

## Supplementary materials

### Control of Micro/Mesoporosity in Non-hydrolytic Hybrid Silicophosphate Xerogels

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### Experimental

**Syntheses.** Si(OAc)<sub>4</sub> (OAc = acetate) was prepared according to the literature.<sup>1</sup> MeSi(OAc)<sub>3</sub>, Me<sub>2</sub>Si(OAc)<sub>2</sub>, <sup>t</sup>BuSi(OAc)<sub>3</sub>, and (AcO)<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>Si(OAc)<sub>3</sub>, (n = 1–3, 6) were prepared by a modified procedure – the complete acetylation of the alkyltrichlorosilanes was attained by distilling off CH<sub>3</sub>COCl from the reaction mixture. PhSi(OAc)<sub>3</sub> and Ph<sub>2</sub>Si(OAc)<sub>2</sub> were prepared according to the literature<sup>2,3</sup> and purified by vacuum sublimation. <sup>t</sup>BuOSi(OAc)<sub>3</sub> was prepared according to literature.<sup>4</sup> SiCl<sub>4</sub> (Merck, 99 %) and acetic acid anhydride (Riedel de Haën, 98 %) were distilled prior to use, <sup>t</sup>BuOH was dried over molecular sieve, NaOAc was dried in an oven at 110 °C, MeSiCl<sub>3</sub> (Sigma-Aldrich, 99 %), Me<sub>2</sub>SiCl<sub>2</sub> (Sigma-Aldrich, 99.5 %), <sup>t</sup>BuSiCl<sub>3</sub> (Sigma-Aldrich, 96 %), Cl<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>SiCl<sub>3</sub> (Gelest, Inc.), PhSiCl<sub>3</sub> (Sigma-Aldrich, 97 %) and Ph<sub>2</sub>SiCl<sub>2</sub> (Sigma-Aldrich, 97 %) were used as received. Toluene was freshly distilled from Na/benzophenone under N<sub>2</sub> before use. *Tris*(trimethylsilyl)phosphate (TTP) was prepared from H<sub>3</sub>PO<sub>4</sub> and Me<sub>3</sub>SiCl and vacuum-distilled. PhP(O)(OSiMe<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>11</sub>P(O)(OSiMe<sub>3</sub>)<sub>2</sub> were prepared from the corresponding phosphonic acids and Me<sub>3</sub>SiCl.<sup>5</sup>

$(\text{Me}_3\text{SiO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OSiMe}_3)_2$  and  $(\text{Me}_3\text{SiO})_2\text{P}(\text{O})\text{C}_6\text{H}_4\text{P}(\text{O})(\text{OSiMe}_3)_2$  were prepared from triethylphosphite by the Arbuzov reaction<sup>6</sup> followed by silylation with  $\text{Me}_3\text{SiBr}$ .<sup>7</sup> Their purification was done by vacuum distillation and vacuum sublimation, respectively.  $\text{PhP}(\text{O})(\text{OH})_2$  (Sigma-Aldrich, 98 %),  $\text{C}_6\text{H}_{11}\text{P}(\text{O})(\text{OH})_2$  (house stock), triethylphosphite (Sigma-Aldrich, 98 %), 1,2-dibromoethane (Sigma-Aldrich, 98 %), 1,4-dibromobenzene (Sigma-Aldrich, 98%) and  $\text{Me}_3\text{SiBr}$  (Sigma-Aldrich, 97 %) were used as received,  $\text{NiCl}_2 \cdot x\text{H}_2\text{O}$  was vacuum dried at 150 °C. Benzene- $d_6$  was dried over and distilled from Na/K alloy and degassed prior to use.  $\text{CDCl}_3$  was dried by  $\text{P}_2\text{O}_5$  and vacuum-transferred to an ampoule.

**Characterization.** The IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded on a Bruker Tensor T27 spectrometer. Samples were prepared as KBr pellets.  $\text{N}_2$  adsorption-desorption experiments were performed at 77 K on a Quantachrome Autosorb-1MP porosimeter.<sup>8,9</sup> Prior to the measurements, the samples were degassed at 25 °C for at least 24 h until the outgas rate was less than  $0.4\text{ Pa min}^{-1}$ . The adsorption-desorption isotherm was measured for each sample at least three times. The specific surface area was determined by the multipoint BET method with at least five data points with relative pressures between 0.05 and 0.23. Micropore volume was established from a t-plot and pore size distribution from DFT procedure with Kernel N2 at 77 K on silica, cylindrical pore, NSDFT equilibrium model. Thermal analysis (TG/DSC) was measured on a Netzsch STA 449C Jupiter apparatus from 25–1000 °C under flowing air ( $70\text{ cm}^3\text{ min}^{-1}$ ) with a heating rate of  $5\text{ K min}^{-1}$ . Solution NMR spectra were recorded on a Bruker Avance II 300 NMR spectrometer at frequencies of 300.1 MHz for  $^1\text{H}$  and 75.5 MHz for  $^{13}\text{C}$  with deuterated solvents as the external lock. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to the residual proton signals or carbon resonances of benzene- $d_6$  (7.15 and 128.0 ppm, respectively) and  $\text{CDCl}_3$  (7.20 and 77.0 ppm). Solid-state  $^{31}\text{P}$  MAS,  $^{29}\text{Si}$  CPMAS, and  $^{13}\text{C}$  CPMAS NMR spectra were acquired on a wide-bore Varian INOVA 400 NMR spectrometer with a broadband Chemagnetic 5mm MAS probe. Inside a dry box, samples were loaded into 5 mm pencil rotors, stoppered with teflon plugs and sealed with silicon grease and paraffin wax. Magic angle spinning rates were 5 kHz for  $^{29}\text{Si}$  and  $^{13}\text{C}$  CPMAS and 10 kHz for  $^{31}\text{P}$  MAS spectra. Chemical shifts were referenced externally to  $^{31}\text{P}$   $\delta$  [ $\text{H}_3\text{PO}_4$  (85%)]: 0.0 ppm;  $^{29}\text{Si}$   $\delta$  [ $(\text{Me}_3\text{SiO})_8\text{Si}_8\text{O}_{20}$ ]: 11.72 ppm;  $^{13}\text{C}$   $\delta$  [adamantane] 38.68 ppm. GC-MS spectra were obtained on a Thermo Scientific Trace GC Ultra – TSQ Quantum XLS mass spectrometer. TS-SQC column (15 m, 0.25 mm, 0.25  $\mu\text{m}$ ) was heated with following program: 50 °C (0 min),  $5\text{ °C min}^{-1}$  up to 80 °C,  $15\text{ °C min}^{-1}$  up to 120 °C,  $35\text{ °C min}^{-1}$  up to 200 °C (0.5 min). Split mode, injector temperature 200 °C, interface temperature 200 °C, detector temperature 200 °C. Column pressure was set to 31.5 kPa and ionization energy to 70 eV. Single-crystal X-ray diffraction data were collected on a KUMA KM-4  $\kappa$ -axis CCD diffractometer

with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The temperature during data collection was 120(2) K. The structure of  $[(\text{Ph}_2\text{Si}\{\text{O}_2\text{P}(\text{O})\text{OSiMe}_3\})_2]$  was solved by direct methods and refined by standard methods using ShelXTL software package.<sup>10,11</sup>

The site occupancy factors of atoms of solvent molecule (disordered near the center of inversion) were set to 0.5 and the rigid bond restrain (RIGU) was applied to whole solvent molecule. Additionally, the geometry of the solvent molecule was restrained by SAME instruction. All hydrogen atoms were placed at calculated positions and were refined as riding with their  $U_{\text{iso}}$  set to either  $1.2U_{\text{eq}}$  or  $1.5U_{\text{eq}}$  (methyl) of the respective carrier atoms. Hydrogens of methyl groups were allowed to rotate about the C—CH<sub>3</sub> bond. Details of the data collection and structure refinement are listed in Tab. 1S. CCDC xxxyyy contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### 1. Mono- and dialkyl/arylacetoxyasilanes and alkyl/arylphosphonic acid esters

**MeSiP.**  $\text{OP}(\text{OSiMe}_3)_3$  (1.450 g; 4.615 mmol) was added dropwise to a stirred solution of  $\text{MeSi}(\text{OAc})_3$  (1.025 g; 4.655 mmol) in toluene (5 cm<sup>3</sup>). After the addition was complete, stirring was stopped and the reaction mixture was kept at 80 °C for one week. The resulting viscous liquid afforded glue-like mixture of oligomers after drying *in vacuo* at room temperature. Further drying at 100 °C provided 0.8722 g of hard glassy product (**MeSiP**) (Tab. 1S).

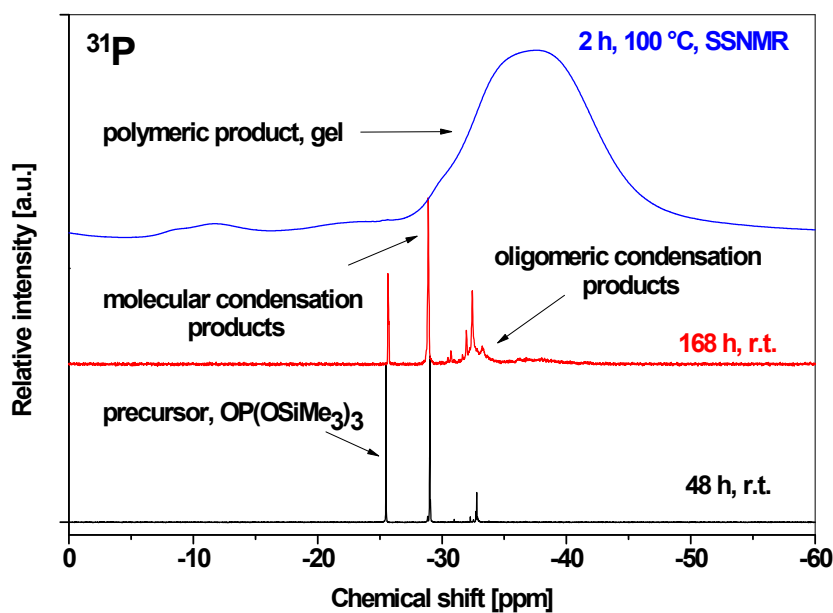


Fig. 1S: The extent of condensation between  $\text{MeSi}(\text{OAc})_3$  and  $\text{OP}(\text{OSiMe}_3)_3$  followed by <sup>31</sup>P NMR.

IR (**MeSiP**, KBr,  $\text{cm}^{-1}$ )  $\nu$ :  $\nu$  500 m, 606 w, 730 m ( $\rho_s$  SiCH<sub>3</sub>), 765 vw ( $\rho_s$  SiCH<sub>3</sub>), 807 s ( $\rho_{as}$  SiCH<sub>3</sub>), 850 s ( $\rho_{as}$  SiCH<sub>3</sub>), 1019 vs ( $\nu$  Si–O–P), 1227 vw, 1260 m ( $\delta_s$  SiCH<sub>3</sub>), 1281 m ( $\delta_s$  SiCH<sub>3</sub>), 1319 m ( $\nu$  P=O), 1377 vw ( $\delta_s$  CH<sub>3</sub>), 1720 w, 1753 m ( $\nu_{as}$  CH<sub>3</sub>COO unident), 2920 vw ( $\nu_s$  CH<sub>3</sub>), 2968 w ( $\nu_{as}$  CH<sub>3</sub>).

<sup>13</sup>C CPMAS NMR (**MeSiP**, ppm)  $\delta$ : –4.1 (POSiCH<sub>3</sub>), 1.1 (O<sub>3</sub>SiCH<sub>3</sub>), 22.7 (CH<sub>3</sub>COO unident), 169.7 (CH<sub>3</sub>COO unident).

<sup>29</sup>Si CPMAS NMR (**MeSiP**, ppm)  $\delta$ : 26 (POSiMe<sub>3</sub>), –61 (MeSiO<sub>3</sub>).

<sup>31</sup>P MAS NMR (**MeSiP**, ppm)  $\delta$ : –37 (O=P(OSi)<sub>3</sub>).

**SiHexP**. C<sub>6</sub>H<sub>11</sub>P(O)(OSiMe<sub>3</sub>)<sub>2</sub> (1.327 g; 4.305 mmol) was added dropwise to a stirred melt of Si(OAc)<sub>4</sub> (0.572 g; 2.16 mmol) at 125 °C. The reaction was stopped after 30 min and drying *in vacuo* afforded 0.747 g of orange xerogel (**SiHexP**). The reaction was carried out also in toluene at 80 °C providing an orange xerogel. Both products showed identical properties.

IR (**SiHexP**, KBr,  $\text{cm}^{-1}$ )  $\nu$ : 451 m, 561 m, 649 w ( $\nu$  SiC<sub>3</sub>), 762 w ( $\rho_s$  SiCH<sub>3</sub>), 851 s ( $\rho_{as}$  SiCH<sub>3</sub>), 894 w, 1021 vs ( $\rho$  CH<sub>3</sub>), 1093 vs ( $\nu$  Si–O–P), 1127 vs ( $\nu$  P–O–Si), 1221 s, 1256 s ( $\delta_s$  SiCH<sub>3</sub>), 1283 m, 1300 sh ( $\nu$  P=O), 1372 vw, 1452 m, 1541 w ( $\nu_{as}$  CH<sub>3</sub>COO bident), 1720 w ( $\nu_{as}$  CH<sub>3</sub>COO unident), 1761 w ( $\nu_{as}$  CH<sub>3</sub>COO unident), 2856 s ( $\nu_s$  CH<sub>2</sub>), 2933 vs ( $\nu_{as}$  CH<sub>2</sub>).

<sup>13</sup>C CPMAS NMR (**SiHexP**, ppm)  $\delta$ : –1.2 (POSiCH<sub>3</sub>), 26.6 (C<sub>6</sub>H<sub>11</sub>), 37.2 (C<sub>6</sub>H<sub>11</sub>), 167.9 (CH<sub>3</sub>COO unident), 192.1 (CH<sub>3</sub>COO bident).

<sup>29</sup>Si MAS NMR (**SiHexP**, ppm)  $\delta$ : 22 (POSiMe<sub>3</sub>), –111 (SiO<sub>4</sub>), –195 (SiO<sub>6</sub>), –214 (SiO<sub>6</sub>).

<sup>31</sup>P MAS NMR (**SiHexP**, ppm)  $\delta$ : 10 (C<sub>6</sub>H<sub>11</sub>P(O)(OSi)<sub>2</sub>), 3 (C<sub>6</sub>H<sub>11</sub>P(OSi)<sub>3</sub>).

**Tab. 1S: Mono- and dialkyl/arylacetoxy silanes and alkyl/arylphosphonic acid esters: Reagent molar amounts, yields, degrees of condensation (DC) and comparison of experimental (ML) and calculated mass losses (ML<sub>calc</sub>) during thermogravimetric analysis of hybrid silicophosphates.**

Sample	n <sub>Si</sub> [mmol]	n <sub>P</sub> [mmol]	Yield [g]	DC [%]	ML [%]	ML <sub>calc</sub> [%]
SiP	11.93	15.84	2.733	85.7	29.4	32.8
MeSiP	4.655	4.615	0.872	87.1	32.1	35.3
Me2SiP	4.20	2.80	0.579	89.4	-	-
PhSiP	3.621	3.636	1.296	63.6	-	-
Ph2SiP	3.30	2.38	1.144	61.9	-	-
BuSiP	2.18	2.40	0.659	69.3	-	-
SiHexP	2.16	4.305	0.747	100	65.0	42.8
SiPhP	4.597	9.318	2.582	58.1	63.5	64.1

Tab. 2S: Gelation properties of various alkyl/arylacetoxy silanes and alkyl/arylphosphonates.

Sample	Si precursor	P precursor	Sol <sup>a</sup>	Gel	Product <sup>b</sup>	SA [m <sup>2</sup> g <sup>-1</sup> ]
SiP	Si(OAc) <sub>4</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	Yes	Yes	X	568
MeSiP	MeSi(OAc) <sub>3</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	Yes	Yes	X	Nonporous
Me <sub>2</sub> SiP	Me <sub>2</sub> Si(OAc) <sub>2</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	Yes	No	O	-
PhSiP	PhSi(OAc) <sub>3</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	Yes	No	O	-
Ph <sub>2</sub> SiP	Ph <sub>2</sub> Si(OAc) <sub>2</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	No	No	M	-
BuSiP	<sup>t</sup> BuSi(OAc) <sub>3</sub>	OP(OSiMe <sub>3</sub> ) <sub>3</sub>	Yes	No	O	-
SiHexP	Si(OAc) <sub>4</sub>	C <sub>6</sub> H <sub>11</sub> P(O)(OSiMe <sub>3</sub> ) <sub>2</sub>	Yes	Yes	X	Nonporous
SiPhP	Si(OAc) <sub>4</sub>	PhP(O)(OSiMe <sub>3</sub> ) <sub>2</sub>	Yes	Yes	P	Nonporous

<sup>a</sup> Results of NMR reactions. <sup>b</sup> X = xerogel, P = precipitate, O = mixture of oligomers, M = molecular products. Nonporous = SA below 10 m<sup>2</sup> g<sup>-1</sup>

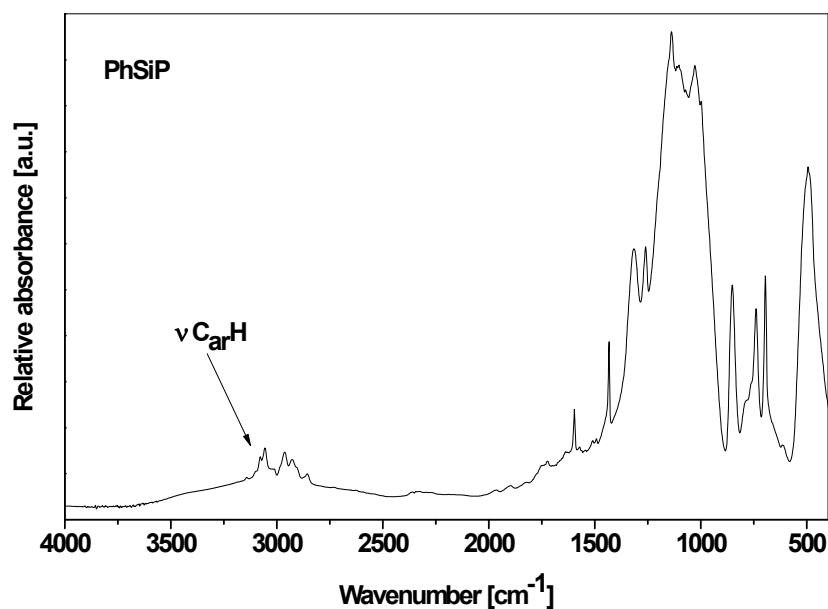


Fig. 2S: IR spectrum of hybrid silicophosphate xerogel with Ph-SiO<sub>3</sub> groups (PhSiP).

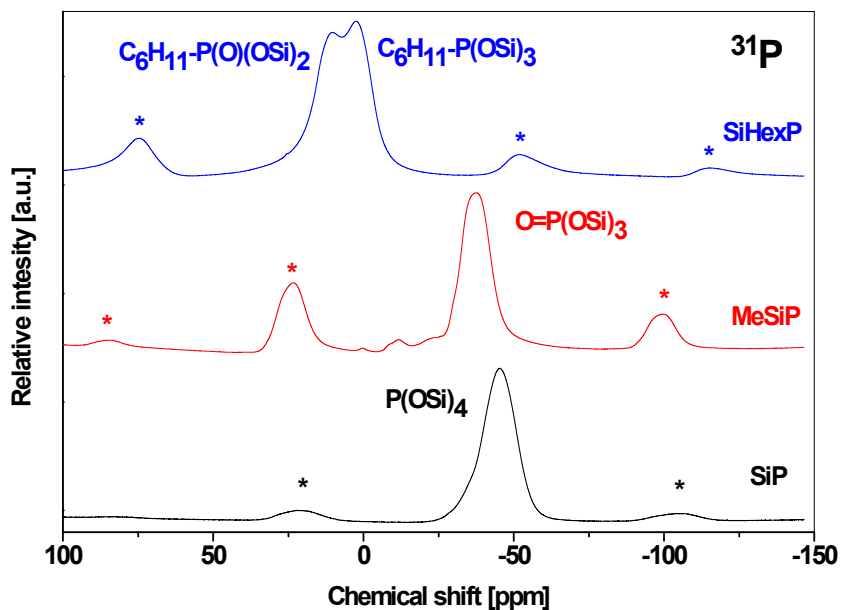


Fig. 3S:  $^{31}\text{P}$  MAS NMR spectra of hybrid silicophosphate xerogel with  $\text{C}_6\text{H}_{11}\text{-P(O)}_2$  groups (**SiHexP**, top), hybrid xerogel with  $\text{CH}_3\text{-SiO}_3$  groups (**MeSiP**, center) and parent silicophosphate sample (**SiP**, bottom). Asterisks denote spinning sidebands.

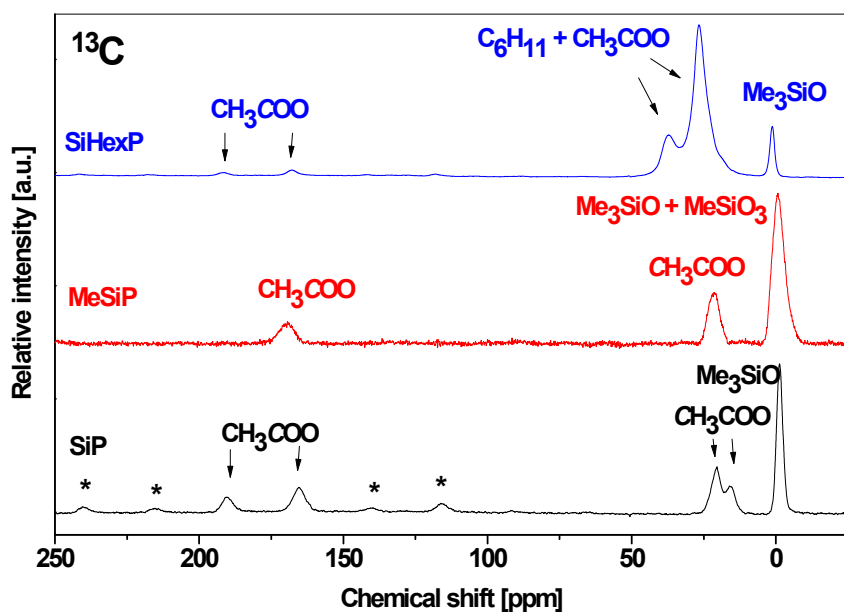


Fig. 4S:  $^{13}\text{C}$  CPMAS NMR spectra of hybrid silicophosphate xerogel with  $\text{C}_6\text{H}_{11}\text{-P(O)}_2$  groups (**SiHexP**, top), hybrid xerogel with  $\text{CH}_3\text{-SiO}_3$  groups (**MeSiP**, center) and parent silicophosphate sample (**SiP**, bottom). Asterisks denote spinning sidebands.

**BuOSiP.** OP(OSiMe<sub>3</sub>)<sub>3</sub> (0.798 g; 2.54 mmol) was added dropwise to a stirred solution of <sup>t</sup>BuOSi(OAc)<sub>3</sub> (0.711 g; 2.55 mmol) in toluene (8 cm<sup>3</sup>). After the addition was complete, stirring was stopped. The reaction mixture was kept at 80 °C for 48 h during which time the viscosity of the mixture increased, however the gel was not formed. The reaction mixture was then dried under vacuum for two days and 0.410 g of a white powder (**BuOSiP**) was obtained.

IR (**BuOSiP**, KBr, cm<sup>-1</sup>)  $\nu$ : 514 m, 763 w ( $\rho_s$  SiCH<sub>3</sub>), 856 s ( $\rho_{as}$  SiCH<sub>3</sub>), 894 w, 1102 vs ( $\nu$  Si–O–P), 1259 s ( $\delta_s$  SiCH<sub>3</sub>), 1305 sh ( $\nu$  P=O), 1373 w, 1397 vw, 1475 w, 1705 w ( $\nu_{as}$  COO unident), 1758 w ( $\nu_{as}$  COO unident), 2906 s ( $\nu_s$  CH<sub>3</sub>), 2980 vs ( $\nu_{as}$  CH<sub>3</sub>).

<sup>13</sup>C CP/MAS NMR (**BuOSiP**, ppm)  $\delta$ : 0.2 (POSiCH<sub>3</sub>), 30.5 ((CH<sub>3</sub>)<sub>3</sub>CO), 75.5 ((CH<sub>3</sub>)<sub>3</sub>CO).

<sup>29</sup>Si MAS NMR (**BuOSiP**, ppm)  $\delta$ : 23 (POSiMe<sub>3</sub>), 14 (POSiMe<sub>3</sub>), –114 (SiO<sub>4</sub>), –215 (SiO<sub>6</sub>).

**[(Ph<sub>2</sub>Si{O<sub>2</sub>P(O)OSiMe<sub>3</sub>})<sub>2</sub>].** A solution of diphenyldiacetoxysilane (0.292 g; 0.972 mmol) in toluene (10 cm<sup>3</sup>) was dropwise added to the solution of TTP (0.307 g; 0.977 mmol) in toluene (10 cm<sup>3</sup>). The reaction mixture was placed into the oil bath and kept at 80 °C for one week. According to <sup>31</sup>P NMR, the starting ester was completely consumed and the reaction mixture consisted of at least four molecular condensation products. The toluene was removed *in vacuo* and the resulting mixture was recrystallized from 10 cm<sup>3</sup> of hexane and 2 cm<sup>3</sup> of THF affording small amount of colorless hexagonal crystals (20 mg, 6 %).

<sup>1</sup>H NMR ([[(Ph<sub>2</sub>Si{O<sub>2</sub>P(O)OSiMe<sub>3</sub>})<sub>2</sub>], ppm)  $\delta$ : 0.09 (s, (CH<sub>3</sub>)<sub>3</sub>Si), 1.29 (s, CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>), 6.9–7.7 (mult., (C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Si).

<sup>31</sup>P NMR ([[(Ph<sub>2</sub>Si{O<sub>2</sub>P(O)OSiMe<sub>3</sub>})<sub>2</sub>], ppm)  $\delta$ : –32.6 (s, O<sub>2</sub>P(O)OSiMe<sub>3</sub>).

[(Ph<sub>2</sub>Si{O<sub>2</sub>P(O)OSiMe<sub>3</sub>})<sub>2</sub>] and [(<sup>t</sup>Bu<sub>2</sub>Si{O<sub>2</sub>P(O)Ph})<sub>2</sub>]<sup>12</sup> are the only structurally characterized examples of Si<sub>2</sub>P<sub>2</sub>O<sub>4</sub> cycles. They resemble the single four-ring (S4R) building units of zeolites. There is a structural difference between these two molecules. In the case of [(Ph<sub>2</sub>Si{O<sub>2</sub>P(O)OSiMe<sub>3</sub>})<sub>2</sub>], the trans trimethylsilyloxy groups on phosphorus atoms point axially with respect to the central Si<sub>2</sub>O<sub>4</sub> plane and the terminal P=O groups are directed equatorially. In the case of [(<sup>t</sup>Bu<sub>2</sub>Si{O<sub>2</sub>P(O)Ph})<sub>2</sub>], the terminal P=O oxygen atoms are in an axial position and phenyl groups are situated in equatorial positions. This is probably due to steric differences between trimethylsilyloxy and phenyl groups.<sup>12</sup> The formation of ring- and cage-containing oligomers is known to prevent gelation to highly cross-linked networks in organotrialkoxysilanes.

**Tab. 3S: Crystal data and structure refinement parameters.**

compound	$[(\text{Ph}_2\text{Si}\{\text{O}_2\text{P}(\text{O})\text{OSiMe}_3\})_2]$
empirical formula	$\text{C}_{37} \text{H}_{48} \text{O}_8 \text{P}_2 \text{Si}_4$
fw	795.05
crystal system	Monoclinic
space group	$P 2_1/n$
temperature, K	120(2)
$\lambda$ , Å	0.71073
$a$ , Å	10.2590(3)
$b$ , Å	11.6835(3)
$c$ , Å	16.8330(4)
$\alpha$ , deg	90
$\beta$ , deg	92.200(2)
$\gamma$ , deg	90
$V$ , Å <sup>3</sup>	2016.13(9)
$Z$	2
$\mu$ , mm <sup>-1</sup>	0.275
no. of reflns collected	7506
no. of indep. reflns ( $R_{\text{int}}$ )	3682 (0.0121)
no. of data / restraints / parameters	3682 / 51 / 266
GoF on $F^2$	1.112
$R_1$ , <sup>a</sup> $wR_2$ <sup>b</sup> ( $I > 2\sigma(I)$ )	0.0306, 0.0882
$R_1$ , <sup>a</sup> $wR_2$ <sup>b</sup> (all data)	0.0383, 0.0906
largest diff. peak / hole, e <sup>-</sup> Å <sup>-3</sup>	0.373 and -0.320

<sup>a</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ . <sup>b</sup>  $wR_2 = [\frac{\sum w (F_o^2 - F_c^2)^2}{\sum (F_o^2)^2}]^{1/2}$ .



**Tab. 4S: Selected bond distances and bond angles for  $[(\text{Ph}_2\text{Si}\{\text{O}_2\text{P}(\text{O})\text{OSiMe}_3\})_2]$**

P(1)=O(4)	
P(1)-O(2)	
P(1)-O(1)	
P(1)-O(3)	
Si(1)-O(3)#1	
Si(1)-O(1)	
Si(1)-C(1)	
Si(1)-C(7)	
O(1)-P(1)-O(3)	
O(3)#1-Si(1)-O(1)	
P(1)-O(1)-Si(1)	
P(1)-O(3)-Si(1)#1	

## 2. Co-condensation of $\text{Si}(\text{OAc})_4$ and $\text{OP}(\text{OSiMe}_3)_3$ partially substituted with $\text{R}_n\text{Si}(\text{OAc})_{4-n}$ ( $n = 1, 2$ ; $\text{R} = \text{Me, Ph}$ ) and $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$

As an example, syntheses and characterizations of samples based on **SiP** xerogel ( $\text{Si}(\text{OAc})_4 + \text{TTP}$ ) with 10.37 % of  $\text{Si}(\text{OAc})_4$  substituted by  $\text{Me}_2\text{Si}(\text{OAc})_2$  (**SiP-Me2SiP2**) and with 12.63 % TTP substituted by  $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$  (**SiP-PhP1**) are described below. Pertinent data for other samples are listed in Tab. 4S.

**SiP-Me2SiP2.**  $\text{OP}(\text{OSiMe}_3)_3$  (0.8843 g; 2.814 mmol) was added dropwise to a stirred solution of  $\text{Si}(\text{OAc})_4$  (0.5284 g, 1.999 mmol) and  $\text{Me}_2\text{Si}(\text{OAc})_2$  (0.0392 g; 0.222 mmol) in toluene (9  $\text{cm}^3$ ). After the addition was complete, stirring was stopped and the reaction mixture was kept at 80 °C for one week. The gel formed in the reaction mixture within few hours. The gel was then dried under vacuum for two days and 0.6383 g of a white xerogel (**SiP-Me2SiP2**) was obtained.

IR (**SiP-Me2SiP2**, KBr,  $\text{cm}^{-1}$ )  $\nu$  :  $\nu$  591 m, 652 w ( $\nu$   $\text{SiC}_3$ ), 764 w ( $\rho_s$   $\text{SiCH}_3$ ), 853 s ( $\rho_{as}$   $\text{SiCH}_3$ ), 1023 vs ( $\rho$   $\text{CH}_3$ ), 1050 vs ( $\nu$   $\text{Si-O-P}$ ), 1121 vs ( $\nu$   $\text{P-O-Si}$ ), 1259 vs ( $\delta_s$   $\text{SiCH}_3$ ), 1303 sh ( $\nu$   $\text{P=O}$ ), 1373 w ( $\delta_s$   $\text{CH}_3$ ), 1418 vw ( $\delta_{as}$   $\text{CH}_3$ ), 1543 w ( $\nu_{as}$   $\text{COO}$  bident), 1718 vw ( $\nu_{as}$   $\text{CH}_3\text{COO}$  unident), 1768 m ( $\nu_{as}$   $\text{CH}_3\text{COO}$  unident), 2907 vw ( $\nu_s$   $\text{CH}_3$ ), 2964 w ( $\nu_{as}$   $\text{CH}_3$ ).

$^{13}\text{C}$  CPMAS NMR (**SiP-Me2SiP2**, ppm)  $\delta$  : 0.5 ( $\text{SiCH}_3$ ), 16.6 ( $\text{CH}_3\text{COO}$  bident), 22.9 ( $\text{CH}_3\text{COO}$  unident), 167.8 ( $\text{CH}_3\text{COO}$  unident), 191.7 ( $\text{CH}_3\text{COO}$  bident).

$^{29}\text{Si}$  MAS NMR (**SiP-Me2SiP2**, ppm)  $\delta$  : 25 ( $\text{POSiMe}_3$ ), -5 ( $\text{Me}_2\text{SiO}_2$ ), -115 ( $\text{SiO}_4$ ), -195 ( $\text{SiO}_6$ ), -214 ( $\text{SiO}_6$ ).

$^{31}\text{P}$  MAS NMR (**SiP-Me2SiP2**, ppm)  $\delta$  : -30 sh ( $\text{O=P}(\text{OSi})_3$ ), -43 ( $\text{P}(\text{OSi})_4$ ).

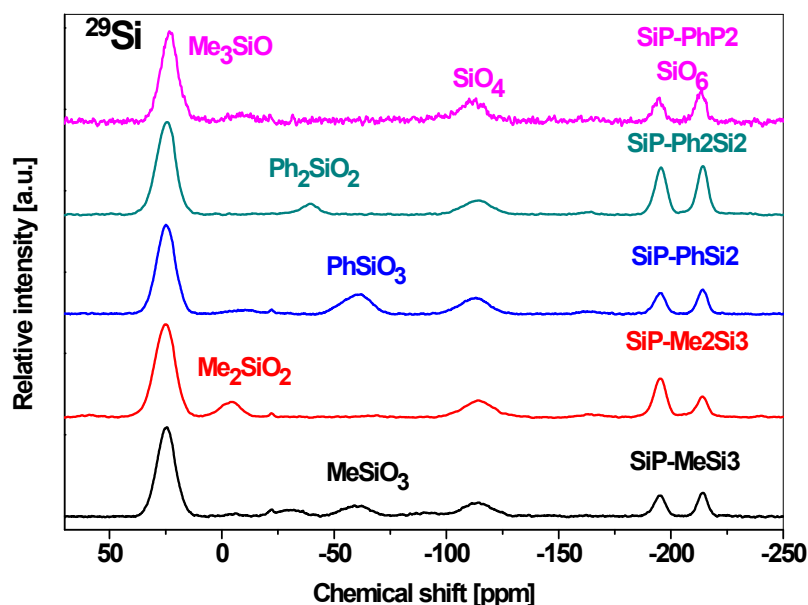


Fig. 5S:  $^{29}\text{Si}$  CPMAS NMR spectra of samples with partially substituted silicon acetate with alkyl- and arylacetoxysilanes and  $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$ .

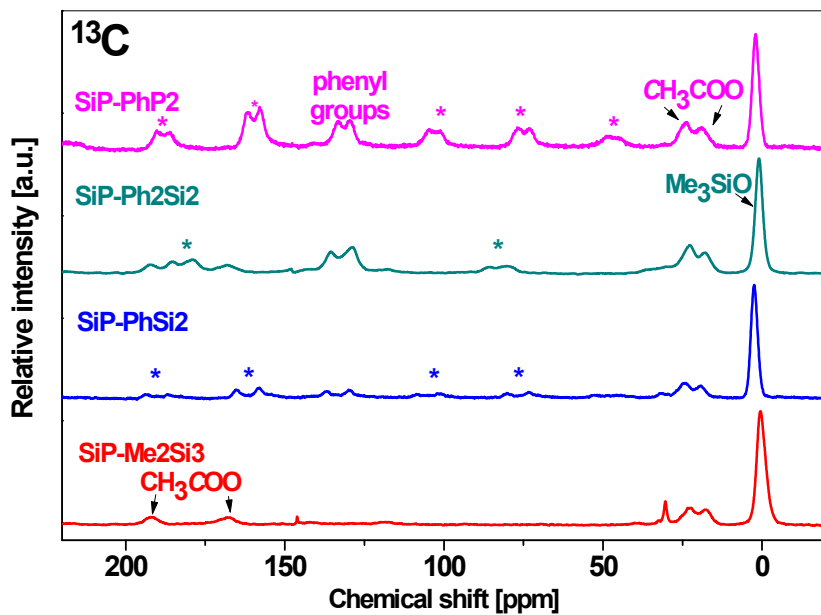


Fig. 6S:  $^{13}\text{C}$  CPMAS NMR spectra of samples with partially substituted silicon acetate with alkyl- and arylacetoxysilanes and  $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$ . Asterisks denote spinning sidebands.

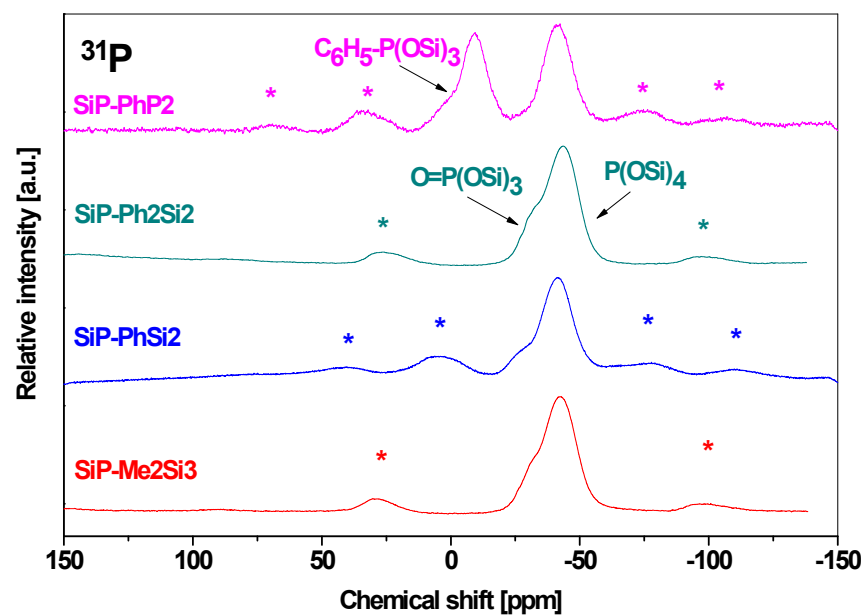


Fig. 7S:  $^{31}\text{P}$  MAS NMR spectra of samples with partially substituted silicon acetate with alkyl- and arylacetoxysilanes and  $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$ . Asterisks denote spinning sidebands.

**SiP-PhP1.** OP(OSiMe<sub>3</sub>)<sub>3</sub> (0.978 g; 3.11 mmol) was added dropwise to a stirred solution of Si(OAc)<sub>4</sub> (0.670 g; 2.54 mmol) in toluene (12 cm<sup>3</sup>). After the addition of TTP was complete, PhP(O)(OSiMe<sub>3</sub>)<sub>2</sub> (0.136 g; 0.450 mmol) was added dropwise to a reaction mixture, which provided a milky gel within 3 hours. The reaction mixture was kept at 80 °C for one week and then dried *in vacuo* affording 0.671 g of a yellowish xerogel (**SiP-PhP1**).

IR (**SiP-PhP1**, KBr, cm<sup>-1</sup>)  $\nu$ : 501 m, 655 w ( $\nu$  SiC<sub>3</sub>), 694 w, 760 w ( $\rho_s$  SiCH<sub>3</sub>), 856 s ( $\rho_{as}$  SiCH<sub>3</sub>), 1021 vs ( $\rho$  CH<sub>3</sub>), 1095 vs ( $\nu$  Si–O–P), 1151 vs ( $\nu$  P–O–Si), 1261 s ( $\delta$  SiCH<sub>3</sub>), 1310 sh ( $\nu$  P=O), 1371 w ( $\delta_s$  CH<sub>3</sub>), 1443 w ( $\delta_{as}$  CH<sub>3</sub>), 1542 w ( $\nu$  CH<sub>3</sub>COO bident), 1718 w ( $\nu$  CH<sub>3</sub>COO unident), 1765 w ( $\nu$  CH<sub>3</sub>COO unident), 2903 vw ( $\nu_s$  CH<sub>3</sub>), 2964 w ( $\nu_{as}$  CH<sub>3</sub>), 3063 vw ( $\nu_{as}$  C<sub>ar</sub>H).

<sup>13</sup>C CPMAS NMR (**SiP-PhP1**, ppm)  $\delta$ : 3.1 (POSiCH<sub>3</sub>), 19.9 (CH<sub>3</sub>COO bident), 25.2 (CH<sub>3</sub>COO unident), 126–140 (C<sub>6</sub>H<sub>5</sub>).

<sup>29</sup>Si MAS NMR (**SiP-PhP1**, ppm)  $\delta$ : 23 (POSiMe<sub>3</sub>), –112 (SiO<sub>4</sub>), –194 (SiO<sub>6</sub>), –213 (SiO<sub>6</sub>).

<sup>31</sup>P MAS NMR (**SiP-PhP1**, ppm)  $\delta$ : –41 (P(OSi)<sub>4</sub>), –9 (PhP(OSi)<sub>3</sub>), 1 sh (PhP(O)(OSi)<sub>2</sub>).

**Tab. 5S:** Co-condensation of Si(OAc)<sub>4</sub> and OP(OSiMe<sub>3</sub>)<sub>3</sub> partially substituted with R<sub>n</sub>Si(OAc)<sub>4-n</sub> (n = 1,2; R= Me, Ph) and PhP(O)(OSiMe<sub>3</sub>)<sub>2</sub>,: Reagent molar amounts, yields, degrees of condensation (DC) and comparison of experimental (ML) and calculated mass losses (ML<sub>calc</sub>) during thermogravimetric analysis of xerogels with partially substituted Si(OAc)<sub>4</sub> or OP(OSiMe<sub>3</sub>)<sub>3</sub>.

Sample	n <sub>Si(OAc)<sub>4</sub></sub> [mmol]	n <sub>OP(OSiMe<sub>3</sub>)<sub>3</sub></sub> [mmol]	n <sup>a</sup> [mmol]	Yield [g]	DC [%]	ML [%]	ML <sub>calc</sub> [%]
SiP	11.93	15.84	-	2.733	85.7	29.4	32.8
SiP-MeSi1	1.92	2.89	0.17	0.547	79.2	35.3	41.4
SiP-MeSi2	1.88	2.81	0.27	0.542	80.7	31.6	39.7
SiP-MeSi3	1.96	3.06	0.37	0.568	82.0	30.6	38.0
SiP-MeSi4	1.94	3.12	0.53	0.575	83.8	29.1	35.6
SiP-MeSi5	1.68	3.79	1.57	0.613	91.0	31.5	24.1
SiP-Me2Si1	3.57	4.88	0.20	1.064	74.8	26.6	46.0
SiP-Me2Si2	1.46	2.05	0.17	0.367	85.3	29.9	33.5
SiP-Me2Si3	1.90	2.73	0.29	0.457	88.2	36.5	27.1
SiP-Me2Si4	1.95	2.86	0.40	0.522	84.9	29.1	34.0
SiP-Me2Si5	1.74	2.63	0.49	0.317	87.5	28.6	-
SiP-Me2Si6	1.80	2.80	0.61	0.539	83.1	30.2	36.4
SiP-PhSi1	1.97	3.17	0.56	0.622	83.7	34.6	39.2
SiP-PhSi2	1.99	3.88	1.26	0.854	81.0	34.9	44.7

SiP-Ph2Si1	2.15	2.94	0.17	0.598	81.0	33.6	41.5
SiP-Ph2Si2	2.21	3.32	0.52	0.727	80.3	38.0	45.3
SiP-PhP1	2.54	3.11	0.45	0.671	83.0	28.2	39.6
SiP-PhP2	2.63	2.22	1.98	0.777	87.3	47.3	41.2

<sup>a</sup>Amount of added organoacetoxysilane/phosphonate component

**Tab. 6S: Textural properties of hybrid xerogels with partially substituted  $\text{Si}(\text{OAc})_4$  with  $\text{R}_n\text{Si}(\text{OAc})_{4-n}$  or  $\text{OP}(\text{OSiMe}_3)_3$  with  $\text{RP}(\text{O})(\text{OSiMe}_3)_2$**

Sample	Additive <sup>a</sup>	Amount of additive [mol%]	SA <sup>b</sup> [ $\text{m}^2 \text{g}^{-1}$ ]	V <sub>total</sub> <sup>c</sup> [ $\text{cm}^3 \text{g}^{-1}$ ]	V <sub>micro</sub> <sup>d</sup> [ $\text{cm}^3 \text{g}^{-1}$ ]	D <sup>e</sup> [nm]	MP <sup>f</sup> [%]
SiP	-	0.00	568	0.280	0.188	2.0	67
SiP-MeSi1	MeSi(OAc) <sub>3</sub>	8.28	529	0.375	0.114	2.9	30
SiP-MeSi2	MeSi(OAc) <sub>3</sub>	12.58	525	0.384	0.093	3.0	24
SiP-MeSi3	MeSi(OAc) <sub>3</sub>	15.97	528	0.344	0.128	2.6	37
SiP-MeSi4	MeSi(OAc) <sub>3</sub>	21.54	517	0.489	0.004	3.8	1
SiP-MeSi5	MeSi(OAc) <sub>3</sub>	48.26	313	0.550	0.000	4.0	0
SiP-Me2Si1	Me <sub>2</sub> Si(OAc) <sub>2</sub>	5.38	522	0.313	0.153	2.4	49
SiP-Me2Si2	Me <sub>2</sub> Si(OAc) <sub>2</sub>	10.37	382	0.217	0.117	2.3	54
SiP-Me2Si3	Me <sub>2</sub> Si(OAc) <sub>2</sub>	13.19	357	0.211	0.105	2.5	50
SiP-Me2Si4	Me <sub>2</sub> Si(OAc) <sub>2</sub>	16.86	380	0.244	0.123	2.5	50
SiP-Me2Si5	Me <sub>2</sub> Si(OAc) <sub>2</sub>	21.96	389	0.233	0.113	2.4	48
SiP-Me2Si6	Me <sub>2</sub> Si(OAc) <sub>2</sub>	25.22	547	0.274	0.175	2.0	64
SiP-PhSi1	PhSi(OAc) <sub>3</sub>	22.22	558	0.550	0.000	4.0	0
SiP-PhSi2	PhSi(OAc) <sub>3</sub>	38.81	251	0.188	0.047	3.0	25
SiP-Ph2Si1	Ph <sub>2</sub> Si(OAc) <sub>2</sub>	7.32	392	0.357	0.005	3.7	1
SiP-Ph2Si2	Ph <sub>2</sub> Si(OAc) <sub>2</sub>	19.05	101	0.102	0.000	4.7	0
SiP-PhP1	PhP(O)(OSiMe <sub>3</sub> ) <sub>2</sub>	12.63	436	0.209	0.140	2.0	67
SiP-PhP2	PhP(O)(OSiMe <sub>3</sub> ) <sub>2</sub>	47.10	424	0.232	0.136	2.2	59

<sup>a</sup> Added  $\text{R}_n\text{Si}(\text{OAc})_{4-n}$  ( $n = 1, 2$ ; R = Me, Ph) or  $\text{PhP}(\text{O})(\text{OSiMe}_3)_2$  components, <sup>b</sup> Surface area, <sup>c</sup> Total pore volume at  $p/p_0 = 0.97$ , <sup>d</sup> Micropore volume by t-plot, <sup>e</sup> Average pore diameter ( $4V_{\text{total}}/\text{SA}$ ), <sup>f</sup> Ratio of micropore volume to total pore volume

11/07/2014

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Autosorb 1 for Windows 1.54

File name:	H:\labdenik Skoskalik_05_11_2014\BET ASTysk\S10PG47\S1P-MeSi1.raw				
Sample ID:	S10PG47	Description:	S10PG47		
Comments:					
Operator:	hugo	Sample weight:	0.0285 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 f./molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	298.00	Analysis Time:	535.1 min
Outgas Temp:	25.0 °C	Outgas Time:	20.0 hrs	End of run:	04/17/2012 20:52
P/Po tolerance:	0	Equil. time:	3	TempComp:	Off
Station #:	1	PC sw. version:	1.54		

A ● D ■

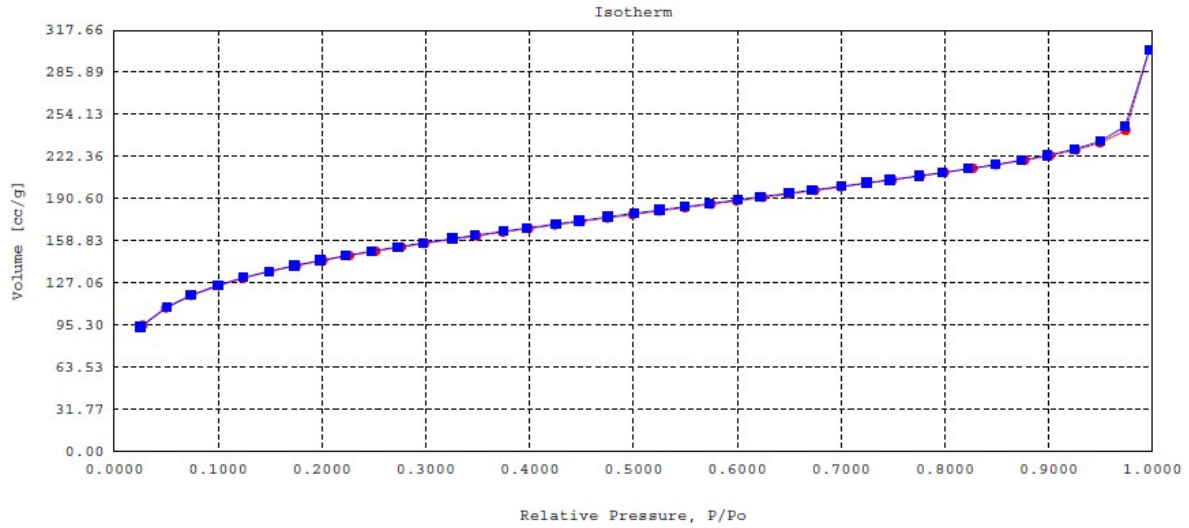


Fig. 8S: Adsorption-desorption isotherm of sample S1P-MeSi1.

11/07/2014

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Autosorb 1 for Windows 1.54

File name:	H:\labdenik Skoskalik_05_11_2014\BET ASTysk\S10PG53\S1P-MeSi5.raw				
Sample ID:	S10PG53	Description:	S10PG53		
Comments:					
Operator:	hugo	Sample weight:	0.057 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 f./molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	298.00	Analysis Time:	640.0 min
Outgas Temp:	25.0 °C	Outgas Time:	7.0 hrs	End of run:	05/23/2012 06:27
P/Po tolerance:	0	Equil. time:	3	TempComp:	Off
Station #:	1	PC sw. version:	1.54		

A ● D ■

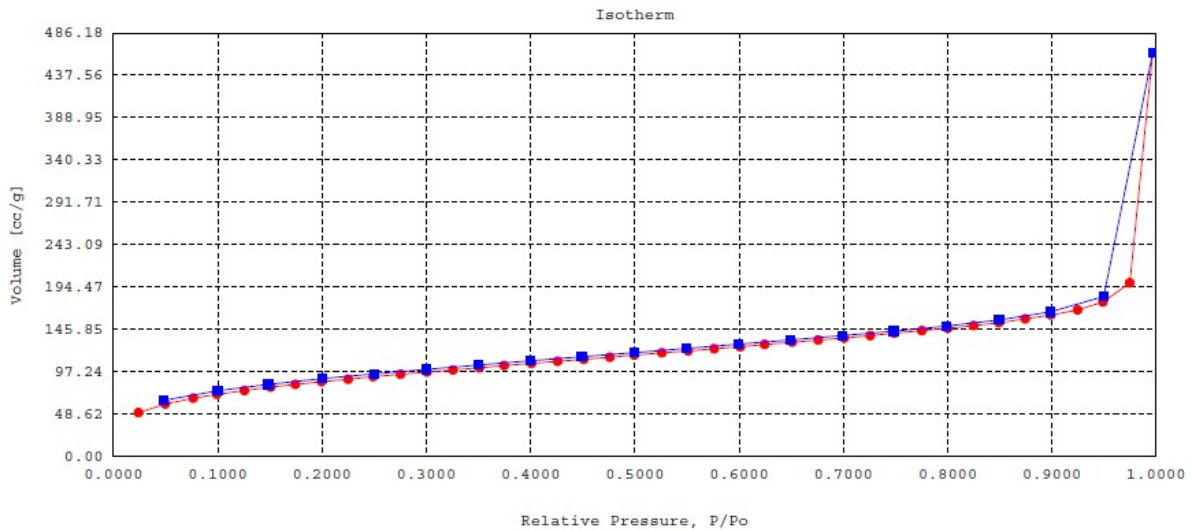


Fig. 9S: Adsorption-desorption isotherm of sample S1P-MeSi5.

11/07/2014

Quantachrome Instruments  
Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

File name:	H:\labdenik škoskalík_05_11_2014\BET ASTysk\S10PG29\S1P-Me2Si1.raw				
Sample ID:	S10PG29	Description:	S10PG29		
Comments:					
Operator:	hugo	Sample weight:	0.032 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 L <sup>2</sup> /molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.40		
Outgas Temp:	25.0 °C	Outgas Time:	8.5 hrs	Analysis Time:	516.8 min
P/Po tolerance:	0	Equil. time:	3	End of run:	12/13/2011 06:19
Station #:	1	PC sw. version:	1.54	TempComp:	Off

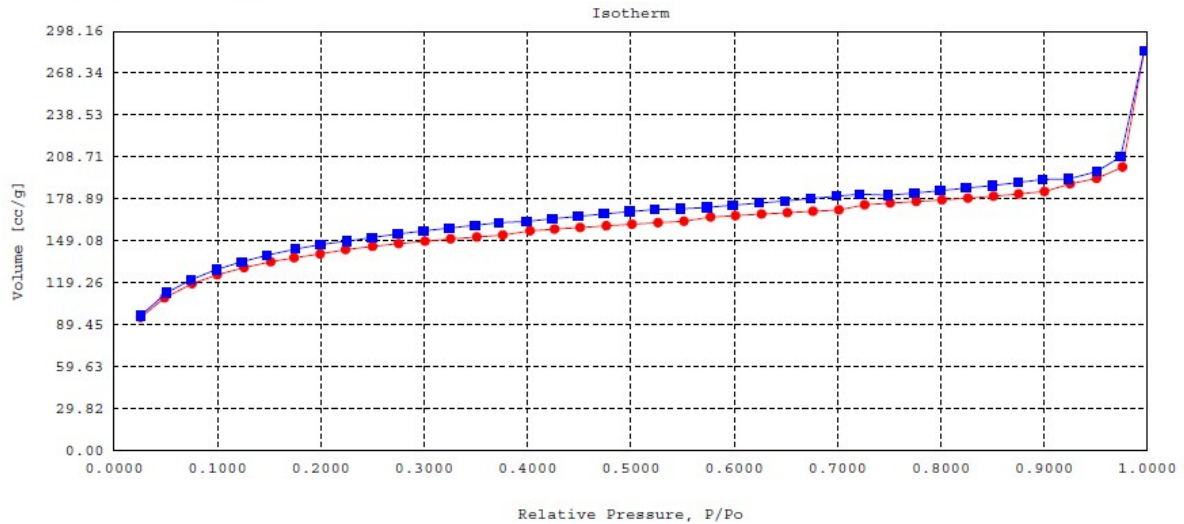


Fig. 10S: Adsorption-desorption isotherm of sample S1P-Me2Si1.

11/07/2014

Quantachrome Instruments  
Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

File name:	H:\labdenik škoskalík_05_11_2014\BET ASTysk\S10PG40\S1P-Me2Si5.raw				
Sample ID:	S10PG40	Description:	S10PG40		
Comments:					
Operator:	hugo	Sample weight:	0.0484 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 L <sup>2</sup> /molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.30		
Outgas Temp:	25.0 °C	Outgas Time:	4.8 hrs	Analysis Time:	448.0 min
P/Po tolerance:	0	Equil. time:	3	End of run:	03/15/2012 02:56
Station #:	1	PC sw. version:	1.54	TempComp:	Off

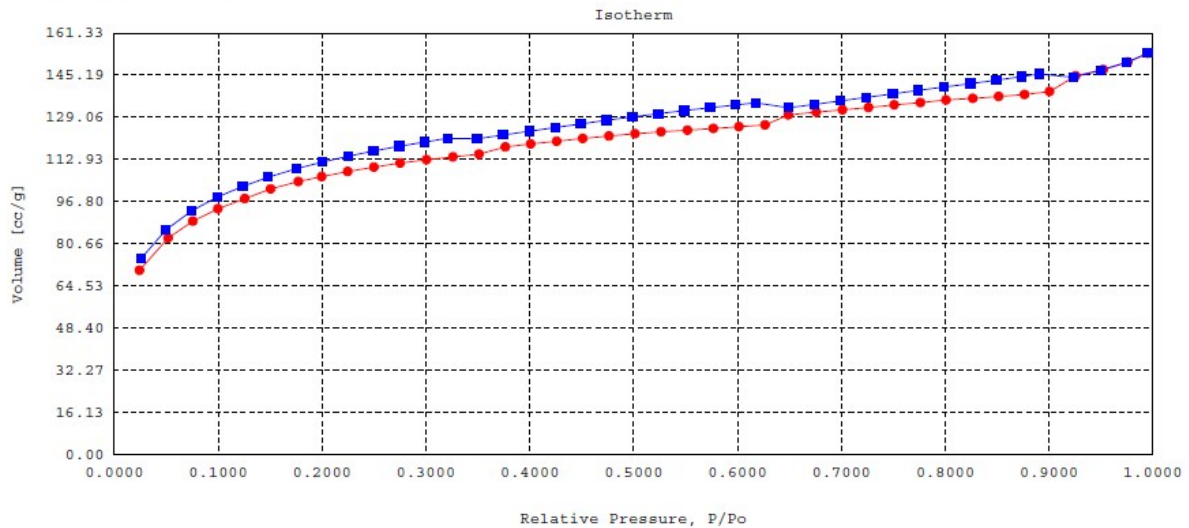


Fig. 11S: Adsorption-desorption isotherm of sample S1P-Me2Si5.

11/07/2014

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Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

File name:	H:\labdenik skoskalik_05_11_2014\BET ASTysk\S1OPG55\S1P-PhSi1.raw				
Sample ID:	S1OPG55	Description:	S1OPG55		
Comments:					
Operator:	hugo	Sample weight:	0.0194 g	Non-ideality:	6.58e-05
Analysis gas:	Nitrogen	X sect. area:	16.2 L/molec		
Adsorbate (DRP):	Nitrogen	Bath Temp.:	298.00		
Outgas Temp:	25.0 °C	Outgas Time:	14.0 hrs	Analysis Time:	604.0 min
P/Po tolerance:	0	Equil. time:	3	End of run:	05/24/2012 22:17
Station #:	1	PC sw. version:	1.54	TempComp:	Off

A ● D ■

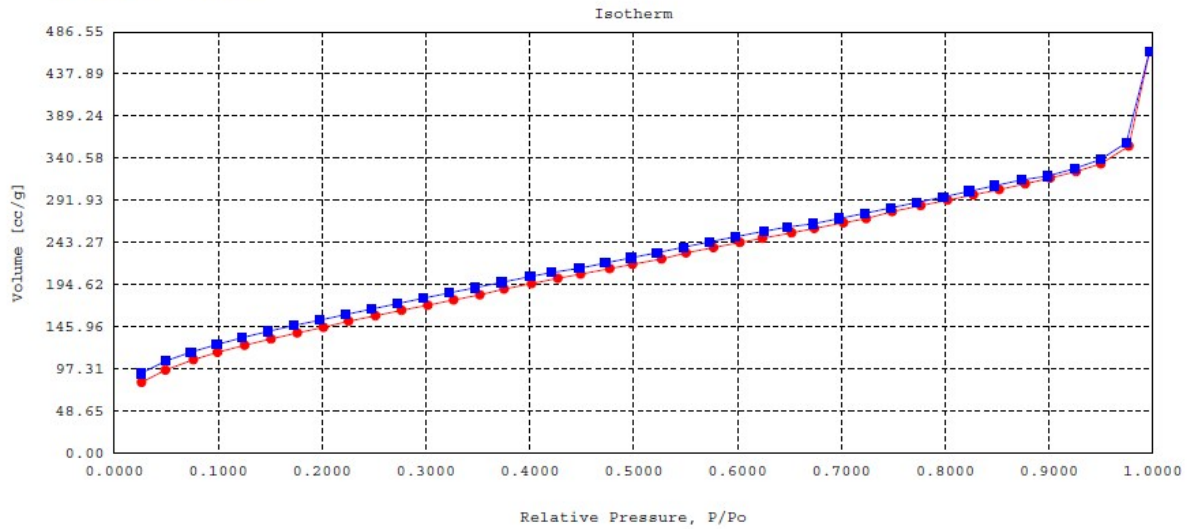


Fig. 12S: Adsorption-desorption isotherm of sample S1P-PhSi1.

11/07/2014

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Autosorb 1 for Windows 1.54

File name:	H:\labdenik skoskalik_05_11_2014\BET ASTysk\S1OPG43\S1P-Ph2Si1.raw				
Sample ID:	S1OPG43	Description:	S1OPG43		
Comments:					
Operator:	hugo	Sample weight:	0.0148 g	Non-ideality:	6.58e-05
Analysis gas:	Nitrogen	X sect. area:	16.2 L/molec		
Adsorbate (DRP):	Nitrogen	Bath Temp.:	298.00		
Outgas Temp:	25.0 °C	Outgas Time:	8.0 hrs	Analysis Time:	500.6 min
P/Po tolerance:	0	Equil. time:	3	End of run:	04/13/2012 03:36
Station #:	1	PC sw. version:	1.54	TempComp:	Off

A ● D ■

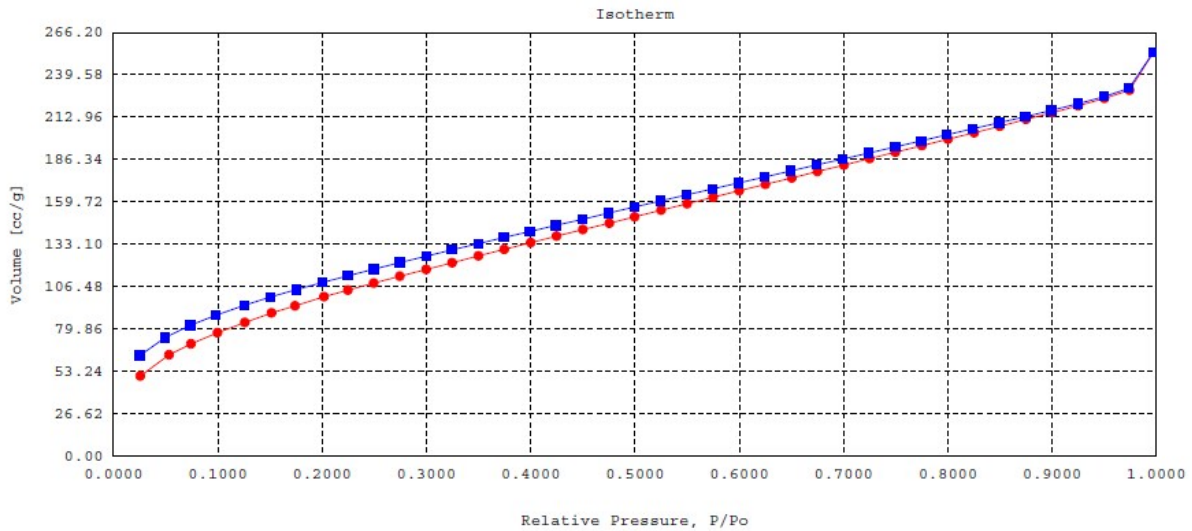


Fig. 13S: Adsorption-desorption isotherm of sample S1P-Ph2Si1.



11/07/2014

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Autosorb 1 for Windows 1.54

File name:	H:\labdenik skoskalik_05_11_2014\BET ASTysk\S1OPG90\S1P-Ph1.raw				
Sample ID:	S1OPG90	Description:	S1OPG90		
Comments:					
Operator:	hugo	Sample weight:	0.062 g		
Analysis gas:	Nitrogen	X sect. area:	16.2 L/molec	Non-ideality:	6.58e-05
Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.40		
Outgas Temp:	25.0 °C	Outgas Time:	23.0 hrs	Analysis Time:	560.5 min
P/Po tolerance:	0	Equil. time:	3	End of run:	03/13/2013 20:13
Station #:	1	PC sw. version:	1.54	TempComp:	Off

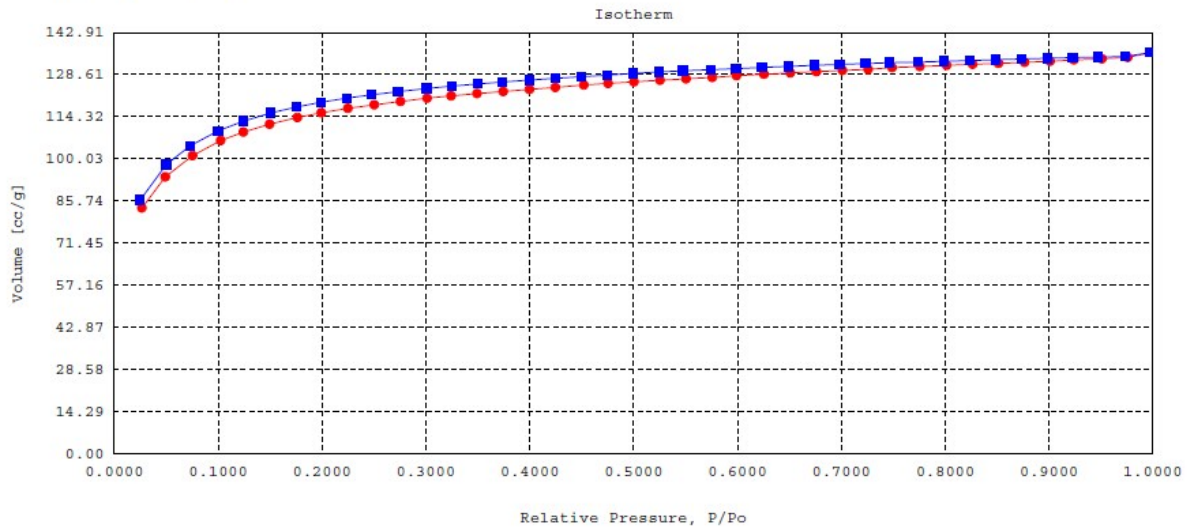


Fig. 14S: Adsorption-desorption isotherm of sample SiP-Ph1.

### 3. Bridged acetoxysilanes and phosphonic acid esters

As an example, syntheses and characterizations of the **SiC2SiP** sample with a CH<sub>2</sub>CH<sub>2</sub> spacer between silicon atoms and the **SiPC6P** sample with C<sub>6</sub>H<sub>4</sub> between phosphorus centers are described below.

Pertinent data for other samples are listed in Tab. 5S.

**SiC2SiP.** OP(OSiMe<sub>3</sub>)<sub>3</sub> (0.704 g; 2.24 mmol) was added dropwise to a stirred solution of (AcO)<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>Si(OAc)<sub>3</sub> (0.471 g; 1.07 mmol) in toluene (10 cm<sup>3</sup>). After the addition was complete, stirring was stopped and the reaction mixture was kept at 80 °C for one week. The reaction mixture provided a milky rigid gel overnight. The reaction was stopped after one week and dried *in vacuo* affording 0.387 g of a white xerogel (**SiC2SiP**).

IR (**SiC2SiP**, KBr, cm<sup>-1</sup>)  $\nu$  :  $\nu$  490 m, 608 vw, 639 vw ( $\nu$  SiC<sub>3</sub>), 763 m ( $\rho_s$  SiCH<sub>3</sub>), 790 sh, 851 m ( $\rho_{as}$  SiCH<sub>3</sub>), 1018 vs ( $\nu$  Si–O–P), 1175 m, 1231 w, 1259 m ( $\delta_s$  SiCH<sub>3</sub>), 1313 s ( $\nu$  P=O), 1374 vw ( $\delta_s$  CH<sub>3</sub>), 1406 vw, 1601 vw, 1754 m ( $\nu_{as}$  CH<sub>3</sub>COO unident), 2906 vw ( $\nu_s$  CH<sub>3</sub>), 2963 w ( $\nu_{as}$  CH<sub>3</sub>).

<sup>13</sup>C CPMAS NMR (**SiC2SiP**, ppm)  $\delta$  : 1.2 (POSiCH<sub>3</sub>), 3.7 shoulder (SiCH<sub>2</sub>CH<sub>2</sub>Si), 22.3 (CH<sub>3</sub>COO unident), 170.6 (CH<sub>3</sub>COO unident).

<sup>29</sup>Si MAS NMR (**SiC2SiP**, ppm)  $\delta$  : 26 (POSiMe<sub>3</sub>), –65 (O<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiO<sub>3</sub>).

<sup>31</sup>P MAS NMR (**SiC2SiP**, ppm)  $\delta$  : –37 (O=P(OSi)<sub>3</sub>).

**SiPC6P.** A solution of  $(\text{Me}_3\text{SiO})_2\text{P}(\text{O})\text{C}_6\text{H}_4\text{P}(\text{O})(\text{OSiMe}_3)_2$  (2.008 g; 3.812 mmol) in toluene (5 cm<sup>3</sup>) was added dropwise to a stirred solution of  $\text{Si}(\text{OAc})_4$  (1.005 g; 3.803 mmol) in toluene (12 cm<sup>3</sup>). After the addition was complete, stirring was stopped and the reaction mixture was kept at 80 °C for one week. The reaction mixture provided a milky rigid gel overnight. The reaction was stopped after one week and dried *in vacuo* affording 1.471 g of a white xerogel (**SiPC6P**).

IR (**SiPC6P**, KBr, cm<sup>-1</sup>)  $\nu$  : 437 w, 534 m, 608 m, 765 w ( $\rho_s$  SiCH<sub>3</sub>), 855 s ( $\rho_{as}$  SiCH<sub>3</sub>), 1019 vs ( $\rho$  CH<sub>3</sub>), 1082 vs ( $\nu$  Si–O–P), 1154 vs ( $\nu$  P–O–Si), 1261 s ( $\delta_s$  SiCH<sub>3</sub>), 1286 sh ( $\nu$  P=O), 1374 w ( $\delta_s$  CH<sub>3</sub>), 1419, 1542 w ( $\nu_s$  CH<sub>3</sub>COO bident), 1716 ( $\nu_{as}$  CH<sub>3</sub>COO unident) 1765 ( $\nu_{as}$  CH<sub>3</sub>COO unident), 2906 vw ( $\nu_s$  CH<sub>3</sub>), 2964 w ( $\nu_{as}$  CH<sub>3</sub>), 3030 vw ( $\nu$  C<sub>ar</sub>-H).

<sup>13</sup>C CP MAS NMR (**SiPC6P**, ppm)  $\delta$  : 3.1 (POSiCH<sub>3</sub>), 19.9 (CH<sub>3</sub>COO bident), 24.6 (CH<sub>3</sub>COO unident), 133.9 (C<sub>6</sub>H<sub>4</sub>).

<sup>29</sup>Si MAS NMR (**SiPC6P**, ppm)  $\delta$  : 25 (POSiMe<sub>3</sub>), -108 (SiO<sub>4</sub>), -195 (SiO<sub>6</sub>), -214 (SiO<sub>6</sub>).

<sup>31</sup>P MAS NMR (**SiPC6P**, ppm)  $\delta$  : -11 (-C<sub>6</sub>H<sub>4</sub>P(OSi)<sub>3</sub>), -1 sh (-C<sub>6</sub>H<sub>4</sub>P(O)(OSi)<sub>2</sub>).

**Tab. 7S: Bridged acetoxysilanes and phosphonic acid esters: Reagent molar amounts, yields, degrees of condensation (DC) and comparison of experimental (ML) and calculated mass losses (ML<sub>calc</sub>) during thermogravimetric analysis of xerogels with bridging organic groups.**

Sample	n <sub>Si</sub> [mmol]	n <sub>P</sub> [mmol]	Yield [g]	DC [%]	ML [%]	ML <sub>calc</sub> [%]
SiC1SiP	1.76	3.52	0.654	85.6	27.2	29.3
SiC2SiP	1.07	2.24	0.387	78.1	35.3	27.4
SiC3SiP	2.18	4.38	0.831	88.5	36.8	31.3
SiC6SiP	1.02	2.03	0.381	-	45.9	-
SiPC2P	2.44	2.45	0.738	83.6	31.9	32.9
SiPC6P	3.80	3.81	1.471	77.0	33.9	47.7

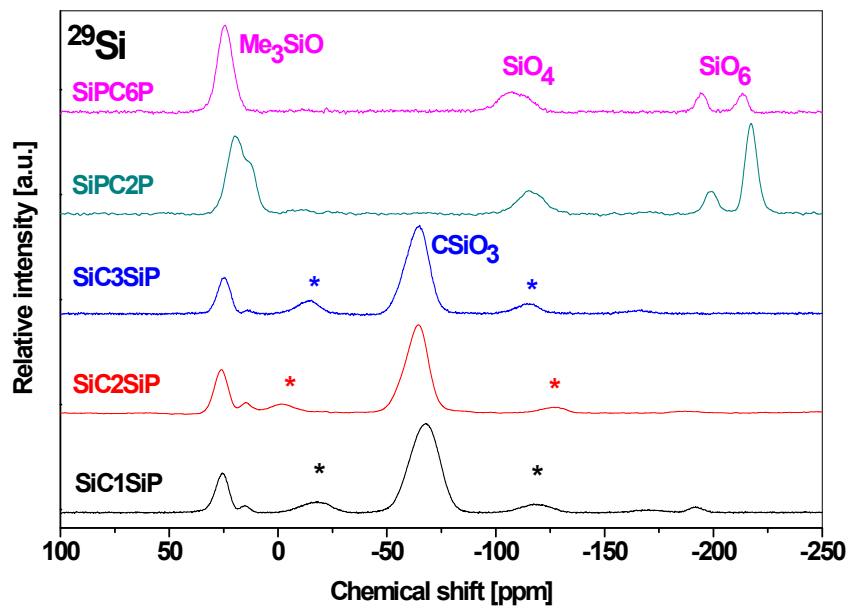


Fig. 15S:  $^{29}\text{Si}$  CPMAS NMR spectra of samples synthesized with bridged acetoxysilanes and phosphonic acid esters. Asterisks denote spinning sidebands.

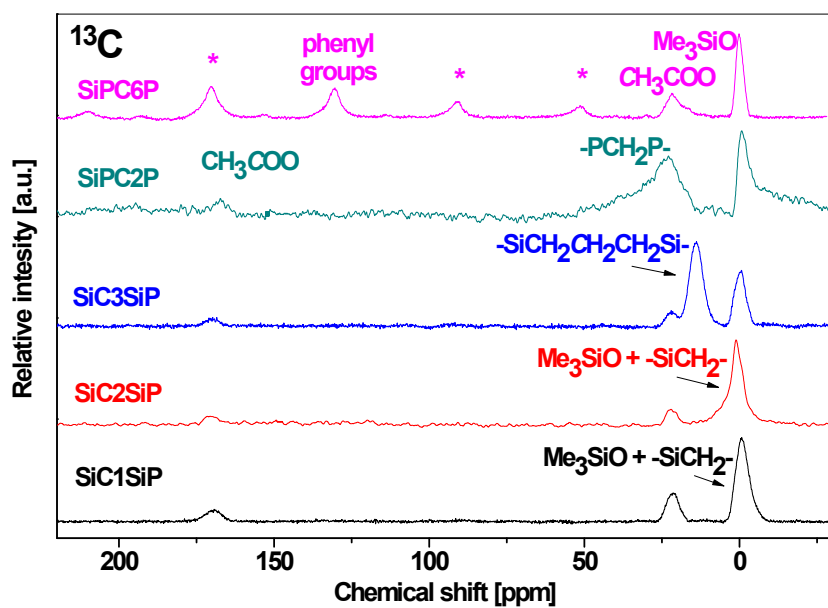


Fig. 16S:  $^{13}\text{C}$  CPMAS NMR spectra of samples synthesized with bridged acetoxysilanes and phosphonic acid esters. Asterisks denote spinning sidebands.

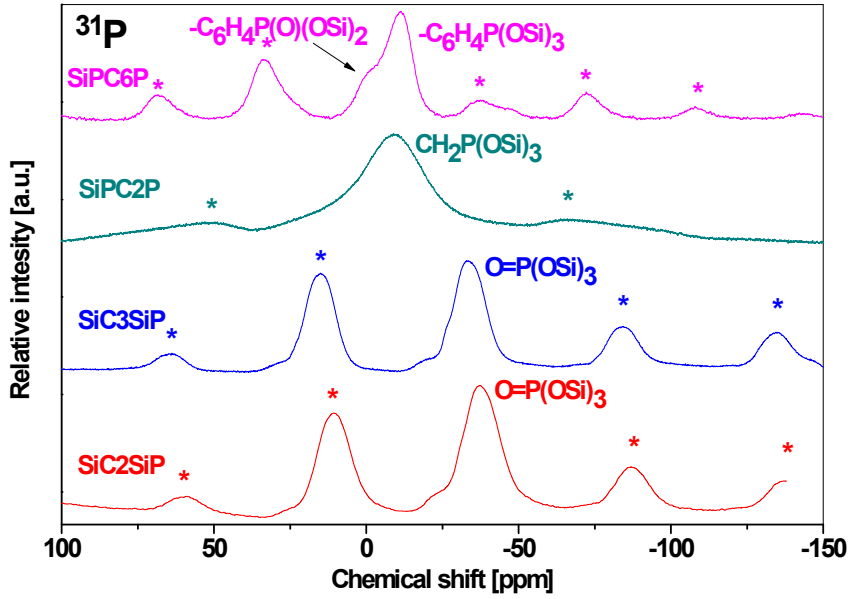


Fig. 17S:  $^{31}\text{P}$  MAS NMR spectra of samples synthesized with bridged acetoxysilanes and phosphonic acid esters. Asterisks denote spinning sidebands.

11/07/2014

Quantachrome Instruments  
Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

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Comments:			
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Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.40
Outgas Temp:	25.0 °C	Outgas Time:	21.0 hrs
P/Po tolerance:	0	Equil. time:	3
Station #:	1	PC sw. version:	1.54
	A ● D ■	Non-ideality:	6.58e-05
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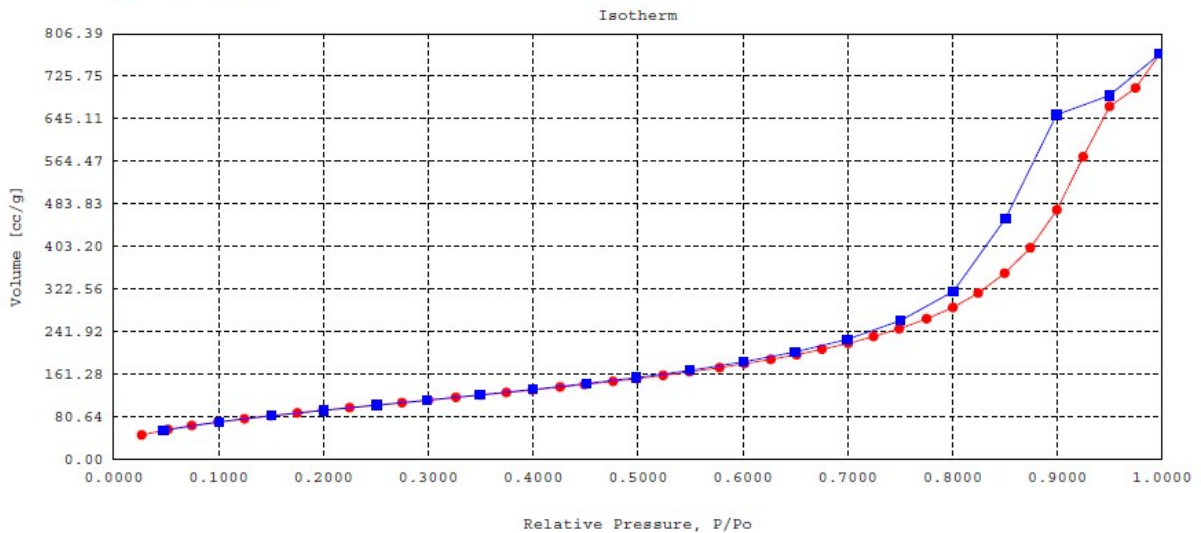


Fig. 18S: Adsorption-desorption isotherm of sample SiC3SiP.

11/07/2014

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Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

File name:	H:\labdenik skoskalik_05_11_2014\BET ASTysk\S10PG62\S1C6S1P.raw				
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Adsorbate (DRP):	Nitrogen	Bath Temp.:	298.00		
Outgas Temp:	25.0 °C	Outgas Time:	9.3 hrs	Analysis Time:	1050.9 min
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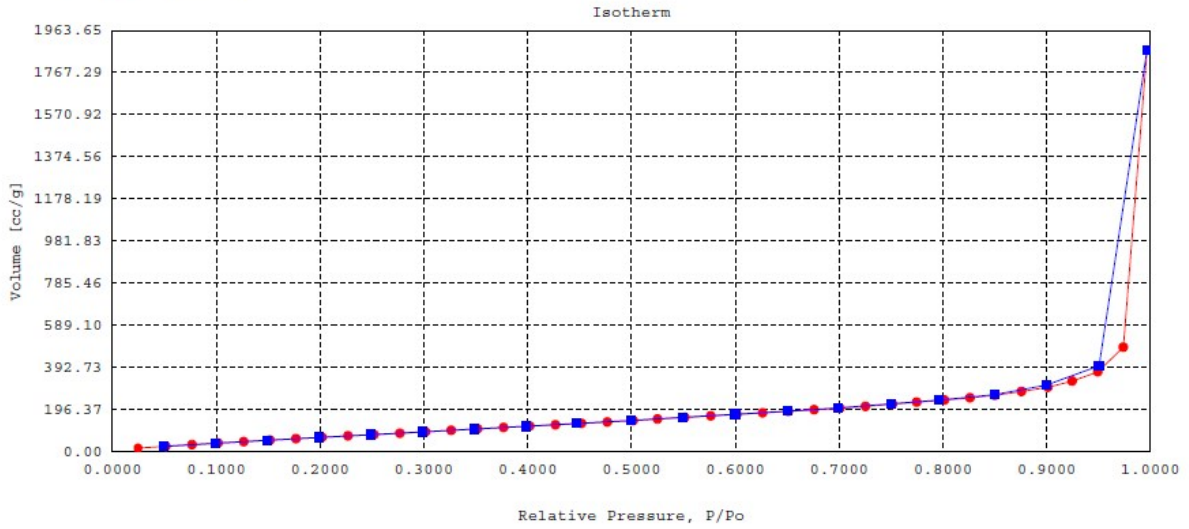


Fig. 19S: Adsorption-desorption isotherm of sample SiC6SiP.

11/07/2014

Quantachrome Instruments  
Quantachrome Autosorb Automated Gas Sorption System Report  
Autosorb 1 for Windows 1.54

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Adsorbate (DRP):	Nitrogen	Bath Temp.:	77.40		
Outgas Temp:	25.0 °C	Outgas Time:	25.0 hrs	Analysis Time:	592.9 min
P/Po tolerance:	0	Equil. time:	3	End of run:	03/02/2013 22:45
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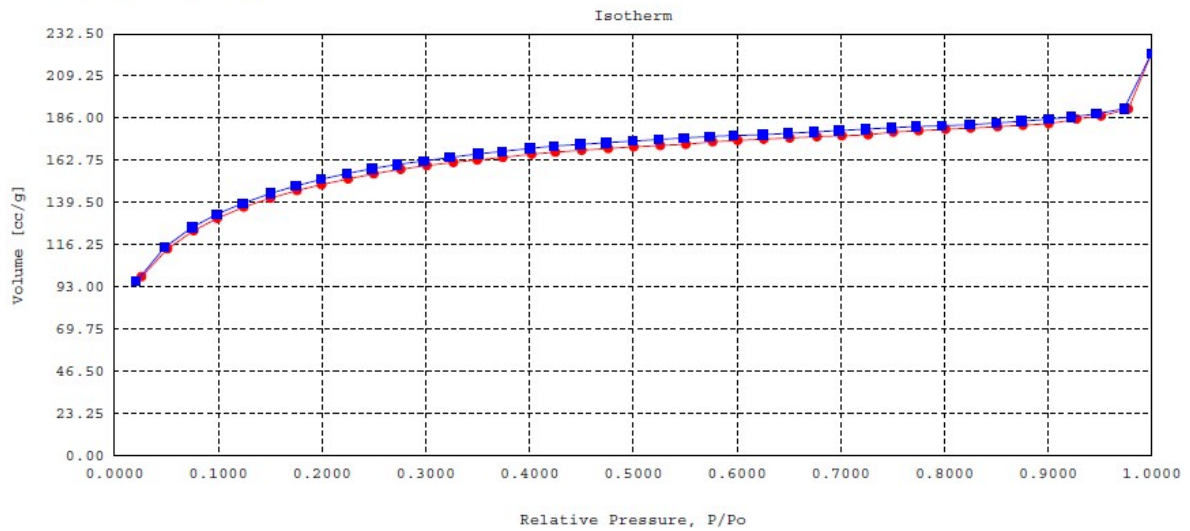


Fig. 20S: Adsorption-desorption isotherm of sample SiPC2P.

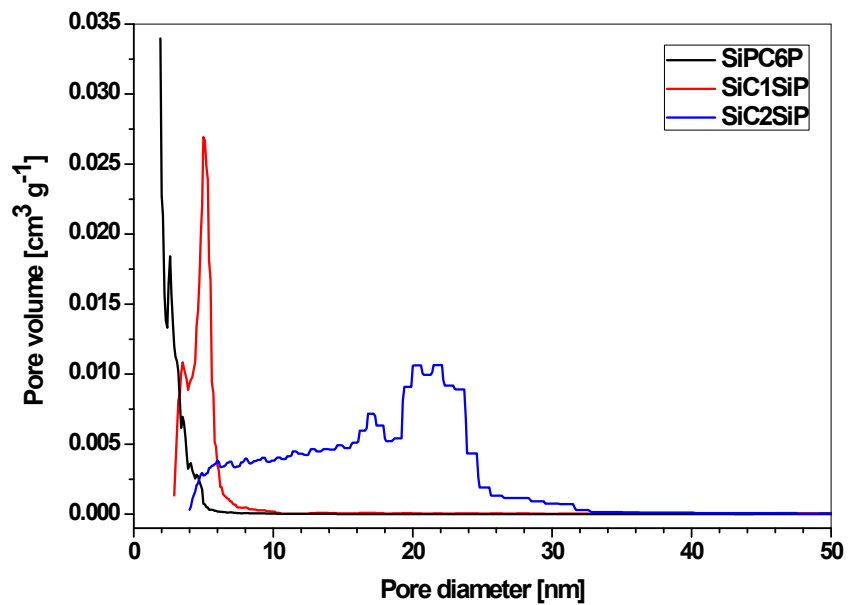


Fig. 21S: Pore size distributions of xerogels with bridging organic spacers (DFT Kernel Used :  $\text{N}_2$  at 77 K on silica, cylindrical pore, NSDFT equilibrium model).

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