Selective Carbonylation of Dimethyl Ether to Methyl Acetate Catalyzed by Acidic Zeolites**

Patricia Cheung, Aditya Bhan, Glenn J. Sunley, and Enrique Iglesia*

Methanol carbonylation is currently used to produce acetic acid with Rh and Ir organometallic complexes and iodide co-catalysts.[1–3] Zeolites[4–9] and Keggin polyoxometallate clusters[10–13] also catalyze the carbonylation of alcohols and ethers (Koch reaction) to form carboxylic acids and esters. Surface alkyl groups, formed by alcohol dissociation, alkene protonation, or alkane deprotonation at acidic sites react with CO to form acylium ions, which then form carboxylic acids and esters, as in the reactions of isobutane on sulfated zirconia[14] and tert-butyl alcohol[5,7,8] on acidic ZSM5, MOR, BEA, and Y-zeolites to form pivalic acid. Carbonylation of methanol and dimethyl ether (DME) on acidic zeolites and polyoxometallate clusters occurs concurrently with side reactions (Scheme 1) and significant catalyst deactivation.[4,6,9–13]

We report herein stable and highly selective (> 99%) halide-free catalysts based on zeolites for DME carbonylation to methyl acetate at low temperatures (423–463 K). The reaction rates are much higher than for methanol carbonylation because water may adsorb competitively at CO binding sites and/or cause parallel methanol dehydration.
DME carbonylation involves the formation of methyl groups, which reform after reaction with CO to generate acetyl species and reactions of DME with acetyl species to give methyl acetate; these propagation steps avoid the formation of methyl groups by the initial direct reaction of DME with H\(^+\), which causes an induction period during the early stages of reaction (see the Supporting Information).

DME carbonylation proceeds at approximately 423–463 K with 99% selectivity to methyl acetate; higher temperatures favor homologation and oligomerization reactions that form hydrocarbons. Figure 1 shows that the rate of methyl acetate synthesis (pertotal Al content) is highest on H-MOR (Si/Al = 10:1; diamonds), H-FER (Si/Al = 33.5:1; triangles), H-MOR (Si/Al = 45:1; circles), and H-ZSM5 (Si/Al = 12.5:1; squares). Conditions: 0.93 MPa CO, 20 kPa DME, 50 kPa Ar.

The addition of water (0.5–1.1 kPa) to DME–CO reactants led to methanol formation and a lower rate of methyl acetate synthesis (Figure 2 and Table 1), without detectable formation of acetic acid. The rate of carbonylation gradually returned to initial values after the removal of water, which is consistent with reversible kinetic inhibition. During methanol carbonylation, parallel dehydration reactions form stoichiometric DME and H\(_2\)O, with the latter inhibiting the carbonylation steps. Inhibition by H\(_2\)O does not reflect its competitive adsorption with DME on Brønsted acid sites or the displacement of DME-derived intermediates by H\(_2\)O because the rates remain zero order with respect to DME pressure, even when H\(_2\)O is present (Figure 2). H\(_2\)O competes with CO for adsorption at the Lewis acid sites; this competition is possibly required to bind CO coreactants\(^{[15–18]}\) or inhibit CO reactions with adsorbed methyl intermediates. IR spectra showed that H\(_2\)O (pre-adsorbed at 298 K) prevents the binding of CO on Lewis acid sites on H-MOR at 123 K, but does not influence CO interactions with H\(^+\).\(^{[19]}\) The involvement of Lewis acid sites in DME carbonylation reactions remains equivocal at this time.

The potential role of surface methyl intermediates and the kinetic relevance of the CO addition steps were examined by DME pulsing studies (addition of DME/Al = 0.73:1–1.00:1) at 438 K on samples treated in flowing dry air at 773 K. Only DME and water were detected in the effluent during subsequent He treatment. DME adsorption ratios per Al

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**Figure 1.** The rate of methyl acetate formation (per total Al content) on H-MOR (Si/Al = 10:1; diamonds), H-FER (Si/Al = 33.5:1; triangles), H-MOR (Si/Al = 45:1; circles), and H-ZSM5 (Si/Al = 12.5:1; squares). Conditions: 0.93 MPa CO, 20 kPa DME, 50 kPa Ar.

**Figure 2.** Effects of DME (squares: 0.5 MPa CO, 438 K; triangles: 0.5 kPa H\(_2\)O, 0.5 MPa CO, 438 K) and CO (diamonds: 2–16 kPa DME, 438 K) concentration on the rate of methyl acetate formation on H-MOR (Si/Al = 10:1).

**Table 1:** Steady-state carbonylation rates with methanol, DME, and DME–H\(_2\)O reactants on H-MOR (Si/Al = 10:1).

<table>
<thead>
<tr>
<th>Reactants</th>
<th>T [K]</th>
<th>(P_{\text{MeOH}}) or (P_{\text{DME}}) [kPa]</th>
<th>(P_{\text{CO}}) [kPa]</th>
<th>(P_{\text{H}_2\text{O}}) [kPa]</th>
<th>Rate of methyl acetate synthesis ([\text{mol \ (g \ atom \ Al)}^{-1} \cdot \text{h}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>DME–CO</td>
<td>423</td>
<td>26</td>
<td>120</td>
<td>0</td>
<td>0.034</td>
</tr>
<tr>
<td>DME–CO–H(_2)O</td>
<td>423</td>
<td>26</td>
<td>120</td>
<td>1.1</td>
<td>0.0025</td>
</tr>
<tr>
<td>DME–CO</td>
<td>438</td>
<td>0.8–8</td>
<td>500</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>DME–CO–H(_2)O</td>
<td>438</td>
<td>8–66.8</td>
<td>500</td>
<td>0.5</td>
<td>0.12</td>
</tr>
<tr>
<td>CH(_3)OH–CO</td>
<td>423</td>
<td>3.7</td>
<td>86</td>
<td>0</td>
<td>not detected (&lt; 0.001)</td>
</tr>
</tbody>
</table>
atom were approximately 0.5:1 (± 0.05) on H-MOR (Si/Al = 6.5:1, 10:1) and H-ZSM5 (Si/Al = 12.5:1; Table 2), which is consistent with DME reactions with H* to form two methyl species [Eq. (1)]. The formation of the methyl species is consistent with IR and NMR spectral evidence of DME interactions with H-zeolites.[20–24]

$$\text{CH}_3\text{OCH}_3 + 2[\text{SiO(H)}\text{Al}] \rightarrow 2[\text{SiO(CH}_3\text{)}\text{Al}] + \text{H}_2\text{O} \quad (1)$$

Table 2: Ratios of dosed and adsorbed DME per Al atom on zeolites at 438 K.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>DME_dosed/Al</th>
<th>DME_ads/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-MOR</td>
<td>10:1</td>
<td>1.00:1</td>
<td>0.45:1</td>
</tr>
<tr>
<td>10:1</td>
<td></td>
<td>0.80:1</td>
<td>0.51:1</td>
</tr>
<tr>
<td>10:1</td>
<td></td>
<td>0.73:1</td>
<td>0.45:1</td>
</tr>
<tr>
<td>6.5:1</td>
<td></td>
<td>0.88:1</td>
<td>0.54:1</td>
</tr>
<tr>
<td>H-ZSM5</td>
<td>12.5:1</td>
<td>0.83:1</td>
<td>0.51:1</td>
</tr>
</tbody>
</table>

Interactions of CO with these methyl groups were probed by replacing DME–CO reactants with pure CO for a specific time interval and then reintroducing DME–CO mixtures. CO reacts with methyl-saturated surfaces to form acetyl complexes that desorb only after DME is reintroduced, at which time the rate of methyl acetate formation increases sharply and then returns gradually to the steady-state values (Figure 3a). Exposing methyl-saturated samples to He led to an immediate return to steady-state rates after DME–CO mixtures were reintroduced. Precursors to methyl acetate form slowly during the contact of methyl groups with CO, but cannot desorb without methylation by DME to form methyl acetate and a new methyl intermediate.

The number of CH$_3$–CO complexes, measured from the rate of methyl acetate formation per Al atom as a function of exposure time in 0.95 MPa CO after exposure to 0.95 MPa CO for varying intervals (0.93 MPa CO, 20 kPa DME, 50 kPa Ar, 438 K). The initial rate derived from Figure 3b is 0.42 methyl acetate (g atom Al)$^{-1}$ h$^{-1}$, which is approximately 50% of the steady-state rate (0.82 methyl acetate (g atom Al)$^{-1}$ h$^{-1}$). The reason is that the reaction of CO with the methyl-saturated sites is the sole kinetically relevant step in DME carbonylation reactions; the remaining differences may reflect a nonuniform reactivity of methyl groups or a different concentration of activated CO in such methyl groups, which would cause only some methyl species to form methyl acetate, while steady-state rates on the saturated surfaces reflect carbonylation rates of the most reactive methyl groups instead.

A plausible chain-transfer sequence involves initiation through reaction of DME with H* to form hydrogen-bonded DME [Eq. (2)] and methyl groups [Eqs. (3) and (4)] in steps that lead to an induction period during DME–CO reactions (see the Supporting Information). CO and water adsorb competitively at sites responsible for CO binding [Eqs. (5) and (6)], and the propagation steps [Eqs. (6)–(8)] dominate in the absence of water. The catalyst surface becomes saturated with stable methyl intermediates that react with CO in the kinetically relevant step to form adsorbed acetyl intermediates [Eq. (7)]. Methyl acetate and subsequent methyl species form by reactions of acetyl species with DME [Eq. (8)].

$$\text{CH}_3\text{OCH}_3 + [\text{SiO(H)}\text{Al}] \rightarrow \text{CH}_3\text{OCH}_3 - [\text{SiO(H)}\text{Al}] \quad (2)$$

$$\text{CH}_3\text{OCH}_3 - [\text{SiO(H)}\text{Al}] \rightarrow [\text{SiO(CH}_3\text{)}\text{Al}] + \text{CH}_3\text{OH} \quad (3)$$

$$\text{CH}_3\text{OH} + [\text{SiO(H)}\text{Al}] \rightarrow [\text{SiO(CH}_3\text{)}\text{Al}] + \text{H}_2\text{O} \quad (4)$$

$$[\text{SiO(CH}_3\text{)}\text{Al}] + \text{CO} \rightarrow [\text{SiO(COCH}_3\text{)}\text{Al}] + \text{CH}_3\text{OCH}_3 \quad (7)$$

$$[\text{SiO(COCH}_3\text{)}\text{Al}] + \text{CH}_3\text{OCH}_3 \rightarrow [\text{SiO(CH}_3\text{)}\text{Al}] + \text{CH}_3\text{COOCH}_3 \quad (8)$$

In summary, acid zeolites catalyze DME carbonylation to methyl acetate at low temperatures (423–463 K) with high selectivity and catalyst stability. DME reacts with Brønsted protons to form methyl-saturated surfaces, which react with CO to form acetyl moieties. These species form methyl acetate by reaction with DME, which also restores the methyl groups initially formed by direct reaction of DME with H* during the induc-
tion period. DME carbonylation preserves anhydrous conditions, as conversion occurs and avoids inhibition of carbonylation pathways by H₂O, a process that leads to much lower carbonylation rates when methanol is used as the reactant. Kinetic and spectroscopic studies are on-going to address the nature of the CO binding sites responsible for these reactions and the apparent requirement for both Bronsted and CO binding centers in DME carbonylation catalysis. The current productivities are below the expected commercial targets but do increase linearly with CO pressure. Taken together with the remarkable selectivity for methyl acetate and the unprecedented low reaction temperatures, these initial reports show significant promise for the practical use of this catalytic chemistry as our knowledge of the nature of CO binding sites increases.

**Experimental Section**

Amorphous silica alumina (Si/Al = 3:1) was obtained from Aldrich. NH₄-MOR (Si/Al = 10:1; Zeolyst), H-MOR (Si/Al = 45:1; Zeolyst), NH₄-FER (Si/Al = 33:5:1; Zeolyst), and NH₄-BEA (Si/Al = 12:5:1; Zeolyst), NH₄-ZSM5 (Si/Al = 12.5:1; AlSi-Penta Zeolithe), and NH₄-USY (Si/Al = 3:1; Engelhard) were treated in flowing dry air at 773 K for 3 h to form acid zeolites. Na-MOR (Si/Al = 6:5:1; Zeolyst) was converted into its NH₄ form by exchanging Na-MOR (10 g) with 1M NH₄NO₃ (48% Ev%0.2 L) at 353 K for 12 h. The samples were dried overnight in ambient air at 393 K before treatment in flowing dry air for 3 h at 773 K.

Carbonylation rates and selectivities were measured using a packed-bed stainless steel reactor (9.5 mm OD) equipped with a multipoint thermocouple held within a 1.6-mm outer thermowell packed-bed stainless steel reactor (9.5 mm OD) equipped with a 125–250 mg catalysts (0.2–0.6 g, 125–250 μm). Catalysts (0.2–0.6 g, 125–250 μm) were treated in flowing dry air (~1.67 cm/s·g⁻¹) for 2 h at 773 K and cooled to reaction temperature (420–513 K) in flowing He (UHP, Praxair) before introducing 2% CO/Ar (UHP, Praxair), and/or 95% CO/Ar (UHP, Praxair). Methanol was added through a saturator using He as the carrier gas, and water was added by a syringe pump (Cole-Parmer, Model 100 series) or by injection of 1.25% H₂/Ar (UHP, Praxair) with CuO at 673 K. Heated lines (423–473 K) transferred the reactor effluent to a mass spectrometer (MKS Spectra Minilab) and a gas chromatograph (Agilent 6890) equipped with a methyl silicone column (HP-1, 50 m × 0.32 mm × 1.05 μm) connected to a flame-ionization detector and a Porapak Q column (80–100 mesh, 12 ft. × 1/8 in.) connected to a thermal conductivity detector.

Transient experiments were carried in the same equipment. He (~3.34 cm²·g⁻¹·s⁻¹, UHP, Praxair) was used to introduce DME (99.5%, Praxair) pulses (1.07 cm³) at 120-s intervals. Samples were then flushed with He (~3.34 cm²·g⁻¹·s⁻¹) for 1.5–2 h to remove physisorbed DME and any water formed. CO, Ar, and He streams were purified of oil and water (Matheson, 451) and of metal carbonyls (Matheson, 454) prior to addition to mixtures containing DME. These streams were further dried using CaH₂ (Aldrich, 99%) held at ambient temperature.

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