Enhancement by SO_2 of initial activity for selective catalytic reduction of NO with CH_3OH over γ-alumina

S.G. Masters and D. Chadwick [*]

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK

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The effect of SO_2 on catalytic activity for NO reduction to N_2 by methanol in excess oxygen over γ-alumina has been investigated. SCR activity increased initially upon exposure of a fresh γ-alumina catalyst to SO_2 which is attributed to formation of Brønsted acid sites. Longer exposure to SO_2 leads to a decline in catalytic activity to a lower steady-state NO_x reduction activity which is independent of the SO_2 content in the feed gas.

Keywords: SO_2, NO reduction, methanol, γ-alumina

1. Introduction

The stringent legislation for nitrogen oxides (NO_x) emission from vehicles and stationary emission sources has been the momentum behind the development of catalysts for NO_x reduction. Abatement of NO_x emission from diesel and lean burn engines requires the development of catalysts which are active in the presence of excess oxygen. Hamada et al. [1–3] have shown that methanol can be applied effectively as a reductant in selective catalytic reduction (SCR) of NO_x over γ-alumina. Diesel fuel contains, depending on different legislation, small quantities of sulphur (0.001–0.4 wt%) which is oxidised to SO_2 during combustion, typically giving a SO_2 content of 20–100 ppm in the exhaust gas. Here we report the effect of SO_2 on the activity of γ-Al_2O_3 catalysts for NO reduction by methanol in excess oxygen. Previous studies have investigated the influence of SO_2 on alumina in SCR using presulphated alumina, while the present study was conducted with SO_2 contained in the feed gas. We demonstrate that initially the presence of SO_2 increases the catalytic activity of NO conversion to N_2 by enhancing the activation of methanol through the formation of Brønsted acidity.

2. Experimental

The surface area, pore volume and pore size distribution of the catalysts were determined by the BET method using an ASAP 2000 Micromeritics instrument (table 1). Ammonia TPD measurements were conducted using a conventional TPD apparatus with a TCD detector and a linear heating rate of 10 °C/min from room temperature and with helium as the carrier gas. The acidity was obtained by NH_3 desorption in the temperature range 90–650 °C. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a VG ESCALAB MK II spectrometer using Al Kα radiation. The quoted binding energies were referenced to the C 1s peak at 284.8 eV from adventitious carbon. Transmission IR spectra were recorded from samples mixed with KBr and pressed into disks.

The catalytic activity was measured in a fixed-bed microflowreactor mounted vertically in an electrically heated furnace [4]. The catalyst sample (25 mg, particle size 106–250 μm) was positioned between pre and post packing of SiC (particle size 106–250 μm) to ensure plug-flow conditions. Gaseous methanol was introduced into the system via an evaporator–condenser system. The catalytic activity was calculated based on NO conversion measured by a chemiluminescence NO_x analyser. Other compounds in the effluent stream were analysed on-line with a Shimadzu 14B gas chromatograph with a TCD detector and a Porapak Q column. The feed gas composition was 1700 ppm NO, 3400 ppm CH_3OH and 3% O_2 containing 0, 17 or 102 ppm SO_2, respectively. The flow rate was maintained at 120 $cm^3\,min^{-1}$ and the quoted GHSV values are based on the measured bulk density of γ-Al_2O_3 (0.49 g/cm^3).

3. Results and discussion

3.1. Effect of SO_2 on catalytic activity

Two commercially available γ-aluminas from different suppliers were studied. The effect upon SO_2 addition on catalyst activity as a function of time-on-stream was monitored at 450 °C, based on a preliminary assessment which showed that both γ-alumina catalysts display maximum NO conversion to N_2 at this temperature [4]. The catalyst was exposed to a $NO/CH_3OH/O_2$ feed gas for approximately 3 h at 450 °C to establish a steady-state NO conversion in

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[*] To whom correspondence should be addressed.

Table 1
Catalyst morphology.

Catalyst	BET surface area (m^2/g)		Average pore size (nm)		NH_3 desorption (mmol NH_3/m^2) × 10^{-3}	
	Fresh	Deactivated	Fresh	Deactivated	Fresh	Deactivated
γ-Al_2O_3 (A)	256	225	11.2	11.5	1.28	1.35
γ-Al_2O_3 (B)	238	195	11.6	13.0	1.80	1.96

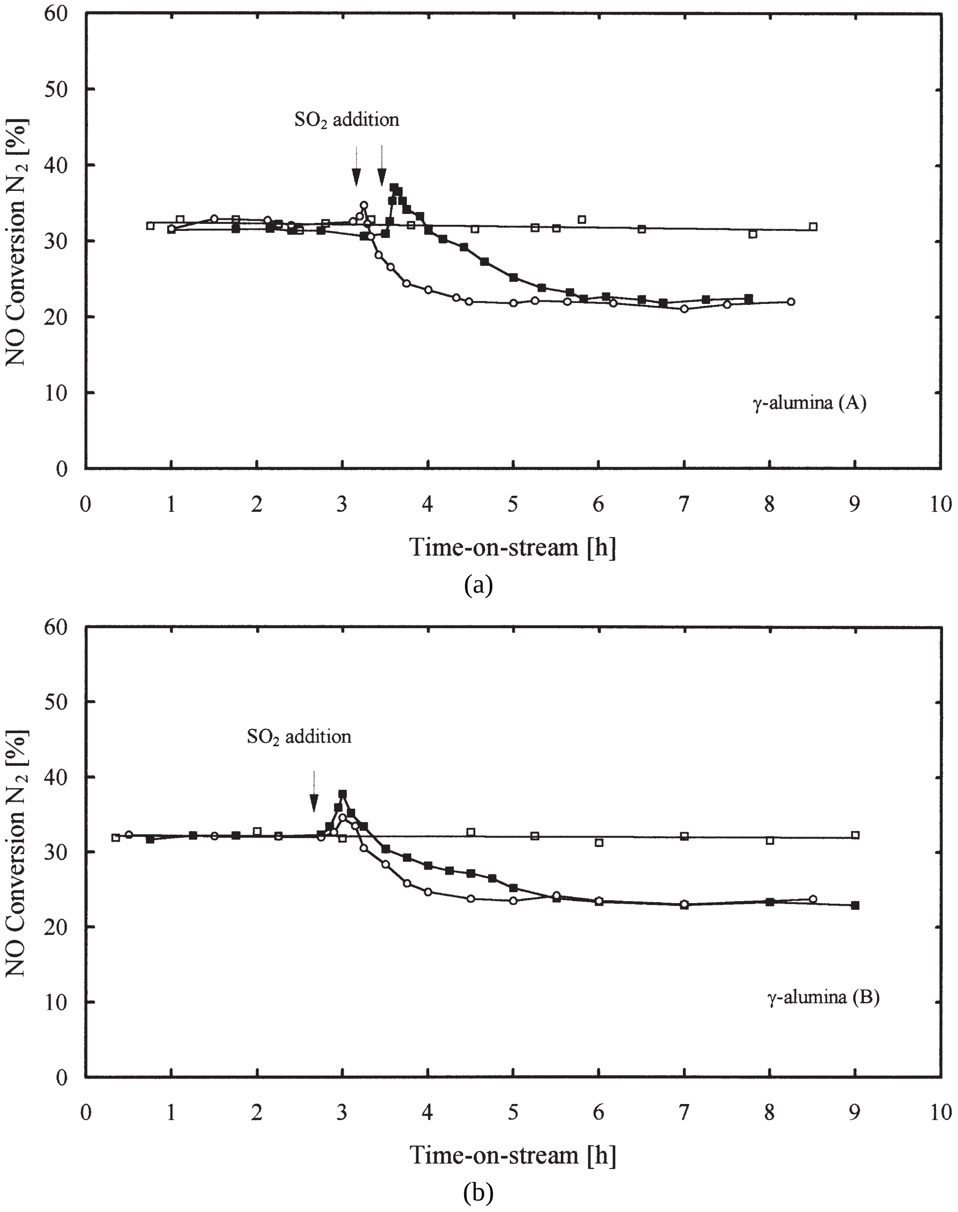

Figure 1. Effect of SO_2 on NO conversion to N_2 by methanol over γ-Al_2O_3 (A) and γ-Al_2O_3 (B) at 450 °C. (□) 0 ppm SO_2, (■) 17 ppm SO_2, (○) 102 ppm SO_2. Conditions: 1700 ppm NO, 3400 ppm CH_3OH and 3% O_2. GHSV = 141000 h^{-1}.

the absence of SO_2. Subsequently, SO_2 was added to the feed gas by replacing helium so that the total flow rate and concentration of the other compounds in the feed gas were unaffected.

The effect on NO conversion to N_2 in excess oxygen upon addition of 17 and 102 ppm SO_2, respectively, over γ-alumina (A) is plotted in figure 1(a). In the absence of SO_2, a steady-state NO conversion to N_2 of 31% at 450 °C was achieved (the GHSV was specifically chosen to maintain NO conversion below 40%). Addition of SO_2 to the feed gas caused an increase in activity, displaying a maximum in NO conversion to N_2 of 37%. This was followed by a gradual decrease in activity over a period of 2.5 h before a steady-state activity level was observed. The pe-

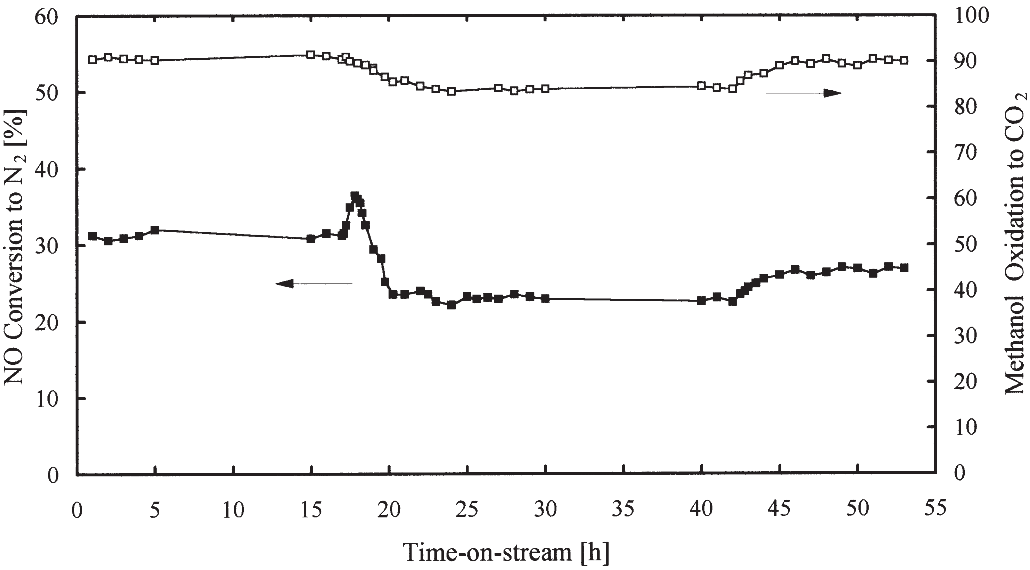

Figure 2. Effect of SO_2 on NO conversion to N_2 by methanol over γ-Al_2O_3 (B) at 450 °C. (□) CH_3OH conversion to CO_2, (■) NO conversion to N_2. Conditions: 1700 ppm NO, 3400 ppm CH_3OH and 3% O_2. GHSV = 141000 h^{-1}.

riod of enhanced activity was about 30 min at the condition used. A similar increase in SCR activity occurred on addition of 102 ppm SO_2 to the feed gas. However, the maximum measured activity was lower than for the feed gas containing 17 ppm SO_2 and the duration of the enhancement was shorter – only 10 min. Thereafter, the activity declined more quickly than for 17 ppm SO_2 and steady state was reached after 1 h. These results were entirely reproducible.

The effect of SO_2 on the catalytic activity was also monitored for a different γ-alumina catalyst (figure 1(b)). As seen, upon addition of SO_2 to the feed gas stream, near-identical features to that observed for γ-alumina (A) were observed. The rate of decline in SCR activity after the peak maximum value was found to be faster for the higher SO_2 concentration as was the case for alumina (A). For both aluminas the final steady-state activity was observed to be the same for both concentrations of SO_2 in the feed gas. The catalytic activity for NO conversion to N_2 could be partly recovered by replacing SO_2 with helium in the feed gas without affecting the concentration of the other reactants, as shown in figure 2.

To our knowledge, this feature has not previously been demonstrated for SCR over γ-alumina. However, a similar increase in SCR activity for NO conversion to N_2 upon addition of SO_2 and subsequent decrease to a lower steady-state level has been reported previously for NO reduction by methane in lean conditions over Cu-ZSM-5 [5]. Li and Armor [5] argued that the activity increase upon SO_2 injection was due to inhibition of methane combustion, hence improving the methane selectivity for NO reduction over Cu-ZSM-5. Figueras et al. [6] reported an increase in NO conversion to N_2 by decane over Cu/TiO_2 and Cu/ZrO_2 in the presence of SO_2. It was suggested that the activity enhancement observed for these catalysts was not due to the selective inhibition of decane oxidation, but could be explained by the promotion of the decane activation by a bifunctional mechanism involving acid sites created on the support by SO_2 adsorption [6]. These observations by Figueras and co-workers are consistent with earlier work on titania and zirconia, which have shown that sulphation introduces an increase in acidity [7]. Several previous studies have characterised the properties of sulphated γ-alumina catalysts. Przystajko et al. [8] have shown by pyridine adsorption that sulphated γ-alumina has increased acidity relative to γ-alumina. This increase in solid acidity has been explained by Saur et al. [9] in the following way. In the absence of water, three oxygens of the sulphate are bonded to Al, whereas in the presence of water this structure is converted into a bridged bidentate sulphate, thus accounting for the increase in acidity by formation of Brønsted acid sites. Ziolek et al. [10] demonstrated by IR measurements of adsorbed N-containing basic probe molecules (pyridine and 2,6-dimethylpyridine) that Brønsted acidity was formed on γ-alumina which had been pretreated with SO_2. This was confirmed by the study of a test-reaction for the presence of Brønsted acidity – cumene cracking to propene and benzene. It seems highly likely, therefore, that the initial enhancement of SCR activity seen in the present work is associated with an increase in acidity by formation of Brønsted acid sites (see below).

3.2. Characterisation of sulphated alumina

After conclusion of the steady-state experiments (after 8 h time-on-stream) corresponding to figure 1 (a) and (b), the γ-Al_2O_3 samples were characterised by X-ray photoelectron spectroscopy (XPS) and transmission IR. Both methods confirmed accumulation of sulphur on the surface as expected. The IR analysis showed a S=O vibration band at $\nu = 1383$ and 1385 cm^{-1} for γ-Al_2O_3 (A)

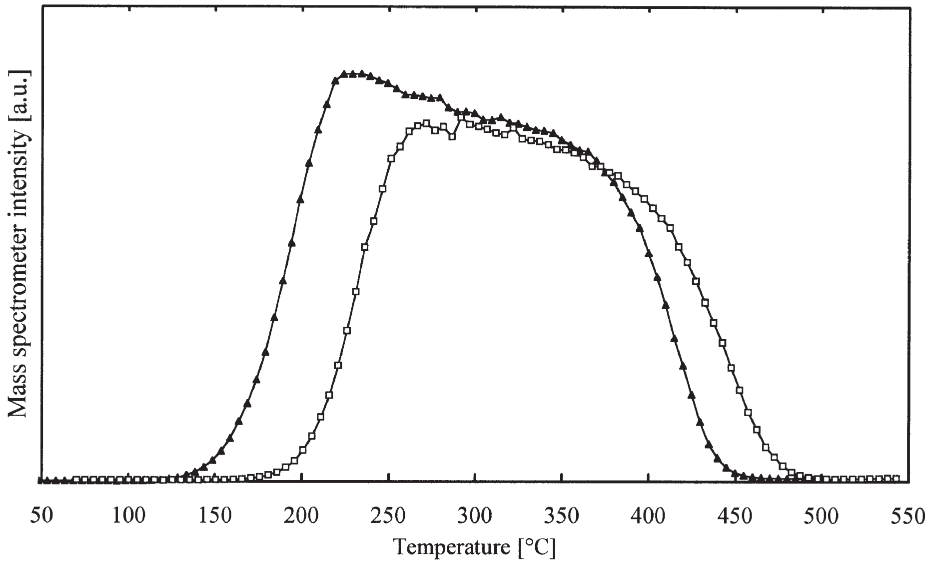

Figure 3. Temperature-programmed reaction (TPRx) of methanol dehydration to dimethyl ether in absence of oxygen over γ-Al_2O_3 (A). Only γ-Al_2O_3 (A) is shown for reasons of clarity. Conditions: (□) 3400 ppm CH_3OH and (▲) 3400 ppm CH_3OH, 102 ppm SO_2. GHSV = 55000 h^{-1}. Heating range 25–500 °C at 5 °C/min.

and γ-Al_2O_3 (B), respectively. This vibration band corresponds well to the sulphate vibration band recorded for $Al_2(SO_4)_3 \cdot xH_2O$ ($\nu = 1387$ cm^{-1}) which was used as reference compound. It is noteworthy that these IR vibration bands are in good agreement with previous studies of SO_2 adsorption and surface reaction on γ-alumina [3,8–10].

The binding energies of S 2p (Al 2p) were determined to be at 169.6 (74.8) and 169.4 eV (74.9 eV) for γ-Al_2O_3 (A) and γ-Al_2O_3 (B), respectively, after 8 h time-on-stream, compared to the S 2p (Al 2p) binding energy at 169.3 eV (75.6 eV) for $Al_2(SO_4)_3 \cdot xH_2O$. For comparison, Arata et al. [11] reported the S 2p binding energy for γ-Al_2O_3 treated with 2.5 M H_2SO_4 to be 169.5 eV, and TGA data, following heating at 500 °C for 3 h, showed a weight decrease of 10.9% in the temperature range 550–1000 °C, corresponding to decomposition of sulphate on the alumina to form SO_3 [11]. The lower Al 2p values for the sulphated catalysts are consistent with the underlying material being γ-Al_2O_3. From the XPS intensity ratios it can be estimated that the $Al_2(SO_4)_3$ exceeds a monolayer coverage after 8 h on-stream.

3.3. CH_3OH activation over γ-alumina

The development of Brønsted acidity [7–10] when SO_2 was added to the feed gas was investigated for the present aluminas by the use of a test-reaction. It is well-known that methanol dehydration to dimethyl ether is catalysed by Brønsted acidity [12–14]. Indeed, alcohol dehydration and dimethyl ether formation in particular, over sulphonated styrene divinylbenzene copolymers are well-known processes [15]. Hence, this reaction was used as the test-reaction. The experiments were performed by temperature-programmed reaction (TPRx) using a feed gas composition of 3400 ppm CH_3OH, with and without 3% O_2 containing either 0, 17 or 102 ppm SO_2.

In absence of oxygen, the addition of SO_2 to the feed gas stream increased the activity for methanol dehydration to dimethyl ether, as seen in the decreasing temperature required for dimethyl ether formation (figure 3) (complete conversion of methanol was achieved). Hence, these TPRx results are consistent with the proposition that introducing SO_2 leads to an increase in acidity by creation of Brønsted acid sites. TPRx results of methanol dehydration over γ-Al_2O_3 (A) and γ-Al_2O_3 (B) in excess oxygen with 0, 17 and 102 ppm SO_2, respectively, are shown in figure 4. Comparison of the TPRx results for methanol dehydration with and without the presence of excess oxygen, show that approximately the same degree of enhancement was established by addition of SO_2. The increase in acidity was confirmed by NH_3-TPD after SCR in the presence of SO_2. The total amount of NH_3 desorbed increased after sulphation (table 1) and the desorption peak broadened to higher temperature.

The rise and fall in SCR activity when SO_2 is present in the feed gas can be explained by a bifunctional mechanism similar to that proposed by Figueras et al. [6]. SO_2 adsorbs creating Brønsted acid sites which can activate methanol. This is consistent with the TPRx data. Furthermore, SO_2 will form sulphate species resulting in blockage of the sites which are required for NO_x activation. (Recent DRIFTS studies of NO adsorption on γ-Al_2O_3 [16] have shown intense bands characteristic of NO_x adsorption complexes, e.g., NO_2^- and NO_3^- which were confirmed by ^{15}NO isotopic substitution and by doping Al_2O_3 with $NaNO_2$ and $NaNO_3$.) These two effects act in opposite direction. However, ultimately, it is the suppression of NO_x activation which leads to the observed decline in the NO conversion to N_2 shown in figures 1 and 2. Burch et al. [17] in

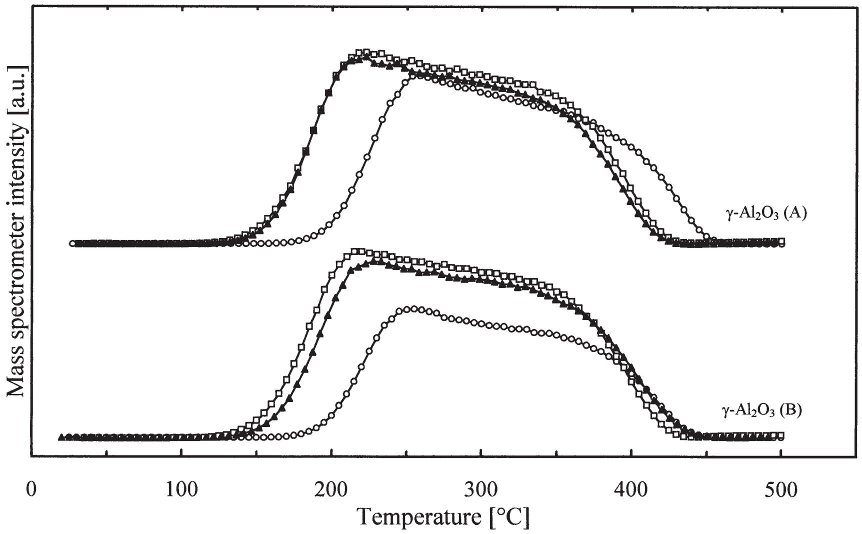

Figure 4. Temperature-programmed reaction (TPRx) of methanol dehydration to dimethyl ether in excess oxygen over γ-Al_2O_3 (A) and γ-Al_2O_3 (B). Conditions: 3400 ppm CH_3OH, 3% O_2, (○) 0 ppm SO_2, (▲) 17 ppm SO_2 and (□) 102 ppm SO_2, GHSV = 55000 h^{-1}. Heating range 25–500 °C at 5 °C/min.

their study of SCR of NO over γ-Al_2O_3 and presulphated γ-Al_2O_3 reported TPD results which show that less NO could be desorbed from sulphated alumina as compared to the amount desorbed from fresh alumina. In addition, NO was found to be significantly less strongly bound on presulphated alumina as evidenced by a decrease in the temperature required to desorb the strongly adsorbed NO_x species. On this basis, Burch and co-workers concluded that a site competition between NO and SO_4^{2-} species exists.

An important feature of the present results and data reported in [17], is the fact that the sulphated γ-Al_2O_3 surface retains a reasonable, if lower, activity for SCR by methanol. Since the Brønsted acid sites created by SO_2 adsorption activate the methanol, this lower rate involves the reaction of activated methanol with either weakly bound NO_x species or with gas-phase NO_x by an Eley–Rideal mechanism, as proposed by Burch et al. [17].

4. Conclusion

It has been demonstrated that the SCR activity of NO reduction by methanol is initially enhanced upon exposure of a fresh alumina catalyst to SO_2. This is attributed to formation of Brønsted acid sites which promote methanol activation. However, longer exposure time to SO_2 causes formation of sulphate and results in a decline in SCR activity reaching a lower a steady-state NO_x reduction activity. This decline is due to site competition between NO and SO_4^{2-} species and the suppression of NO_x activation.

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