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The mechanism of dimethyl carbonate synthesis on Cu-exchanged zeolite Y

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Abstract

The mechanism of dimethyl carbonate (DMC) synthesis from oxidative carbonylation of methanol over Cu-exchanged Y zeolite has been investigated using *in situ* infrared spectroscopy and mass spectrometry under transient-response conditions. The formation of DMC is initiated by reaction of molecularly adsorbed methanol with oxygen to form either mono- or di-methoxide species bound to Cu^+ cations. Reaction of the mono-methoxide species with CO produces monomethyl carbonate (MMC) species. DMC is formed via two distinct reaction pathways—CO addition to di-methoxide species or by reaction of methanol with MMC. The rate-limiting step in DMC synthesis is found to be the reaction of CO with mono-methoxide or di-methoxide species. The first of these reactions produces MMC, which then reacts rapidly with methanol to produce DMC, whereas the second of these reactions produces DMC directly. Formaldehyde was identified as an intermediate in the formation of dimethoxy methane (DMM) and methyl formate (MF). Both byproducts are thought to form via a hemiacetal intermediate produced by the reaction of methanol with adsorbed formaldehyde at a Cu^+ site.

Keywords: Dimethyl carbonate; Methanol oxidative carbonylation; Cu-Y zeolite; Infrared spectroscopy

1. Introduction

Dimethyl carbonate (DMC) has many potential applications. It can serve as an oxygen-containing fuel additive, a precursor for synthesis of carbonic acid derivatives, a methylating agent, and as an intermediate in the synthesis of polycarbonates and isocyanates [1–3]. Cu-exchanged zeolites are particularly attractive catalysts for the synthesis of DMC, because they promote the oxidative carbonylation of methanol to DMC in the gas phase [4–9]. Previous investigations have shown that Cu-X and Cu-Y are the most active catalysts for producing DMC, whereas Cu-ZMS-5 and Cu-MORD are less active and exhibit a high selectivity to producing dimethoxy methane (DMM).

Several studies of the mechanism and kinetics of DMC synthesis over Cu-exchanged zeolites have been reported. Based on evidence from in situ IR spectroscopy, King [4,5] has proposed that methanol adsorbs on extra-framework Cu cations in Cu-Y and reacts with oxygen to form methoxide groups. When CO is present in the gas phase, new bands appeared which were attributed to carbomethoxide species (CH_3OCO–); however, a definitive assignment of these features could not be made. DMC was envisioned to form upon reaction of methanol with the carbomethoxide species. The rate-limiting step was proposed to be CO addition to adsorbed methoxide species to form carbomethoxide species. These findings are supported by the studies of Anderson and Root [6,7], which show that the rate of DMC over Cu-X is first order in CO partial pressure and nearly zero order in both methanol and oxygen partial pressures. More recently, we have carried out studies of the kinetics of DMC synthesis on a fully characterized sample of Cu-Y prepared by dry exchange of H-Y with CuCl [8–10]. Analysis of the catalyst after preparation showed that all of the protons in H-Y had been exchanged one-for-one by Cu, and XANES data confirmed that all of the exchanged Cu was present as Cu^+. In agreement with the work, of Anderson and Root, it was also shown that the kinetics of DMC formation are nearly first order in CO partial pressure, whereas the dependencies on methanol and oxygen partial pressures are nearly zero order. In situ infrared spectra revealed that while CO is strongly adsorbed by extra-framework Cu^+ cations, this adsorbate is almost com-

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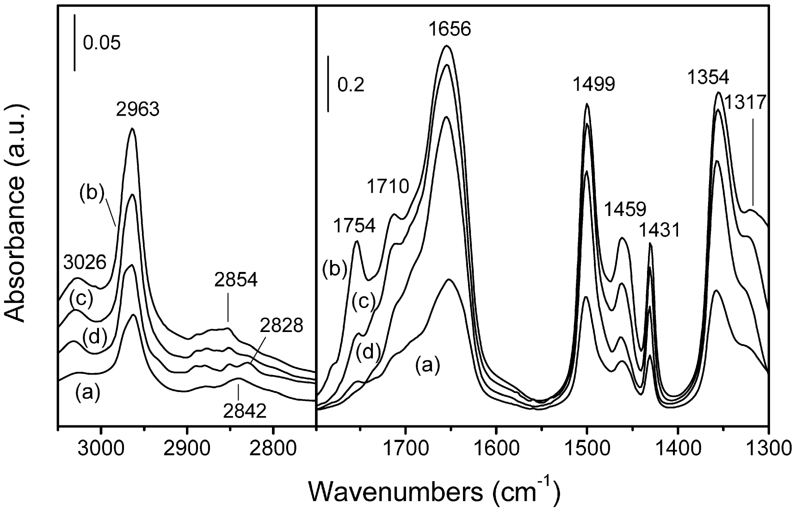

Fig. 1. IR spectra of Cu-Y exposed to DMC (5.57 kPa): (a) 12 s and (b) 20 min; and flushing with He: (c) 1.7 min and (d) 20 min.

pletely displaced by methoxide groups when methanol and oxygen are present together with CO.

The present study was undertaken to elucidate the mechanism for DMC formation on Cu-Y. The same catalyst sample was used as in our previous work [8,10]. Transient-response IR spectroscopy was used in combination with measurements of the temporal evolution of products in the gas phase, to identify the sequence of elementary steps involved in the formation of DMC. Additional transient-response experiments were conducted to gain information on the pathways for forming DMM and methyl formate (MF), the byproducts of DMC synthesis.

2. Experimental

2.1. Catalyst preparation

Cu-Y zeolite was prepared by solid-state ion exchange of H-Y zeolite (Si/Al = 2.5) with CuCl at 923 K [8]. A detailed discussion of the extent of cation exchange and the oxidation state of Cu in the sample of Cu-Y used for the present study has been presented previously [8,10]. This work demonstrated that all of the Brönsted acid protons are replaced quantitatively by Cu^+ cations during solid-state exchange of H-Y by CuCl. The presence of Cu^+ cations as the exclusive form of Cu was confirmed by the observation of a well-defined, CuK-preedge peak at 8983.8 eV by XANES. Analysis of EXAFS data demonstrated that the Cu^+ cations are coordinated to framework oxygens with a coordination number of $\sim$2.1 at a distance of 1.99 ± 0.02 Å.

2.2. Transient-response IR and mass spectrometry experiments

Transient-response IR experiments were carried out using 15 mg of catalyst pressed into a 20 mm-diameter pellet. The pellet was placed into an *in situ* IR cell, and spectra were recorded using a Thermo-Nicolet NEXUS 670 FTIR spectrometer. Eight scans were averaged using a resolution of 4 cm^{-1}. Prior to adsorbate exposure, the catalyst was heated in He at 673 K. The products formed during transient-response experiments were monitored by mass spectrometry (MKS Mini-Lab quadrupole). In a typical experiment, the temperature was reduced to 403 K prior to the introduction of CH_3OH (12.12 kPa). All flow rates were approximately 40 cm^3 min^{-1}. After 30 min of exposure to CH_3OH, 2.02 kPa O_2 was added into the stream. Once steady-state was reached, the stream was switched to He in order to remove gas-phase CH_3OH and O_2 from the atmosphere, as well as any weakly adsorbed species. A flow of CO (20.2 kPa, balance He) was then introduced for a fixed period of time after which the cell was again flushed with He. Next, a flow of CH_3OH/O_2 (12.12 kPa CH_3OH, 2.02 kPa O_2) was reintroduced into the cell. Finally, a flow of $CH_3OH/O_2/CO/He$ (4.0/1.0/9.0/19.3) was passed through the cell at the rate of 40 cm^3 min^{-1}. Since the concentration of reaction products leaving the infrared cell was too small to measure accurately, a parallel experiment was carried out using a larger amount of catalyst (150 mg) [9]. The same protocol used for the transient-response IR experiments was used for the observation of products formed during the transient-response reaction experiments. Separate experiments were carried out to identify the formation for DMM/MF. In this case, a He stream containing formaldehyde was introduced into the system, after which was switched to one containing methanol and formaldehyde. The flow of formaldehyde was turned off and turned on again to identify the role of formaldehyde in the formation for DMM and MF.

3. Results

3.1. Infrared spectra of adsorbed DMC and DMM

Infrared spectra of DMC and DMM adsorbed on Cu-Y were recorded to aid the interpretation of the spectra observed under transient-response conditions. Spectra of DMC adsorbed on Cu-Y at 403 K are shown in Fig. 1. After a contact time of 12 s, bands appear at 3026 and 2963 cm^{-1}, due to the antisymmetric and symmetric C–H stretching vibrations of the CH_3