The first synthesis of organosilyl-substituted aluminophosphate molecular sieves†

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Organosilyl groups were successfully incorporated in AFI and VFI aluminophosphate frameworks using organoalkoxysilanes to modify hydrophobicity and acidity of the molecular sieves.

Tailored synthesis of nanoporous materials with controlled pore size/shape and surface properties is desired in view of various applications, such as catalysts and adsorbents. To this end, various modifications of frameworks of zeolites and related open framework materials have been attempted. Recently, incorporation of organic groups in nanoporous metal oxide-based frameworks has drawn particular attention.[1] With regard to mesoporous materials, there are many reports on organo-hybrid materials including terminal or bridging organic groups.[2] These materials showed varied structural regularity derived from inorganic framework architectures and specific properties such as hydrophobicity/hydrophilicity, acidity/basicity, and coordination to metal ions, depending on the incorporated organic functional groups. In contrast, there are a limited number of reports in the realm of microporous zeolite-like organo-hybrid materials[3–6] apart from MOF-type materials based on coordination compounds.[7] We previously reported on microporous aluminomethylphosphonates AlMepO-α and AlMepO-β with methyl-lined one-dimensional channels.[3] The organic-lined channels were proved to have unique gas and vapour adsorption properties[8,9] though their neutral frameworks made the potentials of the materials limited. Incorporation of organosilyl groups in existing zeolite frameworks is also another approach towards organo-hybrid zeolitic materials. Jones introduced phenethylsilyl groups in beta-zeolite frameworks to enable further functionalisation inside the micropores.[4] Yamamoto and co-workers developed a series of ZOL (zeolite with organic groups as lattice) materials based on several known zeolite frameworks.[5] ZOL includes Si–CH_2–Si linkages instead of a part of Si–O–Si in the frameworks. However, considerable cleavage of Si–C bonds in the frameworks was observed because the synthesis requires strongly alkaline reaction conditions for crystallization and calcination process for template removal, as is general in most of zeolite synthesis procedures.

Aluminophosphate molecular sieve $AlPO_4$-*n*, first reported by Wilson and co-workers[10] in 1982, is the most important family in non-silicate microporous materials. $AlPO_4$-*n* materials are generally prepared in weakly acidic to weakly basic solutions. Isomorphous substitution of phosphorus or aluminium sites with heteroatoms is known of for many $AlPO_4$-*n* frameworks. Silicon-substituted aluminophosphates (SAPOs) lead to the formation of Brønsted acid sites, especially when Si atoms are incorporated instead of P atoms.[11] As far as we know, incorporation of organosilyl groups in microporous aluminophosphate ($AlPO_4$) frameworks, however, has not been noticed, although incorporation of organophosphonate in the framework of VPI-5 has been reported.[6] In this study we report, for the first time, incorporation of organosilyl groups in known aluminophosphate frameworks. Both improved hydrophobicity in the nanopore and acidity such as that of SAPO materials can be expected for the organosilyl-substituted aluminophosphate materials. As base frameworks $AlPO_4$-5 (AFI) and VPI-5 (VFI) were selected because of their large pore sizes, mild synthetic conditions and the possibility of extraction of templates. Under such synthetic conditions no cleavage of organosilyl groups is expected. Incorporation of organoalkoxysilanes (OAS), such as methyltriethoxysilane (MTES), phenyltriethoxysilane (PTES), and bis-triethoxysilylmethane (BTESM) in $AlPO_4$ frameworks was attempted, based on typical synthesis procedures of $AlPO_4$-5 and VPI-5.‡ The aluminophosphate products prepared with MTES, PTES, and BTESM were denoted by MeSi, PhSi, and bisSi, respectively. The OAS/Al_2O_3 ratio in the starting gel composition is indicated as *x* and the products are designated as *x*MTES, for example.

According to the XRD patterns of the products prepared using Et_3N as a template (Fig. 1(a)), addition of MTES up to $x = 1.2$ resulted in formation of pure AFI phase with good crystallinity, and the crystallinity of the products was considerably lowered by addition in a larger amount ($x = 1.4$–1.8). According to the SEM images, all the samples giving pure AFI phase were spherical polycrystalline aggregates of plate-like crystals like those of SAPO-5 prepared in a similar procedure, and no other morphology of particles were observed. Addition of BTESM, however, resulted in formation of a mixture of AFI and AlPO-C phase and no pure AFI phase was obtained.

When Pr_2NH was used as a template, the XRD patterns of the products (Fig. 1(b)) prepared with MTES up to $x = 0.2$ showed the single VFI phase. At $x = 0.3$ a small amount of AlPO-C was recognized as a by-product phase and the addition of a larger amount of MTES resulted in decreasing intensity of VFI-derived reflections. When PTES was added the resulting phase was mostly VFI irrespective of the amount added, although addition of large excess of PTES resulted in formation of an amorphous phase separately as a by-product. When BTESM was added up to $x = 0.2$

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† Electronic supplementary information (ESI) available: compositions of Me-Si-$AlPO_4$-5 and VPI-5 samples, SEM images, nitrogen adsorption isotherms and preparative procedures for organosilyl-substituted compounds. See DOI: 10.1039/b613454h

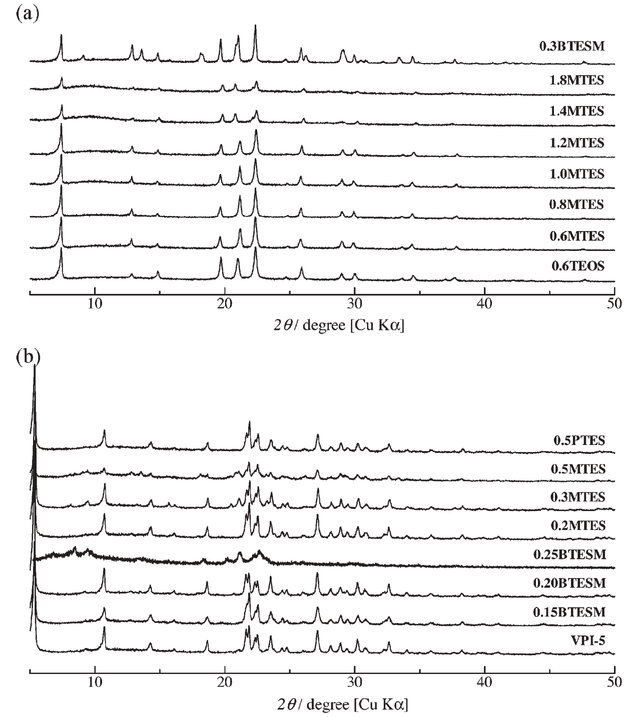

Fig. 1 XRD patterns of organosilyl-substituted (a) $AlPO_4$-5 and (b) VPI-5.

pure VFI phase was obtained. With addition of BTESM more than $x = 0.25$ no VFI diffraction pattern was observed but an amorphous-like product was obtained. According to the SEM images (ESI†), these samples were solely composed of spherical polycrystalline aggregates of needle-like crystals. Although VPI-5 can also be prepared with a mixture of triisopropanolamine and tetramethylammonium hydroxide, no crystalline phase was obtained when BTESM was mixed in the starting gels.

The ^{29}Si MAS NMR of MeSi-$AlPO_4$-5 shown in Fig. 2(a) gave a line at −66 ppm, which was assigned to CH_3–Si(–OT)$_3$ (T-site), and no peak was observed in the higher field (Q-site) region. According to the ^{13}C CP/MAS NMR shown in Fig. 3(a), the signal appearing at −3 ppm was assigned to the methylsilyl group, and the remaining two signals at 10 and 48 ppm to the ethyl group of the occluded Et_3N as a template. The above results indicate that MTES was incorporated in $AlPO_4$-5 phase with no cleavage of the Si–C bonds during the hydrothermal reaction. Regarding bisSi-VPI-5, the ^{29}Si MAS NMR (Fig. 2(b)) gave signals at −60 and −66 ppm, which are assigned to T-sites. The assignment is consistent with the observation that ZOL materials prepared from BTESM gave resonances around −60 ppm.[5] No peak was observed in Q-site region. The ^{13}C CP/MAS NMR shown in Fig. 3(b) gave a peak at −1 ppm assigned to the methylene group. The other three signals at 11, 19, and 50 ppm are assigned to the propyl group of the occluded Pr_2NH molecules. The above results clearly showed that BTESM was also incorporated in the VPI-5 phase with no cleavage of the Si–C bonds.

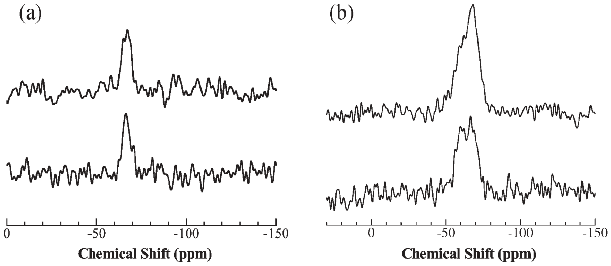

Fig. 2 ^{29}Si CP/MAS NMR spectra of: (a) MeSi–$AlPO_4$-5 (0.6MTES), and (b) bisSi-VPI-5 (0.15BTESM) before (upper) and after (lower) SDA extraction.

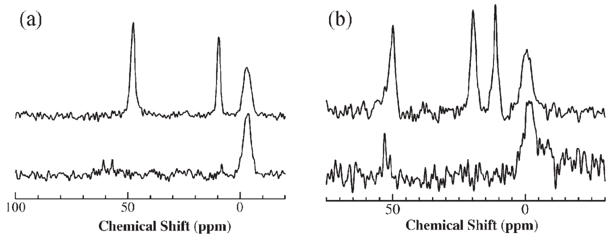

Fig. 3 ^{13}C CP/MAS NMR spectra of: (a) MeSi–$AlPO_4$-5 (0.6MTES), and (b) bisSi-VPI-5 (0.15BTESM) before (upper) and after (lower) SDA extraction.

Removal of the occluded SDA was attempted by extraction using HCl/MeOH. According to the XRD patterns, both the AFI and VFI frameworks were retained intact after the extraction procedure. In the CHN elemental analyses, negligible amounts of nitrogen were detected in the samples after the extraction, and the carbon contents were considerably decreased. The ^{13}C MAS NMR shown in Fig. 3 also revealed that the SDAs occluded in MeSi-$AlPO_4$-5 and bisSi-VPI-5 were successfully extracted. The ^{29}Si MAS NMR in Fig. 2 showed that the organosilyl moieties were virtually intact.

According to the ICP-AES of SDA-extracted samples, the P/Al molar ratios in organosilyl-substituted $AlPO_4$-5 and VPI-5 were close to 1.00 in most cases irrespective of OAS amounts of the starting gels, and the Si/Al molar ratios increased depending on the OAS amounts in the starting gels (ESI†). For example, the molar percentages of Si (Si/(Al + P + Si)) in samples obtained as a single phase were 4.3 mol% for MeSi-$AlPO_4$-5 (1.0MTES), 0.9 mol% for MeSi-VPI-5 (0.2MTES), and 2.4 mol% for bisSi-VPI-5 (0.15BTESM). While there are many reports on synthesis of SAPO-5, relatively a small number of reports are found for synthesis of Si-substituted VPI-5. The Si contents in reported Si-VPI-5 phases are as high as 4 mol% for samples prepared with DPA as a template.[12] Those of SAPO-5 can be generally much higher than that of VPI-5. The reason may be related to difference in allowed framework distortion generated by incorporation of the heteroatoms. Our results in incorporation of organosilyl groups showed apparently similar tendency in this regard.

Regarding Si substitution in $AlPO_4$ frameworks, two extreme models are proposed, *i.e.*, the SM IIa type, in which a P site is replaced by a Si atom, and the SM III type, in which a pair of neighbouring Al and P sites are replaced by two Si atoms.[11] The SM IIa model should give a lower P/Al ratio than one, while the P/Al ratio should be close to one for the SM III model. According to the above P/Al ratios, it is reasonable to assume that OAS fundamentally substitutes a pair of neighbouring Al and P sites (SM III) in organosilyl-substituted $AlPO_4$. Generally, the SM IIa and SM III mechanisms in the case of Si substitution can be distinguished according to the ^{29}Si MAS-NMR because a Q^4(*n*Al) signal generally shows a low-field shift as *n* increases. Regarding 3-connected T-sites, however, a clear relationship between peak positions and

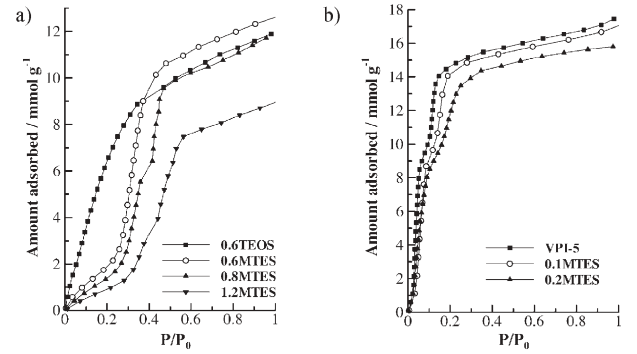

Fig. 4 Water vapour adsorption isotherms of: (a) MeSi–AlPO$_4$-5, (b) MeSi-VPI-5 at 298 K.

neighbouring Al substitution has not been established, unlike in the case of Q-site as far as we understand. From the above results, we conclude that organosilyl groups substitute the AlPO$_4$ frameworks to form organosilica domains mainly, in an SM III manner.

The nitrogen adsorption isotherms (ESI†) of MeSi-AlPO$_4$-5 samples were of type I with adsorption amounts comparable to that of SAPO-5 irrespective of MTES amounts. The nitrogen adsorption isotherms of organosilyl VPI-5 were also of type I. Especially, bisSi-VPI-5 gave an adsorption amount comparable with VPI-5, while MeSi- and PhSi-VPI-5 gave less adsorption. The water vapour adsorption isotherms of MeSi-AlPO$_4$-5 samples (Fig. 4(a)) were of Type V, showing basically hydrophobic nature of the micropores similar to non-substituted AlPO$_4$-5, rather than SAPO-5 prepared with the same molar amount of TEOS which gives a Type I isotherm. By increasing the amount of MTES the steep rise in the isotherm became less steep and the adsorption amount decreased. This clearly shows that more MTES incorporated in the aluminophosphate leads to the more hydrophobic channels. The water vapour isotherm of VPI-5 is known to have three adsorption steps,[13] as is shown in Fig. 4(b). Although the incorporation of MTES did not change the fundamental feature of the isotherms, the slope became less steep with increasing MTES, indicating improved hydrophobicity. The difference was, however, small because of the limited amount of incorporated organosilyl groups.

The NH$_3$-TPD curve shown in Fig. 5 indicates the existence of a small number of strong acidic sites; this was observed around 330 °C. The strong acidity observed for bisSi-VPI-5 could be elucidated in two possible mechanisms. In the SM III mechanism the organosilicate domains surrounded by aluminium atoms can cause small amounts of strong acidic sites. Otherwise, an aluminium atom can be located in organosilicate domains to form an acidic site such as that in aluminosilicate zeolites.

In the case of the ZOL series, calcination for removal of SDA as well as strong alkaline reaction conditions caused a loss of organosilyl moieties to considerable extents. This clearly shows the potential merit of AlPO$_4$ systems in organic modification. Thus, organosilyl-incorporation in AlPO can open a new possibility for nanoporous inorganic–organic hybrid frameworks.

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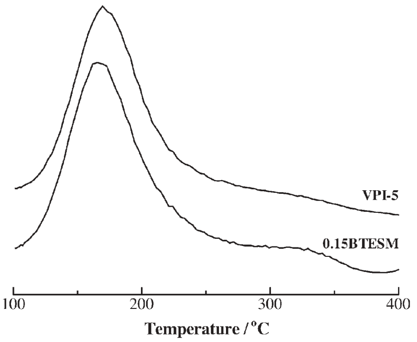

Fig. 5 NH$_3$-TPD curves for VPI-5 and bisSi-VPI-5.

Notes and references

‡ Experimental: SAPO-5 and VPI-5 were prepared by using the reported procedures.[14,15] The composition of the starting gel for AFI synthesis was $x\mathrm{OAS}\cdot 1\mathrm{Al_2O_3}\cdot(1.3 - x/2)\mathrm{P_2O_5}\cdot 1\mathrm{Et_3N}\cdot 40\mathrm{H_2O}$ (x = 0.6–2.0). The gels (ESI†) were hydrothermally reacted in a Teflon-lined stainless-steel autoclave under an autogenous pressure at 200 °C for 18 h. The template was extracted in HCl/MeOH at 100 °C for 20 h in an autoclave. The AFI samples used for adsorption study were de-gassed in advance at 450 °C for 6 h. The composition of the starting gel for VFI synthesis was $x\mathrm{OAS}\cdot 1\mathrm{Al_2O_3}\cdot 1\mathrm{P_2O_5}\cdot 1\mathrm{Pr_2NH}\cdot 40\mathrm{H_2O}$ (x = 0.1–0.5). The gels (ESI†) were hydrothermally reacted at 140 °C for 24 h. The template was removed with HCl/MeOH at 100 °C for 16 h in an autoclave. The VFI samples used for adsorption study and NH$_3$-TPD were de-gassed in advance at 300 °C (N$_2$ adsorption) or 350 °C (NH$_3$-TPD) for 6 h at the heating rate of 1 °C min^{-1}. It was confirmed by XRD that the samples were not decomposed nor transformed to other phases such as AlPO$_4$-8 under those heating conditions.

1 K. Maeda and F. Mizukami, *Catal. Surv. Jpn.*, 1999, **3**, 119.
2 F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem., Int. Ed.*, 2006, **45**, 3216; A. Stein, B. J. Melde and C. Schroden, *Adv. Mater.*, 2000, **12**, 1403.
3 K. Maeda, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2335; K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1199; K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, *J. Chem. Soc., Chem. Commun.*, 1995, 1033.
4 C. W. Jones, K. Tsuji and M. E. Davis, *Nature*, 1998, **393**, 52; K. Tsuji, C. W. Jones and M. E. Davis, *Microporous Mesoporous Mater.*, 1999, **29**, 339; C. W. Jones, K. Tsuji and M. E. Davis, *Microporous Mesoporous Mater.*, 1999, **33**, 223.
5 K. Yamamoto, Y. Sakata, Y. Nohara, Y. Takahashi and T. Tatsumi, *Science*, 2003, **300**, 470; K. Yamamoto, Y. Nohara, Y. Domen, Y. Takahashi, Y. Sakata, J. Plévert and T. Tatsumi, *Chem. Mater.*, 2005, **17**, 3913.
6 W. F. Yan, E. Hagaman and S. Dai, *Chem. Mater.*, 2004, **16**, 5182.
7 S. Kaskel, *in Handbook of Porous Solids*, ed. F. Schüth, K. S. W. Sing and J. Weitkamp, Wiley-VCH, Weinheim, 2002, vol. 2, p. 1139.
8 K. Maeda, Y. Kiyozumi and F. Mizukami, *J. Phys. Chem. B*, 1997, **101**, 4402.
9 C. Schumacher, J. Gonzalez, P. A. Wright and N. A. Seaton, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2351; J. Gonzalez, R. N. Devi, P. A. Wright, D. P. Tunstall and P. A. Cox, *J. Phys. Chem. B*, 2005, **109**, 21700.
10 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
11 S. T. Wilson, *Stud. Surf. Sci. Catal.*, 2001, **137**, 229; J. A. Martens and P. A. Jacobs, *Stud. Surf. Sci. Catal.*, 1994, **85**, 653.
12 B. Kraushaar-Czarnetzki, R. J. Dogterom, W. H. J. Stork, K. A. Emeis and J. P. van Braam Houckgeest, *J. Catal.*, 1993, **141**, 140.
13 M. B. Kenny, K. S. W. Sing and C. R. Theocharis, *J. Chem. Soc., Chem. Commun.*, 1991, 974.
14 D. Young and M. E. Davis, *Zeolites*, 1991, **11**, 277.
15 H. He and J. Klinowskii, *J. Phys. Chem.*, 1994, **98**, 1992.