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A new solid acid catalyst: the first phosphonate and phosphonic acid functionalised microporous polysilsesquioxanes†

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A novel microporous solid acid, the phosphonic acid modified polysilsesquioxane $[(HO)SiCH_2CHPO(OH)_2CH_2CH_2SiO_2(OH)]_n$ P2, from the new single precursor compound $[(EtO)_3SiCH_2CHPO(OCH_2CH_3)_2CH_2CH_2Si(OEt)_3]$ 1, is reported, along with the catalytic activity of P2 for the pinacol–pinacolone rearrangement.

The development of functionalised porous silicas[1a,b] and polysilsesquioxane materials[1c,d] for various applications is proceeding at great pace as evidenced by recent reviews and reports on synthesis and applications in this area. Functional groups or their precursors may be attached to silica *via* compounds $(RO)_3Si(CH_2)_nX$ where X may be further modified if required. Such materials offer a wide spectrum of potential applications for example as acid, base, or oxidation catalysts or asymmetric carbon–carbon coupling catalysts, or as biocompatible surface groups.[1a,b,2] In the context of the present report efforts are also being directed towards the synthesis of functionalised porous polysilsesquioxanes, where the functional group is an integral part of a single framework precursor. Examples include polysilsesquioxanes with built-in NLO and luminescence chromophores,[3a,b] built-in crown-ether[4] or cyclam[5] groups for ion sensing applications or ferrocenyl groups for electrochemical applications.[6]

It occurred to us that phosphonic acid functionalised silicas and polysilsesquioxanes might offer a new class of solid acid materials with wide-ranging potential to act as catalysts, ion exchange and separation materials. There were no examples of such materials previously reported in the literature.

We report here on unique examples of the uniformly modified phosphonate and phosphonic acid polysilsesquioxanes $[(HO)SiCH_2CHPO(OCH_2CH_3)_2CH_2CH_2SiO_2(OH)]_n$ **P1** and $[(HO)SiCH_2CHPO(OH)_2CH_2CH_2SiO_2(OH)]$ **P2** prepared from the new precursor compound $[(EtO)_3SiCH_2CHPO(OCH_2CH_3)_2CH_2CH_2Si(OEt)_3]$, **1**, 1,4-bis(triethoxysilyl)-2-(diethylphosphonato)butane. Compound **1** was formed‡ as shown in eqn. (1) by radical addition of $HPO(OEt)_2$ to the *ene* fragment in 1,4-bis(triethoxysilyl)but-2-ene[7] and was fully characterised by solution phase NMR, mass spectrometry and elemental analysis.

$$\begin{aligned}&HPO(OEt)_2 + \\ &[(EtO)_3SiCH_2CH{=}CHCH_2Si(OEt)_2] \xrightarrow{Bu^tOOBu^t} \\ &\underset{\mathbf{1}}{[(EtO)_3SiCH_2CHPO(OCH_2CH_3)_2CH_2CH_2Si(OEt)_3]} \qquad (1)\end{aligned}$$

P1 was obtained as a transparent monolith after acid-catalysed sol–gel processing of **1** in THF.§ The solid state ^{13}C CP MAS NMR spectrum of **P1** had peaks close to those observed for compound **1**; the ^{29}Si spectrum showed one broad resonance at −63 ppm consistent with predominantly T^2 type silicon sites while the ^{31}P NMR showed a single peak at 35 ppm similar to that of **1**. Treatment of **P1** with concentrated hydrochloric acid gave the corresponding phosphonic acid modified material **P2**.¶ The absence of any Q^n type resonances in the ^{29}Si CP MAS NMR of **P2** indicates that the transformation from ester to acid occurred without any Si–C cleavage. The decrease in C : P ratio and changes in the NMR spectra from **P1** to **P2** (in particular the disappearance of the signals due to the phosphonate ester group $-PO(OCH_2CH_3)_2$ at 63 ppm, see Fig. 1), is consistent with the formation of the phosphonic acid from the ester. Average formulae for these materials derived from C : P ratios and based on predominantly T^2 environments (66% condensation) are $[(HO)SiCH_2CHPO(OEt)_2CH_2CH_2SiO_2(OH)]_n$ **P1** and $[(HO)SiCH_2CHPO(OH)_2CH_2CH_2SiO_2(OH)]_n$ **P2**.

The material **P2** was found to be microporous by nitrogen sorption porosimetry with very narrow pore size distribution.

It is our intention initially to utilise the phosphonic acid functionality in these and related materials we have prepared for various catalytic transformations. Preliminary experiments based on catalytic pinacol–pinacolone rearrangement and dehydration of cyclohexanol were used to test the reactivity of the phosphonic acid functionality in **P2**. A range of solid acid catalysts have been reported to catalyse pinacol–pinacolone rearrangements; examples include metal substituted aluminophosphates,[8] lanthanide substituted zeolites,[9] heteropolytungstates,[10] various SAPOs (silicoaluminophosphates)[11] and polyphosphoric acid.[12]

A reaction between **P2** (0.2 g) and pinacol (6.0 g) at 140 °C (no solvent) resulted in 80% conversion to pinacolone after 12 h. Control experiments‖ using mesoporous or microporous silicas under the same conditions afforded no rearranged product. Attempted dehydration reactions using **P2** (0.25 g) and cyclohexanol (25 cm³) ($C_6H_{11}OH : PO(OH)_2 = 60 : 1$) at 120 °C resulted in about 15% conversion to cyclohexene (^1H NMR of the cooled reaction mixture) after 12 h. In control experiments using mesoporous or microporous silica under the same conditions no cyclohexene was produced. Industrial processes for production of cyclohexene require high temperature and pressure whereby cyclohexanol is fed to activated catalysts such as silica, alumina or zinc aluminate at 380–450 °C (see ref. 13 for example). Neat phosphoric acid used in large excess is also active between 160–170 °C.[14]

A detailed systematic study of both reaction types will be carried out to optimise the catalyst performance.

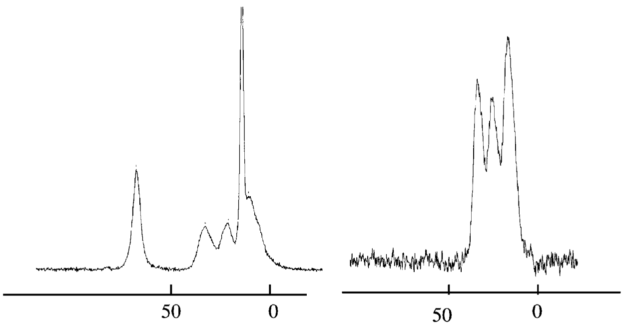

Fig. 1

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† Electronic supplementary information (ESI) available: Fig. 2 nitrogen sorption isotherm of **P2** and Fig. 3 BJH pore size distribution of **P2**. See http://www.rsc.org/suppdata/cc/b0/b008192m/

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Our material **P2** and related materials we have prepared[15] are also subjects for other studies including rearrangements, condensations, ion exchange and binding of biological molecules.

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Notes and references

‡ 1,4-Bis(triethoxysilyl)-2-(diethylphosphonato)butane **1**: 1,4-bis(triethoxysilyl)but-2-ene (30.0 g, 78.8 mmol) and diethyl phosphite (21.8 g, 158 mmol, 20.3 ml) and di-*tert*-butyl peroxide (0.58 g, 3.9 mmol, 0.72 ml) were heated at 140 °C for 18 h under nitrogen. The resultant mixture was distilled under reduced pressure to yield **1** (22.5 g, 55%) bp 147 °C, 0.4 mm Hg; Calcd C 46.3, H 9.1. Found C 46.1, H 9.0; *m/z* 541.5 $(M + \mathrm{Na})^+$ 519.5 (M^+), 473.4 $(\mathrm{M} - \mathrm{OCH_2CH_3})^+$; Calcd for $C_{20}H_{48}Si_2P$ 519.2574; Found 519.2569; NMR: $[(^6CH_3{}^5CH_2O)_3Si^1CH_2{}^2CH\{PO(O^9CH_2{}^{10}CH_3)_2\}$-$^3CH_2{}^4CH_2Si(O^7CH_2{}^8CH_3)_3]$ superscripts indicate proton or carbon environments as appropriate ^{1}H(CDCl$_3$) δ 0.51–1.03 (complex m, 4H, $^1CH_2$, $^4CH_2$), 1.05 (t, 9 H, $^8CH_3$, $^3J_{HH}$ 8 Hz), 1.06 (t, 9 H, $^6CH_3$, $^3J_{HH}$ 8 Hz), 1.27 (t, 6 H, $^{10}CH_3$, $^3J_{HH}$ 8 Hz), 1.56–1.91 (complex m, 3H, ^2CH, $^3CH_2$), 3.66 (q, $^7CH_2$, $^3J_{HH}$ 8 Hz), 3.69 (q, $^5CH_2$, $^3J_{HH}$ 8 Hz), 3.95 (m, $^9CH_2$, $^3J_{PH}$ 10 Hz); ^{13}C (CDCl$_3$) δ 8.17 (d, $^4CH_2$, $^3J_{PC}$ 4 Hz), 8.92, 9.01 (d, $^1CH_2$, $^2J_{PC}$ 6.5 Hz), 16.30, 16.39 (d, $^{10}CH_3$, $^2J_{PC}$ 6.5 Hz), 18.10 (s, $^6CH_3$,$^8CH_3$), 23.56 (s, $^3CH_2$, $^2J_{PC}$ 4 Hz), 32.16, 34.35 (d, ^2CH, J_{PC} 138 Hz), 58.09 (s, $^5CH_2$), 58.29 (s, $^7CH_2$), 61.16, 61.25 (d, $^9CH_2$, $^2J_{PC}$ 6.5 Hz); ^{29}Si (CDCl$_3$) δ −45.65 (s, ^{4}C-Si), −47.66, −47.94 (d, ^{1}C-Si, $^3J_{PSi}$ 40 Hz); ^{31}P (CDCl$_3$) δ 36.13 (s).

§ **P1**: Compound **1** (4.45 g, 8.58 mmol), THF (37 ml) and 1 M HCl (0.8 ml) were stirred under dynamic nitrogen for 1 h and stored in a polythene bottle. Gelation occurred after 11 d. The transparent monolithic gel obtained was air dried for 1 week and then dried at 60 °C in an oven for 24 h. A transparent monophasic crack-free glass was produced. This was powdered, washed with water, ethanol and ether consecutively, and then dried under vacuum at 120 °C for 24 h; ^{13}C CP MAS δ 14.3, 16.9, 23.2, 33.2, 63.1; ^{29}Si CP MAS δ −63.5; ^{31}P CP MAS δ 34.5; Calculated average formula based on T^2 environments $[(HO)SiCH_2CHPO(OEt)_2CH_2CH_2SiO_2(OH)]_n$ C : P = 3.1, Found C/P = 2.8; Calculated for **P1**·3H$_2$O C, 26.2; H, 6.3, P 8.5. Found C 26.6, H 6.0, P 9.6%.

¶ **P2**: Powdered **P1** (1.00 g) and concentrated HCl (100 ml) were refluxed for 24 h. The mixture was filtered through a fritted funnel and washed with excess H$_2$O to remove all traces of HCl, followed by ethanol and ether. The residue was dried under vacuum at 120 °C for 24 h; ^{13}C CP MAS δ 16.5, 23.1, 33.6; ^{29}Si CP MAS NMR δ −66.2; ^{31}P CP MAS NMR δ 33.5; Average formula based on T^2 environments $[(HO)SiCH_2CH$-$PO(OH)_2CH_2CH_2SiO_2(OH)]_n$ C : P = 1.55, Found C : P = 1.35; Calculated **P2**·2H$_2$O C 16.3, H 5.1, P 10.5. Found C 14.2, H 4.3, P 10.5%; BET surface area 354 $m^2\ g^{-1}$; micropore surface area 345 $m^2\ g^{-1}$; micropore volume 0.192 $cm^3\ g^{-1}$; total pore volume 0.219 $cm^3\ g^{-1}$.

‖ Control experiments were carried out with microporous and mesoporous silicas prepared by standard methods from TEOS and with samples of these treated with concentrated HCl and washed in the manner described above for **P2**.

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