

Roles of supports, Pt loading and Pt dispersion in the oxidation of NO to NO₂ and of SO₂ to SO₃

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Abstract

Three types of platinum catalysts, Pt/SiO₂, Pt/γ-Al₂O₃ and Pt/ZrO₂ were examined for the oxidation of NO to NO₂ and of SO₂ to SO₃. The activity order for both oxidation reactions was found to be: Pt/SiO₂ > Pt/γ-Al₂O₃ > Pt/ZrO₂. The effect of Pt loading and Pt dispersion on the catalytic activity and selectivity was examined. Over Pt/SiO₂, the specific activities were found to be strongly size-dependent, the larger Pt particles exhibiting higher specific activity than the smaller ones. Over the Pt/γ-Al₂O₃ catalysts, however, the size-dependence appeared to be much less significant than that of the Pt/SiO₂ catalysts. The results for Pt/ZrO₂ catalysts, however, showed that the specific activities for both reactions were most probably size-independent. The catalytic selectivity for the oxidation of NO relative to that of SO₂ appeared to be size-independent for all the catalysts. The interaction of NO, NO₂ and SO₂ with the catalysts and the effect of the support on the interaction were investigated using TPD technique.

Keywords: Diesel particulate removal; Nitric oxide oxidation; Sulphur dioxide oxidation; Platinum/silica; Platinum/alumina; Platinum/zirconia

1. Introduction

Among several technical possibilities for the control of diesel engine particulate emission is the combustion of soot by nitrogen dioxide (NO₂); this can be generated by catalytic oxidation of nitric oxide (NO) in the exhaust [1,2]. The

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oxidation of NO under diesel exhaust conditions is not a difficult task and the reaction can be catalysed by an oxidation catalyst, for example a platinum-based material. However, any sulphur compound present in the diesel fuel will be converted to sulphur dioxide (SO_2) during engine combustion. In the presence of an oxidation catalyst SO_2 will oxidise to sulphur trioxide (SO_3), which can then form sulphates by reacting with water and other compounds in the exhaust and be adsorbed on the soot, leading to an increase in the weight of the particles emitted from the exhaust. To reduce soot emission from the exhaust the formation of sulphate has to be kept to a minimum by minimising the oxidation of SO_2 and/or using a diesel fuel with a low sulphur content [3].

In an earlier paper, we reported on the oxidation of NO and SO_2 over a model Pt/ SiO_2 catalyst (EUROPT-1) [1]. The catalyst was found to be very active for the oxidation of both NO and SO_2 ; a significant mutual influence between NO and SO_2 was observed, i.e. the presence of SO_2 suppressed drastically the oxidation of NO while the presence of NO in the reaction mixture enhanced SO_2 oxidation.

In this work we have expanded our investigation to other supported platinum catalysts. The catalysts studied were Pt/ SiO_2 , Pt/ $\gamma\text{-Al}_2\text{O}_3$ and Pt/ ZrO_2 . A series of platinum catalysts supported on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and ZrO_2 with various Pt loadings (0.1 to 5 wt.-%) and Pt dispersions were prepared and examined under simulated diesel exhaust conditions in order to see any effect of the nature of the support, the platinum loading and the platinum dispersion on the oxidation of NO and SO_2 .

2. Experimental

2.1. Catalysts

Table 1 lists the catalysts examined in this work, together with the corresponding Pt loadings, the measured Pt dispersions and the BET surface areas.

The support materials used were SiO_2 (Fluid Silica F-7, Akzo B.V., The Netherlands), $\gamma\text{-Al}_2\text{O}_3$ (Alumina 000–1.5E Akzo B.V., The Netherlands), and monoclinic ZrO_2 (RC-100, Daiichi Kigenso Kagaco Kogyo Inc., Japan). All materials were pre-calcined in air at 500°C for 15 h using a linear heating rate of 2°C min^{-1} . The materials were then pressed into discs, and crushed and sieved to obtain grains of size 0.3 to 0.6 mm. The grains were dry-impregnated with $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (Johnson Matthey Chemicals, UK), dried at 100°C and the resultant materials were finally calcined in air at 500°C for 2 h.

The platinum contents of the catalyst samples were determined by the atomic absorption (AA) technique. The platinum dispersion were measured using a Pulse Chemisorb 2700 apparatus (Micromeritics Ltd. USA) by means of hydrogen chemisorption, assuming the ratio of surface Pt to the adsorbed hydrogen

Table 1
The catalysts tested and their characterisations

Catalyst	Pt loading (wt.-%)	Pt dispersion (%)	BET surface area (m ² g ⁻¹)
SiO ₂	–	–	260
0.1 Pt/SiO ₂	0.1 ± 0.05	4	285
0.4 Pt/SiO ₂	0.4 ± 0.1	9	284
2.0 Pt/SiO ₂	2.0 ± 0.2	22	269
5.0 Pt/SiO ₂	5.0 ± 0.5	10	246
γ-Al ₂ O ₃	–	–	197
0.1 Pt/γ-Al ₂ O ₃	0.1 ± 0.05	72	197
0.4 Pt/γ-Al ₂ O ₃	0.4 ± 0.1	100 ^a	175
2.0 Pt/γ-Al ₂ O ₃	2.0 ± 0.2	13	185
5.0 Pt/γ-Al ₂ O ₃	5.0 ± 0.5	34	179
ZrO ₂	–	–	43
0.1 Pt/ZrO ₂	0.1 ± 0.05	28	44
0.4 Pt/ZrO ₂	0.4 ± 0.1	28	43
2.0 Pt/ZrO ₂	2.0 ± 0.2	41	46
5.0 Pt/ZrO ₂	5.0 ± 0.4	19	42

^a Measured value very close to unity.

atom of 1 to 1. During the dispersion measurement, several cycles of hydrogen/oxygen titration were applied prior to the determination of the amount of hydrogen being chemically adsorbed on the platinum of the catalysts, in order to get reproducible platinum dispersion values [4]. The measurements of the total surface areas of the catalysts were carried out using a Micromeritics ASAP2400 system (Micromeritics Ltd. USA), these being based on nitrogen physisorption at –196°C.

2.2. Activity measurements

The experiments were carried out in a fixed-bed tubular reactor system described previously [1]. The reaction temperature was detected by a K-type thermocouple inserted into the catalyst bed and controlled by a Eurotherm. The concentrations of NO and NO₂ were measured using a Nitrogen Oxides Analyzer, Model 8840 (Monitor Labs Inc. USA). The SO₂ concentration was monitored by a Defor SO₂ Analyzer (Maihak GmbH, Germany). All the concentrations of NO, NO₂ and SO₂ were continuously detected and recorded during the experiments. The conversion of NO and SO₂ were calculated based on the following equation:

$$\text{Conversion}(\%) = \frac{Y_{\text{in}} - Y_{\text{out}}}{Y_{\text{in}}} \times 100\% \quad (1)$$

where Y_{in} and Y_{out} are the number of moles of NO or SO₂ entering and leaving

the catalyst bed in unit time, respectively. All the activity measurements were obtained using a feed of volume flow rate $400 \text{ cm}^3 \text{ (STP) min}^{-1}$ consisting of 500 ppm of NO, 50 ppm of SO_2 , 10 vol.-% of O_2 and balance N_2 with a catalyst load of 500 mg in the reactor.

2.3. TPD experiments

Temperature programmed desorption (TPD) experiments were carried out with the same experimental set-up and catalyst load in the reactor as those used for the activity experiments. The experiments were normally done after an activity measurement and the inlet gas used in the activity experiment thus served as the gas for the pre-treatment. After the activity measurement, the catalyst was cooled to room temperature in the same gas stream and the catalyst bed was then purged in N_2 for about 1 h. When the signals of NO, NO_2 and SO_2 from the detectors had dropped to zero, the TPD experiment was started in a N_2 stream (using the same volume flow as that in the activity experiments) with a heating rate of $10^\circ\text{C min}^{-1}$. The maximum temperature for TPD experiment was limited by the set-up and was normally below 480°C . The concentrations of the desorbed NO, NO_2 and SO_2 were recorded as a function of temperature.

3. Results and discussion

3.1. Catalytic activity

Table 2 summarises the results of activity measurements over the three types of catalysts with different Pt loadings at different temperatures; the activity data of the corresponding support materials are also given in the table. It is seen that the Pt catalysts, supported respectively on SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ or ZrO_2 showed very different activities for the oxidation of NO and SO_2 , the SiO_2 supported materials exhibiting the highest. Over all the Pt/ SiO_2 catalysts, the conversion of NO increased with temperature and approached the equilibrium value at about 400°C ; the conversion of SO_2 over these catalysts was also very high and 100% conversion was reached at temperatures about 350°C . The SiO_2 support showed negligible activity compared to the Pt/ SiO_2 catalysts. The $\gamma\text{-Al}_2\text{O}_3$ -supported Pt catalysts also showed increases of both NO and SO_2 conversions with the reaction temperature; over those with the higher Pt loading, i.e. 2 Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 5 Pt/ $\gamma\text{-Al}_2\text{O}_3$, the equilibrium conversion of NO was reached at about 400°C (note that the equilibrium conversions of NO decrease as temperature increases) and the conversion of SO_2 was about 100% above 350°C . The Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts were generally slightly less active for both oxidation reactions than the Pt/ SiO_2 samples with the same Pt loading. The $\gamma\text{-Al}_2\text{O}_3$

Table 2
The conversions of NO and SO₂ over the various catalysts

Catalyst	NO conversion (%)				SO ₂ conversion (%)			
	250°C	300°C	350°C	400°C	250°C	300°C	350°C	400°C
SiO ₂	0	0	0	0	0	0	0	0
0.1 Pt/SiO ₂	21	44	64	50	39	81	100	99
0.4 Pt/SiO ₂	23	50	66	50	46	89	100	99
2.0 Pt/SiO ₂	33	70	71	50	77	100	100	99
5.0 Pt/SiO ₂	33	75	71	50	87	100	100	99
γ-Al ₂ O ₃	0	0	3	4	0	0	1	4
0.1 Pt/γ-Al ₂ O ₃	3	5	9	13	0	4	17	40
0.4 Pt/γ-Al ₂ O ₃	4	8	16	26	9	22	71	77
2.0 Pt/γ-Al ₂ O ₃	27	52	67	50	57	91	100	99
5.0 Pt/γ-Al ₂ O ₃	16	35	58	50	40	82	100	99
ZrO ₂	0	0	0	2	0	2	5	12
0.1 Pt/ZrO ₂	0	0	1	2	1	7	13	26
0.4 Pt/ZrO ₂	0	2	6	12	7	7	17	42
2.0 Pt/ZrO ₂	6	16	26	38	8	26	57	88
5.0 Pt/ZrO ₂	9	25	42	49	20	40	73	93

support showed negligible activity. The ZrO₂-supported Pt catalysts showed the lowest activities for the oxidation of both NO and of SO₂ and the conversions over the ZrO₂ support were much lower than those of the Pt/ZrO₂ catalysts.

3.2. The effect of Pt loading and Pt dispersion

The fact that the Pt-containing catalysts showed much higher activities for the oxidation reactions than did the corresponding support materials implies that the Pt is the active phase for these reactions. In this section, the dependence of the catalytic activity on the Pt loading and on the area of Pt surface exposed are discussed for the Pt/SiO₂, Pt/γ-Al₂O₃ and Pt/ZrO₂ catalysts. To facilitate the discussion, the reaction rates (R_{NO} , R_{SO_2}) and the specific activities in terms of turnover frequency (f_{NO} , f_{SO_2}) for the oxidation of NO and SO₂, as well as the selectivity for the oxidation of NO over that of SO₂ over each of the catalysts are tabulated in Tables 3–5. The size of surface Pt particles (d_{Pt}) and the number of moles of Pt exposed (Pt_s) on the catalyst surface were calculated from the Pt dispersion values and the results are given in the tables.

3.2.1. Pt/SiO₂

Table 3 shows that the reaction rate for NO oxidation increased as the Pt loading increased up to 2 weight percent; however, the rate remained almost constant when the Pt load increased further from 2 to 5 wt.-%. The same rates for NO oxidation observed at 400°C over all the catalysts were due to the fact that the conversions of NO at this temperature were limited by thermodynamic

Table 3
The activities and selectivities of the Pt/SiO₂ catalysts

Catalyst	Pt_s ($\mu\text{mol g}^{-1}$)	d_{Pt} (nm)	T ($^{\circ}\text{C}$)	r_n ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	r_s ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	f_n (h^{-1})	f_s (h^{-1})	$S_{n/s}$ –
0.1 Pt/SiO ₂	0.21	21	250	225	41.8	1097	204	5.4
			300	471	86.8	2298	423	5.4
			350	685	107	3343	522	6.4
			400	536	106	2612	517	5.1
0.4 Pt/SiO ₂	1.85	9	250	246	49.3	133	26.7	5.0
			300	536	95.3	290	51.7	5.6
			350	707	107	383	58.0	6.6
			400	536	106	290	57.5	5.1
2 Pt/SiO ₂	22.6	3.7	250	353	82.5	15.7	3.66	4.3
			300	750	107	33.2	4.75	7.0
			350	760	107	33.7	4.75	7.1
			400	536	106	23.7	4.70	5.1
5 Pt/SiO ₂	25.6	8.2	250	353	93.2	13.8	3.64	3.8
			300	803	107	31.3	4.18	7.5
			350	760	107	29.7	4.18	7.1
			400	536	106	20.9	4.18	5.1
EUROPT-1 (6.3Pt/SiO ₂) 323	1.3	300	300	642	61.8	3.06	0.29	10.4
			350	1178	174	5.64	0.83	6.8

Pt_s : Pt exposed on the surface in $\mu\text{mol g}^{-1}$, calculated from Pt dispersion.

d_{Pt} : size of surface Pt particles in nm, assuming surface particles being cubic shape and calculated using the equation from Ref. [5]: $d_{Pt} = 0.821(1/D_{Pt})$, where D_{Pt} is Pt dispersion.

r_n , r_s : reaction rate of NO or SO₂ over catalyst in $\mu\text{mol g}^{-1} \text{h}^{-1}$.

f_n , f_s : turnover frequency of NO or SO₂, defined as the number of moles of i converted over each mole of the surface Pt per h.

$S_{n/s}$: selectivity, the number of moles of NO converted over that of SO₂ on a catalyst.

equilibrium. The reaction rate for SO₂ oxidation increased with Pt loading. It should be noted that SO₂ conversion reached 100% above 350°C over all the catalysts and at 300°C over the catalysts with 2 and 5% of Pt loadings, see also the data in Table 2.

It is interesting to note that a fifty-fold increase in the Pt loading (from 0.1 to 5 wt.-%) brought an increase of the reaction rate of only about 57% at 250°C (from 225 to 353 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and by about 70% at 300°C (from 471 to 803 $\mu\text{mol g}^{-1} \text{h}^{-1}$), and an increase in SO₂ oxidation rate by about 120% at 250°C (from 41.8 to 91.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$).

Table 3 also shows that the reaction rates for NO and SO₂ oxidation increase as the number of moles of the Pt exposed on the surface per gram of the Pt/SiO₂ catalysts increases but the relation does not seem to be linear; this may indicate that the exposed Pt atoms do not all have the same specific activity. The specific activities of Pt/SiO₂ catalysts are expressed in Table 3 as the number of moles of NO or SO₂ converted per mole of the surface Pt per hour and are denoted as f_{NO} and f_{SO_2} , respectively.

The size of Pt particles is calculated by a formula which is based on the assumption that the surface Pt particles are cubic in shape, given by White [5] as follows:

$$d_{\text{Pt}} = 0.821 (1/D_{\text{Pt}}) \text{ (nm)} \quad (2)$$

where d_{Pt} is the size of surface Pt cluster in nm and D_{Pt} is the Pt dispersion. From the results of Table 3 for the SiO_2 supported materials it is seen that the larger Pt particles seem to have higher specific activities than the smaller ones; for instance, values of 1097 and 204 h^{-1} for f_{NO} and f_{SO_2} , respectively were obtained with the surface Pt particles with size of 20.5 nm while these were only 15.7 and 3.66 for f_{NO} and f_{SO_2} for those Pt particles of size 3.7 nm. This may imply that there is a particle size effect for Pt/ SiO_2 catalysts for the oxidation of both NO and SO_2 , larger Pt particles being more active.

From the point of view of the dependence of the specific activity on the particle size of an active component in a catalyst, two types of reaction have been identified: (a) cases in which the reaction rate depends on the size of the particles, so-called *structure-sensitive* reactions; and (b) cases in which the reaction rate is independent of the size of the particles so-called *structure-insensitive* reactions. The present results seem to indicate that both NO and SO_2 oxidation reactions are structure-sensitive over the Pt/ SiO_2 catalysts. Why they are structure-sensitive is not clear from the present study and further investigation is required to explain this phenomenon.

Table 4
The activities and selectivities of the Pt/ Al_2O_3 catalysts

Catalyst	Pt_s ($\mu\text{mol g}^{-1}$)	d_{Pt} (nm)	T ($^{\circ}\text{C}$)	r_n ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	r_s ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	f_n (h^{-1})	f_s (h^{-1})	$S_{n/s}$ –
0.1 Pt/ Al_2O_3	3.69	1.1	250	32.1	0.0	8.7	0	–
			300	53.6	4.3	14.5	1.16	12.5
			350	96.4	18.2	26.1	4.93	5.3
			400	139.2	42.8	37.7	11.6	3.3
0.4 Pt/ Al_2O_3	20.5	0.8	250	42.8	9.6	2.09	0.47	4.4
			300	85.7	23.6	4.18	1.15	3.6
			350	171.4	76.0	8.36	3.71	2.3
			400	278.5	82.5	13.6	4.02	3.4
2 Pt/ Al_2O_3	13.3	6.3	250	289.2	61.0	21.7	4.58	4.7
			300	556.9	97.5	41.8	7.31	5.7
			350	717.6	107.1	53.8	8.04	6.7
			400	535.5	106.0	40.2	7.96	5.1
5 Pt/ Al_2O_3	87.1	2.4	250	171.4	42.8	1.97	0.49	4.0
			300	374.9	87.8	4.3	1.01	4.3
			350	621.2	107.1	7.13	1.23	5.8
			400	535.5	106.0	6.15	1.22	5.1

Symbols are the same as those in Table 3.

Table 5
The activities and selectivities of the Pt/ZrO₂ catalysts

Catalyst	Pt_s ($\mu\text{mol g}^{-1}$)	d_{Pt} (nm)	T (°C)	r_n ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	r_s ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	f_n (h^{-1})	f_s (h^{-1})	$S_{n/s}$ –
0.1 Pt/ZrO ₂	1.44	2.9	250	0.0	1.1	0.0	0.7	–
			300	0.0	7.5	0.0	5.2	–
			350	10.7	13.9	7.5	9.7	0.8
			400	21.4	27.8	14.9	19.4	0.8
0.4 Pt/ZrO ₂	5.74	2.9	250	0.0	7.5	0.0	1.3	–
			300	21.4	7.5	3.7	1.3	2.9
			350	64.3	18.2	11.2	3.2	3.5
			400	128.5	45.0	22.4	7.8	2.9
2 Pt/ZrO ₂	42.0	2.0	250	64.3	8.6	1.5	0.2	7.5
			300	171.4	27.8	4.1	0.7	6.2
			350	278.5	61.0	6.6	1.5	4.6
			400	407.0	94.2	9.7	2.2	4.3
5 Pt/ZrO ₂	48.7	4.3	250	96.4	21.4	2.0	0.4	4.5
			300	267.8	42.8	5.5	0.9	6.3
			350	449.8	78.2	9.2	1.6	5.8
			400	524.8	99.6	10.8	2.0	5.3

Symbols are the same as those in Table 3.

The reaction rates and specific activities of the EUROPT-1 (6.3 Pt/SiO₂) obtained under the same experimental conditions are also given in Table 3, calculated from the data reported previously [1]. A comparison of these data shows that the reaction rates for the oxidation of both NO and SO₂ over the EUROPT-1 catalyst are in the same order as those over the Pt/SiO₂ catalysts in this work; however, the values of either f_{NO} or f_{SO_2} for the EUROPT-1 catalyst are much lower than those for the Pt/SiO₂ catalysts. This is consistent with the trend observed in the present study — that smaller Pt particles (higher Pt dispersion) give lower specific activity — since the size of Pt particles on EUROPT-1 surface is known to be relatively small [6], compared with the Pt/SiO₂ in this work.

3.2.2. Pt/ γ -Al₂O₃

Pt/ γ -Al₂O₃ catalysts were examined in the same manner as the Pt/SiO₂ catalysts. Table 4 shows the amount of the surface Pt exposed and the calculated Pt particle size of the Pt/ γ -Al₂O₃ catalysts and their corresponding reaction rates and turnover frequencies for the oxidation of NO and SO₂. Increasing the Pt loading in the Pt/ γ -Al₂O₃ catalysts caused both the reaction rates of NO and of SO₂ to go up. Similar trends were also observed when the dependence of the reaction rates on the number of moles of the surface Pt were examined. The 2 Pt/ γ -Al₂O₃ catalyst showed somehow even higher rates than the 5 Pt/ γ -Al₂O₃; the reason for this is not yet clear. The turnover frequencies of NO and SO₂

seem to increase slightly as the size of the Pt particles becomes larger; however, the tendency appears to be much less for the Pt/ γ -Al₂O₃ catalysts than was the case for the Pt/SiO₂ catalysts.

In the case of Pt/SiO₂ catalysts, we concluded that the oxidation of NO and SO₂ over this type of catalysts is structure-sensitive; in the case of the Pt/ γ -Al₂O₃ catalysts, however, the influence of Pt particle size on the rate is less and it is difficult to classify the type of reaction from the present set of experimental results.

3.2.3. Pt/ZrO₂

Table 5 summarises the activity and selectivity data of the Pt/ZrO₂ catalysts. The oxidation reaction rates for NO and SO₂ increased with the Pt loading, the increase in the rate being greater when the Pt loading was changed from 0.1 to 2 wt.-% than when the Pt loading was changed from 2 to 5 wt.-%. The reaction rates for NO and SO₂ oxidation appeared to increase proportional to the Pt surface exposed. However, there was no fixed relation between the specific activity of the catalysts and the size of surface Pt particles; the reaction is most likely to be structure insensitive over the range of Pt particle sizes studied.

3.3. Catalytic selectivity

The catalytic selective, $S_{n/s}$, defined as the number of the moles of NO converted versus that of SO₂ converted over each catalyst is also given in Tables 3–5. The values of selectivity generally fall in the range between 2 to 8. A change in the Pt size appeared to have no significant influence on the selectivity of any of the catalysts. This would be expected as all the catalysts exhibited the same trends in the size effect (either size-dependent or size-independent) for the oxidation of NO as that of SO₂. These results imply that the selectivity of these catalysts cannot be improved by optimising the size of surface Pt particles.

3.4. Effect of the support

The large differences in the activity for the oxidation reactions of the catalysts with the same Pt loading but supported on different materials suggest that the support may play an important role in the oxidation reactions. To examine how the reactant gases interact with the different catalysts as well as to gain information on the effect of the different support materials on the interaction, temperature-programmed desorption (TPD) experiments were performed and the results are presented in Figs. 1–3.

Fig. 1a and b show the recorded signals of NO and SO₂, respectively, from TPD experiments for Pt/SiO₂ materials with various Pt loadings and for the SiO₂ support. It is seen that the desorption of NO from the support SiO₂ (Fig.

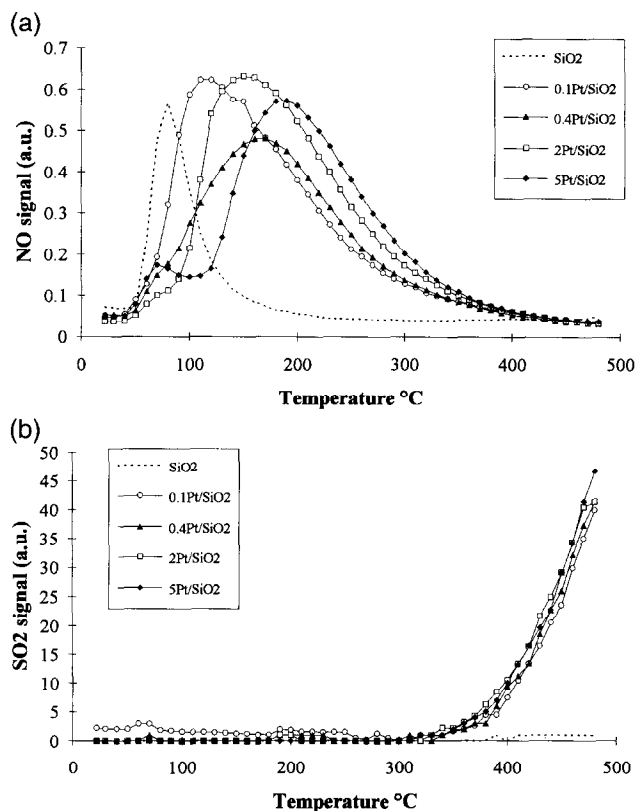


Fig. 1. (a) NO TPD signals over SiO_2 and Pt/ SiO_2 catalysts. (b) SO_2 TPD signals over SiO_2 and Pt/ SiO_2 catalysts.

1a) showed a narrow peak centred at about 80°C and the desorption was complete at 200°C . In the case of the Pt-containing catalysts, the desorption of NO occurred over the whole temperature range measured (25°C to 400°C) and the peak maxima shifted to higher temperatures than in the case of the support alone; there is no relation found between the areas of the desorption peaks and the Pt loadings. The NO_2 signals recorded in parallel TPD runs (not plotted) showed exactly the same trend as for the NO signals for all the catalysts. Fig. 1b shows that the sample of SiO_2 support did not adsorb SO_2 over the whole temperature range examined and that all the Pt-containing catalysts showed nearly the same characteristics for the SO_2 desorption, this starting at around 340°C and increasing continuously up to 480°C , the highest temperature used. These results seem to indicate that the adsorption of NO (and also of NO_2) and of SO_2 occurs predominantly on the surface Pt sites of the Pt/ SiO_2 catalysts in the reaction temperature range (200 to 400°C) and that the SiO_2 support contributes very little to the adsorption of these molecules on the Pt-containing catalysts. The adsorption of NO and NO_2 on the SiO_2 support also appears to be

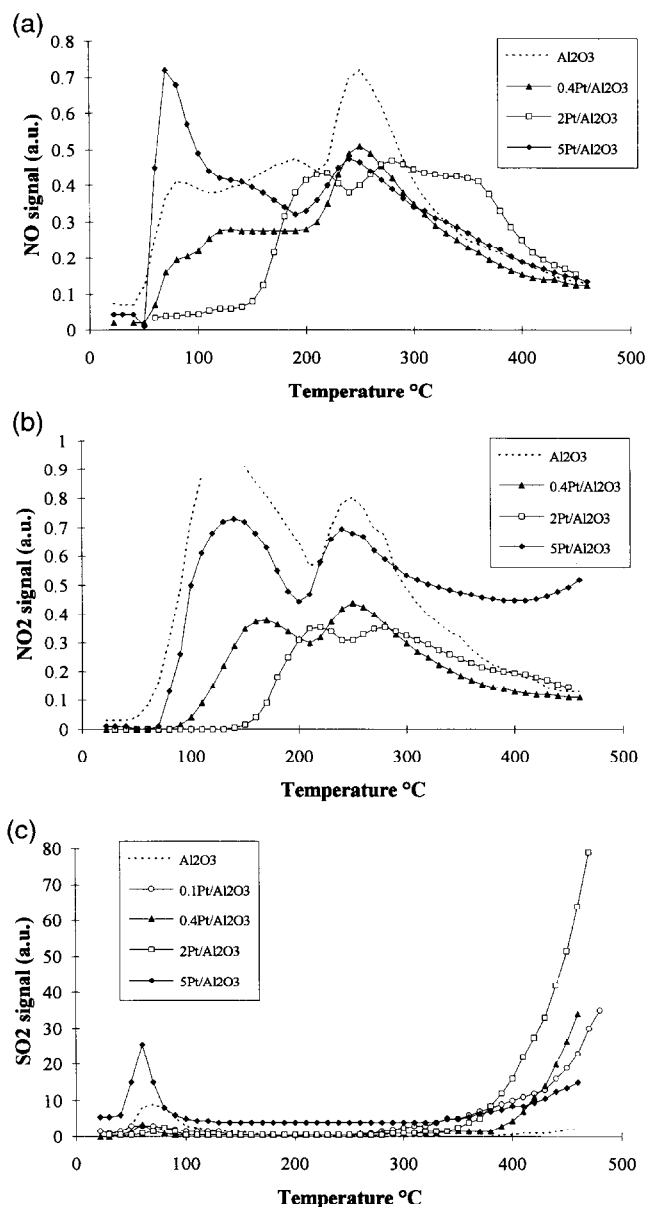


Fig. 2. (a) NO TPD signals over γ -Al₂O₃ and Pt/ γ -Al₂O₃ catalysts. (b) NO₂ TPD signals over γ -Al₂O₃ and Pt/ γ -Al₂O₃ catalysts. (c) SO₂ TPD signals over γ -Al₂O₃ and Pt/ γ -Al₂O₃ catalysts.

relatively weaker than that on the Pt sites of Pt/SiO₂; there was no SO₂ adsorption on the support.

The measured signals of NO, NO₂ and SO₂ in the TPD experiments with Pt/ γ -Al₂O₃ and γ -Al₂O₃ are shown in Fig. 2a to c. Fig. 2a shows that the

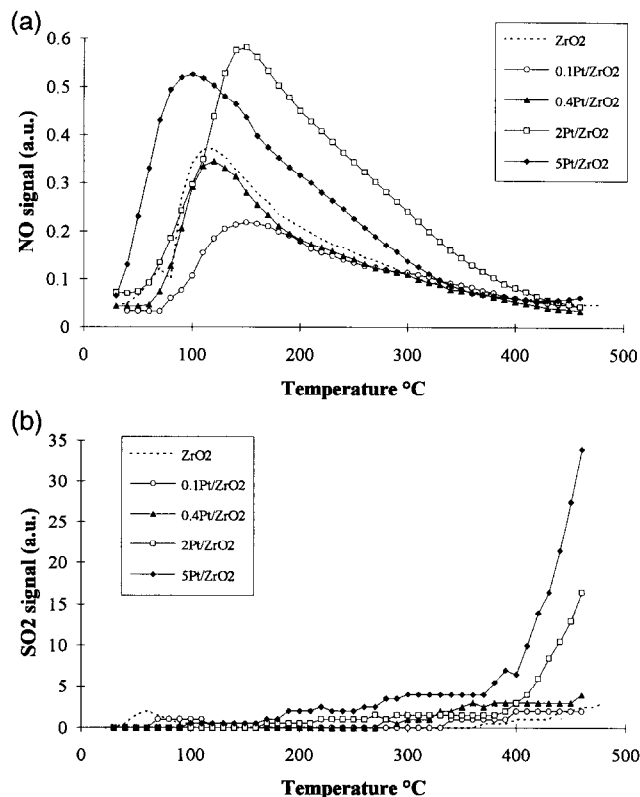


Fig. 3. (a) NO TPD signals over ZrO_2 and Pt/ ZrO_2 catalysts. (b) SO_2 TPD signals over ZrO_2 and Pt/ ZrO_2 catalysts.

desorption of NO from both Pt/ $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ is rather complicated, showing multiple peaks which cover the entire temperature range measured. Looking at the NO desorption in the temperature range in which the activities of the catalysts were examined (250 to 400°C), it appears that nearly all the Pt-containing catalysts gave desorption at a similar temperature but with a lower intensity than that of the $\gamma\text{-Al}_2\text{O}_3$ support alone; an exception was the 2 Pt/ $\gamma\text{-Al}_2\text{O}_3$ (open squares) which gave two desorption peaks both having higher peak temperatures than those of the other catalysts. A similar trend to that observed for NO was also found for NO_2 desorption for each catalyst (Fig. 2b). Considering again only the temperature range from 250 to 400°C, it appears that the $\gamma\text{-Al}_2\text{O}_3$ support seems to govern the desorption characteristics of the Pt-loaded samples. The desorption of SO_2 from both the support and from the Pt-containing catalysts (Fig. 2c) showed one small peak in the low temperature region, centred at 60 to 70°C, and another peak starting at about 350 to 380°C. The low intensity of the SO_2 signal from the $\gamma\text{-Al}_2\text{O}_3$ support (dotted line) in comparison with the Pt-containing catalysts may be an indication that the SO_2

adsorption occurred predominantly on the Pt sites of the catalysts. Comparing these TPD results with those of SiO_2 and Pt/SiO_2 , it seems that the desorption behaviour of the $\gamma\text{-Al}_2\text{O}_3$ support had more influence on the behaviour of the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalysts than did the SiO_2 in the case of the Pt/SiO_2 materials. The adsorption of NO and NO_2 on $\gamma\text{-Al}_2\text{O}_3$ also appears to be stronger than that on the SiO_2 support.

Fig. 3a and b show the desorption of NO and SO_2 , respectively, from the ZrO_2 support and from the Pt/ZrO_2 catalysts. (Similar trends in the NO_2 signals as in those for NO were observed and so the NO_2 data are not shown here). It is seen that the desorption of NO (and NO_2) occurred in one broad peak between 20 to 400°C for all the samples. The presence of Pt in the catalysts, however, did not affect the shapes of curves for the desorption of NO (and NO_2) compared with that for the ZrO_2 support alone, although the peak temperatures varied slightly and the peak intensity changed. The desorption of SO_2 (Fig. 3c) appeared mainly at high temperatures, there being more SO_2 desorption from the catalysts with the higher Pt loadings. As in the case of $\gamma\text{-Al}_2\text{O}_3$, the desorption behaviour of the ZrO_2 support appears to have a great influence on the desorption curves of the Pt/ZrO_2 catalysts, especially on those for NO (and NO_2).

From the above results, it appears that the SiO_2 support is very inert in the reactions and has little influence on either the adsorption features (Fig. 1) or the catalytic activities for oxidation (Table 2) of the Pt/SiO_2 materials with different Pt loadings; the Pt/SiO_2 catalysts, even with a very low Pt loading, gave very high conversions of both NO and SO_2 (Table 2). These observations suggest that the Pt in the catalyst may have a very high intrinsic activity for the oxidation reactions and this intrinsic activity may remain unaffected by the presence of the SiO_2 support. In the cases of the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ and Pt/ZrO_2 catalysts, however, the contributions of the supports to the overall reactions seemed to be more pronounced than in case of the Pt/SiO_2 catalysts. As is seen from the results shown above, the characteristics of these supports for the adsorption of NO and NO_2 appear to be more influential on these catalysts, especially in the temperature range where the catalytic activities were measured. The reactant (NO) is probably adsorbed mainly on the support and then migrates to the Pt sites where it reacts; the product molecules (NO_2) may be held more strongly on $\gamma\text{-Al}_2\text{O}_3$ and ZrO_2 than on SiO_2 (the NO_2 peaks in the TPD runs of these catalysts occurring at higher temperatures); the overall reaction rates over the catalysts supported on these materials may therefore decrease. In the presence of SO_2 and O_2 (or SO_3), the materials such as Al_2O_3 and ZrO_2 can undergo sulphation, which can in turn alter the catalytic properties of the samples. This may also contribute to the strong influence of alumina and zirconia supports on the behaviour of the corresponding catalysts in the reactions [7]. Other factors such as the difference in the population of surface OH^- groups on the different support materials and in the nature of the adsorption of oxygen

on the catalysts could also be important in determining the overall activities of these catalysts. Detailed studies are necessary to reveal the exact nature of the influence of the nature of the supports on the reaction mechanisms and this was beyond the scope of this work.

The relative reactivity of the supports towards the reactant gas molecules observed in this work agrees well with the known behaviour of these materials. For example, SiO_2 is known to be inert in an acidic environment [8], and so little interaction between SiO_2 and the acidic molecules such as NO and SO_2 used in this work would therefore be expected. On the other hand, $\gamma\text{-Al}_2\text{O}_3$ is known to react with acidic molecules such as NO, NO_2 and SO_2 because of its amphoteric nature; for instance, it has been reported that SO_2 can be adsorbed on $\gamma\text{-Al}_2\text{O}_3$, forming aluminium sulphate [9]. A ZrO_2 material has both acidic and basic sites on the surface [10], thus adsorption of acidic molecules, such as the NO, NO_2 and SO_2 used in this study, may be expected on the surface of ZrO_2 .

4. Conclusions

Among the three groups of catalysts investigated, the following activity order for both the oxidation of NO and SO_2 was observed: $\text{Pt}/\text{SiO}_2 > \text{Pt}/\gamma\text{-Al}_2\text{O}_3 > \text{Pt}/\text{ZrO}_2$. The activities of all three groups of the catalysts for the oxidation of NO and SO_2 were observed to increase as the Pt loadings increased in the range examined (from 0.1 to 5 wt.-%) and as the amount of the Pt exposed on the surface went up. However, the dependence of the specific activities on the particle sizes of the surface Pt varied from catalyst to catalyst. Over the Pt/SiO_2 materials, the specific activities were found to be strongly size-dependent, the larger Pt particles exhibiting higher specific activity than the smaller ones; the reactions taking place on this type of catalyst were probably mainly of the structure-sensitive type. Over the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalysts, the size-dependence appeared to be much less significant than that of the Pt/SiO_2 catalysts and it is difficult to classify the reaction type from the present experimental results. The results for Pt/ZrO_2 catalysts, however, showed that the catalytic reactions were most probably size-independent. SiO_2 was found to have very little influence on the corresponding Pt/SiO_2 catalysts for the oxidation reactions studied. However, the $\gamma\text{-Al}_2\text{O}_3$ and ZrO_2 support materials showed a relatively large influence on the behaviour of the corresponding Pt-containing catalysts.

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