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Effects of SO_2 on the alkane activity of three-way catalysts

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Over current Pt-Rh/CeO_2-Al_2O_3 catalysts, the conversion of alkanes occurs by two principal mechanisms: direct oxidation ($HC+O_2$) and steam reforming ($HC+H_2O$). Sulphur dioxide can influence both these mechanisms. Direct oxidation, which predominates when the exhaust-gas is fuel-lean, is *promoted* by the adsorption of SO_x species by the support. Under fuel-rich atmospheres, the presence of SO_2 severely *inhibits* steam reforming. The poisoning is associated with the formation of S^{2-} on the platinum and of SO_4^{2-} on the support, but there is no indication of S-species being retained by the rhodium. It is proposed that each of the two mechanisms is sensitive to a different type of interaction at the metal-support interface. Direct oxidation is enhanced by the transfer of electrons from the precious metal to the support; steam reforming occurs at interfacial sites, which can be blocked by adsorbed SO_x species.

Keywords: Three-way catalysts; sulphur dioxide, poisoning, promotion, oxidation, steam reforming

1. Introduction

The internal combustion engine effectively converts traces of organo-sulphur compounds (generally present in European and US fuels) to sulphur dioxide. If the emissions subsequently pass through a catalytic converter, the SO_2 can undergo a number of changes, which are dependent on the composition and temperature of the exhaust-gas stream, and on the composition of the catalyst.

Sulphur poisoning of platinum-group metals has been widely studied (e.g. see reviews [1,2]) and, ever since the work of Maxted [3], it is usually attributed to the occurrence of either sulphide or sulphite species. In the presence of a three-way catalyst, S^{2-} can be formed under fuel-rich engine cycles [4–6]. When the engine runs fuel-lean, however, the exhaust-gas becomes oxidising, and

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S(VI) species are formed both in the gas-phase [7] and on the catalyst support (CeO_2-Al_2O_3) [5,7]. Using Pt/Al_2O_3 catalysts, Yao and co-workers have shown that the formation of SO_4^{2-} on the support can promote dissociative adsorption on the metal surface [8].

In the present study we have examined how the changes in sulphur species impinge on the mechanisms of alkane conversion, over Pt-Rh/CeO_2-Al_2O_3 automotive catalysts. In turn, the results provide insights into the nature of the interactions between the precious metals and the supporting oxides.

2. Terminology and conventions in three-way catalysis

The composition of an exhaust-gas is often represented by an equivalence ratio (λ). The value of λ is calculated from the amount of oxygen which can be supplied by the oxidising gases, divided by the total amount of oxygen which can be consumed by the reductants. The terms "fuel-lean" or "lean" are used to describe an exhaust-gas when $\lambda > 1.00$; "fuel-rich" or "rich" refer to $\lambda < 1.00$.

Catalytic performance of three-way catalysts is traditionally presented in the form of an activity profile (conversion as function of temperature), which is often referred to as a "light-off curve". However, in its strictest usage, the term "light-off" specifically indicates a sudden increase in rate, when a reaction is driven (to near completion) by an exotherm.

3. Experimental

Catalysts were prepared by impregnating the support material (25 mass% $CeO_2 + 75\%$ γ-Al_2O_3) with aqueous solutions of standard precursors of platinum and/or rhodium, to give a total metal loading of ca. 1% (by mass). Before testing, the samples were dried (110°C), and calcined (500°C) under air.

The metal dispersion was measured by CO chemisorption. Each sample was reduced (300°C; 30 min), before CO was injected into the H_2 gas-stream at room temperature. From the amount of CO adsorbed, CO/M (extent of exposed metal) values were calculated by assuming that each exposed metal atom adsorbs one molecule of CO.

Samples were rich-aged by heating (at fixed temperatures between 300 and 900°C, for 2 h) under a gas-mixture which was both reducing and sulphur-rich (1% H_2; 10% H_2O; 20 mol ppm SO_2; N_2). For lean-ageing, the H_2 was replaced by O_2. The samples were allowed to cool under the gas-mixture used for ageing.

Fresh and aged samples were characterised by XPS (using Kratos XSAM 800; Mg K_α radiation at 130 W; 80 and 40 eV pass energies; C 1s reference, BE = 284.8 eV) and by temperature-programmed reduction (TPR) under 10% H_2/N_2 (40 cm^3 min^{-1}) at 10 K min^{-1}.

Table 1
Composition (mol%) of simulated exhaust-gas mixtures

λ	H_2	O_2	CO	CH_4	C_3H_8	C_3H_6	CO_2	H_2O	NO	SO_2	N_2
0.98	0.43	0.72	1.30	0.067	0.0223	0.0223	15.0	9.2	0.15	0.002	rest
1.02	0.23	0.97	0.70	0.037	0.0123	0.0123	15.0	9.2	0.15	0.002	rest

Activity profiles were obtained during temperature-programmed heating (5 K min^{-1}; 150 to 600°C) of catalysts under either a fuel-rich ($\lambda = 0.98$) or a fuel-lean ($\lambda = 1.02$) simulated exhaust-gas (table 1) at a flow rate of 2 dm^3 min^{-1} g^{-1}. In some experiments SO_2 was excluded from the gas stream.

4. Inhibition and promotion

At $\lambda = 0.98$, the presence of SO_2 in the exhaust-gas severely inhibited the conversion of alkanes over Pt-Rh/CeO_2-Al_2O_3 (fig. 1), particularly at temperatures between ca 275 and 550°C. (From our experience, the distinct plateau is characteristic of ceria-containing catalysts.) There was also an associated effect on the hydrogen concentration, which resulted in the activity trace changing from an almost symmetrical peak when SO_2 was absent (fig. 2a) to a more conventional light-off curve in its presence (fig. 2b). The occurrence of the maximum at ca 300°C can be attributed to competing processes of H_2-conversion and H_2-formation, with the latter predominating at the higher tempera-

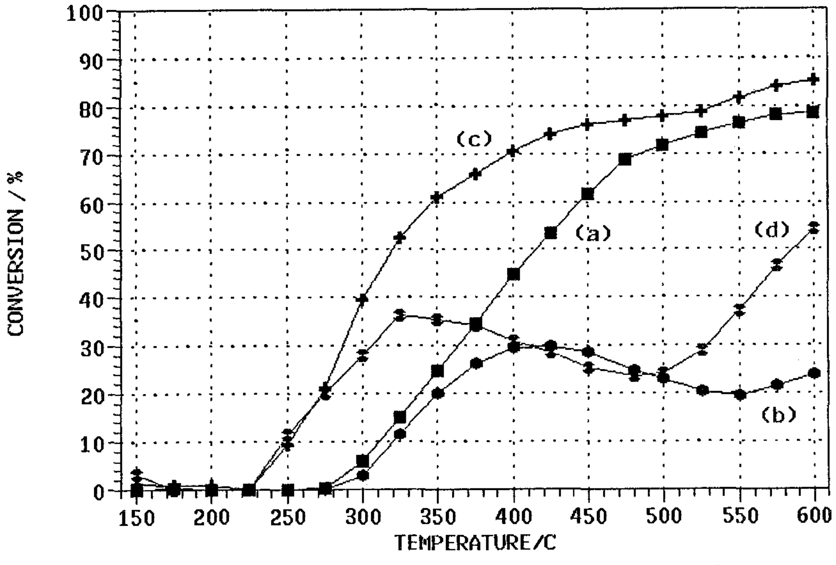

Fig. 1. Alkane activity of Pt-Rh/CeO_2-Al_2O_3 at $\lambda = 0.98$. CH_4 conversion (a) in absence of SO_2, (b) in presence of SO_2; C_3H_8 conversion (c) in absence of SO_2, (d) in presence of SO_2.

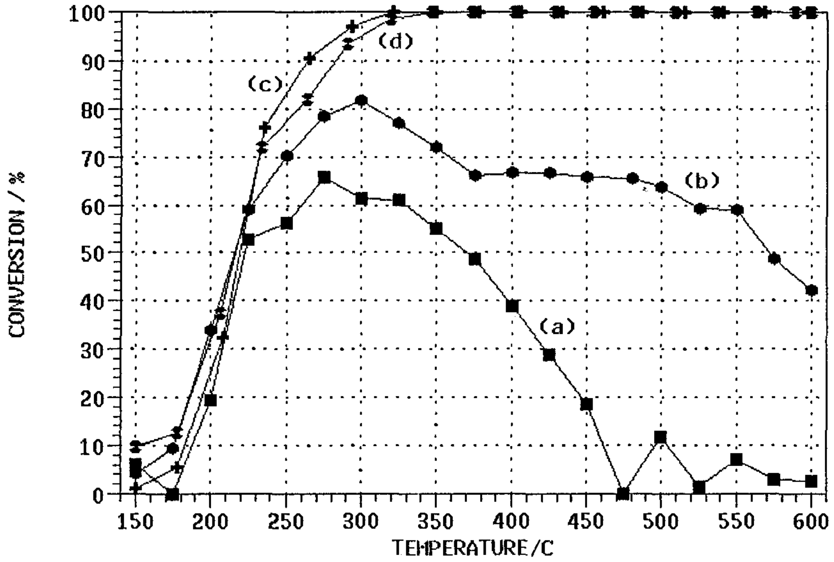

Fig. 2. Hydrogen activity of Pt-Rh/CeO_2-Al_5O_3. At $\lambda = 0.98$ (a) in absence of SO_2, (b) in presence of SO_2; At $\lambda = 1.02$ (c) in absence of SO_2, (d) in presence of SO_2.

tures but being very susceptible to S-poisoning. Although the water-gas shift reaction does occur [9,10], we did not observe any correlation between CO activity and the changes in H_2 concentration when SO_2 was excluded from the gas stream. The changes in hydrogen formation over this catalyst are almost certainly due changes in steam-reforming, which is known to occur over supported forms of both Pt [9] and Rh [9,11]. Indeed, previous work [12] in this laboratory has shown that the alkane activity of Pt-Rh/CeO_2-Al_2O_3 is substantially diminished when H_2O is removed from the gas-phase (the activity is not suppressed totally because H_2O is still being generated in-situ).

The turn-around in H_2-activity was not observed at $\lambda = 1.02$ (figs. 2c and d), indicating either that steam-reforming no longer plays a dominant role in alkane activity under fuel-lean conditions, or that any H_2 generated is immediately converted to H_2O by the presence of excess oxygen. However, the alkane activity did not diminish when H_2O was removed from the gas-stream, confirming that direct oxidation was in fact ocurring.

The presence of SO_2 at $\lambda = 1.02$ promoted the oxidation of propane (figs. 3a and b), but had negligible effect on methane conversion (figs. 3c and d). It should be remembered that, under these (oxidising) conditions, sulphur is retained by the catalyst as SO_4^{2-} on the support [5,7]. The present results are consistent, therefore, with previous work (of Yao et al. [8]) which has demonstrated that oxidation reactions occurring on a platinum-group metal are sensitive to the species adsorbed on the support.

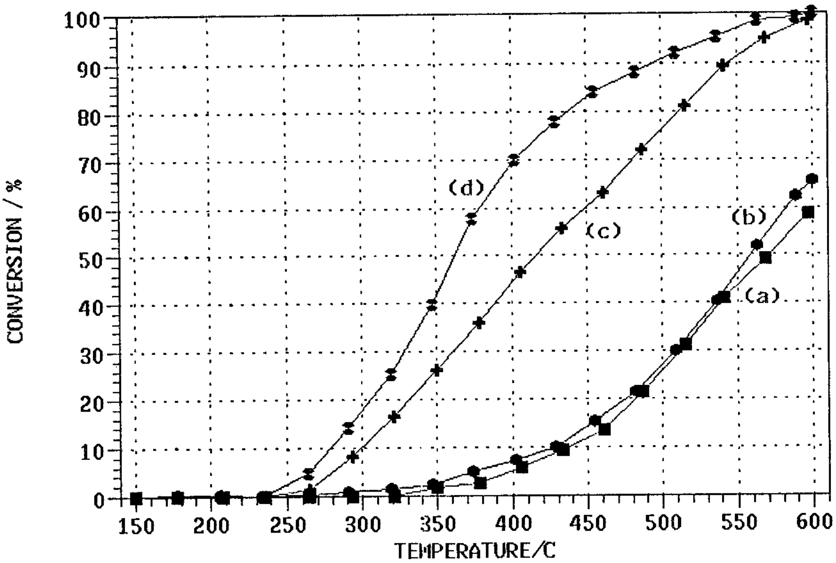

Fig. 3. Alkane activity of Pt-Rh/CeO_2-Al_2O_3 at $\lambda = 1.02$. CH_4 conversion (a) in absence of SO_2, (b) in presence of SO_2; C_3H_8 conversion (c) in absence of SO_2, (d) in presence of SO_2.

5. Nature of S-poisons

There was a substantial loss in the CO-chemisorption capacity of Pt-Rh/CeO_2-Al_2O_3 after rich-ageing in the presence of SO_2 (table 2). This was due in part to sintering of the metal crystallites (especially at temperatures above 550°C), but it also reflected changes in the support (sulphate formation; see later) [8] and the retention of stable species on the metal surface. For example the CO/M value dropped from 0.79 to 0.20 after rich-ageing at 400°C; $< 2\%$ of the change can be attributed to thermally induced sintering (table 2), and $< 55\%$ to sulphate formation (estimated by *lean*-ageing the catalyst in the presence of SO_2 at the same temperature, ie under conditions where sulphur is not expected to be retained by the metal surface [13]). However, even allowing for sintering and support effects, the net changes in CO/M do not provide direct measures of metal surface covered by sulphur, but indicate the combined

Table 2
Effect of rich-ageing Pt-Rh/CeO_2-Al_2O_3 in presence and absence of SO_2

Ageing temperature/°C	CO/M * after ageing	CO/M * after ageing
	$+SO_2$	$-SO_2$
320	0.10	0.75
400	0.20	0.78
550	0.12	0.69
700	0.10	0.39

* CO/M for fresh sample = 0.79.

effects [13–15] of site blocking and the inhibition of adsorption. In fact, the Joyner-Pendry method [16] predicts that the poisoning range for a single S adatom is 0.5–0.7 nm, which corresponds to 10–20 close-packed surface Pt atoms. Previous thermodynamic calculations [4,7,17] have led us to predict that the only stable sulphur species likely to be formed at $\lambda = 0.98$ are H_2S, PtS (<450°C) and $RhS_{0.88}$ (<550°C). After rich-ageing Pt-Rh/CeO_2-Al_2O_3 at 400°C, XPS confirmed the presence of S^{2-} (S 2p, BE = 162 eV) on the catalyst surface. However, the rhodium appeared to be in the form of an oxide (Rh $3d_{7/2}$, BE = 308 eV), suggesting that the decrease in net CO/M value was due to the formation of surface PtS. Furthermore, the surface analysis showed that the concentration of S^{2-} was exceeded by that of oxidised sulphur (S 2p, 169 eV). It was also apparent that the ageing treatment resulted in an increase in the Al/Ce ratio, implying either that the surface of the support had become enriched in aluminium, or that sulphate formation had occurred preferentially on the ceria. Certainly, the cerium had been reduced to Ce^{3+} (Ce $3d_{5/2}$, 882.7 eV), which was consistent with the formation of surface $Ce_2(SO_4)_3$. During TPR, samples which had been rich-aged gave rise to a large reduction peak centred at 480°C. As this peak also appeared when the catalysts were aged in an oxidising atmosphere, we ascribe it to reduction of the sulphate species formed on the support. The peak position seems characteristic of the reduction of such species by spillover-hydrogen generated by Pt [18].

After rich-ageing a supported-Rh catalyst (Rh/CeO_2-Al_2O_3) at 400°C, surface analysis again showed that sulphur had been retained as SVI. However, no S^{2-} was detected, in this case.

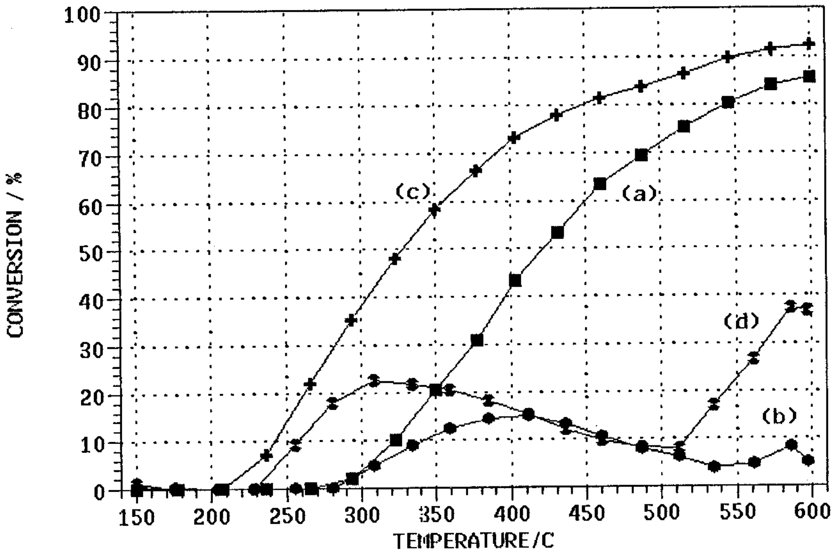

Fig. 4. Alkane activity of Rh/CeO_2-Al_SO_3 at $\lambda = 0.98$. CH_4 conversion (a) in absence of SO_2, (b) in presence of SO_2; C_3H_8 conversion (c) in absence of SO_2, (d) in presence of SO_2.

If it were to be assumed that poisoning occurs only when reduced sulphur species are retained by a catalyst, the above results would indicate that S^{2-} is a highly specific poison, which selectively inhibits steam-reforming reactions over platinum. However, when we tested the activity of the individual supported-metals, we found that SO_2 *does* inhibit steam-reforming over Rh/CeO_2-Al_2O_3 (fig. 4), and that the loss in activity is even greater than for the analogous Pt catalyst. In the absence of any stable species being detected on the rhodium, the inhibition must be caused by

(a) Short-lived species;

(b) re-structuring of the metal surface;

or (c) the sulphate species on the support. As there was no sign of other reactions (notably CO + NO) being inhibited on the Rh surface, we favour explanation (c).

6. Conclusions

During fuel-lean engine cycles, the conversion of alkanes occurs by direct oxidation on the metal sites of a three-way catalyst. The presence of SO_2 in the exhaust-gas induces the following related changes:

(i) the formation of sulphate species on the catalyst support;

(ii) enhanced conversion of higher alkanes. We interpret the response in oxidation activity as showing that the electronic properties of the precious metal are modified by the species adsorbed on the support.

When the exhaust-gas becomes reducing, the prevalent mechanism changes to steam-reforming, which is highly prone to the inhibiting effects of sulphur. The only stable reduced-S species formed on the catalyst are sulphide ions, which appear to be associated with the Pt but not the Rh. As the alkane activity of supported-Rh is, nonetheless, very sensitive to the presence of SO_2, we suggest that changes in the support can hinder the steam-reforming mechanism. We envisage, therefore, that fuel-rich alkane activity can occur at the metal-support interface, and involves reaction between hydrocarbon (adsorbed on the metal) and hydroxyl species (on the support). We believe that formation of sulphates on the support can suppress the interfacial reaction (probably by an associative re-arrangement of the sulphates involving –OH [19]). The range of inhibition is, therefore, closely related to the stability range of the sulphate species.

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