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In situ synthesis of $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films on alumina substrates

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The *in situ* synthesis of $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films supported on alumina substrates was reported in this paper. Continuous $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films could be formed on alumina substrates at 170–200°C for 24 h. It was found that after calcination, $AlPO_4$-14 films peeled off from the alumina supports, while CoAPO-44 films turned to be amorphous. No changes could be observed on ZnAPO-34 films before and after calcination, indicating good thermal stability of ZnAPO-34 films.

1. Introduction

Zeolite molecular sieves are usually produced in the form of powders. For practical utilization, they have to be formed to certain configuration using binders. The present technology can make zeolite molecular sieve films by growing them directly on the surfaces of supports, so that they can be used as catalysts and adsorbents. Furthermore, zeolite molecular sieve films are very good candidates for gas separation membranes, sensors, and nonlinear optical materials [1]. Because of these, they have been of great interests for the past decade.

Up to now, some kinds of aluminosilicate zeolite films have been reported. Many groups around the world successfully prepared MFI-type zeolite films on ceramic, metals, and metal oxide supports by *in situ* hydrothermal synthesis [1, 2]. In addition, Zeolite A, X, ZSM-5, silicalite-1, UTD-1, and L films were also synthesized by secondary growth [3–8]. ZSM-5, ZSM-35, ferrierite, and mordenite zeolite films were fabricated by the so-called vapor-phase transport method [9–11]. Even meso- and micro-porous silicate MCM-41, MCM-48, and MCM-22 films could synthesize on mica, water, graphite, stainless steel, and glass surfaces, respectively [12–16].

Aluminophosphate and isomorphorous substituted aluminophosphate with metal cations, denoted as $AlPO_4$-n and MeAlPO-n respectively, is another family of molecular sieves with unique zeolitic pore structure. For aluminophosphate molecular sieves films, Sano *et al.* [17] synthesized polycrystalline SAPO-5 film on a Teflon slab, and Wu *et al.* [18] prepared $AlPO_4$-5, $VAPO_4$-5 and CoAPO-5 films on anodic alumina substrates, both by *in situ* hydrothermal synthesis. Mintova *et al.* [19] reported the preparation of $AlPO_4$-5 molecular sieve films by microwave synthesis. Balkus *et al.* [20, 21] prepared FeAPO-5 and MAPO-39 films by secondary growth. Zhang *et al.* [22] and Poshusta *et al.* [23] reported the successful preparation of SAPO-34 films on alumina supports and used as gas-separation membranes.

Compared with aluminosilicate zeolite films, aluminophosphate molecular sieve films are not much in terms of variety. Most of the research lay in the AFI-type molecular sieves. AFI-type molecular sieves consist of 12-membered ring channels with a diameter of 0.73 nm and unidimensional channel structure, which limit the use of AFI-type molecular sieve films in some aspects, such as gas separation membranes and permanent gas sensors.

We herein reported the preparation of $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films on alumina supports by *in situ* hydrothermal synthesis. Unlike AFI-type molecular sieves, all of these molecular sieves have a pore size of 0.43 nm and three-dimension channel structure.

2. Experimental

2.1. Materials

Two kinds of alumina supports were used. One was non-porous alumina film substrate from Intertec Southwest LLC (99.8%, 1" × 0.5" × 0.040"), which was cut into 2 cm × 1 cm squares. Another was porous alumina tube from Coors Ceramic Company. The tube had an outer diameter of 8 mm, inner diameter of 6 mm, and

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TABLE I Compositions and conditions for the synthesis of molecular sieve films

Molecular sieve	Composition	Synthesis condition
$AlPO_4$-14	$1Al_2O_3 : 1P_2O_5 : 2i\text{-}PrNH_2 : 400H_2O : 0.25H_2SO_4$	200°C, 24 h
CoAPO-44	$0.4CoO : 0.8Al_2O_3 : 1P_2O_5$: Cyclohexylamine : $50H_2O$	170°C, 24 h
ZnAPO-34	$1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 2TEAOH : 225H_2O$	170°C, 24 h

average pore size of 0.2 μm. The tube was cut into 2 cm pieces in length. All substrates were cleaned by boiling in acetone for 2 h, treating in ultrasonic for 5 min, rinsing with distilled water and drying at 100°C overnight before use.

Regents used were zinc (II) acetate dehydrate, cobalt acetate tetrahydrate, aluminum isopropoxide, orthophosphoric acid (85%), isopropylamine (99%, i-$PrNH_2$), cyclohexylamine (99%), tetraethylammonium hydroxide (TEAOH, 35%), and sulfuric acid (H_2SO_4). All the chemicals were from Aldrich and used as received.

2.2. Synthesis

Materials and compositions for the preparation of reaction mixtures and crystallization conditions were listed in Table I. The detail procedures for the preparation of the hydrogel were similar to those reported in literatures for synthesis of $AlPO_4$-14 [24], CoAPO-44 [25] and ZnAPO-34 molecular sieves [26].

Syntheses of the films were carried out in 23 ml Teflon-lined autoclaves from Parr Instrument Company. The substrates, both nonporous alumina plates and porous alumina tubes, were installed vertically in Teflon holders so that no crystals formed in the solution could deposit on the substrates. For the synthesis of $AlPO_4$-14 films, only porous alumina tubes were used; while for CoAPO-44 films and ZnAPO-34 films, only nonporous alumina plates were used.

Calcination of the films were conducted in a quartz tube at 380°C or 400°C in air or under vacuum for 4 h with a heating rate of 1°C/min.

2.3. Characterization

X-ray diffraction (XRD) was used to determine the structure of the molecular sieve films, which was carried out on a Scintag XDS 2000 diffractometer using Cu-K$_\alpha$ radiation, with a scan speed of 5°/min.

Scanning electron microscopy (SEM) was used to observe the morphology, the crystal size, the film thickness and the continunity of the molecular sieve films, using a Camscan Instrument operating at 15 KV.

3. Results and discussions

3.1. $AlPO_4$-14 films

$AlPO_4$-14 films were prepared on porous alumina tubes. Fig. 1a shows the XRD patterns of the film. Since the support was not flat, the XRD peaks shifted a little. The patterns were composed of the peaks ascribed to α-alumina and $AlPO_4$-14. Fig. 2a shows the SEM photograph of the surface of the film. It could be seen that all the support surface was covered by tabular crystals and most crystals were oriented to the c-direction. $AlPO_4$-14 powders have tabular habit [27], which was the same as those on the film. Both XRD and SEM results revealed that $AlPO_4$-14 could form films on porous alumina supports. Voids could be observed on the surface of the film from the SEM picture. The surface of the porous alumina support could not be seen, however. The cross-sectional view of the film (see Fig. 1b) shows that the film was compact. The thickness of the film was ca. 25 μm.

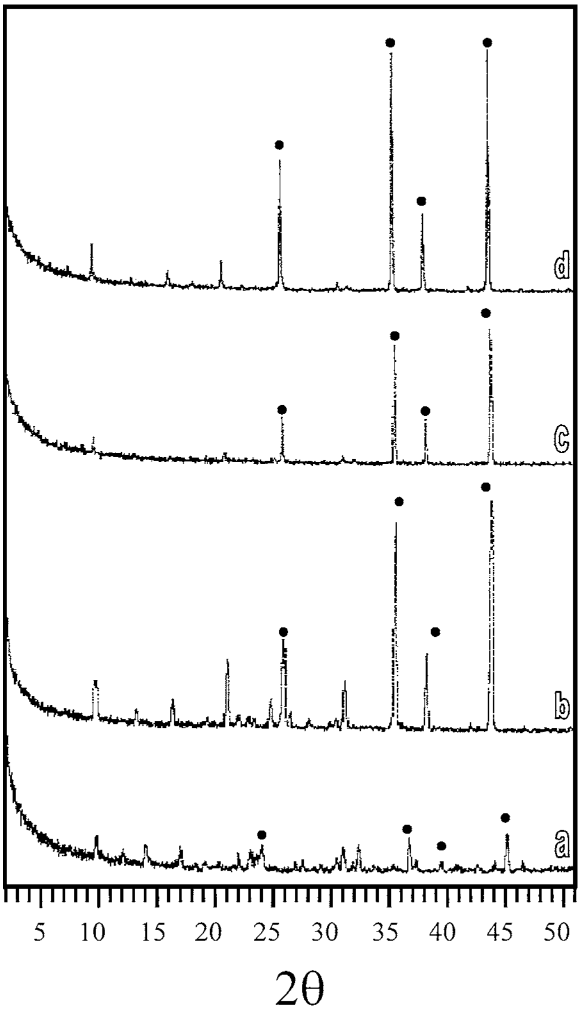

Figure 1 XRD patterns of aluminophosphate molecular sieve films. (a) as-synthesized $AlPO_4$-14 film on porous alumina tube, (b) as-synthesized CoAPO-44 film on dense alumina plate, (c) calcined CoAPO-44 film on dense alumina plate, (d) as-synthesized ZnAPO-34 film on dense alumina plate.

3.2. CoAPO-44 films

CoAPO-44 films were prepared on dense alumina plates. When the plate was taken out of the autoclave

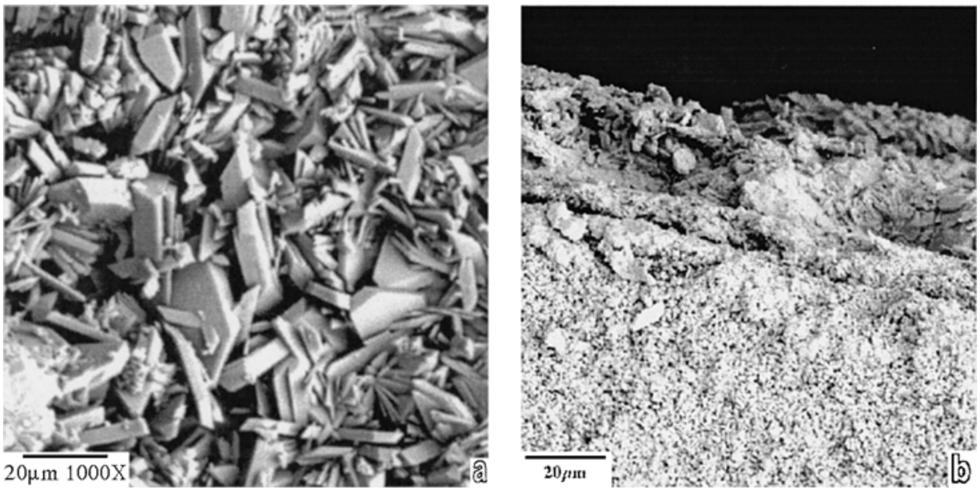

Figure 2 SEM photographs of $AlPO_4$-14 film on a porous alumina substrate. (a) Top-view, (b) cross-sectional view.

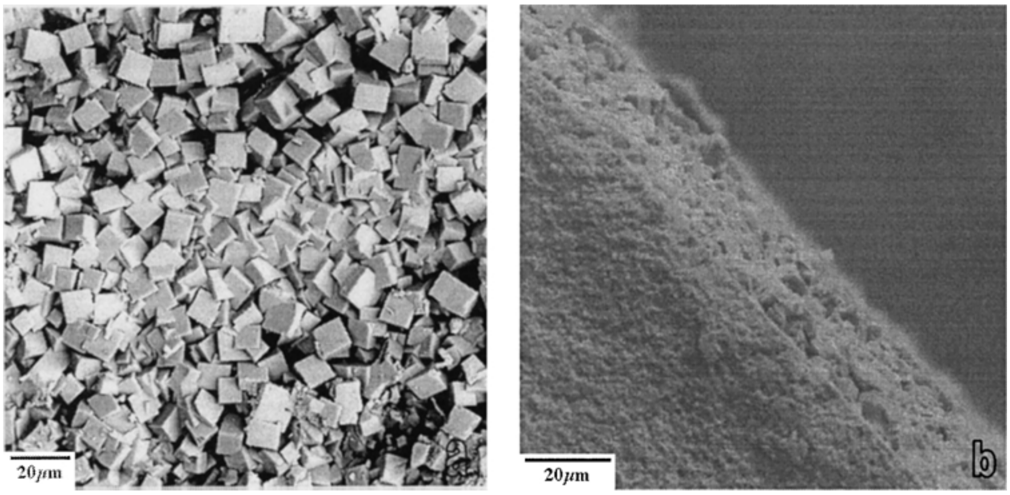

Figure 3 SEM photographs of a CoAPO-44 film on a dense alumina plate. (a) Top-view, (b) cross-sectional view.

after the completion of the synthesis, the white color of the alumina plate turned to be blue, indicating the attachment of new substance to the plate. The color was consistant to the color of CoAPO-44 powders, which had a color of deep blue to light blue depending on the cobalt content [28]. Fig. 1b shows the XRD patterns of the film. It could be seen that the patterns were composed of the characteristic peaks ascribed to α-alumina and CoAPO-44 molecular sieve. Fig. 3a shows the SEM photograph of the surface of the film, which reveals that the film was composed of cube-like crystals, which was the habit of CoAPO-44 crystals [28]. Most of the crystals were intergrown together and oriented to one direction. The crystal size was very uniform and was ca. 10 μm. Although some parts of the film had large voids, the surface of the alumina support could not be observed. On the other hand, the cross-sectional view of the film (see Fig. 3b) shows that the film was compact. The thickness of the film was ca. 20 μm.

3.3. ZnAPO-34 films

Preparation of ZnAPO-34 films was conducted on dense alumina plates using composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 2TEAOH : 225H_2O$. XRD patterns of the film, as shown in Fig. 1d, were composed of the characteristic peaks ascribed to α-alumina and ZnAPO-34 molecular sieve. Fig. 4a shows the SEM photograph of the surface of the film. Most of the support surface was covered with cube-like crystals, which was intergrown together. The crystal size was very uniform and was less than 10 μm. The surface of the alumina could also be seen from this SEM picture, indicating that the ZnAPO-34 film was not continuous. In this case, repeated syntheses were conducted. Fig. 4b shows the SEM photograph of the the film after 4 cycles of syntheses. It was apparent that all the surface of the support were covered with crystals. The crystals were all intergrown together and the size was a little bit bigger than the that after only one synthesis. Fig. 4c shows the SEM picture of the cross-section of the film. The thickness of the film was ca. 15 μm.

3.4. Calcination of the films

Zeolite molecular sieve films synthesized in the presence of organic template should be activated to free the organics which block the pores of the molecular sieves before they can be used. Before calcination at high temperature, the thermal stability of the molecular sieve should be considered since the high temperature stability of $AlPO_4$s is dependent on the Al coordination [29].

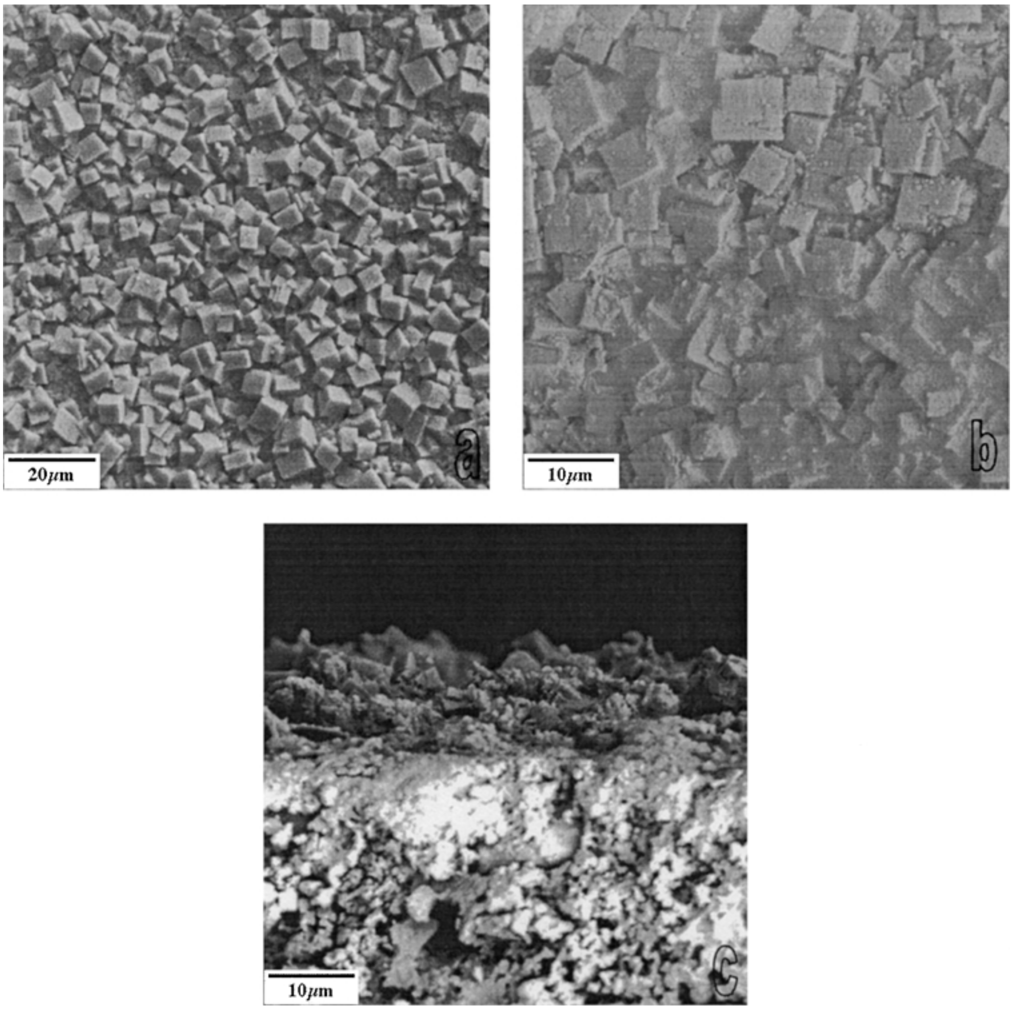

Figure 4 SEM photographs of a ZnAPO-34 film on a dense alumina plate. (a) one synthesis, (b) 4 cycles of synthesis, (c) cross-sectional view.

For metal substituted $AlPO_4$s, some of them were reported to be unstable at high temperature. For example, MAPO-43 starts to collapse above only 653 K [30].

After calcined at 380°C both in air and under vacuum, $AlPO_4$-14 films were observed to peel off. XRD patterns of the peeled powder were amorphous. Fig. 5a illustrates the SEM picture of the calcined $AlPO_4$-14 film. It could be seen that only a few broken $AlPO_4$-14 crystals scattered on the support. In order to test if the film was not strong even before the calcination, an as-synthesized $AlPO_4$-14 film was sonicated in water for 20 min. No any falling of powders could be observed after the sonication. The reason for the peel-off was not clear. However, solid-state NMR spectroscopy showed that both octahedrally and tetrahedrally coordinated aluminum existed in as-synthesized $AlPO_4$-14 molecular sieve, and that calcination transformed all aluminum atoms into tetrahedral coordination [27]. Accordingly, calcination of as-synthesized $AlPO_4$-14 powder led to pronounced structured changes [27]. Perhaps it was the structural changes that resulted in the peel-off of $AlPO_4$-14 films after calcination.

Calcination of CoAPO-44 films were conducted at 380°C under vacuum. When the calcination was completed, it was found that the color of the films turned from blue to black. XRD patterns of the calcined film (Fig. 1c) shows that most peaks ascribed to CoAPO-44 vanished. SEM photograph of the calcined film (Fig. 5b) reveals that cubic crystals of CoAPO-44 could not be observed, and only amorphous substance existed on the support. The above result indicated that there must be some structure change of the CoAPO-44 films after the calcination.

Lohse *et al.* [28] reported that CoAPO-44 was stable under 873 K and the green color was characteristic of the calcined sample. Their research results indicated that the color of calcined CoAPO-44 changed from green to black after adsorption of water [28]. However, it seemed impossible in our experiment that the calcined film may adsorb water in vacuum. They also reported that heating of the calcined, hydrated CoAPO-44 powder at 473 K led to the destruction of the structure [28]. In our case, the structure of CoAPO-44 film seemed to be destroyed even after the finishing of calcination without being rehydrated and heated. Further work should be done to tackle the reasons.

For ZnAPO-34 powder, when calcination is performed in air, a structure transformation occurs alreadly at 400°C [26]. Therefore, calcination of ZnAPO-34 films were conducted under vacuum or in an inert atmosphere. Fig. 5c shows the morphology of a ZnAPO-34 film calcined under vacuum. No significant changes can be observed, except for some small particles, which were assumed to be carbon orignated from calcination under vacuum. XRD patterns of the calcined film show no difference from those of as-synthesized

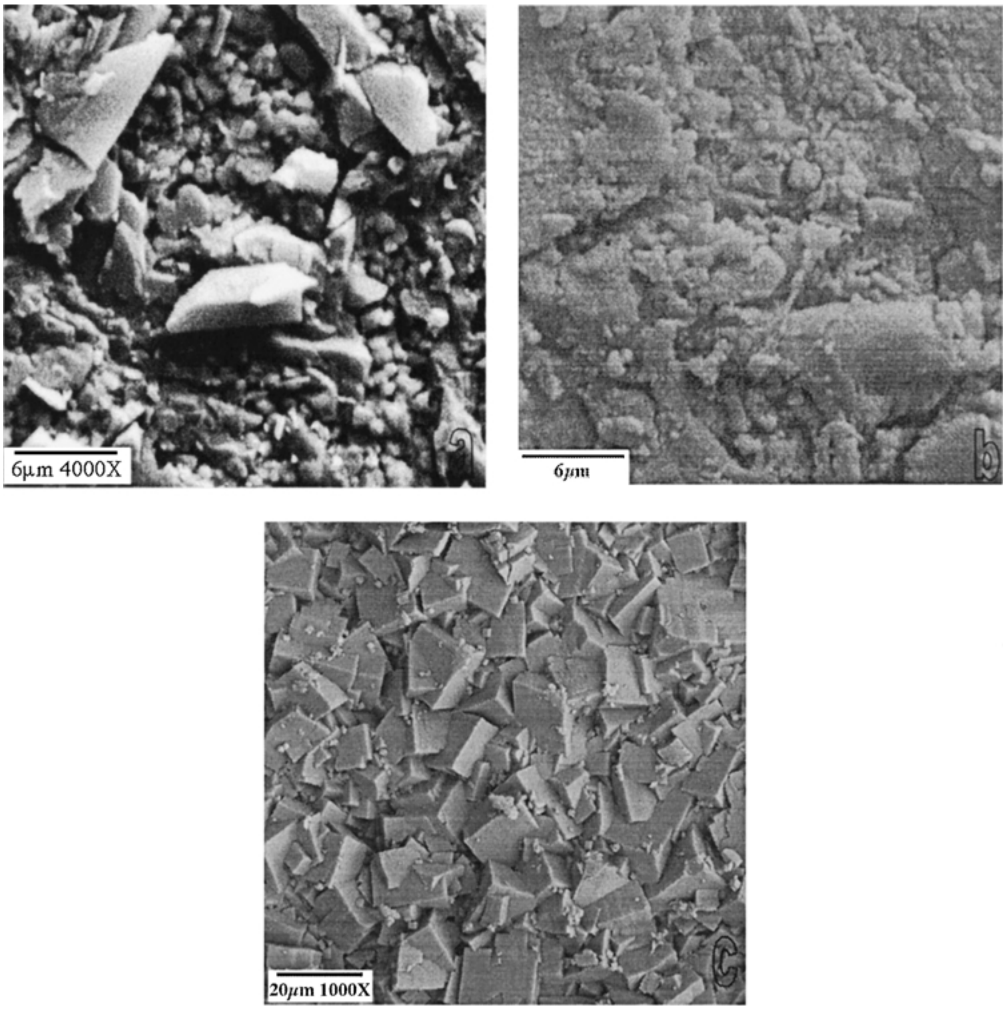

Figure 5 SEM photographs of calcined molecular sieve films. (a) $AlPO_4$-14 film, (b) CoAPO-44 film, (c) ZnAPO-34 film.

sample. ZnAPO-34 films had reasonable thermal stability.

From the above experimental results, it could be seen that $AlPO_4$-14 films could not stand at 400°C both in air and under vacuum; CoAPO-44 films might encounter structure change after calcined at 380°C in vacuum; ZnAPO-34 had resonable thermal stability. Although CoAPO-44 powder was stable under 873 K [28], CoAPO-44 film was not stable. This phenomena also happened on MAPO-39 films. Balkus *et al.* [21] found that MAPO-39 crystals might be calcined at 500°C for 24 h or 48 h, but MAPO-39 film was not stable to be calcined at this temperature. After calcination in air at 500°C for 4 h, the MAPO-39 film appearance changed from continuous white or light gray to patchy brown and the structure collapsed yielding an amorphous powder XRD pattern [21]. In all, the thermal stability of aluminophosphate molecular sieve films were not well-known. From the limited reports, we knew that SAPO-34 films could be calcined in air at up to 400°C [22, 23] and FeAPO-5 films could be calcined at 400°C for 6–8 h [20].

4. Conclusions

$AlPO_4$-14, CoAPO-44 and ZnAPO-34 films supported on alumina supports could be successfully prepared by *in situ* hydrothermal synthesis. After calcination, $AlPO_4$-14 films peeled off from porous alumina supports, while CoAPO-44 films turned to be amorphous. However, no any changes could be observed on ZnAPO-34 films before and after calcination, implying good thermal stability of ZnAPO-34 films.

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References

1. T. BEIN, *Chem. Mater.* **8** (1996) 1636.
2. R. LAI and G. R. GAVALAS, *Microporous Mesoporous Mater.* **37** (2000) 9.
3. L. C. BOUDREAU and M. TSAPATSIS, *Chem. Mater.* **9** (1997) 1705.
4. A. GOUZINIS and M. TSAPATSIS, *ibid.* **10** (1998) 2497.
5. S. MINTOVA, J. HEDLUND, V. VALTCHEV, B. SCHOEMAN and J. STERTE, *Chem. Commun.* (1997) 15.
6. K. KUSAKABE, T. KURODA, A. MURATA and S. MOROOKA, *Ind. Eng. Chem. Res.* **36** (1997) 649.
7. K. J. BALKUS, JR., T. MUNOZ, JR. and M. E. GIMON-KINSEL, *Chem. Mater.* **10** (1998) 464.
8. M. C. LOVALLO, M. TSAPATSIS and T. OKUBO, *ibid.* **8** (1996) 1579.
9. J. DONG, T. DOU, X. ZHAO and L. GAO, *J. Chem. Soc., Chem. Commun.* (1992) 1056.

10. M. MATSUKATA and E. KIKUCHI, *Bull. Chem. Soc. Jpn.* **70** (1997) 2341.
11. T. MATSUFUJI, N. NISHIYAMA, K. UEYAMA and M. MATSUKAT, *Microporous Mesoporous Mater.* **32** (1999) 159.
12. H. YANG, A. KUPERMAN, N. COOMBS, S. MAMICHE-AFARA and G. A. OZIN, *Nature* **379** (1996) 703.
13. H. YANG, N. COOMBS, I. SAKOLOV and G. A. OZIN, *ibid.* **381** (1996) 589.
14. I. A. AKSAY, M. TRAU, S. MANNE, I. HONMA, N. YAO, L. ZHOU, P. FENTER, P. M. EISENBERGER and S. M. GRUNER, *Science* **273** (1996) 892.
15. N. NISHIYAMA, A. KOIDE, Y. EGASHIRA and K. UEYAMA, *Chem. Commun.* (1998) 2147.
16. M. CHENG, D. TAN and X. BAO, *ibid.* (2000) 1713.
17. T. SANO, Y. KIYOZUMI, K. MAEDA, M. TOBA, S. NIWA, F. MIZUKAWI, I. MUKOYOSHI and H. SHOJI, *J. Mol. Catal.* **77** (1992) L19.
18. C. N. WU, K. J. CHAO, T. G. TSAI, Y. H. CHIOU and H. C. SHIN, *Adv. Mater.* **8** (1996) 1008.
19. S. MINTOVA, S. MO and T. BEIN, *Chem. Mater.* **10** (1998) 4030.
20. T. MUNOZ, JR. and K. J. BALKUS, JR., *ibid.* **10** (1998) 4114.
21. L. WASHMON-KRIEL and K. J. BALKUS, JR., *Microporous Mesoporous Mater.* **38** (2000) 107.
22. L. ZHANG, M. D. JIA and E. MIN, *Stud. Surf. Sci. Catal.* **105** (1997) 2211.
23. J. C. POSHUSTA, V. A. TUAN, J. L. FALCONER and R. D. NOBLE, *Ind. Eng. Chem. Res.* **37** (1998) 3924.
24. C. FERNANDEZ, J. P. AMOUREUX, J. M. CHEZEAU, L. DELMOTTE and H. KESSLER, *Microporous Mater.* **6** (1996) 331.
25. H. S. HAN and H. CHON, *ibid.* **3** (1994) 331.
26. N. N. TUSAR, V. KAUCIC, S. GEREMIA and G. VLAIC, *Zeolites* **15** (1995) 708.
27. B. ZIBROWIUS, U. LOHSE and J. RICHTER-MENDAU, *J. Chem. Soc., Faraday Trans.* **87** (1991) 1433.
28. U. LOHSE, R. BERTRAM, K. JANCKE, I. KURZAWSKI and B. PARLITZ, *ibid.* **91** (1995)1163.
29. J. A. MARTENS and P. A. JACOBS, *Stud. Surf. Sci. Catal.* **85** (1994) 653.
30. D. B. AKOLEKAR and S. K. KALIAGUINE, *Zeolites* **14** (1994) 620.

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