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## Synthesis and characterization of nanocrystalline CoAPO-5: Structural and morphological analysis by alteration on hydrothermal parameters

### ABSTRACT

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Nano-zeolite CoAPO-5 as a member of AFI family, was synthesized via a hydrothermal treatment, and structurally characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive X-ray analysis (EDAX). The effects of crystallization temperature and time on the structure of these powder products were studied. XRD patterns of the synthesized powders revealed a high-crystallinity and pure phase of AFI. SEM images and Scherrer equation showed the nano-size of the obtained CoAPO-5. Also, SEM images showed nano-wires as small as 30-50 nm in CoAPO-5 structures. According to EDAX analysis, P/Al ratio of the prepared CoAPO-5 powder was about 1.5. Crystal sizes and the crystallinity of CoAPO-5 reduced at higher temperatures of hydrothermal treatment. On the other hand, the larger crystals grew by increasing the crystallization time from 24 to 48 h.

**Keywords:** Nano-Zeolite; CoAPO-5; Synthesis; Characterization; Structure; Temperature.

### INTRODUCTION

Zeolites, with crystalline frameworks involving nanometer or subnanometer pores, were discovered by Cronstedt in 1756 [1,2]. Aluminophosphate was reported in 1982 by Wilson et al. [3]. Historical review of zeolites and molecular sieves showed in Figure 1. Incorporate of metals into the Aluminophosphate's structures, such as Fe, Cu and Mg have already studied [4, 5]. MeAPO-5 (Me = metal) was used in many reactions (e.g. benzene alkylation [6], dehydrogenation of ethane to ethane [7], selective oxidation of cyclohexane [8,9], and oxidation of p-cresol to p-hydroxybenzaldehyde [10]) and showed good catalytic performance; on the other hand, the incorporation of a single metal into aluminophosphate's is well recognized [11,12].

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CoAPO-5 which is categorized in AFI type has a hexagonal open framework structure with  $a = 13.827 \text{ \AA}$ ,  $b = 13.827 \text{ \AA}$ ,  $c = 8.580 \text{ \AA}$  and  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ . The X-ray single crystal refinement of AFI type is  $R_w = 0.042$  [13-15]. This structure composed of alumina and phosphate, is located alternative with O-bridge. The tetrahedral structure with the main porosity along the [001] plane and the composite building units is shown in Figure 2. The pore size of CoAPO-5 is  $7.3 \text{ \AA}$ . The space group is P6/mcc (mass centered cubic), and the largest ring size is 12 atoms [16, 17]. The typical unit cell composition is  $[\text{CoAl}_{11}\text{P}_{12}\text{O}_{48}] : w\text{H}_2\text{O}$  ( $w = 0.1$  to  $0.2$ ) and the elemental analysis of this zeolite is:  $0.7 \text{ TEA} : (\text{Co}_{0.08}\text{Al}_{0.92}\text{P})\text{O}_4 : 20 \text{ H}_2\text{O}$  [18].



Fig. 1. Historical review of zeolite and molecular sieves

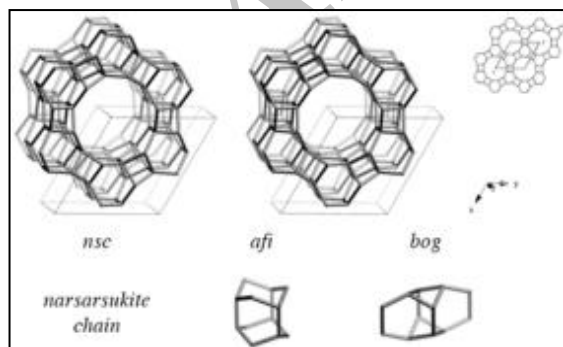


Fig. 2. a) Framework viewed along [001] (upper right: projection down [001]), and b) composite building units [17]

## EXPERIMENTAL

### Materials

Aluminum tri isopropylate (LOBO Chem,  $\text{Al}(\text{C}_3\text{H}_7\text{O})_3$ ) and orthophosphoric acid (Merck, 85%  $\text{H}_3\text{PO}_4$ ) were used as sources of Al and P, respectively. Triethylamine (Riedel de Haen, 99.5%  $(\text{C}_2\text{H}_5)_3\text{N}$ ) and Cobalt nitrate (Merck,  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ ) were also used as inorganic template and metal phase, respectively.

### CoAPO-5 nano-zeolite preparation

Batch composition applied for preparation of CoAPO-5 nano-zeolite using hydrothermal treatment was:  $0.7 \text{ TEA} : (\text{Co}_{0.08}\text{Al}_{0.92}\text{P})\text{O}_4 : 20 \text{ H}_2\text{O}$ . D.I. water and phosphoric acid (85 wt %  $\text{H}_3\text{PO}_4$ ) were mixed and chilled to  $0^\circ\text{C}$ . Cobalt nitrate was added to the mixture and stirred until dissolved. Aluminum tri isopropylate was introduced to the mixture and hold under continuous stirring at room temperature to be homogenized. TEA was then added to the mixture dropwise at continuous stirring for 1 hour. The TEA addition caused an exothermic reaction; therefore, should be performed at  $0^\circ\text{C}$  under temperature control. Initial pH of the mixture was 3. The prepared gel was transferred to a Teflon-lined steel autoclave. The autoclave was tumbled in the oven and the gel was crystallized under four conditions different in time and temperature of crystallization ( $180$  and  $200^\circ\text{C}$ ;  $24$  and  $48 \text{ h}$ ). After crystallization, the autoclave was cooled at room temperature. Product recovery of the product zeolite was done using a Buchner vacuum filtration funnel. Finally, the powder product calcined at  $600^\circ\text{C}$  for 4 h.

### Characterization

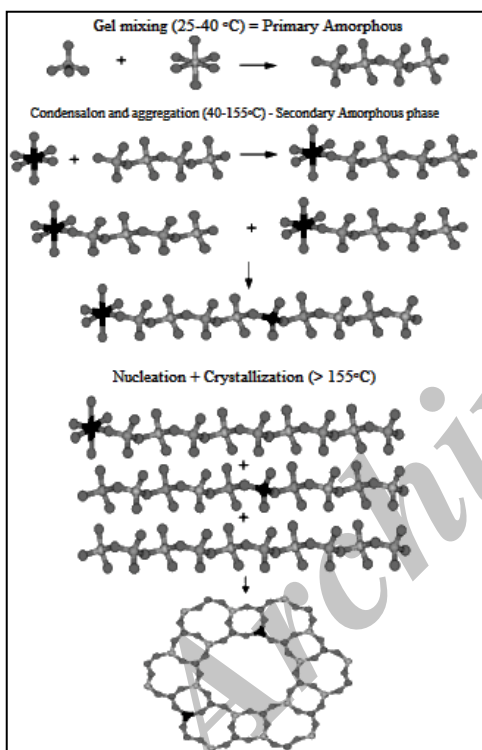
The crystallinity, purity and pore diameter of the prepared CoAPO-5 crystals was established using XRD, SEM and EDAX analysis. SEM and EDAX analyses were carried out using a "Philips XL30 Scanning Electron Microscope and EDAX" analyzer. XRD patterns of powders were recorded with a "Philips PW1800" powder diffractometer by  $0.02$  steps.

## RESULTS AND DISCUSSION

### *Mechanism of gel combination and crystals formation*

Mechanism of gel combination, crystals formation and incorporation of  $\text{Co}^{2+}$  into the crystal structure is shown in Figure 3. This combination and crystallization occurred in 3 states:

1. Gel mixing containing aluminum and phosphor amorphous phase reaction at 25-40°C;
2. Aggregation at 40-155°C and formation of the secondary amorphous phase; and
3. Nucleation and crystallization to constitute final AFI structure at higher temperature than 155°C [19].



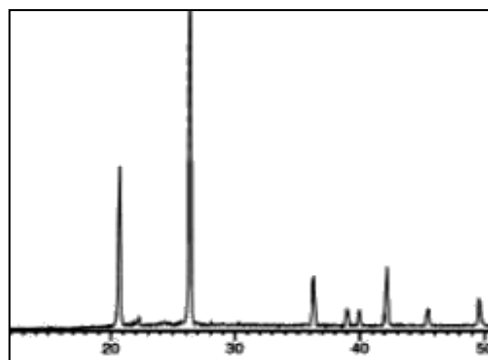
**Fig. 3.** Schematic of molecular structure of crystallization model: black =  $\text{Co}^{2+}$ , white =  $\text{Al}^{3+}$ , gray in the center =  $\text{P}^{5+}$ , and the other gray =  $\text{O}^{2-}$  [19]

This model shows a microscopic view of crystallization. Base of this structure is Al–O–P units which are composed from reaction of alumina and phosphoric acid in water under continuous stirring at 0°C. It has been already shown that the aluminophosphate structures can be formed from single Al–O–P linear chain [19]. The Al–O–P chains formed at gel mixing process are contained

tetrahedral aluminum which is linked to phosphate groups with O–bridge. The phosphate groups are more stable than the Aluminum ones. The heavy metal phase can decrease the interaction between chains. The substitutions of metal with aluminum and attaching to phosphor occur at higher temperature (40–155°C) which makes aluminophosphate chains more weak. Afterward, 3 kinds of chains are formed from the gel. These chains can easily solve and interact with the inorganic template and remain counterpart in the gel. This reaction allowed amorphous phase to crystallize from solution. As seen in Figure 3, these chains are so flexible at high temperature that interact together and rotate to form a porous layer or an open-framework structure. These framework is too weak and unstable. Therefore the heating treatment causes the amorphous structure to be strong and organize the final crystalline structure [20].

### *Product crystallinity and morphology*

The XRD pattern of CoAPO-5 nanozeolites shown in Figure 4 revealed that the CoAPO-5 crystals were the only crystalline phase present in the product. As seen, all peaks match those for AFI crystals with respect to the positions and intensities of the observed reflections, and no additional peaks are observed. The intensity of the XRD peaks and low background intensity indicate an acceptable degree of zeolite crystallinity. The XRD pattern of other synthesized CoAPO-5 is similar to Figure 4.



**Fig. 4.** XRD pattern of the prepared CoAPO-5 crystals

The Scherrer equivalent based on the XRD data used for calculating particle size of the synthesized CoAPO-5 (Eq. 1):

$$D = 0.9\lambda / \beta_{\text{sample}} \cos(\theta)$$

The particle size of each synthesized CoAPO-5 was calculated. The estimated sizes of the zeolite particles in different crystallization times and temperatures are listed in Table 1.

**Table 1.** Estimated particles sizes of CoAPO-5 using Scherrer equivalent.

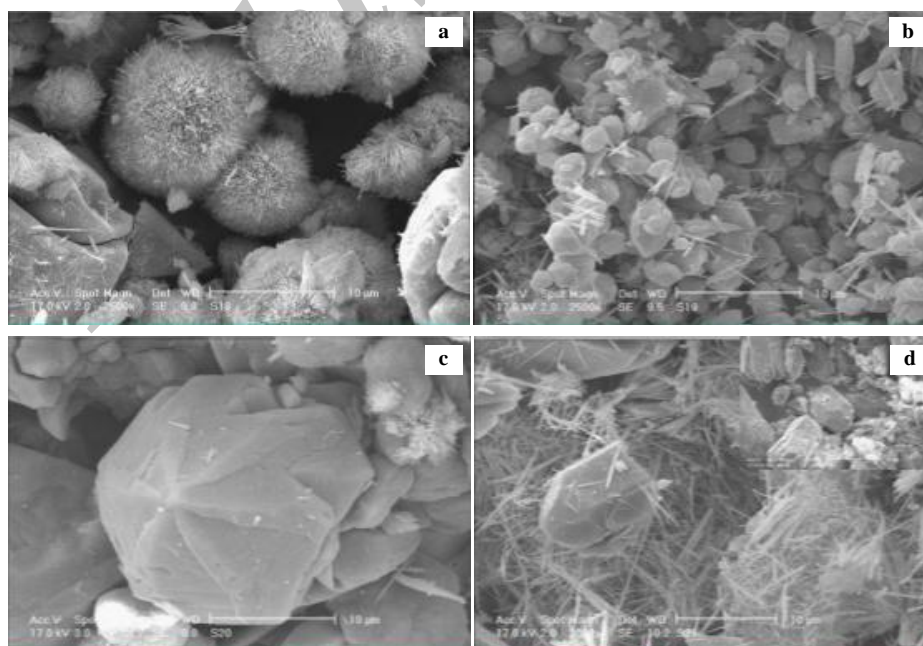
Crystallization Temp (°C)	Crystallization Time (h)	Particles Sizes (nm)
200	24	58
200	48	48
180	24	68
180	48	48

The SEM images of synthesized CoAPO-5 are illustrated in Figure 5. Figure 5a (crystallization at 200°C, 24 h) shows bundles of acicular crystals which are consist of nano-wires. The length and diameter of these nano-wires respectively falls in the range of 1-5  $\mu\text{m}$  and 10-100 nm. Three different shapes of crystal, hexagonal, octahedral crystals, and nano-wires, can be recognized in Figure 5b (@ 200°C, 48 h). In some crystals, the octahedral shapes were transformed into spherical shapes. The crystal size of the powder product in Fig. 5b was about 2-5  $\mu\text{m}$ .

The large size of the octahedral crystals of CoAPO-5 from the hydrothermal at 180°C, 24 h (Figure 5c) was around 20  $\mu\text{m}$ . Also, as seen in Figure 5d, the crystals size of the powder obtained at 180°C after 48 h was about 50-70  $\mu\text{m}$ .

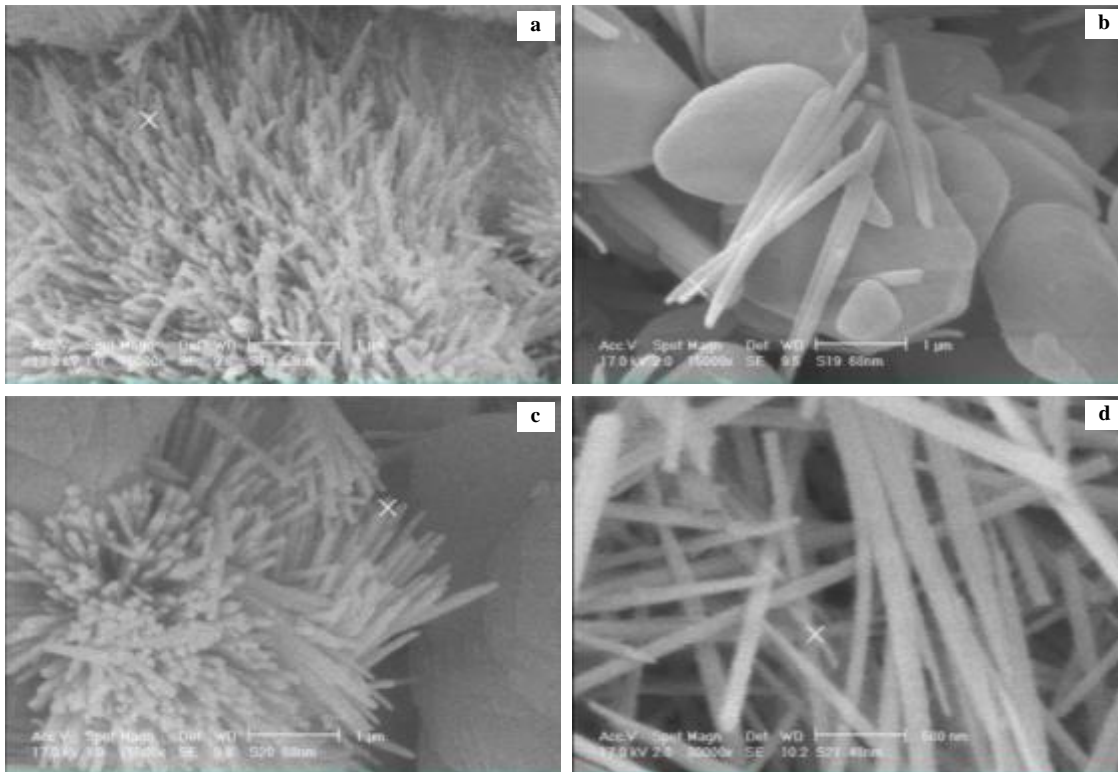
As shown in Figure 5, the crystals synthesized for 48 h indicated a higher level of crystallinity and smaller size than those synthesized for 24 h. In fact, the amorphous phase had more time to form crystals in longer hydrothermal time and can be form more number of crystals with higher crystallinity and smaller sizes. The diameter of nano-wires was decreased in longer duration of crystallization (Figure 6 and Table 1). The morphology of the crystals was affected by changes in crystallization temperature. Increasing the crystallization temperature from 180°C to 200°C led more and smaller crystals with less crystallinity to be formed (Figure 5). The molecules of amorphous phase had more interaction in higher crystallization temperatures; therefore, the molecules can fit out in free spaces and can be formed smaller crystals.

The analyze data of CoAPO-5 are listed in Table 2. According to EDAX analysis of Table 2, the P/Al ratio in the prepared CoAPO-5 powder was about 1.5.



**Fig. 5.** SEM images of the prepared CoAPO-5 crystals(2500x): a) 200°C, 24 h; b) 200°C, 48 h; c) 180°C, 24 h; and d) 180°C 48 h.





**Fig. 6.** The diameter of nano-wires in SEM images (30000x): a) 200°C, 24 h; b) 200°C, 48 h; c) 180°C, 24 h; and d) 180°C, 48 h.

**Table 2.** The EDAX test of synthesized CoAPO-5

Element	wt%	at%
Al	20.91	29.89
P	31.03	38.65
Co	48.06	31.46
Total	100.00	100.00

## CONCLUSIONS

Small nano-pore molecular sieve CoAPO-5 zeolites were synthesized using in situ hydrothermal method. The obtained crystals had nano-wires in structures with sizes as small as 30-50 nm. The hydrothermal treatment without any organic template was applied, so the post-treatment calcinations have been omitted. XRD patterns of the powders obtained showed high-crystallinities and pure phases. The SEM images and Scherrer equation revealed the nano-size of the CoAPO-5 powders. In addition, according to the EDAX

results, the P/Al ratio in prepared CoAPO-5 powder was about 1.5. The effect of the crystallization temperature and time on the structure of the zeolitic powder products was studied. Increasing the temperature led smaller crystals with less crystallinity to be formed. On the other hand, the larger crystals were obtained by increasing the crystallization time.

## ACKNOWLEDGEMENTS

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