

# Abstract

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## “Solid acid catalysts based on heteropoly acids for conversion of renewable feedstocks”

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The aim of this work is to investigate homogeneous and heterogeneous catalysis by HPAs for the conversion of renewable feedstocks. This includes the preparation, characterisation and testing of a range of acidic solid materials such as bulk HPAs,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  and the acidic composites comprising  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (HPW) supported on  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ .

The HPW supported on  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  were prepared by impregnation method and then characterised regarding their acid properties and the chemical structure of HPA on the catalyst surface, compared to “standard” HPA catalysts such as bulk and silica-supported  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ . In contrast to the parent acid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , possessing strong Brønsted acid sites, the catalysts supported on  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  possess both Brønsted and Lewis acid sites, with the latter mainly originating from the oxide support. These catalysts possess weaker acid sites than  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , with their acid strength being similar to that of acidic zeolites. The catalytic activity (turnover frequency) in gas-phase isopropanol dehydration decreases in the order:  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} > 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2 > 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2 \gg 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5 > 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ , which is in line with the acid strength determined by  $\text{NH}_3$  adsorption calorimetry.  $^{31}\text{P}$  MAS NMR and FTIR indicate an increasing interaction between support and HPA in the following order:  $\text{SiO}_2 < \text{TiO}_2 < \text{Nb}_2\text{O}_5, \text{ZrO}_2$ , whilst the strength of acid sites decreases in that order.

Esterification of hexanoic acid and transesterification of ethyl propanoate and ethyl hexanoate with excess methanol (1:20 molar ratio) were tested at 60 °C and ambient pressure with a range of HPA catalysts in homogeneous and heterogeneous systems in comparison with conventional homogeneous and solid acid catalysts such as  $\text{H}_2\text{SO}_4$ , Amberlyst-15 and zeolites HY and H-Beta. In these reactions, the intrinsic catalytic activity (turnover frequency, TOF) of HPA catalysts is significantly higher than that of the conventional acid catalysts. The TOF values decrease with decreasing catalyst acid strength in the order:  $\text{H}_3\text{PW}_{12}\text{O}_{40} \approx \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Nb}_2\text{O}_5, 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2, 15\%\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{TiO}_2 > \text{H}_2\text{SO}_4 > \text{HY}, \text{H-Beta} > \text{Amberlyst-15}$ . Supported HPA catalysts suffer from leaching and exhibit significant contribution of homogeneous catalysis by the leached HPA.

The isomerisation of  $\alpha$ -pinene is studied in the gas phase over solid HPA catalysts in a fixed bed continuous flow reactor at 200°C and ambient pressure. The reaction yields camphene as the main product in a mixture with monoterpene by-products such as limonene, terpinolenes, terpinenes,  $\beta$ -pinene, p-cymene and others. The strong Brønsted solid acids exhibit high initial activities, but suffer from catalyst deactivation, resulting in low camphene yields. Conversely, the HPA catalysts supported on  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ , although weaker acids, show more stable performance in  $\alpha$ -pinene isomerisation.