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COMPARATIVE STUDY OF DIPROPYLAMINE-DIRECTED SYNTHESIS OF SAPO MOLECULAR SIEVES

R. SZOSTAK, T.L. THOMAS and D.C. SHIEH

Zeolite Research Program, Georgia Tech. Research Institute, Georgia Institute of Technology, Atlanta, Ga 30332, U.S.A.

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The crystallization of the silicoaluminophosphate MCM-9 occurs successfully under a very narrow range of composition and exhibits a strong sensitivity to the amount of dipropylamine used as a crystal directing agent in this system. The presence of a structural mixture in this system is confirmed through comparison of X-ray diffraction patterns with those of VPI-5 and SAPO-11.

1. Introduction

The introduction of silicon into the structural aluminophosphate framework offers the opportunity to inject potential acid functionality into the neutral $AlPO_4$ framework. Initial reports of successful incorporation by Lok et al. in 1984 of quantities of silicon [1,2] into the framework through direct addition of silicon containing compounds to the aluminophosphate gel were followed by other reports of a modified synthesis procedure by Derouane and von Ballmoos [3,4]. A two phase system, hexanol + water, was observed to act as a vehicle to introduce silicon into the structure. In both cases the introduction of silicon as a component of the starting material was observed to result in the crystallization of new microporous zeolite-like phases.

2. Crystallization studies of MCM-9 and SAPO-11

We have observed in the course of our studies of the synthesis of the recently reported silicoaluminophosphate molecular sieve, MCM-9 [4], that the formation of the material, as identified from the reported X-ray powder diffraction pattern [4], exhibited a strong sensitivity to the concentration of the organic additive used to direct crystallization of this structure. From a component variable study of this two phase crystallization system (see table 1), using dipropylamine as the crystal directing agent, it was observed that the production of the desired MCM-9

Table 1
Parameter study in the Si : Al : P system with dipropylamine (DPA) as a template.

P_2O_5 / Al_2O_3	SiO_2 / Al_2O_3	H^+ / Al_2O_3	H_2O / Al_2O_3	$C_6H_{11}OH$ / Al_2O_3	DPA / Al_2O_3	Phase produced
1	0.36	10.44	20.7	3.7	0	dense phase
1	0.36	3.25	20.7	3.7	0	dense phase
1	0.36	−3.95	20.7	3.7	0	dense phase
1	0.36	−11.14	20.7	3.7	0	dense phase
1	0.36	−17.17	20.7	3.7	0	dense phase
1	0.36	10.14	20.7	3.7	0.74	MCM-9
1	0.36	3.25	20.7	3.7	0.74	amorphous
1	0.36	−3.95	20.7	3.7	0.74	dense phase
1	0.36	−11.14	20.7	3.7	0.74	unknown #
1	0.36	−17.17	20.7	3.7	0.74	unknown #
1	0.36	10.14	20.7	3.7	1.48	SAPO-11
1	0.36	3.25	20.7	3.7	1.48	amorphous
1	0.36	−3.95	20.7	3.7	1.48	unknown #
1	0.36	−11.14	20.7	3.7	1.48	unknown #
1	0.36	−17.17	20.7	3.7	1.48	dense phase
*1	0.36	10.14	20.7	3.7	1.48	amorphous
*1	0.36	3.25	20.7	3.7	1.48	amorphous
*1	0.36	−3.95	20.7	3.7	1.48	amorphous
*1	0.36	−11.14	20.7	3.7	1.48	dense phase
*1	0.36	−17.17	20.7	3.7	1.48	dense phase
1	0	3.0	20.7	0	0.74	$AlPO_4$-11
1	0	0.95	20.7	0	0.74	layer + dense #
1	0	0.03	20.7	0	0.74	layer phase
1	0	−3.53	20.7	0	0.74	amorphous
1	0	−11.41	20.7	0	0.74	amorphous
1	0	−19.39	20.7	0	0.74	amorphous

* Aged at room temperature for 24 hours.
# attributed to the aluminophosphate H3 [7].
Al source: Catapal
P source: H_3PO_4
Si source: $Si(OC_2H_5)_4$
Temperature: 200 °C
Time: 3 days

structure was sensitive to the concentration of the organic amine in the starting mixture. In a system devoid of the dipropylamine, only dense phase material is observed to form. Upon addition of the amine at a ratio of 0.74 relative to the alumina present, the desired MCM-9 is formed. Doubling of the organic additive results in the loss of many peaks in the X-ray diffraction pattern observed for the MCM-9 material. The remaining very intense peaks can, however, be successfully matched to the SAPO-11 X-ray pattern, which is also known to crystallize in the presence of the dipropylamine [2]. Without the presence of the silicon containing

second phase, the related $AlPO_4$-11 structure, as identified from its X-ray powder diffraction pattern, is formed. The diffraction peaks observed in the X-ray pattern of MCM-9, which disappeared when the dipropylamine concentration was doubled, can be identified as another aluminophosphate phase, the silicon

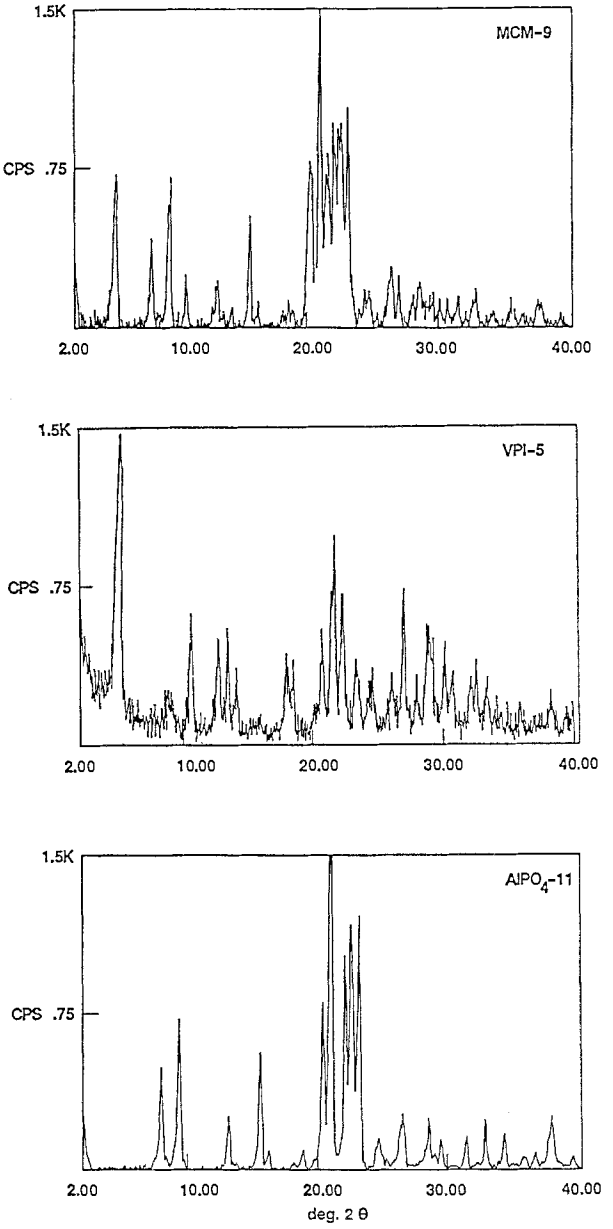

Fig. 1. X-ray powder diffraction patterns of MCM-9 (top); VPI-5 (middle) and $AlPO_4$-11 (bottom) showing the similarities in the X-ray peak positions.

Table 2
Comparison of the X-ray powder diffraction patterns of VPI-5, MCM-9 and SAPO-11 [1,4,6].

VPI-5		MCM-9		SAPO-11	
d(A)	I/I_0	d(A)	I/I_0	d(A)	I/I_0
16.43	100	16.41	vs		
		10.84	w	10.98	20
9.49	2	9.33	w	9.41	36
8.23	14	8.20	m		
		6.68	w	6.76	13
6.21	6	6.17	w		
		5.65	w	5.66	23
5.48	2	5.46	w	5.44	3
4.75	6	4.74	w		
				4.68	5
		4.34	w	4.35	36
		4.21	s	4.23	100
4.08	20	4.10	m		
4.05	22	4.05	m		
3.97	14	4.00	w	4.02	54
3.94	15	3.94	m	3.95	56br
		3.83	m	3.84	66
3.77	10	3.77	w		
3.64	4	3.64	w		
		3.59	w	3.60	8br
3.41	2	3.39	w	3.38	19
3.28	16	3.28	m	3.28	1
3.17	5	3.16	w	3.12	14
3.08	7	3.09	w	3.08	3
3.03	4	3.03	w	3.03	6
2.95	8	2.95	w		
2.90	5	2.90	w		
				2.84	8
2.74	7	2.74	w	2.73	13
2.63	2	2.63	w	2.63	8
2.50	3			2.51	3
2.35	3			2.47	3
				2.38	10br
				2.292	3
				2.238	2
				2.113	6
				2.019	4
				1.941	1
				1.870	2
				1.807	3
				1.684	4

br = broad peak.

containing analog of VPI-5. This was verified through isolation of pure crystalline VPI-5 under milder crystallization temperatures following the reported details of the synthesis of this structure [5].

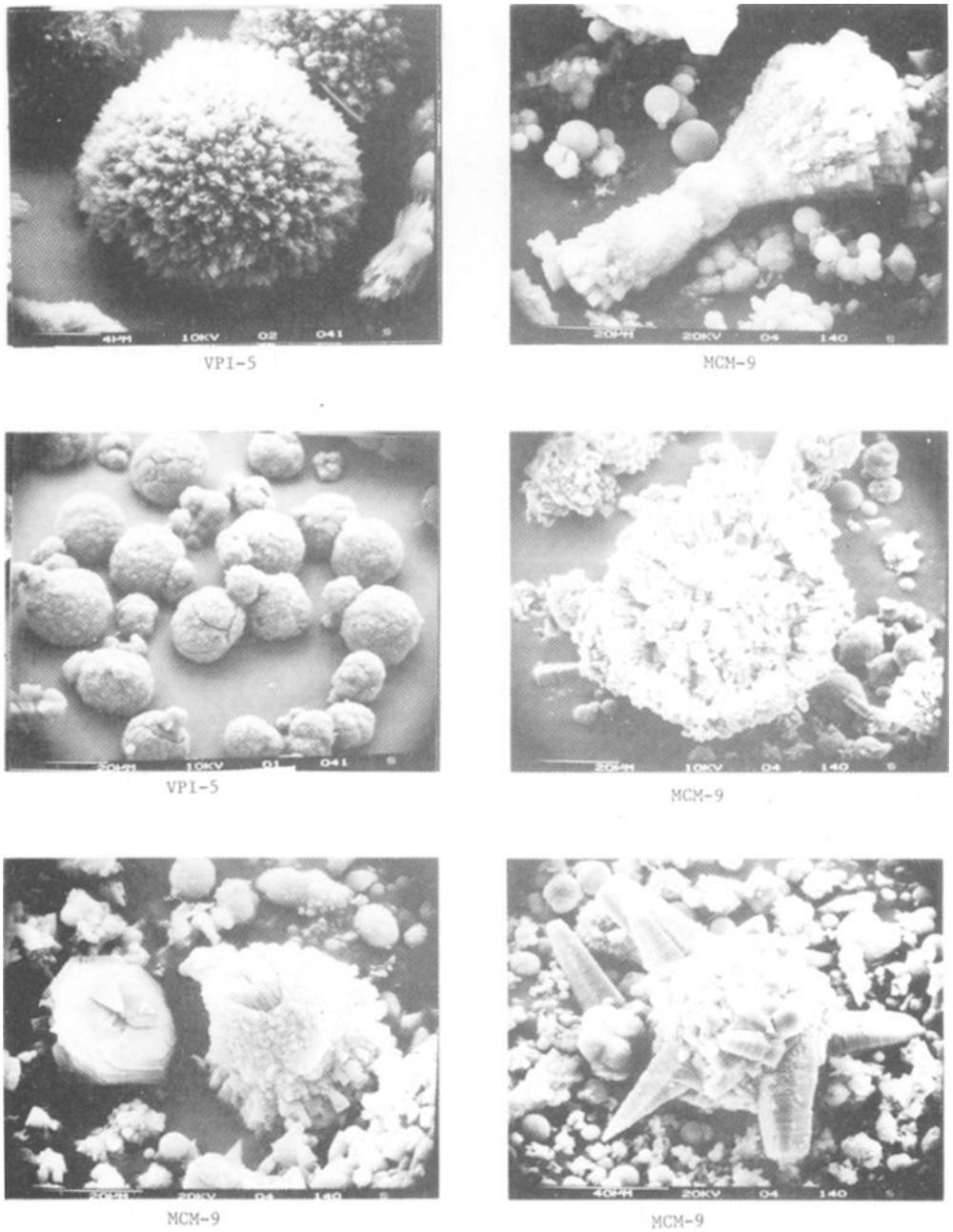

Fig. 2. SEM images of MCM-9 crystals and VPI-5 crystals.

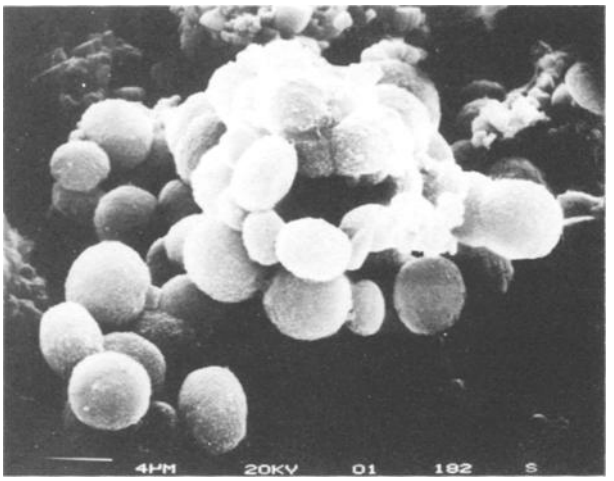

Fig. 3. SEM image of SAPO-11 crystals prepared in the two phase system.

3. Characterization of the products and comparison with VPI-5

A comparison of the X-ray powder diffraction patterns for MCM-9, VPI-5 and $AlPO_4$-11 (comparable to SAPO-11) are shown in fig. 1 and the X-ray peak positions for the three materials are provided in table 2, showing the identification of all of the reported peaks in the MCM-9 X-ray diffraction pattern. The SEM images of MCM-9 and VPI-5 are shown in fig. 2. The images of SAPO-11 as prepared from the two phase system are provided in fig. 3. In addition to the X-ray diffraction pattern comparisons, the presence of numerous crystal habits in the MCM-9 sample also is suggestive of the presence of multiple phases.

4. Experimental procedure

The methodology used in the preparation of MCM-9 was taken from the patent examples 1 and 2 from ref. [4]. The compositions used in the variable study and the resulting crystalline products formed are presented in table 1. The synthesis procedure for VPI-5 was followed exactly as reported in ref. [5]. A Rigaku D/Max-11B Microprocessor Controlled Automated X-ray Powder Diffraction System was used to generate the powder patterns of the samples presented in this study. SEM micrographs were taken on a Cambridge 150 Spectroscan.

Acknowledgements

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