

5th International Conference on Environmental Catalysis

PGM-BASED TECHNOLOGIES FOR NO_x ABATEMENT

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The 5th International Conference on Environmental Catalysis (5ICEC) was held at Queen's University in Belfast, Northern Ireland, from 31st August to 3rd September 2008. The conference was split into five main categories over the course of three days: Autocatalysis, Clean Energy, Renewables, Green Chemistry and Air and Water. In addition to the oral presentations, there were several plenary talks given by keynote speakers, together with poster sessions and vendor booths. This review will focus on the talks related to the use of noble metals, including the platinum group metals (pgms), in autocatalyst applications. The review can be split into three sections: the first details the use of silver/alumina (Ag/Al₂O₃) for the selective catalytic reduction of nitrogen oxides (NO_x) using hydrocarbons (HC-SCR); the second discusses the use of platinum, palladium, rhodium or iridium in lean NO_x traps (LNT) and the third is concerned with platinum, palladium and rhodium used in NO_x storage.

Hydrocarbon-Selective Catalytic Reduction

HC-SCR is a highly desirable technology for the removal of NO_x from diesel and lean-burn gasoline exhausts, although it has proven difficult to develop a suitably active commercial catalyst. One of the most promising candidates is silver supported on alumina, where good SCR activity can be obtained by the addition of hydrogen. This is referred to as the 'hydrogen effect' (1, 2). The activation of Ag/Al₂O₃ by hydrogen has been a matter of some debate, and no clear explanation has yet been provided. It is generally thought that hydrogen causes silver to form active silver clusters; however, it has been reported that the presence of silver clusters by

itself is not sufficient for good SCR activity (3–5). For example, it has been demonstrated that a similar hydrogen effect was obtained through the use of hydrogen peroxide (H₂O₂), which suggests that a hydroperoxy-like species is important for hydrogen-promoted HC-SCR (6).

Atsushi Satsuma (Nagoya University, Japan) argued in his presentation 'Role of Ag Cluster on Hydrogen Effect of HC-SCR over Ag/Alumina' that the silver clusters are not necessary for good SCR activity, but rather promote the formation of the active H₂O₂ species that is essential for the activation of reactants in HC-SCR. The formation of active oxygen species (O₂⁻) was measured by electron spin resonance (ESR) to determine whether silver clusters and hydrogen are required for the promoted HC-SCR to take place. It was argued that an O₂⁻ species is essential for the hydrogen effect due to its high activity towards partial oxidation of hydrocarbons. The lack of detectable O₂⁻ species when silver clusters were treated in a mixture of carbon monoxide and oxygen followed by addition of oxygen indicated that the presence of hydrogen was required. Similarly, no O₂⁻ species were observed on 0.5 wt.% Ag/Al₂O₃ catalysts where no silver aggregation has taken place, even after reduction by hydrogen. It was suggested that this is a consequence of having the silver species fixed as Ag⁺ on the alumina surface.

The O₂⁻ species were only detected on the 2 wt.% Ag/Al₂O₃ that contained silver clusters after exposure to a flow of hydrogen and oxygen followed by addition of oxygen (7). The reaction mechanism was evaluated by density functional theory (DFT) calculations using silver supported on a MFI-type zeolite (Ag/MFI) as the model catalyst. The reaction is suggested to occur *via* the

activation of oxygen by [HHAg₄] clusters to form HOO[HAga] clusters, which in turn leads to the formation of H₂O₂ species. This was to be reported in further detail in a paper pending submission (at the time of writing) by K. Sawabe, T. Hiro, Y. Iwata, K. Shimizu and A. Satsuma.

Similar Ag₄²⁺ clusters were detected by ultra-violet-visible (UV-vis) spectroscopy on both the Ag/MFI and Ag/Al₂O₃ catalysts. However, a larger contribution by Ag-O was found with the latter catalyst. Further details on the nature of the silver structure as analysed through the use of extended X-ray absorption fine structure (EXAFS) and UV-vis spectroscopy can be found in Reference (8).

During the discussions that followed the presentation, it was mentioned that the active silver clusters may not necessarily be solely tetrahedral Ag₄ clusters, as there could be a range of cluster sizes where the average is Ag₄. The important parameters are the agglomeration and charge of the silver cluster. The possible differences between silver supported on the MFI zeolite and supported on alumina were also discussed, as the active silver species and mechanism of reaction may differ between the two.

The next presentation, by Pyung Soon Kim (Pohang University of Science and Technology, Korea), was titled 'Selective Catalytic Reduction of NO_x by Simulated Diesel Fuel Containing Oxygenated Hydrocarbon'. The presentation dealt with methods to improve the low-temperature activity of Ag/Al₂O₃ catalysts through the use of oxygenated hydrocarbons (OHCs) that have been reported to lower the light-off temperatures, as well as preventing catalyst deactivation by coking (9). The NO_x reduction activity was investigated in a packed-bed reactor, using a mixture of simulated diesel fuel (dodecane and *m*-xylene) and ethanol as a reductant. The testing was conducted at a space velocity of 60 h⁻¹ in a mixture of 6% oxygen, 2.5% water vapour and helium, where the C₁:NO_x ratio varied from 2 to 8 over a dual-bed catalyst system with a 0.5 inch coating of Ag/Al₂O₃ catalyst in the front followed by 0.5 inch of copper-exchanged ZSM-5 zeolite (Cu/ZSM-5) catalyst in the rear bed.

Ammonia (NH₃) was found to be a major byproduct, in particular when high amounts of ethanol were used in the fuel mixture. Therefore the Cu/ZSM-5 catalyst was added as an NH₃ oxidation component and to improve the high-temperature activity, as previously reported by Long and Yang (10). The influence of the catalyst preparation procedure and operating conditions were investigated in order to optimise the dual-bed catalyst system. The Ag/Al₂O₃ catalysts were characterised by various techniques, including transmission electron microscopy (TEM), UV-vis spectroscopy, hydrogen temperature-programmed reduction (H₂-TPR) and X-ray (excited) photoelectron spectroscopy (XPS).

Increasing the silver loading improved the low-temperature activity but reduced the high-temperature activity. For high-temperature use, the optimum loading was determined to be 3.8 wt.% Ag. A similar effect was observed with the addition of ethanol, which improved low-temperature activity by around 25% but negatively impacted the activity at temperatures above 350°C. A loss of low-temperature activity was observed when the C₁:NO_x ratio was greater than 8; this is most likely due to the build-up of hydrocarbons coking the catalyst.

The drying temperature used during the preparation of the Ag/Al₂O₃ catalyst was found to have a significant impact on its catalytic activity. The Ag/Al₂O₃ catalyst exhibited poor activity for NO_x conversion to nitrogen (N₂) when dried at 65°C, but was active for the unselective catalytic formation of NH₃. It was reported that the catalysts had to be dried at temperatures above 80°C to achieve good conversion of NO_x to N₂, and the best performance was obtained by using a drying temperature of 110°C. The TEM and UV-vis characterisation results showed that the catalyst dried at 65°C had larger particle sizes (~ 14 nm) and a wider particle size distribution, while the 110°C-dried catalyst contained less metallic silver, and had a smaller average particle size (~ 8 nm) and narrower particle size distribution.

XPS results were also presented. Kim concluded from these that the ionic silver species were the active sites for NO_x reduction to N₂, and that the

metallic silver sites were active for NO_x reduction to NH₃. However, this contradicts the other characterisation results, and together with the large experimental errors reported, this would call into question the accuracy and validity of the XPS results. Further, during the discussions, it was suggested that the most likely influence of the Cu/ZSM-5 catalysts was not NH₃ oxidation, but rather its activity for NH₃-SCR, which leads to an improvement in the high-temperature activity of the catalyst system.

Continuing with presentations based on HC-SCR studies over a Ag/Al₂O₃ catalytic bed, the influence of biodiesel fuel over a microreactor was discussed next. Biodiesel is an interesting and growing area of research, in particular as the EU has mandated the use of certain percentages of biodiesel in vehicle fuel, with set targets for 2010 (11). However, there are a number of challenges involved in the use of biodiesels, including the fact that they are known to produce more NO_x than oil-derived diesel. The presentation given here, by José R. Hernández (Åbo Akademi University, Finland), was entitled 'A Combination between a Low- and a High-Temperature Catalyst for the SCR of NO_x Using Second-Generation Biodiesel in Microchannels'.

The catalytic testing was conducted on a microreactor where ten plates were coated with either Ag/Al₂O₃ or Cu/ZSM-5 catalysts (five plates of each) in a specific arrangement, and the products were measured using a micro gas chromatograph, as described in the presenter's previously published paper (12). The Cu/ZSM-5 catalyst was found to significantly widen the temperature window, especially in the low-temperature region. The cause of the promotion effect when both Ag/Al₂O₃ and Cu/ZSM-5 catalysts are present is not fully understood, but mechanistic studies will be carried out in the future.

Hexadecane was used as the model fuel for simulated second-generation biodiesel, based on the group's previous work (13). The use of hexadecane/biodiesel was found to improve the low-temperature activity, but resulted in the loss of high-temperature activity. The hexadecane concentration was shown to be an important factor, as

the catalytic system could be optimised by controlling the C₁:NO_x ratio. It was reported that, depending on the activity window, the C₁:NO_x ratio should be 6 for low-temperature activity, 9 for mid-range-temperature activity, and 12 for high-temperature activity.

This presentation invited many questions, in particular regarding the relevance of results generated using a microreactor. Hernández stated that the use of a microreactor improves energy efficiency and gives a better yield, increased safety and a better degree of process control. He also asserted that similar conditions are found in a car exhaust system to those in a microreactor. However, it was discussed that this may not always be the case, as the fact that the microreactor's results are based on changes in very small percentages of conversion means that they are prone to higher levels of inaccuracy. Furthermore, additional factors such as mass transfer limitations and exotherms were not addressed. However, it was recognised that limitations in test equipment and reactants, as well as experimental convenience, favour the use of microreactors over testing on larger monolith reactors.

Lean NO_x Traps

The next presentation, 'A NO_x Reduction System Using Ammonia-Storage Selective Catalytic Reduction in Rich/Lean Excursions', by Tadao Nakatsuji (Okayama University, Japan), dealt with a novel approach to the lean NO_x reduction catalyst system. One of the major disadvantages of the lean NO_x trap (LNT) system is its poor low-temperature performance and susceptibility to poisoning by species such as sulfur oxides (SO_x) that require high-temperature regeneration profiles. Furthermore, the LNT only generates nitrogen during the rich phase, as the NO_x is stored during the lean phase.

To address this limitation, a transient catalytic NO_x reduction catalyst was developed by Nakatsuji's group, containing a platinum-based oxygen storage component (OSC) and a solid acid capable of reducing NO_x to N₂ in both the lean and rich phases. This is an extension of the LNT concept with an *in situ* NH₃ formation capability in

order to carry out NH_3 -SCR reactions. The double layer catalyst consists of a solid acid top layer composed of 20% H-mordenite and 80% Pt/CeO₂, and a bottom layer composed of either 2% Pt/Ce-Pr-ZrO_x or 2% Pt/(75% Al-21% BaCO₃-2% K₂CO₃). The ratio between the top layer for NH_3 storage and the bottom layer for NO_x storage was 1:3.

The reaction mechanism over the new catalyst system is proposed to proceed through four main reaction pathways. In the initial lean phase, the NO_x species adsorb onto the OSC component. These are reduced to NH_3 over the platinum catalyst during rich operation, and the NH_3 is then adsorbed onto the solid acid layer. Finally, the stored NH_3 is used to reduce the NO_x species during the lean phase, therefore allowing NO_x reduction to take place during both the lean and rich phases.

The *in situ* Fourier transform infrared (FTIR) spectroscopy results shown during Nakatsuji's presentation supported the proposed mechanism, in which only nitrates are formed during the first thirty seconds, then these rapidly turn into ammonium (NH_4^+) species after a further thirty seconds. After sixty seconds, the NH_4^+ concentration begins to decrease, while concentration of N_2 increases, together with the appearance of some NO_x. Based on the N_2 profiles exhibited during the presentation, there were potentially some selectivity issues. An example of one of the N_2 profiles is sketched in Figure 1.

Akira Obuchi (National Institute of Advanced Industrial Science and Technology (AIST), Japan) presented another interesting novel reactor design

in his talk 'CO and NH_3 -Combined SCR with an Internal Heat Exchanging Reactor'. On newer engine designs, there is a trend towards emission of exhaust gases at lower temperatures to improve fuel economy. As a consequence of this, catalytic reactions are more difficult; therefore a new reactor was developed to integrate a heat exchanging function with catalytic activity. Further details on the reactor design can be obtained from several patents and papers (14–17). This is a challenging process, as combining a catalytic reactor with a heat exchanger system can cause a large drop in pressure and reduce overall efficiency.

The basic design of the reactor system consisted of different types of catalysts washcoated onto several bundled stainless steel sheets at various positions in the reactor. The heat is recovered by use of a counterflow system where the inlet gas is heated by the hot gases generated by the exothermic oxidation reaction towards the centre of the reactor. See Figure 2 for a brief outline of one possible configuration of the reactor scheme with three SCR catalysts.

Obuchi used two different SCR catalysts (Cu/ZSM-5 for NH_3 -SCR, iridium and barium on WO₃/SiO₂ for CO-SCR) with Pt/Al₂O₃ as the oxidation catalyst for combustion of CO to generate the exotherm. In general, there was a ratio of 20 g of Cu/ZSM-5 to each 5 g of IrBa/WO₃-SiO₂ and 3 g of Pt/Al₂O₃ towards the outlet end of the reactor system. There are several different possible configurations, depending on the positions of the catalysts, whether the sheets are coated on one or both sides, and whether one or two different

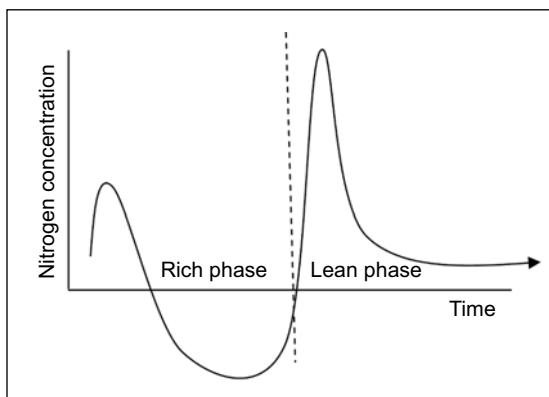


Fig. 1 Nitrogen profile over a modified lean NO_x trap

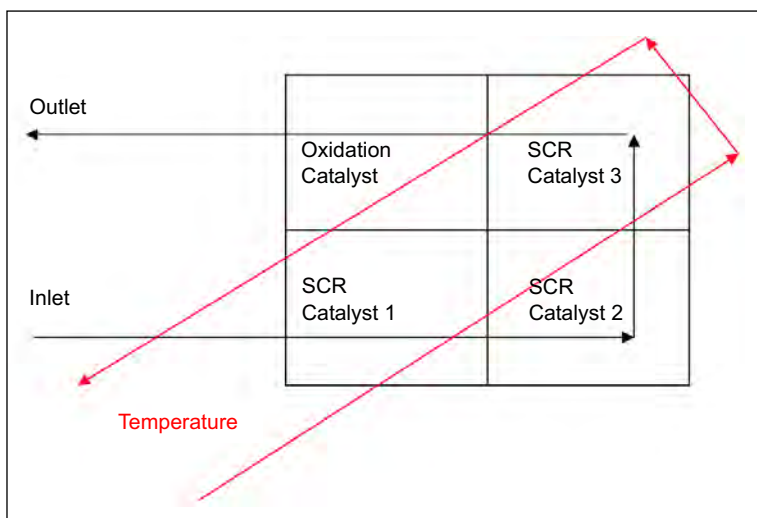


Fig. 2 A possible layout of the combined CO- and NH₃-selective catalytic reduction reactor with an internal heat exchanger, using three SCR catalysts

catalysts are used. The temperature in the reaction zone can be raised to 320°C with an inlet temperature of 100°C, which corresponds to an 80% heat recovery. Under CO-SCR, the NO_x conversion was 25% (NO_x inlet of 100 ppm) which can be raised to 75% when 90 ppm NH₃ is added to allow NH₃-SCR to take place.

The results show a potential for heat recovery, compared to the standard monolith reactor design, that will benefit the catalytic activity of the new system. However, currently between 35 W and 55 W of electrical heating is required at the ends of the reactor to boost the activity of the system and the CO concentration has to be increased artificially.

The last pgm-related presentation of the first day was given by Christophe Dujardin (Unité de Catalyse et de Chimie du Solide, Université des Sciences et Technologie de Lille, France) and discussed the 'Nature and Evolution of Palladium Species on Pd-LaCoO₃ and Pd-Al₂O₃ on the Course of the Reactions NO+H₂+O₂ Followed with *Operando* EXAFS'. Perovskite-supported pgms have been of increasing interest as potential alternatives to ceria-zirconia supported pgms for de-NO_x applications (18, 19). The results presented here showed that there are stronger interactions between palladium and oxide sites on perovskites than on alumina, which suggests that perovskite has a stabilising effect. The reduction of palladium to its metallic form under hydrogen was also shown

to be delayed on perovskites compared to alumina.

The catalysts were synthesised using the sol-gel technique, with addition of 1 wt.% palladium by impregnation, and fired at 400°C followed by a pre-reduction in hydrogen at 250°C. The reaction conditions were 0.1% nitric oxide (NO), 0.5% hydrogen and 3% oxygen in helium. It was interesting to note that pgms supported on perovskite exhibit better catalytic activity compared to those supported on silica, despite their lower surface area.

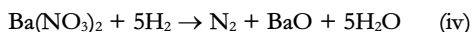
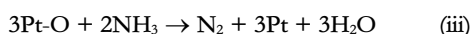
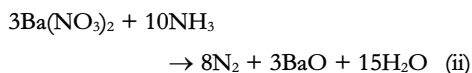
It has been proposed that palladium may actually be inserted into the framework of the perovskite, based on the higher XPS binding energy of PdO at 500°C. However, this is still being debated (20). Results of *in situ* XPS studies were presented that showed preservation of the LaCoO₃ structure and the conversion of Co³⁺ to Co²⁺ and Co⁰ when reduced and re-oxidised under the reaction conditions.

NO_x Storage

The second day of the conference focused on one specific area of NO_x control: NO_x storage. The first talk of the day was by William Epling (University of Waterloo, Canada; in collaboration with Cummins, Inc, U.S.A.) and was entitled 'Evaluating Axial Distributions of Species and Temperature on Monolith-Supported Catalysts *via* Spatially-Resolved Calorimetry'. The technique of IR thermography, which has been successfully

used previously to characterise oxidation catalysts, was used to measure the axial distribution of nitrate species as a function of lean-phase time and temperature, with either NO₂ or NO as the NO_x source, on both model and commercial diesel NO_x adsorber catalysts.

The next presentation was 'Intermediate NH₃ Generation and Utilization Inside a Lean NO_x Trap Catalyst' by Jae-Soon Choi (Oak Ridge National Laboratory, Oak Ridge, U.S.A.). Choi explained how NH₃ is created and where and how it is used in a LNT catalyst. Intra-catalyst measurements were performed using spatially resolved capillary-inlet mass spectrometry (SpaciMS). Lean-rich cycling tests (cycles of 60 s lean, 5 s rich) were carried out on a Pt/Ba/Al₂O₃ washcoated catalyst. NO_x, N₂, NH₃ and H₂ were measured over time and it was seen that the relative amounts of and selectivity towards each species were different at different points along the channel of the monolith. Working at different temperatures, it is possible to see clearly the evolution of the different species during the reaction. At low temperatures (200°C) there is a large amount of NO_x stored on the catalyst, and the NH₃ that was formed upstream is simultaneously consumed to reduce the downstream NO_x. However, increasing the temperature to 325°C reduces the concentration of NH₃, as NO_x is less stable at this temperature and the local H₂:NO_x ratio is also lower. This observation supports the important role of the H₂:NO_x ratio in NH₃ formation. The results obtained suggest that two possible mechanisms exist, depending on the operational temperature. At lower temperatures, NH₃ is formed as an intermediate (Equation (i)) that reduces the NO_x stored in the catalyst (Equations (ii) and (iii)). At higher temperatures, H₂ reacts with the stored NO_x, reducing it directly to N₂ (Equation (iv)):



This study showed that NH₃ plays an important role in the mechanism of a LNT.

After this interesting talk, Hiroyuki Matsubara (Toyota Motor Corporation, Japan) presented 'Novel CeO₂-Al₂O₃ Nano Composite for Inhibiting Platinum Sintering of NSR Catalyst'. It is well known that platinum sintering by thermal ageing decreases NO_x storage capacity. Matsubara and colleagues have developed a new material based on the strong interaction between platinum and ceria to inhibit this effect. After the incorporation of ceria nanoparticles into the matrix of a support with high surface area, in this case alumina, they obtained better platinum dispersion and smaller particle size, which improved the NO_x storage performance of the catalyst, especially at temperatures lower than 300°C.

The other major problem with the use of NO_x traps is poisoning by sulfur present in diesel fuel. 'Kinetics of Sulfur Removal from a Commercial Lean NO_x Trap Catalyst' was presented by Aleksey Yezerets (Cummins Inc, U.S.A.) in partnership with the Emission Control Technologies group of Johnson Matthey, U.S.A. Yezerets and coworkers found one additional effect related to the nature of the sulfur deposited in LNT catalysts. Different forms of sulfur can have different effects on NO_x performance, as well as different kinetics for its removal. The most important species found were the sulfate species, which were shown to be removable at low temperature. The following parameters can affect the desulfation process:

- (a) initial sulfur concentration
- (b) desulfation temperature
- (c) reductant concentration.

This can be summarised as a mathematical expression (Equation (v)):

$$r = A \times \exp(-E_a/8.314 T) \times ([\text{reductant}]^{n_{(i)}}) \times [S]^{n_o} \quad (\text{v})$$

where r is the rate, A is the frequency factor (s⁻¹), E_a is the activation energy (137 ± 8 KJ mol⁻¹), T is the desulfation temperature (K), $[\text{reductant}]^{n_{(i)}}$ is the reductant concentration (mol l⁻¹), $[S]^{n_o}$ is the instantaneous sulfur concentration (mol l⁻¹), $n_{(i)}$ is the reaction order at that moment in time and n_o is the initial reaction order.

Todd J. Toops (Oak Ridge National Laboratory, Knoxville, U.S.A.) talked about 'Thermal Aging of Lean NO_x Trap Catalysts Using Reactor-Generated Exotherms and the Resulting Material Effects'. In this talk, Toops showed that there is a correlation between ageing temperature and surface area losses. Four ageing temperatures (700°C, 800°C, 900°C and 1000°C) were employed over the course of several hundred ageing cycles. At 700°C, there was no impact on the performance of the catalyst at low temperature, at 800°C there could have been a slight influence, and at ageing temperatures above 800°C a significant decrease in NO_x activity and surface area was clearly seen. This was explained by the transition of the alumina support from gamma to delta form at 860°C.

The last day of the conference started with a presentation entitled 'Model NO_x Storage Catalysts: Reaction Mechanisms and Kinetics at the Microscopic Level' by Jörg Libuda (University of Erlangen-Nuremberg, Germany) and colleagues. A catalyst based on Pd/Ba/Al₂O₃ was tested using a combination of scanning tunnelling microscopy, high-resolution photoelectron spectroscopy using synchrotron radiation, time-resolved IR reflection absorption spectroscopy (TR-IRAS), multimolecular beam methods, and combined reactor/TR-IRAS experiments up to ambient pressure conditions. Libuda and his coworkers suggested two possible mechanisms for NO_x storage after NO₂ exposure, depending on the temperature: at low temperatures (~ 100°C) a cooperative mechanism was proposed, in which nitrites are formed first followed by nitrates; at high temperatures (≥ 300°C), it was found to be a non-cooperative mechanism, where all the NO_x is stored as nitrite. Palladium particles were found to be partially covered with BaAl₂O₄. Depending on the structure of these particles, the propensity for nitrite formation will differ. The adsorption properties of the palladium particles depend on the degree of surface oxidation, which changes as a function of particle size and reaction conditions.

The second presentation was entitled 'NSR Catalyst Supported on an Al₂O₃/ZrO₂-TiO₂ Nano-Composite: Sulphur Resistance' and was

presented by Naoki Takahashi (Toyota Central R&D Labs, Inc, Japan). This study compared a NO_x storage and reduction (NSR) catalyst based on two different supports: Ba-K/Pt-Rh/AZT (AZT = 50 wt.% Al₂O₃, 35 wt.% ZrO₂ and 15 wt.% TiO₂) and Ba-K/Pt-Rh/A-ZT (A-ZT = physical mixture of Al₂O₃ and ZT powders, where ZT is a ZrO₂-TiO₂ solid solution). Both catalysts were exposed to a sulfur dioxide-containing oxidising atmosphere at 600°C for 30 min and cooled to 100°C under flowing nitrogen. Then, under reducing conditions, the sample was heated to 800°C. It was found that the sample based on AZT had a higher sulfur tolerance than that on A-ZT, due to a larger surface contact between Al₂O₃ and ZT compared to the physical mixture.

Four-way catalysts allow diesel vehicles to reach Euro 5 legislation while at the same time decreasing the space required by the exhaust aftertreatment system. Claire-Noelle Millet (Institut Français du Pétrole-Lyon, France) and coworkers performed a global kinetic study of four-way catalysts: Pt/Ba/ZrO₂/Al₂O₃. Their presentation, entitled 'Synthetic Gas Bench Study of a 4 Way Catalytic Converter: Catalytic Oxidation, NO_x Storage/Reduction and Impact of Soot Loading and Regeneration', followed the reactions that occur during lean and rich periods. It was found that NO_x storage appeared to be inhibited by carbon monoxide and hydrocarbon oxidation with nitrogen dioxide (NO₂) at low temperatures, possibly due to competition with carbon dioxide for storage sites produced during hydrocarbon oxidation. Soot deposition also affected the catalytic NO_x storage reaction. Continuous oxidation of soot by NO₂ induced a slower NO_x storage rate.

Sandra Capela (Instituto Superior Técnico, Lisboa, Portugal and Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie, Paris, France) and coworkers presented 'An *Operando* 5.8 GHz Microwave-Heated FT-IR Reactor Study of the NO₂-CH₄ Reaction, over a Co/Pd-HFER Catalyst'. HFER is the hydrogen form of ferrierite zeolite. The group performed two tests. The first consisted of a temperature-programmed surface reaction (TPSR), in which a reaction mixture of

500 ppm NO₂ and 5000 ppm methane (CH₄) in argon was supplied to an IR cell-reactor while increasing the temperature from 110°C to 420°C. At ~ 180°C, presence of formaldehyde was detected by the vibration of C=O at 1745 cm⁻¹. -NCO species were also detected at about 250°C. The second test used the same reaction mixture with a 5.8 Hz microwave-heated IR reactor-cell, previously stabilised at either 80°C or 200°C by conventional means. Formaldehyde was again formed as a primary product of the reaction between NO₂ and CH₄; CO was also detected at the surface of the catalyst, probably due to the partial oxidation of CH₄ assisted by nitrate-like species. The use of a microwave field means that it is possible to heat the cell very quickly, which allows results to be obtained faster than with a conventional *operando* cell.

Conclusions

The 5th International Conference on Environmental Catalysis covered a wide range of topics, with autocatalysis being of particular interest. Autocatalysis currently accounts for a large proportion of the world's pgm use and it is important to keep up to date on the latest developments potentially leading to reduced pgm use. Several pertinent topics were covered in the conference and it was interesting to compare academic research with industry requirements and knowledge, as surprising differences between the two were highlighted. The conference is a useful forum for academics and industrial representatives to meet and discuss the ongoing research in pgm use in automotive catalysis.

The conference programme and abstracts of all the papers presented are available on the conference website (21).

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