

IX International Conference on Mechanisms of Catalytic Reactions

Understanding of platinum group metal catalysts essential for new fuels and reactions

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The IX International Conference on Mechanisms of Catalytic Reactions was held in Saint Petersburg, Russia, from 22nd–25th October 2012 and was organised by the Boreskov Institute of Catalysis (BIC), one of the world's largest research centres specialising in catalysis. The Institute has been carrying out research into the understanding and elucidation of the most fundamental aspects of catalysis since 1958 and is currently headed by Professor Valentin N. Parmon. 230 participants, predominantly from academic institutions in 30 countries, applied to attend the conference. Topics included:

- (a) Catalysis from First Principles;
- (b) Mechanisms of Heterogeneous Catalysis;
- (c) Mechanisms of Homogeneous Catalysis;
- (d) Catalytic Processing of Renewables;
- (e) Electrocatalysis, Photocatalysis, Biocatalysis.

The conference included five plenary lectures, nine keynote lectures, 79 oral presentations and 110 posters. The meeting is held every three years. This is the second time the conference's official language has been English, prior to that it had been exclusively in the Russian language. With the change from Russian to English the meeting now inevitably attracts significantly more international interest and this is expected to increase by the time of the next meeting in 2015. Renowned names from the world of catalysis such as Alexis T. Bell (University of California, Berkeley, USA), Notker Rösch (Technical University, Munich, Germany), Robert Schlögl (Fritz-Haber Institute of the Max Planck Society, Berlin, Germany), Bert Weckhuysen (Netherlands Institute for Catalysis Research, Utrecht, The Netherlands) and Rutger Van Santen (Eindhoven University of Technology, The Netherlands) all took part in the organisation of the conference.

This review will discuss the presentations made in terms of those subjects which attracted the greatest attention and are of interest to the platinum group metals (pgms). Other topics including photocatalysis and biomass reforming were also discussed at the meeting; however they go beyond the scope of this review.

Methane Oxidation

Given the abundant resources of methane worldwide there was understandably a significant focus on the possible uses and clean combustion of this carbon-efficient fuel. Methane has the lowest carbon-to-hydrogen ratio of any fossil fuel, and its combustion demonstrates the smallest carbon footprint-to-energy ratio. For this reason there is already widespread use of compressed natural gas (CNG) vehicles worldwide. In North America particularly, the fuel is attractive due to its low cost of around US\$3/MMBtu (million British thermal units, approximately 1.05 GJ). In EU countries, the price is over three times higher at around US\$10/MMBtu, while in Asian countries it is in the US\$13–US\$15/MMBtu range. Representatives from Shell Global Solutions recently stated (1) that developments in 'small scale' liquid natural gas (LNG)/CNG facilities are very important for mobile applications including marine systems which are soon to be subject to emission legislation.

Methane absorbs infrared significantly more strongly than does carbon dioxide, and it is therefore a potent greenhouse gas. Emission of unused CH₄ from LNG/CNG vehicle exhausts must therefore be reduced by use of catalytic converters just as is the case for gasoline or diesel fuelled cars. However, methane is more difficult to oxidise than the majority of other hydrocarbon species. Its strong C–H bond is difficult to break catalytically, and consequently it has a high light-off temperature, with typical values of at least 400°C. Palladium is the most active metal for C–H bond activation and typically high loadings are required. However, high levels of sulfur species and water vapour are typically found in these systems, so modifiers are required to stabilise the activity of the metal over a significant catalyst lifetime. Alexander Konstantinovich Khudorozhkov (Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia) demonstrated that the addition of nickel, cobalt or platinum to a palladium/alumina catalyst stabilised its performance in a 'realistic' automotive gas stream; however Pt was only required in a concentration of 0.2% compared to a requirement of 5% for the other metals. The modifiers were also found to improve activity at lower temperatures compared to the monometallic catalyst. The nature of the Pd precursor was also found to affect stability, with the nitrate prepared catalyst being initially less active than the acetate prepared catalyst but demonstrating improved stability over time. It was shown by X-ray photoelectron spectroscopy (XPS) that deactivation by water was due to oxidation of the

Pd metal, implying that a more stable metallic phase was formed from the nitrate precursor.

Platinum catalysts may also be used for low-temperature CH₄ combustion, although they deactivate very quickly in excess oxygen due to the formation of platinum oxide. It was demonstrated by Ilya Pakharukov (Novosibirsk State University, Russia) that the Pt system demonstrates hysteresis when increasing and decreasing the Pt:O₂ ratio. By this technique the activity could be improved from 11% conversion to 80% under the same external conditions, suggesting an interesting way to improve activity without modifying the catalyst composition. However, under the higher catalyst activity regime, selectivity was sacrificed leading to significant production of carbon monoxide and hydrogen gas as well as carbon dioxide and water vapour. Production of CO would subsequently require a further downstream oxidation catalyst.

Platinum-ruthenium and nickel-copper-chromium catalysts for methane oxidation were presented by Kusman Dossuomov (Institute of Combustion Problems, Al-Farabi Kazakh National University, Almaty, Kazakhstan) and although no comparison was made to Pd catalysts it was suggested that the bimetallic catalysts facilitated the reaction due to the presence of distinct active centres in the same cluster, i.e. CH₄ activation on Pt(0) or Ni(0) and O₂ activation on Ru(0) or Cu(0). It was clear from these studies that the challenge of efficient methane oxidation remains great. Highly stable metallic alloys are required to facilitate methane combustion and, at present, high loadings of pgms are necessary for C–H bond activation. Significant improvements will be required if the increase in natural gas use is continued.

There is increasing interest in using methane more efficiently for heating purposes in domestic and larger boiler systems. Simple combustion of CH₄ leads to CO, H₂ and NO_x pollutants being formed from incomplete combustion. Catalytic combustion in air can lead to improved selectivity to CO₂ and H₂O with lower formation of NO_x as the reaction can take place at temperatures at least 100°C lower than traditional combustion. Several factors must be optimised in order to develop a feasible catalyst for this system which would survive the lifetime of the boiler. Natural gas is denatured with sulfur compounds which inevitably make it difficult to develop a stable catalyst. Stefania Specchia (Politecnico di Torino, Turin, Italy) presented results based on a Pd/BaCeO₃·2ZrO₂ catalyst prepared by solution combustion synthesis starting from metal nitrate/glycine mixtures which resulted in a spongy,

foamy textured material. A simulated sulfur ageing was carried out for up to 450 h under hydrothermal conditions at 800°C under a flow of 9% CO₂, 18% H₂O and 2% O₂ in N₂, including 200 parts per million by volume (ppmv) of SO₂ to emphasise any poisoning effect. This accelerated ageing was said to simulate two years of realistic boiler lifetime. After 150 h ageing the temperature for 50% combustion (T_{50}) of methane had shifted upwards by approximately 100°C relative to the fresh catalyst; however after 300 h ageing the light-off activity had improved by more than 60°C relative to the fresh catalyst (Figure 1) (2). This improvement was explained by the decomposition of the cerium-zirconium mixed oxide into its respective separate oxides under the action of sulfation, subsequently providing enhanced low-temperature oxidation activity. A similar effect was observed with a manganese-cerium-zirconium mixed oxide and was explained in the same way. This effect was not sustained and after the full 450 h ageing the catalyst had lost all useful activity for methane combustion and could not be regenerated.

Automotive Catalysis

Emrah Özensoy (Bilkent University, Turkey) presented a keynote lecture based on his research group's study of lean NOx trap (LNT) model systems using a combination of spectroscopic techniques (3). The presentation covered several aspects of traditional LNT components, including barium dispersion and its effect on reaction intermediates and the effect of titania on the sulfur tolerance of the overall system.

The studies primarily used single crystal Pt(111) as a support surface and barium oxide and/or TiO₂ were deposited thereon. In relation to Ba dispersion, NOx temperature programmed desorption (TPD) was carried out following prolonged exposure to NO₂ (Figure 2) (3). It was observed that there was distinct variation in the NOx desorption profiles depending on whether Ba existed as isolated islands with exposed Pt sites or as an overlayer on the Pt surface. In the former case, NO desorption occurred at temperatures at least 60°C lower than were observed for the overlayer scenario. The temperature of desorption decreased with decreasing Ba loadings, implying that NOx desorption was facilitated by either increasing the exposed Pt area or reducing the Ba particle size. There was evidence of a barium peroxide species in both cases however, which in the overlayer case appeared to be formed *via* the decomposition of NO₃²⁻ into NO₂ and O²⁻. In contrast this species appeared to be permanently present on the isolated Ba islands system. The effect of peroxides on catalyst performance was not discussed.

The TiO₂ modified supports demonstrated an overall greater resistance to sulfate formation on the surface of the catalysts, as evidenced by infrared (IR) spectroscopy; however the NOx uptake capacity was compromised by barium titanate formation. XPS evidenced that the surface Ba:Ti atomic ratio continually decreased with increasing temperature, indicating the diffusion of Ba beneath the surface. When an Al₂O₃ crystal surface was modified with TiO₂ and subsequently Ba, it was observed that the Ba dispersion correlated with that

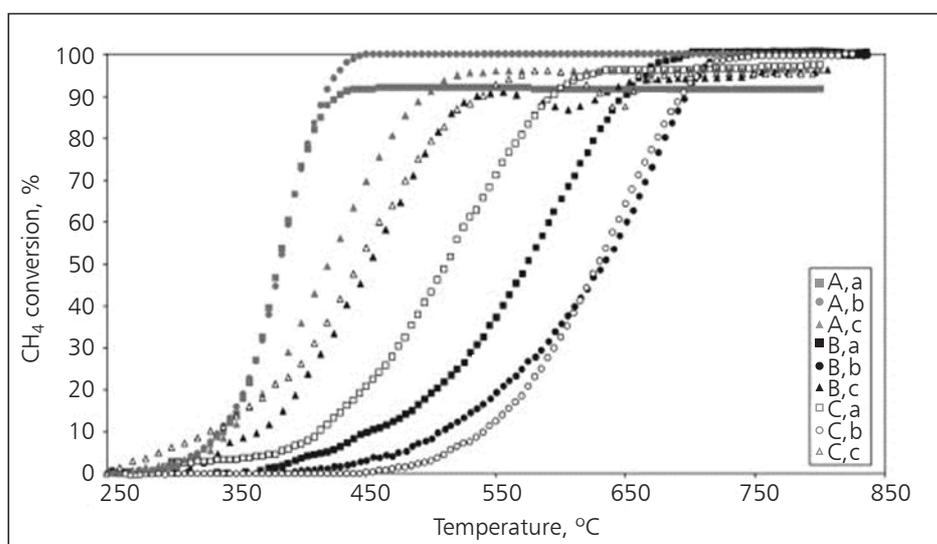


Fig. 1. Catalytic activity towards CH₄ combustion of fresh and aged PdO_x-based catalysts: A = 2%Pd/CeO₂·2ZrO₂; B = 2%Pd/LaMnO₃·2ZrO₂; C = 2%Pd/BaCeO₃·ZrO₂; a = fresh samples; b = 1 week aged samples; c = 2 weeks aged samples (2)

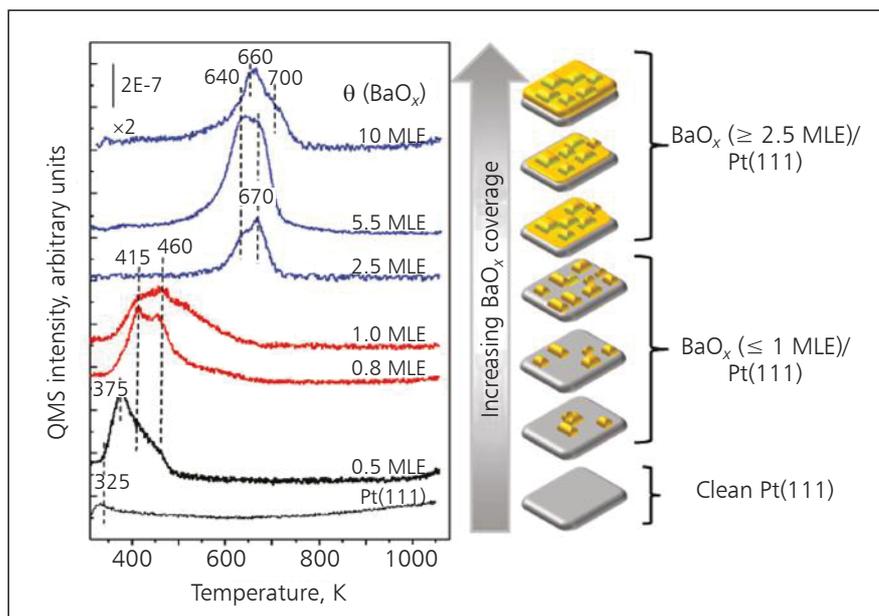


Fig. 2. NO ($m/z = 30$) channel of the TPD spectra obtained after saturation of the $BaO_x/Pt(111)$ surface having different BaO_x surface coverages with NO_2 exposure at 323K. QMS = quadrupole mass spectrometry; MLE = monolayer equivalent (Reprinted with permission from (3). Copyright 2011 American Chemical Society)

of the TiO_2 particles. Well dispersed small particles of TiO_2 encouraged the formation of the same type of BaO particles. Such correlation could prove useful to serve as a templating tool for the Ba species on the surface of alumina and perhaps other supports.

Mikhail Sergeevich Gavrilov (Boreskov Institute) presented his studies on Pd-Rh/ Al_2O_3 systems with the aim of improving the fundamental understanding of deactivation in three-way catalysts. The group have led the way in the use of an analytical technique called laser induced luminescence (LIL) for catalysis for many years with several respected publications on the subject (4, 5). Using this technique they showed that at temperatures above 800°C, Rh^{3+} diffusion into bulk Al_2O_3 occurs in these alloys, accelerating the conversion of the γ to the α phase where the rhodium is permanently encapsulated. The effect of the Pd:Rh ratio was studied and it was shown that a 4:1 Pd:Rh

ratio resulted in a sharp decrease in the encapsulation of the Rh^{3+} ions and hence significantly greater stability.

Evgeny Ivanovich Vovk (Boreskov Institute and Bilkent University) presented the results of a collaboration between the LNT group in Bilkent and the Boreskov Institute. The investigation focused on the effect of adding ceria to Ba/ Al_2O_3 LNT components. A strong Pt-Ce interaction was evidenced by Raman spectroscopy demonstrating the formation of Pt-O-Ce bonds during calcination. It was this interaction which was deemed responsible for the enhanced dispersion and thermal stability of the Pt nanoparticles. NO_x reduction with H_2 was monitored by IR spectroscopy and it was shown that during reduction bridging nitrates were partially converted to monodentate nitrates, with subsequent formation of nitrites. A mechanism for facilitated NO_x reduction with H_2 via these Pt-O-Ce sites was also proposed (Figure 3).

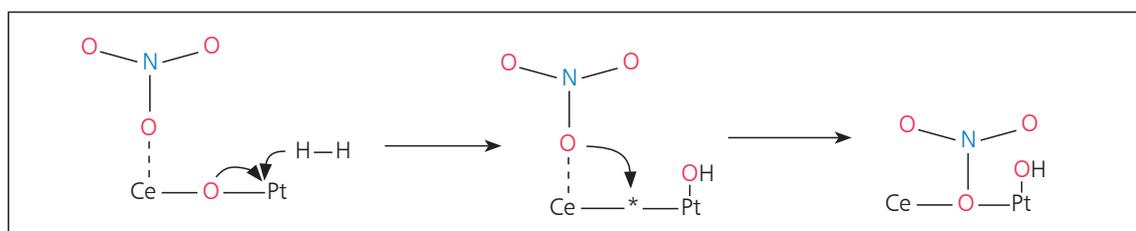


Fig. 3. Schematic representation of the route towards nitrite formation via the oxygen vacancy created in Pt-O-Ce bonds during NO_x reduction with H_2

This suggested that the oxygen vacancies formed between the Pt-Ce centres greatly decreased the barrier for nitrite formation and hence NO_x reduction. These results suggest that further investigations with *in situ* Raman spectroscopy may be able to show the disturbance of this Pt-O-Ce bond during reduction and the presence of the nitrite, although no mention was made of this possibility. The authors also concluded that ceria had no effect on total NO_x uptake of the material when supported on Al₂O₃.

Surface Science and Modelling

In mechanistic discussions there is always a significant contribution from model surfaces and computationally simulated reactions and hence there is often a concern over the 'material gap' in going from these systems to 'real' catalysts. Konstantin M. Neyman (Institutió Catalana de Recerca i Estudis Avancats (ICREA), Barcelona, Spain) presented a keynote lecture focused on surface science studies carried out on single crystal surfaces rather than model nanoparticles. He explained that in some reactions the performance of a Pt(111) slab was more different to that of a Pt₇₉ (79 atom cluster) nanoparticle than Pt would be to Ni. In this sense he cast significant doubt on the application of data obtained from single crystal models to real systems. In particular, where the formation of subsurface carbon or hydrogen is fundamental to the mechanism, such as during olefin hydrogenation on Pd, it was shown that a model cluster correctly simulates the flexibility of the surface atoms on a real system whereas the expansion of a Pd(111) model would be severely restricted and therefore a very different mechanism would be indicated. Likewise the CO oxidation activity of ceria nanoparticles can be up to twice that of bulk ceria and this was attributed to the fact that the energy required for oxygen vacancy formation depends on particle size, suggesting that several different atom cluster sizes must be considered in order to obtain 'real' information. It was further shown that the presence of Pt facilitates the creation of Ce³⁺ centres due to spillover of oxygen to the pgm and this effect is enhanced with increasing temperature.

A keynote lecture presented by Günther Rupprechter (Institute of Materials Chemistry, Vienna University of Technology, Austria) demonstrated that, with careful consideration and complementary information such as *in situ* spectroscopy and surface microscopy, simulated systems can be made to represent the 'true' situation in fine detail. In particular he described the use of Pd-Zn alloys in direct methanol fuel cells

to produce CO₂ and H₂. Cu/ZnO catalysts have been used for this reaction but deteriorate badly over time. Pd-Zn nanoparticles supported on ZnO offer the advantage of higher thermal and chemical stability than their Cu counterparts, giving rise to better long-term stability and less deactivation with time-on-stream. It has been shown that a Pd-Zn alloy at the surface is required for high selectivity and turnover frequency (TOF) but it was observed that on calcination above 600K, Zn diffuses into the bulk and the selectivity is lost. Rupprechter's group used low-energy ion scattering (LEIS) to investigate just the top layer and showed that during this diffusion, the surface alloy is maintained, but it is not sufficient by itself to provide the required selectivity. Subsequently it was determined that multilayers of Pd-Zn alloy are needed. Complimentary XPS data showed that the valence band of Pd is not changed significantly when Zn is only present in the top layer. With thicker layers, the Pd^{3d} band shifts and then H₂O can be activated, facilitating selective conversion of MeOH to CO₂ and H₂ (Figure 4) (6).

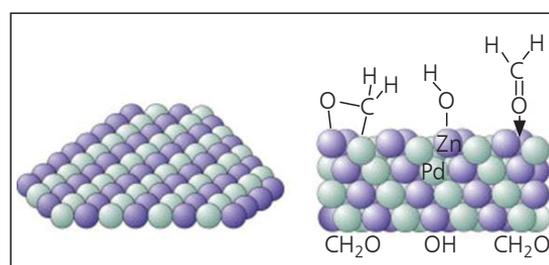


Fig. 4. (a) $p(2 \times 1)$ surface structure of the 1:1 multilayer Pd-Zn alloy on Pd(111); (b) side view of the multilayer Pd-Zn alloy with likely surface intermediates reacting toward CO₂ (6)

Conclusions

The conference, as the name suggests, presented detailed understandings of several systems and elucidated the fact that with proper mechanistic considerations it is possible to tune pgm catalysts so that long-term stability and selectivity can be achieved and in most cases, supersede those of cheaper, less active alternatives. There is significant scope for increased demand for pgm catalysts with inevitably changing fuel trends. More efficient gasoline and diesel engines require better low-temperature catalyst performance which is difficult to accomplish with base metals. The use of methane in engines or boilers

as well as methanol in fuel cells creates an even greater demand for highly active catalysts which can perform the demanding C–H bond breakage step. Likewise, to produce on-board H₂ for fuel cells *via* reforming, catalysts with good low-temperature activity and stability are paramount, and it was shown by many of the presenters at this conference that issues regarding pgm use in these systems can be overcome with better comprehension, such as that achieved for the Pd-Zn system.

As model systems become more widely used and advanced, the data which arise appear more and more relevant to 'real' systems. The use of *in situ* spectroscopy cannot be disputed as an invaluable tool in identifying the crucial sites required for reactions to proceed. There is even scope to extend the already expansive spectroscopy tools commonly used, as demonstrated by the group at the Boreskov Institute who are leading the way in the less well-known laser induced luminescence technique. This appears to be particularly useful in elucidating ageing mechanisms, even with pgm loadings as low as 0.03%.

The organising committee did a fantastic job in providing high quality presentations from worldwide institutions but it cannot be ignored how much extraordinary research is coming from the Boreskov Institute directly on a wide variety of topics. The next conference in this series will take place in 2015.

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The Reviewer



Fiona-Mairéad McKenna studied Physics and Chemistry of Advanced Materials in Trinity College Dublin, Ireland, and went on to obtain a PhD from the University of Aberdeen, UK, on the topic of acetylene hydrogenation over Pd/TiO₂ catalysts. Following a brief period using radio plasmas to deposit hydrophobic layers on carbon fibres, she moved to England to take up a position in the Emission Control Research group at Johnson Matthey Technology Centre, Sonning Common, UK. She is now a Senior Scientist working on pgm-based lean NO_x traps.