

# The Horizons of Platinum Metals Catalysis

A SELECTIVE REVIEW OF THE 17TH NORTH AMERICAN CATALYSIS SOCIETY MEETING IN TORONTO

The 17th meeting of the North American Catalysis Society, organised by the Catalysis Division of the Chemical Institute of Canada, took place in Toronto, from 3rd to 8th June. Held at the Westin Harbour Castle Hotel and Conference Centre on the shores of Lake Ontario, it attracted over 1000 scientists from many backgrounds and countries. The meeting displayed the wide range of areas in which catalysis has a major role. This review of platinum group metals (pgms)-work reflects the interests of the reporters.

## Fuel Cell Catalysis

Platinum alloys continue to be widely used in proton exchange membrane fuel cells and T. R. Ralph (Johnson Matthey, U.K.) reviewed ongoing work. At the cathode, Mn, Fe or Cr alloyed with Pt increase the cell potential by 25 mV over Pt alone. At the anode, Pt-Ru is favoured as it offers resistance to CO and CO<sub>2</sub> poisoning. Other additions are being investigated.

Fuel processors for fuel cells were widely discussed. While many investigation of water gas shift reactors used non-pgm catalysts, S. L. Swartz and coworkers (NexTech Materials, U.S.A.) described the use of Pt deposited onto nanoscale ceria wash-coated on monoliths. These reactors have improved performance above 300°C.

## Three-Way Catalysts for Automobiles

Several presentations described investigations of three-way catalysts (TWCs) for automobiles. H. W. Jen and coworkers (Ford, U.S.A.) examined the effect of pretreatment conditions on the oxygen storage capacity (OSC) of palladium and rhodium model catalysts using Ce<sub>0.63</sub>Zr<sub>0.37</sub>O<sub>2</sub> as the support material. High temperature, lean conditions resulted in Pd catalysts with high OSC, while the OSC for Rh catalysts was better after high temperature, rich conditions. Kinetic studies of CO oxidation were reported by C. Thomas (Université Pierre et Marie Curie, France). Rh<sup>x+</sup>/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> had lower activation energy, lower CO light-off, and

higher turnover rates compared to Rh<sup>0</sup>/SiO<sub>2</sub>.

TWC deactivation was also studied. R. W. McCabe and colleagues (Ford, U.S.A.) characterised phosphorus poisoning of 100,000-mile road-aged catalysts. Phosphorus was deposited on the front face of the monolith either as an overlayer containing phosphates of Mg, Ca or Zn or within the washcoat as phosphates of Ce or Al. The poisoning effect on catalyst activity could be reversed by washing the catalyst with oxalic acid. A. K. Datye (University of New Mexico, U.S.A.) investigated Pd sintering of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts after exposure to high temperature. TEM results showed that regardless of the Pd loading, the sintered Pd particles reached similar sizes. Also, the transformation of  $\theta$ -alumina to  $\alpha$ -alumina played a significant role in the sintering process. A poster by P. J. Andersen and colleagues (Johnson Matthey, U.S.A.) showed the use of large amounts of Ni in Pd-only TWC to suppress hydrogen sulfide (H<sub>2</sub>S) emissions. The Ni was placed in a layer separate from Pd in order to avoid Pd deactivation.

## Lean NO<sub>x</sub> Catalysis

Supported pgm catalysts are active at low temperatures for the selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) by hydrocarbons. They also show reasonable tolerance to both water vapour and sulfur dioxide. Although these catalysts have rather narrow temperature windows, and relatively poor selectivity toward nitrogen, they are still being considered for lean-burn or diesel exhaust treatment applications. Several talks covered this topic, with most focusing on catalyst modification by adding a second metal ion to form a bimetallic system. T. J. Gardner and colleagues (Sandia National Laboratories, U.S.A.) reported their work on Pt-CuO catalysts supported on SiO<sub>2</sub>-doped hydrous titanium oxides. The addition of CuO lowered the NO<sub>x</sub> reduction light-off temperature but did not affect the activity on the high temperature side, thus widening the temperature window. However, adding CuO had no effect on

the selectivity to N<sub>2</sub>. C. Mihut and coworkers (University of South Carolina, U.S.A.) presented work on Pt-Au catalysts prepared from organo-bimetallic cluster precursors. In the cluster-derived catalysts, Pt and Au were intimately mixed. With the Au modifier, catalyst selectivity toward N<sub>2</sub> increased from 45 to 80 per cent, and the maximum temperature of NO<sub>x</sub> reduction shifted from 300 to 450°C. A Ce-Pd/mordenite (HMOR) system was described by L. Cordoba and coworkers (Universidad de Antioquia, Colombia). The Ce suppressed Pd agglomeration, while Pd improved the NO adsorption capacity of Ce/HMOR. Under test conditions, no N<sub>2</sub>O, NH<sub>3</sub> or CO was formed.

### Gas Turbine Catalysts

Supported PdO catalysts are a key feature in catalytic combustors for gas turbines. G. Groppi and colleagues (Politecnico di Milano, Italy) characterised the PdO active/Pd inactive transformation in this system and proposed that Pd<sup>0</sup> oxidation occurs in successive steps: Pd<sup>0</sup> is first covered with an oxide layer, then converted to bulk PdO. The oxide layer was more active than bulk PdO for the combustion reaction. This explains the activity hysteresis seen in the methane (CH<sub>4</sub>) + O<sub>2</sub> reaction.

### Catalytic Reforming

Pt-Re catalysts are widely used in catalytic reforming of paraffins and naphthenes. J. T. Richardson and coworkers (University of Houston, U.S.A.) reviewed past studies, especially theories proposed to explain how Re modifies the catalytic properties of Pt. He also presented recent work by his group on Pt-Re catalysts for CH<sub>4</sub> reforming with CO<sub>2</sub>. On adding Re catalyst stability improved. The Re may dissociate the CO<sub>2</sub> at high temperature and the released oxygen will then remove the C deposits which may otherwise deactivate the Pt.

### Gas-Liquid Reactions

Various pgm catalysts coated on monoliths have found novel use in gas-liquid reactions. F. J. Waller and coworkers (Air Products and Chemicals, U.S.A.) studied the hydrogenation of nitrobenzene to aniline and the acid-catalysed polymerisation of furfuryl alcohol, as model reactions over monoliths.

Reactor design is critical for gas-liquid interactions, but hydrogenation rates for catalysts on monoliths were higher than the corresponding slurry catalysts.

### Catalyst Characterisation and Sulfur Poisoning

Characterising Pt catalysts is important to understand activity and deactivation, and synchrotron techniques are becoming more widely used. J. T. Miller and colleagues (BP, U.S.A.) used EXAFS to correlate the CH<sub>4</sub> oxidation activity of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts prepared from Cl-containing or Cl-free Pt precursors. The Cl-free catalyst consisted of small metallic particles with exposed Pt atoms, while the Cl-poisoned catalysts had Pt-O or Pt-Cl bonds on their surfaces. Metal-support interactions were also studied in Pt/zeolite catalysts during H<sub>2</sub> adsorption using NEXAFS. As the charge on the oxide support became more positive, the binding energy of the Pt valence orbitals increased. The shift of valence orbitals makes molecular bonding with Pt more favourable and corresponds to measured TOF.

Sulfur poisoning and regeneration is always an issue for pgm catalysts. A. Amberntsson and colleagues (Chalmers University of Technology, Sweden) reported on the effect of conditions and type of pgm on the poisoning and regeneration of a NO<sub>x</sub> storage catalyst. They showed that poisoning evolves throughout the entire storage-reduction cycle. Rh is more sensitive to S poisoning than Pt under oxidising conditions but is easier to regenerate under reducing conditions.

A. V. K. Westwood and coworkers (University of Leeds, U.K.) mentioned poisoning effects on catalysts used for CH<sub>4</sub> combustion. The catalyst activity: Pd > Rh > Pt did not change when poisoned with H<sub>2</sub>S, or after regeneration. However, when poisoned with S-carbon compounds, the activity ranking changed to Rh > Pd > Pt, before and after regeneration. Resistance to both poisons, and ease of catalyst regeneration is Rh > Pd > Pt.

The next 18th NACS meeting in the series will be held in June 2003 in Cancun, Mexico.

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