Catalysts for Nitrogen Oxides Control under Lean Burn Conditions

THE OPPORTUNITY FOR NEW TECHNOLOGY TO COMPLEMENT PLATINUM GROUP METAL AUTOCATALYSTS

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Regulations to control the exhaust emissions from motor vehicles are being adopted by more and more countries around the world, and in future more stringent regulations will be introduced, particularly in the U.S.A. and Europe. This, together with the need to show good pollution control under real-world driving conditions, has led to the widespread introduction of closed-loop, three-way catalysts based on the use of platinum group metal technology. The increasing concern about emissions of carbon dioxide, as well as the three traditional pollutants, offers an opportunity for catalyst technology to control nitrogen oxides from both fuel efficient lean burn petrol engines and from diesel engines, thus complementing the use of platinum group metals catalysts to control nitrogen oxides and other emissions. This paper reviews the development of "lean-NOx" technology based on the use of zeolite supported catalysts; it highlights the promise shown and the shortcomings still to be overcome.

Over the last 25 years the motor vehicle has increasingly become a cause for concern on environmental issues. This initially led to the control of carbon monoxide, because of the potential build-up of this toxic gas in congested city centres, and of hydrocarbons and nitrogen oxides, both precursors of the photochemical smog and low level ozone prevalent in some regions, particularly in the Los Angeles basin.

Now the motor vehicle is identified as the contributor of around 15 per cent of carbon dioxide emissions. Carbon dioxide is the main "greenhouse" gas contributing to perhaps 50 per cent of the predicted global warming and is of course the inevitable product of burning carbon-containing fossil fuels.

The twin goals of low and efficient fuel use and minimum emissions are increasingly being addressed by research in both the motor and the catalyst industries of the world.

The Lean Burn Engine

In various prototype forms the lean burn engine has been around for nearly 25 years. However, successful and widespread usage of this engine has been restricted by increasingly strict control on the level of pollutants emitted under the full range of engine operating conditions (1). Recent developments have included the evolution of lean operating two-stroke engines (Figure 1).

Lean burn operation involves the burning of

Fig. 1 Among lean burn engines under development that would benefit from using lean-nitrogen oxides catalysts is the Orbital 2-stroke engine, shown here
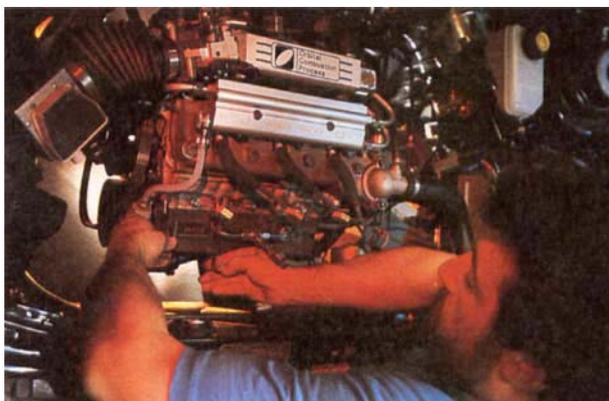
fuel with an excess of air, in ratios up to 24 parts of air to one part of fuel. Under these conditions nitrogen oxides and carbon monoxide emissions are at a minimum, but hydrocarbons can rise at the onset of unstable combustion, as can be seen in Figure 2. Engine design to increase the swirl of the air/fuel charge can increase the air:fuel ratio at which misfire starts and minimise, but not prevent, hydrocarbon emissions.

The main reason that lean burn engines have not so far had widespread acceptance has been that the power output from an engine falls as the fuelling moves to leaner operation. This means that to meet driver expectations of performance and drivability a rich fuel setting is
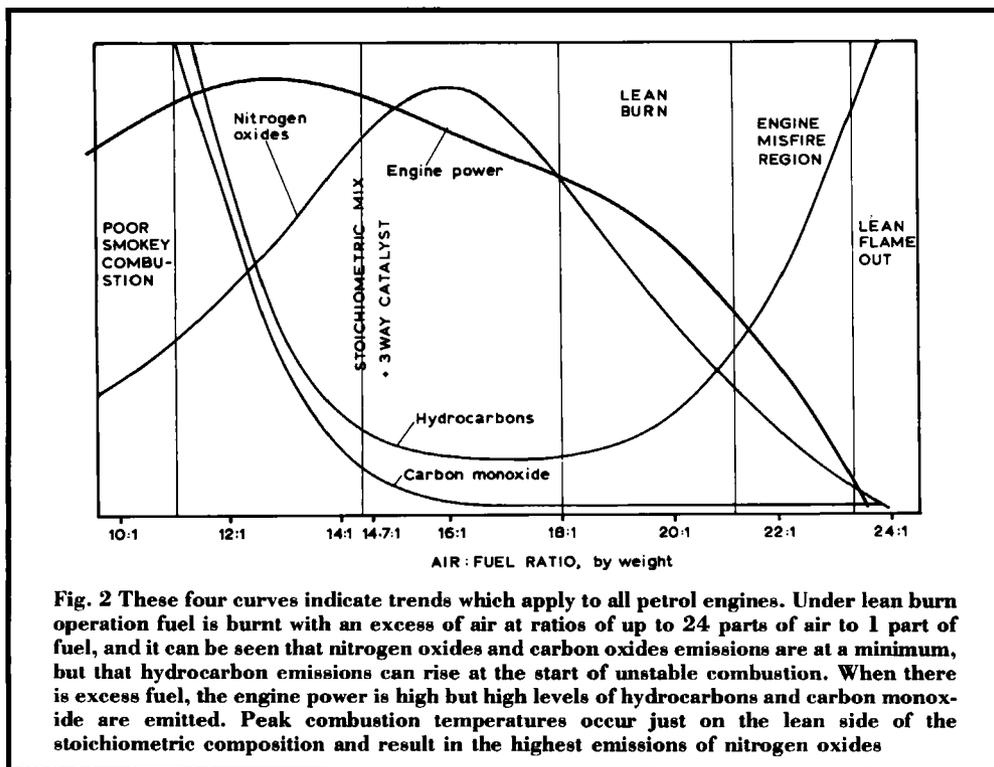

Fig. 2 These four curves indicate trends which apply to all petrol engines. Under lean burn operation fuel is burnt with an excess of air at ratios of up to 24 parts of air to 1 part of fuel, and it can be seen that nitrogen oxides and carbon oxides emissions are at a minimum, but that hydrocarbon emissions can rise at the start of unstable combustion. When there is excess fuel, the engine power is high but high levels of hydrocarbons and carbon monoxide are emitted. Peak combustion temperatures occur just on the lean side of the stoichiometric composition and result in the highest emissions of nitrogen oxides

Table I
European Regulations

1992 Standards in grams/km		
Pollutants	Type approval	Production
Carbon monoxide	2.72	3.16
Hydrocarbons + nitrogen oxides	0.97	1.13
Particulates/diesel	0.14	0.18
On 1/7/92 applies to new models; on 31/12/92 applies to all new registrations		

provided for acceleration, high speed cruising and hill climbing, thus causing nitrogen oxides emissions to increase.

The Diesel Engine

The only true lean burn engine in widespread use is the diesel engine. The diesel engine stays in the lean operating region under all engine conditions. The petrol engine is throttled on the air intake, and ultimate power from a given engine is limited by the amount of air that the engine can "breathe". Conversely the diesel engine is unthrottled and its power output is determined by the amount of fuel that is injected into the combustion chamber. The maximum fuel input level is controlled by the onset of unacceptable levels of smoke or particulate formation. To limit particulate emissions to acceptable or legislated levels it is necessary for the diesel engine always to operate in the lean region (2). This means that the diesel engine has a significantly lower power output than a petrol engine of the same capacity.

Three-Way Catalyst Operation

Conventional three-way catalysts, based on the use of combinations of platinum group metals - platinum, palladium and rhodium - can convert over 90 per cent of the three main pollutants carbon monoxide, hydrocarbons and nitrogen oxides (3). They do this by the exhaust gas being controlled by an air:fuel ratio (or lambda) sensor around the so-called
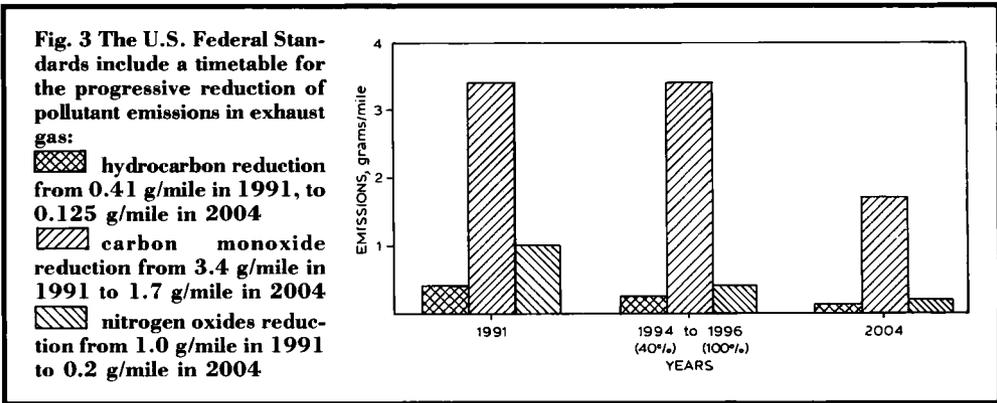
stoichiometric point at which neither air nor fuel is in excess at the intake to the engine; for a typical petrol composition this is at a ratio of 14.7 parts of air to 1 part of petrol.

Under lean conditions the three-way catalyst will act as an oxidation catalyst controlling carbon monoxide and hydrocarbon emissions, but the conversion of the nitrogen oxides emissions falls to very low levels.

Limitations to Lean Operation as Legislation Tightens

The introduction of lean burn engines is limited by a number of key factors. The European driving cycle, during which the emissions from motor cars are measured against the legislated levels, has been changed. The original City Test Cycle was based on inner city driving in congested traffic with a top speed of 50 k.p.h. (31 m.p.h.) and an average speed of 18.8 k.p.h. (11.7 m.p.h.). Under these conditions a typical car might need to use only 15 per cent of its maximum available power, so that lean operation would be possible throughout the cycle. However, the realisation that a major contribution to regional and global pollution is made by motor vehicles operating at high speeds on highways led to the addition of the Extra Urban Driving Cycle (EUDC), which includes speeds up to 120 k.p.h. (75 m.p.h.) and needs more power than the City Test Cycle. This causes greater nitrogen oxides emissions.

The new European Community directive,

Fig. 3 The U.S. Federal Standards include a timetable for the progressive reduction of pollutant emissions in exhaust gas:

▨▨▨ hydrocarbon reduction from 0.41 g/mile in 1991, to 0.125 g/mile in 2004

▨▨▨ carbon monoxide reduction from 3.4 g/mile in 1991 to 1.7 g/mile in 2004

▧▧▧ nitrogen oxides reduction from 1.0 g/mile in 1991 to 0.2 g/mile in 2004

published on 30th August 1991 (4), sets maximum pollution levels for all sizes of motor cars (Table I) and is based on the combined City and EUDC cycles. The standards will necessitate the use of closed loop, three-way catalysts on all new models sold from 1st July 1992 and on all new cars registered for sale after 31st December 1992.

In the U.S. new, more demanding Federal and Californian standards have been set. The former will reduce the allowed hydrocarbon emissions by 40 per cent and nitrogen oxides emissions by 60 per cent, by 1996 (Figure 3). Californian standards call for increasingly lower and lower emissions, culminating in a requirement for all motor vehicle manufacturers to include 10 per cent of zero emissions vehicles in their fleets by 2003 (Figure 4 and Table II). The Californian standards are also expected to be adopted by 13 states in north eastern U.S.A., which together account for nearly 40 per cent of U.S. car sales.
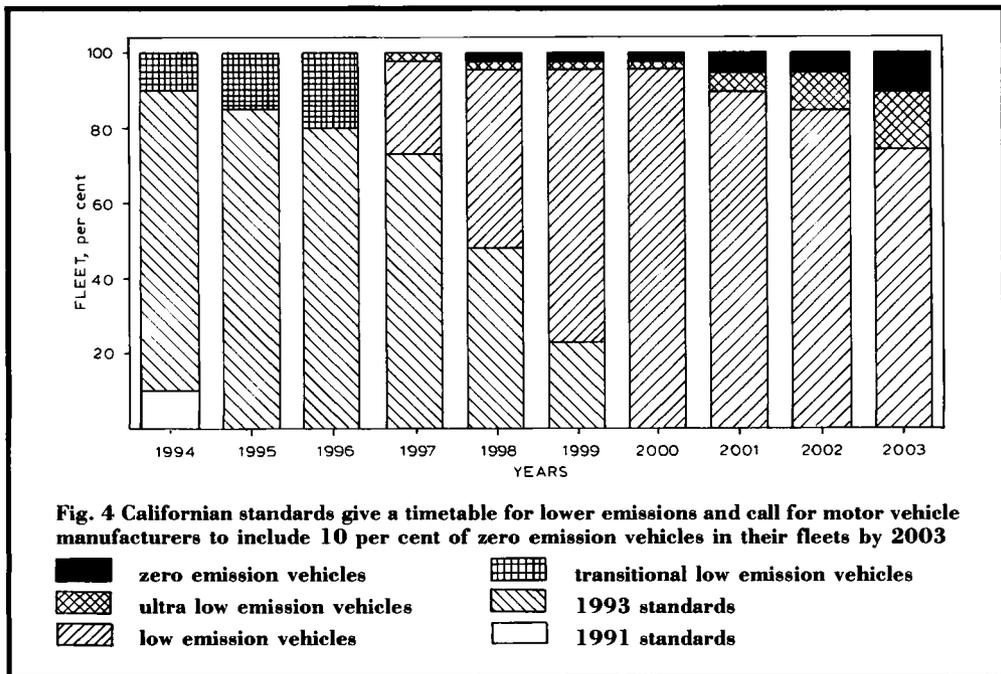

Fig. 4 Californian standards give a timetable for lower emissions and call for motor vehicle manufacturers to include 10 per cent of zero emission vehicles in their fleets by 2003

■ zero emission vehicles
▨▨ ultra low emission vehicles
▨▨ low emission vehicles

▦ transitional low emission vehicles
▨▨ 1993 standards
☐ 1991 standards

Table II

Californian Standards

	Emission limits, grams/mile		
Year and standard	Hydrocarbons	Carbon monoxide	Nitrogen oxides
1991	0.39	7.0	0.4
1993	0.25	3.4	0.4
1994 (TLEV)	0.125	3.4	0.4
1997 (LEV)	0.075	3.4	0.2
1997 (ULEV)	0.04	1.7	0.2
1998 (ZEV)	0	0	0

The European Commission will propose tougher standards for the European Community by the end of 1992, for agreement during 1993 and with implementation expected in 1996. It is anticipated that these will be similar to the new U.S. Federal standards.

These increasing restrictions on nitrogen oxides emissions and the inclusion of real-world driving conditions mitigates against the use of lean burn engines, unless the emissions of nitrogen oxides can be limited in the engine or controlled externally.

Removal of Nitric Oxide under Lean Operation

Nitric oxide is thermodynamically unstable relative to nitrogen and oxygen under the full range of exhaust gas stoichiometries and temperatures encountered in internal combustion engines (5). A number of catalysts were studied during the 1970s, including platinum group metals and metal oxides (6) and some were found to decompose nitric oxide, but none of these had sufficiently high activity to be of practical importance. In their reduced states, these catalysts are rapidly oxidised by nitric oxide, with release of nitrogen. Oxygen is retained on the catalyst surface, however, inhibiting further nitric oxide adsorption and decomposition. Reducing agents are required to remove this surface oxygen and regenerate catalyst activity. Selective catalytic reduction using ammonia as the reducing agent has been utilised for the removal of nitric oxide from industrial boilers and gas turbines under conditions of excess oxygen (7). Careful stoichiometric control of the ammonia must be maintained to assure efficient nitric oxide removal without emission of surplus ammonia. For transportation applications this process is not practical because of the problems associated with the storage of ammonia, and controlling ammonia injection under transient conditions. An active and durable nitric oxide decomposition catalyst, or a selective reduction catalyst utilising reducing species present in the engine exhaust stream would be a major breakthrough for the control of nitric oxide in transportation applications. Recent literature reports and work conducted by Johnson Matthey now indicate that progress is being made towards developing these catalyst technologies employing platinum group metals.

New Nitric Oxide Decomposition Catalysts

Copper-exchanged zeolites have high activity for the catalytic decomposition of nitric oxides according to Iwamoto and co-workers (8). A number of zeolite systems were investigated including Mordenite, Ferrierite, L-type and ZSM-5, with the Cu-ZSM-5 system showing the highest activities (9, 10). Using gas mixtures of 0.5–2.1 per cent nitric oxide in helium, with gas hourly space velocities of 10–80,000

per hour, nitric oxide conversions of 13 to 60 per cent were reported. Maximum conversions to nitrogen were observed at about 500°C, with the degree of decomposition decreasing at higher temperatures. This is apparently due to a change in mechanism, as opposed to catalyst degradation, as the same conversions were observed with decreasing catalyst temperature after high temperature operation. Water and carbon monoxide additions to the gas mixture did not greatly influence activity. The addition of oxygen resulted in a decrease in nitric oxide decomposition activity, although it is claimed that this effect is dependent upon the level of copper exchange in the zeolite, with high levels of exchange resulting in less oxygen inhibition. The addition of sulphur dioxide was found to poison catalyst activity completely in the 400 to 600°C temperature range, with restoration of activity being achieved after the high temperature desorption of sulphur.

Detailed kinetic studies of nitric oxide decomposition over the Cu-ZSM-5 system have been reported by Li and Hall (11, 12). Their work has shown that the reaction is first order in nitric oxide pressure and inhibited by oxygen. The kinetics can be described in the Langmuir-Hinshelwood form with the inhibition being half-order in oxygen pressure. As with Iwamoto and co-workers, they observed that the nitrogen formed was significantly less than the equivalent nitric oxide which disappeared. This discrepancy was accounted for by nitrogen dioxide which appears in the products as a result of homogeneous reaction of product oxygen with undecomposed nitric oxide downstream of the catalyst. The redox capacity of Cu-ZSM-5 was found to be near 0.5 O:Cu, that is $1e^-$. In particular, it was shown that oxygen could be desorbed isothermally from the catalyst surface upon reducing the oxygen partial pressure in the gas stream and that Cu^{+2} was reduced to Cu^{+1} during the desorption of oxygen. Since it is generally believed that the rate of removal of strongly adsorbed product oxygen from the surface limits the nitric oxide decomposition on most catalysts, the continuous desorption of oxygen from the active sites of the Cu-ZSM-5 catalyst during steady-state reaction is felt to be the key to their high sustained activity.

Although the above results represent a significant advancement in the development of catalysts for nitric oxide decomposition, major improvements will be required before such systems can be used to control nitric oxide emissions from combustion sources. Nitric oxide concentrations in exhausts of internal combustion engines are generally <3000 ppm, significantly lower than those used in the work reported above. Tests in our laboratories at these concentrations with 5 per cent oxygen present and gas hourly space velocities of 20,000 per hour show little nitric oxide conversion. In addition, the almost complete poisoning of activity by sulphur dioxide in the reaction gas mixture would preclude use with present petroleum-derived fuels.

Selective Catalytic Reduction of Nitric Oxide by Hydrocarbons

Another significant, and potentially more practical, breakthrough has been the reports by Iwamoto (10, 13, 14), Hamada (15, 16, 17) and Held (18) and co-workers demonstrating the selective catalytic reduction of nitric oxide by hydrocarbons in the presence of excess oxygen. Hamada and co-workers have studied nitric oxide reduction over solid acid (15), transition metal promoted alumina and silica (17), and H-form zeolites (16). Some of their results using C_3H_8 as the selective reducing agent are summarised in Table III. Alumina, titania and zirconia all showed modest activity for the selective reduction of nitric oxide with C_3H_8. The addition of transition metals to alumina resulted in substantially higher activity, with cobalt and iron presenting the highest conversions. Interestingly, the observation was made that a correlation exists between cobalt aluminate formation and nitric oxide reduction activity. Of the platinum group metals, platinum exhibited the highest activity. As the results presented in Table III show, the H-form zeolites were the most active catalysts tested by these workers. In all these studies nitric oxide

Selective Reduction of Nitric Oxide over Solid Acid (15), Transition Metal Promoted Alumina (17) and Zeolite (16) Catalysts

Catalyst	Nitric oxide conversion to nitrogen, per cent		
	at 300°C	at 400°C	at 500°C
SiO_2	< 0.4	< 0.6	< 1.1
Al_2O_3	0.5	13.0	32.0
TiO_2	0.8	4.8	8.9
ZrO_2	—	23.0	20.0
2% Co/Al_2O_3 (blue)	4.2	49.0	29.0
2% Cu/Al_2O_3 (green)	14.0	23.0	11.0
2% Fe/Al_2O_3 (orange)	19.0	35.0	17.0
2% Ni/Al_2O_3 (green)	4.5	31.0	40.0
2% Mn/Al_2O_3 (brown)	13.0	13.0	7.4
0.5% Pt/Al_2O_3	9.0	28.0	12.0
0.5% Pd/Al_2O_3	12.0	5.6	5.4
0.5% Rh/Al_2O_3	13.0	8.9	8.5
H-ZSM-5	49.0	59.0	38.0
H-Mordenite	58.0	65.0	48.0
HY	9.0	19.0	26.0

1000 ppm NO, 329 ppm C_3H_8, 10% O_2 at 3.7 L/HG MHSV (l/hg mass hourly space velocity)

conversion to nitrogen was observed to go through a maximum with increasing reaction temperature. In the region where significant nitrogen was formed carbon monoxide, in addition to carbon dioxide, was found in the product gas stream. At higher temperatures where nitrogen formation decreases, the hydrocarbon was completely oxidised to carbon dioxide. It was also found that the temperature of maximum nitric oxide reduction to nitrogen was dependent upon the hydrocarbon species, with maximum conversion occurring at a temperature about 100°C lower when C_3H_6 was used as reductant, instead of C_3H_8.

A number of ion-exchanged zeolites have been examined for their selective nitric oxide reduction activity by hydrocarbons (10, 13, 14). Using a gas mixture containing 1000 ppm nitric oxide, 250 ppm C_2H_4, and 2 per cent oxygen at a mass hourly space velocity of 18 litres/hour/gram, the order of activity (temperature for maximum nitric oxide reduction to nitrogen) was copper (250°C)<cobalt (350°C)<H (400°C)<silver (450–600°C)<zinc (600°C). Maximum conversions to nitrogen were 30–40 per cent and were relatively independent of the cation. Activities of various copper ion-exchanged zeolites were (conversion to nitrogen at 250°C): Cu-ZSM-5 (31%)>Cu-Mordenite (26%) ~ Cu-L-type (25%)>Cu-Ferrierite (23%). The effect of space velocity on conversion was studied for Cu-ZSM-5, H-ZSM-5, and alumina catalysts. Conversion over alumina dropped rapidly at gas hourly space velocities greater than about 5000 per hour, H-ZSM-5 conversions showed a modest decline in the range of 5–20,000 per hour with a rapid fall at higher space velocities, and conversion over Cu-ZSM-5 was stable up to 48,000 per hour with a fall at higher values. These results show that transition metal ion-exchanged zeolites can have substantially higher activity than the H-form systems, with the copper-exchanged catalysts showing most promise.

Using laboratory gas mixtures more typical of engine exhaust, together with actual engine

evaluation, Held and co-workers (18) have reported results on a number of transition metal ion-exchanged zeolites. Cu-Mordenite; Cr-, Fe-, Mn-, V-, Cu-, Co-, Ni-, and Ag-Y zeolite; Cu-X zeolite; and Ir-, Pt-, Rh-, Ni-, Co-, and Cu-ZSM-5 were all reported to have some activity for selective reduction of nitric oxide by hydrocarbons in the presence of excess oxygen. The Cu ion-exchanged systems showed the highest activities of those tested. They also showed that there was an inhibition of activity when water was added to the reaction gas mixture. Studies of the two most active catalyst systems, Cu-ZSM-5 and Cu-Mordenite, with a gas mixture containing 1000 ppm nitric oxide, 400 ppm C_2H_4, and 1.5 per cent oxygen at 350°C and a gas hourly space velocity of 13,000 per hour showed that nitric oxide conversions over Cu-Mordenite dropped from 37 to 17 per cent with the inclusion of 10 per cent water vapour. Under the same conditions, the more hydrophobic Cu-ZSM-5 catalyst showed a drop in nitric oxide conversion from 50 to 37 per cent. A conventional autocatalyst monolithic substrate was coated with Cu-ZSM-5 for engine evaluation. Under steady-state conditions at about 400°C inlet temperature and a gas hourly space velocity of

approximately 15,000 per hour, nitrogen oxides conversions of 35 to 45 per cent were observed at air:fuel ratios of 17.5–19:1. A correlation exists between nitrogen oxides conversion and the hydrocarbon:nitrogen oxides ratio in the exhaust gas mixture, with the highest nitrogen oxides conversions occurring at the highest hydrocarbon:nitrogen oxides ratios.

In our laboratories, monolithic substrates have been coated with Cu-Mordenite and Cu-ZSM-5 catalysts for laboratory flow reactor and engine evaluation. Laboratory flow reactor results are summarised in Table IV. It should be noted that under these conditions no significant nitric oxide conversion was observed in the absence of hydrocarbons, indicating that direct decomposition was not contributing to nitric oxide conversion. As was found by other workers, nitric oxide conversion went through a maximum as a function of temperature. Carbon monoxide formation was observed during the onset of nitric oxide conversion. Complete conversion of hydrocarbon to carbon dioxide was observed at higher temperatures associated with declining nitric oxide conversion. These results show that zeolite type, the hydrocarbon:nitric oxide ratio, and the hydrocarbon species all have a significant effect on nitric

oxide reduction activity. Consistent with other reports, the Cu-ZSM-5 catalyst gave higher conversions than the Cu-Mordenite catalyst. Maximum conversions increased with increasing hydrocarbon concentrations (increasing HC:NO ratio). The use of C_3H_8 instead of C_3H_6 as reductant resulted in an increase in temperature for maximum nitric oxide conversion from ~400°C to ~500°C. The use of CH_4 resulted in minimal nitric oxide reduction at temperatures up to 600°C. The dependence on hydrocarbon species and concentration, together with the observation that carbon monoxide formation occurs simultaneously with nitric oxide reduction, implies that hydrocarbon partial oxidation or decomposition products are involved in the reaction mechanism. In separate experiments we have exposed a Cu-ZSM-5 catalyst first to a C_3H_6/O_2 mixture and subsequently to a NO/O_2 mixture. Immediately upon switching to the NO/O_2 mixture, significant nitric oxide conversion is observed which decays with time, implying that hydrocarbon-containing species deposited on the catalyst surface are involved in the reaction, and are being depleted with time. We have also shown that carbon monoxide and hydrogen are much less effective than hydrocarbon for selective nitric oxide reduction over these catalyst systems. Iwamoto has classified reductants into two groups, selective (C_2H_4, C_3H_6, C_3H_8, C_4H_8) and non-selective (H_2, CO, CH_4 and C_2H_6) based upon similar observations (10). His group has also investigated the role of oxygen, showing that up to about 2 per cent oxygen in the reactant stream strongly activates nitric oxide reduction with a slight inhibition observed at higher concentrations. Our studies have shown similar effects with the added observation that exposure of a Cu-Mordenite catalyst to nitric oxide and C_3H_8 in the absence of oxygen resulted in a reddish colour change to the catalyst, implying the presence of reduced metallic copper. This occurs even when the reactant gas mixture is net oxidising and may indicate that the importance of oxygen is in maintaining copper in an active oxidation state.

At present there is very little information available on catalyst durability but, as expected, there are indications that the zeolite systems would be limited to temperatures less than 600°C to avoid thermal degradation. Initial resistance to sulphur dioxide poisoning has been indicated (14) although longer term poisoning effects remain to be assessed.

Future Work and Requirements for a Practical Emission Catalyst

A much better understanding of the mechanism(s) involved in the selective nitric oxide reduction reaction with hydrocarbons must be obtained as a basis for development of improved catalyst systems. These studies, together with engine evaluations, must address a number of possible limitations of present technology for vehicle applications. Some of these limitations include:

★ Thermal stability of the present Cu-zeolite systems

★ Effects of potential poisons, particularly sulphur compounds

★ The relatively narrow range of temperatures and low space velocities associated with optimum performance

★ The effects of cyclic engine operation, particularly the effects of varying emission rates of hydrocarbons versus nitrogen oxides on catalyst function.

The importance of these last two effects is demonstrated by the work of Held and co-workers (18). They tested Cu-ZSM-5 catalysts on a vehicle under the transient FTP cycle. Nitrogen oxides conversions of about 15 per cent were obtained during cold-start (bag 1) and about 30 per cent during hot-start (bag 3) tests. The lower conversions were ascribed to low catalyst temperatures during cold-start and the generally higher space velocities incurred in the FTP during the hot-start test. It was also noted that under acceleration conditions where significant nitrogen oxides are formed, the nitrogen oxides:hydrocarbon ratio was unfavourable for nitrogen oxides reduction. The requirement for high hydrocarbon:nitrogen oxides ratios was found to be a major problem in

studies using a diesel engine. Diesel engines have inherently low hydrocarbon emissions and injection of hydrocarbons into the exhaust stream was necessary to obtain significant nitrogen oxides conversion.

Finally, a complete automotive emission control catalyst system must have adequate hydrocarbon and carbon monoxide activity in addition to nitrogen oxides removal. The catalyst systems described above show deficiencies in hydrocarbons and, particularly, carbon monoxide activity which would require the use of a dual function catalyst system. The first component would be the selective nitrogen oxides reduction catalyst, followed by a conventional platinum group metal catalyst for hydrocarbons and carbon monoxide removal. Such concepts are already described in the patent literature. It is obvious that a practical selective nitrogen oxides reduction catalyst for automotive applications is some time away, but the exciting results obtained in the past several years and the high level of activity in this area are reasons for encouragement.

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Rhodium-Iron Resistance Thermometer

For some twenty years the rhodium-iron resistance thermometer has been regarded as one of the most reliable for low temperature measurement, and in various forms has been used from millikelvin regions up to room temperature. Although it is known that the annealing treatment is one of the most important factors controlling the thermometric properties of such thermometers, only limited information is available about their stability when the rhodium-iron (mole fraction 0.5 per cent) is in the form of wire.

A recent communication from the National Research Laboratory of Metrology, Japan, reports on the effects of annealing on a new type of rhodium-iron thermometer, in which the 50 μm diameter wire is wound bifilarly around a cross-shaped frame machined from fused silica. (O. Tamura and H. Sakurai, "Rhodium-Iron Resistance Thermometer with Fused-Silica Coil Frame", *Cryogenics*, 1991, **31**, (10), 869–873). The use of fused silica enables the sensing element to be annealed at temperatures above 600°C. The four lead wires and the protective sheath are made of platinum. The influence of annealing temperatures between 700 and 900°C upon the resistance of the thermometer has been investigated, and a calibration method proposed for cryogenic use of the thermometers.

It is concluded that an annealing temperature of 800°C is required to remove the strain produced in the wire by coiling; thermometers annealed at or above this temperature have similar temperature-resistance characteristics and, after calibrating the deviation from a reference function at only three calibration points, can be used with an accuracy better than 0.5 mK over the range 4.2 to 25 K. Self-heating effects were found to be of a reasonable magnitude.