



Deoxygenation of propionic acid on heteropoly acid and bifunctional metal-loaded heteropoly acid catalysts: Reaction pathways and turnover rates

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ABSTRACT

Reaction pathways of the gas-phase deoxygenation of propionic acid in the presence of heteropoly acid and bifunctional metal-loaded heteropoly acid catalysts were investigated in a fixed-bed reactor at 250–400 °C in flowing H₂ or N₂. Silica-supported H₃PW₁₂O₄₀ (HPW) and bulk acidic salt Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW), both in H₂ and in N₂, exhibited ketonisation activity between 250 and 300 °C to yield 3-pentanone, CsPW being more selective than HPW. At 400 °C, HPW and CsPW were active for decarbonylation and decarboxylation of propionic acid to yield ethene and ethane, respectively. Loading Pd or Pt onto CsPW greatly enhanced decarbonylation in flowing H₂ but had little effect in N₂. Similar performance exhibited Pd/SiO₂ and Pt/SiO₂, giving almost 100% selectivity to ethene in H₂. These results are consistent with hydrodeoxygenation of propionic acid on Pd and Pt, suggesting that hydrogenolysis of C–C bond plays essential role. In contrast to the Pd and Pt catalysts, Cu catalysts, Cu/CsPW and Cu/SiO₂, were both active in hydrogenation of C=O bond to yield propanal and 1-propanol. Turnover rates of propionic acid conversion on metal catalysts followed the order Pd > Pt > Cu for both CsPW-supported and silica-supported metal catalysts.

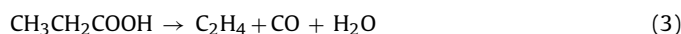
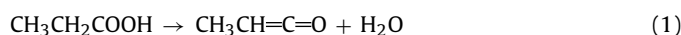
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1. Introduction

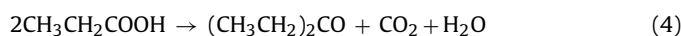
Carboxylic acids are readily available from natural resources and are attractive as renewable raw materials for the production of value-added chemicals and biofuel components [1,2]. For fuel applications, carboxylic acids require reduction in their oxygen content, i.e., deoxygenation [3]. Therefore, much recent research has been focussed on deoxygenation of carboxylic acids using heterogeneous catalysis [4–10].

Previously, thermal and catalysed decomposition of lower C₁–C₃ acids in the gas phase had been addressed in considerable detail ([11–14] and references therein). The decomposition of formic acid is straightforward due to simplicity of this molecule. In the case of acetic and propionic acids, that are more relevant to biomass-derived higher carboxylic acids, the products are more varied reflecting a wider variety of the possible reaction pathways. Both dehydration via C–O bond cleavage and decarboxylation via C–C bond cleavage occur in the pyrolysis of C₁–C₃ carboxylic acids. Thus propionic acid between 496 and 580 °C dehydrates to form methylketene (Eq. (1)), simultaneously decarboxylating to produce CO₂ and ethane (Eq. (2)) [8]. Further decomposition of methylketene gives CO and ethene together with other

hydrocarbon products, resulting in decarbonylation of propionic acid (Eq. (3)) [11,12].



In catalysed decomposition of carboxylic acids the process depends on the catalyst. On metal surfaces, the decomposition may occur via surface carboxylate intermediates [13,14]. Surface acetate species give ketene by dehydrogenation accompanied by C–O bond cleavage, as well as CO₂ and CH₄ by C–C bond cleavage. On metal oxide surfaces carboxylic acids adsorb both in molecular form and as carboxylates. These surface species may decompose via dehydration and/or decarboxylation giving ketene, CO₂, CO and hydrocarbons. Principal decomposition products on metal oxide catalysts often include ketones with 2n – 1 carbon atoms such as acetone and 3-pentanone for acetic and propionic acid, respectively (Eq. (4)) [13,15].



Current studies on catalysed deoxygenation of higher carboxylic acids have been focussed on liquid-phase and gas-phase processes, either in the presence of H₂ (hydrodeoxygenation) or in hydrogen-free systems [4–10]. The principal concern has been to discover active catalysts that are selective towards deoxygenation and

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