Synthesis of Co-Rich CoAPO-5 Molecular Sieves: A Comparison between Glycerol and Water as Solvent

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CoAPO-5 molecular sieves have been synthesized with glycerol and water as solvent in order to maximize the degree of isomorphous substitution of Co^{2+} ions in the AFI framework. These CoAPO-5 molecular sieves have been characterized with X-ray diffraction, inductively coupled plasma-atomic emission spectroscopy, scanning electron microscopy, electron microprobe microanalysis, N_2 sorption, and UV-visible-NIR-diffuse reflectance spectroscopy techniques. Optimum conditions for the synthesis of Co-rich single-phase and highly crystalline CoAPO-5 molecular sieves were obtained by varying the $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel and the synthesis time. It will be shown that highly crystalline hexagonal single-phase CoAPO-5 crystals with a size between 3 and 10 μm and a substitution degree of about 13% can be obtained from a $0.7\text{CoO} \cdot 0.65\text{Al}_2\text{O}_3 \cdot 1\text{P}_2\text{O}_5 \cdot 1(\text{C}_2\text{H}_5)_3\text{N} \cdot 40\text{HOCH}_2\text{CHOHCH}_2\text{OH}$ gel at 190 °C after 14 days of synthesis. This substitution degree is substantially higher than that for CoAPO-5 materials synthesized in the presence of water (i.e., about 7.5%).

Keywords: CoAPO-5 Molecular Sieves, Synthesis, XRD, SEM.

1. INTRODUCTION

$\text{AlPO}_4\text{-5}$ is a well-studied microporous crystalline aluminophosphate material with a unique framework structure, relatively large nanopores, and a good thermal stability. Transition-metal-containing $\text{AlPO}_4\text{-5}$ molecular sieves have been proved to be promising heterogeneous catalysts for both liquid-phase and gas-phase reactions.^{1,2} An example is CoAPO-5, which is known to be highly active and selective in the autooxidation of *p*-cresol to *p*-hydroxybenzaldehyde.² The number of acid or redox sites and, consequently, the catalytic activity depend on the Co^{2+} content in the framework.³ Thus, it is of paramount importance to get insight into the synthesis parameters, which control the amount of framework Co^{2+} ions in $\text{AlPO}_4\text{-}n$ molecular sieves.

It has been shown that the amount of framework Co^{2+} strongly depends on the $\text{AlPO}_4\text{-}n$ structure,⁴ and, based on analytical data, the highest substitution degrees in open $\text{AlPO}_4\text{-}n$ structures have been reached for CoAPO-50 (37.5%) and CoAPO-46 (26%).^{5,6} In contrast, in the hydrothermal synthesis of CoAPO-5, less than 8% of

the Al^{3+} ions can be replaced by Co^{2+} ,⁷⁻¹⁴ and attempts to synthesize CoAPO-5 materials with higher substitution degrees usually lead to low-crystallinity products and amorphous and/or crystalline impurities. This is mainly due to other competing phases, such as CoAPO-34, CoO, and $\text{Co}_x\text{Al}_{2-x}\text{O}_3$, are formed when more Co^{2+} ions are present in the synthesis gel.^{9,10}

In a recent study, we have shown that the substitution degree of Co^{2+} can be increased by adding CsCl to the synthesis gel.¹⁵ In a further attempt to increase the substitution degree of Co^{2+} ions in CoAPO-5 molecular sieves, water has been replaced by glycerol as a solvent in this work. Based on a combination of physical, chemical, and spectroscopic techniques, it will be shown in this work that the substitution degree of Co^{2+} in an $\text{AlPO}_4\text{-5}$ molecular sieve can be increased to about 13.5%, nearly doubling the amount of framework Co^{2+} in this material.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

Table I gives an overview of the CoAPO-5 materials synthesized, together with the gel composition, the chemical composition after synthesis, the sample color, and the sample code. Two series of CoAPO-5 molecular sieves

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Table I. Overview of the CoAPO-5 materials prepared with water or glycerol as a solvent, including the sample code, sample color, chemical composition of the gel and the solid, and the [Co]:[Al] ratio in the gel and the solid.

Sample name	Solvent	Color of solid	Composition of synthesis gel			[Co]:[Al] in gel	[Co]:[Al] in solid	([Co] + [Al]):[P] in solid
			(Co)	Al	P)O ₂			
0.00-G	Glycerol	White	0.00	0.50	0.50	0.00	0.00	1.008
0.08-G	Glycerol	Blue	0.037	0.462	0.50	0.08	0.051	0.982
0.25-G	Glycerol	Dark-blue	0.10	0.40	0.50	0.25	0.150	1.040
0.33-G	Glycerol	Dark-blue	0.125	0.375	0.50	0.33	0.241	1.061
0.43-G	Glycerol	Dark-blue	0.15	0.35	0.50	0.43	0.383	1.072
0.54-G	Glycerol	Dark-blue + pink spots	0.175	0.325	0.50	0.54	0.447	1.106
0.67-G	Glycerol	Dark-blue + pink spots	0.20	0.30	0.50	0.67	0.535	1.136
0.00-W	Water	White	0.00	0.50	0.50	0.00	0.00	1.001
0.05-W	Water	Blue	0.025	0.475	0.50	0.05	0.044	1.000
0.11-W	Water	Blue	0.05	0.45	0.50	0.11	0.081	1.024
0.18-W	Water	Dark-blue	0.075	0.425	0.50	0.18	0.136	1.016
0.25-W	Water	Dark-blue	0.10	0.40	0.50	0.25	0.162	1.064

were prepared starting from a synthesis gel containing H₃PO₄ (85 wt% in water solution, Acros) as a phosphorus source, triethylamine (TEA) (99%, Acros) as a template, cobalt acetate (97%, Acros) as a cobalt source, pseudo-boehmite (70 wt% Al₂O₃, Catapal) as an aluminum source, and glycerol (99%, Acros) or water as a solvent. The sample notation is as follows: *x* - *y*, where *x* is the [Co]:[Al] ratio in the synthesis gel and *y* is the use of glycerol (symbol G) or water (symbol W) as a solvent. The preparation method is similar to the procedure used in previous work in the hydrothermal synthesis of CoAPO-5 materials.¹⁵ Only the synthesis time was prolonged, since it was found that the synthesis of highly crystalline CoAPO-5 materials in glycerol required about 14 days. For example, 2.34 g of H₃PO₄ was dissolved in 30 ml of glycerol, followed by the addition of 1.29 g of cobalt acetate. Pseudo-boehmite (1.11 g) was added after 30 min to the solution with continuous stirring. Finally, 1.05 g of TEA was added dropwise to the synthesis mixture after 20 min, and the gel obtained was continuously stirred for 1 h in an ice bath. The resultant gel was transferred into a Teflon-lined cylindrical autoclave (with a capacity of 35 ml), and the crystallization was carried out under autogenous pressure without stirring at 190 °C for 14 days. After synthesis the solids were subsequently recovered and filtered, washed three times with bi-distilled water, and dried at 60 °C. The as-synthesized solids were later calcined at 550 °C for 5 h in air.

2.2. Characterization

The crystalline phase of the as-synthesized materials was identified with a Siemens D5000matic X-ray diffractometer with Cu K α radiation. Because the ionic radius of tetrahedral Co²⁺ is larger than the ionic radius of tetrahedral Al³⁺ (0.57 vs. 0.39 Å), an increase in the unit cell volume of the AFI crystal structure is expected.¹ This

expansion can be directly measured by X-ray diffraction (XRD) according to $4/3[(h^2 + h \cdot k + k^2)/a^2] + l^2/c^2 = (4 \sin^2 \theta)/\lambda^2$ where *a* and *c* are the cell parameters of the unit cell, θ is the diffraction angle, and λ is the wavelength of the incident X-rays. The unit cell volume is then equal to $a^2 \cdot c$ (Å³). Crystal morphology of the materials was determined with scanning electron microscopy (SEM) on a JEOL super 733 microscope. The chemical compositions of the solids were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and electron microscope microprobe analysis (EMMA). N₂ sorption experiments at -196 °C with the calcined CoAPO-5 materials were performed on an Omnisorp 100 Analyser from Coulter, operating in the continuous gas introduction and continuous-pressure mode. Before measuring, the calcined samples were heated in vacuum at 200 °C for 8 h. Pore volumes of the materials were determined from the desorption curve by the Barrett-Joyner-Halende (BJH) method. Diffuse reflectance spectra (DRS) in the UV-visible-NIR region of the solids were recorded at room temperature with a Varian Cary 5 spectrometer. The spectra were measured with an integration sphere against a Halon white reference standard in the range of 200–2500 nm. The DRS spectra were deconvoluted in Gaussian bands with the Grams/386 software of Galactic Industries Corp., and the absorption bands obtained were used for quantitative estimation of the amount of tetrahedral Co²⁺ ([Co²⁺]_{Td}) and octahedral Co²⁺ ([Co²⁺]_{Oh}).

3. RESULTS AND DISCUSSION

Table I summarizes the chemical composition of the freshly prepared CoAPO-5 materials synthesized with glycerol or water as a solvent. The analytical data indicate an increase in the cobalt content and a corresponding decrease in the aluminum content in the as-synthesized CoAPO-5 material with increasing [Co]:[Al] ratio in the synthesis gel. This process is expected if Co²⁺

ions replace Al^{3+} ions in the AlPO_4 -5 framework. The $[\text{Co}]:[\text{Al}]$ ratio reached a level of 0.162 in the case of hydrothermally synthesized CoAPO-5 materials and a much higher level of 0.535 in the case of glycerol-based synthesized materials. Additional experiments to prepare single-phase CoAPO-5 materials from a synthesis gel containing water as a solvent and a $[\text{Co}]:[\text{Al}]$ ratio of 0.33 or higher failed. Similar observations were made for the glycerol-based materials when the $[\text{Co}]:[\text{Al}]$ ratio was higher than 0.67. In this respect, Table I shows that the $([\text{Co}] + [\text{Al}]):[\text{P}]$ ratio in the as-synthesized materials is close to unity at low $[\text{Co}]:[\text{Al}]$ ratios but gradually increases with increasing $[\text{Co}]:[\text{Al}]$ ratio in the solids for higher $[\text{Co}]:[\text{Al}]$ ratios. This gradual increase suggests that some of the Co^{2+} ions are present in the CoAPO-5 material as amorphous cobalt oxide, cobalt-aluminum oxide, or cobalt-phosphorus oxide at the external surface of the crystallites or occluded in the pore structure. Another possibility is the formation of Co^{2+} at ion exchange sites, which originate from the substitution of Co^{2+} for Al^{3+} in the lattice. The analytical data of Table I also indicate that the $[\text{Co}]:[\text{Al}]$ ratio in the as-synthesized materials is always lower than the $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel, suggesting that part of the Co^{2+} initially present in the synthesis gel is removed by washing the solid after synthesis. No substantial differences in Co^{2+} uptake by the solid could be observed between the synthesis procedure in glycerol or water.

As examples, Figure 1 shows the XRD patterns of samples 0.25-G, 0.43-G, and 0.54-G. It is clear that these XRD patterns contain only the diffraction lines characteristic for the AlPO_4 -5 structure. All of the materials of Table I are single-phase CoAPO-5 molecular sieves without any contamination by other crystalline phases, although there are clear differences in their crystallinity degree and the relative intensities of the diffraction lines. It is evident from Figure 1 that relative to the sum of the intensity of the diffraction lines at the 210, 002, and 211 facets, the 100 diffraction line decreases in intensity with increasing $[\text{Co}]:[\text{Al}]$ ratio in the solid. The $[P_{100}]:[P_{210} + P_{002} + P_{211}]$ ratio (where P is the intensity

Fig. 1. XRD patterns of samples. (A) 0.25-G. (B) 0.43-G. (C) 0.54-G.

Fig. 2. SEM picture of sample 0.25-G.

of the corresponding diffraction line) for the samples 0.25-G, 0.43-G, and 0.54-G is 0.637, 0.427, and 0.278, respectively. Such intensity changes have been ascribed in the literature to isomorphous substitution processes in molecular sieves.^{10,11} Another important observation from XRD is the decrease in crystallinity with increasing $[\text{Co}]:[\text{Al}]$ ratio in the solid. Figure 2 shows the SEM picture of sample 0.25-G, which illustrates the presence of hexagonal CoAPO-5 crystals with sizes of 3–10 μm . No other crystalline phases could be observed in this sample. The same observations were made for the other samples, with the exception of sample 0.67-G. SEM in combination with EMMA indicates that sample 0.67-G also possesses chunks of Co- and Al-rich material, and this most probably explains the relatively high $([\text{Co}] + [\text{Al}]):[\text{P}]$ ratio of 1.136 (Table I).

Figure 3 shows the relationship between the unit cell volume expansion (ΔV) and the $[\text{Co}]:[\text{Al}]$ ratio in the

Fig. 3. Unit cell volume expansion (ΔV) for as-synthesized CoAPO-5 materials as a function of the $[\text{Co}]:[\text{Al}]$ ratio in the solid with glycerol (♦) and water (■) as a solvent.

as-synthesized CoAPO-5 solids prepared in the presence of water or glycerol as a solvent. It was found that

1. The unit cell volume of the CoAPO-5 crystals gradually increases with increasing [Co]:[Al] ratio in the synthesis gel for both synthesis procedures. The increase in unit cell volume is a clear indication of the incorporation of Co^{2+} ions in the AlPO_4 -5 structure, since the Co—O bond is longer than the Al—O bond (1.90 vs. 1.72 Å).¹ Thus, the higher the unit cell volume expansion, the higher the isomorphous substitution degree of Co^{2+} in the AlPO_4 -5 framework.
2. The unit cell volume of the as-synthesized materials is always substantially higher for the samples prepared from glycerol-containing gels than from water-containing gels. This clearly indicates that the isomorphous substitution of Co^{2+} ions in AlPO_4 -5 molecular sieves is facilitated when glycerol is used as a solvent.
3. The increase in unit cell volume levels off at a high [Co]:[Al] ratio, that is, at a value of about 0.13 for the hydrothermally synthesized materials and at a value of about 0.38 for the CoAPO-5 materials prepared with glycerol as a solvent. This could indicate the formation of, for example, the extra framework Co species, which are blocking the pore structure of AlPO_4 -5 molecular sieves.

To verify the latter hypothesis, the CoAPO-5 samples were calcined and characterized by N_2 adsorption techniques to determine the accessible pore volume of the molecular sieves. Figure 4 summarizes the results by plotting the pore volume of the CoAPO-5 materials as a function of the [Co]:[Al] ratio in the solids. This figure indicates that the pore volume is close to the theoretical value of 0.140 ml/g and gradually decreases with increasing [Co]:[Al] ratio in the solids. At a low [Co]:[Al] ratio no pore blocking could be observed for the water- and glycerol-based materials. However, for the CoAPO-5 materials synthesized with water the pore volume starts

Fig. 4. Pore volume of the calcined CoAPO-5 materials as a function of the [Co]:[Al] ratio in the solid with glycerol (◆) and water (■) as a solvent.

to decrease at a [Co]:[Al] ratio of 0.08. In contrast, pore blocking started to occur at a [Co]:[Al] ratio of about 0.15 in the case of glycerol-based synthesized materials. These results are quite in line with the unit cell expansions observed with XRD.

All of the as-synthesized solids have a blue or deep blue color, although some traces of pink impurities could be observed as well (Table I). This suggests the presence of tetrahedral Co^{2+} in the framework of the as-synthesized CoAPO-5 and octahedral Co^{2+} present as amorphous cobalt oxide, cobalt-aluminum oxide, or cobalt-phosphorus oxide or present at ion exchange sites. This observation can be studied in more detail by UV-visible-NIR DRS spectroscopy, since this technique is directly probing the d-d transitions of tetrahedral and octahedral Co^{2+} species.¹ As an example, the DRS spectra of sample 0.25-G and 0.25-W are given in Figure 5. It can be concluded that as-synthesized CoAPO-5 material are characterized by a well-resolved triplet band at about 540, 580, and 620 nm, indicating that a substantial fraction of the Co^{2+} ions are present in tetrahedral coordination. The broad band centered around 480 nm, however, is indicative of the presence of octahedral Co^{2+} ions. It is also clear that the amount of octahedral Co^{2+} is higher in sample 0.25-W than in sample 0.25-G. This observation is in line with the XRD and N_2 sorption experiments.

Fig. 5. Deconvoluted UV-visible DRS spectra of as-synthesized CoAPO-5 materials. (a) 0.25-G. (b) 0.25-W.

In an attempt to obtain a more quantitative estimation of the amount of framework Co^{2+} we have deconvoluted the UV-visible-NIR DRS spectra between 400 and 800 nm into a set of four Gaussian bands. The absorption band at 480 nm is due to octahedral Co^{2+} , whereas the three other absorption bands between 500 and 650 nm are assigned to tetrahedral Co^{2+} (Ref. 1). The intensity of the band at 480 nm can then be taken as a measure of the amount of octahedral Co^{2+} ($[\text{Co}^{2+}]_{\text{Oh}}$), whereas the sum of the intensities of the triplet bands in the 500–650-nm range can be used for estimating the amount of tetrahedral Co^{2+} ($[\text{Co}^{2+}]_{\text{Td}}$). The result of this analysis is shown in Figure 5 for samples 0.25-G and 0.25-W. The UV-visible-NIR DRS spectra of the other CoAPO-5 samples were deconvoluted in a similar way, and Figure 6 shows the $[\text{Co}^{2+}]_{\text{Td}}:[\text{Co}^{2+}]_{\text{Oh}}$ ratio in the CoAPO-5 materials obtained with water or glycerol as a solvent as a function of the $[\text{Co}]:[\text{Al}]$ ratio in the solid. It is clear that the $[\text{Co}^{2+}]_{\text{Td}}:[\text{Co}^{2+}]_{\text{Oh}}$ ratio of the as-synthesized samples decreases with increasing $[\text{Co}]:[\text{Al}]$ ratio in the synthesis gel. Taking the $[\text{Co}^{2+}]_{\text{Td}}:[\text{Co}^{2+}]_{\text{Oh}}$ ratio as a measure for substitution degree of Co^{2+} , one can conclude that the substitution degree is always higher in a CoAPO-5 material synthesized with glycerol as a solvent compared with a CoAPO-5 material synthesized with water as a solvent.

Based on the XRD, N_2 -sorption, analytical, and UV-visible-NIR DRS data, it is fair to estimate that the substitution degrees for CoAPO-5 materials prepared in the presence of water and glycerol are about 7.5% and 13%, respectively. The effect of glycerol as a solvent on the isomorphous substitution process is most probably related to the chelating effect of glycerol on Co^{2+} ions. This will result in a slow release of Co^{2+} in the synthesis mixture and a gradual incorporation of Co^{2+} in the growing CoAPO-5 crystals. This may also explain the slow synthesis process of CoAPO-5 materials in the presence of glycerol. Further synthesis studies should be directed toward confirming this hypothesis.

Fig. 6. Estimated $[\text{Co}]_{\text{tetra}}:[\text{Co}]_{\text{octa}}$ ratio of the as-synthesized CoAPO-5 materials as a function of the $[\text{Co}]:[\text{Al}]$ ratio in the solid with glycerol (♦) and water (■) as a solvent.

4. CONCLUSIONS

The following conclusions can be drawn from this study:

1. Glycerol is a much better solvent than water for the synthesis of Co-rich CoAPO-5 molecular sieves. The substitution degree in glycerol-based materials is about 13%, which is substantially higher than that for water-based CoAPO-5 solids.
2. Glycerol results in a slowdown of the crystallization process of CoAPO-5 molecular sieves, and highly crystalline CoAPO-5 materials are obtained after 14 days of synthesis.
3. Attempts to further increase the substitution level failed and led to the formation of an impure, pink amorphous material.
4. A combination of lattice expansion determinations, pore blocking measurements, chemical determination of the $([\text{Co}] + [\text{Al}]):[\text{P}]$ ratios, and spectroscopic determination of the $[\text{Co}^{2+}]_{\text{Td}}:[\text{Co}^{2+}]_{\text{Oh}}$ is necessary for estimating the true substitution degree of Co^{2+} in CoAPO-5 materials.

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