Catalytic behavior of Cu, Ag and Au nanoparticles. A comparison

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A comparative study of the selective oxidation of NH_3 to N_2 over gold, silver and copper catalysts and the effect of addition of Li_2O and CeO_x

This paper describes the selective oxidation of ammonia into nitrogen over copper, silver and gold catalysts between room temperature and 400°C using different NH_3/O_2 ratios. The effect of addition of CeO_x and Li_2O on the activity and selectivity is also discussed. The results show that copper and silver are very active and selective toward N_2. However the multicomponent catalysts: $M/Li_2O/CeO_x/Al_2O_3$ (M:Au,Ag,Cu) perform the best. On all three metal containing catalysts the activity and selectivity is influenced by the particle size and the interaction between metal particles and support.

3.1 Introduction

The catalytic oxidation of ammonia is an important heterogeneous catalytic process and subject of many studies. The oxidation of ammonia can proceed via the following three principal reactions:

$$4\,\mathrm{NH_3} \;\; + 5\,\mathrm{O_2} \;\; \rightarrow \;\; 4\,\mathrm{NO} \;\; + \;\; 6\,\mathrm{H_2O} \tag{3.1}$$

$$4\,\mathrm{NH_3} \;\; + 4\,\mathrm{O_2} \;\; \rightarrow \;\; 2\,\mathrm{N_2O} \;\; + \;\; 6\,\mathrm{H_2O} \tag{3.2}$$

$$4\,\mathrm{NH_3} \;\; + 3\,\mathrm{O_2} \;\; \rightarrow \;\; 2\,\mathrm{N_2} \;\; + \;\; 6\,\mathrm{H_2O} \tag{3.3}$$

Reaction (3.1) is the first step in the so-called Ostwald process, where the formed NO reacts with O_2 to form NO_2. The nitric acid produced in this way is used for the production of, among others, fertilizers. For this process high temperatures (800-900°C) are required and a Pt/Rh gauze is used as catalyst. The N_2O which is formed in reaction (3.2) can be used as a precursor of atomic oxygen and may, therefore, potentially be used as selective oxidant of hydrocarbons [1, 2]. Therefore, there is recent interest in development of catalysts which convert NH_3 into N_2O with high selectivity. The process described in reaction (3.3) is potentially an efficient and simple method to abate ammonia pollution. It also may be used for the small scale production of pure nitrogen as a safety gas. In literature, many papers dealing with this reaction over various kinds of noble metal and metal oxide catalysts can be found. The earlier work has been reviewed by Il'Chenko et al. [3]. In more recent years various unsupported and supported catalysts have been extensively studied [4–7] for the selective oxidation of ammonia. A variety of metals including Ni, Mn, Fe, Cu, Pt, Ru and Ag supported on γ-Al_2O_3 have been tested mainly in the temperature range 200-600°C. The maximum N_2 selectivity obtained, ranges between 82 and 98%. Copper catalysts are very selective to nitrogen [5] but only at elevated temperatures, while silver catalysts convert ammonia already at temperatures below 200°C [4], but do not have a high selectivity to nitrogen.

In this study we prepared catalysts based on gold, silver and copper nano-particles on γ-Al_2O_3. In addition, the effect of adding Li_2O and CeO_x has been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in CO oxidation [8–10]. It was argued that the active oxygen was supplied by the ceria, rather than from the gasphase. Moreover it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [11]. A detailed study of Gluhoi et al. [12,13] on the effects of addition of (earth) alkali metals to a Au/Al_2O_3 catalyst revealed that the main role of the (earth) alkali metals is that of a structural promoter. It stabilizes the gold particles. It was also found that the combination CeO_x + Li_2O acts as a very efficient promoter for Au based catalyts in many reactions, such as oxidation of hydrocarbons, CO and NH_3 [12,14,15] or reduction of NO by H_2 [16]. Comparable results have been found for copper and silver based catalysts [17]. The results of the gold catalysts in NH_3 oxidation have already been published in other papers of our group [12,14,15].

3.2 Experimental

3.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and/or Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_3 (Engelhard) with the corresponding nitrates. After calcination at 350°C these oxides were used as supports for the Au, Cu or Ag based catalysts. The prepared mixed oxides have an intended atomic ratio Ce/Al and Li/Al of 1/15. The copper, silver and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [18]. An appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals) or $CuNO_3$.3aq was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al atomic ratio was 1/75 (M=Cu, Ag or Au). This ratio of 1:75 is equal to 0.53at% M and resulted in 5wt% for gold, 2.5wt% for silver and 1.5wt% for copper. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Because urea and silver atoms can form a soluble $Ag[NH_3]_2^+$ complex a large surplus of silver was needed to deposit enough silver on the Al_2O_3. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen for 2 hours.

3.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV and 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [19].

3.2.3 Activity measurements

Activity tests of the catalysts were performed in a micro reactor system. The amount of catalyst used was 200mg for the Au/γ-Al_2O_3, Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts. When the catalyst contained CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of metal atoms (Au, Ag or Cu) was similar for all the catalysts with and without additives. Four different gas mixtures of NH_3 and oxygen were used. Both gases were 4vol% balanced in argon. The different NH_3:O_2 ratios used were 1:1, 1:5, 1:10 and 1:25. Typically a total gas flow of 40ml/min (GHSV $\approx$ 2500h^{-1}) was maintained. The effluent stream was analyzed on-line by a quadrupole mass spectrometer(Balzers). The experiments were carried out at a pressure of 1 bar. Each measurement consists of at least four temperature programmed cycles of heating and cooling, with a rate of 4°C/min. Unless otherwise stated the results of the second cooling stage are depicted in the figures. The only hydrogen containing product that was detected was water.

3.3 Results

3.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of the XRD (3nm). The results of the characterization of the catalysts after the reaction are shown in table 3.1. The catalysts without additives contain small particles of 3-4nm. With ceria and Li_2O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [12, 13, 20]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts.

Table 3.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Metal loading (at%)	Average particle size (nm)
Au/Al_2O_3	4.8±0.1	0.51	4.5±0.1
$Au/CeO_x/Al_2O_3$	4.0±0.2	0.42	3.3±0.3
$Au/Li_2O/Al_2O_3$	4.5±0.3	0.48	<3.0
$Au/CeO_x/Li_2O/Al_2O_3$	4.0±0.2	0.42	<3.0
Ag/Al_2O_3	2.2±0.1	0.47	4.9±0.2
$Ag/CeO_x/Al_2O_3$	1.8±0.1	0.39	3.9±0.2
$Ag/Li_2O/Al_2O_3$	2.2±0.1	0.47	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6±0.1	0.34	<3.0
Cu/Al_2O_3	1.3±0.1	0.46	3.6±0.3
$Cu/CeO_x/Al_2O_3$	1.0±0.1	0.35	<3.0
$Cu/Li_2O/Al_2O_3$	1.4±0.1	0.49	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0±0.1	0.35	<3.0

3.3.2 Copper catalysts

The used supports Al_2O_3, Li_2O/Al_2O_3, CeO_x/Al_2O_3 and $Li_2O/CeO_x/Al_2O_3$ without noble metal are inactive for the selective oxidation of ammonia at temperatures below 400°C. The results of the ammonia oxidation over copper catalysts with three different NH_3:O_2 ratios are presented in figure 3.1 and 3.2. In agreement with literature [5] the selectivity to N_2 on these copper catalyst is very high, almost 100%. The NH_3 conversion starts at 300°C with a NH_3:O_2 ratio of 1:1. When the O_2:NH_3 ratio is increased to 5, the temperature onset is not changed but full conversion is already reached at 350°C. When the oxygen content is further increased to a ratio of NH_3:O_2 = 1:25 the onset temperature is lowered to 200°C and the temperature of maximum conversion to 300°C. The results of addition of ceria and Li_2O are depicted in figure 3.3. Addition of Li_2O results is a small improvement of the performance of the Cu/Al_2O_3 catalyst. Addition of CeO_x has a more pronounced effect. The temper-

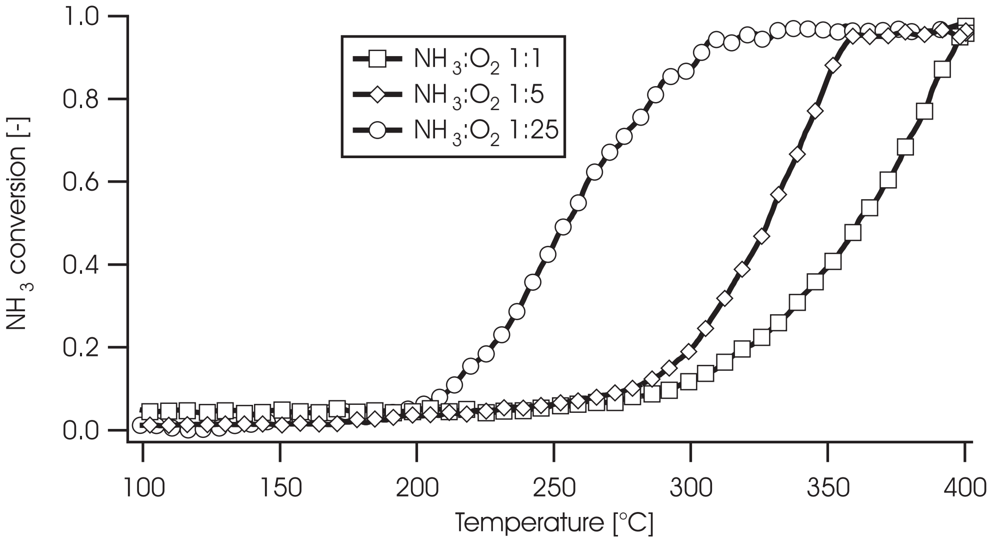

Figure 3.1: NH_3 conversion on Cu/Al_2O_3 catalyst for different NH_3:O_2 ratios.

ature onset of NH_3 conversion is lowered from 300°C towards 225°C. If also Li_2O is added to the $Cu/CeO_x/Al_2O_3$ catalyst again a small improvement is observed in the activity of the catalyst. Figure 3.4 shows the selectivity of the $Cu/Li_2O/CeO_x/Al_2O_3$ catalyst with a NH_3:O_2 ratio of 1:1. Only at temperatures below 200-250°C some N_2O is formed. Above that temperature only N_2 is formed.

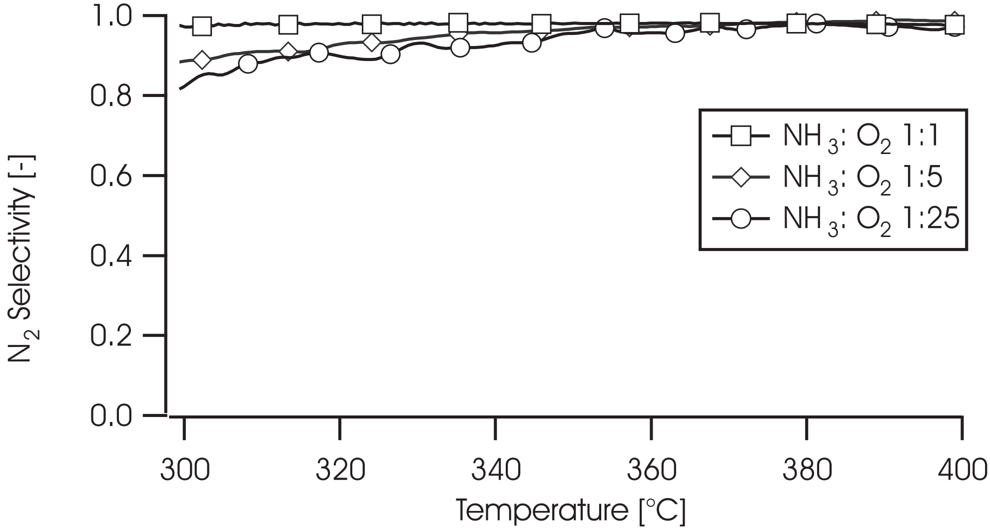

Figure 3.2: N_2 selectivity of the Cu/Al_2O_3 catalyst for different NH_3:O_2 ratios.

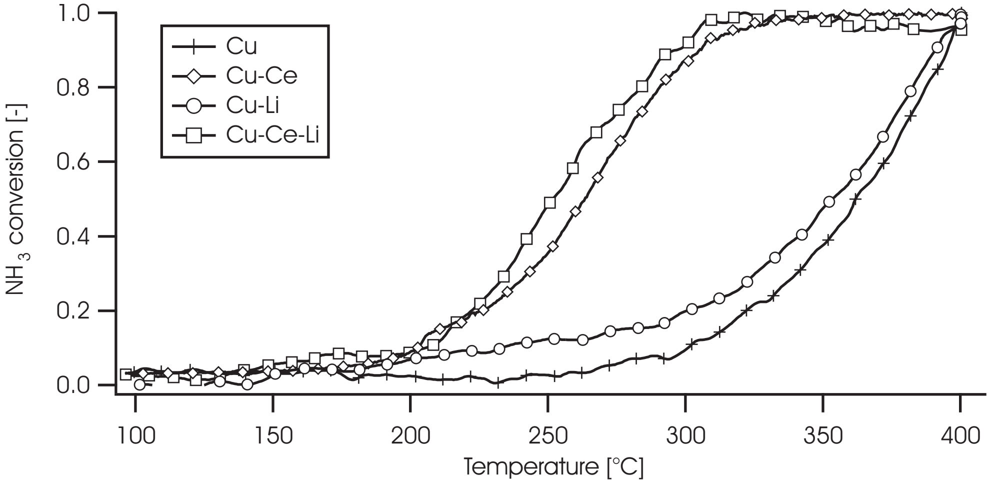

Figure 3.3: Effect of addition of Li_2O, CeO_x and Li_2O + CeO_x on the NH_3 conversion over Cu/Al_2O_3 catalysts, NH_3:O_2 = 1.

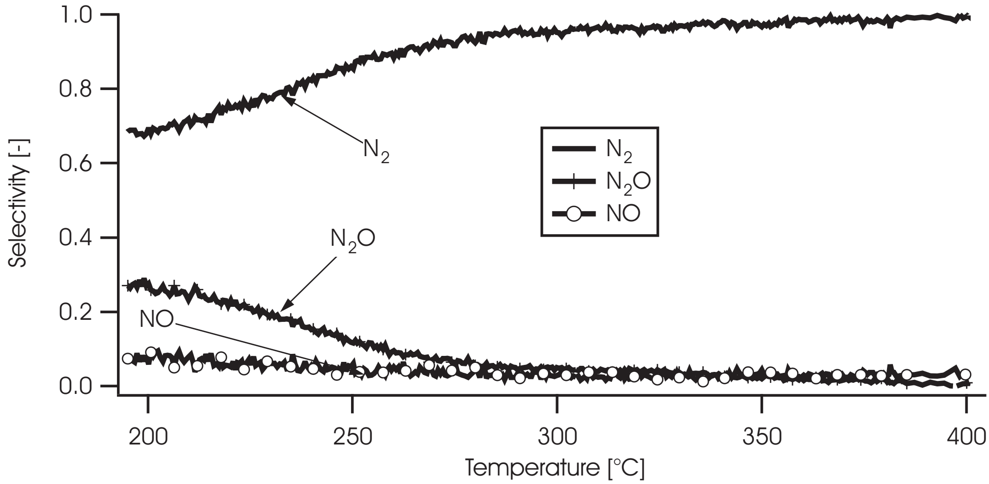

Figure 3.4: Selectivity of the $Cu/Li_2O/CeO_x/Al_2O_3$ catalyst, NH_3:O_2 =1.

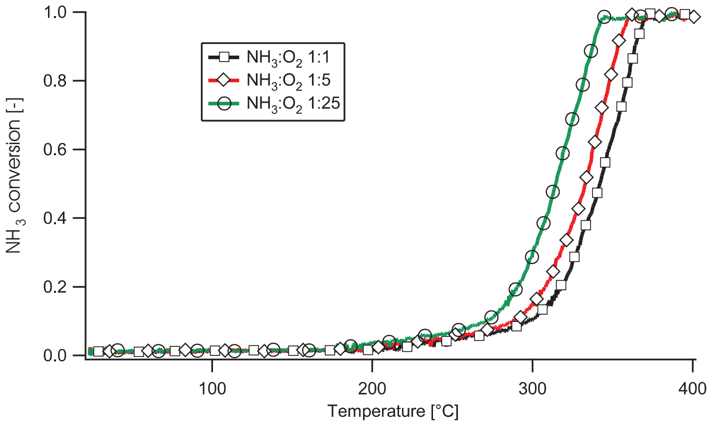

Figure 3.5: NH_3 conversion of Ag/Al_2O_3 catalyst for different NH_3:O_2 ratios.

3.3.3 Silver Catalysts

The NH_3 conversion over the Ag/Al_2O_3 catalysts is shown in figure 3.5. At a NH_3/O_2 ratio of 1, the onset temperature of NH_3 conversion is 300°C. Increasing the O_2/NH_3 ratio results in only a slightly lower onset temperature. In the temperature region of 300 - 400°C mainly N_2 is formed as can be seen in figure 3.6. With the NH_3/O_2 ratios of 1:1 and 1:5 the selectivity starts from 90% at 300°C and increases to 100% at 400°C. When the amount of oxygen is further increased to a ratio of NH_3:O_2 = 1:25 the selectivity at 300°C is increased to 98%. At temperatures above 360°C the selectivity drops towards 80%. In this temperature region some N_2O is formed. The results of addition of CeO_x and Li_2O are shown in figure 3.7. Similar to the copper catalysts, addition of Li_2O has a very small effect on the activity of the Ag based catalyst, while the selectivity was not affected by addition of Li_2O. Addition of CeO_x results in a shift of the onset temperature from 300°C to 200°C. Again no effect on the selectivity is detected. When Li_2O is added to the $Ag/CeO_x/Al_2O_3$ catalyst a further improvement on the activity is obtained. The onset temperature remains about 200°C. The temperature where the conversion reaches maximum is decreased from 340°C to 260°C. The selectivity of this catalyst is shown in figure 3.8. Below 300°C small amounts of NO and N_2O are formed, but the main product is N_2. The selectivity increases with increasing temperature and reaches 100% at 300°C.

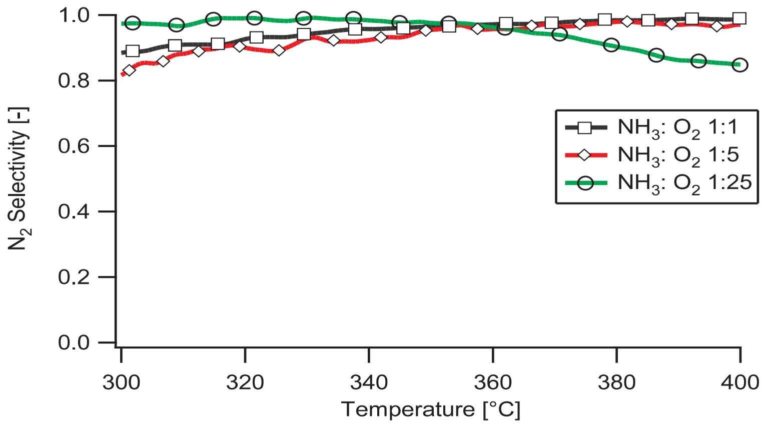

Figure 3.6: N_2 selectivity on the Ag/Al_2O_3 catalyst for different NH_3:O_2 ratios.

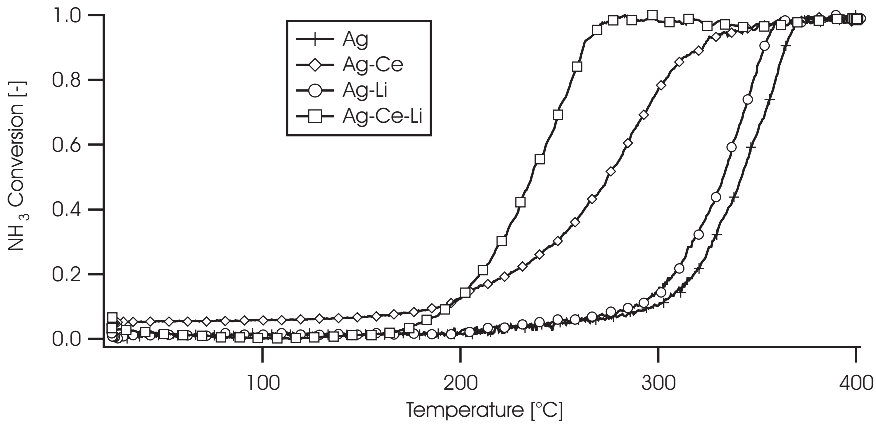

Figure 3.7: Effect of addition of Li_2O, CeO_x and Li_2O + CeO_x on the NH_3 conversion of Ag/Al_2O_3 catalysts, NH_3:O_2 = 1.

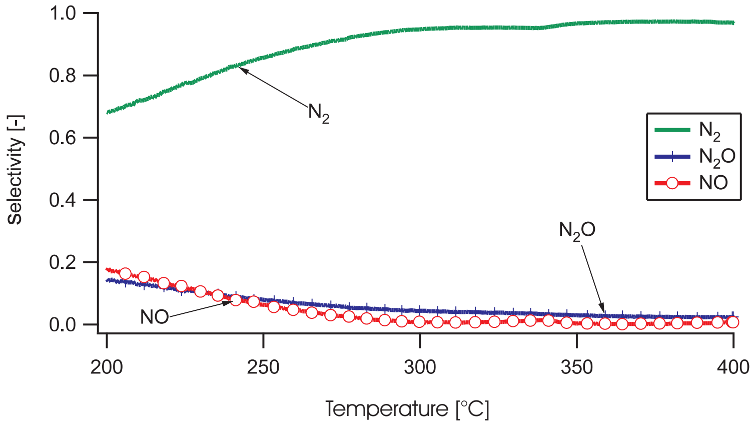

Figure 3.8: Selectivity of the $Ag/Li_2O/CeO_x/Al_2O_3$ catalyst, NH_3:O_2 = 1.

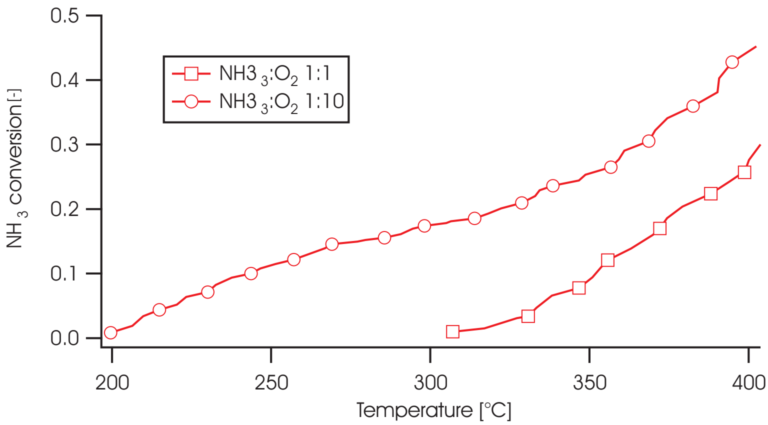

Figure 3.9: NH_3 conversion of Au/Al_2O_3 catalyst for different NH_3:O_2 ratios [12].

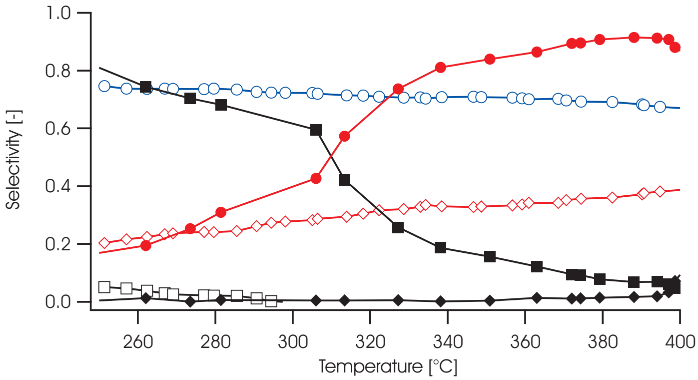

Figure 3.10: Product distribution vs temperature during NH_3 oxidation over Au/Al_2O_3 for two different reactant ratios. Full symbols: NH_3:O_2 = 1:1, open symbols: NH_3:O_2 = 1:10. Selectivity to N_2O(♦), Selectivity to N_2 (●), Selectivity to NO(■) [12].

3.3.4 Gold Catalysts

Figure 3.9 and 3.10 show that over gold based catalysts, at a NH_3/O_2 ratio of 1 a maximum conversion of 30% is obtained at 400°C with a selectivity to N_2 above 80%. The NH_3 conversion increases with increasing O_2 in the feed. For a O_2/NH_3 ratio of 10 the onset temperature is 200°C and a conversion of 45% is reached at 400°C. At 200°C the selectivity towards N_2 is about 78% and slowly decreases to 65% as the temperature is increased to 400°C. This decrease in N_2 selectivity is due to an increase in the N_2O selectivity. Figure 3.11 compares the catalytic activity of the gold based catalysts when the promoters are also present. Clearly the $Au/CeO_x/Li_2O/Al_2O_3$ catalyst showed the best activity [12]. The catalyst is already active at 230°C. In contrast to the copper and silver catalysts the addition of Li_2O to the Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ catalysts results in a large improvement of the activity. If figure 3.12 is compared to figure 3.10 it can be seen that the addition of ceria has a significant effect on the selectivity. At temperatures below 280°C mainly N_2 is formed. At higher temperatures the main product becomes N_2O. The $Au/CeO_x/Li_2O/Al_2O_3$ catalyst shows an increase in N_2 selectivity at the expense of selectivity to N_2O above 380°C. If also Li_2O is added no increase of N_2 production, in this temperature region, is observed.

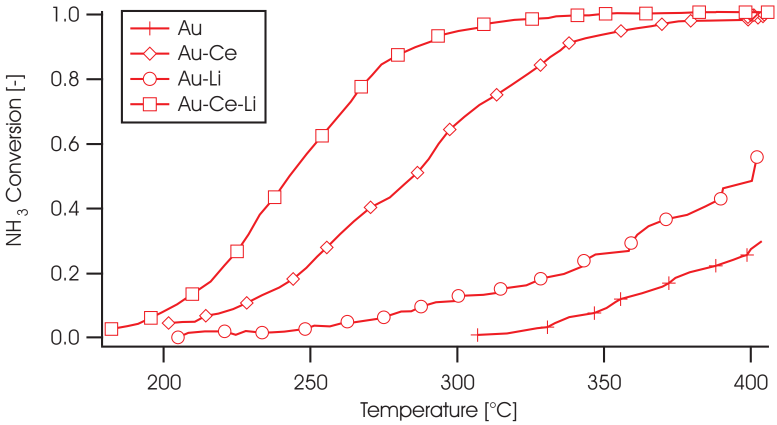

Figure 3.11: Effect of addition of Li_2O, CeO_x and $Li_2O + CeO_x$ on the NH_3 conversion of Au/Al_2O_3 catalysts [12].

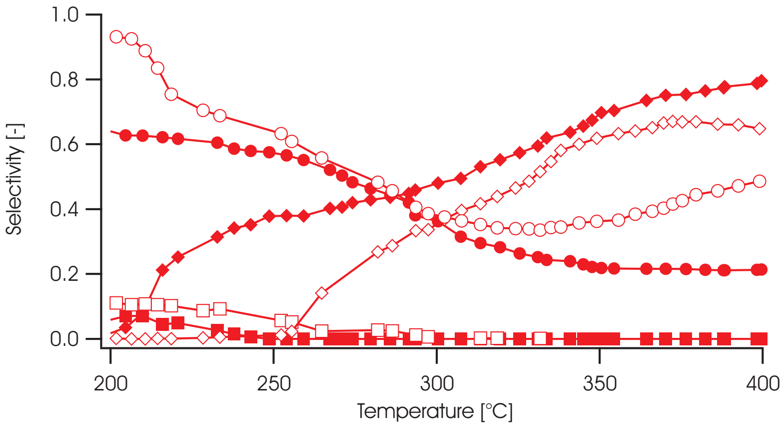

Figure 3.12: Product distribution vs temperature during NH_3 oxidation over $Au/CeO_x/Al_2O_3$ (full symbols) and $Au/Li_2O/CeO_x/Al_2O_3$ (open symbols): Selectivity to N_2O(♦), Selectivity to N_2 (●), Selectivity to NO(■) [12].

3.4 Discussion

3.4.1 Copper catalyst

An extensive study concerning ammonia oxidation on Cu/Al_2O_3 catalyst was reported by Friedman et al. [21] in 1978. Together with the results of another group [22] the authors came to the conclusion that at low copper loadings and calcination temperatures below 500°C the copper mainly exists as surface spinels ($CuAl_2O_4$). This was confirmed by results of Gang et al. [5,23]. They could not detect copper particles with HRTEM on catalysts with loadings of 10% or lower. With higher loading CuO particles were detected. Because the catalysts with lower loading were more active they concluded that the $CuAl_2O_4$ particles were more active than the CuO phase. Based on TPD measurements they also concluded that both surface and lattice oxygen can react with NH_3 to produce N_2. They stated that the first mentioned O-species was the most active one. Increasing the O_2/NH_3 ratio does increase the conversion but decreases the selectivity to N_2. Using a different preparation method and reduction in hydrogen instead of calcination in air we were able to produce small metallic copper particles at low loadings before reaction. These metallic particles are readily oxidized to copper oxide especially in oxygen rich reaction mixtures. The 1.5wt% Cu/Al_2O_3 catalyst showed a similar activity as the 5wt% catalyst of Gang et al. [5] and almost 100% selectivity to N_2. In agreement with that study increasing the O_2/NH_3 ratio enhanced the conversion. If CeO_x is added a great improvement in activity is obtained without loss in selectivity to N_2. This improvement can be explained by giving ceria a role as cocatalyst which consists in providing active oxygen to the active copper species. In the preparation of the catalyst the cerium oxide was deposited first and the copper was deposited afterwards. In this case it is not likely that surface spinels ($CuAl_2O_4$) were formed. CuO-CeO species may be formed but according to [24] those species are only active above 300°C in ammonia oxidation. Therefore, it is not likely that these species cause the improved actvitity of the $Cu/CeO_x/Al_2O_3$ catalyst. Possibly the reaction takes place at the interface of the copper nanoparticles and the ceria.

3.4.2 Silver catalysts

The activity of silver in the selective oxidation of ammonia has been previously studied by Gang et al. [4,23]. They compared silver powder with Ag/SiO_2 and Ag/Al_2O_3. The silver powder was very active, similar to Ag/SiO_2. These catalysts were superior to noble metal catalysts, such as Pt and Ir at temperatures below 200°C, but were not very selective at low temperatures and reached a maximum selectivity to N_2 of around 75% at 300°C. The Ag/Al_2O_3 catalyst showed a better selectivity of around 80% to N_2 at low temperatures. At temperatures above 300°C the selectivity dropped due to the large NO production. They suggested a mechanism which consisted of two steps. The first one is a fast oxidation of NH_3 to NO on the silver particles. The second step is a reduction of the NO to N_2 or N_2O. They suggested that the second step was enhanced by the interaction between silver and the alumina, resulting in an improved selectivity to N_2. The possible effect of the difference in particle size of the Ag/Al_2O_3 (8nm) and Ag/SiO_2(24nm) catalyst has not been discussed in that paper. The silver catalysts we studied have a smaller Ag particle size (table 3.1). With these smaller particles no activity was found below 250°C. With all three O_2/NH_3 ratios the conversion is similar. It is well known that atomically adsorbed oxygen desorbs at around 280°C from a silver surface [25]. Possibly the ammonia oxidation is hindered by these atomically adsorbed oxygen. In the temperature region that the silver catalyst is active in NH_3 oxidation a very high selectivity towards N_2 is obtained. The chemical behavior is very different from the catalysts studied by Gang et al. [23]. Besides the differences in activity they found a large effect of the O_2/NH_3 ratio. It might be that the mechanism on the very small silver particles is different. Li_2O can act as a structural promoter [13, 16, 17]. It stabilizes the small silver particles which results in smaller particles (table 3.1). As addition of Li_2O shows only a small effect on the activity and no effect on the selectivity, it is unlikely that Li_2O influences the reaction chemistry. Addition of CeO_x or the combination of CeO_x and Li_2O does greatly influence the activity but not the selectivity. As the oxygen storage capability in oxidation reactions of ceria is well known, it is possible that the promoting role of CeO_x is related to an improved supply of active oxygen to the silver particles. Clearly, as Gang et al. [4] stated, the interaction between silver and the support has a great influence on the ammonia oxidation. But also the particle size should be taken into account. The smaller the particles the higher the selectivity to N_2. This suggests a model in which the reactions at the interface of silver with the ceria support is very important for high selectivity to nitrogen.

3.4.3 Gold Catalysts

When the oxygen content of the gas feed is increased, the performance of the Au/Al_2O_3 catalysts is improved in terms of conversion. A higher O_2 content does not influence the adsorption of the NH_3 [14]. Hence, probably the surface is mainly covered with

NH_3 and the reaction is very dependent on the availability of oxygen atoms. This is probably also the reason for the beneficial effect of addition of ceria, which is known to be able to provide and store oxygen. When Li_2O is added an improvement of activity is measured for the gold catalysts whereas on the copper and silver catalysts hardly any difference was noted. A possible role of the Li_2O is decreasing the surface acidity of the γ-Al_2O_3. It is expected that on a less acidic surface the NH_3 adsorption is hindered, which can give room for more oxygen adsorption on the support. This is supported by the observation that a post treatment of NaOH increases the activity of several catalysts in this reaction [4, 5]. The mechanistic route to N_2, NO and N_2O is considered in literature to proceed via a sequential NH_3 dissociation (hydrogen abstraction) [7, 26]. Amblard et al. [7] stated a mechanism in which surface NO_x can be reduced by surface NH_x. They considered the activation of surface NH_x to be the rate limiting step. As the addition of CeO_x to the Au/Al_2O_3 catalyst affects besides the activity also the selectivity of the catalyst, it is possible that CeO_x also affects the activation of surface NH_x. In an earlier paper [14] it is shown with FTIR measurements that gold seems to enhance the H-abstraction of NH_3 and from the observation that the selectivity of the ammonia oxidation is dependent on the CeO_x additive, it can be concluded that all components of the catalysts have an influence on the selectivity, suggesting that the chemical reactions may take place at the metal-support interface.

3.4.4 Comparison of the copper, silver and gold catalysts

If the activity and selectivity of the silver and copper catalysts are compared to the results of the gold catalysts published earlier by our group [12, 14, 15], some similarities are observed. For all three catalysts the addition of CeO_x or CeO_x + Li_2O is beneficial for the activity. In all cases the multicomponent catalyst with both oxides is the most active one. Possibly, the metal oxides have an important role in the ammonia oxidation chemistry. The copper, silver and gold metals are needed to create active catalysts as the supports only are inactive at temperatures below 400°C as shown in the present study and in [14]. These results may suggest that for all three metals used the reaction takes place at the metal-support interface. In addition for all three metals (copper, silver and gold) the size of the particles is important. For gold the particle size is crucial for the high oxidation activity [27]. The catalysts with copper nanoparticles also show an improved activity compared to literature data in which large Cu particles (10nm) have been used [5,23]. For the silver catalysts the selectivity is improved if smaller particles are used. In terms of selectivity, copper and silver catalysts differ from the gold catalysts. Addition of ceria to the Au/Al_2O_3 influences the selectivity, whereas the selectivity of copper and silver containing catalysts was not affected by CeO_x. A study by Lin et al. [14] showed that the catalytic ammonia oxidation activity of gold catalysts does not strongly depend on the average gold particle size, but is strongly influenced by the nature of the additive, which suggests a certain metal-support interaction which not only influences the activity but also the selectivity. Possibly, both the gold and ceria play an active role in the NO and N_2O production. On the silver and copper based catalysts the additive ceria only influences the activity but not the selectivity.

3.5 Conclusions

Based on the results presented above, it is concluded that silver and copper catalysts are very active and selective in the selective oxidation of ammonia to nitrogen. For both metals the interaction or nature of the support greatly influences the activity. Addition of Li_2O results in smaller particles for silver and copper, as was reported before for gold based catalysts. Addition of CeO_x increases the activity of the silver, gold and copper catalysts and for the gold catalysts influences also the selectivity. The particle size of the copper, silver and gold is very important for high activity and selectivity.

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