Dehydration of methanol and ethanol over silica-supported heteropoly acids in the gas phase: surface-type versus bulk-type catalysis mechanism

Rawan Al-Faze (Investigation)<ce:contributor-role>Writing – original draft), Amy Finch (Investigation), Elena F. Kozhevnikova (Supervision) (Methodology), Ivan V. Kozhevnikov (Conceptualization) (Supervision)<ce:contributor-role>Writing – review and editing)



PII:	S0926-860X(20)30142-3
DOI:	https://doi.org/10.1016/j.apcata.2020.117549
Reference:	APCATA 117549
To appear in:	Applied Catalysis A, General
Received Date:	9 March 2020
Revised Date:	29 March 2020
Accepted Date:	30 March 2020

Please cite this article as: AI-Faze R, Finch A, Kozhevnikova EF, Kozhevnikov IV, Dehydration of methanol and ethanol over silica-supported heteropoly acids in the gas phase: surface-type versus bulk-type catalysis mechanism, *Applied Catalysis A, General* (2020), doi: https://doi.org/10.1016/j.apcata.2020.117549

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

Dehydration of methanol and ethanol over silica-supported heteropoly acids in

the gas phase: surface-type versus bulk-type catalysis mechanism

Rawan Al-Faze,^{a,b} Amy Finch,^a Elena F. Kozhevnikova,^a Ivan V. Kozhevnikov^{a*}

^aUniversity of Liverpool, Department of Chemistry, Liverpool L69 7ZD, UK

^bTaibah University, Department of Chemistry, P.O Box 30002, Al-Madinah Al-Munawarah

41147, Saudi Arabia

¹ Corresponding author. Tel.: +44(0)1517942938 *E-mail address: kozhev@liverpool.ac.uk* (I. V. Kozhevnikov)

Graphical abstract



Highlights

- The acid strength of HPA/SiO₂ catalysts increases with HPA loading
- Activity of HPA/SiO₂ in alcohol dehydration scales with H⁺ surface site density
- Activity-H⁺ density correlation supports mechanism of surface-type HPA catalysis

Abstract

Dehydration of MeOH to dimethyl ether and EtOH to diethyl ether and ethene was studied at the gas-solid interface in the presence of bulk and SiO₂-supported Keggin heteropoly acids (HPAs) H₃PW₁₂O₄₀ (PW) and H₄SiW₁₂O₄₀ (SiW) as catalysts. The catalysts were prepared by HPA impregnation from water and MeOH. Their acid strength, texture and structural integrity was characterised using NH₃ adsorption calorimetry, BET, XRD and DRIFT spectroscopy. The strength of acid sites in HPA/SiO₂ catalysts increased monotonously with HPA loading. In the dehydration of MeOH and EtOH, the turnover reaction rate for PW catalysts was higher than for SiW catalysts in agreement with their acid strength. HPA catalysts in alcohol dehydration. The steady-state catalyst activity was found to correlate with the density of catalyst proton surface sites rather than with the HPA loading. This indicates that alcohol dehydration occurred via a mechanism of surface-type HPA catalysis at the gas-solid interface rather than a bulk-type (pseudo-homogeneous) catalysis.

Key words: Methanol; Ethanol; Dehydration; Heteropoly acid; Silica support.

1. Introduction

Dehydration of MeOH to dimethyl ether (DME) and EtOH to diethyl ether (DEE) and ethene (Eq. (1)–(3)) is of significant interest in relation to sustainable development [1]. DME is a multimarket product, which has attracted interest as a supplement to LPG (liquefied petroleum gas) and a clean diesel alternative [2,3]. The dehydration of EtOH has long been of interest to produce ethene and DEE from non-petroleum renewable feedstock [1,4]. Ethene is the feedstock for about 30% of all petrochemicals [5], and DEE is a valuable chemical and a green fuel alternative [6].

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{1}$$

$$CH_3CH_2OH \rightarrow CH_2 = CH_2 + H_2O$$
⁽²⁾

$$2CH_3CH_2OH \rightarrow (CH_3CH_2)_2O + H_2O \tag{3}$$

Typically, the dehydration of MeOH and EtOH is carried out in the gas phase in the presence of solid acid catalysts. Metal oxides, zeolites and heteropoly acids (HPAs) are among the most studied catalysts in these reactions ([7-18] and references therein). HPAs have a higher activity, in agreement with the relative acid strength of these catalysts [8,9,13].

HPAs of Keggin structure, represented by the formula $H_{8-x}[X^{x+}M_{12}O_{40}]$ (X = P⁵⁺ or Si⁴⁺, M = W⁶⁺ or Mo⁶⁺), are very strong Brønsted acids. These are widely used as acid catalysts in homogeneous and heterogeneous systems [7,19-22]. The acid strength of bulk solid Keggin HPAs decreases in the order: $H_3PW_{12}O_{40}$ (PW) > $H_4SiW_{12}O_{40}$ (SiW) > $H_3PMo_{12}O_{40}$ (PMo) > $H_4SiMo_{12}O_{40}$ (SiMo) [7,19-22]. The strongest 12-tungstophosphoric acid (PW) and 12tungstosilisic acid (SiW) are the most studied HPAs, and their acid properties are well documented in the literature ([7,8,19-32] and references therein). The most accurate information about HPA acid strength and proton site distribution has been obtained from adsorption microcalorimetry (MC), which provides the heat of adsorption of base probe molecules (e.g., NH₃ and pyridine) as a function of surface coverage [7,8,19-32].

Bulk HPAs have a low surface area $(1-10 \text{ m}^2\text{g}^{-1})$, hence a low density of surface acid sites [7,19-22]. For this reason, supported HPA catalysts are mainly used in heterogeneous acid catalysis. Silica is the most frequently used support because it is relatively inert towards HPAs and available in a wide textural variety. An X-ray spectroscopy study [33] has shown that structural distortion of Keggin unit in supported PW catalysts increases in the series of supports $SiO_2 < TiO_2 < ZrO_2$. Boron nitride has also been reported as an inert support for HPAs, however with a downside of a low surface area [18]. In contrast, basic and amphoteric supports such as MgO and Al₂O₃ are rarely used, as these decrease the acidity of HPAs and may cause

disintegration of HPA structure [7,19-22]. Silica-supported tungsten HPAs have found industrial applications as solid acid catalysts. SiW/SiO₂ is used for the synthesis of ethyl acetate from ethene and acetic acid in vapour-phase processes commercialized by Showa Denko in Japan [34] and BP Chemicals in the UK [35]. A silica-supported HPA catalyst is also used in the Hummingbird[®] technology for the dehydration of bioethanol to polymer grade ethene [36].

Gas-phase dehydration of MeOH and EtOH has been studied extensively [7-18]. The formation DME and DEE is favourable at relatively low temperatures, whereas the more demanding EtOH-to-ethene conversion occurs at higher temperatures. The ethanol-to-ethene dehydration is suggested to proceed through E2 elimination pathway (bimolecular elimination), which involves concerted cleavage of C–O and C–H bonds in alcohol by a pair of acid (H⁺) and base (B⁻) catalyst sites (Scheme 1) [37].

$$CH_3CH_2OH + HB \iff H^{---OH}_{H-C} \longrightarrow CH_2=CH_2 + H_2O + HE$$

Scheme 1. E2 elimination of ethanol to ethene by a pair of acid (H⁺) and base (B⁻) catalyst sites.

The mechanism of alcohol-to-ether dehydration may be represented by associative and dissociative pathways (Scheme 2), both are thought to take place at Brønsted acid sites [12,16]. The associative pathway is a concerted reaction of two alcohol molecules to form ether directly. The dissociative pathway involves initial alcohol adsorption to form a surface alkoxy group with water elimination, followed by reaction with a second alcohol molecule to form ether.



Scheme 2. Associative and dissociative pathways for alcohol-to-ether dehydration.

Kinetics and mechanism of MeOH and EtOH dehydration in the gas phase over HPA catalysts has been the subject of several studies ([8,9,12-15] and references therein). Rigorous mechanistic investigation of MeOH and EtOH dehydration over a series of highly dispersed silica-supported HPAs (5 wt% HPA loading), including reaction kinetics and DFT analysis of elementary steps, has been published [12-14]. Typically, at 100–140 °C, these reactions follow the Langmuir-type rate equation and are zero-order in alcohol at a not too low alcohol partial pressure due to saturation of surface acid sites with alcohol molecules.

In contrast to the finely dispersed supported HPAs, bulk and heavily loaded supported HPAs could catalyse the dehydration of light C₁–C₄ alcohols via a bulk-type (pseudo-homogeneous) mechanism, with all HPA protons, bulk and surface, being catalytically active sites [7]. This is backed by the ability of bulk HPAs to absorb alcohol molecules in large quantities into interstitial space. It has been argued, however, that the bulk-type process would be diffusion controlled [22], hence inconsistent with high activation energies (E_a) of alcohol dehydration. The reported E_a values for MeOH dehydration over bulk PW and SiW are 82 and 85 kJ mol⁻¹ [9]; for i-PrOH dehydration over bulk PW, $E_a = 90$ kJ mol⁻¹ [32]. Linear Brønsted-type correlations between the turnover rates, ln(TOF), and catalyst acid strengths, represented by the initial enthalpies of ammonia adsorption, have been established for MeOH, EtOH and

i-PrOH dehydration over HPA catalysts, which hold for both bulk and supported HPAs [8,9,32]. For MeOH-to-DME dehydration, this correlation holds for bulk and supported HPAs (15% loading) as well as for HZSM-5 zeolite catalysts, which suggests that the reaction with all these catalysts occurs via the mechanism of surface acid catalysis [9]. On the other hand, it has been reported recently that the bulk-type mechanism may be realized for the dehydration of MeOH over bulk PW if the HPA is thermally pre-treated to remove crystallization water from the interstitial space thus making it available for absorption of MeOH [17].

The aim of this work is to provide new mechanistic insights regarding the role of the bulk-type and surface-type HPA catalysis in MeOH and EtOH dehydration over silica-supported HPA catalysts, PW/SiO₂ and SiW/SiO₂, prepared by HPA impregnation from water and MeOH. We look at the effect of HPA loading and acid strength on the dehydration reactions at conditions relevant to practice (5–100% HPA loading). The acid properties of these catalysts are systematically characterised at a gas-solid interface using ammonia adsorption calorimetry (NH₄⁺–MC and TGA–DSC) complemented by BET, XRD and IR spectroscopic characterisation of catalyst texture and HPA structural integrity.

2. Experimental

2.1. Chemicals

H₃PW₁₂O₄₀ hydrate (99%) was puchased from Sigma–Aldrich and H₄SiW₁₂O₄₀ hydrate (99.9%) was from Fluka; these contained 20–28 H₂O molecules per Keggin unit from thermogravimetric analysis (TGA). Anhydrous MeOH (99.8%), EtOH (99.8%) and 2,6-di-*tert*-butylpyridine (>97%) were purchased from Sigma–Aldrich. Commersioal Aerosil 300 silica support ($S_{BET} \approx 300 \text{ m}^2\text{g}^{-1}$) was from Degussa. NH₃ (99.99% pure) was supplied by the British Oxygen Company.

2.2. Catalyst preparation

Silica-supported HPA catalysts, 5–70% HPA/SiO₂, were prepared by wet impregnation of Aerosil 300 silica (~300 m²g⁻¹ surface area) with aqueous and methanol HPA solutions as described elsewhere [32,38] and dried at 150°C/1 Pa for 1.5 h. Previously, it was found that such catalyst pre-treatment gives best performance in alcohol dehydration [8,9,32] and other low-temperature reactions of polar molecules [20] in terms of both activity and catalyst stability. The catalysts prepared from water are hereafter designated HPA/SiO₂ and those prepared from methanol HPA/SiO₂(m). HPA loading in the catalysts was determined from W analysis by ICP-AES (inductively coupled plasma atomic emission spectroscopy). Water content, essential for acidity and activity characterisation, was determined by TGA. The finished SiO₂-supported catalysts prepared from water exhibited a 5±1% weight loss to 600 °C attributable to the loss of adsorbed water and silanol groups of silica. For comparison, pure Aerosil 300 compacted by wetting with water and dried at 150°C/1 Pa for 1.5 h had a 3.8% weight loss to 600 °C. PW/SiO₂(m) catalysts prepared from MeOH had a 4±1% weight loss to 600 °C largely attributable to water loss, as MeOH would be partly removed and partly dehydrated during catalyst drying. Bulk PW and SiW dried at 150°C/1 Pa for 1.5 h exhibited 4±1% weight loss to 300 °C; this characterised the bulk PW and SiW as hexahydrates. Further catalyst drying was not practical because alcohol dehydration yielded water as a by-product. From TGA, spent HPA catalysts after alcohol dehydration had a similar water content to the fresh catalysts. Moreover, the catalysts dried at higher temperatures (250°C/1 Pa/1.5 h) showed significant decline in activity before reaching steady state, which may be due to adsorption of water formed during alcohol dehydration. Acidity characterisation (see below) was carried out on the catalysts with the specified water content to determine catalyst acid strength at conditions close to reaction conditions. Information about the catalysts prepared is given in Tables 1 and 2.

2.3. Techniques

The surface area and porosity of catalysts was characterised by the BET method from nitrogen physisorption measured at -196 °C on a Micromeritics ASAP 2010 instrument. TGA was carried out on a Perkin Elmer TGA-7 instrument under nitrogen atmosphere. Powder X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical Xpert diffractometer with CuK α radiation ($\lambda = 1.542$ Å) and attributed using the JCPDS database. DRIFT (diffuse reflectance infrared Fourier transform) spectra were recorded on a Nicolet Nexus FTIR spectrometer using powdered catalyst mixtures with KBr. The spectra were recorded at room temperature by averaging 254 scans in the range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹. The ICP–AES analysis of catalysts was carried out on a Spectro Ciros ICP–AES instrument; catalyst samples were digested by boiling in aqueous 15% KOH.

Ammonia adsorption on HPA catalysts was measured using a Setaram TG-DSC 111 differential scanning calorimeter by a pulse method in a flow system (N₂ carrier gas) as described previously [32]. Catalyst samples (20–80 mg) were placed in the calorimeter and pre-treated under nitrogen flow (30 mL min⁻¹) at 150 °C. After sample weight stabilization (~1 h), the measurement was performed at 150 °C by successive 2–5 mL pulses of pure ammonia into the N₂ flow using a loop fitted in a 6-port valve. Sufficient time was allowed after each pulse for adsorption equilibrium to be reached (~30 min). Weight gain due to NH₃ adsorption and the corresponding heat of adsorption were recorded, from which the total amount of NH₃ adsorbed and the average enthalpy of NH₃ adsorption (ΔH) were determined.

Table 1

Information about PW/SiO₂ catalysts.

Catalyst ^a	Surface	Pore	Pore	d ^e	HPA	$-\Delta H_{ m o}{}^{ m g}$	NH_3/KU^h
	area ^b	volume ^c	diameter ^d	g cm ⁻³	partical size ^f	kJ mol ⁻¹	
	m^2g^{-1}	cm ³ g ⁻¹	Å		nm		
SiO ₂ ⁱ	283	1.2	164	0.38			
$SiO_2(m)^j$	279	0.7	94	0.21			
5.8% PW/SiO ₂	265	1.1	161	0.34		137	
11% PW/SiO ₂	237	1.1	189	0.38		166	2.9
$19\% PW/SiO_2$	233	1.0	166	0.39		169	2.4
16%PW/SiO ₂ (m)	226	0.6	100	0.19	16	167	
$26\% PW/SiO_2$	188	0.8	178	0.46	13	167	2.7
24%PW/SiO ₂ (m)	193	0.5	98	0.23	18	175	
$45\% PW/SiO_2$	153	0.7	177	0.56	18	177	2.5
48%PW/SiO ₂ (m)	152	0.4	99	0.32	20	175	
68% PW/SiO ₂	104	0.4	140	0.87	24	192	2.1
66%PW/SiO ₂ (m)	101	0.2	88	0.53	22	184	
PW	5.7	0.01	74	3.25	56	203	2.4
PW (300 °C) ^k						144	2.7

^a PW/SiO₂ catalysts prepared by impregnation from water and PW/SiO₂(m) from methanol, both calcined at 150°C/1 Pa for 1.5 h; HPA loading from ICP analysis; prior to BET analysis, the catalysts pre-treated at 250 °C in vacuum. ^b BET surface area per gram of catalyst. ^c Single point total pore volume at $p/p_o = 0.97$ per gram of catalyst. ^d Average BET pore diameter. ^e Bulk density of catalyst powder. ^f From XRD, calculated using the Scherrer equation. ^g Initial enthalpy of NH₃ adsorption from NH₃-MC at 150 °C, average values from 2–3 measurements (±6 kJ mol⁻¹); the catalysts pre-treated at 150 °C. ^h Molecules of NH₃ adsorbed per Keggin unit from TGA–DSC; the catalysts pre-treated at 150 °C. ⁱ Aerosil 300 compacted by wetting with water and dried at 150°C/1 Pa for 1.5 h. ^j Aerosil 300 compacted by wetting with methanol and dried at 150°C/1 Pa for 1.5 h. ^k ΔH_0 from TGA–DSC at 150 °C; prior to measurement, PW pre-treated at 300 °C.

Table 2

Information about SiW/SiO₂ catalysts.

Catalyst ^a	Surface	Pore	Pore	d^{e}	HPA	$-\Delta H_{ m o}{}^{ m g}$	NH ₃ /KU ^h
	area ^b	volume ^c	diameter ^d	g cm ⁻³	partical size ^f	kJ mol ⁻¹	
	m ² g ⁻¹	cm ³ g ⁻¹	Å		nm		
5.8%SiW/SiO ₂	259	1.0	150	0.32		138	
11%SiW/SiO ₂	242	1.0	170	0.36		152	3.5
$17\% SiW/SiO_2$	225	0.9	160	0.36	8.3	156	3.7
$27\% SiW/SiO_2$	184	0.8	163	0.44	11	153	3.9
$46\% SiW/SiO_2$	143	0.5	146	0.56	15	157	3.7
$71\% SiW/SiO_2$	87	0.3	118	0.96	20	160	3.5
SiW	8.0	0.01	68	3.50	43	177	2.9
SiW (300 °C) ⁱ						138	3.2

^a The catalysts prepared by impregnation from water and calcined at 150°C/1 Pa for 1.5 h; HPA loading from ICP analysis; prior to BET analysis, the catalysts pre-treated at 250 °C in vacuum. ^b BET surface area per gram of catalyst. ^c Single point total pore volume at $p/p_o = 0.97$ per gram of catalyst. ^d Average BET pore diameter. ^e Bulk density of catalyst powder. ^f From XRD, calculated using the Scherrer equation. ^g Initial enthalpy of NH₃ adsorption from NH₃-MC at 150 °C, average values from 2–3 measurements (±6 kJ mol⁻¹); the catalysts pre-treated at 150 °C. ^h Molecules of NH₃ adsorbed per Keggin unit from TGA–DSC; the catalysts pre-treated at 150 °C.

Differential heats of ammonia adsorption on HPA catalysts were measured at 150 °C and ambient pressure by a pulse method in a gas flow system (N₂ flow) using a Setaram C80 Calvet calorimeter fitted with a Metrohm DMS Titrino 716 titrator as described elsewhere [8]. Catalyst samples (0.2–1 g) were pre-treated in situ at 150 °C in dry nitrogen flow (20 mL min⁻¹) for 3 h. After temperature and heat flux stabilization, the measurement of adsorption heat was performed by successive pulses of gaseous ammonia (0.25–0.50 mL, 0.01–0.02 mmol) into the N₂ flow using a stainless steel loop fitted in a Valco valve. Sufficient time (~40 min) was allowed after each pulse for adsorption equilibrium to be established. 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. The latter was

determined by titration with 0.01 M sulfamic acid in aqueous buffer solution made of 1 M NH₄Cl (30 mL) and saturated boric acid (2 mL) using a Metrohm combined pH glass electrode with an end point set at pH 5.0. 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_0 . The mean absolute error in ΔH_0 was within ±6 kJ mol⁻¹. Batch to batch reproducibility was also within this range. Our ΔH_0 values for the bulk PW and SiW were in good agreement with those reported in the literature [25,39,40].

2.4. Catalyst testing

The dehydration of MeOH and EtOH was carried out at 100–160 °C, mainly at 120 °C, under ambient pressure in a Pyrex fixed-bed downflow reactor (9 mm internal diameter) fitted with on-line GC analysis (Varian Star 3400 CX instrument with a flame ionization detector and a 30 m×0.32 mm×0.5 μ m SUPELCOWAX 10 capillary column for MeOH dehydration and CP-WAX 52CB 30 m×0.32 mm×0.5 μ m capillary column for EtOH dehydration) as described previously [8,9]. The temperature in the reactor was controlled by a Eurotherm controller using a thermocouple placed at the top of catalyst bed. The alcohols were supplied by passing nitrogen carrier gas (20 ml min⁻¹) controlled by a Brooks mass flow controller through a saturator, which held liquid anhydrous alcohol at 0 °C (ice bath) to maintain the chosen alcohol partial pressure (3.83 kPa for MeOH and 1.48 kPa for EtOH [41]) unless stated otherwise. Before reaction the catalysts (0.20 g, 45–180 μ m particle size) were pre-treated in situ at the reaction temperature for 1 h in N₂ flow. Bulk PW and SiW catalysts, having high densities, were diluted with 0.1 g silica to achieve plug-flow regime. At regular time intervals (~20 min), the downstream gas flow was analyzed by the on-line GC to obtain alcohol conversion and product selectivity. The selectivity was defined as the percentage of MeOH

converted into DME and EtOH to DEE and ethene taking into account reaction stoichiometry; for example, 100% DME selectivity would mean 1 mole of MeOH converted to form 0.5 mole of DME. The mean absolute percentage error in alcohol conversion was \leq 5%.

Reaction rate (R, mol g⁻¹h⁻¹) was determined as R = XF/W, where X is the fractional conversion of alcohol, W/F (g h mol⁻¹) is the contact time, W is the catalyst weight and F is the inlet molar flow rate of alcohol. At chosen reaction conditions, the reaction order in alcohol was zero (±0.1), hence alcohol conversion was equivalent to the reaction rate. Turnover rates (per accessible Brønsted site) were calculated as explained in the text.

The number of accessible proton sites in HPA catalysts was determined by in-situ titration with 2,6-di-*tert*-butylpyridine (DTBP) during alcohol dehydration [12-14]. DTBP pulses (6.5–13 μ mol, 25–50 μ L of 0.26 M DTBP solution in MeOH or EtOH) were injected using a microsyringe into the gas feed before the reactor at regular time intervals until the reaction was terminated. The DTBP pulses were injected ~15 min prior to sampling the gas flow for on-line GC analysis to allow sufficient time for DTBP adsorption onto the catalyst. The DTBP that passed through the catalyst was absorbed in a trap and analysed by GC. The number of accessible H⁺ sites in the HPA catalysts was assumed to be equal to the amount of DTBP (per mole basis) required to terminate the alcohol dehydration.

3. Results and discussion

3.1. Catalyst texture and HPA structural integrity

The surface area and porosity of bulk HPAs and silica-supported HPA catalysts prepared by wet impregnation of silica with aqueous and methanol HPA solutions is presented in Tables 1 and 2, together with the texture of silica support. It can be seen that the catalyst surface area (per gram of catalyst) decreases monotonously with increasing HPA loading. Analysis shows that this is mainly the result of the addition of dense HPAs to the silica without significant

change of the pore structure. Fig. S1–S3 show that HPA loading had only a small effect on the surface area and the pore volume per gram of silica up to ~70% HPA loading, which corresponds to an average HPA surface coverage of ~2 monolayers (calculated assuming an HPA cross section of 144 Å² [7,20,21] and the surface area of Aerosil 300 silica support of ~300 m²/g). Also the pore diameter practically did not change up to ~50% HPA loading (Fig. S4) This suggests that HPAs did not block the pores in silica support, at least in the range of 0–50% HPA loading which is the most important for practical use of these catalysts.

The PW catalysts prepared from water and MeOH have very close surface areas per gram of catalyst, however their porosity is different (Table 1). Those prepared from water have a pore diameter and pore volume about 2-fold greater than those prepared from MeOH. As a result, given practically the same surface area, the catalysts prepared from water are more compact, having a 2-fold greater bulk powder density (*d*) than the ones prepared from MeOH (Table 1). The same applies to Aerosil 300 silica support (d = 0.054 g cm⁻³): the support compacted with water is more dense (d = 0.38 g cm⁻³) than with MeOH (d = 0.21 g cm⁻³) (Table 1). This is the result of predictably stronger interaction of silica with water than with MeOH.

DRIFT spectra for PW/SiO₂, SiW/SiO₂ and PW/SiO₂(m) catalysts together with the spectra of bulk PW and SiW are shown in Fig. S5–S7. Bulk HPAs display the well-known infrared bands of metal-oxygen stretching vibrations in the range of 700–1100 cm⁻¹ characteristic of Keggin heteropoly anions [1,42]. PW shows four bands at 808 cm⁻¹ (W–O–W edge-sharing), 889 cm⁻¹ (W–O–W corner-sharing), 984 cm⁻¹ (W=O) and 1082 cm⁻¹ (P–O). The corresponding bands for bulk SiW occur at 792 cm⁻¹ (W–O–W edge-sharing), 881 cm⁻¹ (W–O–W corner-sharing), 927 cm⁻¹ (Si–O) and 980 cm⁻¹ (W=O). It can be seen that these bands are present unchanged in the spectra of silica-supported HPAs, except for the bands of P–O at 1082 cm⁻¹ and W–O–W at 808 cm⁻¹ for PW/SiO₂ and PW/SiO₂(m) and the band of W–O–W at 792 cm⁻¹ for SiW/SiO₂, which are obscured by the intense bands of silica centred at 804 and

1108 cm⁻¹. This shows that the structure of Keggin units (primary structure) in all HPA catalysts is largely intact, in agreement with previous reports [31,32].

XRD patterns for PW/SiO₂, SiW/SiO₂ and PW/SiO₂(m) are shown in Fig. S8–S10. In PW/SiO₂ catalysts, PW crystal phase appears from 11% PW loading, whereas in SiW/SiO₂ catalysts, SiW crystallites are seen from a higher SiW loading of 17%. The HPA crystal phase in supported catalysts exhibits the diffraction patterns exactly matching those for the bulk HPAs [7,24,31,39,43,44]. This confirms the structural integrity of PW and SiW on the silica surface, i.e. the same crystal structure of bulk and supported HPA crystallites. The average size of HPA crystallites on the silica surface (Tables 1 and 2) was estimated from the Scherrer equation, with FWHM (full width at half maximum) calculated using the Origin. As expected, the size of PW and SiW crystallites increases with HPA loading. PW crystallites formed from aqueous and methanol solutions at similar PW loadings have a similar size (Table 1), which suggests that these solvents make little difference to HPA crystallization. Notably, the SiW crystallites are smaller than the PW ones at similar HPA loadings, indicating a higher SiW dispersion on the silica surface in comparison to PW. These results point to a higher density of surface proton sites in SiW/SiO₂ catalysts compared to PW/SiO₂ at equal HPA loadings. This is not only because SiW has more protons than PW per Keggin unit, but also due to the higher dispersion of SiW on the silica surface compared to PW. This can affect the activity of these catalysts (see below).

3.2. Acid properties of PW and SiW supported on silica

The acid properties of silica-supported PW and SiW have been documented in the literature, although less systematically than those of the bulk HPAs, especially regarding the

effect of HPA loading on the acid strength ([7,19-23,31] and references therein). This information is important for mechanistic studies of HPA catalysis as well as for catalyst optimization. Most NH₃-MC and NH₃-TPD studies [19-23,29,45] point to decreasing the acid strength when HPA is supported on silica, which is attributed to HPA-support interaction. However, a NH₃-DSC study [31] claims that the strength of PW supported on silica does not depend on the PW loading above 6% and is close to the strength of bulk PW. It should be noted that the calorimetric results from different sources are not easy to compare because the heat and the amount of NH₃ adsorption depend on HPA pre-treatment and adsorption temperature [19,24,25].

¹H and ³¹P MAS NMR studies indicate chemical interaction of PW with SiO₂ support [38,46-49], leading to the formation of weaker proton sites on the silica surface, probably via dehydroxylation reaction (4) with the surface Si–OH groups ($m \le 3$):

$$H_{3}[PW_{12}O_{40}] + m(\equiv Si - OH) \rightarrow (Si)_{m}^{+}(H_{3-m}[PW_{12}O_{40}])^{m} + mH_{2}O$$
(4)

In PW/SiO₂ catalysts prepared by conventional wet impregnation of SiO₂ with a PW aqueous solution, different HPA species have been observed by ³¹P MAS NMR, including those resonating at -15 ppm with intact Keggin structure and others resonating from -13 to -14 ppm [38,48], which may be "interacting" species (=Si $-OH_2^+)_m(H_{3-m}[PW_{12}O_{40}]^{m-})$ [48] or dimeric heteropoly acids $H_6[P_2W_{18}O_{62}]$ or $H_6[P_2W_{21}O_{71}]$ formed from PW in the course of catalyst preparation [38]. The relative amounts of these species depend on the PW loading, the Keggin species by far dominating above 30% loading [38]. In contrast, the PW/SiO₂ catalysts prepared from MeOH solution contain exclusively Keggin-type species over the whole range of PW loading [38]. The formation of "interacting" HPA species may be avoided by immobilizing anhydrous Keggin HPAs onto dehydroxylated SiO₂ support using surface organometallic chemistry [50]. It would be interesting, therefore, to compare the acid strength and the catalytic

activity of the silica-supported HPA catalysts prepared from water and MeOH.

Here we determined the initial enthalpies of ammonia adsorption on bulk and silicasupported PW and SiW catalysts, ΔH_0 , representing the strongest catalyst proton sites, at different HPA loadings from 5 to 100% using NH₃-MC (Table 1 and Table 2). The silicasupported PW and SiW were prepared by impregnating HPAs from aqueous solution. For comparison, PW/SiO₂(m) catalysts prepared from MeOH were also studied.

Previously, several studies have reported the ΔH_o values for bulk PW and SiW [8,24,25,32,39,40]. It has been firmly established that these values depend on the adsorption and pre-treatment temperature. The heat of adsorption ($-\Delta H_o$) decreases when the pre-treatment temperature is increased [24,25,40]. At the same time, the amount of NH₃ adsorbed increases with the pre-treatment temperature [24]. These effects have been correlated with the amount of hydration water present in bulk HPAs. At lower temperatures, larger amounts of water present in HPA can hydrate NH₄⁺ ions, thus increasing the heat of adsorption. Simultaneously, the water can block access for NH₃ molecules to the HPA bulk, thus reducing the amount of NH₃ adsorbed [24]. Within the temperature range of 150–200 °C, the ΔH_o values are typically around -200±10 kJ mol⁻¹ for bulk PW and -180±10 kJ mol⁻¹ for bulk SiW [8,25,32,39,40]. Our results from NH₃-MC, $\Delta H_o = -203\pm6$ kJ mol⁻¹ for PW (Table 1) and -177±6 kJ mol⁻¹ for SiW (Table 2) at the pre-treatment and NH₃ adsorption temperature of 150 °C, are in good agreement with the literature. Increasing the pre-treatment temperature to 300 °C, while keeping the NH₃ adsorption temperature at 150 °C, led to a decrease in the heat of adsorption: $\Delta H_o = -144$ kJ mol⁻¹ for PW (Table 1) and -138 kJ mol⁻¹ for SiW (Table 2), as expected.

Fig. 1 shows the initial heat of NH_3 adsorption ($-\Delta H_0$) as a function of HPA loading. As seen, the strength of HPA catalysts increases monotonously with HPA loading, with PW, as expected, being stronger than SiW at any loading. This trend can be rationalized assuming that HPA-support interaction reducing the strength of HPA proton sites should decline with

increasing HPA loading, thus leading to an increase in the catalyst acid strength. The drop in the adsorption heat below 10% loading may be due to a stronger HPA-support interaction causing partial decomposition or dehydroxylation of HPA by reaction (4). The plots of ΔH_0 versus HPA loading above 10% HPA loading (Fig. 1) can be represented by linear regressions (5) and (6) for PW/SiO₂ and SiW/SiO₂, respectively, where (PW%) and (SiW%) are the HPA loadings in wt%. These regressions can be used for calculating ΔH_0 at any HPA loading above 10% for the catalyst system under study.



Fig. 1. Effect of HPA loading on initial heat of NH₃ adsorption on SiO₂-supported HPAs at 150 °C.

The increase in adsorption heat with HPA loading is significant: by 37 kJ mol⁻¹ for PW/SiO₂ and 25 kJ mol⁻¹ for SiW/SiO₂ as the HPA loading increases from 10 to 100%. This should affect the turnover catalyst activity (per accessible proton site), which, in general, scales with

the catalyst acid strength obeying the Brønsted relationship. This is indeed the case, as demonstrated below for the dehydration of MeOH and EtOH.

The PW/SiO₂ catalysts prepared from water and PW/SiO₂(m) prepared from MeOH have practically the same acid strength at the same PW loading (Fig. 1). Therefore, the dimeric heteropoly acids $H_6[P_2W_{18}O_{62}]$ and $H_6[P_2W_{21}O_{71}]$, if formed [38], do not significantly affect the catalyst acid strength as these HPAs are quite strong themselves [25,26]. From NH₃–MC study [26], bulk $H_6[P_2W_{18}O_{62}]$ is weaker than bulk PW, but silica-supported 20% $H_6[P_2W_{18}O_{62}]/SiO_2$ and 20%PW/SiO₂ have similar acid strengths.

The total ammonia uptake was determined for the HPA/SiO₂ catalysts prepared from water, as well as for bulk PW and SiW, using TGA–DSC. The NH₃ adsorption was measured at 150 °C after catalyst pre-treatment at 150 °C. For the bulk HPAs, it was also measured after pre-treatment at 300 °C (TGA–DSC traces for bulk PW and SiW are shown in Fig. S11 and S12). The results are given in Tables 1 and 2 in terms of the number of NH₃ molecules adsorbed per Keggin unit, NH₃/KU. All supported HPA/SiO₂ catalysts exhibited NH₃ uptakes close to the stoichiometric values, i.e., 3 for PW catalysts and 4 for SiW catalysts, in agreement with previous reports [29,31]. As expected, bulk PW and SiW adsorbed less than stoichiometric amounts of NH₃ after pre-treatment at 150 °C than after pre-treatment at 300 °C, (see the last entries in Table 1 and Table 2).

In summary, our acidity characterisation demonstrates that the acid strength of silicasupported HPA catalysts increases monotonously with HPA loading all the way up to 100% loading. It might have been expected that at high loadings, ~70%, HPA-silica interaction would be minimal, and the protons would be as strong as in the bulk HPA. In fact, at 70% loading, the average HPA coverage of silica surface is only ~2 monolayers, hence the HPA-support interaction should still be significant to affect the acid strength. The question is how can the HPA-silica interaction affect the acid strength of HPA ensembles on the surface? Two

mechanisms can be suggested. The first one is via dehydroxylation reaction (4) with the surface Si-OH groups. The second, and more important one, arises from the fact that protons generally tend to reside on the most basic sites. In bulk HPA, the surface protons are located on the bridging outer oxygen atoms in the Keggin anion [20, 40]. In silica-supported HPA, the protons are likely to be located on the neighbouring oxygen atoms of support, which are more basic than the outer oxygen atoms in the Keggin anion. Fast proton mobility in bulk HPAs is well documented; the proton mobility is accelerated by water present in HPA [7,20-22]. The presence of water in HPA/SiO₂ catalysts should, therefore, enhance proton migration from the Keggin anion to the neighbouring oxygen atoms of silica. A previous ¹H MAS NMR study [46] has reported different proton locations in bulk and silica-supported PW. Bulk PW exhibits a signal of strong proton sites at 9.3 ppm. In the spectrum of PW/SiO₂, only the signal of silanol groups at 1.8 ppm can be seen up to 20% PW loading. 37% PW/SiO₂ shows a signal at 5.0 ppm from weaker proton sites. The signal of strong protons at 9.3 ppm appears only above 50% PW loading. This shows that proton sites in PW/SiO₂ have a different chemical structure from the bulk PW. It has been suggested that in PW/SiO₂, the proton sites are located on silanol (A) and siloxane (B) groups of silica rather than on the outer oxygen atoms in the $PW_{12}O_{40}^{3-}$ polyanion [38,52]:

$$\begin{pmatrix} -S_{i} - OH_{2}^{+} \end{pmatrix} (H_{3-n}[PW_{12}O_{40}]^{n-}) \qquad \begin{pmatrix} -S_{i} \\ -S_{i} \\ -S_{i} \end{pmatrix} (H_{3-n}[PW_{12}O_{40}]^{n-})$$

$$A \qquad B$$

Bulk and supported HPA catalysts exhibit different compensation affects in isopropanol dehydration, which has been attributed to the different chemical structures of surface proton sites in these catalysts [51].

3.3. Effect of HPA loading in dehydration of MeOH and EtOH over HPA/SiO₂ catalysts

Here we examined the effect of HPA loading and acid strength on alcohol conversion and product selectivity in the dehydration of MeOH to DME and EtOH to DEE and ethene (Eq. (1) - (3)) at the gas-solid interface over HPA/SiO₂ catalysts over a wide range of HPA loadings (5–100%), seeking to provide new mechanistic insights regarding the role of bulk-type and surface-type HPA catalysis in these reactions. The dehydration reactions were mainly carried out 120 °C at low to medium alcohol conversions to keep the reactions under kinetic control. Typically, the reaction time was 4 h, during which practically no catalyst deactivation was observed (see reaction time courses in Fig. S13–S15). PW and SiW retained the Keggin structure after reaction, as shown by DRIFT spectroscopy of spent HPA/SiO₂ catalysts. Representative results on the effect of HPA loading on steady-state alcohol conversion and product selectivity at a constant contact time *W/F* are shown in Fig. 2–4.

As can be seen from Fig. 2, MeOH conversion for both PW and SiW catalysts passes through a maximum at an HPA loading between 25 and 70%. This shows that catalyst activity scales with the number of surface proton sites in HPA/SiO₂ catalysts, which follows a similar trend passing a maximum at 40–50% HPA loading [45]. Notably, SiW catalysts have a slightly higher activity than PW catalysts in terms of the conversion per gram of catalyst despite the opposite order of their acid strength. For both catalysts, the selectivity to DME was 100%, no other products observed. Similar results were obtained for HPA/SiO₂(m) catalysts prepared from MeOH (Fig. S16). The higher activity of SiW than PW per catalyst weight can be explained by the larger density of accessible proton sites in SiW catalysts than in PW ones. This is because SiW has the larger number of protons per Keggin unit and the higher dispersion on the silica surface compared to PW (see Sect. 3.1). The turnover reaction rate for PW catalysts, however, is higher than for SiW catalysts in agreement with their acid strength (see below).



Fig. 2. Effect of HPA loading on MeOH-to-DME conversion over silica-supported HPA (0.20 g catalyst, 120 °C, 3.83 kPa MeOH pressure, 20 mL min⁻¹ N₂ flow rate, contact time W/F = 105 g h mol⁻¹, 4 h time on stream; 100% DME selectivity in all cases).

PW/SiO₂(m) catalysts prepared from MeOH exhibited similar activities to PW/SiO₂ prepared from water (Fig. 3) in agreement with their similar acid strengths (Fig. 1); the same was observed for SiW/SiO₂(m) and SiW/SiO₂ catalysts (Fig. S17).



Fig. 3. Effect of HPA loading on MeOH-to-DME conversion over PW/SiO₂ prepared from water and PW/SiO₂(m) prepared from MeOH (0.20 g catalyst, 120 °C, 3.83 kPa MeOH

pressure, 20 mL min⁻¹ N₂ flow rate, contact time W/F = 105 g h mol⁻¹, 4 h time on stream; 100% DME selectivity in all cases).

EtOH dehydration showed similar activity trends to MeOH dehydration (Fig. 4A), with SiW also more active than PW per catalyst weight. The selectivity to ethene scaled with EtOH conversion (Fig. 4B), passing a maximum, whereas the selectivity to DEE, as expected, was a mirror image of the ethene selectivity. PW catalysts gave a higher ethene selectivity than SiW catalysts despite the higher EtOH conversion for the SiW catalysts. It has been shown that the selectivity depends not only on the catalyst acid strength and the number of accessible proton sites, but also on the geometry of, and local charges in, the transition states, which are likely to be different for PW and SiW catalysts [14].



Fig. 4. Effect of HPA loading on EtOH conversion (A) and DEE and ethene selectivity (B) over silica-supported HPA (0.20 g catalyst, 120 °C, 1.48 kPa EtOH partial pressure, 20 mL min⁻¹ N₂ flow rate, contact time W/F = 271 g h mol⁻¹, 4 h time on stream).

Overall, these results show that HPA loading of about 25% is an optimum one to achieve the maximum MeOH and EtOH conversion; further increase in HPA loading gives no significant rise in alcohol conversion. However, ethene selectivity in EtOH dehydration peaks at about 70% HPA loading (Fig. 4B). In these experiments performed at 120 °C, the maximum ethene selectivity was 60% at 80% EtOH conversion. The selectivity to ethene reached 100% at 100% EtOH conversion (100% ethene yield) at 160 °C and W/F = 271 g h mol⁻¹ for 26% PW/SiO₂ and 27% SiW/SiO₂ catalysts. For comparison, one of the most active zeolites, HZSM-5 (Si/Al = 12.5), gives 98% ethene yield at 220 °C [52].



Fig. 5. Arrhenius plots for MeOH dehydration over 26%PW/SiO₂ (dotted line) and 27%SiW/SiO₂ (solid line) (HPA/SiO₂ catalysts (0.05 g) diluted with SiO₂ (0.15 g), 3.83 kPa MeOH partial pressure, 20 mL min⁻¹ N₂ flow rate, *W/F* = 26 g h mol⁻¹; *R* is the reaction rate in mol g⁻¹h⁻¹); *E*_a = 79 kJ mol⁻¹ for 26%PW/SiO₂ and 74 kJ mol⁻¹ for 27%SiW/SiO₂.

With the optimum HPA catalysts, 26% PW/SiO₂ and 27% SiW/SiO₂, the dehydration of MeOH and EtOH was zero order in alcohol at 120 °C and 1.5–21 kPa alcohol partial pressure. From zero-order kinetics, MeOH dehydration had a true activation energy (E_a) of 79 kJ mol⁻¹ for 26% PW/SiO₂ and 74 kJ mol⁻¹ for 27% SiW/SiO₂ in the temperature range of 110–140 °C (see the Arrhenius plots in Fig. 5). EtOH dehydration had the same activation energy $E_a = 72$ kJ mol⁻¹ for both catalysts in this temperature range. The high E_a values indicate no diffusion limitations in these reaction systems, which is also supported by the Weisz–Prater analysis reported previously [9]. These results are in agreement with previous reports on alcohol dehydration on supported HPA catalysts with sub-monolayer HPA loadings [8,9].

3.4. Mechanistic considerations

The finding that the steady-state alcohol conversion passes a maximum upon increasing the HPA loading at a constant contact time (Fig. 2–4) has an important mechanistic implication. It shows that the catalyst activity scales primarily with the number of surface proton sites (H⁺ surface site density) rather than with HPA loading or HPA acid strength (the latter increases with HPA loading (Fig. 1)). The H⁺ surface site density in HPA/SiO₂ catalysts is well known to go through a maximum at a medium HPA loading; it increases with HPA loading up to 40– 50% and then declines at higher HPA loadings due to the sharp decrease in catalyst surface area to less than 10 m²g⁻¹ for bulk HPA [45]. Thus in SiW/SiO₂ catalysts, the proton surface site density peaks at 50% SiW loading, as found using adsorption of benzonitrile, which adsorbs only on the surface proton sites [45]. The activity of this catalyst in n-butane isomerization and 1-butene double bond migration occurring via surface-type catalysis correlates with the proton surface site density [45].

The number of surface proton sites accessible for alcohol molecules in HPA/SiO₂ catalysts was determined by in-situ titration with 2,6-di-*tert*-butylpyridine (DTBP) during

alcohol dehydration using a modified pulse method based on the titration procedure previously applied for finely dispersed HPA/SiO₂ and zeolites [12-14,53,54]. Sterically hindered DTBP, unable to penetrate into HPA bulk, titrates only surface H⁺ sites in HPA [12-14]; it does not titrate Lewis acid sites. Previous studies [12,14] have found an under stoichiometric number of active H⁺ in 5% HPA/SiO₂ for dehydration of MeOH and EtOH: 2.0–2.5 and 1.9–3.0 per PW and SiW Keggin unit, respectively. The loss of HPA protons may be explained by the dehydroxylation reaction (4) [12]. At a higher PW loading, in 10% PW/SiO₂, all three PW protons have been found active in EtOH dehydration, and the result did not depend on the alcohol partial pressure [14].



Fig. 6. Titration with 2,6-di-*tert*-butylpyridine (6.5 μ mol DTBP injections at each point starting at 100 min time on stream) during EtOH dehydration over 26%PW/SiO₂ (0.20 g catalyst, 140 °C, 13.6 kPa EtOH pressure, 20 mL min⁻¹ N₂ flow rate); reaction time course (A) and effect of DTBP uptake per mole of PW (B).

Here, the DTBP titration was used to determine the number of active proton sites in HPA/SiO₂ catalysts accessible for alcohol dehydration over a wide range of HPA loading. The number of active H⁺ sites found was close to the stoichiometric values for 10-30% HPA loading. Fig. 6 shows the DTBP titration during EtOH dehydration over 26%PW/SiO₂. The reaction was completely suppressed at a titrant uptake DTBP/PW = 3.0 mol/mol, which means that all three protons in PW were active and accessible for the reaction. The same result was obtained for MeOH dehydration. Interestingly, in EtOH dehydration, after the first DTBP pulse, a step change in reaction selectivity occurred showing an increase in DEE selectivity at the expense of ethene (Fig. 6). Evidently, DTBP primarily inhibited the more demanding pathway of ethene formation. Similar effect on reaction selectivity was also observed for 27% SiW/SiO₂ catalyst. The DTBP titration during EtOH dehydration over 27% SiW/SiO₂ (Fig. 7) gave an extrapolated titrant uptake DTBP/SiW = 2.8, which tailed further beyond DTBP/SiW \approx 4 to completely terminate the reaction. This may indicate that initially all four protons in H₄SiW₁₂O₄₀ were equivalent and accessible for the reaction. But the last titrated proton in $[HSiW_{12}O_{40}]^{3-}$ may be weaker than the first three and/or less accessible for DTBP, hence required more DTBP for neutralization.

In the case of bulk and supported HPA catalysts with higher HPA loadings (>40%), the addition of DTBP, although greatly reduced alcohol conversion, did not completely terminate the reaction (Fig. S18–S20). Probably alcohol molecules could penetrate through the layer of adsorbed DTBP and react with the protons underneath. Hence for these catalysts it was not possible to accurately measure the number of active proton sites. DRIFT spectrum of bulk PW

catalyst after titration with DTBP during EtOH dehydration (Fig. 8) shows the bands at 1530, 1616 and 3370 cm⁻¹ characteristic of the protonated DTBP [53,54]. The same bands are seen in the spectrum of DTBP adsorbed on bulk PW.



Fig. 7. Titration with 2,6-di-*tert*-butylpyridine (6.5 μ mol DTBP injections at each point) during EtOH dehydration over 27%SiW/SiO₂ showing EtOH conversion versus DTBP uptake per mole of SiW (0.20 g catalyst, 140 °C, 13.6 kPa EtOH pressure, 20 mL min⁻¹ N₂ flow rate).



Fig. 8. DRIFT spectra: (1) DTBP (KBr mixture), (2) DTBP adsorbed on bulk PW (KBr mixture versus KBr + PW background) and (3) spent bulk PW catalyst after titration with DTBP during EtOH dehydration (KBr mixture versus KBr + PW background; see reaction details in Fig. S8). The labelled bands at 1530, 1616 and 3370 cm⁻¹ are attributed to the protonated DTBP.

Table 3

Catalyst	HPA loading	Surface H ^{+ b}	Conversion	$10^3 R^{c}$	TOF ^d	$-\Delta H_o^{\rm e}$
	%	mmol g ⁻¹	%	mol g ⁻¹ h ⁻¹	h ⁻¹	kJ mol ⁻¹
PW/SiO ₂	11	0.12	15	1.4	12	166
	17	0.18	26	2.5	14	167 ^f
	26	0.27	29	2.8	10	167
	100	0.020	6.2	0.59	30	203
SiW/SiO ₂	11	0.15	17	1.6	12	152
	15	0.21	24	2.3	11	152 ^f
	27	0.38	35	3.3	8.9	153
	100	0.037	8.5	0.81	22	177

Dehydration of MeOH over HPA/SiO₂ catalysts.^a

^a 0.20 g catalyst, 120 °C, 3.83 kPa MeOH partial pressure, 20 mL min⁻¹ N₂ flow rate, contact time W/F = 105 g h mol⁻¹. ^b Proton surface site density per gram of catalyst. ^c Reaction rate R = XF/W, where X is the fractional alcohol conversion, F is the inlet molar flow rate of alcohol and W is the catalyst weight. ^d TOF per H⁺ surface site. ^e Initial enthalpy of ammonia adsorption ±6 kJ mol⁻¹. ^f Calculated from Eq. (5) and (6).

Tables 3 and 4 show the density of H^+ surface sites and the initial enthalpies of NH_3 adsorption for the bulk and SiO₂-supported PW and SiW catalysts together with turnover frequencies (TOF) for MeOH and EtOH dehydration. The H^+ density for 11–27% HPA loading was calculated assuming that all HPA protons were accessible, as follows from the DTBP

titration. The H⁺ density for the bulk HPAs was calculated using the Keggin unit cross section of 144 Å² [7,20,21] and the HPA surface area from Table 1 and 2. The H⁺ surface site density increases from 0.12 to 0.27 mmol g⁻¹ for PW/SiO₂ and from 0.15 to 0.38 mmol g⁻¹ for SiW/SiO₂ with increasing HPA loading in the range of 11–27%. For bulk HPAs, the proton site density is 10-fold lower (0.020 and 0.037 mmol g⁻¹ for PW and SiW) – only ~2% of the total number of HPA protons.

Table 4

Catalyst	HPA loading	Surface H ^{+ b}	Conversion	$10^3 R^c$	TOF ^d	$-\Delta H_o^{\rm e}$
	%	mmol g ⁻¹	%	mol g ⁻¹ h ⁻¹	h ⁻¹	kJ mol ⁻¹
PW/SiO ₂	11	0.12	36	1.3	12	166
	19	0.20	50	1.9	9.3	169
	26	0.27	72	2.7	9.8	167
	100	0.020	58	2.1	110	203
SiW/SiO ₂	11	0.15	41	1.5	9.9	152
	17	0.24	56	2.1	8.8	156
	27	0.38	72	2.7	7.1	153
	100	0.037	64	2.4	64	177

Dehydration of EtOH over HPA/SiO₂ catalysts.^a

^a 0.20 g catalyst, 120 °C, 1.48 kPa EtOH partial pressure, 20 mL min⁻¹ N₂ flow rate, contact time W/F = 271 g h mol⁻¹. ^b Proton surface site density per gram of catalyst. ^c Reaction rate R = XF/W, where X is the fractional alcohol conversion, F is the inlet molar flow rate of alcohol and W is the catalyst weight. ^d TOF per H⁺ surface site. ^e Initial enthalpy of ammonia adsorption ± 6 kJ mol⁻¹.

The TOF values for MeOH and EtOH dehydration, determined from zero-order kinetics, are almost constant at lower HPA loadings between 10–30%, where the catalyst acid strength changes very little. The TOF values increase significantly for bulk HPAs: almost 3-fold for MeOH and 10-fold for EtOH dehydration, which is in line with the catalyst acid strength represented by the enthalpy of NH₃ adsorption. PW catalysts have greater turnover rates than SiW catalysts, especially for the bulk HPAs, in agreement with their acid strength. From the TOF values, the reactivity of MeOH and EtOH is very close at relatively low HPA loadings of 10–30%. Unexpectedly, in the case of bulk HPAs, EtOH is 3–4 times more reactive than MeOH. This could be caused by a different adsorption geometry of these alcohols on the surface of bulk crystalline HPAs.

The results obtained clearly show that the steady-state activity of silica-supported HPA catalysts in alcohol dehydration correlates with the density of HPA surface proton sites since both the activity and the proton site density change in parallel with HPA loading. This indicates that under the reaction conditions studied, MeOH and EtOH dehydration over bulk and silica-supported HPA catalysts, prepared from water as well as from MeOH, occurs via the mechanism of surface-type HPA catalysis within the whole range of HPA loading rather than via the bulk-type (pseudo-homogeneous) HPA catalysis. For the bulk-type mechanism, the conversion is expected to scale directly with the HPA loading. This conclusion applies to the typical HPA/SiO₂ catalysts – i.e., those prepared and pre-treated by conventional methods. Such catalysts contain variable quantities of water within the HPA interstitial space resulting from both catalyst preparation and alcohol dehydration. Bulk anhydrous HPAs might absorb alcohol molecules into the interstitial space and possibly initially react through the bulk-type mechanism as claimed elsewhere [17], although once steady state reached, the interstitial space would be filled with water formed in the dehydration reaction. Most of our catalytic activity tests was carried out at 120 °C to keep reactions under kinetic control; at higher reaction

temperatures, more relevant to practice, the bulk-type mechanism appears even less likely due to reduction in total adsorption of alcohol molecules as well as possible diffusion limitations.

Previously, a linear relationship between the turnover frequency of ethanol dehydration over PW and SiW catalysts and the initial enthalpy of NH₃ adsorption, ΔH_o , has been reported [8]. This relationship includes PW supported on SiO₂, TiO₂, ZrO₂ and Nb₂O₅ at a submonolayer coverage of 15%, 15%SiW/SiO₂, as well as acidic salts Cs_{2.5}H_{0.5}PW₁₂O₄₀ and Cs_{2.25}H_{0.75}PW₁₂O₄₀, all operating via the surface-type mechanism [8]. Fig. 9 shows this plot, with our new results for bulk PW and SiW from Table 4 added. Excellent fit of these results into the relationship further strengthens the conclusion about the surface-type mechanism of HPA catalysis in alcohol dehydration.



Fig. 9. Plot of ln (TOF) for ethanol dehydration (TOF in h^{-1}) over HPA catalysts vs. initial heat of NH₃ adsorption (120 °C, 0.2 g catalyst, 1.48 kPa ethanol partial pressure, 20 mL min⁻¹ N₂ flow rate) [8]. The added data for bulk PW and SiW (open circles) are from the present work.

4. Conclusions

In this study, we have examined the effect of HPA loading and acid strength in the dehydration of MeOH and EtOH over HPA/SiO₂ catalysts with a wide range of HPA loadings 5–100% prepared by HPA impregnation from water and MeOH. SiW and PW catalysts show close catalytic activities per HPA weight, with SiW having a slightly higher activity despite its weaker acid strength. This can be explained by the larger number of protons per Keggin unit and the higher dispersion of SiW compared to PW. The turnover reaction rate for PW catalysts is higher than for SiW catalysts in agreement with their acid strength. The catalysts prepared from water and MeOH had a very close acid strength and exhibited similar activities in alcohol dehydration. It has been established that the steady-state catalyst activity correlates with the surface proton site density of silica-supported HPA catalysts rather than with the HPA loading or HPA acid strength. This indicates that alcohol dehydration occurs via the mechanism of surface-type HPA catalysis. This conclusion is further strengthened by fitting the activity of bulk PW and SiW into the activity–acid strength relationship for supported HPA catalysts.

CRediT author statement

Rawan Al-Faze - Investigation, Writing - Original Draft

Amy Finch – Investigation

Elena F. Kozhevnikova - Supervision, Methodology

Ivan V. Kozhevnikov - Conceptualization, Supervision, Writing - Review & Editing

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

We thank Taibah University, Medina, Saudi Arabia for PhD studentship (R. Al-Faze).

References

- A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, Chem. Rev. 107 (2007) 2411-2502.
- [2] T.H. Fleisch, A. Basu, R.A. Sills, Introduction and advancement of a new clean global fuel: The status of DME developments in China and beyond, J. Nat. Gas Sci. Eng. 9 (2012) 94–107.
- [3] F. Pontzen, W. Liebner, V. Gronemann, M. Rothaemel, B. Ahlers, CO₂-based MeOH and DME – Efficient technologies for industrial scale production, Catal. Today 171 (2011) 242–250.
- [4] D. Fan, D.-J. Dai, H.-S. Wu, Ethylene formation by catalytic dehydration of EtOH with industrial considerations, Materials 6 (2013) 101-115.
- [5] K. Weissermel, H.-J. Arpe, Industrial organic chemistry, 4th ed., Wiley–VCH, Weinheim, 2003.
- [6] T. Kito-Borsa, D. A. Pacas, S. Selim, S. W. Cowley, Properties of an EtOH-diethyl etherwater fuel mixture for cold-start assistance of an EtOH-fueled vehicle, Ind. Eng. Chem. Res. 37 (1998) 3366–3374.
- [7] T. Okuhara, N. Mizuno, M. Misono, Catalytic chemistry of heteropoly compounds, Adv. Catal. 41 (1996) 113-252.
- [8] W. Alharbi, E. Brown, E.F. Kozhevnikova, I.V. Kozhevnikov, Dehydration of EtOH over heteropoly acid catalysts in the gas phase, J. Catal. 319 (2014) 174–181.

- [9] W. Alharbi, E.F. Kozhevnikova, I.V. Kozhevnikov, Dehydration of MeOH to dimethyl ether over heteropoly acid catalysts: The relationship between reaction rate and catalyst acid strength, ACS Catal. 5 (2015) 7186–7193.
- [10] A. Ciftci, D. Varisli, C.K. Tokay, N.A. Sezgi, T. Dogu, Dimethyl ether, diethyl ether and ethylene from alcohols over tungstophosphoric acid based mesoporous catalysts, Chem.
 Eng. J. 207-208 (2012) 85–93.
- [11] R.M. Ladera, J.L.G. Fierro, M. Ojeda, S. Rojas, TiO₂-supported heteropoly acids for lowtemperature synthesis of dimethyl ether from MeOH, J. Catal. 312 (2014) 195–203.
- [12] R.T. Carr, M. Neurock, E. Iglesia, Catalytic consequences of acid strength in the conversion of MeOH to dimethyl ether, J. Catal. 278 (2011) 78–93.
- [13] A.J. Jones, R.T. Carr, S.I. Zones, E. Iglesia, Acid strength and solvation in catalysis by MFI zeolites and effects of the identity, concentration and location of framework heteroatoms, J. Catal. 312 (2014) 58–68.
- [14] W. Knaeble, E. Iglesia, Kinetic and theoretical insights into the mechanism of alkanol dehydration on solid Brønsted acid catalysts, J. Phys. Chem. C 120 (2016) 3371–3389.
- [15] M.C.H. Clemente, G.A.V. Martins, E.F. de Freitas, J.A. Dias, S.C.L. Dias, Ethylene production via catalytic EtOH dehydration by 12-tungstophosphoric acid@ceria zirconia, Fuel 239 (2019) 491–501.
- [16] P.G. Moses, J.K. Nørskov, MeOH to dimethyl ether over ZSM-22: A periodic density functional theory study, ACS Catal. 3 (2013) 735–745.
- [17] J. Schnee, E.M. Gaigneaux, Elucidating and exploiting the chemistry of Keggin heteropolyacids in the MeOH-to-DME conversion: enabling the bulk reaction thanks to operando Raman, Catal. Sci. Technol. 7 (2017) 817-830.
- [18] J. Schnee, A. Eggermont, E.M. Gaigneaux, Boron nitride: A support for highly active heteropolyacids in the MeOH-to-DME reaction, ACS Catal. 7 (2017) 4011-4017.

- [19] E.F. Kozhevnikova, I.V. Kozhevnikov, A calorimetric study of the acidity of bulk and silica-supported heteropoly acid H₃PW₁₂O₄₀, J. Catal. 224 (2004) 164-169.
- [20] I.V. Kozhevnikov, Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions, Chem. Rev. 98 (1998) 171-198.
- [21] I.V. Kozhevnikov, Catalysts for fine chemicals. Vol. 2. Catalysis by Polyoxometalates, Wiley, Chichester, England, 2002.
- [22] J.B. Moffat, Metal-Oxygen Clusters. The surface and catalytic properties of heteropoly oxometalates, Kluwer: New York, 2001.
- [23] G.I. Kapustin, T.R. Brueva, A.L. Klyachko, M.N. Timofeeva, S.M. Kulikov, I.V. Kozhevnikov, A study of the acidity of heteropoly acids, Kinet. Katal. 31 (1990) 1017-1020.
- [24] L.C. Jozefowicz, H.G. Karge, E. Vasilyeva, J.B. Moffat, A microcalorimetric investigation of heteropolyacids, Micropor. Mater. 1 (1993) 313-322.
- [25] F. Lefebvre, F.X. Lui-Cai, A. Auroux, Microcalorimetric study of the acidity of tungstic heteropolyanions, J. Mater. Chem. 4 (1994) 125-131.
- [26] S. Shikata, S. Nakata, T. Okuhara, M. Misono, Catalysis by heteropoly compounds. 32.
 Synthesis of methyl tert-butyl ether catalyzed by heteropolyacids supported on silica, J.
 Catal. 166 (1997) 263-271.
- [27] J.A. Dias, J.P. Osegovic, R.S. Drago, The solid acidity of 12-tungstophosphoric acid, J. Catal. 183 (1999) 83-90.
- [28] F.X. Lui-Cai, B. Sahut, E. Faydi, A. Auroux, G. Herve, Study of the acidity of carbon supported and unsupported heteropolyacid catalysts by ammonia sorption microcalorimetry, Appl. Catal. 185 (1999) 75-83.

- [29] B.B. Bardin, R.J. Davis, Effect of water on silica-supported phosphotungstic acid catalysts for 1-butene double bond shift and alkane skeletal isomerization, Appl. Catal. 200 (2000) 219-231.
- [30] V. Rakic, V. Dondur, U. Mioc, D. Jovanovic, Microcalorimetry in the identification and characterization of the most reactive active sites of heterogeneous catalysts, Top. Catal. 19 (2002) 241-247.
- [31] A.D. Newman, D.R. Brown, P. Siril, A.F. Lee, K. Wilson, Structural studies of high dispersion H₃PW₁₂O₄₀/SiO₂ solid acid catalysts, Phys. Chem. Chem. Phys. 8, (2006) 2893–2902.
- [32] A.M. Alsalme, P.V. Wiper, Y.Z. Khimyak, E.F. Kozhevnikova, I.V. Kozhevnikov, Solid acid catalysts based on H₃PW₁₂O₄₀ heteropoly acid: Acid and catalytic properties at a gas–solid interface, J. Catal. 276 (2010) 181-189.
- [33] E.I. García-López, G. Marcì, I. Krivtsov, J.C. Espina, L.F. Liotta, A. Serrano, Local structure of supported Keggin and Wells–Dawson heteropolyacids and its influence on the catalytic activity, J. Phys. Chem. C 123 (2019) 19513–19527.
- [34] M. Misono, A view on the future of mixed oxide catalysts. The case of heteropolyacids (polyoxometalates) and perovskites, Catal. Today 100 (2005) 95-100.
- [35] I.D. Dobson, Leaps of innovation, Green Chem. 5 (2003) G78-C81.
- [36] <u>https://www.bio.org/sites/default/files/1500%20Langston.pdf</u> (accessed 27 February 2020).
- [37] H. Noller, P. Andreu, M. Hunger, The mechanism of contact elimination, a contribution to understanding the function of polar catalysts, Angew. Chem. Int. Ed. 10 (1971) 172-181.
- [38] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. van Bekkum, Study of catalysts comprising heteropoly acid H₃PW₁₂O₄₀ supported on MCM-41

molecular sieve and amorphous silica, J. Mol. Catal. A, 114 (1996) 287-298.

- [39] T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, Microstructure of cesium hydrogen salts of 12-tungstophosphoric acid relevant to novel acid catalysis, Chem. Mater. 12 (2000) 2230-2238.
- [40] B.B. Bardin, S.V. Bordawekar, M. Neurock, R.J. Davis, Acidity of Keggin-type heteropolycompounds evaluated by catalytic probe reactions, sorption microcalorimetry, and density functional quantum chemical calculations, J. Phys. Chem. B 102 (1998) 10817-10825.
- [41] CRC Handbook of chemistry and physics, 80th ed., 1999–2000.
- [42] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum(VI) and tungsten(VI) compounds related to the Keggin structure, Inorg. Chem. 22 (1983) 207-216.
- [43] D.B. Taylor, J.B. McMonagle, J.B. Moffat, Cation effects on the surface and bulk structure of the salts of 12-tungstosilicic acid, J. Colloid Interface Sci. 108 (1985) 278-284.
- Y. Yamamoto, S. Hatanaka, K. Tsuji, K. Tsuneyama, R. Ohnishi, H. Imai, Y. Kamiya, T. Okuhara, Direct addition of acetic acid to ethylene to form ethyl acetate in the presence of H₄SiW₁₂O₄₀/SiO₂, Appl. Catal. A 344 (2008) 55–60.
- [45] J. Zhang, M. Kanno, Y. Wang, H. Nishii, Y. Miura, Y. Kamiya, Changes in surface acidity of silica-supported dodecatungstosilicic acid in relation to the loading amount, J. Phys. Chem. C 115 (2011) 14762–14769.

- [46] V.M. Mastikhin, S.M. Kulikov, A.V. Nosov, I.V. Kozhevnikov, I.L. Mudrakovsky, M.N. Timofeeva, ¹H and ³¹P MAS NMR studies of solid heteropolyacid and H₃PW₁₂O₄₀ supported on SiO₂, J. Mol. Catal. 60 (1990) 65-70.
- [47] K. Mohana Rao, R. Gobetto, A. Iannibello, A. Zecchina, Solid state NMR and IR studies of phosphomolybdenum and phosphotungsten heteropoly acids supported on SiO₂, γ-Al₂O₃, and SiO₂-Al₂O₃, J. Catal. 119 (1989) 512-516.
- [48] F. Lefebvre, ³¹P MAS NMR study of H₃PW₁₂O₄₀ supported on silica: formation of (≡SiOH₂⁺)(H₂PW₁₂O₄₀⁻), J. Chem. Soc. Chem. Commun. (1992) 756-757.
- [49] A. Ghanbari-Siahkali, A. Philippou, J. Dwyer, M.W. Anderson, The acidity and catalytic activity of heteropoly acid on MCM-41 investigated by MAS NMR, FTIR and catalytic tests, Appl. Catal. A 192 (2000) 57-69.
- [50] E. Grinenval, X. Rozanska, A. Baudouin, E. Berrier, F. Delbecq, P. Sautet, J.-M. Basset, F. Lefebvre, Controlled interactions between anhydrous Keggin-type heteropolyacids and silica support: Preparation and characterization of well-defined silica-supported polyoxometalate species, J. Phys. Chem. C 114 (2010) 19024–19034.
- [51] G. C. Bond, S. J. Frodsham, P. Jubb, E. F. Kozhevnikova, Ivan V. Kozhevnikov, Compensation effect in isopropanol dehydration over heteropoly acid catalysts at a gas– solid interface J. Catal. 293 (2012) 158–164.
- [52] C.-Y. Wu, H.-S. Wu, Ethylene formation from ethanol dehydration using ZSM- 5 catalyst, ACS Omega 2 (2017) 4287–4296.
- [53] A. Corma, V. Fornes, L. Forni, F. Marquez, J. Martinez-Triguero, D. Moscotti, 2,6-Di-Tert-Butyl-Pyridine as a Probe Molecule to Measure External Acidity of Zeolites J. Catal. 179 (1998) 451–458.
- [54] H. Hattori, Y. Ono, Solid acid catalysis. From fundamentals to applications, CRC Press, 2015, p. 98.

ournal pre-proó