

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

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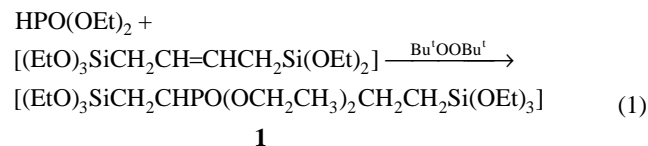
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A novel microporous solid acid, the phosphonic acid modified polysilsesquioxane [(HO)SiCH₂CHPO(OH)₂CH₂CH₂SiO₂(OH)]_n **P2**, from the new single precursor compound [(EtO)₃SiCH₂CHPO(OCH₂CH₃)₂CH₂CH₂Si(OEt)₃] **1**, is reported, along with the catalytic 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(CH₂)_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-ether⁴ or cyclam⁵ 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)SiCH₂CHPO(OCH₂CH₃)₂CH₂CH₂SiO₂(OH)]_n **P1** and [(HO)SiCH₂CHPO(OH)₂CH₂CH₂SiO₂(OH)]_n **P2** prepared from the new precursor compound [(EtO)₃SiCH₂CHPO(OCH₂CH₃)₂CH₂CH₂Si(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-ene⁷ and was fully characterised by solution phase NMR, mass spectrometry and elemental analysis.



P1 was obtained as a transparent monolith after acid-catalysed sol–gel processing of **1** in THF.§ The solid state ¹³C CP MAS NMR spectrum of **P1** had peaks close to those observed for compound **1**; the ²⁹Si spectrum showed one broad resonance at –63 ppm consistent with predominantly T² type silicon sites while the ³¹P 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 Qⁿ type resonances in the ²⁹Si 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(OCH₂CH₃)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 T² environments (66% condensation) are [(HO)SiCH₂CHPO(OEt)₂CH₂CH₂SiO₂(OH)]_n **P1** and [(HO)SiCH₂CHPO(OH)₂CH₂CH₂SiO₂(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) (C₆H₁₁OH: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.

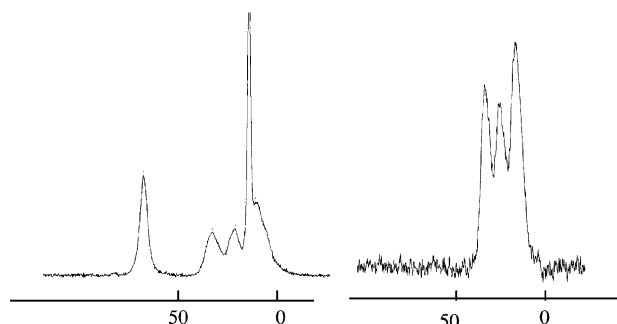


Fig. 1

† 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/>

Our material **P2** and related materials we have prepared¹⁵ 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* + Na)⁺ 519.5 (*M*⁺), 473.4 (*M* - OCH₂CH₃)⁺; Calcd for C₂₀H₄₈Si₂P 519.2574; Found 519.2569; NMR: [(⁶CH₃⁵CH₂O)₃Si¹CH₂²CH{PO(O⁹CH₂¹⁰CH₃)₂}-³CH₂⁴CH₂Si(O⁷CH₂⁸CH₃)₃] superscripts indicate proton or carbon environments as appropriate ¹H(CDCl₃) δ 0.51–1.03 (complex m, 4H, ¹CH₂, ⁴CH₂), 1.05 (t, 9 H, ⁸CH₃, ³J_{HH} 8 Hz), 1.06 (t, 9 H, ⁶CH₃, ³J_{HH} 8 Hz), 1.27 (t, 6 H, ¹⁰CH₃, ³J_{HH} 8 Hz), 1.56–1.91 (complex m, 3H, ²CH, ³CH₂), 3.66 (q, ⁷CH₂, ³J_{HH} 8 Hz), 3.69 (q, ⁵CH₂, ³J_{HH} 8 Hz), 3.95 (m, ⁹CH₂, ³J_{PH} 10 Hz); ¹³C (CDCl₃) δ 8.17 (d, ⁴CH₂, ³J_{PC} 4 Hz), 8.92, 9.01 (d, ¹CH₂, ²J_{PC} 6.5 Hz), 16.30, 16.39 (d, ¹⁰CH₃, ²J_{PC} 6.5 Hz), 18.10 (s, ⁶CH₃, ⁸CH₃), 23.56 (s, ³CH₂, ²J_{PC} 4 Hz), 32.16, 34.35 (d, ²CH, ¹J_{PC} 138 Hz), 58.09 (s, ⁵CH₂), 58.29 (s, ⁷CH₂), 61.16, 61.25 (d, ⁹CH₂, ²J_{PC} 6.5 Hz); ²⁹Si (CDCl₃) δ -45.65 (s, ⁴C-Si), -47.66, -47.94 (d, ¹C-Si, ³J_{PSi} 40 Hz); ³¹P (CDCl₃) 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; ¹³C CP MAS δ 14.3, 16.9, 23.2, 33.2, 63.1; ²⁹Si CP MAS δ -63.5; ³¹P CP MAS δ 34.5; Calculated average formula based on T² environments [(HO)SiCH₂CHPO(OEt)₂CH₂CH₂SiO₂(OH)]_n C:P = 3.1, Found C/P = 2.8; Calculated for **P1**·3H₂O 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 H₂O to remove all traces of HCl, followed by ethanol and ether. The residue was dried under vacuum at 120 °C for 24 h; ¹³C CP MAS δ 16.5,

23.1, 33.6; ²⁹Si CP MAS NMR δ -66.2; ³¹P CP MAS NMR δ 33.5; Average formula based on T² environments [(HO)SiCH₂CHPO(OH)₂CH₂CH₂SiO₂(OH)]_n C:P = 1.55, Found C:P = 1.35; Calculated **P2**·2H₂O C 16.3, H 5.1, P 10.5. Found C 14.2, H 4.3, P 10.5%; BET surface area 354 m² g⁻¹; micropore surface area 345 m² g⁻¹; micropore volume 0.192 cm³ g⁻¹; total pore volume 0.219 cm³ 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**.

- (a) P. M. Price, J. H. Clark and D. J. Macquarrie, *J. Chem. Soc., Dalton Trans.*, 2000, 101; (b) J. H. Clark and D. Macquarrie, *Chem. Commun.*, 1998, 853; (c) D. A. Loy and K. J. Shea, *Chem. Rev.*, 1995, **95**, 1431; (d) R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420.
- I. Rodriguez, S. Iborra, A. Corma, F. Rey and J. L. Jorda, *J. Chem. Soc., Chem. Commun.*, 1999, 593; J. A. Elings, R. Ait-Meddour, J. H. Clark and D. J. Macquarrie, *J. Chem. Soc., Chem. Commun.*, 1998, 2707; R. Ciriminna, J. Blum, D. Anvir and M. Pagliaro, *J. Chem. Soc., Chem. Commun.*, 2000, 1441; Y. Wang, T. Ju Su, R. Green, Y. Tangt, D. Styrkas, T. N. Danks, R. Bolton and J. R. Lu, *J. Chem. Soc., Chem. Commun.*, 2000, 587; S. J. Bae, S.-Wook Kim, T. Hyeon and B. Moon Kim, *J. Chem. Soc., Chem. Commun.*, 2000, 31.
- H. W. Oviatt, K. J. Shea, S. Kalluri, Y. Shi, W. H. Steier and L. R. Dalton, *Chem. Mater.*, 1995, **7**, 493; A.-C. Franville, D. Zambon and R. Mahiou, *Chem. Mater.*, 2000, **12**, 428.
- S. Brandes, R. J. P. Corriu, F. Denat, G. Dubois, R. Guillard and C. Reye, *J. Chem. Soc., Chem. Commun.*, 1999, 2283.
- C. Chuit, R. J. P. Corriu, G. Dubois and C. Reye, *J. Chem. Soc., Chem. Commun.*, 1999, 723.
- P. Audebert, P. Calas, G. Cerveau, R. J. P. Corriu and N. Costa, *J. Electroanal. Chem.*, 1994, **372**, 275.
- R. J. P. Corriu, J. J. E. Moreau, P. Thepot and M. Wong Chi Man, *Chem. Mater.*, 1992, **4**, 1217.
- B. Y. Hsu and S. F. Cheng, *Microporous Mesoporous Mater.*, 1998, **21**, 505.
- C. P. Bezouhanova and F. A. Jabur, *J. Mol. Catal.*, 1994, **87**, 39.
- Y. Toyoshi, T. Nakato and T. Okuhara, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2817; Y. Toyoshi, T. Nakato, R. Tamura, H. Takahashi, H. Tsue, K. Hirao and T. Okuhara, *Chem. Lett.*, 1998, 135.
- F. A. Jabur, V. J. Penchev and C. P. Bezoukhanova, *J. Chem. Soc., Chem. Commun.*, 1994, 1591.
- M. A. Kakimoto, T. Seri and Y. Imai, *Bull. Chem., Soc. Jpn.*, 1988, **61**, 2643.
- T. K. Shioyama and O. K. Bartlesville, Phillips Petroleum Company, US1980000113948 April 7, 1981.
- W. M. Dehn and K. E. Jackson, *J. Am. Chem., Soc.*, 1933, **55**, 4285.
- A. Aliev, D. Li Ou, B. Ormsby and A. C. Sullivan, *J. Mat. Chem.*, 2000, **10**, 2758.