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Effects of Si/Al ratio on Cu/SSZ-13 NH_3-SCR catalysts: Implications for the active Cu species and the roles of Brønsted acidity

Feng Gao *, Nancy M. Washton, Yilin Wang, Márton Kollár, János Szanyi, Charles H.F. Peden *

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, United States

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ABSTRACT

Cu/SSZ-13 catalysts with three Si/Al ratios of 6, 12 and 35 were synthesized with Cu incorporation via solution ion exchange. The implications of varying Si/Al ratios on the nature of the multiple Cu species that can be present in the SSZ-13 zeolite are a major focus of this work, as highlighted by the results of a variety of catalyst characterization and reaction kinetics measurements. Specifically, catalysts were characterized with surface area/pore volume measurements, temperature programmed reduction by H_2 (H_2-TPR), NH_3 temperature programmed desorption (NH_3-TPD), and DRIFTS and solid-state nuclear magnetic resonance (NMR) spectroscopies. Catalytic properties were examined using NO oxidation, ammonia oxidation, and standard ammonia selective catalytic reduction (NH_3-SCR) reactions on selected catalysts under differential conditions. Besides indicating the possibility of multiple active Cu species for these reactions, the measurements are also used to untangle some of the complexities caused by the interplay between redox of Cu ion centers and Brønsted acidity. All three reactions appear to follow a redox reaction mechanism, yet the roles of Brønsted acidity are quite different. For NO oxidation, increasing Si/Al ratio lowers Cu redox barriers, thus enhancing reaction rates. Brønsted acidity appears to play essentially no role for this reaction. For standard NH_3-SCR, residual Brønsted acidity plays a significant beneficial role at both low- and high-temperature regimes. For NH_3 oxidation, no clear trend is observed suggesting both Cu ion center redox and Brønsted acidity play important and perhaps competing roles.

1. Introduction

The mechanism for ammonia selective catalytic reduction (NH_3-SCR) over Cu ion exchanged zeolite catalysts is still widely debated. Some key points of disagreement are as follows. (1) Whether the catalytically relevant Cu species are monomeric or dimeric (even, perhaps, very small Cu ion clusters) [1–3]. (2) Which NO_x and NH_x species are most relevant in the formation of key reaction intermediates? Specifically, whether NO oxidation to NO_2 is an indispensable step in standard SCR [2,4–6], and which NH_x species, NH_4^+, molecular NH_3, or even $NH_{2(a)}$, is the most relevant reductant? (3) Which reaction mechanism best describes NH_3-SCR? In particular, Langmuir–Hinshelwood, Eley–Rideal, and Mars van Krevelen (redox) mechanisms have been previously proposed for NH_3-SCR [7]. Note specifically that most prior mechanistic understanding for NH_3-SCR has been derived from the exhaustively studied VO_x/TiO_2 system. However, the applicability of such knowledge to the zeolite system is questionable since the latter has different catalytically active centers, much higher NH_3 storage capabilities and unique structural characteristics (confinement at a nanometer scale that also gives rise to electrostatic field effects). Most recently, the involvement of redox of metal ions as part of the reaction mechanism, seems to gain common agreement for zeolite-based catalysts [8–10]. (4) Whether Cu/CHA are dual functional in SCR; that is, whether both Cu ion sites and Brønsted acid sites collectively provide the catalytic functionality.

There have been numerous recent studies on the nature of Cu catalytic centers in Cu/SSZ-13 [9–20]. Cu has been suggested to stay predominately as isolated Cu^{2+} ions in SSZ-13; under dehydrated conditions they prefer windows of 6MR as noted above. However, depending on the Al content/distribution and Cu loading, even when only isolated Cu^{2+} ions are considered, there is still a high degree of complexity regarding their locations [10,13–15]. For example, at relatively low Si/Al ratios and low Cu loadings, one expects that (again, in dehydrated form) the majority of isolated Cu^{2+} ions reside near the windows of 6MR and bind with 2 Al T-sites [11,16]. In contrast, at very high Si/Al ratios where the possibility for finding 2 Al sites in one 6MR is highly unlikely, it is possible that isolated Cu^{2+} ions will interact with 2 Al sites that are farther apart (e.g.,. 2 Al sites in one 8MR). Alternatively, Cu ions

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* Corresponding authors.
E-mail addresses: feng.gao@pnnl.gov (F. Gao), chuck.peden@pnnl.gov (C.H.F. Peden) .

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at high Si/Al ratios may charge-balance only one Al site. In this latter case, $[Cu^{II}(OH)]^+$ or Cu^+ species are required in order to appropriately balance the negative framework charge [21]. Recently, Andersen et al. [22] studied the location of Cu^{2+} in CHA zeolite by X-ray diffraction using the Rietveld/maximum entropy method. These authors confirmed the presence of $[Cu^{II}(OH)]^+$ located in windows of 8MRs for high Cu-loaded Cu/SSZ-13, a notion fully consistent with theoretical studies [23].

Very recently, we conducted a detailed kinetic study of NH_3-SCR and two relevant reactions – i.e., NO and NH_3 oxidation – on a series of Cu/SSZ-13 catalysts with Si/Al = 6 and various Cu/Al ratios [10]. In terms of the nature of catalytically active Cu species, our results suggested the following key findings. (1) Below a reaction temperature of ~300 °C, strong solvation effects from H_2O and NH_3 render high mobility for isolated Cu^{2+} ions such that transient Cu-ion dimers form (in equilibrium with monomers) at low to intermediate Cu loadings. These transient dimeric species are catalytically relevant for standard NH_3-SCR and NH_3 oxidation reactions. (2) For standard NH_3-SCR, Cu-ion monomers are also catalytically active and even become the dominant catalytic centers at intermediate Cu loadings below ~300 °C. However, low-temperature active monomers are not located at windows of 6-membered rings (6MR). (3) Cu-ion monomers migrate to windows of 6MR at elevated reaction temperatures (>350 °C) and become the high-temperature catalytically relevant species. Because of the high redox barriers for Cu ion monomers in these locations, NH_3-SCR is characterized by high apparent reaction activation energies (~140 kJ/mol), much higher than typical apparent activation energies obtained on Cu/SSZ-13 zeolites at lower temperatures [9,15]. (4) At high Cu loadings (more than one Cu^{2+} ion per unit cell), permanent Cu-ion dimers form under SCR reaction conditions. While these moieties are active in NO oxidation to NO_2 and are believed to be (even highly) active for NH_3-SCR, they do not appear to improve catalyst performance. This can be rationalized by internal mass transfer limitations induced by these species since they both block pore openings and occupy space within CHA cages.

Overall, the interplay between Cu ion loading, Cu ion mobility and reaction temperature makes the entire NH_3-SCR reaction network quite complicated. Indeed, SCR catalysis is further influenced by CHA zeolite Si/Al ratios, and the effects are at least twofold: Si/Al ratios affect Cu ion locations as briefly discussed above, as well as significantly altering Brønsted acidity and, therefore, NH_3 storage of the catalysts. With regard to the roles of Brønsted acidity in SCR, the literature has been rather controversial. For V_2O_5-based SCR catalysts, reactive NH_3 in the form of NH_4^+ has been frequently proposed [7,24–27]. In explaining the beneficial effects of low Si/Al ratio to SCR on zeolite-based SCR catalysts, Yang and coworkers adapted the same argument and proposed that this is because more NH_4^+ species are formed at lower Si/Al ratios (i.e., more Brønsted acid sites) [28,29]. However, titration experiments in a few recent studies on Cu/CHA catalysts demonstrate that NH_4^+ species are far less reactive toward NO_x than molecular NH_3 adsorbed on Cu sites [30–32]. Interestingly, in V_2O_5-based catalysts, NH_4^+ binds to the catalysts more weakly than NH_3 adsorbed on Lewis acid sites [7], while it is the opposite for zeolite-based catalysts. Therefore, if one makes the reasonable argument that more weakly bound NH_x species are more reactive, consistency still maintains for the two classes of catalysts. In any case, for zeolite-based SCR catalysts, Brønsted acidity may be expected to influence the reaction by affecting Cu ion location and NH_3 storage (the latter plays a more significant role under transient rather than steady-state reaction conditions), rather than the formation of reactive NH_4^+. Indeed, in recent studies by Bates et al. [9,33] on a series of Cu/SSZ-13 SCR catalysts with Si/Al = 4.5 and a narrow range of Cu/Al ratios, the authors found an apparent zero-order dependence of SCR rates on the number of residual Brønsted acid sites measured from NH_3 titration. In our recent study, TOFs were also found to be largely insensitive to Cu/Al ratios under certain reaction conditions [10]. Note, however, that this zero-order dependence on Brønsted acidity may not be general: using samples with the same Si/Al ratio and a narrow range of low Cu/Al ratios (<0.2), the numbers of residual Brønsted acid sites in different samples are not expected to vary dramatically to allow reliable correlations between SCR rate and Brønsted acid density.

Importantly, correlation between SCR rates and residual Brønsted acid density requires the latter to be quantified *in situ* (i.e., under SCR reaction conditions). This is experimentally challenging. Recently, Gounder and coworkers developed protocols for *ex situ* quantification of Brønsted acid sites using NH_3-TPD [33,34]. These authors showed that, for Cu/SSZ-13 samples with high Al content and low Cu/Al ratios, Brønsted acid sites are exchanged by Cu^{2+} ions stoichiometrically (i.e., $2H^+$ per Cu^{2+}). However, this trend does not extend to high Cu loadings and is suggested to be due to the formation of Cu_xO_y clusters that do not play a charge-balancing role [34]. Recent studies by others also revealed the presence of substantial residual Brønsted acid sites in Cu/SSZ-13 at high Cu loadings. For example, one study by Giordanino et al. [35] determined that Brønsted sites are still present even if the Cu/Al ratio is not far from the stoichiometric exchange level. They suggested that some of the Brønsted sites are exchanged by monovalent copper complexes $[CuOH]^+$. In another study, Lezcano-Gonzalez et al. [31] showed that the intensity of ν_{OH} vibrations (bands at 3605 and 3585 cm^{-1} assigned to Brønsted acid sites) in their Cu/SSZ-13 sample at a 100% ion exchange level (i.e., Cu/Al = 0.5), was still comparable to their parent H/SSZ-13.

Clearly, from the recent publications described above, there is still much to learn about the nature of Cu ion species and the roles of Brønsted acidity in Cu/SSZ-13 SCR catalysts. For example, a catalytic property comparison between Cu^{2+} and $[Cu(OH)]^+$ active sites has not yet been established and SCR performance between catalysts with vastly different Brønsted acid site densities has not yet been studied. In the present study, we aim to obtain a more general picture on the roles of Cu ion location and Brønsted acidity in NH_3-SCR by using a relatively large number of samples with various Si/Al and Cu/Al ratios.

2. Experimental

2.1. Catalyst synthesis

Based on the above considerations, three SSZ-13 substrates with different Si/Al ratios were synthesized and used in the present study. The synthesis for SSZ-13 with Si/Al = 6 via a static hydrothermal method has been described in detail elsewhere [11,12] and will not be repeated here. For the two higher Si/Al ratio samples, synthesis was conducted hydrothermally under stirring using a method modified from a protocol developed recently by Deka et al. [16]. Composition of the gel is as follows: $10SDA:10NaOH:xAl_2O_3:100SiO_2:2200H_2O$, where x varies to allow preparation of samples with different Si/Al ratios. The gel is prepared first by dissolving NaOH (99.95%, Aldrich) in water and adding the SDA (TMAda-OH, Sachem ZeoGen 2825). Following which, $Al(OH)_3$ (contains ~54% Al_2O_3, Aldrich) and fumed silica (0.007 μm average particle size, Aldrich) were added sequentially under vigorous stirring until the gel was homogenized. The gel was then sealed into a 125 ml Teflon-lined stainless steel autoclave with a stir bar in. Thereafter, the autoclave was placed in a salt bath on top of a hot plate stirrer to carry out hydrothermal synthesis at 160 °C for 96 h under stirring. Note that continuous stirring during