on-line analysis of hydrogenation reactions over a Cu-based catalyst. It will be demonstrated that ATR-FT-IR spectroscopy is usually much more sensitive than Raman spectroscopy.

The second part of the presentation will be focused on the understanding of the chemical reactivity of alcohols over catalytic materials, showing a second advantage of analysis with ATR-FT-IR spectroscopy over Raman spectroscopy. It will be shown that in the case of Silica based supports, the interaction of the alcohol with the support can be observed, even without the necessity of applying a coating on the ATR crystal. The formation of alkoxides, diminishing the hydrophilicity of the support, is proposed to lead to physical interactions with the ATR crystal, thus inducing the visibility of the support particles in the ATR spectra. Finally, directions for future research within the COST program will be discussed.

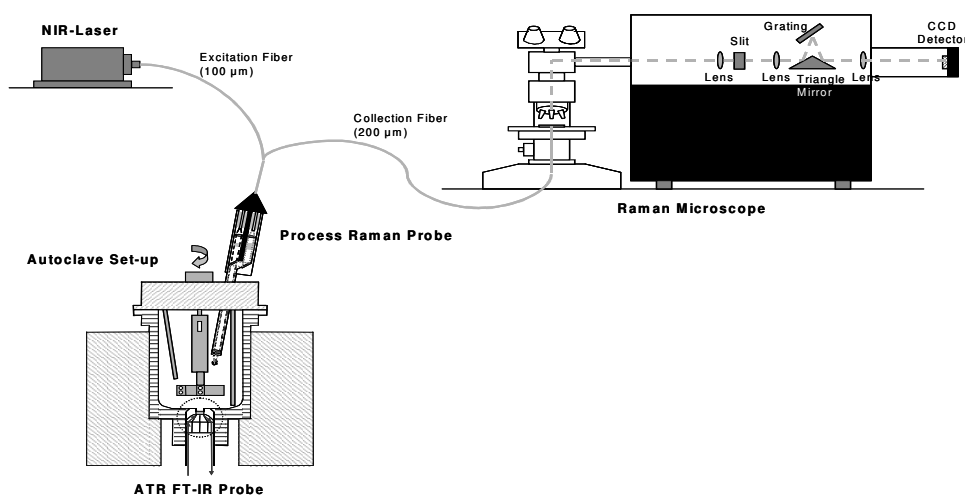


Figure 1. Coupling of the fiber optic Raman probe with ATR-Autoclave and Raman set-up

# Notes



## NO reduction by CO on gold catalysts supported on ceria, modified by $\text{Me}^{3+}$ : effect of water in the gas feed

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The reduction of  $\text{NO}_x$  by CO has been extensively investigated in view of strict automobile emission regulations. Recently, it was established that supported nanosized gold behaves as a catalytically active noble metal in  $\text{NO}_x$  reduction by  $\text{H}_2$ , CO or hydrocarbons [1-3]. The selection of gold catalysts and reaction conditions, which would maximize the catalytic activity preserving a high selectivity to  $\text{N}_2$ , is an important task. In the present study the effect of the modifier both aluminium and lanthanides (La, Sm, Gd, Yb) on the NO reduction by CO over gold/ceria catalyst was investigated. In addition the presence of water in gas feed was evaluated. The mixed oxide supports were prepared by mechanochemical activation. The amount of modifier was 10 wt %. Gold (2-3 wt.%) was introduced by deposition-precipitation method. The catalysts were characterized by XRD, TPR and Raman spectroscopy. The catalytic activity in NO reduction by CO was tested in a wide temperature interval using different composition of gas feed (with and without water) at a WHSV of  $60000 \text{ ml g}^{-1}\text{h}^{-1}$ .

The average size of ceria crystallites was calculated on the basis of XRD measurements. The addition of lanthanides leads to the systematically higher lattice parameters of ceria, while in the presence of alumina the lattice parameters of ceria are quite the same as in stoichiometric  $\text{CeO}_2$ . Both gold and ceria particles are lower than 10 nm. The amount of oxygen vacancies in the defective  $\text{CeO}_y$  structure were discussed on the basis of the FWHM (full width at half maximum) parameter of the dominant ceria line in the Raman spectra. The addition of alumina as well as of lanthanides leads to a widening of the FWHM parameter. From the TPR spectra the  $\text{H}_2$  consumption of the fresh catalysts and after reoxidation were calculated. The catalytic activity measurements were carried out at different conditions: 1) in the presence of hydrogen in the feed and 2) adding both hydrogen and water to the feed. Following the 1<sup>st</sup> route of experiments, the conversion of NO and CO was higher for the gold samples containing lanthanides in comparison to the sample with alumina. However, the selectivity to  $\text{N}_2$  was better for  $\text{Au/CeO}_2\text{-Al}_2\text{O}_3$ , the  $\text{N}_2\text{O}$  formation was registered below  $150^\circ\text{C}$ , ammonia was detected above  $250^\circ\text{C}$  and no methane was found in the whole temperature interval and practically the selectivity was 100 % at about  $200^\circ\text{C}$ . On the contrary, when ceria was modified by lanthanides, a low selectivity to  $\text{N}_2$  was observed, methane and ammonia formation started at above  $150^\circ\text{C}$ . Concerning the 2<sup>nd</sup> route, the same selectivity for the samples containing alumina was found, while a drastically improvement of the selectivity was registered for the gold samples, supported on mixed oxide support modified by lanthanides. Adding water, the NO and CO conversion increased with highest catalytic activity on  $\text{Au/CeO}_2\text{-Yb}_2\text{O}_3$ .

The results obtained indicate that the presence of water in the gas feed, generally found in real exhaust gases, enhances the activity in all modified ceria supported gold catalysts. Mostly important, the presence of water in the case of lanthanides doped samples improves the selectivity to  $\text{N}_2$  making these catalysts more promising in comparison to alumina containing one.

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### References:

1. A. Ueda, M. Haruta, *Gold Bull.*, 32 (1999) 3, and references therein.
2. M.A.P. Dekkers, M.J. Lippits, B.E. Nieuwenhuys, *Catal. Today* 54 (1999) 381.
3. J.R. Mellor, A.N. Palazov, B.S. Grigorova, J.F. Greyling, K. Reddy, M.P. Letsoalo, J.H. Marsh, *Catal. Today*, 72 (2002) 145.

# Notes





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Soghomon	BOGHOSIAN	Greece
Magali	BOUTONNET	Sweden
Wendy	BROWN	United Kingdom
Sarah	BURNHAM	Ireland
Petrica	DULGHERU	Ireland
Jacques	FRAISSARD	France
Laszlo	GUCZI	Hungary
Olga	GUERRERO	Spain
Dolores	HERNANDEZ-ALONSO	Netherlands
Justin	HOLMES	Ireland
Luyba	ILIEVA	Bulgaria
Maria Rosa	INFANTE	Spain
Sven Gunnar	JÄRÅS	Sweden
Jan	KAŠPAR	Italy
Anna	LEWANDOWSKA	Spain
Leonarda	LIOTTA	Italy
Maria	MONTES de OCA	United Kingdom
Elaine	NEVILLE	Ireland
Viorica	PARVULESCU	Romania
Vasile	PARVULESCU	Romania
Lubomir	POSPISIL	Czech Republic
Virginia	RUIZ FERNÁNDEZ	Finland
Agnieszka	RUPPERT	Netherlands
Klaus	SCHIERBAUM	Germany
Robert	SCHOONHEYDT	Belgium
Linda	SHERRY	Ireland
James	SULLIVAN	Ireland
Maciej	TREJDA	Poland
Kostas	TRANTAFYLLIDIS	Greece
SC Edman	TSANG	United Kingdom
Anna-Maria	VENEZIA	Italy
Graeme	WATSON	Ireland
Kai Man	YU	United Kingdom