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# The effect of support and Cu precursor on the activity of supported CuO catalysts in the Selective Catalytic Reduction of NO<sub>x</sub>

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## Abstract

A series of Cu catalysts were studied as a function of support (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>) and Cu precursor (ex-SO<sub>4</sub> and ex-NO<sub>3</sub>) for activity in the SCR-NH<sub>3</sub> reaction. The catalysts were characterised using NO<sub>x</sub> TPD and SEM/EDAX analysis and the effects of residual sulphur interpreted in terms of site-blocking and NH<sub>3</sub> activation mechanisms.

**Keywords:** SCR, NO<sub>x</sub>, NH<sub>3</sub>, 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<sub>2</sub> in the gas phase (and hence SO<sub>4</sub> species on an oxide catalyst surface) has *promoted* the rate of particular reactions. Examples include the total oxidation of propane over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, [5-7], the selective reduction of NO<sub>x</sub> using NH<sub>3</sub> over V<sub>2</sub>O<sub>5</sub> /Carbon catalysts [8] and the combustion of CH<sub>4</sub> over Pd/ZrO<sub>2</sub> [9].

In dealing with the emissions from stationary or mobile power sources the presence of SO<sub>2</sub> - 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  $\text{SO}_{4\text{ads}}$  species following preparation) on the SCR- $\text{NH}_3$  reaction over supported copper catalysts.

The SCR- $\text{NH}_3$  reaction is used to remove  $\text{NO}_x$  emissions from the exhaust gas of stationary power sources (where an excess of  $\text{O}_2$  is present) and is possibly a candidate for use in the after-treatments of heavy duty diesel automotive exhaust gasses using reservoirs or urea as an  $\text{NH}_3$  precursor.

## 2. Experimental

Commercial  $\gamma$   $\text{Al}_2\text{O}_3$  (Criterion Catalysts) (S.A. =  $195 \text{ m}^2\text{g}^{-1}$ ),  $\text{TiO}_2$  (Degussa P25) (S.A. =  $49 \text{ m}^2\text{g}^{-1}$ ) and  $\text{SiO}_2$  (Grace) (S.A. =  $256 \text{ m}^2\text{g}^{-1}$ ) were used as supports. Before doping with Cu these were crushed and sieved to particle sizes of 212-600  $\mu\text{m}$ . 1% loaded catalysts were prepared using conventional incipient wetness impregnation using  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  precursors. They were then dried ( $100 \text{ }^\circ\text{C}$ ) and calcined ( $500 \text{ }^\circ\text{C}$ ) 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%  $\text{NO}$  and 1%  $\text{NH}_3$  in He (BOC Special Gases), Zero Grade Air (Air Products) and  $\text{N}_2$  (BOC) to give a reaction mixture of  $[\text{NO}] = 1000 \text{ ppm}$ ,  $[\text{NH}_3] = 1500 \text{ ppm}$  and  $[\text{O}_2] = 7.4\%$  in a total flow of 100 ml/min. The reaction was studied under temperature programmed conditions with a ramp rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . During the  $\text{NO}_x$  TPD studies the sample was pre-oxidised at  $500^\circ \text{C}$ , dosed for 1h at  $100 \text{ }^\circ\text{C}$  in 1220 ppm  $\text{NO} + 7\% \text{ O}_2$ , purged in  $\text{N}_2$  at  $100 \text{ }^\circ\text{C}$  for 1 min, cooled in  $\text{N}_2$  to  $50 \text{ }^\circ\text{C}$  and ramped to  $600 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C}/\text{min}$  in 88.5 ml/min  $\text{N}_2$ .

Continuous analysis of  $\text{NO}_x$  was carried out following dilution using a Monitor Labs Inc Nitrogen Oxides Analyser (Model 8840) connected to a PC. The

samples were also characterised 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 Characterisation 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<sub>3</sub> catalysts there was a peak due to N present on the un-calcined samples, which was much diminished following calcination. This was difficult to fully de-convolute due to its proximity to the Oxygen peak in the spectrum so no quantitative results are shown. Decomposition of NO<sub>3</sub> species is seen upon calcination using FTIR (*i.e.* the removal of a peak at 1385 cm<sup>-1</sup>).

The NO<sub>x</sub> TPD experiments provide a measure of the NO<sub>x</sub> 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<sub>x</sub> adsorption. Here we consider solely the overall amount of NO<sub>x</sub> adsorbed. The histogram presented (Figure 1) shows the *total* amount of NO<sub>x</sub> 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<sub>x</sub> adsorption (and desorption) is primarily a function of the support used, with Al<sub>2</sub>O<sub>3</sub>-supported materials adsorbing large amounts, TiO<sub>2</sub>-supported materials intermediate amounts and SiO<sub>2</sub>-supported materials very small amounts.

In the case of *all* supports the addition of ex-NO<sub>3</sub> (clean) CuO increases the concentration of NO<sub>x</sub> that can adsorb (by providing extra adsorption sites on CuO)

while the addition of ex-SO<sub>4</sub> CuO decreases [NO<sub>x</sub>] that can adsorb (by poisoning sites for the adsorption of NO<sub>x</sub>). The competition between sulphur oxide species and NO<sub>x</sub> 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<sub>3</sub> + O<sub>2</sub> 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<sub>2</sub> (upper three profiles) being more active than TiO<sub>2</sub> (middle three profiles). Al<sub>2</sub>O<sub>3</sub> (lowest three profiles) shows no activity for the reaction under these conditions. There are some general observations that hold for all three sets of catalysts. Firstly, the presence of CuO on the surface generally increases the activity of all the supports. This is true at lower temperatures for the SiO<sub>2</sub> and TiO<sub>2</sub> supported catalysts and at all temperatures for the Al<sub>2</sub>O<sub>3</sub> supported materials.

At higher temperatures however, in some catalysts the conversion of the copper loaded samples drops below that of the supports. This is due to the activity of the CuO species in promoting the NH<sub>3</sub> → N<sub>2</sub> (thereby removing reductant) and NH<sub>3</sub> → NO (thereby directly forming NO<sub>x</sub>) reactions. The ex-NO<sub>3</sub> catalysts are more active for the desired reaction at lower temperatures than the ex-SO<sub>4</sub> materials while at higher temperatures their activity drops far more quickly than that of the ex-SO<sub>4</sub> catalysts. From the TPD results we can suggest a reason for the decreased activity of the ex-SO<sub>4</sub> catalysts at lower temperatures, *i.e.* competition between NO<sub>x</sub> and SO<sub>4</sub> 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  $\text{NH}_3$  oxidation to  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ). The presence of Sulphate on the catalyst ameliorates this effect to some extent, *i.e.* the presence of  $\text{SO}_4$  groups on the surface poisons the catalyst for the  $\text{NH}_3$  oxidation reaction – allowing the reaction to proceed with a higher selectivity to de $\text{NO}_x$ . This decreased  $\text{NH}_3$  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  $\text{NH}_3$  molecules, *i.e.* they are activated in a manner favourable to de $\text{NO}_x$  (or in a manner less favourable to  $\text{NH}_3$  oxidation).

The higher “high temperature” de $\text{NO}_x$  activity of the ex- $\text{SO}_4$  catalysts seen over the  $\text{SiO}_2$  and  $\text{TiO}_2$  supported materials is not seen in the case of the  $\text{Al}_2\text{O}_3$  supported catalysts. This is possibly due to  $\text{SO}_4$  species adsorbing all over the  $\text{Al}_2\text{O}_3$  surface rather than on sites close to or interfacing with the  $\text{CuO}$  species.

As well as maintaining the higher temperature activity relative to its ex- $\text{NO}_3$  analogue the Cu ex- $\text{SO}_4$   $\text{SiO}_2$  material also shows a higher temperature *increase* in de $\text{NO}_x$  activity as the temperature increases between 450 and 500 °C. In order to probe what causes this effect several more experiments were carried out. Firstly, the  $\text{SiO}_2$  support was dosed with  $\text{H}_2\text{SO}_4$  (at the same level of  $\text{SO}_4$  as had been present during the synthesis of the ex- $\text{SO}_4$  Cu catalyst) and dried/calcined. This material lost all of its de $\text{NO}_x$  activity (compare ( $\Delta$ ) in figure 3 with (\*) in figure 2) showing that sulphate species alone do not cause the increase in high temperature activity.

Secondly, an ex- $\text{NO}_3$  Cu-containing catalyst was dosed with  $\text{H}_2\text{SO}_4$  (again at the same  $\text{SO}_4$  levels as were used in making the Cu ex- $\text{SO}_4$  catalyst) and its activity tested in the temperature programmed reaction.

Here (( $\diamond$ ) in figure 3) the lower (200-300°C) temperature activity present on the Cu/SiO<sub>2</sub> catalyst ((v) in figure 2) is removed (presumably as SO<sub>4</sub> blocks NO<sub>x</sub> 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<sub>4</sub> catalyst in figure 2 ( $\tau$ )) 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<sub>4</sub> catalyst was out-gassed in flowing N<sub>2</sub> at 600 °C for 30 minutes and its activity in the temperature programmed reaction analysed. Figure 3 shows that the increase in activity previously seen between 450-500 °C is now lost (compare ( $\tau$ ) in figure 2 with ( $\tau$ ) 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<sub>x</sub> reaction between 450-500 °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<sub>3</sub> oxidation).

The treatment at 600 °C in N<sub>2</sub> 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<sub>4</sub> species into SO<sub>2</sub> (g) with the remaining 2 O atoms either desorbing as O<sub>2</sub> or remaining as lattice O atoms (in SiO<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub> reaction – and poisons at lower temperature) remain would account for the observed results.

## Conclusions

Sulphur species remain on the supported CuO catalyst surfaces when ex-SO<sub>4</sub> precursors are used. The presence of SO<sub>4</sub><sup>2-</sup> affects the surface of the catalyst in that the capacity for adsorption of NO<sub>x</sub> is decreased. The sulphur species affect the catalyst deNO<sub>x</sub> activity in two ways – (1) decreasing activity at lower temperatures and (2) ameliorating the decrease in activity seen at higher temperatures due to the NH<sub>3</sub> → O<sub>2</sub> reaction (an even more striking *increase* in deNO<sub>x</sub> activity is seen over the ex-SO<sub>4</sub> SiO<sub>2</sub> supported catalysts at higher temperature).

The first effect – removal of low temperature activity is due to the fact that some NO<sub>x</sub> adsorption sites are removed and therefore reaction cannot proceed at the same rate (assuming that the adsorption of NO<sub>x</sub> onto the surface plays a role in the reaction mechanism). It is proposed that the second effect involves the way that the NH<sub>3</sub> molecules co-ordinate to the catalyst surface in the presence of sulphate groups. This coordination decreases the extent of the NH<sub>3</sub> → NO reaction and thus delays the decrease in NO<sub>x</sub> 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 characterise these interfacial SO<sub>4</sub> groups using *in-situ* DRIFTS spectroscopy.

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Table 1: [Cu]/[S] ratios for the calcined and un-calcined catalysts as measured using coupled SEM and X-Ray Analysis. \* refers to a sample of Cu(ex-SO<sub>4</sub>) / SiO<sub>2</sub> that had been treated in N<sub>2</sub> at 600 °C for 30 minutes, \*\* refers to a sample of Cu(ex-NO<sub>3</sub>) / SiO<sub>2</sub> that had been treated with H<sub>2</sub>SO<sub>4</sub> and calcined.

Figure 1: Histogram showing TOTAL amount of NO<sub>x</sub> desorbed during TPD from all calcined catalysts.

Figure 2: Temperature programmed NO+NH<sub>3</sub>+O<sub>2</sub> reaction over Al<sub>2</sub>O<sub>3</sub> (σ), Cu/Al<sub>2</sub>O<sub>3</sub> ex NO<sub>3</sub>(ν), Cu/Al<sub>2</sub>O<sub>3</sub> ex SO<sub>4</sub> (λ), TiO<sub>2</sub> (Δ), Cu/TiO<sub>2</sub> ex NO<sub>3</sub> (□), Cu/TiO<sub>2</sub> ex SO<sub>4</sub> (○), SiO<sub>2</sub> (\*), Cu/SiO<sub>2</sub> ex NO<sub>3</sub> (◇), Cu/SiO<sub>2</sub> ex SO<sub>4</sub> (τ). Each third of the figure represents conversion from 0 to 100 %.

Figure 3: Temperature Programmed NO+NH<sub>3</sub>+O<sub>2</sub> reaction over Sulphated SiO<sub>2</sub> (Δ), Cu/SiO<sub>2</sub> ex NO<sub>3</sub> treated with H<sub>2</sub>SO<sub>4</sub> (◇) and Cu/SiO<sub>2</sub> ex SO<sub>4</sub> out-gassed at 600 °C in N<sub>2</sub> (τ).

Catalyst	Un-calcined	Calcined
Cu(ex-SO <sub>4</sub> ) / Al <sub>2</sub> O <sub>3</sub>	2.7	2.5
Cu(ex-SO <sub>4</sub> ) / TiO <sub>2</sub>	3.2	3.2
Cu(ex-SO <sub>4</sub> ) / SiO <sub>2</sub>	1.2	1.4
Cu(ex-SO <sub>4</sub> ) / SiO <sub>2</sub> *	-	2.1
Cu(ex-NO <sub>3</sub> ) / SiO <sub>2</sub> **	-	1.2

Table 1

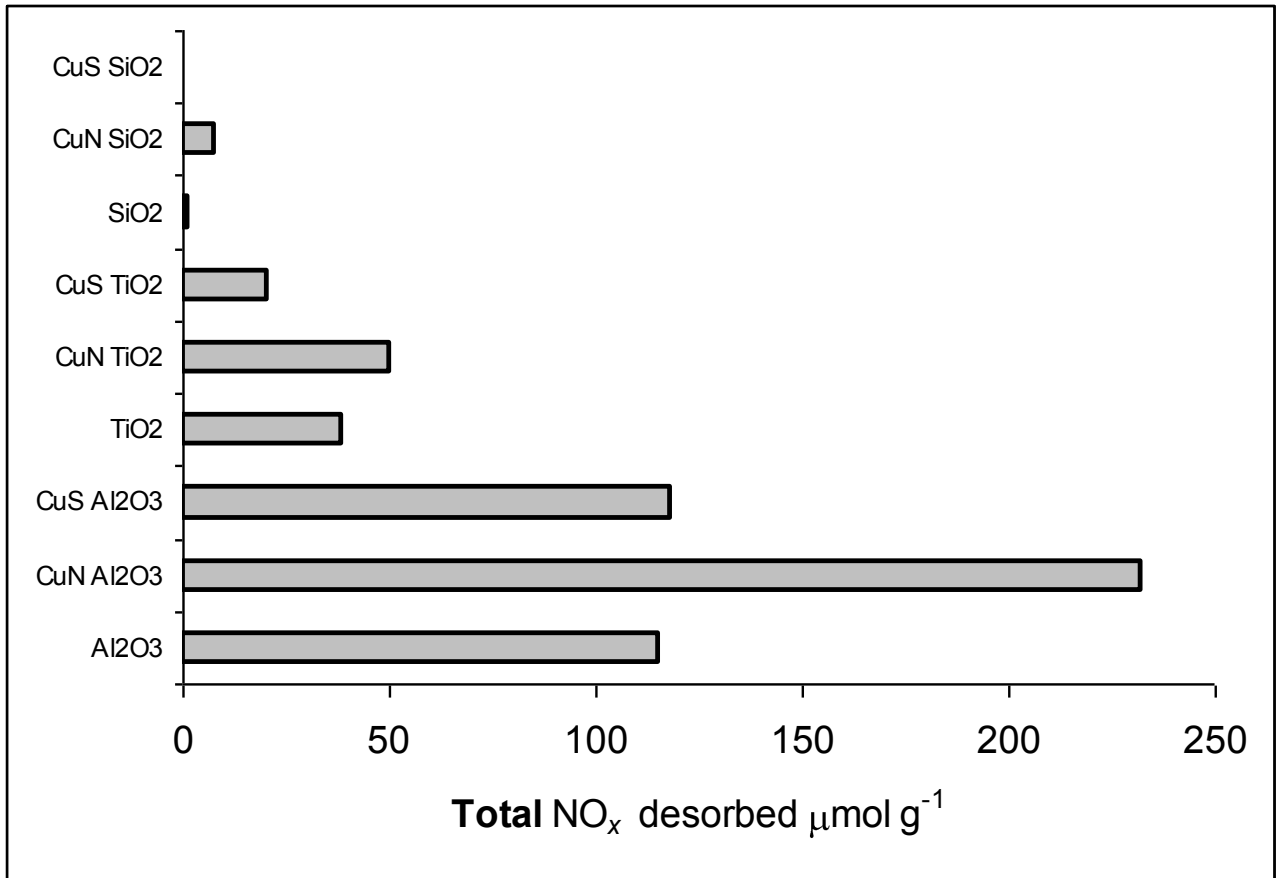


Figure 1

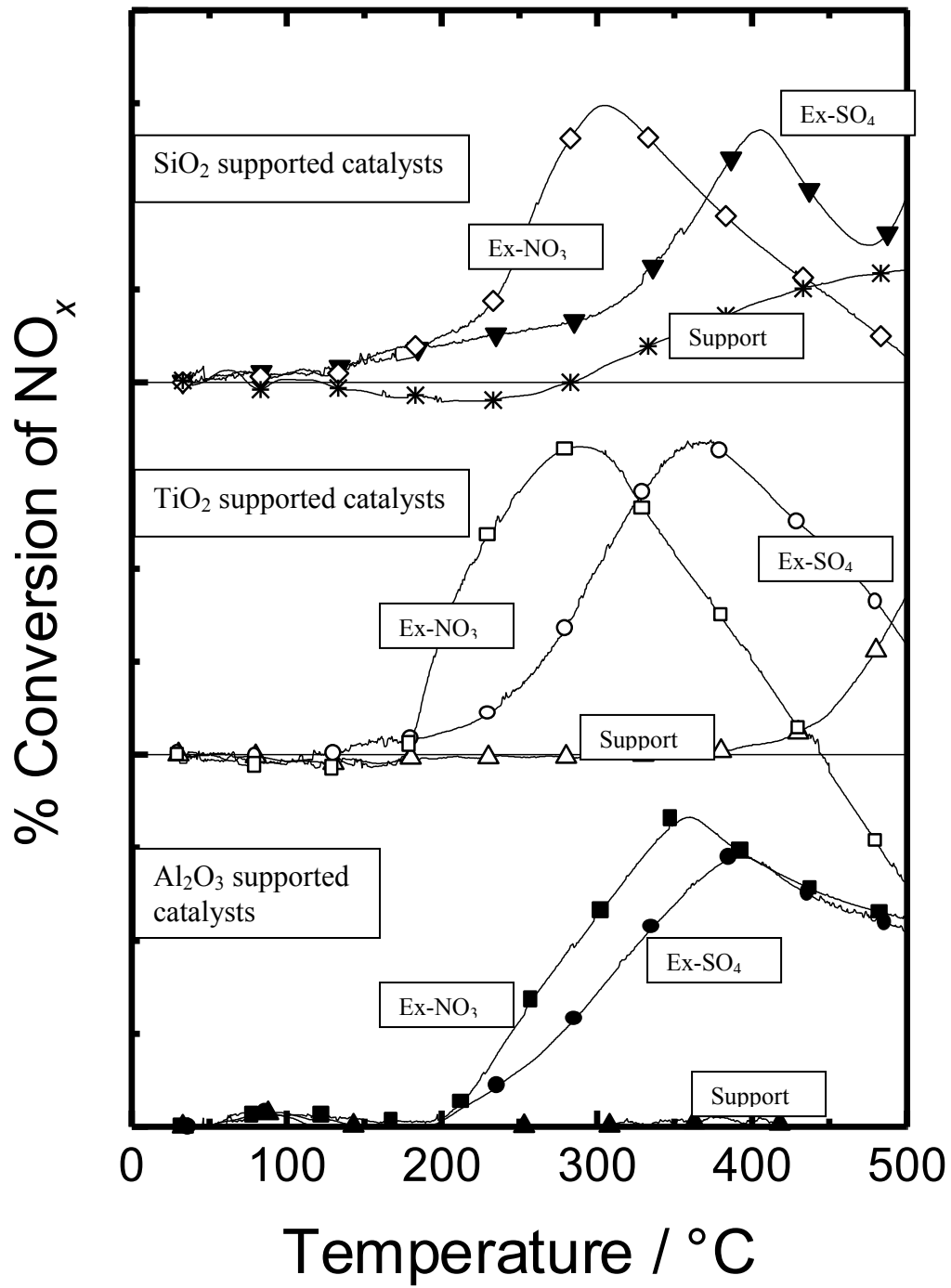


Figure 2

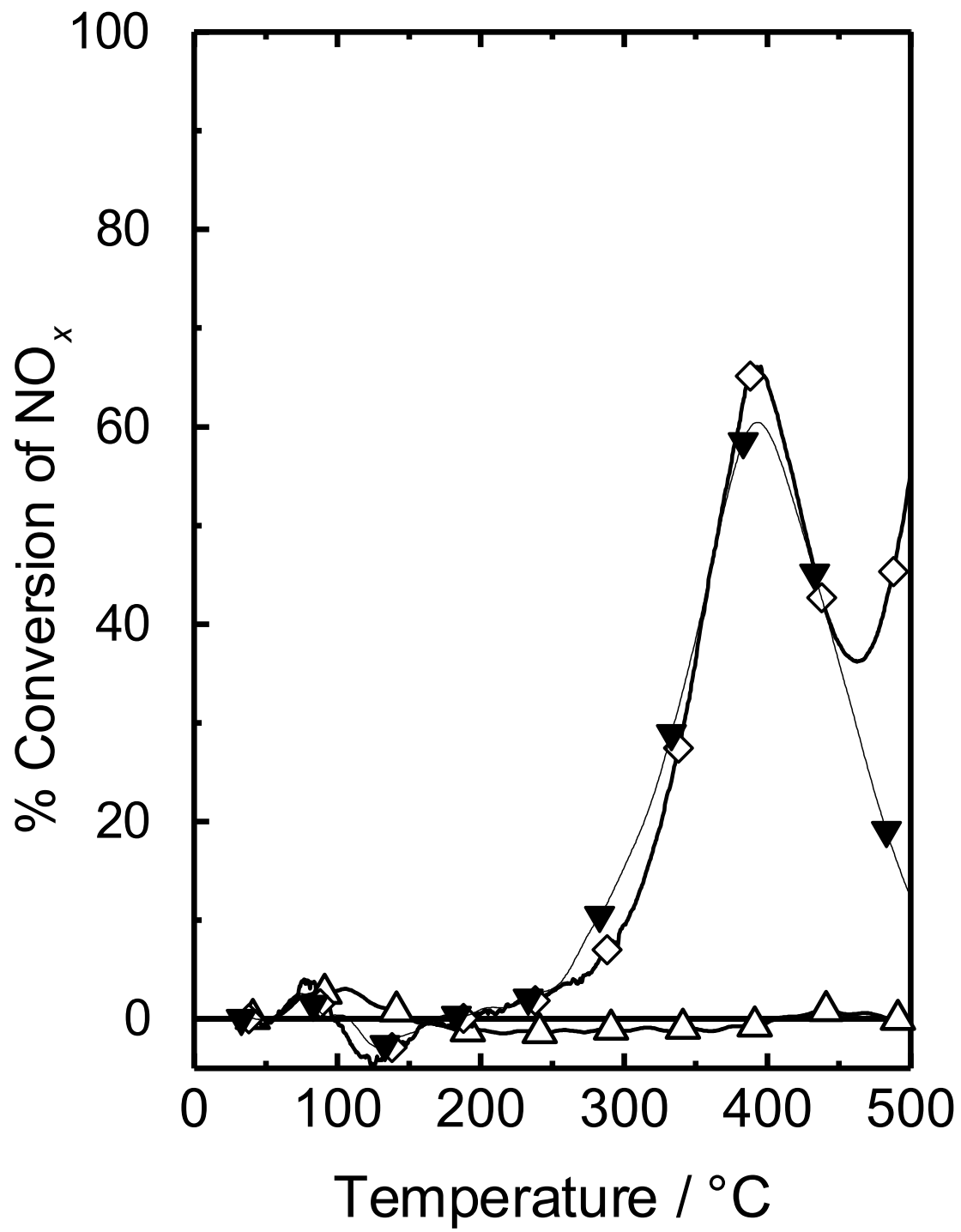


Figure 3