Growth of Oriented Molecular Sieve Thin Films from Aligned Seed Layers

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Oriented aluminum phosphate five ($AlPO_4$-5) molecular sieve thin films were grown onto glass surfaces seeded with aligned $AlPO_4$-5 crystals. The novel aligned seed layer was formed by depositing rod-shaped seed crystals from a colloidal suspension under an electric field. Alignment of the seed layer promotes adhesion of the seed crystals to the underlying substrate and enhances surface nucleation and growth to allow secondary crystallization of oriented thin films. There was no correlation between the crystal orientation of the seed layer and the orientation of the secondary crystals grown in the thin film. The orientation of the secondary crystals could be varied from parallel to perpendicular to the underlying seed layer depending on the synthesis conditions. The technique presented here offers a novel method for growing oriented molecular sieve membranes that are useful for separations and catalysis.

Introduction

Molecular sieves and zeolites are crystalline materials with open framework structures that result in nanometer-scale pores. Depending on the crystal structure, pore sizes can range from 0.3 to 3 nm.[1] The very small pore sizes allow zeolites and molecular sieves to selectively adsorb compounds on the basis of molecular size and shape. These nanoporous crystals are widely used in separation and catalysis and are finding advanced application in areas such as optics and microelectronics.[2,3] Several approaches have been developed to create thin films of zeolites and molecular sieves with controlled pore direction.[4−12] Such oriented thin films have promising applications in molecular sieving membranes, optical materials, and low-dielectric materials for microelectronics. One route to the synthesis of continuous zeolite films is by secondary crystal growth onto a seed layer deposited on a substrate. The continuous film often consists of randomly intergrown crystals, but recent reports have shown that the crystal orientation of the siliceous zeolite ZSM-5 can be controlled by the organic templates used during secondary growth.[10] Another recent study shows that crystallization of silicalite-1 onto polyurethane films results in aligned crystals with the orientation controlled through the properties of polymer films.[11]

The focus of the present study is the molecular sieve aluminum phosphate number five ($AlPO_4$-5). The crystals of $AlPO_4$-5 typically appear as short hexagonal columns and have one-dimensional pores approximately 0.73 nm in diameter running parallel to the longest axis.[13] Films of $AlPO_4$-5 crystals with controlled pore direction have application in molecular sieving membranes. When the pores of $AlPO_4$-5 are filled with certain dyes, the crystal displays nonlinear optical properties. Thus, thin films of $AlPO_4$-5 with aligned pore direction may also offer a route to novel nonlinear optical materials. Several approaches have been taken to create $AlPO_4$-5 thin films with controlled pore direction.[4,5,7−9] When a gold surface is modified with a multilayer organophosphonate film, $AlPO_4$-5 crystals will nucleate on the surface and grow as a thin film of vertically aligned, rod-shaped $AlPO_4$-5 crystals.[5] Vertically oriented $AlPO_4$-5 crystals can also be synthesized by templated crystallization in the pores of anodic alumina membranes.[7−9] Electric fields can be used to align $AlPO_4$-5 crystals, so that they are oriented vertically[4] or horizontally[12] on a substrate. Here, we show that $AlPO_4$-5 crystals deposited parallel to a substrate can act as a seed layer for oriented secondary crystal growth. This novel synthesis approach can be used for producing aligned $AlPO_4$-5 membranes. The orientation of the crystals can be adjusted from normal to parallel to the substrate depending on the synthesis conditions and surface coverage of the seed layer.

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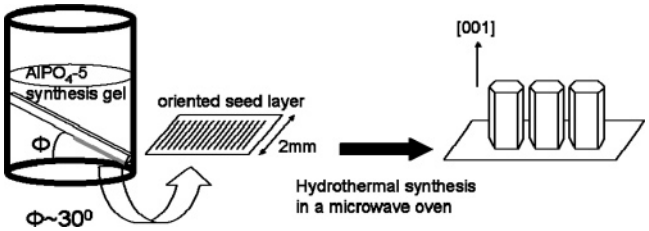

Figure 1. Procedure for secondary crystal growth from an aligned $AlPO_4$-5 seed layer. A 2 mm wide glass slide was placed in a Teflon-lined vessel and tilted on an angle of around 30° with the oriented film facing down. The glass slide was immersed in $AlPO_4$-5 synthesis gel. After hydrothermal synthesis under microwave radiation, hexagonal $AlPO_4$-5 crystals were grown with the [001] axis preferentially oriented perpendicular to the seed layer.

Experimental Section

Fibrous $AlPO_4$-5 crystals were synthesized as described previously.[14] The crystals were approximately 500 nm to 1 μm in width and 40−80 μm in length. The $AlPO_4$-5 crystals were then aligned into a thin film on a glass slide under an applied electric field following a published procedure.[12] The aligned film of crystals served as a seed layer for secondary growth. Figure 1 shows the experimental setup for secondary growth onto the aligned thin film. The glass slide coated with the aligned seed layer was placed in a Teflon-lined vessel with the seed layer facing down and tilted up ~30° relative to the bottom of the vessel. The gel for secondary crystal growth comprised aluminum triisopropoxide, phosphoric acid, triethylamine, deionized water, and hydrofluoric acid in a 1:1.3:0.8:160:0.5 molar ratio. The procedure for preparing the synthesis gel can be found in the literature.[13] The synthesis gel was then added so that the seed layer was immersed in the gel. Hydrothermal synthesis was carried out at 180 °C for 17 min in a Milestone Ethos Plus microwave oven to grow secondary $AlPO_4$-5 crystals onto the seed layer. The synthesized thin film was rinsed with ethanol and dried in air overnight. The morphology of membranes was observed by scanning electron microscopy (SEM), and the structure was confirmed by powder X-ray diffraction (XRD).

Results and Discussion

The aligned crystal seed layer was formed on a glass substrate by depositing crystals from a colloidal suspension under an applied electric field.[12] The applied electric field causes a dipole to form on each crystal in a dilute suspension.[15] The dipole lies along the longest axis of the crystals and the torque acting on the dipole from the applied field will drive the particles to align with the longest axis parallel to the applied field. The particles are deposited by sedimentation from a dilute solution under an applied field. A single deposition step results in low surface coverage of crystals. Repeated deposition cycles are used to control the surface coverage and build up a continuous coating of aligned seed crystals. Complete coverage of the surface with seed crystals occurs after 4−5 deposition cycles, as described previously.[12] The seed layer was formed on a 2 mm wide glass slide and the crystals were aligned across the width of the slide and along a length of approximately 2.5 cm. Secondary crystallization onto the seed layer was achieved by placing the slide into a reaction vessel, as illustrated in Figure 1, and heating via microwave oven.

Heating for 17 min at 180 °C results in secondary crystal growth directly onto the seed layer. Figure 2 shows electron microscopy images of seed layers and the secondary crystals grown onto these seed layers. At low surface coverage of seed crystals (Figure 2A), the secondary crystals are randomly oriented on the surface (Figure 2B). As the surface coverage of seed crystals is increased (images C and E of Figure 2), the secondary crystals grow with a preferred orientation with the *c* axis normal to the underlying substrate (images D and F of Figure 2). Top-view images D and F of Figure 2 clearly show the typical hexagonal prism morphology of $AlPO_4$-5, with crystal widths around 3−5 μm. Crystals grown on the continuous seed layer (Figure 2F) have nearly all crystals preferentially oriented, with the *c* axis tilted slightly from a 90° angle relative to the substrate. The tilting of the crystals becomes more prominent as the surface coverage of the seed layer is reduced (Figure 2D). Crystal orientation eventually becomes random at very low surface coverage of seed crystals (Figure 2B).

Figure 3 shows a side view of a broken section of the thin film shown in top view in Figure 2F. The side-view image reveals a membrane thickness of 25−30 μm and clearly shows the preferred orientation of the crystals. The fibrous seed crystals are still present at the base of the membrane, but the seed layer is only ~1 μm thick. It is apparent from Figure 3 that a layer of disordered crystals is present at the base of the thin film. The layer of disordered crystals appears thicker than the seed layer. Therefore, it appears that the crystals grow initially with a random orientation at the base of the membrane, but with preferential orientation as the membrane gets thicker. For comparison, Figure 4 shows the $AlPO_4$-5 crystals collected from the bulk synthesis solution. The crystals that nucleate and grow in the bulk are also hexagonal prisms with widths of 5−10 μm and lengths of 10−20 μm. The crystals in the bulk are slightly larger than those grown on the membrane. Oriented crystals grown on the surface by secondary crystallization also have a larger aspect ratio (length to width) than those grown in bulk.

Powder X-ray diffraction (XRD) was used to confirm the structure and orientation of the membrane formed by secondary growth. Panels A and B of Figure 5 are XRD patterns of the vertically oriented membrane and the $AlPO_4$-5 crystals collected from the bulk solution, respectively. Both of the diffraction patterns are characteristic of the AFI structure of $AlPO_4$-5. It should be noted that the peak at a 2θ angle of 20.97° is assigned to the (002) planes of the crystals.[16] The intensity of the (002) peak is strongly enhanced when the crystals are oriented normal to the substrate.[5] The pattern from the membrane also shows the other AFI peaks, although the (002) peak is the strongest one. The overall peak intensity is lower for the vertically aligned film than for the crystals collected from the bulk

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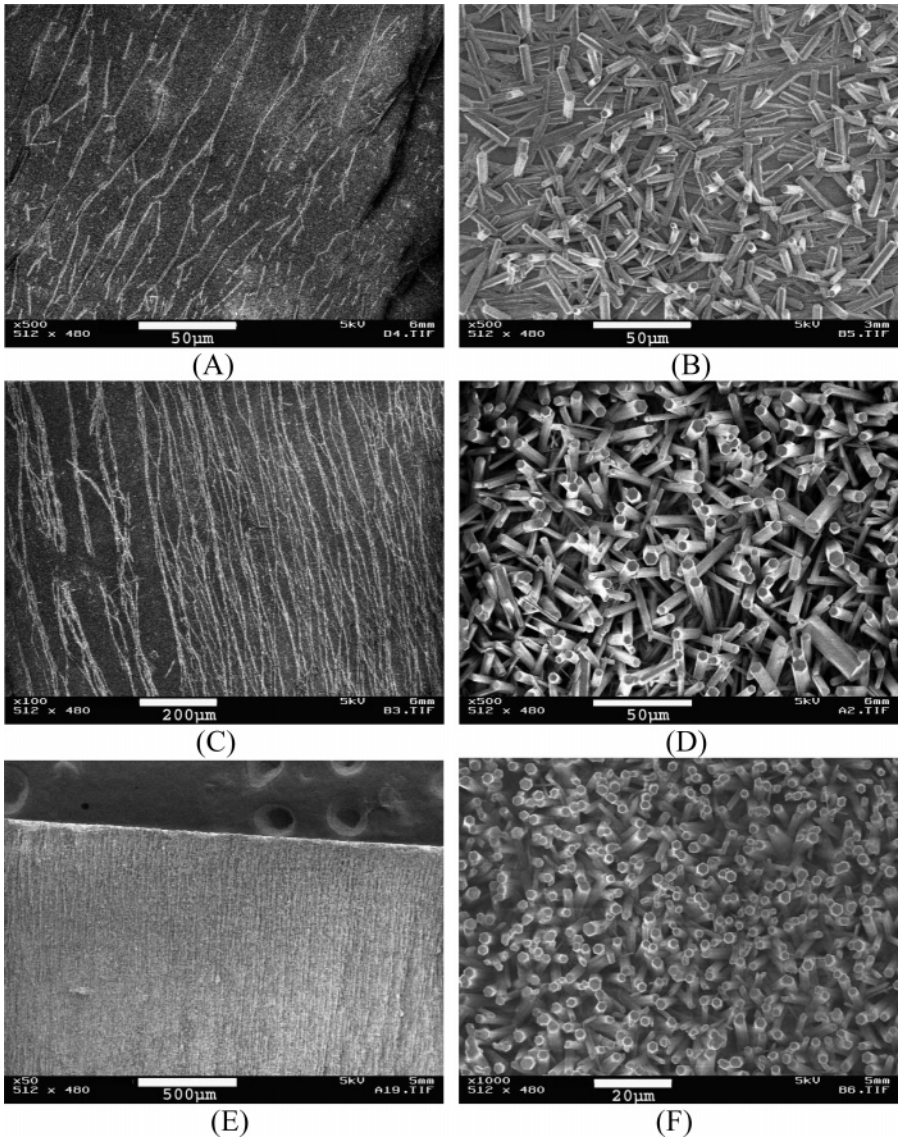

Figure 2. Aligned seed layers (on left) and molecular sieve thin film formed on the seed layer by secondary crystallization (on right). (A) At low surface coverage of seed crystals; (B) secondary growth results in randomly oriented crystals. As surface coverage of seeds is increased (C and E), crystals grown onto the seed layer become oriented with the [001] axis oriented preferentially normal to the surface (D and F).

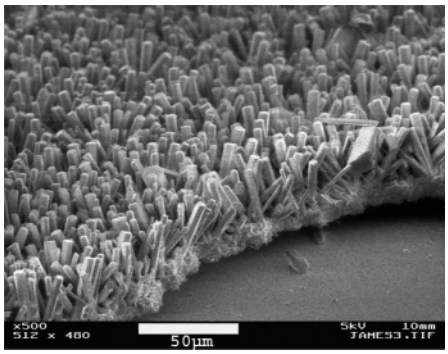

Figure 3. Side view of oriented crystals grown onto an aligned seed layer. The top view of this sample is shown in Figure 2F.

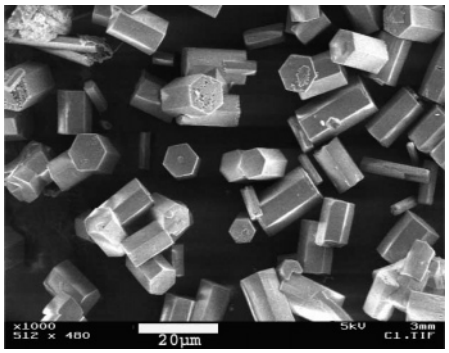

Figure 4. $AlPO_4$-5 crystals collected from bulk solution used for secondary crystal growth.

solution, because the X-ray beam was focused on a smaller area of the surface to ensure data were collected from only the vertically aligned film. The SEM image in Figure 3 shows that there is a disordered layer a few micrometers thick at the base of the membrane. The disordered layer will also contribute to the X-ray diffraction and could cause the intensity of the (002) peak to decrease relative to the other peaks.

The results show that secondary crystal orientation depends on the surface coverage of the seed layer, but is independent of the orientation of the crystal seeds. Even so, we found an aligned seed layer, such as that shown in Figure 2E, provided

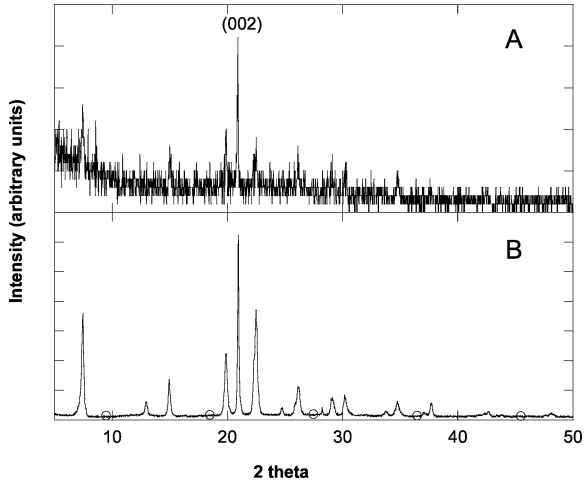

Figure 5. X-ray diffraction of (A) vertically aligned $AlPO_4$-5 crystals as shown in Figure 3, and (B) $AlPO_4$-5 crystals collected from solution as shown in Figure 4.

the best growth of secondary crystals. For comparison, a seed layer was formed by suspending seed crystals in acetone and then depositing the suspension onto a glass slide by evaporation. Without an applied electric field, the particles are deposited with random orientation. Figure 6A shows the disordered seed layer obtained by solvent evaporation. The rapid evaporation of acetone coupled with particle aggregation during evaporation causes the disordered seed film to have greatly varying thickness. The randomly oriented crystals overlap each other and have less direct surface contact with the glass substrate than oriented fibers deposited with the longest axis in the plane of the thin film. As a result, the disordered film adheres weakly to the glass and is much more fragile than the oriented film. When the disordered film shown in Figure 6A was used as a seed layer for secondary crystallization, a significant fraction of the film detached during hydrothermal synthesis, exposing the bare glass surface. In areas where secondary crystal growth occurred, the secondary crystals appeared to be randomly oriented (Figure 6B). A control experiment was also conducted using a bare glass slide with no seed layer. Without a seed layer, no secondary growth on the surface was possible (data not shown). Therefore, the thin, uniform film of aligned crystals created by deposition under an electric field offers a superior seed layer for secondary growth of vertically aligned $AlPO_4$-5 crystals.

The water content in the hydrothermal synthesis gel plays a critical role in enabling secondary crystal growth of $AlPO_4$-5. The water:aluminum triisopropoxide molar ratio used to grow vertically aligned crystals was 160:1. When the water:aluminum triisopropoxide molar ratio was increased to 320:1 or decreased to 50:1, there was no vertical growth. The oriented seed layer was cracked for both cases, and no crystals were grown on the surface. Attempts were also made to grow crystals on the surface using the synthesis gel confined in a water-in-toluene microemulsion that produces $AlPO_4$-5 fibers.[14] However, no crystals were grown on the surface when the microemulsion was used, and the oriented seed layer was cracked after hydrothermal synthesis. From the results, it is clear that water plays an important role for secondary growth. Water content in the gel may affect factors such as nucleation and growth kinetics and transport of nutrients to the growing oriented film. The morphology and orientation of $AlPO_4$-5 crystals grown on a modified gold surface were also observed to strongly depend on the water content of the synthesis gel.[5]

As illustrated in Figure 1, crystals grow normal to the substrate when the oriented seed layer is facing down in the Teflon vessel. However, with the oriented film facing directly upward, the crystals grow with a preferential orientation parallel to the substrate, as shown in Figure 7. The dependence of crystal orientation on the placement of the seed layer suggests that the transport of nutrients to the crystals growing on the surface may be influencing the preferred orientation on the surface. In a study of $AlPO_4$-5 crystallization on an anodic alumina membrane, it was postulated that upward fluid flow during hydrothermal synthesis was responsible for aligning loglike nuclei and allowing vertically aligned crystals to be formed.[9] Convection currents in the microwave-heated cell may influence the transport of nutrients to the surface. For synthesis in the upward orientation, the surface also has many randomly oriented crystals that nucleate and grow in the bulk synthesis solution, then deposit onto the surface by sedimentation. The size and shape of many of the crystals on the upper surface appear to be similar to those collected in the bulk for synthesis with the seed layer facing directly upward. The crystals that deposit by sedimentation onto the surface complicate the interpretation of results of secondary crystallization. Therefore, the downward orientation of the seed layer is preferred for growth of oriented thin films.

Preferential orientation during crystal growth on solid surfaces has been observed for a variety of materials, including zinc oxide (ZnO),[17−19] ferric oxides (Fe_2O_3),[20] tin dioxide (SnO_2),,[21] the zeolite ZSM-5,[10] and $AlPO_4$-5 on organophosphonate functionalized gold surfaces,[5] Even so, there is no well-established mechanism that can predict crystal orientation during growth on surfaces. In general, surface nucleation is favored when the crystal/surface interfacial free energy is low. Deposition of a seed layer helps to promote surface nucleation, but there is no correlation between the seed crystal orientation and the crystal orientation in the grown film. In a study of ZSM-5 zeolite crystal growth on a seeded substrate, it was found that the axis of the crystal with the fastest growth rate is always oriented normal to the substrate, regardless of the orientation of the underlying seed layer.[10] For $AlPO_4$-5, the *c* axis is the fastest growing, and it is thus expected that the most favored orientation would be with the *c* axis normal to the substrate. However, the results demonstrate that crystals of $AlPO_4$-5 are not always oriented with the *c* axis normal to the substrate onto which they are grown. In particular, the results in Figure 2 reveal that the number of seeds deposited on the substrate

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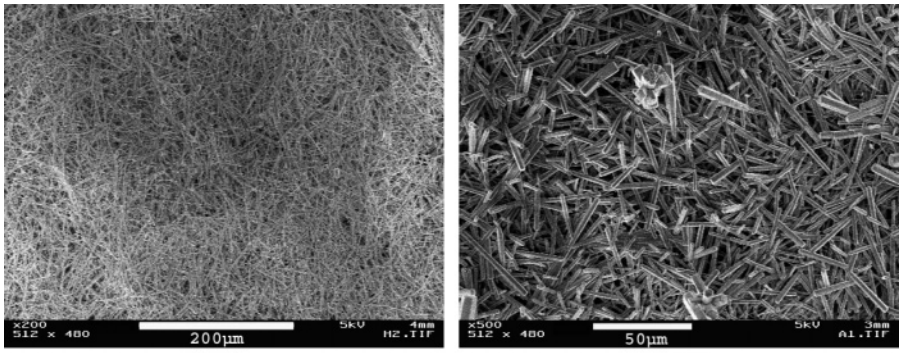

Figure 6. SEM images of (A) a random seed layer formed by evaporative deposition from an acetone suspension and (B) crystals grown onto the seed layer by secondary crystallization.

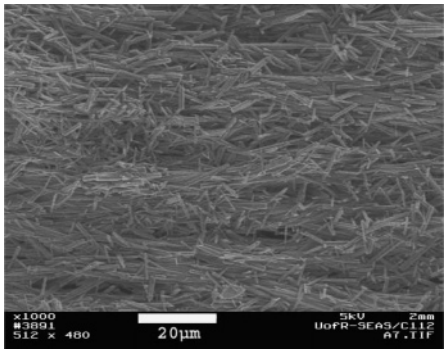

Figure 7. Secondary growth of $AlPO_4$-5 membranes from an aligned seed layer oriented upward during secondary growth. The scale bar is 20 μm.

plays an important role in determining crystal orientation. Previous studies of surface nucleation and growth of hexagonal metal oxide crystals show that the crystals grow with the *c* axis oriented preferentially normal to the surface when the surface density of nucleation sites is high, but grow with the *c* axis oriented parallel to the substrate when the surface nucleation site density is low.[18] The data in Figure 2 show that $AlPO_4$-5 shows similar behavior in the dependence of crystal orientation on the number density of seeds on the surface.

Conclusions

In conclusion, the novel thin film of aligned crystals offers excellent performance as a seed layer for secondary growth of preferentially oriented $AlPO_4$-5 thin films. Alignment of the rod-shaped seed crystals promotes adhesion of the seed crystals to the underlying substrate. The surface coverage of seed crystals can easily be adjusted to promote the growth of oriented $AlPO_4$-5 membranes. The preliminary study here provides a potential route for making molecular sieving membranes with controlled pore direction. By altering the synthesis conditions, we can control the orientation and morphology of the crystals grown on the surface. The molecular sieve pore orientation can be adjusted both parallel and normal to the substrate. To form a continuous membrane, we could possibly fill the space between the aligned crystals by galvanic nickel deposition.[22] In a study of the formation of needlelike titanosilicate molecular sieve film, it was reported that the space between the oriented needlelike crystals can be filled with another molecular sieve possessing similar structure by heteroepitaxial growth to form continuous membranes.[23] It may be possible that "tertiary" crystallization of a compatible material with similar crystal structure such as $AlPO_4$-8 could allow for intergrown crystals that form a continuous membrane.

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