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Solid-State Ion-Exchange of Copper into Zeolites Facilitated by Ammonia at Low Temperature

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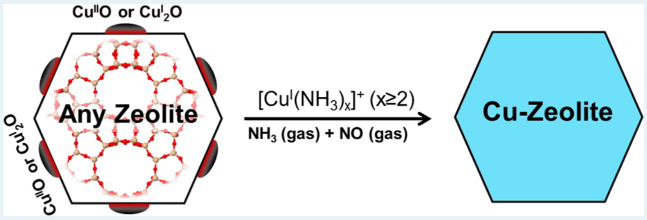
S *Supporting Information*



ABSTRACT: The effect of the gas phase during solid-state ion-exchange of copper into zeolites was studied by exposing physical mixtures of copper oxides (Cu^{I}_2O and $Cu^{II}O$) and zeolites (MFI, *BEA, and CHA) to various combinations of NO, NH_3, O_2, and H_2O. It is shown that heating these mixtures to 250 °C results in active catalysts for the selective catalytic reduction of NO with NH_3 (NH_3-SCR), indicating that the Cu has become mobile at that temperature. Such treatment allows for a fast (<5−10 h) preparation of copper-exchanged zeolites. Scanning transmission electron microscopy analysis of Cu-CHA prepared using this method shows homogeneous distribution of the Cu in the primary particles of the zeolite. In situ XRD reveals that the Cu ion-exchange is related to the formation of Cu^{I}_2O. When the zeolite is mixed with $Cu^{II}O$, addition of NO to the NH_3-containing gas phase enhances the formation of Cu^{I}_2O and the Cu ion-exchange. The mobility of Cu at low temperatures is proposed to be related to the formation of $[Cu^{I}(NH_3)_x]^+$ ($x \geq 2$) complexes.

KEYWORDS: *low-temperature, solid-state ion-exchange, copper, zeolites, ammonia, nitric oxide*

Zeolites exchanged with copper show unique properties in catalytic redox reactions, and therefore, these materials offer promising perspectives to numerous technological applications. One example is the direct selective oxidation of methane to methanol over, for example, Cu-MFI[1,2] and Cu-MOR,[1] which would eliminate the need for energy intensive steam reforming. The reaction is catalyzed by specific $[Cu_2O]^{2+}$ sites hosted in the zeolite matrix[1,2] at Cu/Al ratios >0.5. Another, already implemented, application of Cu-zeolites is for the abatement of environmentally harmful nitrogen oxides in diesel engine exhausts. This technology is based on selective catalytic reduction with ammonia (NH_3-SCR),[3,4] according to the stoichiometry in Reaction 1.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

As environmental legislation becomes more stringent in many parts of the world, the use of NH_3-SCR catalysts is expected to grow substantially in the near future.

The zeolite systems commonly used for NH_3-SCR are Cu-MFI and Cu-*BEA. These framework structures have medium and large pore sizes containing 10 (MFI) and 12 (*BEA) O atoms in the window openings of the structure. However, such systems do not show the required hydrothermal stability, in particular, when using active regeneration of upstream soot filters, where the temperature can reach 700 °C or higher. Recently, materials with the CHA structure such as Cu-SSZ-13 and Cu-SAPO-34, which has smaller window size (8 O atoms) and high hydrothermal stability,[5] have been introduced as SCR catalysts.

The conventional method to introduce the active copper species into zeolites is by exchange with Cu^{2+} ions in aqueous solution. A drawback of this method is that the exchange procedure has to be repeated several times to obtain high ion-exchange levels. For CHA structures, the narrow window openings (0.38 nm in diameter) further impedes the introduction of copper from aqueous solution, especially for SAPO-34, due to its polar framework.[5] This limits the applicability of solution-based ion-exchange procedures.

An alternative method to introduce metal ions into zeolites is by solid-state ion-exchange (SSIE) in the absence of a solution. A dry powder mixture of a metal salt or oxide and the zeolite in the NH_4^+ or H^+ form is heated to high temperature, typically 700−800 °C, which results in diffusion of the metal ions into the zeolite. This process is reported to be driven by the release of water upon exchange with protons in the zeolite.[6−10] There is no need for consecutive washing, filtration and drying, which makes the method simple compared to solution-based ion-exchange. The high temperature required to initiate the exchange restricts SSIE to thermally stable zeolites. However,

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even the stable CHA structure shows some damage after SSIE at 800 °C.[10]

Recently, it was shown that copper ions can be transferred from $Cu^{II}O$ into H-ZSM-5 at 550 °C in a typical NH_3-SCR atmosphere consisting of NO, NH_3, O_2, H_2O, and N_2, with levels of exchanged Cu similar to those obtained by aqueous ion-exchange.[11] This demonstrates that control of the atmosphere can facilitate copper migration at lower temperatures than normally used in SSIE. In the present work, we explore the effect of the gas phase during SSIE of copper into zeolites with CHA, MFI, and *BEA framework structure. We expose physical mixtures of copper oxides and zeolites to various combinations of NO, NH_3, H_2O, and O_2 at considerably lower temperatures than commonly used in SSIE. Because active NH_3-SCR catalysts are formed by exchange of Cu, the degree of copper exchange is conveniently determined by monitoring the catalytic activity. Furthermore, STEM-EDS analysis is used to monitor the copper distribution in the primary particles of the zeolite, and in situ XRD is used to follow the course of the copper migration.

To perform the SSIE, dry powder mixtures of 12.5 wt % $Cu^{II}O$ and zeolite with either the MFI, *BEA, or CHA framework structure and with Si/Al ratios between 12 and 15 were prepared by simple grinding. A 10 mg sample of the copper oxide and zeolite mixture (150−300 μm sieve fraction) was placed in a quartz U-tube reactor, connected to an FTIR analyzer (Gasmet CX4000) to measure the gas-phase composition in the reactor outlet. The sample was then exposed to a well-defined gas atmosphere at constant temperature. After the treatment, the sample was cooled to 200 °C, and the SCR activity was determined by measuring the NO conversion, using a flow of 225 NmL/min of an NH_3-SCR feed (500 ppm of NO, 530 ppm of NH_3, 5% H_2O, and 10% O_2 in nitrogen). The SCR activity monitors the efficiency of the zeolite ion-exchange, as Cu oxides do not contribute to the NO conversion at 200 °C[11]

To first determine the extent of SSIE for the different zeolite structures under SCR conditions (NH_3, NO, H_2O and O_2), the corresponding $Cu^{II}O$−zeolite mixtures were treated between 250 and 550 °C for 60 min in an NH_3-SCR feed. For MFI and *BEA, a low SCR activity was observed already after heating to 250 °C whereas for CHA, activity for SCR was observed only after heating to 450 °C. (see Supporting Information Figure S1). Even though the NO conversion after treatment in the SCR feed at 250 °C is lower than that obtained with solution-based ion-exchanged Cu-zeolites, this indicates that in the presence of an NH_3-SCR feed, SSIE can take place already at 250 °C for MFI and *BEA. The higher temperature required for exchange of Cu into the CHA structure indicates increased difficulty of exchange, probably due to the more narrow pores in this framework structure.

The temperature of 250 °C is considerably lower than any other reported temperatures for SSIE using $Cu^{II}O$, showing that one or several components in the NH_3-SCR feed enhances the exchange of copper from $Cu^{II}O$. To identify that component, the MFI zeolite was systematically exposed to various combinations of NO, NH_3, O_2, and H_2O at 250 °C. Table 1 summarizes the SCR activities at 200 °C measured after these treatments. In the presence of oxygen and/or water, no significant activity increase is seen ($X_{NOx} < 3\%$), which we interpret as migration of copper does not take place, in full agreement with previous reports on SSIE of copper from $Cu^{II}O$ into zeolites.[11] However, when heated in NH_3 in the absence of O_2, the SCR activity at 200 °C increases considerably (X_{NOx} = 36%), pointing to NH_3 as the critical component for the SSIE of copper at low temperatures. Quite surprisingly, an even higher activity is observed (X_{NOx} = 53%) after heating in NH_3 in combination with NO, whereas NO alone (X_{NOx} = 5%) does not seem to have any significant effect on the exchange.

Table 1. Measured NH_3-SCR Activity at 200 °C of $Cu^{II}O$ + H-MFI after Treatment in Different Gas Compositions at 250 °C for 10 h[a]

SSIE treatment conditions	X_{NOx} (%)	reaction rate × 10^{-3} (mmol/s g $_{sample}$)
fresh	1	0.07
O_2 + H_2O	2	0.13
NO + O_2 + H_2O	2	0.13
NH_3 + O_2 + H_2O	2	0.13
NH_3 +NO + O_2 + H_2O	7	0.47
O_2	1	0.07
NO + O_2	2	0.13
NH_3 + O_2	11	0.73
NH_3 + NO + O_2	12	0.80
H_2O	3	0.20
NH_3 + NO + H_2O	18	1.20
NO	5	0.33
NH_3	36	2.40
NH_3 + NO	53	3.53

[a] NH_3-SCR conditions: 500 ppm of NO, 530 ppm of NH_3, 5% H_2O, 10% O_2, and N_2 as inert gas at a total flow of 225 N mL/min using 10.0 mg catalyst.

Furthermore, halving or doubling the NO or NH_3 concentrations during the treatment do not affect the degree of copper exchange (Supporting Information Figure S2).

To investigate if heating in NO and NH_3 enhances the SCR activity for CHA and *BEA as well, these zeolites mixed with $Cu^{II}O$ were heated in such gas composition at 250 °C (see Table 2). The results show that copper is ion-exchanged into these zeolites as well and to approximately the same extent as for the MFI zeolite, despite the differences in pore size. From a comparison of the NH_3-SCR activity of Cu-*BEA obtained from solution-based ion-exchange, we estimate that the extent of copper exchange through [NH_3+NO]-SSIE at 250 °C is at least as high as obtained with conventional aqueous ion-exchange (see Table 2) where the highest copper loading (2.6 wt %, Cu/Al = 0.39) was obtained for a surplus of copper in solution of $Cu^{2+}{}_{solution}/Al_{zeolite} = 3$.

The observation that the NO conversion during NH_3-SCR is similar after 5 and 10 h SSIE shows that the exchange process primarily takes place during the first few hours of the treatment.

To confirm that Cu actually is introduced into the zeolite, STEM-EDS analyses of the CHA zeolite after [NH_3+NO]-SSIE were performed. Figure 1 shows the distribution of Si, Al, and O compared to the distribution of Cu over a representative zeolite crystal. The results reveal that copper is homogeneously distributed in the zeolite crystals analogous to aluminum. A small unreacted copper oxide particle stuck to the crystal surface can also be seen in the Cu map as highlighted by the red circle. The line scan shows the distribution of each of the elements across the crystal width. Prepeak background measured for the Cu peak has also been included in the line scan to demonstrate that the Cu peak signal observed is well above the background.

Table 2. Measured NH_3-SCR Activity at 200 °C of $Cu^{II}O$ + Zeolite (*BEA, CHA, and MFI) Mixtures after Treatment in NO (500 ppm) and NH_3 (530 ppm), and Cu^{I}_2O for MFI Treated in 530 ppm of NH_3 at 250 °C for 5 and 10 h in Comparison with Aqueous Ion-Exchanged Cu-*BEA Together with the Molar Cu/Al Ratio

sample		X_{NOx} (%)	reaction rate × 10^{-3} (mmol/s g $_{sample}$)	Cu/Al
0.8 wt % Cu-*BEA[a]		7.4	0.49	0.12[b]
1.4 wt % Cu-*BEA[a]		16	1.07	0.20[b]
2.0 wt % Cu-*BEA[a]		28	1.87	0.27[b]
2.6 wt % Cu-*BEA[a]		43	2.87	0.39[b]
$Cu^{II}O$ + H-*BEA	fresh	1.7	0.11	-
	5 h	49	3.27	-
	10h	50	3.34	-
$Cu^{II}O$ + H–CHA	fresh	1.0	0.06	-
	5 h	45	3.00	-
	10 h	46	3.07	-
$Cu^{II}O$ + H-MFI	fresh	1.6	0.11	-
	5 h	51	3.40	-
	10 h	53	3.53	-
Cu^{I}_2O + H-MFI	fresh	1.2	0.08	-
(treated in	5 h	59	3.94	-
NH_3 only)	10 h	61	4.04	-

[a] Prepared by aqueous ion-exchange. [b] Measured by ICP-AES.

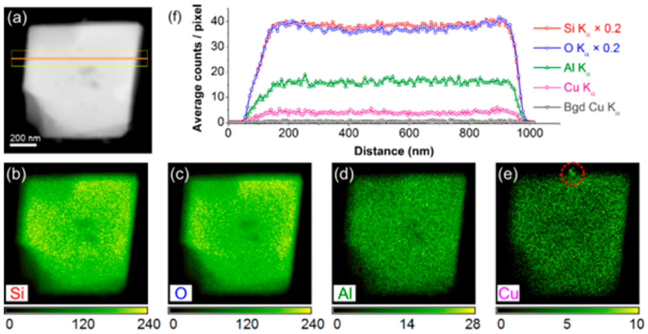

Figure 1. (a–e) STEM dark field image and EDS maps from a representative CHA crystal after [NO+NH_3]-SSIE of $Cu^{II}O$ for 10 h. The color scale shows the color intensity assigned corresponding to the elemental X-ray counts at each pixel. (f) Line scan showing the average counts per pixel observed for each of elements in the crystal in the area indicated in (a). The prepeak background signal for Cu has also been included for comparison.

To determine which Cu-species are responsible for the mobility of Cu, the course of the introduction of Cu ions into the zeolite was followed by in situ XRD. Figure 2 shows the evolution of the phase composition and the lattice parameters of *BEA, CHA, and MFI, respectively, during SSIE at 250 °C obtained by quantitative Rietveld analysis. When the zeolite + $Cu^{II}O$ mixture is treated in NH_3 and NO $Cu^{II}O$ is initially reduced to Cu^{I}_2O and metallic Cu appears when the reduction into Cu^{I}_2O is complete. During the reduction of the Cu-phases, there is in all cases a significant increase in the relative amount of the zeolite phase. This observation is consistent with an interpretation of Cu migrating into the zeolite. Additionally, changes in zeolite lattice parameters are expected when ionic species are exchanged into zeolite extra-framework positions. As shown in Figure 2b, changes in lattice parameters are observed for all the copper oxide-zeolite mixtures, and these are well correlated with the observed increase of the zeolite phase fraction. This independent observation further supports the interpretation of Cu migrating into the zeolite to ion-exchange positions. The changes in zeolite phases are directly correlated to the appearance of Cu^{I}_2O suggesting that the mobile copper species are in oxidation state +1.

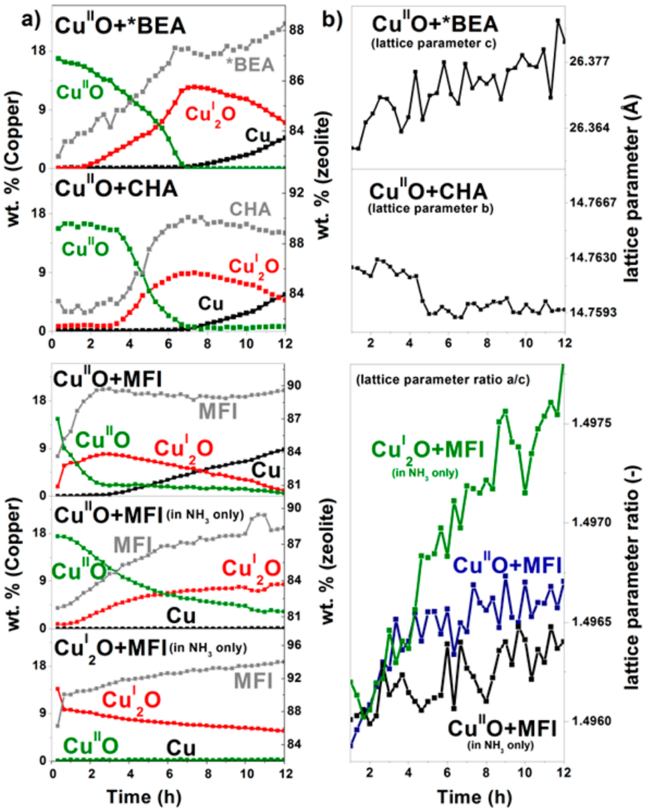

Figure 2. Results of quantitative Rietveld analysis. (a) Phase fractions of zeolite and the copper phases ($Cu^{II}O$, Cu^{I}_2O, and metallic Cu) and (b) evolution of zeolite lattice parameters during [NO+NH_3]-SSIE of $Cu^{II}O$ at 250 °C for *BEA, CHA, and MFI, as well as [NH_3]-SSIE of $Cu^{II}O$ and Cu^{I}_2O for MFI using 2000 ppm of NO and NH_3 respectively.

These results are in good agreement with the findings of Giordanino et al., who have recently shown that linear $[Cu^{I}(NH_3)_2]^+$ complexes are formed in Cu-CHA in the presence of NH_3.[12] Because these complexes are linear, the diameter is similar to that of an ammonia molecule, making it possible for these species to penetrate the pore system. Moreover, with two ammonia molecules coordinated to Cu^{I}, the complex becomes loosely bound to the framework,[12] which is consistent with a high mobility of such complexes that is required for an efficient SSIE process. These observations in combination with the correlation between Cu^{I}_2O and copper migration into the zeolite leads us to conclude that the complexes responsible for the migration of copper are related to Cu^{I} species coordinated to NH_3.

The consistency between formation of Cu^{I} phases and the migration of copper ions into the zeolite also explains the role of NO. When starting from $Cu^{II}O$, the NO in combination with NH_3 facilitates the reduction into Cu^{I}_2O wherefrom the mobile copper species can be formed. This facilitating effect of NO is seen when comparing the [NO+NH_3]-SSIE and [NH_3]-SSIE of $Cu^{II}O$ with the MFI zeolite, as shown in the middle-bottom part of Figure 2, where the formation of Cu^{I}_2O is slower when NO is omitted and is further corroborated by the results in

Table 1. The NO also facilitates the reduction of Cu^I_2O into metallic copper, which does not seem to form mobile species thus giving a "window" wherein the SSIE can occur.

The hypothesis that $[Cu^I(NH_3)_x]^+$ ($x \geq 2$) complexes are responsible for the mobility of the Cu suggests that starting from Cu^I_2O eliminates the need for NO during the SSIE. This is indeed the case (see lower part of Figure 2). For the $[NH_3]$-SSIE of Cu^I_2O the initial SSIE (up to 4 h) proceeds in an identical manner to the $[NO+NH_3]$-SSIE of $Cu^{II}O$. However, because Cu^I_2O is not reduced to metallic copper in NH_3 alone, the SSIE continues throughout the entire course of the treatment as the "window" of migration is kept open. From a comparison of the a/c ratio of the zeolite lattice parameters, even higher exchange ratios for $[NH_3]$-SSIE from Cu^I_2O are expected as seen by the larger increase compared to the other experiments (lower part Figure 2b) and the even higher NO_x conversion in the NH_3-SCR reaction (bottom part, Table 2). We do note that the increased copper exchange ratio expected when increasing the SSIE time from 5 to 10 h does not lead to much increase in the NH_3-SCR activity, as seen from Table 2. This is due to the fact that above Cu/Al ratios of ca. 0.5−0.6 the NO_x conversion in the NH_3-SCR reaction is no longer increased with increasing exchange degrees as reported elsewhere.[5]

We also note that the SSIE depends on the zeolite framework, with a rate of ion exchange that follows the order of MFI>*BEA > CHA, as indicated by the increase in the zeolite phase fractions in Figure 2a.

By conventional ion-exchange methods using aqueous Cu^{2+} solutions, an exchange level around Cu/Al = 0.5 is typically the maximum exchange level that can be achieved. The present results show that by transportation of copper in oxidation state +1 as amine complexes Cu/Al ratios up to 1.0 could in principle be reached. This opens up for an efficient method to prepare overexchanged Cu-zeolites, which, in addition, can be applied to zeolites that are not stable at high temperatures or in aqueous media.

In summary, we have shown that in the presence of NH_3 copper becomes mobile at considerably lower temperatures ($T \leq 250$ °C) than conventionally used in solid-state ion-exchange. Such treatment in NH_3 can be used to prepare ion-exchanged zeolites that are active for NH_3-SCR, for example, on a time scale below 5−10 h, irrespective of framework structure. For $Cu^{II}O$ as a Cu precursor, the migration rate can be enhanced by also adding NO to the treatment atmosphere. The time window of migration can be even further extended using Cu^I_2O in combination with NH_3. We propose that the mobility of the copper at low temperatures is related to the ability of ammonia to form $[Cu^I(NH_3)_x]^+$ ($x \geq 2$) complexes. Cu-zeolites with a Cu/Al ratio of 1.0 could in principle be produced in this way, because copper is in oxidation state +1. Such Cu-zeolites with high copper loading are potentially interesting catalysts for a number of technical applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs5015139.

Additional experimental details and further results (PDF)

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Notes

The authors declare no competing financial interest.

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