

6th International Conference on Environmental Catalysis

PGM-based technologies for NO_x, CO, HC and PM abatement

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Reviewed by Noelia Cortes Felix

Johnson Matthey Technology Centre, Blounts Court,
Sonning Common, Reading RG4 9NH, UK

Email: felixn@matthey.com

The 6th International Conference on Environmental Catalysis (ICEC) was held in Beijing, China, from 12th to 15th September 2010. It was organised by the Research Centre for Eco-Environmental Sciences (RCEES), Beijing, of the Chinese Academy of Sciences (CAS). The topics of this conference covered five important fields: automotive exhaust catalysis; clean air and water; clean energy; reducing greenhouse gases; and green chemistry. Around 500 people from around the world attended. The organisers selected 16 keynotes, 119 oral presentations and 322 posters.

This review solely focuses on automotive exhaust catalysis. The talks have been divided depending on their application, including: particulate matter (PM) control; three-way catalysts (TWCs); ammonia-selective catalytic reduction (NH₃-SCR); hydrocarbon-selective catalytic reduction (HC-SCR); and lean nitrogen oxides (NO_x) traps.

Particulate Matter Control

The first keynote talk was presented by Atsushi Satsuma (University of Nagoya, Japan) and titled 'Combustion of Carbon Using Ag/Ceria Prepared by Self-Dispersion of Ag Powder into Nano-particles'. Satsuma and coworkers presented an innovative method of preparing silver/ceria. This preparation process consisted of mixing silver powder with ceria, followed by calcination at 500°C. Upon calcination, the activity of the prepared catalyst improved, due to redispersion of the silver metallic particles, the reverse of what occurs when the catalysts are prepared by wet impregnation. The same experiment was tried with other metals: copper, gold and platinum, but no improvements in the activity were seen. The effect of the support was also studied; it was found that ceria was the best, with others following the order: ceria > titania > zirconia > zinc oxide > tin(II) oxide > niobia, however ceria is not very thermally stable. To improve thermal stability alumina was added to the ceria prior to mixing with silver.

Yasutake Teraoka (University of Kyushu, Japan) focused on the effects of supported metals and

support oxides on PM combustion activity in his talk 'Catalytic Activity of Supported Metal Catalysts for Diesel Particulate Combustion'. In their experiments, carbon black (CB) and hexadecane were used as substitutes for soot and for the soluble organic fraction (SOF), respectively. Comparing different precious metals supported on titania, platinum showed the greatest activity for SOF oxidation ($\text{Pt} > \text{Pd} > \text{Ag}$); however, the silver catalyst was by far the best for soot oxidation ($\text{Ag} \gg \text{Pt} \sim \text{Pd}$). The effect of the support was only studied for soot oxidation. As silver was the most active metal, this was impregnated on different support oxides. It was concluded that the chemical nature of the oxide is more important than the physical characteristics of the catalyst. Cobalt(II,III) oxide (Co_3O_4) was the best support for soot oxidation, with others following the order: cobalt(II,III) oxide > titania > ceria > lanthanum cobalt oxide > α -alumina > lanthanum manganese oxide > γ -alumina.

Three-Way Catalysts

Sarayute Chansai (Queen's University Belfast, UK) presented the work of his colleagues Alexandre Goguet *et al.* (Queen's University Belfast; Universidade de Aveiro, Portugal; and Oak Ridge National Laboratory, USA). The presentation was titled 'Spatial Resolution of Kinetic Oscillations within a Catalytic Monolith'. Due to the lack of techniques available to study *in situ* reactions inside a monolith, the group from Queen's University Belfast worked on a technique called spatially resolved capillary-inlet mass spectrometry

(SpaciMS). To demonstrate the high accuracy of SpaciMS, carbon monoxide oxidation over platinum-rhodium/alumina was studied. The technique is non-invasive and non-conductive, and it is therefore possible to resolve kinetic oscillations and their dependence on local reaction conditions (1).

The effect of doping palladium/ceria-zirconia (Pd/CZ) materials was presented by Guangfeng Li (University of Zhejiang, China) in 'The Influence of Iron Doping on the Physicochemical Properties of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ and the Catalytic Behaviour of Pd-Only Three-Way Catalyst for Automotive Emission Control'. Li and colleagues showed that the introduction of iron into CZ replaces cerium atoms, creating a more homogeneous Ce-Zr-Fe-O ternary solid solution. This substitution enhances the surface area of the catalyst as well as the average pore diameter and broadens the range of pore distribution. 1% Fe showed the maximum improvement (Figure 1) (2). As a result of the structural changes, the order of activity followed: Pd/CZFe (1%) > Pd/CZFe (2.5%) > Pd/CZFe (5%) > Pd/CZFe (0.5%) > Pd/CZ. Unfortunately, the results shown here were for fresh catalysts. The experiments with their aged counterparts are ongoing. Li stated that for the moment the results with iron-doped CZ are still better than the undoped catalysts.

The following lecture, presented by Naoki Takahashi (Toyota Central R&D Labs Inc, Japan), focused on the improvement of the stability of TWCs using platinum/ceria-based supports. The talk was titled 'Increasing the Lifetime of Automotive TWC Thanks to Pt-O-Ce

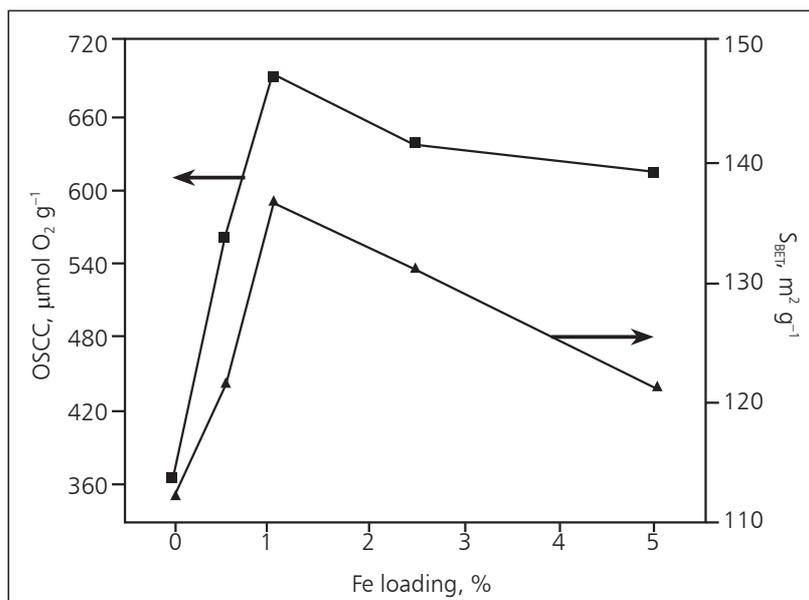


Fig. 1. Oxygen storage complete capacity (OSCC) and surface area (S_{BET}) of doped palladium/ceria-zirconia samples as a function of iron loading (2)

Bonds'. The CZ support was calcined at 1323 K before impregnation of platinum to avoid support sintering later on. During ageing, reducing and oxidising conditions were alternated at 1223 K. The catalysts were then regenerated in air at 1073 K for 30 minutes and treated in a reducing atmosphere at 773 K for 10 minutes. Carbon monoxide adsorption experiments showed that at low platinum loading (<0.25 wt%) it was possible to inhibit platinum sintering and to redisperse the agglomerated platinum. This is believed to be due to platinum anchoring on specific surface sites (Pt-O-Ce) that act as the driving force for the redispersion (3,4).

Ammonia-Selective Catalytic Reduction

Chen Xu (Cummins Inc, USA) focused on the issue of ammonia slip in SCR catalysts. Xu's talk 'New Insights into Reaction Mechanism of Selective Ammonia Oxidation Catalyst in Diesel Aftertreatment Applications' presented an ammonia slip catalyst (ASC) based on platinum that is positioned in front of the SCR catalyst. The ASC controls ammonia oxidation to NO_x when running under lean conditions. This catalyst was hydrothermally aged at 650°C for different periods of time. It was seen that ammonia conversion was unaffected by the ageing time. However, the selectivity changed towards undesired byproducts with longer ageing times. A. Scheuer (Technische Universität Darmstadt, Germany) presented a similar work in their talk 'Design of Dual Layer Catalysts for NH₃ Oxidation in Automotive Exhaust'. In this case, instead of positioning a platinum-based catalyst in front of the

NH₃-SCR catalyst they incorporated it to the actual catalyst as a lower layer. The problem found with this catalyst was the difficult diffusion of ammonia to the platinum layer, emphasising the need to optimise the thickness of the washcoat layer.

Hydrocarbon-Selective Catalytic Reduction

The presentation entitled 'A Mechanistic Study of the H₂-Assisted Reduction of NO_x by Octane on Ag/Al₂O₃ Using SSITKA-DRIFTS-MS Technique', was given by Sarayute Chansai (Queen's University Belfast, UK). They presented work on the role of hydrogen in the HC-SCR reaction (5–7), finding the intermediates involved and differentiating between spectator and active forms of the same surface species. Using isotopic transient kinetics they could see that, under full steady state conditions, the intermediates found were isocyanates and cyanides. However, experiments using steady state isotopic transient kinetic analysis (SSITKA) and fast transient diffuse reflectance fourier transform infrared spectroscopy-mass spectrometry (DRIFTS-MS) with pulses of hydrogen revealed that under non-steady state conditions the isocyanates are the active intermediates, and the cyanides are only spectator species (Figure 2) (8).

Mingli Fu (South China University of Technology, China) incorporated rhodium into silver/ceria-zirconia/alumina (CZA), finding a positive synergistic effect between silver and rhodium in their presentation 'DRIFTS Study of the Selective Catalytic Reduction of NO by C₃H₆ under Lean-Burn Conditions over Ag-Rh/CZA'. Having rhodium and silver together make it

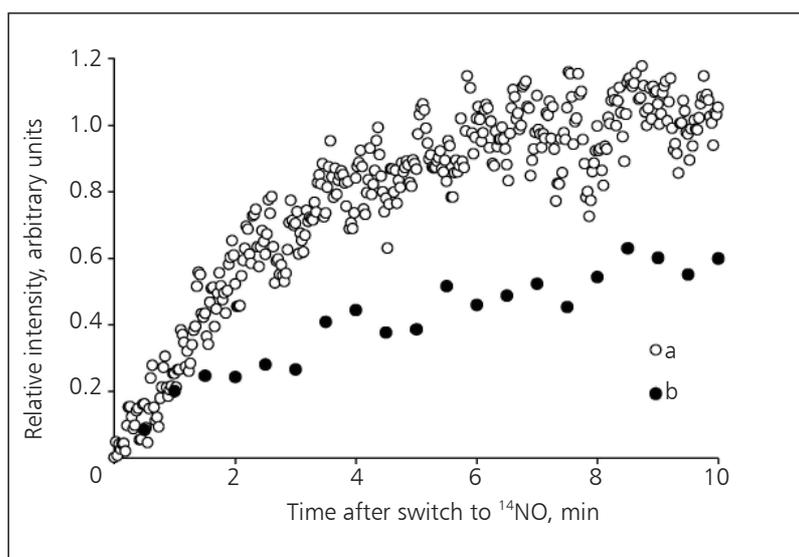


Fig. 2. Evolution of (a) the DRIFTS spectra of ¹⁴N-containing species and (b) the MS intensity of gas phase ¹⁴N₂ over a Ag/Al₂O₃ HC-SCR catalyst (8)

possible to have a wider activity window (300–500°C) and higher NO conversion with propene.

Lean NO_x Traps

The first talk about NO_x storage and reduction (NSR) catalysts was presented by Roberto Matarrese (Politecnico di Milano, Italy), and was entitled 'Interplay between NO_x and Soot Removal over Pt-Ba NSR Catalysts'. Matarrese focused on the influence of soot on the NO_x storage process, studying the stability of stored NO_x in the presence and absence of soot in the system. They concluded that the presence of 10 wt% soot during the storage process at 350°C decreases the NO_x storage capacity by nearly 30%. The reduction part was not seen to be affected. The stability of the stored nitrates was also lower in the presence of soot, indicating a possible interaction between the stored nitrates and soot particles. Matarrese concluded that there is evidence supporting the oxidation of soot with NO_x by direct participation of the adsorbed NO_x and/or releasing NO₂ and O₂, both of which actively oxidise soot.

One ideal system for NO_x abatement would be to use a NSR catalyst with an NH₃-SCR catalyst in order to increase conversion to nitrogen and avoid ammonia slip. The difficulty of controlling the selectivity towards ammonia during the regeneration of the NO_x trap and the different temperatures in both systems makes this a difficult process. Mark Crocker (University of Kentucky, USA) focused on the optimisation of the ammonia selectivity during the regeneration process in his talk titled 'The Effect of Regeneration Conditions on the Selectivity of NO_x Reduction in a Fully Formulated Lean NO_x Trap Catalyst'. They found that several

conditions could have a significant impact on the selectivity of the purge: purge length; reductant concentration; temperature; reductant type; and the state of the catalyst (fresh or aged). One of the most interesting parts of the talk was the influence of using hydrogen or propene as a reductant. When using hydrogen the selectivity towards ammonia would mainly depend on the H₂:NO_x ratio. In contrast, when using propene the selectivity increases with increasing temperature. This is due to the conversion of propene to hydrogen *via* steam reforming. The catalyst used for the study was a fully formulated catalyst based on Pt-Rh-BaO-[La-stabilised CeO₂]-[La-stabilised Al₂O₃] (9).

Do Heui Kim presented 'Effect of the Reductive Treatments on Pt Dispersion and NO_x Storage in Lean NO_x Trap Catalysts'. Do Heui Kim (Institute for Interfacial Catalysis, USA) discovered that the loss of available platinum after a reductive treatment in hydrogen (300–800°C) on a Johnson Matthey catalyst (Pt-BaO/Al₂O₃) was not due to platinum sintering as originally thought (Figure 3) (10). Characterisation tests showed that the loss of platinum active surface area was due to platinum being covered with mobile barium and not as a result of platinum sintering. The reoxidation of the samples resulted in barium moving back to the support, thus increasing the accessible platinum area.

Concluding Remarks

More groups from academia than from industry attended the 6th ICEC. The poster sessions were a great opportunity for discussions, allowing people to share ideas. A major focus of the conference were the mechanistic studies of the reactions that take place on

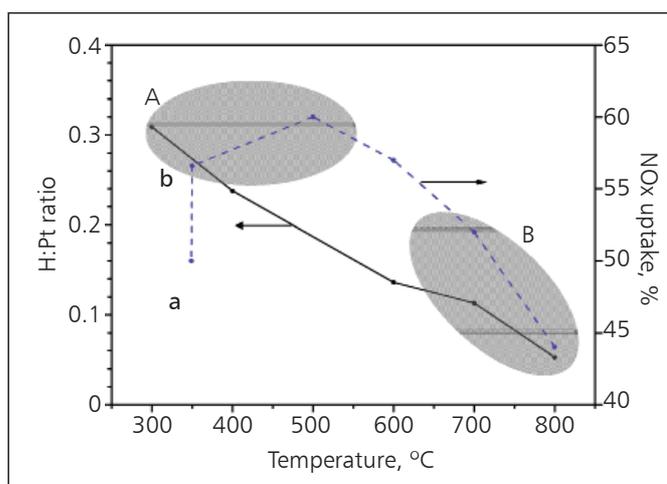


Fig. 3. Change in the H:Pt ratios and NO_x uptake (%) as a function of reduction temperature for a model Pt-BaO/Al₂O₃ catalyst. Region A shows the uptake of NO_x increasing, in contrast to the decreasing accessible Pt surface area. In region B where reduction temperatures exceed 600°C, the decrease of NO_x uptakes may be explained by multiple factors. Point a is the NO_x uptake of the fresh sample without any reduction treatment; point b is the NO_x uptake after a reduction treatment at 350°C (10)

autocatalysts. Several groups have developed new techniques such as SpaciMS to study these reactions, although many reactions remain poorly understood.

Much work has been carried out on applications using platinum group metals (pgms), although most of the talks mentioned the high cost of these catalysts. Several studies into possible substitutes for the pgms were presented, but despite some benefits these alternatives are still far away from competing with the pgms.

Overall, ICEC 2010 provided high quality work and proved once more to be one of the most important conferences specialising in environmental catalysis.

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The Reviewer



Noelia Cortes Felix studied Chemical Science at the Autònoma University of Barcelona, Spain. As a student she followed an Erasmus programme at Twente University, The Netherlands, studying the impregnation of platinum and palladium on carbon nanofibres for their use as catalysts. Following this, she carried out research into novel precious metal catalysts for the control of NO_x emissions at the Johnson Matthey Technology Centre, Sonning Common, UK. She is currently conducting research into three-way catalyst technology, which she combines with a PhD programme in the same subject within The Open University, UK.