Microporous and Mesoporous Materials 265 (2018) 70–76

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

One-step ionothermal synthesis of oriented molecular sieve corrosion-resistant coatings

Tongwen Yu, Yanchun Liu, Wenling Chu**, Rui Cai*, Weishen Yang

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

ARTICLE INFO

Keywords:
Molecular sieve films
Orientation
Ionothermal synthesis
Corrosion-resistant coatings

ABSTRACT

In-situ synthesis of oriented molecular sieve films remains a great challenge. Random oriented films are mostly obtained by this simplest synthesis strategy. Here, we demonstrate that the oriented molecular sieve films as corrosion-resistant coatings can be one-step ionothermally formed by interface chemistry of substrate-solution. In detail, an in-plane oriented AEL molecular sieve film was generated by adjusting the interfacial chemical reaction between substrate and the synthetic solution for appropriate nuclei density. Moreover, the corrosion-resistant performance of oriented film coated Al sample is two orders of magnitude higher than that of random oriented film coated one, reflecting a much more passive corrosion behavior.

1. Introduction

Molecular sieves or zeolite films offer molecular-size and shape selectivities for separating particular components in petrochemical refinery [1–3]. Recently, there are interests in moving beyond the molecular sieve effect of separation membrane and catalysis to explore new applications such as corrosion-resistant coating [4,5], low-*k* dielectric films [6], heat pumps [7] and hydrophilic and antimicrobial coatings [8] by utilizing their intrinsic properties. Among them, molecular sieve film as corrosion-resistant coating has drawn much attention due to its non-toxicity, inert nature and impermeability (the structure-directing agents (SDA) are usually trapped thus blocking the pores of as-prepared molecular sieve films) [9–12]. Therefore, it opens up a promising alternative to chromate conversion coating with high carcinogenicity.

Serving as a guide to corrosion-resistant molecular sieve coating development, the performance is generally dependent on the microstructures, especially the orientation. It is anticipated that an in-plane oriented molecular sieve coating in which pore channels parallel to the substrate surface would have fewer penetrable pathways (e.g., defects, nonselective transport pathways) for corrosive media into the protected metals than that coating with random or out-of-plane orientation. Thus, the particular in-plane orientation would primarily lead to corrosion behaviors inhibition. However, simply *in-situ* synthesis of molecular sieve coatings with particular orientation remains challenging.

In contrast to secondary (seeded) growth method that requires multi-steps to carefully deposit the seeds or modify the substrate for the desirable oriented film growth [13,14], *in-situ* synthesis of molecular sieve films directly on the substrate could considerably improves the adhesion and mechanical stability of the resulting films. However, the most widely used *in-situ* hydrothermal crystallization is rather difficult to obtain oriented molecular sieve films [15,16]. Recently, ionic liquids were introduced to replace water and organic template as both the solvent and SDA for the synthesis of zeolite powders [17,18]. With the assistance of microwave, the above so-called ionothermal synthesis was firstly reported by Yan and co-workers [19] to form an out-of-plane oriented molecular sieve anti-corrosion coatings through two-steps process, in which silane was used to sealed the pore channels of coatings. Tian and co-workers [20] ionothermally fabricated permeable aluminophosphate molecular sieve membranes on alumina disks that also act as the Al source. Furthermore, we recently developed a novel *in-situ* electrochemical ionothermal method that combines electric fields with the open ionothermal system for the control of orientations in molecular sieve films on Al substrate, in which an in-plane oriented, defect-free film [21] or an out-of-plane oriented film [22] were obtained by elaborate programming of the applied electric fields, respectively.

Accordingly, through the interfacial chemical interaction between active Al substrate and synthetic solution, herein we demonstrate one-step *in-situ* ionothermal synthesis for fabrication of in-plane oriented $AlPO_4$-11(AEL framework topology) molecular sieve coatings directly on an aluminum substrate without the assistant of applied electric field. And the oriented $AlPO_4$-11 coatings exhibited excellent corrosion-resistant performance.

* Corresponding author.
** Corresponding author.
E-mail address: cairui@dicp.ac.cn (R. Cai).

https://doi.org/10.1016/j.micromeso.2018.01.030
Received 8 November 2017; Received in revised form 21 January 2018; Accepted 22 January 2018
Available online 06 February 2018
1387-1811/

2. Experimental

2.1. Preparation of $AlPO_4$-11 films

The pure Al substrates were first cleaned by an alconox detergent solution at 60 °C for 1 h and washed by deionized (DI) water, then dried with compressed air.

$AlPO_4$-11 films were prepared by the ionothermal method using Al substrate as both substrate and Al source in a Teflon autoclave. First, a synthesis solution was produced according to the following procedure: 35 g of 1-ethyl-3-methlyimidazolium bromide ([emim]Br) was combined with 1.7 g of phosphoric acid (H_3PO_4, 85% in water, AR) and 0.2 g of hydrogen fluoride (HF, 40% in water, AR), and this solution was mixed by stirring for 30 min at about 90 °C. Then, the reaction mixture (molar ratio of 10.7[emim]Br: 0.27 HF: H_3PO_4) was poured into a Teflon-lined autoclave in which the treated Al substrate was previously placed vertically. The final reaction mixtures were heated to the required temperature for certain times under conventional heating for crystallization and growth of the zeolite films. For DC polarization test, the sample was further ionothermally treated at 175 °C for 4 h with 0.2 g of aluminum isopropoxide. After the syntheses, the films were thoroughly washed with DI water, and dried at 80 °C for 2 h in a vacuum oven.

For comparison, $AlPO_4$-11 films were also prepared by the same way except that the appropriate amount of aluminum isopropoxide was introduced into the synthesis solution, which was stirring for 5 h at 90 °C.

2.2. Characterization

The structures and phase identification of the films were analyzed using X-ray diffraction (XRD, Japan Rigaku D/MAX 2500/PC) with Cu Kα radiation (λ = 0.154 nm) at 40 kV and 200 mA.

Coating morphology and surface covering grade were evaluated by a Scanning Electron Microscope (SEM, Hitachi TM 3000).

The corrosion resistance of the films or bare substrates was measured by electrochemical test. The polarization curves were carried out using a EG&G 263A potentiostat in a three-electrode configuration with the sample as working electrode, platinum foil as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The corrosive medium was 0.1 M NaCl aqueous solution. $AlPO_4$-11 coating were immersed in the corrosive medium for 30 min prior to the polarization test with a sweep rate of 1 mV/s.

3. Results and discussion

3.1. One-step synthesis of in-plane oriented $AlPO_4$-11 film

$AlPO_4$-11 with AEL topology is a representative $AlPO_4$-based molecular sieve and it consists of one-dimensional 10-membered ring channels (6.5 × 4.0 Å) packed parallel to the *c*-axis with alternate AlO_4 and PO_4 tetrahedral forming a neutral framework [23]. In general, the assembly of rod-shaped particles with AEL structure into the orientation-controlled films proved rather difficult by *in situ* hydrothermal/ionothermal method in the presence of additional Al source (e.g., aluminum isopropoxide), in which the homogeneous nucleation [24] readily results in random oriented $AlPO_4$-11 films [15,16]. Our experiment further confirms the random orientation of $AlPO_4$-11 film synthesized by addition of aluminum isopropoxide in a Teflon-lined autoclave (Fig. 1a, Figure S1). In order to obtain a particular in-plane oriented $AlPO_4$-11 film, it is necessary to hinder the homogeneous nucleation induced by a large amount of Al source in the bulk. To ensure nucleation occurring on the substrate surface (heterogeneous nucleation) rather than in the bulk, we excluded the Al source (e.g., aluminum isopropoxide) from the ionothermal synthetic system and used a pure Al plane as the dual role of substrate and sole Al source. In the synthetic solution containing ionic liquid [emim]Br, phosphorus source H_3PO_4, and the mineralizing agent HF, the following process possibly comes true under the optimized conditions. By optimizing crystallization temperature and time, an in-plane oriented

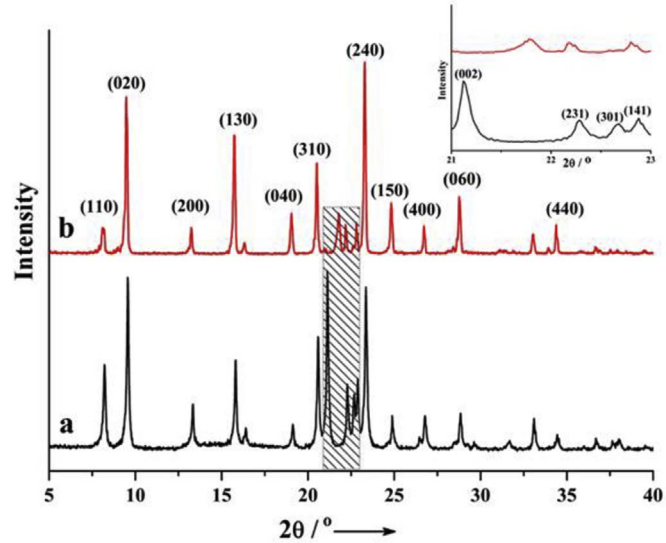

Fig. 1. XRD patterns of $AlPO_4$-11 molecular sieve films on Al substrate. a) a randomly oriented film ionothermally obtained with additional aluminum source; b) an in-plane oriented film ionothermally obtained with sole Al source from the substrate. Inset: expansion of the hatched region.

$$2Al + 2H_3PO_4 \xrightarrow{[emim]^+,\ F^-} 2AlPO_4 - 11 + 3H_2$$

and compact $AlPO_4$-11 molecular sieve coating with flower-like morphology (Fig. 2a) was successfully *in-situ* synthesized on the pure Al substrate at 190 °C after 4 h in a Teflon autoclave, and no $AlPO_4$-11 powder was observed in the bulk, indicating the absence of homogenous nucleation. Furthermore, the cross-sectional scanning electron microscope (SEM) image (Fig. 2b) showed the well-developed intergrowth between the crystals in the coating with the thickness of about 30 μm. Moreover, the hexagonal rods of $AlPO_4$-11 crystals were preferentially oriented parallel to the substrate surface. The in-plane orientation was strongly validated by X-ray diffraction (XRD) result because the (002) reflection peak expected at 2θ = 21.02° almost entirely disappeared, meanwhile (231), (301) and (401) peaks dramatically weakened (Fig. 1b and insert). This characteristic pattern with several (*hk*0) peaks is distinctly different from that of the randomly oriented $AlPO_4$-11 film shown in Fig. 1a due to the observed several rational orders of (00*l*) peaks revealing a wire array phase.

3.2. Effect of the crystallization temperature

During molecular sieve crystallization process, it is well known that the kinetic and thermal dynamic factors governed the growth of crystals and controlled the orientation of the films [25,26]. Accordingly, the effect of crystallization temperature on the formation of $AlPO_4$-11 films was evaluated by SEM analysis. Initial ionothermal trial at 170 °C for 4 h shows no crystals on the pure Al substrate (Fig. 3a), revealing significantly slow interfacial reaction rate of substrate-solution as well as low nucleation and growth rate. A discontinuous (Fig. 3b) but in-plane oriented $AlPO_4$-11 layer (Fig. 4a) is more acceptably observed at higher temperature of 180 °C, indicating the nucleation rate is faster than the growth rate, and therefore the temperature can be further improved. The synthesis at 190 °C is optimum for yielding an in-plane oriented and compact $AlPO_4$-11 molecular sieve coating (Fig. 3c) due to a better match between the nucleation rate and growth rate. With further increasing temperature to 250 °C, a denser and in-plane oriented (Fig. 4b)