

## New phosphonic acid polysilsesquioxane mild solid acid catalysts

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### ABSTRACT

A simple easily scalable one-pot route to new phosphonic acid polysilsesquioxanes, PAPSQ,  $[(O_{3/2}SiCH_2R)_x(O_{3/2}SiCHR(CH_2)_2SiO_{3/2})_y]_n$  where  $R = CH_2PO_3H_2$ , is described in this paper. Nuclear magnetic resonance (NMR), electron microscopy (SEM), thermogravimetric analysis, nitrogen sorption porosimetry, phosphorus and available acid analysis were used to characterise the new PAPSQ materials. The materials were shown to be very efficient and recyclable mild solid acid catalysts for organic transformations including those relevant to biomass conversion such as esterification, transesterification and dehydration of fructose to the important intermediate 5-hydroxymethylfurfural.

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### 1. Introduction

Molecular cages, resins, glasses and ordered mesoporous solids derived from precursor organotrialkoxysilanes such as  $RSi(OMe)_3$  or the bridged type precursors  $(MeO)_3SiRSi(OMe)_3$  are polysilsesquioxanes, PSQ, and are represented as  $[RSiO_{3/2}]_n$  or  $[O_{3/2}SiRSiO_{3/2}]_n$  in the fully condensed forms. The organic groups R are important in determining the properties and applications PSQ display. Polysilsesquioxane, PSQ, materials,  $[RSiO_{3/2}]_n$  or  $[O_{3/2}SiRSiO_{3/2}]_n$  where R is a functional organic group are of great current interest with potential application areas in energy materials, drug delivery systems and as separation media [1–6]. The organic–inorganic hybrid composition provides excellent thermal stability and built-in chemical functionality makes these materials ideal candidates for heterogeneous catalysis applications. New PSQ materials and their catalytic applications are frequently reported [7–13] but the translation of this research to industrial application is apparently limited by the complexity of synthesis and cost [7,8]. PSQs with phosphonic acid functional groups are a relatively little explored class. Compared to stronger Brønsted acid functions such as sulfonic acid, phosphonic acid is relatively mild and consequently may be less prone to promotion of side reactions. We report here on new phosphonic acid functionalised PSQs which are readily synthesised on a large scale, along with studies that demonstrate their use as solid Brønsted acid heterogeneous catalysts.

### 2. Experimental

Solvents and reagents used were purchased from Aldrich. Proton, carbon and phosphorus NMR spectra of PAPSQ materials dispersed in NaOD/D<sub>2</sub>O were recorded on Bruker AMX 400 or 600 MHz instruments. Solid state spectra were obtained using a Bruker AMX 600 MHz instrument: <sup>29</sup>Si HPDec MAS, frequency 119.2 MHz, spinning speed 12 kHz; 1 min recycle delay, with 2 μs ~45° pulse; <sup>31</sup>P CP MAS; frequency 242.9 MHz, spinning speed 12 kHz, 1 ms contact time, 1.5 s delay, 90° pulse for 2.0 μs. SEM was recorded on a JEOL 6300F scanning electron microscope and TGA on a TA Q500 ramped at 10 °C/min under nitrogen. Nitrogen adsorption–desorption was recorded on a Qantachrome Nova porosimeter. Phosphorus elemental analysis was obtained from Medac Ltd.

#### 2.1. Preparation PAPSQa and PAPSQb

$[(O_{3/2}SiCH_2R)_{1.5}(O_{3/2}SiCHR(CH_2)_2SiO_{3/2})]_n$   $R = CH_2PO(OH)_2$

To dimethyl phosphite (37.2 g, 31 mL, 0.338 mol) was added vinyltrimethoxysilane (33 mL, 0.215 mol) and the mixture heated with stirring at 110 °C for 2 h. Di-*tert*-butyl peroxide (1 drop) was added every 15 min for 2 h after which no vinyl resonances could be detected by <sup>1</sup>H NMR. The excess dimethyl phosphite was removed under reduced pressure and the residual colourless liquid containing, **1**, dimethylphosphonatoethyltrimethoxysilane and **2**, 2,4-bis(trimethoxysilyl)-1-dimethylphosphonato butane in ratio 1.5:1 (<sup>31</sup>P NMR (CDCl<sub>3</sub>) **1** 35.68(s) **2** 35.48(s)) was treated further.

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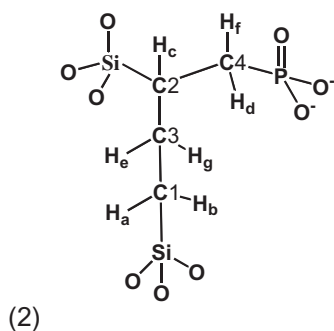
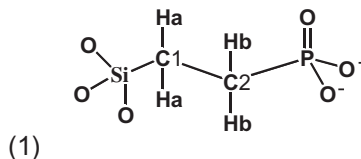
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### 2.1.1. PAPSQa

HCl (160 mL of 5 M) was added to 20 g of the colourless liquid (from Section 2.1) and then stirred under reflux for 5 h. On cooling to room temperature the white solid was filtered and washed extensively with distilled water and methanol. The solid was dried under reduced pressure at 120 °C for 4 h to afford a white powder **PAPSQa** (10.9 g, 89.7%). Surface area: 65 m<sup>2</sup> g<sup>-1</sup>, <sup>29</sup>Si MAS  $\delta_{\text{Si}}$ : -63 (br s) deconvoluted peaks at -53, -58, -63. <sup>31</sup>P CPMAS NMR  $\delta_{\text{P}}$  33 (PO(OH)<sub>2</sub>, 90%) 24 (Si-OH-O=P(OH)<sub>2</sub>, 10%). Found *P* 4.96 mmol g<sup>-1</sup>.

**2.1.1.1. Accessible acid measurement.** In a typical measurement to determine the phosphonic acid first proton exchange capacity, a sample of **PAPSQa** 0.2040 g was shaken in 50 mL of 0.5 M sodium formate solution for 60 h. The formic acid produced was titrated with 20 mM NaOH. Accessible acid in **PAPSQa**: 3.3 mmol g<sup>-1</sup>.

**2.1.1.2. NMR **PAPSQa** dispersed in (NaOD/D<sub>2</sub>O).** **PAPSQa** was dispersed in NaOD/D<sub>2</sub>O wherein the phosphonate is fully ionised while Si-C bonds remain intact. This is a convenient way to confirm presence of components (1) and (2) (see below)



$\delta_{\text{P}}$  (**PAPSQa**) 26.8 (s, *P* (1)), 25.6 (s, *P* (2)) intensity ratio 1.5:1.  $\delta_{\text{H}}$  (1) 0.65 (Ha, m, 2H), 1.36 (Hb, m, 2H);  $\delta_{\text{C}}$  (1) 7.6 (C1), 22.6 (d, C2) (Assignments confirmed by HSQC [14]),  $\delta_{\text{H}}$  (2) 0.53 (m, Hb, J(b,a), 15.27 Hz, J(b,e), 3.43 Hz, J(b,g), 8.73 Hz), 0.73 (m, Ha, J(a,b), 15.27 Hz, J(a,e), 10.45 Hz, J(a,g), 4.2 Hz), 0.99 (m, Hc, J(c,d), 5.22 Hz, J(c,e), 9.76 Hz, J(c,f), 9.32 Hz, J(c,g), 4.27 Hz, J(c,p), 14.10 Hz), 1.27 (m, Hd, J(d,f), 14.90 Hz, J(d,p), 17.62 Hz), 1.55 (m, He, J(e,g), 13.48 Hz), 1.63 (m, Hf, J(f,p), 16.2 Hz), 1.89 (m, Hg, J(e,g), 13.48 Hz),  $\delta_{\text{C}}$  (2) 11.6 (C1), 21.1 (C2), 26.6 (C3), 31.0 (d, C4) (Assignments confirmed by HSQC [14]).

**Note:** the NUMERIT [15] simulated and experimentally observed <sup>1</sup>H NMR spectrum features of the complex seven proton spin system in component (2) are shown in Supplementary Information Fig. A.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2013.03.021>.

### 2.1.2. PAPSQb

To 6.0 g of the mixture of **1** and **2** mole ratio 1.5:1 (from Section 2.1) was added aqueous hydrochloric acid (1 M, 15 mL) and methanol (180 mL). The resultant solution was placed in a polypropylene plastic bottle and warmed to 90 °C for 16 h. The formed glass was ground to a powder. To this powder, hydrochloric acid (5 M, 50 mL) was added slowly and the resultant mixture was

stirred under reflux for 12 h. On cooling to room temperature the solid was filtered and then washed extensively with distilled water, methanol and diethyl ether. The solid was then dried at 120 °C for 4 h to yield a white powder **PAPSQb** (2.9 g, 79%).

Surface area: 80 m<sup>2</sup> g<sup>-1</sup>, <sup>31</sup>P NMR (NaOD/D<sub>2</sub>O)  $\delta_{\text{P}}$ : 25.2, 26.3 ratio 1:1.5; <sup>31</sup>P CPMAS NMR  $\delta_{\text{P}}$  32.2 (br s), <sup>29</sup>Si MAS  $\delta_{\text{Si}}$ : -63 (br s) deconvoluted peaks at -58, -64, found *P* 5.1 mmol g<sup>-1</sup> Accessible acid by titration 3.3 mmol g<sup>-1</sup>.

### 2.2. Catalysis

Quantity of catalyst used (mol%) was based on the available acid determined by titration. Percentage conversions were determined by <sup>1</sup>H NMR spectroscopy or isolated products. Turnover numbers are based on three cycles in each case. Blank reactions were performed in the absence of catalyst. The catalyst was recycled either after filtration and washing or after removal of the product solution and addition of fresh reagent and solvent. Leaching was assessed by interrupting the reaction (ketalisation, esterification and transesterification) at partial conversion (1 h), separating the liquid phase from the catalyst using a 0.2  $\mu\text{m}$  filter and measuring conversion again at the specified reaction time. No evidence of leaching was detected. The ketalisation, esterification and transesterification experiments were also run using the equivalent quantity of phosphoric acid as catalyst.

#### 2.2.1. Protection of ketones (ketalisation)

A mixture of acetophenone (4.8 g, 40.0 mmol, 4.7 mL), ethane-1,2-diol (6.7 g, 107.6 mmol, 6.0 mL) catalyst (30 mg, 0.25 mol%) in toluene (30 mL) was refluxed 10 h using a Dean-Stark apparatus. The reaction was followed by TLC. The reaction mixture was cooled to room temperature, the catalyst filtered off and washed with ether (20 mL). The ketal product 2-methyl-2-phenyl-1,3-dioxolane was obtained as a white solid from the filtrate after washing with water (3  $\times$  20 mL) and drying over magnesium sulfate.

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta_{\text{H}}$ : 1.67 (s, 3H), 3.78 (t, 2H), 4.02 (t, 2H), 7.25–7.56 (m, 5H<sub>arom</sub>).

#### 2.2.2. Esterification of oleic acid

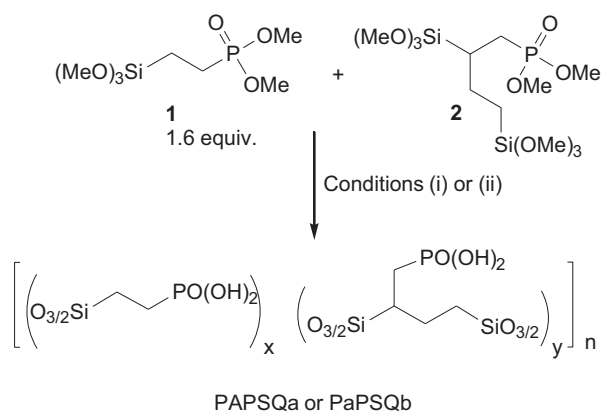
Oleic acid (1 g, 3.54 mmol), catalyst (20 mg, 1.9 mol%) and ethanol (6 mL) were combined and the reaction mixture was refluxed for 8 h then heated to 90 °C for 2 h using an air condenser. The evaporated solvent was replaced with dry ethanol and the mixture heated a further 2 h using an air condenser. Ether (30 mL) was added to the cooled mixture and the catalyst was filtered off, washed with diethyl ether and retained for recycling. The organic solvents were removed from the filtrate. Conversion to the ethyl oleate was determined by integration of the total alkene proton signal at  $\delta_{\text{H}}$  5.33 (m, 2H) against the ester methylene signal at  $\delta_{\text{H}}$  4.11 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>).

#### 2.2.3. Transesterification of ethyl oleate

Ethyl oleate (1.55 g, 5 mmol), catalyst (50 mg, 3.3 mol%) and pentanol (10 mL) were refluxed for 12 h. The reaction was followed by TLC. On cooling, ether (30 mL) was added and the catalyst was filtered off. The organic solvents were removed. Conversion was determined by integration of the alkene proton signals at  $\delta_{\text{H}}$  5.35 and the ester methylene signal at  $\delta_{\text{H}}$  4.13 (t, 2H, OCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>).

#### 2.2.4. HMF synthesis

Fructose (206 mg, 1.14 mmol) was dissolved in deionized water (1.8 g) and **PAPSQa** (209 mg) was added to this solution. An organic phase (2 g) containing MIBK and 2-butanol in 7:3 ratio was added to the reaction vessel to obtain a biphasic mixture. The reaction mixture was heated to 130 °C, while stirring at 600–700 rpm for 12 h. The reaction mixture was then cooled to 90 °C without stirring,



**Scheme 1.** Conditions: (i) direct hydrolysis with 5 M HCl gives PAPSQa  $x/y = 1.5$ ; or (ii) sol-gel process **1** and **2** (MeOH, aqueous HCl) and hydrolysis of xerogel with 5 M HCl gives PAPSQb  $x/y = 1.5$ .

the organic phase (top layer) removed, another batch of fructose (200 mg) and organic phase added and the process repeated. In this manner three catalytic cycles were assessed. In each case pure HMF (by NMR) was obtained from the removed organic phase. The isolated yields of HMF from the organic layers based on D-fructose taken in each cycle were 51, 57 and 57%.

Repeating this process with PAPSQb (203 mg) and fructose (204 mg) in three catalytic cycles afforded HMF product yields of 59, 72 and 73%.

### 2.2.5. Comparative catalytic activity for ketalisation, esterification and transesterification

The reactions as described above in Section 2.2.1, Section 2.2.2, and Section 2.2.3 and identical ones employing phosphoric acid as catalyst at the same mol% phosphorus were sampled at regular intervals up to 5 h and the % conversion evaluated.

### 2.2.6. Comparative catalytic activity for ketalisation

A mixture of acetophenone (4.8 g, 40.0 mmol, 4.7 mL), ethane-1,2-diol (6.7 g, 107.6 mmol, 6.0 mL) and catalysts PAPSQa, PAPSQb or phosphoric acid, adjusted to give 0.2 mol% acid, was refluxed as in Section 2.2.1 and samples taken for analysis at regular intervals.

## 3. Results and discussion

### 3.1. Synthesis

The objective of this work was to explore simple routes for the synthesis of new phosphonic acid functionalised polysilsesquioxanes, PAPSQ and to investigate the solid acid catalytic activity of these materials. We have previously reported on the microporous PAPSQ material  $[(O_{3/2}OSiCH_2CH(PO(OH)_2)CH_2CH_2SiO_{3/2})_n]$  which has an in-framework phosphonic acid group [16]. The precursor for this material required the tedious synthesis of 1,4-bis(triethoxysilyl)but-2-ene and subsequent radical addition of  $HPO(OEt)_2$  to the *ene* fragment making this a relatively long and costly method. Others have reported [17] on the 2-component PAPSQ system  $[(O_{3/2}SiCH_2CH_2(PO(OH)_2))_x(O_{3/2}Si(CH_2)_2SiO_{3/2})_y]_n$  obtained by co-hydrolysis and condensation of the precursors  $[(EtO)_3SiCH_2CH_2PO(OEt)_2]$  and  $[(MeO)_3Si(CH_2)_2Si(OMe)_3]$ .

New phosphonic acid polysilsesquioxanes, PAPSQ  $[(O_{3/2}SiCH_2R)_x(O_{3/2}SiCHR(CH_2)_2SiO_{3/2})_y]_n$  where  $R = CH_2PO_3H_2$ , were synthesised starting from the *mono* and *bis*-trialkoxysilylalkylphosphonate esters (Scheme 1). The known phosphonate ester compounds, **1**, dimethylphosphonate ethyl trimethoxysilane [18] and **2**, 2,4-bis(trimethoxysilyl)

-1-dimethylphosphonatobutane [19], were formed in this work as a two-component mixture in a simple radical addition reaction between dimethylphosphite and vinyltrimethoxysilane in the presence of di-*tert*-butylperoxide. Both compounds were produced even when excess dimethylphosphite was employed. For dimethylphosphite:vinyltrimethoxysilane 1.6:1, compounds **1** and **2** were formed in 1.5:1 ratio as evidenced by the relative integration of  $^{31}P$  NMR resonances at  $\delta$  35.68 for **1** and  $\delta$  35.48 for **2**. The percentage of **2** in the mixture may be increased by increasing the proportion of vinyltrimethoxysilane in the reaction. For example, at dimethylphosphite:vinyltrimethoxysilane ratio of 0.5 the ratio of **1**–**2** formed was 0.9:1. This simple reaction allowed for easy one-pot formation of precursors to bridged polysilsesquioxane materials PAPSQ with very high phosphonic acid loading. In contrast the multi-step routes to  $[(O_{3/2}OSiCH_2CH(PO(OH)_2)CH_2CH_2SiO_{3/2})_n]$  and  $[(O_{3/2}SiCH_2CH_2(PO(OH)_2))_x(O_{3/2}Si(CH_2)_2SiO_{3/2})_y]_n$  mean that these are significantly more demanding to synthesise.

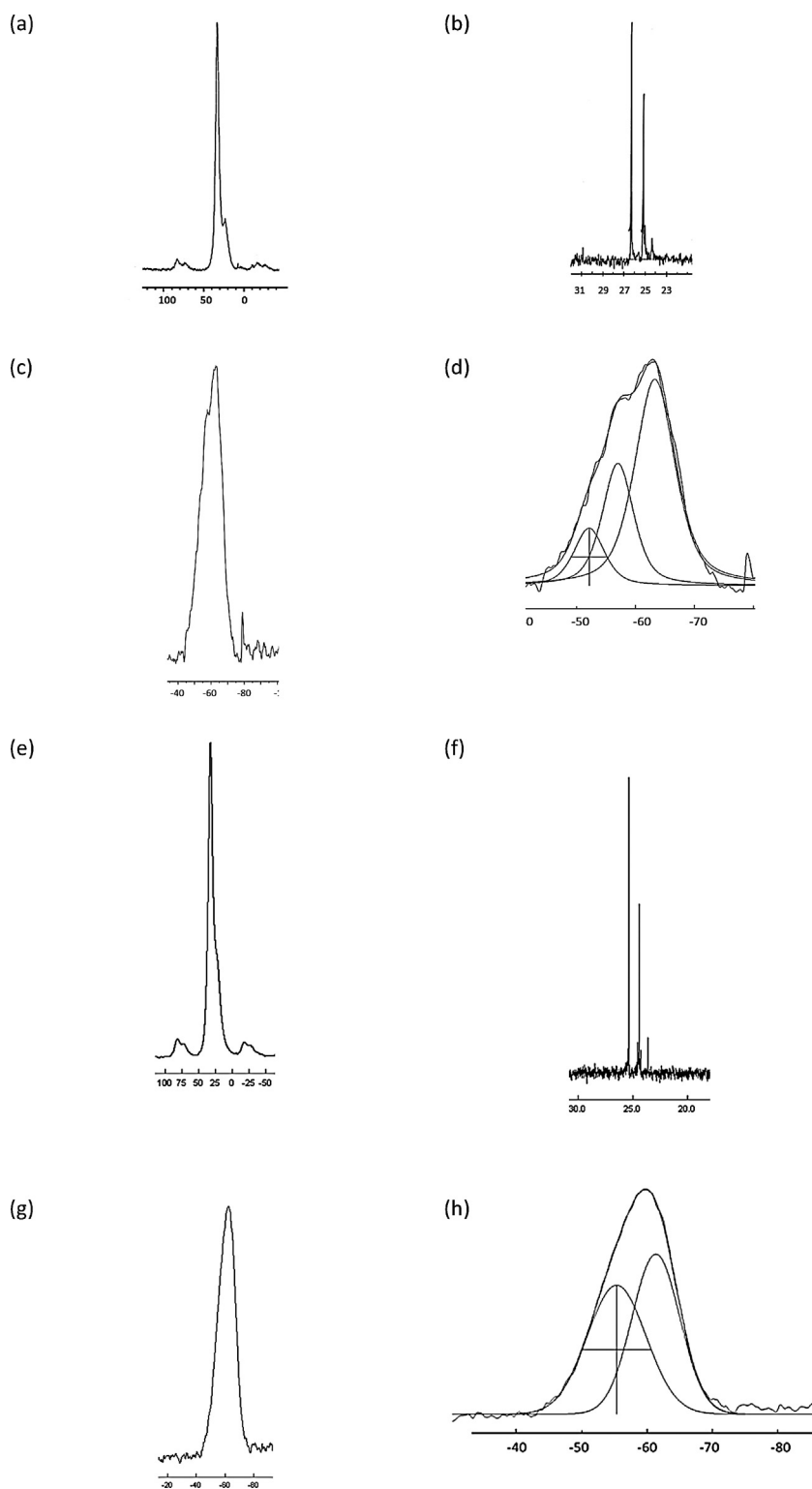
The phosphonate ester mixture was converted to two-component amorphous phosphonic acid polysilsesquioxane materials, PAPSQ. This was achieved either by a one-pot hydrolytic co-polycondensation of the mixture of **1** and **2**, using 5 M HCl to give directly the phosphonic acid polysilsesquioxane designated PAPSQa or by sol-gel processing to an isolated intermediate ethylphosphonate ester xerogel followed by hydrolysis of the crushed xerogel with 5 M HCl to give the material PAPSQb (see Scheme 1). The materials obtained were washed extensively with distilled water, methanol and diethyl ether. Of the two routes, the one pot direct hydrolysis route had the advantage of avoiding any need to form, isolate and grind an intermediate ethylphosphonate ester xerogel  $[(O_{3/2}SiCH_2R)_x(O_{3/2}SiCHR(CH_2)_2SiO_{3/2})_y]_n$  where  $R = CH_2PO(OEt)_2$ . It avoided the need for large quantities of methanol and facilitated the synthesis of much larger batches of material in  $\sim 10$  h compared to  $\sim 30$  h. In addition the direct hydrolysis route also afforded a 10% higher overall yield of product.

### 3.2. NMR features

Materials PAPSQa and PAPSQb had similar NMR spectroscopic features. The ratio  $x/y$  of phosphorus components in the PAPSQs shown in Scheme 1 was determined from the  $^{31}P$  NMR of materials dispersed in NaOD/D<sub>2</sub>O solution (Fig. 1). The  $^{31}P$  CPMAS NMR of the solid PAPSQ appeared as broad peaks around  $\delta$  33 ppm (Fig. 1). A small peak was also present at  $\delta$  24 ppm indicative of some Si–OH–O=P(OH)<sub>2</sub> interaction [20,21].

When the materials were dispersed in NaOD/D<sub>2</sub>O the  $^{31}P$  resonances of the two fully ionized phosphonic acid components were clearly distinguished and shifted to higher field compared to the phosphonic acid (Fig. 1(b) and (f)). Under these conditions the bulk material Si–O–Si framework was sufficiently hydrolysed to facilitate dissolution while Si–C bonds remained intact and this was a convenient way to observe the different phosphorus containing components. Solid state  $^{29}Si$  NMR on PAPSQa and PAPSQb gave broad resonances centred at  $\delta$  –63 ppm, Fig. 1(c) and (g) which after deconvolution, Fig. 1(d) and (h) were found to have the silicon environments in (PAPSQa)PAPSQb  $T^1(12.7\%)0\%$ ,  $T^2(27.8\%)49.8\%$ , and  $T^3(59.5\%)50.2\%$ , with overall condensation (82%)83% respectively.  $T^n$  denotes the number of Si–O–Si bonds at the trifunctional silicon.

The silicon–carbon–phosphorus skeletons of the two phosphorus components in PAPSQa were observed in the  $^1H$  and  $^{13}C$  NMR spectra of a sample dispersed in NaOD/D<sub>2</sub>O (see experimental). Spectral assignments of the different proton environments in dispersed PAPSQa were made after simulation using HSQC (Hetero Single Quantum Coherence) [14] and NUMERIT [15] experiments (see supplementary information Fig. A).



**Fig. 1.**  $^{31}\text{P}$  CPMAS NMR (a) PAPSQa (e) PAPSQb  $^{31}\text{P}$  NMR in NaOD/D<sub>2</sub>O (b) PAPSQa (f) PAPSQb  $^{29}\text{Si}$  MAS NMR (c) PAPSQa (g) PAPSQb and Deconvoluted  $^{29}\text{Si}$  MAS NMR (d) PAPSQa (h) PAPSQb.

### 3.3. Texture

The as synthesised PAPSQa and PAPSQb were ground to fine powders. The ground powders were non porous and had surface areas and pore volumes of 65 m<sup>2</sup>/g, 0.09 cm<sup>3</sup>/g (PAPSQa) and 200 m<sup>2</sup>/g, 0 cm<sup>3</sup>/g PAPSQb. A fused nanoparticle surface texture was seen for both materials as shown in Fig. 2 where PAPSQb displays a finer texture.

### 3.4. Thermal properties

The TGA profiles of as-formed PAPSQa and PAPSQb materials pre-dried at 120 °C were recorded under nitrogen and are shown in Fig. 3. Weight loss from PAPSQa(PAPSQb) of 1.3%(5%) due to retained solvent or water was observed below 150 °C. Further gradual weight loss ~8%(5%) was observed between 150 and 475 °C. This may reflect further condensation of silanol. The weight loss

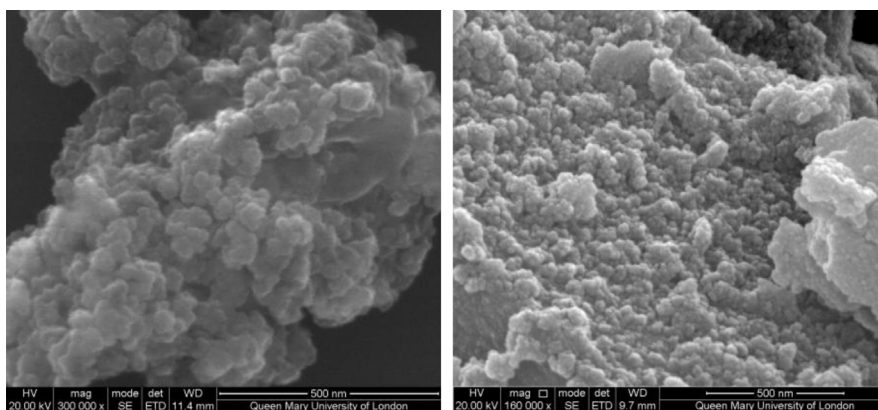


Fig. 2. SEM of (a) PAPSQa (b) PAPSQb.

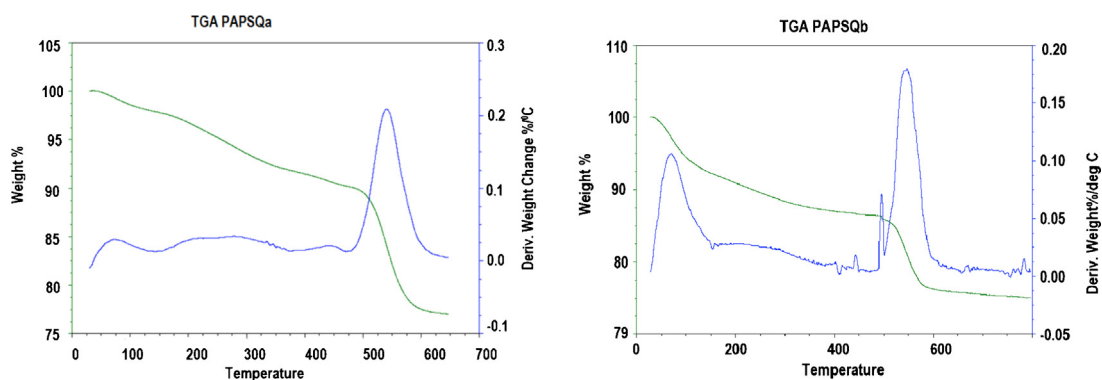


Fig. 3. TGA of (a) PAPSQa (b) PAPSQb.

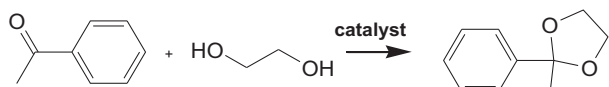
12%(10%) above 475 °C could represent condensation due to P–O–P bond formation and/or elimination of small hydrocarbon fragments. Overall weight loss at 600 °C was less than 23% in both cases.

### 3.5. Catalytic studies

To assess stability and activity the PAPSQ materials were initially assessed as catalysts in organic transformations including protection of ketones and esterification/transesterification of acids and esters respectively. This was followed by a more complex transformation involving dehydration of fructose where there are several potential products. All results are summarised in the Table 1.

The % conversions (92–98%) for ketalisation of acetophenone (Scheme 2) measured after 10–12 h from catalysts PAPSQa and PAPSQb were high.

Both catalysts were easily separated from reaction media by filtration and were recycled further without loss of activity. To achieve a comparison between the catalysts PAPSQa, PAPSQb and a homogeneous analogue, the initial progress of reaction was followed for the ketalisation of acetophenone using the solid acids and phosphoric acid under identical conditions and with 0.2 mol% of the acid in each case. The results (Fig. 4) showed steady rates of conversion in all three cases with 94% conversion for PAPSQa after 4.5 h, while phosphoric acid had 85% and PAPSQb 73% conversion in



Scheme 2. Ketalisation of acetophenone.

the same time period. The apparent differences in conversion profiles for the solid acids may in part be due to minor differences in mechanical mixing during the process (powder PAPSQb was considerably finer than powder PAPSQa which affected its distribution

Table 1  
PAPSQ solid acid catalytic data.

Entry	Catalyst	(%) Conversion or yield <sup>e</sup> for cycles 1,2,3 (TON) <sup>f</sup>
1 <sup>a</sup>	PAPSQa	97,97,97 (1175)
2 <sup>a</sup>	PAPSQb	98,97,97 (1175)
3 <sup>a</sup>	Phosphoric acid	90
4 <sup>b</sup>	PAPSQa	97,95,97 (154)
5 <sup>b</sup>	PAPSQb	96,99,99 (154)
6 <sup>b</sup>	Phosphoric acid	50
7 <sup>c</sup>	PAPSQa	92,93,93 (84)
8 <sup>c</sup>	PAPSQb	92,92,92 (84)
9 <sup>c</sup>	Phosphoric acid	93
7 <sup>d</sup>	PAPSQa	51, 57, 57 (2.7)
8 <sup>d</sup>	PAPSQb	59, 72, 73 (3.5)

<sup>a</sup> Ketalisation of acetophenone. Conditions: 40 mmol acetophenone and ethane-1,2-diol (6 mL) in toluene (30 mL) and 30 mg phosphonic acid 0.25 mol% based on titrated acid (or 0.25 mol% phosphoric acid). Blank reactions (no catalyst) gave zero conversion.

<sup>b</sup> Esterification of oleic acid. Conditions: 3.5 mmol oleic acid, 20 mg catalyst corresponding to phosphoric acid, 1.9 mol% based on titrated acid (or 1.9 mol% phosphoric acid); ethanol (6 mL), at 90 °C for 12 h.

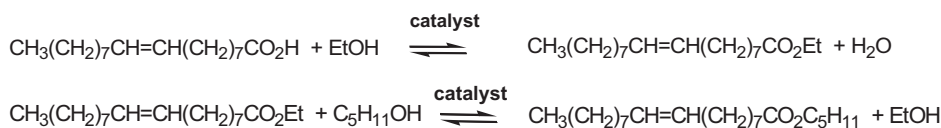
<sup>c</sup> Transesterification ethyl oleate conditions: 5 mmol ethyl oleate, 50 mg catalyst corresponding to phosphoric acid 3.3 mol% based on titrated acid and pentanol (10 mL); refluxed 12 h.

<sup>d</sup> 10 wt% aqueous fructose in 1:1 w/w aqueous/organic phases (organic phase 7:3 MIBK:2-butanol) and 1:1 w/w fructose and PAPSQa.

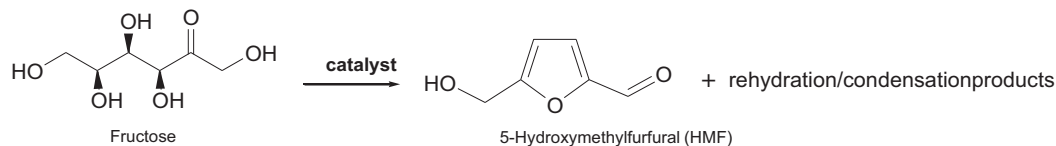
<sup>e</sup> Conversion determined by NMR for entries 1–6 and yield of HMF isolated from organic phase only and confirmed by NMR for entry 7 and 8.

<sup>f</sup> TON = mole product mol<sup>-1</sup> available acid after the 3 cycles.





Scheme 3. Esterification of oleic acid and transesterification of ethyl oleate.



Scheme 4. Dehydration of fructose to HMF.

in this two phase toluene–ethanediol mixture). The PAPSQa profile indicates a slightly faster rate of conversion compared to the homogeneous phosphoric acid catalyst in this reaction.

Both catalysts PAPSQa and PAPSQb gave high conversions for esterification of oleic acid and trans-esterification of ethyl to pentyl oleate (Scheme 3).

These experiments showed that the solid catalysts could be recycled and continued to be active after several runs when held at temperatures in the range 90 °C (ketalisation) to 140 °C (transesterification). Turnover numbers (TON) which reflect the mol% of available acid used (see Table 1) were calculated for the specific conditions employed in each case but it should be noted that experiments to optimise these were only carried out for the ketalisation transformation where the conversion continued to be high as the mol% catalyst was reduced to 0.25 mol% resulting in TON of 1175 mol ketal mol<sup>-1</sup> available acid after three cycles without loss of activity. With an equivalent quantity of phosphoric acid as catalyst and the timescales employed, the conversions were found to be much lower for the esterification and comparable for transesterification reactions. This was considered reasonable since the transesterification reaction was carried out at higher temperatures and water was not a by-product. Compared to organic transformations catalysed by sulfonic acid supported on silica or polysilsesquioxane [8,22–27], reports on catalysis using corresponding phosphonic acid systems are scant. Sulfonic acid has the advantage of significantly greater acid strength with pKa = -1 compared to di-protic phosphonic acid with pKa values typically ~2.3–2.9 and 7.7–9 for the first and second ionizations [28]. A milder acid catalyst might however sometimes be

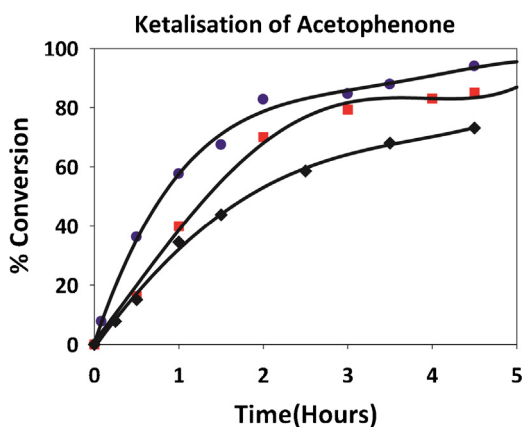


Fig. 4. Reaction profiles for ketalisation of acetophenone with PAPSQa (●), PAPSQb (◆) and phosphoric acid (■) Conditions: 40 mmol acetophenone and ethane-1,2-diol (6 mL) in toluene (30 mL); catalyst at 0.2 mol% P in each case.

preferable particularly where a number of products can be formed and selectivity for a particular product is required. In this context there is great interest in the conversion of fructose to 5-hydroxymethylfurfural, HMF, where rehydration and condensation by-products are a complicating factor in the synthesis (Scheme 4).

HMF is an important intermediate for 2,5-disubstituted furans such as the dicarboxylic acid derivative which has been suggested as an alternative for terephthalic acid and hence a source of biomass derived polymers. The industrial use of HMF is limited by high production costs [29,30]. Some efficient biphasic catalytic systems were recently reported. Dumesic et al. published in-depth studies employing mineral acids including phosphoric acid, the sulfonic acid polystyrene ion-exchange resin catalysts PK-216 and Amberlyst 70 and various silica supported sulfonic acids in biphasic media [31]. We followed conditions reported by Dumesic for a sulfonic acid resin catalyst, consisting of 10 wt% aqueous fructose in 1:1 w/w aqueous/organic phases (organic phase 7:3 MIBK:2-butanol) and 1:1 w/w fructose and catalyst. The reaction with PAPSQa or PAPSQb as catalyst was run at several temperatures up to 130 °C where the highest yield of HMF was isolated. Three cycles were incorporated in the present experiment wherein between cycles the organic MIBK-2-butanol phase (upper layer) containing the product HMF was separated and fresh fructose and organic phase added to the residual hot aqueous phase containing the catalyst. Our analysis was based on isolated HMF from the organic phase only and thus represents the minimum yield since the HMF formed is distributed between aqueous and organic layers. This analysis allowed us to determine whether a constant flow of HMF would result with addition of fresh substrate and organic phase. Rehydration or condensation reaction by-products if formed remain in the aqueous layer. The HMF isolated yields increased after the first cycle for both PAPSQa and PAPSQb catalysts. Thus while leaving the aqueous phase and catalyst unperturbed except for the addition of fresh fructose, the catalysts remained active and the yield of HMF increased during the three cycles of HMF production. Both solid acids resided completely in the aqueous phase of the two-phase mixture and dispersed well in this phase in the stirred mixture. The surface area of catalyst PAPSQb being roughly three times that of PAPSQa may account for the higher 5-HMF yield from PAPSQb. For the identical biphasic system employing the sulfonic acid ion-exchange resin catalyst PK-216, at 90 °C for 8–16 h, or phosphoric acid at 90 °C–180 °C for 8 min the HPLC determined yields of HMF from the organic phase after a single cycle were 23 and 28% respectively [30]. Catalyst stability due to leaching of functional groups was identified as an issue for some silica supported sulphonic acid catalysts when employed in a continuous flow reactor for HMF production [32] but hybrid sulfonic acid catalysts had greater stability in this respect.

#### 4. Conclusion

New phosphonic acid polysilsesquioxane materials, PAPSQs, were readily formed from an easily prepared two-component precursor mixture. Direct hydrolysis of the precursor mixture afforded a simple and fast route to the target material (PAPSQa) that avoids isolating the intermediate phosphonate ester modified material which is an inevitable step of the alternative sol-gel route (to PAPSQb). The mildly acidic glassy particulate materials PAPSQa and PAPSQb displayed effective solid Brønsted acid catalytic activity. Ketalisation proceeded at a faster rate for PAPSQa than with dissolved phosphoric acid or PAPSQb as catalyst. PAPSQs hold much promise as catalysts for transformations that would benefit from a mild acid catalyst such as those where more than one product is routinely formed. In this context the solid acids were used to demonstrate a constant flow of the important intermediate 5-hydroxymethylfurfural, HMF, as the substrate fructose and organic solvent were replenished in this important example of a biomass conversion reaction.

Overall phosphonic acid polysilsesquioxane PAPSQa is a new low cost easy to synthesise organic-inorganic hybrid with good thermal stability and viable catalytic applications can be envisaged for this material. In future work different compositional variations including metal derivatives will be investigated.

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