Kinetic Studies of Carbonylation of Methanol to Dimethyl Carbonate over Copper Zeolite Catalysts

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Introduction

Dimethyl carbonate (DMC) is an attractive "green chemistry" candidate [1] which can be used as a methylating agent in place of dimethyl sulfate and methyl halides. DMC can also be used as a carbonylation agent in place of phosgene for the production of polycarbonates and polyurethanes. A kinetic study of the production of DMC by the gas-phase oxidative carbonylation of methanol with carbon monoxide over copper zeolite catalysts has been conducted. I*n situ* FTIR spectroscopy has been used to probe the catalyst surface under reaction conditions. Comparison of the results obtained for Cu^+X and Cu^+ZSM-5 has been done to examine the importance of the interaction of carbon monoxide with the catalyst surface.

Results and Discussion

The results of the steady-state kinetic study show near-first-order kinetics in carbon monoxide pressure for DMC at low pressure over Cu^+X zeolite, whereas the production of by-products (methylal [MA] and methyl formate [MF]) was independent of carbon monoxide pressure at low pressure. As the pressure of carbon monoxide is increased, competitive adsorption of CO on the surface of the catalyst occurs. Figure 1 shows the effect of this competitive adsorption, which decreases the reaction order for in CO for DMC production. The reaction order for by-production formation becomes negative in CO pressure.

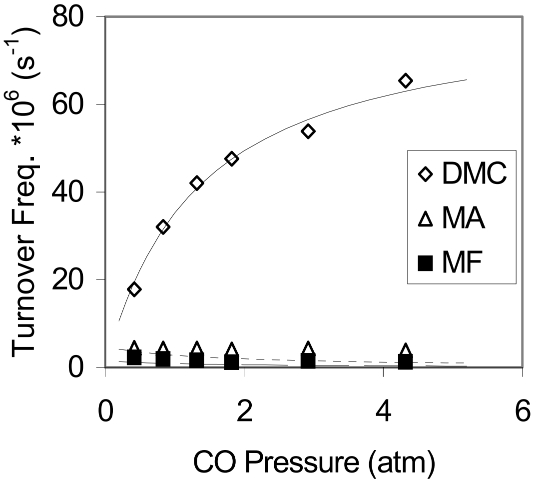

Figure 1 Rates over Cu^+X

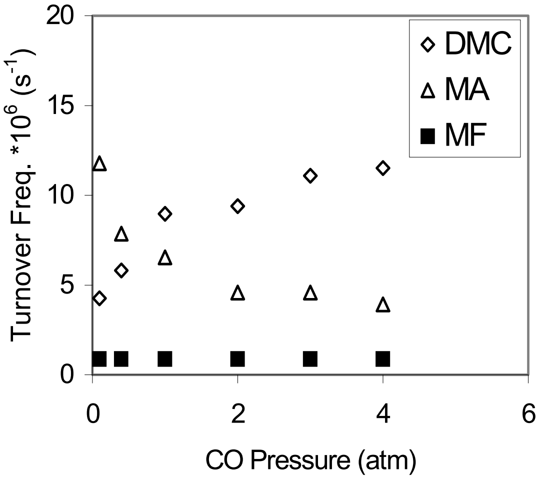

Figure 2 Rates over Cu^+ZSM-5

Comparing the results obtained for DMC production over Cu^+X zeolite with a Cu^+ZSM-5 zeolite provides insight into the importance of the interaction of carbon monoxide with the catalyst surface. Figure 2 shows the effect of carbon monoxide pressure on the rate of DMC and by-product formation. CO adsorbs more strongly on Cu^+ZSM-5 than on Cu^+X, and the observed CO order is lower at all pressures examined.

In situ FTIR spectroscopy has been used to examine the catalyst surface under reaction conditions for both Cu^+X and Cu^+ZSM-5. Figure 3 shows two wavelength windows of interest for detecting the adsorbed species present on the catalyst surface at 130°C under typical reaction conditions. Cu^+ZSM-5 shows a much higher ratio of CO coverage (2130-2170 cm^{-1}) to methanol/methoxide coverage (1300-1500 cm^{-1}) compared to Cu^+X. This result agrees well with the amount of surface CO expected by the results from the kinetic experiments.

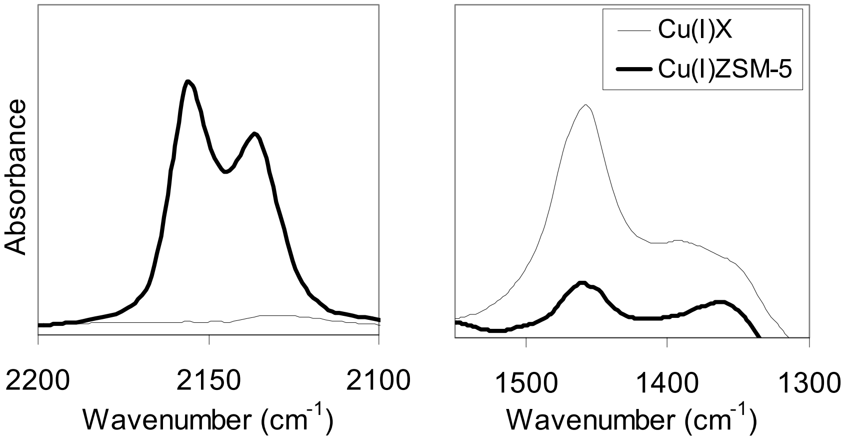

Figure 3 Infrared spectra of adsorbed species on Cu^+X and Cu^+ZSM-5 showing C-O stretching region (2100-2200 cm^{-1}) and the d_{CH} mode of methanol and methoxide.

Microkinetic modeling [2] of the catalytic reaction for DMC production over copper zeolites has shown prospects for improved catalyst design. Experiments conducted with different catalysts show differing activity, selectivity, and variations among by-products. Mechanistic understanding has allowed the identification of important factors for DMC production.

References

1. Ono, Y. *Applied Catalysis A: General* **155** (1997) 133
2. S.A. Anderson and T.W. Root, *J. Catal.* (Submitted)