<100 TON/ 5 h

>40,000 TON/ 5 h

Increased Productivity in Ethylene Carbonylation by Zeolite-Supported Molybdenum Carbonyls

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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.

Keywords: heterogeneous catalysis, carbonylation, ethylene, promotion, molybdenum, metal carbonyl, Y-type zeolite, impregnation

1. Introduction

Carbonylation of alkenes to form carboxylic acids or their esters is typically carried out with homogeneous catalysts. We and others have reported on 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 has 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 of 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 – TON exceed 40,000 in 5 h of reaction – when suspended in acetic acid / water solutions and in the presence of a set of iodide promoters.

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 24.2Å, surface area of 700-800 m²/g, and 0.03 weight % Na_2O . Solid state ²⁷Al NMR shows some extra-framework Al in all the zeolites (see supporting information Figure 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, Figure 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 2h 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 Mo(CO)₆-based catalysts. The reactor was stirred mildly (c.a. 300 rpm), and was pressurized with 10 bar N₂ and vented. This N₂ pressurization and purge was repeated 4 times to remove gaseous and dissolved O₂. 10 ± 1 bar H₂, (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, C₂H₄ and H₂ being charged into the headspace of the reactor; corresponding yields are thus accurate to ±10%. The reactor was heated and the stirring speed was increased to 900 rpm. Within 1 hour, 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 1h 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 x 0.2 mm x 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 mgL⁻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 Kα (λ = 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 Kebulka–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 ThermoStar Q200 mass spectrometer through a fused SiO₂ 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 Mo(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 onto a highly IR transmissive tungsten grid ($\sim 4\text{ cm}^2$) mounted in a custom-built transmission IR cell [16]. The IR cell was sealed with CaF_2 windows and connected to a mechanical pumped gas manifold. After 1 h of vacuum at 20 mtorr, the catalyst was resistively heated from 30 to 180°C ($5^\circ\text{C}/\text{min}$) and the IR spectra were recorded.

3. Results

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

Table 1 shows the results for iodide-promoted ethylene carbonylation using supported and unsupported Mo(CO)_6 . Product selectivity toward propionic acid is high ($> 95\%$) in all cases. To achieve nearly complete conversion for the unsupported Mo(CO)_6 in 5 h requires $\sim 1000\text{ }\mu\text{mol Mo(CO)}_6$, and reducing the Mo reactor charge to $\sim 180\text{ }\mu\text{mol Mo(CO)}_6$ 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 15 bar CO pressure. [2] We have shown that ethyl iodide is a promoter and neither a co-catalyst nor a stoichiometric reagent, as shown by the fate of ^{13}C labeled species, among other experiments. [2] Likewise, complete conversion of stoichiometric CO and ethylene is possible at much lower ethyl iodide loadings, [2] but the relatively high amounts used here help illuminate differences amongst catalysts. Finally, the added H_2 presumably serves to retard water-gas shift and to maintain the Mo in an active state.

In contrast to the productivity of the soluble catalyst, the supported catalyst $\text{Mo(CO)}_x/\text{HY15}$ reaches nearly complete conversion after 5 h for reactor loadings as low as $6\text{ }\mu\text{mol Mo}$, corresponding to a TON as high as 15,000. Further lowering the reactor loading to $2\text{ }\mu\text{mol Mo}$ leads to 40,000 TON over 5h of reaction. TON and yields at $170\text{ }\mu\text{mol Mo}$ decrease with increasing Si/Al ratio of the support, but all the supported catalysts outperform the unsupported Mo(CO)_6 . Bare HY supports show no PA production, and adding both Mo(CO)_6 and HY to the autoclave exhibits similar activity to the equal amount of the unsupported Mo(CO)_6 , demonstrating the synergistic effect of Mo(CO)_6 loaded into the zeolite. Alone, zeolite HY shows no yield of PA. Although the VD catalyst has much lower Mo loadings ($0.1\text{ wt\%}$ vs $2.4\text{ wt\%}$), it reaches similar TON (34,000) as the IM catalyst when similar amounts of Mo are added to the reactor.

Heating the catalysts in flowing He ($30\text{ mL}/\text{min}$) at 200°C has no impact on the loading (as shown in supporting information Table S1), whereas analysis of the used catalysts shows some leaching under reaction conditions (Table 1); $\text{Mo(CO)}_x/\text{HY15}$ loses 85% of its Mo down to a level of $0.3\text{ wt\%}$. The catalysts with higher Si/Al ratios leach even further, losing 90% of their Mo. Interestingly, the Mo/Al ratios for the spent catalysts were around 0.04 in all cases. The VD catalyst does not undergo any significant leaching, consistent with its starting Mo/Al ratio of 0.01 being below the apparent threshold at which the system is stable with respect to leaching. The combination of high CO pressure, additives such as the tetrabutylphosphonium cation, and the condensed

phase all likely contribute to the leaching from all but a small fraction of potential adsorption sites, in spite of the demonstrated thermal stability of these catalysts in helium.

Importantly, when the spent $\text{Mo(CO)}_x/\text{HY15}$ is recovered by filtration, washed with c.a. 250 mL of de-ionized water, and reused in a second reaction, a similarly high PA yield and TON (36,000) is obtained. In this case, the reactor Mo loading was similar for the two cases, achieved by adding much more of the spent catalyst. Thus, even though only a small fraction of the Mo complexes are stable with respect to leaching, all seem to be similarly reactive.

Table 2 shows the dependence on Mo(CO)_6 loading for iodide-promoted ethylene carbonylation. The reactions were performed under identical conditions as shown in Table 1. However, since many of the entries in Table 1 reached nearly complete conversion in 5 h reaction, reactions were also run for 1h to allow for the determination of an approximation of the initial rates. When the reactor charge of Mo is controlled at 20 μmol , 2.4% $\text{Mo(CO)}_6/\text{HY15}$ achieves ~2,000 TON for PA (42% yield) in 1 h. For all loadings on $\text{Mo(CO)}_6/\text{HY15}$ and 30, the 1-h TON is not dependent on Mo(CO)_6 loading, and is approximately 1,900 and 1,600, respectively. These catalysts also leach down to $\text{Mo}/\text{Al} \sim 0.04$, but the near-constant TON again suggests that all of the supported Mo species are catalytically similar, irrespective of loading. These results also show the catalytic relevance of Mo, as opposed to the Al sites in the zeolite, since the latter increase in number dramatically across the entries in Table 2, without a corresponding increase in yield. In contrast, the 1-h TON decreases from 1,700 TON to 70 with increasing loading for $\text{Mo(CO)}_6/\text{HY40}$. This high-silica zeolite does appear to create a distribution of Mo active sites, especially for high Mo loading (3.0 wt%). In the latter case where the activity drops precipitously, the Mo per original acid site (Mo/H^+) is 3.7, much higher than $\text{Mo(CO)}_6/\text{HY15}$ and $\text{Mo(CO)}_6/\text{HY30}$, suggesting that inactive Mo is deposited above a certain threshold. These results indicate that TON increase rather uniformly for supported Mo. More details about the nature of these immobilized Mo species will be discussed in 3.2.

3.2. Identification of sub-carbonyls on $\text{Mo(CO)}_x/\text{HY}$

The catalysts listed in Table 1 were used for all characterizations that follow. As shown in Fig. 1, XRD patterns of the three impregnated $\text{Mo(CO)}_6/\text{HY}$ catalysts show no disruption of the zeolite framework and no crystalline Mo(CO)_6 (three major peaks at 15.5, 16.6 and 17.3° 2 θ). DRUV-vis spectra, in Fig. 2, show two major bands at 240 and 290 nm, both assigned to MLCT (metal-to-ligand charge transfer) features between Mo and CO. [17] Yokota and coworkers previously assigned the 290 nm band and the shoulder at 330 nm to Mo(CO)_6 on NaY, while the 245 nm band was assigned to Mo(CO)_5 . [11] Likewise, Perutz et al. reported the UV-vis spectra of unsupported Mo(CO)_6 during photo-decomposition in methane at 20K. A feature at 285 nm was uniquely assigned to Mo(CO)_6 , whereas Mo sub-carbonyls had blue-shifted absorption band – e.g. 247 nm for Mo(CO)_5 . [18] Here, we assign the 240 nm feature to sub-carbonyls Mo(CO)_x ($x < 6$) and the 290 nm nature to fully-coordinated carbonyls Mo(CO)_6 . We do not attempt to distinguish between sub-carbonyls based on these data. For the impregnated samples, Fig. 2 (a) to (c), the 290 nm feature increases with increasing Si/Al ratio, suggesting that more of the Mo remains as Mo(CO)_6 for the low-

acid samples. As shown in Fig. 2 (d), the 290 nm feature is very weak for the vapor-deposited sample (0.1 wt%).

DRUV-vis spectra were also recorded while heating the supported Mo carbonyls in helium, and the intensity changes at 290 and 240 nm are summarized in Fig. 2 (e) and 2 (f). During heating, there is a slight increase in K-M pseudo-absorbance as temperature increases, likely due to black body radiation. However, as the temperature reaches 110-120°C, absorption at 290 nm drops as Mo(CO)₆ decomposes. The absorbance at 240 nm begins to decrease at slightly higher temperatures, typically near 130°C, suggesting sequential decarbonylation. The temperature for complete decarbonylation increases with increasing Si/Al ratio, from ~140°C to 160°C to 170°C for Mo(CO)_x/HY15, HY30, and HY40, respectively. The decomposition temperature of the latter sample is similar to that of unsupported Mo(CO)₆.

In addition to the temperature of complete decarbonylation, Fig. 2 (e) and 2 (f) also show an increasing ratio of the 290 nm to 240 nm features with increasing Si/Al ratio, indicating that the fraction of sub-carbonyls is highest for the Si/Al=15 sample at all temperatures. The low loadings of the vapor-deposited sample decreases the I₂₉₀/I₂₄₀ ratio to ~0.7 at 120°C, whereas the higher-loaded impregnation sample has a ratio of 1.0 at 120°C. Overall, DRUV-vis spectra indicate that there are relatively more sub-carbonyls on the Si/Al = 15 support and for low loadings, at all temperatures. Described alternately, lower Mo/Al ratios promote the formation and stabilization of Mo sub-carbonyls.

TGA-MS, as shown in Fig. 3, shows the thermal decomposition of supported carbonyls, with a maximum in the rate of mass loss near 110°C for all the HY supported catalysts. An additional decomposition peak at 140°C is observed for Mo(CO)_x/HY40. As noted in Table S1, no significant Mo loss occurs with these thermal treatments. The signal at m/z=28, Fig. 3(b), tracks the mass change, Fig. 3(a), consistent with these events being decarbonylation. In view of the DRUV-vis results discussed earlier, the first peak is assigned to decomposition of sub-carbonyls Mo(CO)_x (x < 6) and strongly adsorbed Mo(CO)₆, while the additional higher temperature peak is assigned to decomposition of physically-adsorbed Mo(CO)₆. Using the mass loss between 60 and 200°C, Fig. 3(c) reports a CO/Mo ratio. This value is an upper limit since loss of adsorbed water may also be measured. The supported catalysts show an upper limit of ~6 CO/Mo, consistent with the starting Mo(CO)₆. The CO/Mo ratio is always lower for HY15 and HY30 than it is for HY40, consistent with the DRUV-vis results showing proportionally more Mo(CO)₆ for the HY40 support. The low loading of the vapor-deposited sample precludes a detailed analysis. However, only a single weight loss peak was observed at 70°C, which includes both water loss and decarbonylation from sub-carbonyls, consistent with a prior literature report [7].

More detailed information about sub-carbonyl species is obtained from FTIR spectroscopy under thermal treatment *in vacuo*, shown in Fig. 4 (a) to (c). Difference spectra are shown, where the spectrum taken after heating to 170°C is used as the background for each of the lower-temperature spectra. Nearly identical traces are obtained if spectra are baselined against the bare HY support, indicating that complete decarbonylation is achieved at 170°C *in vacuo*, in accordance with DRUV-vis and TGA results. Unfortunately, the low loadings of the VD-synthesized catalysts did not permit meaningful analysis by FTIR.

Crystalline Mo(CO)_6 has a strong absorption at 2002 cm^{-1} and a weak shoulder at 1970 cm^{-1} . (see supporting information Figure S4) Others have assigned features to Mo(CO)_6 [19] in the zeolite pore structure (1990 and 2002 cm^{-1}), weakly physisorbed Mo(CO)_6 (2118 and 1970 cm^{-1}) [8, 11], Mo(CO)_5 or strongly chemisorbed Mo(CO)_6 (2045 and 1950 cm^{-1}) [8, 11], Mo(CO)_4 (2020 and 1918 cm^{-1}) [11] and Mo(CO)_3 (1925 cm^{-1}) [8, 11, 20]. These catalysts show a continuum of features from $\sim 1900\text{ cm}^{-1}$ to $\sim 2060\text{ cm}^{-1}$ as synthesized, and they all decompose at higher temperatures. Table 3 summarizes the IR stretching frequencies for the catalysts based on the literature reported assignments.

The Mo carbonyl IR features are not well resolved in the freshly-prepared $\text{Mo(CO)}_6/\text{HY}$ catalysts. Figs. 4 (d) to (f) plot the changes of integrated area in different regions (2060 - 2015 , 2015 - 1960 and 1960 - 1900 cm^{-1}) during heating. We assign the area between 2015 - 1960 cm^{-1} as resulting from adsorbed Mo(CO)_6 . These are the predominant species, consistent with TGA-MS results that correspond to a CO/Mo ratio near 6. The combined area of 2060 - 2015 and 1960 - 1900 cm^{-1} represent various Mo sub-carbonyls, Mo(CO)_x , including Mo(CO)_4 and Mo(CO)_3 . Mo(CO)_6 and all Mo(CO)_x decrease monotonically during thermal treatment *in vacuo* and disappear completely above 140°C , consistent with the TGA-MS results. As with TGA-MS and DRUV-vis, the total area of the Mo(CO)_x features decreases with increasing Si/Al ratio at any given temperature. The reader is cautioned against attempting to make quantitative comparisons of the temperature responses across TGA, DRUV-vis, and FTIR due to the very different cell geometries in each case. [footnote]

It should be mentioned that no evidence is seen for dinuclear Mo carbonyls [$\text{Mo}_2(\text{CO})_8$] or [$\text{Mo}_2(\text{CO})_{10}$] which have been reported over HY at 1931 , 1854 and 1753 cm^{-1} . [6, 21] The absence of these features is likely due to the relatively low loadings for our catalysts, corresponding to a maximum of 3 Mo per HY unit cell, as compared with 17 Mo per NaY unit cell in a literature report [21].

[footnote: Though samples are uniformly heated in TGA, gas sweeps across the powder surface; gas passes through the powder bed in DRUV-vis, the sample has known thermal gradients and the DRUV-vis cell has a large dead volume; gas flows and temperatures are most uniform in the FTIR wire-grid cell. This will change, for example, the extent to which weakly-adsorbed Mo(CO)_6 is removed during pretreatments and how quickly the detected chemical species respond to changes in temperature.]

4. Discussion and Conclusions

This work reports on remarkable increases in catalytic turnover in iodide-promoted ethylene carbonylation for Mo carbonyls immobilized on zeolite HY relative to the analogous homogenous system [2], while maintaining $> 95\%$ selectivity to propionic acid. Productivity is the highest for low Si/Al ratios. The turnover numbers for $\text{Mo(CO)}_x/\text{HY15}$ can exceed 40,000 in 5 h, representing at least a 400-fold improvement over the analogous homogenous systems using Mo(CO)_6 . This turnover number can be regarded as a lower limit to the rate since the reaction may terminate in less than 5 h. This increase in TON is not achieved by using simple combinations of Mo(CO)_6 and the zeolite in the same reactor, and turnovers are relatively insensitive to reuse and to Mo loading and method of deposition, at least up to the values tested (2.4 wt%, or 0.25

Mo/Al for HY zeolite with Si/Al=15). These latter experiments demonstrate that the active catalyst is Mo-based and indeed heterogeneous, in spite of reaction conditions that leach down the Mo loading until very low loadings of Mo/Al < 0.05. It is suspected that much of the leaching occurs after the reaction is complete, and that the particular choice of promoters is partially responsible for the leaching. Work is underway to mitigate leaching to make catalysts that are more productive on a per-gram basis.

We ascribe the enhancement in catalyst productivity to two phenomena. The first is the increase in local acidity. TON and rate increase with decreasing Si/Al and greater acid site density of the support. Our previous mechanistic study indicates that the propionic acid product is liberated from the Mo active site by an acid, regenerating the key Mo hydride intermediate. [2] Higher acid site densities will therefore ensure that this is not a step limiting to catalyst activity.

Secondly, and likely more importantly, is the ability of the zeolite support to stabilize Mo sub-carbonyls. Our recent mechanistic findings [2] demonstrate that under-coordinated Mo sites are required for activation of the ethyl iodide promoter and formation of the crucial Mo hydride. Thus, stabilization of the sub-carbonyls affects the kinetics of the reaction since a larger fraction of the Mo is in an active form at a given CO partial pressure than in the analogous homogeneous systems. Others have reported an inverse dependence of CO partial pressure on the carbonylation rate of the soluble Mo(CO)₆ catalyst [1], which confirms the kinetic relevance of sub-carbonyls.

DRUV-vis and TGA-MS provide evidence for two classes of supported Mo carbonyls, and those assigned as sub-carbonyls are relatively more common on lower Si/Al supports and the lower loadings of the vapor deposition-synthesized sample. This is consistent with the observed enhancement in rate and TON because we believe that the sub-carbonyls (or some fraction of them) are the active species. It has been frequently reported that Mo sub-carbonyls are the major species when materials are synthesized by direct vapor deposition of Mo(CO)₆ over zeolite supports. [5-7] The overall decarbonylation temperature is also lower for lower Si/Al supports and for the VD-synthesized sample, indicating stronger surface-Mo interactions for those samples. Finally, FTIR spectroscopy provides direct evidence that Mo(CO)_x sub-carbonyls are formed over the as-synthesized catalysts and they decarbonylate sequentially as the temperature increases *in vacuo*, suggesting that stabilization of these sub-carbonyls may be responsible for the large increases in catalytic turnover for ethylene carbonylation using the supported catalysts.

We are currently optimizing reaction conditions to better understand and further exploit these enormous productivity enhancements to an industrially-relevant catalytic transformation.

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Table 1. Ethylene carbonylation¹ for unsupported and zeolite(HY)-supported Mo(CO)₆.

catalyst	fresh			used		
	Mo loading ² (wt%)	Mo/Al	TON ³ (μmol)	Yield ⁴ (mol/mol Mo)	Yield ⁴ (%)	Mo loading (wt%) Mo/Al
Mo(CO) ₆	-	-	180	83	16	-
	-	-	1000	96	99	-
	2.4	0.25	2	40500	89	0.3
Mo(CO) ₆ /HY(Si/Al=15) (IM)			6	15300	101	
			20	4550	101	
			170	540	101	
Mo(CO) ₆ /HY(Si/Al=30) (IM)	2.3	0.47	170	410	76	0.2
Mo(CO) ₆ /HY(Si/Al=40) (IM)	2.1	0.57	170	290	53	0.2
Mixture of Mo(CO) ₆ and HY	-	-	170	82	15	-
Used Mo(CO) ₆ /HY(Si/Al=15) (IM)	0.3	0.03	2	35500	78	-
Mo(CO) ₆ /HY(Si/Al=15) (VD)	0.1	0.01	3	33700	107	0.1

¹ Reactor composition: 1.3 mmol Bu₄PI, 76 mmol EtI, 460 mmol H₂O and 760 mmol acetic acid. 10 bar each of H₂, C₂H₄ and CO at 25°C. 190°C reaction temperature, 5h, 900 rpm stirring.

² wt% Mo by ICP-OES. Mo/Al from nominal Al content in the as-received zeolite Y. Mo loading (μmol) gives total Mo in the reactor.

³ TON per mol Mo from propionic acid production after 5 h at 190°C. HY alone shows no PA production.

⁴ Propanoate yield relative to CO fed. Uncertainty of +/- 10% due to variability in charging the gas mixture.

Table 2. Ethylene carbonylation¹ for various loading of impregnated zeolite(HY)-supported Mo(CO)₆.

catalyst	fresh			Yield ⁵ (%)	Used ⁶		
	Mo loading ² (wt%)	Mo/Al	TON ⁴ (mol/mol-Mo)		Mo loading (wt%)	Mo/Al	Mo/H ⁺
Mo(CO) ₆ /HY(Si/Al=15)	0.3	0.03	0.1	1990	39	0.3	0.03
	0.6	0.06	0.2	1780	36	0.2	0.02
	2.4	0.25	0.9	2030	42	0.3	0.03
Mo(CO) ₆ /HY(Si/Al=30)	0.3	0.06	0.2	1520	31	0.3	0.05
	0.6	0.12	0.3	1560	32	0.1	0.03
	3.2	0.68	1.6	1670	36	0.2	0.04
Mo(CO) ₆ /HY(Si/Al=40)	0.2	0.05	0.3	1770	36	0.1	0.03
	0.4	0.10	0.5	1160	24	0.1	0.03
	3.0	0.84	3.7	72	2	0.1	0.03

¹ Reactor composition: 1.3 mmol Bu₄PI, 76 mmol EtI, 460 mmol H₂O and 760 mmol acetic acid. 10 bar each of H₂, C₂H₄ and CO at 25°C. 190°C reaction temperature, 1 h, 20 μmol Mo in the reaction, 900 rpm stirring.

² as-synthesized catalysts. wt% Mo from ICP. Mo/Al from nominal Al content in the as-received zeolite Y.

³ Mo/H⁺ relative to acidity of the bare HY support from NH₃-TPD (Table S2).

⁴ TON from propionic acid production after 1 h at 190°C.

⁵ Propanoate yield relative to CO fed.

Table 3. IR carbonyl stretching frequencies of the species observed during thermal decomposition over zeolite(HY)-supported Mo(CO)₆.

species	ν (cm ⁻¹)	assignment
I	2002	unsupported Mo(CO) ₆ [19]
II	2118, 1990, 1970	physisorbed Mo(CO) ₆ [8, 11]
III	2045, 1950	chemisorbed Mo(CO) ₆ [6] or Mo(CO) ₅ [8, 11]
IV	2020, 1920	Mo(CO) ₄ [11]
V	1925	Mo(CO) ₃ [8, 11, 20]

Fig. 1 XRD patterns of the unsupported and impregnated zeolite(HY)-supported Mo(CO)₆.

Fig. 2 Diffuse reflectance UV-vis spectra of (a) Mo(CO)₆/HY(Si/Al=15) (IM), (b) Mo(CO)₆/HY(Si/Al=30) (IM), (c) Mo(CO)₆/HY(Si/Al=40) (IM) and (d) Mo(CO)₆/HY(Si/Al=15) (VD). The catalysts were heated from 30 to 180°C in He (30mL/min, 5°C/min). (e) Intensity changes at 290 nm during heating. (f) Intensity changes at 240 nm during heating.

Fig. 3 (a) TGA results of the zeolite(HY)-supported Mo(CO)₆. The catalysts were heated from 30 to 200°C in He (100mL/min, 5°C/min). (b) Temperature profile of m/z=28 of evolved gasses; ion current normalized by Mo loading. (c) Calculated CO per Mo during heating, assuming all mass loss in this range is from CO, and is thus an upper limit.

Fig. 4 FT-IR spectra of (a) Mo(CO)₆/HY(Si/Al=15), (b) Mo(CO)₆/HY(Si/Al=30), and (c) Mo(CO)₆/HY(Si/Al=40) heated from 40 to 160°C under vacuum (20 mtorr). Prior to heating, the samples were held at 20 mtorr for 2 h to remove surface adsorbed water. The main set of spectra use the final catalyst heated to 170°C as the background. The integrated area between 2060-2015 cm⁻¹ is assigned to Mo(CO)₆, while the sum of areas between 2015-1960 cm⁻¹ and 1960-1900 cm⁻¹ is assigned as Mo sub-carbonyls. (d), (e) and (f) show the change of the integrated area of Mo(CO)₆ and Mo sub-carbonyls during heating.

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