

Techniques for Catalyst Manufacture

REVIEW OF A ROYAL SOCIETY OF CHEMISTRY MEETING ON APPLIED CATALYSIS

The Industrial Affairs Division of the RSC (Applied Catalysis Group) held a meeting on "Techniques of Catalyst Manufacture" at the Advantica (formerly BG Technology) Research and Technology Centre, in Loughborough, U.K., on 8th November 2000. Delegates were introduced to Advantica's activities in a diverse range of areas, which included the development of natural gas powered vehicles, high-temperature solid oxide fuel cells (SOFCs) and molten carbonate fuel cells as well as catalytic technologies for the functionalisation of methane through partial oxidation, steam reforming and Fischer-Tropsch synthesis.

Industrial Catalyst Preparations

This introduction provided the background for the presentation by Andrew Dicks (Advantica, Loughborough) on the preparation of industrially relevant catalysts by coprecipitation, especially for the activation of methane. Much effort has been directed at the preparation of Al_2O_3 -supported nickel catalysts by coprecipitation, for reactions such as steam reforming and catalytic partial oxidation (CPO). Latterly, supported platinum group metals catalysts, such as Al_2O_3 -supported palladium and platinum in addition to TiO_2 -supported rhodium, have found favour for CPO due to their enhanced rates of reaction and resistance to coke formation. The technique of homogeneous coprecipitation, where hydrolysis of urea at 120°C results in uniform release of OH^- groups throughout the catalyst precursor slurry, has been employed to produce a supported-ruthenium ($\text{Ru}/\text{ZnO}-\text{Al}_2\text{O}_3$) Fischer-Tropsch catalyst. The BET surface area of the final material was shown to be strongly dependent on the $\text{ZnO}:\text{Al}_2\text{O}_3$ ratio. The greatest surface area was obtained with the highest Al_2O_3 content.

These preparation techniques have formed the basis for the catalyst which is used to internally reform CH_4 in a SOFC. More recently, the anode exhaust from a SOFC has been converted by means of shift reactors and a final preferential ox-

idation (PROX) unit to provide a hydrogen-rich feed to a proton exchange membrane (PEM) fuel cell. A SOFC-PEM hybrid system of this type with an electrical output of 500 kW was claimed to be 61 per cent efficient.

Metal Precursors and Catalyst Carriers

Very convincing evidence highlighting the pitfalls associated with deposition of metal precursors on preformed supports was given by Robert Terorde (Engelhard, The Netherlands). While his presentation dealt exclusively with the introduction of iron into a preformed SiO_2 support, it is clear that the lessons learnt would be applicable to the deposition of other metals onto other supports and it would be possible to extend this work to help optimise platinum group metal distributions. He claimed that the final distribution of the metal oxide throughout the support was influenced by properties of the metal precursor, such as its interaction with the support surface, its crystallisation behaviour and the viscosity of the salt solution. The speed of the drying process was also found to be critical. Egg-shell distributions of the metal salts were formed when solutions of strongly crystallising salts, which do not become viscous during the drying step, for example $\text{K}_3\text{Fe}(\text{CN})_6$, were used in the initial impregnation. The microscopic effect of an egg-shell distribution was shown to be the growth of large metal particles.

Addition of a viscosity-increasing agent such as hydroxyethyl cellulose to the iron-containing impregnating solution had the effect of generating a uniform distribution of the deposited metal. It was also shown that an iron precursor, such as an aqueous solution of $\text{NH}_4[\text{Fe}^{\text{III}}(\text{OH})(\text{citrate})]$, will become very viscous when heated, resulting in a very uniform distribution of the metal salt throughout the support pore structure. These data are also applicable to the deposition of platinum group metals on preformed supports and this work may be of value in catalysis for the petrochemical industry.

Andrew Holt (Catal International, Sheffield)

explained the equipment required and process variables associated with producing catalyst carriers in high volume by the cost-effective technique of extrusion. Extruder designs and therefore the shape of the extrudates depend on the material to be extruded. Catalyst supports used for reactions such as hydrotreating are produced using a twin contra-rotating screw. The wet metal oxide pastes, used to make the supports, are normally very abrasive and possess poor flow characteristics. However, in the extrusion process the precursor paste ('dough') needs to possess sufficient plasticity, lubricity and particulate cohesion to pass through a small orifice. In order to achieve this the support powder, for example Al_2O_3 , is normally treated with dilute HNO_3 to help peptisation. The pH of this peptisation step has a large influence on the pore size distribution of the final material. At low pH (< 2) microporous materials could be produced. The plasticity and particulate cohesion of the 'dough' can be controlled by the introduction of one or more of a range of organic modifiers from wood flour to methyl cellulose. Addition of wood flour has the effect producing large voids in the extrudate upon calcination. This can lead to improved gas flow characteristics. Lubricity additives, such as graphite or stearates, can also be introduced.

Progress in Techniques for Catalyst Manufacture

Professor Friedrich Schmidt (Sud-Chemie, Germany) reviewed recent progress in techniques for catalyst manufacture. Large scale catalyst preparation is strongly driven by cost. It is, therefore, necessary to demonstrate a very significant performance benefit before it is viable for industry to make the investment to adopt a new technique for manufacture of a particular catalyst.

If organic solvents or organometallic precursors are to be used in precipitation or sol-gel preparations, significant plant modifications will be required. Such modifications, dictated by safety, environmental and engineering considerations, have prevented large-scale adaptation of these techniques for industrial catalyst manufacture. Exceptions include the manufacture of titanium

silicalite (TS-1) and the Condea process for the manufacture of high purity Al_2O_3 from aluminium alkoxides. Sol-gel preparations are not restricted to stoichiometric compositions and can result in better control of the porosity of the final material. Professor Schmidt also suggested that use of supercritical CO_2 has the potential to greatly simplify solvent removal.

The conference organiser Barry Nay (BP Chemicals, Sunbury-on-Thames) thanked all the participants at the well-attended meeting and suggested that the next meeting of the RSC Applied Catalysis Group may take place outside Britain. Further information on events organised by the RSC Industrial Affairs Division, Applied Catalysis Group are obtainable from nayb@bp.com.

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Heterogenised Rhodium Catalyst

The search for a clean benign replacement for the industrial synthesis of amines (*N*-phenyl-*N'*-isopropyl-*p*-phenyldiamine and *N,N'*-di(1,4-dimethylpentyl)-*p*-phenyldiamine) used as antioxidants in vulcanising rubber, additives in biomimetic sensors and anticorrosive agents, has resulted in a one-pot synthesis using a platinum/carbon-based catalyst. However, this synthesis is not reproducible.

Now researchers at the Universitat Rovira i Virgili, Spain, have developed a reproducible one-pot synthesis to convert a primary amine into a secondary amine by imine intermediate formation (R. Margalef-Català, C. Claver, P. Salagre and E. Fernández, *Tetrahedron Lett.*, 2000, 41, (34), 6583–6588). The catalyst was prepared by immobilising preformed $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{BF}_4$ and its iridium analogue on montmorillonite K10. The rhodium catalyst had the higher activity. The reaction is mild and solvent-free and the catalyst can be easily recovered and reused.