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# **NH<sub>3</sub> and Urea in the Selective Catalytic Reduction of NO<sub>x</sub> over oxide supported copper catalysts.**

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## **Abstract.**

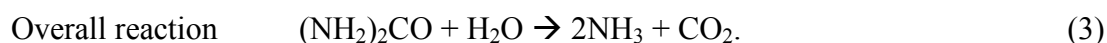
The temperature programmed activity of a series of oxide supported (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>) Cu catalysts formed from two different Cu precursors (Cu(NO<sub>3</sub>)<sub>2</sub> and CuSO<sub>4</sub>) for the selective catalytic reduction of NO<sub>x</sub> using solutions of urea as a reductant have been determined. These activities are compared to those found using NH<sub>3</sub> as a reducing agent over the same catalysts in the presence of H<sub>2</sub>O and it is found that catalysts that are active for the selective reduction of NO<sub>x</sub> with NH<sub>3</sub> are inactive for its reduction using solutions of urea. Poisoning of the surface by H<sub>2</sub>O<sub>ads</sub> is not responsible for all of this decrease in activity and it is postulated that the urea is not hydrolysing to form NH<sub>3</sub> over the catalysts but rather is oxidising to form N<sub>2</sub> or forming passivated layers of polymeric melamine complexes on the surface. The catalysts were characterised by Temperature Programmed Reduction while Temperature Programmed Desorption and Oxidation of NH<sub>3</sub> and Temperature Programmed Decomposition of urea are used to characterise the interaction of both reductants with the various catalysts.

**Keywords: Copper, NO<sub>x</sub>, SCR-NH<sub>3</sub>, Urea.**

## Introduction.

The detrimental effects of NO<sub>x</sub> (NO and NO<sub>2</sub>) are well documented and include the formations of photochemical smog and acid rain as well as direct negative effects on the human respiratory system<sup>1</sup>. NO<sub>x</sub> is formed in all combustion processes from the high temperature reaction between N<sub>2</sub> and O<sub>2</sub><sup>2</sup>. The reduction of Nitric Oxide in gas exhaust streams, from combustion processes, containing a large excess of O<sub>2</sub> remains one of the most intensively studied areas of heterogeneous catalysis<sup>3-8</sup>. The development of an active selective and stable catalyst would find immediate application in the treatment of exhausts from lean burn gasoline and diesel engines. One very successful technique for the removal of NO<sub>x</sub> is used commercially in the treatment of exhaust gases of stationary power generation plants. This involves the selective catalytic reduction of NO<sub>x</sub> with an added reducing agent, *i.e.* NH<sub>3</sub>. The NH<sub>3</sub> selectively reacts with the NO<sub>x</sub> component of a gas stream without reacting with the O<sub>2</sub> (which is present in a large excess)<sup>9</sup>. The catalysts used in these reactions are generally either zeolitic or vanadia based<sup>10</sup>.

For obvious reasons it would not be possible to use NH<sub>3</sub> as a selective reductant on a lean-burn gasoline or diesel powered car, *i.e.* it is corrosive, toxic, a primary and secondary pollutant and, due to its being a gas, difficult to handle requiring pressurised safety systems and very accurate dosage control mechanisms. However, it has been proposed that NH<sub>3</sub> could be replaced by aqueous solutions of urea ((NH<sub>2</sub>)<sub>2</sub>CO)<sup>11-12</sup> and that this could be easily hydrolysed at relatively low temperatures to NH<sub>3</sub> (via formation of HCNO – see equations 1-3)<sup>13</sup>.



Previous work in this laboratory<sup>14</sup> has found that oxide supported CuO catalysts show activity in the SCR-NH<sub>3</sub> reaction with the level of activity being related to the support upon which CuO was dispersed as well as the precursor (ex-NO<sub>3</sub><sup>-</sup> or ex-SO<sub>4</sub><sup>-</sup>) from which the CuO was manufactured. Sulphate species remained on the catalyst surface following calcinations (as monitored by FTIR and EDAX analysis) while the nitrate precursors were removed by calcinations and it is thought that sulphur modifies the activity through altering the acidity of the material as well as in a simple site-blocking manner.

Generally the catalysts were active between ~250–400 °C with activity decreasing at higher temperatures due to competition with the unselective NH<sub>3</sub> oxidation reaction. Residual sulphate had several effects, *i.e.* increasing the temperature at which the SCR-NH<sub>3</sub> reaction gave a maximum conversion and poisoning the catalyst reactivity for the unselective NH<sub>3</sub> combustion reaction at higher temperatures. In the current work the activity of these catalysts were characterised using a variety of temperature programmed techniques and their activity for the deNO<sub>x</sub> reaction using solutions of urea was investigated.

## **Experimental**

*Catalyst Preparation:* Commercial  $\gamma$  Al<sub>2</sub>O<sub>3</sub> (Criterion Catalysts) (S.A. = 195 m<sup>2</sup>g<sup>-1</sup>), TiO<sub>2</sub> (Degussa P25) (S.A. = 49 m<sup>2</sup>g<sup>-1</sup>) and SiO<sub>2</sub> (Grace) (S.A.= 256 m<sup>2</sup>g<sup>-1</sup>) were used as supports. Before doping with Cu these were crushed and sieved to particle sizes of 212-600  $\mu$ m. 1% loaded catalysts were prepared using conventional incipient wetness impregnation using Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O and CuSO<sub>4</sub>.5H<sub>2</sub>O precursors. They were then dried (100 °C) and calcined (500 °C) for 3 h.

*Activity measurements:* The catalyst (25 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<sub>3</sub> in He (BOC Special Gases), O<sub>2</sub> and He (BOC) to give a reaction mixture of [NO] = 1000 ppm, [NH<sub>3</sub>] = 1000 ppm, [H<sub>2</sub>O] = 12% and [O<sub>2</sub>] = 13% in a total flow of 100 ml/min. H<sub>2</sub>O and solutions of urea were introduced into a heated zone before the reactor from a calibrated syringe driver. Aqueous solutions of 5% urea were used at liquid flow rates that gave 300 ppm urea in the final reaction mixture. The reactions (SCR-NH<sub>3</sub> and SCR-Urea) were studied under temperature-programmed conditions with a ramp rate of 10 °C/min between 120 and 500 °C. Levels of NO<sub>x</sub> were continuously analysed, following suitable dilution, using a Monitor Labs Inc. Nitrogen Oxides Analyser (Model 8840) connected to a PC.

*Catalyst Characterisation:* The catalysts were characterised using Temperature Programmed Reduction (TPR) on an in-house constructed apparatus<sup>15</sup>. The catalyst was held in a quartz reactor under a flow of 3%H<sub>2</sub>/Ar as the temperature of the reactor was ramped between room temperature and 1000 °C. Any reduction event was monitored (as a decrease in the H<sub>2(g)</sub> concentration) using a Thermal Conductivity Detector (TCD). Any H<sub>2</sub>O produced during the reduction of the catalyst was trapped using a dry ice trap. Unfortunately H<sub>2</sub>S produced from reduction of sulphate groups on the catalyst was not trapped by the dry ice and thus the formation of H<sub>2</sub>S was also detected by the TCD. The catalyst mass was 50 mg, the flow rate of H<sub>2</sub>/Ar, 22 ml / min and temperature of the furnace ramped at a rate of 8.6 °C / min.

Catalyst acidity, and catalyst interaction with NH<sub>3</sub> was probed using Temperature Programmed Desorption of NH<sub>3</sub>. The catalyst (50 mg) was dosed with NH<sub>3</sub> (2860 ppm) at 110 °C for 30 minutes. The NH<sub>3</sub> was then removed from the

stream and the catalyst cooled to 50 °C in a flow of He (70 ml / min). It is held at this temperature for 20 minutes and then the temperature is ramped from 50 to 550 °C at a ramp rate of 10 °C / min. Temperature programmed oxidation of NH<sub>3</sub> was carried out in the same system using 50 mg of catalyst held in a flow of O<sub>2</sub> (22%) and NH<sub>3</sub> (2222ppm) in a total flow of 90 ml min<sup>-1</sup>.

The interaction of the catalysts with urea was probed using Temperature Programmed Urea Decomposition. The catalyst was wet with an aqueous solution of urea sufficient to does the 50 mg catalyst sample with 53 μmol of urea, dried for 1 h at 50 °C and placed in the reactor in a flow of 70 ml/min of He at a temperature of 50 °C. The temperature was ramped from 50 to 750 °C at a rate of 20 °C / min. The effluent gas was passed through a condenser at 0 °C in order to remove gas phase urea (to prevent its condensation within the capillary or the mass spectrometer chamber). Thus, only the products of the interaction between urea and the catalyst were monitored during decomposition.

In all cases (NH<sub>3</sub> TPD, NH<sub>3</sub> TPO and Urea TP Decomposition) the effluent gas was continuously monitored by mass spectrometry (Prolab Residual Gas Analysis) with the gas phase being introduced to the Prolab *via* a heated continuously evacuated capillary. The mass spectrometer monitors masses at 15, 16, 17, 18 (H<sub>2</sub>O, NH<sub>3</sub> and various fragments of each), 28 (N<sub>2</sub>, CO), 30 (NO), 32 (O<sub>2</sub>) and 44 (CO<sub>2</sub>, N<sub>2</sub>O) as a function of temperature. The data are then corrected for overlapping masses (*e.g.* the contribution of the H<sub>2</sub>O fragment at 17 to the NH<sub>3</sub> signal was removed).

## Results and Discussion.

### Temperature Programmed Reduction

Figure 1 shows the combined TPR profiles from the three sets of catalysts. The lower profiles relate to the SiO<sub>2</sub> supported materials. There is only one peak seen in these profiles at ~285°C. The peak is far more intense from in the case of the ex-SO<sub>4</sub><sup>2-</sup> material than from ex-NO<sub>3</sub><sup>-</sup> catalyst.

In the case of the ex-NO<sub>3</sub><sup>-</sup> catalyst the peak is due to the single reduction of CuO to Cu + H<sub>2</sub>O. This occurs at a lower temperature than that at which bulk CuO reduces (360 °C) and the reason for this decreased temperature of reduction is probably a CuO particle size effect<sup>16</sup>. The increased area of the peak arising from the ex-SO<sub>4</sub><sup>2-</sup> material is due to the reduction of CuO and the concomitant reduction of SO<sub>4</sub><sup>2-</sup> to H<sub>2</sub>S and H<sub>2</sub>O (and also possibly releasing SO<sub>2</sub>). This affects the TCD signal in two ways, firstly removing more H<sub>2</sub> and secondly exposing it to H<sub>2</sub>S causing it to register a further imbalance.

The fact that the SO<sub>4</sub><sup>2-</sup> reduction peak and the CuO reduction peak occur at the same temperature indicates that the sulphate and CuO species are present in closely related agglomerates on the surface. This is not an unfeasible proposition as it is reported that sulphate species analogous to Al<sub>2</sub>(SO<sub>4</sub>) are not stable on an SiO<sub>2</sub> surface<sup>17</sup> and thus the residual sulphur present on the catalyst must be in some way related to the CuO. Once the CuO material is reduced (to Cu + H<sub>2</sub>O) the bonds anchoring the SO<sub>4</sub><sup>2-</sup> to the surface are removed and the sulphate is lost (either as SO<sub>2</sub> or following reduction as H<sub>2</sub>S).

The middle set of profiles in Figure 1 show the reduction of the CuO / Al<sub>2</sub>O<sub>3</sub> catalysts. The ex-NO<sub>3</sub><sup>-</sup> material shows two peaks. There is a very broad peak between

200 and 600°C, which is related to the reduction of CuO. The broadness of the peak suggests that there is a wide distribution of CuO particle sizes on the material. There is another peak seen at higher temperature (850-950 °C), which has previously been related to the reduction of the Al<sub>2</sub>O<sub>3</sub> surface<sup>18</sup>. Both of these peaks are also seen (with exactly the same profiles over the ex-SO<sub>4</sub><sup>2-</sup> catalyst. This suggests that the presence of the SO<sub>4</sub><sup>2-</sup> does not alter the CuO particle size distribution on the Al<sub>2</sub>O<sub>3</sub> support or the reducible characteristics of the Al<sub>2</sub>O<sub>3</sub> support itself. There is another large feature of the ex-SO<sub>4</sub><sup>2-</sup> profile that is seen between 540 and 750 °C. This relates to the reduction of SO<sub>4</sub><sup>2-</sup> species on the Al<sub>2</sub>O<sub>3</sub> surface. The fact that these reduction peaks take place at far higher temperatures than the reduction of most of the supported CuO (200-600 °C) suggests that SO<sub>4</sub><sup>2-</sup> is stable on the Al<sub>2</sub>O<sub>3</sub> support at locations remote from the CuO particles (since it remains on the Al<sub>2</sub>O<sub>3</sub> surface after CuO has been reduced to Cu<sup>0</sup>).

Finally the upper two profiles relate to the reduction of TiO<sub>2</sub>-supported materials. There are two peaks seen over the ex-NO<sub>3</sub><sup>-</sup> sample, one peaking at 225 °C and one at 450 °C. Literature<sup>19</sup> suggests that the first peak is due to the reduction of CuO to Cu (at a lower temperature than the reduction of “bulk” CuO – again probably due to particle size effects). The second peak has previously been ascribed<sup>20</sup> to the reduction of TiO<sub>2</sub> to TiO<sub>2-x</sub>. This reduction in the absence of metallic species on the surface is reported to take place at 630 °C and the reason for the lower temperature in the presence of Cu is reportedly due to the spillover of hydrogen from metallic particles to the oxide surface. With regard to the ex-SO<sub>4</sub><sup>2-</sup> material the peaks are generally larger than those from the ex-NO<sub>3</sub><sup>-</sup> catalyst (for the reasons discussed above). On this material there are still two general areas of reduction (200 – 280 °C and 300 – 500 °C). However, now each of these peaks is split into two, showing complex behaviour related to the reduction of the CuO, the TiO<sub>2</sub> and the SO<sub>4</sub><sup>2-</sup>

components. If we assume that the lower temperature series of peaks is still related to CuO reduction we can suggest that there is  $\text{SO}_4^{2-}$  associated with the CuO on the surface (due to the higher intensity and split nature of the peak).

The splitting of the higher temperature peak is due to the reduction of  $\text{TiO}_2$  (as before) and the reduction of  $\text{SO}_4^{2-}$  deposited upon  $\text{TiO}_2$ . In the absence of  $\text{CuO}_{(s)}$  the reduction of  $\text{SO}_4^{2-}$  on a  $\text{TiO}_2$  surface takes place at  $T > 600\text{ }^\circ\text{C}^{20}$ . We assume that this temperature is again lowered here due to spillover of H- species from Cu.

### **De- $\text{NO}_x$ activity measurements**

*Activity in the SCR- $\text{NH}_3$  reaction in the presence of  $\text{H}_2\text{O}$ .*

Figure 2 shows the activity of all these catalysts in the SCR- $\text{NH}_3$  reaction with  $\text{H}_2\text{O}$  in the reactant stream. It is necessary to know the effect of  $\text{H}_2\text{O}$  since firstly  $\text{H}_2\text{O}$  is a by-product of combustion and so will also appear in the exhaust streams of interest and secondly since urea, if used as a reductant (to generate  $\text{NH}_3$  *in-situ*), would be introduced to the catalyst via aqueous solutions. These results can be compared with those presented previously<sup>14</sup> and while it should be noted that the reaction conditions used here differ from those used previously (in terms of catalyst mass and  $\text{NH}_3$  concentration) and that this leads to some minor changes in overall activity and temperatures of maximum activity the overall trends noted previously still apply, *i.e.* ex- $\text{NO}_3^-$  catalysts are more active at lower temperatures but are less selective at higher temperatures compared to their ex- $\text{SO}_4^{2-}$  analogues.

In the case of  $\text{TiO}_2$  –supported catalysts the temperature at which the catalysts commence de $\text{NO}_x$  is shifted upwards by  $\sim 100\text{ }^\circ\text{C}$  compared to the activities in the absence of  $\text{H}_2\text{O}$  (results not shown). The order of activities remains the same as seen previously with the ex- $\text{NO}_3^-$  catalyst activity being higher than the ex- $\text{SO}_4^{2-}$  at the

lower temperatures while the activity and selectivity of the ex-SO<sub>4</sub><sup>2-</sup> material is better at higher temperatures. One possible explanation for the overall decrease in activity is that there may be competition between the H<sub>2</sub>O and NH<sub>3</sub> for adsorption sites on the surface.

The opposite trend is observed for the Al<sub>2</sub>O<sub>3</sub>-supported materials where the catalysts are now active at 50 °C lower than previously. Again the order of activity is the same as under dry conditions (results not shown) with the ex-NO<sub>3</sub><sup>-</sup> catalysts being slightly more active than the ex-SO<sub>4</sub><sup>2-</sup> samples. One possible explanation for this observed behaviour is that Lewis acid sites on the Al<sub>2</sub>O<sub>3</sub> surface are hydroxylated in the presence of H<sub>2</sub>O generating Bronstead sites, which are more active and selective for the adsorption and activation of NH<sub>3</sub>.

The SiO<sub>2</sub>-supported materials also require higher temperatures before activity commences (350 °C rather than 250 °C when H<sub>2</sub>O is absent - results not shown) suggesting competition between NH<sub>3</sub> and H<sub>2</sub>O for adsorption sites. However, at temperatures above 400 °C the ex-NO<sub>3</sub><sup>-</sup> catalyst is more active in the presence of H<sub>2</sub>O (suggesting that hydroxylation of the surface is important in terms of promoting both activity and selectivity). The ex-SO<sub>4</sub><sup>2-</sup> catalyst is less active at lower temperatures in the presence of H<sub>2</sub>O but is as active at higher T so possibly H<sub>2</sub>O poisons sites as was assumed to be the case with the TiO<sub>2</sub>-supported materials.

Lewis acid centres are known to predominate on TiO<sub>2</sub> surfaces and it seems that these do not hydroxylate to the more selective Bronstead sites as seems to have taken place over the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>- supported catalysts.

*Activity in the SCR-Urea reaction.*

Figure 3 shows the activities of the six catalysts in the de NO<sub>x</sub> reaction when the NH<sub>3</sub> is removed and replaced with a solution of urea. The solution is dosed into the reaction mixture at a rate sufficient to give an overall urea concentration of 300 ppm. This is lower than the 1000 ppm of NH<sub>3</sub> used during the SCR-NH<sub>3</sub> reaction measurements. Each molecule of urea can in theory form two molecules of NH<sub>3</sub> during the decomposition in the presence of H<sub>2</sub>O (see equations 1-3 above) so this equates to 600 ppm NH<sub>3</sub>. Tests have been carried out using larger concentrations of urea (500 – 1000 ppm) and the activities are similar to those reported here.

In almost all cases the activity of the catalysts is much lower than the equivalent reactivities using NH<sub>3</sub> as a reductant. The TiO<sub>2</sub>-supported materials still show some activity at T > 300 °C but this is far decreased relative to the situation where NH<sub>3</sub> is used even in the presence of a large amount of H<sub>2</sub>O (which acts to decrease catalyst activity). The Al<sub>2</sub>O<sub>3</sub>-supported catalyst activities are almost totally suppressed in the presence of urea while there is a small amount of activity remaining over the Cu ex-NO<sub>3</sub><sup>-</sup> SiO<sub>2</sub> supported catalyst. This catalyst remains less active than it was in the presence of 12% H<sub>2</sub>O when NH<sub>3</sub> reductant was used. The activities of the catalysts are too low to allow us to make general statements regarding the effect of surface SO<sub>4</sub><sup>2-</sup> on the activity of the SCR-Urea reaction.

The presence of H<sub>2</sub>O had no severe effect on the SCR-NH<sub>3</sub> activity – pushing the required temperature up for the TiO<sub>2</sub> supported catalysts and improving the activity of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> supported materials. Thus, the explanation for the much decreased activity of the catalysts when NH<sub>3</sub> is replaced by (NH<sub>2</sub>)<sub>2</sub>CO cannot lie in surface poisoning by H<sub>2</sub>O. The only other explanation is that urea does not hydrolyse on the catalyst surface in the manner described in equations 1-3.

One possibility is that urea gets oxidised to  $N_2$  thus not making  $NH_3$  available for  $NO_x$  reduction while another possibility is that the urea forms polymeric melamine complexes<sup>24</sup> on the catalyst surface causing surface passivation.

#### *Temperature Programmed Desorption and Oxidation of $NH_3$ .*

Previous work<sup>14</sup> has shown that the presence of  $SO_4^{2-}$  on the surface decreases the  $NO_x$  sorption capacity of the catalysts and this was used to rationalise the decreased activity of the catalysts at lower temperatures. This work also showed that the ex- $SO_4^{2-}$  materials were more selective at higher temperatures (seen under these conditions also over the  $TiO_2$  and  $SiO_2$  supported catalysts). This was ascribed to either an increased concentration of adsorbed  $NH_3$  at these high temperatures (from an increase in the concentration of surface acid sites) or to an altered manner of activation of  $NH_3$  over these  $SO_4^{2-}$  containing materials (from a change in the strength of the surface acid sites). Interactions between  $NH_3$  and the surfaces were probed using  $NH_3$ TPD and  $NH_3$ TPO.

Figure 4 shows the  $NH_3$  profiles recorded by the mass spectrometer when the various catalysts dosed with  $NH_3$  were subjected to a temperature ramp in a flow of He. Table 1 shows the amounts of  $NH_3$  ( $\mu\text{mol g}^{-1}$ ) detected in the exit gas as a function of catalyst.

In the case of the  $Al_2O_3$  supported catalysts there is a peak seen in the  $NH_3$  desorption profile between 180 and 250 °C. There is an increase in the concentration of  $NH_3$  that is desorbed from the catalyst once  $SO_4^{2-}$  is present (67 versus 58  $\mu\text{mol g}^{-1}$ ). This shows that the presence of  $SO_4^{2-}$  increases the concentration of acid sites on the catalyst<sup>21</sup>. The position and shape of the peak from the  $Al_2O_3$  materials is similar in the presence and absence of  $SO_4^{2-}$ , *i.e.* a sharp peak at ~200 °C and a long tail

towards higher temperature, suggesting that the *strengths* of NH<sub>3</sub> adsorption remained unchanged, *i.e.* there is no change in the strength of acid sites on the surface.

There is a dramatic increase in the concentration of adsorbed NH<sub>3</sub> over the SiO<sub>2</sub> catalysts (lower profiles) once SO<sub>4</sub><sup>2-</sup> is present on the surface (73 versus 12 μmol g<sup>-1</sup>). This shows that again SO<sub>4</sub><sup>2-</sup> increases the concentration of surface acid sites. The distribution of acid site strength is also modified by the presence of SO<sub>4</sub><sup>2-</sup>. In its absence there is a broad plateau in NH<sub>3</sub> desorption between 200 and 400 °C showing a wide range of surface acid strengths. In the presence of SO<sub>4</sub><sup>2-</sup> there is a definite peak at 200 °C with a higher temperature shoulder at ~400 °C. Therefore the SO<sub>4</sub><sup>2-</sup> has formed a new-type of surface acid site (presumably related to the formation of surface NH<sub>4</sub>SO<sub>4</sub>-type species).

The presence of SO<sub>4</sub><sup>2-</sup> has a different effect on the behaviour of the TiO<sub>2</sub> supported catalysts in the NH<sub>3</sub> TPD experiments. In the absence of SO<sub>4</sub><sup>2-</sup> there is a broad peak centred at a temperature of 250 °C and 40 μmol of NH<sub>3</sub> are desorbed g<sup>-1</sup>. When SO<sub>4</sub><sup>2-</sup> is present the overall amount of NH<sub>3</sub> desorbed decreases (to 26 μmol g<sup>-1</sup>) and the temperature of the peak maximum is shifted upward to ~ 380 °C. The latter effect has previously<sup>22</sup> been ascribed to the generation of stronger Lewis acid sites on the surface of TiO<sub>2</sub>. However, the decrease in overall acidity upon the addition of SO<sub>4</sub><sup>2-</sup> is difficult to understand.

One additional point to note is that at higher temperatures minor amounts of N<sub>2</sub>, N<sub>2</sub>O and NO evolved from each of the catalysts with the NO profile in particular being relatively strong from the Al<sub>2</sub>O<sub>3</sub> supported ex-NO<sub>3</sub><sup>-</sup> catalyst. These are not shown for reasons of clarity.

While the TiO<sub>2</sub> and SiO<sub>2</sub>-supported materials do show a change in the manner of activation of NH<sub>3</sub> as a function of SO<sub>4</sub><sup>2-</sup>, *i.e.* the generation of a new type of acid

site, (and thus provide a start point for an explanation for the changed selectivity of these materials in the SCR-NH<sub>3</sub> reaction as a function of the presence or absence of SO<sub>4</sub><sup>2-</sup>) the only changes to the Al<sub>2</sub>O<sub>3</sub> material involve increases in the concentration of acid sites and thus there is no definite explanation for the increased selectivity of the sulphated Al<sub>2</sub>O<sub>3</sub>-supported catalysts at higher temperature.

With this in mind a series of NH<sub>3</sub> oxidation experiments were carried out where the catalyst was held in a flow of NH<sub>3</sub> and O<sub>2</sub> as the temperature was ramped from 50 to 550 °C. NH<sub>3</sub>, N<sub>2</sub>, NO and N<sub>2</sub>O were all continuously monitored by mass spectrometry. The profiles generated from these experiments are shown in figure 5 (a)-(c). It is important to realise that the activities in the NH<sub>3</sub> oxidation reaction do not mirror exactly the interactions that take place during the SCR-NH<sub>3</sub> reaction (in the presence of NO<sub>x</sub>) but this reaction is still a useful probe for how the catalysts behaves in the presence of NH<sub>3</sub> and O<sub>2</sub>.

Figure 5(a) shows the results seen from the SiO<sub>2</sub>-supported catalysts. In both cases (ex-NO<sub>3</sub><sup>-</sup> and ex-SO<sub>4</sub><sup>2-</sup>) the NH<sub>3</sub> profiles from both catalysts behave in exactly the same manner, *i.e.* NH<sub>3</sub> desorption at lower temperatures and the commencement of NH<sub>3</sub> conversion at ~280 °C and complete conversion of NH<sub>3</sub> at 400 °C. There is a significant difference between the two catalysts when the products of NH<sub>3</sub> combustion are considered. The ex-NO<sub>3</sub><sup>-</sup> sample produces significantly less N<sub>2</sub> and significantly more NO than the ex-SO<sub>4</sub><sup>2-</sup> material. This is in agreement with the SCR-activity results above where the selectivity of the ex-SO<sub>4</sub><sup>2-</sup> material is greater than that of the ex-NO<sub>3</sub><sup>-</sup> catalyst, *i.e.* it seems that the ex-NO<sub>3</sub><sup>-</sup> catalyst shows higher activity for the conversion of NH<sub>3</sub> into NO<sub>x</sub> than the ex-SO<sub>4</sub><sup>2-</sup> analogue and thus a lower selectivity for the NO + NH<sub>3</sub> → N<sub>2</sub> reaction.

If it is assumed that the  $\text{NH}_3$  oxidation takes place on the CuO particles rather than the support, and (from the TPR results), that the  $\text{SO}_4^{2-}$  is associated with the CuO rather than on the  $\text{SiO}_2$  support on the catalyst, and then the effect of the proximate  $\text{SO}_4^{2-}$  is to poison reaction of  $\text{NH}_3$  to NO and/or promote its combustion to  $\text{N}_2$ .

Figure 5(b) shows the results for the same experiments over the  $\text{Al}_2\text{O}_3$ -supported catalysts. Again here the  $\text{NH}_3$  profiles are exactly the same over both materials with a desorption of  $\text{NH}_3$  between 100 and 200 °C and commencement of  $\text{NH}_3$  oxidation at ~350 °C. There is a difference in the product profiles here when compared to those seen above with  $\text{N}_2$  being the predominant product formed over both catalysts. Levels of  $\text{N}_2$  formation are also very similar. Low levels of  $\text{N}_2\text{O}$  and NO are seen at higher temperatures. There is no effect of  $\text{SO}_4^{2-}$  on the conversion of  $\text{NH}_3$  or the conversion to  $\text{N}_2$ . The levels of NO and  $\text{N}_2\text{O}$  are too low to allow any definite statement about the amounts of their relative conversion.

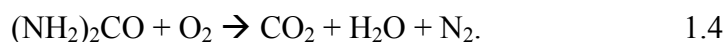
TPR results have shown that most of the  $\text{SO}_4^{2-}$  on  $\text{Al}_2\text{O}_3$ -supported catalysts is located on the  $\text{Al}_2\text{O}_3$  support rather than on the CuO particles and therefore, if it assumed that  $\text{NH}_3$  oxidation takes place at the CuO rather than on the support then the reason that there is no effect of  $\text{SO}_4^{2-}$  on the oxidation of  $\text{NH}_3$  is due to the fact that the  $\text{SO}_4^{2-}$  remains far from the active CuO sites.

Finally figure 5(c) shows the profiles obtained from the  $\text{TiO}_2$ -supported catalysts. Over these materials there is a definite difference in the profiles obtained over the ex- $\text{NO}_3^-$  and the ex- $\text{SO}_4^{2-}$  catalysts. Combustion of the  $\text{NH}_3$  commences at ~100 °C lower temperature over the ex- $\text{NO}_3^-$  catalyst than over the ex- $\text{SO}_4^{2-}$  catalyst. In common with the  $\text{SiO}_2$ -supported catalysts conversion to NO over the former catalyst is higher (and conversion to  $\text{N}_2$  lower) than over the latter. The increased selectivity of the ex- $\text{SO}_4^{2-}$  catalyst in the SCR- $\text{NH}_3$  reaction is mirrored here.

TPR results suggest that over TiO<sub>2</sub>-supported catalysts the SO<sub>4</sub><sup>2-</sup> (when present) is situated both close to CuO particles as well as on the TiO<sub>2</sub> support. Assuming that particles of CuO are the locus of activity for NH<sub>3</sub> oxidation it seems that SO<sub>4</sub><sup>2-</sup> located close to these active centres can affect the selectivity and, in this case activity, of the catalyst in the NH<sub>3</sub> oxidation reaction.

#### *Temperature Programmed Decomposition of Urea*

The SCR-Urea results (figure 3) show that most of the deNO<sub>x</sub> activity of the catalysts is lost once solutions of urea are used in the reaction mixture rather than NH<sub>3</sub>. There does not seem to be any relationship between this reduced activity and the presence or absence of SO<sub>4</sub><sup>2-</sup> on the surface. One possible reason for the difference between NH<sub>3</sub> and urea as a selective reductant is that the urea does not hydrolyse according to equations 1-3 and instead reacts with O<sub>2</sub> to form N<sub>2</sub> (equation 1.4).



or forms a urea-derived polymeric passivating layer on the surface (Equation 1.5).



The Temperature Programmed Decomposition studies are simply a probe experiment and obviously do not equate to what takes place on the surface of the catalyst during the SCR-urea reaction. However they do give valuable information about the behaviour of urea molecules in isolation from other reactants.

Figure 6 shows the major peaks that arise from this decomposition over the various samples having been dosed with 53 μmol of urea from an aqueous solution, dried and having the temperature ramped in Helium from 50 to 750 °C. Any urea that did not decompose (*i.e.* that which sublimed and recrystallised outside the reactor) could not be measured and no gas phase urea was allowed enter the mass

spectrometer. Therefore, all these profiles show is the gas phase decomposition products.

Under these flow conditions in the absence of a catalyst, *i.e.* when urea crystals were placed in the reactor and held alone with quartz wool the urea simply sublimed from the reactor and did not decompose to yield any gaseous products. Therefore we can say that any gaseous products that do evolve during the Temperature Programmed Decomposition arise due to the interaction between the urea and the catalyst.

The main decomposition of urea takes place over all the catalysts between 150 and 250 °C. During this time NH<sub>3</sub>, H<sub>2</sub>O (not shown for clarity) and CO<sub>2</sub> (or N<sub>2</sub>O) are released from the catalysts. At higher temperatures N<sub>2</sub> (or CO) is released from all materials.

Table 2 shows the amounts of NH<sub>3</sub> and CO<sub>2</sub> (assuming N<sub>2</sub>O formation is minimal) released during the experiments. From the 53 μmol urea dosed on the catalyst 106 μmol NH<sub>3</sub> and 53 μmol CO<sub>2</sub> could be formed if the full decomposition of urea to 2 NH<sub>3</sub> + CO<sub>2</sub> took place. However, it is clear that far less of these species are released from the catalyst (the remainder subliming and being removed from the reactor or remaining on the surface to form N<sub>2</sub> / CO at higher temperatures). It should be pointed out that twice as much NH<sub>3</sub> as CO<sub>2</sub> would be expected to be produced from the decomposition. This is not quite the case as seen in Table 2 and the discrepancies could be due to N<sub>2</sub>O or to the decompositions proceeding in a different manner to those discussed above. Overall most decomposition happens over the Al<sub>2</sub>O<sub>3</sub> supported materials, followed by the SiO<sub>2</sub>-supported catalysts with the least amount of decomposition taking place over the TiO<sub>2</sub>-supported materials.

This suggests that  $\text{Al}_2\text{O}_3$  supports interact with more urea than  $\text{SiO}_2$  and  $\text{TiO}_2$  (as all were initially dosed with the same concentration of urea and any “non-interacting” urea sublimates from the reactor and remains undetected). Over the  $\text{TiO}_2$  supported materials there is also a second release of  $\text{CO}_2$  at slightly higher temperatures (280 °C) with no accompanying  $\text{NH}_3$  formation – showing that the mode of adsorption and decomposition of urea differs over the various supports.

All catalysts also release some  $\text{N}_2$  or  $\text{CO}$  at higher temperatures. This arises from the decomposition of some fragments of urea that remain following the initial decomposition that are stable on the surface at temperatures between 300 and 600 °C. the concentration of these is highest over the  $\text{TiO}_2$  materials and lowest over the  $\text{Al}_2\text{O}_3$  supported catalysts.

Fang and DaCosta<sup>24</sup> have reported that molten urea sticks very well to a  $\text{TiO}_2$  surface relative to an  $\text{Al}_2\text{O}_3$  one and relate this to the relative concentration of hydroxyl groups present in each case with the urea coordinating more strongly to the more hydrophobic substrate. This would account for the increased formation of  $\text{N}_2$  (or  $\text{CO}$ ) over the  $\text{TiO}_2$ -supported materials at higher temperatures but is in contrast to the results above where lower temperature urea decomposition is more pronounced over the  $\text{Al}_2\text{O}_3$ -supported materials. We suggest that the decomposition to  $\text{NH}_3$  and  $\text{CO}_2$  discussed above requires the participation of surface hydroxyl groups (water in equations above) and for this reason there is more  $\text{NH}_3$  /  $\text{CO}_2$  formed over  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  supported catalysts. Over  $\text{TiO}_2$  (with a lower concentration of surface OH) the urea decomposes at higher temperature to  $\text{N}_2$  /  $\text{CO}$ .

Over the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ -supported catalysts there is no pronounced effect of  $\text{SO}_4^{2-}$  on the decomposition of urea with roughly the same amount of  $\text{NH}_3$  and  $\text{CO}_2$  being formed over both the ex- $\text{NO}_3^-$  and the ex- $\text{SO}_4^{2-}$  samples. Over the  $\text{TiO}_2$ -

supported materials there is a large effect of  $\text{SO}_4^{2-}$  which results in far less urea decomposing to  $\text{NH}_3$  and  $\text{CO}_2$  and far less  $\text{CO}/\text{N}_2$  formation at higher temperatures in the presence of sulphate. This suggests that the sulphate decreases both the surface-OH concentration (which results in the first peak) and the overall concentration of strongly chemisorbed urea (which leads to the second peak).

The initial decomposition peaks are rather sharp over the  $\text{SiO}_2$  and  $\text{TiO}_2$ -supported materials but are rather spread out over the  $\text{Al}_2\text{O}_3$ -supported catalysts. This is probably due to a chromatographic effect within the  $\text{Al}_2\text{O}_3$  catalyst bed rather than a distribution of urea stabilities on the catalyst surfaces.

Traces for HNCO (an intermediate in the decomposition of urea<sup>13, 25</sup>) were only seen at extremely low levels (not shown) over these catalysts and only in the initial decomposition peak ( $\sim 200$  °C). No HNCO or  $\text{NH}_3$  was seen at the higher temperatures where these catalysts catalyse the  $\text{NO} + \text{NH}_3$  reaction. We suggest that the urea decomposition fragments, which remain on the surface at this temperature, form  $\text{N}_2 / \text{CO}$  rather than decompose to the required  $\text{NH}_3$ . One catalyst that *is* active for the SCR-Urea reaction ( $\text{CuZSM-5}$ )<sup>25</sup> has also been studied using this technique and it shows a release of both  $\text{NH}_3$  and HNCO at these higher temperatures<sup>26</sup>.

Therefore there are three pathways for the removal of urea and its decomposition products from the surfaces of the catalysts under these temperature-programmed conditions. Firstly, the sublimation of non-coordinated urea from the solid phase, secondly the low temperature decomposition of relatively weakly bound urea to yield  $\text{NH}_3$  and  $\text{CO}_2$  (at  $\sim 200$  °C) and finally the combination of decomposition products to form either  $\text{CO}$  or  $\text{N}_2$  at higher temperature  $300 - 650$  °C.

These profiles show that to a greater or lesser degree the supported catalysts are able to convert urea to  $\text{NH}_3$  at low temperatures. However, the experiments

provide no clear picture of why they remain inactive in the SCR-Urea reaction while being active and selective in the SCR-NH<sub>3</sub> reaction.

## Conclusions

CuO catalysts derived from NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> precursors on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> are active for the SCR-NH<sub>3</sub> reaction in the presence of H<sub>2</sub>O. This activity is not transferred to the SCR-urea reaction. Having shown in previous work<sup>14</sup> that the surface capacity for storing NO<sub>x</sub> are affected by the presence of SO<sub>4</sub><sup>2-</sup> on the catalyst, this work shows that over the SiO<sub>2</sub> catalysts the SO<sub>4</sub><sup>2-</sup> is associated with the CuO, over the TiO<sub>2</sub> catalysts the SO<sub>4</sub><sup>2-</sup> is associated both with the CuO and the TiO<sub>2</sub> and over the Al<sub>2</sub>O<sub>3</sub>-supported materials the SO<sub>4</sub><sup>2-</sup> is associated with the support.

NH<sub>3</sub> TPD studies have shown that SO<sub>4</sub><sup>2-</sup> increases the concentration of acid sites on the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> supported materials and changes the acid site distribution over the SiO<sub>2</sub> and TiO<sub>2</sub> catalysts (while reducing the overall acidity of the latter).

NH<sub>3</sub> oxidation studies show that the presence of SO<sub>4</sub><sup>2-</sup> on the surface has no effect on the activity or selectivity of this reaction over Al<sub>2</sub>O<sub>3</sub>-supported materials and decreases the selectivity to NO<sub>x</sub> formation over SiO<sub>2</sub> and TiO<sub>2</sub>-supported materials (while also decreasing the activity of the latter). These results provide an explanation of the SO<sub>4</sub><sup>2-</sup> effect on selectivity in the SCR-NH<sub>3</sub> reaction at higher temperatures.

The urea decomposition studies show that most adsorbed urea is weakly adsorbed on the catalyst surface and that this urea decomposes to NH<sub>3</sub> and CO<sub>2</sub> (through interaction with surface OH groups) at a temperature of ~200 °C. Only very low levels of the proposed urea decomposition product HNCO were recorded and only at this temperature.

Relatively low amounts of urea decomposition products remain on the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-supported catalyst surfaces at temperatures above 300 °C. Far higher concentrations of urea decomposition products remain on the TiO<sub>2</sub>-supported materials (due to the hydrophobicity of the surface). In all cases these decompose under TPD conditions to N<sub>2</sub>/CO at higher temperatures. The presence of SO<sub>4</sub><sup>2-</sup> affects the concentration and temperature of decomposition of these species.

These experiments do not clarify why the activity of catalysts in the SCR-NH<sub>3</sub> reaction is not obtained in the SCR-urea reaction. We suggest that even though the catalysts decompose urea to NH<sub>3</sub> at lower temperatures that this is not the case at higher temperatures and that either urea → N<sub>2</sub> or the formation of a passivating layer on the surface<sup>24</sup> is responsible for this decreased activity.

### **Acknowledgements**

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### Figure Legends.

Figure 1: Displaced Temperature Programmed Reduction profiles from each catalyst (for conditions see text). Cu/SiO<sub>2</sub> (□, ■), Cu/Al<sub>2</sub>O<sub>3</sub> (○, ●), Cu/TiO<sub>2</sub> (△, ▲). Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>.

Figure 2: Displaced Temperature Programmed Activity profiles for the various catalysts in the SCR-NH<sub>3</sub> reaction in the presence of H<sub>2</sub>O. Catalyst mass 25 mg, 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 13% O<sub>2</sub> and 12% H<sub>2</sub>O balanced to 100 ml/min with He. Cu/SiO<sub>2</sub> (□, ■), Cu/Al<sub>2</sub>O<sub>3</sub> (○, ●), Cu/TiO<sub>2</sub> (△, ▲). Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>.

Figure 3: Displaced Temperature Programmed Activity profiles for the various catalysts in the SCR-Urea reaction. Catalyst mass 25 mg, 1000 ppm NO, 300 ppm urea, 13% O<sub>2</sub>, 12% H<sub>2</sub>O balanced to 100 ml / min with He. Cu/SiO<sub>2</sub> (□, ■), Cu/Al<sub>2</sub>O<sub>3</sub> (○, ●), Cu/TiO<sub>2</sub> (△, ▲). Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>.

Figure 4: Displaced Temperature Programmed NH<sub>3</sub> desorption profiles for the various catalysts. Cu/SiO<sub>2</sub> (□, ■), Cu/Al<sub>2</sub>O<sub>3</sub> (○, ●), Cu/TiO<sub>2</sub> (△, ▲). Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>.

Figure 5. Temperature Programmed NH<sub>3</sub> oxidation profiles from the various catalysts. Profiles from (a) Cu/SiO<sub>2</sub>, (b) Cu/Al<sub>2</sub>O<sub>3</sub> and (c) Cu/TiO<sub>2</sub> catalysts. NH<sub>3</sub> (□, ■), N<sub>2</sub> (○, ●), NO (△, ▲), N<sub>2</sub>O (◇, ◆) Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>.

Figure 6. Displaced Urea decomposition products from Urea TPD experiments from (a) Cu/SiO<sub>2</sub>, (b) Cu/Al<sub>2</sub>O<sub>3</sub> and (c) Cu/TiO<sub>2</sub> catalysts. NH<sub>3</sub> (□, ■), N<sub>2</sub>O/CO<sub>2</sub> (○, ●), and CO/N<sub>2</sub> (△, ▲), Open Symbols ex-NO<sub>3</sub><sup>-</sup>, Filled symbols ex-SO<sub>4</sub><sup>2-</sup>. For clarity the m/e=28 signals are \* 20, \*50 and \*10 respectively).

Figure 1

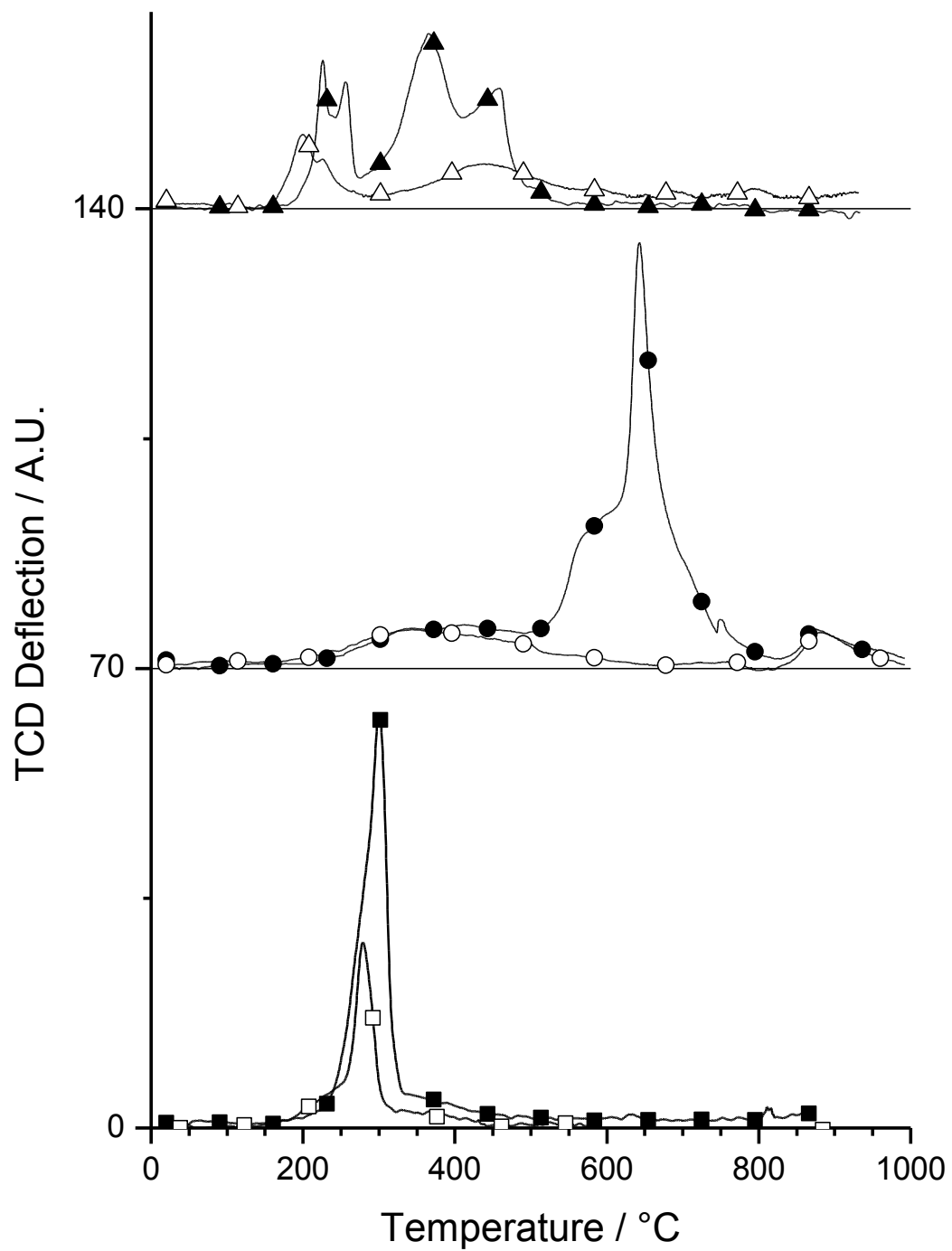


Figure2

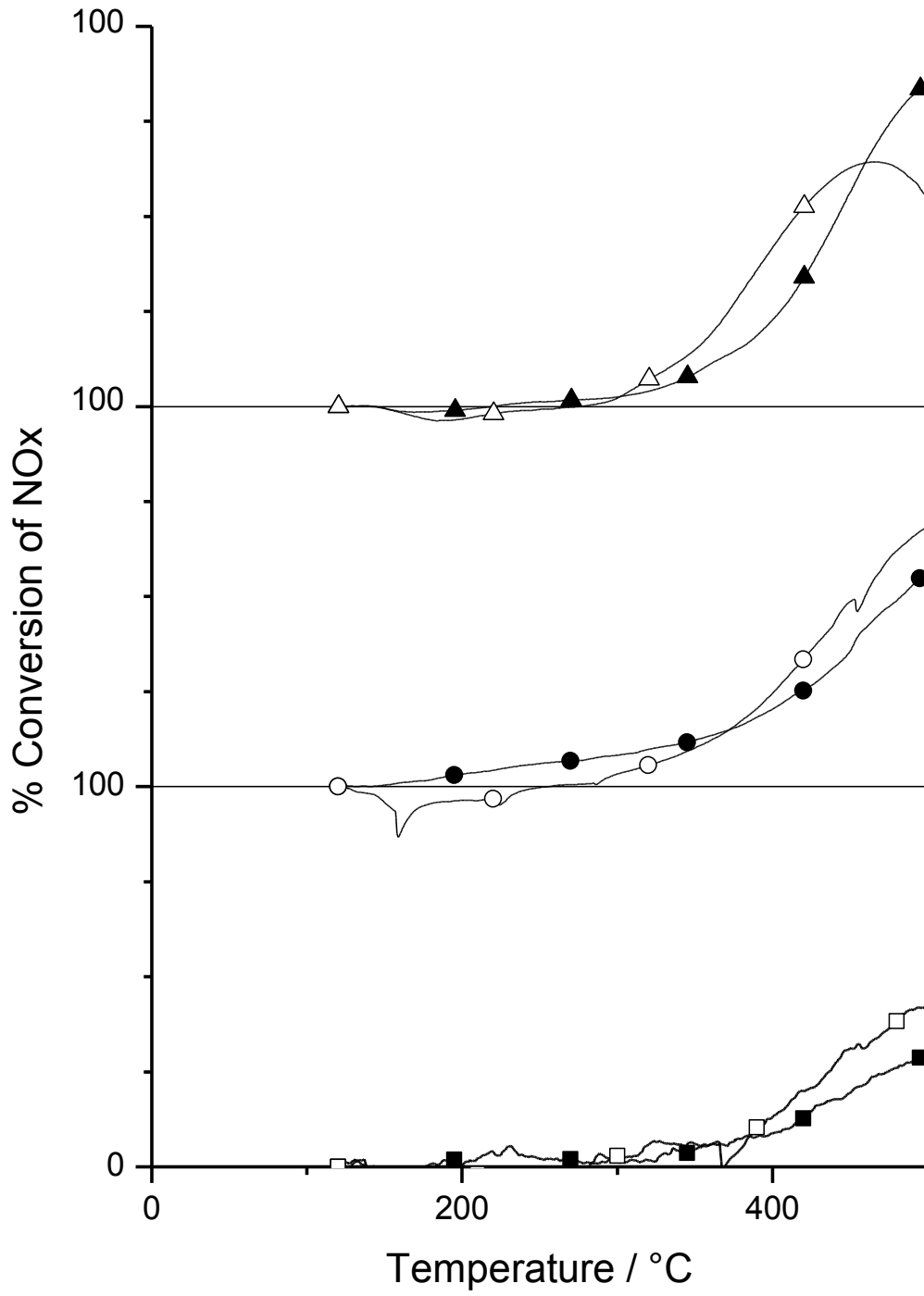


Figure 3

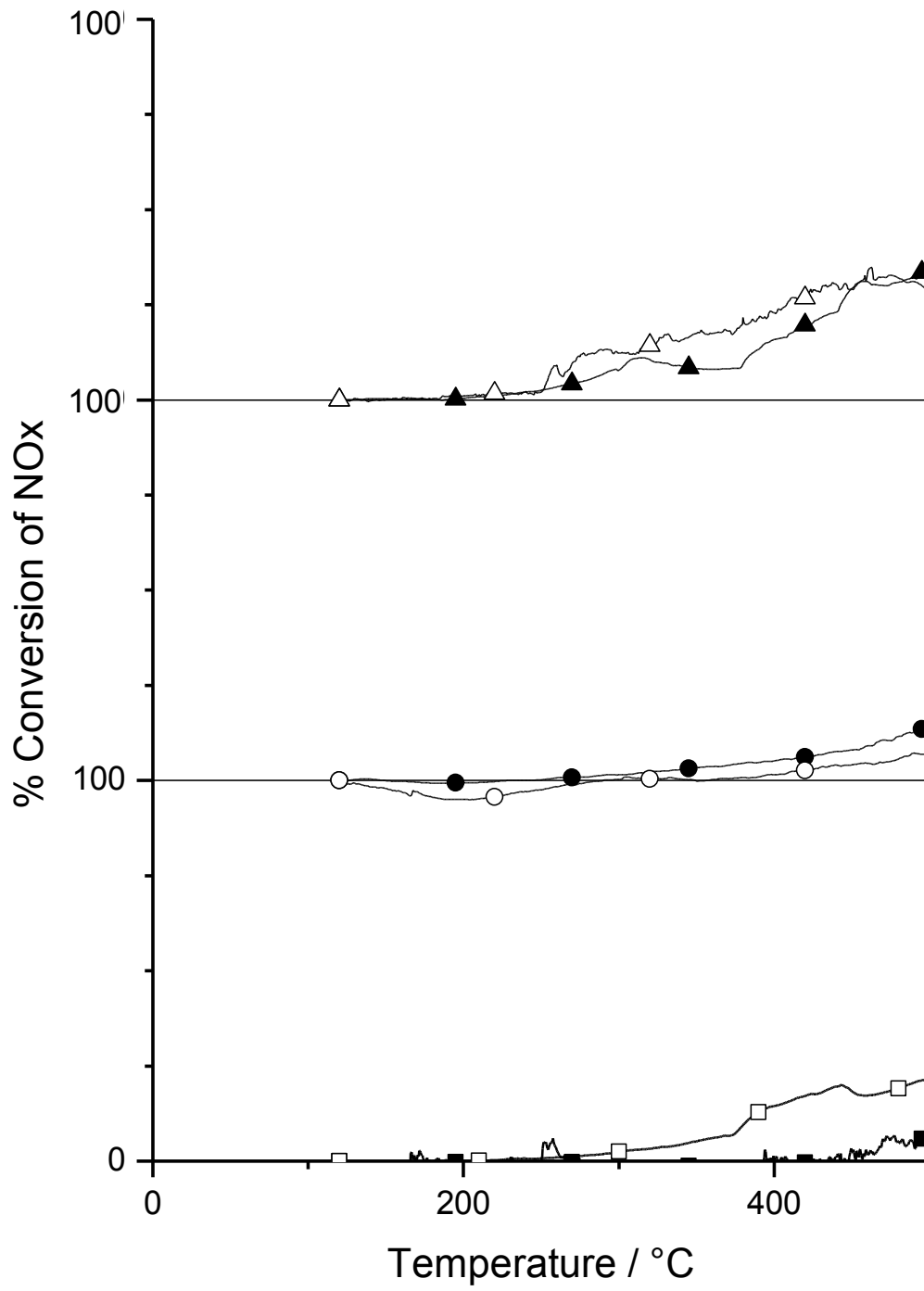


Figure 4

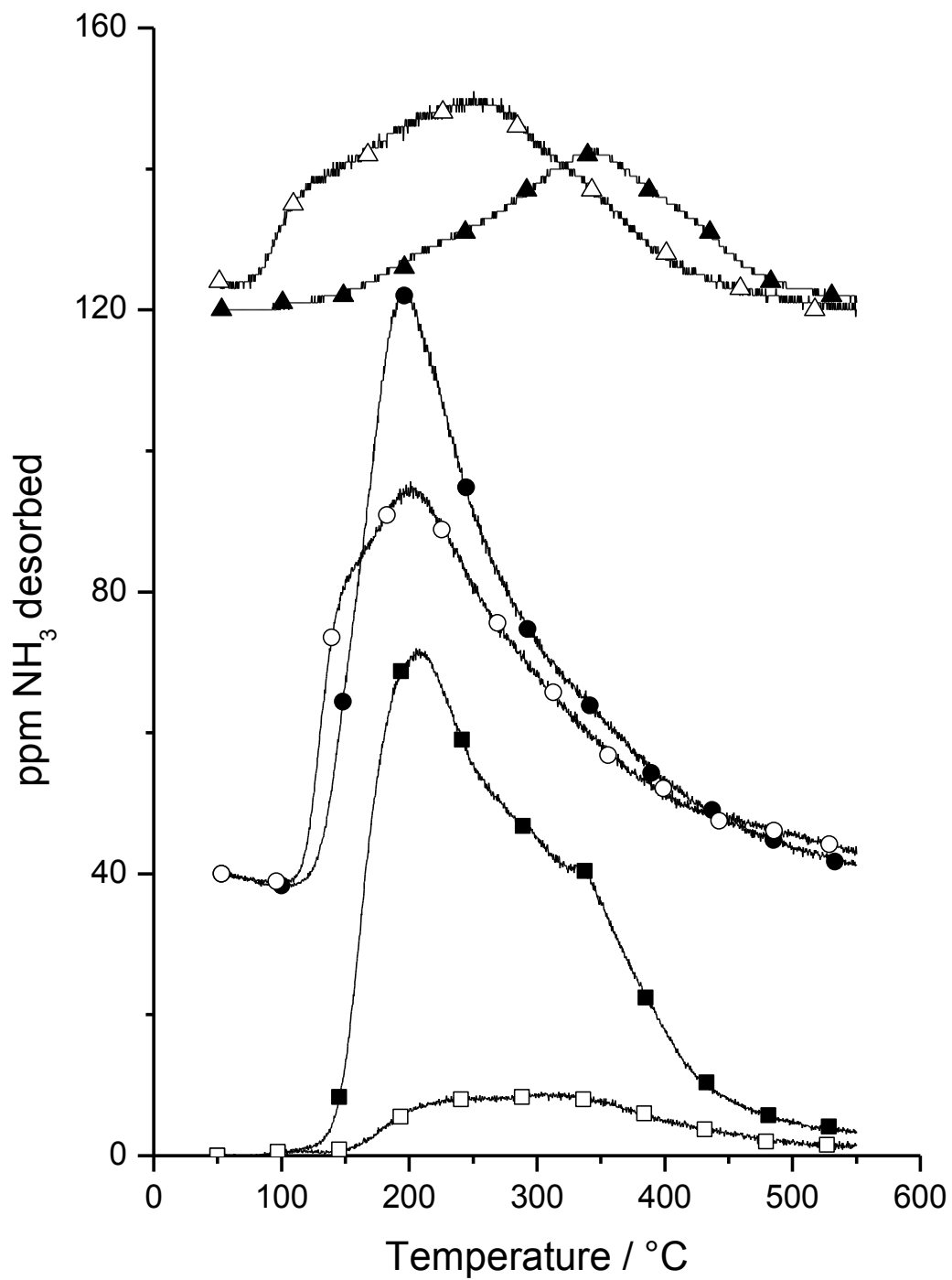


Table 1

	Ex SO <sub>4</sub> <sup>2-</sup>	Ex NO <sub>3</sub> <sup>-</sup>
Al <sub>2</sub> O <sub>3</sub>	67	58
TiO <sub>2</sub>	26	40
SiO <sub>2</sub>	73	12

Table 1:  $\mu\text{mol NH}_3$  desorbed  $\text{g}^{-1}$  of the various catalysts during  $\text{NH}_3$  TPD measurements.

Table 2

	Ex NO <sub>3</sub> <sup>-</sup>		Ex SO <sub>4</sub> <sup>2-</sup>	
	NH <sub>3</sub>	CO <sub>2</sub>	NH <sub>3</sub>	CO <sub>2</sub>
Al <sub>2</sub> O <sub>3</sub>	26.1	12.1	27.7	10.9
TiO <sub>2</sub>	12.7	6.0	6.4	3.7
SiO <sub>2</sub>	12.9	5.8	14.0	6.3

Table 2:  $\mu\text{mol NH}_3$  and  $\text{CO}_2$  desorbed from each catalyst following a dose of 53  $\mu\text{mol}$  urea onto 50 mg of catalyst followed by TPD

Figure 5(a)

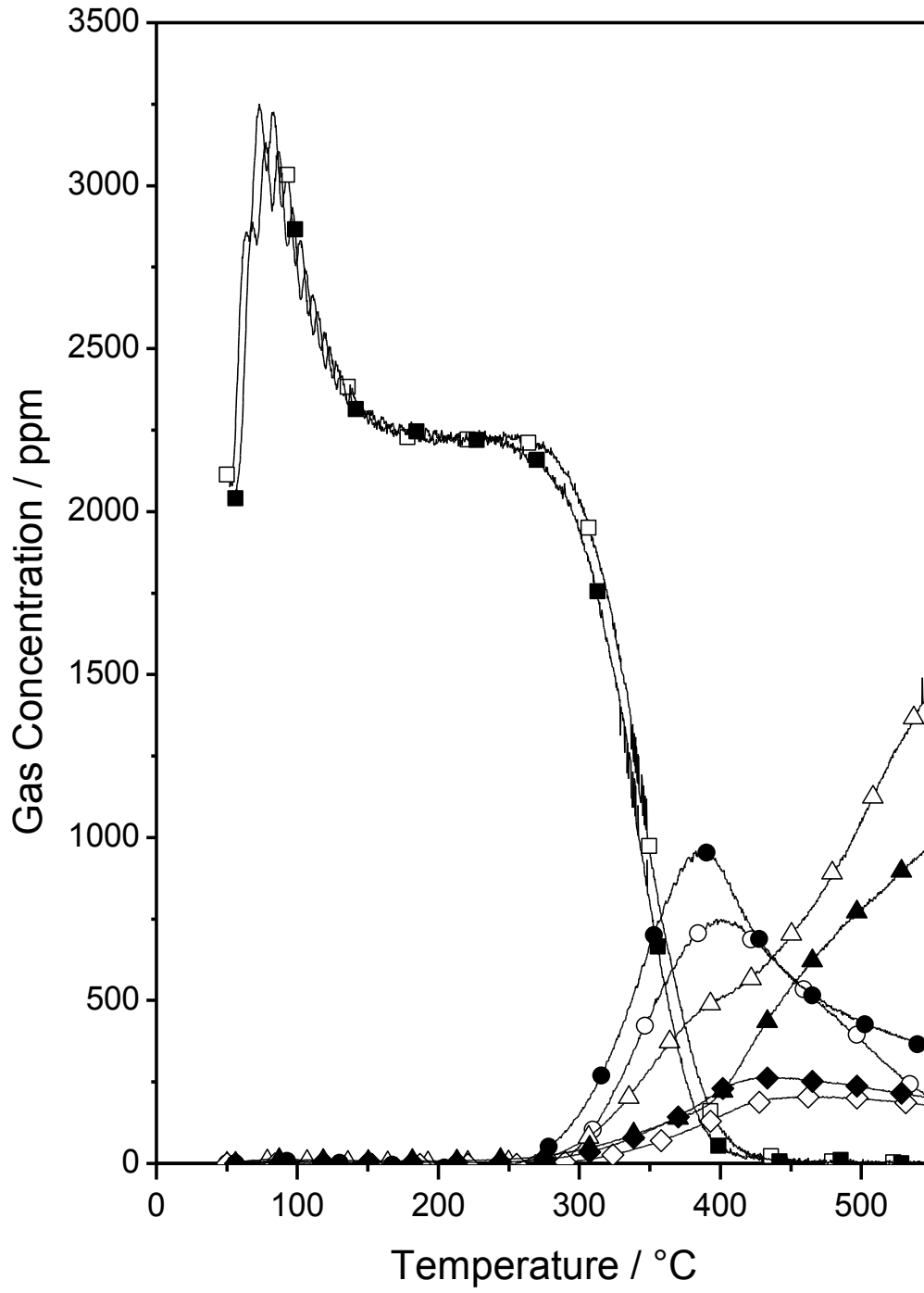


Figure 5(b)

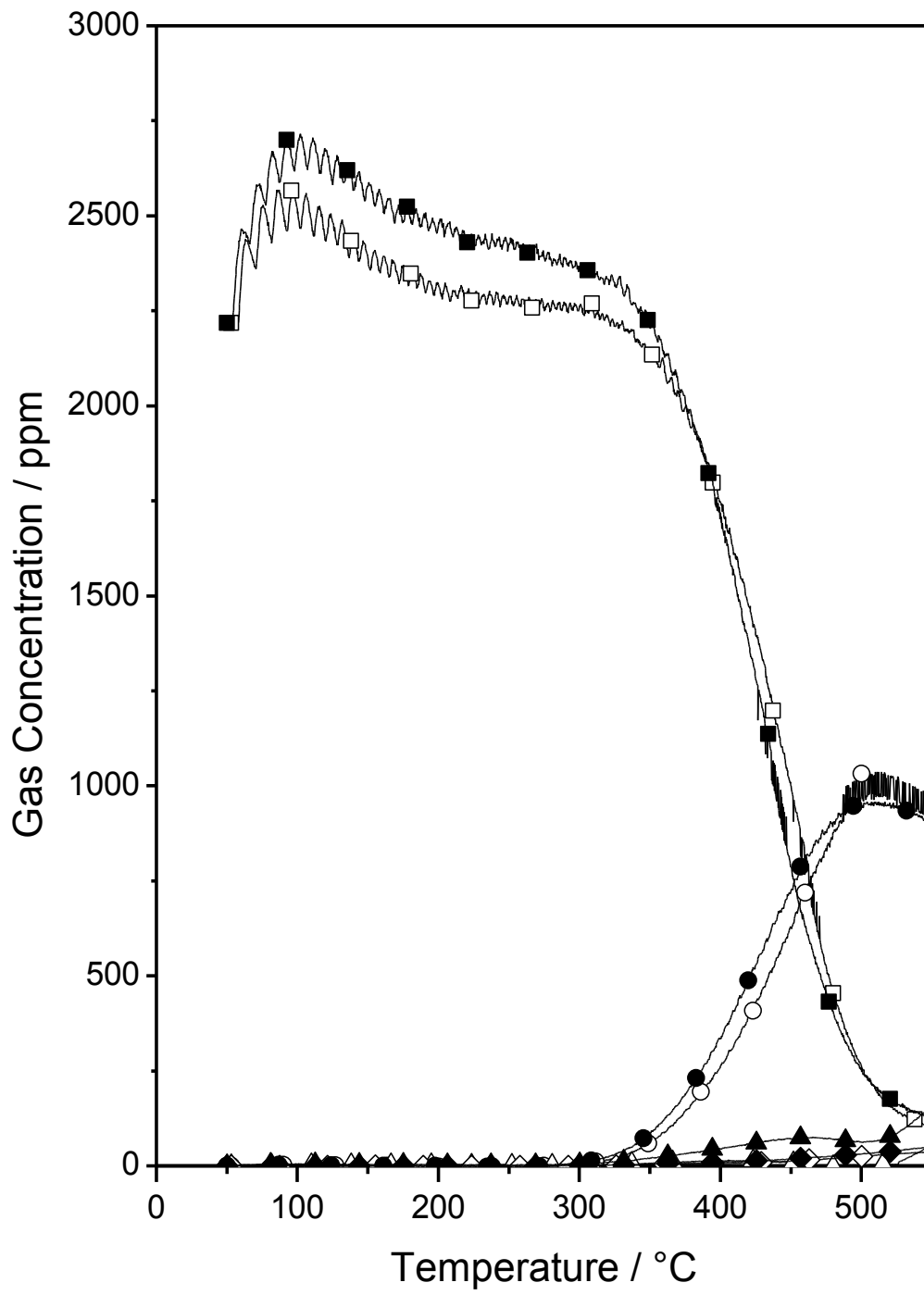


Figure 5(c)

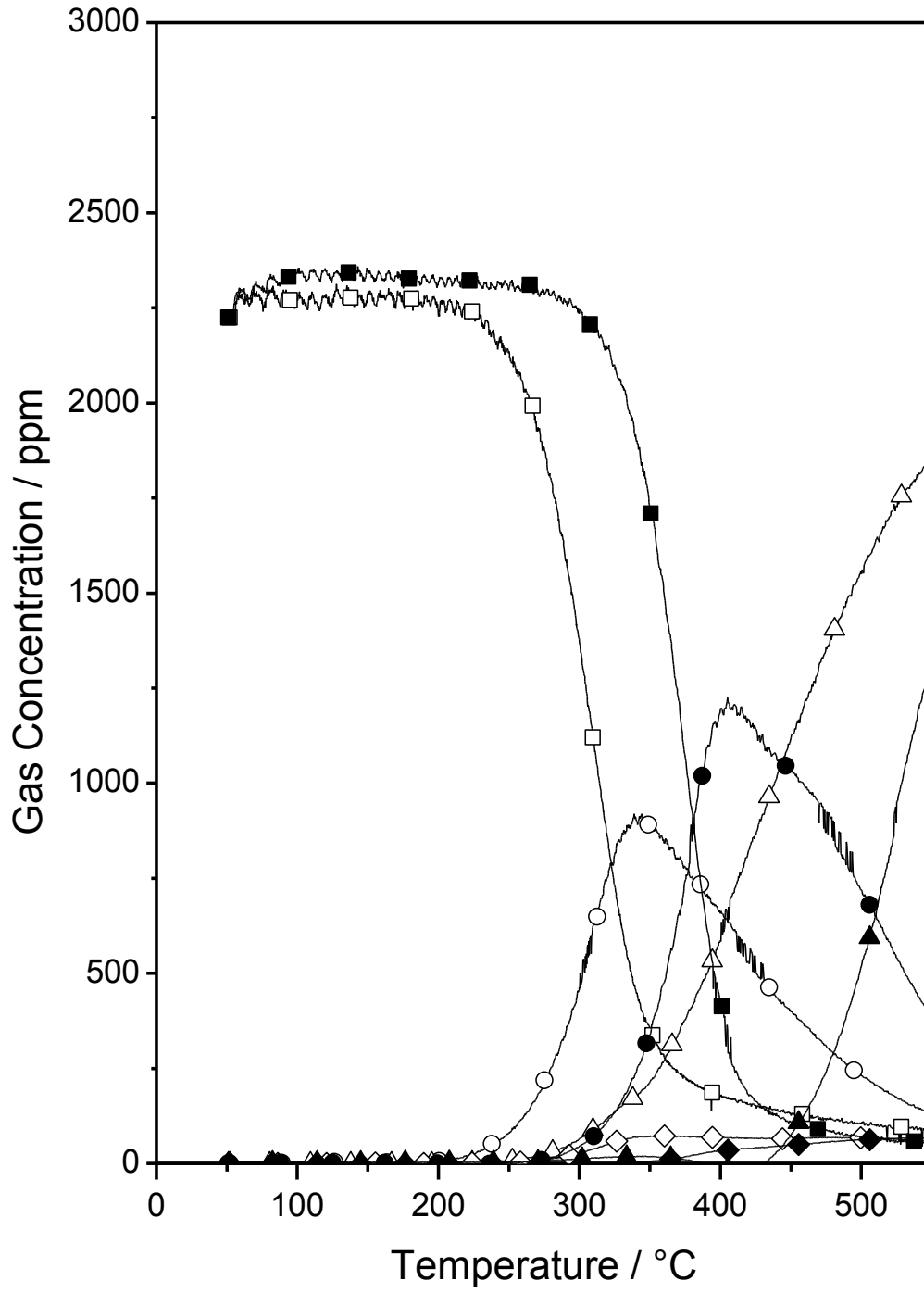


Figure 6(a)

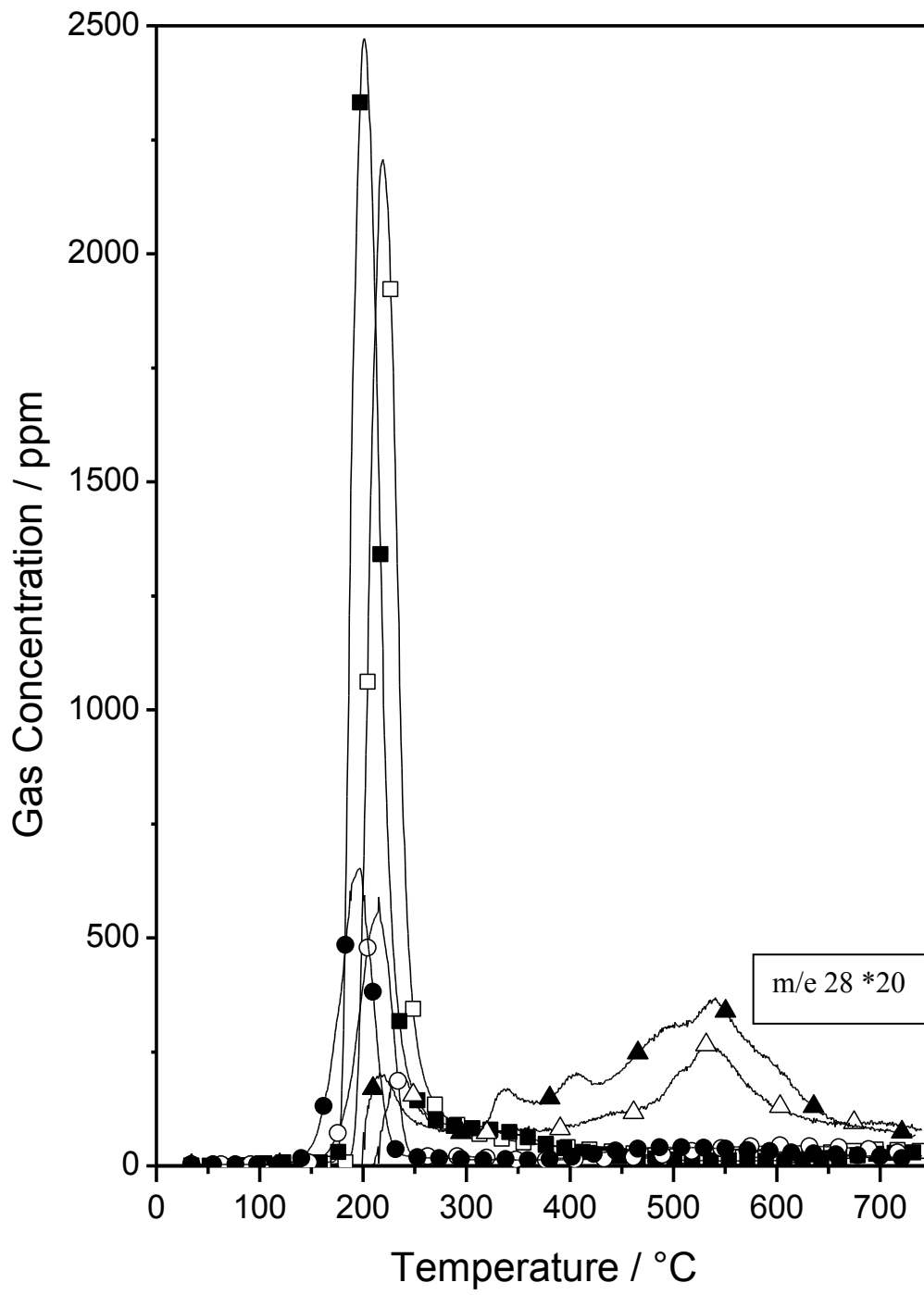


Figure 6(b)

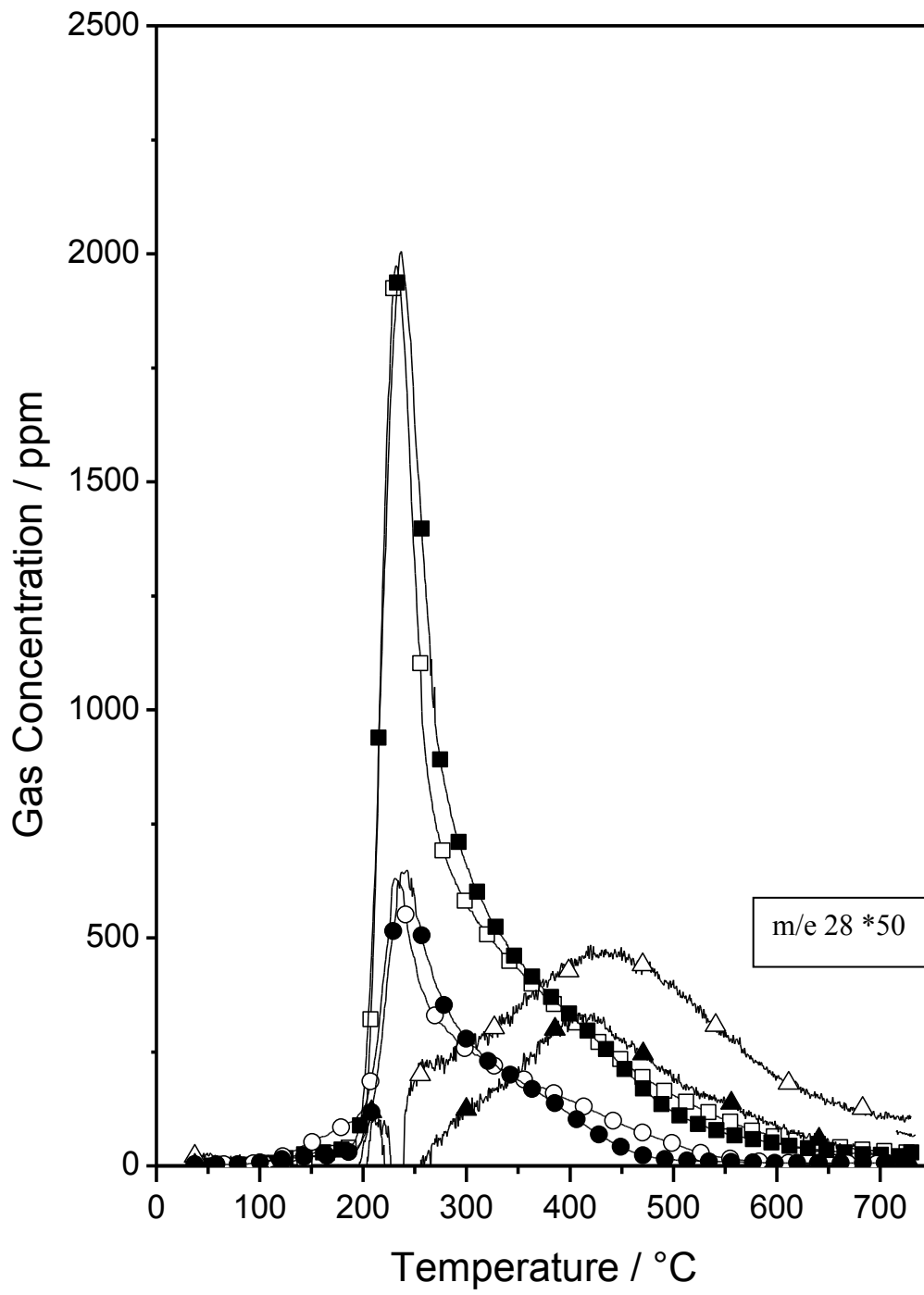


Figure 6(c)

