Effect of zeolite framework type and Si/Al ratio on dimethoxymethane carbonylation

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A B S T R A C T

This work reports on the effects of zeolite framework type and Si/Al ratio on the carbonylation of dimethoxymethane (DMM) to produce methyl methoxyacetate (MMAc). Faujasite (FAU), ZSM-5 (MFI), Mordenite (MOR) and Beta (BEA) showed very similar activity for DMM carbonylation. However, FAU had a very high selectivity to MMAc compared to MFI, MOR and BEA because of very low rates of dimethyl ether (DME) and methyl formate (MF) formation, by-products of the disproportionation of DMM. The high rate of DMM disproportionation observed for MFI, MOR and BEA is ascribed to the small pores of these zeolites, which facilitate a critical initial step in the formation of DME and MF. FER showed very low activity for both carbonylation and disproportionation. Increasing the Si/Al ratio for both FAU and MFI led to an increase in the turnover frequency for DMM carbonylation. It is proposed that the low rate of MMAc formation found at low Si/Al ratios is due to repulsive interactions occurring between adsorbed species located within the same supercage (FAU) or channel intersection (MFI).
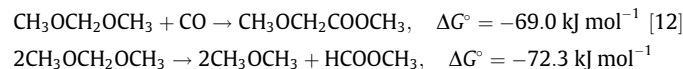
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1. Introduction

Acid-catalyzed formaldehyde carbonylation has been investigated as a means for producing carbon–carbon bonds for 70 years [1–7]. The products of the reaction, consisting of glycolic acid and its esters and ethers, are desirable as precursors to monoethylene glycol (MEG). This approach to the synthesis of MEG is being pursued because formaldehyde can be produced from synthesis gas-derived methanol [8], a cheaper carbon source than ethene the current starting material for the production of MEG [9]. Fig. 1 shows schemes for synthesizing MEG from formaldehyde and dimethoxymethane (DMM) and demonstrates the equivalence of using formaldehyde and its acetal. Both formaldehyde and DMM are synthesized directly by partial oxidation of methanol [8,10]. The key step in each scheme is the formation of a carbon–carbon bond between formaldehyde/DMM and CO. Coupling carbon monoxide and formaldehyde leads to glycolic acid (GA), whereas the carbonylation of DMM leads to methyl methoxyacetate (MMAc), both of which are precursors to MEG.

Previous investigation of formaldehyde carbonylation has been carried out exclusively in the liquid phase, often requiring carbon monoxide pressures over 100 atm in order to achieve reasonable selectivities [1–6]. In a recent report, we demonstrated for the first time the gas-phase carbonylation of a formaldehyde dialkyl acetal,

DMM, over H-Faujasite (H-FAU) [11]. At a CO pressure of 3 atm, 79% selectivity to MMAc could be achieved. Because acetals are often used as protecting groups for aldehydes, this reaction can be considered equivalent to formaldehyde carbonylation. In contrast to liquid-phase carbonylation of formaldehyde, which produces a large number of by-products [2,4,7], the gas-phase carbonylation of DMM involves only two reactions – the carbonylation of DMM to form MMAc and the disproportionation of DMM to form dimethyl ether (DME) and methyl formate (MF).

$$CH_3OCH_2OCH_3 + CO \rightarrow CH_3OCH_2COOCH_3, \quad \Delta G^\circ = -69.0 \text{ kJ mol}^{-1} \text{ [12]}$$

$$2CH_3OCH_2OCH_3 \rightarrow 2CH_3OCH_3 + HCOOCH_3, \quad \Delta G^\circ = -72.3 \text{ kJ mol}^{-1}$$

The aim of the present investigation was to establish the effects of zeolite framework structure and Si/Al ratio on the gas-phase carbonylation of DMM to MMAc. Experiments were carried out to determine the effects of DMM and CO partial pressures and reaction temperature on the rate of MMAc formation as well. The observed effects of zeolite framework structure and Si/Al ratio are interpreted in the light of a proposed reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Zeolite samples were obtained commercially with different Si/Al ratios in either the NH_4^+ form (NH$_4$-FAU, Si/Al ≈ 2.6, Si/Al ≈ 6,

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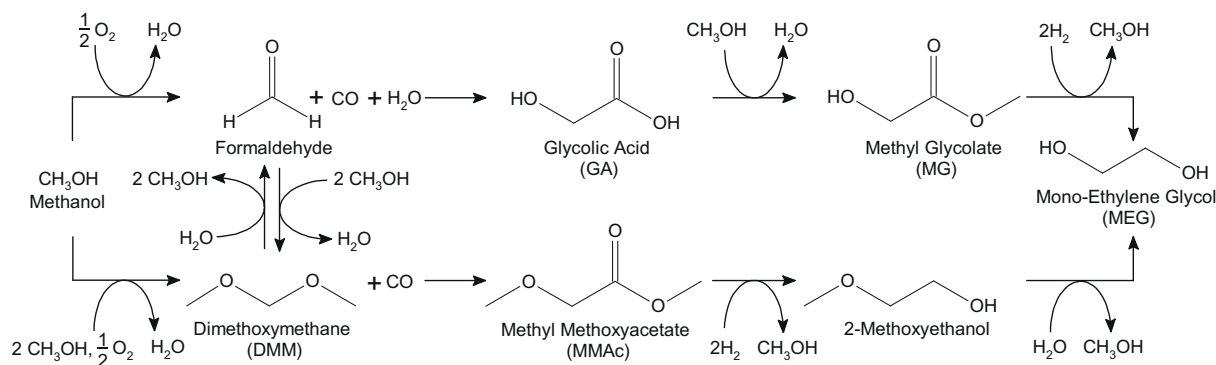E-mail address: bell@cchem.berkeley.edu (A.T. Bell).

Fig. 1. Scheme for the production of ethylene glycol from methanol via formaldehyde or dimethoxymethane.

Zeolyst; NH$_4$-MFI, Si/Al ≈ 13.5, Süd-Chemie, Si/Al ≈ 11.5, Si/Al ≈ 15, Si/Al ≈ 25, Si/Al ≈ 40, Si/Al ≈ 140, Zeolyst; NH$_4$-MOR, Si/Al ≈ 10, Zeolyst; NH$_4$-BEA, Si/Al ≈ 12.5, Zeolyst; NH$_4$-FER, Si/Al ≈ 10, Zeolyst) or the H$^+$ form (H-FAU, Si/Al ≈ 15, Si/Al ≈ 30, Si/Al ≈ 40, Zeolyst). As-received samples were heated to 773 K for 3 h at the rate of 2 K min^{-1} in 100 cm^3 min^{-1} flow of dry air (zero grade) to convert from the NH$_4^+$ form to the H$^+$ form and to drive off any adsorbed water. Dried samples were stored in a desiccator prior to use to minimize further adsorption of water.

One sample (Na-MFI, Si/Al ≈ 27.5, Süd-Chemie) was obtained in the Na$^+$ form and was converted to the NH$_4^+$ form by aqueous exchange with 1 M NH$_4$NO$_3$ solution. 5 g of Na-MFI was exchanged with 0.1 L of solution for 12 h at 353 K three times, filtering and washing with 0.1 L deionized water each time. After the final exchange, the sample was filtered and rinsed again and dried at 383 K for 36 h. Conversion to the H$^+$ form was achieved by treatment in dry air for 3 h at 773 K as described earlier.

2.2. Steady-state catalytic data

Reactions were carried out in a 6.35 mm OD quartz tube reactor with an expanded section (~12.7 mm OD, ~20 mm length "bubble"). The reactor was packed with quartz wool above and below the catalyst bed to hold the catalyst powder in place. The reactor was placed inside a resistively heated ceramic furnace with external temperature control, and the catalyst bed temperature was measured with a K-type thermocouple sheathed in a quartz capillary placed in direct contact with the bed.

Residual moisture was removed from the catalyst by heating it to 773 K for 3 h at a rate of 2 K min^{-1} in 100 cm^3 min^{-1} flow of dry air. Samples were then cooled to the desired 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 (99.999% ultra-high purity, Praxair) 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 a bonded polystyrene–divinylbenzene (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.

The total gas flow rate in the reactor was maintained at 100 cm^3 min^{-1} at the reaction pressure, resulting in a gas flow rate between 100 and 300 cm^3 min^{-1} at STP. Since the active centers for carbonylation of DMM are Brønsted-acids sites and the concentration of these sites is proportional to the Al content in a given zeolite, reactor space time was calculated on the basis of the number

of moles of Al contained in a given zeolite. Using this definition, space time was varied by choosing the weight of catalyst loaded.

Selectivities to MMAc from DMM are reported based on moles of carbon in MMAc that originated from DMM and were calculated as $S_{MMAc} = \frac{3r_{MMAc}}{2r_{DME} + 2r_{MF} + 3r_{MMAc}}$, where r_i is the rate of formation of each product i in molar units. Note that only three atoms of carbon in MMAc are derived from DMM, and the fourth carbon atom is derived from CO.

3. Results

3.1. Effect of zeolite framework type

Fig. 2 shows the effect of zeolite framework type on the steady-state rates of MMAc formation (Fig. 2a), DME, and MF formation (Fig. 2b), MMAc selectivity from DMM (Fig. 2c), and DMM conversion (Fig. 2d) as functions of reaction temperature. Zeolites of similar Si/Al ratios were chosen, and the space time was fixed based on moles of Al in the sample at ~0.8 mmol Al min L^{-1}. The partial pressures of CO and DMM in the feed gas were fixed at 1.98 atm and 0.02 atm, respectively.

The dependence of the MMAc formation rate with temperature was complex and depended on zeolite framework type. The MMAc rate showed a maximum with temperature over each zeolite, but the temperature of the maximum rate depended on the zeolite structure. MOR and BEA possessed higher activity to MMAc than FAU and MFI at temperatures in the range of 363–393 K, whereas FAU and MFI possessed higher activity to MMAc than MOR and BEA at higher temperatures in the range of 393–433 K. FER was almost completely inactive but also showed increasing activity to MMAc formation at higher temperatures. The maximum MMAc formation rates observed for FAU, MFI, MOR and BEA were roughly comparable, varying only by a factor of two from each other.

DME and MF formation rates also showed a dependence on zeolite framework type. The rates of both DME and MF formation increased monotonically with temperature, except for the MF formation rate over MOR as discussed in the following paragraphs. MOR and BEA showed very high disproportionation rates that increased almost linearly with temperature above 353 K. The rate of DMM disproportionation was low for MFI up to 393 K and then rose rapidly at higher temperatures such that DME and MF formation rates exceeded those over MOR and BEA at 453 K. By contrast, FAU and FER showed very low, albeit increasing, disproportionation rates at all temperatures.

The ratio of DME to MF was approximately two in most cases, as expected from the stoichiometry of DMM disproportionation. The DME/MF ratio exceeded two at higher temperatures over all zeolite types tested here, except over FAU, where it remained near two, up to 453 K. The deviation from a DME/MF ratio of two was most