

# Limiting Environmental Pollutants

**Catalytic Control of Air Pollution: Mobile and Stationary Sources ACS Symposium Series 495**

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To improve the quality of the air has become a growing concern around the world. The use of catalysis to limit the amount of pollution released into the atmosphere is by now well established, and the importance of platinum group metals in this activity is fully recognised. Nevertheless, as the regulations are progressively tightened, there is an increasing need to maximise the efficiency of existing catalysts and to develop new catalysts.

This volume encapsulates papers from a symposium, sponsored by the Division of Colloid and Surface Chemistry of the American Chemical Society, held in New York, in 1991. The first part of the volume deals with emission control for mobile sources, while the second is devoted to stationary sources. With few exceptions, the papers contained describe investigations based on platinum group metal catalysts.

The first section begins with a review by J. C. Summers and R. G. Silver of Allied Signal on legislation in the U.S. and elsewhere and the catalyst technologies which are being investigated to meet the legislative requirements. This theme is expanded in a subsequent paper by J. C. Summers, W. B. Williamson and J. A. Scaparo of Allied Signal, who discuss specific catalyst technologies based on palladium.

The beneficial effects of ceria on platinum-based catalysts is reported by J. G. Nunan, R. G. Silver of Allied Signal and S. A. Bradley of UOP, who contribute to the by now substantial literature on this subject. They state that after reduction in hydrogen or rich exhaust gas there appears to be a promotional effect of cerium which extends beyond oxygen storage effects, water gas shift promotion and platinum dispersion. This effect relates to a platinum-cerium interaction and the synergistic reduction of platinum and surface cerium.

Topics of much current interest are the plat-

inum group metal interaction with support materials and the interaction of nitric oxide with platinum group metals. These factors, and the influence of metal particle size, are the subject of a paper by G. Zafiris, S. I. Roberts and R. J. Gorte of the University of Pennsylvania, who have examined nitric oxide adsorption on rhodium supported on zirconia and  $\alpha$ -alumina, and platinum on ceria,  $\alpha$ -alumina and zinc oxide. For rhodium, nitric oxide reduction appears to be structure sensitive due to changes in nitrogen desorption rates; whereas, for platinum, nitric oxide decomposition limits reaction rates and this may be affected by metal-support interaction. The use of steady state isotopic transient kinetic analysis in the study of carbon monoxide oxidation and the carbon monoxide-nitric oxide reaction of a platinum supported on rhodium three-way catalyst is reported by R. Oukaci, D. G. Blackmond, J. G. Goodwin and G. R. Gallaher from the University of Pittsburgh. They suggest that the distribution of sites for carbon dioxide formation is bimodal, with less than 30 per cent of the active sites accounting for 75 per cent of the catalyst activity. Since a similar bimodal activity was also found for rhodium supported on  $\text{La}_2\text{O}_3$ , the authors conclude that low activity (but more stable) sites could be associated with a metal-rare earth interaction.

The oxidation of hydrocarbons and oxygenated compounds commonly found in exhaust is examined by J. M. Bart, M. F. Prigent of Institut Français du Pétrole and A. Pentenero of the Université de Nancy. They find that as the oxygen concentration is increased the rate of removal of hydrocarbon is dependent upon the hydrocarbon species. In the case of oxygenated compounds, the extent of removal appears to be independent of the number of carbon atoms in the molecule. Addition of sulphur dioxide into the gas mix generally inhibits conversion of

hydrocarbons but, under stoichiometric and lean conditions, hydrocarbons with a carbon number less than 3 show increased activity.

Natural gas is being considered as an alternative fuel for automotive applications in many parts of the world. However, methane is a powerful greenhouse gas, so emissions of unburnt methane are of particular concern. The paper by S. H. Oh, P. J. Mitchell and R. M. Siewert, from General Motors, examines the relative performance of platinum, palladium and rhodium on alumina for methane oxidation in a simulated exhaust gas. The results show the order of activity to be palladium > rhodium > platinum, and that optimum performance is obtained slightly rich of stoichiometry. The authors consider some of the mechanistic implications of these results, and conclude that high surface concentrations of oxygen inhibit methane adsorption and reaction, and that water gas shift reactions are unimportant in the system, except possibly for rhodium catalysts.

The second section of this volume deals with pollution control of stationary sources and also begins with a review by J. C. Summers, J. E. Sawyer and A. C. Frost of Allied Signal, who

examine the implications of the U.S. 1990 Clean Air Act. Two other papers in this section deal with laboratory investigations of the catalytic oxidation of trichloroethylene (TCE) over platinum and PdO on alumina. TCE is typical of a range of widely used industrial solvents. The principal products over both catalysts are carbon dioxide, chlorine and hydrogen chloride; the production of chlorine arises from each TCE molecule having a hydrogen:chlorine ratio of 1:3. However, if water or methane is introduced into the reaction system, sufficient hydrogen is provided to increase the proportion of hydrogen chloride, with a corresponding reduction in chlorine. In addition, these reductants lower the proportion of the intermediate tetrachloroethylene appearing in the gas stream.

Thus the emphasis on catalysis, particularly using the platinum group metals, to control gaseous emissions continues to be very great. The full understanding of how these metals can be promoted to achieve extra performance remains elusive. By sponsoring and publishing symposia of this kind a gradual understanding is being built up.

D.E.W.

## Nitrate and Nitrite Removal from Drinking Water

Nitrate contamination of ground water in intensively farmed arable areas may result from the over application of natural or artificial fertilisers. As nitrate can constitute a health risk to humans such contamination must be minimised and the European Community has stipulated that the nitrate concentration in drinking water should not exceed 50 mg/l, and in fact it recommends significantly lower levels. Although a number of different processes are available for the removal of nitrate from water they have disadvantages; now researchers in Germany are working to develop a catalytic process to reduce both nitrate and nitrite with hydrogen (S. Hörold, K.-D. Vorlop, T. Tacke and M. Sell, "Development of Catalysts for a Selective Nitrate and Nitrite Removal from Drinking Water", *Catal. Today*, 1993, 17, (1-2), 21-30).

Nitrite, which is more toxic than nitrate, can be reduced to nitrogen by the use of a number of supported platinum metals hydrogenation catalysts. The removal of nitrate can be achieved by first reducing it to nitrite, which is then

reduced to gaseous nitrogen and/or dissolved ammonia, the latter being undesirable in drinking water. The type of hydrogenation catalyst, activated by the addition of a second metal, determines the reduction products. Of the hydrogenation catalysts tested for the reduction of nitrite, 5 per cent platinum on carbon displayed the highest activity but resulted in substantial ammonia formation; with 5 per cent palladium on alumina the ammonia was significantly less. Palladium-copper bimetallic catalysts were studied for nitrate reduction, and optimum activity and selectivity were achieved with a palladium:copper ratio of 4:1.

A combination of suitable platinum metals nitrate and nitrite reducing catalysts, and strict hydrogen limitation, has enabled the complete removal of 100 mg/l nitrate to be achieved while the formation of ammonia is kept below 0.5 mg/l, which is the level permitted in drinking water. Thus it is suggested that, when optimised, bimetallic catalysts could possibly be applied to the purification of drinking water.