

Synthesis of dimethyl carbonate and dimethoxy methane over Cu-ZSM-5

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Abstract

An investigation was carried out of the oxidative carbonylation of methanol to dimethyl carbonate over Cu-ZSM-5. The catalyst was prepared by solid-state ion exchange of H-ZSM-5 with CuCl and then characterized by X-ray absorption spectra (XAS). The XANES portion of the XAS data showed that all of the copper is present as Cu⁺ cations, and analysis of the EXAFS portion of the data shows the Cu⁺ cations have a Cu-O coordination number of ~2.7, suggesting that the cations are doubly and triply coordinated. Under DMC synthesis conditions, cuprous cations can be identified by two sorts of sites, one site covered by methanol only and a second on which CO and methanol co-absorb. In the absence of CO, DMM is the primary product formed, but when CO is present DMC becomes the primary products. DMM and MF are presumed to form via the coupling of formaldehyde and formic acid, respectively, with methanol. Consistent with this reasoning, the rates of DMM and MF formation increase with oxygen partial pressure. DMC is formed by carbonylation of methanol, and the rate of its formation increases with CO partial pressure. Increasing methanol partial pressure has an equivalent effect on the rates of DMM and DMC formation, suggesting that both products are formed from a common precursor derived from methanol, for example a methoxide group.

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1. Introduction

Dimethyl carbonate (DMC) can be used as a fuel additive to replace methyl tert-butyl ether (MTBE) [1], a precursor for synthesis of carbonic acid derivatives [2], as a methylating agent to replace methyl halides and dimethyl sulfate, and as an intermediate in the synthesis of polycarbonates and isocyanates [2,3]. Whereas DMC has been made from methanol and phosgene, there has been considerable interest in exploring more environmentally benign processes for this product, such as the oxidative carbonylation of methanol; carbonylation of methyl nitrite, ethylenecarbonate, or urea transesterification; direct synthesis from CO₂; alkylation of metal carbonates with organic halides; and decarbonylation of dimethyl oxalate [4]. Of these alternatives, the most promising route is the vapor-phase oxidative carbonylation of methanol, $2\text{CH}_3\text{OH} + \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{H}_2\text{O}$ [5].

A number of copper-based catalysts have been investigated for the vapor-phase oxidative carbonylation of methanol [6–22]. These include CuCl and CuCl₂ supported on activated carbon [6–12]; CuCl, CuCl₂, and bimetallic PdCl₂-CuCl₂ deposited on mesoporous silica supports (HMS silica, MCM-41, and SBA-15) [14–16]; and Cu/silica [23]. There have also been reports that the activity and selectivity of the above-mentioned catalysts can be increased by the incorporation of quaternary ammonium salts such as tetrabutylammonium bromide (TBAB) and tetraethylammonium chloride (TEAC) [16,17]. Because chloride-containing catalysts can lead to reactor corrosion, several authors have examined the potential of copper-exchanged zeolites as catalysts [19,20,24,25]. King [20] have reported that Cu-Y zeolite exhibits good activity and selectivity for DMC synthesis with little catalyst deactivation. Under similar conditions, zeolites exchanged with cuprous cations were found to have higher activity and higher selectivity than catalysts based on cuprous chloride. More recently, Root et al. [19] compared the performance of Cu-X and Cu-ZSM-5, and reported that Cu-X exhibited higher selectivity. In situ infrared studies revealed that CO is more strongly adsorbed on Cu cations ex-

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changed into ZSM-5 than X zeolite. The authors proposed that the synthesis of DMC proceeds via an Eley-Rideal process in which gas-phase CO reacts with the methoxide species bonded to the Cu cations present in the zeolite, and that strong adsorption of CO inhibits the adsorption of methanol, which is required to form methoxide species. Recent work by Drake et al. [24] on Cu-exchanged Y zeolite revealed that all of the Cu exchanged is present as Cu^+ in sites I', II, and III'. In addition to DMC, this catalyst was found to produce dimethoxy methane (DMM) and methyl formate (MF). In situ infrared and XANES showed that both methoxide and carbonyl groups are associated with the Cu^+ cations of the zeolite, in agreement earlier reports of Root and Anderson for Cu-X [19]. Preliminary work by the present authors using well-characterized Cu-ZSM-5 [25] revealed that this catalyst also produces DMC, DMM, and MF; however, in contrast to Cu-Y, the selectivity of DMM is higher than that of DMC. The present work was undertaken with an aim of understanding in greater detail the effects of reaction conditions on the distribution of products. In situ XANES and infrared spectroscopy were used to characterize the oxidation state of Cu cations in the zeolite and the nature of species associated with these cations.

2. Experimental

2.1. Catalyst preparation and characterization

Cu-exchanged ZSM-5 was prepared via solid-state ion exchange (SSIE) of H-ZSM-5 and CuCl at 1023 K, as described previously [25]. Freshly prepared catalyst was stored in a dry-box before use. The oxidation state of Cu in Cu-ZSM-5 was determined by Cu *K*-edge X-ray absorption near-edge analysis (XANES), which was carried out 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. After characterization by XAS, each sample was cooled to 298 K before being exposed to a particular gas or gas mixture. In separate experiments, pretreated Cu-ZSM-5 was exposed to a mixture of He/CH₃OH, He/CO, He/CO/O₂/CH₃OH, or He/O₂. 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 a rate of 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 with the IFEFFIT package [26]. Pre-edge absorptions due to the background and detector were subtracted using a linear fit to the data in the range -200–50 eV relative to the sample edge energy (E_0). Each spectrum was normalized by a constant determined by the average absorption in the range 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.

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. tubular flow reactor made of quartz. Before exposure 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. A CH₃OH/O₂/CO/He mixture (4.0/1.0/9.0/19.3) was fed to the reactor at a nominal total flow rate of 20 cm³/min and was varied between 3 and 80 cm³/min to study the effect of residence time on product distribution at 403 K. A second experiment designed to study the effect of temperature on the oxidative carbonylation of methanol was carried out using a fresh sample of Cu-ZSM-5. For this study, a CH₃OH/O₂/CO/He mixture (4.0/1.0/9.0/19.3) was fed to the reactor at a nominal total flow rate of 20 cm³/min, and the reactor temperature was increased from 298 to 423 K. Studies of methanol oxidation in the absence of CO were also carried out. For these experiments, a CH₃OH/O₂/He mixture (4.0/1.0/28.3) was fed to the reactor at a nominal total flow rate of 20 cm³/min and was varied between 3 and 80 cm³/min to study the effect of residence time on product distribution at 403 K.

2.3. Infrared characterization of adsorbed species

Infrared spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer equipped with an MCT-A detector. Measurements were taken using a resolution of 4 cm⁻¹. The catalyst were pressed into 20-mg self-supporting pellets and then placed into an infrared cell equipped with CaF₂ windows. Before adsorbate exposure, the catalyst was heated in He at 673 K. Either 16 or 32 scans were averaged to obtain each spectrum.

3. Results

3.1. Characterization of Cu-ZSM-5

Fig. 1 illustrates the IR spectrum for the O–H stretching region. Spectra are shown for H-ZSM-5 and Cu-ZSM-5. The intensity of the band at 3610 cm⁻¹, which is characteristic of Brønsted acid protons [27], approached zero for Cu-ZSM-5, indicating that exchange via the reaction $\text{ZH} + \text{CuCl} \rightarrow \text{ZCu} + \text{HCl}$ was nearly complete. In contrast, the IR peak at 3740 cm⁻¹, which is characteristic of Si–OH groups [27], remained essentially unaltered during the course of cation exchange with CuCl, indicating that Si–OH groups did not undergo SSIE.

Cu *K*-edge XANES of Cu-ZSM-5 and reference compounds (CuCl, Cu₂O, and CuO) are shown in Fig. 2a; with the corresponding derivative curves given in Fig. 2b. The features in the near-edge region are very sensitive to the changes in the oxidation state and coordination environment of Cu. Cu²⁺ (CuO) exhibits three features in the XANES region: a weak absorption

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