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Preparation of ZnAPO-34 films on alumina substrates

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The hydrothermal synthesis of ZnAPO-34 films supported on alumina substrates was reported in this paper. Synthesis parameters of the films were extensively examined. Organic content, water content, alumina source, and supports played important roles in the syntheses of ZnAPO-34 films. The best synthesis composition was found to be $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 2TEAOH : 225–550H_2O$ with aluminum isopropoxide as alumina source. However, repeated syntheses were necessary to synthesize contineous ZnAPO-34 films on both nonporous an porous alumina supports.

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1. Introduction

Zeolite and molecular sieve films have attracted much attention in recent years because they can be potentially applied as structured catalysts, membranes and sensors [1]. Up to now, research in this field has been mainly focused on the synthesis of zeolite films and membranes on various substrates, such as zeolite A [2, 3], silicalite-1 [4, 5], ZSM-5 [6, 7], ZSM-35 [8], Y [9], L [10], ferrierite [11], mordenite [12], etc. Among these zeolite films and membranes, most of them have a pore size larger than 0.5 nm. Zeolite films and membranes with pore size around 0.4 nm are not common.

Aluminophosphate, $AlPO_4$-n, and isomorphorous substituted aluminophosphate, MeAlPO-n, are another family of molecular sieves with unique zeolitic pore structure. At present, more than 50 different crystal structure of $AlPO_4$ have been reported, making the aluminophosphates an important class of microporous crystals [13]. Comparing with zeolites which are used for the preparation of molecular sieve films and membranes, alumonophosphate molecular sieves being used are few. Sano *et al.* [14] synthesized polycystalline SAPO-5 film on a Teflon slab by in-situ hydrothermal synthesis. Caro *et al.* [15] prepared "zeolite-in-metal" membrane by aligning and embedding $AlPO_4$-5 crystals in nicked by galvanic deposition. On the other hand, Wu *et al.* [16] prepared $AlPO_4$-5, $VAPO_4$-5 and CoAPO-5 films on anodic almina substates. Likewise, AFI-type molecular sieves consist of 12-membered ring channels with a diameter of 0.73 nm and unidimensional channel structure [16], which limit the use of AFI-type molecular sieve films for applications involving in small size of molecules. In order to develop aluminophosphate molecular sieve films having smaller pore size, Balkus *et al.* [17] prepared MAPO-39 films by secondary growth. Zhang *et al.* [18] and Poshusta *et al.* [19] reported the successful peparation of SAPO-34 membranes on an alumina disk and tubular supports, with promising gas separation properties, respectively. SAPO-34 has a pore size of 0.4 nm and three dimension channel structure. To the best of our knowledge, no other this kind of aluminophosphate molecular sieve films and membranes are reported since then.

In order to explore the possiblility of using other kinds of aluminophosphate molecular sieves with pore size of about 0.4 nm for the preparation of molecular sieve films, we tried to synthesize $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films on alumina substrates [20], all of which have a pore size of 0.4 nm and three-dimension channel structure as SAPO-34. It was found that continuous $AlPO_4$-14, CoAPO-44 and ZnAPO-34 films could be formed on alumina substrates; only ZnAPO-34 films had good thermal stability, however. We herein report the detail preparation of ZnAPO-34 films on both nonporous and porous alumina supports. The preparation conditions of the films were examined.

2. Experimental

2.1. Materials

Two kinds of alumina supports were used. One was nonporous alumina plate from Intertec Southwest

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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, with an outer diameter of 8 mm, inner diameter of 6 mm, and an average pore size of 0.2 μm. The substrates were cleaned by boiling in acetone for 2 h, treated in ultrasonic for 5 min, rinsed with distilled water and dried at 100°C overnight before use.

Regents used were zinc (II) acetate dehydrate, aluminum isopropoxide, pseudoboehmite (Catapal B, 70 wt% Al_2O_3), orthophosphoric acid (85%), and TEAOH (35%). Except that pseudoboehmite was from Vista Chemical Company, all the other chemicals were from Aldrich and used as shipped.

2.2. Synthesis

The detail procedures of preparing the hydrogel for the synthesis of ZnAPO-34 films and membranes were similar to those reported in literature for the synthesis of ZnAPO-34 molecular sieve [21]. Zinc (II) acetate dehydrate, orthophosphoric acid, and TEAOH were used as zinc source, phosphorus source and structure-direction agent, respectively. In most cases, aluminum isopropoxide was used as alumina source, and pseudoboehmite was only used when specified.

The synthesis was carried out in a 23 ml Teflon-lined autoclave from Parr Instrument Company at 170°C for 24 h. 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 deposite on the substrates. The film was prepared on the outer surface of the porous alumina tube since an upside-down T-shaped Teflon rod was inserted into the tube and was installed at the bottom of the autoclave.

Calcination of the film was conducted in a quartz tube at 400°C in vacuum for 4 h with a heating rate of 0.5°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 Kα 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. Synthesis of ZnAPO-34 films

Our first set of experiment trying to prepare the ZnAPO-34 film was conducted using composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 1TEAOH : 225H_2O$ on a nonporous alumina plate. This composition is almost the same as that for the synthesis of ZnAPO-34 powder [21], except that the water content is 3 times higher. We chose higher water content because we thought it would help the growth of ZnAPO-34 on the substrates, since most people used high water content, or even clear solution, to synthesize MFI type zeolite films and membranes [7, 24]. XRD patterns (see Fig. 1) of the alumina plate after synthesis determined that ZnAPO-34 molecular sieve was grown on the plate [22, 23]. It was found from the SEM photograph (Fig. 2) that cubic-like crystals, with crystal size less than 10 μm and good intergrowth, could be observed on the substrate. However, some parts of the substrate were not covered by molecular sieve crystals. Since the coverage of the surface of the substrates was not complete, synthesis parameters, such as organic content, water content, alumina source, were examined to screen an optimized composition by which a contineous ZnAPO-34 film could be produced.

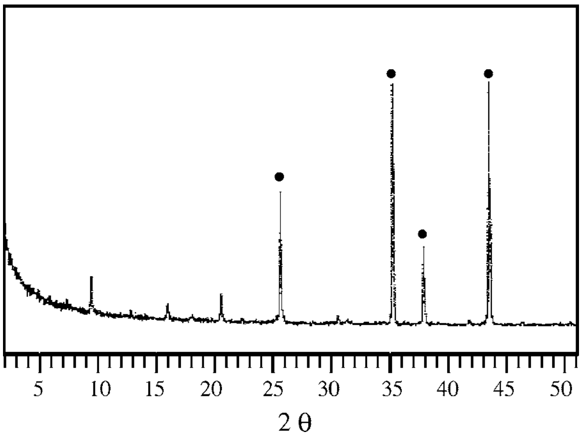

Figure 1 XRD patterns of a ZnAPO-34 film on nonporous alumina plate. Black dots indicated the peaks of α-Al_2O_3.

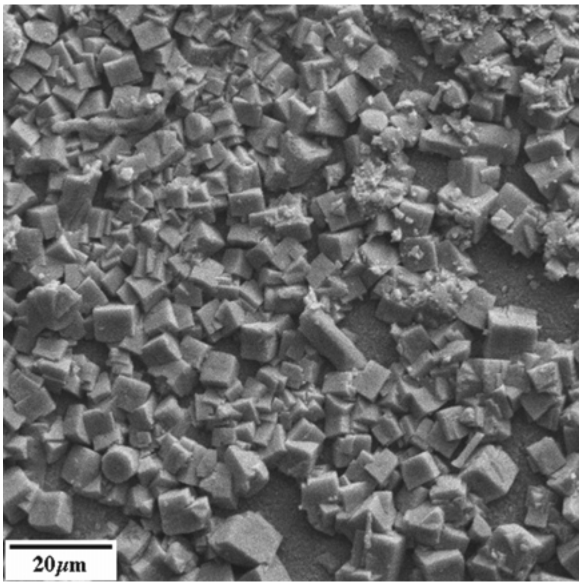

Figure 2 SEM photograph of a ZnAPO-34 film on a nonporous alumina plate prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 1TEAOH : 225H_2O$.

3.1.1. Effect of organic content

For the preparation of ZSM-5 membranes, it was found that alkalinity played an important role in the coverage and intergrowth of crystals on the substrate [7]. With this in mind, the effect of organic content on the quality of ZnAPO-34 film was first examined.

ZnAPO-34 films were synthesized from composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : x$ $TEAOH : 225H_2O$

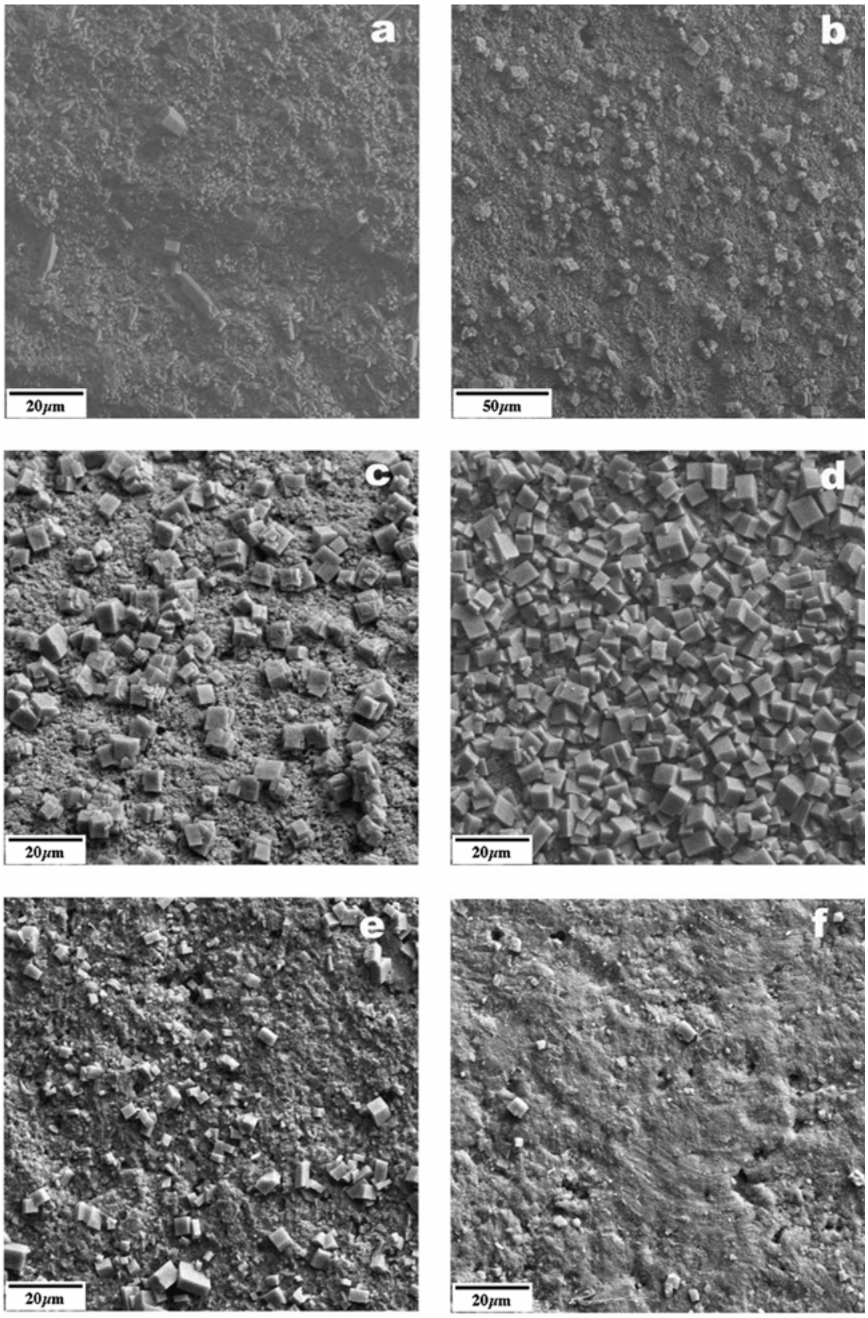

Figure 3 SEM photographs of ZnAPO-34 films on porous alumina tubes prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : x$TEAOH : $225H_2O$. $x =$ (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, and (f) 3.0.

with $x = 0.5$, 1.0, 1.5, 2.0, 2.5 and 3.0 respectively on porous alumina tube. Fig. 3 shows the SEM photographs of the films. Compositions with high (2.5 and 3.0) and low (0.5) TEAOH content cannot produce pure crystals and good coverage. With intermediate TEAOH content, the coverage increases with TEAOH content increasing from 1.0 to 2.0, and the best result can be obtained with TEAOH of 2.0.

It is known that the addition of TPABr increases the number of cryatals [24] and increasing alkalinity increases the nucleation rate [25, 26] in the synthesis of silicalite. In our case, increase of TEAOH content from 0.5 to 2.0 increases both TEA^+ concentration and alkalinity, and favores both the nucleation rate and the number of ZnAPO-34 crystals. Accordingly, good coverage can be achieved with TEAOH of 2.0. Too higher TEAOH content does not fovor the formation of ZnAPO-34 nuclei, which is the same as that in the synthesis of zeolite, due to the high solubility of small subcolloidal species at high alkalinity [24].

3.1.2. Effect of water content

The effect of water content was examined first with TEAOH content of 1.0 using nonporous alumina plates as substrates. The composition was $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 1$TEAOH : xH_2O, $x = 75$, 150, 225, and 300, respectively. Fig. 4 shows the SEM photographs of the films produced with water content of 75 and 150, respectively, while the picture of the film produced with water content of 225 has been shown in Fig. 2. No crystal could be found by SEM with water content of 300, so the SEM picture is not shown. The crystals of ZnAPO-34 film prepared with water

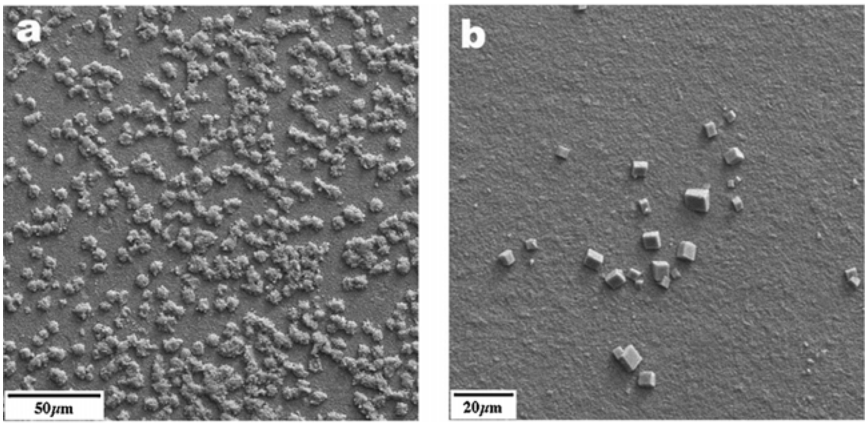

Figure 4 SEM photographs of ZnAPO-34 films on nonporous alumina plates prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 1TEAOH : xH_2O$. $x =$ (a) 75 and (b) 150.

content of 75 are the same as those of ZnAPO-34 powder, i.e., cubic form ball-shaped aggregates. When water content is increased to 150, the crystals change from aggregates into single cubic form, and the coverage decreases greatly. With further increasing the water content to 225, crystals intergrow together and cover most surface of the substrate. However, increase of water content to 300 produces few crystals on the support.

The effect of water content was also examined with TEAOH content of 2.0 on porous alumina tubes. The synthesis composition was $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 2TEAOH : xH_2O$, $x = 75$, 150, 225, 300, and 550, respectively. Fig. 5 shows the SEM photographs of the films produced with water content of 75, 150, 300, and 550, respectively, while the film produced with water content of 225 has been shown in Fig. 3d. When water content is 75, the crystals of the film are also cubic form ball-shaped aggregates. When water content is increased to 150, the aggregates also change to single cubic form with decreased coverage. Further increasing water content from 225 to 550 increases the coverage and intergrowth of the crystals. However, a complete coverage of crystals cannot be achieved as revealed by SEM.

Increase of only the amount of water content decreases simultaneously alkalinity and TEA^+

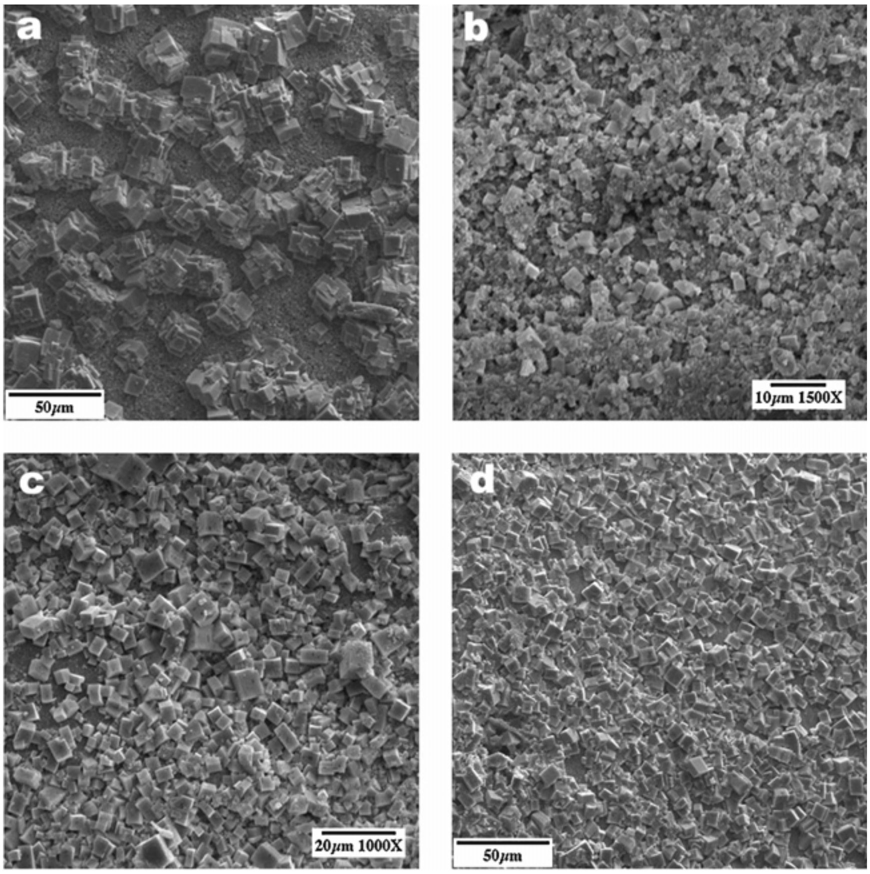

Figure 5 SEM photographs of ZnAPO-34 films on porous alumina tubes prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 2TEAOH : xH_2O$. $x =$ (a) 75, (b) 150, (c) 300, and (d) 550.

concentration, which decreases the nucleation rate and the number of crystals, as discussed above. That would be the reason why few crystals are produced on the film synthesized with water content of 300 and TEAOH content of 1.0. When TEAOH content is 2.0, ZnAPO-34 films with reasonable coverage can be achieved with water content of 225 to 550. That may be because the alkalinity and TEA^+ concentration are not decreased to the point which cannot produce a good ZnAPO-34 film. It seems that $TEAOH/H_2O$ ratio is very important to the synthesis of ZnAPO-34 films.

3.1.3. *Effect of alumina source*

In these experiments, ZnAPO-34 films were synthesized by a composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 1TEAOH : xH_2O$, $x = 75$, 150, 225, and 300, respectively, on nonporous alumina plates using pseudoboehmite as alumina source. Fig. 6 shows the top views of the films with water content of 150, 225 and 300. Almost no crystal could be found by SEM with water content of 75, so the SEM picture is not shown. It can be seen that the coverage is low in all case, with the best coverage when water content is 225, similar to the case when aluminum isopropoxide is used as alumina source. It is very interesting that the morphology of the films is all cubic form ball-shaped aggregates. This phenomena has been observed with composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : xTEAOH : 75H_2O$, $x = 1$ and 2 with aluminum isopropoxide as alumina source (Figs 4a and 5a), which might be due to the different hydrolysis rate between boemite and aluminum isopropoxide, and the different hydrolysis rate with different water content. Slower hydrolysis rate produces large collioid particles, which produce ball-shaped aggregates. It can be concluded that using aluminum isopropoxide as alumina source favored the formation of good ZnAPO-34 films.

3.1.4. *Effect of substrate*

Figs 2 and 3b are the SEM photographs of ZnAPO-34 films synthesized with the same composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 1TEAOH : 225H_2O$ on nonporous alumina plate and porous alumina tube, respectively. It is apparent that the ZnAPO-34 film on the nonporous alumina plate has higher coverage than that on the porous alumina tube. This may be related to the surface roughness of the substrate. SEM pictures of the surfaces of the nonporous alumina plate and the porous alumina tube indicate that the surface of the nonporous alumina plate is flatter than that of the porous alumina tube. Flat surface favores the formation of a good ZnAPO-34 film. That is a very important point in the synthesis of a defect-free molecular sieve film.

3.1.5. *Choice of synthesis condition*

From the above results and discussions, it can be concluded that good ZnAPO-34 films could be

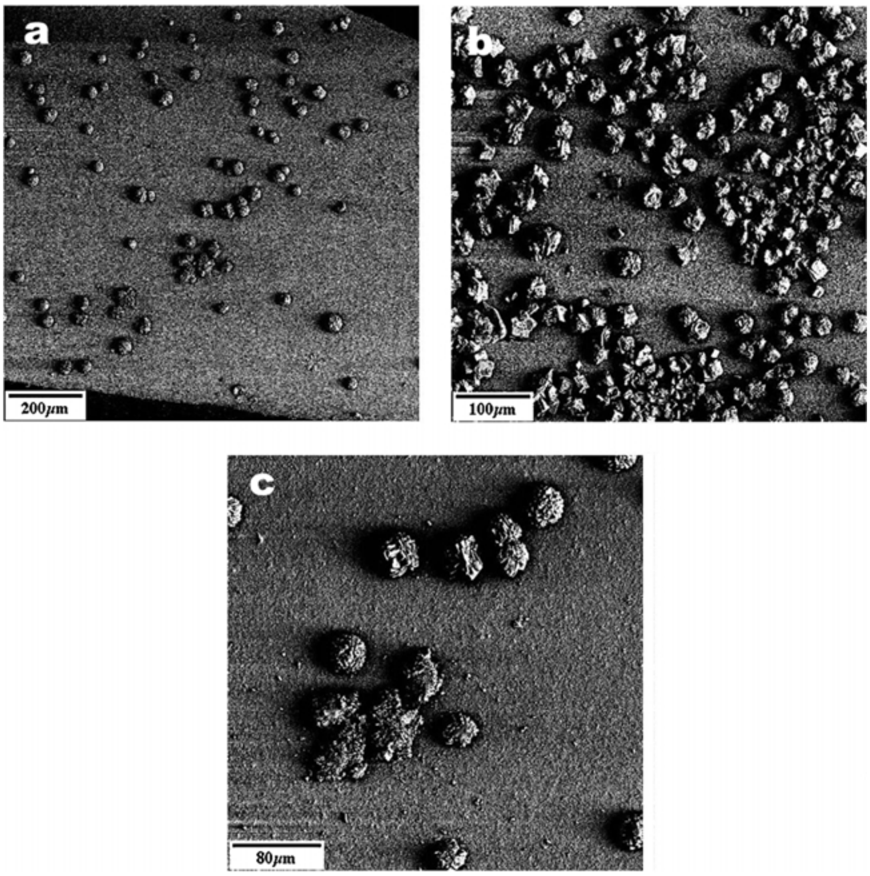

Figure 6 SEM photographs of ZnAPO-34 films on nonporous alumina plates prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 1TEAOH : xH_2O$ using pseudoboehmite as alumina source. $x =$ (a) 75, (b) 150, (c) 225, and (d) 300.

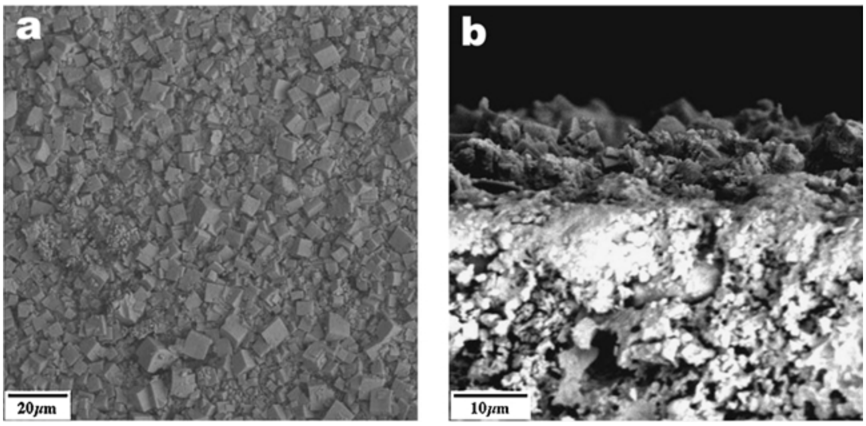

Figure 7 SEM photographs of a ZnAPO-34 film on a porous alumina tube prepared with composition of $1P_2O_5 : 0.8Al_2O_3 : 0.4ZnO : 2TEAOH : 225H_2O$ after 4 cycles of synthesis. (a) surface of the film and (b) cross-section of the film.

synthesized by a composition of $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 2TEAOH : xH_2O$, $x = 225$ to 550 on both nonporous alumina plates and porous alumina tubes, with aluminum isopropoxide as alumina source. However, a ZnAPO-34 film with complete coverage by ZnAPO-34 crystals can not be achieved. In this case, repeated syntheses have to be carried out. Contineous ZnAPO-34 films can be made by several cycles of syntheses. Fig. 7a shows the top-view of a ZnAPO-34 film on porous alumina tube after 4 times of syntheses. It can be seen that the coverage and the intergrowth of the crystals are very good. No voids between the ZnAPO-34 crystals can be observed. Under such circumstance, we think that a continuous ZnAPO-34 film can be produced. The thickness of the film is ca. 10 μm as shown in Fig. 7b.

3.2. Calcination of the films

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 corrdination [27]. For metal substituted $AlPO_4$s, some of them were reported to be unstable at high temperature. For example, MAPO-43 started to collapse above only 653 K [28].

For ZnAPO-34 powder, when calcination was performed in air, a structure transformation occured already at 400°C [20, 21]. Therefore, calcination of ZnAPO-34 should be conducted under vacuum or in an inert atmosphere. The morphology of a ZnAPO-34 film on the porous alumina tube calcined under vacuum, as shown by SEM, are almost the same as Fig. 7a. No significant changes can be observed, except for some small particles, which are assumed to be carbon orignated from calcination under vacuum. XRD patterns of the calcined film show no difference from those of the as-synthesized sample. ZnAPO-34 films has reasonable thermal stability.

Cracks are always formed within the molecular sieve films during the calcination because of the heat- and/or pressure-induced stresses [29]. Under such circumstance, heating rate and gas atmosphere on template decomposition should be carefully chosen to prevent the crack-forming. Gilbert *et al.* [29] found that the least stressful conditions for template removal of TPABr/silicalite powder occurred with a heating rate of 0.5 K/min in an atmosphere containing a mixture of air and ozone (1%). In our case, we chose a heating rate of 0.5 K/min, which would be a safe heating profile. Since we didn't examine the occurance of cracks within ZnAPO-34 films by other techniques than SEM, we couldn't conclude that the ZnAPO-34 films were defect-free. More efforts have to be spent to develop a suitable calcination profile for this kind of molecular sieve films.

4. Conclusions

ZnAPO-34 films supported on nonporous alumina plates and the outer surface of porous alumina tubes can be successful prepared by *in situ* synthesis. It is found that intermediate organic content and water content favor high coverage of ZnAPO-34 crystals on the supports. Alumina source also has influence on the coverage of crystals on the substrates, with aluminum isoporpoxide producing higher coverage than pseudoboehmite. On the other hand, More ZnAPO-34 crystals can be grown on dense alumina plate than on porous alumina tube, even with the same synthesis conditions, indicating that flatter substrate results in higher coverage of the film. The best composition for the synthesis was $0.4ZnO : 0.8Al_2O_3 : 1P_2O_5 : 2TEAOH : 225\text{–}550H_2O$ with aluminum isopropoxide as alumina source. However, a complete covered ZnAPO-34 film cannot be achieved with only one synthesis. In this case, repeated syntheses have to be conducted and contineous films can be prepared with several cycles of syntheses.

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