EuropaCat XI

Highlights of catalysis by pgms and base metals from the biennial congress

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1. Introduction

The 11th EuropaCat meeting was hosted in Lyon, France, on the 20th anniversary of the first meeting held in 1993 in Montpelier – bringing it back to its origin in France. The event was a large gathering of delegates in many disciplines of catalysis from across Europe and further afield. The schedule was busy, with plenary lectures and keynote talks from invited speakers, oral and poster presentations and a full programme of discussion sessions where the presentations were brief and discussion amongst the delegates was promoted. Of particular note was the high quality of the six plenary lectures. These are discussed in more detail below, followed by selected highlights on the themes of emissions control, biomass conversion, process chemistry and catalyst synthesis.

Further information on the EuropaCat XI conference, including details of the scientific programme and biographies of the invited speakers, can be found on the conference website (1).

2. Plenary Lectures

Each session began with a plenary lecture given by a notable professor in the field of catalysis.

The first presenter was Bert Weckhuysen (Utrecht University, The Netherlands) who provided an overview of *in situ* characterisation to understand issues such as catalyst coking and catalyst poisoning in fluid catalytic cracking and methanol-to-olefin processes. Combinations of techniques such as ultraviolet-visible (UV-Vis) microscopy, fluorescence, hard micro-X-ray diffraction, time-of-flight-secondary ion mass spectrometry (ToF-SIMS) and X-ray absorption near edge structure (XANES) spectroscopy using different energies managed to evidence three-dimensional (3D) dis-homogeneities in the elemental distribution of samples (zeolites in particular) and correlate them with the specific reactivity of different regions on the catalyst surface.

Ferdi Schüth (Max-Planck-Institut f. Kohlenforschung, Germany) was invited to present different preparation routes for controlled nanoparticle systems. He proposed the introduction of a size-controlled gold nanoparticle in a zirconium dioxide (ZrO_2) system

starting from a colloidal suspension with the aim of preventing the sintering of catalytically active particles. This has been extended to the formation of alloys (platinum, ruthenium) coated onto carbon shells for fuel cell catalysts and CoPt for biomass conversion. A second interesting idea was the use of ball milling to promote catalytic reactions. For example, carbon monoxide could be oxidised over cobalt(II,III) oxide (Co_3O_4) in a ball mill, but the reaction stopped when the mill was switched off. The milling was thought to generate transient sites on the Co_3O_4 which were highly active.

Marc Fontecave (Collège de France, France) gave a talk on recently developed Co and nickel-based catalysts for the (photo)catalytic production and oxidation of hydrogen. The insertion of Co into iron(III) oxide/tungsten oxide (Fe_2O_3/WO_3) catalysts for the (photo)anode was suggested. Co_3O_4 has been shown to have good storage properties but has no effect on H_2 production. Fe-Ni compounds and some Co complexes are currently used for the production of H_2. More recently, Ni complexes have been grafted onto carbon nanotubes (CNTs) and deposited on an electrode. They have also been modified to be resistant to CO; however, it has been suggested that a diimine-dioxime Co complex binding system may be more robust under acidic conditions. At the moment, other metals such as Ru and iridium are under investigation in the photosynthesis field.

During the Michel Boudart Award lecture, Jens Norskov (Stanford University, USA) gave an interesting overview on the possibilities offered by computational modelling applied to catalysis. The speaker showed how linking catalytic activity to the electronic structure and chemical composition of a material is feasible if the problem is approached correctly. The main message of the presentation lay in the importance of finding the appropriate descriptors for catalytic activity and selectivity. Once this information is available, the design and optimisation of a process becomes possible, and catalyst and process selections can be carried out on a more rational and effective basis. Examples such as ammonia synthesis were provided and illustrated these concepts well.

Enrique Iglesia (University of California, USA) gave the François Gault lecture in which he discussed the challenges presented by the conversion of molecules without a C–C bond, such as methane, methanol and dimethyl ether. Overcoming thermodynamics, the use of inexpensive oxidants, protecting species with weaker C–H bonds, inhibition of carbon and

CO_2 formation are some of the issues faced when working with these reactions. The speaker presented several examples during his talk. When considering CH_4 pyrolysis the C_2–C_{10} yield is limited by both thermodynamics and polynuclear aromatic chain growth. The C_{11+} formation can be controlled by using catalytic materials, such as Mo/H-ZSM5, that can stop chain growth. The thermodynamics and kinetics for this reaction can be improved by removing the hydrogen. Indirect paths can be used to reduce the conversion of CH_4 to the undesired CO_2 or C. The process will include chemically protected intermediates which are less reactive than methane. For example, synthesis gas is a thermodynamically protected form of activated methane. This is quite reactive and can be converted to a broad range of hydrocarbons.

The final plenary lecture, given by Dmitry Murzin (Åbo Akademi University, Finland) was a fascinating insight into the synthesis of pharmaceutical materials from naturally-occurring biomolecules. On the face of it, this may seem like an unpromising avenue, but as both classes of molecule contain high levels of functionality, significant progress can be made by appropriate selection of the starting material and efficient use of catalytic functional group transformations. A good example of material selection was the lignan 7-hydroxymatairesinol (**Figure 1(a)**). The knots found in wood are particularly rich in such lignans and since they cannot be processed into paper due to their hardness they are essentially a low value waste material. 7-hydroxymatairesinol can be converted into a number of useful products, including 7-oxomatairesinol (**Figure 1(b)**) which is has potential anticarcinogenic and antioxidative properties. This conversion was achieved using an Au-catalysed selective oxidation reaction. In these reactions, achieving excellent selectivity to the desired product is critical to applications in pharmaceutical materials.

3. Emission Control Technologies

The catalytic conversion of environmentally hazardous pollutants in automobile exhausts was a thoroughly debated topic in the conference and a wide range of research studies were presented, including theoretical modelling of materials or processes, optimisation of the current state of the art and new ideas and concepts. Those presentations presenting original ideas and newly achieved insight can have a more general appeal and have been selectively covered in this report.
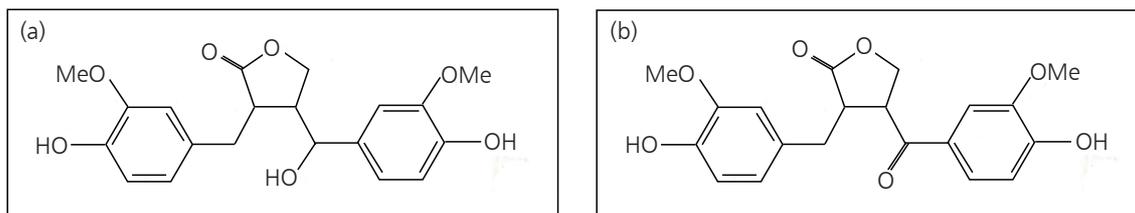
Fig. 1. The structure of: (a) 7-hydroxymatairesinol; and (b) 7-oxo-matairesinol

3.1 Selective Catalytic Reduction

Many advances have been achieved in selective catalytic reduction (SCR) technology over the years. Fe- and copper-zeolite and vanadium-based catalyst technology is still the most studied for the NH_3-SCR reaction. A keynote speaker in this area was Isabella Nova (LCCP Politecnico di Milano, Italy), who proposed a detailed and universal SCR mechanism over the standard commercial catalysts (**Figure 2**) (2). Several speakers provided information on the reaction mechanism and metal active sites in Cu-zeolites. Florian Göltl (Université de Lyon, France) suggested a new type of active site for Cu in chabazite structures (SSZ-13) by modelling the adsorption of CO to a Cu(I) site. Janos Szanyi (Pacific Northwest National Laboratory, USA) also focused his studies on Cu-SSZ13 and proposed that the formation of Cu-nitrosyl adsorbed onto SSZ-13 could be the key intermediate for the NH_3-SCR reaction. Regarding V-based catalysts, a ceria loaded Sb-V/TiO_2 catalyst was mentioned by Heon Phil Ha (KIST, South Korea). The addition of CeO_2 to the Sb-V/TiO_2 catalyst resulted in superior catalytic activity over a wide range of temperatures, higher thermal stability and improved sulfur dioxide tolerance.

The addition of H_2 to the gas feed containing nitric oxide and NH_3 has also been considered over silver/alumina catalysts. Stefanie Tamm (Haldor Topsoe) provided a global kinetic model for this reaction. Another type of SCR system uses hydrocarbons (HC) instead of NH_3 as a reductant, although at the moment these systems cannot offer the performance of NH_3-SCR systems. Asima Sultana (Advanced Industrial Science and Technology (AIST), Japan) showed that by adding NH_3 into a HC SCR over Ag/Al_2O_3 catalyst nitrogen oxides conversion could be improved.

3.2 NOx Storage-Reduction Technology

NOx can be removed from a lean gas stream by chemical adsorption onto a catalyst and subsequently reduced to N_2. Several materials were proposed for NOx storage during the conference. The commercial Pt-Ba/Al_2O_3 catalyst was mentioned by two speakers. Laura Righini (Politecnico di Milano) proposed a mechanism for the reduction by NH_3 of NOx stored on this catalyst, suggesting that the release of stored
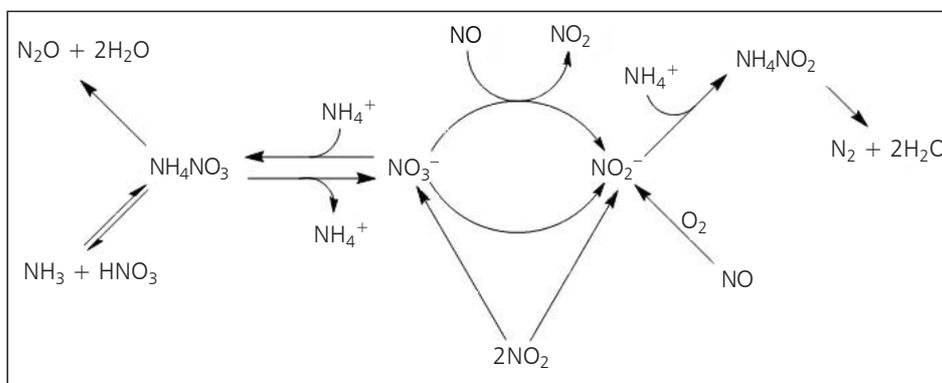

Fig. 2. A proposed mechanistic model for standard and fast NH_3-SCR reaction (2, 3)

NOx is the rate determining step for the reduction of nitrates. Beñat Pereda-Ayo (University of the Basque Country, Spain) provided evidence that the addition of Ce improves the NOx storage capabilities of Pt-Ba/Al$_2$O$_3$. The optimum Ce loading was found to be 5%. Manganese and Co-based lanthanum perovskite doped with Pd were also presented as optimum catalysts with high NOx storage capacity and good S-uptake/release properties. Merve Doğaç and Emrah Özensoy (Bilkent University, Turkey) proposed lanthanum manganite (LaMnO$_3$) perovskite as the best example, with a higher surface area compared to a Co-based equivalent.

3.3 Soot Oxidation

Marzia Casanova (University of Udine, Italy) introduced Fe/V catalysts supported on ceria-zirconia (Ce$_{0.75}$Zr$_{0.25}$O$_2$) for simultaneous activity for both SCR and soot oxidation. Obtaining a good activity for both processes remains challenging and further work seems to be needed before this concept can acquire commercial viability. Michela Klots (Centre National de la Recherche Scientifique (CNRS), Saint-Gobain, France) and Emil Obeid (Institut de Recherches sur la Catalyse et L'Environnement de Lyon (IRCELYON), France) showed how the design of a soot oxidation catalyst can be improved by exploiting knowledge of oxygen and electronic diffusion processes commonly used in designing solid state fuel cells.

By using a theoretical modelling approach, Andrzej Kotarba (Jagiellonian University, Poland) explored the key parameters of the soot oxidation process for a platinum group metal (pgm)-free soot oxidation catalyst. The interaction between the soot grains and the oxide catalyst, topology of the soot molecular framework and influence of potassium doping on the work function were investigated. For K-Fe-O systems a strong correlation was observed between the catalytic activity and the work function. The influence of potassium on the nanostructure of iron oxide, leading to tunnelled and layered forms, together with surface decoration by CeO$_2$ helped to lower the work function, resulting in a substantial increase in catalytic activity. It was proposed that enhanced electron availability is beneficial for the generation of surface reactive oxygen species that initialise the combustion process.

3.4 Methane Oxidation

Zbigniew Sojka (Jagiellonian University) presented a model for rationalising the activity of deposited oxo-clusters for methane oxidation. The crucial parameters of the proposed model are the C–H bond activation energy, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of the surface transition metal oxo-clusters and the properties of the Lewis basic support (gauged by the optical basicity, Λ), accommodating the detached proton. By optimising different parameters at the same time the authors managed to show how catalytic activity can be improved. A very interesting concept for obtaining an active and ageing-resistant CH$_4$ oxidation catalyst was presented by Paolo Fornasiero (University of Trieste, Italy). Core-shell structures of Pd encapsulated in CeO$_2$ appear to stabilise the active phase of the catalyst, not only preventing agglomeration of palladium(II) oxide (PdO) particles during the catalytic reaction, but also preventing PdO from being transformed to Pd at its usual transition temperature. The authors speculated also on the role played by hydroxyl groups on the loss of catalytic performance and how regeneration strategies impact the recovery of catalytic activity.

4. Biomass Processing

In recent years interest in the conversion of biomass into biofuels and biochemicals has increased due to growing demand for energy and more stringent environmental requirements. This interest was reflected throughout the conference. In the area of biofuels, the conversion of glycerol to form hydrogen by aqueous phase reforming (APR) was discussed by Pedro Arias (University of Basque Country). His group compared the activity of Pt/ɣ-Al$_2$O$_3$, Ni/ɣ-Al$_2$O$_3$ and PtNi/ɣ-Al$_2$O$_3$ catalysts prepared by two different methods: sol-gel and impregnation. The catalyst prepared by the sol-gel method initially showed a higher H$_2$ production but subsequent deactivation reduced the levels to the same as those of the impregnated catalysts. For these catalysts the ɣ-Al$_2$O$_3$ was converted into boehmite (ɣ-AlOOH) during APR, resulting in Ni sintering. The stability of the catalyst is a well-known problem in APR and the use of other supports such as carbon may be a solution. Another example of hydrogen production was delivered by Dimitri Bulushev (University of Limerick, Ireland). He explained that the production of hydrogen from biomass-derived formic acid at low temperatures (60ºC) could be improved by doping the Pd/C catalyst with K ions.

Several talks focused on the production of biochemicals. The production of 1,2- and 1,3-propanediol from glycerol using a Pt/WO$_3$/Al$_2$O$_3$

catalyst was examined by Sara Garcia Fernandez (University of Basque Country). The catalyst was prepared by sequential impregnation of Al_2O_3. The Lewis/Bronsted acidity could be tuned by the amount of WO_3. An increase of Lewis sites decreased the selectivity towards 1,2-propanediol. The effect of Pt was also studied, showing an increase in activity with increasing metal content.

The hydrodeoxygenation of biomass derived ketones was presented by several groups. Ivan Kozhevnikov (University of Liverpool, UK) showed high conversion of methyl isobutyl ketone (MIBK) to 2-methylpentane over Pt/H-ZSM-5 at 200ºC. At lower temperatures the use of Pt loaded on acidic heteropoly salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst for the hydrogenation of MIBK and diisobutyl ketone to the corresponding alkanes gave yields of 97%–99%. This catalyst was stable for over 16 h and little coke formation was observed. A bifunctional metal-acid catalysed pathway was identified for these catalysts. The effect of Pd and Pt particle sizes on the hydrodeoxygenation of 5-nonanone to form *n*-nonane and 5-nonanol was investigated by Irina Simakova (Boreskov Institute of Catalysis, Russia). The catalysts studied were Pd/ZrO_2 and Pt/ZrO_2. An increase in selectivity to *n*-nonane was observed with decreasing particle size.

5. Process Chemistry
5.1 Syngas Processing
Freek Kapteijn (Delft University of Technology, The Netherlands) took an engineering approach to the Fischer-Tropsch (FT) reaction, describing the effects of diffusion and H_2:CO ratio. CO diffuses more slowly than hydrogen and so the 'real' H_2:CO ratio in catalyst pores could be much higher than that supplied to the reaction. He also reported a Co/ZSM-5 catalyst which maximised the yield of the petroleum fraction made and decreased C_{21+} to almost zero. The CH_4 selectivity, however, increased from 6% to 15% when compared with a similar Co/SiO_2 catalyst, although the Co/ZSM-5 catalyst was more active. Ye Wang (Xiamen University, China) used Ru/zeolite catalysts for the same reaction. Ru nanoparticles gave lower selectivity to CH_4 and C_{2-4} than Co and using a wide pore zeolite support gave less secondary cracking to low C_n products due to a reduced residence time. A Co/TiO_2-SiC catalyst was described by Y. Liu (University of Strasbourg, France). This performed well, with C_{5+} selectivity at 90% and 50% conversion at a gas hourly space velocity (GHSV) of 2850 h^{-1}.

Processing syngas to higher olefins was also discussed by James Spivey (Louisiana State University, USA). He used a CuCo catalyst and found through modelling that a bimetallic active site gave the best performance. Ard Koeken (Utrecht University) used an Fe catalyst for the same reaction; typically for Fe-based FT, iron carbide was thought to be the active site. The formation of iron carbide was measured using a tapered element oscillating microbalance. The formation of carbon phases was also observed when the catalyst was exposed to 20 bar syngas at 350ºC, although this could be supressed by increasing the H_2/CO ratio from 1 to 2.

Conversion of syngas to alcohols using Pd and Rh catalysts was presented by Shuichi Naito (Kanagawa University, Japan). A Pd/CeO_2 catalyst gave methanol and HCs, whilst Rh/CeO_2 gave mostly hydrocarbons. Increasing Rh particle size increased hydrocarbon selectivity. Addition of lithium to either system decreased hydrocarbon formation and increased selectivity to oxygenates.

5.2 Selective Hydrogenation
Selective hydrogenation was a major theme at the conference. One of the main feedstocks investigated was alkynes which can be selectively hydrogenated to alkenes. One talk of particular interest by Daniel Lamey (Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland) described the use of supported Pd nanoparticles in the hydrogenation of acetylene to ethane in the presence of excess ethane. The nanoparticles were made by reduction of Pd salts in the presence of polymer stabilisers. Catalyst testing showed that the larger particles (10 nm) were the most active, whilst the smallest particles (2 nm) were the most selective to ethane and gave the lowest amounts of the by-product green oil. The best catalyst described was a 4 nm nanoparticle stabilised with polyvinylpyrrolidone (PVP) and using a polyethyleneimine polymer to block unselective sites on the catalyst.

Gianvito Vilé (Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland) reported silver-based catalysts for propyne hydrogenation, supported on titania or silica. Catalytic measurements suggested that splitting H_2 was the rate limiting step on these catalysts – as the hydrogen concentration increased, the rate increased. However density functional theory (DFT) calculations suggested a lower energy route which reacted molecular hydrogen directly with the alkyne (Equation (i)).

$$HC\equiv CH \xrightarrow{\text{hydrogenation}} H_2C=CH_2 \quad (i)$$

The selective hydrogenation of dimethyl oxalate to ethylene glycol was reported using Cu/SiO_2 catalysts by Y. Yuan (Xiamen University, China). The catalyst was reduced at 350ºC prior to reaction, leading to Cu(0) and Cu(I) active sites. Decoration of the catalyst with low levels of Au increased the conversion and the selectivity to ethylene glycol. Meanwhile P. Chen (Ruhr University, Germany) investigated CNTs doped with oxygen or nitrogen as supports for the hydrogenation of olefins. Addition of Pt or Pd gave an active catalyst; X-ray photoelectron spectroscopy (XPS) showed that the N- or O-dopant had an electronic impact on the precious metal.

5.3 Oxidation Catalysis

Again, a wide range of substrates, processing methods and catalysts were described for selective oxidation. Selective oxidation attracted much more attention than total oxidation, despite the relevance of the latter to pollution control. As is often the case in oxidation, a wide range of materials were reported, including pgms, Au, base metals and combinations of two or more of the above. Au catalysts were inevitably well represented. This was especially true of Au/TiO_2 which has taken the role of a benchmark oxidation catalyst, amongst the academic community if not the industrial one. Bimetallic catalysts containing Au were also popular choices, especially PdAu and CuAu on a range of supports.

One notable feature of the oxidation work presented was the range of substrates being investigated. Whilst the oxidation of CO and of benzyl alcohol could be considered as standard gas-phase and liquid-phase reactions, respectively, more complex substrates were also investigated. For example, Stefania Albonetti (Università di Bologna, Italy) and Florentina Neatu (University of Bucharest, Romania) both reported the oxidation of hydroxymethylfurfural to furandicarboxylic acid. Hydroxymethylfurfural is of interest as it can be readily synthesised from cellulose (**Figure 3**). Albonetti used Au and CuAu catalysts whilst Neatu used CuMn and FeMn, illustrating the range of materials which are active oxidation catalysts.

6. Catalyst Synthesis

A number of talks were focussed on materials synthesis rather than understanding of reactions. The main catalyst preparation technologies – impregnation, deposition and so on – were well-represented. The synthesis of catalysts using pre-formed nanoparticles is growing in popularity, as parameters such as particle size and shape and the addition of second metals can be controlled.

One talk which stood out was by Gonzalo Prieto (Utrecht University). He described a Cu/SBA-15 material which was prepared by impregnation and calcined in two ways. When calcined under N_2, the CuO particles were well dispersed through the support, whilst calcination using a 2% NO/N_2 atmosphere led to only some of the support's channels containing the particles. The catalyst calcined under nitrogen resisted sintering as the particles were further apart (**Figure 4**). The work has been reported in full elsewhere (4).

Sintering control was also discussed by Ferdi Schüth in his plenary lecture. He reported a multistep synthesis of Au nanoparticles captured in zirconia shells (**Figure 5**). The shells were porous enough to
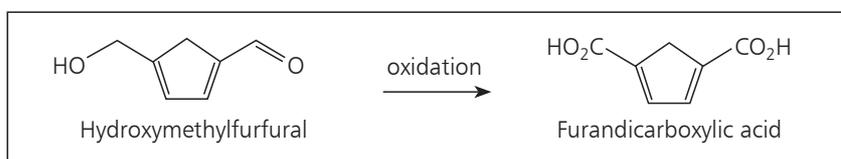
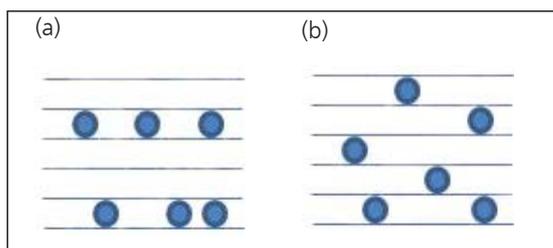Fig. 3. The oxidation of hydroxymethylfurfural to furandicarboxylic acid

Fig. 4. A Cu/SBA-15 material was calcined in two ways: (a) NO/N_2 calcined which sintered easily; and (b) N_2 calcined which resisted sintering
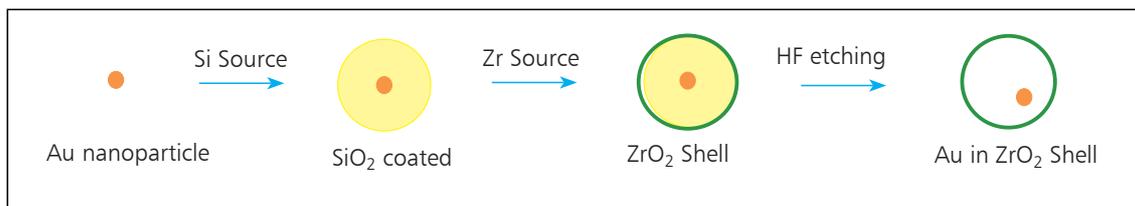
Fig. 5. The multistep synthesis of Au nanoparticles captured in ZrO$_2$ shells

allow reagents and product to diffuse in and out, but the particles were trapped and therefore could not sinter. A similar approach was described by Paolo Fornasiero, as discussed in Section 3.4.

7. Summary

Overall this EuropaCat conference was very well attended and managed in a very efficient way, despite the volume of participants. The different parallel sessions and discussion symposia (up to seven parallel sessions in the same time slot) covered almost all possible topics, established and new, relevant for the catalysis community. As a general feeling heterogeneous catalysis received more attention than homogeneous catalysis, but both were covered.

The next EuropaCat conference (EuropaCat XII) will take place in Kazan, Russia, in 2015, reaching the geographical boundaries between Europe and Asia and hopefully again bringing together a comprehensive and stimulating programme.

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The Reviewers

Silvia Alcove obtained her BSc from Rovira i Virgily University, Spain. She joined the Emission Control Technologies department at Johnson Matthey Technology Centre, Sonning Common, UK, in 2009. , She is currently undertaking an Engineering Doctorate (EngD) in collaboration with Nottingham University. Her research project mainly consists of improving the NH$_3$-SCR catalysis technology for high NOx reduction and better mercury oxidation in power plant industries.

Francesco Dolci obtained a BSc and a PhD from the University of Turin, Italy. He then moved to The Institute of Nanotechnology in Karlsruhe, Germany, and to the Joint Research Centre of the European Commission in Petten, The Netherlands for working on solid state hydrogen storage materials. In August 2012 he joined the Emission Control Research department in Johnson Matthey, working mainly on three-way catalysis development.

Peter R. Ellis gained his BSc and PhD from Durham University, UK. Following post-doctoral placements in Reading University, UK, and Queens University Belfast, UK, he joined Johnson Matthey in 2001. His current research interests are heterogeneous catalysts for a range of processes including Fischer-Tropsch, direct hydrogen peroxide synthesis and selective oxidation and also the utilisation of pre-formed nanoparticles in heterogeneous catalysis.

Cristina Estruch Bosch studied Chemistry followed by a Masters in Catalysis at the Rovira i Virgili University . She carried out her master's final project during an internship at Johnson Matthey Technology Centre, studying liquid phase methane oxidation. After that, she became a Johnson Matthey employee and continued to work in heterogeneous catalysis. She then started a PhD in collaboration with Ghent University, Belgium, within a European project in which Johnson Matthey is a project partner. She is now working on new projects involving biomass conversion and hydrogenation whilst writing up her thesis.