

Novel Vapor-Phase Carbonylation of Dimethoxymethane over Acid Zeolites

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Introduction

Acid-catalyzed formaldehyde carbonylation has been studied as a carbon-carbon bond forming reaction for many years because of its potential to synthesize precursors to ethylene glycol, an important chemical used in polyester synthesis [1-4]. Producing ethylene glycol from derivatives of synthesis gas such as methanol and formaldehyde holds economic promise.

Until now, investigation of acid-catalyzed formaldehyde carbonylation has been restricted to high pressure, liquid-phase batch systems. The present work lifts this restriction and is the first report of carbonylation of formaldehyde dimethyl acetal (a.k.a. dimethoxymethane, DMM) in the vapor phase, catalyzed by acidic zeolites. The reaction proceeds at atmospheric or near atmospheric (up to ~3 atm) pressure, as compared with the hundreds of atmospheres of carbon monoxide required in [1-3].

As formaldehyde carbonylation follows the Koch mechanism [5] which involves carbocations, the authors propose that DMM carbonylation will also follow a carbocation mechanism.

Materials and Methods

Ammonium forms of ZSM-5 (Si/Al 13.5) and Mordenite (Si/Al 10) (from Süd-Chemie) and Faujasite (Si/Al 15), Beta (Si/Al 12.5), and Ferrierite (Si/Al 10) (from Zeolyst) were converted to their proton forms by heating for three hours at 500 °C with a 2 °C/min ramp rate. In a typical experiment, 0.05 g of H-form zeolite was loaded into a quartz reactor tube and held in place by quartz wool. The sample was then reheated to 500 °C to remove residual moisture and then cooled to the reaction temperature. Carbon monoxide was bubbled through a stainless steel saturator filled with liquid DMM and chilled to ~-20 °C. Additional CO or He was mixed with the saturator exit to provide the desired CO/DMM ratio before flowing into the reactor. The reactor exit was equipped with a needle valve used to raise the system pressure for above ambient pressure experiments. Reaction products were analyzed by gas chromatography.

Results and Discussion

The carbonylation product of DMM, methyl methoxyacetate (MMAc) (Equation 1), was produced with 40-50% selectivity over ZSM-5, Mordenite, and Beta, while Ferrierite was almost ineffective for the reaction with selectivity of 10% and the lowest observed rate. Faujasite showed the highest rate and the highest selectivity, ~65%. Dimethyl ether (DME) and methyl formate (MF) were the only byproducts, formed by the Cannizzaro disproportionation of DMM (Equation 2) in a ratio of 2 moles of DME per mole of MF.



For Faujasite, both the rate and selectivity of MMAc formation increased with increasing Si/Al ratio up to Si/Al of 30, reaching a maximum rate of 25 mol MMAc (mol Al)⁻¹ h⁻¹ and selectivity of 70%. By contrast, the rate was only 5 mol MMAc (mol Al)⁻¹ h⁻¹ for a Si/Al ratio of 2.6, with a selectivity of 30%. Further increasing the Si/Al to 40 increased the rate only slightly and did not affect the selectivity compared to Si/Al 30. The effect of Si/Al ratio can be explained by the reduced acidity of high alumina zeolites (Si/Al<10) leading to lower activity, and by a rate enhancement for carbonylation when aluminum centers are spaced further apart.

The MMAc rate increased with CO partial pressure up to 3 atm. This increase was nearly linear over Faujasite (Si/Al 30), with the MMAc selectivity reaching 80% at a CO pressure of 3 atm. The rate of DME synthesis was unaffected by the CO pressure over Faujasite, but was inversely proportional to CO pressure over ZSM-5. The trend over ZSM-5 can be explained by the competition of DMM carbonylation and disproportionation that shifts in favor of carbonylation at higher CO partial pressures. With Faujasite, as the DME rate was independent of CO pressure, carbonylation and disproportionation occur in parallel, perhaps on distinct active sites with different environments.

Increasing the DMM partial pressure favored the disproportionation reaction, and so experiments were typically carried out with a high CO/DMM ratio (10-150). Selectivity was independent of space time while both carbonylation and disproportionation rates increased for short space times and declined for longer space times.

The high activity and selectivity of Faujasite is attributed to the large pore size relative to the other zeolites studied here. The large pores may better stabilize the carbocation intermediates in a Koch-type mechanism. The enhancement in activity and selectivity achieved by reducing the aluminum content of Faujasite is proposed to stem from the separation of aluminum centers from each other, also allowing more space within the framework for each carbocation. In particular, the rate and selectivity increased until the number of aluminum atoms per supercage reached unity (ideally at Si/Al = 23 if all aluminum were equally dispersed) for a Si/Al ratio of 30, but decreasing the aluminum content further to a Si/Al ratio of 40 showed little or no effect.

Significance

This study represents the first case of formaldehyde carbonylation in the vapor phase. The effect of zeolite structure and Si/Al ratio on the activity and selectivity of DMM carbonylation have been explained, and a mechanism for the reaction has been proposed.

References

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