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Vehicle exhaust catalysis.
II: The effect of traces of sulphur dioxide on the performance of three-way vehicle emission catalysts

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Abstract

The effect of small amounts of sulphur dioxide on the performance of a three-way vehicle exhaust catalyst has been studied. Removal of propane from a stoichiometric gas mixture containing oxygen was reduced, but the effect was largely reversible. Small amounts of SO_2 poisoned irreversibly the steam reforming and water-gas shift reactions, apparently as a result of a support sulphate/metal sulphite/sulphide couple under oxidising–reducing conditions.

1. Introduction

The relative importance of catalytic oxidation, steam reforming and water-gas shift has been studied using a three-way vehicle emission catalyst and mono-metallic catalysts [1]. Using simulated exhaust gas, oxidation was found to occur at lower temperatures than either of the other reactions, suggesting that reactions involving steam become significant only when oxygen is absent or when the catalyst temperature is higher.

Vehicle exhaust gases usually also contain traces of sulphur oxides, originating from sulphur in the fuel. In an oxidising medium, the presence of sulphur dioxide is reported to result in a slight decrease in the activity of catalysts for the oxidation of propane and carbon monoxide [2,3] and an increase in activity for the oxidation of light hydrocarbons [2–4]. The effect was found to be, at least in part, reversible [3] and was suggested to arise as a result of the formation of sulphites and sulphates [4].

The effect of SO_2 on the catalytic activity has been found to be much more serious in a reducing mixture [2,3,5,6]. The formation of sulphates and sulphides led to poisoning of Pt [6] and to loss of steam reforming and water-gas shift activity [2,7,8]. Bart et al. [9] found that 20 ppm SO_2 in the feed stream inhibited slightly catalytic oxidation and decreased steam reforming activity considerably. It has been suggested that sulphur deposits (possibly as SO_x) at the metal–support interface to suppress steam reforming and water-gas shift [2].

The present studies are focused on the deactivation of a three-way catalyst caused by addition of sulphur dioxide to the feed. Particular attention is focused on oxidation, steam reforming and on water-gas shift reactions occurring over the catalyst.

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2. Experimental

Catalytic activity was measured in a flow rig in which a sample of monolithic catalyst (9 mm OD × 30 mm) was mounted in a quartz tube reactor. Details of the rig and the analysis have been given previously [1]. The three-way catalyst was kindly prepared by Johnson Matthey and contained 0.3 wt.-% Pt, Pd and Rh supported on a ceria–alumina washcoat promoted with baria, and nickel.

Various gas mixtures were fed to the catalyst. A standard test mixture (0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2 15.1% H_2O, balance N_2) could be used to equilibrate the catalyst and to test steam reforming or water-gas shift activity. 1.7% O_2 was added if it was desired to measure oxidation activity (stoichiometric mixture).

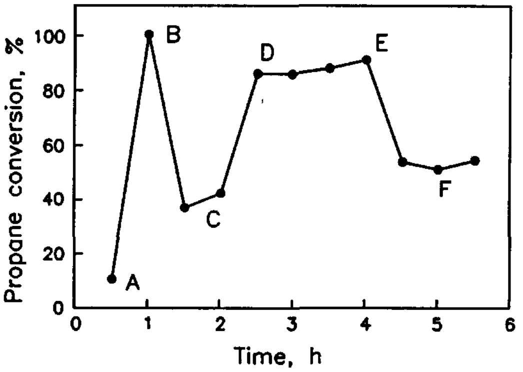

Fig. 1. Effect of SO_2 on the activity of a three-way car exhaust catalyst in terms of propane removal from a gas mixture of 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 1.7% O_2, 13.4% CO_2, 15.1% H_2O and balance N_2 at GHSV 19000 h^{-1}. A —Feed gas admitted into reactor at 300°C; B —temperature increased to 325°C, and catalyst equilibrated; C — 50 ppm SO_2 switched on at 325°C; D —50 ppm SO_2 switched off at 325°C; E —temperature increased to 350°C with SO_2 off; F —50 ppm SO_2 switched on.

A mixture of 13.4% CO_2 and 15.1% H_2O, balance N_2 was used as a rinse gas and a carrier gas. In the latter case, SO_2 (either 20 ppm or 64 ppm), 1.7% O_2 1.7% H_2 or 1.7% CO could be added with the rinse gas, nitrogen being backed off to maintain constant flow.

In all cases, the flow rate was maintained at 600 ml min^{-1} to give a GHSV of 19000–20000 h^{-1} (depending on the reproducibility of the size of the monolith sample). All experiments were duplicated and the carbon balance was accurate to ±2%.

3. Results and discussions

The effect of SO_2 on oxidation of a stoichiometric gas mixture was first examined. The oxidation test mixture was admitted to the reactor at 300°C (point A, Fig. 1) and the temperature slowly raised to 325°C. Light-off occurred and, after equilibrating the catalyst, all propane was removed (point B). 50 ppm SO_2 was then added to the gas stream and, after equilibration, the propane conversion dropped to ca. 40% (point C). Removing SO_2 led to recovery of 85% of the original activity (point D). An increase in reaction temperature failed to increase this value (point E). Subsequent admission of SO_2 again dropped

Table 1
Propane removal over three-way catalysts in the presence and absence of oxygen

Catalyst condition	Propane converted % (stoichiometric mixture)[a]		Propane converted % (reducing mixture)[b]	
	325°C	350°C	400°C	500°C
Fresh	100	100	62.7	100
SO_2 exposed	85.8	90.9	5.4	5.7
SO_2 removed and rinsed with H_2/500°/1 h and air/500°C/1 h	87.1	93.9	2.9	3.1

[a] Stoichiometric mixture = 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 15.1% H_2O, 13.4% CO_2 plus 1.7% O_2, balance N_2 —600 ml min^{-1}.
[b] Reducing mixture = 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 15.1% H_20, 13.4% CO_2, balance —N_2 600 ml min^{-1}.

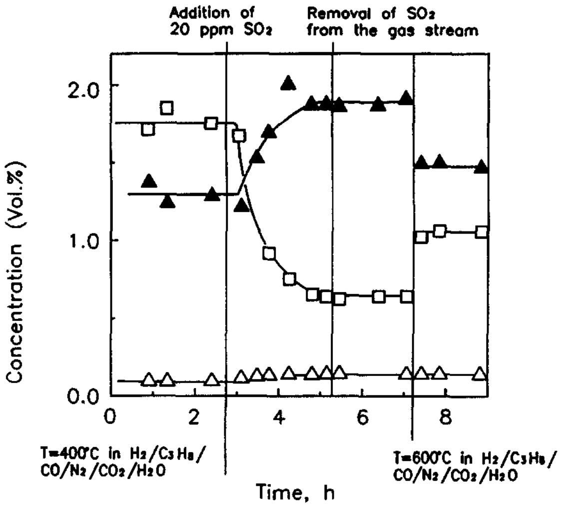

Fig. 2. Effect of addition of SO_2 to a reducing gas mixture over a three-way catalyst. Test conditions 0.5% H_2, 1.6% CO, 0.13% C_3H_8, 13.4% CO_2, 15.1% H_2O, balance N_2: total flow 600 ml min^{-1} (GHSV 19000 h^{-1}). (□) H_2; (▲) CO; (△) C_3H_8.

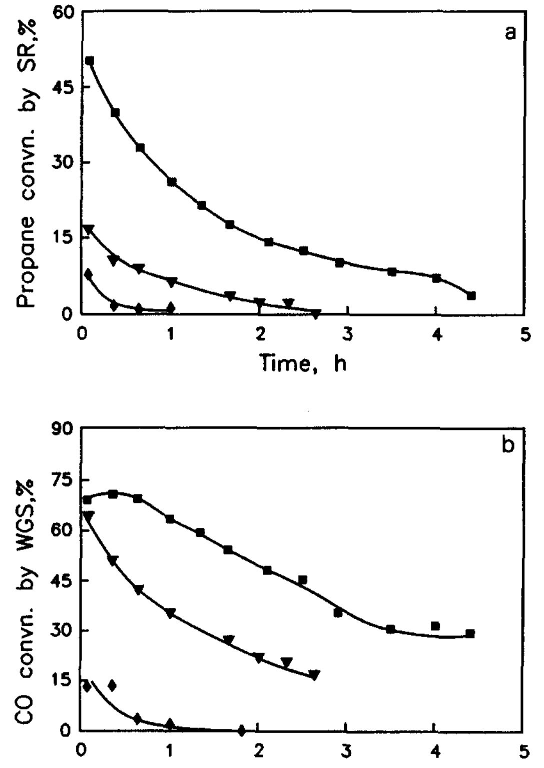

Fig. 3. (a) Steam reforming activity —propane conversion versus time and (b) water-gas shift activity —carbon monoxide conversion versus time, at 400°C of a three-way catalyst poisoned with a total of 4 μmol SO_2 (■); 10 μmol SO_2 (▼); or 21 μmol SO_2 (◆); and then exposed to a mixture containing 0.5% H_2, 1.60% CO, 0.13% C_3H_8, 13.4% CO_2, 15.1% H_2O, balance N_2.

the conversion (F). Results are summarised in Table 1.

The oxidation of propane has been reported to be increased in an oxidising atmosphere containing SO_2 [2–4] but to be decreased in fuel rich gases [2,3,5]. The present results for a stoichiometric gas mixture would indicate that exhaustion of oxygen in the front of the bed may lead to reducing conditions and deactivation at the back of the bed (Table 1). With this in mind, the effect of SO_2 on steam reforming and water-gas shift was examined.

The experiment involved equilibrating a fresh catalyst using a reducing gas test mixture, followed by rinsing using 13.4% CO_2, 15.1% H_2O

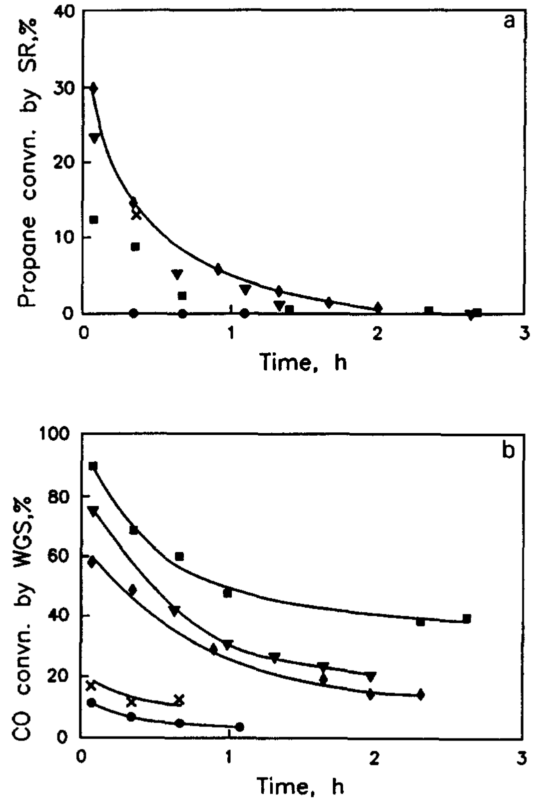

Fig. 4. (a) Steam reforming activity in terms of conversion of C_3H_8 and (b) water-gas shift activity in terms of conversion of CO at 400°C after poisoning a three-way catalyst with 10 μmol SO_2 and then subjecting it to the following conditions: (▼) 600°C/1.7% O_2 for 2 hours, (■) 750°C/1.7% O_2 for 12 hours, (◆) 600°C/N_2 for 2 hours, (×) 600°C/1.7% H_2 for 2 hours, (●) 750°C/1.7% H_2 for 12 hours. (13.4% CO_2, 15.1% H_2O, and N_2 (balance) were additionally present in the above reaction mixtures. Initial SR/WGS activity before regeneration was zero.)

Table 2
Regeneration of SO_2 poisoned catalysts

Regeneration treatment						Subsequent test mixture							
Cycle 1			Cycle 2			Initial conversion (%)				After 2 h conversion (%)			
						$C_3H_8^b$		CO^c		$C_3H_8^b$		CO^c	
Gas[a]	T (3C)	Time (h)	Gas	T (°C)	Time (h)	10[d]	80[d]	10[d]	80[d]	10[d]	80[d]	10[d]	80[d]
1.7% O_2	600	2				24	8	77	25	0	0	22	0
1.7% O_2	750	12				12		90		0		50	
N_2	600	2				30	33	60	66	0	0	20	15
1.7% H_2	600	2				15	0	19	12	0	0	0	0
1.7% H_2	750	12				15		12		0		0	
1.7% H_2	600	2	1.7% O_2	600	2		60		65		20		58
1.6% CO, 0.5% H_2, 0.13% C_3H_8	600	2	1.7% O_2	600	2		45		80		0		10
N_2	600	2	1.7% O_2	600	2		45		67		0		10

[a] 13.4% CO_2, 15.1% H_2O + N_2 balance, were present to give 600 ml min^{-1}.
[b] By steam reforming.
[c] By water-gas shift.
[d] Total SO_2 used to poison the catalyst is 10 μmol or 80 μmol.

balance N_2. SO_2 (20 ppm or 64 ppm) was then mixed with the rinse gas for a period sufficient to pass a known total amount of SO_2 over the catalyst. The monolith was then rinsed (10 min) and the reducing test mixture readmitted. The conversion was followed to equilibration.

Some small deactivation took place during the initial equilibration of the catalyst (Table 1), but this could be reversed by heating to 600°C in oxygen. Addition of SO_2 showed immediate deactivation of steam reforming and water-gas shift (Table 1, Fig. 2). Heating the catalyst to 600°C in the reducing gas mixture did not rejuvenate the catalyst (Fig. 2). Further experiments showed that as little as 4 μmol of SO_2 (there were ca. 35 μmol of active metal in the catalyst) in the samples was sufficient to poison the steam reforming and water-gas shift activity (Fig. 3).

Poisoning of the steam reforming and water-gas shift reactions under reducing conditions has been previously observed [2,3,5] and Gandhi et al. have used IR spectroscopy to show that platinum had a strong affinity for SO_2 under reducing conditions [6]. Thermodynamic calculations based on published data [10,11] suggest that bulk sulphides decompose above ca. 520°C, but two dimensional (layer) sulphides are known to be more stable [12]. Certainly the immediate effect of 21 μmol of SO_2 on activity (Fig. 3) is consistent with direct deactivation of the metal, while the less immediate effect of 4 μmol SO_2 could indicate involvement of the support in the deactivation process.

Both alumina and ceria are known to concentrate sulphur oxides by forming sulphates [13,14]. Under reducing conditions these could revert to sulphites and sulphides to produce some hydrogen sulphide. Adsorption on the surface of catalytically active metals would then lead to deactivation.

Attention was then focused on possible regeneration of catalytic activity. Catalysts were first deactivated by passing either a total of 10 or 80 μmol of SO_2 over the monoliths. The catalysts were then rinsed and the activities determined using the reducing gas mixture. No steam reforming or water-gas shift activity could be observed. Various regeneration procedures were then attempted, and catalyst activities were measured using the reducing test mixture after regeneration. Typical results are summarised in Fig. 4 and Table 2.

It is seen from these results that regeneration does occur on heating in oxygen, but the effect with respect to steam reforming and water-gas shift is temporary. No permanent regeneration was observed on heating in nitrogen or hydrogen. The exception to this behaviour was a reduction–oxidation cycle which led to regeneration of water-gas shift activity (Table 2). This effect was quite reproducible, and the cause is unknown.

It is thought that oxidation of sulphide catalysts generates sulphur oxides, which react readily with alumina and ceria above ca. 500°C to form sulphates [10,11]. Re-admission of the reducing test mixture regenerates sulphites and sulphides which migrate again to the precious metal to renew deactivation.

Overall, however, the effect of sulphur dioxide on the conversion of a stoichiometric gas mixture over a three-way catalyst is significant but largely reversible. Steam reforming and water-gas shift, favoured under reducing conditions, are irreversibly poisoned by small amounts of SO_2.

Acknowledgements

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