durability of catalysts is improving and enhancements in light-off temperature are being achieved with new catalyst formulations. It is likely that platinum and rhodium will continue to be the primary ingredients for controlling carbon monoxide and nitrogen oxides and that palladium will continue to emerge as an important contributor to control hydrocarbon emissions.

New horizons are now being opened for controlling nitrogen oxides under lean operating conditions, and it is felt that the most likely market for such catalyst systems will be the lean burn diesel engine, and possibly the lean burn two-stroke engine. Both copper and platinum catalysts are under development, but problems with the durability of such catalyst systems remain to be resolved. However, this area gives the most challenging and intriguing possibilities for the design of future emission systems.

References

1 B. J. Cooper and S. A. Roth, *Platinum Metals Rev.*, 1991, **35**, (4), 178–187

Nitric Oxide Catalysis as Applied to Vehicles

A recent review paper by Kathleen C. Taylor of General Motors covers the technical literature on nitrogen oxides automotive emission control published during the period 1982–1991 (*Catal. Rev.-Sci. Eng.*, 1993, **35**, (4), 457–481). The paper concentrates on three-way catalysts applied on gasoline engine vehicles, but a brief summary is also presented of recent work on lean nitrogen oxides catalysts for lean burn engine vehicles. The requirement for further reduction in nitrogen oxides emissions from vehicles is highlighted by reference to the recent tightening of standards in the United States; as outlined in the above *Platinum Metals Review* article. The paper considers the fundamentals of three-way catalyst operation and describes rhodium as the preferred metal for nitrogen oxides control, due to its high activity for their reduction and high selectivity to form nitrogen rather than ammonia.

The paper states that wide adoption of rhodium replacements such as palladium or copper appears unlikely at this stage due to the stricter control standards coming into force. It references the use of platinum in three-way catalysts together with ceria, and describes basic work on the role of ceria and its operation in conjunction with platinum and rhodium. Ceria is shown to be capable of extending the time for nitric oxide decomposition over platinum/rhodium/ceria catalysts due to the fact that the ceria absorbs oxygen from nitric oxide decomposition. Thus, ceria prevents the noble metal catalyst becoming deactivated by the accumulation of surface oxygen. Ceria is also claimed to alter favourably the reaction kinetics of carbon monoxide oxidation and nitric oxide reduction, and to decrease the apparent activation energy of the carbon monoxide/nitric oxide reaction, so favouring high conversion at low temperatures. Lower ceria particle size enhances the reduction of nitric oxide over platinum/ceria catalysts and this is attributed to the increased platinum-ceria interaction.

The paper addresses the recent interest in the substitution of palladium for rhodium as a cost reduction move. It describes palladium as having a narrower air:fuel operating range for the control of nitrogen oxides emissions compared to platinum/rhodium, particularly under rich air:fuel conditions. This has been ascribed to poisoning of palladium sites by hydrocarbons in the exhaust, which can be alleviated by the addition of lanthanum and other additives.

The reduction mechanism for nitrogen oxides removal is described as a nitric oxide decomposition process over the noble metals, followed by the removal of oxygen from the noble metal surface via reaction with a reducing agent. Surface chemistry studies of reactions over rhodium surfaces have clearly identified the elementary steps necessary to complete this reaction process. Rhodium is found to be structure sensitive with particle size having a major effect, but crystallographic orientation only a moderate effect, on sensitivity.

The recent Auto/Oil Quality Improvement Research Program has clearly shown that fuel sulphur level can have a dramatic impact on nitrogen oxides emissions from a vehicle. During this study an increase of fuel sulphur from 49 ppm to 466 ppm showed a 9 per cent increase in the emissions with the higher sulphur content fuel. Laboratory studies have confirmed these results. Platinum and rhodium show rapid reversibility when the fuel sulphur level is lowered back to 49 ppm; however, palladium is slower to recover. The presence of ceria in the catalyst prolongs the recovery process due to sulphur adsorbed on the ceria surface.

The review is a useful compendium of the literature published during the period, particularly with respect to the mechanism and reaction of nitric oxide removal over rhodium based three-way catalyst systems. B.J.C.