Nanosized $AlPO_4$-5 Molecular Sieves and Ultrathin Films Prepared by Microwave Synthesis

Svetlana Mintova,[†] Shangyi Mo, and Thomas Bein*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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Nanosized $AlPO_4$-5 molecular sieves and submicron $AlPO_4$-5 films were synthesized by microwave treatment of aluminophosphate precursors. The effects of the chemical composition of the initial solution and the conditions of microwave treatment of aluminophosphate precursors on the synthesis of nanosized $AlPO_4$-5 molecular sieves were investigated. The syntheses were performed under hydrothermal conditions in a microwave oven at temperatures ranging from 90 to 160 °C, using various concentrations of H_2O and organic template and varying aging times. The resulting bulk products were analyzed using X-ray diffraction, scanning electron microscopy, thermogravimetry, dynamic light scattering, and nitrogen sorption. Optimal conditions for the preparation of nanosized molecular sieve crystals were found. Thin films of $AlPO_4$-5 on acoustic wave devices were also prepared, composed of a molecular coupling layer, $AlPO_4$-5 seed crystals, and a homogeneous porous film formed by microwave treatment of an aluminophosphate precursor. The initial mixture composition and microwave conditions affect the thickness and the orientation of the zeolite crystals in the films. Sorption isotherms for *n*-hexane and cyclohexane in these $AlPO_4$-5 films are reported.

Introduction

There is an increasing interest in ultrafine molecular sieve particles in view of their potential applications in catalysis and their use as precursors for thin film formation. Several different film deposition techniques developed in recent years[1−3] include conventional treatment of the zeolite precursors to produce dense and homogeneous crystalline films. The preparation of ultrathin zeolite films based on adsorption of seed layers and further hydrothermal treatment in zeolite precursor solutions was recently reported.[4−8]

During the last few years considerable attention has been focused on the zeotypic or microporous aluminophosphates ($AlPO_4$). These materials have neutral frameworks containing channels and cavities with diameters ranging from 4 to 12 Å, depending on the structure.[9] $AlPO_4$-5 (AFI) is composed of alternating AlO_4 and PO_4 tetrahedra, forming a framework with one-dimensional electrically neutral cylindrical channels of uniform cross section (7.3 Å) extended parallel to the long (*c*) axis of the crystals.

Although numerous procedures have been reported for the synthesis of $AlPO_4$-5 molecular sieves,[10−19] not many have been documented regarding the synthesis of nanosized $AlPO_4$-5. Hydrothermal synthesis of $AlPO_4$-5 molecular sieves in conventional ovens is typically performed from aluminophosphate gels containing organic templates at 150−200 °C and times ranging from several hours to several days. The influence of the concentration of organic template, the pH of the gel, and the crystallization temperature on the $AlPO_4$-5 molecular sieve formation was reported.[11−15] In a different approach, microwave treatment of the $ALPO_4$-5 gel was recently used for the preparation of

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* Author for correspondence. Fax: (765) 494 0239. E-mail: tbein@chem.purdue.edu.

[†] On leave from the Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, 92 Rakovski St., 1000 Sofia, Bulgaria.

(1) Bein, T. *Chem. Mater.* **1996**, *8*, 1636.

(2) Matsukata, M.; Kikuchi, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2341.

(3) Exter, den M. J.; Jansen, J. C.; van de Graaf, J. M.; Kapteijn, F.; Moulijn, J. A.; van Bekkum, H. *Stud. Surf. Sci. Catal.* **1996**, *102*, 413.

(4) Lovallo, M.; Tsapatsis, M. *Chem. Mater.* **1996**, *8*, 1579.

(5) Mintova, S.; Schoeman, B. J.; Valtchev, V.; Sterte, J.; Mo, S.; Bein, T. *Adv. Mater.* **1997**, *9*, 585.

(6) Mintova, S.; Valtchev, V.; Engstrom, V.; Schoeman, B. J.; Sterte, J. *Microporous Mater.* **1997**, *11*, 149.

(7) Lovallo, M.; Tsapatsis, M. *AIChE* **1996**, *42*, 320.

(8) Suzuki, H., U.S. Patent 4,699,892, 1987.

(9) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*, 4th ed.; Elsevier: New York, 1996.

(10) Wilson, S.; Lok, B., Messina, C.; Cannan, T.; Flanigen, E. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(11) Caro, J.; Finger, G.; Kornatowski, J.; Richter-Mendau, J.; Werner, L.; Zibrowius, B. *Adv. Mater.* **1992**, *4*, 273.

(12) Schnabel, K.; Finger, G.; Kornatowski, J.; Loffler, E.; Peuker C.; Pilz, W. *Microporous Mater.* **1997**, *11*, 293.

(13) Newalkar, B.; Kamath, B.; Jasra, R.; Bhat, S. *Zeolites* **1997**, *18*, 286.

(14) Prasad, S.; Liu, S. *Microporous Mater.* **1995**, *4*, 391.

(15) Caro, J.; Marlow, F.; Hoffmann, K.; Striebel, C.; Kornatowski, J.; Girnus, I.; Noack, M.; Kolsch, P. *Stud. Surf. Sci. Catal.***1997**, *105*, 2175.

(16) Caro, J.; Marlow, F.; Wubbenhorst, M. *Adv. Mater.* **1994**, *6*, 413.

(17) Werner, L.; Caro, J.; Finger, G.; Kornatowski, J. *Zeolites* **1992**, *12*, 658.

(18) Demuth, D.; Unger, K. K.; Schüth, F.; Stucky, G. D.; Srdanov, V. I. *Adv. Mater.* **1994**, *6*, 931.

(19) Mahrwald, R.; Lohse, U.; Girnus, I.; Caro J. *Zeolites* **1994**, *14*, 486.

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Table 1. Crystallization Conditions of $AlPO_4$-5 Molecular Sieves

no	$(TEA)_2O$	Al_2O_3	P_2O_5	H_2O	t_{aged} (h)	T_{cr} (°C)	t_{cr} (min)	power (W)	size[a] (nm)	product[b]
1	0.7	1.0	1.28	110		160	20	300	3000	$AlPO_4$-5
2	0.7	1.0	1.28	110		110	20	300		Am + $AlPO_4$-5
3	0.7	1.0	1.28	110	18	110	60	1000		Am + $AlPO_4$-5
4	0.7	1.0	1.28	110		110	60	1000		Am
5	0.7	1.0	1.28	110	18	60	20	300		boehmite
6	1.0	1.0	1.32	110	12	60	60	300		boehmite
7	1.0	1.0	1.32	110		90	60	1000	500	$AlPO_4$-5
8	1.0	1.0	1.32	110	18	90	60	1000	200	$AlPO_4$-5
9	1.0	1.0	1.32	110	18	110	3	1000	150	$AlPO_4$-5
10	1.0	1.0	1.32	110	18	110	3	300		$AlPO_4$-5 + Am
11	1.0	1.0	1.32	110	18	110	3	1000	80	$AlPO_4$-5
12	1.0	1.0	1.32	110	18	110	60	1000	100−600	$AlPO_4$-5
13	1.0	1.0	1.32	110	18	160	3	1000	600	$AlPO_4$-5

[a] Determined with dynamic light scattering. For some samples, crystal sizes were also obtained from SEM: No 9−150 nm, No 11−80 nm and No 12−100 nm. [b] Am, amorphous phase.

Table 2. Crystallization Conditions of $AlPO_4$-5 Molecular Sieves as a Function of Water Content

no.	$(TEA)_2O$	Al_2O_3	P_2O_5	H_2O	t_{aged} (h)	T_{cr} (°C)	t_{cr} (min)	power (W)	size[a] (nm)	product[b]
1	1.00	1.0	1.32	300	12	170	7	500	300	$AlPO_4$-5
2	1.00	1.0	1.32	600	12	170	7	500	1500	$AlPO_4$-5 + T
3	1.00	1.0	1.32	900	12	170	7	500	2000	T
4	1.00	1.0	1.32	50	12	170	7	500	100−600	$AlPO_4$-5
5	1.00	1.0	1.32	110	12	170	7	500	150−200	$AlPO_4$-5
6	1.00	1.0	1.32	600	12	110	7	500		Am
7	1.00	1.0	1.32	900	12	110	7	500		Am
8	1.00	1.0	1.32	110	12	150	7	1000	150	$AlPO_4$-5
9	1.00	1.0	1.32	110	12	150	6 h	oven	3−10 μm	$AlPO_4$-5
10	1.00	1.0	1.32	110	12	150	18 h	oven	10−20 μm	$AlPO_4$-5
11	1.00	1.0	1.32	110	12	110	18 h	oven		boehmite

[a] Determined with dynamic light scattering. For some samples, crystal sizes also were obtained from SEM: No 1−250 nm and No 8−150 nm. [b] T, tridymite; Am, amorphous phase

crystals with sizes of about 10−50 μm.[11,15,16] Large $AlPO_4$-5 crystals are of interest as host matrixes for organizing dye molecules in nonlinear optics applications, as photoluminescent materials, and as inert hosts for control of stereochemistry.[17−19] Using microwave heating for the synthesis of AFI and MFI type structures can drastically reduce the crystallization times, and in some cases the zeolite crystal size can be substantially decreased to 50 nm.[20,21] However, the preparation of aluminophosphate films using microwave treatment has not yet been published.

In this paper, we describe the microwave synthesis of nanosized $AlPO_4$-5 crystals and the preparation of thin films of $AlPO_4$-5 on gold substrates. The sorption of hydrocarbons in $ALPO_4$-5 films grown on the electrodes of quartz crystal microbalances (QCM) was also examined.

Experimental Section

$AlPO_4$-5 molecular sieves were synthesized using aluminum hydroxide oxide (AlOOH, 72% Al_2O_3, Vista Catapal D), orthophosphoric acid (H_3PO_4, 85%, Mallinckrodt, AR), tetraethylammonium hydroxide (TEAOH, 20%, Aldrich), and distilled water as reactants. The gel was prepared by (i) mixing the proper amounts of AlOOH, water, and orthophosphoric acid and stirring the mixture at room temperature for 1 h and (ii) adding TEAOH dropwise, followed by stirring for 4 h. The aluminophosphate precursor solution was aged for 12−18 h (t_{aged}) before microwave treatment. The crystallization was carried out in a QWave 3000 Questron microwave oven. After different treatment times, the bombs were cooled in water and the resulting zeolite crystals were purified by centrifugation at 13 000 rpm for 1 h in a Beckman J2−21M/E centrifuge. Some experiments were carried out in 25 mL PTFE-lined stainless steel autoclaves placed in a preheated conventional oven with forced air circulation. The size of the suspended particles was determined by dynamic light scattering (DLS) in a Coulter N4 Plus Submicron Particle Analyzer. Gel composition, microwave conditions, and resulting particle sizes are summarized in Tables 1 and 2.

$AlPO_4$-5 films were prepared on polished, gold-coated QCMs (Cold Springs R&D, Marcellus, NY; resonance frequency 10 MHz). Before film deposition, the QCMs were plasma cleaned (Opthos Instruments, 50 W, 3 Torr of air) for 20 min. A (3-mercaptopropyl)trimethoxysilane (MPS, FW = 196.3) coupling layer was self-assembled by immersing the QCMs into a 20 mM MPS solution in anhydrous ethanol for 1 h. The $AlPO_4$-5 seed crystals were chemically anchored via MPS by soaking the silane-modified QCMs in an $AlPO_4$-5 sol (6.5 wt % in water) for 1 h. After washing with distilled water, the substrates were calcined at 300 °C in flowing oxygen in order to decompose the MPS. For the hydrothermal treatment the QCM devices were mounted in two Teflon holders and immersed in the initial synthesis solution (Figure 1). The holders were used to prevent the deposition of molecular films on the QCM contacts. The temperature inside the Teflon bombs was controlled by a thermocouple immersed directly into a reference sample bomb. The amount of the initial solution, the size of the Teflon holders, and the QCM substrates in the two bombs were the same. The microwave synthesis conditions of the $AlPO_4$-5 films are shown in Table 3. The film-coated QCMs were heated in oxygen at 350 °C overnight prior to further characterization and sorption studies. The crystallinity of the bulk samples and the orientation of the molecular sieve films were monitored by X-ray diffraction, in $\theta-\theta$ geometry (Scintag XDS 2000, cooled Ge detector, Cu Kα radiation). Crystal morphology and zeolite film thicknesses were determined by SEM (Philips ElectroScan 3.2). The TGA measurements were performed with a 951 DuPont Instruments Analyzer, by placing approximately 17 mg of the sample

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(20) Fang, M.; Du, H.; Xu, W.; Meng, X.; Pang, W. *Microporous Mater.* **1997**, *9*, 59.

(21) Koegler, J.; Arafat, A.; van Bekkum, H.; Jansen, J. C. *Stud. Surf. Sci. Catal.* **1997**, *105*, 2163.

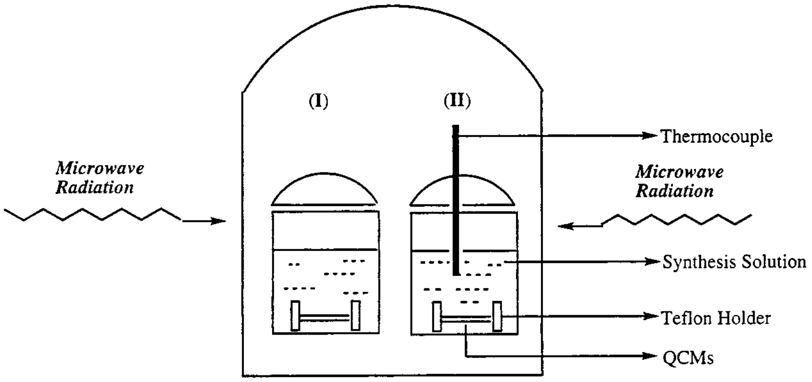

Figure 1. Experimental setup for microwave formation of $AlPO_4$-5 film.

Table 3. Conditions for the Crystallization of $AlPO_4$-5 Films on QCM Gold Electrodes[a]

no.	T (°C)	t_{cr} (min)	power (W)	thickness (SEM) (nm)
S1	110	1	1000	100
S2	110	5	1000	250
S3	90	10	500	150
S4	110	10	1000	200 + large crystals
S5	160	1	300	250
S6	150	7	500	500
S7	150	5	1000	250
S8	150	360	oven	3000

[a] The gel for sample 11 in Table 1 was used.

into a platinum holder on a balance and heating in flowing air with a temperature increment of 10 °C/min to 800 °C. Nitrogen sorption isotherms were obtained (Coulter Omnisorp 100), for confirmation of the zeolitic microporosity of the powder samples. Vapor sorption isotherms on the $AlPO_4$-5 films (at 23 °C) were measured with a computer-controlled gas flow system using an FTIR detector to measure concentrations.

Results and Discussion

Preparation of $AlPO_4$-5 Molecular Sieves. The results of the $AlPO_4$-5 crystallization using different initial solutions and conditions of hydrothermal crystallization in both microwave and conventional ovens are given in Tables 1 and 2. Most of the samples have X-ray diffraction patterns corresponding to the AFI type structure, similar to those published in the literature.[14,20] Microwave heating makes it possible to grow crystals or aggregates with sizes from 80 to 3000 nm by changing the crystallization temperature from 90 to 170 °C and the crystallization time from 3 to 60 min. When decreasing the temperature below 90 °C, no $AlPO_4$-5 crystalline phase was obtained and only peaks corresponding to the boehmite structure are present (samples 5 and 6, Table 1). Increasing the microwave power for heating the precursor solution (from 300 to 1000 W, 110 °C) leads to the formation of nanosized $AlPO_4$-5 crystals in several minutes (samples 10 and 11, Table 1). A relationship between crystallization temperature and crystal size was found, and crystalline materials with sizes of about 80 and 600 nm were obtained at 110 and 160 °C after 3 min (samples 11 and 13, Table 1). The $AlPO_4$-5 product of sample 11 shows almost spheroidal shape, while aggregates of spheroidal $AlPO_4$-5 crystals were obtained after long microwave treatment (sample 12, Table 1). It is necessary to heat the starting solution very quickly (at 1000 W within 20 s) to the crystallization temperature in order to synthesize pure $AlPO_4$-5 (samples 7–9 and 11–13). When the starting solution is heated slowly (in sample 10), the presence of an amorphous phase indicates incomplete conversion, presumably due to slower nucleation and crystallization rates. It should be noted that in the case of long crystallization times, larger crystals precipitate from the solution to the bottom of the bomb, while smaller crystals are still suspended (sample 12, Table 1).

The aging and stirring times are also very important factors in determining the crystal size of $AlPO_4$-5. The size of the crystals in sample 8 is much smaller than in sample 7 (not aged). Increasing the aging time leads to the formation of smaller crystals than those obtained after only 4 h of stirring ($t_{aged} = 0$; see Experimental Part), probably because more nucleation centers are created by aging the gel (sample 8). A similar trend was observed during the synthesis of $AlPO_4$-5 crystals at other temperatures. In sample 3, both $AlPO_4$-5 crystals and amorphous phase were obtained, in contrast to sample 4, where only amorphous material is present. The only one difference between those two samples is the aging time, which confirms the importance of aging on the crystallization of molecular sieves.

The $(TEA)_2O/Al_2O_3$ ratio also plays an important role in the crystallization, as shown in Table 1. With low crystallization temperatures below 160 °C did not show conversion to pure $AlPO_4$-5 (samples 2–5, Table 1). The low concentration of organic template could be compensated with a high temperature of crystallization in order to obtain crystalline $AlPO_4$-5 materials (sample 1, Table 1).

The effect of the water content in the initial solution on the $AlPO_4$-5 formation was investigated by comparing the results obtained for samples 1–5 in Table 2. It should be mentioned that for those samples, the temperature of crystallization was 170 °C and the time of crystallization was 7 min, because at 110 °C only amorphous phase is present (samples 6 and 7, Table 2). When the initial reaction mixture is very dilute, not many nucleation sites are present, and $T_{cr} = 110$ °C is not high enough to achieve significant crystallization. Diluting the reaction mixture beyond $H_2O/Al_2O_3 = 300$ leads to the formation of large spheroidal particles as well as the formation of tridymite (samples 2 and 3, Table 2). In Figure 2, the diffraction peaks of the tridymite are present, as well as those for $AlPO_4$-5. Lower H_2O/Al_2O_3 ratios between 50 and 300 produced uniformly crystalline $AlPO_4$-5 samples. In sample 4

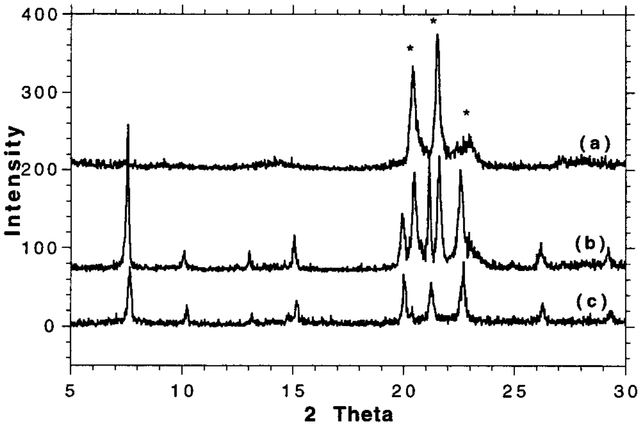

Figure 2. XRD patterns of bulk AlPO$_4$-5 molecular sieves obtained in a microwave oven with a H_2O/Al_2O_3 ratio of (a) 900 (sample 3, Table 2), (b) 600 (sample 2, Table 2), and (c) 50 (sample 4, Table 2). The asterisk denotes tridymite

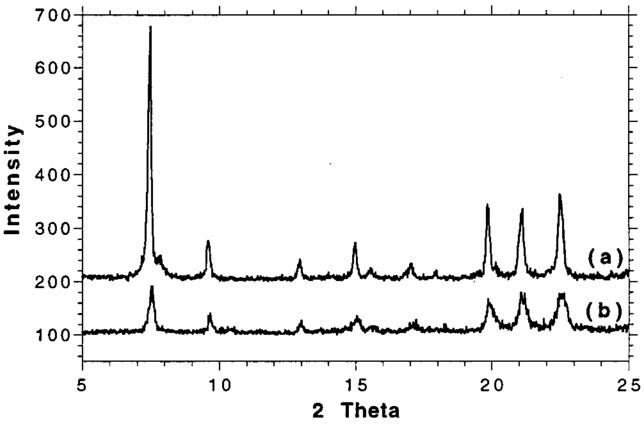

Figure 3. XRD patterns of bulk AlPO$_4$-5 molecular sieve obtained by heating at 150 °C (samples 9 and 8, Table 2, respectively) in (a) a conventional oven for 6 h (9) and (b) a microwave oven for 7 min (8). Important AFI reflections occur at (100) 7.4°, (110) 12.9°, (200) 14.8°, (210) 19.8°, (002) 21.0°, and (102) 22.2°.

(lowest water content) crystals with different sizes were produced.

Sample 9 (Table 2), with the same initial mixture and aging time as sample 8, was heated in a conventional oven at 150 °C for 6 h. The XRD pattern of sample 9 (Figure 3a) is similar to that of sample 8 (Figure 3b), except for broadening of the diffraction lines of samples obtained in the microwave oven, attributed to the small size of the latter. Dynamic light scattering measurements show that sample 8 consists of fine particles with sizes of about 150 nm (Table 2), whereas crystals in samples 9 and 10 have sizes ranging from 3 to 20 μm. We note that aggregation can affect the apparent particle size obtained with dynamic light scattering. However, the size of the crystals in some samples (<300 nm) was confirmed by SEM. When decreasing the temperature of crystallization to 110 °C in the conventional oven with the same initial mixture, only boehmite was obtained (sample 11). The initial mixture used for sample 1 (Table 2) was also hydrothermally treated in a conventional oven, and a mixture of AlPO$_4$-5 and amorphous materials was obtained. These results show that the preparation of pure AlPO$_4$-5 by microwave heating is possible in a broader reagent composition range compared to conventional hydrothermal treatment. Electron micrographs of the products show that the AlPO$_4$-5 crystals obtained in the conventional oven were well-shaped hexagonal prisms up to 20 μm in length.

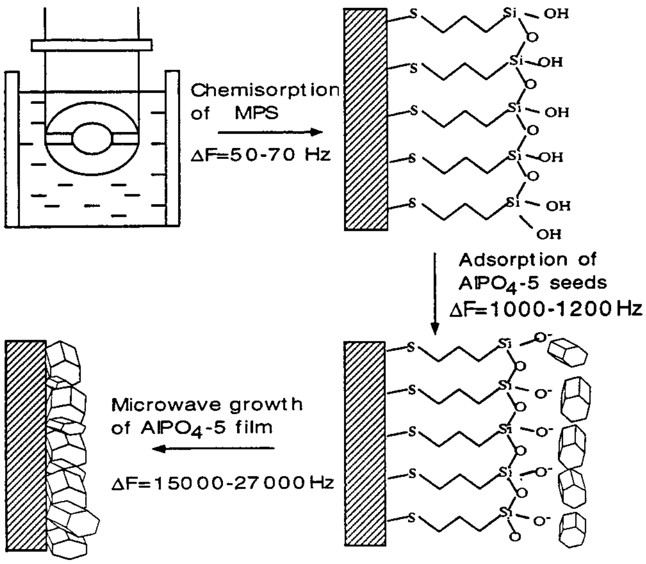

Figure 4. Sequence of the AlPO$_4$-5 film formation: (a) chemisorption of MPS, (b) attachment of AlPO$_4$-5 seed crystals, and (c) microwave formation of AlPO$_4$-5 film. A frequency shift of 1 Hz corresponds to a mass change of 2.2 ng/cm^2.

Thermogravimetric analysis of the uncalcined AlPO$_4$-5 samples was performed. The total weight loss on heating to 800 °C is around 15%, which indicates that water and templates are desorbed from the pores of the molecular sieve. Assuming that desorption of H_2O is complete at the first inflection point at 150 °C and that desorption/combustion of occluded amine in the channel system is complete at 360 °C, the amount of water and amine present is about 4 and 11% respectively, which is comperable with AlPO$_4$-5 synthesized from gels.[13] These data were used to find the minimal calcination temperature for AlPO$_4$-5 films.

The nitrogen adsorption isotherms of the AlPO$_4$-5 samples show the typical shapes, which confirms the zeolitic microporosity of the crystals, and reveal a pore volume of 0.14 mL/g (e.g., sample 11, Table 1), similar to results presented in ref 22.

Preparation of AlPO$_4$-5 Films on QCMs. Figure 4 shows the sequential modification of the QCMs by (3-mercaptopropyl)trimethoxysilane (MPS), AlPO$_4$-5 seed crystals, and the subsequent microwave synthesis of the AlPO$_4$-5 film, as well as the QCM frequency shifts (ΔF) observed after each step. The frequency shifts of the QCMs are proportional to the mass changes on the electrodes. A shift of 1 Hz corresponds to a 2.2 ng/cm^2 mass change. The QCM data for the chemisorption of MPS correspond to a surface loading of 110−154 ng/cm^2 or 3.4−4.7 molecules/nm^2. The loading is close to that expected for a monolayer.[23] Bare QCMs immersed into an initial aluminophosphate mixture and treated in a microwave oven for 1−10 min showed no frequency changes. No aluminophosphate films were formed on

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(22) Chaudhary, V.; Akolekar, D.; Singh, A.; Sansare, S. *J. Catal.* **1988**, *111*, 23.

(23) Kurth, D. G.; Bein, T. *Langmuir* **1993**, *9*, 2965.

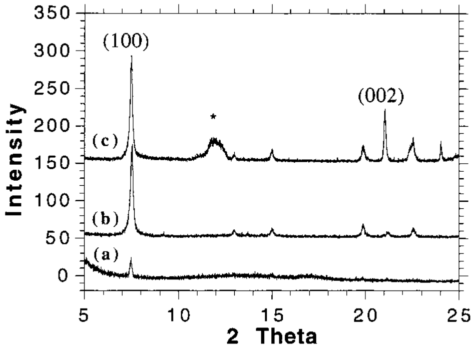

Figure 5. XRD patterns of (a) adsorbed crystals of $AlPO_4$-5 on a QCM electrode, (b) $AlPO_4$-5 molecular sieve film with a thickness of 100 nm (S1), and (c) an $AlPO_4$-5 molecular sieve film with a thickness of 250 nm (S2). Important AFI reflections occur at: (100) 7.4°, (200) 14.8°, (210) 19.8°, (002) 21.0°, (102) 22.2° and (112) 24.7°. * Plasic XRD holder.

QCMs with only an MPS layer (without adsorbed $AlPO_4$-5 seeds), as indicated by the constant frequency. According to the frequency changes of the QCMs after each step presented in Figure 4, the amount of deposited $AlPO_4$-5 seed crystals is about 2.4 μg/cm^2. After hydrothermal treatment, the amount is between 33 and 59 μg/cm^2, depending on the film thickness.

Table 3 presents the results of film preparation experiments in which the conditions were varied. Molecular sieve films with thicknesses ranging from 100 to 3000 nm were obtained using different initial mixtures as well as different conditions of hydrothermal treatment in microwave and conventional ovens. In all cases the crystals form a rather continuous film. Increasing the synthesis time from 1 to 5 min (samples S1−S2) results in the formation of a secondary layer with larger crystals.

The XRD patterns of $AlPO_4$-5 films S1 and S2 (Table 3) are shown in Figure 5. In the diffractogram recorded for the adsorbed $AlPO_4$-5 crystals (Figure 5a) the (100) peak is detected at $2\theta = 7.4°$, in addition to small features around 15° and 20° 2θ. In the case of the 100 nm thick film obtained after 1 min. (Figure 5b), the most intense peak is observed at 7.43° 2θ and a peak of very low intensity corresponding to *hkl* 002 confirms the preferred orientation of the *c*-axis parallel to the substrate. The diffractogram of the 250 nm $AlPO_4$-5 film (Figure 5c) reveals drastic enhancement of the 002 peak (21.0° 2θ) such that it becomes similar in intensity to that of the 100 peak (7.4° 2θ). This result confirms the preferential orientation of the initially grown 100 nm film, corresponding to the orientation of the seed crystals. When the film growth proceeds further, loss of orientation is observed, probably due to secondary nucleation. These observations are similar to those for silicalite-1 films prepared by the seed method.[6]

Very thick but homogeneous $AlPO_4$-5 films were synthesized after 6 h at 150 °C in a conventional oven (sample S8). The XRD patterns of $AlPO_4$-5 films grown on QCMs in (a) a conventional oven for 6 h and (b) in a microwave oven for 5 min (S7) are depicted in Figure 6. The XRD patterns obtained for the films are similar to those for $AlPO_4$-5 powder samples and demonstrate the deposition of pure $AlPO_4$-5 phase in the film (Figure 3). It is apparent that the microwave preparation results in crystals that are aligned along their *c*-axes parallel to the substrate, while heating in the conventional oven leads to nonoriented films. The conventional hydrothermal treatment leads to the growth of big isolated crystals that can only form dense films at much greater thickness (sample S8).

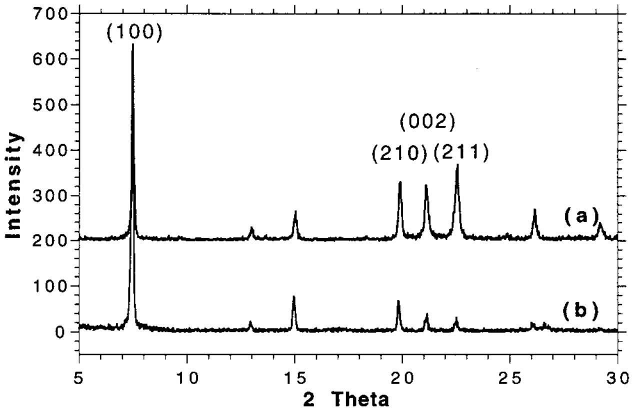

Figure 6. XRD patterns of $AlPO_4$-5 film grown on a QCM electrode in (a) a conventional oven for 6 h (sample S8, at 150 °C) and (b) a microwave oven for 5 min (sample S7, at 150 °C). The intensity of the (100) reflection of the latter sample S7 extends to 650.

Scanning electron microscopy (SEM) was performed to study the changes in the film thickness and morphology as a function of microwave treatment conditions for the QCMs. To obtain a thin and homogeneous film it is necessary to minimize the size of the crystals. Therefore, the formation of zeolite films was carried out at low temperatures (90−110 °C) with short crystallization times. The rate of heating was very high such that the temperature of crystallization was reached in about 20 s. Under these conditions, nucleation and crystal growth occurred in solution together with surface growth, and nanosized crystals covered the entire QCM surface. It was found that the homogeneity is best when the heating rate is maximized.

SEM photographs of $AlPO_4$-5 films obtained for samples S1−S4 show different morphologies, depending on the treatment conditions (Figure 7). The top view of a film formed after 1 min of microwave treatment shows a surface completely covered by $AlPO_4$-5 crystals with sizes of about 80 nm (Figure 7a). The morphology of the film formed after 5 min of crystallization is similar, but the crystals have reached a size of about 100 nm and an incomplete second layer was obtained (Figure 7b). In the case of the syntheses at lower temperatures (sample S3), the zeolite films consist of very small crystals (Figure 7c) and the roughness of the films is higher than that in sample S1. A micrograph of the sample obtained after 10 min at 110 °C is shown in Figure 7d (sample S4). This increased crystallization time results in complete monolayer coverage and in the formation of large crystals (about 2 μm) on top of the first layer. Some of these crystals are more strongly attached to the first molecular sieve film than others. Samples exposed to ultrasonic treatment in both water and acetone lose some of the crystals, but the basic film is very stable.

The results obtained demonstrate that the thickness and morphology of the zeolite films can be controlled by varying the temperature and time of microwave

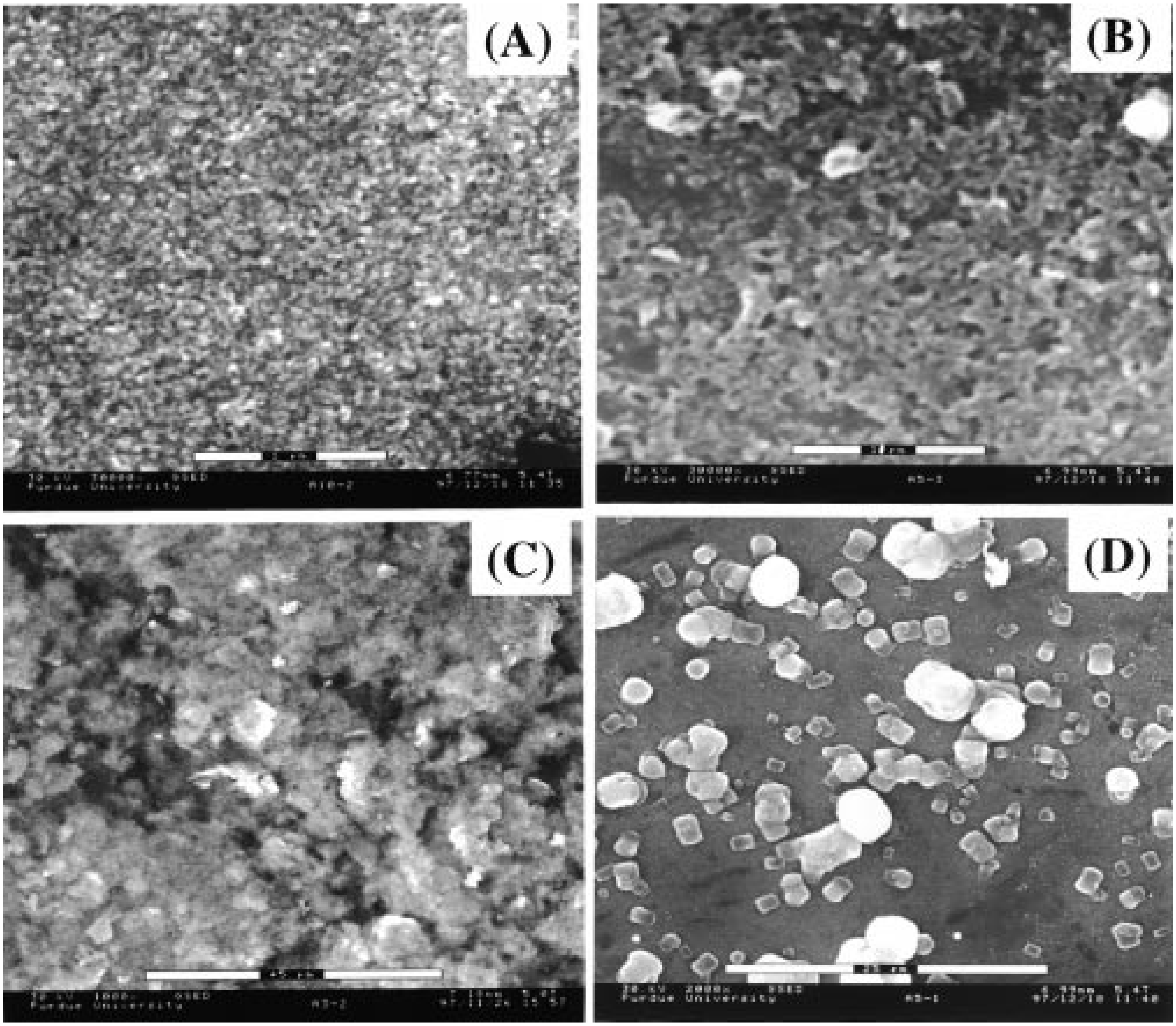

Figure 7. Scanning electron micrographs of AlPO$_4$-5 films on gold of (a) sample S1, (b) sample S2, (c) sample S3, and (d) sample S4. Samples are described in Table 3.

treatment, the heating power, and the time of aging of the zeolite precursor solution.

Sorption of Hydrocarbons in the AlPO$_4$-5 Films. The QCMs covered with AlPO$_4$-5 films were prepared for sorption studies by heating at 350 °C under oxygen flow for 12 h, followed by plasma-cleaning immediately before mounting in the sensor cell. Vapors of hexane and cyclohexane in nitrogen were carried to the sensor cell using a computer-controlled flow and data acquisition system. The response of the sensors is illustrated by the sorption of hexane and cyclohexane vapors (Figure 8). The kinetic diameters of *n*-hexane and cyclohexane are 4.9 and 6.7 Å respectively; hence they can enter the channel system of the AlPO$_4$-5 film (7.3 Å diameter).[22] The equilibration with hexane occurs within 40 min, while cyclohexane equilibration requires about 60 min per concentration point. These results are attributed to the different diffusivities of these organic molecules in the AlPO$_4$-5 film. At $p/p_o = 4 \times 10^{-4}$, the uptake into the film was ~0.03 (g/g) for cyclohexane and ~0.045 (g/g) for *n*-hexane. The sorption capacity for hexane is somewhat higher than that for cyclohexane, due to differences in molecular size and shape and

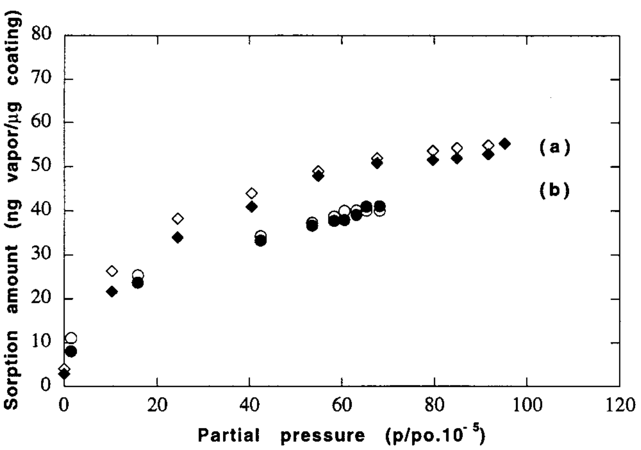

Figure 8. Sorption isotherms for (a) *n*-hexane and (b) cyclohexane on an AlPO$_4$-5 film grown on a QCM device (Film S1): Filled symbols, adsorption; open symbols, desorption.

packing efficiency in the $AlPO_4$-5 channels. The sorption isotherms depicted in Figure 8 show that the sorption is essentially reversible.

Conclusions

The use of microwave heating leads to improved control of both the synthesis of nanosized molecular sieve crystals and the preparation of very thin aluminophosphate films. The results show that the morphology, orientation, and size of the $AlPO_4$-5 crystals can be controlled by varying the temperature, water content, amount of organic template, and the conditions of hydrothermal treatment.

Microwave treatment of aluminophosphate precursors is a superior technique for the preparation of thin zeolite films, requiring only very short crystallization times. Adsorbed seed crystals on modified QCMs and controlled microwave treatment of the initial synthesis gels can lead to homogeneous film growth. The resulting films were shown to have microporosity.

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