



Increased productivity in ethylene carbonylation by zeolite-supported molybdenum carbonyls



Chieh-Chao Yang^{a,b}, Sara Jacob^a, Beata A. Kilos^c, David G. Barton^c, Eric Weitz^b, Justin M. Notestein^{a,*}

^a Chemical & Biological Engineering, Northwestern University, Evanston 60208, IL, USA

^b Department of Chemistry, Northwestern University, Evanston 60208, IL, USA

^c The Dow Chemical Company, Core R&D, Midland 48674, MI, USA

ARTICLE INFO

Article history:

Received 23 December 2015

Revised 8 March 2016

Accepted 9 March 2016

Available online 4 April 2016

Keywords:

Heterogeneous catalysis

Carbonylation

Ethylene

Promotion

Molybdenum

Metal carbonyl

Y-type zeolite

Impregnation

ABSTRACT

Ethylene carbonylation to propionic acid is a powerful route to the synthesis of oxygenates. $\text{Mo}(\text{CO})_6$ is a known homogenous catalyst for this reaction. When supported on HY zeolite, prepared by incipient wetness impregnation from pentane or by vapor deposition, turnover numbers dramatically increase to over 40,000 in 5 h of reaction, particularly for the supports with lower Si/Al ratios. Diffuse reflectance UV–visible spectra and thermogravimetric analysis indicate that lower Si/Al ratios promote more and stronger interactions between $\text{Mo}(\text{CO})_6$ and the support, leading to higher reactivity under liquid-phase reaction conditions. Although some leaching occurs under these conditions, the active catalyst is the supported $\text{Mo}(\text{CO})_x/\text{HY}$, and the recovered catalysts are still stable and active for ethylene carbonylation with turnover numbers exceeding 30,000 mol propionic acid/mol of Mo over 5 h at 190 °C. FTIR provides evidence for the formation and stabilization of under-coordinated carbonyl species during heat treatment, and such sub-carbonyls are known to be relevant in previously-established catalytic mechanisms.

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1. Introduction

Carbonylation of alkenes to form carboxylic acids or their esters is typically carried out with homogeneous catalysts. We and others have reported the reactivity of $\text{Mo}(\text{CO})_6$ and other group VI metal carbonyls with iodide promoters for ethylene carbonylation to form propionic anhydride and propionic acid [1,2]. A practical drawback of using $\text{Mo}(\text{CO})_6$ in solution is that separation of the products from the solvent and catalyst is difficult. More fundamentally, the carbonylation mechanism requires the formation of open coordination sites on Mo, which can lead to catalyst deactivation through the formation of Mo metal or oxide particles. The possible advantages of using supported metals for ethylene carbonylation have been noted. Studies of heterogeneous catalysis for ethylene carbonylation have been limited to silica- and zeolite supported precious metal (Pd, Rh, Ir, Pt, Ru) complexes using bromide promoters and these have not focused on the reaction mechanism [3,4]. There are no reports we are aware of for ethylene carbonylation using supported metal carbonyls.

Although not previously studied for ethylene carbonylation, there have been many studies on the structure of $\text{Mo}(\text{CO})_6$ supported on zeolites by vapor deposition [5–14], or by impregnation

[6,15], typically with the goal of synthesizing metallic Mo or Mo oxides. For example, using FTIR, Howe et al. [6] reported that at least three different sub-carbonyls ($\text{Mo}(\text{CO})_4$, dinuclear anion $\text{Mo}_2(\text{CO})_{10}^{2-}$ and an unassigned species) were formed by heating $\text{Mo}(\text{CO})_6$ adsorbed on HY or NaY. These sub-carbonyls formed reversibly between 50 and 150 °C. Further evacuation above 200 °C partially oxidized (on HY) or reduced (on NaY) the molybdenum, resulting in species that did not re-adsorb appreciable quantities of CO. Okamoto et al. [7,8] also observed the reversible formation of Mo sub-carbonyls at ~100 °C on HY and NaY, and their decomposition by 150 °C. In that study, the sub-carbonyl species was assigned as $\text{Mo}(\text{CO})_3$. Given this evidence for stabilization of sub-carbonyls over Y-type zeolites, one would hypothesize that they would be excellent supports for ethylene carbonylation catalysts.

In this paper, $\text{Mo}(\text{CO})_6$ supported on zeolite HY with Si/Al ratios of 15, 30, and 40 was prepared by impregnation and vapor deposition under water- and air-free conditions. TGA–MS, and FTIR and DRUV–visible spectroscopy were used to identify the nature of the supported Mo carbonyls. These materials were then shown to be extraordinarily effective catalysts for ethylene carbonylation – the TON exceeds 40,000 in 5 h of reaction – when suspended in acetic acid/water solutions and in the presence of a set of iodide promoters.

* Corresponding author.

2. Experimental

2.1. Catalyst preparation

Supported $\text{Mo}(\text{CO})_6$ catalysts were prepared by incipient wetness impregnation (IM) and vapor deposition (VD) under water- and air-free conditions. $\text{Mo}(\text{CO})_6$ and Y-type zeolite (proton form HY, Si/Al = 15, 30, 40) were obtained from Sigma–Aldrich and Zeolyst, respectively. HY zeolite has a unit cell size of 24.2 Å, surface area of 700–800 m^2/g , and 0.03 wt% Na_2O . Solid-state ^{27}Al NMR shows some extra-framework Al in all the zeolites (see supporting information Fig. S1), and NH_3 temperature programmed desorption gives H^+/Al ratios of 0.27, 0.39, and 0.21 for Si/Al = 15, 30, and 40 respectively (see supporting information Table S2, Figs. S2 and S3). Note that only absorption on Brønsted acid sites was found on the bare HY support using NH_3 -TPD-IR. Prior to synthesis, $\text{Mo}(\text{CO})_6$ and the zeolite were held under dynamic vacuum (<30 mtorr) for 2 days at room temperature and 200 °C, respectively, to remove physisorbed water. For the impregnation samples (denoted as IM in the following text and figures), the constituents used to prepare these samples were all transferred to an Ar-filled controlled atmosphere box. $\text{Mo}(\text{CO})_6$ was then dissolved in anhydrous pentane ($\geq 99\%$, with less than 0.001% water content), and the minimum wetting volume of the solution was added to the zeolite sample to give materials with 0.2–3.2 wt% Mo. Catalysts are denoted $\text{Mo}(\text{CO})_x/\text{HY}$ in general, and $\text{Mo}(\text{CO})_x/\text{HY}15$, $\text{Mo}(\text{CO})_x/\text{HY}30$, and $\text{Mo}(\text{CO})_x/\text{HY}40$, for the specific HY supports. The as-prepared samples (IM) were left stirring gently inside the glove box until dry, and used without further calcination. For the vapor deposition samples (denoted as VD in the following text and figures), ~ 30 mg $\text{Mo}(\text{CO})_6$ and 500 mg of the pre-dried HY were evacuated separately to <80 mtorr on a Schlenk line. The valve to the pump was closed, and the two vessels were connected for 2 h to allow vapor transfer from room temperature $\text{Mo}(\text{CO})_6$ to the HY flask held at 0 °C by an ice bath. The loaded HY was finally evacuated at <30 mtorr at room temperature for 30 min to remove excess $\text{Mo}(\text{CO})_6$.

2.2. Ethylene carbonylation

Reactants and solvents were obtained from Sigma–Aldrich and used without further purification. Following the conditions of our prior studies [2], the standard reaction mixture consisted of 1.3 mmol of tetrabutyl phosphonium iodide (TBPI), 76 mmol of ethyl iodide (EtI), 460 mmol of water and 760 mmol of acetic acid in a total volume of 51 mL. A 300 mL Hastelloy® C reactor was used for ethylene carbonylation experiments. This autoclave was filled with the liquid mixture and $\text{Mo}(\text{CO})_6$ -based catalysts. The reactor was stirred mildly (c.a. 300 rpm), and was pressurized with 10 bar N_2 and vented. This N_2 pressurization and purge was repeated 4 times to remove gaseous and dissolved O_2 . 10 ± 1 bar H_2 (99.999%, Airgas), 10 ± 1 bar ethylene (99.999%, Airgas), and 10 ± 1 bar CO (99.9995%, Airgas) were sequentially charged into the reactor at room temperature to reach a total pressure of 30 ± 1 bar. These pressures correspond to 91 ± 8 mmol each of CO, C_2H_4 and H_2 being charged into the headspace of the reactor; corresponding yields are thus accurate to $\pm 10\%$. The reactor was heated and the stirring speed was increased to 900 rpm. Within 1 h, the sample temperature and pressure equilibrated at 190 °C and 50–52 bar. Reaction time $t = 0$ was designated to be when the reaction temperature reached 190 °C. The pressure decreased to 12–14 bar after 5 h of reaction (24–26 bar after 1 h of reaction) after cooling to room temperature; an indication of consumption of CO and ethylene. After the reactor was cooled to room temperature, a liquid aliquot sample was passed through a 0.1 μm PTFE

filter for GC analysis using an Agilent 7890A GC-FID with a HP-INNOWAX column (50 m \times 0.2 mm \times 0.4 μm). Propanoate yield was calculated relative to the added CO. Propionic acid (PA), ethyl propionate (EP), propionaldehyde, ethyl acetate, diethyl ether (DEE) and ethanol signals were calibrated against known standards. The latter three are condensation products between EtI and solvent water or acetic acid. The headspace in most experiments was sampled after cooling to room temperature, and no additional volatile products, such as ethane, acetaldehyde, or dimethyl ether, were detected.

2.3. Catalyst characterization

Mo loading was quantified with a Varian Vista MPX ICP-OES. Molybdenum standards for instrument calibration were prepared from a 1000 mg L^{-1} AAS standard solution in the range of 0–30 ppm of Mo. Materials were dissolved in 48% hydrofluoric acid (HF) and diluted with ultra-pure water before analysis. X-ray diffraction (XRD) patterns were collected using a Rigaku X-ray diffractometer over the range 5–40° 2θ and Cu $K\alpha$ ($\lambda = 1.54059$ Å) radiation. Step size, slit widths, and dwell times were kept constant for all materials.

Diffuse reflectance UV–visible (DRUV–vis) spectra were collected with a UV-3600 Shimadzu spectrophotometer equipped using a Harrick Praying Mantis high temperature reaction chamber to allow measurements at elevated temperature and under gas flow. Polytetrafluoroethylene (PTFE) was used as the background spectrum. The catalysts were heated from ambient temperature to 180 °C (5 °C/min) in Helium at 30 mL/min. Reflectance data were recorded and transformed into the Kubelka–Munk (K–M) function.

Thermogravimetric analysis (TGA) was performed in a TA Instruments Q500 thermogravimetric analyzer with an evolved gas analysis furnace connected to a Pfeiffer Thermostat Q200 mass spectrometer through a fused SiO_2 capillary column maintained at 200 °C. The catalyst was heated from ambient temperature to 200 °C (5 °C/min) in helium at 100 mL/min. No change was seen in the $m/z = 14$ intensity after the first minute, indicating that air was rapidly purged from the system, and that the $m/z = 28$ intensity was due to evolved CO from decarbonylation of $\text{Mo}(\text{CO})_6$.

FT-IR spectra were recorded with a Thermo Scientific Nicolet 6700 infrared spectrometer equipped with a mercury cadmium telluride (MCT) detector. Each spectrum was the average of 128 scans taken at 4 cm^{-1} resolution. The catalyst was supported on a highly IR transmissive tungsten grid (~ 4 cm^2) mounted in a custom-built transmission IR cell [16]. The IR cell was sealed with CaF_2 windows and connected to a mechanically pumped gas manifold. After 1 h of vacuum at 20 mtorr, the catalyst was resistively heated from 30 to 180 °C (5 °C/min) and the IR spectra were recorded.

3. Results

3.1. Promotion in catalytic turnover over $\text{Mo}(\text{CO})_x/\text{HY}$

Table 1 shows the results for iodide-promoted ethylene carbonylation using supported and unsupported $\text{Mo}(\text{CO})_6$. Product selectivity toward propionic acid is high (>95%) in all cases. To achieve nearly complete conversion for the unsupported $\text{Mo}(\text{CO})_6$ in 5 h requires ~ 1000 μmol $\text{Mo}(\text{CO})_6$, and reducing the Mo reactor charge to ~ 180 μmol $\text{Mo}(\text{CO})_6$ decreases yields to 16%. The turnover number is less than 100 in that case. The behavior of this soluble catalyst has been investigated previously by us and others. Increasing CO partial pressures are inhibitory [1], but complete conversion is possible under these conditions up to at least

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