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

Norma B. Castagnola,[1] Christopher L. Marshall,[1,*] and A. Jeremy Kropf[1]
[1]Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

Introduction

Phenol is a valuable commodity produced primarily via the Cumene Process, a multi-step reaction that generates phenol and acetone in equimolar amounts. In the past, several catalysts have been examined using a number of oxidants. While yielding phenol as the only product, the cost of the oxidants makes their commercial application prohibitive. Recently, direct gas-phase oxidation of benzene to phenol using molecular oxygen has been reported [1]. The catalyst used was Cu-ZSM-5, well-known for its unique activity in NO decomposition.

We have studied the selective oxidation of benzene over Cu-ZSM-5 using a single-pass gas-phase reactor. To optimize the system, we analyzed a series of parameters, such as the addition of water to the reaction, the Si/Al ratio of the zeolite, the Cu loading and the temperature. The properties of the Cu-exchanged ions were studied by temperature-programmed reduction and *in situ* XAS analysis.

Results and Discussion

We carried out the reaction using air as the oxidant, with GHSV = 2300 h^{-1}. At 400^oC and using only air, benzene conversion was 10-15% and phenol was produced at 0.83% yield with 9% selectivity, results comparable to those reported [1]. The addition of water improved both the phenol yield (2.3%) and selectivity (21%). The controlled reduction of Cu^{2+} to Cu^+ in H_2 demonstrated that Cu^{2+} is necessary for the formation of phenol. When Cu^+ was the starting material, the initial yield to phenol was almost zero. Once Cu^+ oxidized to Cu^{2+} under the reaction conditions, the yield to phenol increased dramatically.

The reaction generated a large number of by-products. The acidity of the support promoted secondary reactions that lessened the yield to phenol. When the reaction was carried out at 200^oC, the selectivity to phenol increased notably, but the conversion was rather low. Nevertheless, this temperature yielded only a few by-products, which facilitated the study of the catalyst under different conditions. Without the addition of water, no phenol was produced at 200^oC.

The Cu wt% and the Si/Al ratio in Cu-ZSM-5 were varied in order to identify the best catalyst composition. Table 1 shows the selectivity to phenol and CO_2 at different Si/Al ratios and different Cu loadings. The catalyst with a Si/Al ratio of 25 and a Cu loading of 0.85 wt% gave the best selectivity to phenol. Higher Cu loadings favored the formation of CO_2. Previous reports on Cu-ZSM-5 proposed two Cu sites: one predominates at low Cu loadings and the second predominates at high Cu loadings [2]. CuO is formed in Cu-ZSM-5, exchanged at more than the 100% level; this catalyst is far more selective to CO_2 formation.

Table 1. Catalytic results of Cu-ZSM-5 at 200°C

	Si/Al ratio				
	15	25			40
Cu Loading wt %	0.85	0.85	1.5	1.9	0.85
Selectivity to Phenol (%)	59	70	25	20	52
Selectivity to CO_2 (%)	22	14	55	65	21

Temperature-programmed reduction of the Cu-exchanged zeolites showed that the high-temperature reduction peak (Cu^+ to Cu^0) shifts to higher temperatures as the Cu loading decreases. During this second reduction step, the metallic Cu migrates to form small clusters; more dispersed Cu ions require higher temperatures for the reduction.

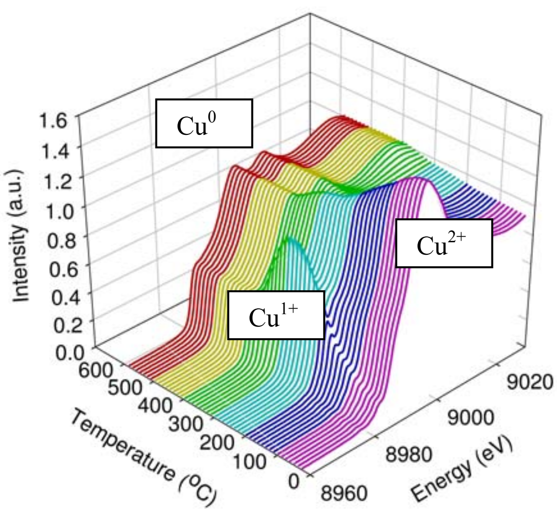

Figure 1. Normalized XANES spectra of Cu-ZSM-5 collected during the temperature-programmed reduction in 4% H_2/He.

In situ XANES temperature-programmed reduction (Figure 1) agreed with these results. Preliminary analysis of the data indicated that $Cu^{2+} \rightarrow Cu^+$ reduction is insensitive to Cu loading. However, high Cu loadings resulted in low-temperature reduction of $Cu^+ \rightarrow Cu^0$. This indicates that at low loadings, the Cu sites are isolated and promote phenol formation. *In situ* EXAFS followed the formation of Cu-Cu bonding as a function of Cu loading and reduction temperature.

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