

# An Update in Heterogeneous Catalysis

A SELECTIVE REVIEW OF THE 19TH NORTH AMERICAN CATALYSIS SOCIETY MEETING

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The North American Catalysis Society (NACS), founded in 1956, was established as a group dedicated:

*“to promote and encourage the growth and development of the science of catalysis”*

as the current president, J. M. Armor, describes it on the NACS website (1). The 19th North American Meeting (19th NAM) organised by the NACS took place in Philadelphia, Pennsylvania, from 22nd to 27th May, 2005 (2). Historically, the organisers aim to cover the most relevant aspects of catalysis for the needs of society both today and tomorrow (3). The meeting was attended by over 1000 attendees and, as has become customary at recent NACS meetings, had a strong international flavour. The twenty-two oral sessions were conducted in parallel over five days in six separate conference halls, while the twenty poster sessions were organised over three days in one conference hall.

The scientific programme covered the broad topics of: Petroleum, Environmental, Chemical, Fuel Cells and Fuel Processing, and each of these topics had several subtopics, such as fuel desulfurisation and processing, gasoline and diesel emissions control, photocatalysis, pharmaceuticals, gas to liquids, nanotechnology, surface science, advances in spectroscopy, etc., covering most of the fields in catalysis.

This selective review describes some of the highlights reported on the platinum group metals (pgms), especially platinum (Pt), palladium (Pd), rhodium (Rh) and ruthenium (Ru), grouped into sections on environmental catalysis for gasoline and diesel engines (particularly emissions control),

fuel reforming and surface science in catalysis.

The commencement of the oral sessions was preceded by the Houdry Award Plenary Lecture given by Dr Henrik Topsøe, winner of the 2005 Eugene J. Houdry Award in Applied Catalysis. The rest of this day was taken up by six parallel oral sessions followed by a poster session. The oral session on “Environmental: Gasoline Engines” seemed to be attended by more participants than the other sessions of the day.

## Environmental Catalysis for Gasoline Engines

This session was mainly focused on nitrogen oxides (NO<sub>x</sub>) catalysis, with presentations and discussion on barium-based NO<sub>x</sub> storage materials, NO<sub>x</sub> reduction mechanisms, the promotion of precious metal catalysts with metal oxides, and the impact of all these aspects on NO<sub>x</sub> storage and reduction (NSR). Also covered were pgms sintering mechanisms in automotive catalysts and the role that cerium redox chemistry plays in gasoline automotive exhaust catalysis.

NO<sub>x</sub> storage mechanisms in Pt/Ba systems were discussed by several authors. R. Vijay *et al.* (University of Delaware, Newark, U.S.A.) reported that metal oxides (Co > Mn > Fe) promoted NO<sub>x</sub> conversion over Pt/Ba based catalysts supported on Al<sub>2</sub>O<sub>3</sub>. E. Fridell (Chalmers University of Technology, Göteborg, Sweden) showed an elegant mechanism for nitrate and nitrite decomposition on Pt/BaO/Al<sub>2</sub>O<sub>3</sub> using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy and temperature programmed reduction (TPR) techniques. The presence of Pt helped to avoid the formation of nitrate species over the

storage material. The Pt/Ba interface helped Ba storage properties by improving both NO<sub>2</sub> and NO + O<sub>2</sub> adsorption. SO<sub>2</sub> deactivated the Pt, Pt sulfate species formed, and bulk carbonate species were removed. NO<sub>x</sub> was capable of the partial decomposition of these Pt sulfate species.

X. Wang *et al.* (Lehigh University, Bethlehem, U.S.A.) attempted to correlate NO<sub>x</sub> adsorption and decomposition with site acidity. On a Pt/BaO system, physisorbed NO<sub>x</sub> desorbed at low temperatures from weak basic sites. At ~ 200°C Pt allows NO<sub>x</sub> to be removed from the storage BaO material, but higher temperatures are needed to remove it from BaO crystals. Barium is suspected of being dispersed over Al<sub>2</sub>O<sub>3</sub>, *via* an interaction with Lewis acid sites; this allows isolated BaO sites to form. NO<sub>x</sub> decomposed better over the isolated BaO sites than over the BaO crystals.

The lecture by Professor A. Datye (University of New Mexico, Albuquerque, U.S.A.) entitled ‘Sintering of Automotive Exhaust Catalysts: Myth and Reality’ tackled the problem of providing an insight into the fundamentals of catalyst sintering mechanisms as pertaining to automobile exhaust catalysts. Experimental data, from Pd/Al<sub>2</sub>O<sub>3</sub> sintering studies conducted at 900°C in N<sub>2</sub>/H<sub>2</sub>O, were obtained using scanning electron microscopy (SEM) over model catalysts. The data indicated a log normal particle size distribution, characteristic of a particle migration mechanism (catalytic particles coalesce into larger particles) with the Ostwald ripening mechanism (catalytic atoms, not particles, are mobile) being the rate-limiting step. The order of higher stability against sintering was: Pt > Pd > Au. Interestingly, Datye also showed that in the case of Pd carried on two different supports, the one with the stronger metal-support interaction (Pd/sapphire) sinters faster than the one with the weaker metal-support interaction (Pd/quartz).

Datye also collaborated with Professor S. S. C. Chuang (University of Akron, U.S.A.), in a study on the effect that Ag addition to Pd/Al<sub>2</sub>O<sub>3</sub> has on the NO-CO reaction. *In situ* infrared (IR) studies conducted by Chuang’s group clearly demonstrated that adding Ag to Pd/Al<sub>2</sub>O<sub>3</sub> prevented the formation of the bridged NO adsorbed species on Pd, directly proving that Ag caused the break-up

of Pd ensembles and, in the process, improved the NO-CO reaction activity.

Y. Nagai (Toyota Central R&D Labs., Nagakute, Aichi, Japan) *et al.* reported that a CeZrYO<sub>x</sub> support inhibited Pt sintering due to Pt atoms being anchored with surface oxygen bonds. Such bonds would not be present in Al<sub>2</sub>O<sub>3</sub>, for instance.

H. Birgersson (KTH-Royal Institute of Technology, Stockholm, Sweden) *et al.* presented a paper about the regeneration of pgms catalysts and washcoats and the importance of expanding this technique for the future when automotive emission control reaches all of Asia and Latin America.

The poster session on the first evening included over one hundred submissions on eight topics. The posters on “Environmental: Gasoline Engines” appeared to attract most attention (as did the oral sessions). One interesting poster was from R. McCabe and coworkers (Ford Motor Company, Dearborn, U.S.A.). This poster highlighted the NO oxidation properties of a Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst, and compared its performance to that of a Pt-containing catalyst.

## Environmental Catalysis for Diesel Engines

Andrew Walker (Johnson Matthey ECT, Wayne, PA, U.S.A.) inaugurated this session with a talk about past, present and future challenges of light- and heavy-duty diesel technology. NO<sub>x</sub> chemistry was a main subject in this session, but particulate and soot oxidation were also covered.

Fifteen talks were dedicated to NO<sub>x</sub> storage materials, reduction mechanisms and reaction promoters, hydrocarbon selective catalytic reduction (HC SCR) and ammonia selective catalytic reduction (NH<sub>3</sub> SCR).

In the HC SCR discussions, Zr pillared clays were reported by V. Sadykov (Boreskov Institute of Catalysis, Russia) to be good supports for creating very active Pt interfaces with surface OH groups, for instance in Pt-Cu/Zr pillared clays, and to react well with propylene and decane. The absence of Lewis acid sites in this material avoided sulfate species from populating the surface. Cu<sup>2+</sup> was claimed to enhance the Pt activity.

H. H. Lamb (North Carolina State University,

Raleigh, U.S.A.) *et al.* suggested that Pd supported on a basic carrier could be a promising alternative to Pt/BaO/Al<sub>2</sub>O<sub>3</sub> systems for NO<sub>x</sub> storage and NSR applications. Their proposal was supported by a novel Pd/MgAlO<sub>x</sub> formulation catalyst and by experimental work using TPR, XPS and extended X-ray absorption fine structure (EXAFS) spectroscopy techniques.

The role of potassium and its interaction with Pt in a Pt/K/Al<sub>2</sub>O<sub>3</sub> system was described as a potential alternative to Pt/BaO systems by T. J. Toops (Oak Ridge National Laboratory, Knoxville, U.S.A.) *et al.* using *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and TPR techniques. P. J. Schmitz (Ford Motor Company, Dearborn, U.S.A.) screened the rates for NO and CO oxidation for sixty-four Pt catalysts over different supports, precursors and ageing atmospheres, and produced a map of activity for the different materials. At around 150°C the factors affecting the rates were: precursors > support > ageing atmosphere.

Professor M. Makkee (Delft University of Technology, The Netherlands) presented interesting work on the impact of model NO<sub>x</sub> storage catalysts on the promotion of soot oxidation. Fresh Pt-K/Al<sub>2</sub>O<sub>3</sub> was shown to promote soot oxidation at lower temperatures in an O<sub>2</sub> containing feed, but this promotion effect disappeared on ageing at 600°C. When Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub> catalysts were exposed to NO and O<sub>2</sub>, soot oxidation could be promoted at lower temperatures by the NO<sub>2</sub> (produced by oxidation of the NO in the feed gas) and by the NO<sub>2</sub> that had been previously stored on the catalyst.

Professor M. Harold (University of Houston, U.S.A.) gave a presentation on TAP<sup>®</sup> (temporal analysis of products) studies investigating the mechanism of NSR reactions. Using NO pulse-probe experiments on a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst he showed evidence of O<sub>2</sub> (produced by the NO reaction to produce N<sub>2</sub>) inhibiting the reaction under lean conditions. Rich pulse experiments showed that this O<sub>2</sub> poisoning could be reversed. Mechanisms for both the NO and NO<sub>2</sub> reaction with the NSR catalyst were proposed.

The performance of NSR catalysts is very dynamic due to the alternating rich and lean feeds needed for them to work effectively. Insight into the dynamics in a monolith coated with a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> NSR catalyst was given by J.-S. Choi (Oak Ridge National Laboratory, U.S.A.). Spatially-resolved capillary-inlet mass spectrometry (SpaciMS) was used to probe the species evolution with time and distance down the monolith channel. The NO<sub>x</sub> reaction and release along with H<sub>2</sub> production and reaction of CO were measured. During the rich event CO oxidation consumed the oxygen at the front of the monolith, whereas H<sub>2</sub> was produced towards the rear of the monolith after the initial NO<sub>x</sub> release and reduction.

The effect of phosphorus poisoning on a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> coated monolith NSR catalyst was described in a presentation by R. Silver (Caterpillar, Peoria, IL, U.S.A.). The catalyst was exposed to phosphorus using a diesel burner and phosphorus-doped fuel to accelerate the expected exposure that would be seen in use on a vehicle, and then tested in a laboratory reactor. The phosphorus poisoning was found to be concentrated more to the front of the monolith. The NO to NO<sub>2</sub> oxidation function promoted by Pt was less affected by phosphorus poisoning than was the NO<sub>x</sub> storage function promoted by Ba in the catalyst.

How sulfur poisoning and thermal ageing affect NO<sub>x</sub> storage on a Pt-Ba/Al<sub>2</sub>O<sub>3</sub> NSR catalyst was described in a talk by Hai-Ying Chen (Johnson Matthey, Wayne, PA, U.S.A.). The degree of deactivation due to thermal ageing was found to be dependent on the ageing atmosphere; redox ageing gave greater deactivation than hydrothermal ageing, while ageing in air-only gave least deactivation. Increasing the ageing temperature was found to have a more significant effect than varying the ageing atmosphere. From BET and XRD studies it was concluded that the deactivation was due to an increased Ba-support interaction, Pt sintering and Pt-Ba separation. Exposure to sulfur was found to affect NO<sub>x</sub> storage capacity on the catalyst, depending on whether it was fresh or aged.

In the earlier mentioned, well-attended, poster session linked to the 'Environmental: Diesel Engines' presentations, highlights included a study

on the role of Pt loading and NSR by J. Anderson (University of Aberdeen, U.K.), and studies of Pt and Ba interactions, by I. Nova (Dipartimento Chimica, Materiali e Ingegneria Chimica “Giulio Natta”, Politecnico di Milano, Italy) *et al.* and by J. H. Kwak (Pacific Northwest National Laboratory, Richland, U.S.A.). R. J. Kudla (Ford Motor Company, Dearborn, U.S.A.) presented a poster of studies of NO oxidation over alumina-supported Pt-Pd and Pt-Rh.

## Fuel Reforming

The session on fuel reforming in the fuel cells and fuel processing section was introduced with a plenary talk from J. Rostrup-Nielsen from Topsøe A/S, Denmark. This quote from his abstract:

*“Hydrogen is an energy carrier which can be produced from a variety of energy sources ranging from fossil fuels, biofuels to a number of sustainable sources and nuclear energy via electricity. Hydrogen can also be produced from other secondary hydrogen carriers such as methanol, ammonia, and syngas.”*

perfectly describes the session in which hydrogen from traditional reforming and from alternative sources and hydrogen purification were covered. It is perhaps in this session that pgms catalysts had the greatest importance – as Pt, Rh, Pd and Ru were mentioned for autothermal reforming (ATR), partial oxidation (PO), steam reforming (SR), selective oxidation (SelOx) and water gas shift (WGS) processes – in almost every talk.

The addition of Cu to Pd and Rh was found to increase the hydrogen production rates during CH<sub>3</sub>OH ATR. Nickel (Ni) was also found to enhance the sulfur tolerance of Rh during the ATR of synthetic fuels. Supports for pgms such as: La-doped Al<sub>2</sub>O<sub>3</sub> for gasoline ATR using Rh, ZnO for CH<sub>3</sub>OH ATR using Pd, and YZrCeO<sub>x</sub> for Pt-Ni ATR of logistic fuels were described. The deposition of Rh nanoparticles in porous Al<sub>2</sub>O<sub>3</sub> was found to be a good method to prepare stable catalysts for PO of methane. The addition of traces of Pt helped these catalysts to be more tolerant to carbon deposition.

Pt and Ru were mentioned as good candidates for SelOx, although the novel chemistry of gold

gathered more attention in this field and in the WGS reaction. Pt supported on ceria was stated to be one of the most significant catalysts for the low temperature WGS reaction. The impact of promoters, such as rhenium and SnO<sub>2</sub>, to Pt to achieve high WGS activity was also discussed.

For fuel reforming, the highlights in the characterisation of pgms catalysts were Raman and DRIFTS isotopic transient kinetics (ITK) *in situ* studies. Raman spectroscopy was used for *in situ* characterisation of high temperature reforming processes to monitor carbon deposition. *In situ* DRIFTS and TPR coupled with mass spectrometry were used to characterise the evolution of the direct and reverse WGS reaction over Pt/CeO<sub>2</sub> catalyst samples using ITK.

## Surface Science in Catalysis

The oral session featured a presentation by Professor F. Zaera (University of California, Riverside, U.S.A.) on the nature of chiral modifiers in improving the enantioselectivity of the  $\alpha$ -keto ester hydrogenation reaction on Pt catalysts. Using data obtained from reflection adsorption infrared spectroscopy (RAIRS), NMR spectroscopy and solubility studies, Zaera clearly demonstrated that the mode of chiral modifier adsorption on Pt (flat geometry being preferred), the presence of peripheral substituents (which improve solubility), and the hindrance of quinuclidine ring rotation, all play vital roles in improving the enantioselectivity.

Professor F. Ribeiro (Purdue University, U.S.A.) gave a talk on the kinetics and structure sensitivity of Pd catalysts during complete CH<sub>4</sub> oxidation. By virtue of experiments on model catalysts under industrial conditions, Ribeiro and coworkers showed that the CH<sub>4</sub> oxidation reaction is structure insensitive to: (a) the Pd metal surface, due to the surface being saturated with oxygen, and (b) the PdO surface, as a result of the surfaces turning amorphous after oxidation.

## NACS Awards at the Banquet

The conference banquet included the presentation of the NACS awards. As mentioned before, the 2005 Eugene J. Houdry Award in Applied Catalysis was awarded to Dr Henrik Topsøe of the

Haldor Topsøe Research Laboratories, Lyngby, Denmark, for his significant contributions to the understanding of hydrotreating catalysts.

Professor Matthew Neurock of the University of Virginia was awarded the 2005 Paul H. Emmett Award in Fundamental Catalysis for his pioneering contributions to theoretical methods for the analysis and prediction of catalytic rates and selectivities.

## Conclusions

The abstracts of the oral and poster presentations given at this conference are available on the meeting's website (2). The website will remain active only until 1st December, 2005. The next meeting is planned to be held in 2007 in Houston, Texas (4).

## References

- 1 North American Catalysis Society, <http://www.nacatsoc.org/>
- 2 19th North American Catalysis Society Meeting, 22-27 May, 2005, Philadelphia, PA, U.S.A., <http://www.19nam.org/>
- 3 T. H. Ballinger and H.-Y. Chen, *Platinum Metals Rev.*, 2001, 45, (4), 164-165; a review of the 17th NACS meeting held in Toronto
- 4 20th North American Catalysis Society Meeting, 17-22 June, 2007, Houston, TX, U.S.A., <http://www.20nam.org/>

### The Reviewers

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