THE NATURE OF THE ACTIVE Cu SPECIES IN Cu/CHA MATERIALS FOR THE SELECTIVE CATALYTIC REDUCTION OF NOx WITH NH_3

Feng Gao, Marton Kollar, Yilin Wang,
Janos Szanyi, and Charles H.F. Peden

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354
chuck.peden@pnnl.gov

Introduction

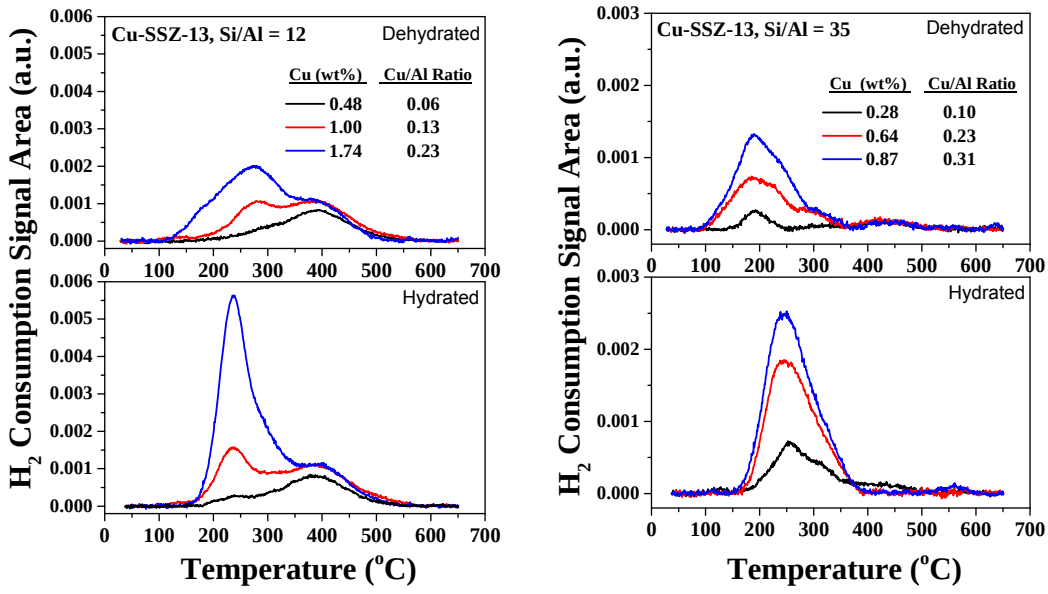
Metal-exchanged molecular sieves with a Chabazite (CHA) structure are of considerable current research interest due to the very recent commercial success of their application for the selective catalytic reduction (SCR) of NOx with ammonia on diesel vehicles [1]. Catalysts with outstanding SCR performance (activity, hydrothermal stability, etc.) include the aluminosilicate zeolite, SSZ-13, and the silico-alumino-phosphate, SAPO-34, with ion-exchanged Cu. Apart from the commercial success, detailed catalyst structures, reaction mechanisms, and structure-activity relationships are still lacking. In this presentation, we will describe results of more recent studies of Cu/SSZ-13 that specifically focus on the nature of the active Cu species under a variety of reaction conditions. Catalysts with varying Si/Al ratios and Cu loadings have been prepared and studied. We use a number of characterization methods including FTIR, x-ray absorption (XAS), and electron paramagnetic resonance (EPR) spectroscopies. Temperature-programmed reduction (TPR) experiments in the presence or absence of water are also highlighted. Besides these catalyst characterization measurements, we will also provide NH_3-SCR and NH_3 oxidation kinetics over these catalysts at high space velocity conditions for the development of structure-activity relationships.

Experimental

Na/SSZ-13 with a Si/Al ratio of ~6 was synthesized using a procedure detailed in reference [2]. For the two higher Si/Al ratio samples, synthesis was conducted hydrothermally using a method modified slightly from a protocol developed recently by Deka, et al. [3] with reactant ratios varied to provide differing Si/Al ratios. After exchange of Na^+ for NH_4^+, aqueous $CuSO_4$ solutions with varying concentrations were used to prepare Cu/SSZ-13 catalysts with Cu loadings. Reaction tests were performed using a plug-flow reactor and products were measured using an online FTIR detector. Catalysts were characterized with ICP, surface area/pore volume measurements, temperature programmed reduction (TPR), and x-ray absorption, electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and FTIR spectroscopies.

Results and Discussion

A portion of the results to be discussed are presented here. Of particular interest is the temperature at which Cu reduces from the +2 to +1 oxidation states during TPR experiments. This occurs at moderate (150-500 ºC) temperatures and often in distinct temperature ranges as a function of Cu loading [1]. For somewhat higher Cu-loaded (Cu/Al > 0.1) SSZ-13 samples with Si/Al = 6, H_2-TPR results for fully hydrated and fully dehydrated samples have been reported previously [4]. In more recent studies [5], experiments under identical conditions were conducted on Si/Al = 12 and 35 samples with various Cu loadings, and the results are plotted in Fig. 1. These results suggest that a number of factors determine the $Cu^{+2} \rightarrow Cu^{+1}$ reduction temperature: 1) Cu-ion location in the SSZ-13 structure (as indicted in our prior studies [4]); 2) the extent of Cu-ion 'bonding' to the zeolite (i.e., whether Cu ions interact with 1 or 2 ion exchange sites); and 3) whether reduction is carried out in the presence or absence of water, with water likely hydrolyzing Cu-zeolite O bonds and resulting in a mobile Cu-ion species.



(a) (b)

Figure 1: Temperature-programmed reduction (TPR) data for Cu-SSZ-13 samples with various Cu loadings for (a) Si/Al = 12 and (b) Si/Al = 35. The upper panels show TPR for dehydrated samples while the lower panels show TPR for fully hydrated samples.

On the basis of FTIR studies of the region of the spectra where T-O-T zeolite vibrations are observed, we recently noted that the presence of water eliminates newly formed (perturbed) T-O-T vibrations that occur in Cu/SSZ-13 catalysts [6]. These results also strongly suggest that the Cu/zeolite-O bonds have been hydrolyzed resulting in mobile Cu-ion species. Significantly, the perturbed T-O-T vibrations reappear when the catalyst is heated to approximately 250 ºC where water is largely removed from the zeolite. This latter result is especially interesting because this is the same temperature range at which an unusual dip in performance (the so-called “seagull” shape) for the “standard” (i.e., NOx = NO) SCR reaction is observed for Cu/SSZ-13 catalysts at lower Cu loadings [5]. We propose that a hydrolyzed, readily reducible and mobile Cu species is responsible for high standard SCR rates at lower temperatures, while Cu ions, strongly interacting with the zeolite upon dehydration, are more difficult to reduce and are only active at higher reaction temperatures.

Acknowledgement. This work was supported by the U.S. DOE/EERE/Vehicle Technologies Office.

References

(1) F. Gao, J.H. Kwak, J. Szanyi and C.H.F. Peden, *Topics in Catal.*, **2013**, 56, 1441, and references therein.
(2) D.W. Fickel and R.F. Lobo, *J. Phys. Chem. C*, **2010**, 114, 1633.
(3) U. Deka, A. Juhin, E.A. Eilertsen, H. Emerich, M.A. Green, S.T. Korhonen, B.M. Weckhuysen and A. M. Beale, *J. Phys. Chem. C* **2012**, 116, 4809.
(4) F. Gao, E.D. Walter, E.M. Karp, J.Y. Luo, R.G. Tonkyn, J.H. Kwak, J. Szanyi and C.H.F. Peden, *J. Catal.*, **2013**, 300, 20.
(5) F. Gao, E.D. Walter, M. Kollar, Y. Wang, J. Szanyi and C.H.F. Peden, *J. Catal.*, **2014**, submitted for publication.
(6) J.H. Kwak, T. Varga, C.H.F. Peden, F. Gao, J.C. Hanson and J. Szanyi *J. Catal.*, **2014**, in press.