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In-situ thickness controlled growth of $AlPO_4$-5 films

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ABSTRACT

Uniformly c-oriented $AlPO_4$-5 films were prepared on a glass substrate by a simple *in-situ* growth method. The water content of the synthesis gel played an important role in the synthesis of *c*-axis-oriented films that were perfectly aligned along the *c*-axis and exhibited high coverage. We also optimized the growth conditions by varying the reaction time and temperature, and suggested a simple and effective strategy for controlling the thickness of $AlPO_4$-5 films. Furthermore, $AlPO_4$-5 films with various thicknesses were obtained by adjusting the height and tilt angle of the substrate in the reaction vessel. We believe that this work provides a simple and effective pathway for controlling the thickness and orientation of $AlPO_4$-5 films and can therefore expand the possible range of applications of molecular sieve films.

1. Introduction

Various types of porous films with different sizes and porous architectures, such as mesoporous materials [1–3], metal–organic frameworks [4,5], and zeolites [6], have been pursued for various applications. Among them, zeolite-based porous films are very attractive owing to their well-defined stable pore structure, their high selectivity of gas molecules, unique ion exchange ability, temperature stability, and durability toward solvents. Considerable emphasis has been placed on the development of synthetic methods for producing continuous zeolite thin films on desired substrates [6]. These films should have controlled orientation and thickness as well as excellent coverage in order to be used in advanced practical applications such as molecular separation membranes [7–11], optical devices [12], membrane sensors [13,14], and electrochemical electrodes [15–17]. Developing synthetic conditions for obtaining oriented zeolite thin films is especially challenging. These films have been extensively studied over the last few decades. Techniques for preparing continuous zeolite thin films can be broadly classified into two categories. The first is the *in-situ* growth method [18–21], in which the supporter or substrate is directly immersed in the synthetic gel and then subjected to hydrothermal conditions. The second is the seed growth technique (also known as the secondary growth method), which requires two main procedures: 1) formation of an oriented seed layer on the supporter and 2) direct immersion of the fabricated seed layer in the synthetic gel and a subsequent hydrothermal reaction for growing the seed layer [20,22–38].

To date, most oriented zeolite thin films on substrates have been produced via the secondary growth method [20,22–38], which allows easy manipulation of the film orientation and morphology by changing the orientation and morphology of the pristine seed layer. However, the seed growth method requires multiple steps owing to the formation process of the inclusion seed layer, bonding stability between the crystals and the substrate, and disorientation from self-crystallization during secondary growth; this method remains, therefore, somewhat challenging.

In contrast, in the *in-situ* growth method, continuous zeolite thin films are formed after the nucleation of zeolite crystals on the supporter, which is directly immersed in the synthetic gel; these crystals are chemically bonded to the substrate and are therefore, quite stable. Despite its simplicity, this method has been used to synthesize a few types of zeolites, such as MFI [18,19], zeolite A [20], and SAPO-34 [21]; applying this method to a wide spectrum of continuous zeolite thin films is currently highly desirable. In fact, there is increasing demand for studies aimed at determining the appropriate *in-situ* growth synthetic condition required for various types of zeolite membrane. However, this method involves homogeneous nucleation and growth on substrates during hydrothermal

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synthesis, systematic control of the film thickness and orientation is quite difficult; the film thickness and orientation, which is essential to improving performance in practical applications, is quite difficult.

$AlPO_4$-5 is composed of alternating tetrahedral shapes of AlO_4 and PO_4, which form an array of opened one-dimensional channels packed in a hexagonal structure. The main channels of $AlPO_4$-5, which are combined with 7.3 Å-diameter twelve-membered ring windows, are one-dimensional, electrically neutral, and parallel to the *c*-axis of the crystal (Scheme 1). Owing to its crystal structure, $AlPO_4$-5 can be used in numerous applications, such as nonlinear optical materials [39], absorbents [40], and host templates [41,42]. $AlPO_4$-5 films with controlled microstructures are especially attractive for a number of other applications, including separation and catalytic applications. The crystal size, crystal orientation relative to the membrane layer, thickness, and uniformity of the zeolite membranes generally determine the performance of these materials.

However, most of the $AlPO_4$-5 films reported to date have been synthesized by the seed growth technique. For example, Lin et al. synthesized fibrous $AlPO_4$-5 crystals via microemulsion-directed synthesis and used an applied electric field to align these crystals into a thin film on a glass substrate [29]. The aligned seed crystals served as the seed layer for the oriented $AlPO_4$-5 film during secondary growth. In addition, Karanikolos et al. created seed layers with covalent links on functionalized silicon substrates and then synthesized continuous *c*-oriented $AlPO_4$-5 films by secondary and tertiary growth [30]. As previously mentioned, these growth processes consist of more than two steps and are therefore complex and time-consuming. Deposition of seed crystals and optimization of the rate and direction of secondary growth are also quite challenging.

Therefore, in this paper, we report the facile preparation of $AlPO_4$-5 films on transparent glass substrates via the *in-situ* growth method. We achieved an optimum synthetic condition for highly *c*-oriented $AlPO_4$-5 films by controlling the water content of the synthetic gel, hydrothermal reaction time, and reaction temperature. Moreover, we demonstrate that the height and tilt angle of the substrate in the reaction vessel during *in-situ* hydrothermal reaction significantly affect the thickness and coverage.

2. Experimental section

2.1. Materials

Pseudoboehmite (Al_2O_3, Catapal B, Viata Chemical), phosphoric acid (H_3PO_4, 85.0% aqueous solution, Samchun), and triethylamine (TEA, Aldrich) were used as received for the synthesis gel of the $AlPO_4$ films. Glass substrates (2.5 cm × 5 cm) were purchased from Marienfeld (Paul Marienfeld GmbH & Co.KG).

2.2. Preparation of synthesis gel for $AlPO_4$ film

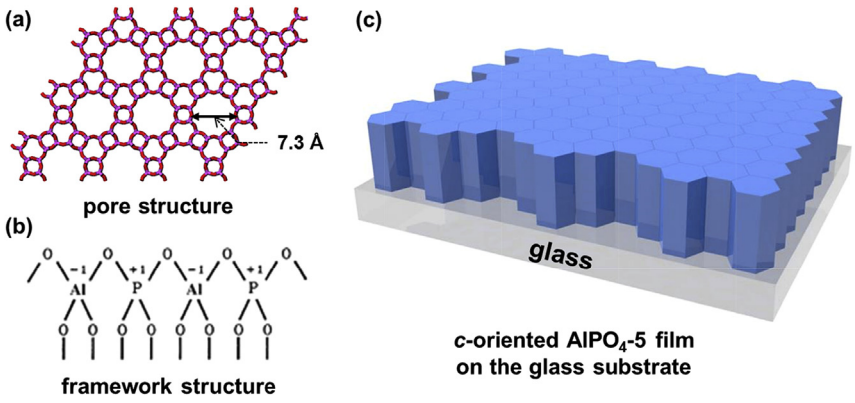
A synthesis gel consisting of Al_2O_3, H_3PO_4, TEA, and H_2O was prepared, where the molar ratio of Al_2O_3:P_2O_5:TEA:H_2O was 0.75:1:1.32:30, according to the following procedure. H_3PO_4 (20.5 mL) was diluted in 111.4 mL of distilled deionized water (DDW). To this solution, 20.6 g of pseudoboehmite was slowly added, and the solution was hydrolyzed for 13 h at room temperature with continuous vigorous stirring. During stirring, the initially thick solution became watery. After hydrolysis was complete, 36.8 mL of TEA as a structure-directing agent was introduced dropwise into the above hydrolyzed solution with an injection speed of 1 drop/sec under vigorous stirring to prevent solidification of the gel solution. This solution obtained a very slightly yellowish tinge and was aged for 4 h at room temperature with continuous stirring.

2.3. Preparation of $AlPO_4$-5 film on the glass substrate

A glass substrate (2.5 cm × 5 cm) was immersed in Mucasol (5%) solution and cleaned by sonication for 10 min. The glass was rinsed with a copious amount of DDW and sonicated for 15 min in isopropyl alcohol. Finally, it was dried by blowing nitrogen gas. For growth of $AlPO_4$-5 on the glass substrate, the glass substrate was placed on a Teflon supporter at a certain angle and put into a Teflon-lined autoclave. Synthetic gels consisting of P_2O_5, $Al(OH)_3$, TEA, and H_2O were prepared in a molar ratio of P_2O_5:$Al(OH)_3$:TEA:H_2O = 0.75:1:1.32:α, where α = 400, 200, 100, or 30. Then 60 mL of synthesis gel was transferred to the Teflon-lined autoclave. The autoclave was placed for 7 h in a convection oven preheated to 200 °C. After the hydrothermal reaction, the synthesized $AlPO_4$-5 film on the glass substrate was washed with DDW. To remove residual $AlPO_4$-5 crystals on top of the film, the obtained $AlPO_4$-5 film was gently swung through deionized water and dried by blowing nitrogen gas.

2.4. Instrumentation

Scanning electron microscope (SEM) images of the zeolite films were obtained from a field-emission SEM (Hitachi S4300) at an acceleration voltage of 20 kV. A platinum/palladium alloy (in the ratio of 8 to 2) was deposited with a thickness of about 15 nm on top of the samples. The X-ray diffraction (XRD) patterns



Scheme 1. (a) Pore size and (b) framework structures of $AlPO_4$-5, and (c) illustration of c-oriented $AlPO_4$-5 films on the glass substrate.