

# Experimental and Theoretical Studies of the Mechanism for the Synthesis of Dimethyl Carbonate on Cu-exchange zeolite Y

Yihua Zhang, Xiaobo Zheng, and Alexis T. Bell\*  
Department of Chemical Engineering  
University of California, Berkeley, CA 94720-1462  
\*bell@cchem.berkeley.edu

## 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 [1,2]. Cu-exchanged zeolite are known to be active for oxidative carbonylation of methanol to dimethyl carbonate [1,2]. This process has been considered as a promising method for DMC synthesis because it avoids of corrosive components such as CuCl or Cu<sub>2</sub>Cl. The present study was undertaken to elucidate the mechanism for DMC formation by oxidative carbonylation of methanol on Cu-Y zeolite. A combination of experimental and theoretical approaches was used.

## Experimental and Theoretical Methods

CuY zeolite was prepared by solid-state ion exchange of HY zeolite (Si/Al = 2.5) with CuCl at 1023 K. The final material was then characterized by IR, NMR, XAFS. The Cu-Y prepared in this manner has Cu/Al ratio of 1.0 and all of the Cu is present as Cu<sup>+</sup>. The structure of adsorbed species and the dynamics of their formation and interconversion were investigated using transient-response FTIR. Prior to adsorbate exposure, the catalyst was heated in He at 673 K. The products formed during transient-response experiments were monitored by both mass spectrometry and gas chromatography.

A six-membered ring cluster model was used to represent the catalytically active site in CuY. Two silicon atoms in the ring were replaced by aluminum atoms. The B3LYP functional and the 6-31G\* basis set was used in Gaussian 03 for geometry optimizations. Accurate energies were obtained using the 6-311+G\*\* basis set. The electronic structure of Cu was described using the cc-pVTZ basis set.

## Results and Discussion

In the presence CH<sub>3</sub>OH and O<sub>2</sub>, methoxide groups are formed on CuY characterized by CH stretching bands at 2925, 2824 cm<sup>-1</sup>. Formation of these groups inhibits CO adsorption, as demonstrated by a decrease in the intensity of CO bands on Cu<sup>+</sup>. Following a He flush of the catalyst to remove methanol and oxygen from the gas phase, CO was introduced. The presence of CO caused a decrease in concentration for adsorbed methoxide groups and a slow growth in bands at 1664, 1349 cm<sup>-1</sup> attributable to C=O and OCO stretching vibrations in DMC. After flushing of CO from the gas phase and exposure of the catalyst to CH<sub>3</sub>OH and O<sub>2</sub>, the pre-adsorbed DMC was displaced and bands attributable to methanol and methoxide groups appeared rapidly. As shown in Figure 1, DMC formation upon CO reaction with methoxide groups is slow, suggesting that it is the rate-limiting step. When CH<sub>3</sub>OH, CO, and O<sub>2</sub> are

present, the primary product formed is DMC and adsorbed methanol and methoxide are the dominant surface species.

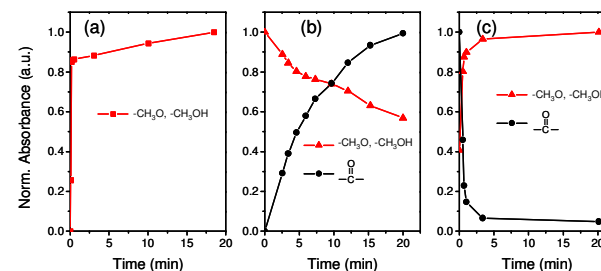


Figure 1 IR observation during transient response experiment with presence of (a) CH<sub>3</sub>OH/O<sub>2</sub>; (b) CO; (c) CH<sub>3</sub>OH/O<sub>2</sub>

Quantum chemical calculations suggest mechanism for DMC synthesis. Reaction begins with O<sub>2</sub> oxidation of CH<sub>3</sub>OH to form methoxide (-OCH<sub>3</sub>) species. The formation of these species greatly reduces heat of CO adsorption. (HO)-Cu-(OCH<sub>3</sub>), a precursor to DMC formation, further reacts with CH<sub>3</sub>OH and CO to form DMC. As shown in Figure 2, two distinct reaction pathways were found for the formation of DMC – one proceeding via mono-methyl carbonate species, Cu-(CH<sub>3</sub>OCOOH), and the other via dimethoxide, (CH<sub>3</sub>O)-Cu-(OCH<sub>3</sub>) species. The proposed reaction mechanism is consistent with the experimental observations.

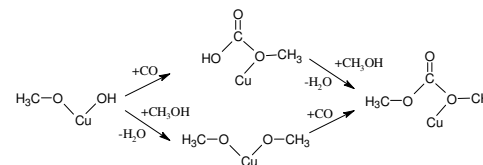


Figure 2 Proposed DMC formation mechanisms

## Significance

This study has shown that oxygen is required for methanol deprotonation to form methoxide species. Cu(OCH<sub>3</sub>)(OH) is proposed as a precursor to DMC formation. DMC is formed via either CO addition to dimethoxide species or methanol addition to mono-methyl carbonate species.

## References

1. Y. Zhang, I. J. Drake, D. N. Briggs and A. T. Bell, I. E., *J. Catal.*, 244 219 (2006).
2. I. J. Drake, Y. Zhang, D. Briggs, B. Lim, T. Chau, A. T. Bell, *J. Phys. Chem.*, 110, 11654 (2006).