

Facile Synthesis of Nanoporous Nickel Phosphates without Organic Templates under Microwave Irradiation

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The syntheses of two nanoporous nickel phosphates, VSB-1 and VSB-5, have been investigated to elucidate the effect of various synthesis parameters such as pH, type of base, reaction time, and heating method. The pH is found to be the most important factor to direct the structure in the synthesis. These molecular sieves are easily synthesized in a suitable pH range even without organic template molecules. VSB-1 is crystallized only in acidic conditions (pH = 3.5–4.8), while VSB-5 is prepared in weakly basic conditions (pH = 7.5–9.2). The reaction yield of VSB-1 increases with increasing pH, while VSB-5 shows the opposite trend. Compared with conventional hydrothermal synthesis, the microwave irradiation method increases the reaction rates of the two nickel phosphates by about 60 times, and the synthesis of VSB-1 and VSB-5 can be completed within 1 min at 190 and 180 °C, respectively. It is demonstrated that the molecular sieves can be synthesized continuously under microwave irradiation due to these fast crystallizations.

Introduction

Porous materials such as zeolites and aluminophosphate molecular sieves (AIPO) are widely used in catalysis and separation processes and are being developed for new applications.¹ Among them, metal phosphate² and metal incorporated aluminophosphate molecular sieves³ have attracted considerable attention for many applications. We have reported the synthesis and applications of the nickel phosphate molecular sieves named VSB-1^{4–6} and VSB-5.^{7,8} These nickel phosphates exhibit genuine zeolitic properties such as high BET surface area, ion exchange capacity, and shape-

selective catalysis.^{4–8} Their structures are based on 3D networks of octahedrally coordinated nickel atoms containing large, unidimensional channels. The unit cell formulas of VSB-1 and VSB-5 are $\text{Ni}_{18}[(\text{HPO}_4)_{14}(\text{OH})_3\text{F}_9(\text{H}_3\text{O}^+/\text{NH}_4^+)_4] \cdot 12\text{H}_2\text{O}^4$ and $\text{Ni}_{20}[(\text{OH})_{12}(\text{H}_2\text{O})_6][(\text{HPO}_4)_8(\text{PO}_4)_4] \cdot 12\text{H}_2\text{O}$,⁷ respectively. VSB-1 has been hydrothermally synthesized in the presence of pyridine and tris(2-aminoethyl) amine (TREN)⁴ and has potential applications in heterogeneous catalysis^{5,6} and as a support for a photocatalyst.⁹ The VSB-5 has several applications including hydrogen storage,⁸ selective hydrogenation, and base catalysis.⁷ In our previous work, VSB-5 was synthesized using expensive organic diamines as templates or structure-directing agents.⁷ Typically, 1,3-diaminopropane (DAP) was used to direct the VSB-5 structure.⁷

The use of organic templates to synthesize porous materials has significant drawbacks in the environment and economics.¹⁰ Moreover, the collapse of their pore structure in open-framework metal phosphates may occur during the heating process to remove organic molecules remaining in the as-synthesized materials.¹¹ Therefore, the synthesis of porous materials without organic template or structure-directing agent is highly desirable in practical applications. Recently, we have reported the template-free synthesis of VSB-5 by controlling the pH of the reactant mixture using inorganic bases.¹¹ In the present work, we have investigated in more detail the facile synthesis of VSB-1 and VSB-5 without

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Table 1. Synthesis Results of VSB-1 According to the Type of Base

sample no.	synthesis condition ^a				synthesis result	
	base	reactant composition (mol)	pH _{initial}	pH _{final}	yield (%) ^b	S _{BET} (m ² /g) ^c composition ((P/(P + Ni), at. %)
A	TREN/Py	1:1:2.4:0.4:1.8:40 Ni:P:HF:TREN:Py:H ₂ O	3.5	3.4	73	160 43.7
B	aqueous ammonia	1:1:1.5:3:100 Ni:P:HF:NH ₃ :H ₂ O	4.9	4.8	78	180 43.8
C	KOH	1:1:1.5:2.5:100 Ni:P:HF:KOH:H ₂ O	4.0	3.7	62	150 43.8
D	TEA	1:1:1.5:2.5:100 Ni:P:HF:TEA:H ₂ O	3.5	3.2	75	180 43.7

^a With microwave heating for 2 h at 180 °C. TREN: tris(2-aminoethyl)amine; Py: pyridine; TEA: triethylamine. ^b Based on the Ni concentration and the unit cell formula of VSB-1, Ni₁₈(HPO₄)₁₄(OH)₃F₉(H₃O⁺/NH₄⁺)₄12H₂O. ^c BET surface area of as-synthesized samples. Samples were heated very slowly (<1 °C/min) to 300 °C under vacuum and dehydrated at 300 °C for 4 h upon surface area measurement.

organic molecules as templating agents. The effect of pH in the synthesis of VSB-1 and VSB-5 is also studied.

So far, microporous materials have been synthesized mainly using conventional electric heating. Since the pioneering works,¹² it is known that the microwave synthesis of porous materials has many advantages such as fast crystallization,^{12,13} increased phase purity and phase selectivity,¹⁴ narrow particle size distribution,¹⁵ and facile morphology control.^{13,14} Very recently, we have shown that the coupled effect of metal incorporation and microwave irradiation during the synthesis of MFI type zeolites produces fibrous Ti-MFI crystals with very interesting properties.¹⁷ The microwave synthesis of porous materials can be a powerful tool to seek efficient synthesis conditions for inorganic materials that are normally prepared by conventional hydrothermal method because it offers the advantage of rapid crystallization. The facile synthesis of VSB-1 and VSB-5 by microwave irradiation method will be discussed.

Porous materials have been generally synthesized in a batchwise manner since the synthesis time is very long, usually several days, although continuous and fast synthesis is desirable. The continuous crystallization of AlPO-5 has been tried by utilization of microwave heating.¹⁸ Seeding has been useful to decrease the nucleation or crystallization time.¹² However, to our knowledge, the continuous synthesis of a porous material including transition metal phosphates has been seldom reported^{18,19} so far and needs further research. The continuous synthesis of a porous material is practical only when the crystallization time is in minutes or less. In this work, the continuous synthesis of the two

nanoporous nickel phosphates is possible under microwave irradiation due to the fast crystallization in suitable synthesis conditions. The aims of this work are to find a facile synthesis methods for nanoporous nickel phosphates in the absence of organic templates and to synthesize them continuously under microwave irradiation.

Experimental Section

VSB-1 was synthesized hydrothermally using NiCl₂·6H₂O, HF, and H₃PO₄ together with different inorganic bases such as aqueous ammonia or KOH, and with pyridine and TREN for comparison. To check the effect of pH, the HF/NH₃ ratio was changed or the concentration of NH₄F was varied. The molar compositions of typical reaction mixtures were 1:1:1.5:x:100 Ni:P:HF:NH₃:H₂O, 1:1:x:3:100 Ni:P:HF:NH₃:H₂O, or 1:1:x:100 Ni:P:NH₄F:H₂O. Synthesis conditions to analyze the type of bases are summarized in Table 1. VSB-5 was synthesized likewise using NiCl₂·6H₂O and H₃PO₄ in the presence of bases such as aqueous ammonia and tri-*n*-propylamine (TPA). The composition of a typical reaction mixture was 1:0.63:x:100 Ni:P:NH₃(or TPA):H₂O.

The synthesis was generally carried out utilizing microwave technique to analyze reaction parameters rapidly. The precursor gel of 30–40 g was loaded in 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 or 190 °C in less than 1 min (microwave power was 1200 W) and maintained at that temperature for a predetermined time (microwave power was 300 W). Unless otherwise specified, the crystallization times for the microwave synthesis of VSB-1 and VSB-5 were usually 2 and 1 h, respectively. For comparison, the same reactant mixture was crystallized in an electric oven for 0.5–60 h. The solid product was recovered with centrifugation, washing, and drying.

In the synthesis using microwave heating, the reaction temperature was controlled using EST-300 Plus system (Electronic Sensor – Temperature) that monitored and controlled temperature conditions inside sample vessels. In this system, a microwave transparent fiber-optic temperature probe was inserted into a thermowell of a sample vessel. The temperature sensor was a phosphor located at the tip of the probe. The decay rate of fluorescent light emitted from the phosphor is temperature-dependent, allowing a precise determination of temperature. For safety, the temperature of the reaction vessel in the microwave oven was measured using an optional TempGuard system. An infrared lens and sensor were located in the microwave oven and the temperature of each vessel was measured as the vessels rotated over the sensor. If the temperature in any vessel was higher than the maximum pre-set temperature, the TempGuard stopped microwave generation.

The structure and crystallinity of the synthesized samples were determined by X-ray powder diffraction (Rigaku, D/MAX IIIB, Cu K α radiation). Materials containing a dense nickel phosphate

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Table 2. Optimum Conditions for Synthesis of VSB-1^a

variables	reactant composition (mol)	ranges to form VSB-1		other phases formed ^b [JCPDS card no.]
		<i>x</i>	pH	
NH ₃	1:1:1.5: <i>x</i> :100 Ni:P:HF:NH ₃ :H ₂ O	2–3	3.8–4.8	low pH: no crystallization high pH: (NH ₄)Ni(PO ₄)(H ₂ O) [86-0586]
HF	1:1: <i>x</i> :3:100 Ni:P:HF:NH ₃ :H ₂ O	1.5–7	3.0–4.8	low pH: no crystallization high pH: (NH ₄)Ni(PO ₄)(H ₂ O) [86-0586]
NH ₄ F	1:1: <i>x</i> :100 Ni:P:NH ₄ F:H ₂ O	1–4	3.2–4.8	low pH: no crystallization high pH: (NH ₄)Ni(PO ₄)(H ₂ O) [86-0586]

^a With microwave heating for 2 h at 180 °C. ^b Other phases formed when the pH is too high (a dense phase) or low (no solid obtained).

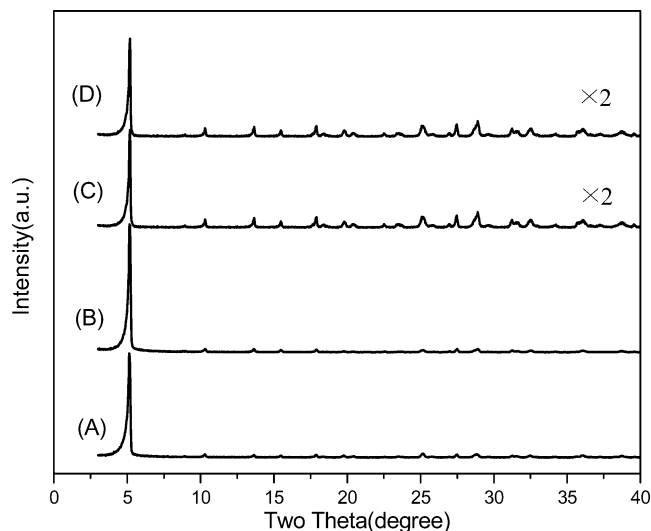


Figure 1. XRD patterns of as-synthesized VSB-1 molecular sieves according to a type of base: (a) sample A (TREN/Py), (b) sample B (aqueous ammonia), (c) sample C (KOH), and (d) sample D (TEA) of Table 1.

phase were identified by comparing XRD patterns with JCPDS cards. The morphology was checked using a scanning electron microscope (Philips, XL30S FEG), and the composition was analyzed by inductively coupled plasma spectrometry (Jovin Yvon Ultima-C). The reaction yield was determined by comparing the weight of the obtained solid (after considering the content of moisture) compared with the expected weight based on the unit cell formulas of VSB-1⁴ and VSB-5.⁷ The XRD intensity was not considered to calculate the yield because the homogeneity of the crystals is usually very high (confirmed by using SEM).

Results and Discussion

Synthesis of VSB-1 with Various Bases. Recently, we reported that the nickel phosphate molecular sieve VSB-5 can be synthesized using inorganic bases instead of an organic templating agent.¹¹ As shown in Table 1, the VSB-1 can also be obtained without an organic base such as pyridine and TREN in suitable acidic conditions, showing that VSB-1 can be synthesized without an organic templating molecule very similar to the template-free synthesis of VSB-5. The X-ray diffraction patterns and morphologies do not show noticeable differences with the type of bases added in the reactant mixture as shown in Figures 1 and 2. Likewise, the physicochemical properties such as chemical composition and BET surface area do not change appreciably with the type of bases used in the synthesis (Table 1). The nitrogen adsorption and desorption on VSB-1 reveal type I isotherms typical for microporous materials (Figure 3). The VSB-1 can be obtained in a suitable pH range (3.5–4.8) that was

adjusted with an inorganic base such as aqueous ammonia, KOH, and NaOH or with the HF/NH₃ or NH₄F (see below). Moreover, the VSB-1 can be synthesized in the presence of several organic amines such as triethylamine (TEA) if the pH lies between 3.8 and 4.5 (Table 1). However, it is not easy to figure out exactly which species plays the role of the template or structure-directing agent in the synthesis of the porous nickel phosphates. Henry et al. have reported that a water cluster, (H₂O)₁₇, can behave as a template in the synthesis of a nanoporous material called MIL-74 which is composed of zinc, aluminum, and phosphate.²⁰ Similar water clusters may play the role of the templates in the synthesis of VSB-1 molecular sieve. However, detailed work is necessary to clarify the templating species.

Effect of pH in the Synthesis of VSB-1 and VSB-5. The synthesis of VSB-1 has been performed in a wide pH range that was controlled by using aqueous ammonia, HF, or NH₄F. The VSB-1 can be obtained only in a limited acidic condition as summarized in Table 2. No crystalline material is obtained in more acidic condition (pH < 3.8) while a dense nickel phosphate, (NH₄)Ni(PO₄)(H₂O), is produced in neutral or alkaline condition. The physicochemical properties of the VSB-1 such as morphology, composition (P/Ni), and BET surface area do not show any noticeable dependence on the pH of 3.5–4.8. However, the crystal size and aspect ratio increase more or less with increasing the NH₄F/Ni ratio from 1 to 4 (data not shown).

The reaction yield of VSB-1 depends remarkably on the pH of the initial reactant mixture as illustrated in Figure 4. It is assumed that the low yield in low pH range is due to the retardation of nucleation/crystallization of nickel phosphates in strong acidic condition because VSB-1 dissolves when the pH is less than about 2 in aqueous solution at 100–180 °C (data not shown). Moreover, the reactivity of phosphoric acid may be lower than the deprotonated phosphoric acid species such as H₂PO₄⁻. The yield of VSB-5 also depends on the pH of the reactant mixture. Contrary to the VSB-1, the yield of VSB-5 decreases with increasing pH in alkaline condition as presented in Figure 5. The effects of pH on the reaction yield of VSB-5 may be explained in terms of the competitive formation of (NH₄)Ni(PO₄)(H₂O) along with the partial dissolution of VSB-5 at higher pH. We have reported that the dense phase, (NH₄)Ni(PO₄)(H₂O), is favorably obtained in more alkaline condition (pH > 9.2).¹¹ The analysis of chemical stability in various pH's reveals that VSB-5 is dissolved in highly basic conditions (pH > 12) at 100–180 °C (data not shown).

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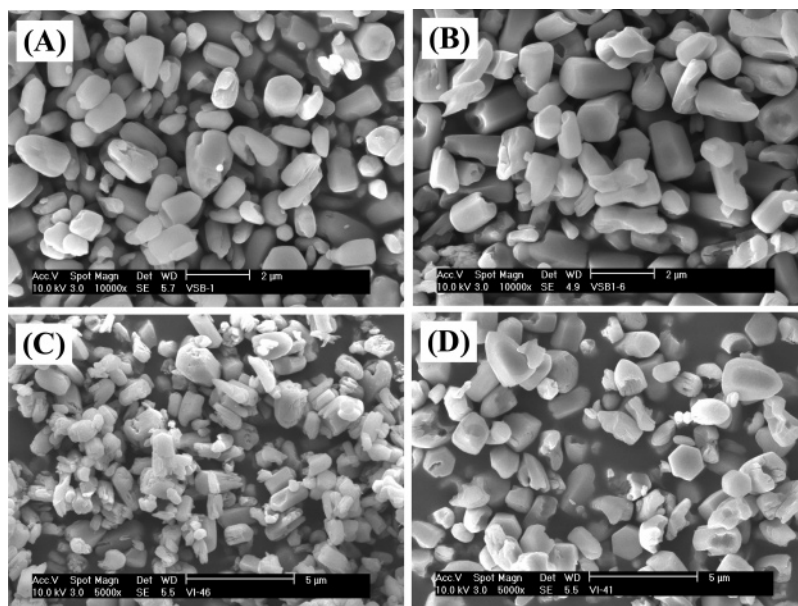


Figure 2. SEM images of as-synthesized VSB-1 molecular sieves according to a type of base: (a) sample A (TREN/Py), (b) sample B (aqueous ammonia), (c) sample C (KOH), and (d) sample D (TEA) of Table 1.

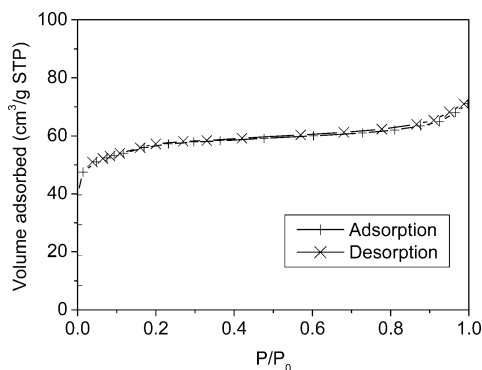


Figure 3. Nitrogen adsorption and desorption isotherms on a porous nickel phosphate, VSB-1, taken from Sample B of Table 1.

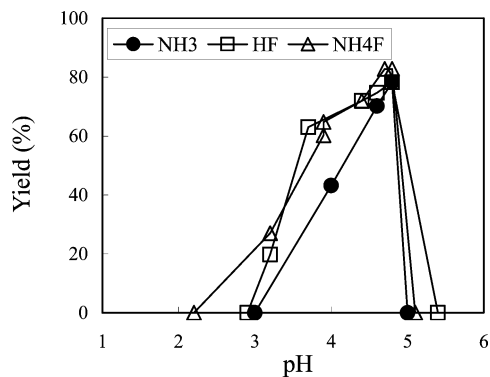


Figure 4. Crystallization yield of VSB-1 as a function of the pH adjusted using aqueous ammonia (composition: 1:1:1.5:*x*:100 Ni:P:HF:NH₃:H₂O), hydrofluoric acid (composition: 1:1:*x*:3:100 Ni:P:HF:NH₃:H₂O) and ammonium fluoride (composition: 1:1:*x*:100 Ni:P:NH₄F:H₂O), respectively.

When the pH is in the region that VSB-1 crystallizes, nickel and phosphorus species exist as Ni²⁺(H₂O)₆ and H₂PO₄⁻, respectively.^{21,22} As mentioned earlier, below this pH, the acidity is too high for the crystallization. If the pH

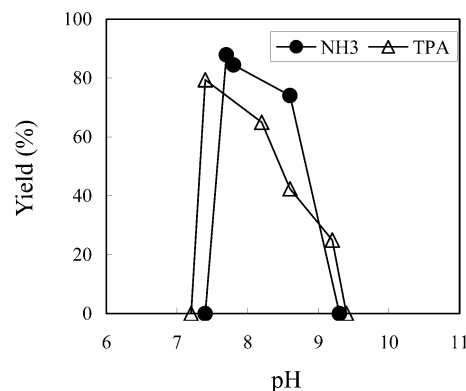


Figure 5. Crystallization yield of VSB-5 as a function of the pH adjusted using aqueous ammonia (composition: 1:0.63:*x*:100 Ni:P:NH₃:H₂O) and tri-*n*-propylamine (composition: 1:0.63:*x*:100 Ni:P:TPA:H₂O), respectively.

is higher than the region to derive VSB-1, nickel and phosphorus species exist as Ni₄(OH)₄⁴⁺ and H₂PO₄⁻ or HPO₄²⁻, respectively.^{21,22} Therefore, the monomeric nickel species may be helpful to the synthesis of VSB-1 that has a lower Ni/P ratio (Ni/P = 1.29)⁴ than that of VSB-5 (Ni/P = 1.67).⁷

When the pH of the reactant mixture is from 7.5 to 9.2, the pH suitable for the VSB-5 synthesis, the major nickel and phosphorus precursor species would be Ni₄(OH)₄⁴⁺ and HPO₄²⁻ (or partly PO₄³⁻), respectively.^{21,22} Therefore, it may be assumed that the oligomeric species Ni₄(OH)₄⁴⁺ plays an important role in the synthesis of VSB-5 as Ni–O–Ni bonds are known to exist in the framework of the VSB-5 molecular sieve.⁷ When the pH of the reaction mixture is above 9.2, it is expected that the major nickel and phosphorus precursor species would be Ni(OH)₃⁻ and PO₄³⁻ (or partly HPO₄²⁻), respectively.^{21,22} Therefore, dense nickel phosphate phases such as (NH₄)Ni(PO₄)(H₂O) and Ni₃(PO₄)₂(8H₂O) may be obtained via the interaction between these species (especially PO₄³⁻) as observed in the crystallization of the precursor gel containing aqueous ammonia and tri-*n*-propylamine, respectively.¹¹ In summary, the VSB-1 and VSB-5 can be

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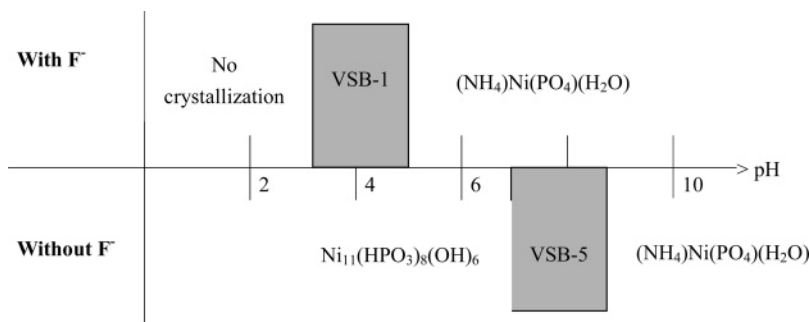


Figure 6. A phase diagram of nickel phosphates to be formed according to a variation of pH and the presence of fluoride anion.

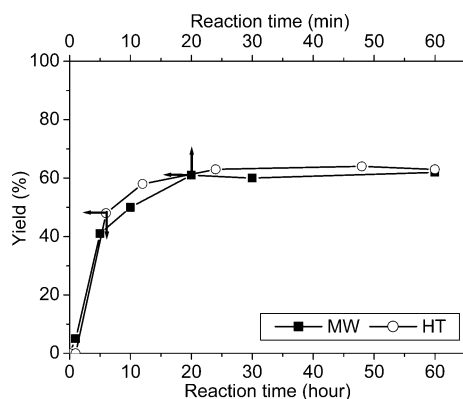


Figure 7. Crystallization yield of VSB-1 with crystallization time and synthesis method (MW: microwave synthesis; HT: conventional hydrothermal synthesis). The molar composition of a reactant mixture was 1:1:2.5:100 Ni:P:NH₄F:H₂O (pH = 4.0).

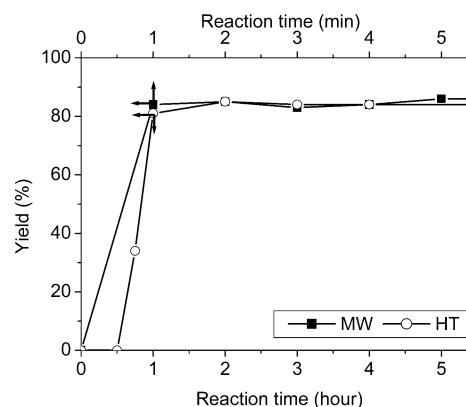


Figure 8. Crystallization yield of VSB-5 with crystallization time and synthesis method (MW: microwave synthesis; HT: conventional hydrothermal synthesis). The molar composition of the reactant mixture was 1:0.63:3:100 Ni:P:NH₃:H₂O (pH = 7.8).

obtained only in a limited pH range and the pH is one of the most important factors in the synthesis of the porous nickel phosphates. The fluoride anion is inevitable in the synthesis of the VSB-1 because fluorine atom is one of the constituents of the VSB-1 structure.⁴ In fact, a dense nickel phosphate compound, Ni₁₁(HPO₃)₈(OH)₆, is obtained in the absence of fluoride even in the acidic condition that VSB-1 can be formed (pH: 3.5–4.8). On the other hand, another dense nickel phosphate, (NH₄)Ni(PO₄)(H₂O), is obtained in the presence of fluoride even if the pH is between 7.5 and 9.2, which is suitable for the synthesis of VSB-5. Based on the results, the phase diagram for the synthesis of VSB-1 and VSB-5 is described in Figure 6.

Facile and Continuous Synthesis of VSB-1 and VSB-5. The crystallization kinetics of VSB-1 and VSB-5 molecular sieves has been checked at 180 °C, and the results are displayed in Figures 7 and 8. The synthesis of VSB-1 from the reactant mixture (1:1:2.5:100 Ni:P:NH₄F:H₂O, pH = 4.0) is completed within about 20 min and 20 h by using microwave heating and conventional electric heating, respectively. Similarly, the VSB-5 can be crystallized from the reactant mixture with the composition of 1:0.63:3:100 Ni:P:NH₃:H₂O (pH = 7.8) within about 1 min and 1 h with microwave heating and conventional electric heating, respectively. To our knowledge, porous metal phosphate materials have not been synthesized within a few minutes even with seeding. The crystallization times for the synthesis of VSB-1 and VSB-5 can be decreased by about 60 times by using microwave heating instead of conventional electric heating (Figures 7 and 8). The fast synthesis of porous materials by microwave heating has been reported quite often

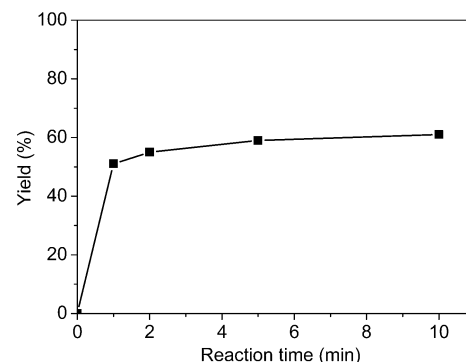


Figure 9. Crystallization yield of VSB-1 with a crystallization time at 190 °C under microwave irradiation. The molar composition of the reactant mixture was 1:1:2.5:100 Ni:P:NH₄F:H₂O (pH = 4.0).

and has been explained with the homogeneous heating or superheating.^{12,13,23} To decrease the crystallization time to minutes, the reaction of VSB-1 was executed at 190 °C using microwave irradiation, and the dependence of reaction yield with time is represented in Figure 9. The synthesis rate increases noticeably with increasing reaction temperature (compare Figures 7 and 9), and the VSB-1 is obtained also in 1 min at 190 °C similar to the fast synthesis of VSB-5 in 1 min at 180 °C.

The continuous synthesis of a porous material is very important in the viewpoint of applications and economics, and synthesis in minutes or less is a prerequisite for the continuous synthesis. Therefore, it can be expected that the VSB-1 and VSB-5 might be produced continuously by using

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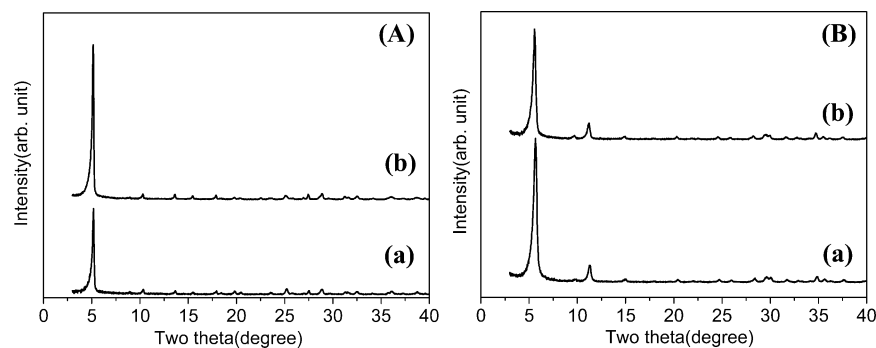


Figure 10. XRD patterns of porous nickel phosphates according to a synthesis method: (A) VSB-1 synthesized with (a) a continuous reactor (residence time: 3 min; temperature: 190 °C) and (b) a batch reactor (crystallization time: 2 h; temperature: 180 °C); (B) VSB-5 synthesized with (a) a continuous reactor (residence time: 3 min; temperature: 180 °C) and with (b) a batch reactor (crystallization time: 1 h; temperature: 180 °C).

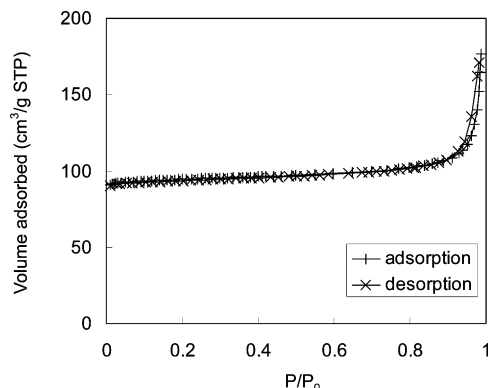


Figure 11. Nitrogen adsorption and desorption isotherms on a porous nickel phosphate; VSB-5 synthesized continuously under microwave irradiation at 180 °C.

microwave heating considering the rapid syntheses in 1 min. Continuous crystallization of nickel phosphates was carried out by using equipment consisting of a microwave oven, tubular reactor, slurry pump, temperature sensor, pressure sensor, etc. The reactant mixture was preheated to about 100 °C and fed to a tubular reactor made of Teflon in the chamber of a microwave oven. The reaction mixture was heated by microwave irradiation and the residence time was maintained to about 3 min.

As shown in Figure 10, the XRD patterns of VSB-1 and VSB-5 synthesized continuously do not show appreciable differences from those synthesized with a batch microwave reactor. The VSB-5 synthesized continuously shows the typical type I nitrogen adsorption and desorption isotherms (Figure 11) and the isotherms are very similar to those of VSB-5 synthesized using a batch reactor.²⁴ The adsorption and desorption isotherms of VSB-1 synthesized using the continuous reactor are very similar to those of Figure 3 (data not shown). Therefore, it can be demonstrated that the VSB-1 and VSB-5 can be produced continuously in a suitable

condition under the microwave irradiation using a tubular reactor. The continuous synthesis of nickel phosphates may be improved further by optimization of reaction parameters such as residence time, reactor volume, composition of reaction mixture, and temperature, and the results will be published elsewhere.

Conclusions

The present work for the synthesis of porous nickel phosphates demonstrates that they can be synthesized without any organic template molecules in contrast to the conventional synthesis of open-framework metal phosphates. The VSB-1 and VSB-5 are synthesized in limited pH ranges of 3.5–4.8 and 7.5–9.2, respectively, and the pH is one of the most important parameters for the synthesis. The reaction yield of VSB-1 increases with increasing pH, whereas the yield of VSB-5 decreases with increasing pH. Compared with conventional synthesis, microwave irradiation increases the crystallization rates of both VSB-1 and VSB-5 by about 60 times. When microwave irradiation is used, the crystallization of VSB-1 and VSB-5 can be completed in 1 min at 190 and 180 °C, respectively. Moreover, the continuous synthesis of the two nanoporous nickel phosphates is accomplished due to the fast crystallization under microwave irradiation.

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