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Neutral and Cation-Free LTA-Type Aluminophosphate ($AlPO_4$) Molecular Sieve Membrane with High Hydrogen Permselectivity

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Zeolites, with their uniform pore structures and high thermal stability, have been widely used in the chemical industry as catalysts and adsorbents. In the last two decades, supported zeolite membranes/layers have attracted intense interest because of their potential applications as separators, reactors, and sensors.[1−3] To date, mainly silicate or aluminosilicate zeolite membranes of the structure types MFI,[4−6] DDR,[7] LTA,[8,9] and FAU[10,11] have been prepared on different types of supports and evaluated in single or multigas permeation. The first industrial application of zeolite membranes was the dewatering of bioethanol using LTA membranes.[12] These LTA membranes failed as molecular sieve membranes, although they were very powerful in hydrophilic separations.[13] Furthermore, the extreme hydrophilicity and the cation content of aluminosilicate LTA complicate its application in gas separation. On the other hand, there have also been reports of silicoaluminophosphate (SAPO-34)[14,15] and aluminophosphate ($AlPO_4$-5/$AlPO_4$-34)[16] membranes for gas separation. However, no neutral and cation-free LTA-type $AlPO_4$ membrane with low hydrophilicity could be prepared until now.

The neutral and cation-free LTA-type $AlPO_4$ zeolite,[17,18] with its cubic three-dimensional nanostructure and a small pore size of ~0.4 nm (Figure 1), is expected to give a powerful membrane for the separation of H_2 from larger molecules such as N_2, O_2, CO_2, CH_4, and C_3H_8. Recently, we developed a synthesis recipe for the preparation of large and well-shaped LTA $AlPO_4$ crystals by modifying a previous synthesis protocol.[19] In the present work, we report the preparation of a supported LTA-type $AlPO_4$ membrane with high hydrogen selectivity. To the best of our knowledge, this is the first successful synthesis of an LTA-type $AlPO_4$ membrane with molecular sieve performance.

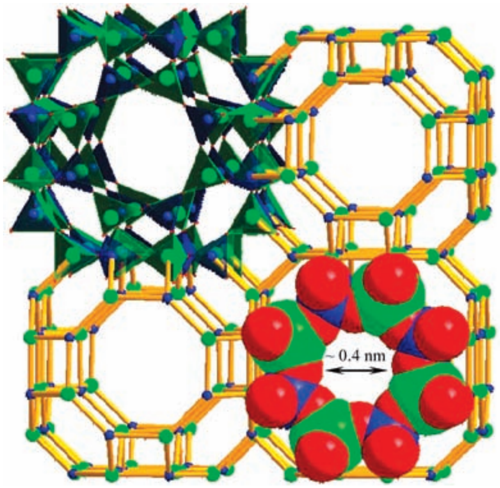

Figure 1. LTA topology of $AlPO_4$ LTA zeolite, including the tetrahedral oxygen coordination of the Al and P cations (top left) and the narrow eight-membered-ring opening through which molecules have to pass (bottom right).

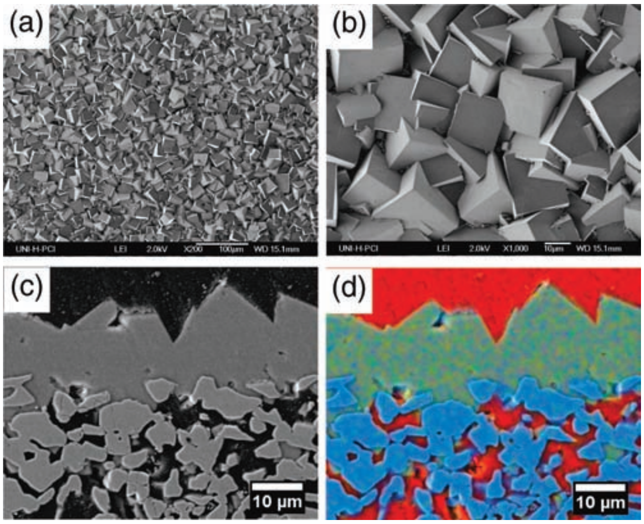

Figure 2. SEM images of the LTA $AlPO_4$ membrane: (a, b) top views at different magnifications; (c) SEM image and (d) EDXS mapping of the sawn and polished $AlPO_4$ membrane cross section. Color code: green, P; blue, Al; red, C from the polymer used for sample preparation.

The LTA-type $AlPO_4$ membrane was prepared by the secondary growth method[6] (for details, see the Supporting Information). After secondary growth for 5 h at 473 K, a pure LTA-type $AlPO_4$ zeolite layer with a high crystallinity was formed on the Al_2O_3 support (Figure S2 in the Supporting Information). Figure 2a,b shows scanning electron microscopy (SEM) top views of the LTA-type $AlPO_4$ membrane at different magnifications. The support surface is completely covered by uniform $AlPO_4$ crystals, and no visible cracks, pinholes, or other defects are observed. From the cross section shown in Figure 2c,d, it can be seen that the membrane is dense and that the former seeds have grown into a well-intergrown continuous layer. From the absence of phosphorus signals in the support region in the energy-dispersive X-ray spectroscopy (EDXS) analysis, it can be concluded that no further nucleation and crystal growth inside the support pores took place during the secondary growth. It was found that the seed layer is indispensable for forming a dense LTA $AlPO_4$ zeolite membrane. Cracks and pinholes were usually observed when no seeds were attached to the support surface before hydrothermal synthesis (Figure S3).

The volumetric flow rates of the single gases H_2, CO_2, O_2, CH_4, and C_3H_8 as well as 1:1 binary mixtures of H_2 with CO_2, O_2, CH_4,

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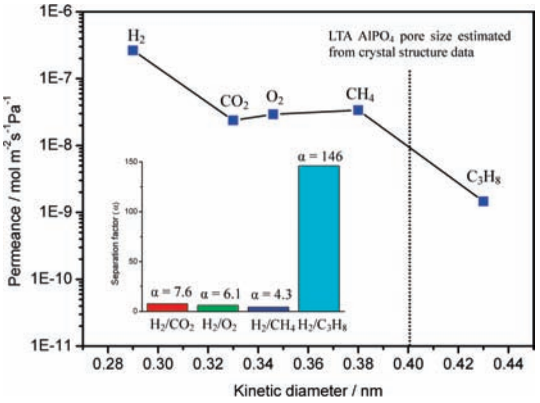

Figure 3. Single-gas permeances of different gases on the LTA-type $AlPO_4$ membrane at 293 K as a function of their kinetic diameter. The inset shows the mixture separation factor for H_2 over other gases, as determined by gas chromatography.

and C_3H_8 were measured using the Wicke−Kallenbach technique (Figure S4). The permeances and separation factors are summarized in Table S1. Figure 3 shows the permeances of the single gases through the LTA $AlPO_4$ membrane as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3, the permeance of C_3H_8 is much lower than those of the other gases, which is in accordance with the pore size of ∼0.4 nm of the LTA $AlPO_4$ zeolite as estimated from crystallographic data, suggesting that the LTA $AlPO_4$ membrane shows molecular sieve performance. In view of the fact that the separation selectivity of a membrane can be estimated as the product of adsorption selectivity and diffusion selectivity,[20] hydrogen shows the highest permeance. It should be noted that FAU,[10] SAPO-34,[14,15] and zeolite T[21] membranes have been found to show a high CO_2 permeance due to the fact that these polar zeolites have a strong adsorption affinity toward CO_2. For the present cation-free LTA-type $AlPO_4$ membrane, which is composed of AlO_4 and PO_4 tetrahedra resulting in a neutral framework, no CO_2 affinity can be expected, leading to a lower CO_2 permeance in comparison with those of O_2 and CH_4, which is in accordance with a previous finding for a mixed-matrix $AlPO_4$ membrane.[16] The ideal separation factors for H_2 from CO_2, O_2, CH_4, and C_3H_8, determined as the ratio of the single-component permeances,[22] are 11, 9, 7.7, and 181, respectively, indicating that the LTA-type $AlPO_4$ membrane is expected to display H_2 selectivity.

The molecular sieve performance of the LTA-type $AlPO_4$ membrane was confirmed by the separation of binary mixtures of H_2 with CO_2, O_2, CH_4, and C_3H_8. As shown in the inset of Figure 3 and in Table S1, the separation factors for H_2/CO_2, H_2/O_2, H_2/CH_4, and H_2/C_3H_8 mixtures, determined as the molar ratios in the permeate and retentate,[22] are 7.6, 6.1, 4.3, and 146, respectively, with H_2 permeances higher than 2.0×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}. These mixture separation factors exceed the corresponding Knudsen constants and are among the highest H_2 separation factors with comparable H_2 permeances (Table S2). It should be noted that an exceptionally high mixture selectivity (>300) was reported for the system H_2O/H_2 on an aluminosilicate LTA membrane,[23] but here water is separated from hydrogen through a hydrophilic separation mechanism instead of molecular sieving. Since H_2 adsorption and diffusion are reduced by the presence of a second mixture component, all of the ideal separation factors are higher than the corresponding mixture separation factors in the binary system (Table S1). Similar results have been reported for $AlPO_4$[16] and LTA zeolite[8] membranes. Figures S5 and S6 show the H_2/CH_4 mixture separation factor and the H_2 permeance as a function of time at 293 and 323 K, respectively. Both the mixture separation factor and the H_2 permeance remain unchanged for at least 48 h at 293 or 323 K, suggesting that the LTA-type $AlPO_4$ membrane has a high stability. When the temperature was increased from 293 to 323 K, the H_2 permeances increased to 2.9×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} while the separation factor was reduced.

In conclusion, in the present work, we have successfully prepared a neutral and cation-free supported LTA-type $AlPO_4$ membrane with high hydrogen permselectivity. For binary mixtures at 293 K, the separation factors for H_2/CO_2, H_2/O_2, H_2/CH_4, and H_2/C_3H_8 are 7.6, 6.1, 4.3, and 146, respectively, with high H_2 permeances of 2.1−2.5 $\times 10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1}. The LTA-type $AlPO_4$ membrane offers potential applications in gas separation and hydrogen purification by molecular sieving.

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Supporting Information Available: Experimental details; SEM image of a seed layer and an LTA $AlPO_4$ membrane prepared without seeding; XRD pattern of the seeded support and LTA $AlPO_4$ membrane; equipment for measurement of gas permeation; separation performance as a function of time; permeance calculation; and comparison of the gas separation performances. This material is available free of charge via the Internet at http://pubs.acs.org.

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