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Thermal investigations of CoAPO materials prepared by using piperidine as a structure-directing agent

Nevenka Rajić[a,b,*], Roman Gabrovšek[a], Venčeslav Kaučič[a,c]

[a]National Institute of Chemistry, P.O. Box 3430, SI-1001 Ljubljana, Slovenia
[b]Faculty of Technology and Metallurgy, University of Beograd, YU-11000 Beograd, Yugoslavia
[c]University of Ljubljana, SI-1001 Ljubljana, Slovenia

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Abstract

Two CoAPO materials (CoAPO-34 and CoAPO-20) with relatively high Co^{2+}/Al^{3+} substitution level were synthesised in either fluoride-free or fluoride-containing reaction mixture using piperidine as a structure-directing agent. Present investigation established that fluoride ions acted only as a mineralising agent and did not impart any structure-directing role. TG-DTG-DSC curves differ considerably for CoAPO-34 and CoAPO-20, thus indicating that thermal decomposition of piperidine proceeds in a different manner for these products. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: CoAPO; Chabazite-like material; Sodalite-like material; Thermal analysis; TG-DTG-DSC

1. Introduction

There have been many efforts directed to the synthesis of transition metal-containing aluminophosphates because of their industrial importance in catalytic processes [1]. Consequently, cobalt is an interesting transition metal cation because the substitution of Co^{2+} for Al^{3+} generates both acid and redox sites in the aluminophosphate framework [2,3].

In the search for catalytic and other properties of metal-containing aluminophosphates (MeAPO-*n*, where *n* denotes specific structure type), a template–host interaction is very important. In that context, we investigated thermal behaviour of piperidine that was used as the template in the crystallisation of two CoAPO materials having relatively high cobalt content.

2. Experimental

The reactants used were piperidine (Aldrich), 85% phosphoric acid (Fluka), aluminium isopropoxide (Aldrich), cobalt(II) acetate tetrahydrate (Merck) and 40% hydrofluoric acid (Fluka).

Two reaction systems were explored in the preparation of CoAPO materials:

$$x\mathrm{CoO} : (0.6 - x)\mathrm{Al_2O_3} : \mathrm{P_2O_5} : 2\mathrm{piperidine} : \mathrm{HF} : 80\mathrm{H_2O}$$

and

$$x\mathrm{CoO} : (0.6 - x)\mathrm{Al_2O_3} : \mathrm{P_2O_5} : 2\mathrm{piperidine} : 80\mathrm{H_2O}$$

The mixtures were prepared by successive additions of phosphoric acid and piperidine to the suspension of aluminium isopropoxide/cobalt-acetate water solution

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[*] Corresponding author. Fax: +386-61-125-9244.

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during vigorous stirring. Hydrofluoric acid was added prior to piperidine for the preparation of fluoride-containing mixture. The hydrothermal crystallisation was performed at 190°C for 24–72 h.

The products were filtered, washed with distilled water and dried at 105°C.

3. Instrumentation

The crystalline products were characterised by X-ray powder diffraction analysis (Phillips PW 1710 diffractometer using Cu Kα radiation). Scanning electron microscopy (SEM) (JEOL JSM 5800) was used for the determination of crystal morphologies and dimensions.

Elemental composition of the products (Al, P, Co) was determined by using JEOL 5800 SEM with energy dispersive X-ray analyser attachment (EDX). Carbon, hydrogen and nitrogen were determined with a standard C-H-N analyser.

Thermal analyses were performed using TG 951 and DSC 910 modules (TA Instruments, USA). Samples were heated in 50 ml/min flow of helium in the temperature range 20–1100°C at a heating rate of 10°C/min.

4. Results and discussion

The fluoride-free and fluoride-containing reaction mixtures were employed for the preparation of CoAPO materials. Namely, fluoride anions have been known to act as a mineralising agent leading to a slower nucleation and yielding crystals of larger size, and thus suitable for structure determination [4,5]. The fluoride ions can also play a structure-directing role and can be incorporated into APO framework [6]. Furthermore, the presence of fluoride ions in a reaction mixture allows the preparation of cobalt(II) substituted pure silica ZSM-5 molecular sieve [7]. The percentage of cobalt(II) substitution is usually low, and that is why we introduced HF into a CoAPO reaction mixture with an attempt to ease the incorporation of Co^{2+} ions into an APO framework to a greater extent.

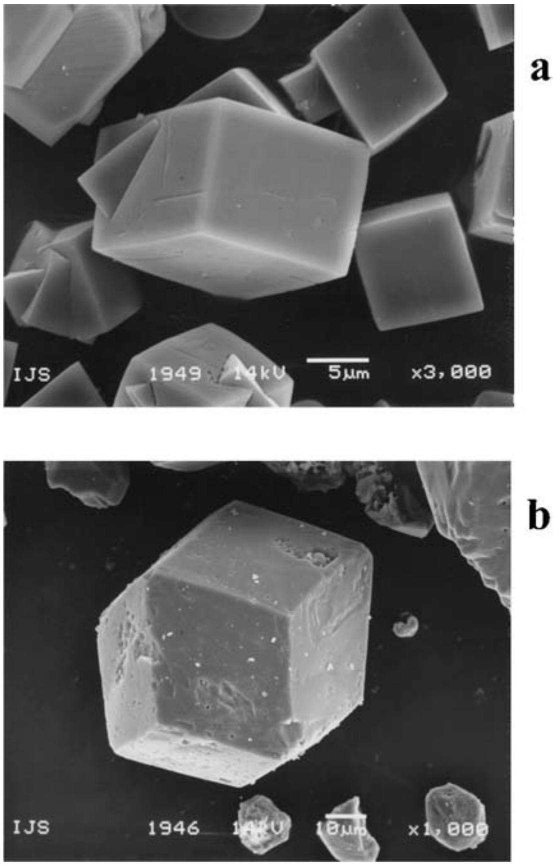

Fig. 1. SEM micrographs of CoAPO-34 (a) and CoAPO-20 (b).

Various reaction mixture compositions were examined in the course of synthesis (see Section 2), and only the composition with x=0.2 resulted in the formation of highly crystalline pure CoAPO phases. The compositions with x<0.2 yielded the products with lower Co contents and with traces of amorphous phases, whereas in the reaction mixtures with x>0.2 products that contained amorphous solids as the major phase were formed. Further discussion thus refers only to the products formed in the reaction systems with x=0.2.

Scanning electron micrographs (Fig. 1) show that synthetic products are highly crystalline and that the morphology of particles depends on the presence of fluoride ions in the reaction mixture. Cubes and truncated-edge cubes with similar size of about 30 µm crystallise from fluoride-free and fluoride-containing reaction mixture, respectively.

The presence of fluoride ions in the reaction mixture also affects the chemical composition of products.

However, since no fluorine was found in the product obtained from the fluoride-containing mixture, it seems likely that in systems investigated fluoride ions only acted as a mineralising agent (i.e. fluoride ions do not impart a templating effect). It is worth noticing that a fluoride-containing CoAPO (i.e. triclinic chabazite-like CoAPO-34) also forms in a similar reaction system with a lower Co/Al and higher Al/P molar ratios [6].

Elemental analysis of the as-synthesised products when considering TGA and C-H-N-analysis results gives the following chemical formulas:

$Co_{0.25}Al_{0.75}PO_4\cdot 0.13$ piperidine$\cdot 0.15$ H_2O for the product formed from fluoride-free mixture, and $Co_{0.2}Al_{0.8}PO_4\cdot 0.4$ piperidine for the product obtained from fluoride-containing reaction mixture.

The molar fraction sum for Co+Al=1 reveals Co^{2+}/Al^{3+} framework substitution in both products. The negative framework charge, resulting from the replacement of Al^{3+} by Co^{2+}, may be compensated by both piperidinium cation and H_3O^+ for CoAPO-34, or by piperidinium cation for CoAPO-20. Additionally, it can be seen that for both products a relatively high level of Co/Al substitution is evident.

The XRD patterns of the products and of dried reaction mixtures[1] are given in Fig. 2. The material obtained from the fluoride-free mixture displays the XRD pattern corresponding to as-synthesised CHA-zeolite (CoAPO-34), whereas the pattern of the product obtained from fluoride-containing medium is in agreement with that of SOD-zeolite (CoAPO-20) [8]. It is interesting to note that SAPO-34 and SAPO-20 were also found as competing phases, but with their formation depending on piperidine content in a fluoride-free reaction mixture [9]. Moreover, it is evident that CoAPO-20 crystallises from an amorphous reaction mixture, whereas CoAPO-34 forms from relatively ordered (polycrystalline) reaction mixture. This is an additional support for the mineralising role of fluoride ions that solubilise framework-forming elements, thus slowing the crystallisation.

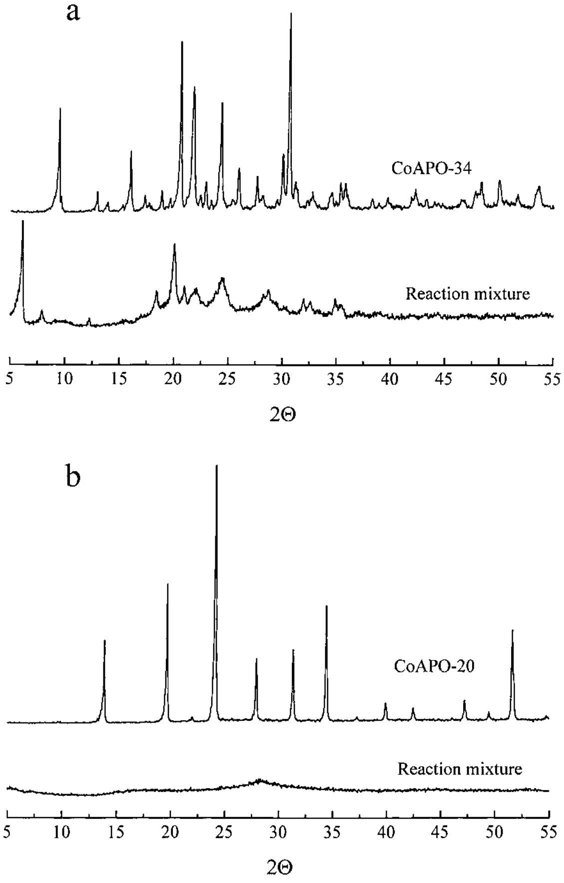

Fig. 2. XRD patterns of CoAPO-34 and the reaction mixture from which it crystallises (a), and CoAPO-20 and its reaction mixture (b).

TG analysis of the fluoride-free containing reaction mixture, shows a 4.5% weight loss up to 150°C, and the overall weight loss up to 700°C of about 45%. The TG curve of the fluoride-containing reaction mixture shows rather continuous weight loss up to 700°C, and the overall weight loss after calcination is about 34% (Fig. 3). DTG curve of the fluoride-free containing mixture shows a major weight loss in the lowest temperature range (up to 200°C there is 30% weight loss) which is due to water elimination. The weight loss for the fluoride-containing mixture in the same temperature range is 15%. This indicates that the fluoride ions not only act as the mineralising agent but also affect the nucleation, i.e. the presence of fluoride ions influences the level of piperidine in the reaction mixture. It is interesting that an increase of SAPO-20 content in the product (comprising the mixture of SAPO-20 and SAPO-34) was correlated with the increase of the piperidine content in the reaction mixture [9].

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[1] The mixtures were dried at a room temperature.

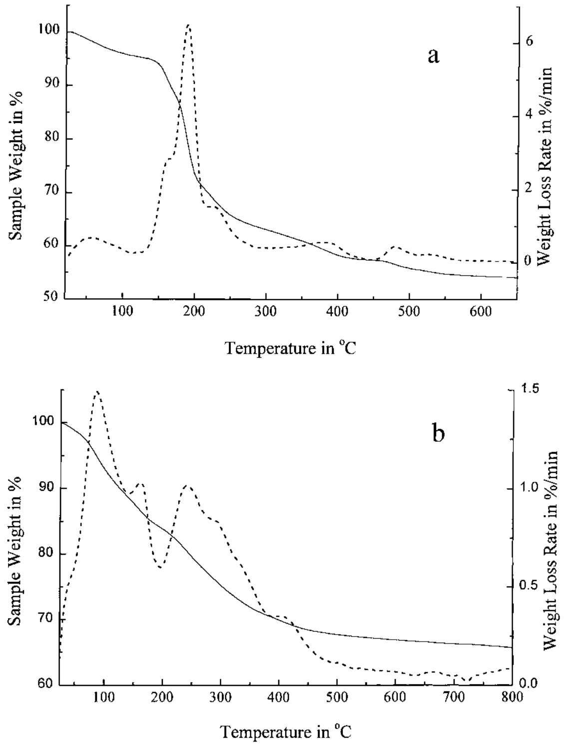

Fig. 3. TG (solid line) and DTG (dashed line) curves of fluoride-free (a) and fluoride-containing reaction mixture (b).

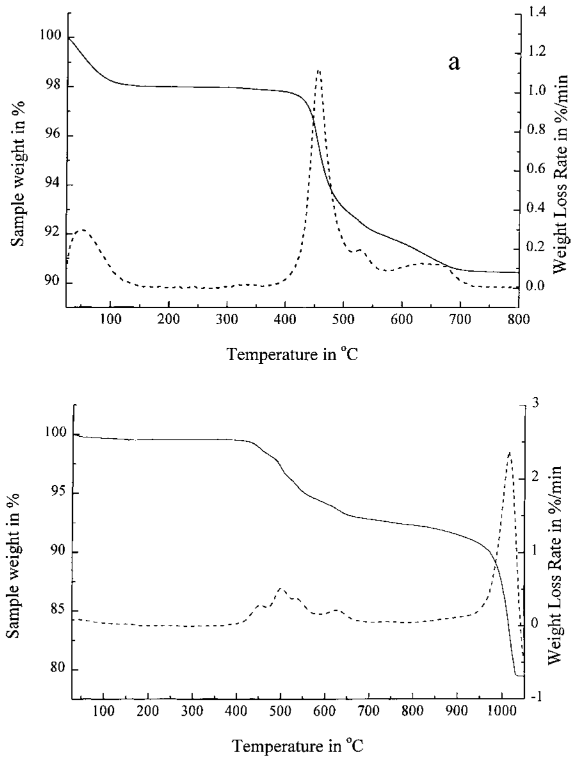

Fig. 4. TG (solid line) and DTG (dashed line) curves of CoAPO-34 and CoAPO-20 (b).

Fig. 4 shows TG curves for the decomposition of the CoAPO products. It can be seen that the decomposition patterns of the CoAPO materials differ. The TG curve of CoAPO-34 exhibits the first weight loss (~2%) which nears completion at ~150°C. The weight loss is accompanied by a broad maximum centred at 50°C in the DTG curve, corresponding to both the physically adsorbed water molecules as well as to water molecules occluded in the pores. Namely, since there is not enough piperidine molecules for adjusting the framework charge neutrality (as a reminder, Al^{3+} replacement by Co^{2+} causes negatively charged framework), some of water molecules must also be protonated. It is most likely that protonated water molecules are trapped inside the cavities. However, a clear distinction between the adsorbed and bound water molecules could not be ascertained.

The TG curve of CoAPO-20 does not exhibit any weight loss up to 400°C, indicating that there are no water molecules trapped inside sodalite cavities. Thus, both CoAPOs exhibit a plateau up to ~400°C. The second part of TG curves (t>400°C) indicates the decomposition of piperidine. It is evident that this decomposition proceeds in a different manner for CoAPO-20 and CoAPO-34. Namely, piperidine gradually decomposes in CoAPO-34 product with the decomposition completed at about 700°C (7.5% weight loss). A sharp maximum in the DTG curve at 454°C suggests a uniform decomposition of piperidine. For CoAPO-20 product, the removal of piperidine proceeds in two distinct stages and the process is terminated at higher temperature (at ~1020°C). The first stage occurs at 400–800°C (9.5% weight loss) and it is accompanied by several, well-resolved DTG maxima (450, 500, 540 and 630°C), whereas the second stage, at 800–1050°C (11.3% weight loss) shows a sharp DTG maximum at 1010°C. This indicates that the piperidine molecules inside the CoAPO-20 framework are non-equivalent. This phenomenon could be related to CoAPO-20 chemical formula.

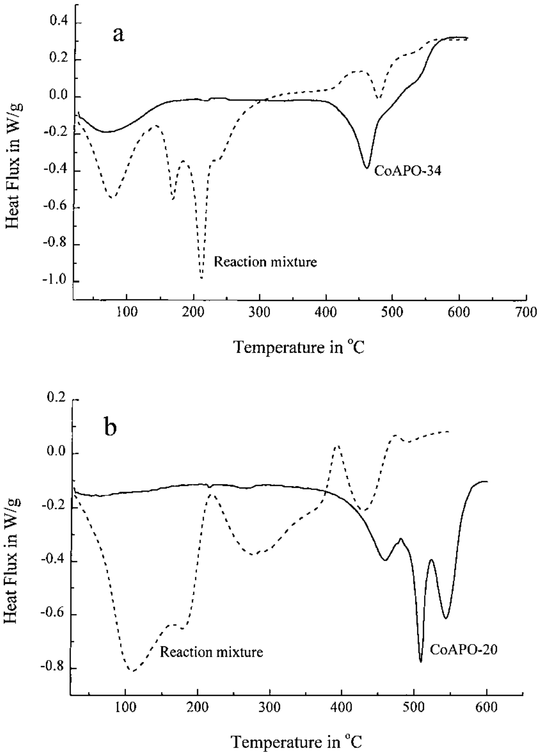

Fig. 5. DSC curves of CoAPO-34 and the reaction mixture from which it crystallises (a), and CoAPO-20 and its reaction mixture (b).

Namely, half of the total amount of piperidine might be protonated since the piperidinium cations act as a compensation for the negative framework charge. Moreover, the high temperature of the last decomposition stage indicates that trapped species are tightly bound to the CoAPO framework. It could also be added that a preliminary single crystal structure determination of the CoAPO-20 shows a peculiar disorder of piperidine molecules inside sodalite cavities.[2]

DSC profiles are given in Fig. 5. Endothermic effects in DSC curves accompany all weight losses. While the reaction mixtures exhibit rather similar DSC patterns, thermal behaviour of CoAPO-34 and CoAPO-20 differs.

The endotherms below 400°C are due to water elimination. There are four endotherms in the range 25–400°C for both reaction mixtures. The fluoride-free mixture exhibits endotherms at 79, 168, 212 and 238°C, while for the fluoride-containing reaction mixture the endotherms appear at 110, 180, 276 and 294°C. It is evident that the fluoride-containing mixture displays the endotherms at higher temperatures if compared with fluoride-free one in the range 25–400°C. It seems likely that the linkages of the water molecules inside (or between) framework building units are also affected by the mineralising role of the fluoride ions. At temperatures above 400°C there is only one endotherm for both reaction mixtures and it corresponds to piperidine decomposition. For fluoride-containing mixture the endotherm is at lower temperature (430°C) than for the fluoride-free one (478°C). This may be due to the fact that the fluoride-free mixture is polycrystalline (in contrast to the fluoride-containing mixture being amorphous) and that piperidine interacts strongly with CoAPO skeleton.

DSC profiles of CoAPO-34 and CoAPO-20 products are significantly different, thus reflecting different thermal behaviour of these materials. CoAPO-34 shows a broad endotherm at around 70°C (due to water desorption), whereas CoAPO-20 does not display any endotherm up to 460°C. CoAPO-20 has three well-resolved endotherms at 460, 540, and 544°C (corresponding to the removal of piperidine) indicating again that all piperidine molecules inside CoAPO-20 skeleton are non-equivalent and that the removal of piperidine does not proceed uniformly. In contrast to CoAPO-20, CoAPO-34 has a sharp endotherm at 458°C and a shoulder at 540°C indicating a rather uniform decomposition of piperidine.

5. Conclusion

Until now, piperidine has been known as a structure-directing agent for the preparation of triclinic $AlPO_4$-34 and MeAPO-34 in a fluoride medium [6]. Recently, piperidine was also used for the preparation of SAPO-34 in a fluoride-free medium [9].

In the present investigation piperidine was found to act as the structure-directing agent for CoAPO-34, but CoAPO-20 formation required also the presence of fluoride ions in reaction mixture. The fluoride ions in the latter case, however, had only a mineralising role and did not impart any structure-directing effect.

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[2] Fluoride synthetic route in this investigation allowed the formation of crystals of CoAPO-20 suitable for single crystal determination. The structure refinement is in progress.

Although both CoAPO materials belong to the class of microporous solids with a small pore size (3–4 Å), the decomposition of piperidine proceeds in a different manner. This fact suggests that piperidine–host interactions strongly depend on the structural type of CoAPO skeleton.

References

[1] G. Bellusi, M.S. Rigutto, in: J.C. Jansen, M. Stocker, H.G. Karge, J. Weitkamp (Eds.), Advanced in Zeolite Science and Applications, Elsevier, Amsterdam, 1994, pp. 177–213.

[2] M. Hartmann, L. Kevan, Chem. Rev. 99 (1999) 635.

[3] K.J. Chao, A.C. Wei, H.C. Wu, J.F. Lee, Catal. Today 49 (1999) 277.

[4] L.V.C. Rees, S. Chandrasekhar, Zeolites 13 (1993) 534.

[5] B. Feron, J.L. Guth, N. Mimouni-Erddalane, Zeolites 14 (1994) 177.

[6] N. Rajic, R. Gabrovsek, A. Ristic, V. Kaucic, Thermochim. Acta 306 (1997) 31.

[7] C.I. Round, C.D. Williams, C.V.A. Duke, J. Chem. Soc., Chem. Commun. (1997) 1849.

[8] M.M. Treacy, J.B. Higgins, R. von Ballmoos, Collection of Simulated XRD Powder Patterns for Zeolites, 3rd Revised Edition, Zeolites 16 (1996).

[9] E. Dumitriu, A. Azzouz, V. Hulea, D. Lutic, H. Kessler, Microporous Mater. 10 (1997) 1.