

Direct Oxidation of Benzene to Phenol in Air over a Zeolite-based Catalyst

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The selective oxidation of benzene to phenol is a reaction of great interest: World production was 7.8 megatons in 2001. The current technology to produce phenol is via the Cumene Process, a 3-step reaction that is energy intensive, generates a large amount of waste and produces acetone as a co-product. Our goal is to find an alternative technology that will directly convert benzene to phenol free of co-products. We have successfully used Cu-ZSM-5 to produce phenol in a one-step process. Among the many parameters that influence the catalysis, the Cu exchange level has a strong effect on the selectivity of the catalyst: Low Cu loadings favored the formation of phenol, while high loadings shift the selectivity to CO₂. Previous reports on Cu-ZSM-5 proposed many different Cu ion sites [1, 2, 3]. In this report, we studied the *in situ* temperature-programmed reduction (TPR) of Cu-ZSM-5. The data were analyzed and fitted to a novel model that supports our catalysis results.

During H₂-TPR, the Cu²⁺ ion exchanged in the zeolite undergoes a two-step reduction to Cu⁺ and Cu⁰. These three species are clearly observed in the XANES region (Fig. 1). The main difference between different Cu loadings is the temperature at which the second reduction step occurs. The high-temperature reduction

peak (Cu⁺ to Cu⁰) shifts to higher temperatures as the Cu loading decreases. During this step, the metallic Cu migrates to form small clusters; more dispersed Cu ions require higher temperatures for the reduction. These results indicated that, at low loadings, the Cu sites are isolated and promote phenol formation.

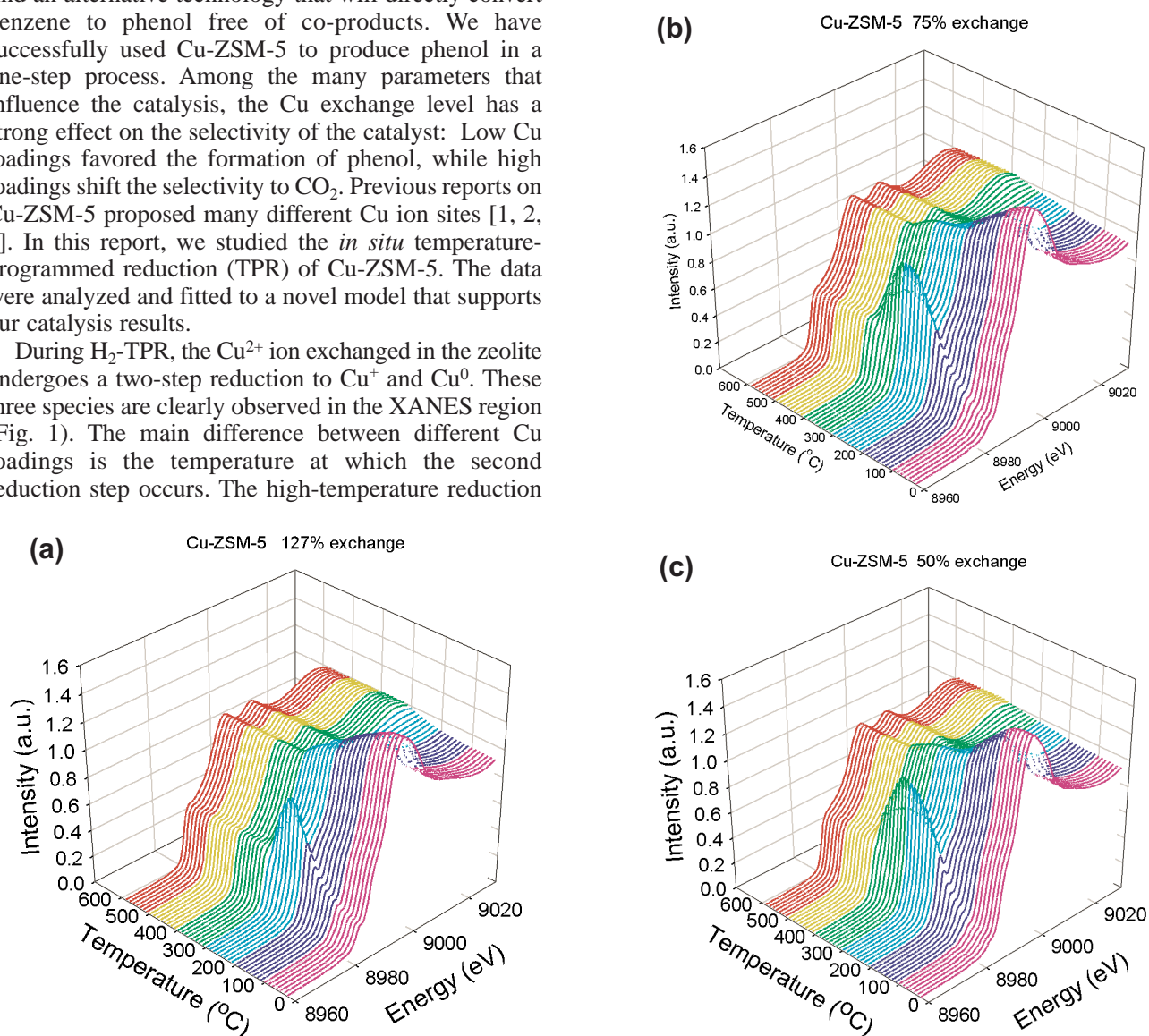


FIG. 1. Normalized XANES spectra of Cu-ZSM-5, (a) 127% exchange, (b) 75% exchange, (c) 50% exchange, collected during the temperature-programmed reduction in 4% H₂/He.

From the XANES data, it appears that isolated Cu sites are the ones responsible for the selectivity of the reaction. A suitable model of an isolated Cu is the octahedral hexaaquacopper complex, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. From the EXAFS data, only five neighboring oxygens could be fit: 4 short Cu-O bonds and 1 longer Cu-O bond. The axial bond is elongated, as expected from the Jahn-Teller theorem. We can predict then that the Cu ion has a square pyramidal configuration (see Fig. 2).

As the reduction temperature increases, a new path appears at 100°C, attributed to a Cu-Cu interaction. At higher temperatures, Cu^{2+} (monomer or dimer) is reduced to Cu^+ . As the Cu loading increases, this Cu-Cu path appears at lower temperatures. In the 127% exchange level sample, these Cu dimers appear from room temperature (see Fig. 3). These species appear to be responsible for the shift in the selectivity of the reaction.

To summarize, this *in situ* XAFS experiment helped us elucidate the structure of the active site responsible for the selectivity of the benzene-to-phenol oxidation. At low Cu loadings, the ions are isolated and have a square pyramidal geometry. At high loadings, Cu dimers are present, and they are responsible for the

deep oxidation of benzene or phenol to CO_2 . Further experiments doping the catalyst with other metals are in progress.

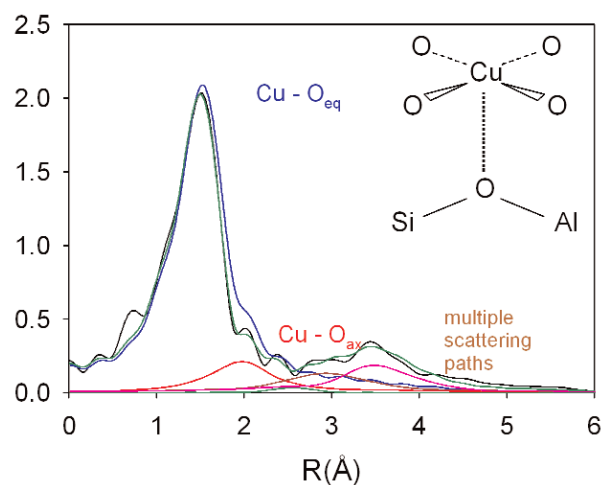


FIG. 2. Fitting results from Cu-ZSM-5, 50% exchange level, EXAFS data at room temperature

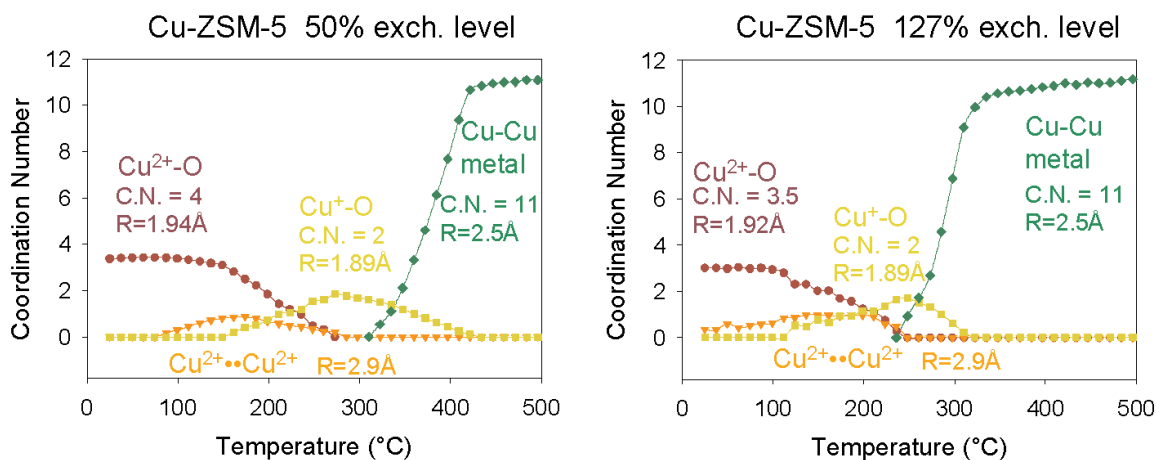


FIG. 3. Coordination numbers of the Cu-O and Cu-Cu species as a function of temperature, as fitted from the EXAFS spectra during H_2 -TPR.