

Studies of Cu-ZSM-5 by X-ray absorption spectroscopy and its application for the oxidation of benzene to phenol by air

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Abstract

The oxidation of benzene to phenol has been successfully carried out in air over Cu-ZSM-5 at moderate temperatures. Several parameters such as Cu loading, calcination temperature and co-exchanged metal ions influence the nature of the catalyst. At low Cu loadings, the catalyst is more selective to phenol while at high Cu loadings CO₂ is the major product. In situ H₂-TPR XAFS studies reveal that at low Cu loadings, Cu exists as isolated pentacoordinated ions, with 4 equatorial oxygens at 1.94 Å and a more distant axial oxygen at 2.34 Å. At higher loadings, monomeric as well as dimeric Cu species exist, with a Cu–Cu distance of 2.92 Å. This suggests that the isolated Cu sites are the active sites responsible for phenol formation. When the catalyst was calcined at 450 °C, the activity peaked in the first hour and then slowly deactivated, but when the calcination temperature was increased to 850 °C, the activity slowly increased until it reached a plateau. Analysis of the XANES region during in situ H₂-TPR shows that at lower calcination temperatures two reduction peaks are present, corresponding to Cu²⁺ → Cu⁺ and Cu⁺ → Cu⁰. At high calcination temperatures, only a small fraction of the Cu undergoes the two-step reduction and most of the Cu remains in the +2 state. Slow deactivation of the catalyst calcined at 450 °C is due to migration of the Cu ions to inaccessible sites in the zeolite; at high calcination temperatures the Cu is tightly bound to the framework and is unable to migrate. EXAFS analysis of the sample calcined at 850 °C reveals two Cu–Si(Al) scattering paths at 2.83 Å. Doping the catalyst with other metals, in particular Ag and Pd, further improves the activity and selectivity of the reaction. The addition of water to the reaction increases the selectivity of the reaction by displacing the product from the active site.

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1. Introduction

Phenol is a widely used chemical and a versatile building block for the plastic industry. Global phenol production was 7.8 million tonnes in 2001 [1]. About 95% of the phenol is produced via the cumene process, a three-step reaction that is energy intensive and produces phenol and acetone in equimolar amounts. The major problem with this process is the difficulty to market the quantity of acetone produced; as a result the economics of the process becomes dependent on the acetone demand. This situation has prompted the development of alternative routes to produce phenol free of co-products. Among these routes, the direct gas phase

oxidation of benzene is an attractive alternative for the current technology; it is a one-step process and environmentally benign. Nitrous oxide has been successfully used over Fe-ZSM-5 [2–5]; conversions of up to 30% with over 95% selectivities were achieved. Unfortunately, this route is not viable unless the oxidant is obtained cost-free, as in the case of Solutia, which has invested in this technology since nitrous oxide is obtained as a by-product from its adipic acid process. In addition, a quick deactivation is observed due to coke formation [6]; about two thirds of the activity is lost after 20 h on stream. In situ formation of nitrous oxide by oxidation of ammonia in air has been used as an oxidant over a Ca,Cu-hydroxyapatite catalyst; about 3.5% conversion with 97% selectivity to phenol was achieved at 450 °C [7]. Hydrogen peroxide is a valuable and desirable oxidizing agent because of its good activity and selectivity at low temperatures. It can

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be formed in situ in the gas phase via the catalytic hydrogenation of oxygen over Pd-membranes. Recently, a thin Pd layer in a shell-and tube-reactor has been successfully used to form phenol, with conversions of 13% with 85% selectivity at 150 °C [8,9]. The drawback of this method is again the cost of cryogenic gases and the risks associated with using both hydrogen and oxygen.

Tsuruya and co-workers [10,11] reported for the first time the use of Cu-ZSM-5 as a catalyst for the one step oxidation of benzene to phenol using molecular oxygen (20% in N₂) as the oxidant. Several conditions were optimized, and at 400 °C, the yield to phenol was 4.9% with ca. 30% selectivity. This is a promising system, since Cu-ZSM-5 is a very convenient and well-known catalyst for the decomposition of NO_x.

In this paper, we study further the Cu-ZSM-5 system to better understand the nature of the active site. Instead of using a combination of pure gases (N₂ and O₂), air is chosen as the oxidant. We use a continuous gas phase plug-flow reactor to determine the performance of Cu-ZSM-5 in the oxidation of benzene to phenol with air. The catalytic results depend strongly on the amount of Cu exchanged in the zeolite and the temperature at which the samples are calcined. In situ H₂-TPR XAFS studies of the catalysts gives us insight about the dispersion of the Cu species and their structure within the zeolite framework. In agreement with previous spectroscopic data published, in particular EPR, the coordination around the Cu ions is proposed and simple models were used to fit the data in the EXAFS region. The samples were further characterized using XRD and NMR to observe changes in crystallinity with temperature. We also propose the role of water in the reaction and the effect of doping the catalyst with other metals, such as Pd and Ag.

2. Experimental

Catalyst samples were prepared by conventional exchange methods. Zeolite NH₄-ZSM-5 (Zeolyst, SiO₂/Al₂O₃ = 30, 55, 80) was calcined at 500 °C for 5 h. Cu-ZSM-5 was prepared by ion exchanging the appropriate amount of a 0.03 M Cu(NO₃)₂ solution in 10 g of freshly calcined H⁺-ZSM-5. The volume of the suspension was leveled to 100 ml with distilled water and the slurry was stirred for a few hours at room temperature. During the exchange, the pH of the solution was slowly raised to 8 by using a dilute solution of NH₄OH. The suspension was stirred for another 24 h, and then filtered, washed and dried at 100 °C. The catalyst was calcined in air in a static oven for 5 h at different temperatures. The Cu content was determined by ICP-MS and the exchange level was estimated based on a Cu/Al ratio of 0.5. To study the effect of the Si/Al ratio, three parent NH₄-ZSM-5 zeolites with Si/Al of 15, 27.5 and 40 were used at a fixed Cu loading of 0.85 wt.%. To study the effect of Cu loading, three samples using H⁺-ZSM-5 (Si/Al = 27.5) were prepared with 0.85,

1.6 and 1.9 wt.% Cu, corresponding to exchange levels of 53, 100 and 120%. These catalysts are referred to as Cu-ZSM-5(53), Cu-ZSM-5(100) and Cu-ZSM-5(120). Additional catalysts were prepared by ion-exchanging silver and palladium after calcination of Cu-ZSM-5 at optimum temperatures. The pH of the exchange was 7 and the final metal loading was 0.85 wt.% Cu, 0.08 wt.% Pd and 1 wt.% Ag. The exchange levels were 53% Cu, 3% Pd and 18% Ag.

The gas phase oxidation of benzene to phenol was carried out at atmospheric pressure in a continuous plug-flow reactor (stainless steel, 8 mm i.d., 380 mm length). One half gram of catalyst (30–40 mesh), with 0.5 g of SiC as diluent (Electro Abrasive, 40 mesh, 350 μm particle size) were placed in the reactor and heated in air (Zero Chromatographic grade, AGA) up to the reaction temperature. Once the desired temperature is reached, benzene and water were pumped separately into the reactor. The reactant feed had the following molar % composition: N₂ 67.5%, O₂ 18%, benzene 8% and water 6.5%; the total flow was 1.47×10^{-3} mol/min, with a space velocity of 2500 h⁻¹. The liquid products were analyzed on-line with a HP 5890 Series II with an FID detector using a DB-5 column (30 m, 0.53 mm i.d., 1.5 μm film). The gas products were analyzed with a HP 5890 Series II Plus with a TCD detector using a 10%TCEP CPAW 80/100 (3 m × 3.2 mm) and a Haysep DB 100/120 (9.1 m × 3.2 mm) packed columns. At moderate temperatures (100–200 °C) the major products were phenol and CO₂. Other liquid by-products were: toluene, benzaldehyde, benzofuran, biphenyl, diphenylmethane, diphenylethane, and dibenzofuran. The selectivity of phenol (%) was defined as the yield of phenol divided by the total yield of products (in mol).

H₂O¹⁸ experiments were carried out at the same conditions as before. One milliliter of a 50% H₂O¹⁸ (Alfa Products) was fed into the reactor at a flow of 0.1 ml/h and the reaction temperature was 100 °C. The liquid products were trapped at -15 °C using an ethylene glycol/dry ice bath. Phenol and phenol enriched with ¹⁸O were analyzed with a HP 5890A GC equipped with a 5970 Series Mass Selective Detector.

Temperature-programmed reduction experiments were done in an Altamira AMI-1 chemisorption unit. Approximately 0.15 g of freshly calcined catalyst was placed in a 3.2 mm quartz U-tube and attached to the unit. Samples were pre-treated at 200 °C for 60 min under a flow of Ar (30 ml/min) and then cooled back to room temperature. For the temperature-programmed reduction, a gas mixture of 4%H₂/Ar (AGA, 30 ml/min) was passed over the sample at room temperature for 30 min, followed by a temperature ramp of 5 °C/min from room temperature to 600 °C. The effluent gas was measured using a thermal conductivity detector.

XRD characterization of freshly calcined Cu-ZSM-5 samples was carried out on a Siemens D5000 instrument using Cu Kα radiation, with a fixed power source (40 kV, 30 mA), a scan rate of 0.6° (2θ)/min and a step size of 0.02°.

²⁷Al MAS NMR spectra were obtained at room temperature using a Bruker DMX-300 spectrometer

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