Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 245 (2007) 110–123
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Site requirements and elementary steps in dimethyl ether carbonylation catalyzed by acidic zeolites

Patricia Cheung [a], Aditya Bhan [a], Glenn J. Sunley [b], David J. Law [b], Enrique Iglesia [a,*]

[a] *Department of Chemical Engineering, University of California at Berkeley, Berkeley, CA 94720, USA*
[b] *BP Chemicals, Hull Research and Technology Centre, Saltend, Hull HU12 8DS, UK*

Received 24 July 2006; revised 18 September 2006; accepted 25 September 2006

Abstract

Steady-state, transient, and isotopic-exchange studies of dimethyl ether (DME) carbonylation, combined with adsorption and desorption studies of probe molecules and infrared (IR) spectroscopy, were used to identify methyl and acetyl groups as surface intermediates within specific elementary steps involved in the synthesis of methyl acetate from DME–CO mixtures with >99% selectivity on H-zeolites. Carbonylation rates increased linearly with CO pressures but did not depend on DME pressures, suggesting that the addition of CO to CH_3 groups present at saturation coverage controls catalytic carbonylation rates. These reactions lead to acetyl groups that subsequently react with DME to form methyl acetate (423–463 K; >99% selectivity) and regenerate methyl intermediates, consistent with kinetic studies of CO reactions with CH_3 groups previously formed from DME and with kinetic and IR studies of DME reactions with acetyl groups formed by stoichiometric reactions of acetic anhydride. These studies show that CO reacts with DME-derived intermediates bound on zeolitic Al sites from the gas phase or via weakly held CO species adsorbed non-competitively with CH_3 groups. These reactions, in contrast with similar reactions of methanol, occur under anhydrous conditions and avoid the formation of water, which strongly inhibits carbonylation reactions.

Keywords: Carbonylation; Acid; Zeolite; Mordenite; Dimethyl ether; Methanol; Carbon monoxide; Methyl acetate; Acetic acid; Carboxylic acid

1. Introduction

Methanol carbonylation accounts for ∼60% of acetic acid production worldwide [1–5]. The Monsanto and BP Cativa^{TM} processes use homogeneous Rh or Ir complexes and iodide co-catalysts to carbonylate methanol (30–60 bar, 423–473 K) [1]. The Acetica process uses an immobilized Rh–carbonyl complex grafted onto a pyridine-containing solid resin and iodide co-catalysts to improve throughput and catalyst recovery [6]. Practical methanol carbonylation catalysts without costly noble metals and corrosive iodide co-catalysis remain unavailable.

Carbonylation of alkenes and alkanols to carboxylic acids via Koch-type reactions [7] is catalyzed by strong acids without metal co-catalysts [8,9]. Acidic zeolites and sulfated zirconia catalyze the carbonylation of alkanols and alkenes to carboxylic acids via Koch-type pathways, which involve CO insertion into C–O bonds within tertiary surface-bound alkoxides and subsequent hydrolysis of the bound acetyl intermediates formed [10–16]. Fujimoto and co-workers first reported methanol carbonylation to acetic acid on zeolites and proposed an intermediate role of surface methyl groups [17]. Similar reactions of methanol and dimethyl ether (DME) were later reported on acidic zeolites and polyoxometallate clusters, but with significant homologation side reactions and catalyst deactivation [18–23]. A preliminary note from our group showed that H-mordenite (H-MOR) and H-ferrierite (H-FER) catalyzed DME carbonylation to methyl acetate with stable rates and >99% selectivity at 423–463 K after an initial induction period, during which acidic protons were replaced by methyl groups and the water co-produced was removed [24]. The rate of DME carbonylation was much higher than for similar reactions of CH_3OH, at least in part because H_2O, formed in parallel CH_3OH dehydration reactions, inhibits carbonylation steps. Methyl acetate synthesis rates did not depend on DME pressure,

---

[*] Corresponding author. Fax: +1 510 219 0142.
E-mail address: iglesia@cchem.berkeley.edu (E. Iglesia).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.09.020

but increased linearly with CO pressure up to ∼1 MPa. This kinetic response is consistent with a sequence of elementary steps involving the formation of surface methyl groups at Brønsted acid sites initially via direct DME reactions with protons and then via chain transfer reactions of DME with surface acetyls formed via rate-determining CO insertion into C–O bonds in methyl groups at the catalytic steady state [24].

Here we provide evidence for these intermediates and elementary steps and for their consistency with the measured kinetic effects of DME, CO, and H_2O using infrared (IR) spectroscopy, isotopic tracer and kinetic effects, and transient reaction studies. We also report that H-MOR samples with similar Si/Al ratio and extra-framework Al content give different carbonylation turnover rates (per H^+); methyl acetate synthesis rates on these H-MOR samples do not correlate with the number of CO binding sites measured from low-temperature CO adsorption uptakes, suggesting that the specific siting and structure of acidic Al–OH groups is critical to stabilize transition states required for kinetically relevant CO insertion steps. In the context of these results, we discuss various possible structures for such active sites, specifically those involved in formation of the C–C bond in methyl acetate synthesis.

2. Experimental

2.1. Catalyst preparation

Na-MOR (Si/Al ∼ 6.5, Zeolyst) was converted to NH_4-MOR via four sequential exchanges of Na-MOR (10 g) with 1 M NH_4NO_3 (0.2 L) at 353 K for 12 h. After each exchange, the NH_4-MOR was washed with 0.2 L of deionized water and isolated by filtration. After the final exchange, the sample was treated overnight at 393 K in ambient air and then in flowing dry air (zero grade, Praxair) for 3 h at 773 K (0.167 $K\,s^{-1}$).

Chemically dealuminated HMOR samples were prepared by refluxing HMOR (Si/Al ∼ 10, Zeolyst) in a 1.5 M aqueous solution of oxalic acid dihydrate (99%, Fluka) (catalyst:oxalic acid solution = 1:5, v/v) at 313, 323, or 343 K for 3 h before washing with (0.2 L) deionized water, filtering, and drying at 393 K in ambient air overnight; this process was carried out to remove detrital Al species, but it also removed some framework Al atoms [25,26]. The samples were subsequently treated at 773 K (0.0167 $K\,s^{-1}$) in flowing dry air (zero grade, Praxair) for 3 h. This treatment was carried out to explore the effects of Al content on DME carbonylation rates.

NH_4-MOR (Si/Al ∼ 10, Zeolyst, ∼14 g) was exchanged with Na using 0.5 L aqueous $NaNO_3$ (99%, EMD Chemicals, 0.014–2.44 M) at 353 K for 12 h and then washed in 2 L of deionized water and treated at 393 K overnight in ambient air and then in flowing dry air (zero grade, Praxair) for 3 h at 773 K (0.167 $K\,s^{-1}$). This treatment was carried out to explore the effects of replacing H^+ with Na^+ on the rate of DME carbonylation on residual protons.

NH_4-MOR (Si/Al ∼ 10, Zeolyst), H-MOR (Si/Al ∼ 44.5, Zeolyst), H-MOR (Si/Al ∼ 10, Sudchemie), H-MOR (Si/Al ∼ 9.5, Tosoh), and NH_4-MFI (Si/Al ∼ 12.5, AlSi-Penta Zeolithe GmbH) samples were treated in flowing dry air (zero grade, Praxair) for 3 h at 773 K (0.0167 $K\,s^{-1}$) to remove residual organics and to convert NH_4^+ cations to H^+.

Table 1
Elemental analysis and extra-framework Al content from ^{27}Al MAS NMR of zeolite samples

Zeolite name	Source	Si/Al_{ICP}	Na/Al_{ICP}	Al_{EF} (%)
HMOR_8.9	Tosoh	8.9	–	20.7
HMOR_10.1	Sudchemie	10.1	–	18.6
HMOR_9.8	Zeolyst	9.8	–	19.5
HMOR_9.5	Zeolyst	9.5	–	19.9
HMOR_6.0	Zeolyst	6.0	<0.002	21.0
HMOR_46	Zeolyst	46	–	–
NaMOR_0.17	Zeolyst	9.1	0.17	–
NaMOR_0.27	Zeolyst	9.0	0.27	–
NaMOR_0.41	Zeolyst	8.7	0.41	–
NaMOR_0.55	Zeolyst	9.0	0.55	6.6
NaMOR_0.90	Zeolyst	9.9	0.90	∼1
HMOR-Ox_15.3	Zeolyst	15.3	–	–
HMOR-Ox_14.2	Zeolyst	14.2	–	–
HMOR-Ox_16.5	Zeolyst	16.5	–	–
HFER_34.5	Zeolyst	34.5	–	3.5
HMFI_12.2	AlSi-Penta	12.2	–	15.4

^{27}Al magic-angle spinning (MAS) NMR spectra were measured with a Bruker AV-500 spectrometer using a 4-mm MAS broadband probe. The spectra were referenced to octahedral Al^{3+} cations in 1 M aluminum nitrate solutions. Acid forms of the zeolites were kept for ⩾12 h in a desiccator containing aqueous 1 M NaCl (∼96% relative humidity), because these hydration protocols sharpen ^{27}Al NMR lines by weakening quadrupole interactions [27]. The amount of extra-framework Al, measured from these ^{27}Al NMR; the Si, Al, and Na contents (Galbraith Laboratories, ICP-OES); and the nomenclature used are reported in Table 1.

2.2. Steady-state catalytic reactions of DME–CO and DME–CO–H_2O mixtures

DME carbonylation rates and selectivities were measured in a packed-bed stainless steel reactor (8.1 mm i.d., 9.5 mm o.d.) held within a three-zone resistively heated furnace (Applied Test Systems, 3210 series). Temperature was measured using an axial multipoint thermocouple contained within a stainless steel thermowell (1.6 mm o.d.). Catalyst samples (0.2–0.6 g, 125–250 µm particle diameter) were treated in flowing dry air (∼1.67 $cm^3\,s^{-1}\,g^{-1}$, zero grade, Praxair) for 2 h at 773 K at a heating rate of 0.167 $K\,s^{-1}$ before cooling in flowing He (∼3.33 $cm^3\,s^{-1}\,g^{-1}$, UHP, Praxair) to reaction temperatures (420–513 K) and introducing DME (99.5%, Praxair), 95% CO/Ar (UHP, Praxair), or 2% DME/5% Ar/93% CO (99.5% DME, UHP Ar/CO, Praxair) reactant mixtures. The reactant mixtures were dried before use by passing through a CaH_2 (0.5 g, 99.99%, Aldrich) bed held at ambient temperature. Water was introduced into the reactant mixture after the CaH_2 bed using a syringe pump (Cole-Parmer, model 100 series) in experiments designed to explore kinetic inhibition of carbonylation reactions by water. The reactor effluent was brought via transfer lines held at 423–473 K into a mass spectrometer (MKS Spectra Minilab) or into a gas chromatograph (Agilent