NH_3 and Urea in the Selective Catalytic Reduction of NO_x over oxide supported copper catalysts.

James A. Sullivan* and Julie A. Doherty Department of Chemistry, University College Dublin, Belfield, Dublin 4,

Ireland

Abstract.

The temperature programmed activity of a series of oxide supported (TiO₂, Al₂O₃ and SiO₂) Cu catalysts formed from two different Cu precursors (Cu(NO₃)₂ and CuSO₄) for the selective catalytic reduction of NO_x using solutions of urea as a reductant have been determined. These activities are compared to those found using NH₃ as a reducing agent over the same catalysts in the presence of H₂O and it is found that catalysts that are active for the selective reduction of NO_x with NH₃ are inactive for its reduction using solutions of urea. Poisoning of the surface by H₂O_{ads} is not responsible for all of this decrease in activity and it is postulated that the urea is not hydrolysing to form NH₃ over the catalysts but rather is oxidising to form N₂ 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 NH₃ and Temperature Programmed Decomposition of urea are used to characterise the interaction of both reductants with the various catalysts.

Keywords: Copper, NO_x, SCR-NH₃, Urea.

Introduction.

The detrimental effects of NO_x (NO and NO₂) are well documented and include the formations of photochemical smog and acid rain as well as direct negative effects on the human respiratory system¹. NO_x is formed in all combustion processes from the high temperature reaction between N₂ and O₂². The reduction of Nitric Oxide in gas exhaust streams, from combustion processes, containing a large excess of O₂ remains one of the most intensively studied areas of heterogeneous catalysis³⁻⁸. 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_x is used commercially in the treatment of exhaust gases of stationary power generation plants. This involves the selective catalytic reduction of NO_x with an added reducing agent, *i.e.* NH₃. The NH₃ selectively reacts with the NO_x component of a gas stream without reacting with the O₂ (which is present in a large excess)⁹. The catalysts used in these reactions are generally either zeolitic or vanadia based¹⁰.

For obvious reasons it would not be possible to use NH₃ 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 NH₃ could be replaced by aqueous solutions of urea $((NH_2)_2CO)^{11-12}$ and that this could be easily hydrolysed at relatively low temperatures to NH₃ (via formation of HCNO – see equations 1-3)¹³.

 $(NH_2)_2CO \rightarrow NH_3 + HNCO$ (1)

$$HNCO + H_2O \rightarrow NH_3 + CO_2.$$
 (2)

Overall reaction
$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2.$$
 (3)

Previous work in this laboratory¹⁴ has found that oxide supported CuO catalysts show activity in the SCR-NH₃ reaction with the level of activity being related to the support upon which CuO was dispersed as well as the precursor (ex- NO_3^- or ex- SO_4^-) 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 NH₃ oxidation reaction. Residual sulphate had several effects, *i.e.* increasing the temperature at which the SCR-NH₃ reaction gave a maximum conversion and poisoning the catalyst reactivity for the unselective NH₃ 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_x reaction using solutions of urea was investigated.

Experimental

Catalyst Preparation: Commercial γ Al₂O₃ (Criterion Catalysts) (S.A. =195 m²g⁻¹), TiO₂ (Degussa P25) (S.A. = 49 m²g⁻¹) and SiO₂ (Grace) (S.A.= 256 m²g⁻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(NO₃)₂.3H₂O and CuSO₄.5H₂O 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% NH₃ in He (BOC Special Gases), O_2 and He (BOC) to give a reaction mixture of [NO] = 1000 ppm, [NH₃] = 1000 ppm, [H₂O] = 12% and [O₂] = 13% in a total flow of 100 ml/min. H₂O 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-NH₃ 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_x 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 apparatus¹⁵. The catalyst was held in a quartz reactor under a flow of 3%H₂/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_{2(g)} concentration) using a Thermal Conductivity Detector (TCD). Any H₂O produced during the reduction of the catalyst was trapped using a dry ice trap. Unfortunately H₂S produced from reduction of sulphate groups on the catalyst was not trapped by the dry ice and thus the formation of H₂S was also detected by the TCD. The catalyst mass was 50 mg, the flow rate of H₂/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_3 was probed using Temperature Programmed Desorption of NH_3 . The catalyst (50 mg) was dosed with NH_3 (2860 ppm) at 110 °C for 30 minutes. The NH_3 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 NH₃ was carried out in the same system using 50 mg of catalyst held in a flow of O₂ (22%) and NH₃ (2222ppm) in a total flow of 90 ml min⁻¹.

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 (NH₃ TPD, NH₃ 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 (H₂O, NH₃ and various fragments of each), 28 (N₂, CO), 30 (NO), 32 (O₂) and 44 (CO₂, N₂O) as a function of temperature. The data are then corrected for overlapping masses (*e.g.* the contribution of the H₂O fragment at 17 to the NH₃ 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 SiO₂ 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-SO₄²⁻ material than from ex-NO₃⁻ catalyst.

In the case of the ex-NO₃⁻ catalyst the peak is due to the single reduction of CuO to Cu + H₂O. 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 effect¹⁶. The increased area of the peak arising from the ex-SO₄²⁻ material is due to the reduction of CuO and the concomitant reduction of SO₄²⁻ to H₂S and H₂O (and also possibly releasing SO₂). This affects the TCD signal in two ways, firstly removing more H₂ and secondly exposing it to H₂S causing it to register a further imbalance.

The fact that the $SO_4^{2^-}$ 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 $Al_2(SO_4)$ are not stable on an SiO_2 surface¹⁷ 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 + H₂O) the bonds anchoring the $SO_4^{2^-}$ to the surface are removed and the sulphate is lost (either as SO_2 or following reduction as H₂S).

The middle set of profiles in Figure 1 show the reduction of the CuO / Al_2O_3 catalysts. The ex-NO₃⁻ 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 Al₂O₃ surface¹⁸. Both of these peaks are also seen (with exactly the same profiles over the ex-SO₄²⁻ catalyst. This suggests that he presence of the SO₄²⁻ does not alter the CuO particle size distribution on the Al₂O₃ support or the reducible characteristics of the Al₂O₃ support itself. There is another large feature of the ex-SO₄²⁻ profile that is seen between 540 and 750 °C. This relates to the reduction of SO₄²⁻ species on the Al₂O₃ 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 SO₄²⁻ is stable on the Al₂O₃ support at locations remote from the CuO particles (since it remains on the Al₂O₃ surface after CuO has been reduced to Cu⁰).

Finally the upper two profiles relate to the reduction of TiO₂-suppoorted materials. There are two peaks seen over the ex-NO₃⁻ sample, one peaking at 225 °C and one at 450 °C. Literature¹⁹ 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 ascribed²⁰ to the reduction of TiO₂ to TiO_{2-x}. 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-SO₄²⁻ material the peaks are generally larger than those from the ex-NO₃⁻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 TiO₂ and the SO₄²⁻

components. If we assume that the lower temperature series of peaks is still related to CuO reduction we can suggest that there is 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 TiO_2 (as before) and the reduction of SO_4^{2-} deposited upon TiO_2 . In the absence of $CuO_{(s)}$ the reduction of SO_4^{2-} on a TiO_2 surface takes place at T > 600 °C²⁰. We assume that this temperature is again lowered here due to spillover of H- species from Cu.

De-NO_x activity measurements

Activity in the SCR-NH₃ reaction in the presence of H_2O .

Figure 2 shows the activity of all these catalysts in the SCR-NH₃ reaction with H_2O in the reactant stream. It is necessary to know the effect of H_2O since firstly H_2O 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 NH₃ *in-situ*), would be introduced to the catalyst via aqueous solutions. These results can be compared with those presented previously¹⁴ and while it should be noted that the reaction conditions used here differ from those used previously (in terms of catalyst mass and NH₃ 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-NO₃⁻ catalysts are more active at lower temperatures but are less selective at higher temperatures compared to their ex-SO₄²⁻ analogues.

In the case of TiO_2 –supported catalysts the temperature at which the catalysts commence deNO_x is shifted upwards by ~100 °C compared to the activities in the absence of H₂O (results not shown). The order of activities remains the same as seen previously with the ex-NO₃⁻ catalyst activity being higher than the ex-SO₄²⁻ at the

lower temperatures while the activity and selectivity of the $ex-SO_4^{2-}$ material is better at higher temperatures. One possible explanation for the overall decrease in activity is that there may be competition between the H₂O and NH₃ for adsorption sites on the surface.

The opposite trend is observed for the Al_2O_3 -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-NO₃⁻ catalysts being slightly more active than the ex-SO₄²⁻ samples. One possible explanation for this observed behaviour is that Lewis acid sties on the Al_2O_3 surface are hydroxylated in the presence of H₂O generating Bronstead sites, which are more active and selective for the adsorption and activation of NH₃.

The SiO₂-supported materials also require higher temperatures before activity commences (350 °C rather than 250 °C when H₂O is absent - results not shown) suggesting competition between NH₃ and H₂O for adsorption sites. However, at temperatures above 400 °C the ex-NO₃⁻ catalyst is more active in the presence of H₂O (suggesting that hydroxylation of the surface is important in terms of promoting both activity and selectivity). The ex-SO₄²⁻ catalyst is less active at lower temperatures in the presence of H₂O but is as active at higher T so possibly H₂O poisons sites as was assumed to be the case with the TiO₂-supported materials.

Lewis acid centres are known to predominate on TiO_2 surfaces and it seems that these do not hydroxylate to the more selective Bronstead sites as seems to have taken place over the Al_2O_3 and SiO_2 - supported catalysts.

Activity in the SCR-Urea reaction.

Figure 3 shows the activities of the six catalysts in the de NO_x reaction when the NH₃ 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 NH₃ used during the SCR-NH₃ reaction measurements. Each molecule of urea can in theory form two molecules of NH₃ during the decomposition in the presence of H₂O (see equations 1-3 above) so this equates to 600 ppm NH₃. 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 NH₃ as a reductant. The TiO₂-supported materials still show some activity at T> 300 °C but this is far decreased relative to the situation where NH₃ is used even in the presence of a large amount of H₂O (which acts to decrease catalyst activity). The Al₂O₃-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-NO₃⁻ SiO₂ supported catalyst. This catalyst remains less active than it was in the presence of 12% H₂O when NH₃ reductant was used. The activities of the catalysts are too low to allow us to make general statements regarding the effect of surface SO₄²⁻ on the activity of the SCR-Urea reaction.

The presence of H_2O had no severe effect on the SCR-NH₃ activity – pushing the required temperature up for the TiO₂ supported catalysts and improving the activity of Al_2O_3 and SiO₂ supported materials. Thus, the explanation for the much decreased activity of the catalysts when NH₃ is replaced by (NH₂)₂CO cannot lie in surface poisoning by H₂O. 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 complexes²⁴ on the catalyst surface causing surface passivation.

Temperature Programmed Desorption and Oxidation of NH₃.

Previous work¹⁴ 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-SO₄²⁻ materials were more selective at higher temperatures (seen under these conditions also over the TiO₂ and SiO₂ supported catalysts). This was ascribed to either an increased concentration of adsorbed NH₃ at these high temperatures (from an increase in the concentration of surface acid sites) or to an altered manner of activation of NH₃ over these SO_4^{2-} containing materials (from a change in the strength of the surface acid sites). Interactions between NH₃ and the surfaces were probed using NH₃TPD and NH₃TPO.

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 (µmol g⁻¹) detected in the exit gas as a function of catalyst.

In the case of the Al₂O₃ supported catalysts there is a peak seen in the NH₃ desorption profile between 180 and 250 °C. There is an increase in the concentration of NH₃ that is desorbed from the catalyst once SO_4^{2-} is present (67 versus 58 µmol g⁻¹). This shows that the presence of SO_4^{2-} increases the concentration of acid sites on the catalyst²¹. The position and shape of the peak from the Al₂O₃ materials is similar in the presence of SO_4^{2-} , *i.e.* a sharp peak at ~200 °C and a long tail

towards higher temperature, suggesting that the *strengths* of NH₃ 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 NH₃ over the SiO₂ catalysts (lower profiles) once SO₄²⁻ is present on the surface (73 versus 12 µmol g⁻¹). This shows that again SO₄²⁻ increases the concentration of surface acid sites. The distribution of acid site strength is also modified by the presence of SO₄²⁻. In its absence there is a broad plateau in NH₃ desorption between 200 and 400 °C showing a wide range of surface acid strengths. In the presence of SO₄²⁻ there is a definite peak at 200 °C with a higher temperature shoulder at ~400 °C. Therefore the SO₄²⁻ has formed a new-type of surface acid site (presumably related to the formation of surface NH₄SO₄-type species).

The presence of $SO_4^{2^-}$ has a different effect on the behaviour of the TiO_2 supported catalysts in the NH₃ TPD experiments. In the absence of $SO_4^{2^-}$ there is a broad peak centred at a temperature of 250 °C and 40 µmol of NH₃ are desorbed g⁻¹. When $SO_4^{2^-}$ is present the overall amount of NH₃ desorbed decreases (to 26 µmol g⁻¹) and the temperature of the peak maximum is shifted upward to ~ 380 °C. The latter effect has previously²² been ascribed to the generation of stronger Lewis acid sites on the surface of TiO₂. However, the decrease in overall acidity upon the addition of $SO_4^{2^-}$ is difficult to understand.

One additional point to note is that at higher temperatures minor amounts of N_2 , N_2O and NO evolved from each of the catalysts with the NO profile in particular being relatively strong from the Al_2O_3 supported ex-NO₃ catalyst. These are not shown for reasons of clarity.

While the TiO₂ and SiO₂-supported materials do show a change in the manner of activation of NH₃ as a function of $SO_4^{2^-}$, *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-NH₃ reaction as a function of the presence or absence of $SO_4^{2^-}$) the only changes to the Al₂O₃ material involve increases in the concentration of acid sites and thus there is no definite explanation for the increased selectivity of the sulphated Al₂O₃-supported catalysts at higher temperature.

With this in mind a series of NH_3 oxidation experiments were carried out where the catalyst was held in a flow of NH_3 and O_2 as the temperature was ramped from 50 to 550 °C. NH_3 , N_2 , NO and N_2O 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_3 oxidation reaction do not mirror exactly the interactions that take place during the SCR- NH_3 reaction (in the presence of NO_x) but this reaction is still a useful probe for how the catalysts behaves in the presence of NH_3 and O_2 .

Figure 5(a) shows the results seen from the SiO₂-supported catalysts. In both cases (ex-NO₃⁻ and ex-SO₄²⁻) the NH₃ profiles from both catalysts behave in exactly the same manner, *i.e.* NH₃ desorption at lower temperatures and the commencement of NH₃ conversion at ~280 °C and complete conversion of NH₃ at 400 °C. There is a significant difference between the two catalysts when the products of NH₃ combustion are considered. The ex-NO₃⁻ sample produces significantly less N₂ and significantly more NO than the ex-SO₄²⁻ material. This is in agreement with the SCR-activity results above where the selectivity of the ex-SO₄²⁻ material is greater than that of the ex-NO₃⁻ catalyst, *i.e.* it seems that the ex-NO₃⁻ catalyst shows higher activity for the conversion of NH₃ into NO_x than the ex-SO₄²⁻ analogue and thus a lower selectivity for the NO + NH₃ → N₂ reaction.

If it is assumed that the NH₃ oxidation takes place on the CuO particles rather than the support, and (from the TPR results), that the SO_4^{2-} is associated with the CuO rather than on the SiO₂ support on the catalyst, and then the effect of the proximate SO_4^{2-} is to poison reaction of NH₃ to NO and/or promote its combustion to N₂.

Figure 5(b) shows the results for the same experiments over the Al_2O_3 supported catalysts. Again here the NH₃ profiles are exactly the same over both materials with a desorption of NH₃ between 100 and 200 °C and commencement of NH₃ oxidation at ~350 °C. There is a difference in the product profiles here when compared to those seen above with N₂ being the predominant product formed over both catalysts. Levels of N₂ formation are also very similar. Low levels of N₂O and NO are seen at higher temperatures. There is no effect of SO₄²⁻ on the conversion of NH₃ or the conversion to N₂. The levels of NO and N₂O are too low to allow any definite statement about the amounts of their relative conversion.

TPR results have shown that most of the SO_4^{2-} on Al_2O_3 -supported catalysts is located on the Al_2O_3 support rather than on the CuO particles and therefore, if it assumed that NH₃ oxidation takes place at the CuO rather than on the support then the reason that there is no effect of SO_4^{2-} on the oxidation of NH₃ is due to the fact that the SO_4^{2-} remains far from the active CuO sites.

Finally figure 5(c) shows the profiles obtained from the TiO_2 -supported catalysts. Over these materials there is a definite difference in the profiles obtained over the ex-NO₃⁻ and the ex-SO₄²⁻ catalysts. Combustion of the NH₃ commences at ~100 °C lower temperature over the ex-NO₃⁻ catalyst than over the ex-SO₄²⁻ catalyst. In common with the SiO₂-supported catalysts conversion to NO over the former catalyst is higher (and conversion to N₂ lower) than over the latter. The increased selectivity of the ex-SO₄²⁻ catalyst in the SCR-NH₃ reaction is mirrored here.

TPR results suggest that over TiO_2 -supported catalysts the SO_4^{2-} (when present) is situated both close to CuO particles as well as on the TiO_2 support. Assuming that particles of CuO are the locus of activity for NH₃ oxidation it seems that SO_4^{2-} located close to these active centres can affect the selectivity and, in this case activity, of the catalyst in the NH₃ oxidation reaction.

Temperature Programmed Decomposition of Urea

The SCR-Urea results (figure 3) show that most of the deNO_x activity of the catalysts is lost once solutions of urea are used in the reaction mixture rather than NH₃. There does not seem to be any relationship between this reduced activity and the presence or absence of SO_4^{2-} on the surface. One possible reason for the difference between NH₃ and urea as a selective reductant is that the urea does not hydrolyse according to equations 1-3 and instead reacts with O₂ to form N₂ (equation 1.4).

$$(NH_2)_2CO + O_2 \rightarrow CO_2 + H_2O + N_2.$$
 1.4

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

$$(x+1) ((NH_2)_2CO + H_2O \rightarrow (HNCO)_x + (x+2)NH_3 + CO_2$$
 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 μ mol 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_3 , H_2O (not shown for clarity) and CO_2 (or N_2O) are released from the catalysts. At higher temperatures N_2 (or CO) is released from all materials.

Table 2 shows the amounts of NH₃ and CO₂ (assuming N₂O formation is minimal) released during the experiments. From the 53 µmol urea dosed on the catalyst 106 µmol NH₃ and 53 µmol CO₂ could be formed if the full decomposition of urea to 2 NH₃ + CO₂ 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 N₂ / CO at higher temperatures). It should be pointed out that twice as much NH₃ as CO₂ 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 N₂O or to the decompositions proceeding in a different manner to those discussed above. Overall most decomposition happens over the Al₂O₃ supported materials, followed by the SiO₂-supported catalysts with the least amount of decomposition taking place over the TiO₂-supported materials. This suggests that Al_2O_3 supports interact with more urea than SiO_2 and TiO_2 (as all were initially dosed with the same concentration of urea and any "noninteracting" urea sublimes from the reactor and remains undetected). Over the TiO_2 supported materials there is also a second release of CO_2 at slightly higher temperatures (280 °C) with no accompanying NH₃ formation – showing that the mode of adsorption and decomposition of urea differs over the various supports.

All catalysts also release some N_2 or 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 TiO₂ materials and lowest over the Al₂O₃ supported catalysts.

Fang and DaCosta²⁴ have reported that molten urea sticks very well to a TiO₂ surface relative to an Al₂O₃ 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 N₂ (or CO) over the TiO₂-supported materials at higher temperatures but is in contrast to the results above where lower temperature urea decomposition is more pronounced over the Al₂O₃-supported materials. We suggest that the decomposition to NH₃ and CO₂ discussed above requires the participation of surface hydroxyl groups (water in equations above) and for this reason there is more NH₃ / CO₂ formed over Al₂O₃ and SiO₂ supported catalysts. Over TiO₂ (with a lower concentration of surface OH) the urea decomposes at higher temperature to N₂ / CO.

Over the SiO₂ and Al₂O₃-suppoorted catalysts there is no pronounced effect of SO_4^{2-} on the decomposition of urea with roughly the same amount of NH₃ and CO₂ being formed over both the ex-NO₃-and the ex-SO₄²⁻ samples. Over the TiO₂-

supported materials there is a large effect of SO_4^{2-} which results in far less urea decomposing to NH₃ and CO₂ and far less CO/N₂ 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 SiO_2 and TiO_2 supported materials but are rather spread out over the Al_2O_3 -supported catalysts. This is probably due to a chromatographic effect within the Al_2O_3 catalyst bed rather than a distribution of urea stabilities on the catalyst surfaces.

Traces for HNCO (an intermediate in the decomposition of urea^{13, 25}) were only seen at extremely low levels (not shown) over these catalysts and only in the initial decomposition peak (~200 °C). No HNCO or NH₃ was seen at the higher temperatures where these catalysts catalyse the NO + NH₃ reaction. We suggest that the urea decomposition fragments, which remain on the surface at this temperature, form N₂ / CO rather than decompose to the required NH₃. One catalyst that *is* active for the SCR-Urea reaction (CuZSM-5)²⁵ has also been studied using this technique and it shows a release of both NH₃ and HNCO at these higher temperatures²⁶.

Therefore there are three pathways for the removal of urea and its decomposition products from the surfaces of the catalysts under these temperatureprogrammed conditions. Firstly, the sublimation of non-coordinated urea from the solid phase, secondly the low temperature decomposition of relatively weakly bound urea to yield NH₃ and CO₂ (at ~200 °C) and finally the combination of decomposition products to form either CO or N₂ 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 NH₃ 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-NH₃ reaction.

Conclusions

CuO catalysts derived from NO₃⁻ and SO₄²⁻ precursors on SiO₂, Al₂O₃ and TiO₂ are active for the SCR-NH₃ reaction in the presence of H₂O. This activity is not transferred to the SCR-urea reaction. Having shown in previous work¹⁴ that the surface capacity for storing NO_x are affected by the presence of SO₄²⁻ on the catalyst, this work shows that over the SiO₂ catalysts the SO₄²⁻ is associated with the CuO, over the TiO₂ catalysts the SO₄²⁻ is associated both with the CuO and the TiO₂ and over the Al₂O₃-supported materials the SO₄²⁻ is associated with the support.

 NH_3 TPD studies have shown that SO_4^{2-} increases the concentration of acid sites on the SiO₂ and Al₂O₃ supported materials and changes the acid site distribution over the SiO₂ and TiO₂ catalysts (while reducing the overall acidity of the latter).

 NH_3 oxidation studies show that the presence of SO_4^{2-} on the surface has no effect on the activity or selectivity of this reaction over Al_2O_3 -supported materials and decreases the selectivity to NO_x formation over SiO_2 and TiO_2 -supported materials (while also decreasing the activity of the latter). These results provide an explanation of the SO_4^{2-} effect on selectivity in the SCR-NH₃ 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_3 and CO_2 (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 SiO₂ and Al₂O₃-supported catalyst surfaces at temperatures above 300 °C. Far higher concentrations of urea decomposition products remain on the TiO₂-supported materials (due to the hydrophobicity of the surface). In all cases these decompose under TPD conditions to N₂/CO at higher temperatures. The presence of SO₄²⁻ affects the concentration and temperature of decomposition of these species.

These experiments do not clarify why the activity of catalysts in the SCR-NH₃ reaction is not obtained in the SCR-urea reaction. We suggest that even though the catalysts decompose urea to NH₃ at lower temperatures that this is not the case at higher temperatures and that either urea \rightarrow N₂ or the formation of a passivating layer on the surface²⁴ is responsible for this decreased activity.

Acknowledgements

We would like to gratefully acknowledge the Irish Research Council for Science, Engineering and Technology for support of this work under grant number SC/02/227.

References.

- Wayne, R.P., *Chemistry of Atmospheres*, 2nd Ed. Oxford Scientific Publishing, (1991)
- 2 Zeldovich, Y.B., Acta. Phisiochem., URSS, 21, (1946) 656.
- 3 Iwamoto, M., Ed. Catal. Today, 22, (1994) and references therein.
- 4 Burch, R., Ed. *Catal. Today*, **26**, (1995) and references therein.
- 5 Kung, M.C., Kung, H. H. Top. Catal., 28(1-4), (2004),
- Burch, R., Breen, J. P. and Meunier, F. C. *Appl. Catal.*, *B: Env.*, **39**, (2002),
 283.
- Muzio, L. J., Quartucy, G. C., and Cichanowicz, J. E. Int. J. Env. Poll., 17, (2002), 4.

- 8 Gilot, P., Guyon, M. and Stanmore, B.R., *Fuel*, **76**, (1997), 507.
- 9 Bosch, H., and Janssen, F., *Catal. Today*, **2**, (1988) 369.
- Sullivan, J.A., Cunningham, J., Morris, M.A. and Keneavey, K., *Appl. Catal. B: Env.*, 7, 1-2, (1995) 137.
- 11 Hug, H.T., Mayer, A. and Hartenstein, A., SAE paper 950809, (1995).
- 12 Held, W., Konning, T. and Puppe, L., SAE paper 900496, (1990).
- M. Koebel, M. Elsener, M. Kleemann, Catal. Today 59 (2000) 335.
 Koebel, M., Elsener, M. and Madia, G., *Ind. Eng. Chem. Res.*, 40, (2001), 52.
- 14 Sullivan, J.A., Catal. Letts., 79, (2002), 59.
- 15 Robertson, S.D., McNicol, B.D., De Baas, J.H., Kloef, S.C., *J.Catal.*, **37**, (1975), 424.
- Bennici, S., Gervasini, A. and Ragiani, V., Ultrason. Sonochem., 8, (2001),
 131.
- 17 F.A. Cotton, F.A. and Wilkinson, G., Advanced Inorganic Chemistry,5th ed.
- 18 Jia, J., Shen, J., Lin, L., Xu, Z., Zhang, T. and Liang, D., J. Mol. Catal. A: Gen., 138, (1999), 177.
- Xu, B., Dong, L. and Chen, Y., J.Chem.Soc. Faraday Trans., 94, (1998), 1905.
- 20 Jung, S.M. and Grange, P., *Appl. Catal. B: Env.*, **32**, (2001), 123.
- 21 Chen, J.P. and Yang, R.T., *J.Catal.*, **139**, (1993), 277.
- 22 Jung, S.M. and Grange, P., *Catal. Today*, **59**, (2000), 305.
- 23 Eight Peak Index of Mass Spectra, 3rd Edn., Unwin Brothers, Surrey, 1983.
- 24 Fang, H.L., DaCosta, H. F. M. Appl. Catal., B: Env., 46, (2003), 17.
- 25 Doherty, J.A., M.Sc. Thesis, UCD, 2004.
- 26 Doherty, J.A. Keane, O., and Sullivan, J.A., *in prep*.

Figure Legends.

Figure 1: Displaced Temperature Programmed Reduction profiles from each catalyst (for conditions see text). Cu/SiO₂ (\Box , \blacksquare), Cu/Al₂O₃ (\bigcirc , \bullet), Cu/TiO₂ (\triangle , \blacktriangle). Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻.

Figure 2: Displaced Temperature Programmed Activity profiles for the various catalysts in the SCR-NH₃ reaction in the presence of H₂O. Catalyst mass 25 mg, 1000 ppm NO, 1000 ppm NH₃, 13% O₂ and 12% H₂O balanced to 100 ml/min with He. Cu/SiO₂ (\Box , \blacksquare), Cu/Al₂O₃ (\bigcirc , \bullet), Cu/TiO₂ (\triangle , \blacktriangle). Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻.

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% O₂, 12% H₂O balanced to 100 ml / min with He. Cu/SiO₂ (\Box ,=), Cu/Al₂O₃ (O, •), Cu/TiO₂ (Δ , ▲). Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻.

Figure 4: Displaced Temperature Programmed NH₃ desorption profiles for the various catalysts. Cu/SiO₂ (\Box , \blacksquare), Cu/Al₂O₃ (\bigcirc , \bullet), Cu/TiO₂ (\triangle , \blacktriangle). Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻.

Figure 5. Temperature Programmed NH₃ oxidation profiles from the various catalysts. Profiles from (a) Cu/SiO₂, (b) Cu/Al₂O₃ and (c) Cu/TiO₂ catalysts. NH₃ (\Box ,=), N₂

 (\bigcirc, \bullet) , NO $(\triangle, \blacktriangle)$, N₂O $(\diamondsuit, \blacklozenge)$ Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻.

Figure 6. Displaced Urea decomposition products from Urea TPD experiments from (a) Cu/SiO₂, (b) Cu/Al₂O₃ and (c) Cu/TiO₂ catalysts. NH₃ (\Box , \blacksquare), N₂O/CO₂ (\bigcirc , \bullet), and CO/N₂ (\triangle , \blacktriangle), Open Symbols ex-NO₃⁻, Filled symbols ex-SO₄²⁻. For clarity the m/e=28 signals are * 20, *50 and *10 respectively).





Figure2



Figure 3



Figure 4



Table 1

	Ex SO ₄ ²⁻	Ex NO ₃ ⁻
Al ₂ O ₃	67	58
TiO ₂	26	40
SiO ₂	73	12

Table 1: μ mol NH₃ desorbed g⁻¹ of the various catalysts during NH₃ TPD measurements.

Table 2

	Ex NO ₃		Ex SO ₄ ²⁻	
	NH ₃	CO ₂	NH ₃	CO_2
Al ₂ O ₃	26.1	12.1	27.7	10.9
TiO ₂	12.7	6.0	6.4	3.7
SiO ₂	12.9	5.8	14.0	6.3

Table 2: μ mol NH₃ and CO₂ desorbed from each catalyst following a dose of 53 μ 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)

