Preparation effects on the activity of Cu-ZSM-5 catalysts for NO decomposition

Yanping Zhang, Katie M. Leo, Adel F. Sarofim, Zhicheng Hu[a]
and Maria Flytzani-Stephanopoulos[b]

Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, MA 02139, USA
[a]*Engelhard Co., Iselin, NJ 08830, USA*
[b]*Department of Chemical Engineering, Tufts University, Medford, MA 02155, USA*

Received 15 July 1994; accepted 17 August 1994

Effects of Cu-ZSM-5 catalyst preparation on the activity of "over-exchanged" copper for NO decomposition are reported. The Cu-ZSM-5 catalysts were prepared by incorporating Cu^{2+} cations into ZSM-5 zeolites from an aqueous cupric acetate solution adjusted to different pH values by adding either acetic anhydride or aqueous ammonia in the solution. The Cu^{2+} exchange levels increased with increasing pH level. STEM/EDX analysis identified CuO particles (5–6 nm) on the zeolite surface for the materials exchanged at $pH > 6$. Conversion and kinetics measurements of NO decomposition to N_2 over these catalysts showed that the "over-exchanged" copper was not active. Short-time wash with aqueous ammonia removed this copper. The catalyst activity correlated very well with the amount of copper remaining in the ZSM-5 channels.

Keywords: NO decomposition; surface Cu and ion-exchanged Cu; pH effects; STEM analysis of Cu-ZSM-5

1. Introduction

The direct catalytic decomposition of nitric oxide is the simplest method for removing NO_x from flue gas streams since it involves no reductant addition, such as ammonia or hydrocarbons. However, a stable active catalyst, resistant to water vapor and poisons, such as SO_2, still eludes the art. The most promising catalyst for NO decomposition is presently the copper ion-exchanged ZSM-5 zeolite, first reported by Iwamoto et al. [1,2] to have stable steady-state activity even in the presence of oxygen.

All reports of Cu-ZSM-5 catalyst activity agree that excessively copper ion-exchanged ZSM-5 catalysts give higher N_2 yields [1–3]. Here, "excessively" indicates above the theoretical ion exchange level, corresponding to one divalent Cu^{2+} ion for every two $[AlO_2]^-$ sites in the zeolites.

The "over-exchanged" copper has been attributed to $[CuOH]^+$, i.e., to both cupric cations, Cu^{2+}, and anions, OH^-, carried into the zeolite from an aqueous solution [4–6]. Iwamoto et al. [7] reported that it is impossible to prepare excessively copper ion-exchanged ZSM-5 zeolites from aqueous solutions of cupric nitrate or sulfate. However, increasing the pH of the solution by addition of basic compounds readily achieved "over-exchanged" copper in the ZSM-5 [8]. The Cu loading increased with pH from 4 to 9 and reached a nearly constant value above pH = 9. The conversion of nitric oxide to nitrogen over catalysts with Cu^{2+} exchange from 130–150% was approximately the same. Campa et al. [9] also reported that the catalytic activity remains almost constant above 100% Cu^{2+} exchange and was suggested to be due to formation of Cu_xO_y microclusters on the surface. Recently, Valyon and Hall [6] reported that the NO decomposition activity of ZSM-5 catalysts correlated with the pH values, 4 and 6, of the aqueous cupric acetate solution used for ion exchange.

Presently, it is still not known what the state of "over-exchanged" copper is in the ZSM-5 materials. The probability exists that at higher pH values deposition of $Cu(OH)_2$ in the zeolite pores takes place, resulting in "deposited" rather than "exchanged" copper. Recently, Sarkany et al. [5] used TPR/TPD and FTIR to characterize the "over-exchanged" copper in ZSM-5. An aqueous solution of $Cu(ac)_2$ at pH = 7 was used for the exchange. Two copper–oxygen species were identified in addition to Cu^{2+} ions and attributed to CuO and $[Cu–O–Cu]^+$ [5]. These results were not correlated with the pH of the salt solution. Thus, it remains unclear whether the oxidic copper is the result of $Cu(OH)_2$ precipitation or $[CuOH]^+$ exchange.

In this study, we prepared Cu-ZSM-5 catalysts from aqueous $Cu(ac)_2$ solutions adjusting the pH in the range of 4.5–7.5, and analyzed the activity of the resulting materials for NO decomposition. The "over-exchanged" copper was characterized by a wet chemical technique (aqueous ammonia wash), followed by inductively coupled plasma (ICP) spectrometry and by scanning transmission electron microscopy (STEM) with energy dispersion X-ray (EDX) microprobe analysis.

2. Experimental

A first set of catalysts was prepared by exchanging Cu^{2+} cations into ZSM-5 from dilute aqueous $Cu(ac)_2$ solutions. The parent zeolite was a Na^+-ZSM-5 (Si/Al = 21.5) zeolite in fine powder form obtained from the Davison Chemical Division of W.R. Grace & Co. (SMR 6-2826-1192). The following preparation procedure was used in this study. First, cupric acetate was dissolved in deionized water to form an aqueous solution with a concentration of 0.007 M and initial pH of 5.74. Second, the pH of the solution was adjusted by adding either acetic anhydride or aqueous ammonia into the solution to a desired pH value. The ZSM-5 particles were added into the solution in amounts corresponding to replacing all the Na^+

ions in the ZSM-5 by half the number of Cu^{2+} in the cupric acetate solution. The mixture was then vigorously stirred by a magnetic stirrer at room temperature for 19 h. Finally, the sample was washed with deionized water at room temperature for 30 min. After filtration, the samples were dried in air at 100°C overnight. Seven Cu-ZSM-5 catalysts were prepared according to this procedure at pH of 4.5, 4.9, 5.74, 6.0, 6.5, 7.0 and 7.5.

Another Cu-ZSM-5 catalyst was prepared in a different fashion for comparison. The ZSM-5 zeolite was first ion-exchanged with Cu^{2+} using the same procedure as above, except that aqueous ammonia was gradually added to the slurry of ZSM-5 and cupric acetate solution to a final pH value of 7.0, after the ZSM-5 zeolite had reached equilibrium in exchange with Cu^{2+} at the pH value of 5.7 at room temperature for 19 h. This catalyst was tested for NO decomposition to examine the effect of increasing the pH of the solution after Cu^{2+}-exchange had taken place at lower pH.

A second set of Cu-ZSM-5 samples with 10–141% Cu exchange levels were prepared at pH = 5.7. The procedure was the same as that described above. Low Cu exchange levels were achieved by adjusting the ratio of Cu^{2+} to Na^+ in the slurry. Repeated exchanges were used to increase the Cu exchange level. The highest Cu exchange level, 141%, was obtained after three consecutive exchanges at the conditions described above.

Elemental analyses were performed by ICP (Perkin-Elmer Plasma 40) after the catalyst samples were dissolved in HF (48%) solution, and the solution was diluted to 2% HF by deionized water. Metal ratios, such as Si, Cu and Na, to Al were calculated based on the elemental contents measured by ICP. In the text, the catalysts are identified in the following way: Cu(exchange level)-ZSM-5(pH), for example, Cu(97)-ZSM-5(6.0), where 100% Cu^{2+} exchange denotes one Cu^{2+} ion neutralizing two Al^-, i.e. the atomic ratio Cu/Al = 0.5.

The preparation and properties of the two sets of Cu-ZSM-5 catalysts in this study are listed in table 1. It is worth noting that the Cu^{2+} ion-exchange with Na^+ is non-stoichiometric in the first set of samples.

The prepared materials were evaluated with respect to copper loss in short-time wash experiments with aqueous ammonia solutions. For these experiments, 0.1 g of Cu-ZSM-5 catalyst was washed with aqueous ammonia (5 ml of 29.5% aqueous ammonia +50 ml of deionized water) at room temperature for 6 min. The washed Cu-ZSM-5 samples were analyzed by ICP to determine potential copper loss from the Cu-ZSM-5 samples.

The catalysts prepared in this study were characterized by X-ray diffraction (XRD, Rigaku 300) to examine the crystal structures, as well as CuO formation on the samples. The diffraction patterns were taken in the 2θ range of 5–80° at a scanning speed of 1°/min.

Characterization of the Cu-ZSM-5 samples by a state-of-the-art STEM (VG Microscopes, HB 603 STEM) was also performed to examine Cu distribution in the Cu-ZSM-5 samples. The fresh samples were calcined in a muffle furnace in air at

Table 1
Cu-ZSM-5 catalyst preparation at various pH[a]

Catalyst	Si/Al[b]	Cu/Al[b]	Na/Al[b]
as-received Na-ZSM-5	21.5 (supplier's)		1.0
first set of samples[c]			
Cu(40)-ZSM-5(4.5)	19.1	0.20	0.09
Cu(74)-ZSM-5(4.9)	19.2	0.37	0.20
Cu(102)-ZSM-5(5.7)	19.0	0.51	0.20
Cu(97)-ZSM-5(6.0)	19.0	0.48	0.18
Cu(154)-ZSM-5(6.5)	18.6	0.77	0.11
Cu(165)-ZSM-5(7.0)	19.0	0.83	0.11
Cu(154)-ZSM-5(7.5)	18.4	0.77	–
Cu(136)-ZSM-5(5.7/7.0)[d]	18.1	0.68	–
second set of samples[e]			
Cu(10)-ZSM-5(5.7)	20.5	0.05	0.89
Cu(30)-ZSM-5(5.7)	19.1	0.15	0.62
Cu(50)-ZSM-5(5.7)	19.4	0.25	0.44
Cu(73)-ZSM-5(5.7)	21.3	0.37	0.20
Cu(97)-ZSM-5(5.7)	21.9	0.48	0.13
Cu(102)-ZSM-5(5.7)	19.0	0.51	0.20
Cu(142)-ZSM-5(5.74)[f]	20.3	0.71	0.00

[a] pH measured before contacting Na-ZSM-5 with the aqueous cupric acetate solution.
[b] Si, Al, Cu and Na contents as measured by ICP.
[c] Cu ion-exchanged with Na-ZSM-5 at room temperature for 19 h once.
[d] Cu first ion-exchanged with Na-ZSM-5 at room temperature and pH = 5.8 for 19 h, then gradually adding aqueous ammonia into the slurry of Na-ZSM-5 and cupric acetate solution to pH = 7.0.
[e] Cu ion-exchanged with Na-ZSM-5 at room temperature for 19 h once.
[f] Cu ion-exchanged with Na-ZSM-5 at room temperature for 19 h thrice.

500°C for 2 h prior to STEM analysis. The calcined samples were placed on a 200 mesh carbon film-covered plain nickel grid for the STEM study. The STEM was equipped with a X-ray microanalytical probe of 0.14 nm optimum resolution. Elemental mapping was performed with this probe on the basis of 128 × 128 data matrix.

The activity of the Cu-ZSM-5 catalysts for NO decomposition was evaluated in laboratory-scale packed-bed, quartz-tube reactors, with i.d. = 1.1 cm (for NO conversion measurement) or 0.4 cm (for kinetic experiments). A porous quartz fritted disk was placed in the middle of the reactor to support the catalyst bed. The reactor was put in a temperature-programmed furnace that was electrically heated and controlled by a temperature controller (Tetrahedron: model Wizard). Two mass flow controllers were used to measure flow rates of a certified standard gas mixture of 4% NO + He (Matheson), and pure He (Airco, 99.999%). A gas chromatograph (HP: model 5890) with a thermal conductivity detector, and a 5A molecular sieve column of 1/8 inch o.d. by 6 feet long was used to measure concentrations of nitrogen, oxygen and nitric oxide in the effluent gas stream. An amount of 0.5 or 0.03 g of catalyst was used in conversion and kinetic tests, respectively. The catalyst packing density in the reactor was 0.5 g/cm^3. The contact time, defined as the ratio of catalyst weight to the total flowrate of the feed gas, was 1 g s/cm^3 or 0.03 g s/cm^3 (STP). The NO concentration was 2 or 4 vol% in the feed gas stream. All measurements were made after steady state had been reached.

3. Results

3.1. EFFECT OF pH ON Cu EXCHANGE LEVEL

Fig. 1 shows the pH dependence of Cu^{2+} ion-exchange levels in the first set of Cu-ZSM-5 samples. The Cu^{2+} exchange level increased with increasing pH, leveled off at about pH = 6.0, then increased further showing a maximum at pH = 7.0. Aluminum was not found by ICP in residual solutions, and no structural change of the zeolite was observed from X-ray diffraction patterns of the Cu-ZSM-5 samples after the ion exchange, which is in agreement with what was reported by Iwamoto et al. [8]. In a separate test, the Cu ion uptake capacity (at pH = 5.7) of the parent zeolite (Na-ZSM-5) after exposure to an acetic anhydride solution at pH = 4.0 at room temperature for 19 h remained unchanged.

The mode of adding aqueous ammonia to the ion-exchange solution affects the Cu exchange level. The Cu exchange level reached 136.8%, when the pH of the slurry of aqueous cupric acetate and ZSM-5 zeolite was adjusted to 7.0 after Cu ion-exchange at pH = 5.7 had taken place for 19 h. This sample is designated as Cu(136)-ZSM-5(5.7/7.0), where 5.7 and 7.0 refer to the two pH values used. However, the Cu^{2+} exchange level of the sample Cu(165)-ZSM-5(7.0) was higher than that of Cu(136)-ZSM-5(5.7/7.0). The former was exchanged once at pH = 7.0 for 19 h.

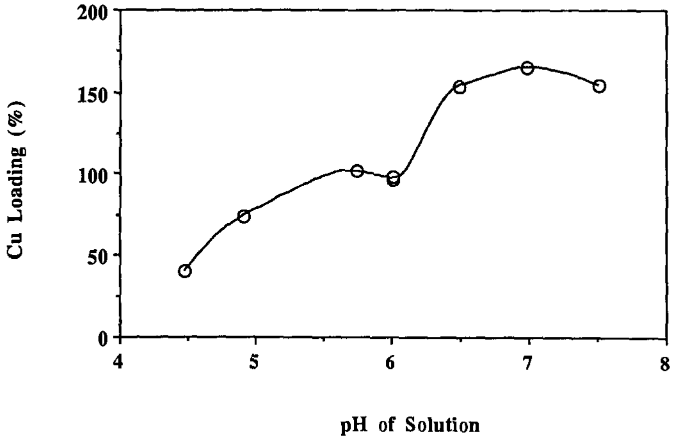

Fig. 1. Dependence of Cu loading on pH of starting cupric acetate solution.

3.2. NO CONVERSION TO N_2 AND O_2

The catalytic activities of the catalysts prepared in this work were evaluated for NO decomposition in a mixture of 2% NO + He at a contact time of 1 g s/cm^3 (STP) and temperature in the range of 350–600°C. NO was introduced into the inlet stream after the catalyst was pretreated in the reactor in pure He stream at 500°C for 2 h at a total pressure of 1.3 atm.

Fig. 2 shows the results for the first set of Cu-ZSM-5 samples. The activity of these catalysts for NO decomposition to N_2 increased with the Cu exchange level when the pH used in preparation was less than 5.74. However, over the rest of this set of catalysts, including Cu(136.8)-ZSM-5(5.7/7.0), prepared at higher pH with high nominal Cu^{2+} exchange levels, the NO conversion to N_2 curves overlap with that of Cu(102)-ZSM-5(5.7) over the whole temperature range. Here, the catalytic activity no longer increases with the Cu^{2+} exchange level. This suggests that part of the copper contained in the samples is not active for NO decomposition. It is noted that the NO conversion to N_2 over the Cu(96)-ZSM-5(6.0) catalyst was almost 20% lower than that over the Cu(102)-ZSM-5(5.74). This is not the case for two catalysts with similar Cu^{2+} exchange levels (here, 97 and 102%) in the second set of Cu-ZSM-5 samples, both prepared at pH = 5.74 (table 1 and fig. 3).

Contrary to the first set of samples, the catalytic activities of the second set of the samples increased monotonically with the Cu exchange level. The NO conversion to N_2 at 500°C over these samples is depicted in fig. 3 as a function of Cu exchange level.

3.3. KINETIC STUDIES

The microcatalytic reactor was used with samples weighing 0.03 g for kinetic

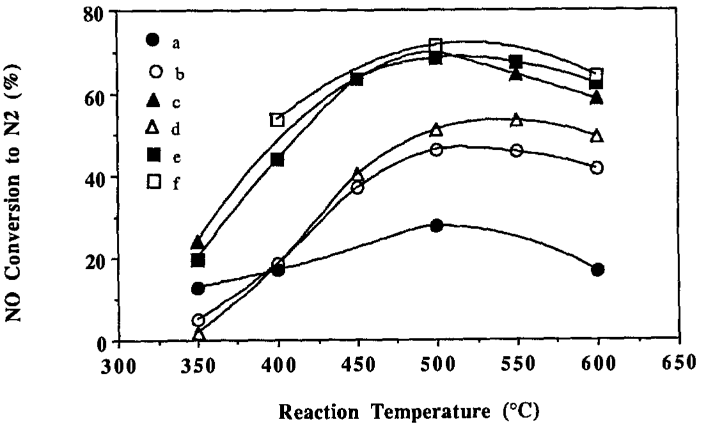

Fig. 2. Effects of catalyst preparation on catalytic activity for NO conversion to N_2 in 2% NO + He and 1 g s/cm^3: (a) Cu(40)-ZSM-5(4.5); (b) Cu(74)-ZSM-5(4.9); (c) Cu(102)-ZSM-5(5.7); (d) Cu(97)-ZSM-5(6.0); (e) Cu(165)-ZSM-5(7.0); (f) Cu(154)-ZSM-5(7.5).

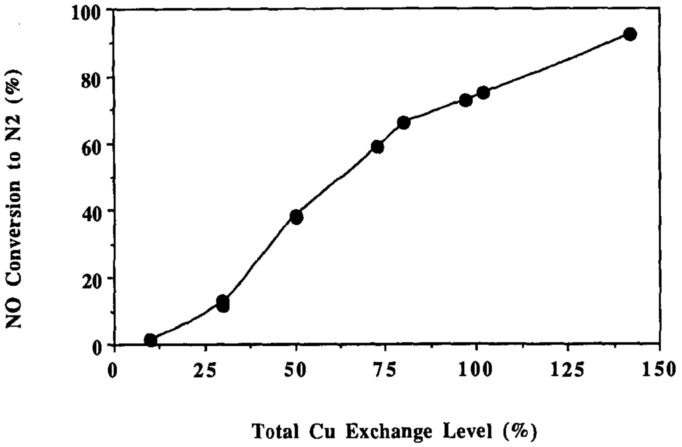

Fig. 3. The effect of Cu exchange level on the catalytic activity for NO decomposition in 2% NO + He, 1 g s/cm^3 and 500°C.

studies and measurements of turnover frequencies of NO decomposition over the first set of the Cu-ZSM-5 samples. A short contact time, 0.03 g s/cm^3 (STP), was chosen at which the reaction was controlled by kinetics. Fig. 4A shows Arrhenius plots for the turnover frequencies over six typical Cu-ZSM-5 catalysts (from the first set, table 1), while fig. 4B displays the TOF as a function of the pH at the temperature of 500°C. The turnover frequency (TOF) defined, here, as the number of NO molecules converted to N_2 per Cu (based on total Cu) per second, generally increases with temperature, reaches a maximum at 500°C (450°C for Cu(40)-ZSM-5(4.5)), then decreases at higher temperatures. The TOF in fig. 4B increases with the pH up to a value of 5.7 for the catalyst Cu(102)-ZSM-5(5.74), then decreases for the samples prepared at higher pH. This is in good agreement with the NO conversion measurements.

3.4. IDENTIFICATION OF "SURFACE COPPER" IN THE FIRST SET OF SAMPLES

As shown in figs. 2 and 4, a certain amount of copper ions in the samples prepared at high pH was not active for NO decomposition, since the NO conversion did not increase with the copper exchange level.The Cu^{2+} distribution in the catalysts can be evaluated in terms of "surface Cu" and "ion-exchanged Cu" cations. Unlike the first set of the samples, Cu^{2+} cations in the second set of Cu-ZSM-5 catalysts were stoichiometrically ion-exchanged with Na^+ ions, as shown in table 1, when Cu ion exchange level was lower than about 90%. The correlation of catalytic activity with the amount of ion-exchanged Cu, as shown in fig. 3, can be used as a standard to determine how much copper was "ion-exchanged" in each of the first set of Cu-ZSM-5 samples. The difference between the total Cu and "ion-exchanged Cu" is, here, designated as "surface Cu", which is not active for NO decomposition. The Cu distribution in the first set of samples is shown in fig. 5.

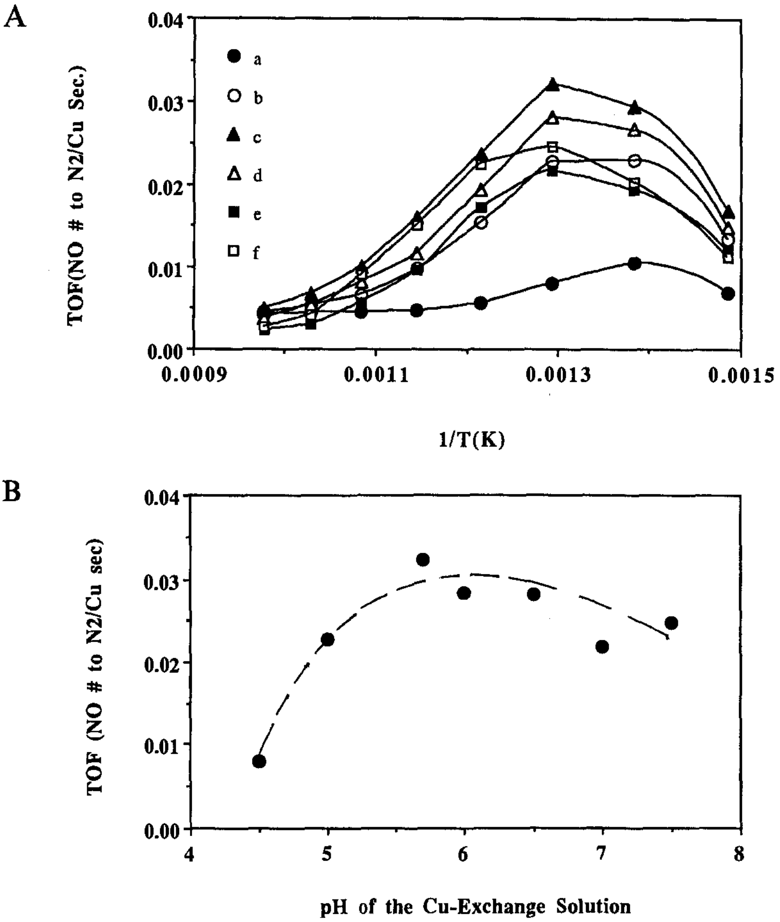

Fig. 4. The effect of catalyst preparation on the catalytic activity (TOF) for NO decomposition in 4% NO + He and 0.03 g s/cm^3: (A) Arrhenius plots: (a) Cu(40)-ZSM-5(4.5); (b) Cu(74)-ZSM-5(4.9); (c) Cu(102)-ZSM-5(5.7); (d) Cu(97)-ZSM-5(6.0); (e) Cu(165)-ZSM-5(7.0); (f) Cu(154)-ZSM-5(7.5). (B) Correlation of TOF with the pH at 500°C.

In order to further examine the contribution of the "surface Cu" and "ion-exchanged Cu" to the catalytic activity, the first set of the Cu-ZSM-5 catalysts was washed by aqueous ammonia solutions (2.7% assay). The amounts of Cu washed out from two samples, namely Cu(97)-ZSM-5(6.0) and Cu(165)-ZSM-5(7.0), did not change 1 min after the catalyst samples were contacted with the solutions. It was decided to contact all samples with the aqueous ammonia solution for 6 min, which is long enough for all cations in the slurry to reach a surface equilibrium. The amount of Cu removed by the aqueous ammonia solutions from each catalyst is determined by the difference of the initial total Cu and the remaining Cu in the samples (as specified by ICP). The results are shown in fig. 6. It can be seen that a little amount of Cu was removed from the catalysts prepared at low pH. However, considerable amount of copper was extracted from the catalysts prepared at high pH.

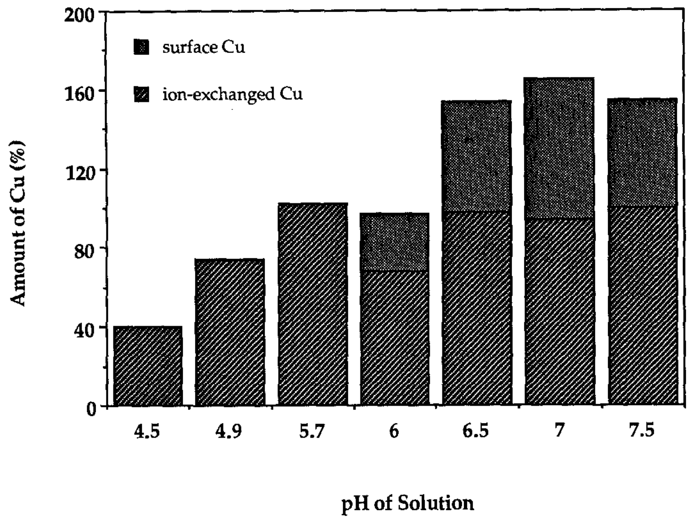

Fig. 5. Cu distribution in the first set of catalysts.

The "surface Cu" and the Cu^{2+} washed out by aqueous ammonia were approximately equal as shown in fig. 6. The Cu removed by aqueous ammonia from the samples prepared at pH values of 4.5, 4.9 and 5.7 is part of the ion-exchanged copper. This is concluded from the following tests. First, the same amount of Cu was removed by aqueous ammonia after calcination of these samples in air at 500°C for 2 h. Second, the same tests for the materials prepared at high pH values showed that only a small amount of Cu (~ 3%) could be removed. It was found by XRD

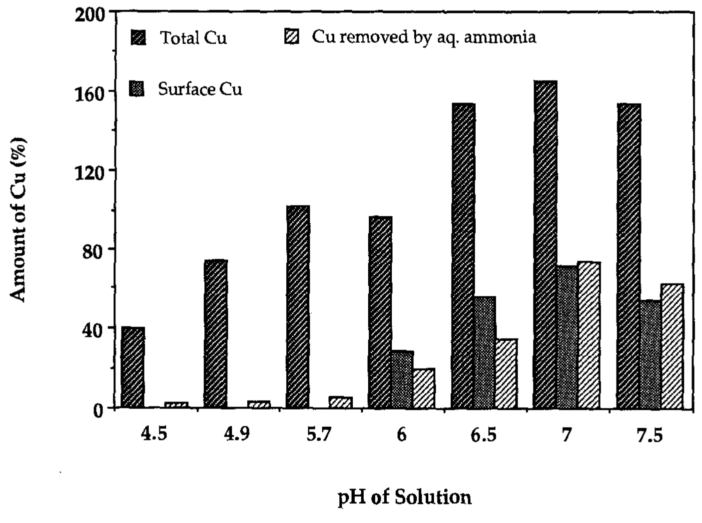

Fig. 6. Comparison of "surface Cu" and Cu washed by aqueous ammonia.

that CuO was formed by the "surface Cu" after calcination in air. A separate test revealed that CuO cannot be removed by the ammonia wash method. Therefore, the removed Cu is the ion-exchanged Cu cations.

Kinetic studies showed that the TOF values of the ammonia-washed catalysts were the same as those of the original samples (prior to washing). This confirms that the extracted Cu was not active for the reaction. The TOF for the catalysts Cu(96)-ZSM-5(6.0) and Cu(165)-ZSM-5(7.0) before and after the ammonia wash is shown in fig. 7. Here the TOF is defined as the number of NO molecules converted to N_2 per Cu (based on ion-exchanged Cu) per second.

When the catalyst Cu(141)-ZSM-5(5.7) was washed with the aqueous ammonia solution under the same conditions as above, it was found that only 6% of total Cu was removed. However, the catalyst Cu (153)-ZSM-5(7.5) lost 28% of its total Cu. Thus, the "surface Cu" is easily removed by aqueous ammonia.

3.5. CHARACTERIZATION OF CATALYSTS BY STEM/EDX AND XRD

Fig. 8a shows a STEM micrograph of the 500°C, 2h-calcined Cu(165)-ZSM-5(7.0) sample. This is representative of the catalysts prepared at high pH (>6.0). The phase contrast imaging demonstrated formation of copper particles (up to 6 nm) clearly distinguishable from the zeolite support. The X-ray spectra of a copper aggregate and the Cu-ZSM-5 background are shown in fig. 8b, in which a very strong copper signal was obtained on the bright spots of the dark field STEM micrograph (fig. 8a). Copper X-ray mapping shows homogeneously dispersed copper in the sample, and confirms formation of copper particles on the edges and voids of the zeolite crystal. This can be seen in the X-ray maps of Cu and Si, as shown in fig. 9 (scale of one elemental mapping: 100 nm by 120 nm), for the same area as that in fig. 8a.

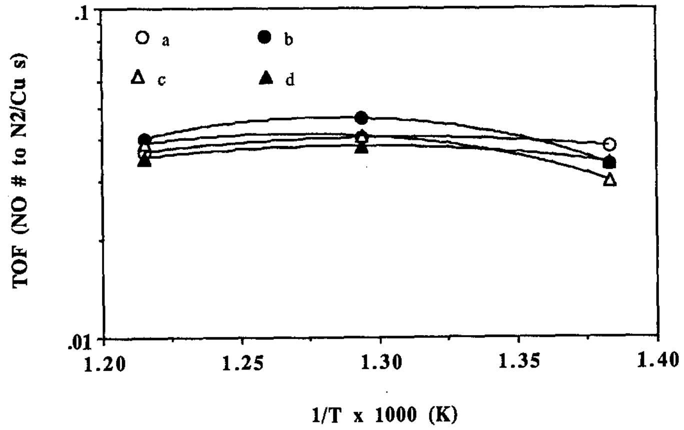

Fig. 7. Activity comparisons of fresh with aqueous ammonia washed samples for NO decomposition in 4% NO + He and 0.03 g s/cm^3: Cu(97)-ZSM-5(6.0) (a) fresh; (b) washed; Cu(165)-ZSM-5(7.0) (c) fresh; (d) washed.

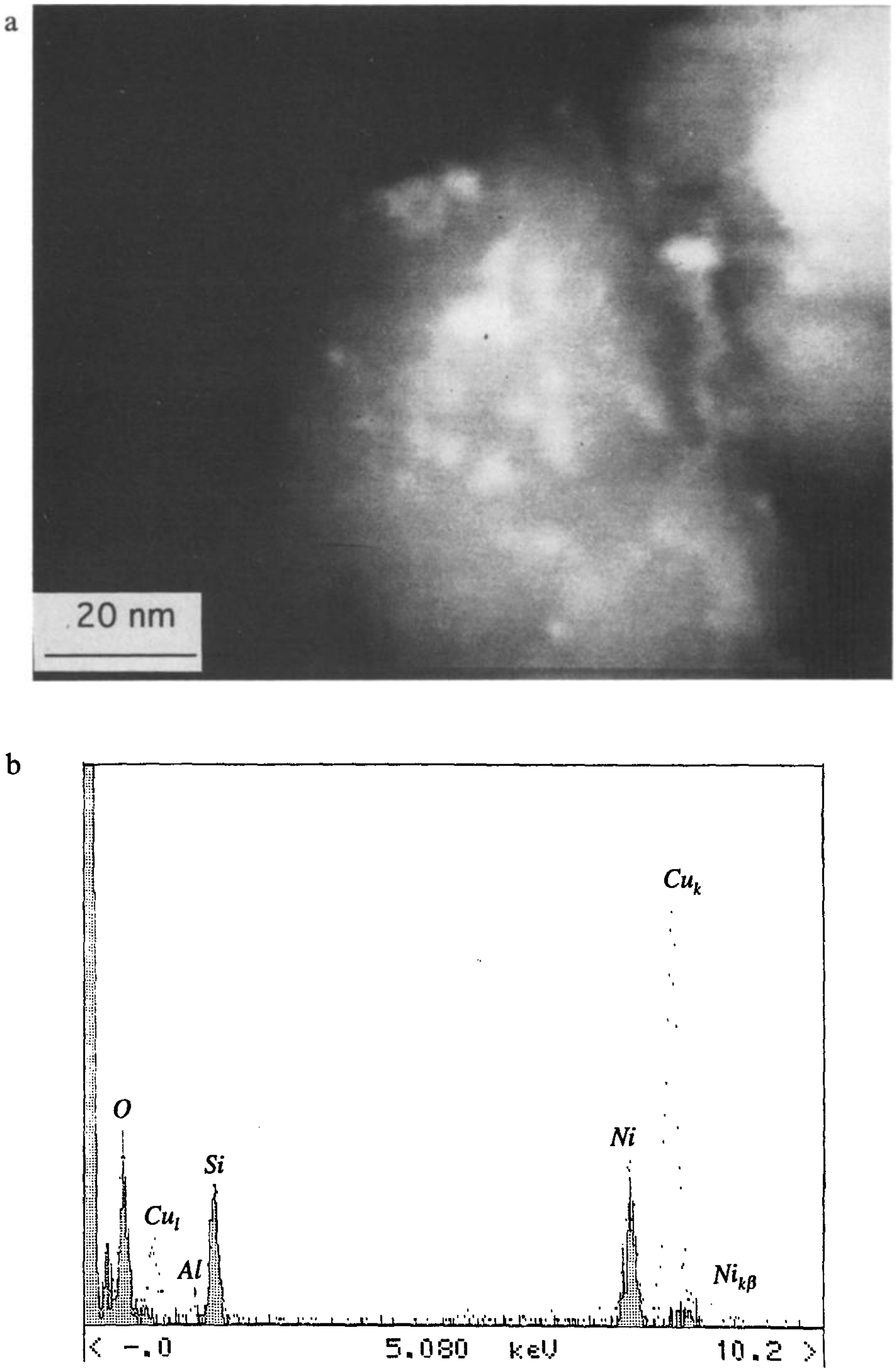

Fig. 8. Characterization of the calcined Cu(165)-ZSM-5(7.0) by STEM: (a) dark field micrograph showing copper aggregates (bright spots); (b) X-ray spectrum of copper aggregates (dots) and catalyst background (bars).

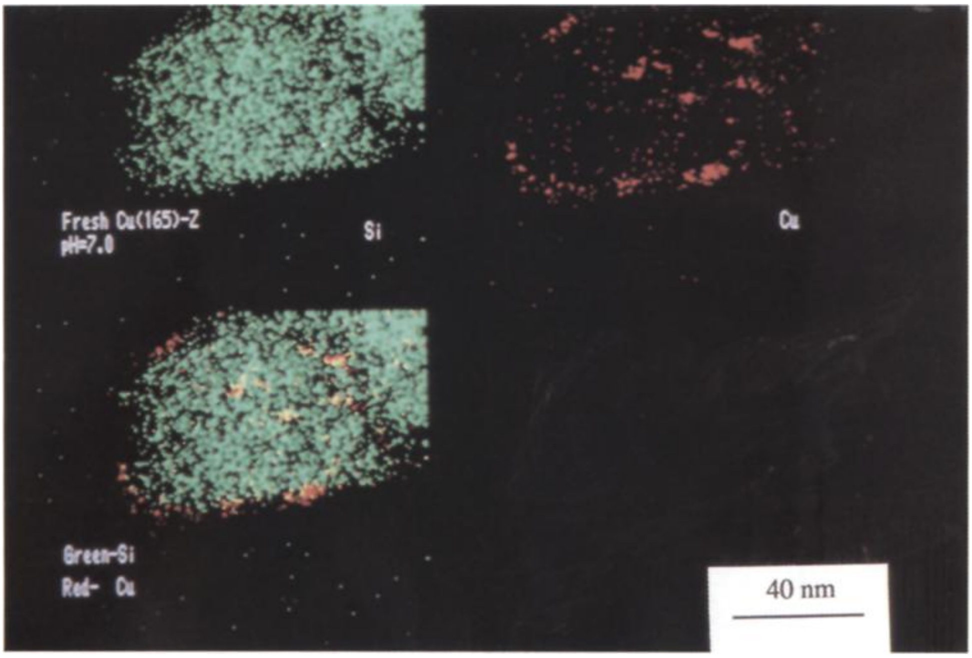

Fig. 9. X-ray mapping of Si and Cu in the calcined Cu(165)-ZSM-5(7.0) sample.

XRD patterns similar to that of the parent ZSM-5 zeolite were obtained for all the materials prepared in this work. No other crystalline phase, such as CuO, was found by XRD in the fresh samples. However, CuO could be clearly seen by XRD in samples prepared at high pH after air calcination. An example is shown in fig. 10 for the Cu(154)-ZSM-5(7.5) after 2 h air calcination at 500°C. For comparison, fig. 10 shows the XRD patterns of this sample as well as that of the parent ZSM-5 in the range of $2\theta = 34-40°$, in which CuO has the strongest diffraction peaks.

4. Discussion

The experimental results in figs. 1 and 2 show that the Cu^{2+} loading and activity are strongly dependent on the initial pH of the starting aqueous cupric acetate solution. It is well known that there are three types of terminal silanol OH-groups in zeolites. The first type is always present at the outer surface of the zeolite crystals to terminate the structure [10], while the second and third silanol groups exist in the framework of zeolites. At low pH, OH-groups adsorb protons and become positively charged. At high pH, they deprotonate, and the edges become negatively charged and have a cation exchange capacity [11]. Adding acetic anhydride into the cupric acetate solution lowers the pH, i.e., more protons are present in the solution. When a certain amount of Cu^{2+} cations exist in the solution, Na^+ cations in

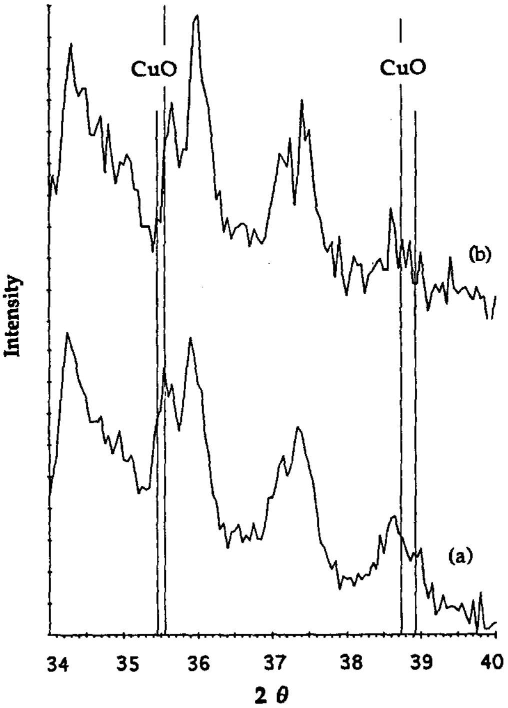

Fig. 10. XRD patterns of (a) 500°C, 2 h calcined Cu(154)-ZSM-5(7.5) showing CuO formation, and (b) parent Na-ZSM-5.

the ZSM-5 zeolites will be exchanged by both Cu^{2+} and H^+, and an equilibrium will be reached. Hence, the presence of H^+ cations in the solution inhibits the ion exchange between Cu^{2+} and Na^+ cations. The higher the H^+ concentration in the solution, the lower the Cu^{2+} ion exchange level. This is the reason why the Cu^{2+} ion exchange with Na^+ is not stoichiometric for the first set of samples shown in table 1. Since OH-groups adsorb protons and become positively charged, Cu^{2+} cations exchanged in the zeolite would only replace Na^+ cations associated with Al in the zeolite framework. This can also be concluded by the low amount of "surface Cu" present in the samples prepared at low pH values. However, by adding aqueous ammonia to the cupric acetate solutions, some Cu complexes can be formed with positive charges. The typical complexes are $[Cu(NH_3)_4]^{2+}$ [12], mononuclear $[CuOH]^+$, and polynuclear $[Cu_2(OH)_2]^{2+}$, $[Cu_2OH]^{3+}$, etc. [13]. It is possible for the positively charged Cu^{2+} complexes and negatively charged edges of the zeolites to attract each other. Thus, some part of copper is deposited in the zeolite pores while the other exchanges with the Na^+ cations associated with $(AlO_2)^-$ in the framework. As a result, higher nominal Cu^{2+} exchange levels are measured by ICP in the first set of samples. The STEM X-ray maps of copper and silicon support this explanation.

From fig. 6, it is further seen that a part of Cu^{2+} cations is easy to remove by the aqueous ammonia solution. The amount of the removed Cu is approximately equal to the increment of the Cu loading at the higher pH, on the basis of Cu(102)-ZSM-5(5.74). Therefore, it is concluded that the removed Cu is the deposited Cu.

The copper aggregates seen by STEM/X-ray microprobe analysis in the first set of Cu-ZSM-5 samples are formed by the deposited Cu on the ZSM-5 crystals, which are labile and upon calcination can form copper oxide particles on the crystal edges and voids. The deposited copper on the zeolite is similar to impregnated Cu-ZSM-5, which is not active for NO decomposition. Characterization of impregnated Cu-ZSM-5 by XPS showed a higher Cu/Si ratio in the zeolite surface region than the bulk value, and was attributed to large copper aggregates [14].

The catalytic activity of Cu-ZSM-5 catalysts depends on the copper exchanged in the zeolite channels. The deposited copper is inactive. As can be seen in fig. 2, the NO conversion to N_2 increases with Cu^{2+} exchange levels for the Cu-ZSM-5 catalysts prepared at starting solution pH equal to or lower than 5.74, but not for those samples prepared at higher pH values. The results from the kinetic study of NO decomposition over these catalysts, shown in fig. 4, are in good agreement with the NO conversion measurements of fig. 2.

From the XRD analyses, it can be concluded that the deposited Cu coalesced and formed CuO after calcination of the Cu-ZSM-5 samples prepared at high pH in air at 500°C for 2 h.

5. Conclusion

"Over-exchanged" Cu-ZSM-5 is desirable as it is a more active catalyst for the NO decomposition reaction than under-exchanged Cu-ZSM-5. While a single-step ion-exchange from a dilute copper salt solution at $pH > 6.5$ can achieve a high copper loading in ZSM-5, not all the copper exists in the ion-exchanged state in the zeolite channels; a fraction of the copper is on the surface, easily forming oxidic particles after calcination. This surface deposited copper is inactive for NO decomposition. The reported multi-step ion-exchange process from dilute cupric salt solutions at $pH = 5.5$–6.0, even if more tedious, is presently the only one that can safeguard the active "over-exchanged" Cu-ZSM-5 state.

Acknowledgement

Dr. A. Garratt-Reed of the MIT Center for Materials Science and Engineering is gratefully acknowledged for assisting with the STEM analyses. Financial support for the project was provided by the US Department of Energy/University Coal Research Program, under Grant No. DE-FG22-91PC91923 with Dr. K. Das (DOE/METC) serving as Technical Project Officer.

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