

Effects of zeolite structure and composition on the synthesis of dimethyl carbonate by oxidative carbonylation of methanol on Cu-exchanged Y, ZSM-5, and Mordenite

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Abstract

The aim of this work was to establish the effects of zeolite structure/chemical composition on the activity and selectivity of Cu-exchanged Y (Si/Al = 2.5), ZSM-5 (Si/Al = 12), and Mordenite (Si/Al = 10) for the oxidative carbonylation of methanol to DMC. Catalysts were prepared by solid-state ion-exchange of the H-form of each zeolite with CuCl and were then characterized by FTIR and X-ray absorption spectroscopy (XAS). The XANES portion of the XAS data showed that all of the copper was present as Cu⁺ cations, and analysis of the EXAFS portion of the data shows the Cu⁺ cations had a Cu–O coordination number of ~2.1 on Cu-Y and ~2.7 on Cu-ZSM-5 and Cu-MOR. Dimethyl carbonate (DMC) was observed as the primary product when a mixture of CH₃OH/CO/O₂ was passed over Cu-Y, whereas dimethoxy methane was the primary product over Cu-ZSM-5 and Cu-MOR. The higher activity and selectivity of Cu-Y for the oxidative carbonylation of methanol can be attributed to the weaker adsorption of CO on the Cu⁺ cations exchanged into Y zeolite. In situ IR observations revealed that under reaction conditions, adsorbed CO was displaced by methoxide groups bound to the Cu⁺ cations. The kinetics of DMC synthesis suggests that the rate-limiting step in the formation of this product was the insertion of CO into Cu–OCH₃ bonds. The yield of DMC decreased with methanol conversion, likely due to the hydrolysis of DMC to methanol and carbon dioxide.

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1. Introduction

Dimethyl carbonate (DMC) can be used as a fuel additive to replace methyl *tert*-butyl ether (MTBE), a precursor for synthesis of carbonic acid derivatives, as a methylating agent to replace methyl halides and dimethyl sulfate, and as an intermediate in the synthesis of polycarbonates and isocyanates [1–3]. Cu-exchanged zeolites have been shown to be active catalysts for the oxidative carbonylation of methanol to dimethyl carbonate, with the principal byproducts being dimethoxymethane (DMM) and methyl formate (MF) [4–9]. Previous studies have shown that the structure and chemical composition of the zeolite influence the activity and selectivity of Cu-exchanged zeolites. For example, Anderson and Root [7] have reported that

Cu-X has greater activity and selectivity for DMC formation than Cu-ZSM-5. The authors proposed that CO adsorption has a negative effect on the formation of DMC. However, the mechanism by which zeolite structure and chemical composition affect the adsorptive and catalytic properties of the catalyst have not been investigated.

The present study was undertaken with aim of assessing the effects of zeolite structure on the activity and selectivity of Cu-exchanged zeolites for the synthesis of DMC. Catalysts were prepared by solid-state ion exchange of H-Y, H-ZSM-5, and H-MOR with CuCl under conditions chosen to minimize the retention of occluded CuCl [8–10]. All catalysts were characterized after preparation by infrared (IR) spectroscopy, to establish the extent to which Brønsted acid OH groups had been exchanged for copper cations, and by XANES, to establish the valence of the exchanged copper cations. The coordination of Cu to framework oxygen atoms was probed by EXAFS. The ac-

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tivity and selectivity of Cu-Y, Cu-ZSM-5, and Cu-MOR were then explored for various conditions. In situ IR and XANES measurements also were carried out to identify the nature of the adsorbed species associated with the copper cations and the oxidation state of the copper cations during the oxidative carbonylation of methanol.

2. Experimental

2.1. Catalyst preparation and characterization

Cu-exchanged zeolites were prepared by solid-state ion exchange (SSIE) of the protonated form of each zeolite (Y:Si/Al = 2.5, Strem; ZSM-5:Si/Al = 12, ALSI-PENTA; MOR:Si/Al = 10, Zeolyst) with CuCl at elevated temperature in a flow of He. Details of this procedure have been described elsewhere [8–11]. Freshly prepared catalysts, designated as Cu-Y, Cu-ZSM-5, and Cu-MOR, were stored in a drybox before use. The level of proton exchange was evaluated by observing the intensity of the IR band for residual Brønsted acid sites.

The oxidation state of Cu in the Cu-exchanged zeolites was determined by Cu K-edge X-ray absorption near-edge spectroscopy (XANES). These data were acquired in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 2–3. This beamline is equipped with a double-crystal monochromator, Si(111), detuned to 70% intensity to minimize the presence of higher harmonics. The samples were pressed into self-supporting wafers (calculated to have an absorbance of 2.5) and then mounted in a controlled-atmosphere cell operated at 101 kPa. Following characterization by XAS, each sample was cooled to 298 K before exposure to a particular gas or gas mixture. In separate experiments, pretreated Cu-exchanged zeolites were exposed to mixtures of He/CH₃OH, He/CO, and He/CO/O₂/CH₃OH. Methanol vapor was introduced using a gas saturator containing liquid methanol at 298 K. To examine the effects of gas adsorption, the sample was exposed to a flow of gas at room temperature, and the temperature was then raised at 10 K min⁻¹ to 403 K and held at this level for 1 h. All XAS measurements were made in situ. Cu XANES data were analyzed using the IFEFFIT package [12,13]. Pre-edge absorptions due to the background and detector were subtracted using a linear fit to the data in the range of -200 to 50 eV relative to the sample edge energy (E_0). Each spectrum was normalized by a constant determined by the average absorption in the range of 100–300 eV relative to E_0 . The edge energy of each sample and reference was taken at the first inflection point beyond any pre-edge peaks.

Extraction of the EXAFS data from the measured absorption spectra was performed with the XDAP code [14]. The pre-edge was subtracted using a modified Victoreen curve. The background was subtracted using cubic spline routines with a continuously adjustable smooth parameter. Normalization was performed by dividing the data by the height of the absorption edge at 50 eV.

Data analysis was performed by multiple-shell fitting in *R*-space using the EXAFS data analysis program XDAP, which

allows minimization of the residuals between both the magnitude and the imaginary part of the Fourier transforms of the data and the fit. *R*-space fitting has significant advantages over the usually applied fitting in *k*-space, as has been explored in depth by Koningsberger et al. [15]. Theoretical phase shift and backscattering amplitude for the Cu–O absorber-scatterer pair, generated using the FEFF8 code, were used in EXAFS data analysis. The theoretical references were calibrated using experimental data for Cu₂O as described previously [10,16].

2.2. Measurement of catalyst activity and selectivity

Measurements of catalyst activity and selectivity were carried out using 150 mg of catalyst loaded into a 10-mm-i.d. quartz tubular flow reactor. Before being exposed to reactants, the catalyst was pretreated at 873 K for 1 h in a stream of high-purity He (99.999%). For the catalytic experiment, a CO/O₂ mixture (25.0% CO, 2.5% O₂, balance He) and He (99.999%) were used. Methanol (CH₃OH) was introduced by passing the CO/O₂ mixture through a saturator maintained at a constant temperature of 293 K. The reaction products were analyzed by gas chromatography equipped with a capillary column (Alltech, AT aquawax; polyethylene glycol stationary phase) connected to a flame ionization detector (FID) and by a packed column (Alltech, Haysep DB packing) connected to a thermal conductivity detector (TCD). The effects of feed space velocity were investigated using a CH₃OH/O₂/CO/He mixture (4.0/1.0/9.0/19.3). The flow rate of this mixture was varied from 3 to 80 cm³/min while the catalyst temperature was maintained at 403 K. A second series of experiments designed to study the effects of CO, CH₃OH, and O₂ partial pressures on reaction rate and product selectivity was carried out using a fresh sample of Cu-exchanged zeolite. In this case, the total flow rate of feed was maintained at 20 cm³/min, and the catalyst temperature was 403 K.

Product selectivity was determined using the following equations:

$$S_{\text{DMC/CO}} = [\text{DMC}] / ([\text{DMC}] + [\text{CO}_2])$$

and

$$S_{i/\text{CH}_3\text{OH}} = n[i] / (2[\text{DMC}] + 2[\text{MF}] + 3[\text{DMM}] + 2[\text{DME}]),$$

where *i* is DMC, MF, DMM, and DME and *n* is the number of carbon atoms derived from methanol.

2.3. IR characterization of adsorbed species

IR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer equipped with an MCT-A detector. Measurements were obtained at a resolution of 4 cm⁻¹. The catalysts were pressed into 15-mg self-supporting pellets and placed into an IR cell equipped with CaF₂ windows. Before absorbate exposure, the catalyst was heated in He at 673 K.

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