

Understanding NH₃-SCR kinetics over Cu-SSZ-13 catalysts from motion of the Cu ions

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Introduction

With the successful implementation of Cu-SSZ-13 (a small pore zeolite with Chabazite (CHA) structure) as part of the emission control systems for diesel passenger vehicles, and light- and medium-duty trucks in the U.S. and Europe, there has been a new surge of research interest in NH₃-SCR over Cu-Chabazite; as evidenced by the more than 40 open literature publications that have appeared in the past 3 years [1,2, and references therein].

Previous studies have proposed that NH₃-SCR is solely catalyzed by isolated Cu²⁺ ions located at faces of 6-membered rings of the CHA structure [1]. However, under typical NH₃-SCR reaction conditions, that is, in the presence of large amounts of NH₃ and H₂O which both bind strongly with Cu ions as ligands at low to moderate temperatures, and an excess amount of O₂ which may interact with isolated Cu ion centers to generate Cu₂O_x complexes, it should not be expected that these ions remain in their dehydrated locations and forms, especially at relatively low temperatures.

Materials and Methods

Cu-SSZ-13 powder catalysts with different Si/Al ratios (6, 12 and 35) and various Cu loadings were synthesized using a traditional aqueous solution ion-exchange method. Standard NH₃-SCR and NO/NH₃ oxidation reactions were carried out using a plug-flow reaction system [3] described previously. The feed gas contained 350 ppm NO, 350 ppm NH₃, 14% O₂, 2.5% H₂O and balance N₂. Typical GHSV was 400,000 h⁻¹. Cu²⁺ mobility and conversions during hydration/dehydration and oxidation/reduction were monitored with H₂-temperature programmed reduction, FTIR, electron paramagnetic resonance (EPR) spectroscopy, among other routine characterization methods.

Results and Discussion

Figure 1 shows EPR spectra for a low Cu loading sample during dehydration. At ambient temperature (black curve), multiple features were found at high field and the low-field hyperfine structures were partially shielded by a large broad signal caused by rapid Cu²⁺ ion mobility and dipolar interactions between Cu²⁺ ions [3]. At 250 °C (blue curve), only one sharp feature was detected at high field, and the low-field hyperfine structures became well-defined indicating a loss of mobility for Cu²⁺ ions. Interestingly, at intermediate temperatures, especially at 150 °C (red curve), intensity for the high-field feature decreases dramatically, and the low-field hyperfine structures are completely absent. This signal loss is caused by dipolar interactions between Cu²⁺ ions, demonstrating that the Cu²⁺ ions are still highly mobile at 150 °C. It is expected that during NH₃-SCR (i.e., in the presence of H₂O and NH₃, ligands that bind strongly with Cu ions at relatively low temperatures), Cu ion mobility can extend to even higher temperatures.

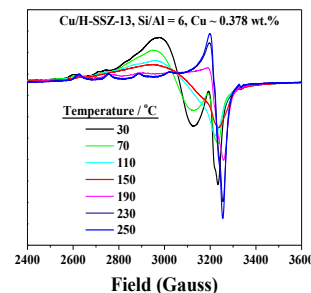


Figure 1 Electron Paramagnetic Resonance (EPR) spectra of a Cu-SSZ-13 sample (Si/Al = 6, Cu/Al = 0.032) during dehydration.

Figure 2 (a) presents standard SCR reaction results collected on a series of low-Cu loading samples. From this graph, the existence of multiple kinetic regimes is obvious. From 100 to ~250 °C, NO_x conversions increase with increasing temperature and Cu loading, while from ~250 to ~350 °C, NO_x conversions decrease with increasing temperature. Above ~350 °C, NO_x conversions increase again very rapidly with increasing temperature. **Figure 2(b)** displays NO_x conversions shown in Figure 2(a) plotted as a function of the square of the Cu loading. As long as NO_x conversions are maintained in the differential regime, a linear relationship exists between NO_x conversion and the square of the Cu loading for temperatures below 250 °C, strongly suggesting that below ~250 °C, the catalytically active centers are a Cu-dimer species. From 250 to 350 °C, the instability of such species causes NO_x conversion to decrease. Only in the high-temperature regime (> 350 °C) are isolated Cu²⁺ ions the active centers.

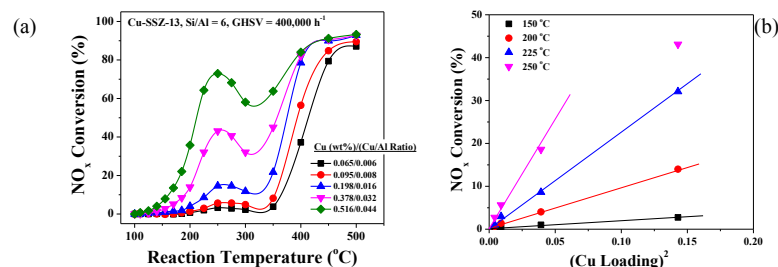


Figure 2(a) NO_x conversions as a function of temperature during standard SCR for Cu-SSZ-13 samples with various Cu-loadings. Different symbols represent samples with different Cu loadings. **Figure 2(b)** NO_x conversions shown in Fig. 2(a) plotted as a function of the square of the Cu loading. Note the linear relationships at differential NO_x conversions.

Significance

Transient Cu-dimers are the relevant active sites at reaction temperatures ≤ 350 °C for NH₃ oxidation and standard SCR reactions. This case study emphasizes the importance of considering the dynamic nature of catalytically active sites under reaction conditions.

References

- [1] U. Deka, I. Lezcano-Gonzalez, B.M. Weckhuysen, A.M. Beale, ACS Catal. 3 (2013) 413.
- [2] F. Gao, J.H. Kwak, J. Szanyi, C.H.F. Peden, Top. Catal. 56 (2013) 1441.
- [3] F. Gao, E.D. Walter, E.M. Karp, J.Y. Luo, R.G. Tonkyn, J.H. Kwak, J. Szanyi, C.H.F. Peden, J. Catal. 300 (2013) 20.