

Scientific Bases for the Preparation of Heterogeneous Catalysts

PGMs FEATURE IN GREATER UNDERSTANDING OF PRECURSORS AND ACTIVE SPECIES

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The 9th International Symposium on the Scientific Bases for the Preparation of Heterogeneous Catalysts took place on the campus of the Université Catholique de Louvain in Louvain-la-Neuve, Belgium, from 10th to 14th September 2006. This series of symposia was initiated in 1975 on a four-yearly cycle; Reference (1) is a review of the 1978 Symposium. In 2006 the 9th Symposium was attended by over 250 delegates, of whom 30% were from industry; about 80% of the delegates originated from Europe. The Symposium programme covered the following topics:

- Key Aspects in Catalyst Preparation
- Structured Catalysts
- Supported Metal Catalysts
- Micro- and Mesoporous Supports
- Tailored Zeolites
- Catalysis by Bases
- Catalysts for Fuel Production.

Precious metal catalysts (including platinum, palladium, ruthenium and gold) were well represented in the first four of these categories. Over the course of four days, forty-one oral contributions were heard, including seven keynote communications. In addition, more than one hundred posters were presented in two sessions.

Catalyst Preparation Issues

During the Symposium, many of the multitude of issues associated with catalyst preparation were referred to, including: the interaction of aqueous precious metal ions with metal oxide supports, controlled preparation of metal nanoparticles, and the single-step preparation of monolithic platinum group metal (pgm)-containing catalysts. Two of the major points that must be addressed in the

development of a new catalyst from bench to production are scale-up and reproducibility, topics that are conspicuous by their absence from the catalysis literature. It was therefore encouraging from an industrial perspective to see groups tackling these issues, including T. Cukic and coworkers (Leibniz Institute for Catalysis, Berlin, Germany) who assessed the preparation of Pd/Al₂O₃ hydrogenation catalysts. Several parameters affecting catalyst activity were identified and, by the use of a regression model, generic rules to reproducibly obtain an active catalyst were defined. The key preparation parameter was identified as the ratio between the amount of impregnation solution and the volume of support.

In addition to this work, R. Prada Silvy and coworkers (Université Catholique de Louvain, Belgium) presented a systematic investigation of the scale-up of a propane ammoxidation catalyst prepared by coprecipitation of vanadium on alumina. They successfully showed the need to generate a thorough understanding of the chemistry involved and to employ flexible catalyst preparation strategies in order to produce larger amounts.

Structured Catalysts

Industrial heterogeneous catalysts tend to be formed as extrudates or from slurries coated onto monoliths or foams. M. Yates and coworkers (Instituto de Catálisis y Petroleoquímica, Spain) presented a simple single-step process for the production of dispersed pgm nanoparticles on formed ceramic supports with customised textural properties. This was achieved by incorporating activated carbon into a pgm-doped mixture; for example, one of alumina/ α -sepiolite (SiO₂, MgO,

Al₂O₃, CaO). The porosity of the product was such that the pgm was still accessible to the reactants, in this case toluene for combustion. This obviated the washcoating step associated with conventional monolith-supported catalysts.

The issue of supports was also raised by M. V. Twigg (Johnson Matthey, U.K.) and J. T. Richardson (University of Houston, U.S.A.), who challenged the delegates with the question of why structured ceramic foams were not more commonly used as catalyst supports. The BET surface areas of ceramic foams can be increased by washcoating, and they have additional useful properties, including a ten-fold decrease in pressure drop compared to pellets, and coefficients of 1D and 2D heat transfer five times higher. The examples selected to highlight the usefulness of catalytic metals loaded or washcoated onto ceramic foams were: silver for ethylene epoxidation, ruthenium for CO₂ methanation and cobalt for Fischer-Tropsch catalysis.

Supported Metal Catalysts

The significance of support morphology was illustrated by a talk on Au/TiO₂ catalysts by V. Caps and coworkers (Institut de Recherches sur la Catalyse, France) who compared the capability of low surface area, poorly functionalised titania to stabilise the formation of small gold particles prepared by the deposition-precipitation method, with the tendency of more highly functionalised titania or titania-doped surfaces to cause agglomeration. An alternative method of controlling particle sizes in platinum, palladium, ruthenium and bimetallic palladium-platinum catalysts was proposed by E. Sulman and coworkers (Tver Technical University, Russia). By this method the pgm precursor was impregnated into hypercrosslinked polystyrene granules where controlled nanoparticle growth can occur in the cavities and pores of the polymer matrix. Reduction with an aqueous reducing agent gave 1–2 nm metal particles which were active in selective oxidation of monosaccharides.

On a more fundamental level, several authors presented work highlighting the importance of comprehending the interaction between precious

metal complexes and metal oxide supports in aqueous solution, i.e. the types of systems associated with catalyst preparation by impregnation and deposition-precipitation. In particular, J. R. Regalbuto and coworkers (University of Illinois, U.S.A.) illustrated in their presentation entitled ‘Simple, scientific syntheses with common catalyst precursors’ that carrying out impregnation at the pH which maximises the electrostatic interaction between the substrate and adsorbing metal complex (of platinum, ruthenium, copper or cobalt) can yield catalysts with a high loading of ultra-small metal particles. This method claims to minimise the contamination of the catalyst by unwanted precursor counterions such as chloride, which may remain if impregnation is carried out under non-optimal conditions. This presentation generated much interest and in the discussion session it was revealed that this approach is applicable to surfaces of relatively low surface functionality, e.g. α -Al₂O₃ shaped catalyst carriers developed for high crush resistance.

The support interactions of pgm precursors also featured in the talk on catalyst preparation by K. Bourikas and coworkers (University of Patras, Greece) who outlined the possible modes of interfacial deposition – electrostatic adsorption and adsorption through coordinative or hydrogen bonding – and illustrated experimental methodologies by which it was possible to establish the predominant mode. It was shown that [PtCl₆]²⁻ and [Pt(NH₃)₄]²⁺ adsorb electrostatically, in contrast to oxo-ions such as [Co(H₂O)₆]²⁺ in which there is inner-sphere coordination. The principles of pH-optimised adsorption were also applied by A. Deffernez (Université Catholique de Louvain, Belgium) to depositing palladium and gold-palladium on carbon by determining the point of zero charge of the carbon support, and determining the precious metal species present across the pH range.

The coordination chemistry theme was continued by S. L. Soled and colleagues (ExxonMobil Research and Engineering Co, U.S.A.) who reported on the use of triethanolamine (TEA) as an impregnation aid in preparing Ru/SiO₂ catalysts from ruthenium nitrosyl nitrate. The multiple

functionality of TEA caused it to bind both to the labile ruthenium precursor and to the hydroxyl groups of the silica support. Partial decomposition then gave a catalyst in which the ruthenium crystals were distributed homogeneously on the silica, since migration of RuO₂ was hindered. Organometallic metal carbonyl Ru₅Pt clusters were used as precursors with mesoporous silica supports by O. Muraza and coworkers (Eindhoven University of Technology, The Netherlands). On decarbonylation by heating, 1.4 nm bimetallic nanoparticles were obtained, a decomposition process which left the mesoporous silica intact.

Innovations in Catalyst Preparation

The Symposium featured several talks demonstrating novel catalyst preparation techniques. G. M. Veith and coworkers (Oak Ridge National Laboratory, U.S.A.) introduced the uses of magnetron sputtering for preparing precious metal catalysts, illustrated by Au/WO₃, Au/C and Pt/C systems. This technique relies on physical vapour deposition of an atomic metal flux onto a constantly tumbling support material, with the metal loading increasing linearly with time. High-purity catalysts with narrow particle size distributions were accessible by this route, and good adhesion was observed, even with supports such as SiO₂ and WO₃ which are less accessible using chemical deposition methods. Gold catalysts were also the focus of the talk by J. K. Bartley and colleagues (Cardiff University, U.K.) who discussed a supercritical carbon dioxide precipitant technique being used to prepare titania supports for gold catalysts. Using this technique, supercritical CO₂ is added to the support precursor, TiO(acac)₂, in methanol, causing it to precipitate as small, amorphous particles with a high surface area (160 m² g⁻¹). These are then calcined to give a TiO₂ support. In CO oxidation, Au/TiO₂ prepared by the supercritical route gave 100% conversion, as compared with only 10% for the untreated analogue.

F. Cambier and coworkers (Centre of Research for Industries, Belgium) presented a method of catalyst production using an inductive atmospheric plasma torch, which is currently being used to

prepare nanopowders, but which they intend using to generate Al₂O₃, ZrO₂ or SiO₂ supported ppm catalysts. A supported ionic liquid catalyst (SILCA) featured in a talk by P. Mäki-Arvela (Åbo Akademi University, Finland), who demonstrated that partial hydrogenation of citral to citronellal can be achieved using [N-butyl-4-methylpyridinium][tetrafluoroborate] and Pd(II) acetylacetonate on active charcoal in a three-phase reaction.

Conclusion

This is a uniquely relevant series of Symposia for anyone in the field of heterogeneous catalysis, and continues to highlight the pivotal role played by pgms in this area. Despite the diversity of the research presented, one of the underlying themes to emerge from the discussions was the importance of gaining a more fundamental understanding of the base metal and precious metal species used as catalyst precursors and of the active metallic species involved in catalysis. For further information readers are directed to the published proceedings (2).

References

- 1 P. A. Sermon, *Platinum Metals Rev.*, 1979, 23, (1), 14
- 2 "Scientific Bases for the Preparation of Heterogeneous Catalysts", Proceedings of the 9th International Symposium, Louvain-la-Neuve, Belgium, 10th–14th September, 2006, eds. E. M. Gaigneaux, M. Devillers, D. E. De Vos, S. Hermans, P. A. Jacobs, J. A. Martens and P. Ruiz, Studies in Surface Science and Catalysis, No. 162, Elsevier, Amsterdam, The Netherlands, 2006

The Reviewers



After gaining a Ph.D. at the University of Reading, Mark Feaviour joined Johnson Matthey in 1999, and worked for six years carrying out research on the preparation of steam reforming, water gas shift, and other fuel processing catalysts. He now works in the Core Science Coatings Group.



After three years as a lecturer at Trinity College in Dublin, Emma Schofield moved to Johnson Matthey in the U.K., where she specialises in developing new synthetic routes to heterogeneous catalysts.