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The catalytic oxidation of ammonia: influence of water and sulfur on selectivity to nitrogen over promoted copper oxide/alumina catalysts

T. Curtin [*], F. O' Regan, C. Deconinck, N. Knüttle, B.K. Hodnett

Department of Chemical and Environmental Sciences University of Limerick, Limerick, Ireland

Abstract

The CuO/Al_2O_3 system is active for ammonia oxidation to nitrogen and water. The principal by-products are nitrous oxide and nitric oxide. Nitrous oxide levels increase with the addition of various metal oxides to the basic copper oxide/alumina system. Addition of sulfur dioxide to the reaction stream sharply reduces the level of ammonia conversion, but has a beneficial effect on selectivity to nitrogen. Added water vapour has a lesser effect on activity but is equally beneficial in terms of selectivity to nitrogen. The CuO/Al_2O_3 is also active for the selective catalytic reduction of nitric oxide by ammonia, but this reaction is not effected by sulfur dioxide addition. A mechanism for ammonia oxidation to nitrogen is proposed wherein part of the ammonia fed to the catalyst is converted into nitric oxide. A pool of monoatomic surface nitrogen species of varying oxidation states is established. N_2 or N_2O are formed depending upon the average oxidation state of this pool. An abundance of labile lattice oxygen species on the catalyst surface leads to overoxidation and to N_2O formation. On the other hand, reduced lability of surface lattice oxygen species favours a lower average oxidation state for the monoatomic surface nitrogen pool and leads to N_2 formation. ©2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The treatment of ammonia from waste streams is becoming an important issue due to ever increasing environmental concerns. Many chemical processes have gaseous or liquid waste streams containing ammonia which will have to be reused or destroyed. Several reviews of different techniques used for the elimination of ammonia have been published [1,2]. Catalytic methods based on the decomposition of ammonia into nitrogen and hydrogen are at an advanced stage of deployment to treat emissions of ammonia from coking plants and from refineries [3] and are useful for waste streams which are predominantly oxygen free. In contrast, catalytic oxidation of ammonia to nitrogen would be suitable for a different range of applications and are the subject of increasing interest.

A technology for ammonia removal from oxygen containing streams would be beneficial for ammonia slip control in selective catalytic reduction (SCR) units, thus allowing these units to operate at higher efficiencies for nitric oxide removal [4]. Catalytic technologies for the oxidation of ammonia to nitric oxide are well established and form the basis of nitric acid production on a commercial scale [5], but catalysts which stop the oxidation at N_2 are less well developed [6].

Work in the area of ammonia oxidation to nitrogen prior to 1975 [7] was reviewed recently by Li and Armor [4] and reveals that precious metal, base oxide and transition metal exchanged zeolite catalysts exhibited a propensity to produce large

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[*] Corresponding author. Tel.: +353-61-202981;
fax: +353-61-202568
E-mail address: teresa.curtin@ul.ie (T. Curtin)

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amounts of nitrous oxide or nitric oxide. In addition, those catalysts which were very selective for nitrogen formation below 300°C exhibited poor activity. Il'chenko and Golodets [8,9] carried out a detailed study on the catalytic oxidation of ammonia over unsupported oxides at low temperatures. The products of reaction observed were N_2 and N_2O. Selectivity to nitrogen increased in the following sequence: $MnO_2 < Co_3O_4 < Fe_2O_3 < CuO < MoO_3 < V_2O_5$. Generally, this sequence also represented the inverse of activity. MnO_2 and Co_3O_4 exhibited the highest selectivity to N_2O.

More recently, studies have appeared describing ammonia oxidation over SCR V/TiO_2 catalysts [10], MoO_3 on SiO_2 [11,12], Cu-Mn binary oxides supported on TiO_2 [13] and Pd, Pt or Rh supported on ZSM-5 or alumina [4]. All show varying propensities for the formation of nitric oxide and nitrous oxide in the temperature range 200–400°C and varying levels of resistance to deactivation by water vapour. Membrane reactors such as those using a palladium ceramic composite were found to oxidise ammonia to inert non-polluting substances at temperatures above 500°C [14].

The work reported here examines the activity of copper oxide on alumina for the oxidation of ammonia in the presence of oxygen to form nitrogen and water and investigates the effect of a second metal oxide on the overall activity of the system. In addition, the catalytic activity is analysed in the presence of SO_2 and added water.

2. Experimental

2.1. Catalyst preparation

A catalyst containing 4.3 wt.% CuO on Al_2O_3 was prepared by dry impregnation, using copper nitrate as the impregnating salt. The required amount of $Cu(NO_3)_2$ was dissolved in a volume of water enough to fill the pores of the pre-calcined alumina (Rhône-Poulenc RP535, pore volume 1.3 ml/g, surface area 122 m^2/g). The resulting solid was dried at room temperature and calcined at 450°C overnight in air. Using a similar procedure, a series of catalysts containing 4.3 wt.% CuO and a second metal oxide (PbO, NiO, CoO, SnO or Cr_2O_3) was also prepared. In these cases, the impregnating solution consisted of copper nitrate and the metal nitrate. All prepared solids were dried at room temperature and calcined at 450°C overnight in air.

2.2. Characterisation

Surface area measurements were carried out using a Micromeritics Gemini 111 2375 system with nitrogen as the adsorbing gas. All samples were outgassed at 200°C before analysis. Temperature programmed reduction in a 5% H_2/N_2 flow (heating rate 10°C/min) was performed on 4.3 wt.% CuO/Al_2O_3 and on the same catalysts following exposure to SO_2.

2.3. Catalyst testing

The oxidation of ammonia was carried out using a continuous flow system operated at ambient pressure. The gas flow rates were controlled by mass flow controllers (Tylan General UK). The feed gas, a mixture of NH_3 (and NO in some cases), oxygen and helium flowed at a rate of 20–200 ml/min over 25 mg of catalyst. The reactor was a quartz glass vertical tube. The catalyst was kept in position by 2 plugs of quartz wool. Before testing, the catalyst was pretreated for 90 min in a stream of helium at 20 ml/min at 420°C. After this pretreatment the samples were cooled to 325°C and the reaction initiated by introducing 0.54% NH_3, 8% O_2 and a helium balance at various total gas flow rates. The gases leaving the catalytic reactor were analysed using a Hewlett–Packard HP5971A Mass Selective Detector. In some experiments, 0.1% SO_2 was added to the reactant stream. In these circumstances, to prevent the deposition of ammonium sulphate, all lines were heated to over 150°C and SO_2 was introduced into the reactant stream at the entrance of the reactor. In these experiments 500 mg of catalyst was used. For experiments with added water, 1% water vapour was added to the stream.

3. Results

Table 1 lists all the catalysts used in this study and the corresponding surface areas. All catalysts present a surface area marginally less than the parent alumina.

Table 1
Surface area of alumina and prepared catalysts

Catalyst name	Surface area (m^2/g)
Al_2O_3	122
4.3 wt.% CuO/Al_2O_3	116
1 wt.% PbO-4.3 wt.% CuO/Al_2O_3	114
1 wt.% NiO-4.3 wt.% CuO/Al_2O_3	112
1 wt.% CoO-4.3 wt.% CuO/Al_2O_3	109
0.6 wt.% SnO-4.3 wt.% CuO/Al_2O_3	106
0.4 wt.% Cr_2O_3-4.3 wt.% CuO/Al_2O_3	110

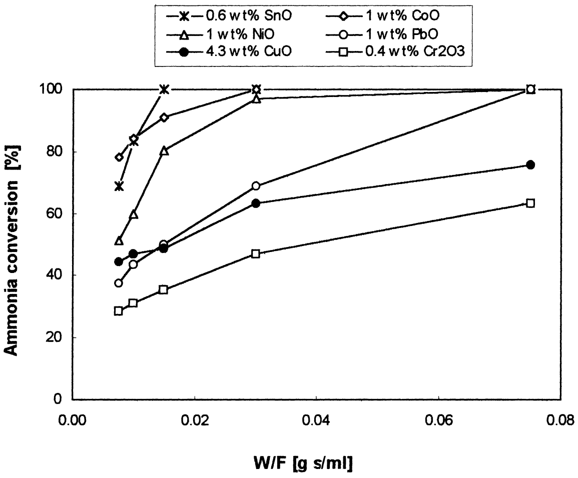

Fig. 1. Ammonia conversion at changing *W*/*F* values using a 4.3 wt.% CuO/Al_2O_3 and catalysts containing both CuO and a metal oxide. (0.54% NH_3, 8% O_2, He balance; 25 mg catalyst, 325°C; *W*/*F* = 0.0075–0.075 g s/ml).

The activities at 325°C of all the catalysts used in this study for the oxidation of ammonia, without added SO_2 or water, are presented in Fig. 1 and the corresponding selectivity to nitrogen presented in Fig. 2. The catalysts of composition 0.4 wt.% Cr_2O_3-4.3 wt.% CuO/Al_2O_3 and 1 wt.% PbO-4.3 wt.% CuO/Al_2O_3 catalysts present similar activities and selectivities to 4.3 wt.% CuO/Al_2O_3. The most active catalyst was 0.6 wt.% SnO-4.3 wt.% CuO/Al_2O_3, but it exhibited the lowest selectivity to N_2 (Fig. 2). Lower selectivities to nitrogen were due to increased production of N_2O, with smaller amounts of NO also detected. For example, in the range of *W*/*F* values studied, the selectivity to N_2O was 10–15% using 0.6 wt.% SnO-4.3 wt.% CuO/Al_2O_3. The corresponding value for NO was 7–8%. Of note in Fig. 2 is the fact that selectivity increased with increasing conversion over those catalysts with activities close to 4.3 wt.% CuO/Al_2O_3, namely the chromium and lead treated samples, whereas selectivity declined with increasing conversion for the more active catalysts.

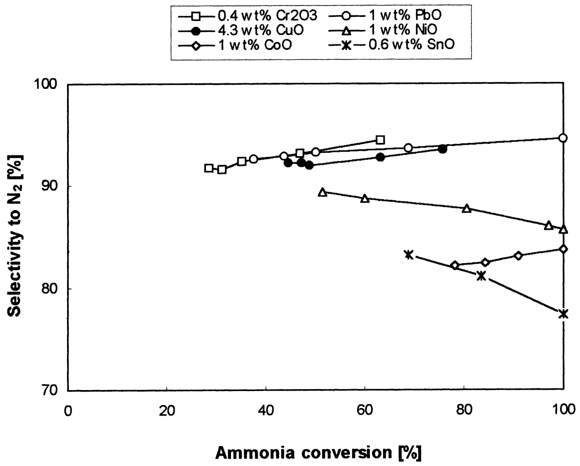

Fig. 2. Selectivity to N_2 with ammonia conversion using a 4.3 wt.% CuO/Al_2O_3 and catalysts containing both CuO and a metal oxide. (0.54% NH_3, 8% O_2, He balance; 25 mg catalyst, 325°C; *W*/*F* = 0.0075–0.075 g s/ml).

Introducing SO_2 into the reactant stream (0.1 vol.%) strongly attenuated the catalytic activity of all the catalysts used in this study. This can be seen from Fig. 3 which presents the conversion of ammonia with variation in *W*/*F* in the presence (closed triangles) and absence (open circles) of SO_2 over all catalysts listed in Table 1.

Addition of SO_2 to the feed stream also had interesting effects on the selectivity to N_2. Fig. 4 presents the selectivity-conversion data for all the catalysts listed in Table 1. Added SO_2 clearly boosts the selectivity towards N_2 over all the catalysts studied here. An important point is that there is some overlap in our data in terms of the % conversion that could be achieved in the absence and presence of SO_2 so that variations in selectivity as a function of conversion do not explain the observed phenomenon.

When ammonia conversion and selectivity was assessed in the presence of added steam, some reduction in activity was noted (square symbols, Fig. 3) but again selectivity to N_2 was improved vis-a-vis the dry conditions (Fig. 4) over all the catalysts studied.

The influence of SO_2 on activity was surprising in view of literature reports that the CuO-$CuSO_4/Al_2O_3$

Table 2
Ammonia and nitric oxide conversion rates over 4.3 wt.% CuO/Al_2O_3 in the presence and absence of (0.1 vol.%) SO_2 at 325°C. (8% O_2, He; 25 mg catalyst; $W/F = 0.03$ g s/ml)

Reactant concentration	Without SO_2		With SO_2	
	NH_3 conversion [%]	NO conversion [%]	NH_3 conversion [%]	NO conversion [%]
0.54% NH_3 0% NO	63	n/a	[a]21	n/a
0.38% NH_3 0.38% NO	68	65	57	51
0.18% NH_3 0.18% NO	82	68	70	57

[a]Tested using 500 mg catalyst; $W/F = 0.6$ g s/ml).

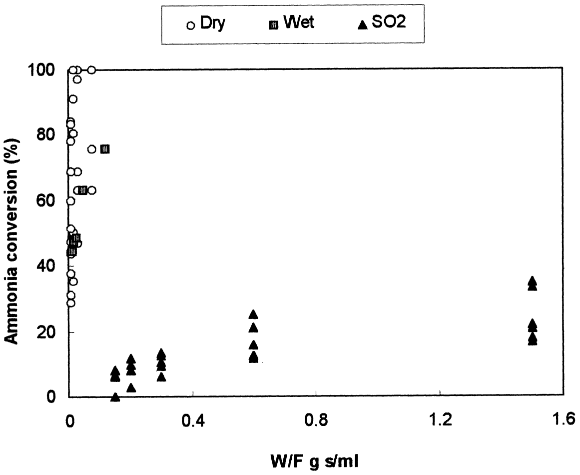

Fig. 3. Ammonia conversion with variation in W/F in the presence and absence of SO_2 and H_2O using 4.3 wt.% CuO/Al_2O_3 and catalysts containing both CuO and a metal oxide. Reaction temperature = 325°C. Dry (No SO_2 or H_2O: 0.54% NH_3, 8% O_2, He; 25 mg catalyst). SO_2 (with SO_2; 0.54% NH_3, 8% O_2, 0.1% SO_2, He; 500 mg catalyst). Wet (with H_2O; 0.54% NH_3, 8% O_2, 1% H_2O, He; 25 mg catalyst).

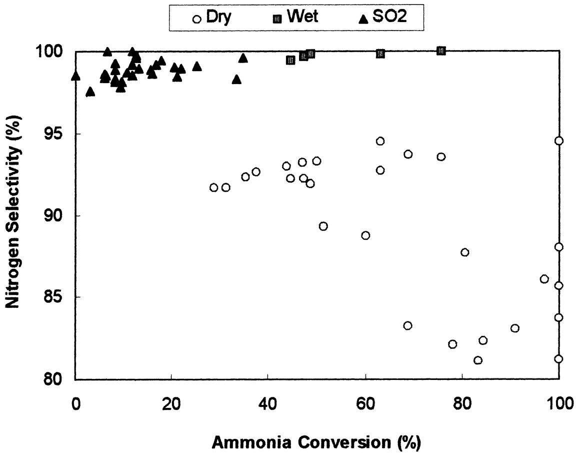

Fig. 4. Selectivity to N_2 with NH_3 conversion in the presence and absence of SO_2 and H_2O using 4.3 wt.% CuO/Al_2O_3 and catalysts containing both CuO and a metal oxide. Reaction temperature = 325°C. Dry (No SO_2 or H_2O: 0.54% NH_3, 8% O_2, He; 25 mg catalyst) SO_2 (with SO_2; 0.54% NH_3, 8% O_2, 0.1% SO_2, He; 500 mg catalyst). Wet (with H_2O; 0.54% NH_3, 8% O_2, 1% H_2O, He; 25 mg catalyst).

system is an efficient SCR catalyst which is totally resistant to poisoning by SO_2 [15]. Hence, a series of experiments was undertaken in which the conversion of ammonia was monitored in SCR conditions, with an equimolar mixture of NH_3 and NO, and in ammonia oxidation conditions, in which feed NO was excluded. The results are summarised in Table 2.

The results clearly show that SO_2 strongly inhibits the ammonia oxidation reaction, as before, but has little effect on the SCR reaction in terms of ammonia or nitric oxide consumption.

The ammonia conversion using 4.3 wt.% CuO/Al_2O_3 was also investigated in the presence of N_2O. When N_2O was introduced into the reactant stream it did not convert to N_2 or NO at 325°C in the absence or presence of SO_2. In addition, the presence of N_2O does not inhibit the conversion of ammonia.

The TPR profiles of 4.3 wt.% CuO/Al_2O_3 and this catalyst following treatment with SO_2 are presented in Fig. 5. These data point to a major change in reducibility following sulphation, indicating reduced reactivity of lattice oxygen with H_2 following treatment with SO_2.

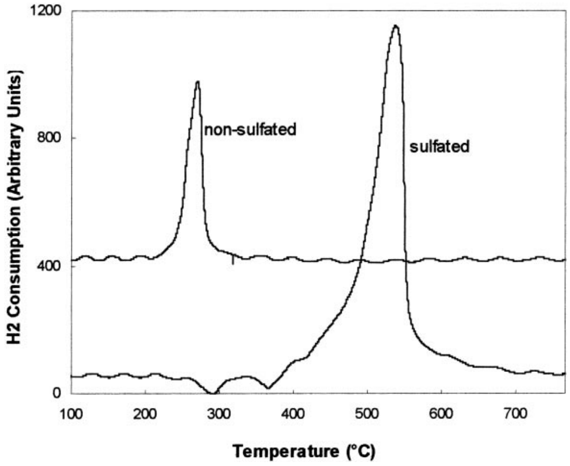

Fig. 5. TPR profiles of sulfated and unsulfated 4.3 wt.% CuO/Al_2O_3. (Flow – 20 ml/min, 5% hydrogen in nitrogen; temperature ramp 10/min; 35 mg catalyst).

4. Discussion

The main points to emerge from this work is that the CuO/Al_2O_3 system is active and selective for the oxidation of ammonia to nitrogen and water and that the selectivity towards nitrogen can be boosted by the addition of SO_2 or water vapour to the feed stream. Work carried out to date on the 4.3 wt.% CuO/Al_2O_3 catalyst showed that the amount of NO detected in the product stream increased as the percent conversion or the contact time decreased. This behaviour is consistent with NO being an intermediate in the reaction to N_2, and this argument is all the more compelling because the 4.3 wt.% CuO/Al_2O_3 catalyst used in this work is an efficient SCR catalyst, as shown in Table 2. Our hypothesis is that a significant amount of the oxidation of ammonia proceeds by the overoxidation of ammonia into NO or even NO_2, which in turn reacts with the remaining ammonia via a standard SCR reaction to yield nitrogen and water

Step 1 $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Step 2 $4NO + 4NH_3 + 3O_2 \rightarrow 4N_2 + 6H_2O$

Another product of reaction observed in this work was N_2O. Indeed there has been a deal of discussion in the literature as to the origins of NO and N_2O produced in ammonia oxidation conditions [4].

A second metal oxide was added to the copper based catalyst in an effort to boost the formation of the oxidation product, NO, which should in turn increase the selectivity to nitrogen. Addition of a second supported component to the basic CuO/Al_2O_3 did result in an increased activity with a number of additives but no benefit was observed in terms of selectivity towards nitrogen. In fact, in many cases the impregnation of the second metal oxide resulted in increased production of N_2O. For example, in the range of W/F studied, the most active catalyst was 0.6 wt.% SnO-4.3 wt.% CuO/Al_2O_3, but it exhibited the lowest selectivity to N_2 (Fig. 2) with N_2O selectivity ranging between 10–15% and NO selectivity ranging between 7–8%. This compared to an N_2O selectivity of 4% and a NO selectivity range of 2–3% for the 4.3 wt.% CuO/Al_2O_3 alone.

The beneficial influence of SO_2 on the selectivity to N_2 is a general effect that was observed with all the catalysts used here, and other workers [6] have reported that CuO/TiO_2 catalysts prepared from $CuSO_4$ give less NO and N_2O than the corresponding catalysts prepared from $Cu(NO_3)_2$.

Certainly in our reaction conditions the SCR reaction is much faster than the ammonia oxidation reaction in the presence of SO_2 and at least as fast in its absence (Table 2). The behaviour of SO_2 in diminishing the activity of the catalyst may now be interpreted in terms of the first step of NO formation being inhibited. Evidence in support of this argument is the finding that when NO is fed to the reactor in SCR reaction conditions (see Table 2) the reaction with NH_3 is clearly unaffected by the added SO_2.

A feature of the catalysts after exposure to SO_2 in the reaction conditions is the formation of bulk $CuSO_4$ and some $Al_2(SO_4)_3$ [15]. In TPR experiments with H_2 as reducing agent, the peak maximum occurs at 520°C for sulfated CuO/Al_2O_3 whereas the peak maximum for CuO/Al_2O_3 is at 250°C. Our hypothesis is, therefore, that added SO_2 inhibits the oxidation of NH_3 into NO by making the extraction of surface lattice oxygen for the reaction more difficult.

$$NH_3 + O_{lattice} \rightarrow NH_{x(ads)} + H_{3-x}O_{ads}$$

The boost in selectivity on adding SO_2 is not due to the often observed kinetic phenomenon in the selective oxidation of hydrocarbons, whereby selectivity to a partial oxidation product often increases when the conversion decreases [16]. With ammonia oxidation selectivity to N_2 over a given CuO/Al_2O_3 was observed to increase or decrease (see Fig. 2) depending on the catalyst used. In addition, there is some overlap, in terms of % conversion, for the data presented in Fig. 4, in the range 30–40%. In this range, for the same conversions, the SO_2 treated catalysts were more selective to N_2 than those not treated with SO_2. For example, using the Cr_2O_3-CuO/Al_2O_3 catalyst, at a conversion of approximately 28%, the selectivity to nitrogen was 92% and this increased to 99% when SO_2 was added to the reaction stream for the same conversion. The effect of SO_2 addition on the N_2O selectivity can also be quite dramatic. For example, added SO_2 reduced N_2O selectivity over 0.6 wt.% SnO-4.3 wt.% CuO/Al_2O_3 from 10–15% to close to 0.

Table 3 illustrates the simplest mononitrogen species which can be involved in ammonia oxidation, and there is ample experimental evidence to support the presence of each of these species on the surface as well as nitrites and nitrates. We follow de Boer et al. [12] with the concept that the pool of mononitrogen species can follow a number of reaction pathways leading to the formation of N_2 or N_2O. Our argument is that N_2 or N_2O will be produced in varying amounts depending on the oxygen availability on the CuO/Al_2O_3 or $CuSO_4/Al_2O_3$ catalysts. Increased surface lattice oxygen availability would push the average oxidation state of the surface nitrogen species towards positive values. The average oxidation state of nitrogen in N_2O is 1+ and 0 in N_2 implying a greater oxygen demand for the reaction which leads to N_2O. Typically, we can envisage N_2 formation via the reaction of any combination of the species listed in Table 3 with combined oxidation numbers less than or equal to 0, e.g.,

$$NH_{2(ads)} + NO_{(ads)} \rightarrow N_2 + H_2O$$

It should be recalled that once N_2 is formed further reaction to N_2O or NO is unlikely on thermodynamic grounds [12].

Table 3
Oxidation states of mononitrogen species

Species	NH_3	NH_2	NH	N	NO	NO_2
Oxidation state	3−	2−	1−	0	2+	4+

N_2O formation would require the reaction of any of the species listed in Table 3 with combined oxidation numbers greater than 0, e.g.,

$$N_{(ads)} + NO_{(ads)} \rightarrow N_2O.$$

The concept of regulating the availability of surface lattice oxygen, often through the dilution of the surface concentration of active surface sites, is widely accepted as an essential feature of oxide catalysts for the selective oxidation of hydrocarbons [16]. Here it is proposed that adding SO_2 to the feed reduces the availability of surface lattice oxygen species in this reaction system, which in turn reduces the average oxidation state of the surface bound nitrogen species, favouring N_2 formation over N_2O. A similar selectivity effect was observed by Il'chenko and Golodets [8]. In their study, a series of unsupported metal oxide catalysts were tested at low temperatures. It was proposed that the activity and selectivity to various products depended on the surface oxygen bond energy of the various metal oxide catalysts. The oxide catalysts with high surface oxygen bond energy resulted in lower rates of reaction and high selectivity to nitrogen. Metal oxides whose surface oxygen bond energy was low led to the formation N_2O. They suggested that the effect was similar to that observed to selective oxidation of hydrocarbons. However, the selectivities observed using the various catalysts were not compared at similar conversions.

The influence of added water to the copper based catalysts can also be assessed. The slightly reduced activity can be associated with competitive adsorption between ammonia and water for active sites. Water adsorbed and blocking oxidation sites would have a similar but lesser effect to sulphation, in that the availability of surface lattice oxygen would be somewhat restricted, favouring the products of partial oxidation [17].

5. Conclusions

The propensity of a CuO/Al_2O_3 system to produced N_2 or N_2O during NH_3 selective oxidation is determined by the average oxidation state of the pool of monoatomic nitrogen species present on the surface. Labile lattice oxygen at the surface of the catalyst increases the average oxidation state of the surface monoatomic nitrogen pool and leads to N_2O formation. Adding SO_2 to the reaction feed reduces the lability of the lattice oxygen and increases the average oxidation state of the pool, favouring N_2 formation. While adding water to the reaction feed restricts access of NH_3 to surface oxidation sites.

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