The effect of support and Cu precursor on the activity of supported CuO catalysts in the selective catalytic reduction of NO_x

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A series of Cu catalysts were studied as a function of support (Al_2O_3, TiO_2 and SiO_2) and Cu precursor (ex-SO_4 and ex-NO_3) for activity in the SCR-NH_3 reaction. The catalysts were characterized using NO_x TPD and SEM/EDAX analysis and the effects of residual sulphur interpreted in terms of site-blocking and NH_3 activation mechanisms.

KEY WORDS: SCR; NO_x; NH_3; copper; sulphur.

1. Introduction

Sulphur has long been thought of as a poison for many catalysts and catalytic processes [1–3]. As well as forming particulate matter that can block catalyst pores and physically disable the catalyst [4], sulphur-containing species can also selectively adsorb on the catalytically active sites, chemically poisoning the catalyst. However, recently several reports have confirmed that the presence of SO_2 in the gas phase (and hence SO_4 species on an oxide catalyst surface) has *promoted* the rate of particular reactions. Examples include the total oxidation of propane over Pt/Al_2O_3 catalysts [5–7], the selective reduction of NO_x using NH_3 over V_2O_5/carbon catalysts [8] and the combustion of CH_4 over Pd/ZrO_2[9].

In dealing with the emissions from stationary or mobile power sources the presence of SO_2—as a combustion product of sulphur-containing species in the fuel—is always an issue. The present work analyses the effect of sulphur (present as $SO_{4\text{ads}}$ species following preparation) on the SCR-NH_3 reaction over supported copper catalysts.

The SCR-NH_3 reaction is used to remove NO_x emissions from the exhaust gas of stationary power sources (where an excess of O_2 is present) and is possibly a candidate for use in the after-treatments of heavy duty diesel automotive exhaust gases using reservoirs or urea as an NH_3 precursor.

2. Experimental

Commercial γ-Al_2O_3 (Criterion Catalysts) (S.A $= 195\,m^2\,g^{-1}$), TiO_2 (Degussa P25) (S.A. $= 49\,m^2\,g^{-1}$) and SiO_2 (Grace) (S.A. $= 256\,m^2\,g^{-1}$) were used as supports. Before doping with Cu these were crushed and sieved to particle sizes of 212–600 μm. 1% loaded catalysts were prepared using conventional incipient wetness impregnation using $Cu(NO_3)_2{\cdot}3H_2O$ and $CuSO_4{\cdot}5H_2O$ precursors. They were then dried (100 °C) and calcined (500 °C) for 3 h.

The catalyst (100 mg) was held in a tubular quartz reactor using plugs of quartz wool. The reactants were blended using electronic mass flow controllers from cylinders of 1% NO and 1% NH_3 in He (BOC Special Gases), Zero Grade Air (Air Products) and N_2 (BOC) to give a reaction mixture of $[NO] = 1000$ ppm, $[NH_3] = 1500$ ppm and $[O_2] = 7.4\%$ in a total flow of 100 ml/min. The reaction was studied under temperature programmed conditions with a ramp rate of 10 °C/min. During the NO_x TPD studies the sample was pre-oxidized at 500 °C, dosed for 1 h at 100 °C in 1220 ppm $NO + 7\%$ O_2, purged in N_2 at 100 °C for 1 min, cooled in N_2 to 50 °C and ramped to 600 °C at 10 °C/min in 88.5 ml/min N_2.

Continuous analysis of NO_x was carried out following dilution using a Monitor Labs Inc. Nitrogen Oxides Analyser (Model 8840) connected to a PC. The samples were also characterized using coupled SEM and EDAX analysis (JOEL 35C SEM) to detect the presence of copper, nitrogen and sulphur species on the surface.

3. Results and discussion

3.1. Characterization studies

The ratio of S to Cu on the surface as measured by the EDAX analysis remains roughly the same before and after calcination (see table 1), showing that obviously some sulphur remains on the catalyst following the preparation procedure.

In the X-ray analysis of the ex-NO_3 catalysts there was a peak due to N present on the uncalcined samples,

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Table 1
[Cu]/[S] ratios for the calcined and uncalcined catalysts as measures using couples SEM and X-ray analysis

Catalyst	Uncalcined	Calcined
Cu(ex-SO_4)/Al_2O_3	2.7	2.5
Cu(ex-SO_4)/TiO_2	3.2	3.2
Cu(ex-SO_4)/SiO_2	1.2	1.4
Cu(ex-SO_4)/SiO_2 [a]	–	2.1
Cu(ex-NO_3)/SiO_2 [b]	–	1.2

[a] A sample of Cu(ex-SO_4)/SiO_2 that had been treated in N_2 at 600 °C for 30 min.

[b] A sample of Cu(ex-NO_3)/SiO_2 that had been treated with H_2SO_4 and calcined.

which was much diminished following calcination. This was difficult to fully deconvolute due to its proximity to the oxygen peak in the spectrum so no quantitative results are shown. Decomposition of NO_3 species is seen upon calcination using FTIR (*i.e.* the removal of a peak at 1385 cm^{-1}).

The NO_x TPD experiments provide a measure of the NO_x sorption capacity of the supports alone and of each of the calcined catalysts. Each different set of supported catalysts has characteristic peak profiles, the temperatures and areas of which can be related to the nature and extent of NO_x adsorption. Here we consider solely the overall amount of NO_x adsorbed. The histogram presented (figure 1) shows the *total* amount of NO_x desorbed from all three supports and the six Cu-loaded catalysts as the temperature is ramped between 50 and 600 °C. It is clear that the extent of NO_x adsorption (and desorption) is primarily a function of the support used, with Al_2O_3-supported materials adsorbing large amounts, TiO_2-supported materials intermediate amounts and SiO_2-supported materials very small amounts.

In the case of *all* supports the addition of ex-NO_3 (clean) CuO increases the concentration of NO_x that can adsorb (by providing extra adsorption sites on CuO) while the addition of ex-SO_4 CuO decreases [NO_x] that can adsorb (by poisoning sites for the adsorption of NO_x). The competition between sulphur oxide species and NO_x for surface adsorption sites is well known [10,11] and seems to be operating here.

3.2. Temperature programmed activity studies

Figure 2 shows the results from the temperature programmed $NO + NH_3 + O_2$ reaction over the supports and catalysts. For clarity the figure is split into three sections, each corresponding to between 0 and 100% for each of the three sets of supported catalysts.

The supports themselves show some activity with SiO_2 (top three profiles) being more active than TiO_2 (middle three profiles). Al_2O_3 (bottom three profiles) shows no activity for the reaction under these conditions. There are some general observations that hold for all three sets of catalysts. First, the presence of CuO on the surface generally increases the activity of all the supports. This is true at lower temperatures for the SiO_2 and TiO_2 supported catalysts and at all temperatures for the Al_2O_3 supported materials.

At higher temperatures, however, in some catalysts the conversion of the copper loaded samples drops

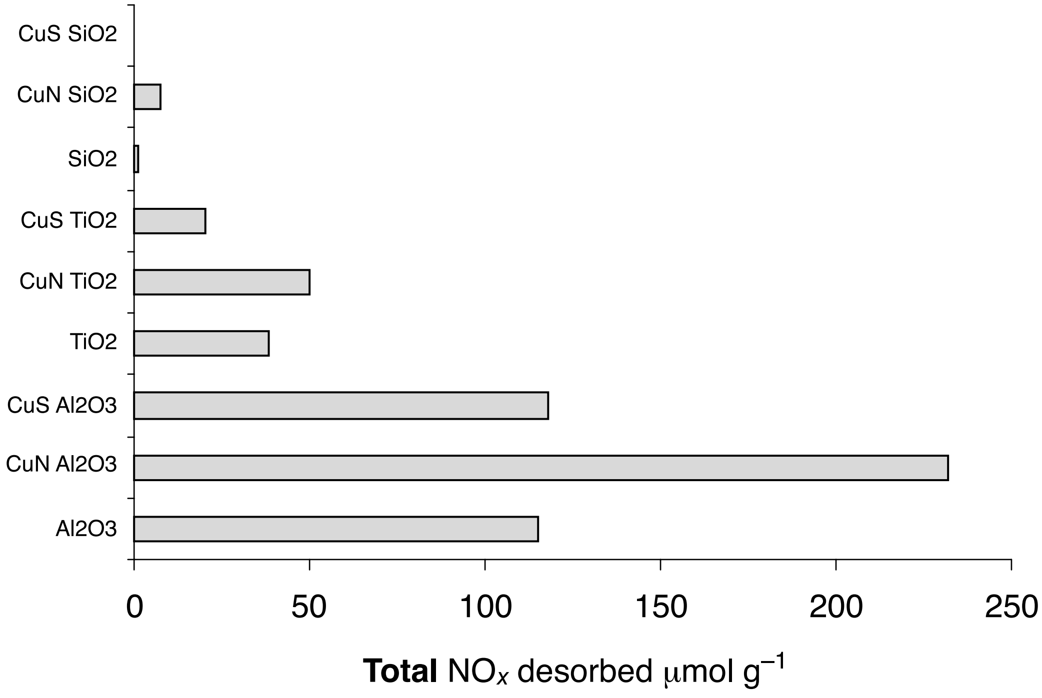

Figure 1. Histogram showing TOTAL amount of NO_x desorbed during TPD from all calcined catalysts.

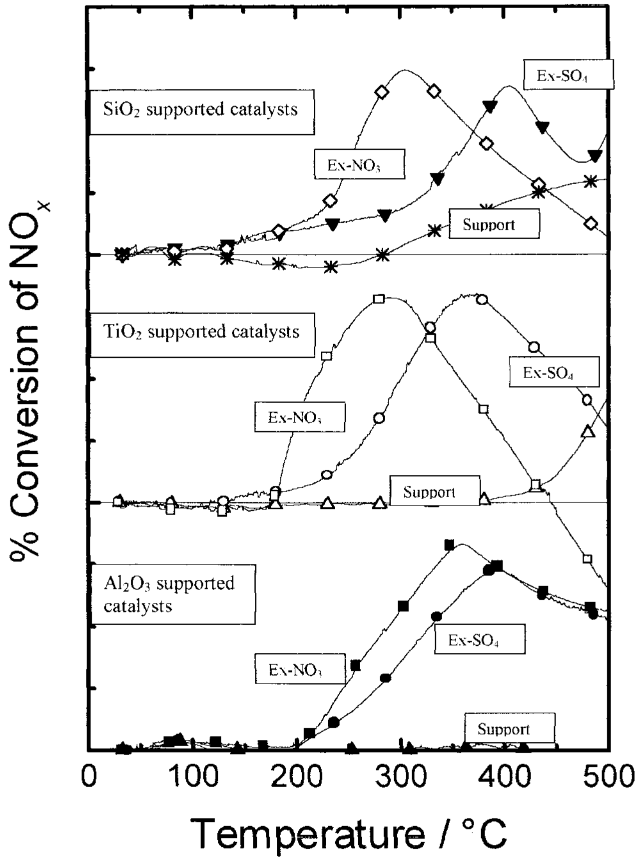

Figure 2. Temperature programmed NO + NH_3 + O_2 reaction over Al_2O_3 (▲), Cu/Al_2O_3 ex-NO_3(■), Cu/Al_2O_3 ex-SO_4 (●), TiO_2 (△), Cu/TiO_2 ex-NO_3 (□), Cu/TiO_2 ex-SO_4 (○), SiO_2 (∗),Cu/SiO_2 ex-NO_3 (◇), Cu/SiO_2 ex-SO_4 (▼). Each third of the figure represents conversion from 0 to 100%.

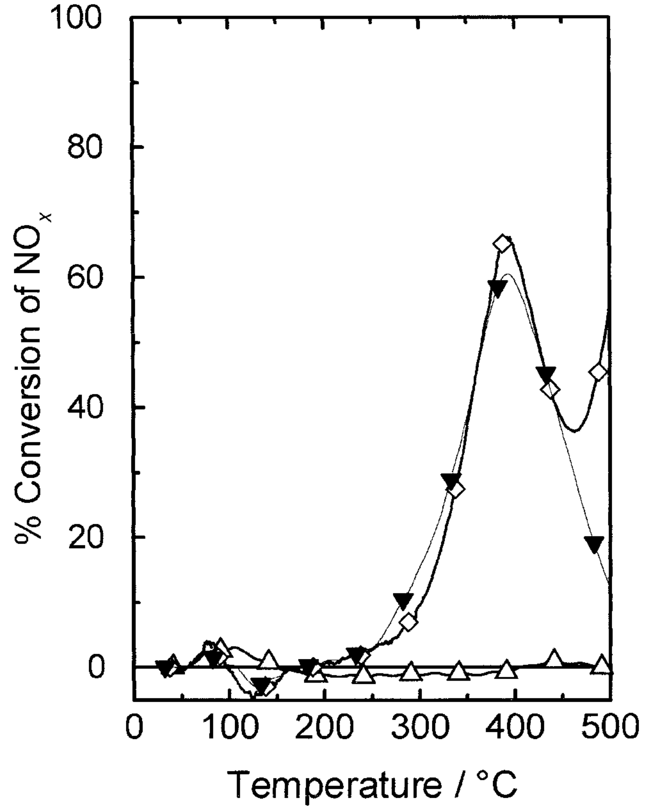

Figure 3. Temperature programmed NO + NH_3 + O_2 reaction over sulphated SiO_2 (△), Cu/SiO_2 ex-NO_3 treated with H_2SO_4 (◇) and Cu/SiO_2 ex-SO_4 out-gassed at 600 °C in N_2 (▼).

below that of the supports. This is due to the activity of the CuO species in promoting the $NH_3 \rightarrow N_2$ (thereby removing reductant) and $NH_3 \rightarrow NO$ (thereby directly forming NO_x) reactions. The ex-NO_3 catalysts are more active for the desired reaction at lower temperatures than the ex-SO_4 materials while at higher temperatures their activity drops far more quickly than that of the ex-SO_4 catalysts. From the TPD results we can suggest a reason for the decreased activity of the ex-SO_4 catalysts at lower temperatures, *i.e.* competition between NO_x and SO_4 for adsorption sites on the surface.

The reason for the drop off in activity at higher temperatures is due to the increased prevalence of competing reactions, particularly NH_3 oxidation to NO_x (NO + NO_2). The presence of sulphate on the catalyst ameliorates this effect to some extent, *i.e.* the presence of SO_4 groups on the surface poisons the catalyst for the NH_3 oxidation reaction—allowing the reaction to proceed with a higher selectivity to deNO_x. This decreased NH_3 oxidation activity is possibly due to the change in acidity of the catalyst upon sulphation and the resultant different mode of activation of the incoming NH_3 molecules, *i.e.* they are activated in a manner favourable to deNO_x (or in a manner less favourable to NH_3 oxidation).

The higher "high temperature" deNO_x activity of the ex-SO_4 catalysts seen over the SiO_2 and TiO_2 supported materials is not seen in the case of the Al_2O_3 supported catalysts. This is possibly due to SO_4 species adsorbing all over the Al_2O_3 surface rather than on sites close to or interfacing with the CuO species.

As well as maintaining the higher temperature activity relative to its ex-NO_3 analogue, the Cu ex-SO_4 SiO_2 material also shows a higher temperature *increase* in deNO_x activity as the temperature increases between 450 and 500 °C. In order to probe what causes this effect several more experiments were carried out. First, the SiO_2 support was dosed with H_2SO_4 (at the same level of SO_4 as had been present during the synthesis of the ex-SO_4 Cu catalyst) and dried/calcined. This material lost all of its deNO_x activity (compare △ in figure 3 with ∗ in figure 2) showing that sulphate species alone do not cause the increase in high temperature activity.

Second, an ex-NO_3 Cu-containing catalyst was dosed with H_2SO_4 (again at the same SO_4 levels as were used in making the Cu ex-SO_4 catalyst) and its activity tested in the temperature programmed reaction.

Here (◇ in figure 3) the lower (200–300 °C) temperature activity present on the Cu/SiO_2 catalyst (■ in figure 2) is removed (presumably as SO_4 blocks NO_x

adsorption sites) and higher temperature activity—in the form of an increase in activity between 450 and 500 °C (as seen in the ex-SO_4 catalyst in figure 2, ▼), is introduced. Therefore the increase in activity at higher temperatures seen between 450 and 500 °C is due to the presence of *both* copper and sulphate species on the surface.

Finally the ex-SO_4 catalyst was out-gassed in flowing N_2 at 600 °C for 30 min and its activity in the temperature programmed reaction analysed. Figure 3 shows that the increase in activity previously seen between 450 and 500 °C is now lost (compare ▼ in figure 2 with ▼ in figure 3). SEM and EDAX analysis (table 1) shows that sulphur remains on the catalyst following this treatment. However, whatever increased activity this sulphur species had for the promotion of the deNO_x reaction between 450 and 500 °C is removed. Therefore either the sulphate species which caused the enhanced activity >450 °C is removed from the catalyst or its structure is changed into a form inactive for the increased promotion for the reaction (suppression of the NH_3 oxidation).

The treatment at 600 °C in N_2 could have had several effects on the surface composition of the catalysts, including sintering of the CuO particles and support or decomposition of the SO_4 species into $SO_{2(g)}$ with the remaining two O atoms either desorbing as O_2 or remaining as lattice O atoms (in SiO_2 or CuO). A situation where the CuO particles sinter and interfacial sulphate groups (active for the high temperature promotion) between the CuO and the SiO_2 are removed from the catalyst—or removed from the CuO interface—during the out-gassing, while sulphate groups remote from the CuO particles (inactive for the deNO_x reaction, and poisons at lower temperature) remain would account for the observed results.

4. Conclusions

Sulphur species remain on the supported CuO catalyst surfaces when ex-SO_4 precursors are used. The presence of SO_4^{2-} affects the surface of the catalyst in that the capacity for adsorption of NO_x is decreased. The sulphur species affect the catalyst deNO_x activity in two ways: decreasing activity at lower temperatures, and ameliorating the decrease in activity seen at higher temperatures due to the $NH_3 \rightarrow O_2$ reaction (an even more striking *increase* in deNO_x activity is seen over the ex-SO_4 SiO_2 supported catalysts at higher temperature).

The first effect, removal of low temperature activity, is due to the fact that some NO_x adsorption sites are removed and therefore reaction cannot proceed at the same rate (assuming that the adsorption of NO_x on to the surface plays a role in the reaction mechanism). It is proposed that the second effect involves the way that the NH_3 molecules coordinate to the catalyst surface in the presence of sulphate groups. This coordination decreases the extent of the $NH_3 \rightarrow NO$ reaction and thus delays the decrease in NO_x conversion. Furthermore the final figure shows that this effect is not solely due to the sulphate groups but rather to an effect of both the copper and the sulphate groups acting together.

Further work is in progress to characterize these interfacial SO_4 groups using *in-situ* DRIFTS spectroscopy.

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