

# Hydrogenation of Carboxylic Acids over P-Mo-V Heteropoly Compounds in Comparison with the Constituent Mo and V Oxides

Hacib Benaissa,<sup>1</sup> Paul N. Davey,<sup>2</sup> Elena F. Kozhevnikova,<sup>1</sup> and Ivan V. Kozhevnikov<sup>1\*</sup>

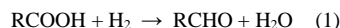
<sup>1</sup>Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

<sup>2</sup>Quest International, Ashford, Kent, TN24 0LT, UK

\*I.V.Kozhevnikov@liverpool.ac.uk

## Introduction

Aldehydes find many uses such as in flavours and fragrances as well as intermediates in the production of dyes, agrochemicals and pharmaceuticals. Most aldehyde syntheses are non-catalytic reactions, producing large amounts of waste. Consequently, considerable interest has attracted direct, environmentally friendly hydrogenation of readily available aromatic and aliphatic carboxylic acids to aldehydes (Eq. 1) using heterogeneous catalysis [1,2]. In particular, metal oxides have been investigated as the catalysts for acid hydrogenation. The hydrogenation of acids possessing  $\alpha$ -hydrogen atoms also produces ketones as by-products (Eq. 2) [1,2]. Mitsubishi has developed commercial hydrogenation of aliphatic and aromatic acids using Cr oxide catalyst in the gas phase to produce aldehydes with  $\geq 90\%$  yield [1].



Heteropoly acids (HPAs) possess controllable acid and redox properties and are widely used as acid and oxidation catalysts [3]. The Keggin HPAs  $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]$  ( $n = 0, 1, 2$ ) are well known as catalysts of partial oxidation [3]. Here we report that these HPAs and their  $\text{Cs}^+$  salts are active catalysts for the gas-phase hydrogenation of propanoic and hexanoic acids to their aldehydes. The HPAs are compared with their constituent oxides –  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$ .

## Materials and Methods

The HPA catalysts were prepared as described elsewhere [4,5] and characterised before and after reaction by XRD, FTIR, TG/DSC and BET analysis. The hydrogenation of carboxylic acids was carried out in a fixed-bed reactor with on-line GC analysis at 350 °C, 1 bar pressure, 80 mL/min  $\text{H}_2$  flow rate and 2 vol% acid concentration in the  $\text{H}_2$  flow [4]. Prior to reaction, the catalyst (0.2 g) was pre-treated in situ in a hydrogen flow at 400 °C for 2 h.

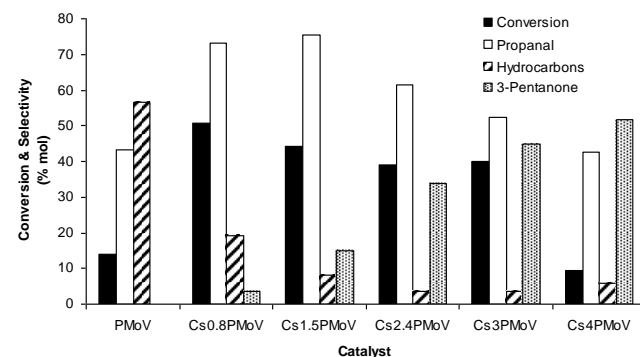
## Results and Discussion

Bulk HPAs and their  $\text{Cs}^+$  salts catalyse the hydrogenation of propanoic and hexanoic acids, yielding aldehydes (propanal and hexanal) together with ketones (acetone and 3-pentanone) and hydrocarbons (propane from propanoic acid and  $\text{C}_4$ - $\text{C}_7$  from hexanoic acid) as the main products. Catalyst acidity (controlled by Cs substitution) has crucial effect on the reaction selectivity (Fig. 1). As the Cs content increases, the selectivity to aldehydes passes a maximum (74-76%). At the same time, the selectivity to hydrocarbons sharply decreases, whereas ketone selectivity increases monotonously. This indicates that the ketones are likely to form via Cs carboxylate intermediate. Initially crystalline, the catalysts become amorphous after reaction, with their surface area significantly reduced. As evidenced by FTIR,  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$  and its Cs salts, possessing a higher thermal stability, retain the Keggin

structure in their bulk after reaction, whereas 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. This shows that the as-made crystalline HPAs are catalyst precursors rather than the true catalysts. The reaction over  $\text{Cs}_{2.4}\text{H}_{1.6}[\text{PMo}_{11}\text{VO}_{40}]$  is zero order in propanoic acid with an activation energy of 85 kJ/mol. The formation of aldehydes is suggested to occur via a Mars–Van Krevelen mechanism, with the rate-limiting step of formation of oxygen vacancy in the catalyst by reaction of lattice oxygen with  $\text{H}_2$ .

The constituent  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  oxides make more active hydrogenation catalysts than the P-Mo-V heteropoly compounds (HPCs). In hexanoic acid hydrogenation, bulk  $\text{MoO}_3$  reduces to  $\text{MoO}_2$ , which performs steadily to give 75% hexanal selectivity at 95% conversion. The bulk  $\text{V}_2\text{O}_5$ , inactive itself, slowly, over 26 h, reduces to the active  $\text{V}_2\text{O}_3$  oxide, which shows excellent performance: 97-100% hexanal selectivity at 80-83% conversion over 72 h on stream – the result of potential practical interest. This suggests that Mo and V oxides that could form upon HPC decomposition might play a role in carboxylic acid hydrogenation over HPCs.

It is demonstrated that hydrogenation of carboxylic acids to aldehydes over bulk HPCs bears a pronounced resemblance to selective oxidation by  $\text{O}_2$  over these HPCs such as the oxidation of methacrolein to methacrylic acid. First, both reactions occur via Mars–Van Krevelen mechanism, utilising redox properties of HPCs. Second, both types of catalysis require precise control of catalyst acidity which can be achieved by cation exchange in HPC (e.g. with  $\text{Cs}^+$ ).



**Figure 1.** Propanoic acid conversion and product selectivity for  $\text{Cs}_x\text{H}_{4-x}[\text{PMo}_{11}\text{VO}_{40}]$  catalysts.

## References

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