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Carbonylation

Vapor-Phase Carbonylation of Dimethoxymethane over H-Faujasite**

*Fuat E. Celik, Tae-Jin Kim, and Alexis T. Bell**

The carbonylation of formaldehyde or formaldehyde derivatives has been investigated as a means for producing glycolic acid and its esters/ethers.[1–8] These products can be converted readily into ethylene glycol, an important industrial chemical used in polyester synthesis. Previous investigations of these reactions have been carried out in the liquid phase, and have required high carbon monoxide pressures (tens to hundreds of atmospheres) to overcome the low solubility of carbon monoxide. It has also been observed that at lower carbon monoxide pressures, the reaction of formaldehyde with itself, the Cannizzaro disproportionation reaction, becomes the dominant process.

We report herein the first example of the vapor-phase carbonylation of dimethoxymethane (DMM), the dimethyl acetal of formaldehyde. Using H-Faujasite (H-FAU; an acid zeolite) as the catalyst, it was possible to produce methyl methoxyacetate (MMAc) by the reaction in Equation 1 with a

$$CH_3OCH_2OCH_3 + CO \rightarrow CH_3OCH_2COOCH_3 \quad (1)$$

selectivity of up to 79% and a yield of up to 20% based on DMM. MMAc is an ether/ester of glycolic acid, and can be converted into glycolic acid and then ethylene glycol by hydrolysis and hydrogenation. Alternatively, MMAc can be reduced directly to 2-methoxyethanol, an industrial solvent. Disproportionation of DMM to produce dimethyl ether (DME) and methyl formate (MF) [Eq. (2)] was the only competing process observed.

$$2\,CH_3OCH_2OCH_3 \rightarrow 2\,CH_3OCH_3 + HCOOCH_3 \quad (2)$$

The effects of temperature on the rate of DMM carbonylation to MMAc and the rate of DMM disproportionation to DME and MF are shown in Figure 1 a.

The products DME and MF were formed in a ratio DME:MF close to two, consistent with the stoichiometry of Equation (2). This observation and the absence of formaldehyde in the reaction products indicate that DMM decomposition to DME and formaldehyde did not occur. The rate of MMAc formation reached a maximum at 393 K, whereas the rate of DMM disproportionation increased monotonically with increasing temperature. As seen in Figure 1 b, while the conversion of DMM increased with increasing temperature, the selectivity of DMM conversion into MMAc reached a maximum at 373 K.

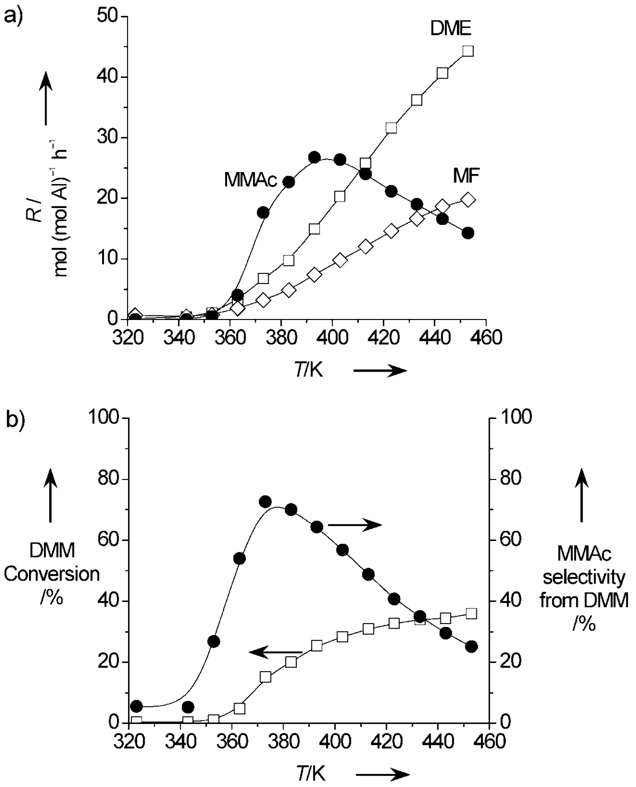

Figure 1. The effect of reaction temperature on a) the rates (R) of MMAc (●), DME (□), and MF (◇) formation, and b) DMM conversion (□; left-hand axis), and selectivity of MMAc from DMM (●; right-hand axis). $P_{CO} = 1.99$ atm, $P_{DMM} = 0.017$ atm, total gas flow rate = 100 cm^3 min^{-1} at pressure, 200 cm^3 min^{-1} at STP.

The rate of DMM carbonylation and the selectivity of DMM conversion into MMAc increased with increasing carbon monoxide partial pressure (P_{CO}) while the DMM pressure was kept roughly constant (Figure 2 a and b). The maximum rate and the MMAc selectivity shifted to lower temperatures as P_{CO} increased, with the selectivity maximum occurring 20–30 K lower than the rate maximum. A maximum selectivity of 79% was reached at 2.99 atm CO pressure and 373 K. Although the maximum rate increased nearly linearly with CO pressure, the maximum selectivity began to level off at CO pressures between 1.99 and 2.99 atm (see Supporting Information). DMM conversion increased with increasing P_{CO}, as the carbonylation rate increased, while the disproportionation rate stayed roughly constant.

Figure 3 a shows that for a fixed CO pressure the rate of DMM disproportionation increased with increasing DMM partial pressure (P_{DMM}), while the rate of carbonylation went

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[*] F. E. Celik, Dr. T. J. Kim, Prof. A. T. Bell
Chemical Engineering, University of California, Berkeley
Berkeley, CA 94720 (USA)
Fax: (+1) 510-642-4778
E-mail: bell@cchem.berkeley.edu

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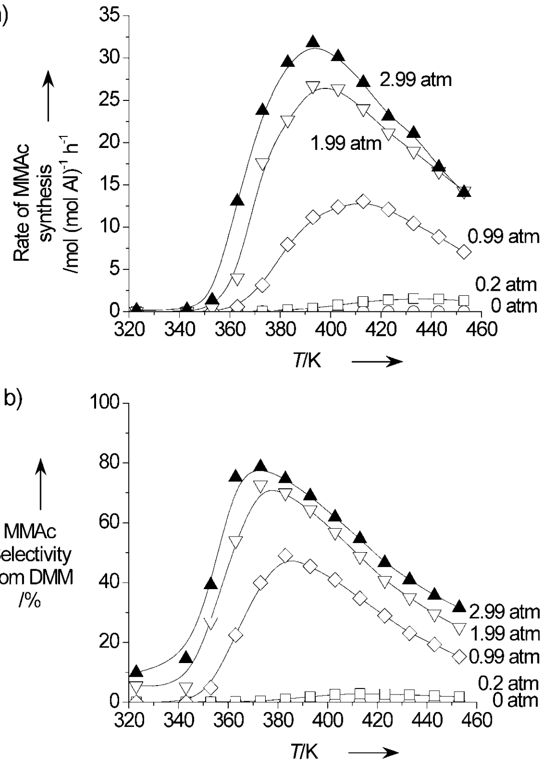

Figure 2. The effect of reaction temperature on a) the rate of MMAc formation at different CO pressures as labeled, and b) the selectivity of MMAc from DMM at different CO pressures as labeled. $P_{DMM} = 0.013$–0.019 atm, total gas flow rate = 100 cm^3 min^{-1} at pressure, 100–300 cm^3 min^{-1} at standard temperature and pressure (STP).

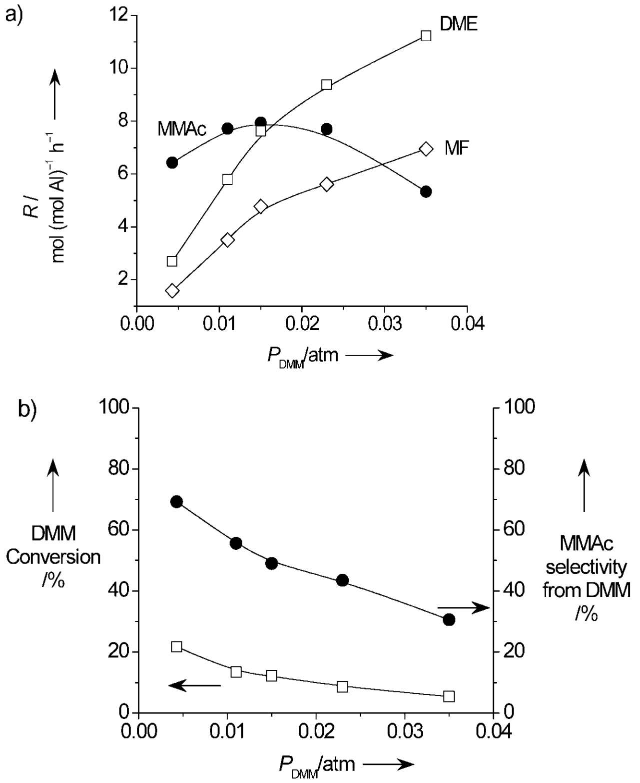

Figure 3. The effect of DMM partial pressure on a) the rate (*R*) of MMAc (●), DME (□), and MF (◇) formation, and b) DMM conversion (□; left-hand axis), and selectivity of MMAc from DMM (●; right-hand axis). $T = 383$ K, $P_{CO} = 1.0$ atm, $P = 2.0$ atm (balance He), total gas flow rate = 100 cm^3 min^{-1} at pressure, 200 cm^3 min^{-1} at STP.

through a maximum. Figure 3 b demonstrates that both DMM conversion and selectivity to MMAc decreased with increasing DMM pressure. These data indicate that higher DMM pressures favor disproportionation over carbonylation, as could be inferred from the stoichiometry of the reactions in Equations (1) and (2). For this reason, DMM pressure was kept low in all experiments, usually between 0.01 atm and 0.02 atm. Figure 3 b suggests that even higher selectivities and conversions could have been achieved at DMM partial pressures below 0.01 atm.

Taken together the results presented in Figures 1–Figure 3 show that the selectivity of DMM conversion into MMAc increases with increasing P_{CO}/P_{DMM} ratio and that the overall rate of MMAc formation could be increased by increasing P_{CO} at a fixed P_{DMM}.

With increasing space time (number of Al centers within the catalyst sample divided by the total gas volumetric flow rate), the conversion of DMM increased but the MMAc selectivity remained nearly constant (see Supporting Information). While the rate of MMAc formation per mole of Al loaded into the reactor decreased with increasing space time, higher yields of MMAc could be achieved without sacrificing selectivity by operating at higher space times.

After an initial transient period of approximately 120 min, the catalyst showed stable steady-state activity and selectivity for at least 24 h. During the transient period, activity and selectivity to MMAc increased as a function of time until reaching their steady-state values.

The observed rate of DMM carbonylation is comparable to that reported for the carbonylation of DME over H-MOR.[9] At 438 K, the turnover frequency for DME carbonylation to methyl acetate was approximately 0.2 h^{-1} at approximately 2 atm of CO and increased to approximately 1.1 h^{-1} at approximately 10 atm of CO with selectivity approaching 100 %. By contrast, the turnover frequency for DMM carbonylation to MMAc over H-FAU reported herein was approximately 13 h^{-1} at approximately 1 atm of CO and 413 K with 35 % selectivity, and increased to approximately 32 h^{-1} at approximately 3 atm of CO and 393 K with 69 % selectivity. A MMAc selectivity of 79 % from DMM was achieved with a turnover frequency of approximately 24 h^{-1} at approximately 3 atm of CO and 373 K. These observations are consistent with the higher reactivity of formaldehyde and its acetals relative to those of ethers.

The maximum MMAc selectivity of 79 % achieved in the present study using a vapor-phase reaction is comparable to that reported previously for formaldehyde carbonylation using solid acids and carbon monoxide pressures of 314 atm (79 %)[3] and 238 atm (81 %)[5] in liquid-phase reactions with solid acid resin catalysts.

In conclusion, we have shown that high-selectivity, vapor-phase, carbonylation of DMM to MMAc can be achieved at low pressure using H-FAU as the catalyst. DMM disproportionation to DME and MF can be minimized by keeping the ratio of P_{CO} to P_{DMM} high.

Experimental Section

NH_4-faujasite (Si/Al = 30, Zeolyst), was heated for 3 h at 773 K (2 K min^{-1} ramp rate) in 100 cm^3 min^{-1} dry air to convert it into the H^+ form and remove water. Characterization by FT-IR using a Thermo Nicolet Nexus 6700 FTIR spectrometer showed no evidence for extra-framework aluminum formation following catalyst pretreatment (see Supporting Information).

Reactions were carried out using 0.05 g of catalyst in a 6.35 mm outer diameter (OD) quartz reactor tube with an expansion in the middle (ca. 12.7 mm OD) packed with quartz wool to hold the catalyst in place. A quartz-sheathed K-type thermocouple was placed in direct contact with the catalyst bed. The catalyst was pretreated for 3 h at 773 K in dry air (100 cm^3 min^{-1}) to remove residual moisture, and cooled to reaction temperature. CO (99.99% pure research grade, Praxair) was bubbled through a stainless steel saturator filled with DMM (99%, Sigma–Aldrich) and chilled to provide the desired vapor pressure. Additional CO or He was mixed with the saturator exit flow to set the desired CO/DMM ratio and the total gas volumetric flow rate. Reaction products were analyzed using an Agilent 6890n GC equipped with an HP-PLOT Q capillary column connected to a flame ionization detector. Experiments at elevated pressure were carried out by throttling a needle valve located downstream from the reactor.

Activity and selectivity data were collected as a function of temperature by increasing the reaction temperature at a fixed reactant composition and flow rate. Each temperature was held constant for 45 min.

The total gas flow rate in the reactor was maintained at 100 cm^3 min^{-1} at the reaction pressure, resulting in gas flow rates between 100 and 300 cm^3 min^{-1} at STP. The reactor space time, calculated on the basis of mole of aluminum in the zeolite framework, was held constant at 0.27 (mmol Al) min L^{-1} except where noted otherwise. When varied, changes in space time were accomplished by increasing the amount of catalyst used in the experiment.

Selectivities to MMAc from DMM are reported on the basis of mole of carbon using the following formula: 3(mole of MMAc formed)/[2(mole of DME formed) + 2(mole of MF formed) + 3(mole of MMAc formed)]. The selectivity to MMAc from CO was 100%.

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