

Deoxygenation of Propionic Acid in Gas Phase over Cobalt Molybdenum Catalyst

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The gas-phase deoxygenation of propionic acid was investigated in the presence of Co-Mo catalysts in N₂ or H₂ flow at 200-400 °C. In the presence of N₂, the main product was 3-pentanone with other deoxygenates and some light gases *e.g.*, ethane and ethene. Using H₂ flow, the catalyst was active for decarboxylation and decarbonylation of acid and the yields of ethane and ethene. The decarboxylation and decarbonylation reactions increased with increasing temperature. Cobalt-molybdenum supported on alumina showed better performance than bulk catalyst, especially at 400 °C in the presence of N₂ for the ketonization of propionic acid to form 3-pentanone as the main product. Bulk and supported catalysts were characterized by surface area porosity (BET), thermogravimetric analysis and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of pyridine adsorption.

Keywords: Deoxygenation, Propionic acid, Gas-phase, Cobalt-molybdenum catalyst.

INTRODUCTION

Value-added chemicals and biofuel components have been produced from carboxylic acids because these are renewable raw materials attractively and readily available from natural sources [1-6]. Deoxygenation of carboxylic acids has been used in the production of fuel [1-6]. Heterogeneous catalysis has recently received attention in these deoxygenation reactions [7-9]. Propionic acid, which can be derived from carbohydrate feed stocks, is chosen as an illustrative carboxylic acid with six carbon atoms [10].

Molybdenum and cobalt or nickel, supported on γ -Al₂O₃, have been used in hydro treating reactions. Molybdenum sulfide supported catalysts were more active in hydro treatment for removing sulfur, nitrogen and oxygen than others such as Co and Ni sulfide. Cobalt and nickel were used as active promoters [11]. Co(Ni)Mo(W) supported on alumina has been used to catalyze commercial petroleum refining for a century [12]. Fe-Co/sulfonated polystyrene was an efficient catalyst for heterogeneous reactions of cyclic ketones and H₂O₂ to lactones. Yield and selectivity of lactones were high [13]. Molybdenum catalysts based on carbide have attracted attention for reactions including the synthesis of ammonia [14], hydrogenation, dehydrogenation, hydrodenitrogenation, hydrodesulfurization and isomerization [11,15-18]. In the current work, cobalt molybdenum catalysts in bulk form and supported on alumina were tested in the gas-phase deoxygenation of propionic acid at 200-400 °C at ambient pressure.

EXPERIMENTAL

All chemicals were used as received from Sigma-Aldrich without further purification. The purity of propionic acid was ≥ 99.5 %. The aluminium oxide used for supporting catalysts was obtained from Degussa. Throughout the experiments, double distilled water was used to prepare catalysts.

Catalyst preparation: Cobalt-molybdenum catalyst was prepared by dissolving cobalt acetate and 12-molybdophosphoric acid H₃PMo₁₂O₄₀·13H₂O in a minimum amount of water separately at room temperature. The solutions were mixed by adding them simultaneously to a vessel at room temperature and stirred for at least 3 h. The mixture was rotary evaporated at 35 °C and the resulting material was dried overnight in an oven at 110 °C. Co-Mo was supported on γ -Al₂O₃ using the impregnation method. The amount of Co-Mo bulk catalyst was added to the support and the mixture was stirred for 3 h at room temperature, then the catalyst was dried at 110 °C overnight. The products were finally calcined at 400 °C for 2 h to form metal oxides.

Catalyst characterization: The specific surface area and porosity of catalysts were measured by the BET method from nitrogen physisorption determined at -196 °C on a Micromeritics ASAP2010 instrument. Prior to analysis, the catalyst was evacuated *in situ* at 250 °C for 3 h. Thermogravimetric analysis of 20-50 mg sample was carried out on a Perkin-Elmer TGA 7 instrument, under nitrogen flow at a heating rate of 20 °C min⁻¹ to raise the temperature from room temperature

to 700 °C. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of adsorbed pyridine was performed on the Nico-let Nexus FTIR spectrometer in Professor Ivan Kozhevnikov's Laboratory. Catalyst samples were ground with KBr (10 wt % in KBr) and pretreated at 150 °C/10⁻⁵ bar for 1h. The samples were then exposed to pyridine vapour at room temperature for 1 h, followed by pumping out at 150 °C/10⁻⁵ bar for 1 h to remove physisorbed pyridine, as explained elsewhere [3,4,19-21]. The DRIFT spectra of adsorbed pyridine were recorded at room temperature at a resolution of 5 cm⁻¹.

Catalyst testing: The gas-phase deoxygenation of propionic acid was performed in flowing N₂ or H₂ at 200–400 °C under atmospheric pressure using a down flow quartz fixed-bed reactor (9 mm i.d.) with online GC analysis (Varian 3800 instrument with a 30 m × 0.32 mm × 0.5 µm Zebron ZB-WAX capillary column and a flame ionization detector). For hydrocarbon products, a 60 m × 0.32 mm GS-GasPro capillary column was used, which allowed for full separation of these hydrocarbons. The reaction temperature was controlled by using a thermocouple placed at the top of the catalyst bed inside the glass reactor. Propionic acid was fed into the carrier gas and the flow of acid was controlled by a Brooks mass flow controller through a stainless steel saturator, which held the liquid acid at an appropriate temperature to maintain the chosen reactant concentration in the gas flow. All system lines and GC valves were maintained at 180 °C to prevent downstream condensation of propionic acid and its reaction products. The reactor was packed with 0.2 g catalyst powder of 45–180 µm particle size. Typically, the reaction was carried out with 0.2 g of catalyst and 2 vol % of propionic acid concentration under N₂ or H₂ at a flow rate of 20 mL min⁻¹. Before the reaction started, the catalysts were pretreated at the same conditions of temperature and flow rate for 1 h. The products were analyzed using the gas chromatography equipment in Kozhevnikov's laboratory at Liverpool University, UK.

RESULTS AND DISCUSSION

Table-1 shows the resulting catalyst porosity in terms of BET surface area, pore size and pore diameter. Co–Mo had only 45 m² g⁻¹ of surface area, 0.06 cm³ g⁻¹ of pore volume and 23 Å pore diameter, whereas the values for the supported catalyst were 97 m² g⁻¹, 0.12 cm³ g⁻¹ and 49 Å, respectively.

TABLE-1
CATALYST CHARACTERIZATION

Catalyst	S _{BET} ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore diameter ^c (Å)
Co–Mo	45	0.06	23
Al ₂ O ₃	164	0.22	53
Co–Mo/Al ₂ O ₃	97	0.12	49

^aBET surface area; ^bSingle point total pore volume; ^cAverage BET pore diameter.

Figs. 1 and 2 show infrared adsorption bands for heteropoly-oxometalate catalysts H₃PMo₁₂O₄₀·13H₂O and Co_{1.5}PMo₁₂O₄₀·13H₂O respectively. Keggin structure can be assigned in the range of 750–1150 cm⁻¹ [10]. It can be seen that there are some bands in 1,080–1,060, 990–960, 900–870 and 810–760 cm⁻¹ region, which are assigned to (P–O), (M–O), (M–O–M) and (M–O–M) vibrations respectively, whereas M is Co or Mo [10,22].

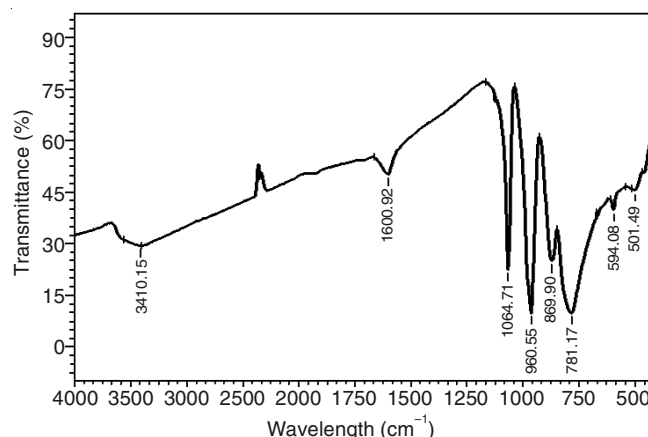


Fig. 1. IR spectra of H₃PMo₁₂O₄₀·13H₂O

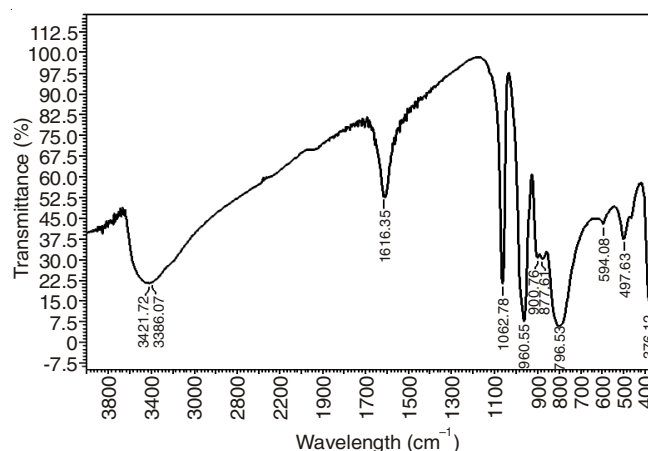


Fig. 2. IR spectra of Co_{1.5}PMo₁₂O₄₀·13H₂O

Figs. 3 and 4 show the TGA results for H₃PMo₁₂O₄₀·13H₂O and Co_{1.5}PMo₁₂O₄₀·13H₂O respectively. From Fig. 3 it can be seen that the bulk catalyst had two thermal areas. The first, from 50–240 °C, may be attributed to loss of physisorbed water or hydration water. The peak at 240–450 °C is due to the decomposition of the catalyst's Keggin structure [10,22,23].

Catalyst acidity was determined by pyridine adsorption. Both bulk and supported catalysts had very high numbers of Lewis acid sites, but fewer Brønsted acid sites. The acidity was not affected by supporting Co–Mo on Al₂O₃ as shown in Fig. 5.

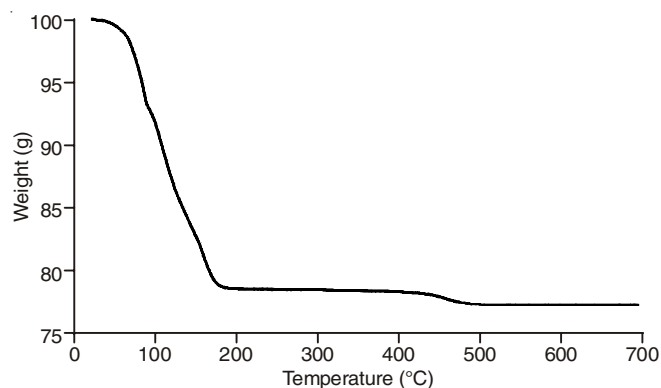
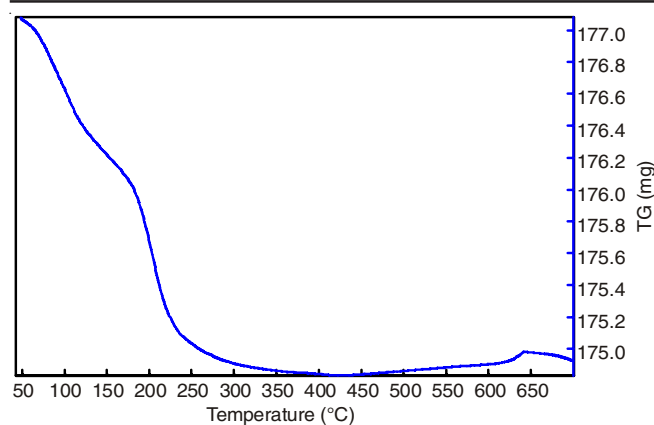
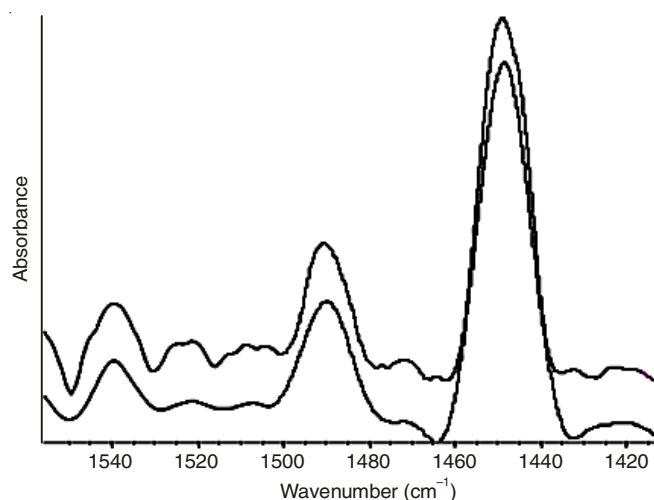


Fig. 3. TGA analysis for H₃PMo₁₂O₄₀·13H₂O

Fig. 4. TGA analysis for $\text{Co}_{0.5}\text{PMo}_{12}\text{O}_{40}\cdot 13\text{H}_2\text{O}$ Fig. 5. DRIFT spectra for (a) bulk Co-Mo and (b) Co-Mo/ Al_2O_3

Catalyst performance

Deoxygenation of propionic acid over Co-Mo bulk catalyst and N_2 flow: Table-2 lists the conversion and selectivity results for the deoxygenation of propionic acid over bulk and supported cobalt/molybdenum catalysts under various conditions. The flow of N_2 was used and the reactor was packed with 0.2 g of catalyst and 2 vol % of acid in the temperature range of 200–400 °C. It can be seen that catalyst performance improved as temperature increased. At 400 °C, bulk catalyst gave 65 % selectivity of 3-pentanone at 31 % conversion and no hydrocarbons were produced at any temperature. Co-Mo/ Al_2O_3 , with $97 \text{ m}^2 \text{ g}^{-1}$ surface area, $0.12 \text{ cm}^3 \text{ g}^{-1}$ pore volume and 49 Å pore diameter showed better performance, giving 67 % and 5 % selectivity of 3-pentanone and propanal, respectively at 65 % propionic acid conversion (44 % yield of 3-pentanone).

Deoxygenation of propionic acid over Co-Mo bulk catalyst and H_2 flow: Similar reaction conditions for temperature, concentration of acid and catalyst weight were applied to the gas-phase deoxygenation of propionic acid, using H_2 instead of N_2 . Table-3 shows that the conversion of acid increased with increasing temperature. Under H_2 at 400 °C, Co-Mo bulk catalyst gave 45 % and 10 % of 3-pentanone and propanal selectivity respectively, at 99 % of propionic acid conversion. The supported catalyst gave only 16 % 3-pentanone and 18 % propanal selectivity at 100 % acid conversion.

TABLE-2
DEOXYGENATION OF PROPIONIC ACID
OVER BULK Co-Mo AND Co-Mo/ Al_2O_3

Temp. (°C)	Conv. (%)	Selectivity (%)				
		Ethane	Ethene	Propanal	3-Pentanone	Others ^c
200 ^a	4	0	0	8	5	87
250 ^a	9	0	0	8	11	81
300 ^a	15	0	0	9	22	69
350 ^a	22	0	0	6	29	65
400 ^a	31	0	0	1	64	35
200 ^b	5	0	0	7	0	93
250 ^b	4	0	0	8	0	92
300 ^b	6	0	0	6	11	71
350 ^b	14	0	0	3	65	32
400 ^b	65	0	0	5	67	28

^a0.2 g catalyst, 20 mL min^{-1} N_2 flow rate and 2 vol % PA for 4 h over Co-Mo. ^b0.2 g catalyst, 20 mL min^{-1} N_2 flow rate and 2 vol % PA for 4 h over Co-Mo/ Al_2O_3 . ^cIsopropanol and acetone together.

TABLE-3
DEOXYGENATION OF PROPIONIC ACID
OVER BULK Co-Mo AND Co-Mo/ Al_2O_3

Temp. (°C)	Conv. (%)	Selectivity (%)				
		Ethane	Ethene	Propanal	3-Pentanone	Others ^c
200 ^a	7	5	9	20	0	66
250 ^a	18	8	12	42	2	36
300 ^a	47	9	14	38	0	39
350 ^a	90	13	13	18	25	31
400 ^a	99	12	16	10	45	16
200 ^b	9	2	4	8	0	86
250 ^b	12	2	7	19	22	50
300 ^b	32	5	9	39	34	13
350 ^b	96	2	10	31	25	32
400 ^b	100	5	8	18	16	53

^a0.2 g of catalyst, 20 mL min^{-1} of H_2 flow rate and 2 vol % of PA for 4 h over Co-Mo. ^b0.2 g of catalyst, 20 mL min^{-1} of H_2 flow rate and 2 vol % of PA for 4 h over Co-Mo/ Al_2O_3 . ^cIsopropanol and acetone together.

Stability of Co-Mo/ Al_2O_3 : The best catalytic performance was that of 0.2 g Co-Mo/ Al_2O_3 at 400 °C under N_2 flow. Fig. 6 shows that supported Co-Mo/ Al_2O_3 was stable for at least 15 h on stream. The catalyst reached the steady state in the 1st h. In the last 3 h there was only a slight drift in acid conversion from 58 to 52 %, while selectivity of the product remained stable. Loss of conversion may have resulted from the deposition of carbon on the catalyst as coke. C, N, H measurement showed that 4 % of carbon and 2 % of hydrogen were deposited on the catalyst. In addition, the surface area may have decreased at higher reaction temperature, thus reducing catalytic activity.

Conclusion

This work has demonstrated that Co-Mo in bulk and supported on alumina are active and durable catalysts for the gas-phase deoxygenation of propionic acid at 200–400 °C and 1 bar of pressure under N_2 and H_2 flow. Co-Mo/ Al_2O_3 showed the best performance at 400 °C and it was stable for at least

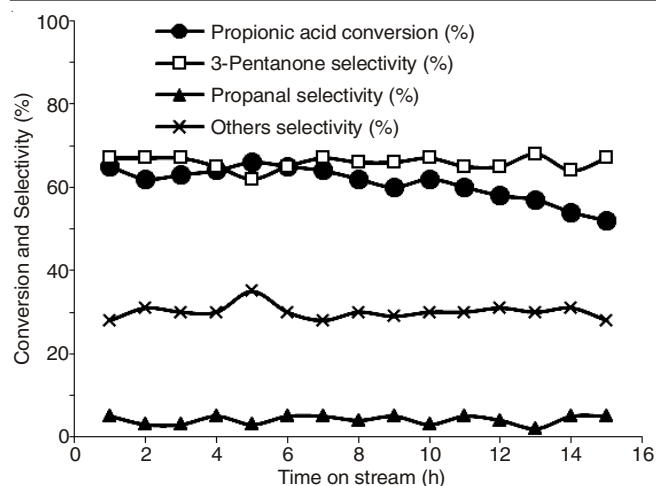


Fig. 6. Deoxygenation of propionic acid on Co-Mo/Al₂O₃ (0.2 g catalyst, 400 °C, 1 bar pressure, 20 mL min⁻¹ N₂ flow rate and 2 vol % propionic acid)

15 h on stream, with a small decrease in the last 3 h, probably because of catalyst deactivation by coking. Co-Mo and its metal oxide supports were characterized by BET, TGA and DRIFTS of pyridine.

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