

Following the movement of Cu ions in a SSZ-13 zeolite during dehydration, reduction and adsorption: a combined *in situ* TP-XRD, XANES/DRIFTS study

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Introduction

Stringent environmental regulations require the development of new catalysts that are able to remove harmful components of automotive exhaust gases. The small pore, Cu ion exchanged-zeolite, SSZ-13, with chabasite (CHA) structure shows remarkable activity, N₂ selectivity and hydrothermal stability in the selective catalytic reduction (SCR) of NO_x with NH₃ under lean conditions [1]. In spite of the extensive studies aimed at understanding this catalyst, the locations of the Cu ions in the CHA framework are still debated. The results of earlier studies have suggested that Cu ions were located exclusively in the center (or off center) of the six member ring building blocks of the double six member ring prisms [2]. Our FTIR and H₂ TPR studies indicated that Cu ions were located in two distinct cationic positions, and exhibited rather different reducibilities [3]. Furthermore, these studies also revealed that due to the strong interaction between Cu ions and certain reactants (e.g., NH₃ and H₂O) the location of Cu ions strongly dependent on the gas environment. In this study we used a combined diffraction/spectroscopy (XRD/XANES/DRIFTS) method to identify the positions of Cu ion in the CHA framework under different environments (calcination, oxidation and reduction with CO). The results unambiguously show the dynamic nature of the active Cu ion sites in the CHA structure. These results help understanding the variations in catalytic activity of this material under different reaction conditions.

Materials and Methods

The Cu-SSZ-13 catalyst used throughout this study was synthesized in house following the procedure reported in the literature [2]. The Cu-SSZ-13 sample had a Si/Al ratio of 6, ion exchange level of 80%, and the rest of the charges were balanced by protons. All the experiments discussed here were conducted at beam line X18A at the National Synchrotron Light Source at Brookhaven National Laboratory. For the XANES/TP-XRD measurements, a Kapton tube was loaded with the Cu-SSZ-13 catalyst sample and mounted onto a sample holder assembly that allowed for controlled heating, and ensured constant gas flow through the catalyst bed. The combined XANES/DRIFTS measurements were carried out in the reactor cell of a praying mantis DRIFTS assembly. In both experimental set-ups the gas delivery to the reactors were controlled by mass flow controllers.

Results and Discussion

Temperature-programmed XRD experiments were carried out on the Cu-SSZ-13 sample in an O₂/He gas stream from 25 to 400 °C in order to substantiate the movement of Cu²⁺ ions during dehydration. The series of XRD patterns collected during calcination is displayed in Fig. 1 in the narrow 2-theta range of 15.5-23.0°. Variations in both the intensities and positions of the diffraction peaks indicate the movement of cations in the zeolite framework as water is being removed. DRIFTS and XANES spectra collected simultaneously during the calcinations of the Cu-SSZ-13 sample in O₂/He flow are also displayed in Fig. 1, middle and left panels, respectively. Some of the T-O-T vibrations of the zeolite framework are sensitive to the electrostatic environment of the charge compensating cation. This interaction manifests itself in the development of perturbed T-O-T vibrational feature in the 800-1000 cm⁻¹ spectral region. This band is sensitive to both the oxidation state and the coordination environment of the cation. The series of IR spectra shown here clearly indicate changes in the perturbed T-O-T feature as the sample is gradually losing water. At high H₂O content Cu²⁺ ions are fully hydrated, and interact weakly with the zeolite framework. As water is being removed, well defined aqua complexes form first, then as all the water is removed from the hydration shell of the cation, Cu²⁺ strongly interact with zeolite framework as it moves to its crystallographic position. The presence of two features is the consequence of two well defined cationic position in the CHA structure. The differential XANES spectra displayed in the left panel of Fig. 1 also shows the progression of H₂O removal from the Cu-SSZ-13 sample. The XANES spectrum is also very sensitive to both the oxidation state of the Cu ions, and their coordination environment. Similar experiments were carried out during reduction with CO as well.

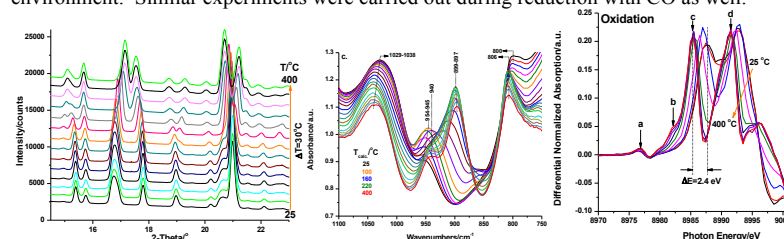


Figure 1. TR-XRD (left), DRIFTS (middle) and XANES (right) spectra recorded during the calcination of a Cu-SSZ-13 sample from 25 to 400 C in an O₂/He flow.

Significance

Understanding the state of cations under reaction conditions is essential to establish a viable reaction mechanism for the SCR of NO_x with NH₃. All the results obtained in this study clearly show the dynamic nature of cation positioning, and movement in the CHA framework.

References

1. J.H. Kwak, R.G. Tonkyn, D.H. Kim, J. Szanyi, C.H.F. Peden, J.Catal. 275 **2010** 187; J.H. Kwak, D. Tran, S.D. Burton, J. Szanyi, J.H. Lee, C.H.F. Peden, J.Catal. 287 **2012** 203.
2. D.W. Fickel, R.F. Lobo, J Phys.Chem.C 114 **2010** 1633; U. Deka, A. Juhin, E.A. Eilertsen, H. Emerich, M.A. Green, S.T. Korhonen, B.M. Weckhuysen, A.M. Beale, J.Phys.Chem. C 116 **2012** 4809.
3. J.H. Kwak, H. Zhu, J.H. Lee, C.H.F. Peden and J. Szanyi, Chem.Comm., **48** **2012** 4758–4760.