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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_x

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Abstract

A series of Cu catalysts were studied as a function of support (Al₂O₃, TiO₂ and SiO₂) and Cu precursor (ex-SO₄ and ex-NO₃) for activity in the SCR-NH₃ reaction. The catalysts were characterised using NO_x TPD and SEM/EDAX analysis and the effects of residual sulphur interpreted in terms of site-blocking and NH₃ activation mechanisms.

Keywords: SCR, NO_x, NH₃, 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 SO₂ in the gas phase (and hence SO₄ species on an oxide catalyst surface) has *promoted* the rate of particular reactions. Examples include the total oxidation of propane over Pt/Al₂O₃ catalysts, [5-7], the selective reduction of NO_x using NH₃ over V₂O₅ /Carbon catalysts [8] and the combustion of CH₄ over Pd/ZrO₂ [9].

In dealing with the emissions from stationary or mobile power sources the presence of SO₂ - 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- 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 gasses using reservoirs or urea as an NH_3 precursor.

2. Experimental

Commercial γ Al_2O_3 (Criterion Catalysts) (S.A. = $195 \text{ m}^2\text{g}^{-1}$), TiO_2 (Degussa P25) (S.A. = $49 \text{ m}^2\text{g}^{-1}$) and 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 μm . 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°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 $[\text{NO}] = 1000 \text{ ppm}$, $[\text{NH}_3] = 1500 \text{ ppm}$ 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 $10^\circ\text{C}/\text{min}$. During the NO_x TPD studies the sample was pre-oxidised at 500°C , dosed for 1h 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 $10^\circ\text{C}/\text{min}$ 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 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-NO₃ 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 NO₃ 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 Al₂O₃-supported materials adsorbing large amounts, TiO₂-supported materials intermediate amounts and SiO₂-supported materials very small amounts.

In the case of *all* supports the addition of ex-NO₃ (clean) CuO increases the concentration of NO_x that can adsorb (by providing extra adsorption sites on CuO)

while the addition of ex-SO₄ 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 + NH₃ + O₂ 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 SiO₂ (upper three profiles) being more active than TiO₂ (middle three profiles). Al₂O₃ (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 SiO₂ and TiO₂ supported catalysts and at all temperatures for the Al₂O₃ 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 NH₃ → N₂ (thereby removing reductant) and NH₃ → NO (thereby directly forming NO_x) reactions. The ex-NO₃ catalysts are more active for the desired reaction at lower temperatures than the ex-SO₄ materials while at higher temperatures their activity drops far more quickly than that of the ex-SO₄ catalysts. From the TPD results we can suggest a reason for the decreased activity of the ex-SO₄ catalysts at lower temperatures, *i.e.* competition between NO_x and SO₄ 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 ($\text{NO} + \text{NO}_2$). 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 de NO_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 de NO_x (or in a manner less favourable to NH_3 oxidation).

The higher “high temperature” de NO_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 de 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 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 de NO_x activity (compare (Δ) in figure 3 with (*) in figure 2) showing that sulphate species alone do not cause the increase in high temperature activity.

Secondly, 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 ((\diamond) in figure 3) the lower (200-300°C) temperature activity present on the Cu/SiO₂ catalyst ((v) in figure 2) is removed (presumably as SO₄ 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-SO₄ catalyst in figure 2 (τ)) 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-SO₄ catalyst was out-gassed in flowing N₂ 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 (τ) in figure 2 with (τ) 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 450-500 °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 NH₃ oxidation).

The treatment at 600 °C in N₂ could have had several effects on the surface composition of the catalysts including sintering of the CuO particles and support or decomposition of the SO₄ species into SO₂ (g) with the remaining 2 O atoms either desorbing as O₂ or remaining as lattice O atoms (in SiO₂ or CuO). A situation where the CuO particles sinter and interfacial sulphate groups (active for the high temperature promotion) between the CuO and the SiO₂ 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.

Conclusions

Sulphur species remain on the supported CuO catalyst surfaces when ex-SO₄ precursors are used. The presence of SO₄²⁻ 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 – (1) decreasing activity at lower temperatures and (2) ameliorating the decrease in activity seen at higher temperatures due to the NH₃ → O₂ reaction (an even more striking *increase* in deNO_x activity is seen over the ex-SO₄ SiO₂ 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 onto the surface plays a role in the reaction mechanism). It is proposed that the second effect involves the way that the NH₃ molecules co-ordinate to the catalyst surface in the presence of sulphate groups. This coordination decreases the extent of the NH₃ → 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 characterise these interfacial SO₄ groups using *in-situ* DRIFTS spectroscopy.

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Table 1: [Cu]/[S] ratios for the calcined and un-calcined catalysts as measures using couples SEM and X-Ray Analysis. * refers to a sample of Cu(ex-SO₄) / SiO₂ that had been treated in N₂ at 600 °C for 30 minutes, ** refers to a sample of Cu(ex-NO₃) / SiO₂ that had been treated with H₂SO₄ and calcined.

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

Figure 2: Temperature programmed NO+NH₃+O₂ reaction over Al₂O₃ (σ), Cu/Al₂O₃ ex NO₃(ν), Cu/Al₂O₃ ex SO₄ (λ), TiO₂ (Δ), Cu/TiO₂ ex NO₃ (□), Cu/TiO₂ ex SO₄ (○), SiO₂ (*), Cu/SiO₂ ex NO₃ (◇), Cu/SiO₂ ex SO₄ (τ). Each third of the figure represents conversion from 0 to 100 %.

Figure 3: Temperature Programmed NO+NH₃+O₂ reaction over Sulphated SiO₂ (Δ), Cu/SiO₂ ex NO₃ treated with H₂SO₄ (◇) and Cu/SiO₂ ex SO₄ out-gassed at 600 °C in N₂ (τ).

Catalyst	Un-calcined	Calcined
Cu(ex-SO ₄) / Al ₂ O 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 *	-	2.1
Cu(ex-NO ₃) / SiO ₂ **	-	1.2

Table 1

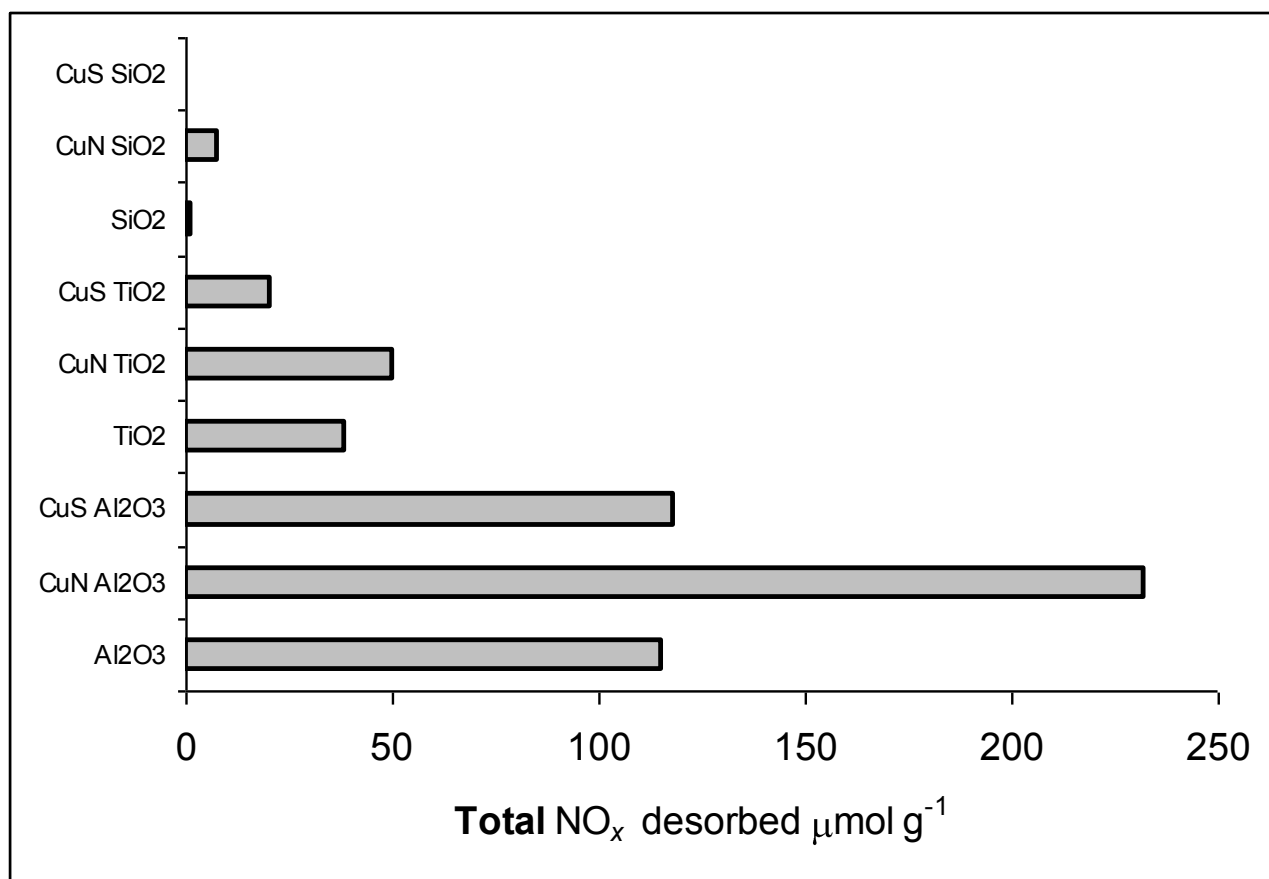


Figure 1

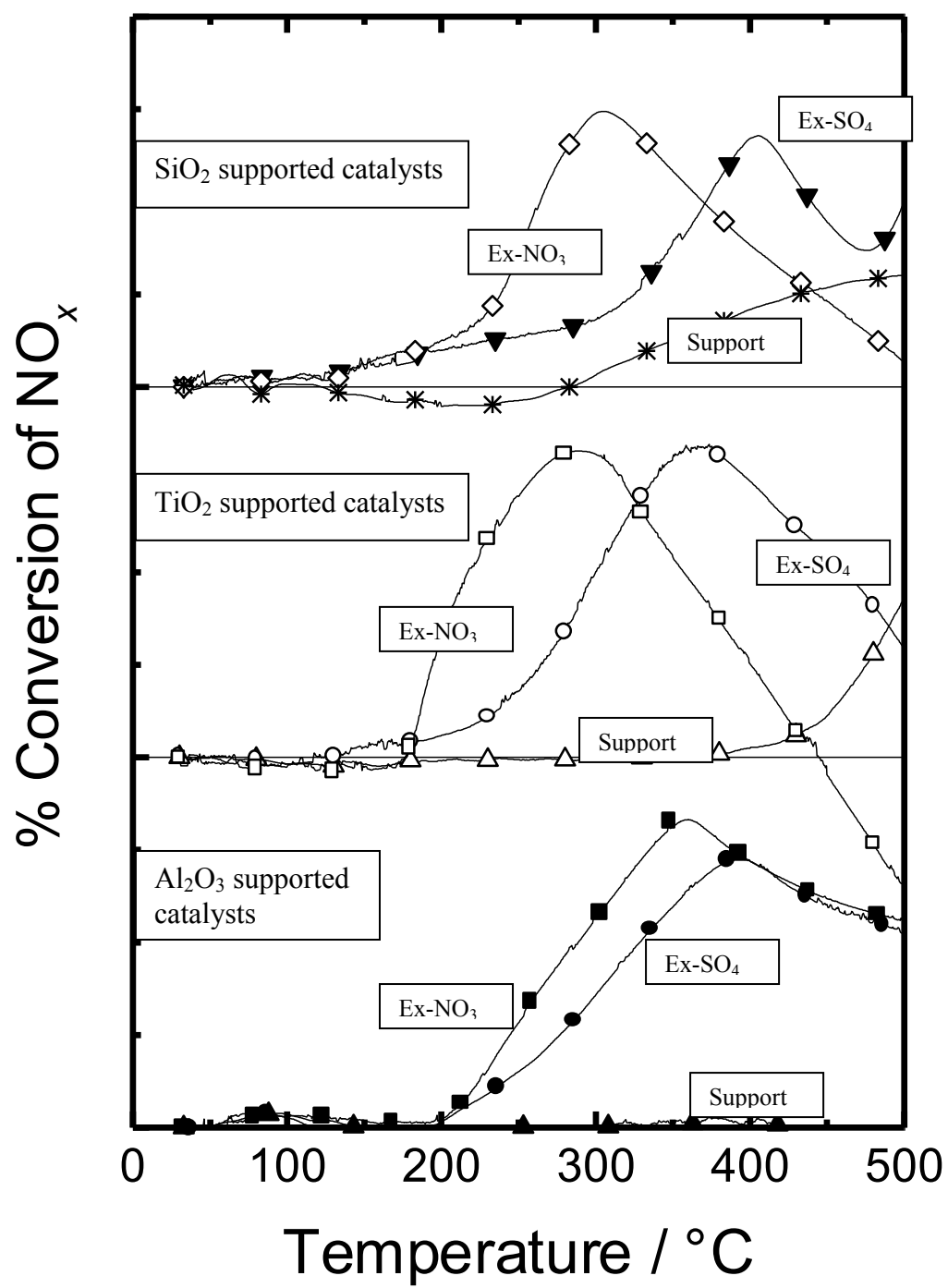


Figure 2

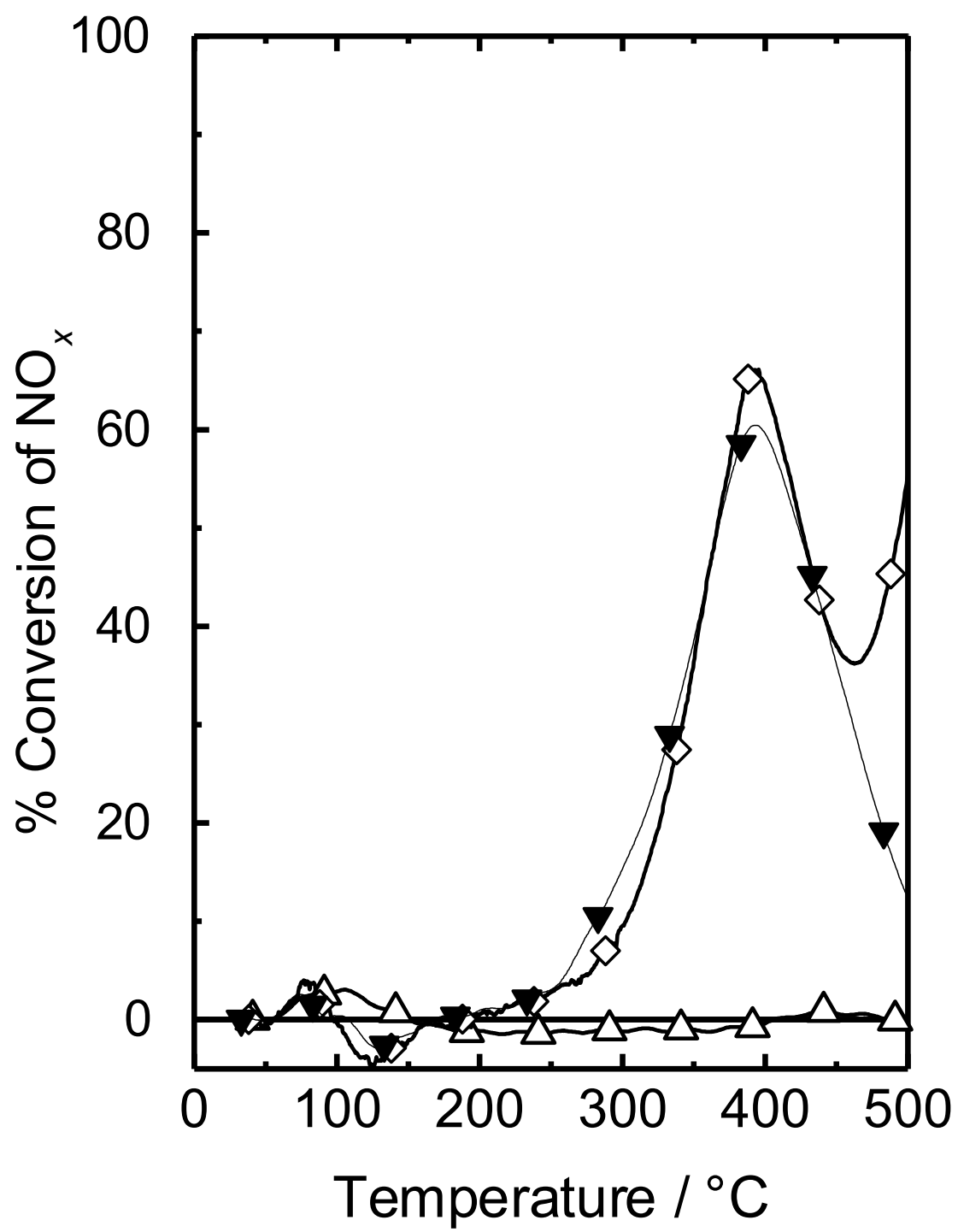


Figure 3