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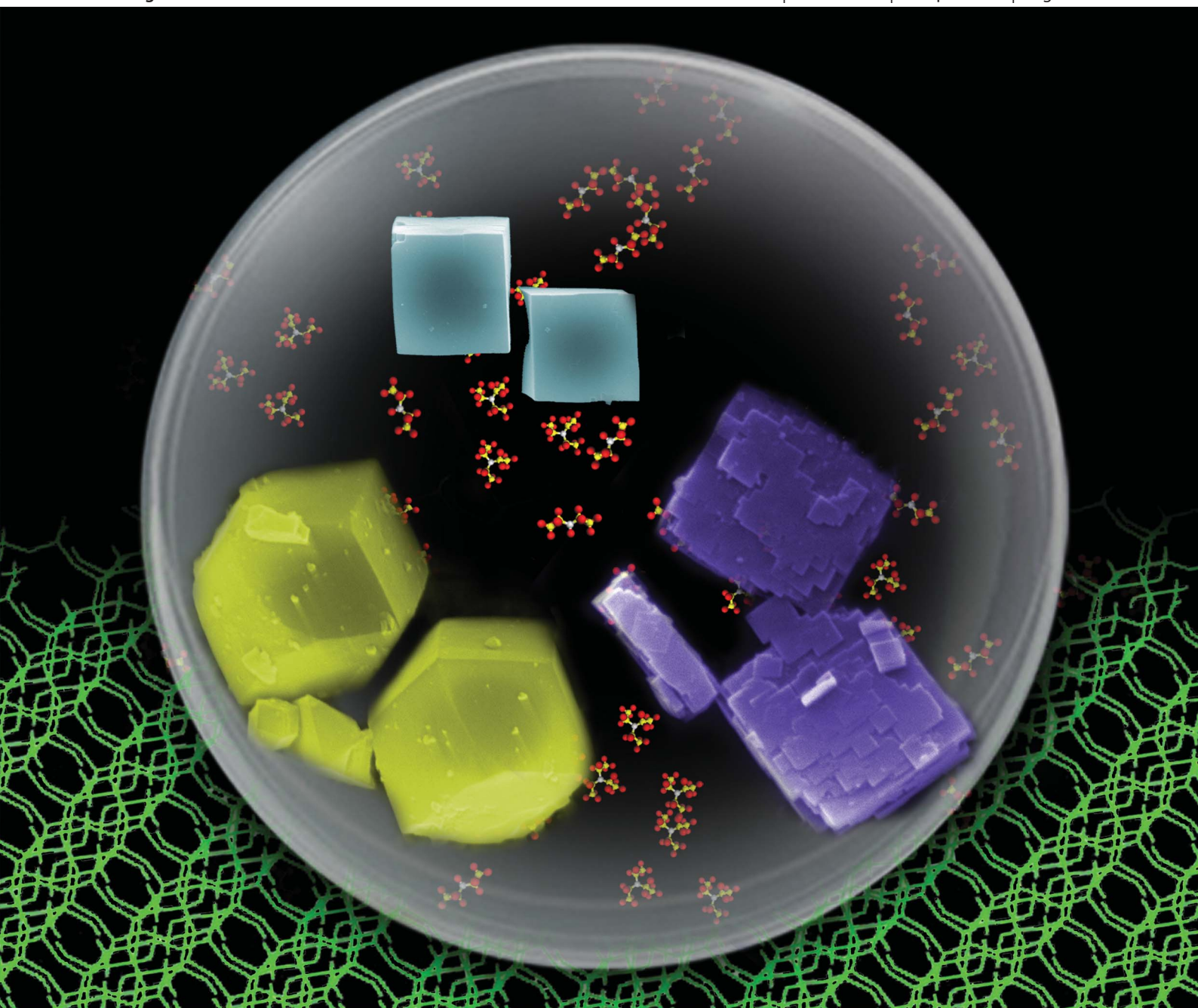
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amines as the solvent and template

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PAPER

A novel solvothermal approach to synthesize SAPO molecular sieves using organic amines as the solvent and template

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A novel solvothermal synthesis route designated as aminothermal synthesis, in which organic amines are used as both the dispersing medium and the template, is developed for the synthesis of SAPO molecular sieves. Three synthetic systems based on triethylamine (TEA), diethylamine (DEA) and TEA-DEA binary mixture were studied. SAPO-34 with good crystallinity and high yield (*ca.* 90%) was successfully synthesized from TEA and TEA-DEA systems. By adjusting the crystallization temperature, SAPO-18 was for the first time obtained using TEA template. In the case of DEA, a small-pore molecular sieve DNL-6 with RHO topology was synthesized. In an attempt to make the synthetic process environmentally benign and reduce the waste emission, organic liquid was collected after the synthesis of SAPO-34 and reused in next crystallization. It was found that the crystalline product and yield were almost the same as those synthesized with fresh amines. Moreover, CO_2 and CH_4 were chosen as the probe molecules to investigate the adsorption properties of products. SAPO molecular sieves synthesized by aminothermal method exhibited good adsorption capacities and high CO_2/CH_4 ratios.

Introduction

Silicoaluminophosphate molecular sieves (SAPOs), invented by Union Carbide Corporation in 1980s, are important crystalline materials with uniform pores.[1,2] They have exhibited many attractive properties as adsorbents, ion-exchangers, catalysts and catalyst supports.[3,4] Hitherto, hydrothermal method is a predominant strategy to synthesize SAPO molecular sieves.[5] In addition, solvothermal,[6–12] ionothermal[13–16] and dry-gel conversion methods[17–19] have also been explored for the preparation of SAPO molecular sieves. Novel synthetic methods are always attractive in the field of molecular sieves, which may have the possibility to create new materials or known phases with specific properties.[20]

Solvothermal method was firstly introduced into the zeolite synthesis by Bibby and Dale, in which organic solvents instead of water were used as mass and heat transfer medium.[6] One of the advantages with solvothermal method is to prepare large

crystals. Kuperman *et al.* obtained a series of giant zeolite crystals with diameters ranging from 0.4 to 5 mm in HF-alkylamine and HF-pyridine systems.[8] Xu and co-workers extended this method to the synthesis of aluminophosphate (AlPO) molecular sieves.[20] By employing alcohols as solvents, they synthesized many novel aluminophosphate materials with anionic frameworks, among which JDF-20 possessing 20-ring extra-large pores is the most attractive one.[9,10] Up to now, several SAPO molecular sieves have been synthesized through solvothermal route, such as SAPO-5, 11, 21, 31, 35 *etc.*[7,11,12] It is noteworthy that most solvothermal preparation of molecular sieves is not truly anhydrous, and the presence of small amount of water is essential to the crystallization process.[21,22] Liu *et al.* studied the effect of water amount on the solvothermal synthesis and found that the crystallization rate could be greatly accelerated with the increasing amount of water in the system.[22]

SAPO-34 as one of the most important members of silicoaluminophosphate molecular sieves has attracted great attention, because it behaves good property for CO_2 separation from CH_4[23–25] and exhibits excellent catalytic performance in methanol-to-olefin (MTO) reaction.[26,27] A commercial MTO process has been established based on SAPO-34 catalyst in 2010.[28] SAPO-34 was normally synthesized with a hydrothermal method. Many organic amines have been reported as structure directing agents or templates, including tetraethylammonium hydroxide (TEAOH),[1,2] dipropylamine,[2] isopropylamine,[29] piperidine,[30] morpholine,[31] triethylamine (TEA),[32] and

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diethylamine (DEA),[33] *etc.* Other synthetic approaches for SAPO-34 involve microwave-assisted synthesis,[34] ionothermal synthesis[13,35] and dry-gel conversion method.[18] However, there is no open report on the solvothermal synthesis of SAPO-34. The main drawbacks associated with the conventional synthesis of SAPO-34 lie in the incomplete conversion of reagents and the generation of large amount of mother liquids, which would waste chemicals and cause environmental pollution, especially for the industrial production of SAPO-34. Dry-gel conversion may help to avoid such problems, but pitifully has difficulties in scaling up. Recycling unused reagents has been applied in the synthesis of aluminosilicate zeolites to increase the product yield and reduce the waste disposal. However, efficient utilization of unreacted chemicals from the synthesis of SAPO/AlPO molecular sieves has attracted less attention up to now.[36]

In this paper, we report the use of organic amines as the solvent and template in the synthesis of SAPO-34 molecular sieve, in which the synthesis route was named as aminothermal synthesis. Two organic amines TEA and DEA, usually used as templates for hydrothermal synthesis of SAPO-34, were chosen to explore the aminothermal synthesis. Fortunately, some encouraging results have been achieved.

Experimental

General procedure of aminothermal synthesis

Organic amines used in the synthesis were TEA (99.5 wt%), DEA (99.5 wt%) and their mixtures. Pseudoboehmite (70.5 wt%), phosphoric acid (85 wt%), and silica sol (27.5 wt%) were used as inorganic precursors.

A typical synthesis procedure was as follows. Organic amine, pseudoboehmite, silica sol and water were added in sequence into a glass beaker. In some experiments, no additional water was added since water amount from reagents could satisfy the gel compositions. The mixture was stirred at room temperature for 5 min, and then transferred into a stainless steel autoclave. After further addition of phosphoric acid, the autoclave was sealed quickly, placed in an oven and rotated at 60 rpm for 20 min to get a homogeneous mixture. Subsequently, the autoclave was heated in 60 min to the desired temperature under rotation and kept for a certain time. After the crystallization, organic liquid was collected from the autoclave with a burette or by decantation. The solid product was washed with distilled water and dried in air.

The solid yield of samples was calculated by the following formula: Yield (%) = $(M_{sample} \times 85\%) \times 100/(M_{Al_2O_3} + M_{P_2O_5} + M_{SiO_2})_{gel}$, where M_{sample}, 85% and $(M_{Al_2O_3} + M_{P_2O_5} + M_{SiO_2})_{gel}$ stand for the weight of solid sample, an estimated value of framework compounds included in the sample, and the dry mass of three inorganic oxides in the starting mixture, respectively.

Characterization

The powder XRD pattern was recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.54059$ Å), operating at 40 kV and 40 mA. The chemical composition of the solid samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy (SEM, KYKY-

AMRAY-1000B). All NMR experiments were performed on a Varian Infinity plus 400WB spectrometer with BBO MAS probe operating at a magnetic field strength of 9.4 T. The resonance frequencies were 104.2, 161.9, 79.4, and 100.5 MHz for ^{27}Al, ^{31}P, ^{29}Si, and ^{13}C, respectively. Chemical shifts were referenced to 1.0 M Al(NO$_3$)$_3$ for ^{27}Al, 85% H$_3$PO$_4$ for ^{31}P, and 2, 2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ^{29}Si and ^{13}C. The spinning rates of the samples at the magic angle were 4, 10, 6 and 8 kHz for ^{29}Si, ^{27}Al ^{31}P and ^{13}C, respectively. Textural properties of the calcined samples were determined by N$_2$ adsorption at 77 K on a Micromeritics ASAP 2020 system. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evaluated using the *t*-plot method. The collected organic amine solution was analyzed by a Varian GC3800 gas chromatograph equipped with a FID detector and a SE-30 capillary column.

Adsorption experiments

Adsorption isotherms of CH$_4$ and CO$_2$ of the samples were measured with a Micromeritics ASAP 2020 apparatus at 25 °C and pressure up to 1 bar. The temperature was controlled by using a Dewar bottle with a circulating jacket connected to a thermostatic bath utilizing water as the coolant. Before analysis, all samples were degassed under vacuum at 350 °C for 6 h. The free space of the tube was determined with helium gas. Ultra-high purity grade CH$_4$ and CO$_2$ were used for all the adsorption experiments.

Results and discussion

Aminothermal synthesis of SAPO molecular sieves based on TEA system

The synthesis conditions for the SAPO molecular sieves using TEA as the solvent and template are summarized in Table 1. At 160 °C, pure phase of SAPO-34 (samples 2 and 3) could be obtained after 2 days of crystallization by the novel synthetic route. The product yields for samples 2 and 3 were calculated to be 89.5 and 88.1%, respectively. These values were higher than those obtained from the conventional hydrothermal synthesis performed at 200 °C (75.4%, sample 10). The present yields became more prominent when compared with the hydrothermal yield of SAPO-34 synthesized at 160 °C (46.8%, sample 11). This suggests that aminothermal environment could accelerate the crystallization rate of SAPO-34. Prolonged synthetic time from 2 to 4 days led to a slight increase of crystal yield (sample 4), indicating that the crystallization had approached completion after 2 days. It is important to note that the existence of certain amount of water in the aminothermal system was necessary for a successful synthesis. If the water amount was too low ($V_{amine/water} \geq 8$), only amorphous solid was produced (sample 1), in agreement with the previous finding that water amount in the solvothermal system had significant effect on the crystallization rate.[22] The elemental compositions of the obtained samples were determined by XRF and shown in Table 1. The solid compositions of samples 2–4 were similar to one another and close to their initial mixtures. It seems that small changes in water amount and crystallization time had little effect on the product composition.

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Table 1 Aminothermal synthesis of SAPO molecular sieves based on TEA system and DEA system

| Sample	Gel composition[a] R : Al$_2$O$_3$: P$_2$O$_5$: SiO$_2$: H$_2$O	V$_{amine/water}$	T/°C	t (day)	Product[b]	Yield	Product composition
1[c]	R = TEA 7.0 : 1.0 : 0.9 : 0.3 : 6.9	8.0	160	2	amorphous	—	—
2	R = TEA 7.0 : 1.0 : 0.9 : 0.3 : 9.6	5.8	160	2	SAPO-34	89.5%	Al$_{0.490}$P$_{0.444}$Si$_{0.066}$
3	R = TEA 7.0 : 1.0 : 0.9 : 0.3 : 15.7	3.5	160	2	SAPO-34	88.1%	Al$_{0.486}$P$_{0.446}$Si$_{0.068}$
4	R = TEA 7.0 : 1.0 : 0.9 : 0.3 : 15.7	3.5	160	4	SAPO-34	90.4%	Al$_{0.480}$P$_{0.454}$Si$_{0.066}$
5	R = TEA 7.0 : 1.0 : 0.9 : 0.5 : 11.3	4.9	200	2	SAPO-18	84.2%	Al$_{0.461}$P$_{0.421}$Si$_{0.118}$
6	R = TEA 7.0 : 1.2 : 0.9 : 0.5 : 16.6	3.4	200	2	SAPO-18	79.3%	Al$_{0.479}$P$_{0.459}$Si$_{0.063}$
7	R = DEA 9.0 : 1.2 : 0.9 : 0.5 : 16.6	3.3	160	2	amorphous	—	—
8	R = DEA 9.0 : 1.2 : 0.9 : 0.5 : 16.6	3.3	160	4	DNL-6	32.9%	Al$_{0.489}$P$_{0.306}$Si$_{0.205}$
9	R = DEA 9.0 : 1.0 : 0.9 : 0.5 : 11.3	4.7	200	2	DNL-6(16%) SAPO-34(84%)	44.1%	Al$_{0.475}$P$_{0.326}$Si$_{0.200}$
10	R = TEA 3.0 : 1.0 : 0.9 : 0.3 : 50	0.46	200	2	SAPO-34	75.4%	—
11	R = TEA 3.0 : 1.0 : 0.9 : 0.3 : 50	0.46	160	2	SAPO-34	46.8%	—
12	R = DEA 2.0 : 1.0 : 0.8 : 0.6 : 50	0.23	200	2	SAPO-34	39.5%	Al$_{0.490}$P$_{0.350}$Si$_{0.150}$
13[d]	R = TEA 3.0 : 1.0 : 1.0 : 0.5 : 15.7 : 20EG	—	200	2	SAPO-5	73.0%	Al$_{0.489}$P$_{0.467}$Si$_{0.044}$

[a] For samples 1, 2, 5 and 9, all water in the initial mixture came from reagents and no extra water was added. [b] The value in the brackets was calculated based on the relative intensity of the first peak of each phase in the XRD pattern. [c] Fumed silica was used as Si source in order to reduce the water amount in the system. [d] Experiment using ethylene glycol (EG) as the solvent.

When the synthesis temperature was increased to 200 °C, SAPO-18 (samples 5 and 6) instead of SAPO-34 was crystallized. SAPO-18 was previously synthesized utilizing expensive *N,N*-diisopropylethylamine[37,38] or TEAOH[39] as the template *via* a hydrothermal route. To the best of our knowledge, this is the first report of SAPO-18 synthesis using TEA template. However, the result was not very unexpected, considering the structure similarity between SAPO-18 (AEI) and SAPO-34 (CHA). Both of them consist of layers of double six-rings, which are connected along *z*-axis *via* O-bridges to form three-dimensional structures. The lateral shift between the layers is zero for the CHA structure, while a rotation of 180° about *z* gives the AEI structure. Additionally, solvothermal synthesis with ethylene glycol as the solvent and TEA as the template was also investigated as a comparison. SAPO-5 was obtained as the final product (sample 13). This implies that solvent property could exert a great influence on the synthesis, and the strong basic environment arising from TEA solvent was important for the formation of SAPO-18.

Fig. 1 displays the XRD patterns of the as-synthesized samples. For SAPO-34 (samples 2–4), both the crystallinity and relative intensity of each peak were comparable to those of sample 10 by hydrothermal method. The XRD patterns of SAPO-18 were similar to those reported in the previous literatures.[37,38,40] The SEM images (Fig. 2) reveal that SAPO-34 had a typical rhombohedral morphology. SAPO-18 was consisted of square-shaped plate-like crystals, in consistence with previous report.[39] The textual properties of samples are presented in Table 2. All samples possessed large surface areas and high pore volumes. These values were close to those of samples synthesized with hydrothermal method, implying that the aminothermal route was an effective methodology to synthesize SAPO molecular sieves with good crystallinity.

Solid-state ^{29}Si, ^{31}P and ^{27}Al MAS NMR spectra were determined to investigate the local atomic environments in the as-synthesized SAPO-34 (sample 4) and SAPO-18 (sample 6). The results are shown in Fig. 3. For SAPO-34, both ^{29}Si and ^{31}P MAS NMR spectra gave one single resonance peak, in accordance with Si (4Al) and P (4Al) environments. Two peaks centred at 39.3 and 12 ppm were observed for the as-synthesized SAPO-34

in the ^{27}Al MAS NMR spectrum. The strong peak at high field should arise from tetrahedrally coordinated aluminium atoms. The weak peak was ascribed to penta-coordinated Al formed by an additional interaction of one water or template molecule to the framework aluminium.[41] The assignment was confirmed by the ^{27}Al spectrum of the calcined SAPO-34, in which only one signal with a chemical shift of 33.8 ppm appeared. The ^{29}Si MAS NMR spectrum of SAPO-18 was complex and showed the co-existence of several Si environments. Since the silicon contents in SAPO-18 and SAPO-34 were low and very close, it could be inferred that the framework of SAPO-18 was facilitating the formation of Si islands. Chen *et al.* investigated the Si environments in SAPO-18 prepared by hydrothermal method to observe a similar phenomenon.[38] The ^{31}P spectrum of SAPO-18 consisted of a single peak centered at −29 ppm and the other small one at
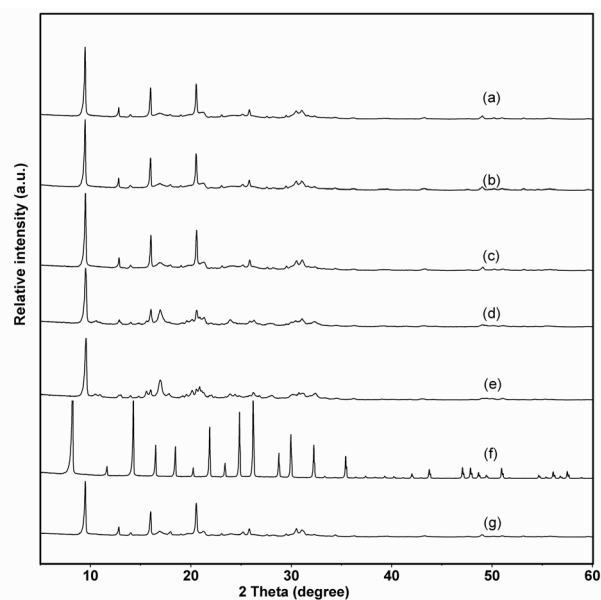
Fig. 1 XRD patterns of as-synthesized samples 2(a), 3(b), 4(c), 5(d), 6(e), 8(f) and 10(g).
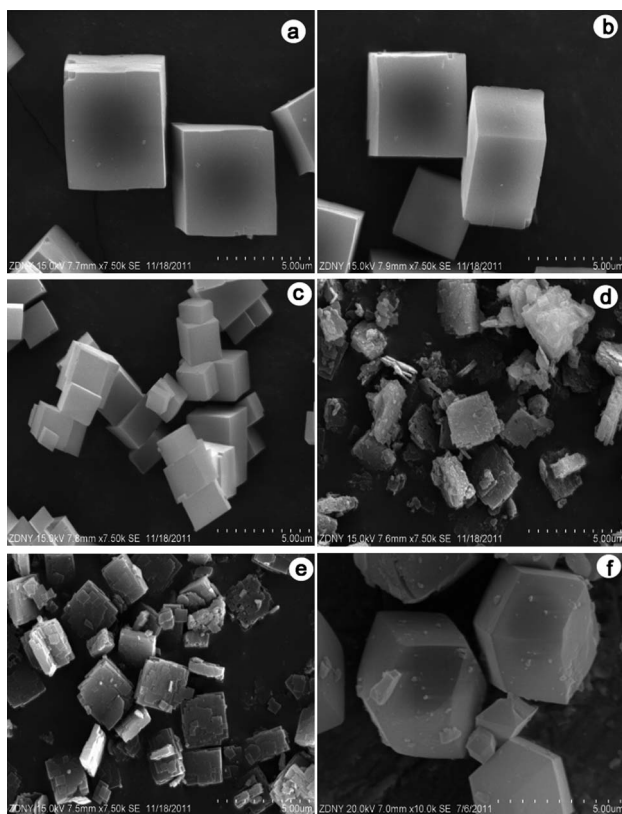
Fig. 2 SEM images of as-synthesized samples 2(a), 3(b), 4(c), 5(d), 6(e) and 8(f).

Table 2 Textual properties of the samples

Sample	Surface area (m² g⁻¹)			Pore volume (cm³ g⁻¹)	
	S_{total}[a]	S_{micro}[b]	S_{ext}[c]	V_{total}	V_{micro}[d]
3	577	569	8	0.27	0.26
4	546	544	2	0.26	0.25
5	554	531	22	0.31	0.24
6	575	562	13	0.29	0.26
8	629	586	43	0.31	0.27
10	562	559	3	0.27	0.26
12	510	461	49	0.28	0.23
14	526	520	5	0.31	0.30
15	546	540	6	0.26	0.25
16	565	554	11	0.27	0.25
17	679	659	20	0.31	0.30

[a] BET surface area. [b] t-Plot micropore surface area. [c] t-Plot external surface area. [d] t-Plot micropore volume.

−12.3 ppm. According to the literature,[42] the framework structure of AlPO-18 contains three phosphorus and three aluminium crystallographic positions. Therefore, these two signals should be ascribed to P (4Al) with different local geometries. Correspondingly, several peaks were observed in the ²⁷Al spectrum. The strong splitting signals were due to tetrahedral Al atoms at different crystallographic sites, and the small peak at *ca.* 9 ppm arose from penta-coordinated Al. Generally, the chemical environments of Si, P and Al in samples 4 and 6 were similar to those of the samples prepared by hydrothermal method.
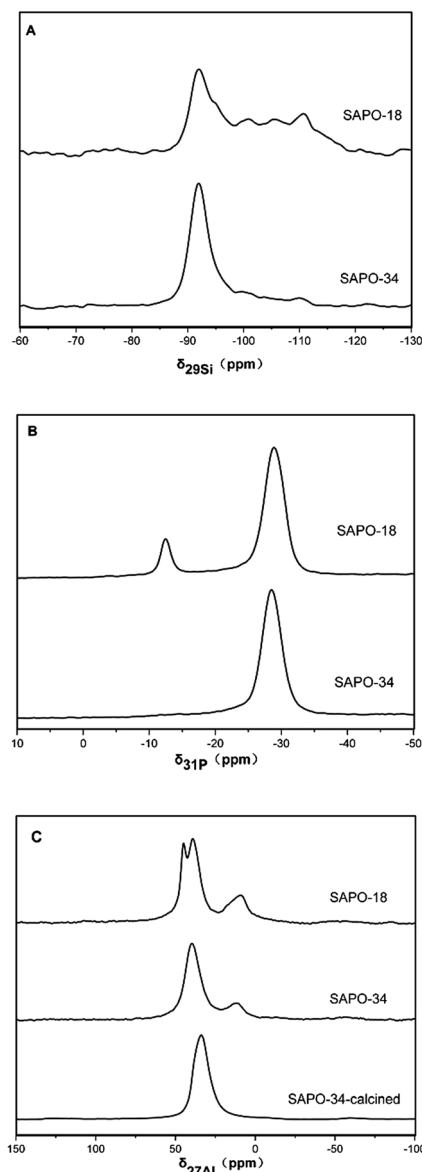
Fig. 3 ²⁹Si MAS NMR (A), ³¹P MAS NMR (B) and ²⁷Al MAS NMR (C) spectra of as-synthesized samples 4 (SAPO-34) and 6 (SAPO-18).

Aminothermal synthesis of SAPO molecular sieves based on DEA system

Diethylamine (DEA) is a kind of versatile structure-directing agent frequently employed in the synthesis of SAPO molecular sieves. Aminothermal synthesis of SAPO-molecular sieves based on DEA system was carried out. Detailed synthesis conditions and product compositions are listed in Table 1. XRD patterns and SEM images of the as-synthesized sample are shown in Fig. 1 and 2, respectively.

It can be seen that DNL-6 with a good crystallinity was formed from a starting composition of 9.0DEA : 1.0Al₂O₃ : 0.9P₂O₅ : 0.5SiO₂ : 16.6H₂O at 160 °C for 4 days (sample 8). DNL-6 was a novel SAPO molecular sieve with RHO framework type. Our laboratory recently reported its first synthesis under hydrothermal conditions by using DEA as the template in the presence of cetyltrimethylammonium bromide

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(CTAB).[43,44] Along with increasing the synthetic temperature to 200 °C, the product became a mixture of SAPO-34 and DNL-6 (sample 9). It should be mentioned that the solid yields of samples 8 and 9 were obviously lower than those synthesized with TEA solvent, but close to that obtained by the hydrothermal route with DEA template (sample 12). Possibly, the high Si incorporation into the framework of molecular sieves induced by DEA possibly resulted in the low yield.[33]

SEM image reveals that DNL-6 has a rhombic dodecahedral morphology with crystal size distribution of 2–5 μm. The micropore surface area and volume of DNL-6 were respectively determined to be 586 m^2 g^{-1} and 0.27 cm^3 g^{-1} (see Table 2). The values were comparable to those of SAPO-34 and SAPO-18, in consistence with the similar framework densities of three molecular sieves.

Aminothermal synthesis of SAPO molecular sieves based on TEA-DEA system

The mixture of TEA and DEA was explored as the solvent and template to synthesize SAPO molecular sieves. A series of experiments with different TEA/DEA ratios were investigated and the results are shown in Table 3. Interestingly, SAPO-34 with a solid yield of ~90% could be obtained from the systems with higher TEA/DEA ratios at 200 °C for 2 days (samples 14, 15 and 18), different from the induction behaviour of any single amine under the same synthesis conditions. With the gradual increase of DEA concentration in TEA-DEA mixture, the product phase would change from SAPO-34 to DNL-6 containing a small amount of SAPO-34 impurity, accompanied with an obvious decrease of the solid yield. Elemental analyses by XRF (see Table 3) revealed that the product synthesized with the highest DEA concentration possessed the largest silicon content (sample 17), which was identical to that of sample 8 crystallized in individual DEA solvent. Thus, the low yield of sample 17 might be ascribed to the high Si incorporation induced by DEA template.

The XRD patterns of as-synthesized samples are presented in Fig. 4. All samples exhibited good crystallinity. However, a clear distinction in the relative peak intensity was observed when comparing the XRD patterns of SAPO-34 synthesized from binary amines system with those from TEA system. According to the literature, the former had a pure CHA structure, but the latter was a CHA/AEI intergrowth with CHA as a dominant phase.[45] This suggests that the mixture of TEA and DEA have a strong structure-directing ability to the formation of pure CHA framework. Textual properties shown in Table 2 indicated that
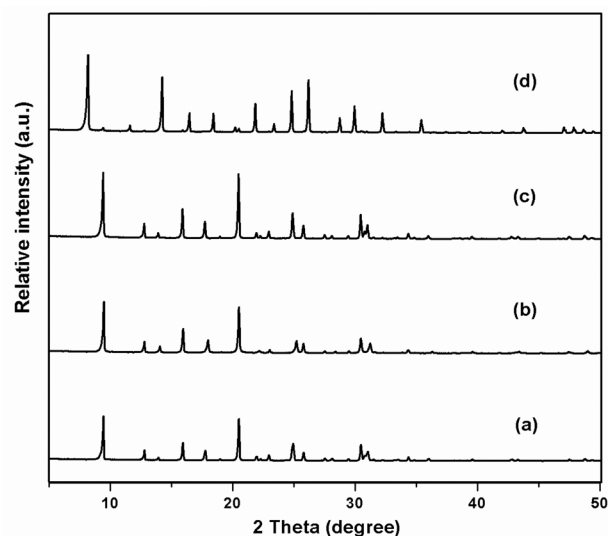

Fig. 4 XRD patterns of as-synthesized samples 14(a), 15(b), 16(c) and 17(d).

samples 14–17 possessed large micropore surface area and micropore volume, further confirming the excellent crystallinity of the products.

^{13}C MAS NMR was employed to investigate the incorporation of DEA and TEA into the products (see Fig. 5). The assignments of all peaks were labelled in the spectra. The strong peak centred at ca. 11 ppm was ascribed to –CH$_3$ group of two amines. The –CH$_2$– group in DEA and TEA gave signals at 47–49 and 39–42 ppm, respectively. It can be seen that the signals from both TEA and DEA appeared in the spectra of all four samples, suggesting co-templated role of two amines. Deconvoluted results revealed that the molar ratio of TEA/DEA in the products was lower than that in the starting gels, possibly indicating that DEA was more easily incorporated into the as-synthesized sample than TEA.

Synthesis of SAPO-34 using recycled amines

Also, synthesis of SAPO-34 using recycled amines was investigated based on samples 3 (TEA system) and 18 (TEA-DEA binary system). Organic amines could be collected easily by a burette or by decantation after the synthesis, since there was a clear interface between organic solution and viscous gel-like product. It should be mentioned that experiment without extra water addition was not suitable for recycling synthesis due to the

Table 3 Aminothermal synthesis of SAPO molecular sieves based on TEA-DEA system

Sample	Gel composition[a] TEA : DEA : Al$_2$O$_3$: P$_2$O$_5$: SiO$_2$: H$_2$O	T/°C	t (day)	Product[b]	Yield	Product composition
14	7.0 : 0.5 : 1.0 : 0.9 : 0.5 : 11.3	200	2	SAPO-34	89.1%	Al$_{0.456}$P$_{0.427}$Si$_{0.117}$
15	7.0 : 1.5 : 1.0 : 0.9 : 0.5 : 11.3	200	2	SAPO-34	89.7%	Al$_{0.475}$P$_{0.397}$Si$_{0.128}$
16	4.5 : 3.5 : 1.0 : 0.9 : 0.5 : 11.3	200	2	SAPO-34	85.6%	Al$_{0.478}$P$_{0.396}$Si$_{0.123}$
17	2.5 : 7.0 : 1.0 : 0.9 : 0.5 : 11.3	200	2	DNL-6(94.3%) + SAPO-34(5.7%)	60.3%	Al$_{0.475}$P$_{0.326}$Si$_{0.200}$
18	7.0 : 1.5 : 1.0 : 0.9 : 0.5 : 15.7	200	2	SAPO-34	90.2%	—

[a] For samples 14–17, all water in the initial mixture came from reagents and no extra water was added. [b] The value in the brackets was calculated based on the relative intensity of the first peak of each phase in the XRD pattern.
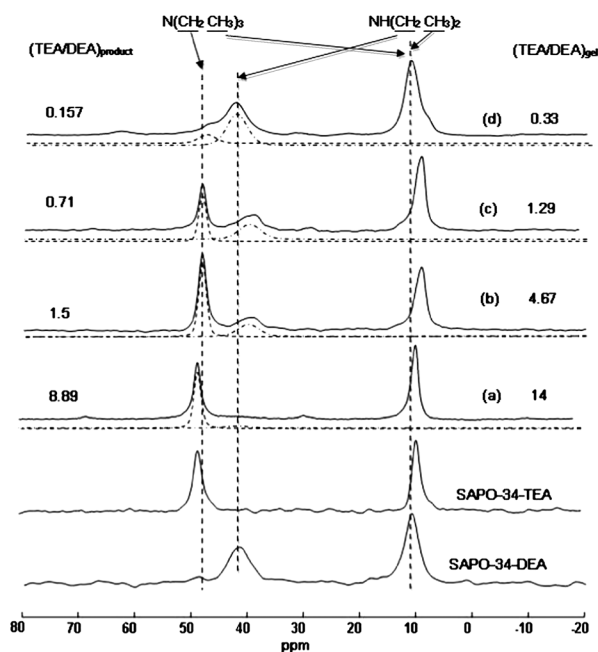
Fig. 5 ^{13}C MAS NMR spectra of as-synthesized samples 14(a), 15(b), 16(c) and 17(d). Standard samples: SAPO-34-TEA and SAPO-34-DEA were synthesized hydrothermally with TEA and DEA templates, respectively.

existence of small amount of water in the collected organic liquids.

The detailed information of recycled liquids and the synthesis conditions are listed in Table 4. It can be seen that only small quantities of organic amines and water were added to attain the same solvent environment as the first batch. Pure SAPO-34 with good crystallinity and high yield was obtained in both experiments, almost identical to the product synthesized with fresh amines. This proves that recycled amines could be readily reused to synthesize SAPO-34 with high quality.

CO_2 and CH_4 adsorption

Molecular sieves with small pore size are promising adsorbents for CO_2 separation from methane. Adsorption isotherms of

Table 4 Repeated synthesis of SAPO-34 with collected liquids

	Sample 3[a]	Sample 18[b]
Collected liquid mass	35.0 g	39.8 g
Liquid component	TEA 33.0 g	TEA 34.4 g
	H_2O 2.0 g	DEA 2.95 g
		H_2O 2.4 g
Added liquids	TEA 2.4 g	TEA 0.94 g
	H_2O 3.64 g	DEA 2.53 g
		H_2O 1.39 g
Product	SAPO-34	SAPO-34
Crystalline yield	90%	89.7%

[a] Initial gel composition for sample 3 : 7.03 g pseudoboehmite, 10.37 g phosphoric acid, 3.20 g silica sol, 5.64 g water and 35.35 g TEA.
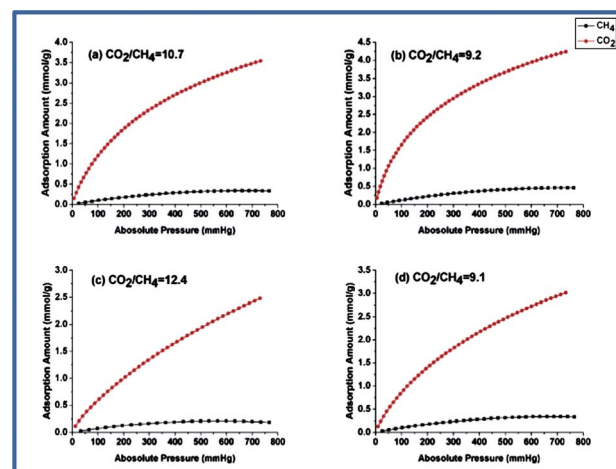[b] Initial gel composition for sample 18 : 7.03 g pseudoboehmite, 10.37 g phosphoric acid, 5.36 g silica sol, 3.79 g water, 35.35 g TEA and 5.48 g DEA.

CO_2 and CH_4 on SAPO-34, SAPO-18 and DNL-6 synthesized by aminothermal method were collected and shown in Fig. 6. To evaluate the effect of the present synthesis method on the sorption properties of the samples, SAPO-34 synthesized by hydrothermal method (sample 10) was used as a reference material.

Compared with the reference sample 10, sample 15 (SAPO-34) exhibited a large CO_2 adsorption capacity and high CO_2/CH_4 ratio, which is attractive for the separation of CO_2/CH_4 mixture. The highest CO_2/CH_4 adsorption ratio was observed for SAPO-18 (sample 6), though its adsorption capacities for both gases were relatively low. DNL-6 (sample 8) displayed the largest uptakes for CO_2 and CH_4. The CO_2/CH_4 ratio on DNL-6 was 9.2, quite close to 9.1 on the reference sample. These preliminary results indicate good adsorption/separation properties of SAPO molecular sieves synthesized by aminothermal method.

Conclusions

The present work demonstrates that the aminothermal method is an effective route to synthesize SAPO molecular sieves. SAPO-34 with ~90% yield was obtained using TEA or TEA-DEA mixture as the solvent and template. Pure SAPO-18 could be synthesized by changing the crystallization temperature of the TEA system, which is the first synthesis report of SAPO-18 with TEA as the template. Employing DEA as the solvent and template, a novel SAPO molecular sieve DNL-6 was formed. Characterization results revealed that DEA could induce a high Si incorporation into the framework of molecular sieves to cause a low solid yield. In addition, DEA showed a stronger ability than TEA to incorporate into the as-synthesized sample when TEA-DEA binary mixture was used for aminothermal synthesis. Environmental benign approaches could be realized through recycling organic liquids collected after the synthesis. Finally, SAPO molecular sieves were evaluated as adsorbents for the CO_2/CH_4 separation. As compared with the reference sample, SAPO-34 synthesized by the present route exhibited better adsorption capacity and high CO_2/CH_4 ratio. The present work will further

Fig. 6 CO_2 and CH_4 adsorption isotherms of samples 15(a), 6(b), 8(c) and 10(d).

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arouse our interests to explore the aminothermal synthesis of other SAPO molecular sieves with a wide range of organic amines.

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