

Heteropoly compounds as catalysts for hydrogenation of propanoic acid

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Abstract

Bulk Keggin heteropoly acids (HPAs) $H_{3+n}[PMo_{12-n}V_nO_{40}]$ ($n = 0-2$) and their Cs^+ salts catalyse the vapour-phase hydrogenation of propanoic acid at 350 °C and 1 bar H_2 pressure, yielding propanal together with 3-pentanone and propane as the main products. Catalyst acidity (controlled by Cs substitution) has crucial effect on the reaction selectivity. As the Cs content increases, the selectivity to propanal passes a maximum (74–76%). At the same time, the selectivity to propane sharply decreases, whereas 3-pentanone selectivity increases monotonously. This indicates that 3-pentanone is likely to form via Cs propanoate intermediate. Partial substitution of Mo(VI) by V(V) in the $PMo_{12}O_{40}^{3-}$ anion has a small effect on the catalyst performance. Initially crystalline, the catalysts become amorphous after reaction, with their surface area significantly reduced. As evidenced by FTIR, $H_4[PMo_{11}VO_{40}]$ and its Cs salts, possessing a higher thermal stability, retain the Keggin structure in their bulk after reaction, whereas less stable $H_3[PMo_{12}O_{40}]$ and $H_5[PMo_{10}V_2O_{40}]$ derivatives undergo decomposition. This shows that the as-made crystalline heteropoly compounds are catalyst precursors rather than the true catalysts. The reaction over $Cs_{2.4}H_{1.6}[PMo_{11}VO_{40}]$ is zero order in propanoic acid with an activation energy of 85 kJ/mol. The formation of propanal is suggested to occur via a Mars–Van Krevelen mechanism.

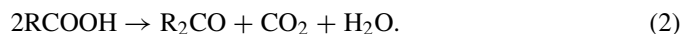
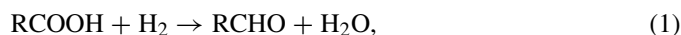
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Keywords: Heteropoly compounds; Hydrogenation; Propanoic acid; Propanal; Catalysis

1. Introduction

Aldehydes are widely used as flavours and fragrances as well as intermediates in the production of dyes, agrochemicals and pharmaceuticals. A variety of aldehydes is produced on a small or medium scale. Most aldehyde syntheses are non-catalytic reactions, producing large amounts of waste. Direct hydrogenation of carboxylic acids to aldehydes (Eq. (1)) by heterogeneous catalysis has attracted considerable interest as an environmentally friendly route using readily available and inexpensive aromatic and aliphatic acids as feedstock ([1,2] and references therein). In particular, metal oxides have been investigated as the catalysts for this reaction [1]. Oxides with intermediate metal–oxygen bond strength and relatively weak acid–base properties have been found to be the more efficient catalysts [2]. The hydrogenation of acids possessing α -hydrogen

atoms also produces ketones as byproducts (Eq. (2)) [1,2]. In the past decade, Mitsubishi developed commercial hydrogenation of aromatic acids using Cr/ZrO₂ oxide catalyst and aliphatic acids with Cr₂O₃ catalyst to produce the corresponding aldehydes with $\geq 90\%$ yield [1].



Heteropoly compounds (HPCs), i.e., heteropoly acids (HPAs) and their salts, also frequently termed polyoxometalates, have found broad applications as catalysts in homogeneous and heterogeneous systems due to their unique acid and redox properties [3–9]. HPCs are often considered “molecular oxides” because of their discrete molecular structure and chemical analogy to the constituent metal oxides [4,7,8]. Particularly important are the most stable and readily available Keggin HPCs [3–9]. The Keggin HPAs $H_{3+n}[PMo_{12-n}V_nO_{40}]$, where $n = 0-2$, and their salts are well-known catalysts for partial oxidation of organic compounds by oxygen [4,7–9]. The oxidation

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of methacrolein to methacrylic acid is utilised commercially over these catalysts [7–9]. There is compelling evidence that this reaction occurs via redox Mars–Van Krevelen mechanism, with catalyst acidity (controlled by ion exchange, e.g., with Cs⁺ cations) playing an important role [4,7–9]. To our knowledge, no attempt to use these HPAs as hydrogenation catalysts has been made so far.

Here we report that the H_{3+n}[PMo_{12-n}V_nO₄₀] acids (*n* = 0–2) and their Cs⁺ salts are active catalysts for the vapour-phase hydrogenation of propanoic acid. It is demonstrated that the performance of these catalysts in hydrogenation bears close resemblance to that in selective oxidation.

2. Experimental

2.1. Chemicals and catalysts

H₃[PMo₁₂O₄₀] hydrate (PMo) and propanoic acid were purchased from Aldrich. Heteropoly acids H₄[PMo₁₁VO₄₀] (PMoV) and H₅[PMo₁₀V₂O₄₀] (PMoV₂) were prepared as crystalline hydrates by refluxing stoichiometric amounts of MoO₃, V₂O₅ and H₃PO₄ in water for 48 h to yield orange solutions of HPAs, followed by removing water in a rotary evaporator and drying the solids in an oven at 110 °C overnight [10,11]. Cs salts of these HPAs, Cs_{*x*}H_{3-*x*}[PMo₁₂O₄₀] (Cs_{*x*}PMo), Cs_{*x*}H_{4-*x*}[PMo₁₁VO₄₀] (Cs_{*x*}PMoV) and Cs_{*x*}H_{5-*x*}[PMo₁₀V₂O₄₀] (Cs_{*x*}PMoV₂), were prepared using the Izumi's procedure for the preparation of Cs_{*x*}H_{3-*x*}[PW₁₂O₄₀] [12] by adding dropwise 0.25 M aqueous solution of Cs₂CO₃ to an aqueous solution of HPA at 70 °C, followed by ageing the aqueous slurry overnight at room temperature. Water was rota-evaporated at 50 °C to afford solid Cs salt which was finally dried in an oven at 110 °C overnight.

2.2. Techniques

The BET surface area, *S*_{BET}, and porosity of catalysts were measured by nitrogen physisorption at 77 K on a Micromeritics ASAP 2000 instrument. Before the measurement, the samples were evacuated at 250 °C for 4–6 h. Water content in the catalysts was measured by thermogravimetric analysis (TGA) using a Perkin–Elmer TGA 7 instrument. Diffuse reflectance IR spectra were recorded on a Nicolet NEXUS FTIR spectrometer using powder mixtures of catalysts with KBr. ³¹P MAS NMR spectra of catalysts were recorded at room temperature and 4 kHz spinning rate on a Bruker Avance DSX 400 NMR spectrometer in a 4 mm sample probe using 85% H₃PO₄ as a reference. ICP-AES chemical analysis was carried out on a Spectro Ciros CCD emission spectrometer. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a Siemens D-5000 diffractometer with a monochromatic CuK_α radiation in the angular range 10° ≤ 2θ ≤ 80°, with a step width of 0.036° and count-time of 1 s per step. XRD patterns were attributed using JCPDS database. In situ XRD experiments were carried out using the same diffractometer in a XRK900 reactor chamber (Anton Paar GmbH). The XRD spectra were

measured in a hydrogen flow (25 mL/min), ramping the temperature from room temperature to 400 °C at a rate of 5 °C/min. Thermal stability of heteropoly compounds was estimated using a Setaram TG-DSC 111 differential scanning calorimeter from exothermic peak corresponding to the formation of oxides. Ammonia adsorption measurements were performed using the Setaram TG-DSC 111 instrument at 100 °C by pulse method. Catalyst samples were pretreated at 350 °C/1 h in dry He flow (30 mL/min). Then the temperature was lowered to 100 °C. After stabilisation, successive 2 mL-pulses of gaseous NH₃ were injected in the He flow using a loop fitted in a 6 port valve. Catalyst reduction was performed at 340 °C under hydrogen flow using the Setaram TG-DSC 111 instrument. In a typical experiment, a catalyst sample (30 mg) was packed into the TGA-DSC crucible. Prior to reduction, the sample was heated under N₂ flow (40 mL/min) up to 350 °C at a rate of 5 °C/min and held for 1 h at that temperature. Then the temperature was decreased to 340 °C and stabilised for 30 min. This operation was to prevent any additional water loss because of the slight heating of the sample caused by exothermic reduction. After temperature stabilisation, reduction was commenced by switching nitrogen flow to a mixture of H₂ and N₂.

2.3. Catalyst testing

The hydrogenation of propanoic acid was carried out in a Pyrex glass fixed-bed reactor (9 mm internal diameter) with on-line GC analysis (Varian Star 3400 CX gas chromatograph equipped with a 30 m × 0.25 mm HP INNOWAX capillary column and flame ionisation detector). The reactor was placed in a vertical tubular furnace and fed from the top. The reaction temperature was controlled by a Eurotherm controller using a thermocouple placed in the centre of the catalyst bed. The hydrogenation of propanoic acid to propanal is slightly endothermic ($\Delta H^0 = 28.3$ kJ/mol), therefore temperature gradients across the catalyst bed could be neglected. The reactor was packed with 0.2 g catalyst powder. Prior to reaction, the catalyst was pretreated in situ in a hydrogen flow (40 mL/min), ramping the temperature to 400 °C at a rate of 10 °C/min then dwelling at 400 °C for 2 h, unless otherwise stated. The hydrogenation of propanoic acid was carried out at 350 °C, 1 bar pressure, 80 mL/min H₂ flow rate and 2 vol% acid concentration in the gas flow. The hydrogen flow was controlled by Brooks mass flow controllers. Propanoic acid was supplied by bubbling the H₂ flow through a glass saturator containing the acid, which was kept at a certain temperature to maintain the acid concentration in the gas flow. All gas lines were made of stainless steel. The gas lines after the saturator and sampling valves were heated at 170 °C to prevent reactant and product condensation. At regular time intervals, the downstream gas flow was analysed by the on-line GC which was calibrated for each product. The products were collected in an ice trap and analysed by the off-line GC-MS. Propanoic acid conversion (%) was calculated as $X = 100 \times ([\text{acid}]_0 - [\text{acid}]) / [\text{acid}]_0$, where $[\text{acid}]_0$ is the concentration of propanoic acid in the feed flow, which was measured using a bypass line. Product selectivities were calculated as the molecular percentage of all organic prod-

Table 1
Characterisation of fresh catalysts

Catalyst	Atomic ratio				S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Water content ^a	Thermal stability ^b ($^{\circ}\text{C}$)
	P	V	Mo	Cs				
PMo	1.0	0	12.3	0	1	–	15.3	438
Cs _{1.5} PMo	1.0	0	11.4	1.5	5	0.009	6.7	432
Cs _{2.5} PMo	1.0	0	12.1	2.5	28	0.065	3.8	440
Cs ₃ PMo	1.0	0	12.1	3.2	9	0.063	4.0	440
PMoV	1.0	0.9	10.4	0	1	–	10.7	471
Cs _{0.8} PMoV	1.0	1.0	11.5	0.76	7	0.007	–	–
Cs _{1.5} PMoV	1.0	1.0	11.1	1.52	14	0.049	5.7	483
Cs _{2.4} PMoV	1.0	1.0	11.2	2.44	85	0.105	4.6	487
Cs ₃ PMoV	1.0	1.0	11.3	3.05	102	0.097	5.9	–
Cs _{4.0} PMoV	1.0	1.0	11.5	4.0	98	0.141	–	–
PMoV ₂	1.0	2.1	10.8	0	4	0.006	13.8	425
Cs _{1.3} PMoV ₂	1.0	2.1	10.2	1.25	2	0.007	6.8	457
Cs _{2.5} PMoV ₂	1.0	2.1	10.4	2.5	30	0.055	3.2	490
Cs ₄ PMoV ₂	1.0	2.1	10.7	4.0	13	0.070	–	–
Cs ₅ PMoV ₂	1.0	2.0	10.2	5.0	13	0.082	2.6	–

^a Crystallisation water (molecules per Keggin unit) from TGA weight loss in the temperature range of 30–200 $^{\circ}\text{C}$.

^b Exothermic peak corresponding to the formation of oxides.

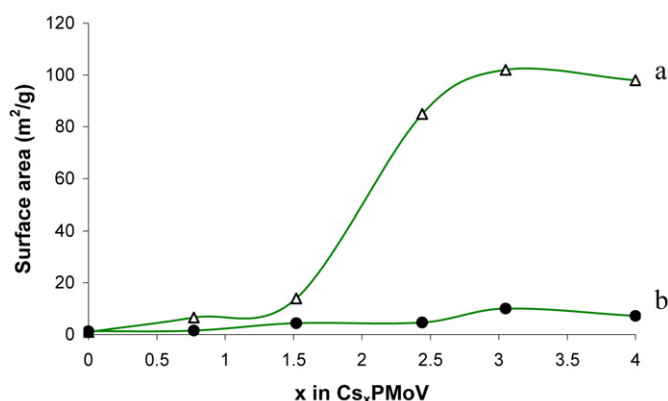


Fig. 1. BET surface area of Cs_xPMoV catalysts: (a) before reaction and (b) after reaction.

ucts obtained. Carbon balance was estimated as the percentage of the reacted carbon atoms found in products.

Kinetic studies were carried out under differential conditions at a propanoic acid conversion $\leq 10\%$, other conditions being: 0.07 g catalyst sample, 60 mL/min flow rate, 2–7 vol% acid concentration balanced by H₂, and 320–380 $^{\circ}\text{C}$ temperature range. The reaction rate, r , was determined as the rate of propanoic acid consumption ($\text{mol/g}_{\text{cat}} \text{h}$): $r = F_0 X / W$, where F_0 is the propanoic acid flow rate (mol/h), X , the conversion of propanoic acid (dimensionless) and W , catalyst weight (g).

3. Results and discussion

3.1. Catalyst characterisation: fresh catalysts

Three series of bulk solid Cs heteropoly salts based on PMo, PMoV and PMoV₂ heteropoly acids with a varied Cs content were prepared and, prior to use as hydrogenation catalysts, characterised regarding their chemical composition, surface area, porosity and thermal stability (Table 1). In agreement

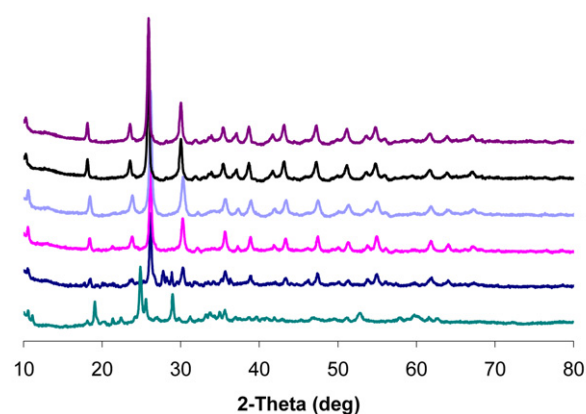


Fig. 2. XRD patterns for fresh Cs_xPMoV catalysts: (a) PMoV, (b) Cs_{0.8}PMoV, (c) Cs_{1.5}PMoV, (d) Cs_{2.4}PMoV, (e) Cs₃PMoV, (f) Cs₄PMoV.

with the previous reports [4,6,7,9], the parent HPAs had very low surface areas which increased with increasing the Cs content (Table 1, Fig. 1). The porosity of these compounds was low, also increasing with Cs content. Their thermal stability, determined from the exotherms corresponding to the formation of oxides [7], was in the order: PMo < PMoV \geq PMoV₂, in agreement with the literature [4,7,9]. The compounds prepared were crystalline solids, as exemplified by the XRD patterns for Cs_xPMoV (Fig. 2). The parent HPAs, that contained 11–15 H₂O per Keggin unit (Table 1), were triclinic. Their Cs salts containing 3–6 H₂O were cubic, as expected [7,13]. ³¹P MAS NMR confirmed the Keggin structure of PMo, PMoV and PMoV₂ heteropoly acids (Fig. 3). The first two exhibited single lines at –3.6 and –3.7 ppm, respectively, in agreement with the literature [4,9]. PMoV₂ showed two broad overlapping resonances at –3.2 and –3.7 ppm which can be attributed to isomeric PMoV₂ polyanions [14]. Some PMoV might be present in this PMoV₂ sample because the hydrothermal synthesis of PMoV₂ from MoO₃ and V₂O₅ takes long time to

complete [11]. FTIR spectra (Figs. 4 and 5) also confirmed the structure of the compounds prepared. All the samples exhibited four infrared bands characteristic of the Keggin structure: 780–800, 860–880 cm^{-1} (Mo–O–Mo), 960–990 cm^{-1} (Mo=O) and 1060–1080 cm^{-1} (P–O) [4].

Keggin heteropoly acids and their Cs salts are purely Brønsted acids [4,6,7]. The acidity of the catalysts (number of proton sites) was measured by ammonia adsorption. Table 2 shows the results for fresh Cs_xPMoV catalysts. As can be seen, the mea-

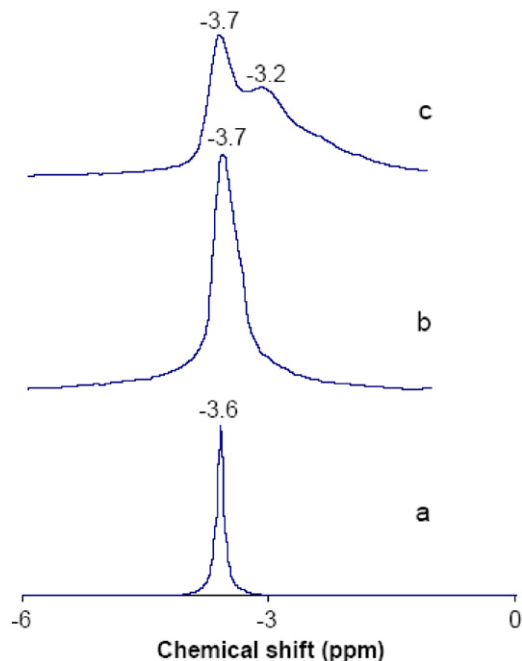


Fig. 3. ^{31}P MAS NMR spectra for heteropoly acids: (a) PMo, (b) PMoV, (c) PMoV₂.

asured values are in good agreement with the theoretical bulk Brønsted acidity (total number of proton sites) of these catalysts. Therefore, the acidity measured is the bulk acidity rather than the surface one. As expected, the acidity decreases with increasing Cs content. The acid strength of proton sites probably

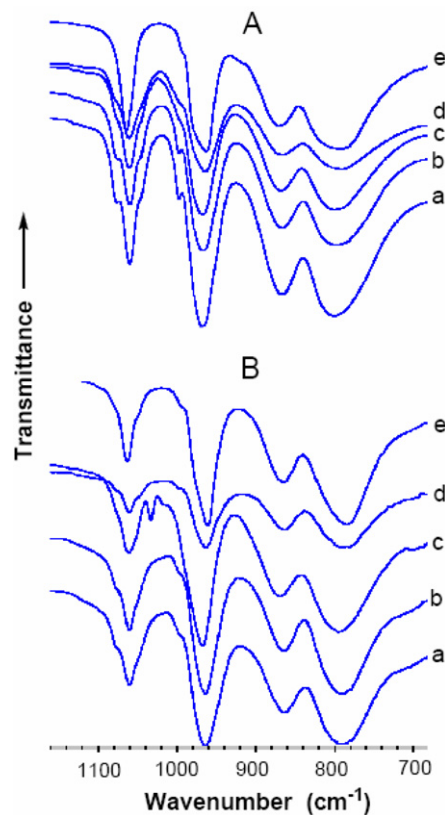


Fig. 5. FTIR for fresh (A) and used (B) catalysts: (a) PMoV, (b) $\text{Cs}_{0.8}\text{PMoV}$, (c) $\text{Cs}_{1.5}\text{PMoV}$, (d) $\text{Cs}_{2.4}\text{PMoV}$, (e) Cs_3PMoV .

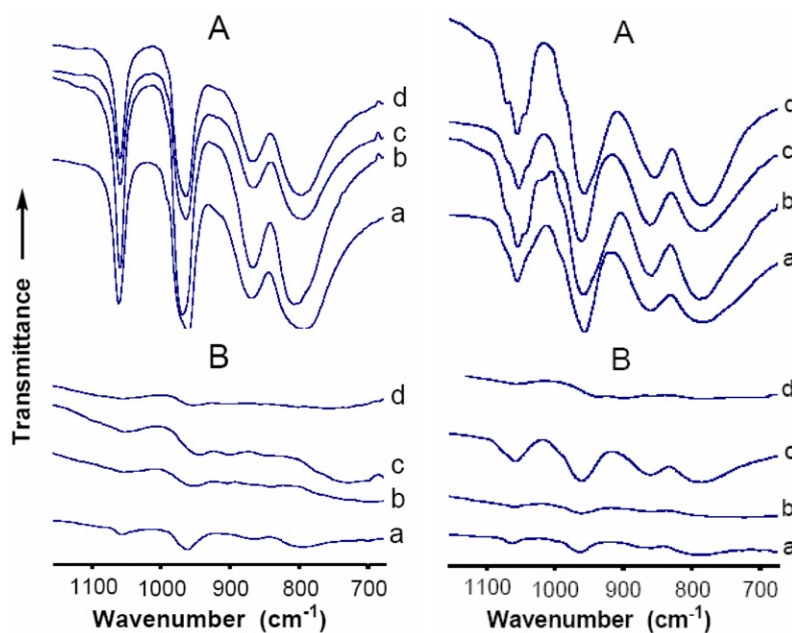


Fig. 4. FTIR for fresh (A) and used (B) catalysts. Left: (a) PMo, (b) $\text{Cs}_{1.5}\text{PMo}$, (c) $\text{Cs}_{2.5}\text{PMo}$, (d) Cs_3PMo ; right: (a) PMoV₂, (b) $\text{Cs}_{1.3}\text{PMoV}_2$, (c) $\text{Cs}_{2.5}\text{PMoV}_2$, (d) Cs_5PMoV_2 .

Table 2
Ammonia adsorption on fresh Cs_xPMoV catalysts at 100 °C

Catalyst $Cs_xH_{4-x}[PMo_{11}VO_{40}]$	NH_3 adsorbed (mmol/g)	Theoretical amount of Brønsted sites ^a (mmol/g)
PMoV	2.78	2.25
$Cs_{0.8}PMoV$	1.65	1.72
$Cs_{1.5}PMoV$	0.68	1.25
$Cs_{2.4}PMoV$	0.40	0.74
Cs_3PMoV	0.31	0.44
$Cs_{4.0}PMoV$	0	0

^a The total number of proton sites in the catalyst bulk.

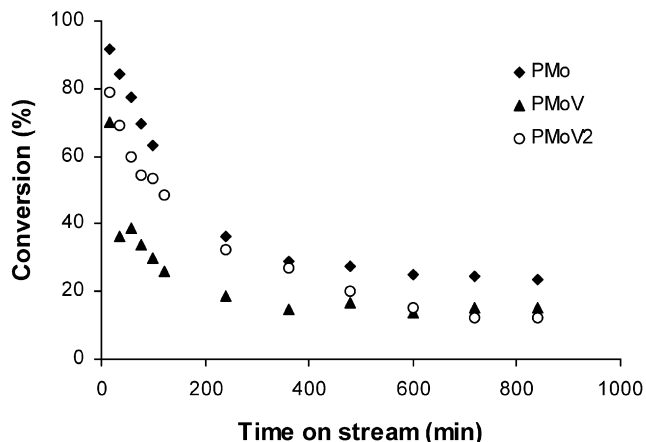


Fig. 6. Conversion of propanoic acid over heteropoly acids PMo, PMoV and PMoV₂ as a function of time on stream.

decreases upon Cs substitution as well, which can be expected from the weaker acid strength of $Cs_{2.5}H_{1.5}[PW_{12}O_{40}]$ compared the parent heteropoly acid $H_3[PW_{12}O_{40}]$ [15].

3.2. Catalyst performance

Hydrogenation of propanoic acid over the bulk heteropoly compounds was found to yield a range of products, with propanal, 3-pentanone and hydrocarbons (mostly propane) being the main products, together with small amounts of 1-propanol. Catalyst acidity that was controlled by Cs substitution in the parent HPAs [4,7] had crucial effect on the hydrogenation activity and selectivity of these catalysts. In contrast, partial substitution of Mo(VI) by V(V) in the $PMo_{12}O_{40}^{3-}$ anion, which is known to affect redox properties and stability of the polyanion [4,7,9], had relatively small effect on the catalyst performance.

Heteropoly acids PMo, PMoV and PMoV₂ exhibited very high initial catalytic activities (70–91% conversion) which declined to 13–23% steady-state conversion in 6–10 h on stream (Fig. 6). Initially, carbon balance was low, improving with the time on stream (Table 3). The deactivation of catalysts and loss of carbon can be explained by coking (see below). The lower carbon balance for PMo compared to PMoV and PMoV₂ can be explained by the stronger acidity of PMo [6,9] hence more significant coking. The HPAs gave mainly propane, with propanal, some butane and traces of ethane as co-products (Table 3). No 3-pentanone was found in the presence of HPAs. The

Table 3
Initial and steady-state performance of heteropoly acids in propanoic acid hydrogenation^a

Catalyst performance	Catalyst					
	PMo		PMoV		PMoV ₂	
	15 min	12 h	15 min	12 h	15 min	12 h
Conversion (%)	91.4	23.6	70.0	15.0	79.1	12.5
Selectivity (%)						
Propane	89.7	53.9	79.0	56.8	68.8	60.9
Butane	5.7	0.0	3.8	0.0	6.1	0.0
Propanal	4.6	46.1	12.7	43.2	23.9	39.1
1-Propanol	0	0	4.5	0	0	0
C balance	50.8	87.6	62.3	92.1	60.0	97.1

^a Reaction conditions: 350 °C, 1 bar, 80 mL/min H₂ flow rate, 2 vol% propanoic acid, 0.2 g catalyst.

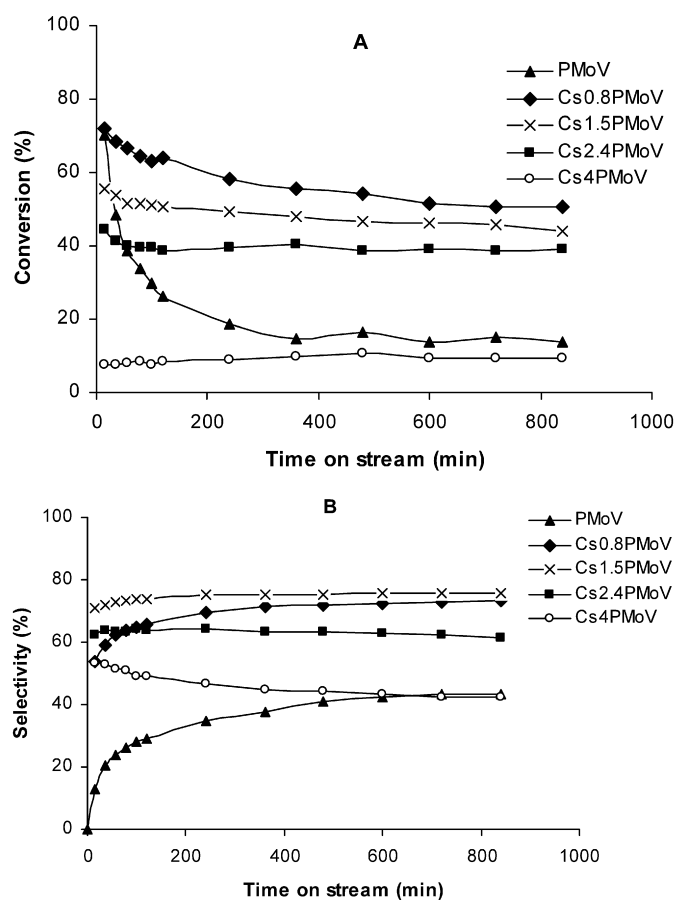


Fig. 7. Conversion of propanoic acid (A) and selectivity to propanal (B) over Cs_xPVMo catalysts as a function of time on stream.

propanal selectivity increased with the time on stream at the expense of hydrocarbons.

Cs salts showed more stable performance than the parent acids (Fig. 7). It took only 1–2 h for Cs salts to reach steady state. The catalytic activity of Cs salts, both initial and steady-state, decreased with Cs content. As the Cs content increased, the selectivity to propanal passed a maximum to make propanal the main product for partially substituted Cs salts. At the same time, the selectivity to propane sharply decreased, whereas 3-pentanone selectivity increased monotonously. 3-Pentanone

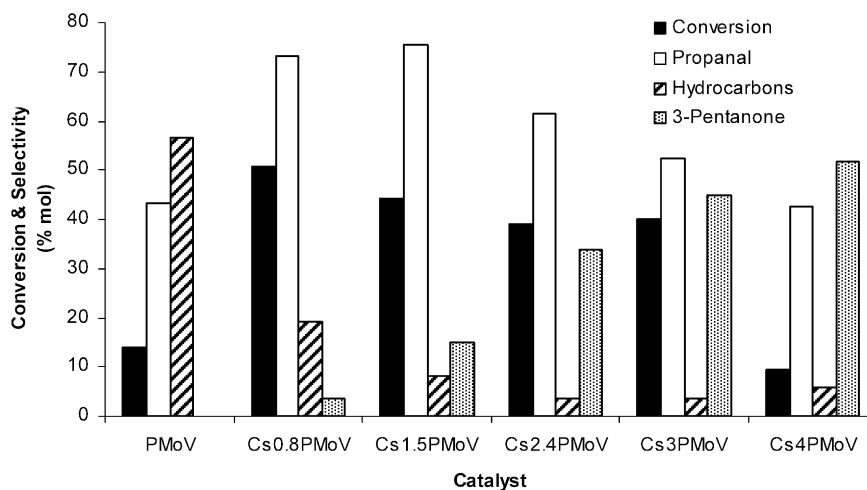


Fig. 8. Propanoic acid conversion and selectivity to main reaction products for Cs_xPMoV catalysts after 12 h time on stream.

Table 4
Steady-state catalyst performance in propanoic acid hydrogenation after 12 h reaction time^a

Catalyst	Conversion (%)	Selectivity (%)			
		HC ^b	Propanal	1-Propanol	3-Pentanone
PMo	24.0	53.9	46.1	–	–
Cs _{1.5} PMo	40.1	21.7	71.1	1.7	5.5
Cs _{2.5} PMo	41.1	7.8	74.4	1.6	16.1
Cs ₃ PMo	39.7	6.6	75.1	1.5	16.9
PMoV	14.0	56.7	43.3	–	–
Cs _{0.8} PMoV	50.6	19.3	73.1	3.9	3.7
Cs _{1.5} PMoV	44.2	8.1	75.3	1.7	14.9
Cs _{2.4} PMoV	38.9	3.6	61.4	–	33.8
Cs ₃ PMoV	40.0	2.6	52.5	–	44.9
Cs ₄ PMoV	9.5	5.9	42.6	–	51.6
PMoV ₂	17.9	60.0	40.0	–	–
Cs _{1.3} PMoV ₂	41.7	8.6	76.0	1.4	13.9
Cs _{2.5} PMoV ₂	30.2	2.5	46.7	–	50.8
Cs ₅ PMoV ₂	7.6	–	31.5	–	68.5

^a Reaction conditions: 350 °C, 1 bar, 80 mL/min H₂ flow rate, 2 vol% propanoic acid, 0.2 g catalyst.

^b Hydrocarbons, mainly propane.

was the main product in case of neutral Cs salts (Fig. 8). Usually, the selectivity to propanal increased with the time on stream at the expense of hydrocarbons (Fig. 7).

Table 4 summarises the catalyst performance at steady state after 12 h on stream. Regarding the propanal production, the three series of catalysts, Cs_xPMo, Cs_xPMoV and Cs_xPMoV₂, showed similar performance. Better results were obtained for the Cs salts containing 0.8–1.5 Cs ions per Keggin unit which provided 74–76% propanal selectivity at 41–51% conversion. Cs_{0.8}PMoV gave the highest propanal yield of 37% (73.1% selectivity at 50.6% conversion).

It was found that increasing the time of catalyst pretreatment (at 400 °C under H₂) improved the yield of propanal due to an increase in catalyst activity (conversion), with the propanal selectivity practically unchanged (Fig. 9). For Cs_{0.8}PMoV, an increase of the pretreatment time from 2 to 10 h increased the yield of propanal from 37 to 52% (70% selectivity at 74% con-

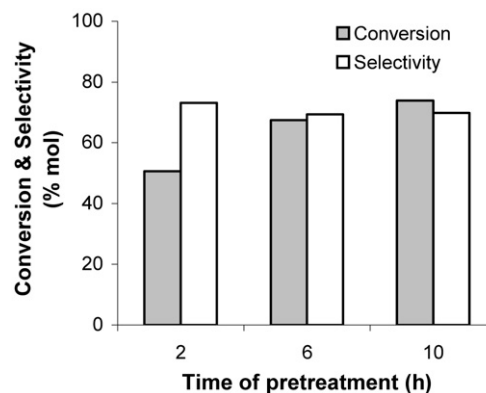


Fig. 9. Effect of pretreatment of Cs_{0.8}PMoV catalyst (at 400 °C under H₂) on propanoic acid conversion and propanal selectivity after 12 h time on stream.

version). This may be explained by formation of catalytically active vanadium and molybdenum oxides upon catalyst pretreatment (see below).

3.3. Catalyst evolution

In situ XRD was used to study the catalyst evolution during catalyst pretreatment. Fig. 10 shows the results for Cs_{2.4}PMoV which is one of the most stable catalysts studied here (Table 1). Crystalline at room temperature (cubic cell), the catalyst becomes amorphous after heating at 400 °C under H₂ for 1.5 h and remains such after subsequent heating at the reaction temperature 350 °C for 5 h. Therefore, our usual pretreatment (400 °C/2 h, under H₂) would break the secondary structure of the catalyst to turn it into an amorphous material. These results demonstrate that the as-made crystalline heteropoly compounds are catalyst precursors rather than the true catalysts in the hydrogenation of propanoic acid.

3.4. Characterisation of spent catalysts

The spent catalysts were characterised by chemical analysis, XRD, FTIR and BET surface area/porosity analysis. The post reaction characterisation showed that the catalysts went through

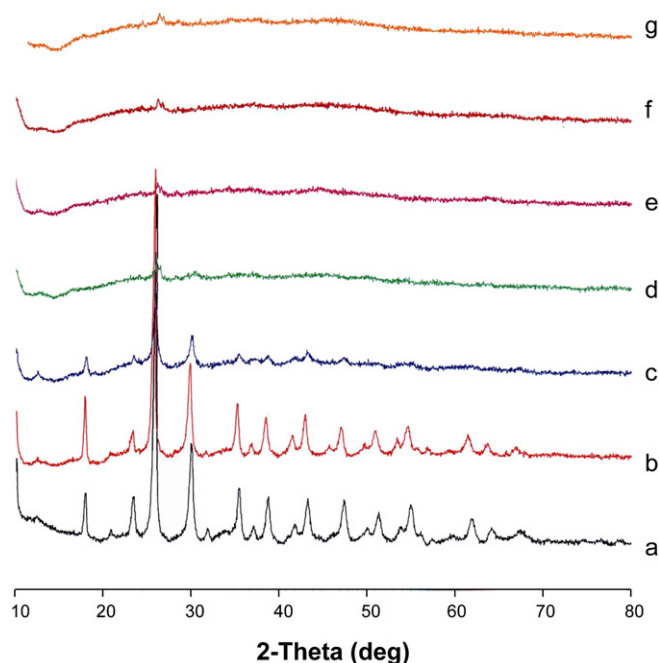


Fig. 10. In situ XRD for $\text{Cs}_{2.4}\text{PMoV}$ under H_2 at different temperatures: (a) room temperature, (b) $400^\circ\text{C}/0.5$ h, (c) $400^\circ\text{C}/1.0$ h, (d) $400^\circ\text{C}/1.5$ h, (e) $400^\circ\text{C}/2.0$ h, (f) after (c) the temperature was decreased to 350°C and kept for 2.5 h at 350°C , (g) $350^\circ\text{C}/5$ h.

a dramatic structural change during the hydrogenation process. All spent catalysts were amorphous, exhibiting the XRD patterns similar to those in Fig. 10 e–g, i.e., the crystallinity characteristic of fresh catalysts was lost. Catalyst surface area decreased significantly to less than $10\text{ m}^2/\text{g}$ (Fig. 1), indicating catalyst particle agglomeration. As evidenced by FTIR, $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ and its Cs salts possessing a higher thermal stability (Table 1) retained the Keggin (primary) structure in their bulk (Fig. 5), although there is no guarantee that the structure remained intact at the catalyst surface. In contrast, the less stable $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ and $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ derivatives largely lost the Keggin structure (Fig. 4), except for the more thermally stable $\text{Cs}_{2.5}\text{PMoV}_2$ (Table 1).

Coke was found in spent catalysts, its amount depended on the Cs content (i.e., catalyst acidity). As expected, the HPA catalysts possessing strong acidity had a larger amount of coke (3.5 wt% for PMo) than the Cs salts. The neutral Cs salts had hardly any coke deposition at all. Coking could be the reason for the strong deactivation of HPA catalysts (Fig. 6). Coke could also cause the increase in propanal selectivity at the expense of propane with increasing the time on stream (Table 3).

3.5. Kinetic studies

The kinetic measurements for propanoic acid hydrogenation were carried out in steady state under differential conditions (conversion $\leq 10\%$) using $\text{Cs}_{2.4}\text{PMoV}$ as the catalyst. The rate of propanoic acid conversion was measured at 320 – 380°C and propanoic acid concentration 2–7 vol% in H_2 flow. Under these conditions, the selectivity to propanal was 74–76%. The reaction rate did not depend on the flow rate at constant contact

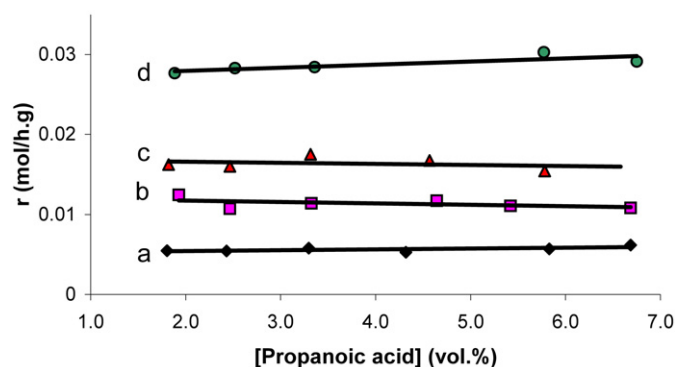


Fig. 11. The rate of propanoic acid conversion over $\text{Cs}_{2.4}\text{PMoV}$ at different temperatures as a function of propanoic acid concentration: (a) 320°C , (b) 340°C , (c) 360°C , (d) 380°C .

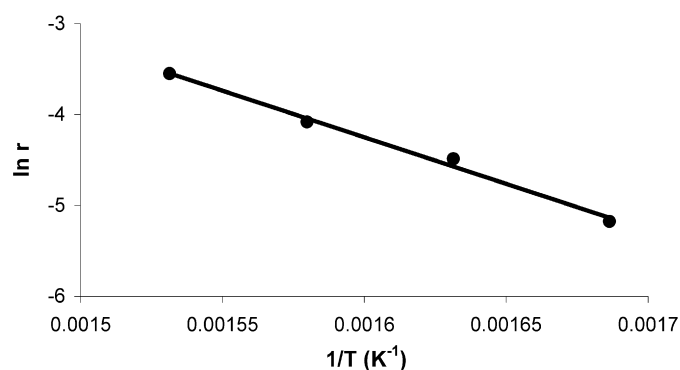


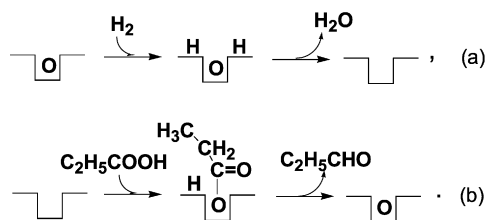
Fig. 12. Arrhenius plot for propanoic acid hydrogenation (2.5 vol% propanoic acid).

time. This indicates that the reaction was not affected by external mass transfer. In the whole temperature range studied, the reaction was zero order in propanoic acid (Fig. 11) and obeyed the Arrhenius equation with an activation energy of 85 kJ/mol (Fig. 12). These results suggest that the reaction occurred in chemical regime without diffusion limitations.

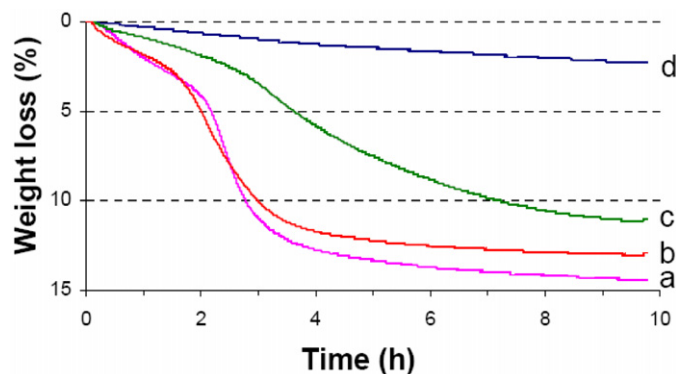
3.6. Mechanism

Hydrogenation of carboxylic acids to the corresponding aldehydes over metal oxides has been suggested to proceed via a Mars–Van Krevelen redox mechanism [1,2]. This mechanism adopted for the hydrogenation of propanoic acid is shown in Scheme 1. It involves two steps in which lattice oxygen plays a key role. In the first step (a), lattice oxygen reacts with adsorbed hydrogen to generate an oxygen vacancy on the catalyst surface by desorption of water molecule. In the second step (b), this vacancy is refilled by an oxygen from the acid acting as an oxidant to form aldehyde and regenerate the catalyst in its oxidised form. For this mechanism to be efficient, metal–oxygen bond should be of an intermediate strength, neither too strong nor too weak [2]. If it is too strong, step (a) will be very slow. If too weak, step (b) will limit the reaction due to the low ability of the lattice to abstract oxygen from the acid.

Redox properties of the Keggin heteropoly molybdovanadates $[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n)-}$ are well documented, both in the



Scheme 1. Surface mechanism of carboxylic acid hydrogenation [2].

Fig. 13. Weight loss upon reduction of catalysts with H_2 at 340°C : (a) PMoV, (b) $\text{Cs}_{0.8}\text{PMoV}$, (c) $\text{Cs}_{2.4}\text{PMoV}$, (d) Cs_4PMoV .

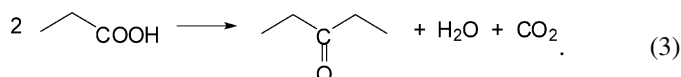
solid state [4,7–9] and solution [3,5,6,9], and utilised in many catalytic oxidations [3–9], including industrial vapour-phase oxidation of methacrolein to methacrylic acid [4,8,9]. Misono et al. [4] have shown that reduction of solid Keggin HPAs (e.g., $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$) by H_2 occurs in several steps, first without evolving water then, especially at higher temperatures, water evolves to form polyanions with oxygen vacancies. Partial reduction of HPA is a reversible process, further reduction may be irreversible. It has been found that the reduction rate does not depend significantly on the specific surface area of HPA, which has been explained by a bulk-type mechanism for this reaction [4]. This mechanism implies that protons and electrons that form initially on the surface rapidly diffuse into the HPA bulk, resulting in nearly uniform reduction of the bulk solid [4].

To examine whether or not the formation of oxygen vacancies in bulk molybdovanadophosphates under our reaction conditions was feasible, we monitored catalyst weight upon heating under H_2 using in situ TGA. Fig. 13 shows the results for Cs_xPMoV catalysts treated at 340°C as a function of time. In these experiments, the weight of catalyst samples had been stabilised at 340°C prior to exposure to H_2 . As can be seen, all the catalysts were losing weight upon reduction due to water evolution, creating oxygen vacancies. The higher the Cs content, x , the higher was the catalyst stability towards reduction. After heating for 10 h, Cs_4PMoV lost only 2 wt% due to oxygen loss, whereas PMoV lost 14 wt%, i.e., 39% of its oxygen, which should have caused decomposition of PMoV. Under reaction conditions in the presence of propanoic acid, the feed flow was less reducing than the pure H_2 , therefore the steady-state reduction of the catalyst was probably less than that.

With these results, the hydrogenation of propanoic acid over bulk heteropoly compounds fits well into the Mars–Van Krev-

elen redox mechanism (Scheme 1). Zero order in propanoic acid (Fig. 11) indicates that the formation of oxygen vacancy (step (a)) is likely to be the rate-limiting step in the process. This is also supported by the fact that Cs_4PMoV , which is the most stable catalyst towards reduction in the Cs_xPMoV series (Fig. 13), is the least active one for propanoic acid hydrogenation (Table 4). Another observation supporting this mechanism is that there is no relation between the catalyst activity and the catalyst surface area (cf. the data for Cs_xPMoV in Table 4 and Fig. 1). As mentioned above, similar behaviour has been observed for the reduction of HPAs by H_2 [4]. This suggests that step (a) in propanoic acid hydrogenation might occur via bulk-type mechanism, resulting in the formation of oxygen vacancies on the catalyst surface as well as in catalyst bulk.

In addition to aldehydes, the hydrogenation of carboxylic acids possessing α -hydrogen atoms produces ketones [1,2], 3-pentanone in our case (Eq. (3)). This reaction does not involve hydrogen. The yield of ketones usually increases with the number of α -hydrogens [1,2]. For the formation of ketones, several mechanisms have been proposed. These include: (i) decomposition of metal carboxylate, (ii) via acid anhydride as intermediate, (iii) via β -keto acid intermediate and (iv) ketene intermediate route ([2] and references therein). In our case, the selectivity to 3-pentanone correlates well with the Cs content in the catalysts (Table 4, Fig. 8). As the Cs content increases, so does the selectivity to 3-pentanone at the expense of hydrocarbons and propanal. Therefore, in our system, 3-pentanone is likely to form via Cs propanoate as intermediate. Propane probably resulted from reduction of propanoic acid to 1-propanol followed by acid-catalysed dehydration to propene and its hydrogenation to propane, which agrees with the formation of small amounts of 1-propanol (Table 4). Ethane and butane could form by cracking and alkylation of the primary products and decarboxylation of propanoic acid. The decline in hydrocarbon selectivity with increasing the Cs content can be explained by decreasing the catalyst acidity (Table 2). Simultaneously, the propanal selectivity decreases due to a slowdown of step (a) because of the increase in catalyst stability to reduction (Fig. 13).



Keggin structure does not seem to be vital for the effectiveness of these catalysts in the hydrogenation of propanoic acid. Thus the catalysts of the PMo and PMoV₂ series, which largely lose the Keggin structure during reaction, and those of the PMoV series, which retain it, show similar performances (Table 4). This suggests that surface oxide species produced by decomposition of heteropoly anions at the catalyst surface may play a role in the hydrogenation process with all these catalysts. It could be the reason for the small effect of partial substitution of Mo(VI) by V(V) in the $\text{PMo}_{12}\text{O}_{40}^{3-}$ polyanion on the catalyst performance (Table 4).

Hydrogenation of carboxylic acids to aldehydes over bulk heteropoly compounds appears to bear a pronounced resemblance to selective oxidation by oxygen over these HPCs such as the oxidation of methacrolein to methacrylic acid and oxidative dehydrogenation of isobutyric acid to methacrylic acid

[4,8]. First, both reactions occur via Mars–Van Krevelen redox mechanism, utilising redox properties of HPCs. Secondly, the acidity of HPCs plays a fundamental role in these reactions. Both types of catalysis require precise control of the acidity which can be achieved by cation exchange (e.g., with Cs^+). This resemblance can be further extended to homogeneous oxidation with O_2 catalysed by $[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]^{(3+n)-}$ heteropoly anions (HPA-n). Many of such reactions occur by a two-step redox mechanism involving oxidation of substrate by HPA-n followed by reoxidation of reduced form of HPA-n by O_2 [3,5,6,9]. In the homogeneous oxidation, control of acidity is crucial for catalyst efficiency like in the above heterogeneous redox reactions. Hence there is a close relation between heterogeneous and homogeneous redox catalysis by these heteropoly compounds.

4. Conclusions

Keggin heteropoly acids $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]$ ($n = 0-2$) and their Cs^+ salts are active catalysts for the vapour-phase hydrogenation of propanoic acid at 350 °C and 1 bar H_2 pressure. Catalyst acidity has crucial effect on the reaction selectivity. Tuning the catalyst acidity by Cs substitution in heteropoly acids allows for the propanal selectivity to be maximised. It is demonstrated that the as-made crystalline heteropoly compounds are catalyst precursors rather than the true catalysts. After reaction, the catalysts become amorphous, with their surface area significantly reduced. $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ and its Cs salts, which possess a higher thermal stability, retain the Keggin structure after reaction. In contrast, less stable $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$

and $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$ derivatives undergo decomposition to a large extent. Evidence is provided that the formation of propanal occurs via Mars–Van Krevelen mechanism. It is noted that hydrogenation of carboxylic acids to aldehydes over bulk heteropoly compounds bears a pronounced resemblance to selective oxidation by oxygen over these HPCs, which probably stems from the “molecular oxide” nature and multifunctionality of HPCs.

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