

Emission Control for Gas Turbines

PLATINUM-RHODIUM CATALYSTS FOR CARBON MONOXIDE AND HYDROCARBON REMOVAL

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Johnson Matthey are reporting successful commercialisation of oxidation catalysts for the clean-up of gas turbine exhaust. The reduction of carbon monoxide and hydrocarbons is achieved with a platinum-rhodium catalyst which minimises the formation of sulphur trioxide. The catalyst system, supported on an energy saving, low pressure drop metal monolith, has been used continuously for five years on large industrial gas turbines.

The catalytic control of atmospheric pollutants from automobiles has been firmly established in the U.S.A. and Japan, and is increasingly being adopted by European and other industrial countries. Nitrogen oxides, carbon monoxide and hydrocarbons in car exhaust gas are reduced by controlling the air : fuel ratio and by simultaneous conversion of all three pollutants in either a dual bed catalytic converter or in a single bed "three-way" catalytic converter (1). The accumulated benefits from this control technology (2) have not been paralleled in the control of emissions from stationary sources. Over half of the man-made carbon monoxide, hydrocarbons and nitrogen oxides reaching the atmosphere is emitted from stationary sources including power station boilers, industrial boilers, stationary internal combustion engines and gas turbines (3). Strict emission limits for controlling nitrogen oxides, carbon monoxide, hydrocarbons and sulphur oxides have been enacted by many states in the U.S.A. and in West Germany.

With the exception of rich-burn internal combustion engines, all stationary combustion is carried out using a large excess of oxygen, in order to maximise fuel efficiency. This precludes a direct extension of automotive three-way catalyst technology to stationary sources.

The control of nitrogen oxides from gas tur-

bines in a large stoichiometric excess of oxygen consists of two parts. The first level of control is practised by injecting water or steam into the combustion zone to lower the combustion temperature. This "wet firing" allows nitrogen oxide levels to be reduced by 50 per cent, from 100 ppm to 50 ppm. The second step is the selective catalytic reaction of ammonia with the remaining nitrogen oxide, a process known as Selective Catalytic Reduction (SCR). The ammonia is injected into the flue gas and the mixture is then passed over a base metal oxide catalyst, typically supported on alumina or titania (4). The SCR method can achieve nitrogen oxide levels below 10 ppm, and it is used in Japan, California and West Germany.

While the water/steam injection minimises nitrogen oxides formation, it increases the amount of carbon monoxide and hydrocarbons in the combustion products which then require flue gas treatment to lower the emissions. The well-established catalytic oxidation technology used for automotive emission control can be extended to control carbon monoxide and hydrocarbon emissions from gas turbines. Johnson Matthey, a leader in automotive catalyst technology, has developed oxidation catalyst and reactor technology for this purpose, the technology being introduced into the market in 1982. It is currently available as a stand-alone product or in conjunction with Johnson



Fig. 1 A Johnson Matthey emission control reactor is located in the centre of this picture, between the gas turbine and the stack. This reactor contains several catalyst panels measuring 10 feet by 14 feet, and purifies 4 million cubic feet of flue gas per hour. The steam from this plant is pumped underground to assist in the recovery of viscous oil

Matthey SCR catalyst and control systems as shown in Figure 1. This paper describes the oxidation catalyst and the reactor technology.

Reactor Design

Automotive oxidation reactors are required to treat relatively small volumes of gas over approximately 2,000 hours of operation at temperatures varying from ambient, during start-up, to occasional excursions up to 1,000°C. In contrast, gas turbine exhaust reactors treat much larger quantities of gas, for example, 7.5 million cubic feet per hour (SCFH) for a 20 MW gas turbine. The catalyst temperature is controlled between 250 and 650°C, and the catalyst is required to operate without replacement for more than 20,000 hours. A typical gas turbine exhaust heat recovery system, where combustion gases are expanded through a turbine to produce electricity, is shown in Figure 2. Before they go to the stack the exhaust gases pass through a superheater, boiler and economiser, where heat is recovered in the form of low and high pressure steam. The exhaust temperature is normally 470°C at the inlet to the

superheater and 260°C at the inlet of the economiser. When duct burners are used to make more steam, the temperature at the inlet to the superheater can be as high as 650°C.

Each application has a unique set of emission objectives which the catalyst and reactor are custom designed to achieve. The main design considerations which most oxidation reactors have in common are:

- High reactor productivity to minimise volume and cost.

- Low pressure drop to maximise useful work from the expanding gas.

- Low sulphur dioxide conversion to sulphur trioxide to minimise sulphate particulate emissions.

- Continuous operation exceeding 20,000 hours.

- Some co-generation installations require frequent start-up and shut-down features, for which thermal shock resistance is required.

- Proper relationship to the SCR reactor to meet overall emission control objectives, that is to minimise the reconversion of ammonia to nitrogen oxides. The interaction of the

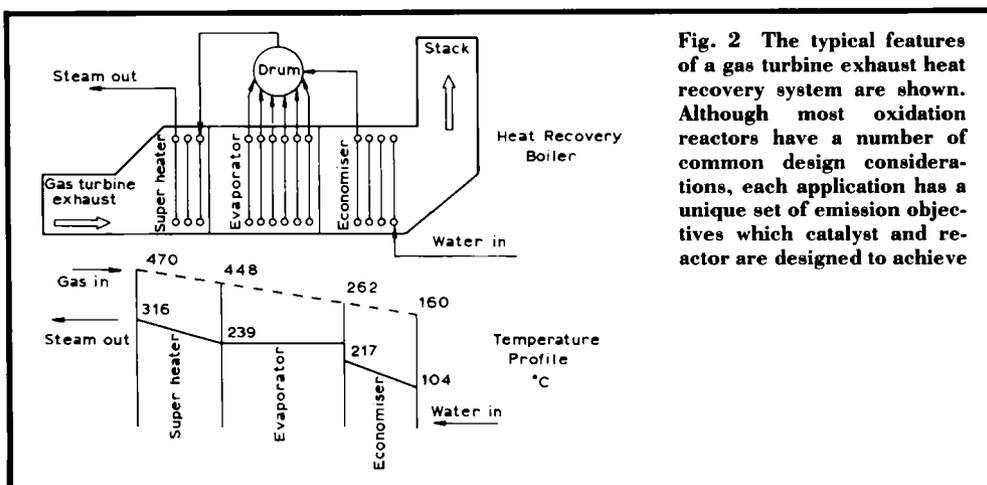


Fig. 2 The typical features of a gas turbine exhaust heat recovery system are shown. Although most oxidation reactors have a number of common design considerations, each application has a unique set of emission objectives which catalyst and reactor are designed to achieve

SCR reactor with the oxidation reactor has been reported elsewhere (5).

The productivity of a reactor is measured by the hourly gas volume which each unit volume of reactor can clean up to the specified emission level. This is referred to as the gas hourly space velocity (GHSV). The productivity of oxidation reactors equipped with noble metal catalysts varies from 50,000 to 150,000 gas volumes per hour, per volume of reactor. The oxidation reactor consists of four components:

- [1] A panel of catalyst blocks which fits into the reactor housing, sized to minimise the pressure drop of the flue gas through the reactor.
- [2] A metal honeycomb substrate which provides the low pressure drop unit cell of the catalyst panel, and forms the interfacial area between the gas and the catalyst. This area is relevant when the reactor is operated in the mass transfer limited region of the temperature range.
- [3] A high surface area refractory oxide coating which provides the internal surface area for the dispersion of the catalyst ingredients.
- [4] The active catalyst material.

The active catalyst material used in the Johnson Matthey reactors described here is a combination of platinum and rhodium. This catalyst provides high carbon monoxide conversion and high conversion of both unsaturated

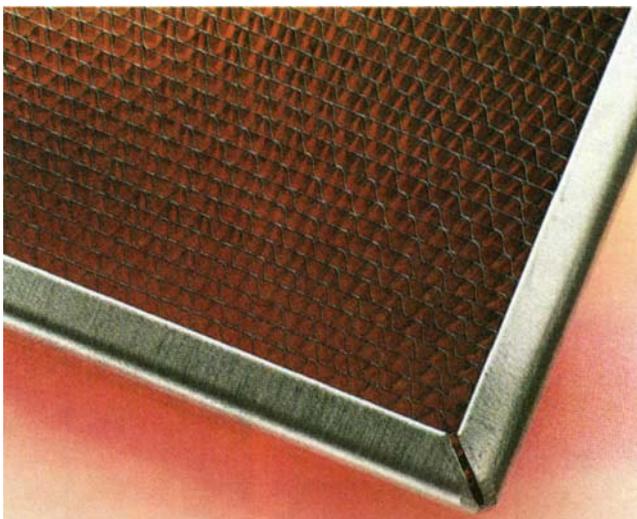
and saturated hydrocarbons, while minimising the oxidation of sulphur dioxide.

Metal Honeycomb Substrate

Industrial emission control reactors must result in only a low pressure drop at high flow rates, since minimising co-generation operating costs depends upon minimising the pressure drop. It is generally assumed by turbine operators that every 4 inches of water gauge backpressure causes a 0.4 to 1.5 per cent loss of power output. The thin walls of metal substrate allow a minimum pressure drop for a given amount of catalyst coating. Thus the combined thickness of support and catalyst coating is less than the wall thickness of a ceramic substrate of equivalent surface area.

Johnson Matthey's metal honeycomb technology was originally developed for automotive emission control in the 1970s (6). The high temperature-resistant ferritic stainless steel monoliths and the catalyst coating technology developed then have now been adapted and modified to suit the large industrial catalyst blocks used in SCR and oxidation reactors. These blocks measure 2 ft square by 3.5 inches deep and constitute one cubic foot of effective reactor volume. In addition to the low pressure drop characteristics, the metal substrate offers significant advantages over ceramic substrate in situations where thermal shock is experienced.

Fig. 3 The use of heat resistant metal substrates provides low pressure drop characteristics and superior resistance to thermal shock. A common foil configuration is shown here



A number of metal substrate designs are available. The most common is a stack of alternate layers of flat and corrugated foil strips, Figure 3. Cell densities of 100, 200 and 400 cells per square inch (16, 31 and 62 cells per square cm) are fabricated by this technique. A high surface area alumina washcoat applied to this monolith serves as the support for the catalyst ingredients. Proprietary coating technology ensures that the adhesion of the washcoat to the metal is as good as the adhesion to a ceramic substrate.

Platinum-Rhodium Catalyst

Although base metal oxides such as CoO, Cr₂O₃ and CuO have some activity for carbon monoxide and hydrocarbon reactions, noble metals are more active catalysts (7, 8). Among the noble metals, platinum and palladium have been used most widely because of their relative cost and their thermal stability (9). Rhodium is a good oxidation catalyst but is less economical.

The choice of noble metal precursors and fabrication technology significantly affects the metal dispersion, the catalyst distribution within the high surface area support material and consequently the activity and stability of the resulting catalyst system. Extensive research has been carried out to develop and implement these dispersion and stabilisation phenomena, and this research forms the basis of Johnson Matthey's leading technological position in the environmental catalyst field.

As shown in the Table, a platinum-rhodium catalyst prepared using Johnson Matthey proprietary technology is significantly more active

than platinum, palladium and platinum-rhodium catalysts prepared using conventional impregnation techniques. The carbon monoxide and hydrocarbon conversion data were obtained in a tubular reactor operating at 110,000 GHSV, using a simulated gas turbine exhaust gas consisting of: 80 ppm carbon monoxide, 31 ppm ethylene, 31 ppm ethane,

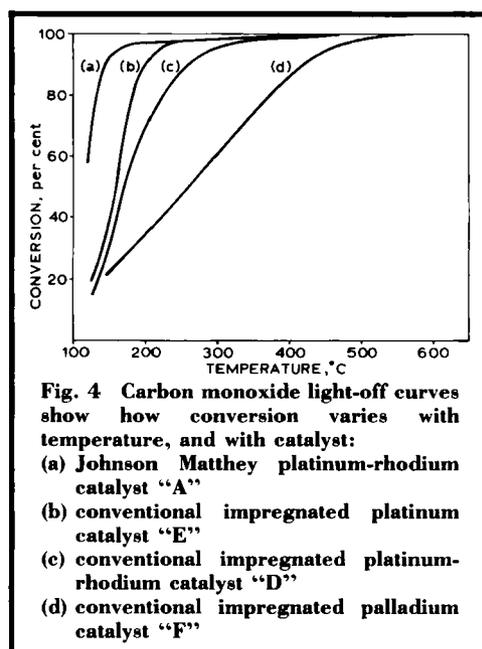


Fig. 4 Carbon monoxide light-off curves show how conversion varies with temperature, and with catalyst:

- (a) Johnson Matthey platinum-rhodium catalyst "A"
- (b) conventional impregnated platinum catalyst "E"
- (c) conventional impregnated platinum-rhodium catalyst "D"
- (d) conventional impregnated palladium catalyst "F"

Oxidation Activity of Noble Metal Catalysts						
Designation	Formulation	Relative metal loading	Conversion, per cent			
			At 150°C during light-off		At 480°C steady-state	
			CO	C ₂ H ₄ /C ₂ H ₆	CO	C ₂ H ₄ /C ₂ H ₆
A	Johnson Matthey Pt-Rh	1.0	92	24	100	85
B	Johnson Matthey Pt-Rh	0.45	82	15	100	74
C	Conventional impregnated Pt-Rh	1.71	84	10	100	74
D	Conventional impregnated Pt-Rh	0.60	30	0	100	55
E	Conventional impregnated Pt	2.63	40	4	100	69
F	Conventional impregnated Pd	1.85	23	0	99	65

46 ppm sulphur dioxide, 3 per cent carbon dioxide, 8 per cent oxygen, 10 per cent water and the balance nitrogen. The high activity of this proprietary platinum-rhodium catalyst enables the size of the reactor used in gas turbines to be reduced, compared to a reactor employing a conventional oxidation catalyst.

Carbon Monoxide and Hydrocarbon Light-Off Temperatures

The activity of a catalyst is often measured by the lowest temperature required to achieve conversion of the reactant, the so-called light-off temperature. The carbon monoxide light-off curves for four of the catalysts featured in the Table are shown in Figure 4. The Johnson Matthey platinum-rhodium catalyst requires only 120°C to exceed 50 per cent carbon monoxide conversion, compared with 160°C for a highly loaded platinum catalyst. Both show the characteristic steep conversion versus temperature dependence, indicating a high activation energy. The conventionally prepared platinum-rhodium catalyst and the palladium catalyst require higher temperatures to reach 50 per cent conversion, while the palladium cata-

lyst shows a lower activation energy, but much lower activity.

Hydrocarbons are more difficult to oxidise than carbon monoxide. Some qualitative rules for the relative ease of oxidising hydrocarbons have been published by Stein (10). The ease of oxidation is as follows:

- [a] Branched chain > straight chain
- [b] Acetylenes > olefins > saturated
- [c] C_n > . . . C₃ > C₂ > C₁

The catalytic oxidation of saturated hydrocarbons over a platinum filament was also studied by Hiam and co-workers (11). They reported the ease of oxidation as:

n-butane > isobutane > propane > ethane.

As shown in Figure 5, the Johnson Matthey platinum-rhodium catalyst exhibits similar features. For the ethylene/ethane mixture the ethylene reacts first at about 130°C and the conversion exceeds 90 per cent above 200°C. Ethane starts to react at about 400°C and conversion exceeds 80 per cent above 480°C. Butane is easier to oxidise than ethane; its conversion reaches 80 per cent at 430°C. The non-methane hydrocarbons in the exhaust of turbines fuelled with natural gas are predominantly

ethane and propane. Where high conversions of saturated hydrocarbons are required, a relatively high operating temperature of between 450 and 500°C is recommended.

Oxidation of Sulphur Dioxide and Sulphur Trioxide

Most gas turbines are fuelled with natural gas. The flue gas from these turbines contains only minor amounts of sulphur dioxide which are of small significance compared with the particulate emission requirements. However, some installations burn refinery gas which contains 50–300 ppm sulphur, while other installations are permitted to burn oil as a back-up fuel. When refinery gas or liquid fuels are burned, the exhaust gas contains sulphur dioxide. An effective carbon monoxide/hydrocarbon oxidation catalyst is normally also active for the oxidation of sulphur dioxide. However, this oxidation needs to be minimised to reduce the downstream formation of sulphate particulates from sulphur trioxide. The activity of the Johnson Matthey platinum-rhodium catalyst for sulphur trioxide formation can be reduced by increasing the rhodium content in the catalyst, or by thermal treatment. This concept has been applied to minimise sulphate formation in automotive catalysts (12, 13, 14).

Sulphur dioxide oxidation over various automotive catalysts has been reported by Truex, who showed that the conversion is strongly dependent on the platinum:rhodium ratio, and decreases rapidly as the rhodium content is increased (15). A similar rhodium effect has been measured with the Johnson Matthey platinum-rhodium catalyst, as shown in Figure 6. At a gas turbine exhaust temperature of 480°C, a 9:1 platinum-rhodium catalyst gives 71 per cent sulphur dioxide conversion, while a 2:1 platinum-rhodium catalyst gives only 37 per cent sulphur dioxide conversion. Both of these catalysts had been calcined at 650°C because initial tests showed less difference in their performance, as a function of the platinum:rhodium ratio.

Controlled thermal treatment reduces the oxidation activity for sulphur dioxide more

than that for carbon monoxide and hydrocarbons. As illustrated in Figure 7, an 800°C thermal treatment lowers sulphur dioxide conversion at 480°C from 70 per cent to 18 per cent, but after thermal treatment the catalyst still provides 80 per cent conversion of ethane/ethylene, and 100 per cent conversion of carbon monoxide.

Catalyst Stability

Catalysts are degraded in use by mechanical vibration, by particulate abrasion and pore

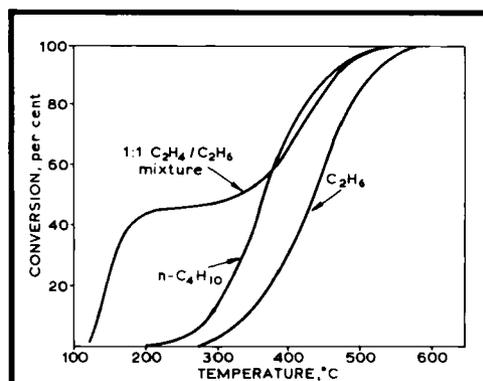


Fig. 5 These light-off curves show the relative ease of oxidising hydrocarbons with the Johnson Matthey platinum-rhodium catalyst "A"

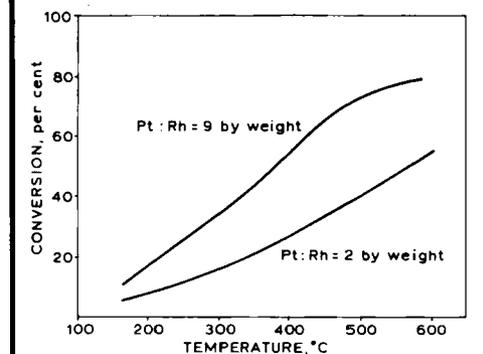


Fig. 6 At a fixed conversion temperature, the oxidation of sulphur dioxide is strongly dependent upon the platinum:rhodium ratio. These data show the effect of varying the proportions of the two elements in a Johnson Matthey platinum-rhodium catalyst, the low rhodium catalyst being superior at any particular temperature

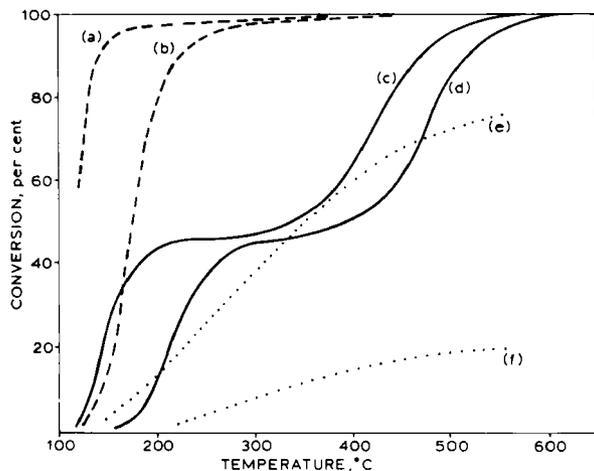


Fig. 7 Thermal treatment can change the oxidation activity of a catalyst for various gases by differing degrees. The information presented here relates to Johnson Matthey platinum-rhodium catalyst "A":
 (a) CO, fresh
 (b) CO, treated at 800°C
 (c) C₂H₄/C₂H₆, fresh
 (d) C₂H₄/C₂H₆, treated at 800°C
 (e) SO₂, fresh
 (f) SO₂, treated at 800°C

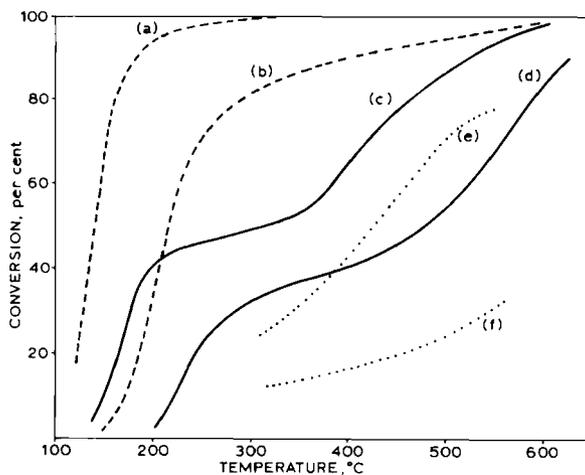


Fig. 8 The light-off behaviour of the Johnson Matthey platinum-rhodium catalyst "A" is affected by thermal ageing. This is shown here for carbon monoxide, an ethylene/ethane mixture and sulphur dioxide
 (a) CO aged at 500°C for 23 hours
 (b) CO aged at 650°C for 258 hours
 (c) C₂H₄/C₂H₆, aged at 500°C for 23 hours
 (d) C₂H₄/C₂H₆, aged at 650°C for 258 hours
 (e) SO₂, aged at 500°C for 23 hours
 (f) SO₂, aged at 650°C for 258 hours

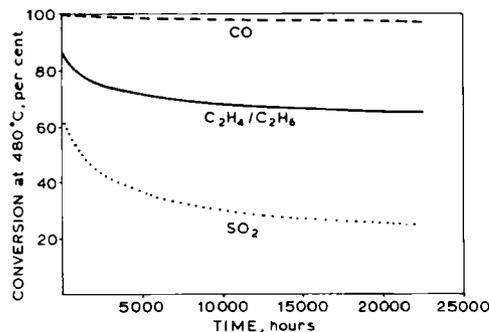


Fig. 9 From the thermal deactivation curves for Johnson Matthey platinum-rhodium catalyst "A", it is projected that after the catalyst has been aged for three years at 480°C conversions of carbon monoxide and ethylene/ethane will still exceed 95 and 65 per cent, respectively

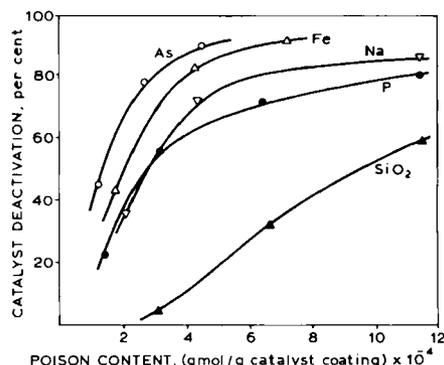


Fig. 10 The poison susceptibility of Johnson Matthey platinum-rhodium catalyst "A" has been determined using a number of synthetic poisons; the deactivation they cause is shown here

fouling, thermal shock, thermal sintering and poisoning by trace impurities. Mechanical vibration and thermal shock affect catalyst performance if they attack the physical integrity of the catalyst. The main causes of catalyst deactivation in normal turbine operation are thermal sintering, poisoning of the catalyst metals and fouling of the catalyst pores.

Thermal sintering of the alumina support is of little concern since the operating temperature is below 700°C. However, sintering of noble metals on the support is significant at turbine operating conditions. The effect of prolonged thermal exposure on the activity of the Johnson Matthey platinum-rhodium catalyst is shown in Figure 8. At low temperatures, where conversion is controlled by the reaction rate, conversion is greatly decreased, reflecting the loss of intrinsic catalytic activity. Catalysts are designed to operate at temperatures where small changes in activity do not significantly affect conversion. At these higher temperatures, where bulk mass transfer of the carbon monoxide and hydrocarbons to the catalyst controls conversion, the drop in performance is much less. However, the activity for sulphur dioxide oxidation, which is reaction rate controlled at the catalyst surface, is significantly reduced.

A thermal deactivation model has been obtained from laboratory ageing experiments conducted at temperatures from 450 to 700°C, for various lengths of time. From the model, the activity-time behaviour can be projected, as illustrated in Figure 9 for operation at 480°C. From this it is predicted that the catalyst will still give carbon monoxide conversions in excess of 95 per cent and ethylene/ethane conversions greater than 65 per cent after thermal ageing for three years. Actual catalyst durability in commercial operations is described below. The decrease in hydrocarbon conversion is primarily due to loss of ethane oxidation activity. If high hydrocarbon conversions are required, the catalyst volume can be increased. When the catalyst is operated at 480°C, the sulphur dioxide conversion drops gradually to below 30 per cent after 1 year.

The poison susceptibility of the Johnson Matthey platinum-rhodium catalyst is determined by using synthetic poisons. Aqueous solutions of ferric nitrate, sodium nitrate, orthophosphoric acid, arsenic(III) oxide and colloidal silica are applied to the catalyst at various concentrations, and the activity is measured after thermal treatment. The faster, mass transfer controlled carbon monoxide and ethylene conversions at 480°C are unchanged by any of these poisons up to a level of 2 per cent, based on total catalyst coating weight. However, the slower, kinetically controlled ethane and sulphur dioxide conversions decrease notably on exposure to these poisons. Figure 10 shows the degrees of catalyst deactivation due to poisoning, estimated from the ethane conversion at 480°C. On a molar basis the severity of poisons are in the order:



Silica can act as a poison or a masking agent, depending on its source and the precursor chemistry. In these tests, however, the colloidal silica acts as a masking agent rather than as a catalyst poison.

Where the contents of poisons and foulants in the turbine exhaust are high, extra catalyst can be introduced to maintain high conversion of saturated hydrocarbons.

Commercial Operation

The longest running Johnson Matthey carbon monoxide/hydrocarbon oxidation reactor is installed in the Texaco refinery in Long Beach, California. Here a refinery gas containing 50 ppm sulphur is burnt in a water injected 35 MW United Technologies FT4 gas turbine. The exhaust contains 100 to 200 ppm carbon monoxide depending on the turbine load. The oxidation reactor was guaranteed to reduce carbon monoxide emissions below 13 ppm for two years. The reactor contains 150 cubic feet of catalyst and is operated at 460°C. From start-up in 1982 when the catalyst reduced the carbon monoxide emission to below 5 ppm, the original catalyst has provided nearly five years of satisfactory performance, maintaining the carbon monoxide levels below the required

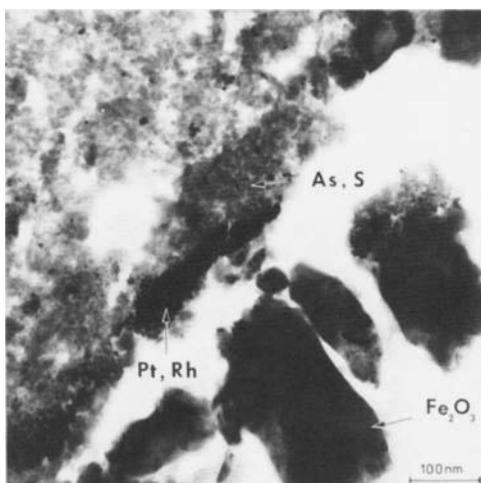


Fig. 11 A section of the surface layer showing iron oxide crystals, a band of platinum + rhodium and a region containing arsenic and sulphur

13 ppm. The ethane oxidation activity deteriorated to 10 per cent of its original activity after two years. At that time a proprietary catalyst wash treatment, which primarily removes foreign materials from the catalyst, restored the original carbon monoxide activity and 70 per cent of the original ethane oxidation activity. The irreversible deactivation of the catalyst is therefore estimated at 30 per cent.

A transmission electron micrograph of the catalyst after two years of service is presented in Figure 11. The catalyst surface is covered with iron oxide particles which have crystallite sizes ranging from 40 nm to 120 nm. The catalyst contains 1.8 per cent iron. Other contaminants are 1.3 per cent sodium, 1.0 per cent sulphur and 1.0 per cent arsenic. These contaminants are distributed fairly uniformly throughout the porous washcoat and appear to arise from corrosion of upstream steel parts, vaporised lubricating oil components and impurities in the fuel, air and water.

The surface area of a sample from the used catalyst was 80 m²/g compared with 150 m²/g for a fresh catalyst. This loss of surface area is attributed to micropore blockage by the contaminants. In turbines fired with natural gas, which is cleaner, exhaust catalyst contamination and degradation are expected to be sig-

nificantly less. Catalyst life for natural gas fuelled turbines is therefore expected to be longer than that for the catalyst in the refinery gas fuelled Texaco installation.

Conclusions

Oxidation catalyst technology developed to reduce automotive exhaust emissions has been extended to reduce the carbon monoxide and hydrocarbon emissions from gas turbines. Platinum-rhodium catalysts have been developed to maximise activity for carbon monoxide and hydrocarbon conversion, while minimising the undesired conversion of sulphur dioxide to sulphate. Commercial operation of metal supported catalyst arrays in large gas turbines has been successful for five years of operation, and continues to be an effective means of reducing carbon monoxide and hydrocarbon emissions from stationary sources.

References

- 1 B. Harrison, B. J. Cooper and A. J. J. Wilkins, *Platinum Metals Rev.*, 1981, **25**, (1), 14
- 2 M. P. Walsh, *Platinum Metals Rev.*, 1986, **30**, (3), 106
- 3 B. Harrison, A. F. Diwell and M. Wyatt, *Platinum Metals Rev.*, 1985, **29**, (2), 50
- 4 J. R. Kiovisky, P. B. Koradia and C. T. Lim, *Ind. Eng. Chem., Prod. Res. Dev.*, 1980, **19**, 218
- 5 R. Lis, H. Jung and E. R. Becker, 80th Annual Meeting of A.P.C.A., New York, Paper No. 87-52.2, 21 June 1987
- 6 A. S. Pratt and J. A. Cairns, *Platinum Metals Rev.*, 1977, **21**, (3), 74
- 7 V. V. Popovskii, *Kinetics and Catalysis*, 1972, **13**, 1065
- 8 J. G. Firth, *J. Catal.*, 1974, **34**, 159
- 9 G. J. K. Acres, *Platinum Metals Rev.*, 1970, **14**, (1), 2
- 10 K. C. Stein, 52nd Annual Meeting of A.P.C.A., Los Angeles, 21-26 June 1969
- 11 L. Hiam, H. Wise and S. Chaikin, *J. Catal.*, 1968, **9**, 272
- 12 B. J. Cooper, B. H. Harrison, E. Shutt and I. Lichtenstein, S.A.E. Paper No. 770367, 1977
- 13 B. J. Cooper, E. Shutt and M. J. Scullard, S.A.E. Paper No. 760035, 1976
- 14 R. H. Hammerle and T. J. Truex, S.A.E. Paper No. 760090, 1976
- 15 T. J. Truex, Symp. on the Status of Automotive Sulfate Emissions, 2nd Joint Conf. of the Chem. Inst. of Canada and Am. Chem. Soc., Montreal, 31 May 1977