

Controlling Nitrogen Oxide Emissions from Industrial Sources

AN APPLICATION FOR SELECTIVE CATALYTIC REDUCTION

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The pollution problem known as acid rain has focused attention on the need to control all major sources of contributing emissions. The use of platinum metal catalysts to control automobile exhaust gases is now well developed but in fact over half the man-made nitrogen oxides exhausted into the atmosphere are emitted from sources other than vehicles, and include power station boilers, industrial boilers and stationary internal combustion engines. Several methods may be used to prevent these emissions, and platinum catalysts, either alone or in combination with one or more of the base metal catalysts currently used, appear to have considerable potential for this application.

The pollution of the atmosphere by nitrogen oxides has been a subject of growing concern during the past decade. Photochemical smog (1, 2), to which nitrogen oxides contribute, and which causes respiratory and eye damage, was first recognised as a problem and characterised in Los Angeles and Tokyo, and has led to control of emissions from motor vehicles in the U.S.A., Japan and Australia (3). Vehicle emissions legislation, requiring tight control of nitrogen oxides, has been proposed recently in West Germany and it seems likely that other European countries will follow. In the European context, the major perceived problem is that of "acid rain", which has been implicated in vegetation damage, acidification of freshwater lakes and rivers, corrosion and the weathering of buildings (4, 5). Nitrogen oxides can also be a problem in the food industry where they are formed in direct fired drying and baking operations. The interaction of nitrogen oxides with proteins in foodstuffs (6) can cause the formation of N-nitrosamines which are hepatotoxic and carcinogenic. To avoid this the food industry now widely uses indirect methods of heating even though it is generally accepted that these can increase the

energy consumption by as much as 15 per cent.

Man-made emissions of nitrogen oxides can be divided conveniently into those arising from stationary sources and those from mobile sources, as shown in Figure 2, where the primary non-combustion source is nitric acid manufacture. Since the control of nitrogen oxide emissions from mobile sources, using noble metal catalysts, is now well developed (3), this article will concentrate largely on the control of stationary source emissions, which amount to just over 50 per cent of the total nitrogen oxides (NO_x) burden. Data on nitrogen oxide emissions from stationary sources in the U.S.A. are given in Figure 3, and it is clear that the major contributors are utility power station boilers, industrial boilers and reciprocating internal combustion engines. The latter are used primarily for local electricity generation, gas and oil pumping, heat pumps, and combined heat and power systems. As will be shown later, a different control strategy to that used for mobile sources is often required for these stationary sources, because high oxygen levels in the flue gas preclude the use of three-way catalysts (3).

Oxides of nitrogen formed during combus-

Fig. 1 There is growing anxiety about the condition of forests in the European Communities, particularly in West Germany where damage is widespread. Although there may be a number of causes it is probable that a major contributing factor is air pollution from nitrogen oxides, either alone or in combination with other emissions such as sulphur dioxide and ozone



tion can be caused either by the thermal fixation of atmospheric nitrogen in the air used for combustion, leading to "thermal NO_x" (7), or by conversion of chemically bound nitrogen in the fuel, which results in "fuel NO_x" (8). Nitric oxide is the major oxide formed; there is also a small fraction of nitrogen dioxide,

although more of this is formed later in the atmosphere. In addition there is a third kind of nitrogen oxides formation known as "prompt NO_x", which is used to describe the nitrogen oxides formed in the reaction zone of a rich pre-mixed flame (9). Thermal nitrogen oxides formation can be reduced very significantly by

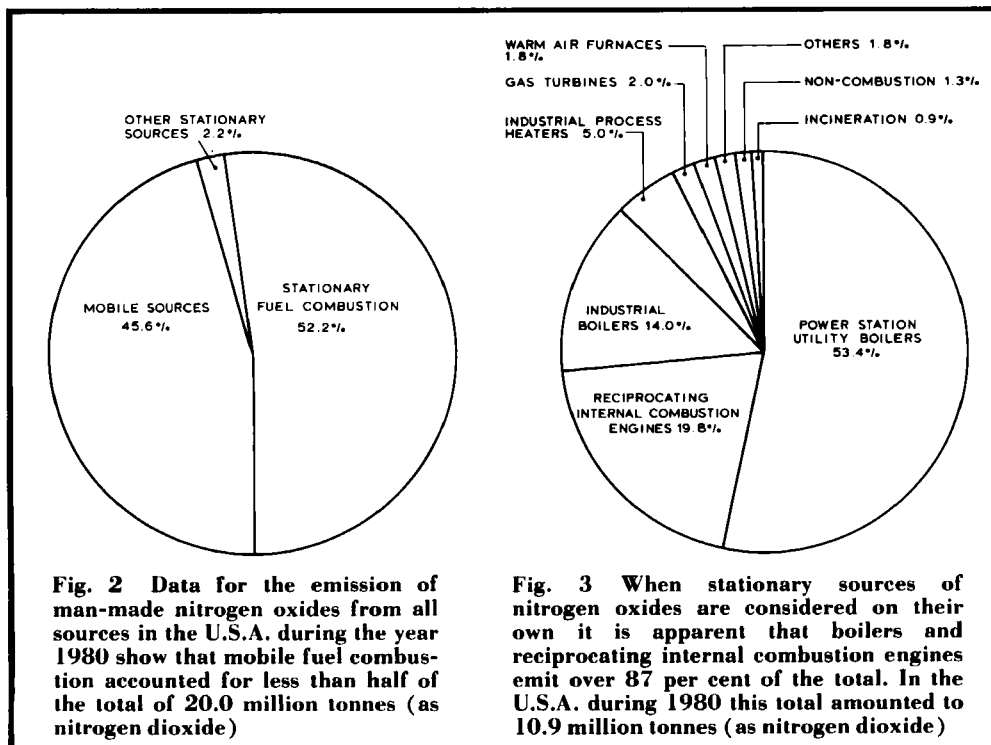


Fig. 2 Data for the emission of man-made nitrogen oxides from all sources in the U.S.A. during the year 1980 show that mobile fuel combustion accounted for less than half of the total of 20.0 million tonnes (as nitrogen dioxide)

Fig. 3 When stationary sources of nitrogen oxides are considered on their own it is apparent that boilers and reciprocating internal combustion engines emit over 87 per cent of the total. In the U.S.A. during 1980 this total amounted to 10.9 million tonnes (as nitrogen dioxide)

Table I			
Achievable Levels of Nitrogen Oxides Reduction			
Per cent reduction from the baseline			
Method of Control	Source of Emissions		
	Coal	Oil	Gas
COMBUSTION MODIFICATION			
Low excess air	10-30	10-30	10-30
Off-stoichiometric combustion	10-50	10-50	20-50
Flue gas recirculation	10-20	10-60	20-50
Water/steam injection	—	10-50	—
Low nitrogen oxides burner	30-60	10-60	20-70
FLUE GAS DENITRIFICATION			
Selective catalytic reduction	90	90	90
Non-catalytic reduction	—	40-70	40-70
Wet chemical scrubbing	90	90	90

using platinum metal based catalytic combustors (10, 11) instead of flame combustors. However, this technology is still under development and, generally, it is not possible to introduce it retrospectively in place of flame combustors.

Methods of Controlling Nitrogen Oxides

Various approaches to the problem of nitrogen oxides control may be envisaged; these are:

1. fuel switching
2. fuel pre-treatment
3. combustion (or chemical process) modification
4. flue (or tail) gas denitrification.

Switching from one fuel with a high nitrogen and sulphur content to another containing lesser proportions of these elements is currently utilised in the Netherlands, where power stations are switched from oil to natural gas on days when high concentrations of nitrogen oxides and sulphur oxides are expected at ground level (12). This, however, is a short-term, rather than a long-term solution to the problem. An alternative to this is to pre-treat the fuel in order to remove nitrogen compounds prior to combustion, thereby minimising fuel-NO_x emissions. The third option is to modify the conditions under which combustion takes

place, which can have an effect both on thermal NO_x and fuel NO_x formation, or, in the case of a chemical process, to modify the process conditions in some way. Finally one can denitrify the flue (or tail) gas from a combustion or chemical process, by one of a large number of possible methods, including catalytic reduction, non-catalytic reduction, wet absorption, adsorption on a solid and electron beam irradiation (13).

By far the most important of the above approaches are combustion modification and flue gas denitrification. The achievable levels by which nitrogen oxides from various combustion sources may be reduced using common examples of these techniques are given in Table I (8). It will be seen that the maximum reduction claimed for the best available low nitrogen oxides burner is 60 to 70 per cent, whereas 90 per cent is obtainable either by selective catalytic reduction by ammonia or by wet chemical scrubbing. However, combustion modification is the first approach in controlling nitrogen oxides from combustion processes, in view of its low cost; this being put at only 20 to 33 per cent of the cost of installing selective catalytic reduction equipment. Nevertheless, if high levels of nitrogen oxides reduction are required to meet stringent legislation, as has existed in Japan for some years, then it becomes necessary also to

Table II	
Reaction Mechanisms of the Catalytic Reduction of Nitrogen Oxides	
$\text{NO}_2 + \text{R} \xrightarrow{\text{catalyst}} \text{RO} + \text{NO}$... i
$2\text{NO} + \text{O}_2 \xrightarrow{\text{catalyst}} 2\text{NO}_2$... ii
$\text{NO} + \text{R} \xrightarrow{\text{catalyst}} \text{RO} + \text{N}_2 \text{ or } \text{N}_2\text{O}$... iii
$\text{NO}_2 + \text{NH}_3 \xrightarrow{\text{catalyst}} \text{NH}_4\text{NO}_{2/3}$... iv
$\text{NH}_4\text{NO}_{2/3} \longrightarrow \text{N}_2 \text{ or } \text{N}_2\text{O} + \text{H}_2\text{O}$... v
R = hydrocarbon, hydrogen, carbon monoxide	

apply flue gas denitrification. Selective catalytic reduction has been shown to be the most cost-effective option available (13). For combined nitrogen oxides and sulphur oxides control from a U.S. power plant, it is significantly cheaper to apply selective catalytic reduction combined with wet flue gas desulphurisation than it is to use wet methods for controlling both pollutants simultaneously.

The Catalytic Control of Nitrogen Oxide Emissions

Catalytic control of nitrogen oxides can be achieved by two methods, known as non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR). NSCR uses hydrogen, carbon monoxide or hydrocarbons as the reducing agent (14), while SCR employs ammonia; both routes can be characterised by the mechanisms shown in Table II (15). Nitrogen dioxide is readily reduced to nitric oxide over a catalyst as shown in Reaction i. However, in the presence of oxygen, nitric oxide is rapidly re-oxidised to the equilibrium concentration of nitrogen dioxide for the prevailing temperature, as in Reaction ii. If hydrogen, carbon monoxide or hydrocarbons, are used as the reducing species, oxygen must be removed from the system before the process can proceed through Reaction iii. Thus, when NSCR is used to control nitrogen oxides, it is common practice to use excess reductant to remove oxygen from the feedstream prior to nitrogen oxides reduction (14).

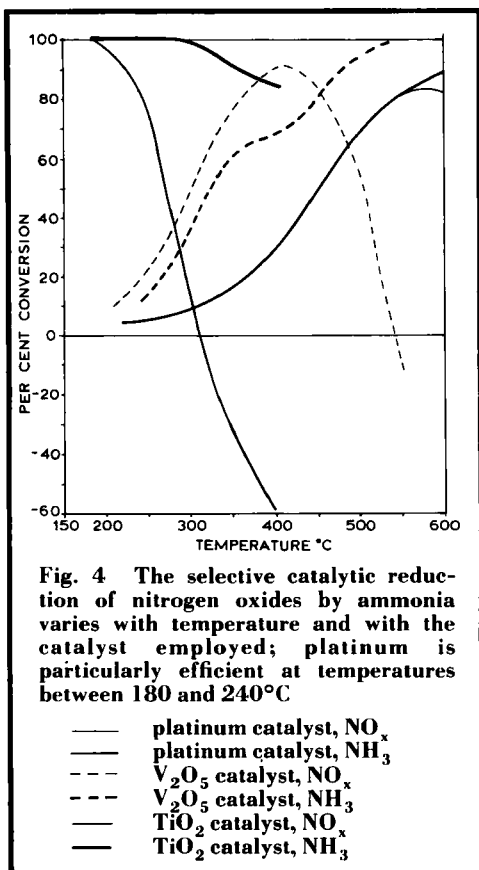
In contrast, SCR uses ammonia as the reducing agent and this is able to react directly with

nitrogen dioxide on the catalyst surface, as in Reaction iv, to give an ammonium salt type intermediate. This intermediate then decomposes to produce nitrogen or nitrous oxide as shown in Reaction v. This is a fundamental change in mechanism compared to NSCR, which explains why SCR is capable of operating under oxygen rich conditions. The mechanism is supported by infrared studies in which the presence of nitrogen dioxide and an ammonium ion have been observed on the surface of a SCR catalyst (16). It also explains why the SCR process is accelerated by oxygen, shifting the product towards nitrous oxide. Indeed, the selective catalytic reduction process can be represented by a number of chemical equations, as shown in Table III, which can proceed either in the presence or absence of oxygen and which possess widely different ammonia/nitrogen oxides stoichiometries.

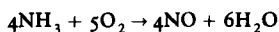
Catalysts for Selective Catalytic Reduction

Both platinum group metal and base metal catalysts are able to promote the selective catalytic reduction process and some typical results for both types of catalyst, supported on alumina-washcoated ceramic monoliths, are shown in Figure 4. The results show a characteristic increase in ammonia and nitrogen oxides conversion with temperature (light-off), except for the platinum catalyst, which was highly active even at 180°C, the lowest temperature at which conversion was measured. The reason for the latter was that, at temperatures below 180°C, there was a tendency for ammonium nitrite or nitrate species to accumulate on the catalyst surface,

Table III	
Possible Routes for Selective Catalytic Reduction	
$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \longrightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$	
$4\text{NH}_3 + 2\text{NO}_2 + \text{O}_2 \longrightarrow 3\text{N}_2 + 6\text{H}_2\text{O}$	
$4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 \longrightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O}$	
$4\text{NH}_3 + 6\text{NO} \longrightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$	
$2\text{NH}_3 + 8\text{NO} \longrightarrow 5\text{N}_2\text{O} + 3\text{H}_2\text{O}$	



resulting in the potential danger of explosive decomposition. For all systems, conversion of nitrogen oxides rises to a maximum, clearly seen in Figure 4, and then decays, ultimately giving apparently a negative conversion. The explanation for this lies in the fact that most catalysts which are effective for SCR will also catalyse the ammonia oxidation reaction which

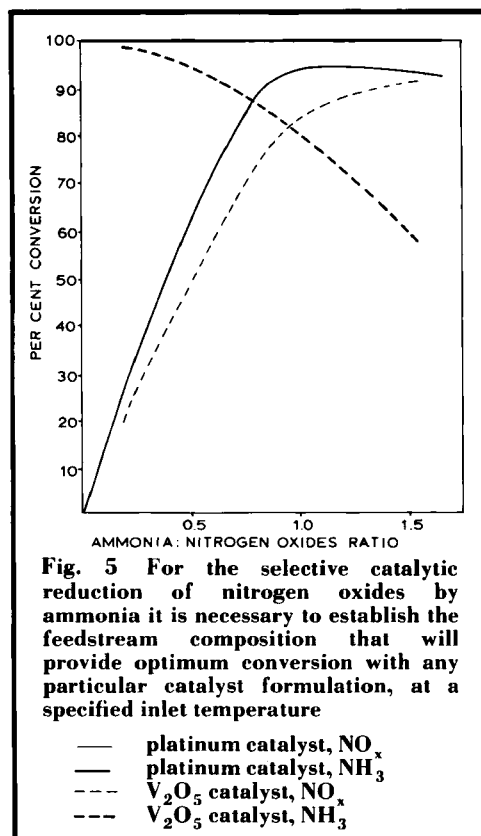


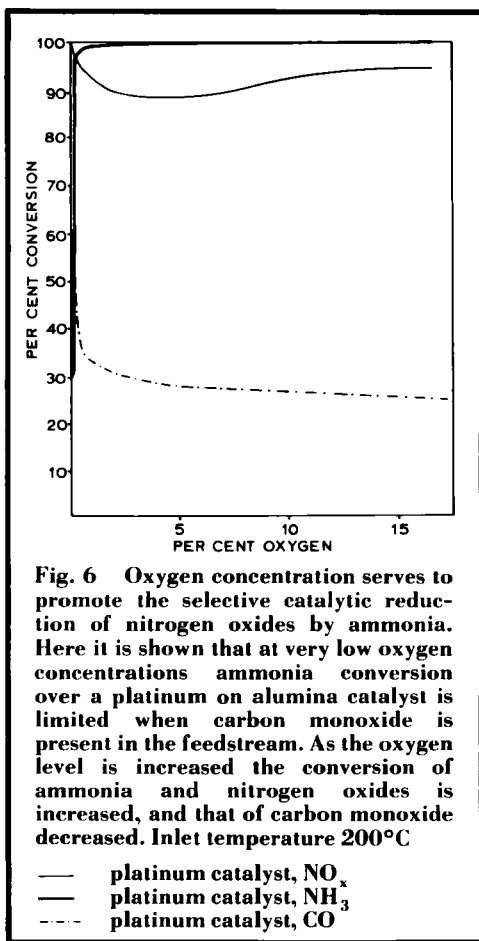
is the basis of nitric acid manufacture (17). Thus, above a certain threshold temperature, which varies for different catalysts, nitric oxide is produced, leading to a nitrogen oxides conversion which is negative overall. At the same time ammonia conversion remains high.

A further feature of note is that the ratio of ammonia and nitrogen oxides conversions varies according to catalyst formulation, as seen by comparing the lines in Figure 4. This may be

due to the ability of different catalysts to catalyse more than one of the reactions shown in Table III over the relevant temperature range, giving rise to variable stoichiometry. It is clear, therefore, that for each catalyst formulation it is necessary to establish the optimum ammonia:nitrogen oxides inlet ratio at the desired operating temperature in order to maximise nitrogen oxides conversion and minimise ammonia breakthrough. Examples of such optimisation exercises for both a noble metal and a base metal catalyst are shown in Figure 5.

The oxygen content of the feedstream to the catalyst is important, since oxygen promotes the SCR process. This is illustrated in Figure 6, where it can be seen that, at very low oxygen concentration and over a platinum on alumina catalyst, ammonia conversion is limited. In the experiment shown here, carbon monoxide was





also included in the feedstream and it appears that this is largely responsible for the high nitrogen oxides conversion at low oxygen levels. However, as soon as the oxygen level is increased, the ammonia conversion rises to almost 100 per cent at the expense of carbon monoxide conversion, confirming the promoting effect of oxygen and the change in mechanism of nitrogen oxides conversion under these conditions.

In summary, both platinum group metals and base metals will catalyse the SCR process, indeed base metal formulations are now available commercially (18). However, platinum group metal catalysts have the advantage of lower light-off temperatures, but must not be operated at temperatures which allow bulk for-

mation of ammonium nitrate or ammonium nitrite because of the explosion hazard. All SCR catalysts have a relatively narrow operating temperature "window" which is limited by light-off and by the onset of ammonia oxidation. It is clear that the judicious choice of components offers the possibility of formulating catalysts capable of accommodating a wide range of feedstream conditions. It seems probable that the addition of platinum group metals to the currently used base metal catalysts will enable the best features of both to be combined.

Some Applications of Selective Catalytic Reduction

For the reasons described above, NSCR is limited to applications where there exists, or where can readily be provided, an excess of fuel over available oxygen, for example, nitric acid plant tail gas (14) and rich-running gas-fuelled engine exhaust (3). In contrast, being able to operate under net oxidising conditions, SCR finds a much wider range of applications, including boiler flue gas, furnace emissions, gas turbine exhaust, lean-operating (and thus more efficient) gas-fuelled engines and nitric acid plant tail gas (where no excess fuel need be provided). Other advantages which are claimed for SCR include a relatively low reaction temperature, a long catalyst life and a relatively low catalyst cost (18). On the other hand, some disadvantages have been listed; these include the necessity for good temperature control, the greater expense of ammonia as compared with hydrocarbon fuels, the possibility of side reactions to form ammonium nitrate/nitrite—with the risk of explosions, and the requirement for a relatively large catalyst volume.

In view of their importance as the major stationary source of nitrogen oxides emissions, boilers represent the largest potential application for SCR, and in Japan base metal catalysts are used to meet the stringent legislation in that country. At first, several problems with fly ash (in the case of coal fired boilers) and sulphur were encountered, but these have now largely been overcome by a number of measures including the development of sulphur tolerant

base metal catalysts. There are, however, several applications where platinum group metals are at a potential advantage over base metals. These include lean-running natural gas-fuelled engines, where both exhaust temperatures and sulphur levels are generally low, and nitric acid plant tail gas treatment, where there is an advantage in operating at low temperature and where sulphur is not a problem. In the latter case, the main market lies in fitting SCR units to existing acid plants, since the current trend is to larger plants with extended absorption of nitrogen oxides. However, stationary engines represent a much larger market, given their use

in gas pumping, heat pumps, and combined heat and power systems. Furthermore, legislation to limit nitrogen oxides emissions from this source is expected to become widespread in the future. It is anticipated that superior catalysts will be developed to meet the generally agreed need for a much cleaner, healthier environment in a more cost effective manner. The base metals currently used as catalysts for the SCR process, particularly for controlling emissions from stationary engines, are likely to be promoted with platinum group metals to achieve optimum performance over the widest possible range of feedstream conditions.

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The Behaviour of Platinum-Enriched Superalloys

The continuing development of the gas turbine engine results in an associated demand for improved materials from which critical components can be fabricated. These materials must be capable of providing not only the necessary creep strength at elevated temperatures but also adequate resistance to cyclic oxidation and hot corrosion.

With conventional superalloys, compositional changes made to improve the mechanical properties may result in inferior resistance to high temperature oxidation and corrosion. However, enhanced resistance can be obtained by enriching nickel based superalloys with platinum. An examination of the microstructures that form when platinum is added to superalloys has been conducted by Dr. G. J. Tatlock and T. J. Hurd, of the University

of Liverpool who have compared, in their oxidised and hot corroded forms a conventional superalloy with another which had 4.5 per cent of platinum substituted for some of the nickel. The results of their oxidation investigations have now been published (*Oxid. Met.*, 1984, **22**, (5/6), 201-226).

Morphological studies confirm that the two alloys behave in a very similar way at 900°C, but that at 1100°C notable differences occur. At the higher temperature platinum appears to have a small but significant effect on the diffusion of the other elements present in the alloy. By a complex sequence of events, this results in the formation of a protective alumina scale which provides the platinum-containing alloy with a distinct improvement in oxidation resistance.