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Vehicle exhaust catalysis: I. The relative importance of catalytic oxidation, steam reforming and water-gas shift reactions

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Abstract

The activity of a monolithic three-way catalyst has been compared with the performance of the individual metals (Pt, Pd, Rh) for oxidation, steam reforming and water-gas shift. The presence of ceria was found to accelerate the last two reactions. The orders of activity were found to be: oxidation — presence or absence of ceria, Pt > Pd > three-way > Rh; steam reforming — no ceria in the catalysts, Pd > Rh > Pt; steam reforming — ceria in the catalyst, three-way ~ Rh > Pd > Pt; water-gas shift — no ceria, Pd > Pt > Rh; water-gas shift — ceria, three-way > Pt > Pd > Rh. Both the water-gas shift and the steam reforming reactions became significant only at higher temperatures than those needed to facilitate oxidation. As a result, both reactions are probably important only after oxygen has been exhausted in the monolithic bed.

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1. Introduction

The use of three-way catalytic converters to minimise air pollution caused by automotive exhaust gases is now well established [1,2]. The catalysts contain small amounts of noble metals (Pt, Pd, Rh) deposited together with a washcoat (alumina modified with small amounts of lanthana or baria and with ca. 10–20% ceria) on a ceramic or metallic monolith [2]. Provided the air:fuel ratio is controlled within a narrow operating window, both the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides is promoted [3,4].

Exhaust gases do not only contain carbon monoxide, hydrocarbons and nitrogen oxides: large amounts of steam and carbon dioxide are also present. As a result, there is significant interest in the effect of these gases on catalyst performance [5–12]. Reactions occurring over the catalyst could include:

Oxidation	$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$	(1)
Partial oxidation	$C_3H_8 + 7/2O_2 = 3CO + 4H_2O$	(2)
Oxidation	$2H_2 + O_2 = 2H_2O$	(3)
Water-gas shift	$CO + H_2O = CO_2 + H_2$	(4)
Steam reforming	$C_3H_8 + 3H_2O = 3CO + 7H_2$	(5)
CO_2 reforming	$C_3H_8 + 3CO_2 = 6CO + 4H_2$	(6)

Of these, CO_2 reforming is too slow to compete with steam reforming [13]. Both steam reforming and water-gas shift are known to be promoted by three-way catalysts [5–13].

The relative importance of oxidation, steam reforming and water-gas shift over different cat-

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alysts has been the subject of some study [5,6]. The role of ceria, known to be a promoter for the water-gas shift reaction [9,14] and steam reforming [7,10,15] has also been studied. However, few systematic studies of the separate and the combined reactions over directly comparable catalysts have been attempted.

The present paper reports such studies using various catalysts used in conjunction with a simulated exhaust gas. The subsequent paper reports the effect of traces of sulphur oxides on catalytic activities.

2. Experimental

All catalysts used in this study were kindly supplied by Johnson Matthey. The performance of a fully formulated monolithic three-way catalyst containing 0.3 wt.-% Pt, Pd and Rh supported on a ceria–alumina washcoat and promoted with baria, vanadia and nickel was compared with the same catalyst system without precious metals and with 0.3 wt.-% of each individual precious metal. Comparisons were also made with monometallic catalysts containing everything except ceria in the washcoat.

A cylindrical (9 mm O.D. × 30 mm length) sample of catalyst was mounted in a quartz tube reactor over a portion of untreated monolith. The reactor was heated electrically to a constant (±2°C) temperature. Thermocouples at the inlet and outlet of the catalytic monolith were used to record the temperature of the catalyst bed. Gas flow-rates were controlled by Brooks mass flow controllers, with water being injected into the gas stream via an evaporator from a syringe pump. Exit gases were analysed gas chromatographically, separating components on a CTR-1 column before both a TCD and a FID detector, used to detect hydrocarbons. Carbon dioxide was also analysed using an on-line non-dispersive infra-red detector. In both cases, water was removed before analysis using an ice–salt bath.

A total flow-rate of 600 ml min^{-1} ($\text{GHSV} = 19000\,\text{h}^{-1}$) was maintained unless otherwise specified. A stoichiometric gas mixture (A) containing 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 15.1% H_2O, 13.4% CO_2, 1.7% O_2 and balance N_2 was used for tests of oxidation. The effect of steam was assessed by replacing steam by N_2 (dry mixture B). The importance of steam reforming and water-gas shift were assessed by replacing oxygen by N_2 (reducing mixture C). A mixture of 3% CO, 18% H_2O balance N_2 at a GHSV of 16000 h^{-1} (WGS mixture) was also used to assess the water-gas shift reaction.

Catalytic activity was measured in terms of conversion and temperature. Using the stoichiometric gas mixture, oxidation was measured in terms of the disappearance of propane, carbon monoxide or hydrogen. Using the gas mixture containing no oxygen, steam reforming was measured in terms of the disappearance of propane. Water-gas shift was assessed in the same mixture from a balance across reactions 4 and 5.

$$CO_{\text{inlet}} + \underset{\substack{\text{consumed in}\\ \text{reaction 5}}}{3C_3H_8} = CO + \underset{\substack{\text{consumed in}\\ \text{reaction 4}}}{CO_{\text{outlet}}}$$

The conversion of CO via the water-gas shift is their

$$X = \left(1 - \frac{\text{CO out}}{\text{CO in} + 3C_3H_8\ \text{consumed}}\right) \times 100\%$$

The importance of the water-gas shift reaction was assessed from the disappearance of CO and the appearance of CO_2 when using the CO/H_2O mixture.

3. Results and discussion

Catalytic oxidation was first examined, using the three-way catalyst and mono-metallic catalysts prepared in the absence and presence of ceria. Oxidation was examined using gas mixtures in the absence (Fig. 1 and Fig. 3 and presence (Fig. 2) of steam.

Platinum, as expected [1,2,5] is found to be the best catalyst for propane oxidation with ceria, if anything, reducing activity (Fig. 1). Palladium

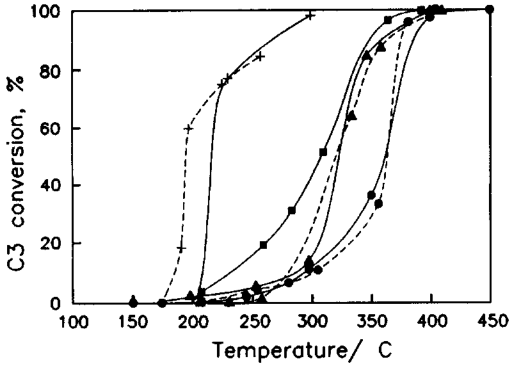

Fig. 1. Oxidation activity of different car exhaust catalysts in terms of conversion of propane in dry feed gas. Feed gas: 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 1.7% O_2 and balance N_2 at GHSV 19000 h^{-1}. Solid curves refer to catalysts containing ceria, dashed curves to catalysts containing no ceria. (■) Three-way, (+) Pt/alumina, (▲) Pd/alumina, (●) Rh/alumina.

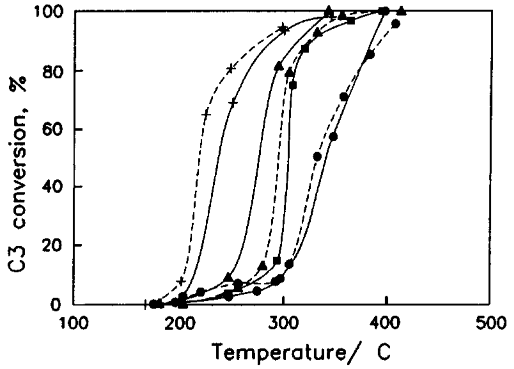

Fig. 2. Activity comparisons of different car exhaust catalysts in terms of conversion of propane in a feed gas containing steam. Feed gas: 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 15.1% H_2O, 1.7% O_2 and balance N_2 at GHSV 19000 h^{-1}. Solid curves refer to catalysts containing ceria, dashed curves to catalysts containing no ceria. (■) Three-way, (+) Pt/alumina, (▲) Pd/alumina, (●) Rh/alumina.

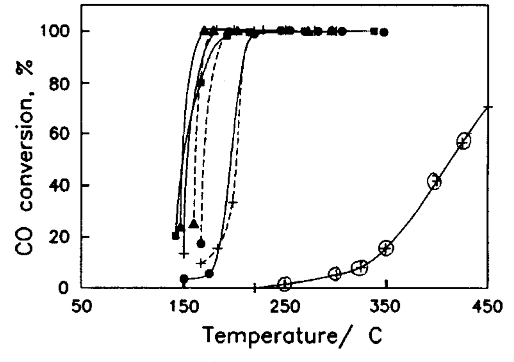

Fig. 3. Oxidation activity of car exhaust catalysts in terms of conversion of carbon monoxide in a dry feed gas. Feed gas: 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 1.7% O_2 and balance N_2 at GHSV 19000 h^{-1}. Solid curves refer to catalysts containing ceria, dashed curves to catalysts containing no ceria. (■) Three-way, (+) Pt/alumina, (▲) Pd/alumina, (●) Rh/alumina, ( ) washcoat.

was found to be the best catalyst for carbon monoxide oxidation (Fig. 3).

The presence of steam was found significantly to enhance the conversion of propane over both Pd and Rh while having little effect in the performance of Pt (compare Fig. 1 and Fig. 2: Table 1). Ceria is also seen to enhance propane conversion, particularly over Pd (Fig. 2). Thus it would seem, in agreement with the findings of Gandhi et al. [10], Lobo et al. [16] and Bart et al. [12], that steam reforming could be responsible for at least part of the conversion of propane.

In order to confirm this, catalysts were tested using reducing mixture C to assess the importance of steam reforming and water-gas shift (Fig. 4). The expected order of activity for steam reforming (Rh > Pd > Pt) [9–11] was observed, with ceria being formed to promote the activity of all catalysts. However, the temperatures at which steam reforming became important (> 350°C) were significantly higher than those involved in oxidation (ca. 200–320°C) (Fig. 2). Thus it seems probable that, in agreement with Barbier Jr. and Duprez [11], steam reforming becomes significant only after oxygen has been consumed. The important reaction is not necessarily the removal of oxygen, but the resulting increase in temperature.

Despite this finding, it is clear from Fig. 1 and Fig. 2 and from Table 1, that the presence of water accelerates the conversion of propane over Pd and Rh and decreases activity over Pt where steam reforming is less likely [10]. The most probable explanation is that oxidation raises the temperature of the catalyst to a value where, over Pd and Rh, further conversion via steam reforming can occur. The temperature increase would not necessarily be measured experimentally, with the thermocouples located near to, but outside the monolith.

The importance of water-gas shift over the catalysts was also examined (Fig. 5, Table 1). As reported by Gandhi et al. [13], the order of activity was found to be Pt > Pd ≥ Rh (Fig. 5) and the presence of caria promoted the reaction (Table 1). The difference in results between the two gas streams (Table 1) reflects the negative

Table 1
Catalytic activities: temperatures needed to achieve 50% conversion

Catalytic activity tested	Reaction mixture[a]	Temperature needed to achieve 50% conversion (°C)						
		Three-way catalyst	Catalytically active metal					
			Pt	Pt/CeO$_2$	Pd	Pd/CeO$_2$	Rh	Rh/CeO$_2$
Oxidation propane	Dry gas B ($-H_2O$)	305	195	216	317	321	360	360
Oxidation propane	Stoichiometric mix A ($+H_2O$)	302	218	237	293	275	333	339
Oxidation CO	Dry gas B ($-H_2O$)	148	201	152	159	148	179	199
Steam reforming propane	Reducing mixture C	385	451	411	415	394	433	385
Water-gas shift	Reducing mixture C	368	315		357		357	
Water-gas shift	3% CO, 18% H_2O, water-gas shift mixture	363	411	374	398	408	450	468

[a]Full details are given in the Experimental section.

order dependence on carbon monoxide [13].

Comparison of the activities of the catalysts for oxidation (Fig. 3) and water-gas shift (Fig. 5) again shows that the water-gas shift reaction does not affect low-temperature reaction. Oxidation of carbon monoxide is favoured at 150–170°C: water-gas shift becomes important only at about 300°C.

Thus it is clear that both steam reforming and water-gas shift can occur in a three-way catalyst, but only at temperatures above those necessary to initiate oxidation. This may not necessarily be the case for all hydrocarbons (methane catalytic oxidation and steam reforming both become important only at ca. 500°C [12,17] but, in the case of propane and carbon monoxide, an increase in catalyst temperature above that needed to induce oxidation is required.

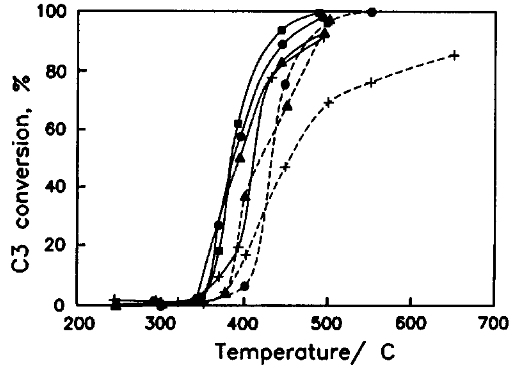

Fig. 4. Steam reforming activity of car exhaust catalysts in terms of conversion of propane in a gas feed: containing steam. Feed gas: 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 15.1% H_2O and balance N_2 at GHSV 19000 h^{-1}. Solid curves refer to catalysts containing ceria, dashed curves to catalysts containing no ceria. (■) Three-way, (+) Pt/alumina, (▲) Pd/alumina, (●) Rh/alumina.

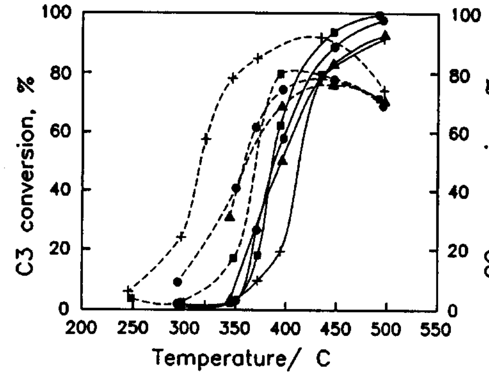

Fig. 5. The contribution of steam reforming and water-gas shift for different catalysts. Gas feed: 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 15.1% H_2O and balance N_2 at GHSV 19000 h^{-1}. Solid curves refer to steam reforming in terms of removal of propane, dashed curves to water-gas shift —in terms of conversion of carbon monoxide. (■) Three-way, (+) Pt/ceria/alumina, (▲) Pd/ceria/alumina, (●) Rh/ceria/alumina.

Vehicle emissions may also contain traces of sulphur oxides. Deactivation and regeneration of catalysts caused by such traces are considered in a subsequent paper [18].

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