Microwave assisted phase transformation of silicoaluminophosphate zeolite crystals

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1. Gel Synthesis

Aluminum isopropoxide (>99.99% metal basis, Aldrich), phosphoric acid (85 wt % aqueous solution, Sigma-Aldrich), and Ludox (40 wt % in suspension, Sigma-Aldrich) were used as the inorganic precursors. Tetraethylammonium hydroxide (35 wt %, Sigma-Aldrich) and dipropylamine (99 wt %, Aldrich) were used as the primary and secondary templates, respectively. Aluminum isopropoxide, phosphoric acid, and water were mixed and stirred for about 2 h. Then, Ludox was added and stirred for another 2 h to form an homogeneous solution. The primary and secondary templates were added to the homogeneous solution. The resulting gel was aged for 3 days while stirring at 50 °C. The gel was transferred to a glass tube and MW heating for different times was carried out with continuous stirring in a computer controlled MW oven (Mars 5, CEM corp.) at 150^{o}C and 250 psi. After cooling, the product was separated using centrifugation and dried overnight at 60^{o}C. The dried samples were calcined at 550^{o}C for 5 h with heating and cooling rates of 1^{o}C/min to remove the organic templates.

2. Characterization

The crystalline structure of the resultant phases was studied using XRD (Bruker D8 Discover). Particle size and morphology of the samples were determined using FE-SEM (FEI Nova 600). The ICP analysis was carried out on an Applied Research Laboratories ARL3410+ ICP-OES and CHN analysis was done on 440 CHN/O/S analyzer. TEM

images were collected on a Technai F20 FEI TEM. The surface area and adsorption isotherms of CO_2, CH_4 gases of the samples were obtained using Micromeritics Tristar-3000 porosimeter after degassing the samples at 300^oC for 180 min. BX FTIR (Perkin-Elmer) was used to determine the lattice vibrations in the SAPO framework.

3. Calculation of % relative amounts of silicoaluminophosphates

The SAPO-5 to SAPO-34 phase transition was followed by determining the relative amounts of SAPO phases by using XRD patterns as shown in Figure S1. Results are summarized in Table S1. The most prominent peak for SAPO-5 is present at 2θ ~7.4^o and for SAPO-34 is present at 2θ ~9.9^o. The area under the curve for these two peaks was quantified using origin software, after baseline correction, to determine the relative amounts of SAPO-34. The SAPO-34 relative amounts were calculated using the ratio of the area under the curve for the 2θ ~9.9^o reflection over the total area (2θ ~7.4^o + 2θ ~9.9^o). Example: For B: % SAPO-34 relative amount is (103/(103 + 319))x100 = ~ 24%.

Table S1: Relative amounts of silicoaluminophosphate phases as a function of microwave synthesis time

Sample ID	**microwave synthesis time (min)**	**Area under the Curve**		**SAPO-34 relative amount (%)**
		2θ ~7.4^o (1 0 0)	**2θ ~9.9^o (1 1 0)**	
A	30	327	0	0
B	60	319	103	24
C	120	439	235	35
D	300	208	265	56
E	420	112	491	81
F	500	0	677	100

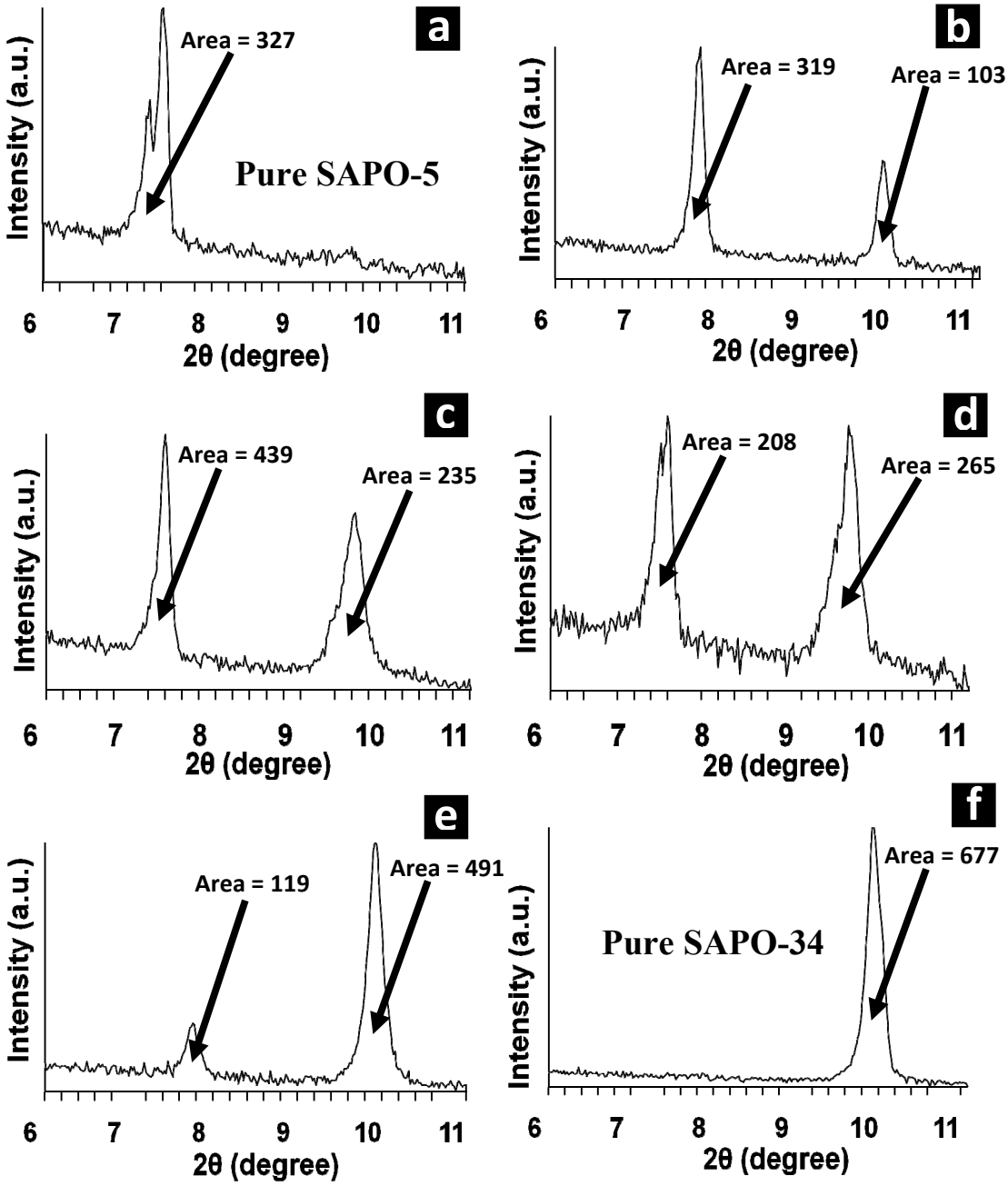

Figure S1: Calculation of the area under the most prominent XRD peaks of SAPO-5 and SAPO-34 synthesized using microwave assisted approach after a) 30; b) 60; c) 120; d) 300; e) 420; and f) 500 min.

4. Phase change observed by TEM

The crystal morphology and size observed using TEM are in agreement the SEM images and confirmed that SAPO-5 is transformed to SAPO-34 (Figure S2).

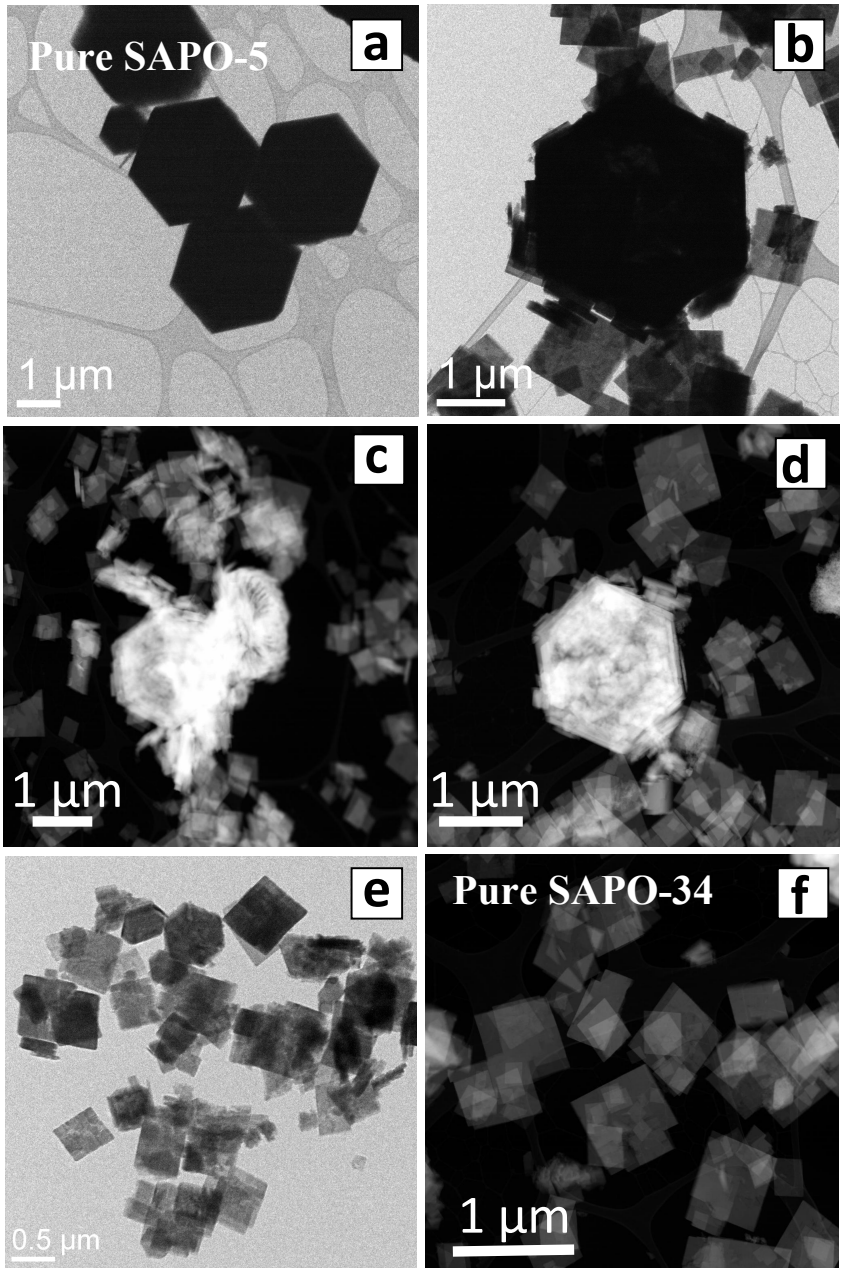

Figure S2: TEM images of the silicoaluminophosphate phases synthesized using microwave assisted approach after a) 30; b) 60; c) 120; d) 300; e) 420; and f) 500 min.

5. FTIR analysis of SAPO phases:

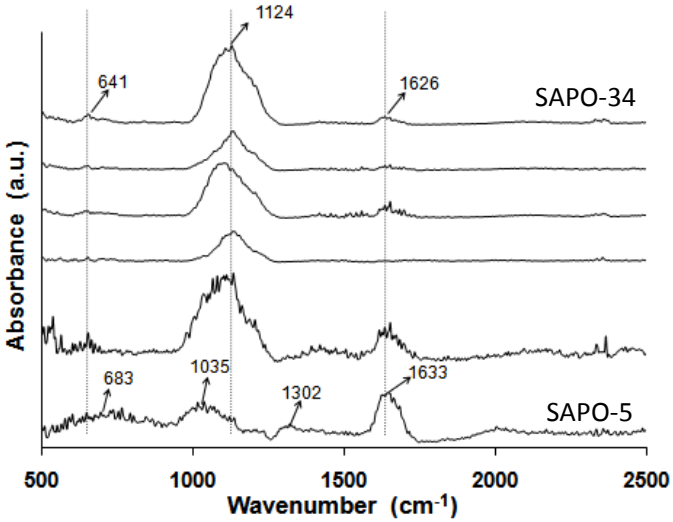

Figure S3: FTIR spectra of the silico-aluminophosphate samples

Figure S3 shows the FTIR spectra of the samples synthesized for different times. The lattice vibrations of SAPO-5 are 683, 1035, 1302, and 1633 cm^{-1} , which are in well agreement with previous reports [1] and clearly shifted to typical lattice vibrations of SAPO-34 at 641, 1124 and 1626 cm^{-1},[2] with increased times. The peak around 650 is assigned to the vibration of double-6 rings and the bending of T-O tetrahedra. The main peak which is present around 1100 is due to the asymmetric stretching of T-O tetrahedra. The peak around 1630 and 1300 are more intense in SAPO-5 due to the presence of remained templated and adsorbed water even after calcination, which are typical for SAPO-5 [1c] and they are almost disappeared in SAPO-34. The frequency of the peak around 1100 shifts slightly because of the differences in bond lengths and angles of highly strained and not yet thoroughly cross-linked unstable SAPO-5 lattices compared to the stable lattices of SAPO-34 [1b]. The FTIR spectra of the SAPO-34 and SAPO-5 clearly showed that structure changes have taken place during the phase transformation.

[1] a) G. Ciobanu, G. Carja, O. Ciobanu, *Microporous Mesoporous Mater.* 2008, **115**, 61; b) M. Briend, M.J. Peltre, P. Massaiani, P.P. Man, Vomscheid, M. Derewinski, D. Barthomeuf, *stud. Surf. Sci. Catal.* 1994, **84**, 613; c) T.G. Tsai, H.C. Shih, S.J. Liao, K.J. Chao, *Microporous Mesoporous Mater.* 1998, **22**, 333

[2] D.B. Akolekar,S. Bhargava, W. V. Bronswijk, *Appl. Spectroscopy,* 1999, **53**, 931; b) G. Liu, P. Tian, Y. Zhang, J. Li, L. Xu, S. Meng, Z.Liu, *Microporous Mesoporous Mater.* 2008, **114**, 416; c) J. Tan, Z. Liu, X. Bao, X, Liu, X. Han, C. He, R. Zhai, *Microporous Mesoporous Mater.* 2002, **53**, 97.

6. Effect of crystal size on CO_2/CH_4 adsorption capacity

The effect of crystal size of SAPO-34 phase on CO_2/CH_4 adsorption capacities is shown in Figure S4. The CO_2/CH_4 adsorption ratios were calculated at 100 KPa. As the crystal size decreases, the CO_2/CH_4 adsorption ratio increased significantly.

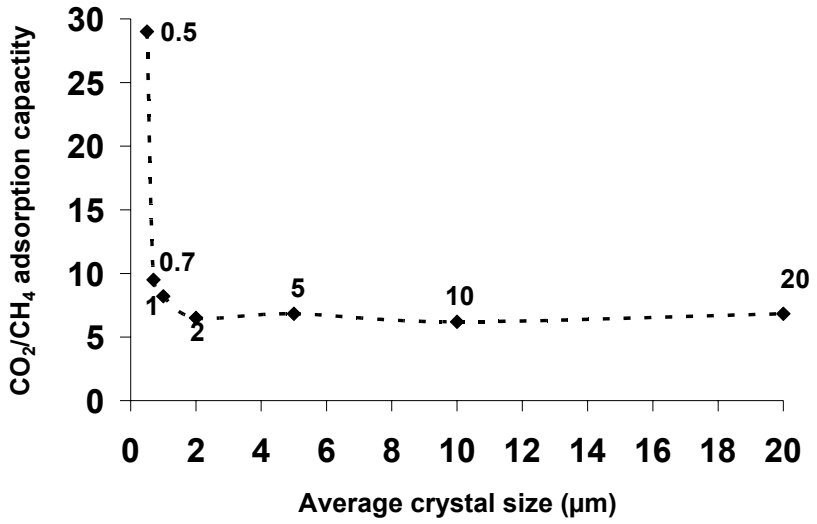

Figure S4: Effect of crystal size of SAPO-34 on CO_2/CH_4 adsorption capacity

Note: Samples with crystal size of ~0.7μm and larger were prepared by conventional hydrothermal synthesis method.

7. CHN analysis

The carbon, hydrogen and nitrogen content of silicoaluminophosphate phases were quantified using 440 CHN/O/S analyzer. The results are presented in Table S2.

Table S2: CHN analysis of SAPO phases as a function of microwave synthesis time

Sample ID	synthesis time (min)	Amounts in mg/ 30mg of sample		
		Carbon	Hydrogen	Nitrogen
A	30	0.02	2.02	0.00
B	60	0.04	1.90	0.01
C	120	0.03	1.64	0.00
D	300	0.04	1.79	0.00
E	420	0.04	1.92	0.01
F	500	0.05	1.27	0.00