

IN SITU XAFS OF Cu-ZSM-5 NO_x-REDUCTION CATALYSTS

Increasing governmental restrictions on the release of nitrogen oxides (NO_x) from combustion sources has intensified the need for innovative techniques to accurately analyze catalytic systems. One particularly promising catalytic system is a copper-exchanged zeolite (Cu-ZSM-5) that has been found to be useful in the decomposition and selective catalytic reduction of NO_x by using short-chain hydrocarbons. However, the performance of this system has not been fully studied or optimized for NO_x removal. Recently, researchers at the Materials Research Collaborative Access Team (MR-CAT) beamline 10-ID were able to probe the Cu-ZSM-5 system *in situ* to provide a more complete understanding of the working catalyst [1]. The *in situ* technique, coupled to an improved experimental setup (hardware and software) at the MR-CAT sector, has resulted in a more detailed fundamental understanding of Cu-ZSM-5, with the potential for improving the catalyst for NO_x abatement to meet newer environmental standards.

The Cu-ZSM-5 system has been researched extensively by means of a number of methods, but a fundamental understanding of the nature of the catalytic system under reactive conditions had yet to be achieved. *In situ* x-ray absorption fine structure (XAFS) spectroscopy, as previously demonstrated in work by Iwasawa and colleagues [2-4], is an optimal catalyst probe. The MR-CAT team realized that a possible clue — the existence of a Cu¹⁺ state — was not well resolved in the previous work, because to adequately resolve the appearance and disappearance of the Cu¹⁺ pre-edge feature, the data needed to be taken at a higher energy resolution. The MR-CAT facility was outfitted with hardware and software that permit rapid scanning of the Cu K absorption edge (less than 2 min per scan) and allow the design of temperature-programmed experiments that can be completed within a few hours. During a typical 3-h run, more than 40 scans can be collected for a sample at a temperature resolution of ~15°C. This temperature resolution allows for fine analysis of the critical events in the reduction or oxidation processes as a function of temperature. To demonstrate the capabilities, the team studied the temperature-programmed reduction of Cu-ZSM-5 in both H₂ and CO atmospheres. During H₂ reduction (Fig. 1), the Cu¹⁺ pre-edge is clearly visible, and the transitions of Cu²⁺ to Cu¹⁺ and of Cu¹⁺ to Cu⁰ are in good agreement with data collected from *ex situ* reduction. With this quantity and resolution of data, the team used factor analysis to identify the various states of copper reduction on the basis of features in the near-edge region and observed the presence of two separate Cu¹⁺ phases that differed only in their local coordination geometries. Separation of such phases would not have been possible without the rapid, high-energy-resolution scans made possible at MR-CAT.

With the new data collection equipment installed at the MR-CAT insertion device beamline, the MR-CAT team is now able to study catalytic systems under real reaction conditions with the high energy resolution and on the timescales necessary for complete analysis. Further improvements in beamline hardware and catalytic cells will allow rigorous scanning under true flow conditions and high pressures. A new sample cell design is currently allowing the analysis of multiple catalyst samples under identical operating conditions.

REFERENCES

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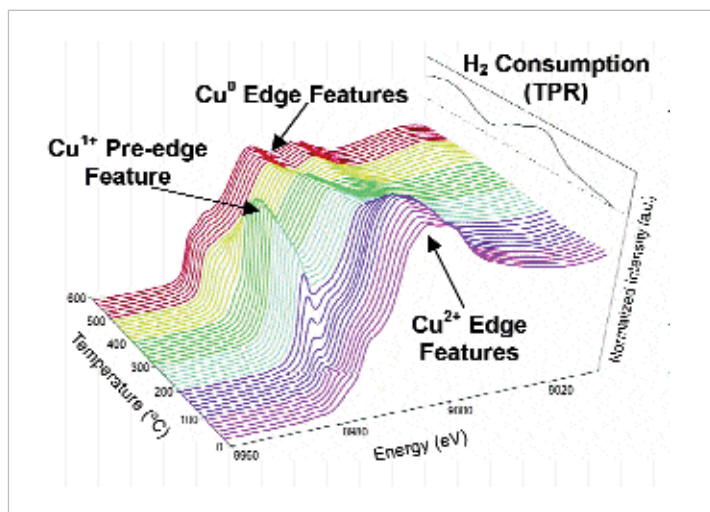


Fig. 1. Normalized XANES spectra across the Cu K edge collected during the temperature-programmed reduction (TPR) of Cu-ZSM-5 in 5% H₂/He at a rate of 3°C/min. Note the H₂ consumption.