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Highly oriented, neutral and cation-free $AlPO_4$ LTA: from a seed crystal monolayer to a molecular sieve membrane†

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An oriented, neutral and cation-free $AlPO_4$ LTA molecular sieve membrane with high hydrogen selectivity was prepared on porous α-Al_2O_3 supports through secondary growth of a highly oriented $AlPO_4$ LTA monolayer.

Zeolites with their uniform pore structure and high thermal stability are widely used in the chemical industry as catalysts, ion exchangers and adsorbents.[1] Apart from the use of zeolites as powders, supported zeolite layers are of interest for many potential applications as separators, reactors, sensors and electrical insulators.[2–6] It is well recognized that control of the microstructures of zeolite layers, such as grain orientation and grain boundaries, plays an important role in their performances.[2,7,8] Mostly, oriented zeolite layers exhibit superior performances compared to randomly oriented zeolite layers.[9] Therefore, intense research efforts have been made towards the preparation of oriented zeolite layers,[10–13] mainly focused on the preparation of *b*-oriented MFI membranes.[14–16] Lai *et al.* reported the synthesis of *b*-oriented MFI membranes with a high *p*-xylene/*o*-xylene selectivity of about 500.[17] Highly *b*-oriented MFI membranes have been prepared by both direct *in situ* growth[18] and secondary growth.[19] The secondary growth method is considered to allow a better control of the growth of oriented zeolite films since the quality of the films is less influenced by the characteristics of the substrate, thus enhancing the reproducibility of membrane preparation.[20] For secondary growth of oriented membranes, a highly oriented monolayer of zeolite seeds is helpful.

Much effort has been made to assemble zeolite crystals as an oriented seed monolayer. The preparation of a packed zeolite A monolayer was first realized by physical adsorption of the micro-crystals onto a substrate.[21] Recently, Yang *et al.* reported the deposition of highly *b*-oriented silicalite-1 seeds on various substrates by a Langmuir–Blodgett technique.[16,22] Pre-treated zeolite crystals were also chemically attached on substrates for the fabrication of an oriented monolayer by a simple ionic or covalent bonding.[23] Another great contribution for the assembling of an oriented zeolite monolayer with dense packing was achieved by introducing dual covalent bonds between the zeolite crystals and the substrate. Yoon and coworkers have developed a novel "two-component modification" strategy for the assembly of a highly oriented LTA and MFI zeolite films on glass slides *via* covalent linkages,[24–26] where the reactive groups on the substrate surfaces were effectively linked to the matching groups on the zeolite crystals to yield a uniform and oriented zeolite monolayer with high coverage and close packing. However, these covalent linkages are not suitable for the assembly of large-sized zeolite crystals (usually smaller than 3 μm).[27] Further, a rather long reaction time (usually several hours) is required to obtain a high coverage monolayer.[28] Therefore, the development of a simple, effective and versatile road to assemble highly oriented zeolite monolayers is desired.

We are interested in the development of molecular sieve zeolite membranes exploiting the shape-selectivity in gas separation.[29–31] Recently, we have reported a novel neutral and cation-free aluminophosphate ($AlPO_4$) LTA molecular sieve membrane with a random orientation microstructure.[32] Attributing to its neutral and cation-free framework as well as a small pore size of about 0.4 nm, the aluminophosphate LTA membrane displayed better gas separation performance than the aluminosilicate LTA zeolite membrane since the highly polar structure of the aluminosilicate LTA zeolite with a strongly negative zeta potential causes problems in closing up inter-crystalline gaps. In combination with ultrasonication, herein we report a simple, effective and versatile strategy to prepare a highly oriented $AlPO_4$ LTA monolayer through the use of polyethyleneimine (PEI) as an interlayer, which can attach seed crystals as hydrogen-bonding mediators.[33–35] After the attachment of oriented seed crystals, hydrothermal secondary growth follows to prepare an oriented $AlPO_4$ LTA membrane. It can be expected that a highly oriented $AlPO_4$ LTA molecular sieve membrane will show superior separation performances compared to a randomly oriented $AlPO_4$ LTA molecular sieve membrane.

As shown in Fig. S1 (ESI†), a highly oriented $AlPO_4$ LTA seeds monolayer with a uniform crystal size of about 15 μm (Fig. S2, ESI†) was prepared by ultrasonication using PEI as a mediator among the $AlPO_4$ LTA crystals and the substrate. The close packing is attributed to a certain degree of surface migration by repeated bond breaking (by ultrasonication) and

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bond formation (by PEI) between the $AlPO_4$ LTA microcrystals and the alumina support as described by Yoon *et al.*[29,33,36]

From the SEM image of the $AlPO_4$ LTA layer on a glass plate in Fig. 1a, it can be seen that almost the entire plate is covered by a uniform monolayer of $AlPO_4$ LTA crystals with a high-density packing. The higher magnification SEM image (Fig. 1b) indicates that only a crystal monolayer is well assembled on the glass plate, and all the zeolite crystals are aligned with a face parallel to the glass surface, indicating a perfect one-dimensional orientation. Similar to the previous reports of highly oriented aluminosilicate LTA crystals assembled *via* covalent linkages,[24–26] the $AlPO_4$ LTA crystals show a strong tendency to pack closely each other during the attachment onto the substrate. Due to a strong face-to-face interaction between the amino-modified faces of two separate $AlPO_4$ LTA crystals through a large number of hydrogen bonds between the terminal NH_2 groups,[24,34–36] the PEI mediated $AlPO_4$ LTA crystals tend to act as a template for positioning the next crystal once mounted on the substrate. The advantage of using PEI as the interlayer hydrogen-bonding mediator was well recognised for the assembly of highly oriented LTA and MFI monolayers.[27,34,35] Actually, without PEI in the suspension, a less oriented layer with low coverage is observed on the glass plate (Fig. S3, ESI†).

The formation of an oriented $AlPO_4$ LTA monolayer on the glass plate was confirmed by the XRD pattern as shown in Fig. 2. Different to the randomly oriented XRD pattern of $AlPO_4$ LTA zeolite powder (inset in Fig. 2), the oriented $AlPO_4$ LTA monolayer shows only (h00) peaks that correspond to [200], [400], [600] and [1000] planes of the $AlPO_4$ LTA zeolite (the reflection of [800] located at about $2\theta = 29.09$ seems lost due to its intrinsically low intensity even for powder), indicating a parallel orientation of the (h00) face relative to the substrate surface. Such a simple pattern strongly contrasts with the more complex pattern of the random $AlPO_4$ LTA powder shown in the inset of Fig. 2.

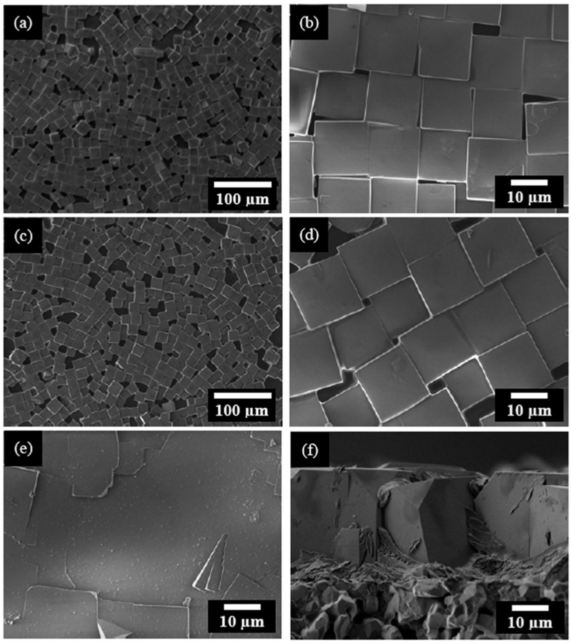

Fig. 1 SEM images of a $AlPO_4$ LTA seed monolayer on a glass plate (a), (b) and on a porous α-Al_2O_3 disk (c), (d), and α-Al_2O_3 supported continuous $AlPO_4$ LTA molecular sieve membrane after secondary growth (e: top view, f: cross-section).

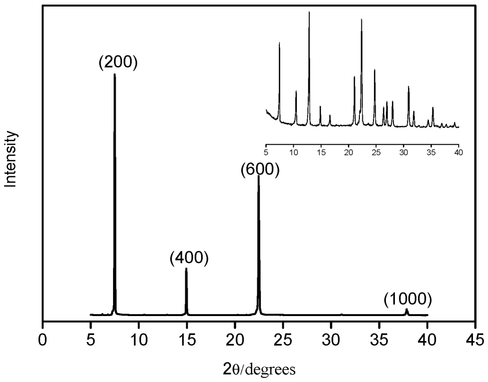

Fig. 2 XRD pattern of the highly oriented $AlPO_4$ LTA seeds monolayer on a glass plate as shown in Fig. 1a and b. The inset shows the XRD pattern of the randomly oriented $AlPO_4$ LTA powders.

It is found that the ultrasonic treatment is vital to obtain an oriented monolayer. A randomly oriented $AlPO_4$ LTA layer is observed in the case of ultrasonic-free treatment (Fig. S4, ESI†). Presumably the ultrasonication can provide sufficient kinetic energy to the functional groups to form the interlayer hydrogen-bonding. As reported previously,[28] compared to the deposition rate by refluxing and stirring, strong ultrasonic agitation led to more than a 10^3-fold increase in the rate of microcrystals attachment to glass slides as monolayers with molecular linkages. Fig. S5 (ESI†) shows SEM images of the highly oriented $AlPO_4$ LTA monolayer with a crystal size larger than 60 μm. To the best of our knowledge, this is the largest crystal size so far assembled as an oriented monolayer. The present strategy through ultrasonication of PEI mediated microcrystals works equally well to prepare other oriented monolayers like aluminosilicate LTA (Fig. S6, ESI†). Besides on the non-porous flat glass plates, a highly oriented $AlPO_4$ LTA monolayer can be consistently formed on the porous Al_2O_3 substrates regardless of their surface conditions (Fig. 1c and d), further confirming the universality of this method.

The oriented $AlPO_4$ LTA molecular sieve membrane on a porous Al_2O_3 substrate was prepared through secondary growth of an oriented $AlPO_4$ LTA monolayer as reported previously.[32] After secondary growth for 5 h at 200 °C, the former seeds monolayer have merged with each other and formed a well-intergrown continuous layer with a thickness of about 25 μm (Fig. 1e and f). No visible cracks, pinholes or other defects are observed. Further, the as-synthesized $AlPO_4$ LTA membrane still keeps its dominant (h00) orientation (Fig. S7, ESI†).

To investigate the separation performance of the oriented $AlPO_4$ LTA membrane, the volumetric flow rates of the single gases H_2, CO_2, N_2, CH_4 and C_3H_8 as well as the binary 1 : 1 mixtures of H_2 with CO_2, N_2, CH_4 and C_3H_8 through the activated $AlPO_4$ LTA membrane were measured using the Wicke–Kallenbach technique (Fig. S8, ESI†). Fig. 3 shows the permeances of the single gases on the oriented $AlPO_4$ LTA membrane as a function of the kinetic diameters of the permeating

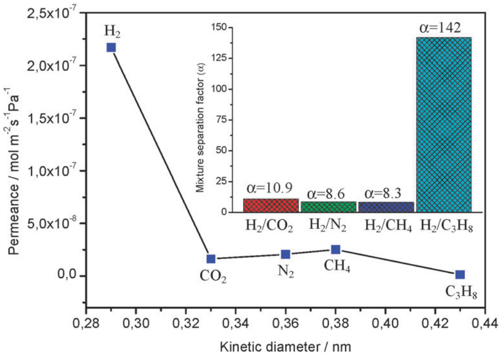

Fig. 3 Single gas permeances of different gases through the oriented $AlPO_4$ LTA membrane at 200 °C as a function of the kinetic diameter. The inset shows the mixture separation factors for H_2 over other gases from equimolar mixtures as determined by gas chromatography.

molecules at 200 °C. As shown in Fig. 3, the permeance of C_3H_8 is much lower than those of the other gases since the pore size of $AlPO_4$ LTA is estimated from crystallographic data to be ~0.4 nm, which is in accordance with our previous report of a randomly oriented $AlPO_4$ LTA membrane.[32] The ideal separation factors of H_2 from other gases, are 13.3, 10.5, 8.6 and 160.7, respectively.

This molecular sieving performance of the $AlPO_4$ LTA membrane has been confirmed by the separation of binary mixtures of H_2 with CO_2, N_2, CH_4 and C_3H_8. As shown in the inset of Fig. 3, the separation factors of H_2/CO_2, H_2/O_2, H_2/CH_4 and H_2/C_3H_8 are 10.9, 8.6, 8.3 and 142, respectively, with H_2 permeances of about 1.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. These mixture separation factors far exceed the corresponding Knudsen separation coefficients (4.7, 3.7, 2.8 and 4.7, respectively). Compared with our former report of a random $AlPO_4$ LTA membrane,[32] the oriented $AlPO_4$ LTA membrane in this study shows a highly enhanced H_2 selectivity along with decreased permeances (Fig. S9, ESI†). It seems that the oriented growth can minimize the defect density and the transport pathways through the grain boundaries, thus leading to an enhancement of selectivities. It is expected that the membrane permeance can be further increased by reducing the membrane thickness through the use of smaller-sized seed crystals. So far, there are many studies on the small pore-sized zeolite membranes for gas separation.[37,38] Comparing with literature data of mixed gas separation, the oriented $AlPO_4$ LTA membrane developed in this study are among those with high separation performances (Table S1, ESI†).

In conclusion, through the use of PEI as a hydrogen-bonding interlayer in combination with ultrasonication, we have developed a simple, effective and versatile strategy to assemble highly oriented $AlPO_4$ LTA monolayers on various substrates. After secondary growth, the former oriented monolayer grew into a well-intergrown oriented membrane with a preferential (h00) orientation. For separation of single and binary mixtures, the oriented $AlPO_4$ LTA membrane showed a higher H_2 selectivity than a random $AlPO_4$ LTA membrane since the oriented growth could minimize the defect density and the transport pathways through the grain boundaries. Further work is in progress to extend this strategy to prepare other oriented zeolite membranes.

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