Journal of Catalysis **208,** 15–20 (2002)
doi:10.1006/jcat.2002.3572, available online at http://www.idealibrary.com on IDEAL®

NO Reduction by Urea under Lean Conditions over Single-Step Sol–Gel Cu/Alumina Catalyst

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Received June 28, 2001; revised February 13, 2002; accepted February 13, 2002

We present the catalytic activity of 1% Cu on alumina catalyst prepared using a single-step sol–gel process (designated 1% Cu–SG) as a function of oxygen, water, and SO_2 in the feed for the reduction of NO with an aqueous urea solution. Our results show that NO_x conversion activity of 1% Cu–SG is dependent on oxygen in the feed. The maximum conversion increased from 91 to 99% when the amount of oxygen in the feed was changed from 2 to 14%. Also, the location of maximum conversion temperature decreased from 400 to 377°C. Short-term and long-term exposure of the catalyst to a gas mixture containing 25 ppm SO_2 did not result in activity loss at any temperature as long as aqueous urea was present in the feed. However, temporary interruption of aqueous urea solution resulted in permanent activity loss. Our attempt to reactivate the catalyst with propene failed to recover the original activity.

Key Words: **selective NO reduction; copper/alumina catalyst; sol–gel preparation; urea; SO_2.**

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1. INTRODUCTION

The removal of nitrogen oxides from the exhaust of a diesel vehicle is still a very challenging problem even though there have been many studies. Hydrocarbons and oxygenated hydrocarbons seemed to be possible reducing agents in the reduction of nitrogen oxides (1, 2). However, it was soon discovered that they had low-to-moderate reducing efficiency and resulted in undesired by-products. Ammonia, on the other hand, has been used as a reducing agent to remove NO_x from the flue gas streams of power plants. Using ammonia as a reductant for the removal of NO_x from automobile exhaust gas may not be commercially viable because there are difficulties in the storing and handling of ammonia and a robust controller is required to accommodate the rapidly changing load conditions of automobile exhaust gas with little ammonia slip. To overcome the difficulties associated with pure ammonia, urea can be hydrolyzed and decomposed *in situ* to generate ammonia.

$$CO(NH_2)_2 \Rightarrow NH_3 + HNCO \quad [1]$$

$$HNCO + H_2O \Rightarrow NH_3 + CO_2 \quad [2]$$

It seems that urea, as ammonia source, is the best choice for such applications because urea is not toxic and also can be easily transported as a high-concentration aqueous solution. As a result, NO_x can be reduced with not only ammonia but also the urea itself and its decomposition by-product, HNCO, as shown in reactions [3]–[5].

$$2CO(NH_2)_2 + 6NO \Rightarrow 5N_2 + 2CO_2 + 4H_2O \quad [3]$$

$$4HNCO + 6NO \Rightarrow 5N_2 + 4CO_2 + 2H_2O \quad [4]$$

$$4NH_3 + 4NO + O_2 \Rightarrow 4N_2 + 6H_2O \quad [5]$$

Even though the use of urea in the reduction of NO_x from the flue gas streams of power plants is a well-established method (3), there have not been many studies on the use of urea as a reductant in treatment of the exhaust of lean-burn engines.

Held *et al.* (4) was the first to demonstrate that a Cu/ZSM-5-coated monolith catalyst was active in the reduction of NO_x by urea under laboratory conditions. However, catalysts based on zeolites proved to be unstable in the hydrothermal environment of engine exhaust. In addition, V_2O_5-based catalysts were studied for the reduction of NO_x by urea in real diesel exhaust gas (5–7). These studies raised questions as to urea dosage control and, for automotive applications, the appropriateness of using highly toxic vanadia-based catalysts. Even though there have been many studies on the selective catalytic reduction of NO with urea under oxidizing conditions, there are limited reports on the hydrolysis of HNCO and urea. Koebel and Elsener (8) studied the decomposition/hydrolysis products of urea over a SCR catalyst and also evaluated urea as a possible reducing agent for the catalytic reduction of NO. They found low emissions of higher molecular mass compounds, such as melamine, formed during the hydrolysis and decomposition of urea. They also pointed out that the emission of urea, isocyanic acid, and NH_3 was possible under nonideal

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operating conditions of the catalyst. Dumpelmann *et al.* (9) reported that the hydrolysis of HNCO over alumina reached completion but the hydrolysis mechanism of HNCO over alumina was unclear. Kleemann *et al.* (10) also studied the hydrolysis of HNCO over SCR catalysts and reported that a typical vanadia on titania catalyst was highly active for HNCO hydrolysis.

In this paper, we report the catalytic activity of 1% Cu on alumina catalyst, prepared by a single-step sol–gel method, for NO_x reduction with aqueous urea solutions under oxidizing conditions in the absence and presence of SO_2.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparations

We prepared the 1% Cu on alumina catalyst using a sol–gel method. Aluminum tri-sec-butoxide, 95% pure (from Alfa Aesar, Inc.), was used to synthesize the catalyst in one step at room temperature. Aluminum tri-sec-butoxide was first mixed with the water–ethanol solution (35 mol of ethanol/1 mol of Al and 8 mol of water/1 mol of Al) and then the necessary amount of cupric nitrate, 99%+ (from Aldrich, Inc.), was added to the sol solution to obtain 1% Cu loading. Details are given in Ref. (11). The gel was dried in air at 100°C for 12 h to remove the solvent and water. The dry gel was put in a furnace and its temperature was increased from room temperature to 600°C with an 8°C/min heating rate. Once 600°C was reached, it was kept at this temperature in air for 24 h and was ground and sieved to 80–120 mesh size.

2.2. Catalyst Testing

In all experiments, 0.1 g of catalyst was held between two quartz wool plugs in a quartz U-tube (I.D., 3 mm) flow reactor and tested under a total flow rate of 176 ml/min at 1 atm and room temperature. The reactant gas mixture was blended by using four independent mass flow controllers to give 300 ppm NO (plus ~10 ppm NO_2 impurity in the NO cylinder), 2–14% O_2, 2–8% water, 25 ppm SO_2 (when used), and He as balance.

Water and aqueous urea solution were used to get the desired water and urea concentration in the feed. The necessary amount of urea (0.6–1.2 g) was first dissolved in 50 ml of water and then injected into the feed stream with a peristaltic tube pump (Cole Palmer) set to the desired flow rate to obtain 2–8% water and corresponding urea concentration in the gas phase. The aqueous solution mixed with the feed gas stream was heated in the entrance section of the U-tube reactor (the residence time in this heating section was around 0.2 s) before entering the catalyst bed. The temperature of this section was the same as that of the reactor bed. Even though the pump was set to a flow rate to obtain 150 ppm urea in the gas phase, we found that the urea fed to the reactor was higher, especially at high temperatures, due to the receding interface of gas and liquid in the urea feeding tube, resulting in an increased rate of urea injection. For this reason, we report the urea concentration as ~300 ppm, which was found to be the maximum and stayed constant above 300°C, determined through CO_2 measurement with FTIR.

The reactor outlet stream was analyzed by using a Thermo Environmental 42CHL NO_x chemiluminescence analyzer to determine unreacted NO_x and also a FTIR with a 10-cm path length gas cell (Galaxy 7020 Spectroscopy by Mattson, Inc., and WinFirst Software version 3.61 for data analysis) for quantitative determination of CO_2, CO, and N_2O at each temperature. The activity measurements were reproducible within ±2% and the N_2O selectivity measurements were accurate to ~5 ppm, resulting in an error bar of ±2% in N_2 selectivity at 50% NO_x conversion.

2.3. Catalyst Characterization

Approximate crystallite size and phases present in the catalyst were determined by X-ray diffraction (Rigaku powder diffractometer, operated at 40 kV and 100 mA). BET surface area was measured with a Micromeritics 2010 instrument. Prior to analysis, the sample was degassed under vacuum at 300°C until the vacuum inside the sample tube stayed constant at around 5 μm Hg. A standard Micromeritics program was employed to calculate both BET surface area and BJH pore size distribution (using the desorption isotherm).

3. RESULTS

3.1. Catalyst Characterization

XRD spectrum of the fresh 1% Cu–SG catalyst showed alumina peaks (γ and η) at 2θ of ~39, ~45.5, and ~66.8°. However, we did not observe any peak corresponding to Cu, CuO, or Cu_2O. The sol–gel synthesis and calcination treatment that we used produced 1% Cu–SG catalyst with BET surface area of ~297 m^2/g and a narrow pore size distribution centered at $D \sim 55$ Å. In contrast, when alumina is synthesized alone there is no change in surface area but the average pore size becomes ~77 Å.

3.2. Oxygen and Water Effect on the Activity

Figure 1 shows the catalytic activity of 1% Cu–SG catalyst as a function of oxygen concentration. Catalyst (0.1 g) was tested under 176 ml/min (1 atm and room temperature) of a reactant gas mixture containing 300 ppm NO, 4% water, 300 ppm urea (based on CO_2 amount measured with FTIR), 2–14% oxygen, and He as balance. For all oxygen concentrations, the conversion versus temperature had an S shape. At 2% oxygen in the feed, the catalyst showed ~5% conversion at 250°C and ~60% at 350°C. The maximum

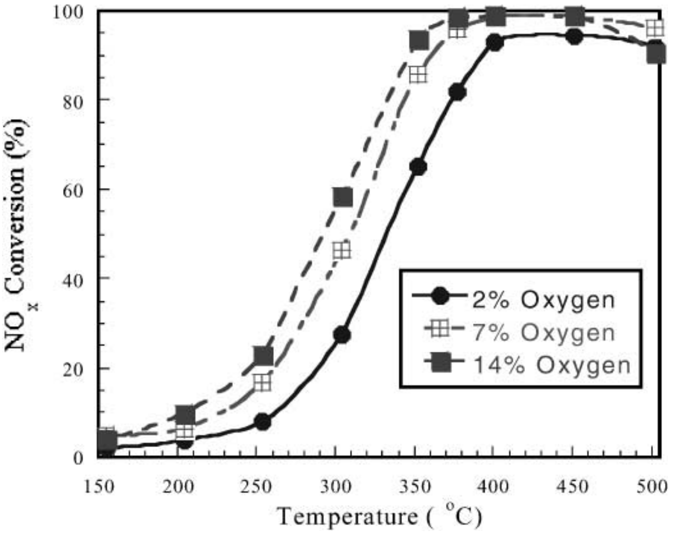

FIG. 1. The activity of 1% Cu–SG as a function of oxygen. Reaction conditions: 300 ppm NO, the above oxygen concentrations, 4% water, 300 ppm urea, and He as balance. Also, 0.1 g of catalyst and 176 ml/min (1 atm and room temperature) of flow rate.

conversion, ~91%, was reached at 400°C and conversion stayed at this level until 500°C. When oxygen in the feed is increased to 7%, ~15% NO_x conversion occurs at 250°C and the conversion reaches ~86% at 350°C. The maximum ~98% conversion is obtained at 400°C and stays at 98% until 500°C. Increasing the oxygen concentration to 14% did not change the activity of 1% Cu–SG above 350°C within our experimental error even though we observed a slight enhancement in the activity between 250 and 300°C. Also, at all temperatures and oxygen concentrations we did not observe any N_2O formation in the feed. The only product was N_2.

CO_2 analysis of the reactor outlet with FTIR showed that 12 ppm CO_2 formed at 150°C and increased to 54 ppm at 200°C. CO_2 formation further increased to 190 ppm at 250°C and 300 ppm at 300°C. Then it stayed at this level until 500°C. Our preliminary NH_3 analysis of the reactor outlet revealed fewer than 100 ppm NH_3 at temperatures below 300°C but above 350°C there was no NH_3 at the outlet. This was also confirmed with the determination of N_2 production, measured by the GC, at all temperatures. In fact, we found that the amount of N_2 produced above 300°C was ~47% higher than the amount expected through the selective reduction reaction.

We also tested the activity of 1% Cu–SG catalyst as a function of water concentration in the feed. We found that the conversion-versus-temperature curve up to 450°C did not change when water concentration was changed from 2 to 8% (data not shown). For all water concentrations, ~15% conversion occurred at ~250°C and the conversion reached ~98% at 400°C and stayed there until 450°C within our experimental error.

3.3. Comparison of the Activity Obtained with Urea to that Obtained with NH_3

Figure 2 shows the activity of 1% Cu–SG as a function of NH_3 and urea in the feed. A mixture of 300 ppm NO, 600 ppm NH_3 or 300 ppm urea, 7% oxygen, 4% water, and helium as balance was passed over 0.1 g of the catalyst. In this case, NH_3 was introduced as a gas and the necessary amount of water was injected into the hot section of the reactor. When urea was used instead of NH_3, it was first dissolved in 50 ml of water and then aqueous urea solution was injected into the heated section of the reactor entrance. As seen in the figure, when ammonia in the feed is 600 ppm, the conversion versus temperature curve up to 400°C is similar to that obtained with 300 ppm urea in the feed. Conversion (~15%) at 250°C increased to ~83% at 350°C and the maximum conversion, ~97%, was reached at 400°C. In contrast, the constant conversion of ~98% between 450 and 500°C obtained with aqueous urea dropped to ~81% at 450°C and to ~31% at 500°C when there was 600 ppm NH_3 in the feed. In addition, we found that as seen in Fig. 3, the oxidation of NH_3 to N_2 in the absence of NO over 1% Cu–SG was highly selective to N_2. Conversion (~10%) to N_2 occurred at 350°C and ~77% conversion to N_2 was reached at 450°C and stayed at this level until 500°C. The only by-product was NO and we did not observe any N_2O or NO_2. The conversion to NO reached a maximum of 2% at 500°C.

3.4. SO_2 Effect on the Activity

Figure 4 shows the comparison of the catalytic activities obtained under steady state condition with 25 ppm SO_2

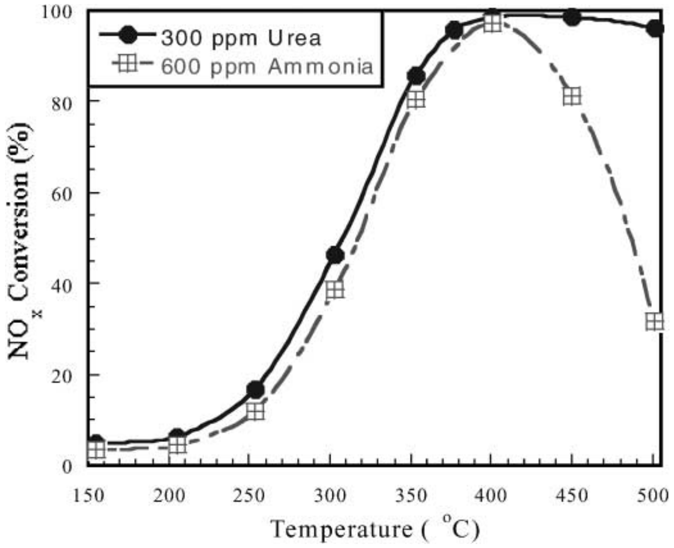

FIG. 2. The activity of 1% Cu–SG as a function of urea and ammonia. Reaction conditions: 300 ppm NO, 7% oxygen, 4% water, the above urea and NH_3 concentrations, and He as balance. Also, 0.1 g of catalyst and 176 ml/min (1 atm and room temperature) of flow rate.

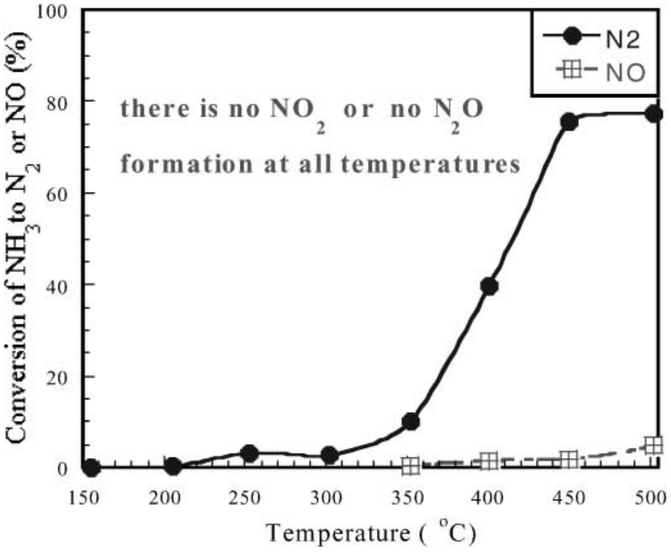

FIG. 3. The NH_3 oxidation to N_2 activity of 1% Cu–SG as a function of temperature. Reaction conditions: 600 ppm NH_3, 7% oxygen, 4% water, and He as balance. Also, 0.1 g of catalyst and 176 ml/min (1 atm and room temperature) of flow rate.

in the feed to that obtained after keeping the catalyst under the gas mixture containing 25 ppm SO_2 in the feed for 2 days on stream. For a steady state test, we used a reactant gas mixture containing 300 ppm NO, 7% oxygen, 4% water, 25 ppm SO_2, 300 ppm urea, and He as balance. For the long-term effect of SO_2 on the activity, we kept a 1% Cu–SG catalyst at 300°C for 2 days under the reaction gas mixture containing SO_2. At the end of this period, the catalyst was treated with 5% oxygen in helium at 500°C for 20 h.

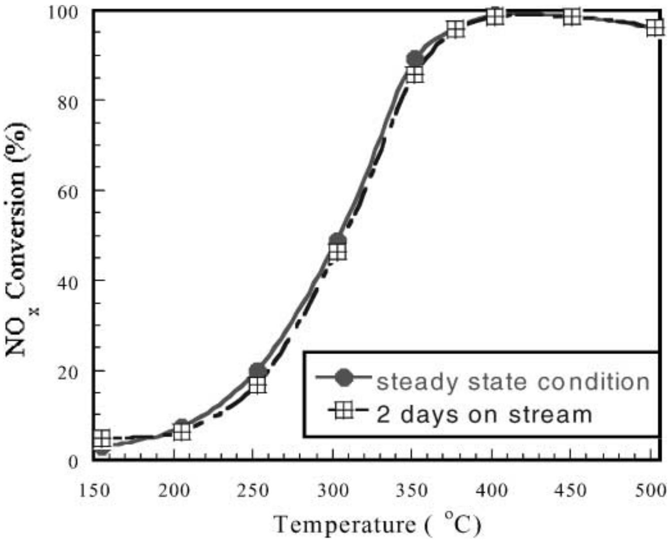

FIG. 4. Long- and short-term activity of 1% Cu–SG under the gas mixture containing 25 ppm SO_2. Reaction conditions: 300 ppm NO, 7% oxygen, 4% water, 300 ppm urea, and He as balance. Also, 0.1 g of catalyst and 176 ml/min (1 atm and room temperature) of flow rate.

Then we retested the catalyst with the gas mixture containing 300 ppm NO, 300 ppm urea, 4% water, 7% oxygen, and helium as balance. As seen in Fig. 4, the activity of 1% Cu–SG did not change at any temperature. In both cases, ~17% conversion occurred at 250°C and the conversion reached 98% at 400°C and stayed until 450°C was reached. We observed a slight decrease in conversion, ~96%, at 500°C.

4. DISCUSSION

To our knowledge, this is the first report ever published in the literature on the activity of Cu on alumina catalyst for NO reduction with aqueous urea solution under oxidizing conditions. On the other hand, there are many studies on NO reduction with NH_3 and also on the oxidation of NH_3 to N_2 over Cu on alumina. It is difficult to make a sound comparison between different laboratories because of different reaction conditions, preparation methods, and copper loading. However, we will try to explain why the observed activity and N_2 selectivity of our 1% Cu–SG changed as a function of oxygen, water and SO_2 in the feed.

4.1. Oxygen and Water Effect

Our results showed that water concentration in the feed did not change the NO conversion activity of the 1% Cu–SG catalyst. This may be due to the constant amount of ammonia formation regardless of water concentration in the feed. Indeed, we found that the decomposition/hydrolysis of urea during the NO reduction yielded similar CO_2 amounts for all water concentrations in the feed within our experimental error. This indicates that the decomposition of urea seems to be the rate-determining step and also strongly depends on the temperature, whereas the hydrolysis of HNCO seems to be very fast and reaches completion and, hence, is independent of water concentration for the constant urea in the feed.

At 4% water, an S-shape conversion versus temperature was obtained regardless of oxygen content in the feed, as shown in Fig. 1. When oxygen in the feed was increased from 2 to 14%, the activity of the catalyst roughly doubled and the maximum conversion temperature dropped to 377 from 400°C while the conversion increased from ~91 to ~99%. In contrast, Held *et al.* (4) reported that the activity of Cu/ZSM-5 monolith catalyst did not change as a function of oxygen in the feed when an aqueous urea solution was the reductant. Also, they showed that the NO_x conversion reached ~100% between 300 and 350°C and then dropped to ~90% at 400°C. Similarly, Morimune *et al.* (7) found that over TiO_2/V_2O_5 monolith catalyst, the maximum NO conversion, ~80%, occurred at 400°C when the ratio of NH_3 (generated by hydrolysis of urea) to NO was 1.5, and above 400°C, the conversion decreased and the formation of N_2O increased. However, over 1% Cu–SG catalyst under similar reaction conditions, we observed ~99% NO_x conversion between 377 and 450°C and 96% conversion at 500°C. Also, at no temperature did we observe N_2O formation and N_2 was the only product seen. Even though the concentration of urea in the feed was higher than the stoichiometric amount ($N_{reducing}/NO_x = 2$), our preliminary NH_3 analysis revealed that approximately 100 ppm NH_3 at the exit of the reactor was present below 300°C. However, above 350°C, we did not observe the formation of NH_3. The reason is most likely oxidation of the excess amount of N-containing compounds, such as NH_3 or HNCO, to N_2 or NO during the reduction of NO. It is plausible that the excess amount of urea is decomposed and hydrolyzed to NH_3 and HNCO and that these N-containing compounds are oxidized to N_2 above 350°C during the reduction of NO. In fact, we found that the amount of N_2 measured using the GC was $\sim$47% higher than the amount of N_2 that one could calculate for the reduction of NO with NH_3, HNCO, or urea at temperatures above 350°C. However, N_2 balance calculation still shows less than 30 ppm NH_3 slip above 350°C. This difference between NH_3 analysis and N_2 balance seems to be due to either adsorption of NH_3 on the catalyst or losses during the NH_3 analysis. This is plausible because it is known that NH_3 adsorbs on alumina. At this time, we do not have the necessary analytical instrumentation for a detailed analysis of the product stream. The difference between this study and others may be due to the different Cu loading, the nature of support, and the preparation technique. We will report the effect of Cu loading and the preparation method on the activity of Cu on alumina catalyst in the near future.

Katona *et al.* (12) reported that over polycrystalline platinum, NO was reduced by ammonia at a very high rate in the presence of oxygen. Also, Ramis *et al.* (13) showed that dissociative adsorption of NH_3, leading to adsorbed NH_2 and H, was the first possible step in the reduction of NO with NH_3 in the presence of oxygen. Similarly, we could speculate that the increased NO conversion activity as a function of oxygen may be due to the dissociative adsorption of ammonia over copper oxide to adsorbed NH_2 or N- and H-containing species and that these N- and H-containing species react with NO to yield nitrogen. This is plausible because 1% Cu–SG catalyst decomposes and hydrolyzes urea starting at 250°C, thus resulting in NH_3 or HNCO. Increased oxygen concentration will accelerate the reoxidation of copper patches formed as a result of the dissociative adsorption of NH_3 on CuO_x particles and move the NO reduction to lower temperatures, similar to the effect of oxygen on the oxidation of propene (17).

As seen in Fig. 2, above 400°C, NO_x conversion decreased sharply when gaseous NH_3 was the reductant instead of urea under similar reaction conditions. This indicates that NH_3 is not the only reductant during the reduction of NO with urea in the presence of oxygen and water over 1% Cu–SG catalyst. This is plausible because Koebel *et al.* (5) reported that the formation of HNCO and NH_3 increased with temperature during the decomposition/hydrolysis of urea. In addition, we found that 1% Cu–SG was highly active and selective to N_2 in the oxidation of NH_3, as shown in Fig. 4. As a result, NO reduction with NH_3 under the oxidizing condition above 400°C decreases sharply because of the increased rate of the oxidation of NH_3 to N_2.

As compared to that of 1% Cu on alumina and 3% Cu/ZSM-5 catalysts reported in Refs. (19) and (20) under similar reaction conditions, the oxidation of NH_3 and also NO reduction with NH_3 under oxidizing conditions over our 1% Cu–SG catalyst is highly active and selective to N_2. This may be due to the stabilized small CuO_x crystallites (diameter less than 5 nm based on XRD measurements) in the Al_2O_3 network induced during the sol–gel preparation used in this study. Because Centi *et al.* (19) and Ramis *et al.* (13) showed that the copper oxide was the active phase for NO reduction with NH_3 and the oxidation of NH_3 to N_2 under the oxidizing conditions, respectively.

4.2. SO_2 *Effect*

Centi *et al.* (18) reported that above 325°C, a deep sulfation of the alumina support in addition to sulfation of copper oxide was favored in the presence of SO_2 and oxygen, resulting in a detrimental effect on the regenerability and the stability of the alumina. As shown in Fig. 4, under steady state conditions (1-h reaction time for each temperature) or 2 days of exposure to the reaction gas mixture, the presence of 25 ppm SO_2 did not hinder the NO_x conversion activity at any temperature. This seems to indicate that neither deep sulfation of alumina nor the formation of $CuSO_4$ occurred during the steady state or long-term tests when there was urea in the feed. In the literature, there are conflicting reports on the activity of $CuSO_4$ for NO reduction by NH_3. Recently, Centi *et al.* (19) showed that the copper oxide was more active than the copper sulfate. This is also in agreement with our findings. In fact, we found that the activity of the catalyst decreased if the supply of aqueous urea was interrupted temporarily, e.g., for 1 h. In this case, the maximum conversion irrecoverably dropped from 99 to 89% at 450°C. Our attempt to reactivate the catalyst using propene failed. This may be due to bulk aluminum sulfate formation, leading to plugging of pores. Indeed, the measurement of BET and pore size distribution of this used catalyst revealed loss of surface area from $\sim$297 to 199 m^2/g and an increase in the average pore diameter from $D \sim 55$ to $\sim$83 Å.

5. CONCLUSIONS

- Urea is a more efficient reductant than ammonia under the same reaction conditions.
- The maximum NO_x conversion temperature is dependent on oxygen in the feed. Regardless of oxygen concentration, an S-shaped conversion-versus-temperature curve is observed under our reaction conditions.

- N_2 is the only product of NO reduction with urea and also nitrogen selectivity is independent of oxygen in the feed.
- NO_x conversion and decomposition/hydrolysis of urea was not dependent on water concentration in the feed above 2% water.
- Exposure of 1% Cu–SG to the reaction gas mixture containing 25 ppm SO_2 either under steady state condition or after 2 days on stream did not hinder activity at any temperature.
- Comparison of the activity of 1% Cu–SG obtained with 300 ppm urea to that obtained with 600 ppm NH_3 shows that the reduction of NO proceeds through not only NH_3 but also other N-containing compounds.
- The oxidation of NH_3 under the oxidizing conditions in the absence of NO over 1% Cu–SG is highly selective to N_2 and the only by-product is NO.

ACKNOWLEDGMENT

Partial financial support of this research by Ford Motor Company and NSF CTS 9985449 is gratefully acknowledged.

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