



Dehydration of ethanol over heteropoly acid catalysts in the gas phase



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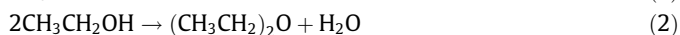
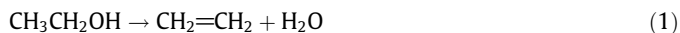
ABSTRACT

Dehydration of ethanol was studied at a gas–solid interface over a wide range of solid Brønsted acid catalysts based on Keggin-type heteropoly acids (HPAs) in a continuous flow fixed-bed reactor in the temperature range of 90–220 °C focussing on the formation of diethyl ether (DEE). The catalysts included $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW) supported on SiO_2 , TiO_2 , Nb_2O_5 and ZrO_2 with sub-monolayer HPA coverage, as well as bulk acidic Cs salts of HPW ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.25}\text{H}_{0.75}\text{PW}_{12}\text{O}_{40}$) and the corresponding core–shell materials with the same total composition (15%HPW/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and 25%HPW/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, respectively) comprising HPW supported on the neutral salt $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. The ethanol-to-DEE reaction was found to be zero order in ethanol in the range of 1.5–10 kPa ethanol partial pressure. The acid strength of catalysts was characterised by ammonia adsorption microcalorimetry. A fairly good correlation between the catalyst activity (turnover frequency) and the catalyst acid strength (initial enthalpy of ammonia adsorption) was established, which demonstrates that Brønsted acid sites play important role in ethanol-to-DEE dehydration over HPA catalysts. The acid strength and the catalytic activity of core–shell catalysts HPW/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ did not exceed those of the corresponding bulk Cs salts of HPW with the same total composition, which contradicts the literature claims of the superiority of the core–shell HPA catalysts.

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1. Introduction

The dehydration of ethanol (Eq. (1) and (2)) has long been of interest to produce ethene and diethyl ether (DEE) from non-petroleum renewable feedstock [1]. In the last decade, this reaction has attracted significant attention in the context of sustainable development [2]. Ethene is the feedstock for about 30% of all petrochemicals [3], and diethyl ether is a valuable chemical and a green transportation fuel alternative [4]. Typically, the dehydration of ethanol is carried out in the gas phase in the presence of solid acid catalysts such as metal oxides and zeolites [5–8]. DEE is the thermodynamically favored product; it is predominantly formed at lower temperatures, whereas the selectivity to ethene increases with increasing reaction temperature at the expense of DEE.



Heterogeneous acid catalysis by heteropoly acids (HPAs) has attracted much interest in both fundamental and applied research because of its potential to generate significant economic and environmental benefits [9–13]. The majority of catalytic applications use the most stable and easy available Keggin HPAs comprising

heteropoly anions of the formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$, where X is the heteroatom (P^{V} , Si^{IV} , etc.) and M is the addendum atom (Mo^{VI} , W^{VI} , etc.). HPAs possess strong Brønsted acidity superior to that of conventional solid acid catalysts such as acidic oxides and zeolites. Amongst various heteropoly acids, tungsten HPAs are usually chosen as acid catalysts because of their stronger acidity and higher thermal stability compared to molybdenum HPAs [9–13]. HPAs and their acidic salts have been applied as the catalysts for ethanol dehydration and found to exhibit higher catalytic activities than the oxide and zeolite catalysts [14–16].

The aim of this work was to investigate a wide range of HPA-based catalysts in ethanol dehydration at a gas–solid interface focusing on the formation of DEE rather than ethene, which has been the target of much previous work. In particular, we looked at the effect of catalyst acid strength on the turnover rate of this reaction. Amongst the catalysts studied are $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (HSiW) supported on SiO_2 , TiO_2 , Nb_2O_5 and ZrO_2 with sub-monolayer HPA coverage. Also we studied bulk acidic Cs salts of HPW ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.25}\text{H}_{0.75}\text{PW}_{12}\text{O}_{40}$, thereafter abbreviated as $\text{Cs}_n\text{H}_{3-n}\text{PW}$) and the corresponding core–shell materials with the same total composition (15%HPW/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ and 25%HPW/ $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, respectively) comprising HPW supported on the neutral salt $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$. It has been claimed that the core–shell catalysts are superior to the bulk Cs salts regarding their acid strength and catalytic activity [17].

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2. Experimental

2.1. Chemicals and catalysts

Ethanol ($\geq 99.8\%$) and other chemicals were obtained from Aldrich and used as supplied without further purification.

Preparation of catalysts and supports and catalyst characterisation techniques have been described elsewhere [18,19]. Catalyst supports P25 titania (anatase/rutile = 3:1) and Aerosil 300 silica were from Degussa. ZrO_2 and Nb_2O_5 oxides were prepared in-house [18] and calcined at 400 °C in air for 5 h. Supported HPA catalysts were prepared by wet impregnation of the oxide supports with an aqueous HPA solution [18] and calcined at 150 °C/ 10^{-3} kPa for 1.5 h.

The caesium salts $Cs_nH_{3-n}PW_{12}O_{40}$ ($n = 2.25, 2.5$ and 3) were prepared according to the literature procedure [20] by adding dropwise the required amount of aqueous solution of caesium carbonate (0.47 M) to aqueous solution of $H_3PW_{12}O_{40}$ (0.75 M) at room temperature with stirring. The precipitate obtained was aged in aqueous mixture for 48 h at room temperature and dried in a rotary evaporator at 45 °C/3 kPa and after that in an oven at 150 °C/ 10^{-3} kPa for 1.5 h.

The core-shell catalysts 15%HPW/ $Cs_3PW_{12}O_{40}$ and 25%HPW/ $Cs_3PW_{12}O_{40}$ were prepared by wet impregnation of $Cs_3PW_{12}O_{40}$ powder with the required amount of HPW aqueous solution, followed by drying in a rotary evaporator at 45 °C/3 kPa and after that in an oven at 150 °C/ 10^{-3} kPa for 1.5 h. The $Cs_3PW_{12}O_{40}$ support was pre-calcined at 300 °C in air for 3 h to harden its structure.

The catalysts prepared were ground and sieved to 45–180 μm particle size. Their texture is given in Table 1.

2.2. Catalyst characterisation

The texture of catalysts (specific surface area and porosity) was characterised by the BET method from nitrogen physisorption measured at -196 °C on a Micromeritics ASAP 2010 instrument.

Before analysis, the samples were evacuated in situ at 250 °C for 3 h.

Differential heats of ammonia adsorption on the catalysts were measured at 150 °C and ambient pressure by a pulse method in a gas flow system using a Setaram C80 Calvet calorimeter fitted with a Metrohm DMS Titrino 716 titrator (Supplementary Information, Fig. S1). Catalyst samples (0.5–1 g) were placed in a stainless steel percolation cell of 2.8 cm^3 volume (Fig. S2), which was set in the sample compartment of the C80 calorimeter and pre-treated in situ at 150 °C in dry nitrogen flow (20 $mL\ min^{-1}$) for 1.5 h. After temperature and heat flux stabilisation, the measurement of adsorption heat was performed by successive pulses of gaseous ammonia (0.5 mL, 0.02 mmol) into the N_2 flow using a stainless steel loop fitted in a 10 port Valco valve. Sufficient time (~ 30 min) was allowed after each pulse for adsorption equilibrium to be established. Precise amount of ammonia in the pulse was determined by titration with sulphamic acid (see below) in a blank test. The downstream gas flow after the sample cell was passed through the titration vessel (50 mL) containing an aqueous buffer solution made of 1 M NH_4Cl (15 mL) and saturated boric acid (1 mL) to absorb any ammonia broken through the catalyst sample. This ammonia was titrated with 0.01 M aqueous solution of sulphamic acid using a Metrohm combined pH glass electrode with an end point set at pH 5.0, as described elsewhere [21]. The amount of ammonia adsorbed was determined as the difference between the amount of ammonia supplied in the pulse and the amount of ammonia broken through the sample cell. From these results, the differential enthalpies of ammonia adsorption per mole of ammonia adsorbed were obtained. Extrapolation of these values to zero ammonia uptake gave the initial enthalpy of ammonia adsorption, ΔH_{NH_3} . Typically, in the first 4–5 pulses, the entire ammonia supplied was adsorbed on the catalyst sample, without any ammonia breakthrough observed. This allowed accurate determination of the ΔH_{NH_3} values without the need of ammonia titration. The mean absolute error in ΔH_{NH_3} was found to be ± 3 $kJ\ mol^{-1}$. The measurement procedure is illustrated in Figs. S3 and S4.

Table 1
Catalyst characterisation.

| Catalysts ^a | S_{BET}^b ($m^2\ g^{-1}$) | Pore volume ^c ($cm^3\ g^{-1}$) | Pore size ^d (\AA) | $\Delta H_{NH_3}^f$ ($kJ\ mol^{-1}$) |
|------------------------|-------------------------------|---|---|--|
| Nb_2O_5 | 183 | 0.15 | 33 | |
| ZrO_2 | 107 | 0.10 | 39 | |
| TiO_2 (P25 Degussa) | 44 | 0.10 | 90 | |
| SiO_2 (Aerosil 300) | 300 ^e | | | |
| HPW | 2 | 0.04 | 81 | −197 |
| Cs_3PW | 145 | 0.11 | 31 | |
| $Cs_{2.25}H_{0.75}PW$ | 128 | 0.07 | 22 | −162 |
| $Cs_{2.5}PW$ | 132 | 0.10 | 29 | −164 |
| 15%HPW/ Cs_3PW | 130 | 0.09 | 29 | −151 |
| 25%HPW/ Cs_3PW | 116 | 0.07 | 24 | −165 |
| 15%HPW/ Nb_2O_5 | 126 | 0.11 | 34 | −132 ^g |
| 15%HPW/ ZrO_2 | 109 | 0.09 | 36 | −121 ^g |
| 15%HPW/ TiO_2 | 45 | 0.20 | 174 | −143 ^g |
| 5%HPW/ SiO_2 | 235 | 0.86 | 146 | |
| 10%HPW/ SiO_2 | 237 | 1.02 | 173 | |
| 15%HPW/ SiO_2 | 202 | 1.00 | 169 | −154 ^g |
| 20%HPW/ SiO_2 | 213 | 0.81 | 152 | |
| 5%HSiW/ SiO_2 | 168 | 0.76 | 181 | |
| 10%HSiW/ SiO_2 | 244 | 1.16 | 191 | |
| 15%HSiW/ SiO_2 | 221 | 1.02 | 185 | −154 |
| 20%HSiW/ SiO_2 | 200 | 0.90 | 180 | |

^a All HPA catalysts calcined at 150 °C under vacuum for 1.5 h; in-house made supports ZrO_2 and Nb_2O_5 calcined at 400 °C in air for 5 h and Cs_3PW at 300 °C in air for 3 h.

^b BET surface area.

^c Single point total pore volume.

^d Average BET pore diameter.

^e Manufacturer's value.

^f Initial enthalpy of NH_3 adsorption at 150 °C (± 3 $kJ\ mol^{-1}$).

^g From [18].

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