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# Vapor-phase ethanol carbonylation with heteropolyacid-supported Rh

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ABSTRACT

Ethanol carbonylation is a potential route to valuable C3 products. Here, Rh supported on porous, Cs-exchanged heteropolyacid $Cs_3PW_{12}O_{40,}$ is demonstrated as an effective catalyst for vapor-phase ethanol carbonylation, with higher selectivity and conversion to propionates than existing catalysts. Residual acidity or a Mo polyatom was strongly detrimental to yields. Propionate selectivity was maximized at 96% at 170 °C and with added $H_2O$. The catalyst displayed stable selectivity over 30 h on stream and up to 77% conversion. Ethyl iodide is a required co-catalyst but at levels as low as 2% relative to ethanol. XPS and *in situ* XANES indicate partial Rh reduction, consistent with the formation of low-valent reactive intermediates and slow deactivation through formation of Rh nanoparticles. With further optimization and understanding, these Rh/heteropolyacid catalysts may lead to stable and selective catalysts for the production of propionates through ethanol carbonylation.

## 1. Introduction

Alcohol carbonylation is an important commercialized process, particularly for the production of acetic acid from methanol, which is one of the largest industrial processes to use homogeneous catalysts [1–4]. A common system for alcohol carbonylation uses a group VIII metal complex and an iodide co-catalyst in the condensed phase. Alkyl iodides are formed *in situ*, which oxidatively add to the transition metal complex, followed by CO insertion into the M–C bond, and reductive elimination [5–7]. Much less studied are processes for the ethanol carbonylation to propionates, alcohol carbonylation in the vapor phase, or alcohol carbonylation using supported, heterogeneous catalysts. Vapor-phase heterogeneous catalysts include the mechanistically distinct carbonylation of methanol and dimethyl ether with mordenite-type zeolites [8–11], and variants on the Reppe carbonylation of ethylene [10–14]. Only a very limited number of studies have investigated solid catalysts for ethanol carbonylation to propionic acid or ethyl propionate, and all are for group VIII metals promoted with alkyl iodides [15–18]. Both Nefedov and Scurrell separately showed that Rh supported on X-type zeolites are effective heterogeneous catalysts for vapor-phase alcohol carbonylation with added iodide [15–22]. Rh has also been supported on various materials including carbon [23,24] or ligand-modified oxides [25] for carbonylation of methanol in the vapor phase. Several other insoluble resins have been developed for methanol carbonylation, both in the vapor and liquid phases. Critically, Christensen and Scurrell found decreasing selectivity for propionates with increasing ethanol conversion [15,16]. This was not due to sequential reactions, but rather due to the strong competition from ethanol dehydration to ethylene and diethyl ether. Although the references cited above demonstrate that ethylene and ethers can participate in carbonylation chemistry, the water that forms as a co-product appears to be detrimental to carbonylation reactivity in those systems. Given ethanol's strong propensity to dehydrate, this must be addressed for any acid catalyst [26,27]. Therefore, there is a need for development and testing of new catalyst formulations that suppress ethanol dehydration and promote carbonylation in the vapor phase.

An important other class of carbonylation catalysts are those based on heteropolyacids. Heteropolyacids have been widely used as homogeneous and heterogeneous acid and redox catalysts [28–30]. Limited reports have shown that these catalysts are capable of methanol [31,32] or dimethyl ether [33] carbonylation to acetic acid and methyl acetate, respectively. Both reports considered it essential to have a Brønsted acidic support. There are many structural classes of heteropolyacids such as Keggin [34], Wells–Dawson [35], Finke–Droege [36], and Pope–Jeannin–Preyssler [37]. Among the various heteropolyacids, Keggin heteropolyacids have been broadly investigated because they are the most stable and readily synthesized. Keggin heteropolyacids are comprised of heteropolyanions of the formula $[XM_{12}O_{40}]^{n-}$, where X is the

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heteroatom (P, Si, etc.) and M is the polyatom (W, Mo, etc.) [28–30,34]. Changing the heteroatom and polyatom controls the acidic and redox properties of these heteropolyacids, and these properties have been investigated in various catalytic reactions [29,30]. The use of $H_3PW_{12}O_{40}$ in alcohol and ether carbonylation has been reported [38]. Heteropolyacids are highly soluble in polar solvents including water and alcohols, while heteropolyacid salts with large cations are insoluble and have high surface area by forming a tertiary structure [28,29]. Examples of cations commonly used include $K^+$, $Rb^+$, $Cs^+$, and $NH_4^+$, and the acidity of a heteropolyacid salt can be tuned by the amount of the large cation exchanged on the heteropolyanion, leading to wide use as solid acid catalysts [28]. $Cs^+$-modified heteropolyacids have been demonstrated in dimethyl ether carbonylation [39].

This work describes the novel application of Rh supported on heteropolyacids as a promising heterogeneous catalyst for vapor-phase ethanol carbonylation, including identification of suitable operating conditions and catalyst compositions, spectroscopic analysis of the active catalyst, and mechanistic insight into the working state of the catalyst. The mechanism appears to be broadly analogous to that of condensed-phase methanol carbonylation by similar, soluble catalysts. As compared to existing catalysts known for vapor-phase ethanol carbonylation, the catalysts described here have higher selectivity to the desired carbonylation products, including at high conversion.

## 2. Experimental

### 2.1. Catalyst preparation

Heteropolyacid (HPA) salts were prepared through an ion-exchange method. Keggin HPAs, phosphotungstic acid $H_3PW_{12}O_{40}(H_2O)_x$, and phosphomolybdic acid $H_3PMo_{12}O_{40}(H_2O)_x$ were purchased and used as received from Sigma–Aldrich. $Cs^+$ or $NH_4^+$ was used as exchange cations. $Cs^+$ was incorporated with stoichiometries from $x = 1.5–3.0$ in $Cs_xH_{3-x}PW_{12}O_{40}$ or $Cs_x(NH_4)_{3-x}PW_{12}O_{40}$ to cover the range where surface area and acidity vary significantly [28]. $NH_4^+$ was incorporated with stoichiometries from $x = 0–1.5$ in $Cs_x(NH_4)_{3-x}PW_{12}O_{40}$. Water was purified to 18 MΩ resistivity using a Barnstead Nanopure Infinity system and passed through a 0.2 μm filter before use. A known amount of cesium nitrate ($CsNO_3$, Sigma–Aldrich) and/or ammonium nitrate ($NH_4NO_3$, Sigma–Aldrich) was dissolved in 20 mL of distilled water to form 0.13–0.15 M solutions and slowly added to 20 mL of 0.05 M aqueous solution of phosphotungstic acid or phosphomolybdic acid while stirring. The resulting composite solution was heated at 60 °C overnight to obtain a solid product. The solid product was dried for 1–3 h in a 150 °C oven and then calcined at 350 °C in static air for 2 h ramping at 5 °C/min.

Rh was then loaded on HPA salts by incipient wetness impregnation using $RhCl_3(H_2O)_x$ obtained from Sigma–Aldrich and used as received. Rh content was controlled in the range of 0.5–5 wt%. The impregnated solid was dried for 1–3 h in a 150 °C oven and then calcined at 350 °C in static air for 2 h ramping at 5 °C/min. A comparison Rh catalyst was synthesized on Na13X zeolite by ion exchange between $RhCl_3(H_2O)_x$ and Na13X molecular sieve (Sigma–Aldrich). The Rh precursor was dissolved in water, and a known amount of Na13X molecular sieve was added such as to make 1 wt% Rh. The resulting solution was heated to 80 °C and stirred overnight. Filtration yielded solid particles, which were washed with ~200 mL of purified water and dried in a 150 °C oven overnight. After drying, the catalyst was calcined at 400 °C in static air for 2 h ramping at 5 °C/min. These materials showed no indication of framework disruption by $^{27}$Al MAS SS NMR (Appendix A, Fig. S1).

A silica-supported 1 wt% $Rh/Cs_3PW_{12}O_{40}/SiO_2$ catalyst was synthesized as follows. 1 g $H_3PW_{12}O_{40}$ was loaded onto 2 g of silica gel (Selecto Scientific, ~500 $m^2/g$, ~6 nm pore diameters, 40–63 μm particle size) by incipient wetness impregnation from water, dried at 150 °C for 1–3 h, and calcined at 300 °C for 2 h. 0.19 g of $CsNO_3$ was dissolved in 30 mL of distilled water. 1.9 g of $H_3PW_{12}O_{40}/SiO_2$ was then dispersed in the solution with constant stirring, and the mixture was stirred for 12 h. The solid product was filtered, washed with distilled water, dried at 150 °C for 1–3 h, and calcined at 350 °C for 2 h to obtain $Cs_3PW_{12}O_{40}/SiO_2$ support. $RhCl_3(H_2O)_x$ was then supported onto $Cs_3PW_{12}O_{40}/SiO_2$ by incipient wetness impregnation as above at a loading of 1 wt% relative to the $Cs_3PW_{12}O_{40}$. The impregnated solid was dried at 150 °C for 1–3 h and calcined at 350 °C for 2 h.

### 2.2. Catalyst characterization

Cs and W contents in the catalysts were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Rh contents on the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. Materials were found to dissolve well in a solution of 95 wt% water, 3 wt% nitric acid, 1 wt% hydrofluoric acid, and 1 wt% hydrochloric acid. For calibration, samples were compared to known concentrations of Rh, Cs, and W in the same stock solutions that samples were dissolved in. All elemental ICP standard solutions were acquired from Sigma–Aldrich at an original concentration of 1000 ppm.

Surface areas of the catalysts were measured using $N_2$ physisorption on a Micromeritics 2010 ASAP. Prior to $N_2$ physisorption, all samples were degassed under vacuum overnight at 140 °C. X-ray diffraction (XRD) patterns of the catalysts were acquired using Cu Kα radiation operated at 40 kV and 20 mA using a Rigaku Geigerflex X-ray powder diffractometer. X-ray photoelectric spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250 Xi. Peak locations were identified using Advantage Software v5.5.3. The spectrometer binding energy was calibrated through energy shifts to the reference C 1s (284.9 eV). Thermogravimetric analysis (TGA) was done on a Q500 from TA Instruments. An 80 mg sample was subjected to a temperature ramp from ambient to 350 °C at a rate of 5 °C/min under oxygen flow.

Rh K-edge X-ray absorption near edge structure (XANES) spectral measurements were performed at the Advanced Photon Source, Argonne National Laboratory. The DuPont–Northwestern–Dow Collaborative Access Team (DND-CAT) bending magnet D beamline at Sector 5 was used. XANES spectra were recorded in transmission mode by employing a Si(111) double crystal monochromator. Transmission intensities were measured with Canberra ionization chambers. For the Rh K-edge, all XANES spectra were scanned in the range of 23,100–23,450 eV. The photon energy for each scan was calibrated using Rh foil, setting the first inflection point at the known edge energy of $Rh^0$, 23,220 eV. 2–5 scans of each reference were averaged to optimize signal-to-noise ratio. XANES of the as-synthesized catalyst was compared to metallic Rh, $Rh_2O_3$, $RhCl_3(H_2O)_x$, and $RhI_3$.

Temperature-programmed desorption (TPD) of $NH_3$ was carried out in an Altamira Instruments AMI-200 to measure catalyst acidity. 0.1 g of each catalyst charged into a quartz reactor and pretreated at 200 °C for 1 h with a stream of He (25 mL/min). A mixed stream of $NH_3$ and He (25 mL/min) was then introduced into the reactor at 50 °C for 30 min. Physisorbed $NH_3$ was removed at 100 °C for 1 h under a flow of He (25 mL/min). After cooling the catalyst, furnace temperature was increased from 50 °C to 600 °C at a heating rate of 20 °C/min under a flow of He (25 mL/min). Desorbed $NH_3$ was detected using a thermal conductivity detector (TCD). For calibration, known amounts of $NH_3$ were injected into the empty reactor under a flow of He (25 mL/min).