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Template-Free Synthesis of the Nanoporous Nickel Phosphate VSB-5 under Microwave Irradiation

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Metal phosphate[1] and metal incorporated aluminophosphate molecular sieves[2] have attracted considerable attention for applications in catalysis, adsorption, and separations, etc. The synthesis of VSB-5, a large-pore nickel phosphate molecular sieve, has been reported recently by us[3] and applications such as hydrogen storage,[4] selective hydrogenation, and base catalysis have been explored.[3] The original preparation involved hydrothermal synthesis at 180 °C for 5 days using expensive organic diamines as templates or structure-directing agents. Typically, 1,3-diaminopropane (DAP) was used to synthesize the VSB-5 in the pH range 7.3−11.0.[3] The P/Ni ratio of the reaction mixture (2.1) was considerably higher than that in the product VSB-5 (0.6),[3] requiring high concentrations of DAP (typically DAP/Ni = 5.3)[3] to maintain alkaline conditions. Furthermore, the use of organic diamines in the synthesis of VSB-5 necessitated high-temperature (about 350 °C) calcination or activation to remove the amine and open up the pore structure.[5]

The use of organic templates to synthesize porous materials has the following significant drawbacks:[6] (i) organic templates are normally very expensive and environmentally unfriendly; (ii) calcination to remove the template may cause destruction of the pore structure and irreversible aggregation of crystals; and (iii) synthesis with a template may change the Si/Al ratio of the final products in systems such as LTA and FAU zeolites. To the best of our knowledge, large-pore metal phosphate molecular sieves, especially thermally unstable ones such as iron phosphates and vanadium phosphates, have not been hydrothermally synthesized without organic amines. However, several thermally stable molecular sieves composed of Si, Al, or P, including MFI[7] (10-membered ring (MR)), $AlPO_4$−H1 (18MR), H2 (10MR), H3[8] (8MR), and a silicoaluminophosphate molecular sieve[9] ($Si_2AlP_3O_{13}$, pore diameter <0.6 nm) have been synthesized without organic template molecules. The shortest O−O distance across the pore of VSB-5 is 11.6 Å.

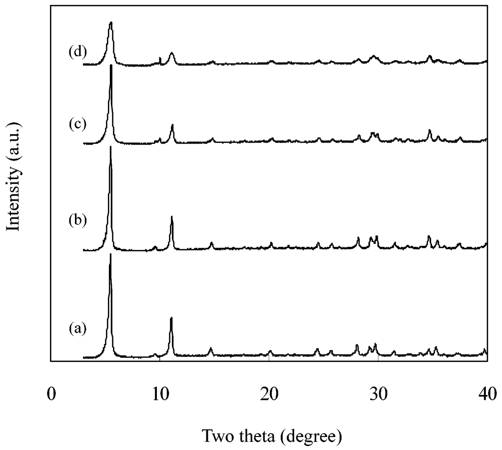

Figure 1. XRD patterns of synthesized VSB-5: (a) Sample A, (b) Sample B, (c) Sample C, and (d) Sample D.

Recently, microwave synthesis has been applied to the fast crystallization of various nanoporous materials.[10] It can be a powerful tool to seek efficient synthesis conditions for inorganic materials normally made hydrothermally because it offers advantages such as rapid crystallization, phase selectivity, and facile morphology control, etc.[11] In this work, we report the template-free and facile synthesis of VSB-5 with inorganic bases such as aqueous ammonia or NaOH under microwave irradiation.

VSB-5 was synthesized using $NiCl_2{\cdot}6H_2O$ and H_3PO_4 together with different inorganic bases such as NaOH and aqueous ammonia, and with diaminopropane (DAP) for comparison. The synthesis conditions are summarized in Table 1. The precursor gel of 30−60 g was loaded in

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Table 1. Synthesis Conditions of VSB-5 Materials under Microwave Irradiation and Properties of the Synthesized VSB-5 Materials

	synthesis condition[a]			synthesis result			
sample	base	molar composition (mol %)	pH	crystallization yield (%)[c]	composition ((P/(P+Ni), atomic %)	BET surface area[d] (as-synthesized) (m^2/g)[e]	BET surface area[d] (activated at 350 °C) (m^2/g)[f]
A	DAP[b]	Ni/P/DAP/H_2O (1:2.1:5.2:132)	10.5	50.2	37.9	54	300 (0.24)
B	DAP	Ni/P/DAP/H_2O (1:0.63:3.5:100)	9.8	50.4	37.8	42	290 (0.20)
C	aqueous ammonia	Ni/P/NH_3/H_2O (1:0.63:3.0:103)	7.7	87.9	37.8	400 (0.28)	340
D	NaOH	Ni/P/NaOH/H_2O (1:0.63:2.5:100)	7.8	83.8	37.6	240	200

[a] With microwave irradiation at 180 °C for 4 h. [b] DAP: 1,3-diaminopropane. [c] Based on the Ni content and the unit cell formula of VSB-5, $Ni_{20}[(OH)_{12}(H_2O)_6][(HPO_4)_8(PO_4)_4]12H_2O$.[3] [d] The figures in parentheses mean the total pore volume (cc/g) at $P/P_o = 0.99$. [e] Samples were dehydrated at 300 °C for 4 h in vacuo upon surface area measurement. [f] Samples were activated at 350 °C for 4 h in air before surface area measurement.

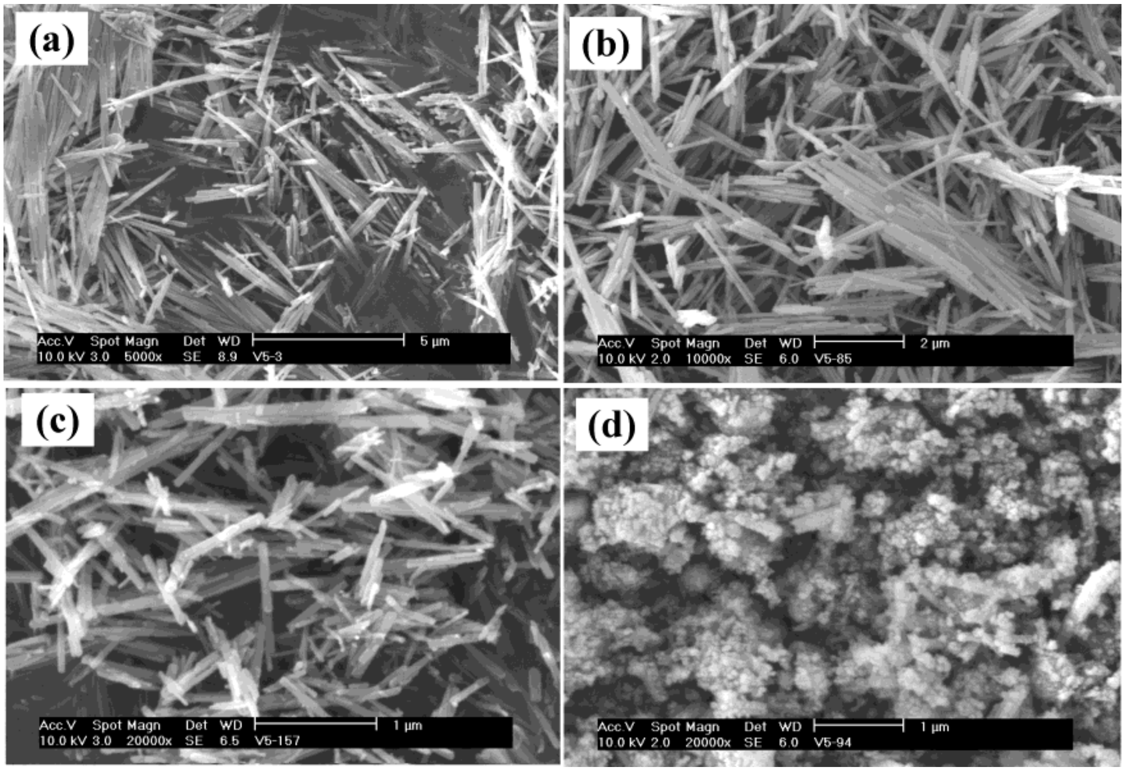

Figure 2. SEM images of VSB-5 materials using the different base under microwave irradiation: (a) Sample A, (b) Sample B, (c) Sample C, and (d) Sample D. The magnifications are 5000, 10 000, 20 000, and 20 000 times for (a), (b), (c), and (d), respectively.

a 100-mL Teflon autoclave, which was sealed and placed in a microwave oven (Mars-5, CEM, maximum power of 1200 W). The reaction mixture was heated to the reaction temperature of 180 °C in less than 2 min (microwave power was 600 W) and maintained at that temperature for 4 h (microwave power was 300 W). The solid product was recovered with centrifugation, washing with deionized water, and drying. The structure and crystallinity of the synthesized samples were determined by X-ray powder diffraction (Rigaku, D/MAX IIIB, Cu Kα radiation). Materials containing a dense nickel phosphate phase were identified by comparing XRD patterns with JCPDS cards. The morphology and composition (Ni, P) were analyzed with a scanning electron microscope/energy dispersive X-ray spectrometer (Philips, XL30S FEG). The composition was cross-checked by inductively coupled plasma spectrometery (Jovin Yvon Ultima-C).

Figure 1 shows the XRD patterns of the nickel phosphate products obtained from different bases. The patterns are very similar to those of VSB-5 reported previously.[3] However, the XRD intensities of VSB-5 synthesized with NaOH are very low while their peak widths are wide, as compared to those synthesized with DAP. These results appear to be due to the formation of smaller crystals (vide infra) upon using NaOH because its BET surface area (Table 1) is comparable to the material with DAP. It can also be seen that the VSB-5 is formed at a relatively low concentration of expensive diamine if the P/Ni ratio is low (Samples A and B). The VSB-5 crystals have rodlike morphologies except in the case of VSB-5 synthesized with NaOH (Figure 2). The morphology does not change with the DAP/Ni ratio (Samples A and B), but the crystal size decreases somewhat if aqueous ammonia is used to control the pH. The crystal size of VSB-5 synthesized

Table 2. Optimal Synthesis Conditions of VSB-5 Materials[a]

	conditions to form VSB-5		
base	base/Ni ratio	pH	other phases formed[b] [JCPDS card]
DAP	1.5−6.0	7.5−11.6	low pH: $Ni_{11}(HPO_3)_8(OH)_6$ [44-1327] high pH: $Ni_3(PO_4)_2(8H_2O)$ [33-0951]
aqueous ammonia	2.8−6.0	7.5−9.2	low pH: $Ni_{11}(HPO_3)_8(OH)_6$ [44-1327] high pH: $(NH_4)Ni(PO_4)(H_2O)$ [86-0586]
NaOH	2.5	7.8	low pH: $Ni_{11}(HPO_3)_8(OH)_6$ [44-1327] high pH: $Ni(OH)_2$ [14-117]

[a] Reactant composition Ni/P/base/H_2O (1:0.63:*x*:100). [b] Dense phases formed when the pH is too high or low.

with NaOH is very small (about 100 nm) and the homogeneity is not so high (Sample D).

Optimization results for the different bases show that the VSB-5 can be synthesized only in weak alkaline conditions, as illustrated in Table 2. However, the range of pH or base/Ni ratio required to synthesize VSB-5 depends on the type of base. When the P/Ni ratio is 0.63, the optimal range of base/Ni ratio in the reactant solution is 1.5−6.0 for DAP, 2.8−6.0 for aqueous ammonia, and 2.5 for NaOH (Table 2). Similarly, the optimal pH range to synthesize the molecular sieve is 7.5−11.6 for DAP, 7.5−9.2 for aqueous ammonia, and 7.8 for NaOH when the P/Ni ratio is 0.63 (Table 2). We also confirmed that VSB-5 could be synthesized with various organic bases such as trialkylamines, dialkylamines, and diamines (not presented here).

As shown in Table 2, dense nickel phosphates are obtained if the pH is too high or too low compared with the optimal range. At low pH, the dense phase $Ni_{11}(HPO_3)_8(OH)_6$ was obtained. At high pH, the resulting phases were identified as $(NH_4)Ni(PO_4)(H_2O)$, $Ni_3(PO_4)_2(8H_2O)$, and $Ni(OH)_2$ with ammonia, DAP, and NaOH, respectively.

The VSB-5 materials have very similar P/(P + Ni) ratios irrespective of the bases used in the synthesis. The BET surface areas of the materials made with inorganic bases after thermal treatment at 350 °C ranged from 200 to 340 m^2/g, indicating porosity comparable to that of the sample made conventionally (300 m^2/g, Sample A). The surface areas of VSB-5s synthesized with DAP are very low (less than 55 m^2/g) before thermal treatment at 350 °C. However, high surface areas (240−400 m^2/g) are easily obtained with only dehydration at 300 °C in vacuo when using inorganic bases. This result shows that the synthesis method of VSB-5 using inorganic bases is very effective and convenient for producing the nanoporous structure. It can also be seen that the BET surface area decreases with thermal treatment at 350 °C (Samples C and D), indicating partial degradation of the structure. Additionally, the crystallization yield of VSB-5 synthesized with inorganic bases is high compared to that from the synthesis with DAP or organic amines. However, the yield increases with the decrease of DAP/(Ni + P) ratio and the yield can reach 78% when the reactant mixture has the composition of 1:0.63:3.35:100 Ni/P/DAP/H_2O.

This work demonstrates that VSB-5 may be easily synthesized with simple and inexpensive inorganic bases such as aqueous ammonia and NaOH. The reaction time in the microwave synthesis is only 4 h. The synthesis method described here offers a cost-effective preparation that yields materials that do not require high-temperature activation. Moreover, the method is more environmentally benign because it does not require the use or decomposition of organic amines. The preparation of large-pore molecular sieves without the use of templating molecules suggests that other porous metal phosphates may form under similar conditions. Because the vast majority of the open-framework transition-metal phosphates synthesized to date are not sufficiently stable to remain crystalline following the removal of template molecules, our strategy of avoiding organic templates entirely may permit the preparation of other porous transition-metal phosphate materials.

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