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Project Director:	Dr. Rosemarie Szostak
Telephone Number:	(404) 880-6861
Prepared by:	Dr. Rosemarie Szostak Dr. Godfried Abotsi Dr. Mark Mitchell Dr. Conrad Ingram Dr. Eugene Dai Miss Crystal McClure Mr. Dolon Silimon
Institution:	Clark Atlanta University 223 James P. Brawley Drive Atlanta, Georgia 30314

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Co-APO-5 and -11 have been synthesized hydothermally both from a clear solution and from a gel, Various amounts of cobalt have been used. The materials have been characterized by XRD, ICP, and BET. Rapid crystallization together with well formed hexagonal crystals is obtained for CoAPO-5 from a clear homogeneous F-containing solution. Magnetic susceptibility indicates a mixture of electronic configurations for cobalt in the framework. Strong indications of tetrahedral coordinated cobalt is found.

Introduction

The aim of this phase of our study is to demonstrate how cobalt-containing aluminophosphate molecular sieves with structure types AFI and AEL can be synthesized from a clear homogeneous solution. The advantage of beginning with a clear solution is that transient phases, either crystalline or amorphous, can be more easily identified. The nature of these phases and their role in the crystallization process can be seen more easily. HF is used as a mineralizing agent. It has been reported that the presence of F anions in the synthesis mixture can improve considerably the $AlPO_4$-5 type crystals.[1]

Experimental Procedure

The batch composition for the starting gel in the case of CoAPO-5 is:

$0.8\ Al_2O_3 : 1\ P_2O_5 : 0.2\ CoO : 1\ TEA : 40\ H_2O$

using pseudoboehmite (VISTA), 85% orthophosphoric acid (FLUKA), cobalt acetate, $Co(OAc)_2{*}4H_2O$ (FLUKA), triethylamine, TEA,(FLUKA), and deionized water. The reaction mixture is heated in a teflon lined steel autoclave previously rinsed with HF to ensure clean autoclaves. Crystallization occurs at 200C after 14 hours. The batch composition for the clear solution system is:

$0.9\ Al_2O_3 : 1.2\ P_2O_5 : x\ CoO : 2.3\ R : 1.9\ HF : 143\ H_2O$

with x ranging from 0.1 to 0.01, R= TEA for CoAPO-5 and DPA(dipropylamine) for CoAPO-11. The chemicals used include aluminum hydroxide, $Al(OH)_3$, nH_2O (50-58.5wt%, Aldrich), 85% ortho phosphoric acid (FLUKA), cobalt acetate, $Co(OAc)_2{*}4H_2O$ (FLUKA), triethylamine (FLUKA), dipropylamine (KODAK), 40% HF (Aldrich), and deionized water. The solution is stirred until a completely clear solution is formed, dark pink in color, normally requiring 3 hours. The solution is then heated in a teflon lined steel autoclave at 170C for 3-6 hours.

Results and Discussion

Synthesis

Table 1 shows the batch compositions for the synthesis of CoAPO-11 and the phases obtained. These batches do not make a clear solution, rather a thin gel. When increasing the amount of DPA from 1.5 to 2.0, unidentified additional peaks appear in the x-ray diffraction pattern. Also, at 170C increasing the crystallization time results in impure CoAPO-11. When DiPA is used as organic additive AlPO4-quartz appears when R/P_2O_5 is 1. Increasing the amount of R results in CoAPO-11 with some unidentified impurities. Pure CoAPO-11 is never obtained with this organic base. What can be seen from this is that an increased amount of DiPA depresses the formation of AlPO4-quartz. DiPA is not used for further synthesis experiments because pure phases were not obtained. Based on experience, the times chosen for the crystallization of both CoAPO-5 and-11 was three hours.

Table 1: Batch composition for the synthesis of CoAPO-11 from composition: 0.9 Al_2O_3 : 1.0 P_2O_5 : 0.1 CoO : x R : 1.0 HF : 50 H_2O.

sample	R	pH_i/pH_f	time/h	T/deg C	color	phase
3101C	1.5 DPA	3.5/3.	16	190	blue	CoAPO-11
0502B	2.0 DPA	6.1/6.1	17	190	blue	CoAPO-11*
0602D	1.0 DiPA	4.2/4.6	18	190	blue	$AlPO_4$-quartz
0602E	1.5 DiPA	5.6/6.3	18	190	blue	CoAPO-11*
0502D	2.0 DiPA	6.4/6.5	17	190	blue	CoAPO-11*
1902A	1.5 DPA	6.0/5.8	23	170	blue	CoAPO-11
1902B	1.5 DPA	6.0/5.5	48	170	blue	CoAPO-11*

* extraneous peaks due to unidentified impurities.

Table 2 shows the synthesis parameters for the crystallization of CoAPO-5 and CoAPO-11 from a clear homogeneous solution.

Table 2: Synthesis of CoAPO-11 and CoAPO-5 from a clear solution with molar ratio: 0.9 Al2O3 : 1.2 P2O5 : 0.1 CoO : 2.3 R : 1.9 HF : x H2O, r=DPA for CoAPO-11 and TEA for CoAPO-5. Crystallization time is 3h.

sample	*R*	*x*	*pHi/pHf*	*temp/deg C*	*result*
0204A	DPA	143	3.8/3.9	190	CoAPO-11
0404A	DPA	100	4.3/4.2	170	CoAPO-11
0105A	DPA	143	5.6/4.9	170	CoAPO-11
0905	DPA	50	5.4/5.6	170	CoAPO-11

sample	*R*	*x*	*pHi/pHf*	*temp/deg C*	*result*
0204B	TEA	143	4.0/4.1	190	CoAPO-5+$AlPO_4$-quartz
0404B	TEA	100	4.3/4.1	170	CoAPO-5
0105B	TEA	143	5.7/5.1	170	CoAPO-5
0905B	TEA	50	5.5/5.5	170	CoAPO-5/ CoAPO-11

Synthesis of samples with an increased amount of cobalt were not successful. In this work further effort on incorporation of more than 0.1 CoO was not made. One series of CoAPO-5 with varied amounts of cobalt was synthesized successfully from the batch composition: 0.9 Al2O3 : 1.2 P2O5 : x CoO : 2.3 TEA : 1.9 HF : 143 H2O, x being 0.1, 0.05, 0.02, and 0.01 CoO. The synthesis time was 4 hours at 170C. In the gel system a CoAPO-5 was made with 0.2 CoO in the starting gel. This is summarized in Table 3:

Table 3: Synthesis of CoAP0-5 from gel and clear solution with various amounts of cobalt.

sample	Al_2O_3	P_2O_5	*CoO*	*TEA*	H_2O	*HF*	*Co/u.c.*

5-1-14*	0.8	1.0	0.20	1.0	40	--	2.4
1105B	0.9	1.2	0.10	2.3	143	1.9	1.2
1105C	0.9	1.2	0.05	2.3	143	1.9	0.6
2194B	0.9	1.2	0.02	2.3	143	1.9	0.3
2104C	0.9	1.2	0.01	2.3	143	1.9	0.1

* This was made from a gel

The last column in Table 3 indicates the theoretical number of cobalt in the unit cell if all cobalt incorporates at aluminum sites. In this study the experiments were done to develop an adequate synthesis procedure for obtaining pure material. The samples described in Table 3 were characterized further.

XRD

The x-ray powder diffractograms of CoAPO-5 from a clear solution is shown together with CoAPO-5 from a gel in Figure 1. It is clearly shown that the intensity of the 002 peak is significantly lower in the clear solution system. This might be due to orientation effects. To rule out explanations of this effect other than orientation, diffractograms were obtained both with a Guinier camera and a powder diffraction method. The Guinier method is based on transmitted radiation whereas the diffractometer reflects radiation. Therefore one should obtain very high intensity for the 002 peak, opposite for the powder method, from the Guinier film if the effect has other reasons than orientation. This is not the case, and one can conclude from this that the drop in intensity of the 002 peak is due to orientation effects. This is visualized in Figure 2 where diffractograms of CoAPO-4 from clear solution is obtained both from a Guinier film and a diffractometer.

Long hexagonal well-defined rods 100 microns in size are obtained from the clear solution synthesis. From the gel smaller particles, not so well defined in shape, are obtained. This is suggested to result in the orientation effects observed in the XRD for the long crystals obtained from clear solution.

Elemental analysis

Table 4 shows elemental analysis of CoAPO-5 with various amounts of cobalt.

Table 4; Element analysis of CoAPO-5 by ICP-AES.

sample	*Al(atom %)*	*P(atom %)*	*Co(atom %)*
5-1-14	44.9	49.3	5.8
1105B	46.9	50.1	3.0
1105C	46.7	50.6	2.8
2104A	45.9	53.4	0.7

Elemental analysis has also been performed by microprobe. IT was observed an inhomogeneous distribution of cobalt in the samples. This has recently been described by de Navarro et al..[2]

BET

Table 5 shows the BET surface area of calcined CoAPO-5 with various amounts of cobalt.

Table 5: BET surface area of CoAPO-5 with various amounts of cobalt.

sample	*CoO in reactant*	*Co/u.c.*	*BET(m2/g)*
5-1-14	0.20	2.4	283
1105B	0.10	1.2	265
1105C	0.05	0.6	292
2104B	0.02	0.3	244
2104A	0.01	0.1	190

Unit Cell Parameters

Unit cell parameters for CoAPO-5 with various amounts of cobalt has been calculated using the program UNITCELL.[3] Figure 3 shows unit cell volume with increasing cobalt content. The x-axis represents the number of cobalt atoms per unit cell, calculated from the reaction mixture. The measured amount of cobalt is shown in Table 4. It is anticipated here that all cobalt available substitutes for aluminum at the tetrahedral positions in the structure. This is not likely to happen, but gives an indication on what can be expected. From 0.1 Co-atoms per unit cell to 0.2 no significant increase in the unit cell volume is observed with increasing cobalt content. The ionic radius for Co(II) (0.72A) is much larger than Al(III) (0.51A). One should expect an increase in unit cell dimensions with increasing cobalt content if one assumes that the bonds are exclusively ionic in character. However, the covalent radius for cobalt (1.16A) is smaller than for aluminum (1.25A). If he character of the bonds were covalent one should observe a contraction of unit cell volume with increasing amounts of cobalt. The character of the bonds in aluminophosphate molecular sieves will be a mixture of covalent and ionic. Ab initio calculations of the charge on aluminum in a Al-O-P cluster show that the real charge is +1.51.[4] This has not been calculated yet for cobalt. The model used is a very simplified aluminophosphate structure, but can give an indication on charges I the lattice. Finally, if one assumes that the character of the bonds both for cobalt and aluminum are half ionic, half covalent, cobalt (0.94A) will be larger than aluminum (0.88A) so an increase in the unit cell volume would still be expected to increase upon increasing amounts of cobalt in the structure. This is what is observed.

Conclusions

Highly crystalline CoAPO-5 and CoAPO-11 have been synthesized from clear homogeneous solutions. Various amounts of cobalt have been incorporated in CoAPO-5. Orientation effects are observed in the XRD for long hexagonal rods. The coordination of cobalt is predominately half ionic/half covalent.

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[1] S. Qiu, W. Pang, H. Kessler, J. Guth, *Zeolites*, 9, 440 (1989)

[2] U. C. de Navarro, F. Machado, M. Lopez, D. Maspero, J. Perez-Pariente, *Zeolites*, 15, 157 (1995)

[3] Swedish Energy Data, Test Application, Version 1.0 (1995)

[4] Private communications with Klaus Schøffel, Hydro, Norway

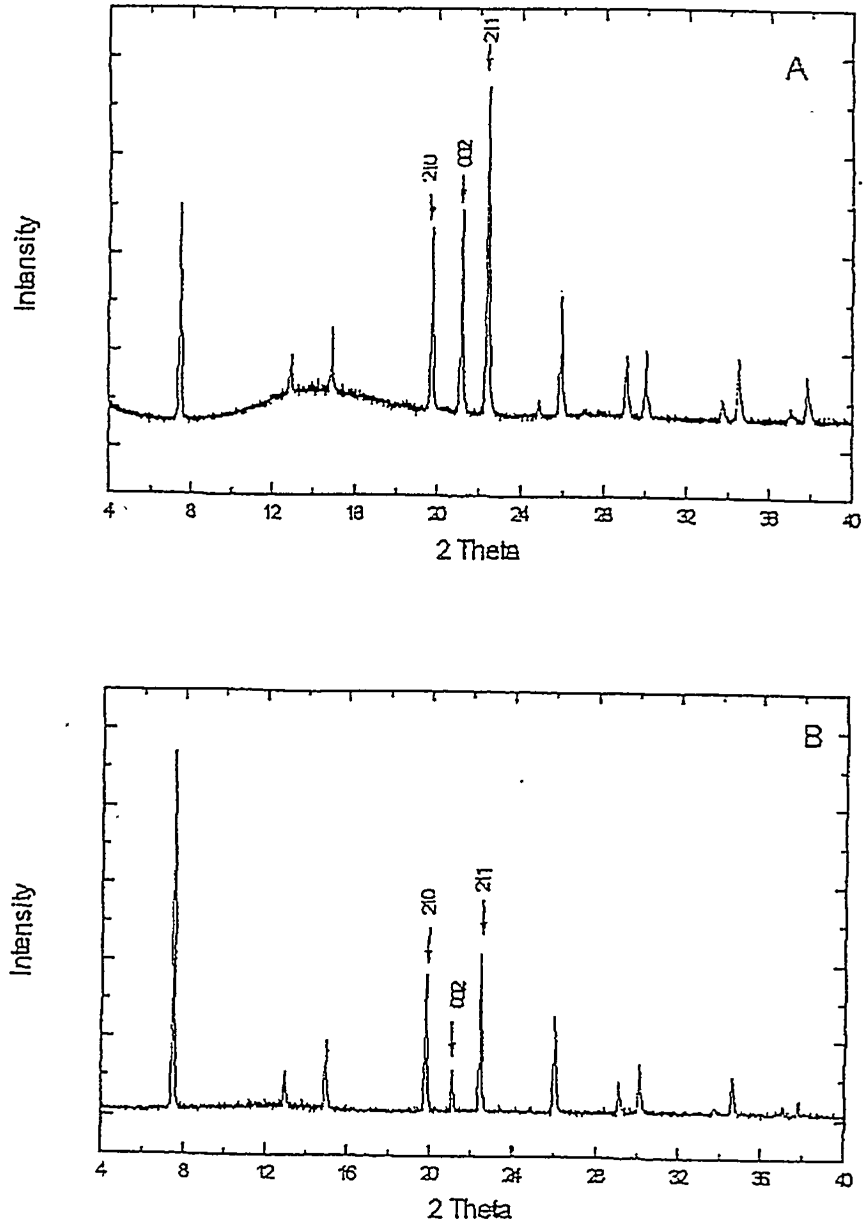

Figure 1. CoAPO-5 from A) gel, 5-1-14 Table 3 B) clear solution 1105 B Table 3

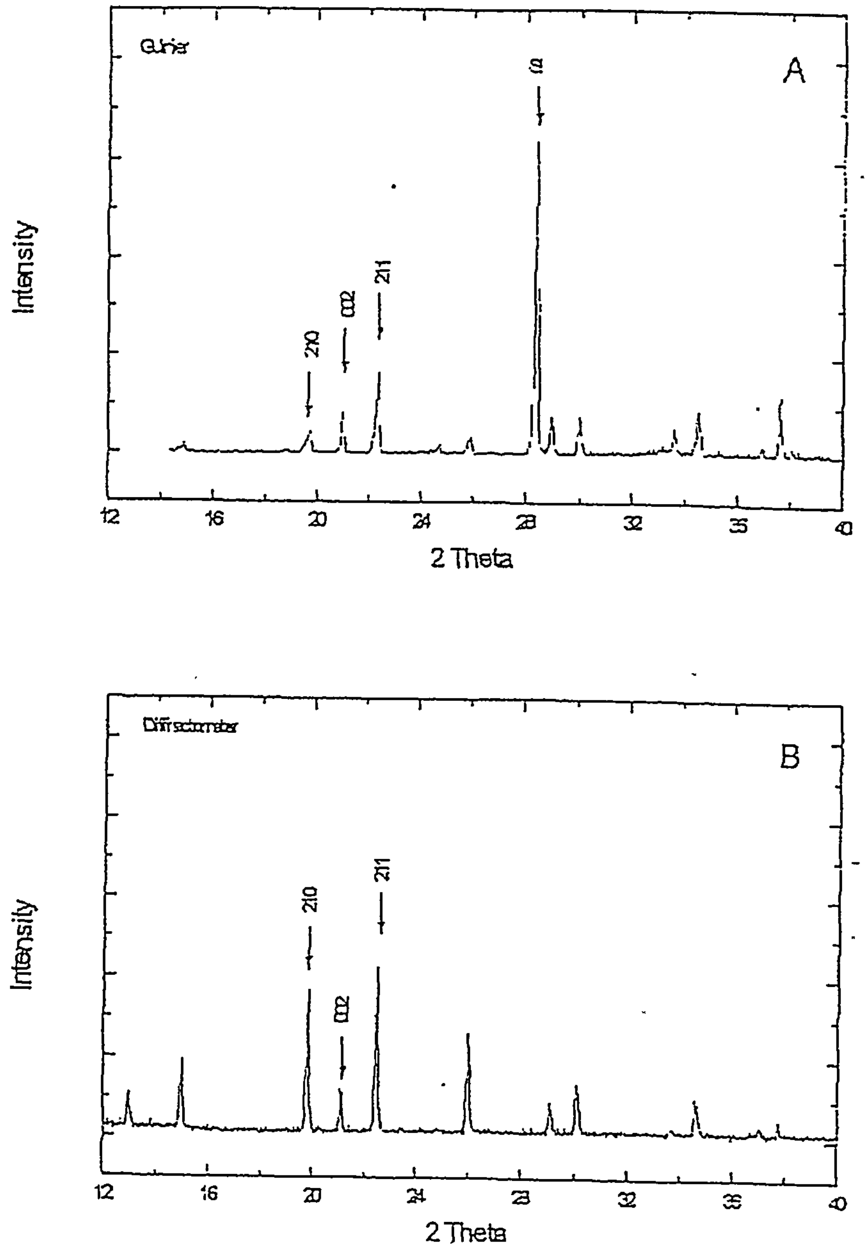

Figure 2. Diffraction patterns of CoAPO-5 from clear solution A) based on Guinier method, transmitted radiation B) based on a diffractometer, reflected radiation.

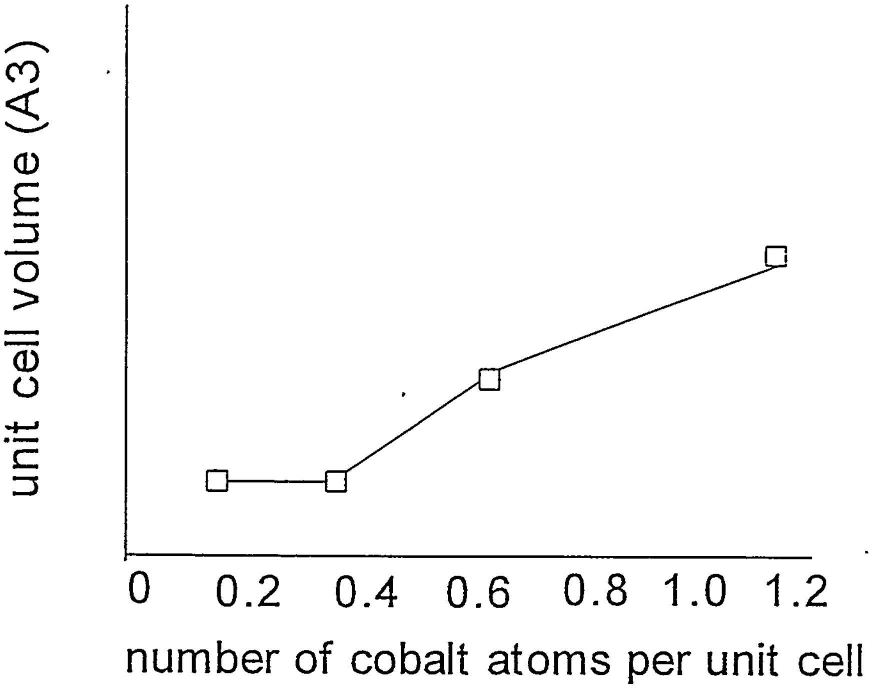

Figure 3: Unit cell volume as a function of coblat content