Fully Copper-Exchanged High-Silica LTA Zeolites as Unrivaled Hydrothermally Stable NH_3-SCR Catalysts

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Dedication ((optional))

Abstract: *Diesel engine technology is still the most effective solution to meet tighter CO_2 regulations in the mobility and transport sector. In implementation of fuel-efficient diesel engines, the poor thermal durability of lean nitrogen oxides (NO_x) aftertreatment systems remains as one major technical hurdle. Here, divalent copper ions when "fully exchanged" into high-silica LTA zeolites are demonstrated to exhibit excellent activity maintenance for NO_x reduction with NH_3 under vehicle simulated conditions even after hydrothermal aging at 900 °C – a critical temperature that the current commercial Cu-SSZ-13 catalyst cannot overcome due to thermal deactivation. Detailed structural characterizations confirm the presence of Cu^{2+} ions only at the center of single 6-rings that act not only as a catalytically active center, but also as a dealumination suppressor. The overall results of our work renders the copper-exchanged LTA zeolite attractive as a viable substitute for Cu-SSZ-13.*

Tighter CO_2 emission standards from mobile sources are being legislated globally in order to address the concerns regarding anthropogenic climate change. Hence, automotive manufacturers have developed a variety of new propulsion systems, including battery electric, plug-in hybrid, and even fuel cell electric vehicles.[1] However, there is a general consensus that internal combustion engines will continue to dominate the market for the foreseeable future.[1,2] As such, fuel-efficient combustion technologies like diesel engines offer superior green-house gas reduction potential. One technical obstacle to broader diesel implementation is the required lean NO_x aftertreatment system, especially to meet upcoming strict emission regulations.

NO_x is extremely difficult to reduce under an oxygen-rich environment.[3] Although its selective catalytic reduction by urea (urea-SCR) has recently been commercialized, the operation window of this technology is severely limited by the decomposition temperature (~ 200 °C) of urea into NH_3 and by SCR catalyst deactivation at temperatures higher than 750 °C.[4] This prohibits closer placement of the catalyst to the engine, requiring an aggressive warm-up with extra fuel burning during the cold-start. Furthermore, when integrating a mandatory particulate filter in the modern diesel aftertreatment system to mitigate soot and ash, the frequent regeneration of diesel particulate filters is required before a certain accumulation of soot, resulting in large temperature spikes. Improvement of the thermal durability of the SCR catalysts would, therefore, be the key to maximizing the fuel efficiency, as well as to producing clean emissions from diesel engines.

Metal-exchanged zeolites have drawn much attention as diesel vehicle SCR catalysts, and with copper-exchanged ZSM-5 and SSZ-13, which are medium- and small-pore zeolites with MFI and CHA topologies, respectively,[5] have been most widely studied for this reaction.[4] Cu-SSZ-13 has recently been implemented as the current standard catalyst in the mobile SCR technology because of its superior thermal durability compared to already known catalysts. When aged at 850 °C, however, even this catalyst, whose fresh form achieves greater than 90% NO_x conversion at 250 - 400 °C in steady state, loses its CHA structure and forms copper oxide (CuO_x) species, leading to severe activity loss.[6]

Although zeolite A (framework type LTA) is the first synthetic zeolite to be prepared,[7] its catalytic applications have long been severely restricted due to its poor thermal stability originating from the high framework Al content (Si/Al = 1.0). However, a recent success in the benzylimidazolium-mediated synthesis of its unprecedented high-silica (Si/Al > 8) form provides a key advantage in terms of structural stability with tunable loading of catalytically-active metal centers.[8] Here we report that when the copper ion exchange level increases to 100% (Cu/Al = 0.50), the high-silica (Si/Al = 16-23) Cu-LTA catalysts hydrothermally aged at 900 °C, i.e., the current regeneration temperature which the commercial Cu-SSZ-13 catalyst cannot withstand, show remarkable NO reduction activities.

Figures 1a and 1b show NO conversion as a function of temperature over Cu-LTA and Cu-SSZ-13 catalysts with essentially equivalent Si/Al and Cu/Al ratios, respectively. In the temperature range studied, all Cu-LTA catalysts produced a little amount of N_2O (Figure S1), an undesired by-product of this reaction, together with much lower NH_3 oxidation activities than the Cu-SSZ-13 catalysts with the corresponding Si/Al and Cu/Al ratios (Figure S2). While a notable increase in low-temperature activity was observed for fresh Cu-LTA catalysts as the Cu/Al

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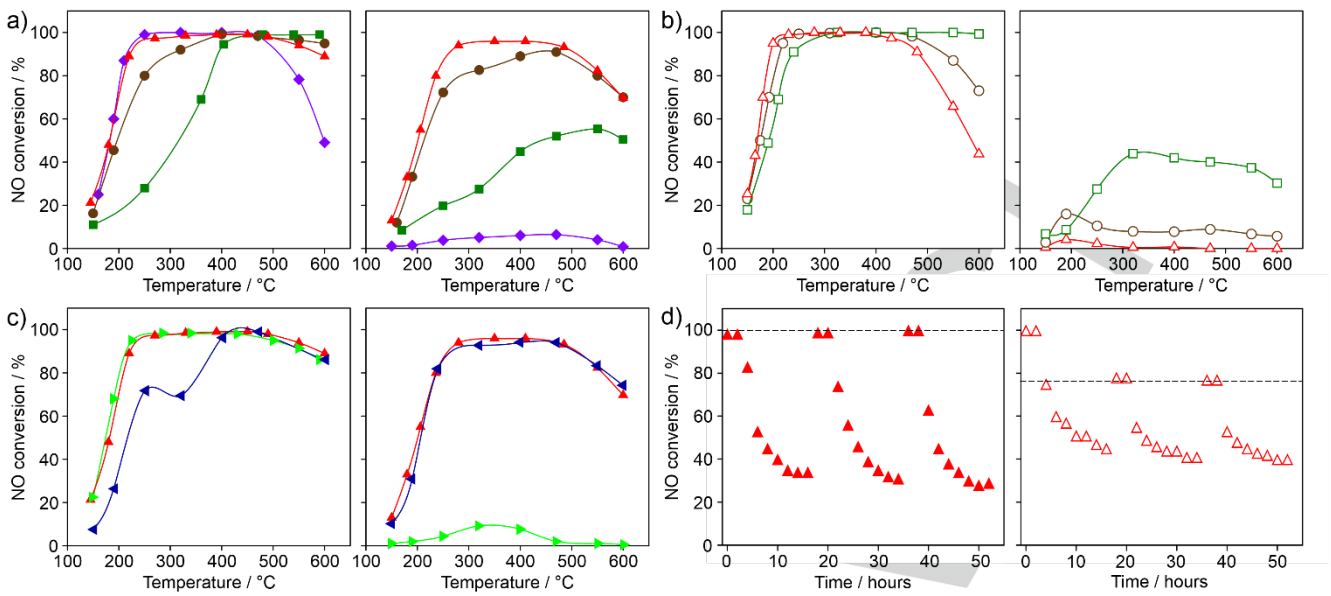

Figure 1. a) to c) NO conversion as a function of temperature over the (left) fresh and (right) 900 ºC-aged forms of Cu-LTA-16-0.14 (■), Cu-LTA-16-0.32 (●), Cu-LTA-16-0.48 (▲), Cu-LTA-16-0.65 (♦), Cu-LTA-11-0.48 (▶), Cu-LTA-23-0.50 (◀), Cu-SSZ-13-16-0.15 (□), Cu-SSZ-13-16-0.34 (○), and Cu-SSZ-13-16-0.49 (△). The feed contains 500 ppm NH_3, 500 ppm NO, 5% O_2, 10% H_2O balanced with N_2 at 100,000 h^{-1} gas hourly space velocity. Hydrothermal aging was performed under flowing air containing 10% H_2O at 900 ºC for 12 h. The last two values of the catalyst identification correspond to the Si/Al and Cu/Al ratios of the catalysts, respectively. d) Effects of 20 ppm SO_2 exposure as a function of time at 270 ºC on the NO conversion over fresh Cu-LTA-16-0.48 (▲) and Cu-SSZ-13-16-0.49 (△). The feed composition is the same as that described above.

ratio approaches 0.50, on the other hand, there are no significant differences in the high-temperature activity. These results substantially differ from those of fresh Cu-SSZ-13 catalysts. More interestingly, when hydrothermally aged in air containing 10% water vapor at 850 °C for 24 h, a larger difference in the $deNO_x$ activity between the best catalysts (i.e., Cu-LTA-16-0.48 and Cu-SSZ-13-16-0.15, where the last two numbers indicate the Si/Al and Cu/Al ratios, respectively) in the Cu-LTA and Cu-SSZ-13 series was found (Figure S3).

This trend becomes more apparent when aged at 900 °C for 12 h. None of the Cu-SSZ-13 catalysts prepared here exhibited NO conversions higher than 50%. However, the Cu-LTA-16-0.48 catalyst was still active and gave excellent stability (Figures 1a and 1b), although it lost its $deNO_x$ activity upon extending the aging time to 24 h at the same temperature (Figure S4). We also tested the $deNO_x$ activity of an over-exchanged Cu-LTA catalyst, i.e., Cu-LTA-16-0.65. While exhibiting similar activity after aging at 750 °C, as recently reported,[8b] it became almost zero when further aged at 900 °C, unlike the others with lower Cu/Al ratios (Figure 1a). This may be due to the easy formation of CuO_x clusters in the over-exchanged catalyst during hydrothermal treatment,[6] which has a detrimental effect on the stability of the zeolite support.

We next compared the SCR activities of three Cu-LTA catalysts with very similar Cu/Al ratios (0.49 ± 0.01) but different Si/Al ratios (11-23) and thus different Cu contents (3.6-2.0 wt%) (Figure 1c). There are no detectable differences in the activity of fresh Cu-LTA-11-0.48 and Cu-LTA-16-0.48, whereas the former catalyst became practically inactive upon hydrothermal aging at 900 °C. However, Cu-LTA-23-0.50, i.e., the Cu-LTA catalyst with the lowest Cu content (2.0 wt%), showed a significantly lower activity in the temperature region below 400 °C, revealing some influence of the Cu content. A striking finding is the notable enhancement of its low-temperature activity after aging at 900 °C for 12 h, as found in the copper ions exchanged into SAPO-34, the silicoaluminophosphate analog of SSZ-13.[9] Consequently, the overall activity became nearly the same as that of aged Cu-LTA-16-0.48. Moreover, no severe decrease in activity was observed even after 24 h of aging (Figure S4). This can be attributed to further stabilization or relocation of low-temperature active sites in Cu-LTA-23-0.48 during high-temperature treatment, making them more active.[10]

Various sulfur compounds present in most transportation fuels and lubricants are converted mainly into sulfur dioxide (SO_2) with a kinetic diameter of 4.1 Å,[11] a notorious catalyst poisoning agent, during the combustion. The time-on-stream activity of Cu-LTA-16-0.48 was compared with the Cu-SSZ-13 catalyst with similar Si/Al and Cu/Al ratios (Cu-SSZ-13-16-0.49) at 270 °C in the presence of 20 ppm SO_2 (Figure 1d). Their deactivation behavior was similar with a marginal difference rationalized by considering the slightly larger 8-ring widow size (4.1 vs 3.8 Å) of Cu-LTA catalysts.[5] However, the regeneration behavior was very different in that Cu-SSZ-13-16-0.49 reached less than 80% of the original activity, while Cu-LTA-16-0.48 was fully regenerated after post-treatment in air at 500 °C for 2 h (Figure 1d). This suggests the formation of ammonium sulfate-like species rather than more stable copper sulfate-like ones in the Cu-LTA catalyst. We also examined the effect of propylene (C_3H_6), another possible source of poisoning during SCR, on the activity maintenance of these

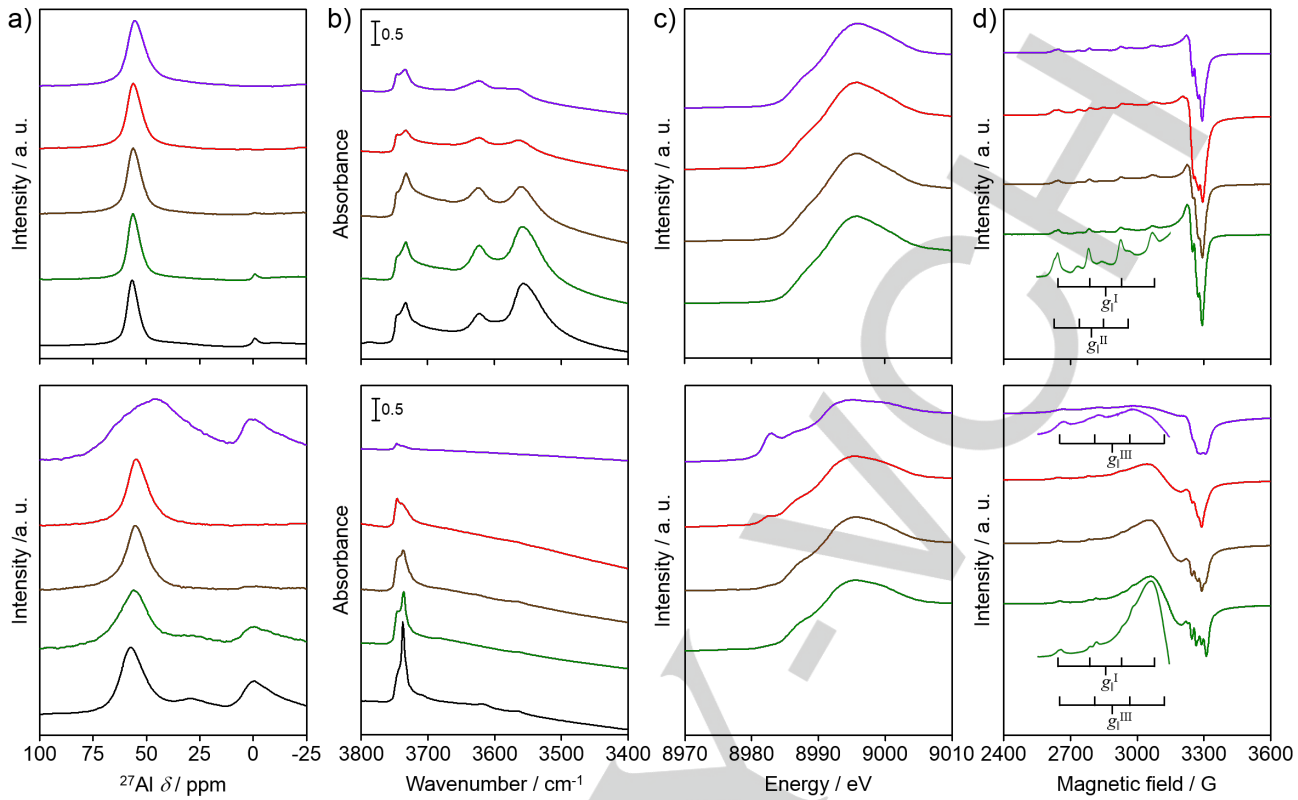

Figure 2. a) ^{27}Al MAS NMR spectra, b) IR spectra, in the 3800-3400 cm^{-1} region, c) Cu K-edge XANES spectra, and d) ESR spectra at room temperature of Cu-LTA catalysts with the same Si/Al ratio (16) but different Cu/Al ratios (0-0.65) before (top) and after (bottom) hydrothermal aging at 900 ºC for 12 h. In each panel, the spectra from top to bottom are for Cu-LTA-16-0.65, Cu-LTA-16-0.48, Cu-LTA-16-0.32, Cu-LTA-16-0.14, and Cu-LTA-16-0, respectively. Prior to ESR experiments, each catalyst was oxidized at 400 ºC and evacuated at the same temperature. The spectra of Cu_2O and CuO, XANES reference compounds, and of Cu^{2+} species supported on γ-Al_2O_3, an ESR reference material, can be found in Figure S8.

two catalysts, although this hydrocarbon would be easily removed in the presence of oxygen at elevated temperatures.[12] As expected from the kinetic diameter (4.7 Å) of C_3H_6 larger than the pore size of LTA framework,[11] no significant hydrocarbon poisoning by C_3H_6 was observed (Figure S5).

All fresh Cu-LTA catalysts, with the same Si/Al ratios (16) but different Cu/Al ratios (0 – 0.65), show one resonance around 57 ppm, typical of tetrahedral Al, in the ^{27}Al magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra (Figure 2a). A very weak signal around 0 ppm due to octahedral Al is also observable for the catalysts with Cu/Al ratios ≤ 0.32. However, this does not mean that no or little dealumination has occurred during Cu-LTA preparation, because paramagnetic Cu^{2+} ions have stronger interactions with octahedral Al species than with framework Al atoms.[4b] Hydrothermal aging at 900 °C for 12 h led to a notable increase of the octahedral ^{27}Al resonance that weakens as the Cu/Al ratio increases to 0.50. Particularly, aged Cu-LTA-16-0.48 with nearly 100% exchange level, which exhibits the best deNO_x performance (Figure 1a), still shows no octahedral ^{27}Al resonance (Figure 2a). A combination of powder X-ray diffraction (XRD) and N_2 sorption experiments reveals that all aged catalysts, except over-exchanged Cu-LTA-16-0.65, maintain their structural integrity (Figures S6 and S7). This indicates increased resistance against dealumination in Cu-LTA catalysts as the copper exchange level approaches 100%.

IR spectroscopy reveals that when fresh, both two OH bands around 3620 and 3550 cm^{-1} due to bridging Si-OH-Al groups[13] become weaker in intensity with increasing Cu/Al ratio up to 0.48, as expected (Figure 2b). Interestingly, upon severe hydrothermal aging at 900 °C, these are hardly observed for all catalysts. The Cu K-edge X-ray absorption near-edge structure (XANES) spectra in Figure 2c show that the copper species in Cu-LTA catalysts with Cu/Al ≤ 0.48 exist mainly as the divalent cation, even after aging at 900 °C. We also note that aged Cu-LTA-16-0.65 gives two pre-edge features around 8983 and 8987 eV due to the 1*s* → 4*p* transition of Cu^{+} and Cu^{2+} ions, respectively,[14] which may be responsible for the fairly lower structural stability of this over-exchanged catalyst compared to the other catalysts (Figures S6 and S7). In line with the ^{27}Al MAS NMR results (Figure 2a), therefore, it is clear that while zeolite Brønsted acidity does not play an important role in NH_3-SCR, the degree of removal of framework Al atoms, unbalanced by Cu^{2+} ions in Cu-LTA catalysts, is inversely proportional to the Cu/Al ratio. This led us to conclude that the Cu^{2+} ions in Cu-LTA

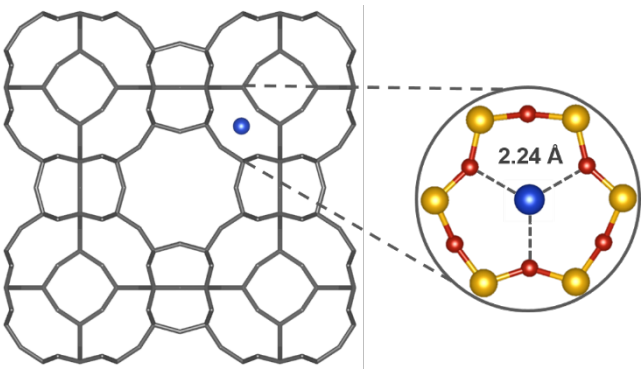

Figure 3. Structure of the fresh, dehydrated Cu-LTA-16-0.48 catalyst with one distinct Cu^{2+} site. A Cu^{2+} cation located at the center of single 6-rings are shown at the right. Color code: yellow, Si; red, O; blue, Cu.

serve not only as a catalytic center, but also as a dealumination suppressor. If such is the case, the electrostatic interactions between the divalent cation and two AlO_4^- tetrahedra with a single negative net charge would then be considerably stronger than expected.

We also used electron spin resonance (ESR) spectroscopy to obtain information on the local structure of isolated Cu^{2+} ions within Cu-LTA. The ESR spectra at room temperature of all fresh Cu-LTA catalysts in their dehydrated form are characterized by the two signals with $g_{\parallel}$ = 2.358, $A_{\parallel}$ = 145 G and $g_{\parallel}$ = 2.415, $A_{\parallel}$ = 110 G, respectively (Figure 2d). The $g_{\parallel}$ and $A_{\parallel}$ values of the signal with a much higher intensity are essentially the same as those of Cu^{2+} ions in the dehydrated form of LTA-type zeolites such as zeolite A and its high-silica analog ZK-4 that occupy single 6-ring (*s6r*) sites.[15] Also, the ESR parameters of the weak signal, which is hardly observable upon aging at 900 °C, are similar to those of the Cu^{2+} ions adjacent to the *s6r* but displaced into the *lta* cage.[15a] It is worth noting that unlike the other three Cu-LTA zeolites, aged over-exchanged Cu-LTA-16-0.65, which already lost crystallinity (Figure S6), exhibits only one ESR signal with $g_{\parallel}$ = 2.332, $A_{\parallel}$ = 155 G, corresponding to the Cu^{2+} ions supported on γ-Al_2O_3.[14]

The LTA structure is built from 14-hedral ($[4^6 6^8]$) *sod* cages linked together via 6-hedral ($[4^6]$) double 4-ring (*d4r*) cages in a cubic array to enclose the larger 26-hedral ($[4^{12}6^8 8^6]$) *lta* cage,[5] and at least eight crystallographic sites for extraframework cations are reported.[16] We did not attempt to locate the Cu^{2+} ions in Cu-LTA-16-0.32 and Cu-LTA-16-0.14 due to their low copper contents (< 2 wt%). However, we were able to determine the extraframework cation locations in fresh, dehydrated Cu-LTA-16-0.48 with a copper content of 2.7 wt% using synchrotron powder XRD and Rietveld analyses (Figure S9 and Tables S1-S3). The Cu^{2+} ions were found to be located only at the *s6r* centers where they are coordinated to three framework oxygen atoms at 2.24 Å along the three-fold axis (Figure 3), like those in copper-exchanged zeolite A.[15c] Remarkably, no Cu^{2+} ions in this Cu-LTA catalyst exist within 8-ring windows, in contrast to the case of Cu-SSZ-13 with quite similar Si/Al (15.5) and Cu/Al (0.45) ratios.[17] The Cu-LTA-16-0.48 catalyst was also hydrothermally aged at 750 °C for 24 h to minimize the intrazeolitic formation of CuO_x species (Figure 2c) that encumber locating extraframework cations, and were then subject to powder XRD and Rietveld analyses (Figure S10 and Tables S4 and S5). No noticeable changes in the local environment of Cu^{2+} ions are observed (Figure S11). Combined with the catalytic results in Figure 1, therefore, the efficient zeolite support for Cu^{2+} ions as an NH_3-SCR catalyst may not be necessarily limited to the cage-based, small-pore zeolites containing 8-hedral ($[4^6 6^2]$) double 6-rings as a structure-building unit like SSZ-13.

The framework structure of zeolites has long been recognized as one of the most important factors governing the extraframework cation positions in these microporous materials and, ultimately, their stability.[18] Indeed, our work demonstrates that the local Cu^{2+} environment in Cu-LTA is significantly different from that in Cu-SSZ-13.[4,19] The Cu-LTA catalysts described here opens up a completely new research direction for lean NO_x catalysts, even for gasoline-powered vehicles, and eliminates one of the road blocks in expanding the use of fuel-efficient diesel engines for future mobile transportations.

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Keywords: Cu-LTA • heterogeneous catalysis • hydrothermal stability • NH_3-SCR • zeolites

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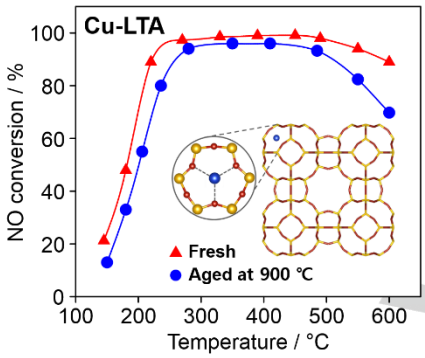
Layout 1:

COMMUNICATION

Fully copper-exchanged high-silica LTA zeolites show unprecedented activity for selectively reducing NO_x with NH_3 even after hydrothermal aging at 900 °C.



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