

# Selective Low Temperature NH<sub>3</sub> Oxidation to N<sub>2</sub> on Copper-Based Catalysts

Lu Gang, J. van Grondelle, B. G. Anderson, and R. A. van Santen

*Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology,  
P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

Received December 23, 1998; revised March 18, 1999; accepted April 14, 1999

TPD, TPR, UV-visible spectroscopy, and high-resolution electron microscopy (HREM) have been used to characterize the state and reactivity of alumina-supported copper-based catalysts for the oxidation of ammonia to nitrogen. The results of HREM and UV spectra show that a CuAl<sub>2</sub>O<sub>4</sub>-like phase is more active than a CuO phase for the ammonia oxidation reaction. Both surface oxygen and copper lattice oxygen can react with NH<sub>3</sub> to produce N<sub>2</sub> but surface oxygen is much more active than lattice oxygen at low temperature. For copper zeolite catalysts [Cu–O–Cu]<sup>2+</sup>-like species or small copper oxygen aggregates are the likely forms of the catalytically active centers at low temperature. The activity of CuY was increased by treating the sample with NaOH. This treatment presumably increases the amount of low temperature active centers.

© 1999 Academic Press

**Key Words:** ammonia; oxidation; copper oxides; copper zeolite; copper catalysts.

## 1. INTRODUCTION

Gas phase ammonia oxidation to nitrogen may find application in the treatment of ammonia containing industrial flue gases, in the SCR de-NO<sub>x</sub> process for ammonia slipstream treatment, in the purification of reformates for fuel-cell systems, in the deodorization of ammonia/amine containing gas, and for the small scale production of pure nitrogen as a safety gas. Previous studies show that noble metals such as Pt and Ir are very active for this reaction but are less selective. Significant amounts of nitrous oxide or nitric oxide are produced on these catalysts (1–3). Supported molybdenum and vanadium catalysts show higher selectivity but the reaction temperature needed is too high for most of the industrial applications (4–6).

Copper oxide is one of the most active catalysts and has been considered as a potential substitute for noble metal-based emission control catalysts. Sazonova *et al.* (7) investigated the activity of various catalysts for ammonia oxidation at temperatures between 250 and 400°C. They concluded that the most active and selective catalysts are V/TiO<sub>2</sub>, Cu/TiO<sub>2</sub>, and Cu-ZSM-5. Topsøe of Denmark (8) recently patented a process for catalytic low temperature

oxidation of ammonia in off-gas at temperatures between 200 and 500°C. The catalysts used were silica-supported Cu, Co, and Ni oxides doped with small amounts of noble metals (100 to 2000 ppm). They claimed that the selectivity and activity of the catalysts was improved when the catalysts were sulfated either during or prior to contact with the ammonia-containing gas. Their data show that the selectivity can be improved from 53 to 99% by sulfation. Wollner reported that high ammonia conversion (80–100%) was obtained over mixed copper–manganese oxides supported on titania catalysts at temperatures greater than about 300°C (9). However, the selectivity was not reported clearly. The results of Hodnett (10) show that Cu/Al<sub>2</sub>O<sub>3</sub>, which is a very active SCR catalyst, is also very active and selective for ammonia oxidation at a temperature of about 325°C. A pulse reaction study of various transition metal-exchanged zeolite Y catalysts revealed CuY as the most active catalyst for ammonia oxidation at low temperature (11).

The aforementioned studies show that copper oxides supported on alumina, SiO<sub>2</sub>, TiO<sub>2</sub>, or zeolites are all active ammonia oxidation catalysts. The operating temperature for these catalysts is still rather high (greater than 300°C). Little is known about the relationship between catalyst preparation and the active phase for these copper-based ammonia oxidation catalysts. In the present study various kinds of copper oxides supported on alumina and on zeolite Y have been prepared and tested as catalysts for the ammonia oxidation reaction. TPD, TPR, UV-visible spectroscopy, and high-resolution electron microscopy (HREM) were used to characterize these catalysts in an attempt to shed light on the optimal preparation for active and selective low-temperature ammonia oxidation catalysts.

## 2. EXPERIMENTAL

### 2.1. Catalyst Preparation

The starting zeolite was a commercial NaY zeolite from Akzo Co. with a Si/Al ratio of 2.4 (Na<sub>56</sub>Al<sub>56</sub>Si<sub>136</sub>O<sub>384</sub> · 249H<sub>2</sub>O). NaY was ion-exchanged in an aqueous solution of copper nitrate at room temperature for 24 h. After

filtration, it was washed with deionized water three times, dried at 110°C, and then calcined at 400°C for 2 h. The copper contents were 3.7 and 8.4 wt%, respectively. The samples will be referred to as CuY-3.7 and CuY-8.4 in the subsequent discussion.

Three Cu/Al<sub>2</sub>O<sub>3</sub> samples with Cu loadings of 5, 10, and 15 wt%, respectively, were prepared by incipient wet impregnation. The precursor for these catalysts was Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O distributed over the Al<sub>2</sub>O<sub>3</sub> support. The samples were calcined in air at 600°C for 24 h before testing. These samples will be referred to as Cu-Al-5, Cu-Al-10, and Cu-Al-15.

## 2.2. Catalyst Testing

Catalytic activity measurements were carried out in a quartz, fixed-bed reactor (4 mm internal diameter). The amount of catalyst used was about 0.2 g (250–425 μm particles). Ammonia, oxygen, and helium flow rates were controlled by mass flow meters. Water vapor was introduced by passing the helium flow through a water saturator at elevated temperature. The inlet and outlet gas compositions were analyzed using an on-line gas chromatograph equipped with a thermal conductivity detector. A quadrupole mass spectrometer was also used to monitor the different products.

## 2.3. Catalyst Characterization

High-resolution transmission electron microscopy measurements were done on a Philips CM30-T electron microscope at the National Centre for HREM at the Delft University of Technology. Diffuse reflectance UV-visible spectra were recorded at room temperature using a Shimadzu UV-2401PC spectrometer in the 190- to 900-nm wavelength range. The Kubelka–Munk function  $F(R)$  was plotted against the wavelength (in nm).

NH<sub>3</sub> and O<sub>2</sub> TPD experiments were performed using a fixed-bed flow reactor system equipped with a computer interfaced quadrupole mass spectrometer. After adsorption of NH<sub>3</sub> or O<sub>2</sub> at room temperature the TPD data were recorded by mass spectrometer while the temperature was increased from 50 to 500°C at a heating rate of 5°C/min. The TPR data were obtained on a typical computer-controlled temperature programmed reduction apparatus. The hydrogen consumption was measured using a thermal conductivity detector. The temperature was ramped from 25 to 800°C at a rate of 5°C/min.

## 3. RESULTS

### 3.1. Catalytic Oxidation of NH<sub>3</sub> on Copper Based Catalysts

The results of Table 1 show that the performance of the copper alumina catalysts is comparable to that of the copper zeolite catalysts at high temperature (>300°C). At lower

TABLE 1  
Ammonia Oxidation over Various Copper Catalysts

Catalyst	Temperature (°C)	NH <sub>3</sub> conversion (%)	N <sub>2</sub> selectivity (%)
Cu-Al-5	250	0	—
	300	21	97
	350	75	96
Cu-Al-10	250	12	96
	300	90	97
	350	100	90
Cu-Al-15	250	9	97
	300	46	96
	350	100	94
CuY-3.7	250	16	97
	300	54	98
	350	100	97
CuY-8.4	250	23	97
	300	88	98
	350	100	98
CuY-3.7 (With aftertreatment)	200	21	97
	250	56	98
	300	100	98
CuY-8.4 (With aftertreatment)	200	35	95
	250	68	97
	300	100	98

Note. Reaction condition: NH<sub>3</sub>, 1.14%; O<sub>2</sub>, 8.21%; flow rate, 74.7 N ml/min; cat. weight, 0.2 g.

temperature, the copper zeolite catalysts become superior. An optimal copper loading exists for the copper alumina catalysts. For CuY catalysts, increased loading led to higher activity.

Ione *et al.* (12) and Schoonheydt *et al.* (13) reported that the polynuclear nickel or copper ions were formed in the framework of zeolite Y when NaY was ion exchanged with an aqueous Ni(NO<sub>3</sub>)<sub>2</sub> or Cu(NO<sub>3</sub>)<sub>2</sub> solution at pH 6–7. These polynuclear cations gave a higher activity for CO oxidation than the mononuclear state. Suzuki *et al.* (14, 15) successfully prepared a highly dispersed nickel oxide catalyst, which was also a very good CO oxidation catalyst, by hydrolyzing the Ni<sup>2+</sup> exchanged zeolite Y with an aqueous solution of NaOH or ammonia at various pH values. In this research the effect of NaOH aftertreatment has also been examined. We have used the procedure reported by Suzuki *et al.* (14, 15) to study the effect of NaOH aftertreatment on CuY catalysts. The results are included in Table 1.

As can be seen in Table 1, the activity of the two copper zeolite catalysts for ammonia oxidation increased significantly following NaOH treatment. This significantly higher activity was probably induced by the formation of small metal oxides in the zeolite. It should be noted that the CuY catalysts are active at temperatures as low as 200°C. Temperatures of at least 250°C are necessary for reaction on Cu alumina catalysts.

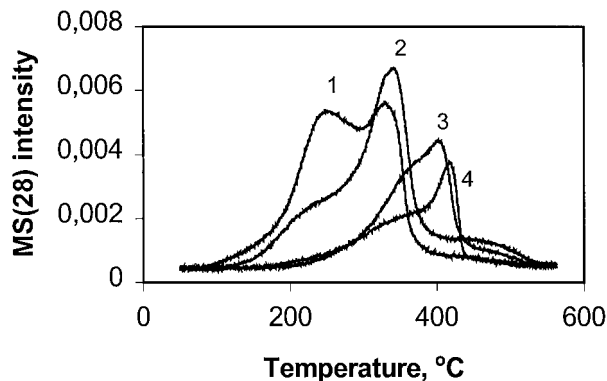


FIG. 1.  $N_2$  production profiles on an oxidized Cu-Al-10 catalyst during  $NH_3$  TPD (obtained during four consecutive  $NH_3$  exposures).

### 3.2. TPD and TPR Profiles for Copper Based Catalysts

Four successive cycles consisting of isothermal  $NH_3$  adsorption at  $50^\circ C$  followed by TPD up to  $500^\circ C$  were carried out on an oxidized Cu-Al-10 catalyst. The catalyst was heated in  $O_2/He$  flow at  $500^\circ C$  for 2 h before the first cycle.

After a TPD run the sample was cooled in flowing helium to  $50^\circ C$ .  $NH_3$  was then re-adsorbed and the  $N_2$  TPD spectrum was measured. The nitrogen production profiles for four such successive cycles of  $NH_3$  TPD experiments are shown in Fig. 1. It can be seen that there are two peaks around  $250$  and  $330^\circ C$  for the first cycle TPD. In the second cycle, the first peak almost disappeared while the second peak shifted to a slightly higher temperature. In the third and fourth cycles, the peak moved to even higher temperatures. As copper is dispersed very well on alumina (see HREM results) and since no nitrogen is produced during  $NH_3$  TPD on alumina alone, the possibility of different active centers for the two peaks can be excluded. We propose that the first peak is caused by the reaction of adsorbed surface oxygen with  $NH_3$  and that the second peak is caused by reaction of ammonia with subsurface or possibly with lattice oxygen. After the first TPD cycle the surface oxygen is almost totally consumed. This explains the disappearance of the first peak in the latter cycles.

Figures 2 and 3 compare  $NH_3$  and  $N_2$  desorption profiles measured during  $NH_3$  TPD experiments on copper zeolite catalysts that had been subjected to NaOH after-treatment. The zeolite catalysts were pretreated in  $O_2$  at  $400^\circ C$  for 2 h prior to the experiments. The amount of catalysts is same for all the samples used in these experiments. Only one cycle of  $NH_3$  TPD data are shown in Figs. 2 and 3 since the successive cycles measured on these zeolite catalysts showed no  $N_2$  production. This means that either no oxygen existed on the copper zeolite catalysts or that the copper was completely reduced after the first cycle of the  $NH_3$  TPD experiment. The desorption of  $NH_3$  on NaY showed only one peak at  $150^\circ C$ , whereas two peaks (at  $150$  and  $350^\circ C$ ) were

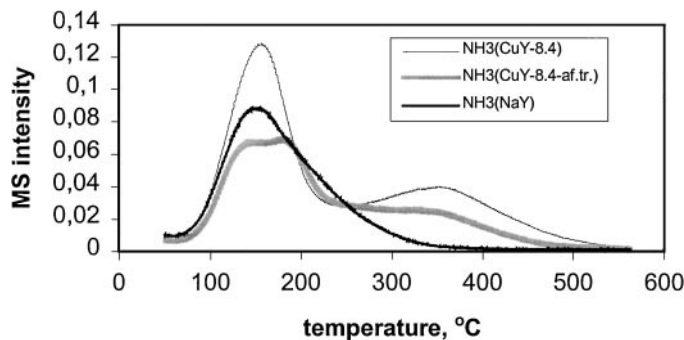


FIG. 2.  $NH_3$  TPD profiles on copper zeolite catalysts (catalyst pretreatment,  $400^\circ C$  in  $O_2$  heated for 2 h).

observed on the CuY-8.4 catalyst. The introduction of Cu into NaY not only creates a more strongly bonded  $NH_3$  adsorption center but it also increases the amount of weakly bonded  $NH_3$  centers. After NaOH treatment, a third ammonia adsorption center seemed to be produced, although this center is not very strong. There was almost no  $N_2$  produced on NaY, while on CuY-8.3 there were two  $N_2$  peaks at the temperature at which ammonia desorption occurred. This shows that apparently there were two active ammonia oxidation centers created by the introduction of Cu into NaY. The first active center (at around  $150^\circ C$ ) is very interesting as it indicates that ammonia oxidation at low temperature on copper catalysts is possible. A third active center (at around  $190^\circ C$ ) for ammonia oxidation is created following NaOH treatment. Comparison of the  $N_2$  production profiles measured on the alumina-based catalyst (Cu-Al-10) and on the zeolite-based catalyst shows that CuY is apparently much more active than Cu-Al $_2$ O $_3$  at low temperature ( $<200^\circ C$ ).

Catalysts used in  $O_2$  TPD were all treated in  $O_2$  at  $400^\circ C$  for 2 h and then cooled to room temperature. For  $H_2$  TPR experiments, however, all of the catalysts were pretreated in He at  $400^\circ C$  for 2 h. The amount of catalyst used for

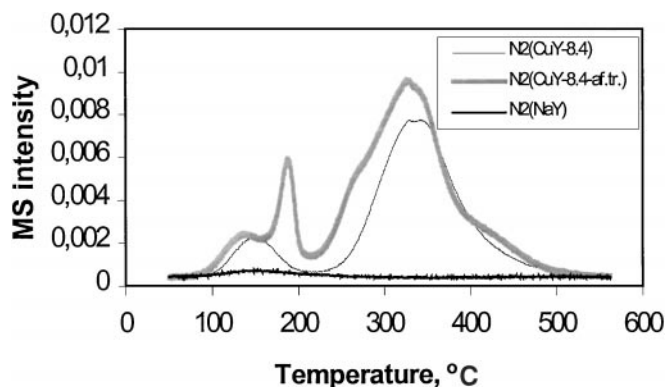


FIG. 3.  $N_2$  production profiles on CuY catalysts during  $NH_3$  TPD (catalyst pretreatment,  $400^\circ C$  in  $O_2$  heated for 2 h).

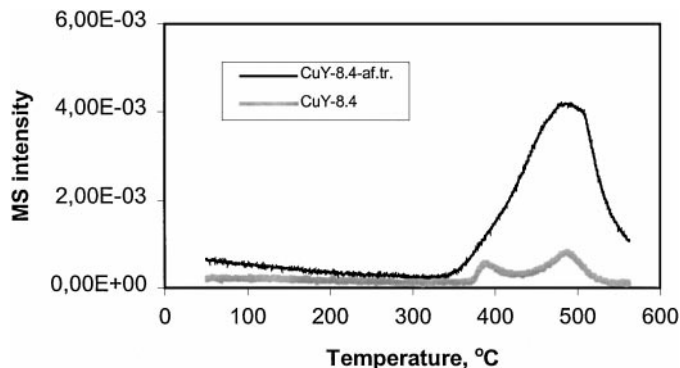


FIG. 4. O<sub>2</sub> desorption on CuY catalyst with and without aftertreatment.

all O<sub>2</sub> TPD and H<sub>2</sub> TPR experiments is the same, so the peak areas of different catalysts can be compared directly with each other. It can be seen from Fig. 4. that two peaks exist in the O<sub>2</sub> TPD profiles on the CuY-8.4 catalyst. Since no O<sub>2</sub> desorption was observed on NaY, these two O<sub>2</sub> desorption peaks must be caused by the Cu in the zeolite. After the NaOH treatment the amount of O<sub>2</sub> desorbed was greatly increased. Many investigations (16, 17) on the complete oxidation of CO and hydrocarbons have shown that their reactivities directly depend on the capacity of oxygen adsorption. Here it also appears that oxygen adsorption relates to the rate of ammonia oxidation. Figure 5 shows the TPR profiles of the CuY catalyst with and without the aftertreatment. Integration of the peaks reveals that the amount of reducible copper ions increased by a factor of 1.4 when the CuY catalyst was treated with NaOH.

### 3.3. HREM Results

No metal oxide particles were observed on the alumina surface of the Cu-Al-5 and the Cu-Al-10 catalysts (see Fig. 6). Metal particles with diameters ranging between 5 and 10 nm were observed on the Cu-Al-15 catalyst (see Fig. 7). The Cu-Al-15 catalyst was black in color, probably

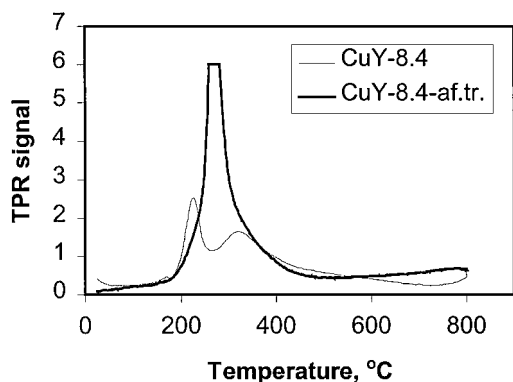


FIG. 5. TPR by H<sub>2</sub> profiles for CuY with and without aftertreatment.

due to the formation of these CuO particles on the alumina surface. By contrast the catalysts with lower copper loadings (Cu-Al-5 and Cu-Al-10), on which no particles could be detected, were green in color.

No differences in the HREM images were observed on samples of the catalyst CuY-3.7 before and after NaOH treatment. However, a very small amount of particles was discovered on the outer surface of the zeolite crystals for CuY-8.4 (see Figs. 8 and 9). Again there was no big difference observed before and after NaOH treatment.

### 3.4. UV-Visible Spectroscopy

The Cu<sup>2+</sup> ion has a 3d<sup>9</sup> electronic structure. In the presence of a crystal field generated by ligands or oxygen ions, *d-d* transitions appear in the visible or near-infrared range. For an octahedral environment, transitions appear between 600 and 800 nm depending on the crystal field strength. Table 2 shows the summary of our assignments of the UV spectral bands measured on different kind of catalysts.

Figure 10 shows the UV spectra measured on copper-alumina catalysts with different copper loadings. It can be seen that there is a weak absorption band at about 740 nm for Cu-Al-5 and Cu-Al-10 catalysts. This band shifts to 650 nm for the Cu-Al-15 catalyst. According to previous studies (18) the band at 650 nm corresponds to a CuO phase. A UV spectrum measured on CuO showed indeed that a broad band around 650 nm exists (see Fig. 11). The shift of this band to higher wavelength indicates that the distance between Cu<sup>2+</sup> and the ligands or oxygen ions increases; i.e., the Cu<sup>2+</sup>-O<sup>2-</sup> bond should exhibit greater ionic character.

It can be seen from Fig. 12 that the absorption band appears at about 840 nm for CuY samples without NaOH aftertreatment. This indicates the existence of isolated Cu<sup>2+</sup> ions of square pyramid symmetry (19–21). After NaOH treatment, this band shifts to about 750 nm, similar to the bands observed on the alumina-based copper catalysts (Cu-Al-5 and Cu-Al-10).

CuY-3.7 and CuY-3.7 (with and without aftertreatment) were reduced in H<sub>2</sub>/He at 500°C for 2 h before measuring the UV spectra (see Fig. 13). The appearance of an

TABLE 2

Summary of the Assignments of UV Spectral Bands Measured on Different Copper Catalysts

Absorption wavelength	Copper species	Support
840 nm	Cu <sup>2+</sup> ions	Zeolite Y
740–750 nm	CuAl <sub>2</sub> O <sub>4</sub> -like phase or [Cu-O-Cu] <sup>2+</sup> species	Al <sub>2</sub> O <sub>3</sub> , Zeolite Y
650 nm	CuO phase	No support or Al <sub>2</sub> O <sub>3</sub>
560 nm	Cu <sup>0</sup> metal phase	No support or Zeolite Y

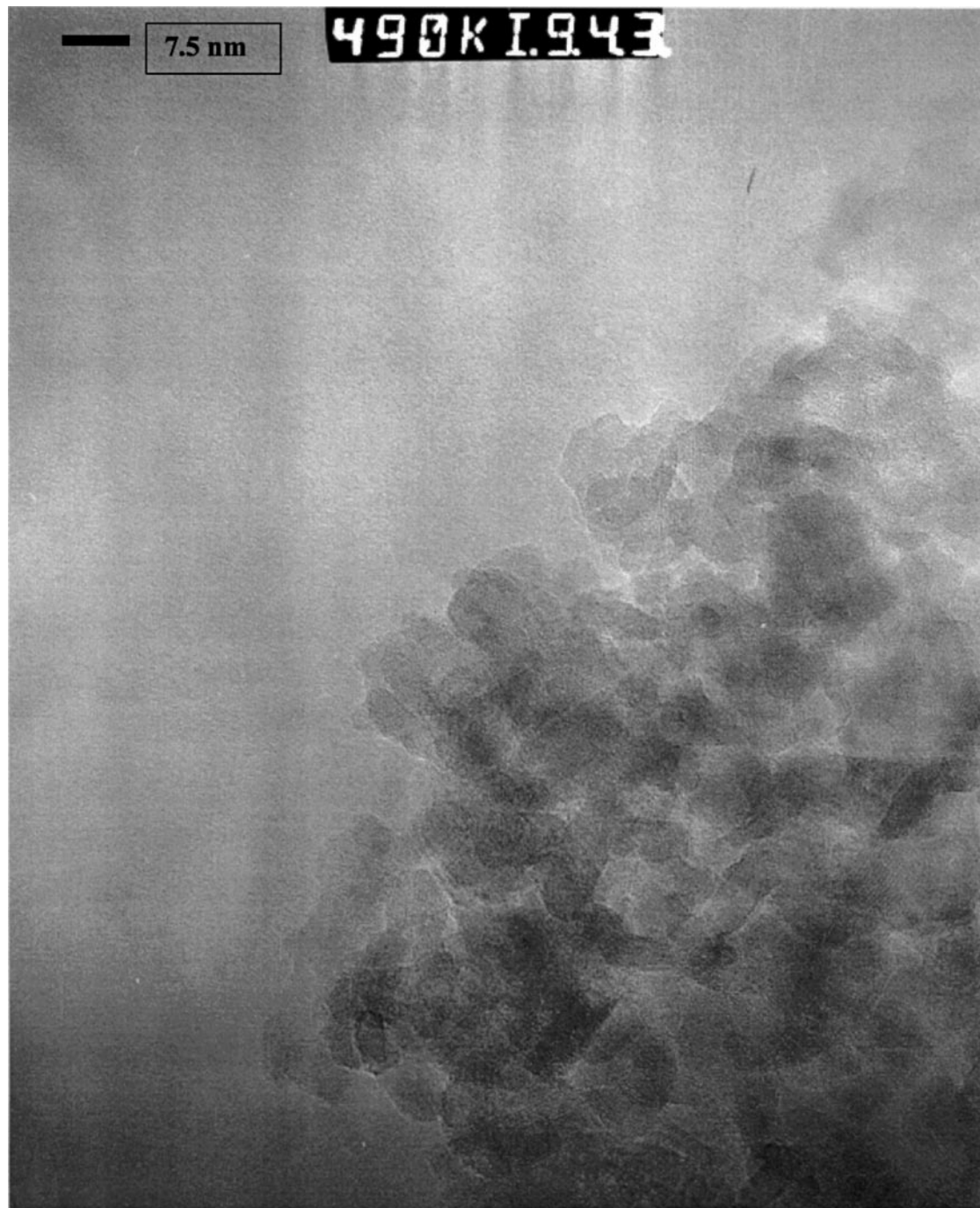


FIG. 6. An HREM image of the Cu-Al-10 catalyst showing the absence of any detectable metal oxide particles.

absorption maximum at 560 nm indicates the creation of a metallic copper phase (21). The absorption band at 840 nm measured on CuY-3.7 means that some  $\text{Cu}^{2+}$  ion cannot be reduced. The intensity of the absorption band at 560 nm ( $\text{Cu}^0$ ) did increase at the expense of the 840-nm band ( $\text{Cu}^{2+}$ ), indicating that some reduction of copper is possible following NaOH treatment.

#### 4. DISCUSSION

The most extensive investigation of  $\text{Cu}/\text{Al}_2\text{O}_3$  catalysts has been performed by Friedman *et al.* (22). By applying several techniques and combining results with previous work, a coherent model of the surface structure was developed, resulting in the following conclusions

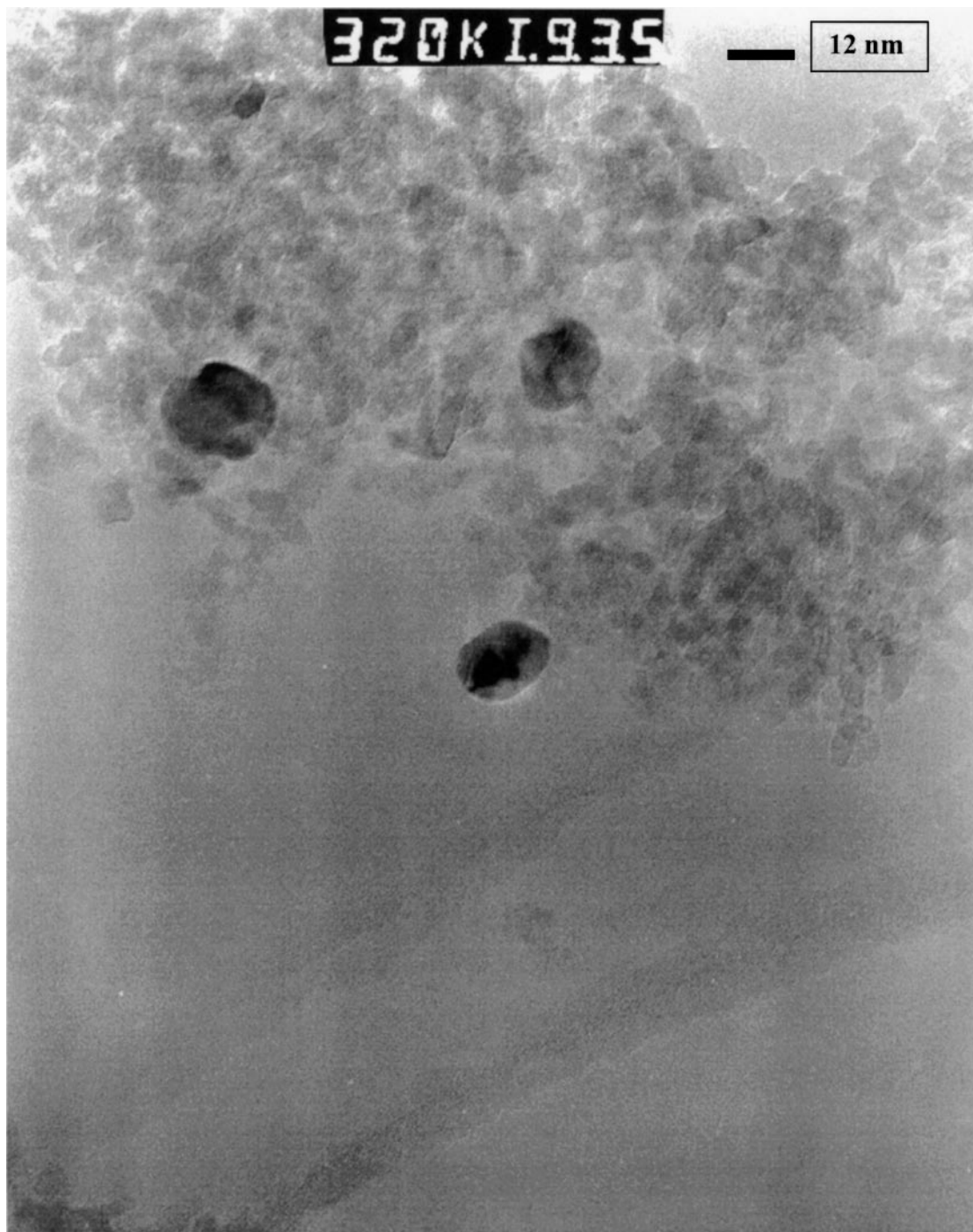
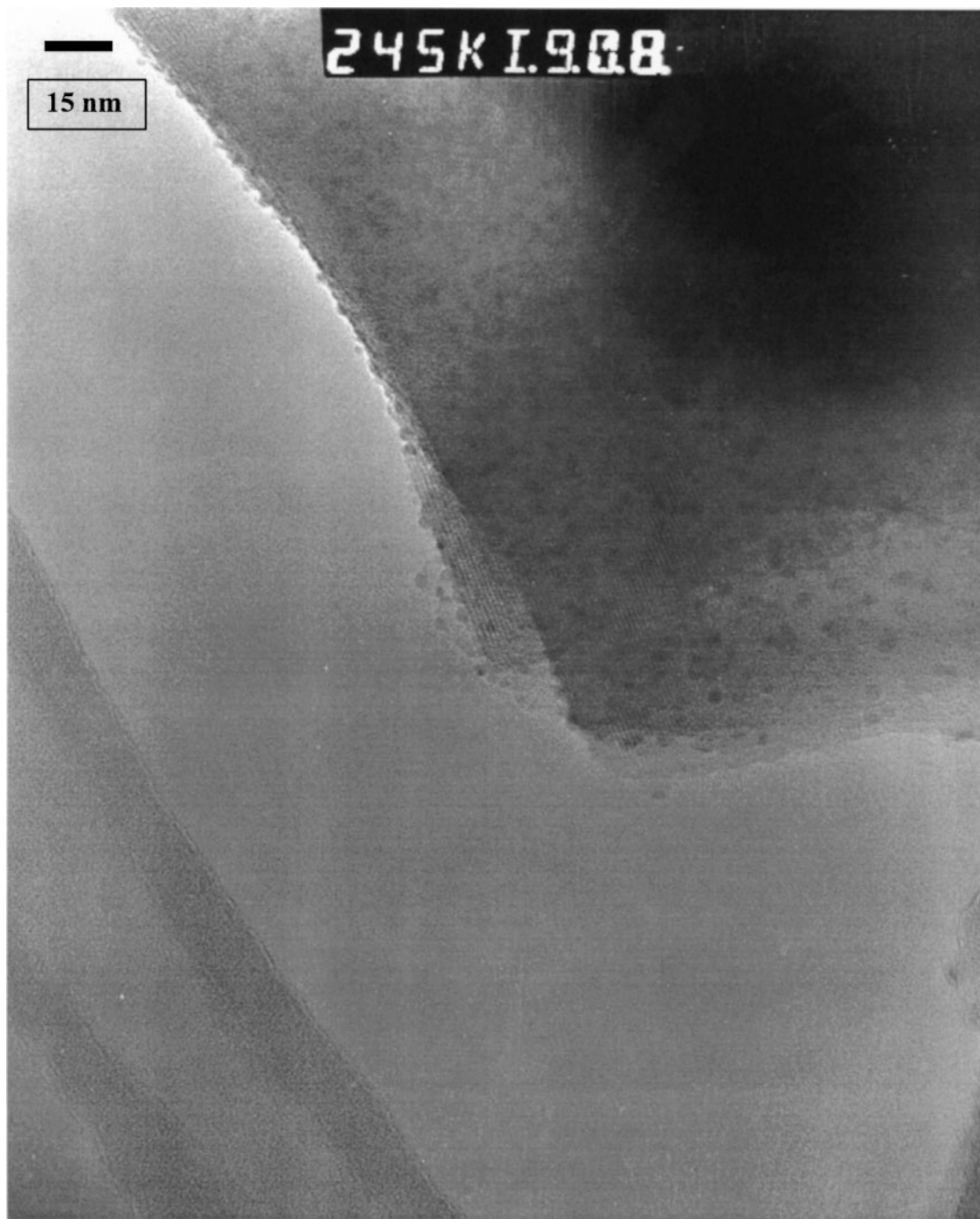


FIG. 7. An HREM image of the Cu-Al-15 catalyst showing the presence of metal oxide particles with diameters between 5 and 10 nm.

(22, 23): (i) At low metal loadings and at calcination temperature below 500°C the formation of a surface spinel (which resembles  $\text{CuAl}_2\text{O}_4$ ) predominates. Most of the  $\text{Cu}^{2+}$  ions are in a distorted octahedral geometry, unlike bulk  $\text{CuAl}_2\text{O}_4$ , where about 60% are tetrahedral and 40% octahedral. (ii) At higher metal loadings,

segregation of bulk-like CuO may also occur. (iii) Calcination at 900°C leads to formation of bulk  $\text{CuAl}_2\text{O}_4$ . Our HREM and UV measurements also show that no CuO particles form on the alumina surface for Cu-Al-5 and Cu-Al-10 catalysts but that particles are present on the Cu-Al-15 sample. The fact that the performance of Cu-Al-10



**FIG. 8.** An HREM image of the CuY-8.4 catalyst (without NaOH aftertreatment) showing the presence of very small particles (diameter  $<5$  nm) on the outer surface of the zeolite Y crystal.

is better than that of the Cu-Al-15 catalyst supports the conclusion that a  $\text{CuAl}_2\text{O}_4$ -like phase is more active than CuO phase in the ammonia oxidation reaction.

At least three types of copper species in CuY have been described in the literature: (i) Isolated ions interacting with the framework Al, either without an extraframework ligand

or with an extraframework O or OH ligand. These species show a different reactivity (24). (ii) Polymeric chains or multinuclear species (often called small copper-oxygen aggregates), for instance  $[\text{Cu-O-Cu}]^{2+}$  inside the zeolite supercage (25-27). (iii) CuO particles on the external surface of zeolite crystals (28). Although at high loading the HREM



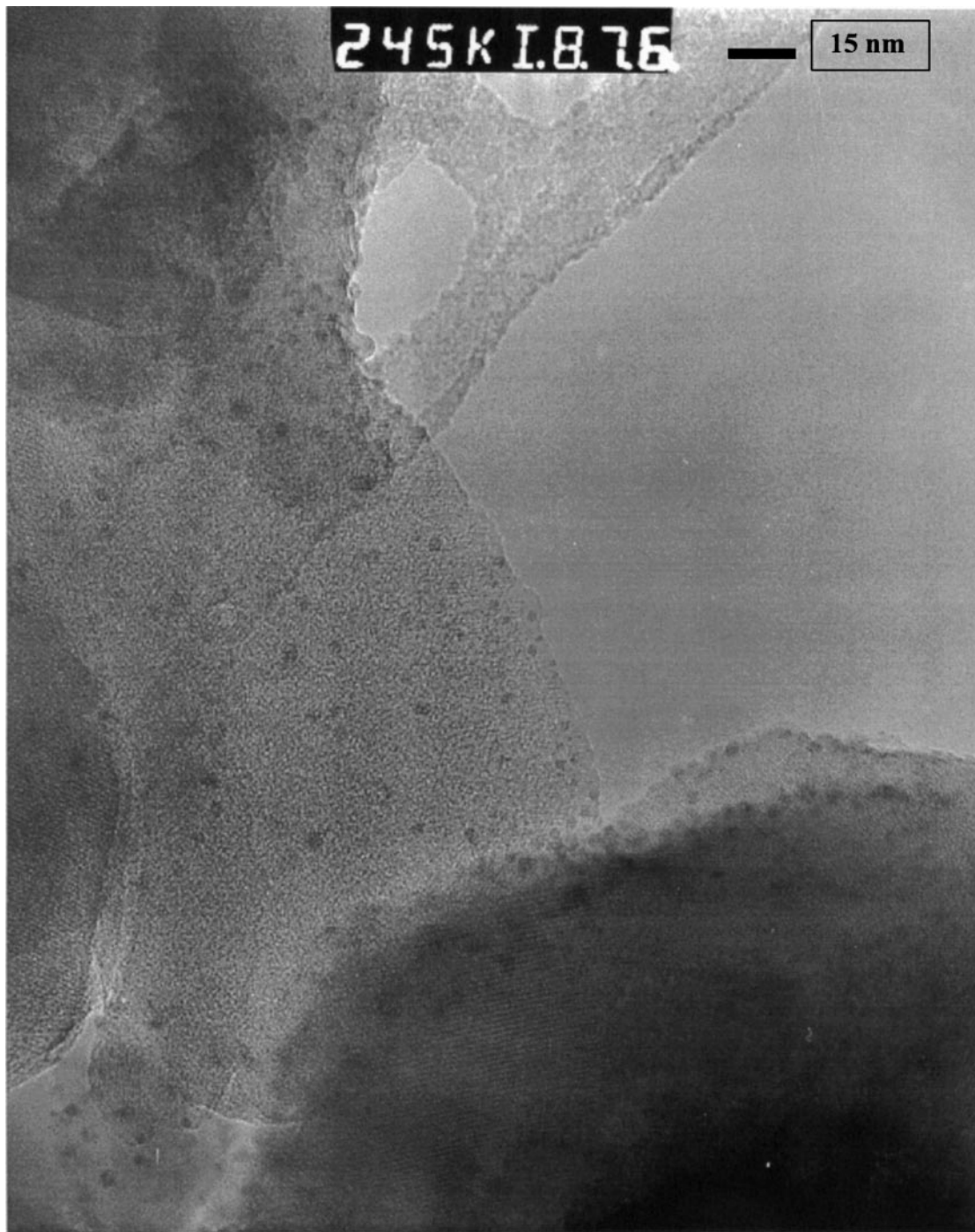


FIG. 9. An HREM image of the CuY-8.4 catalyst (following NaOH aftertreatment) shows that NaOH treatment produces no visible effects on the size of the small particles present on the zeolite outer surface.

results show some CuO particles on the outer surface of the zeolite, the UV spectra show no apparent CuO adsorption band intensity at 650 nm. This means that only a small amount of copper is on the surface of the zeolite crystals as CuO as compared with the amount of copper inside the pores of zeolite. Since the CuO phase is not very active

for ammonia oxidation it can be concluded that a copper phase occluded in the micropores of the zeolite, different from CuO, forms the main active centers.

Since the diameter of an ammonia molecule is larger than the diameter (2.2 Å) of entrance windows into the sodalite cages in CuY zeolites, Cu<sup>2+</sup> ions that are accessible to



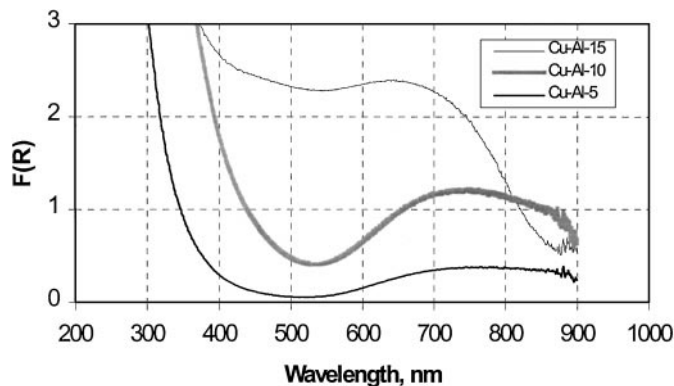


FIG. 10. UV spectra measured on copper alumina catalysts with different copper loadings (5, 10, and 15% (by weight)).

adsorbed  $\text{NH}_3$  have to be located in the supercages. According to earlier studies (29), they are localized at  $\text{S}_{\text{II}}$  sites, i.e., near the centers of six-membered rings of the sodalite cages. A different chemical composition of six-membered rings (Si/Al ratio) could result in the existence of three types of  $\text{S}_{\text{II}}$  sites in the supercages, since according to Lowenstein's rule the number of aluminum atoms in the ring can be either one, two, or three. The results of  $\text{NH}_3$  TPD on CuY-8.4 show only two active centers ( $\text{S}_{\text{II}}^1$  and  $\text{S}_{\text{II}}^2$ ). However, a third center ( $\text{S}_{\text{II}}^3$ ) appears after NaOH treatment. It is suggested that either the  $\text{S}_{\text{II}}^1$  and  $\text{S}_{\text{II}}^3$  are very similar or that the amount of  $\text{S}_{\text{II}}^3$  centers is small. After NaOH treatment, some of the  $\text{Cu}^{2+}$  ions in  $\text{S}_1$  (in the center of the hexagonal prism) migrate to the  $\text{S}_{\text{II}}^3$  sites of the supercages. The results of  $\text{O}_2$  TPD and TPR strongly indicate this migration. The UV spectra for reduced CuY samples also indicate that more  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^0$  after NaOH treatment.

Comparison of the UV spectra for CuY samples with and without aftertreatment shows that there are mainly isolated copper ions in the zeolite before NaOH treatment. The shift of the absorption band from 840 nm to 750 nm after treatment indicates the creation of  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  inside the zeolite supercage or the presence of small copper-oxygen

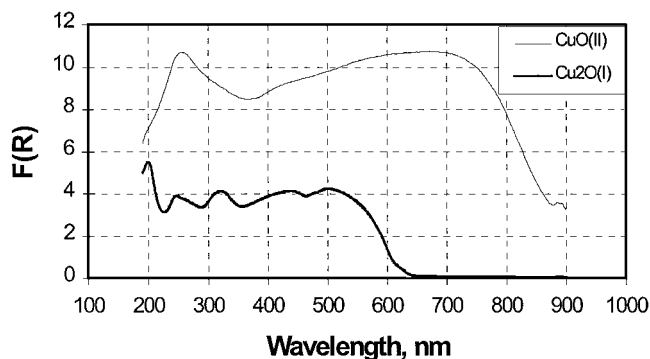


FIG. 11. UV spectra measured using bulk  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  oxides.

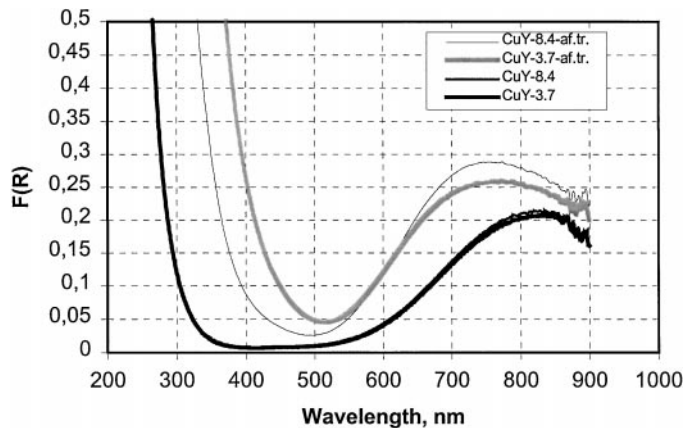


FIG. 12. UV spectra for CuY-based catalysts.

aggregates (25–27). Perhaps copper ions are first deposited as  $\text{Cu}(\text{OH})_2$  by hydroxylation both in the supercages and in the sodalite cages. Part of the  $\text{Cu}(\text{OH})_2$  then moves to the three  $\text{S}_{\text{II}}$  sites in the supercages during this hydroxylation process. Upon dehydration of  $\text{Cu}(\text{OH})_2$ ,  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  complexes are produced which are thought to be the active centers for low temperature ammonia oxidation. Actually  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  already exists in CuY prior to NaOH treatment. According to prior studies (30),  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  species are present even at low ion-exchanged levels in CuY. The concentration of  $[\text{Cu}-\text{O}-\text{Cu}]^{2+}$  species increases with the Cu loadings. This is in agreement with the finding that low temperature active centers for ammonia oxidation exist on an untreated CuY catalyst.

## 5. CONCLUSIONS

HREM and UV-visible spectral measurements showed that no metal oxide particles form on alumina at copper loadings below 10% (by weight). At higher loadings a  $\text{CuO}$  phase was detected. The fact that the performance of

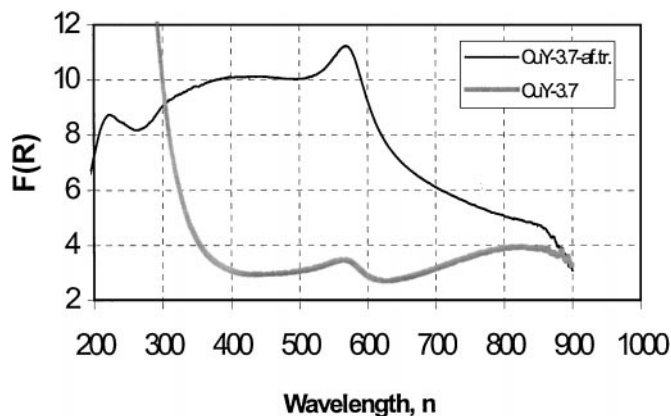


FIG. 13. UV spectra for reduced CuY samples.

10 wt% Cu/Al<sub>2</sub>O<sub>3</sub> was better than that of 15 wt% (Cu–Al–15) supports the conclusion that a “CuAl<sub>2</sub>O<sub>4</sub>”-like surface phase is more active than a CuO phase in the ammonia oxidation reaction. NH<sub>3</sub> TPD profiles on Cu–Al–10 indicate that both surface oxygen and lattice oxygen can react with NH<sub>3</sub> to produce N<sub>2</sub>. However, surface oxygen is much more active than lattice oxygen at low temperature.

NH<sub>3</sub> TPD on CuY catalysts shows three types of active centers. Two of these are active at low temperature (below 200°C) and one is active at a higher temperature (above 300°C). The existence of low temperature active centers indicates that ammonia oxidation at low temperature on copper catalysts is possible. According to the UV spectra, the [Cu–O–Cu]<sup>2+</sup>-like species or small copper oxygen aggregates are responsible to the low temperature active centers. However, the amount of low temperature active centers or the concentration of [Cu–O–Cu]<sup>2+</sup> species is small prior to NaOH treatment. The NaOH treatment of CuY increases the amount of low temperature active centers.

The above results apparently indicate that the environment or the type of active copper species is very important for low temperature ammonia oxidation and is strongly related with different supports and preparation methods.

#### ACKNOWLEDGMENTS

The authors kindly thank Dr. P. J. Kooyman, National Centre for High Resolution Electron Microscopy, Delft University of Technology, The Netherlands, for performing the HRTM experiments. Financial support has been supplied by the Netherlands Foundation for Chemical Research (SON) of STW.

#### REFERENCES

- Li, Y., and Armor, J. N., *Appl. Catal. B* **13**, 131 (1997).
- Delaney, J. E., and Manogue, W. H., “Proceedings, 5th International Congress on Catalysis, Palm Block, 1972” (J. W. Hightower, Ed.), North Holland, Amsterdam, 1973.
- Ostermaier, J. J., Katzer, J. R., and Manogue, W. H., *J. Catal.* **41**, 277 (1976).
- Boer, M. de, van Dillen, A. J., and Geus, J. W., *Catal. Lett.* **11**, 227 (1991).
- Biermann, J. J. P., Janssen, F. J. J. G., and Geus, J. W., *J. Mol. Catal.* **60**, 229 (1990).
- Vogt, E. T. C., Ph.D. thesis, University of Utrecht (1988).
- Sazonova, N. N., Simakov, A. V., and Veringa, H., *React. Kinet. Catal. Lett.* **57**(1), 71 (1996).
- Dannevang, F., US patent 5,587,134 (1996).
- Wollner, A., and Lange, F., *Appl. Catal. A* **94**, 181 (1993).
- Deconinck, C., Knuttel, N., Curtin, T., and Hodnett, B. K., Presented at the “2nd World Conference on Environmental Catalysis, Miami, USA, Nov. 1999.” [Conference proceedings to be published in *Catal. Today*.]
- Al'tshuller, O. V., and Kushnerev, M. Ya., *Probl. Kinet. Katal.* **15**, 56 (1973).
- Ione, K. G., Kuznetsov, P. N., and Romannikov, V. N., “Application of Zeolite in Catalysis.” Akademiai Kiado, Budapest, 1979.
- Schoonheydt, R. A., Ione, K. G., Kuznetsov, P. N., and Romannikov, V. N., *J. Catal.* **43**, 292 (1976).
- Suzuki, M., Tsutsumi, K., Takahashi, H., and Saito, Y., *Zeolites* **8**, 284 (1988).
- Suzuki, M., Tsutsumi, K., Takahashi, H., and Saito, Y., *Zeolites* **8**, 387 (1988).
- Watanabe, N., Yamashita, H., Miyadera, H., and Tominaga, S., *Appl. Catal. B* **8**, 405 (1996).
- Golunski, S. E., Hatcher, H. A., Rajaram, R. R., and Truex, T. J., *Appl. Catal. B* **5**, 367 (1995).
- Marion, M. C., Garbowski, E., and Primet, M., *J. Chem. Soc. Faraday Trans.* **86**(17), 3027 (1990).
- Lever, A. B. P., “Inorganic Electronic Spectroscopy.” Elsevier, Amsterdam, 1984.
- Strohmeier, B. R., Leyden, D. E., and Hercules, D. M., *J. Catal.* **94**, 514 (1985).
- Praliaud, H., Mikhailenko, S., Chajar, Z., and Primet, M., *Appl. Catal. B* **16**, 359 (1998).
- Friedman, R. M., Freeman, J. J., and Lytle, F. W., *J. Catal.* **55**, 10 (1978).
- Park, P. W., and Ledford, J. S., *Appl. Catal. B* **15**, 221 (1998).
- Centi, G., and Perathoner, S., *Appl. Catal. A* **132**, 179 (1995).
- Wang, Z., Sklyarov, A. V., and Keulks, G. W., *Catal. Today* **33**, 291 (1997).
- Beutel, T., Sarkany, J., Lei, G. D., Yan, J. Y., and Sachtler, W. M. H., *J. Phys. Chem.* **100**, 845 (1996).
- Dedecek, J., and Wichterlova, B. N., *J. Phys. Chem.* **98**, 5721 (1994).
- Praliaud, H., Mikhailenko, S., Chajar, Z., and Primet, M., *Appl. Catal. B* **16**, 359 (1998).
- Breck, D. W., “Zeolite Molecular Sieves.” Wiley-Interscience, New York-London-Sydney-Toronto, 1974.
- Conesa, J. C., and Soria, J., *J. Chem. Soc. Faraday Trans. I* **75**, 406 (1979).