

6th European Congress on Catalysis

COMPREHENSIVE COVERAGE OF HETEROGENEOUS CATALYSIS AND SURFACE SCIENCE FROM FUNDAMENTALS TO INDUSTRIAL USES

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The 6th European Congress on Catalysis (EuropaCat-VI) took place in Innsbruck, Austria, from the 31st August to 4th September 2003, and was attended by more than 1000 participants. Many aspects of homogeneous and heterogeneous catalysis were covered, with four oral sessions running simultaneously. Three poster sessions contained a large number of presentations. This selective review covers aspects of the presented heterogeneous work featuring the platinum group metals.

Sir John Meurig Thomas (The Royal Institution, U.K.) opened the conference by giving a plenary lecture, emphasising the importance of pursuing *in situ* studies at pressures and temperatures which simulate real conditions, that is, atmospheric pressure and temperatures greater than 500°C, in order to understand the mechanisms of chemical reactions that need to be catalysed under the conditions of industrial use. The lecture highlighted a number of specific examples where deployment of two or more parallel *in situ* techniques, such as X-ray absorption spectroscopy, X-ray diffraction and chemical analysis (by gas chromatography/mass spectrometry (GC/MS)), shed considerable light on the nature of both the short- and long-range structures of an active catalyst. Such studies describe some of the chemical modifications that could be implemented in the vicinity of active centres in order to boost catalytic performance.

In a keynote lecture, Professor Robbie Burch (Queen's University Belfast) talked about the use of transient techniques to understand and control catalytic reactions, especially when used in conjunction with *in situ* spectroscopy such as FTIR. In his talk he gave several examples of catalytic reactions where the reaction rate can be significantly enhanced by periodic perturbation of the reactant

composition. He also discussed the use of transient techniques to investigate detailed catalytic reaction mechanisms. An example given was the reduction of nitric oxide (NO) over 0.3% Pt/Al₂O₃ under lean-burn conditions using octane as reductant. Below a critical temperature (< 185°C) the steady state activity is very unstable and self-poisoning of the catalyst rapidly leads to deactivation. However, it was demonstrated that periodic perturbation of the surface state of a catalyst can result in a dramatic change in its steady state activity. Professor Burch showed that the low temperature activity for NO reduction can be maintained indefinitely by creating short temperature spikes on the Pt surface by addition of pulses of methanol as a fuel.

Lean DeNO_x Catalysis

In the symposium on lean deNO_x catalysis, Professor Angelos M. Efstathiou (University of Cyprus) described the use of Pt/Mg-Ce-O as a novel stable, active and selective catalyst for the reduction of NO to nitrogen (N₂) with the use of hydrogen in the presence of excess oxygen. The Pt/Mg-Ce-O catalyst gave the highest N₂ production yield ever reported in the open literature for the NO/H₂/O₂ reaction. The catalyst operates extremely well in the 100–400°C temperature range and shows excellent stability in the presence of 5% H₂O and 20 ppm SO₂ in the reaction feed stream.

Poster Display

There were also a large number of posters on display. A poster by S. Morandi (University of Bologna, Italy) tackled the removal of NO_x from lean-burn gasoline and diesel engines. This requires the development of alternative catalysts to the conventional three-way catalysts (TWC) which are inactive in converting NO_x under lean exhaust conditions, that is in excess oxygen. A potential

solution was represented by Toyota-type NO_x storage-reduction (NSR) catalysts, containing Pt and Ba supported on alumina – NO_x are adsorbed and stored in the catalyst under lean driving conditions, and then released and reduced to N₂ during rich operation. The main drawbacks of the NSR catalysts are low resistance to sulfur, low activity at temperatures < 200°C and low resistance towards hydrothermal treatment. NSR catalyst containing 1 wt.% Pt and Pt-Cu (1 wt.% Pt and 4 wt.% Cu) supported on calcined Mg/Al hydrotalcite-type (HT) compounds were shown to have higher activity than Pt-BaO/Al₂O₃ systems at temperatures below 300°C and better resistance to sulfur poisoning. Also for the Pt-Cu catalysts, higher resistance to hydrothermal treatment was observed compared to the Pt-BaO/Al₂O₃ sample.

In a separate study, the effect of the addition of a solid solution of ceria-zirconia on the Pt-BaO/Al₂O₃ matrix was investigated by C. Manfredotti (University of Torino, Italy). The presence of the ceria-zirconia solid solution enhances both the metal dispersion and the Pt surface area accessible to reactant gases with respect to a NSR catalyst. The barium-containing phase favours reducibility of the Pt particles and generation of more electron-rich metallic sites compared to Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃. Furthermore, the sample was shown to have higher sulfur resistance of the NO_x storage capacity than the corresponding Pt-BaO/Al₂O₃ system, probably due to ceria-zirconia acting as a trap for SO_x.

Light-Driven Alkane Oxygenation by Ruthenium(II)

Photocatalysts can activate unreactive C-H bonds of complex saturated hydrocarbons, such as alkanes, to functionalise them: an important reaction in organic chemistry. The dissociation of a ligand often starts the reaction, catalysed by a transition metal complex. Ru(II) polypyridyl complexes take part in photosubstitution reactions, probably by excitation in the metal to ligand charge transfer (MLCT) region by dissociation.

Now, researchers from the Tokyo Metropolitan University, Japan, have developed, under visible light irradiation (> 385 nm), stereospecific and photoregulated catalytic alkane oxidation reactions using chloro(Me₂SO)Ru(II) complexes with tris(2-pyridylmethyl)amine or its derivative in the presence of

R. Villa (Politecnico di Milano, Italy) looked at the effect of calcination and ageing treatment on the activity and stability of alumina and zirconia supported PdO for methane combustion. Alumina supported systems, calcined at low temperature (~ 600°C), showed the best activity. However, calcination treatments at high temperature (> 900°C) caused PdO decomposition to Pd. This had a strong negative impact on the catalytic activity and stability. The study demonstrated that using ZrO₂-based supports strongly increases the stability of the catalytic system upon high temperature calcination and ageing treatments. It was proposed that zirconia-type supports significantly narrow the hysteresis of the PdO-Pd redox by facilitating the onset of Pd reoxidation during cooling.

Concluding Remarks

In summary, four parallel oral sessions, together with the large number of posters meant that only a few of the many papers and posters presented could be attended and reviewed. The Congress, held in the beautiful city of Innsbruck, did, however, cover all the main aspects of heterogeneous catalysis from fundamental catalysis and surface science to industrial catalysis.

The EuropaCat website is: www.europacat.org

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2,6-dichloropyridine *N*-oxide (M. Yamaguchi, T. Kumano, D. Masui and T. Yamagishi, *Chem. Commun.*, 2004, (7), 798–799). Excitation in the MLCT band selectively substituted the S-bound Me₂SO ligand by a solvent molecule.

When adamantane, the most stable C₁₀H₁₆ isomer, was catalytically oxidised, 1-adamantanol and adamantane-1,3-diol were selectively formed in good yields. The Ru complex and irradiation were both necessary for oxidation to proceed; without irradiation the reaction diminished, but irradiation restored it. Thus the reaction is photoassisted, not photoinitiated. Irradiation may initiate the catalytic reaction and generate the active species for alkane oxidation.