

***IDECAT Conference on Catalysis***

**Concepts, complexity and diversity in catalysis**

**Porquerolles 12 - 17 May 2007**

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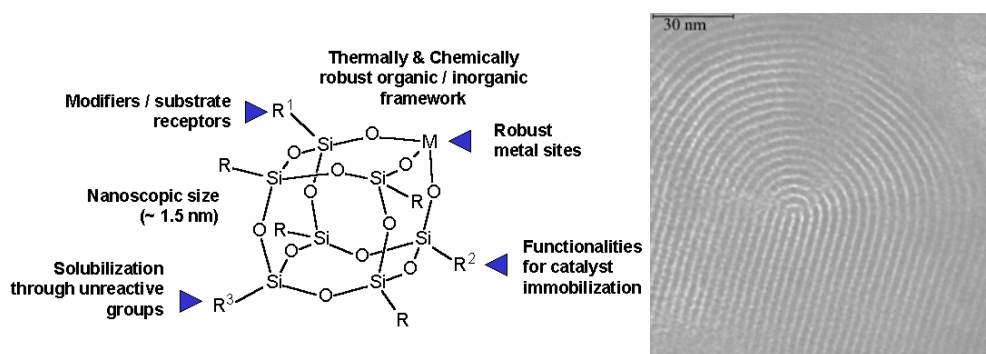
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## Prof Abbenhuis Erik

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### Hybrid Catalysis with Nanostructured POSS Metal derivatives

We have pioneered the development of a new chemical technology for catalysis. This technology bridges the property space between hydrocarbon-ligated metal complexes and oxidic supported catalysts. It imparts new or improved properties to catalytic materials achieving uncannily precise molecular architectures. Catalysts are derived from chemicals known as polyhedral oligomeric silsesquioxanes (POSS) rendering silanolate metal derivatives. POSS catalysts have unique features:



- The chemical composition of the support is a hybrid, intermediate ( $\text{RSiO}_{1.5}$ ) between that of silica ( $\text{SiO}_2$ ) and silicones ( $\text{R}_2\text{SiO}$ ). The support is electron-withdrawing and increases Lewis acidic catalyst activity.
- POSS catalysts can contain one or more covalently bonded reactive functionalities suitable for polymerization, grafting, surface bonding, or other transformations covering the generation of precise catalytic materials and catalyst supports.
- POSS catalysts are physically large and range approximately 1-3nm in size. They can be molecularly enlarged (POSS building block chemistry) to cover applications from homogeneous catalysis via membrane catalyst retention to truly heterogeneous catalysis, either in gas or liquid phase application.

Presented are newly developed catalysts for alkene metathesis, oligomerization, polymerization and epoxidation.

L. Zhang, H.C.L. Abbenhuis, N. Ni Bhriain, P.C.M.M. Magusin P.C.M.M. et al., *Chem. Eur. J.*, **2007**, *13*, 1210-1221.

R. W. J. M. Hanssen, R. A. van Santen, H. C. L. Abbenhuis, *Eur. J. Inorg. Chem.*, **2004**, 675-683.

J.I. van der Vlugt, J. Ackerstaff, T.W. Dijkstra, A.M. Mills, H. Kooijman, A.L. Spek, A. Meetsma, H.C.L. Abbenhuis, D. Vogt; *Adv. Synt. Catal.*; **2004**, 346(4), 399-412.

M. D. Skowronska-Ptaskinska, M. L. W. Vorstenbosch, R. A. Van Santen, H. C. L. Abbenhuis, *Angew. Chem. Int. Ed.* **2002**, *41*, 637-639.

H. C. L. Abbenhuis, *Chem. Eur. J.* **2000**, *6*, 25-32.

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### **Noels' and Grubbs' catalysts: two different systems, one unique active species**

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The catalytically active propagating species involved in the self-metathesis of ethyl oleate obtained from the multi-component Noels' catalytic system {[RuCl<sub>2</sub>(p-cymene)(PCy<sub>3</sub>)] + Me<sub>3</sub>SiCHN<sub>2</sub>} are probably the same as these of the single-component well-defined Grubbs' 1st generation catalyst, [Cl<sub>2</sub>Ru=CHPh(PCy<sub>3</sub>)<sub>2</sub>] (1-Ph). In the case of the Noels' catalyst, it involves the de-coordination of p-cymene, and the redistribution of PCy<sub>3</sub> ligands to generate only 5-10 % of [Cl<sub>2</sub>Ru=CHR(PCy<sub>3</sub>)<sub>2</sub>], where R = CH-(CH<sub>2</sub>)<sub>6</sub>-CH<sub>3</sub> (1-Oct) and R = CH-(CH<sub>2</sub>)<sub>6</sub>-COOEt (1-E), while 1-Ph can generate 100% of these species.

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### Colloids as building blocks for nanosized supported catalysts

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It is now accepted that for preparation of supported catalysts, control at the atomic level is needed to design active sites because the chemical and catalytic properties of atoms at terraces, corners, and edge of a metal crystallite are different. Since the synthesis of nanoparticles is more controllable in liquid phase, a promising way for the preparation of nanosized supported catalysts is the deposition of sols, where the active particles are already preformed, on the support surface. In polyol mediated synthesis, the tailoring of the particles characteristics is obtained through the control of the nucleation and growth steps by chelating effect of polyol which avoids agglomeration of particles during the preparation. Recently, this method has received considerable attention because of its simplicity and the advantage, over the most other methods, to prepare metal alloy and highly pure mixed oxides (1). In the present work, we summarize our earlier experiences on preparation of supported catalysts by utilizing nanoparticles synthesized in liquid phase reduction or formed in the solid/liquid interfacial layer of the support. In particular, we will present our data on: 1.V2O5 supported on TiO2. Catalytic activity and stability of prepared samples were tested in the total oxidation of chlorinated organic compounds (2). 2.Pd/Rh and Pd/Pt catalysts supported on different mesoporous materials. The catalytic behaviour of these catalysts was investigated in the hydrogenation and hydrogenolysis/ring-opening of naphthalene (3). The key features of the polyol method are the broad applicability and the chance to produce nanoscaled and crystalline oxides. Moreover, this technique allows preparing metal alloy and mixed oxides sols with a very close contact between different active phases, such as requested from polyfunctional catalyst. Taking into account parameters as polarity and charge of the support surface, a reliable adhesion between these preformed active phases and support can be obtained leading to stable catalysts. References

[1]G. Baldi, A. Barzanti, M. Bitossi "Ceramic colorants in the form of nanometric suspensions " PCT WO03/076521 A1, 2003, assigned to Colorobbia Italia SpA.

[2]S. Albonetti, G. Baldi, A. Barzanti, A.L Costa, J. Epoupa Mengou, F. Trifirò, A. Vaccari " Chlorinated organics total oxidation over V2O5/TiO2 catalysts prepared by polyol mediated synthesis" Appl Catal. A (2007) doi:10.1016/j.apcata.2007.02.031, in press.

[3]S. Albonetti, G. Baldi, A. Barzanti, E. R. Castellon, A. J. Lopez, D. E. Quesada and A. Vaccari "Nanosized Pd/Pt and Pd/Rh catalysts for naphthalene hydrogenation and

## M. Baldé Cornelis

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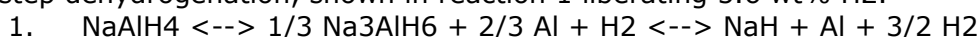
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### **Hydrogen storage in Nanostructured NaAlH<sub>4</sub> deposited on Carbon Nanofibers**

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Sodium alanate (NaAlH<sub>4</sub>) is a promising hydrogen storage material due to its high reversible hydrogen storage capacity and optimal thermodynamic stability for reversible hydrogen storage at low to medium temperatures. When NaAlH<sub>4</sub> is heated, it decomposes via a two-step dehydrogenation, shown in reaction 1 liberating 5.6 wt% H<sub>2</sub>.



Due to kinetic barriers, hydrogen desorption rates are slow and reloading of undoped NaAlH<sub>4</sub> is also slow and not possible under practical conditions. A possible strategy to facilitate hydrogen kinetics, is to decrease the particle size of NaAlH<sub>4</sub> to the nanometer-range.[1] This presentation will deal with synthesis of nano-sized sodium alanate particles by deposition on a support material (carbon nanofibers). Results of XRD, TEM and TPD experiments will be presented.

1. Baldé, C.P.; Hereijgers, B.P.C.; Bitter, J.H.; De Jong, K.P.; *Angew. Chem. Int. Ed.* 2006,



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### **Arene-pincer hybrids for catalysis: metal-to-metal interactions through simultaneous sigma- and pi-coordination.**

We want to present a new family of dinuclear organometallic complexes in which each of the two metal is bonded via a different carbon-to-metal binding mode to the same hydrocarbon fragment: a linear, sigma-bond in the one case (E,C,E-pincer complex), and a piano-stool-like, pi-bond in the second (arene complex). Different bridging units between the sigma- and pi-coordination frameworks have been investigated, with a view to test electronic communication between the sigma- and pi-electron systems. Despite the orthogonal coordination mode of the two metals, metal-to-metal interactions have been experimentally observed, which led in some cases to pronounced effects on the chemical reactivity of the corresponding complexes. The synthesis, reactivity and catalytic properties of these complexes will be presented, including proofs of metal-to-metal interactions, and interpretation by DFT calculations. Ultimately, as arene- and E,C,E-pincer complexes are both known as catalysts, some of these structures could lead to monomolecular, bifunctional catalysts, which would enable tandem or cascade reactions in one pot.

## Prof Bordes-Richard Elisabeth

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### **Multicomponent oxides in selective oxidation of alkanes: Theoretical acidity vs. Selectivity**

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Semi-empirical relationships between the 'optical basicity'  $L$  (so-called after Duffy [1]) of solid oxides and the 'thermodynamic' selectivity in mild and total oxidation of hydrocarbons have recently been set up [2-4]. They can be used to determine the optimum acidity or to account for the observed selective properties of a solid catalyst in a given reaction. For example, in the Lewis-related acidity scale related to the same  $O_2^-$  base, the acidity of a series of solid oxides decreases along (hydrogen or cationic) zeolites > heteropolyacids >  $(VO)_2P_2O_7$  >  $MoO_3$  >  $V_2O_5 \sim NiMoO_4$  >  $Bi_2MoO_6$  >  $Cu_2O$  >  $Sb_2O_4/SnO_2$  >  $Ag_2O$  >  $K_2O$ , and  $SiO_2$  >  $\gamma-Al_2O_3$  >  $\alpha-Al_2O_3$  >  $CeO_2$  >  $ZrO_2 \sim TiO_2$  >  $MgO$ , catalysts and supports, respectively. The value of  $L$  can be calculated for any formula including those of multicomponent oxides and depends on the oxidation state, coordination and spin of the cation(s). On the reaction side, the difference of ionization potential  $DI$  of reactant-to-product was proposed to account for selectivity. Plotting  $DI$ , the electron donor power of gas phase, against  $L$ , the electron donor power of oxygen in the selective solid, gives linear relationships, the slope of which depend on the chemical nature of the reactant (alkane, alkene, alcohol, etc.) and on the extent of oxidation (mild to total oxidation). Examples will be shown in several cases, particularly the influence of dopants in VPO (butane to maleic anhydride), MoVO (propane or acrolein to acrylic acid, ethane to acetic acid) and of Co, Fe, Ni in multicomponent molybdates (propene to acrolein), on selectivity in the respective reactions. The variation in the structure and composition of the respective catalysts will be discussed.

1.J.A. Duffy, *Geochim. Cosmochim. Acta*, 57 (1993) 3961-3970.

2.P. Moriceau, A. Leboutellier, E. Bordes and P. Courtine, *Phys. Chem. Chem. Phys.*, 1 (1999) 5735-5744.

3.P. Moriceau, B. Taouk, E. Bordes, P. Courtine 11th Int. Cong. Catal., Granada, July 2000; *Stud. Surf. Sci. Catal.*, 130 (2000) 1811.

4.E. Bordes-Richard and P. Courtine in *Metal Oxides: Chemistry and Applications*, J.L.J.

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### Delaminated zeolitic materials for replacing mineral acid catalysts in industrial processes

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**Introduction:** The industrial synthesis of many commodities and fine-chemicals is usually catalyzed by strong mineral acids, which have to be neutralized at the end of the reaction and the resulting salts disposed (1). In order to minimize residual water it would be expedient to replace such acid solutions by regenerable and non-polluting solid acid catalysts. In this sense, zeolites have found wide application due to their strong acidity and the possibility to impose shape selectivity on the reaction products (2), although the reaction can be controlled by diffusion, particularly when bulky molecules are involved. Then, one way to overcome such drawback is by delamination of a layered zeolite precursor. The resulting material presents well defined aluminosilicate nanolayers and very large external surface area, the catalytic sites being plenty accessible to the reactant molecules whilst allowing a fast desorption of products. Here we present the results obtained in the application of the delaminated material ITQ-2 for substitution of mineral acids in two industrial processes for preparation of commodities: the synthesis of  $\omega$ -laurolactam ( $\omega$ -LRL), the monomer in the production of nylon-12 and the synthesis of diamino diphenyl methane (DADPM), intermediate for the production of polyurethanes.

**Experimental:** ITQ-2 (Si/Al=15, 25 and 50 M) was prepared by delamination of the layered MCM-22 precursor following a previously described recipe (3). For comparison, a sample of the MCM-22 (Si/Al=15 M) was also synthesized (4).  $\omega$ -LRL was obtained by Beckmann rearrangement of cyclododecanone oxime (CDOX) in benzonitrile at low temperature (130 °C). Batch reaction experiments were done along 7 h with a catalyst:oxime:solvent ratio of 1:1:200 (wt/wt/wt). Products and non-reacted oxime were analyzed by GC-MS. For the synthesis of DADPM, a neutral condensate (aminal, <1% H<sub>2</sub>O) was prepared following a known recipe (5). Then, the isomerization of the aminal was performed at 150 °C in a batch reactor in the presence of ITQ-2 (20 wt% catalyst). Reaction samples were analyzed by GC and <sup>1</sup>H-NMR.

**Results:** a) Synthesis of  $\omega$ -LRL: the liquid-phase Beckmann rearrangement of CDOX over ITQ-2 and MCM-22 yields  $\omega$ -LRL with selectivity of 100 %, although ITQ-2 shows clear superior catalytic activity than its homologue zeolitic layered precursor (Figure 1). Nevertheless, the catalytic activity is seriously affected by the Si/Al molar ratio, and the order of activity is: ITQ-2(25)~ITQ-2(15)>ITQ-2(50) (see Figure 2); b) Synthesis of DADPM: the isomerization of the aminal over zeolitic materials yields a mixture of primary amines (diamines and triamines), secondary amines, N-methylated derivatives and quinoxalines. ITQ-2 shows again higher catalytic activity than MCM-22, although the selectivity to linear diamines (ratio 4,4'-DADPM/2,2'+2,4'-DADPM) is lower in the exfoliated material (Figure 3). Conversely, the catalytic activity is also influenced by the Si/Al molar ratio and the order of activity is: ITQ-2(25)~ITQ-2(15)>ITQ-2(50) (see Figure 4).

**Discussion:** The accessibility of acid sites to reactant molecules is drastically enhanced in an exfoliated structure (3). This is reflected in the superior performance shown by ITQ-2 versus MCM-22 both in the production of  $\omega$ -LRL and DADPM. Further, the delaminated material allows faster desorption of products, then minimizing secondary reactions and catalytic deactivation (3,5). Occasionally, the delamination process can lead to some loss of the shape selectivity effect, as it is the case in the synthesis of linear isomers of DADPM (4,4'-DADPM and its higher homologues). In any case, the acidity and adsorption properties of the catalyst can be tailored by changing the Si/Al molar ratio. Best results correspond to the range Si/Al=15-25 M, which shows a compromise between the level of dealumination (and hence external surface area and molecular accessibility) and the acidity.

**Conclusion:** Delaminated zeolite ITQ-2 constitutes a real challenge for replacing mineral acids in the industrial synthesis of some commodities as  $\omega$ -LRL and DADPM. This material presents an appropriate acidity and fully accessibility to active sites though the outer surface, then showing higher activity and extended life than conventional zeolitic materials. The results presented here are pretty competitive regarding to the current industrial process particularly in the case of the DADPM synthesis.

**References:** 1) K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry* (VCH, New-York, 1997); 2) I.E. Maxwell W.H.J. and Stork, in *Introduction to Zeolite Science and Practice* (eds. Van Bekkum, H. et al.) 571-630 (Elsevier, Amsterdam, 1991); 3) A. Corma, V. Fornés, S.B. Pergher, Th.L.M. Maesen and J.G. Buglass, *Nature* 396, 353 (1998); 4) M.E. Leonowicz, J.A. Lawton, S.L. Lawton and M.K. Rubin, *Science* 264, 1910 (1994); 5) A. Corma, P. Botella, & C. Mitchell, *Chem. Commun.* 2008 (2004).

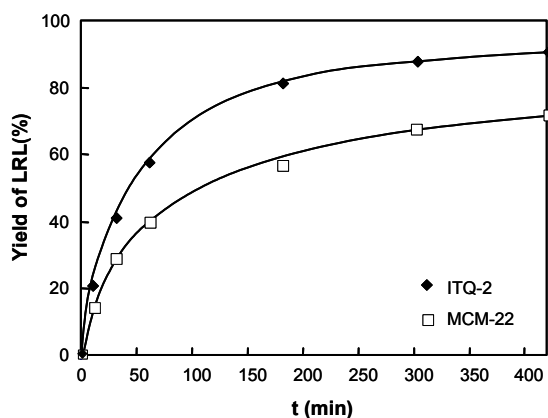


Figure 1. Beckmann rearrangement of CDOX over ITQ-2(15) and MCM-22(15). Experimental conditions as in the text.

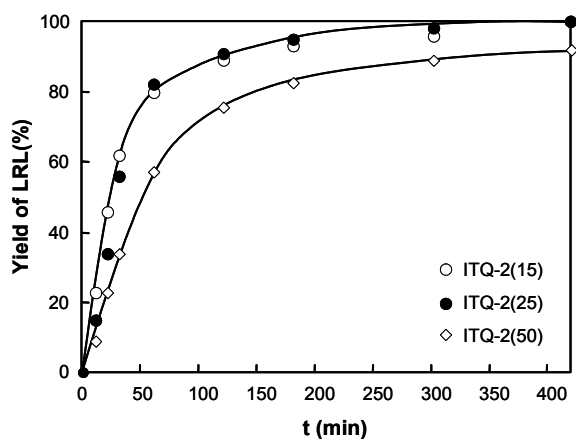


Figure 2. Beckmann rearrangement of CDOX over ITQ-2 with different Si/Al molar ratio. Experimental conditions as in the text.

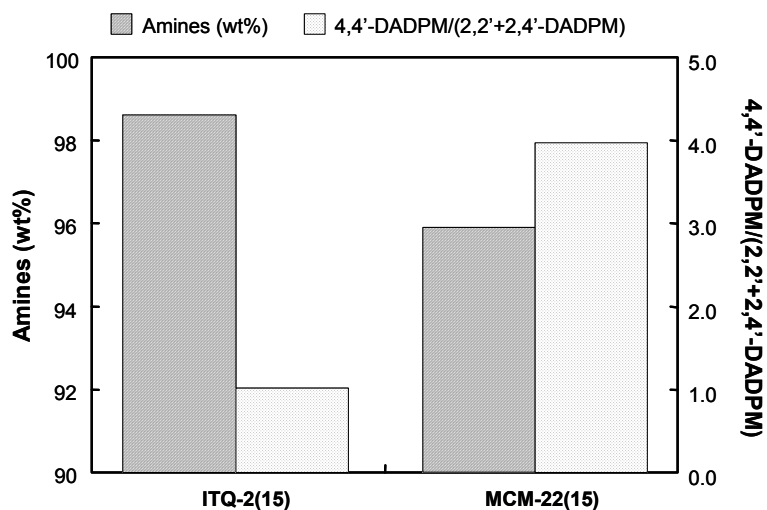


Figure 3. Production of primary amines and diamines distribution in the isomerization of the neutral condensate (aminal) over ITQ-2(15) and MCM-22(15). Experimental conditions as in the text.

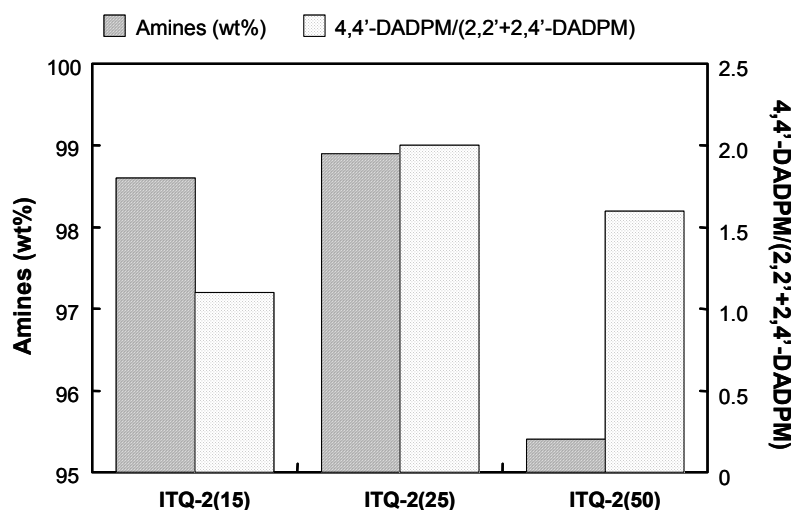


Figure 4. Production of primary amines and diamines distribution in the isomerization of the neutral condensate (aminal) over ITQ-2 with different Si/Al molar ratio. Experimental conditions as in the text.

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### **A study on the nature of the surface active layer in Vanadyl Pyrophosphate, catalyst for the oxidation of n-butane to maleic anhydride**

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The industrial catalyst for n-butane oxidation to maleic anhydride (MA) is a vanadium/phosphorus mixed oxide, in which bulk vanadyl pyrophosphate (VPP)  $(VO)_2P_2O_7$  is the main component. The nature of the active surface in VPP has been studied by several authors, often with the use of in-situ techniques [1]. Different hypothesis were formulated; while bulk VPP is in all cases assumed to constitute the core of the active phase, differences concern the nature of the first atomic layers which are in direct contact with the gas phase. In the present work we report the results of an investigation about the transient reactivity and the changes of the surface V oxidation level of an equilibrated VPP in response to modifications of the gas-phase composition, for catalysts having different P/V atomic ratios. The latter is one of the most important factors affecting the catalytic performance. Data obtained were used to make hypothesis about the nature of the surface active layer, and on how the latter is modified in function of the gas-phase. Catalysts were prepared by the "organic procedure" for the synthesis of  $VOHPO_4 \cdot 0.5H_2O$ , the precursor of VPP [2]. Three samples were prepared, having P/V ratio equal to 0.99, 1.03 and 1.15. The catalytic properties at steady-state (i.e., after the equilibration period of 100 hours reaction time) are considerably different according to the P/V ratio of the samples. The differences are relevant at intermediate reaction temperature (between 340°C and 400°C), whereas they are minimal at  $T < 340^\circ\text{C}$  and at  $T > 400^\circ\text{C}$ . These differences are attributed to changes in the nature of the active surface layer, due to reversible oxidation and hydrolysis phenomena occurring on VPP. The latter indeed depends on the reaction conditions (temperature, gas-phase composition) and on the catalyst P/V ratio. In order to reproduce the transformations occurring at the surface of the VPP, the equilibrated catalyst performance was studied in forced-unsteady regime, by applying conditions different from those underwent by the catalyst under reaction. Specifically, we chose three representative temperatures: 320°C, 380°C and 440°C, and at each temperature either oxidizing treatments (feed of air), or hydrolyzing treatments (feed of 4% steam in He), or both, were applied. Then, the reaction mixture was fed again, and the variation of catalytic performance that occurred along time-on-stream was examined during the transition from the forced regime to the so-called "stable" one. For example, the transient catalytic performance of P/V 1.15, after treatment of the equilibrated sample with air at 380°C, showed that, (i), the equilibrated active surface onto which P is in excess is not in a fully oxidized state, and that, (ii), this active surface is less selective to MA and equally active than a more oxidized active surface in stable reaction conditions. The other conditions of treatments were applied at the chosen temperatures to the samples varying by P/V. In-situ UV-Vis DRS also indicated that feeding the reaction mixture favoured the development of a more oxidized active surface, and that the extent of transformation depends on the reaction temperature. The results allowed us to propose a model of the active surface layer of VPP in reaction conditions. The main points of the model of the active layer are the following: (a) The nature of the surface under stable reaction conditions is substantially close to equilibrated VPP at low reaction temperatures ( $T < 340^\circ\text{C}$ ), regardless of the P/V ratio. (b) At reaction temperatures  $340^\circ\text{C} < T < 400^\circ\text{C}$ , the nature of the active layer depends on the P/V ratio. For P/V  $\approx$  1.0 samples, the development of

an oxidized, but non-hydrolyzed, surface layer leads to a very active but poorly selective catalyst. For  $P/V > 1.0$  samples, instead the surface is stabilized against oxidation by excess P, but it is hydrolyzed under stable reaction conditions. This active layer is moderately active, but selective. (c) Finally, at  $T > 400^{\circ}\text{C}$ , all samples develop a hydrolyzed and oxidized surface that is moderately active but selective. The modifications of the active surface characteristics are reversible, provided hydrolyzing or oxidizing treatments are not carried out at temperatures higher than  $440^{\circ}\text{C}$ . References

[1] H. Bluhm, M. Hävecker, E. Kleimenov, A. Knop-Gericke, A. Liskowski, R. Schlögl, D.S. Su, *Topics Catal.* 23 (2003) 99

[2] N. Ballarini, F. Cavani, C. Cortelli, M. Ricotta, F. Rodeghiero, F. Trifirò, C. Fumagalli, G. Mazzoni, *Catal. Today*, 117 (2006) 174.

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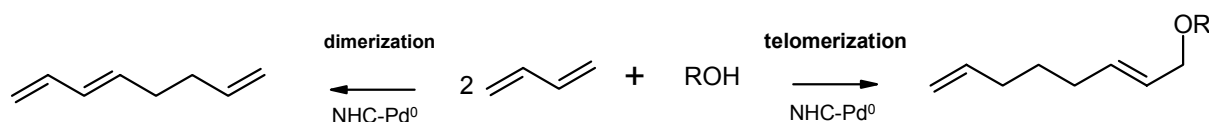
### Industrially useful 100% atom efficient reactions: the Pd-catalysed telomerization and dimerization of butadiene. A theoretical and experimental mechanistic study

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The coupling of two molecules of 1,3-butadiene in the presence of a nucleophile (ROH) and a palladium(0)-N-heterocyclic-carbene catalyst leads either to the production of telomers (with TON > 1.5 million with MeOH)<sup>1</sup> or 1,3,7-octatriene (TON > 80 000 with iPr-OH)<sup>2</sup>. The telomeric products are useful building blocks for plasticizer alcohols, solvents, corrosion inhibitors and monomers for polymers, whereas octatriene is a useful intermediate for the manufacturing of different polymers.<sup>1-2</sup> Despite the importance of these industrially interesting chemical processes, no mechanistic studies has been performed on such catalytic systems. We report in this contribution detailed theoretical and experimental studies on the catalytic cycle of these two palladium-catalysed reactions and demonstrate the detrimental effect of the ligand properties on the different catalytic intermediates.



#### References:

- (a) Jackstell, R.; Andreu, M. G.; Frisch, A.; Selvakumar, K.; Zapf, A.; Klein, H.; Spannenberg, A.; Röttger, D.; Briel, O.; Karch, R.; Beller, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 986-989. (b) Jackstell, R.; Harkal, S.; Jiao, H.; Spannenberg, A.; Borgmann, C.; Röttger, D.; Nierlich, F.; Elliot, M.; Niven, S.; Cavell, K. J.; Navarro, O.; Viciu, M. S.; Nolan, S. P.; Beller, M. *Chem. Eur. J.* **2004**, *10*, 3891-3900.
- Harkal, S.; Jackstell, R.; Nierlich, F.; Ortmann, D.; Beller, M. *Org. Lett.* **2005**, *7*, 541-544.



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### **Operando studies of alumina-supported oxomolybdates for methanol selective oxidation**

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The partial oxidation of methanol is of great interest for industrial applications but is also a good probe reaction to test the catalytic properties of new preparations. Raman spectroscopy can give insights into catalytic systems under reaction conditions enabling to obtain information on the nature of the active phase. However it cannot give information at the atomic level. This can be obtained by XPS although the vacuum required by this technique prevents its use in situ or operando conditions. XAS does not suffer from such limitations but the spectra can sometimes be difficult to interpret without guidelines from other experiments. The combination of complementary techniques can lead to a fine interpretation of the mechanisms occurring on a catalyst surface. Raman spectra recorded during the methanol oxidation reaction were collected at different temperatures under catalytic conditions. In absence of oxygen, on the high Mo content catalyst (20 wt. % Mo/Al<sub>2</sub>O<sub>3</sub>), at 523 K, products from the oxidation reaction of methanol (formaldehyde and methyl formate) are evidenced, but a fast deactivation of the oxidative function is observed with the time of stream although methanol conversion remains stable and equal to 86% yielding mainly dimethylether (DME). A broad line in the Raman spectra at c.a. 800 cm<sup>-1</sup> is characteristic of a reduced polymolybdate phase. Its intensity increases during the course of the reaction in the absence of oxygen. The presence of oxygen in the reactive mixture induces an almost complete restoration of the initial signal. At the same time, the methanol conversion increases up to 92% as well as the selectivity of the reaction to formaldehyde indicating that the oxidative functions are restored by oxygen. All these data indicates that, in the absence of oxygen, methanol reacts with the active oxomolybdate phase to give oxidation products until all accessible centers are reduced. When the number of available oxidized sites, "active sites" decreases, the percentage of oxidation product decreases down to zero and the selectivity towards dehydration products (mainly DME) increases. The reduction of the catalyst has also been monitored by the XANES spectra. Indeed the oxidized state shows a characteristic pre-edge peak that drastically decreases upon reduction along with a shift of the absorption edge towards lower energies (c.a. 3eV) indicating reduction of the metallic centers. The EXAFS region of the XAS spectra leads to complementary informations and shows that the oxygen environment around the molybdenum is a distorted tetrahedron and that no significant evolution in the first coordination sphere occurs upon reduction of the catalyst. These data, however do not give the crucial information that is the oxidation degree of the molybdenum centers. In order to assess this point, we performed XPS analyses after a pre-treatment at 573 K under a He/CH<sub>3</sub>OH gas flow in a microreactor settled in the preparation chamber, which allows experiments to be performed without exposing catalysts to air. XPS spectra show the presence of 28% of MoVI, 72% of MoV and no MoIV and clearly show that, on this oxomolybdic phase, methanol oxidation proceeds through the reduction of MoVI to MoV. Methanol oxidation to formaldehyde being however a two electrons process, the presence of large amount of MoV implies that at least two molybdenum atoms are required for the reaction to take place. We can conclude that the redox function of oxomolybdenum species deposited on alumina is efficient only if a polymolybdate phase is present. According to this interpretation monomeric molybdenum centers on alumina should not be active in selective oxidation. We then prepared a 3 % wt. Mo on Al<sub>2</sub>O<sub>3</sub> that contains only monomeric oxomolybdenum centers as evidenced by the Raman line at 920 cm<sup>-1</sup> before calcination. The catalytic test on methanol transformation on this low loading catalyst shows that no oxidation products are formed even in the presence of oxygen. Furthermore, XAS spectroscopy does not show any evolution of the signal and we can

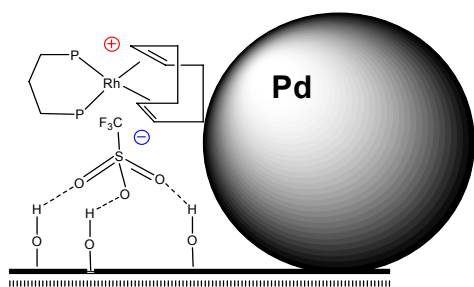
### SYNERGISTIC EFFECT IN ARENES HYDROGENATION OVER HYBRID BIMETALLIC SITES Rh(I)-Pd(0)

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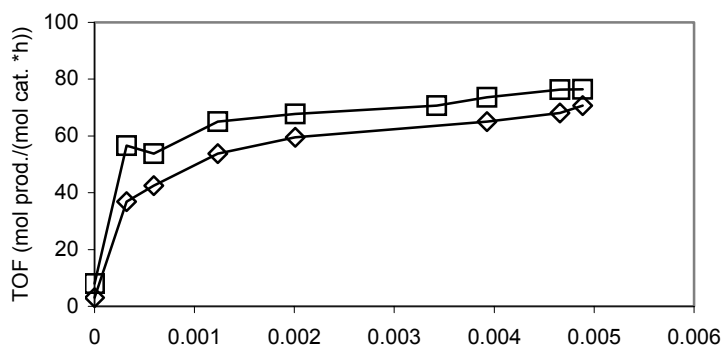
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The combination, on the same support material, of a grafted molecular rhodium complex (Rh(sulphos(COD))) and palladium nanoparticles results in an amplification of reaction rates of arenes hydrogenation reactions, as demonstrated in previous works [1,2]. Such effect was ascribed to the formation, under H<sub>2</sub> atmosphere of Rh(I)(μ-H)<sub>x</sub>Pd(0) sites between grafted complex and palladium nanoparticles, resulting in a highly active catalyst. Here we will report about a new system based on (CF<sub>3</sub>SO<sub>3</sub>)Rh(dppp)(COD) grafted on Pd(0)/SiO<sub>2</sub> as shown in Figure 1. The hybrid catalyst was from 10 to 20 times more active for the hydrogenation of toluene, than supported palladium alone (see Fig. 2). The catalytic conversion promptly increase even at low Rh loadings then is almost constant with Rh content up to 1%. Hydrogen pressure and substrate concentration effects on conversions were studied and respectively a linear increase vs H<sub>2</sub> pressure and a first to zero order transition vs. substrate concentration were found.



**Fig.1** Scheme of Rh(dppp)(COD)-Pd/SiO<sub>2</sub> catalyst



**Fig.2** TOF(Pd) vs Rh amount (mmol) for benzene (squares) and toluene (diamonds)

Moreover air exposure of both fresh and post catalysis samples results in a increase of catalyst activity. Such effect was deeply investigated by the means of EXAFS and CO probe molecule-DRIFTS spectroscopies suggesting that the air exposure at room temperature leaves the Rh<sup>I</sup> complex stable but modifies the charge distribution and/or the fraction of more coordinatively unsaturated Pd site so favouring the Rh<sup>I</sup> site proximity to surface metal Pd particles, leading to the formation of bimetallic sites stable under reaction conditions and responsible for the increased synergistic effect.

#### References:

1. C. Bianchini, V. Dal Santo, A. Meli, M. Moreno, R. Psaro, L. Sordelli and F. Vizza, *Angew. Chem. Int. Ed.* **2003**, *42*, 2636.
2. P. Barbaro, C. Bianchini, V. Dal Santo, A. Meli, M. Moreno, R. Psaro, L. Sordelli and F. Vizza, *J. Am. Chem. Soc.* **2006**, *128*, 7065

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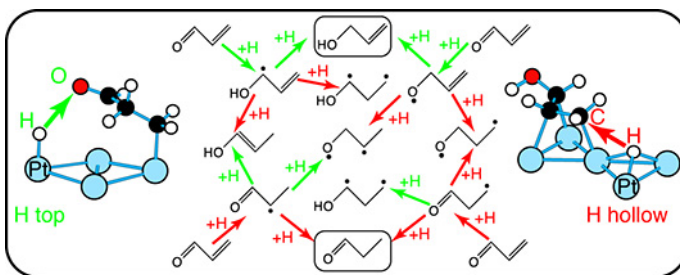
### DFT study of a selective reaction: acrolein hydrogenation on Pt(111)

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The hydrogenation of  $\alpha$ - $\beta$  unsaturated aldehydes (crotonaldehyde, prenal, cinnamaldehyde, citral) is an important reaction in numerous processes of fine chemistry (pharmaceuticals, perfumes). The challenge is to obtain selectively the unsaturated alcohol by hydrogenation of the C=O bond or the saturated aldehyde by hydrogenation of the C=C bond, the former being the most interesting product. The selectivity origin, that depends on the molecule and on the catalyst, is not known. The knowledge of the mechanism is though essential to design new, more selective catalysts. Quantum chemistry is a very useful tool to explore the reaction mechanisms because it allows the characterization of the reaction intermediates and of the transition states, which are not accessible to the experimentalists.

We have first studied acrolein, the most simple of these aldehydes, on a Pt(111) surface. Periodic calculations, based on the density functional theory (DFT), have allowed the exploration of the various adsorption structures. Then, on the most stable adsorption state (flat  $\eta_4$  form), we have compared the competitive hydrogenation pathways of the two double bonds. There are numerous competitive pathways. All the reactants, intermediates, products and transition states have been optimized, which allowed us to obtain the activation energies and to perform a kinetic treatment of the two first hydrogenations. In our kinetic model, based on the transition state theory, all the competitive steps have been included and the rate constants have been calculated from DFT activation energies. The calculated selectivity is in agreement with the experimental results (96% selectivity in propanal). It seems controlled by competition between the propenal desorption and the second hydrogenation leading to propanal.



This work is the first

comprehensive theoretical study of a heterogeneous catalytic reaction showing several competitive ways and dealing with complex molecules. From a more general point of view, it is interesting to explain the selectivity inversion (preferential formation of the unsaturated alcohol) when acrolein is substituted (case of prenal) or when the catalyst is an alloy (case of  $Pt_xSn$ ). Considering these first theoretical results, one can suggest that, if the desorption energy of the unsaturated alcohol is smaller, the selectivity in this alcohol will increase, on condition that the other elementary steps remain identical.

F. Delbecq et P. Sautet, *J. Catal.* **2002**, 211, 398-406.

F. Delbecq et P. Sautet, *J. Catal.* **2003**, 220, 115-126.

D. Loffreda, F. Delbecq, F. Vigné et P. Sautet, *Angew. Chem. Int. Ed.* **2005**, 44, 5279-5282.

D. Loffreda, F. Delbecq, F. Vigné et P. Sautet, *J. Am. Chem. Soc.* **2006**, 128, 1316-1323.

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### **Structure and reactivity of chromocene confined into nanovoids with a different polarity: from organometallic chemistry to catalysis**

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CrCp<sub>2</sub> supported on silica, which is a modification of the well known Cr/SiO<sub>2</sub> Phillips catalyst [1] is highly active in ethylene polymerization (Union Carbide catalyst) [2]. The structure of the active sites resulting from the reaction of CrCp<sub>2</sub> with the silanol groups of the silica surface, and their reaction with the ethylene monomer are not completely understood. The experimental approach recently applied to give an insight into the structure of the active sites and into the reaction mechanism of the parent Cr/SiO<sub>2</sub> catalyst [3], does not give the same successful results in the case of the CrCp<sub>2</sub>/SiO<sub>2</sub> system, whose complexity mainly arises from the tendency of CrCp<sub>2</sub> to cluster. For this reason, in fact, the majority of the spectroscopic techniques give information on the dominating but inactive CrCp<sub>2</sub> clusters, and not on the grafted and active species. It is clear that, in order to clarify the structure and the reactivity of CrCp<sub>2</sub> and to allow a direct comparison with theoretical calculations, it is necessary to be in presence of molecularly dispersed CrCp<sub>2</sub> species. In this contribution we discuss the effect of CrCp<sub>2</sub> confinement into the nanovoids of two porous matrices characterized by a different polarity: a nanoporous polystyrene and a Na-Y zeolite. The structural, vibrational and optical properties of molecular CrCp<sub>2</sub> hosted inside these two matrices and its reactivity towards different molecules (CO, NO, H<sub>2</sub>O, CH<sub>3</sub>OH, etc.) is fully characterized by means of several spectroscopic techniques (FTIR, Raman, UV-Vis DRS, EXAFS, etc.) and compared to the theoretical results obtained by DFT calculations, adopting several Hamiltonians (e.g. BP86, B3LYP) and using the Gaussian03 code. The confined CrCp<sub>2</sub> molecules show an enhanced reactivity with respect to the corresponding bulk or with the CrCp<sub>2</sub> in solution. As an example, in the CrCp<sub>2</sub>/PS system, reversible CrCp<sub>2</sub>⋯(CO) complexes are formed in mild conditions (room temperature and PCO = 100-300 Torr), in contrast to the drastic conditions required in toluene solution (below 0 °C and PCO = 1-10 bar) [4]. The CrCp<sub>2</sub> molecules confined inside the ionic environment of the Na-Y zeolite show a much higher reactivity towards CO, in that the CrCp<sub>2</sub>⋯(CO) complexes immediately lose a Cp ring and form tri-carbonyl species stabilized by the zeolitic walls. The conclusion arising from this work is that the CrCp<sub>2</sub>/nanoporous systems can be considered as materials having a model character, useful to understand the structure and reactivity of the more complex and real CrCp<sub>2</sub>/SiO<sub>2</sub> catalyst. Furthermore, these systems offer a good opportunity to verify the potentialities of DFT calculations in predicting the properties of open shell metallocenes. The peculiarity of this approach consists in the possibility to characterize an organometallic complex by working in heterogeneous standard experimental conditions (i.e. without using gaseous matrices or solvents); therefore, it is an outstanding example of the possibility to connect together organometallic (homogeneous) chemistry with heterogeneous catalysis. The financial support of NoE IDECAT is acknowledged. References

[1] Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. Chem. Rev. 2005, 105, 115-183.

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### Maps of LiGand space

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Transition metal complexes catalyse many reactions important in synthetic organic chemistry. A range of reaction variables, such as the metal centre, ligands, substrate, solvent and reaction conditions, contribute to the control of reactivity and selectivity in homogeneous catalysis. Modification of any of these variables can be used to fine-tune catalyst efficiency, but the overall effect of such changes can be difficult to predict *a priori*. The development of new catalysts therefore rarely involves a truly "rational" design process, but instead relies on chemical intuition as well as the screening and optimisation of a range of likely candidates.<sup>1</sup>

Maps of chemical space derived from both experimental and calculated descriptors have been developed to guide such screening efforts.<sup>2</sup> In addition, regression models have been derived from suitable parameters to aid in the interpretation, and sometimes prediction, of experimental data.<sup>2,3</sup> However, experimental data is often not available for novel catalytic systems, making computational approaches the method of choice.

We have recently developed a ligand knowledge base (LKB) of descriptors calculated with density functional theory (DFT) for a range of phosphorus(III) donor ligands.<sup>4</sup> This LKB was explored with multivariate statistical methods. Projections of the descriptors can be used to map chemical space and visualise clustering of ligands in chemically coherent subsets. Available external datasets can be projected onto such maps, highlighting trends and guiding ligand screening. In addition, linear regression models can be developed to describe the relationships between the descriptors and both calculated and experimental parameters. This contribution will illustrate potential applications of such maps of ligand space. In addition, the challenges associated with the application of statistical methods to chemical data will be discussed.

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<sup>1</sup> Hoveyda, A. H.; Hird, A.W.; Kacprzynski, M. A., *Chem. Commun.*, **2004**, 1779.

<sup>2</sup> Bjørsvik, H.-R.; Hansen, U. M.; Carlson, R., *Acta Chem. Scand.*, **1997**, *51*, 733; Cooney, K. D.; Cundari, T. R.; Hoffman, N. W.; Pittard, K. A.; Temple, M. D.; Zhao, Y., *J. Am. Chem. Soc.*, **2003**, *125*, 4318; Burello, E.; Rothenberg, G., *Adv. Synth. Catal.*, **2003**, *345*, 1334; Burello, E.; Marion, P.; Galland, J. C.; Chamard, A.; Rothenberg, G., *Adv. Synth. Catal.*, **2005**, *347*, 803.

<sup>3</sup> Joerg, S.; Drago, R. S.; Sales, J., *Organometallics*, **1998**, *17*, 589 and references therein; Wilson, M. R.; Prock, A.; Giering, W. P.; Fernandez, A. L.; Haar, C. M.; Nolan, S. P.; Foxman, B. M., *Organometallics*, **2002**, *21*, 2758 and references therein; Bunten, K. A.; Farrar, D. H.; Poë, A. J. *Organometallics*, **2003**, *22*, 3448 and references therein; Lipkowitz, K. B.; Pradhan, M. J. *Org. Chem.*, **2003**, *68*, 4648; Cruz, V.; Ramos, J.; Munoz-Escalona, A.; Lafuente, P.; Pena, B.; Martinez-Salazar, J., *Polymer*, **2004**, *45*, 2061.

<sup>4</sup> Fey, N.; Tsipis, A. C.; Harris, S. E.; Harvey, J. N.; Orpen, A. G.; Mansson, R. A., *Chem. Eur. J.* **2006**, *12*, 291-302.

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### Selective Catalysts for Hydrogenolysis/Ring opening of Tetralin

Environmental themes and changes in market demand [1,2] are at the present time the main driving forces for the development of new refinery processes or the modification of the existing one to meet the demand in terms of quality. As for the diesel fuel, owing to the adverse effect on engine emission it is most likely that the polycyclic aromatic compounds (PACs) and more in general the aromatics content will be the subject of more restrictive legislation [3-5]. Besides, the diesel percentage of European car fleet is expected to rise significantly in the next years with a consequent increase of gasoil demand. A possible route to accomplish this twofold objective is the upgrading of high aromatic cuts such as light cycle oil (LCO). However, simple dearomatization leads to the formation of naphthenic compounds and consequently to a modest improvement of product characteristics. A more substantial improvement in this way may be achieved by saturation and selective hydrogenolysis/ring opening of naphthenic rings [6]. In recent years, transition or noble-metals based catalysts have been widely investigated in the hydrogenation and hydrogenolysis/ring opening of PACs present in LCO fractions [7-9]. Although the catalytic performances have been widely investigated, few and partial data are available on the mechanism of the above reaction and on the role of the different parameters. The aim of this study was to investigate the catalytic behaviour of platinum and iridium based catalyst for the hydrogenation and ring opening of tetrahydronaphthalene (THN or tetralin) chosen as a model reactant. Particularly, this contribution was focused on assessing the role played by the metallic phase and support characteristics, as well as operating conditions on selectivity for the different classes of products during THN conversion. The metal phase (1 %wt) was loaded on the selected support by incipient wetness impregnation of noble metal solution [10]. The different catalysts were fully characterized using different techniques (BET surface area, XRD surface total acidity and Brønsted/Lewis distribution, TPR, metal dispersion, etc.). Conversion tests of THN with different noble-metal containing catalysts were performed in a lab-scale plant operating up to 6.0 MPa, checking different reaction conditions (temperature, pressure, WHSV, H<sub>2</sub>/THN ratio). Nature of the metal and support exhibited a strong influence on hydrogenation and ring opening activity. Particularly, the platinum based catalyst showed a higher hydrogenation activity respect to the iridium loaded catalyst. Besides, for the same metal a significant effect on the hydrogenating activity was observed for different supports. Temperature and pressure play a key role on the selectivity, the hydrogenolysis/ring opening activity being favoured at low temperature and low H<sub>2</sub> pressure. However, while Pt showed significant hydrogenation activities, forming high amounts of fully saturated compounds, very interesting performances were obtained using Ir-based catalyst, previously reported as slightly active in the hydrogenation and hydrogenolysis/ring opening of naphthalene. References

[1] R. Catani, M. Mandreoli, S. Rossini, A. Vaccari, *Catal. Today* 75 (2002) 125.

[2] Partinelli Tecnon, in : Proceedings of EniTecnologie Conference, "Long Term Refinery Outlook", San Donato Milanese, M1, Italia, November 21, 2000.

[3] P.T. Vasudevan, J.G.L. Fierro, *Catal. Rev.-Sci. Eng.* 38 (1996) 161.

[4] M. Yamada, K. Segawa, Y Ohtsuka (Eds.), *Catal. Today* 39 (1997) 1.

[5] C. Song, *Chemtech* (29 Marzo 1999) 26.

[6] R.C. Santana, P.T. Do, M. Santikunaporn, W.E. Alvarez, J.D. Taylor, E.L. Sughrue, D.E. Resasco, *Fuel* 85 (2006) 643.

[7] P.T. Do, W. E. Alvarez, D.E.

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### **A View on the Mechanism of the Catalytic Partial Oxidation of Methane**

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The Catalytic Partial Oxidation (CPO) of methane over noble metals has received increased attention in the last years [1] due to its key role in the production of synthesis gas or higher value chemicals from natural gas. CPO can be accomplished autothermally and selectively in very short contact times (ms range) over Pt- and/or Ph- based catalysts. The conversion is characterized by a complex interplay between transport processes and chemical reactions, which may also occur in the gas phase. Homogeneous reactions are suspected to play a role in this high temperature oxidation reaction. The catalyst may produce and release reactive intermediates and energy into the gas phase, so that surface and gas phase reaction steps can occur simultaneously. Radicals are thought to be key intermediates. [2,3] Consequently, identified intermediates and reaction products can lead to a better understanding of mechanistic. Our goal was to identify reactive species and products during the high temperature process of methane conversion. The use of a Molecular Beam Mass Spectrometer (MBMS) equipped with a high temperature catalytic wall reactor [4] allowed studying this reaction in situ. A small gas portion is expanded through a tiny nozzle (125  $\mu\text{m}$ ) in the Pt/Rh reactor wall into a three stage pumped vacuum. An arrangement of skimmer and collimator allows quenching intermediates in a molecular beam to prevent further reaction. A quadrupole mass spectrometer with tunable ionization energy offers the possibility to detect intermediates in presence of interfering species (same  $m/z$ ) in the molecular beam. Methyl radicals with an ionization energy of approx. 10 eV have been detected and distinguished using the threshold ionization method from methane (Appearance Potential = 14 eV) during oxidation at 1100 to 1300 °C. At temperatures with increased concentrations of methyl radicals the product composition, investigated by on line GC analysis, indicates new reaction pathways leading to formation of C2 to C6 compounds. Acetylene and various unsaturated higher hydrocarbons have been observed, pointing towards recombination of methyl radicals followed by stepwise dehydrogenation. This is the first in situ observation of radicals in methane partial oxidation under reaction conditions. Radical formation starts at 1100 °C and increases significantly with temperature. In agreement with the GC data it follows that the radicals are directly involved in the conversion of methane to higher hydrocarbons.

1.D. A. Hickman and L. D. Schmidt, *Science*, 1993, 259, 343-346.

2.O. Deutschmann and L. D. Schmidt, *AIChE Journal*, 1998, 44, 2465-2477.

3.C. A. Mims, R. Mauti, A. M. Dean and K. D. Rose, *J. Phys. Chem.*, 1994, 98, 13357-13372.

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### Functionalization of nanoporous polystyrenes by means of an organometallic approach: new materials exploitable for catalytic applications

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In the recent years metal-containing polymers [1] are becoming very attractive owing to their possible applications as catalysts for organic synthesis, X-ray absorbers or materials having optical properties, etc. In addition, unsaturated organometallic compounds of transition metals have been investigated actively in recent years as novel chromophores suitable for nonlinear optical applications [2,3]. Furthermore, functionalized nanoporous polystyrenes could be extremely interesting in the field of H<sub>2</sub> storage, since the transition metal able to adsorb H<sub>2</sub> is confined inside a light matrix providing a higher capacity of hydrogen storage in more favorable conditions (RT) in contrast to the conditions required by the non-functionalized polymers (77 K).

In this contribution we report our first results obtained in the field of functionalization of nanoporous polystyrenes by means of an organometallic approach. Two nanoporous polystyrenes have been investigated, differing in composition, hydrophilic character and surface area: (i) a poly(4-ethylstyrene-co-divinylbenzene) in the following PS, showing a BET surface area of 1000 m<sup>2</sup>g<sup>-1</sup>, and (ii) a poly(4-vinylpyridine), in the following PS-N, 25% cross linked with divinylbenzene, showing a surface area of 60 m<sup>2</sup>g<sup>-1</sup>. PS is highly hydrophobic, while in PS-N the presence of the pyridine unit determine its hydrophilic character.

Cr has been successfully incorporated inside PS by a simple chemical vapor deposition method starting from Cr(CO)<sub>6</sub>, by following an approach similar to that adopted in the preparation of inorganic-organic hybrid materials [4]. FTIR and UV-Vis spectroscopies demonstrate that, by heating Cr(CO)<sub>6</sub>/PS at 150 °C, Cr is immobilized on the benzene groups of the PS in the form of Cr-arenetricarbonyl complexes [-(C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub>-]. The formation of these complexes confers to the PS the yellow color typical of the (C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> organometallic complex. As (C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> molecular solid easily sublimate under moderate vacuum, the stability up to 200 °C of (C<sub>6</sub>H<sub>6</sub>)Cr(CO)<sub>3</sub> complexes hosted inside the PS nano-cavities is ascribed to a stabilization effect of the hosting matrix. Furthermore, the Cr-functionalized polymer retains its yellow color also after exposure to air. This functionalized PS could be used in the development of unique heterogeneous catalysts, since the arenetricarbonyl complexes exhibit effective catalytic activity for some reactions, such as the hydrogenation of polyunsaturates into cis-unsaturated products.

The PS-N matrix has been successfully functionalized also with Cu(II), by impregnation with an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>. The inclusion of Cu(NO<sub>3</sub>)<sub>2</sub> units strongly perturbed the vibrational properties of the PS-N related with the pyridine groups. The Cu(II) cations are reduced to Cu(I) by treatment in CO at 150°C. As Cu(I) ions hosted in zeolites are able to adsorb H<sub>2</sub> even at RT [5], the insertion of Cu(I) species inside the lighter PS-N hosting matrix can result in a promising H<sub>2</sub> storage material. The financial support of NoE IDECAT is acknowledged.

#### References

- [1] Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217-3274.
- [2] Long, N. J. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 6.
- [3] Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
- [4] Kamegawa, T.; Sakai, T.; Matsuoka, M.; Anpo, M. *J. Am. Chem. Soc.* **2005**, *127*, 16784-16785.



[5] Spoto, G.; Gribov, E.; Bordiga, S.; Lamberti, C.; Ricchiardi, G.; Scarano, D.; Zecchina, A. *Chem. Commun.* 2004, 2768-2769

## **EXAFS study of the impregnation and reduction processes of Pd/C catalysts**

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We investigated, with in-situ Pd K-edge EXAFS, all the steps related with the preparation of Pd/C catalysts, starting from the Pd<sup>2+</sup> precursor precipitation from solution, through the partial reduction from the basic support, to the chemical reduction from the liquid phase. EXAFS data have been obtained at the BM26A DOUBBLE beamline at the ESRF. In all steps, samples were measured in wet conditions, to be as close as possible to the catalysts inserted into the industrial reactor. These results complement those obtained by conventional techniques, investigating the catalysts in dried conditions. Following variables were considered: (i) origin of the carbon; (ii) Pd loading; (iii) impregnation method; (iv) reducing agent. Comparison with Pd/Al<sub>2</sub>O<sub>3</sub> is also made.

From the evaluation of the whole set of data, the main results can be summarized as follows. (i) The as-impregnated samples contain only oxidized Pd<sup>2+</sup> phase and no metallic Pd is observable. (ii) The chemical reduction agents from the liquid phase do not completely penetrate inside the Pd particles, even H<sub>2</sub>, so that a relevant fraction of Pd is still in the oxidized form after this step. (iii) The reducing efficiency of a given chemical agent depends on the type of the support: Al<sub>2</sub>O<sub>3</sub> > C from wood > C from peat. (iv) The drying procedure does not alter significantly the oxidation state of Pd. (v) A complete reduction of Pd is achieved only by interaction with H<sub>2</sub> from the gas phase. The average particle size and the dispersion of the Pd particles on the samples reduced in H<sub>2</sub> atmosphere, estimated by TEM, EXAFS and CO chemisorption, are compared and discussed.

## **CH<sub>2</sub>Cl<sub>2</sub> as a selective modifying agent to create a new family of highly reactive Cr polymerization sites**

*E. Groppo,<sup>1</sup> C. N. Nenu,<sup>2</sup> C. Lamberti,<sup>1</sup> T. Visser, A. Zecchina<sup>1</sup> and B. M. Weckhuysen<sup>2</sup>* <sup>1</sup>Department of Inorganic, Physical and Materials Chemistry, NIS Centre of Excellence and INSTM Centro di Riferimento, University of Turin, Via P. Giuria 7, I-10125 Torino, I, elena.groppo@unito.it <sup>2</sup>Utrecht University, Department of Chemistry, Inorganic Chemistry and Catalysis, Sorbonnelaan 16, The CrII/SiO<sub>2</sub> Phillips catalyst, although used in industrial plants since the 1960s, is still one of the most debated systems, concerning both the molecular structure of the active sites and the related initiation mechanism, for which a unifying picture is still missing [1-4]. The main reasons why these two strictly connected questions are not properly addressed are the high intrinsic heterogeneity of the CrII sites formed at the surface of amorphous silica and the high Cr dilution (typically less than 1 wt.% Cr). The second point is related to the formation of catalytically inactive Cr<sub>2</sub>O<sub>3</sub> clusters at higher Cr loadings.[5] As for the first point, the presence of at least three families of CrII species, differing in their ability to coordinate ligand molecules and thus in their catalytic activity, has been fully demonstrated [2-6]. Attempts to reduce the complexity of the catalyst surface have been continuously made over the last decades. In this respect, the annealing method of McDaniel and co-workers,[1] further developed by Groppo et al. [4], represents a way to fine-tune the relative population of CrII sites. van Kimmenade et al. [7], by grafting Cr species on a flat SiO<sub>2</sub>/Si(100), succeeded in obtaining better defined Cr species. This approach is ideal for the application of any surface science specific method, such as XPS and AFM. Very recently, a method to completely remove the heterogeneity of the CrII/SiO<sub>2</sub> system has been reported [8, 9]. By using the complex TAC (1,3,5-tribenzylhexahydro 1,3,5-triazine) ligand - as a surface-modifying agent - a single site Cr species was made, resulting in the formation of polyethylene with a very low polydispersity

index. In this contribution we show that the much simpler CH<sub>2</sub>Cl<sub>2</sub> molecule acts on the CrII/SiO<sub>2</sub> system as a surface-modifying agent, having the dual function to selectively enhance the catalytic activity of a small fraction of Cr sites, while poisoning the remaining ones [10]. This approach represents a much simpler method to reduce the Cr heterogeneity, increasing at the same time the catalytic performances of the system. In situ UV-Vis and IR spectroscopies suggest that the highly active Cr polymerization site is created by the dissociative chemisorption of CH<sub>2</sub>Cl<sub>2</sub> representing a species that does not need the first initiation step by ethylene [10]. This work is supported by research grants from ATOFINA Research and NWO CW-VICI and by an EU Marie-Curie trainingship to C.N. to visit the University of Torino. IDECAT support is acknowledged for the travels of C.L. and E.G. to Utrecht.

#### References

- [1] M.P. McDaniel, *Adv. Catal.*, 33 (1985) 47.
- [2] B.M. Weckhuysen, I.E. Wachs and R.A. Schoonheydt, *Chem. Rev.*, 96 (1996) 3327.
- [3] E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.*, 105 (2005) 115.
- [4] E. Groppo, C. Lamberti, G. Spoto, S. Bordiga, G. Magnacca and A. Zecchina, *J. Catal.*, 236 (2005) 233.
- [5] E. Groppo, C. Prestipino, F. Cesano, F. Bonino, S. Bordiga, C. Lamberti, P.C. Thüne, J.W. Niemantsverdriet and A. Zecchina, *J. Catal.*, 230 (2005) 98.
- [6] B.M. Weckhuysen, R.A. Schoonheydt, J.M. Jehng, I.E. Wachs, S.J. Cho, R. Ryoo, S. Kijlstra and E. Poels, *J. Chem. Soc. Faraday Trans.*, 91 (1995) 3245.
- [7] E.M.E. van Kimmenade, J. Loos, J.W. Niemantsverdriet and P.C. Thune, *J. Catal.*, 240 (2006) 39.
- [8] C.N. Nenu and B.M. Weckhuysen, *Chem. Commun.*, (2005) 1865.

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### **Polystyrene supported L-proline: a recyclable organocatalyst for the asymmetric aldol reaction in the presence of water**

The straightforward synthesis of a polystyrene-supported proline catalyst has been reported. The supported L-proline was used in the reaction between cyclohexanone and several substituted benzaldehydes. Results showed that the reaction takes place only in the presence of water or methanol. Without solvent or in the presence of solvents such as DMSO, DMF, CHCl<sub>3</sub>, dioxane or ethanol no reaction was observed. High yields (50-99%) diastereoselectivities (85/15-99/1) and enantioselectivities (90-98%) were obtained. The reaction was also carried out using other ketones. A model of the supported catalyst will be given. The recyclability of the catalyst was tested. After five cycles we obtained the same yield (88%) and stereoselectivity (95/5 anti/syn; 98% ee).

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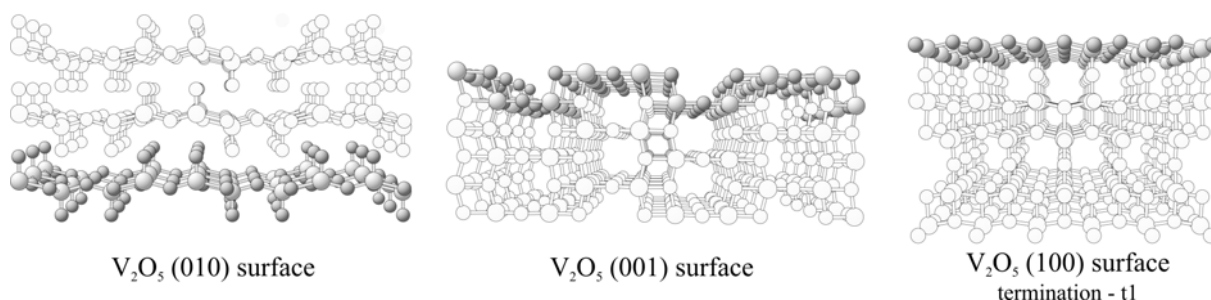
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### Ammonia Activation at Low-indices V<sub>2</sub>O<sub>5</sub> Surfaces in SCR Reaction – Cluster DFT Study.

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Vanadia-based catalysts are of a great importance in an abatement of NO<sub>x</sub> from waste gases. The interest of using these catalysts in industry is also caused by its resistance to SO<sub>2</sub> poisoning. The SCR of nitrogen oxides in the presence of NH<sub>3</sub> can proceed according to two mechanisms: the first one - Eley-Rideal mechanism in which ammonia is adsorbed at the Brönsted acidic sites present on the surface, and reaction proceeds between strongly adsorbed NH<sub>3</sub> species and NO molecules from the gas phase and the second mechanism - Langmuir-Hinschelwood type-mechanism where in the first stage of the catalytic reaction NO from the gas phase is oxidized and adsorbed as NO<sub>2</sub> species, and than reacts with adsorbed NH<sub>3</sub>. However, Topsøe et al. suggested, that SCR reaction proceeds according to the hybrid of Eley-Rideal and Langmuir-Hinschelwood mechanisms and it is necessary to consider both of them, in order to fully understand this process.

The V<sub>2</sub>O<sub>5</sub> catalyst's crystallites may exhibit different types of faces: surfaces built of chemically saturated atoms (the (010) netplane) and those built of unsaturated cations and anions ((001) and (100) netplanes) (see Fig.1). The fact of 15% overall contribution of the (001) and (100) surfaces into crystallite structure [1] indicates that all low-indices surfaces might be important in catalytic process. In these study, the adsorption of ammonia on all Brönsted acidic centers present at low-indices V<sub>2</sub>O<sub>5</sub> surfaces is discussed.



The calculations were carried out by means of *ab initio* DFT (RPBE exchange-correlation functional) method using StoBe code. To mimic surface clusters cut out from the surface with Brönsted acidic sites were used. Dangling bonds of peripheral oxygen atoms were saturated by hydrogen atoms. The electronic structure was described by atomic charges gained from Mulliken population analyses and Mayer bond indices.

Results of the calculations show that ammonia molecule is stabilized on all OH surface groups at any V<sub>2</sub>O<sub>5</sub> surface, however the mechanism and adsorption geometry depend on surface and type of Brönsted center. The calculations show that in some cases hydrogen bonds are bi- or tri-furcated, and can also be of more complexed nature. Both NH<sub>4</sub> as well as OH groups can play role of the proton donor in the hydrogen bond. In most cases the adsorbed NH<sub>3</sub> appears as NH<sub>4</sub><sup>+</sup> cations.

[1] J. Goclon, R. Grybos, M. Witko, *unpublished results*

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### **Supported Ionic Liquid Phase Catalysis with Supercritical Flow**

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*Supported Ionic Liquid Phase (SILP) catalysts have been tested in a continuous flow system using Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as transport vector for both substrates and products. The hydroformylation of a long chain alkene with a homogeneous rhodium-phosphine catalyst was taken as a model reaction in order to test the concept. High activity giving rapid hydroformylation of 1-octene (rates up to 800 h<sup>-1</sup>) with the catalyst remaining stable for at least 40 hours at very low rhodium leaching levels (0.5 ppm) could be demonstrated. The process involving a fixed bed catalyst in a tubular reactor is very economic, Liquid Hourly Space Velocities of over 2.8 h<sup>-1</sup> can be achieved in a continuously flowing process where no product isolation step is needed. Advantages of this concept include excellent diffusion of the substrate and gases to the catalyst, excellent solubility of the substrates and gases within the supported ionic liquid and extraction of heavy products that might otherwise foul the catalyst by filling the pores. A stable, efficient catalyst system with very low catalyst losses is obtained.*

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### **Interactions of NH<sub>3</sub> with Co ions in the zeolite framework studied by FTIR/UV-Vis spectroscopy**

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Transition metal ions coordinated to framework oxygens of specific local framework structure forming cationic site exhibit in zeolites unique co-ordinations, which can serve as adsorption or reaction centers. Simultaneous FTIR and UV-Vis in situ spectroscopy under dynamic conditions is used to detail analysis of the ammonia interaction with individual Co sites in the zeolite framework. Co-zeolite samples with different Co loading were prepared for this study. FTIR and UV-Vis spectra were measured over sample in a form of a thin pellet (ca 80 - 120 μm) exposed to reaction stream in a high temperature catalytic micro-reactor (ISRI, U.S.) modified for combined FTIR (Nexus 670, Thermo Nicolet Co.) and UV-Vis (Avantes Fiber Optic) spectrometers. Quantitative analysis of the response to concentration change of the feed was based on mathematic modelling of the response in the IR/UV-VIS cell and the thin pellet of sample

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### **Fe-zeolite catalysts doped with second noble metal for N<sub>2</sub>O decomposition.**

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The Fe-zeolite catalysts represent promising catalytic system candidates for abatement of N<sub>2</sub>O from various sources, including tail gas resulting from burning processes, and particularly tail gases arising from chemical industry. The activity of Fe-zeolite catalysts for decomposition of N<sub>2</sub>O can be improved by several ways. Recently synergetic effect between Fe active sites in the zeolite and second metallic sites created by a second metal added into Fe-zeolite has been reported as effective way for catalyst function improvement [1-4]. Advantages of doping Fe-zeolite with noble metals, Pt, Rh, Ru, inducing increased activity under realistic conditions is presented. Fe-zeolites were prepared from NH<sub>4</sub>-zeolite by interaction with FeCl<sub>3</sub> solution in acetylacetone [5]. Pt, Rh, Ru-zeolites were prepared by a classical ion exchange with solutions of corresponding metal complexes in water. Bimetallic Fe/Me-zeolites were then prepared by subsequent Fe ions loading as described above. Catalytic N<sub>2</sub>O decomposition was studied in a flow reactor. Feed typically consisted of 1000 ppm N<sub>2</sub>O, 25-1000 ppm NO<sub>x</sub>, balanced by He, with flow 300 cm<sup>3</sup>.min<sup>-1</sup>, over 100 mg catalyst. Analysis was carried out with N<sub>2</sub>O IR analyzer Advance Optima (ABB co., Germany) and NO chemiluminescence analyzer MLU Model 200AH (TELEDYNE co., U.S.A.). Flow steady state conversions obtained over bimetallic Fe/Me-ferrierites at temperatures ranged from 250 to 500 °C clearly showed a synergy between Fe and all second noble metal ions. The noble metal ions added into Fe-ferrierite increased the catalytic activity of the Fe ions in this order: Pt < Rh = Ru. Addition of NO substantially decreased the decomposition of N<sub>2</sub>O over Rh-ferrierite and Ru-ferrierite, but substantially increased over Fe-ferrierites as well as over bimetallic Fe/Me-ferrierites. The evidence of complexity of decomposition mechanism as influenced by noble metals was documented also by appearance of oscillation [6] of N<sub>2</sub>O decomposition over either pure iron-ferrierites or bimetallic-ferrierites. The character of oscillation and its parameters depended on reaction conditions and presence of noble metal. All these observations indicated several possible decomposition mechanisms, operating with various NO<sub>x</sub> species, either formed during N<sub>2</sub>O decomposition or added to the reaction, the specific of them probably prevailed depending on presence of Pt, Rh or Ru ions. The synergetic effect was evidenced for Pt, Rh, Ru noble metal ions added into Fe-zeolite. Detailed description of bimetallic catalyst behavior, under realistic streams, i.e. under composition close to potential practical application, was provided.

References.

[1] J.A.Z. Pieterse, G. Mul, I. Melian-Cabrera, R.W.van den Brink, Catal. Letters 99, 1-2 (2005) 41.

[2] J.A.Z. Pieterse, S. Booneveld, G. Mul, R.W. van den Brink, Stud. Surf. Sci. Catal. 158 (2005) 1915.

[3] G.D. Pirngruber, L. Frunz, J.A.Z. Pieterse, J. Catal. 243 (2006) 340.

[4] Z. Sobalík, K. Jíša, D. Kaucký, A. Vondrová, Z. Tvar&#367;žková, J. Nováková, Catal. Lett. 113 (2007) 124.

[5] Z. Sobalík, J.E. Šponer, Z. Tvar&#367;žková, A. Vondrová, S. Kuriyavar, B. Wichterlová, Stud. Surf. Sci. Catal. 135 (2001) 136.

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### **Development of new laboratory tools for the heterogeneous catalysis**

The oligomerization of ethylene is currently the primary source of higher olefins, which are versatile chemical intermediates to a wide variety of industrial and consumer products. Recently we have reported that Ni-exchanged molecular sieves with large pores and tuneable acidity, such as Ni-Al-MCM-41, Ni-Al-MCM-48 and Ni-SBA-15 revealed very interesting properties as heterogeneous catalysts for the selective ethylene oligomerization performed in slurry batch mode. However, this experimental technique showed some drawbacks generated by the important changes in the reaction mixture composition. Thus, the ethylene solubility strongly decreases in the oligomers phase and the rate of catalysts deactivation is accelerated by the heavy products accumulation in reactor. In order to overcome these problems and to establish the kinetic parameters and the longer term behaviour of these catalysts, new investigations, using a continuously operated slurry reactor (CSTR), were performed in our laboratory. Generally, the as synthesized catalytic materials need to be formed into suitable sized particles for use in the commercial CSTRs. Because the mesoporous materials reveal relatively low mechanical stability, we developed a new experimental CSTR system, in which the powdered catalyst was used. The aim of this contribution is to describe this new tool and to present the catalytic behaviours of our catalysts in ethylene oligomérisation. With this reactor, under mild conditions ( $T = 50^{\circ}\text{C}$ ,  $P = 35 \text{ bar}$ ), the long-term stability of the Ni-Al-MCM-41 was

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### **Nanovoid-structured TiO<sub>2</sub> encapsulating (I<sub>2</sub>)<sub>n</sub> molecules: a way to tune the photoactivity in the visible region**

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Between all the various semiconductors used in photocatalysis, TiO<sub>2</sub> is essentially the best material for environmental purification [1, 2]. The only drawback of TiO<sub>2</sub>, is that its band gap lies in the near UV of the electromagnetic spectrum: 3.2 eV (285 nm) and 3.0 eV (410 nm) for anatase and rutile respectively. As a consequence, only UV light is able to create electron-hole pairs and to initiate photocatalytic process. As UV light constitutes only 5% of the solar spectrum [3], 95% of the solar photons are useless for TiO<sub>2</sub> photocatalysts. It is therefore evident that any modification of the TiO<sub>2</sub>-based photocatalysts resulting in a lowering of its band gap, or in the introduction of stable optical sensitizers, will represent a breakthrough in the field. A new strategy to synthesize a TiO<sub>2</sub> characterized by the presence of internal nanovoids is presented. It consists in the hydrolysis at room temperature of pure Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> in air (30-40% humidity), according to Equation:  $Ti(OC_3H_7)_4 + 2H_2O \rightarrow TiO_2 + 4 C_3H_7OH$ . After 36 hours the white powder obtained was dried at 373 K in an oven and then calcined in air at 773 K for 6 hours. The walls of the internal cavities are populated by adsorbed molecular species derived from the partial combustion of isopropoxide groups. Addition of iodine as dye molecule in the synthesis procedure results in a new nanovoid structured titanium oxide characterized by (I<sub>2</sub>)<sub>n</sub> adducts encapsulated inside the cavities that in this way are protected from degradation. The resulting material is able to absorb visible photons of the solar light and to photodegrade methylene blue. Thus surface area of the nanovoid structured TiO<sub>2</sub> is about one order of magnitude lower than that of the P25 commercial TiO<sub>2</sub> photocatalyst, but its ability to degrade methylene blue is comparable. This implies that the surface specific degradation efficiency of this new material is about ten times higher than that of the P25.

#### References

[1] Linsebigler, A.L., Lu, G.Q. and Yates, J.T., Chem. Rev., 95 (1995), 735-758.

[2] Hoffmann, M.R., Martin, S.T., Choi, W.Y. and Bahnemann, D.W., Chem. Rev., 95 (1995), 69-96.

[3] Yin, S., Zhang, Q.W., Saito, F. and Sato, T., Chem. Lett., 32 (2003), 358-359.

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### Kinetic study and modelling of peroxypropionic acid synthesis from propionic acid and

### hydrogen peroxide using homogeneous catalysts

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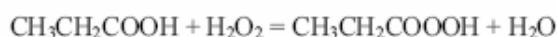
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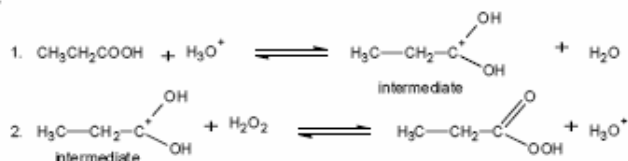
#### Introduction

Peroxy-carboxylic acids are widely used for disinfection in food industry and as bleaching agents in paper industry. The synthesis of peroxypropionic acid is prepared by the following reversible reaction, which is usually catalyzed by sulfuric acid:



#### Kinetic study

Apparently there are no kinetic expressions which take into account the catalyst and water concentration in the literature. The following steps are proposed to explain the perhydrolysis of propionic acid:



The quasi-equilibrium hypothesis was applied, assuming that the rate determining step is the reversible reaction 2, leading to the following rate expression:

$$r = r_2 = [\text{H}_3\text{O}^+] * \left( k_2 * \frac{[\text{PA}] * [\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}]} - \frac{[\text{PPA}]}{K_2^c} \right) \quad (1)$$

#### Equilibrium parameters

It was noted, that for the description of reaction equilibrium non-ideality should be taken into account. Analysis of the parameter  $K_2^c$ , which is the equilibrium constant of the overall reaction ( $K_1^c$  is assumed to be equal at 1) based on the products and reactants concentration demonstrated that there is non-ideality due to the presence of a strong electrolyte, i.e. sulfuric acid. By plotting the equilibrium constant  $K_2^c$  versus the concentration of sulfuric acid (see Fig.1.), one can notice that in the studied temperature range 30-60°C there is a linear relationship between sulfuric acid concentration and the true thermodynamic constant ( $K^T$ ):

$$K_2^c = 1.39 * [\text{H}_2\text{SO}_4] + K_2^T \quad (2)$$

The heat of reaction  $\Delta H_r$  can be considered to be constant in the same temperature range; therefore the true thermodynamic constant can be expressed by:

$$K_2^T = K_{2,reference}^T \exp\left[\frac{-\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_{reference}}\right)\right] \quad (3)$$

where the reference has been taken at 30°C.

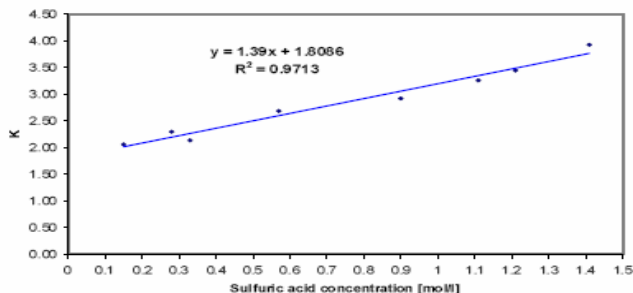


Figure 1. Equilibrium constant  $K_2^e$  versus sulfuric acid concentration at 40°C.

The model gave statistically well defined values:  $\Delta H_r = -4.17 \text{ kJ}\cdot\text{mol}^{-1}$  and  $K_{2,reference}^T = 2.05$ .

### Kinetics parameters

The temperature dependences of the rate constants were described by a modified Arrhenius equation:

$$k = k_{ref} \exp\left(\frac{-Ea}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (4)$$

where  $k_{ref} = A \exp\left(\frac{-Ea}{R T_{ref}}\right)$ ,  $Ea$  is the activation energy,  $A$  the frequency factor and  $T_{ref}$  the reference temperature usually the average temperature of the experiments.

Some results from the modeling are shown on Fig.2. :

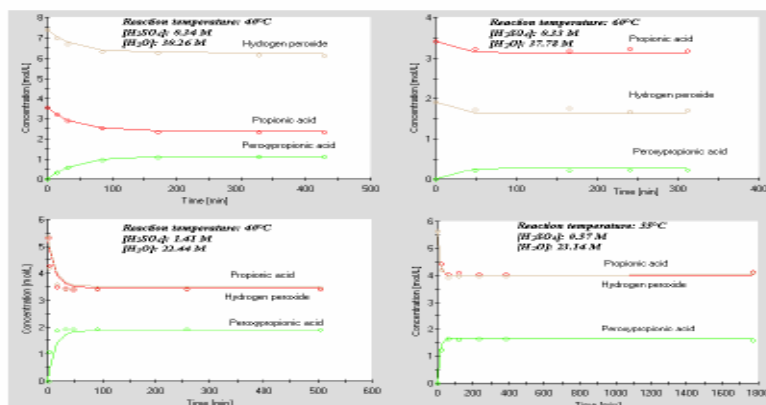


Figure 2. Fit of the model to different experiments.

The explanation coefficient of the model was 99.17%. At 44.7°C the value of the rate constant and the activation energy were respectively  $0.118 \text{ l}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$  and  $44.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

### Conclusions

The statistic data of the models are correct and the fitting is reasonable. The model can describe such reactions within the temperature range 30-60°C and for low concentration of catalyst ( $< 1.4 \text{ M}$ ). The non-ideality of this system is due the presence of strong electrolyte and thus the equilibrium constant should be expressed by the equation (2) and (3).

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### **SO<sub>2</sub> poisoning effect on the activity of Pd/Co<sub>3</sub>O<sub>4</sub> and Pd/Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalysts for CH<sub>4</sub> combustion**

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Pd supported catalysts are among the most effective systems for the abatement of unburned methane from natural gas fuelled vehicles. However, the strong sensitivity of PdO to SO<sub>2</sub> traces represents a serious drawback to its practical application [1]. On the basis of previous findings on the enhanced redox and thermal properties of Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> with respect to Co<sub>3</sub>O<sub>4</sub> [2], in the present work we investigate the catalytic performances and sulphur resistance of two Pd(0.7wt%)/Co<sub>3</sub>O<sub>4</sub> and Pd(0.7wt%)/Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalysts, working in both stoichiometric and lean conditions. The samples were characterized by BET, XRD, TPR/TPO and XPS analyses.

Preliminary results indicate that the catalysts Pd/Co<sub>3</sub>O<sub>4</sub> and Pd/Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> behave differently during the CH<sub>4</sub> combustion in lean conditions and in the presence of SO<sub>2</sub>: contrary to Pd/Co<sub>3</sub>O<sub>4</sub> which deactivates noticeably, Pd/Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> maintains its high activity. The results are explained in terms of the preferential formation of the cerium sulphate with respect to the inactive palladium sulphate that is predominant in the Co<sub>3</sub>O<sub>4</sub> supported catalyst.

### **Acknowledgements**

Support by the European Community, Network of Excellence (NoE) IDECAT (Integrated Design of Catalytic Nanomaterials for a Sustainable Production) is acknowledged.

### **References**

- [1] Gélin, P., Urfels, L., Primet, M., Tena, E., Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn naturalgas fuelled vehicles emissions: influence of water and sulphur containing compounds, *Catalysis Today*, 83 (2003), 45-57.
- [2] Liotta, L.F., Di Carlo, G., Pantaleo, G., Venezia, A.M., Deganello, G., Co<sub>3</sub>O<sub>4</sub>/CeO<sub>2</sub> composite oxides for methane emissions abatement: Relationship between Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> interaction and catalytic activity, *Applied Catalysis B: Environmental*, 66 (2006) 217-227.

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### **Direct and reverse shape-selective catalysis by metal-organic frameworks**

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Metal-organic frameworks (MOFs) are crystalline materials which are made up by linking single metal ions or small metal clusters together with multidentate organic molecules. Depending on the nature of the metal and the organic components and on the way in which they are linked, the layout of structural units can lead to a porous system of regular size, analogous to that found in zeolites and related materials. We have observed remarkable differences between the catalytic behaviour of external and internal surfaces of these MOFs microporous solids. To exemplify these remarkable differences, in this contribution we will introduce the results obtained using two MOFs (containing respectively Pd<sup>2+</sup> and Zn<sup>2+</sup>) in the hydrogenation of olefins and in the photodegradation of organic molecules, respectively. These two types of reactions illustrate the interplay between the MOF surface properties (size and shape of the internal cavities) and the dimensions of the reactant molecules, which are responsible for shape-selective properties of the catalytic processes. In the first case, a "classic" shape-selectivity effect was found; i.e., those molecules that can not diffuse inside the pores of the material can not reach the catalytic sites, so that they are not converted, as opposite to those molecules that have access to the metal centers. On the contrary, the second reaction exemplifies a case of "reverse" shape-selectivity: small molecules can enter inside the internal cavities of the MOF, where they are protected against photodegradation, while large molecules remain at the external surface and they are transformed.

[1] F. X. Llabrés i Xamena, A. Corma and H. García, *J. Phys. Chem. C*, 2007, 111, 80.

[2] F. X. Llabrés i Xamena, A. Abad, A. Corma and H. García,

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### **Theoretical Insight of Adsorption Thermodynamics and Soft Vibrations of Multifunctional Molecules on Metal Surfaces**

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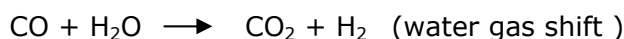
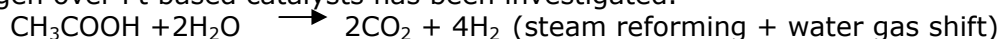
A promising route for the recognition of the adsorption structure of multifunctional molecules on metal surfaces is the assignment of the soft vibrations.[1,2] Here a systematic DFT study of the vibrational spectra of four conjugated molecules on six metals demonstrates that the symmetric and antisymmetric molecule-metal vibrations are correlated with the adsorption structure and strength. On noble metal surfaces (Au, Ag), the stable  $\mu_1$  structure is weakly adsorbed and these vibrations are softer. In contrast, on transition metal surfaces (Pt, Pd, Ni), the stable  $\mu_3$  structure is strongly stabilized and these modes are strengthened. On Cu, the stable structure  $\mu_3$  is atypical and intermediate between previous cases.

[1] D. Loffreda, *Angewandte Chemie International Edition*, (2006), vol. 45, p. 6537.

### Influence of the oxide support and oxygen addition on the steam reforming of acetic acid Pt based catalysts

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Hydrogen as an energy carrier, especially when derived from renewable sources such as biomass, is of considerable interest in the future for use in fuel cells. In order to develop efficient catalysts for the gasification of biomass, understanding the mechanism of catalytic action is essential. Thus, steam reforming of acetic acid (AcOH), which is one of the major components in flash-pyrolysis oil, to produce hydrogen over Pt based catalysts has been investigated.



Coke / oligomer formation is the most difficult problem in the development of catalysts, and hence the life time of catalyst is usually short (fig 1(I)). Coke oligomer formation is, to a large extent, influenced by the properties of the support. One possible way to overcome coke/oligomer deposition on the catalyst is to take advantage of, if any, redox properties of the support and carry out steam reforming in the presence of oxygen. The target of this would be to selectively combust any coke formed and extend catalyst life.

Steam reforming activity of Pt/ZrO<sub>2</sub> catalyst was lost even in the presence of oxygen in the feed (fig 1 (I)). In the case of a support with redox properties (CeO<sub>2</sub>) the catalyst life was extended remarkably (> 44 h on stream), without any decrease in the hydrogen yield; in other words, H<sub>2</sub> oxidation is prevented (fig 1 (II)). Therefore, the approach of oxygen addition in the presence of a support with redox properties shows promising results in the development of stable catalysts for biomass gasification.

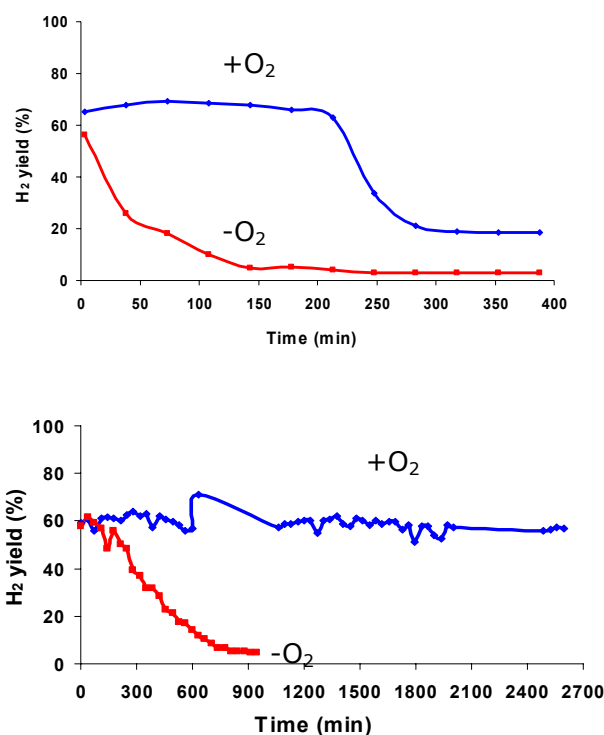


Figure 1. Hydrogen yields vs. time of (I) 0.5% Pt/ZrO<sub>2</sub> and (II) 0.5% Pt/CeO<sub>2</sub> for steam reforming of AcOH. (975 K, SV = 64,000 h<sup>-1</sup>, H<sub>2</sub>O/C =

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### **The effect of Lewis acid in supported ionic liquid catalysts (SILCA) applied in the hydrogenation of $\alpha,\beta$ -unsaturated aldehydes**

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Ionic liquids, or room temperature salt melts, have been under intensive study recently. There are many special characteristic features common to most of them. Some of the most important ones are the negligible vapour pressure ( $\sim 10^{-8}$  bar), wide liquidus range, unique solvation properties, wide electrochemical window and good ion conductivity<sup>1,2</sup>. Ionic liquids have shown good performance in various kinds of catalytic reactions as well as in preparation of nanostructured materials and nanoparticles for catalysis<sup>3,4</sup>. However, the wider use of ionic liquids is still hampered by their high cost as well as the limited knowledge on their physical and chemical properties as well as biodegradability. On the other hand, catalysis is one of the areas where ionic liquids represent considerable potential, also including the fact that the immobilized ionic liquid phase catalyst concept results in a very efficient use of the ionic liquid and relatively short diffusion distances for the reactants compared to those in two-phase systems. For these reasons, supported ionic liquid catalysts with a catalytic amount of an ionic liquid immobilized on a solid surface represent a noteworthy alternative from the industrial point of view.

Immobilization or supporting of ionic liquids can be carried out in many different ways, such as simple impregnation, grafting, polymerization, sol-gel method, encapsulation or pore trapping, among others<sup>5,6,7,8,9,10</sup>. A novel straight-forward preparation method is based on impregnation of the support material with an ionic liquid diluted with a molecular solvent such as acetone. The dilution followed by the evaporation of the co-solvent results in a uniform and thin ionic liquid layer on the support material. Simultaneously, during the ionic liquid immobilization, transition metal ions or complexes can be dissolved into an ionic liquid layer and, thus, be immobilized. These metal ions can further be reduced to metallic nano-particles. Previously introduced preparation method was utilized also in this study<sup>11</sup>. However, our aim was now to alter the selectivity profiles by addition of a Lewis acidic compound to the catalysts. Various Lewis acids and reaction conditions were screened and the results will be presented at the occasion. Naturally, an alternative approach available is presented by ionic liquids containing Lewis acidic building blocks.

The catalysts were used in the hydrogenation of citral. Selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes, ketones and esters, in general, is a versatile method to obtain many desired products for the perfumery industry, hardening of fats, preparation of pharmaceuticals and synthesis of organic chemical intermediates<sup>12</sup>. Citral and its hydrogenation products are widely used in the perfumery and fine chemical industry<sup>12</sup>. Our experiments showed that adding compound which has property of withdrawing electrons to ionic liquid layer of SILCA has major effects to the activity of the catalyst as well as the product distribution, resulting e.g. into one-pot synthesis of menthol from citral. A sample hydrogenation experiment is presented in Fig.1.



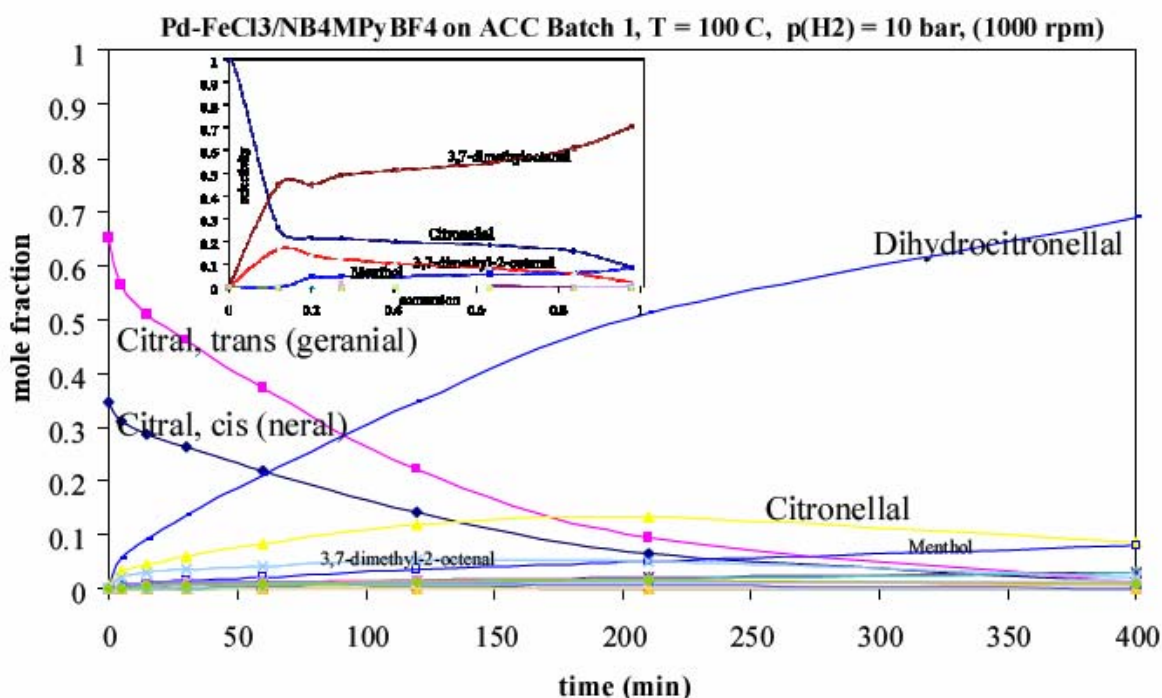


Figure 1. Hydrogenation of citral to various perfumery and fine chemical industry products.

## References:

- <sup>1</sup> Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168
- <sup>2</sup> Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792
- <sup>3</sup> Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228
- <sup>4</sup> Sheldon, R. *Chem. Comm.* **2001**, 2399
- <sup>5</sup> Valkenberg, M. H.; deCastro, C.; Hölderich, W. F. *Green Chem.* **2002**, *4*, 88
- <sup>6</sup> Kim, D. W.; Chi, D. Y. *Angew. Chem. Int. Ed.* **2004**, *43*, 483
- <sup>7</sup> Riisager, A.; Fehrmann, R.; Flicker, S.; van Hal, R.; Haumann, M.; Wasserscheid, P. *Angew. Chem. Int. Ed.* **2005**, *44*, 815
- <sup>8</sup> Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. *Angew. Chem. Int. Ed.*, **2004**, *43*, 1397
- <sup>9</sup> Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50
- <sup>10</sup> Carlin, R. T.; Cho, H. T.; Fuller, J. *Proc. Electrochem. Soc.* **1998**, *11*, 180
- <sup>11</sup> Virtanen, P.; Karhu, H.; Kordas, K.; Mikkola, J.-P. *Chem. Eng. Sci.*, **2007**, DOI: 10.1016/j.ces.2007.03.029
- <sup>12</sup> Claus, P. *Top. Catal.* **1998**, *5*, 51

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### **A new efficient and environmentally sound synthesis of the catalyst Methyltrioxorhenium (MTO)**

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Methyltrioxorhenium (MTO) is a highly active catalyst in oxidation reactions (e.g. epoxidations, oxidation of aromatics) as well as in numerous other catalytic reactions, among them olefin metathesis and aldehyde olefination [1]. Though, a major drawback for the use of MTO has been its synthesis employing expensive and highly toxic tin organyls [2]. Herein we report a new synthetic pathway to MTO using non-toxic and easy-to-handle zinc compounds, in particular methyl zinc acetate. With this reagent and perrhenyl carboxylates originating from dirhenium heptoxide, MTO can be synthesized in yields > 80 %. Methyl zinc acetate itself can be gained by reaction of anhydrous zinc acetate with trimethyl aluminum. Both are readily available and in particular cheap chemicals, making the presented route economically interesting.

[1] a) F. E. Kühn, A. Scherbaum, W. A. Herrmann, *J. Organomet. Chem.* 2004, 689, 4149; b) F. E. Kühn, A. M. Santos, W. A. Herrmann, *Dalton Trans.* 2005, 2483; c) W. A. Herrmann, F. E. Kühn, *Acc. Chem. Res.* 1997, 30 169.

[2] a) W. A. Herrmann, J. G. Kuchler, J. K. Felixberger, E. Herdtweck, W. Wagner, *Angew. Chem.* 1988, 100, 420; *Angew. Chem. Int. Ed.* 1988, 27, 394; b) W. A. Herrmann, F. E. Kühn, R. W. Fischer, W. R. Thiel, C. C. Romão, *Inorg. Chem.* 1992, 31, 4431; c) W. A. Herrmann, R. M. Kratzer, R. W. Fischer, *Angew. Chem.* 1997, 109, 2767; *Angew. Chem. Int. jeudi 19 avril 2007* Page 28 sur 34

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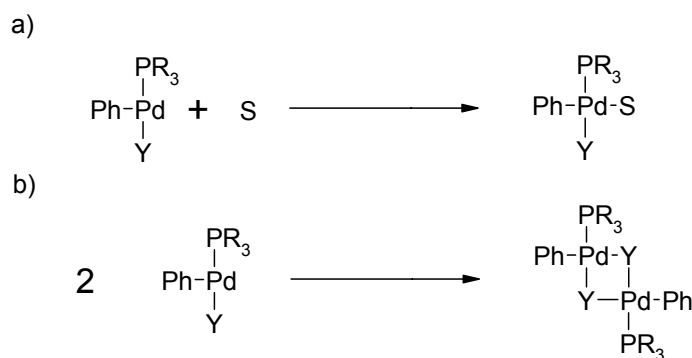
### The relative stability of 14-electron T-shaped palladium complexes from a computational point of view

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Many organometallic reactions occur through paths with intermediate electron deficient complexes that possess an open coordination site. In this line, three-coordinated palladium complexes with 14 electrons are usually proposed as intermediate species in catalytic cycles; but there are some controversy about this stability<sup>1,2</sup>.

In the present work the stability of 14-electron Pd complexes over (a) solvent coordination (solvation) and (b) dimerization processes is evaluated (see scheme) by means of computational methods. A systematic study was performed to analyse how the different ligands affect the relative stability of the T-shaped complex: (i) the Y ligands considered were halides, amides, the hydroxyl group and similar ones; (ii) the phenyl ligand (Ph) was modified by including fluorine, hydroxy, methoxy or amine substituents; (iii) several phosphines (PR<sub>3</sub>) as PH<sub>3</sub>, P(Me)<sub>3</sub>, P(<sup>t</sup>Bu)<sub>3</sub> and P(Ph)<sub>3</sub> were also considered. The existence of agostic interactions occupying the vacant site was also analyzed in complexes with P(<sup>t</sup>Bu<sub>3</sub>).



<sup>1</sup> Yamashita, M; Hartwig, J. F. *J. Am. Chem. Soc.*, **2004**, *126*, 5344-5345.

<sup>2</sup> Casares, J. A.; Espinet, P.; Salas, G. *Chem. Eur. J.*, **2002**, *8*, 21, 4843-4853

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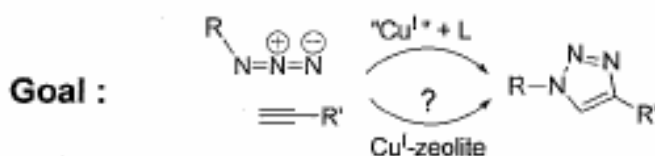
### Click Chemistry in CuI-Zeolites

Institut de Chimie, UMR 7177, Strasbourg, France

**Click Chemistry** = set of chemical tools for easily connecting (bio)molécules

The Cu<sup>I</sup>-catalyzed version of the Huisgen [3+2]-cycloaddition is to date the most practical and useful "click" reaction.

Can we design and develop a more practical way ? Modified Zeolites ?



### Conditions Set up :



catalyst	T. (°C)	time (h)	yield (%)
none	rt	96	< 5
none	110	48	70
CuCl	rt	48	70
CuI-USY	rt	15	83
CuI-USY	110	5	87
CuI-Y	rt	15	68
CuI-Y	110	5	75
CuI-MOR	rt	15	69
CuI-MOR	110	5	79
CuI-ZSM5	rt	15	63
CuI-ZSM5	110	5	79
CuI-β	rt	15	47
CuI-β	110	5	73
H-USY	rt	15	-

solvent	%
PhCH <sub>3</sub>	83
PhH	64
CH <sub>2</sub> Cl <sub>2</sub>	82
THF	62
CH <sub>3</sub> CN	61
CH <sub>3</sub> OH	61

### Scope :

Alkyne	Azide	Adduct	Yield
$\text{≡-Ph}$	$\text{Ph-N}_3$	$\text{Ph-N=N-C=C-Ph}$	
$\text{≡-C}_6\text{H}_5$		$\text{Ph-N=N-C=C-C}_6\text{H}_5$	
$\text{≡-C(OH)Ph}$		$\text{Ph-N=N-C=C-C(OH)Ph}$	
$\text{≡-C(O)OEt}$		$\text{Ph-N=N-C=C-C(O)OEt}$	
$\text{≡-C(O)NHPh}$			
$\text{≡-Ph}$	$\text{Ph-N}_3$	$\text{Ar-N=N-C=C-Ph}$	
"	$p\text{-MeOPh-N}_3$		
"	$p\text{-O}_2\text{NPh-N}_3$		
$\text{≡-C(O)OEt}$	$\text{Cyclohexane ring with OH and N}_3$	$\text{Cyclohexane ring with OH and N=N-C=C-COOEt}$	
$\text{≡-C(OH)Ph}$	$\text{Cyclohexane ring with BzO, TsO, OMe and N}_3$	$\text{Cyclohexane ring with BzO, TsO, OMe and N=N-C=C-R}$	
$\text{≡-C(O)OEt}$			
"	$\text{Cyclohexane ring with OMe, OH, SPh and N}_3$	$\text{Cyclohexane ring with OMe, OH, SPh and N=N-C=C-COOEt}$	

**Conclusions :** Modified Zeolites practical & useful tool in organic synthesis  
A step forward **Green Chemistry**

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### Highly Active, Stable, and Selective Well-Defined Silica Supported Mo Imido Olefin Metathesis Catalysts

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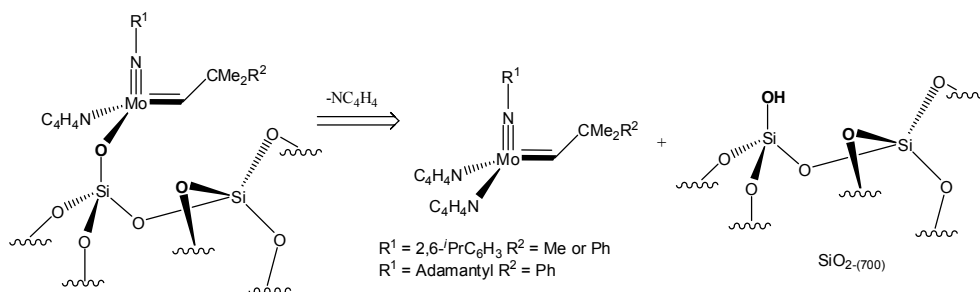
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Surface OrganoMetallic Chemistry (SOMC) allows the formation of well-defined complexes bonded to the surface of an inorganic material. One of its main goals is to establish structure-reactivity relationships, as in homogeneous catalysis, so as to develop tunable heterogeneous catalysts.

In the last years, it has been shown that monosiloxy Mo-, W- and Re-based catalysts, of general formula  $[(\equiv\text{SiO})\text{M}(\equiv\text{ER})(=\text{CH}t\text{Bu})(\text{CH}_2t\text{Bu})]$  are highly active olefin metathesis catalysts (M = Re, ER = CtBu; M = Mo, ER = NH; M = Mo or W, ER = NAr), that often display reactivity and stability greater than their homogeneous analogues,  $[(\text{RO})_2\text{M}(\equiv\text{ER})(=\text{CH}t\text{Bu})]$  (RO = Me(CF<sub>3</sub>)<sub>2</sub>CO or POSS). However, with these systems, traces of 1-butene are formed in the metathesis of propene. This could be due to the pending neopentyl ligand (this phenomenon is not observed with the parent bisalkoxide system), and therefore we have investigated the replacement of this neopentyl ligand with others  $\sigma$ -donor ligands.

Recently it has been reported that a variety of bis(pyrrolyl) complexes  $[\text{Mo}(\equiv\text{NR}_1)(=\text{CHCMe}_2\text{R}_2)(\text{NC}_4\text{H}_9)_2]$  react rapidly with two equivalents of monoalcohols (e. g. Me<sub>3</sub>COH or (CF<sub>3</sub>)<sub>2</sub>MeCOH) or 1 equiv of a biphenol or binaphthol to give 2 equivalents of pyrrole and bisalkoxide or biphenolate or binaphtholate species in ~100% yield.

We have therefore investigated the reaction between bis(pyrrolyl) complexes,  $[\text{Mo}(\equiv\text{NR}_1)(=\text{CHCMe}_2\text{R}_2)(\text{NC}_4\text{H}_9)_2]$  (R<sub>1</sub> = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R<sub>2</sub> = Me or Ph; R<sub>1</sub> = Adamantyl, R<sub>2</sub> = Ph) and partially dehydroxylated silica (SiO<sub>2</sub>-(700)) in order to generate well-defined asymmetric systems having no alkyl ligand.





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### **Structure and nuclearity of active sites in Fe-zeolites: comparison with iron sites in enzymes and homogeneous catalysts**

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Fe-ZSM-5 and Fe-silicalite zeolites efficiently catalyse several oxidation reactions which find close analogues in the oxidation reactions catalyzed by homogeneous and enzymatic compounds [1,2]. The iron centres are highly dispersed in the crystalline matrix and on highly diluted samples, mononuclear and dinuclear structures are expected to become predominant. The crystalline and robust character of the MFI framework has allowed to hypothesize that the catalytic sites are located in well defined crystallographic positions. For this reason these catalysts have been considered as the closest and best defined heterogeneous counterparts of heme and non heme iron complexes and of Fenton type Fe<sup>2+</sup> homogeneous counterparts [3]. On this basis, an analogy with the methane monooxygenase has been advanced several times. The examination of the structure, nuclearity and catalytic activity of the iron species obtained with various characterization techniques already reported in literature, we conclude that Fe-ZSM-5 and Fe-silicalite are not the ideal samples conceived before and that many types of species are present, some active and some other silent from adsorptive and catalytic point of view. The relative concentration of these species changes with thermal treatments, preparation procedures and loading. Only at lowest loadings the catalytically active species become the dominant fraction of the iron species. On the basis of the spectroscopic titration of the active sites by using NO as probe [1,2,4,5], we conclude that the active species on very diluted samples are isolated and highly coordinatively unsaturated Fe<sup>2+</sup> grafted to the crystalline matrix. Indication of the constant presence of a smaller fraction of Fe<sup>2+</sup> presumably located on small clusters is also obtained. The nitrosylic species have been analyzed in detail and the similarities and differences with the cationic, heme and non heme homogeneous counterparts have been evidenced. The same has been done for the oxygen species formed by N<sub>2</sub>O decomposition on isolated

### References

[1] G. Berlier, G. Spoto, S. Bordiga, G. Ricchiardi, P. Fisticaro, A. Zecchina, I. Rossetti, E. Selli, L. Forni, E. Giamello and C. Lamberti, *J. Catal.*, 208 (2002) 64.

[2] G. Berlier, A. Zecchina, G. Spoto, G. Ricchiardi, S. Bordiga and C. Lamberti, *J. Catal.*, 215 (2003) 264.

[3] A. Wanat, T. Schnepf, G. Stochel, R. van Eldik, E. Bill and K. Wieghardt, *Inorg. Chem.*, 41 (2002) 4.

[4] A. Zecchina, M. Rivallan, G. Berlier, C. Lamberti and G. Ricchiardi, *Phys. Chem. Chem. Phys.*, invited paper, submitted (2007).

[5] M.T. Nechita, G. Berlier, G. Ricchiardi, S. Bordiga and A. Zecchina, *Catal. Lett.*, 103 (2005) 33.

[6] G. Mul, J. Perez-Ramirez, F. Kapteijn and J.A. Moulijn, *Catal. Lett.*, 80 (2002) 129.

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### **Hydrogen function at decane-SCR-NO<sub>x</sub> over Ag/alumina**

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Ag/Al<sub>2</sub>O<sub>3</sub> catalysts highly active at H<sub>2</sub>/C<sub>10</sub>H<sub>22</sub>-SCR-NO<sub>x</sub> were studied with an attempt to elucidate the active Ag site and hydrogen function. Isotopic H<sub>2</sub> - D<sub>2</sub> exchange at RT over oxidised and reduced Ag/Al<sub>2</sub>O<sub>3</sub> showed high rate of HD formation on Ag<sup>+</sup> contrary to that over Ag<sup>0</sup>. It suggests that Ag-H like species are formed from Ag<sup>+</sup>. Accordingly, the presence of Ag<sup>+</sup> clusters is not the exclusive reason for the enhanced activity of Ag/alumina by the addition of hydrogen to the C<sub>10</sub>H<sub>22</sub>-SCR-NO<sub>x</sub>, hydrogen itself has to take part in the reaction. We speculate that the formed Ag-hydride immediately reacts with oxygen to form highly active oxygen species. These oxygen species might dramatically enhance the propagation of the SCR-NO<sub>x</sub> reaction.



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### CO induced reconstruction of Ru clusters

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CO has been a prototypical molecule to understand the catalytic activity and selectivity of several transition metal surfaces, clusters and supported clusters.

Moreover, dissociation of CO forms the basis for the Fischer-Tropsch reaction. In recent years the focus of the catalytic study has been on the activity of small transition metal clusters. These clusters provide several active sites due to different coordination of the metal atoms. It has been shown that the active sites are strongly dependent on the size and morphology of the cluster. It is known that during the catalytic reactions the surface of the single crystal or large particles locally restructure. However, this effect is expected to be more global in small particles.

In the present theoretical work, we investigate the effect of the chemisorption of CO on different stable Ru clusters from Ru<sub>4</sub> to Ru<sub>13</sub>. The results reveal that the structure of Ru<sub>13</sub> undergoes a reconstruction. Interestingly, orthobicuola reconstructs into a more stable geometry of pentagonal prism. In this study we will discuss the electronic, magnetic and structural properties of these reconstructed structures. Moreover, this work will give a new insight into the catalytic effect of Ru clusters on CO adsorption and dissociation.

#### References

- [1] P. Biloen and W. M. H. Sachtler, *Adv. Catal.* (1981), 30, 165.//
- [2] S. E. Colley, R. G. Copperthwaite, G. J. Hutchings, S. P. Terblanche, M. M. Thackeray. *Nature* (1989), 339, 129.//
- [3] G. A. Somorjai. *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994), p. 442.//
- [4] R. A. van Santen and M. Neurock *Catal. Rev. Sci. Eng.* (1995), 37, 557.//
- [5] C. M. Chang and M. Y. Chou. *Phys. Rev. Lett.* (2004), 93, 133401-1

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### **Non-uniform catalytic behavior of zeolite crystals as revealed by in-situ optical micro-spectroscopy**

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In-situ spectroscopic methods are essential to a fundamental understanding of catalytic reactions thanks to their ability to unravel useful structure-function relationships. Recent developments have broadened the range of chemical reactions catalyzed by high surface area solids, which can be investigated in the act. However, most techniques average information over the whole catalyst sample, while in many cases it is of utmost importance to probe distinct areas of catalyst particles or grains, revealing how the structural features render into catalytic function. Here, we investigate the oligomerization of styrene derivatives occurring in the micro-pores of ZSM-5 zeolite crystals using an in-situ optical micro-spectroscopic technique, developed in our laboratory. With this setup, spatially-resolved optical absorption from the sample placed inside an in-situ catalytic cell can be mapped with a spatial resolution down to several microns. ZSM-5 crystals turn strongly colored upon exposure to 4-methoxystyrene, featuring two absorption bands at ~590 and 635 nm in the optical spectra. Their intensity ratio was found to vary at the different regions of the crystal. The spectral bands were assigned to the dimeric and trimeric carbocations, respectively, implying that the styrene oligomerization at the crystal edges leads preferentially towards dimeric products while in the main crystal body both styrene trimers and dimers are being formed in comparable quantities. Furthermore, optical absorption measurements with polarized light reveals that the carbocations are entrapped and aligned within the straight pores of the zeolite. Based on this information, we propose a reaction mechanism which explicates how the zeolite channel geometry at different crystal regions is translated into different reaction products distribution. Experimental results obtained with the series of substituted styrenes allowed us to elucidate the effect of reactivity and diffusion of the reactants in the zeolite pores. In addition, we have demon

#### References

M. H. F. Kox, E. Stavitski, B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2007, in press

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### **Controlling the properties of gold atoms and clusters on supported model catalysts by the oxide film thickness.**

In this contribution we present a low-temperature scanning tunnelling microscopy investigation on the properties of gold atoms and clusters adsorbed on the surface of Ag(001)-supported MgO thin films. This particular system has received attention since it was found that charge transfer from surface defects onto adsorbed gold, leading to negatively charged gold clusters, may contribute to enhanced catalytic activity in the low-temperature oxidation of CO [1]. Charging of gold, however, must not necessarily involve the presence of defects: on the basis of density functional theory calculations it was proposed that charge transfer may also occur for gold atoms on the regular terrace sites of thin MgO films, provided that the film thickness does not exceed a few monolayers [2]. Here, we have studied gold adsorption at 5-10 K on MgO films of different thickness with the aim to provide experimental evidence for charging of gold on very thin films and the corresponding differences in adsorption properties compared to thick MgO films. The adsorption of Au on a 3 ML thin MgO film leads to a highly ordered structure that can be explained by the repulsive interaction between partially negatively charged Au atoms. The influence of charging is further manifested by the possibility for Au nucleation both on Mg and O sites as well as the formation of 2-dimensional, one atomic layer thin Au islands after annealing to room temperature. In comparison, for 8 ML thin MgO films Au nucleation occurs exclusively on O sites and annealing leads to 3-dimensional clusters, as expected for neutral Au atoms on the MgO(001) surface. We find no influence of the film thickness for Pd adsorption on MgO thin films, which shows that the particular electronic properties of Au are essential to observe the charging effect on thin MgO films.

[1] B. Yoon et al., Science

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### **Nanocarbons as Robust catalysts for Oxidative Dehydrogenation of Ethylbenzene to Styrene**

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Here we report on the applications of nanocarbons (e.g. nanographite, nanotube, nanodiamond) as metal-free catalyst for styrene syntheses from ethylbenzene. Long-time test reveal the high-stability of nanocarbons in oxidative dehydrogenation reactions, while activated carbons are rapidly deactivated. Kinetic analyses of carbon-mediated oxidative dehydrogenation (ODH) and direct dehydrogenation (DH) will be presented. Our work will provide vital evidences on metal-free catalysis by nanostructured carbons in catalysis

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### **FUNCTIONALIZATION OF ALKENES CATALYZED BY GOLD COMPLEXES: SOLVENT AND COUNTERIONS ARE NOT MERE SPECTATORS DURING THE REACTION**

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The preconceived idea that gold is chemically inert has changed quite rapidly since the beginning of the XXI century. The number of reactions catalyzed by gold is growing up astonishingly, both homogeneous and heterogeneous reactions. In the present work, two homogeneous catalyzed reactions by gold(I) and gold(III) complexes are analyzed by means of theoretical (DFT) methods and the results checked by experiment.

The study of a hydrogenation reaction catalyzed by a Au(III)-Shift base complex shows that the hydrogen molecule is activated in two different ways by the gold(III) catalyst. The initial step corresponds to a H<sub>2</sub> heterolytic activation to form a gold-hydride intermediate, without previous coordination of the H<sub>2</sub> molecule. In this step (the reaction controlling step), the solvent is playing a critical role as suggested by theoretical calculations and corroborated by experiments (scheme 1). Once the gold-hydride intermediate (the real catalytic species) is formed, the proper hydrogenation catalytic cycle takes place; in here, the H<sub>2</sub> activation is preceded by its coordination to the metal centre.

The mechanistic study on the hydroamination reaction by a gold(I)-PR<sub>3</sub> complex shows that the reaction proceeds without the coordination of the amine to the catalyst. A novel reaction mechanism for the proton transfer from the amine to the olefin is proposed: it implies a tautomerization process. In addition, the ligand (triflate) liberated during the process is shown to play a critical role catalyzing the proton-transfer step acting as a proton shuttle.

These results can give some hints for the mechanistic description of other gold homogeneous catalyzed reactions. In addition, they illustrate that other species (as the solvent or liberated ligands during the process) usually considered as spectators during

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### **Selective adsorption of small olefins on zeolites**

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Separation of light hydrocarbons from cracking fractions by sorption on siliceous materials is an important field of research. Ideally, for an economically feasible separation, a molecular sieve is required with small, uniform pores and a hydrophobic character. RUB-41 is such a material. RUB-41 is a new zeolite structure with framework type RRO possessing a 2-dimensional pore system with almost uniform pore size distribution. RUB-41 has selective sorption properties for small, linear molecules in the gas phase. Moreover, olefins are adsorbed much more strongly than alkanes.\* In this study, the sorption properties of RUB-41 were examined for small olefins in the liquid phase. Separation processes in the liquid phase allow the use of smaller units and separate larger volumes in shorter periods. RUB-41 showed interesting selectivity patterns for linear butenes in different organic solvents. This holds great promise for the liquid phase separation of butene mixtures. Further, the possibility of incorporation of hetero-atoms is investigated; this opens the way to applications as shape selective catalyst.

\* Wang, Y.X., Gies, H., Marler, B., Müller, U. Synthesis and crystal structure of zeolite RUB-41 obtained as calcination product of a layered precursor: a systematic approach to a new

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### Investigation of CpMoO<sub>2</sub>CH<sub>3</sub> as an epoxidation catalyst, the next chapter in the MTO success story

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In the past decade trioxorhenium and dioxomolybdenum complexes have been shown to be excellent epoxidation catalysts<sup>[1, 2]</sup>. Although these catalytic systems have been widely studied, many questions regarding their reactivity remain. We herein report our studies on CpMo(CO)<sub>3</sub>CH<sub>3</sub>, including the isolation and characterization of a catalytic intermediate, CpMo(O-O)OCH<sub>3</sub>, which provides insight into the reaction pathway of this system. Previous work done by our group with the MTO<sup>[3, 4]</sup> provides a basis for discussion of our proposed reaction pathway and heterogenisation of this Molybdenum species.

- [1] C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.*, **1997**, 97, 3197
- [2] C. Freund, M. Abrantes, F. E. Kühn, *J. Organomet. Chem.*, **2006**, 691, 3718
- [3] W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem.*, **1993**, 105, 1209
- [4] D. Veljanovski, A. Sakthivel, W. A. Herrmann, F. E. Kühn, *Adv. Synth. Catal.*, **2006**, 348, 1752

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### **Pd and PdAu on mesoporous silica for methane oxidation: effect of SO<sub>2</sub>**

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Pd and PdAu catalysts supported on mesoporous silica were prepared by incipient wetness impregnation. They were characterized by XPS, XRD and BET measurements. The activity was tested in the oxidation of methane under experimental conditions close to those used in industrial

application. The effect of SO<sub>2</sub> addition to the reactant mixture was studied. Test reactions were consecutively performed in order to evaluate the thermal stability and the poisoning reversibility.

The palladium catalyst performed quite well in terms of the light off temperature (T<sub>50</sub> < 300°C) and

in terms of SO<sub>2</sub> tolerance. Moreover, the activity, which decreased after a night treatment in SO<sub>2</sub> at

350°C, was completely recovered in subsequent cycles. The presence of gold determined a slight

decrease of the activity without altering the SO<sub>2</sub> tolerance. Evidence for a dynamic reductionoxidation

process occurring at the palladium surface was obtained from the gold promoted sample in which reduced Pd was observed after the SO<sub>2</sub> treatment.