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Steam-Stable Zeolitic Imidazolate Framework ZIF-90 Membrane with Hydrogen Selectivity through Covalent Functionalization

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Abstract: A novel covalent functionalization strategy was developed to prepare reproducible ZIF-90 molecular sieve membranes by using 3-aminopropyltriethoxysilane as a covalent linker between the ZIF-90 layer and Al_2O_3 support via imines condensation. The ZIF-90 membranes show high thermal and hydrothermal stabilities, and they allow the separation of hydrogen from larger gases by molecular sieving.

Since the discovery of metal−organic frameworks (MOFs), microporous MOFs have attracted intense attention due to their potential applications in gas adsorption and storage, molecular separation, and catalysis.[1−6] Further, their highly diversified structures and pore size as well as specific adsorption affinities recommend MOFs as fascinating candidates for fabrication of superior molecular sieve membranes. The potential of MOFs as membrane material has been well recognized both experimentally and computationally.[7−11] Zeolitic imidazolate frameworks (ZIFs), a MOF subfamily based on transition metals and imidazolate linkers, have emerged as a novel type of crystalline porous material for the fabrication of molecular sieve membranes due to their zeolite-like properties such as permanent porosity, uniform pore size, and exceptional thermal and chemical stability.[12,13] Very recently, a few ZIF membranes with reasonable gas separation performances have been developed.[14−17] Despite much progress in the preparation of MOF membranes, there is still a long road ahead before robust synthetic strategies can be developed that allow the facile synthesis of highly selective MOF membranes, as highlighted recently.[18] One major obstacle to growing MOF films on supports is that the organic linkers in MOF materials usually cannot provide additional linkage groups that can form bonds with OH groups on the support surface. As reported previously,[9,10] it is rather difficult to prepare continuous MOF membranes by a direct solvothermal synthesis route since the heterogeneous nucleation of MOF crystals on support surfaces is very poor. Therefore, chemical modifications[10,17] and seed coating[7,15] of the supports are usually indispensable to direct the nucleation and growth of the MOF layers.

Recently, Yaghi and co-workers reported the new sodalite (SOD) topology ZIF-90 through solvothermal reaction of zinc(II) salt and imidazolate-2-carboxyaldehyde (ICA).[19] ZIF-90 is not only highly stable but also shows permanent microporosity with a narrow size of the six-membered ring pores (∼3.5 Å).[14,19] It can be expected, therefore, that a ZIF-90 membrane is able to separate H_2 (kinetic diameter ∼2.9 Å) from larger molecules.

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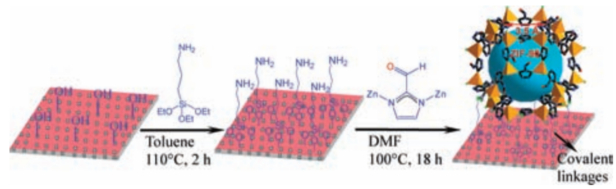

Figure 1. Scheme of preparation of ZIF-90 membranes by using 3-aminopropyltriethoxysilane (APTES) as a covalent linker between ZIF-90 membrane and Al_2O_3 support via an imine condensation reaction.

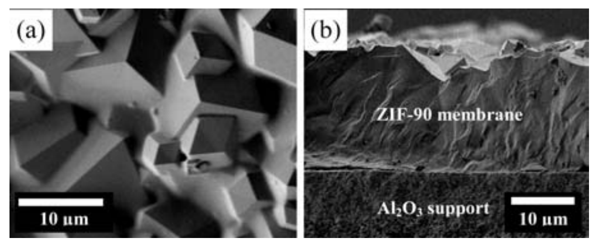

Figure 2. (a) Top view and (b) cross section SEM images of the ZIF-90 membrane supported on the APTES modified Al_2O_3 support.

In particular, the presence of the free aldehyde groups in the framework allows the covalent functionalization of ZIF-90 with amine groups via an imine condensation reaction.[19] Based on this coupling between the aldehyde and amine groups,[19,20] we report a novel covalent functionalization strategy to prepare molecular sieve ZIF-90 membranes by using 3-aminopropyltriethoxysilane (APTES) as covalent linkers between the ZIF-90 layer and Al_2O_3 support, as shown in Figure 1. In the first step, the ethoxy groups of the APTES react with surface hydroxyl groups of the Al_2O_3 support.[21] In the second step, the amino groups react with the aldehyde groups of ICA via imines condensation, and then the nucleation and crystal growth of the ZIF-90 start at these fixed sites on the surface of the porous ceramic supports.

After solvothermal reaction for 18 h at 100 °C (see Supporting Information), the surface of the APTES modified support has been completely covered with well intergrown rhombic dodecahedrons and a compact ZIF-90 layer with a thickness of about 20 μm. No cracks, pinholes, or other defects are visible (Figure 2). On the contrary, no continuous layer can be formed if the support surface was not treated with APTES (Figure S1). This result strongly indicates that the covalent linkages between the ZIF-90 and Al_2O_3 support indeed facilitate the formation of a compact ZIF-90 layer on the APTES modified support. Actually, due to the high organic functionality and flexibility with which the organic linkers can be modified, MOFs have been exemplified as ideal candidates for the covalent functionalization of materials through a host−guest reaction of pendant functional groups.[22−24]

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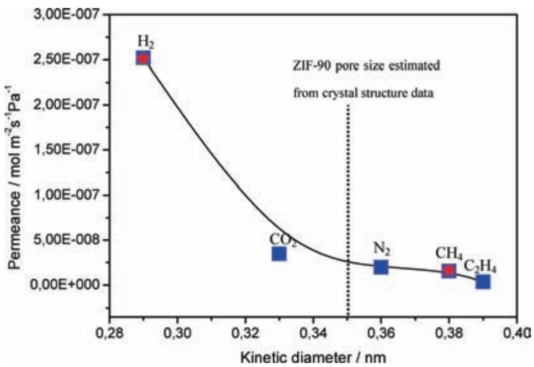

Figure 3. Single gas permeances of different gases on the ZIF-90 membrane at 200 °C as a function of their kinetic diameter. The pentacles show the permeances of H_2 and CH_4 from an equimolar binary mixture.

A typical X-ray diffraction pattern of the ZIF-90 membrane (Figure S2) shows a high degree of crystallinity, and all of the peaks match well with those of ZIF-90 reported previously in addition to Al_2O_3 signals from the support.[19]

Before gas permeation, the as-synthesized ZIF-90 membrane was on-stream activated at 200 °C by using an equimolar H_2-CH_4 mixture in the Wicke−Kallenbach permeation apparatus (Figure S3). Figure S4 shows the variation of the H_2 and CH_4 permeances from their binary mixture during the on-stream activation. Whereas the H_2 permeance increases with increasing temperature, the CH_4 permeance only slightly increases. The activation is completed at 200 °C with H_2 permeances of about 2.5×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and a H_2/CH_4 mixture selectivity of 15.2.

The volumetric flow rates of the single gases H_2, CO_2, N_2, CH_4, and C_2H_4 as well as the eqimolar binary mixtures of H_2 with CO_2, N_2, CH_4, and C_2H_4 were measured by using the Wicke−Kallenbach technique (Figure S3). The permeances and separation factors are summarized in Table S1. Figure 3 shows the permeances of the single gases through the activated ZIF-90 membrane as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3 and Table S1, the permeances clearly depend on the molecular size of the gases, and the permeance of H_2 is much higher than those of the other gases. However, due to the well-known fact of lattice flexibility, also molecules with a kinetic diameter larger than the crystallographic pore size can pass through the membrane. The ideal separation factors[25] of H_2 from CO_2, N_2, CH_4, and C_2H_4 are 7.2, 12.6, 15.9, and 63.3, respectively, suggesting that the ZIF-90 membrane displays molecular sieve performance with high H_2 permselectivity.

The molecular sieve performance of the ZIF-90 membrane was confirmed by the separation of the equimolar mixtures at 200 °C and 1 bar. Upon comparison with the H_2 single gas permeance, the H_2 permeances in mixtures were observed to differ only slightly; H_2 permeances between 2.32×10^{-7} and 2.51×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} were measured. For the 1:1 binary mixtures, the mixture separation factors[25] of H_2/CO_2, H_2/N_2, H_2/CH_4, and H_2/C_2H_4 are 7.3, 11.7, 15.3, and 62.8, respectively, which by far exceed the corresponding Knudsen coefficient (4.7, 3.7, 2.8, and 3.7, respectively). It is found that the novel synthesis strategy through covalent functionalization is very helpful to enhance the reproducibility of membrane preparation (Table S2). The average H_2/CH_4 selectivity is 15.13 ± 0.21 (standard deviation) for the three membranes in Table S2.

When the permeation temperature was increased from 25 to 225 °C at 1 bar, the H_2 permeances increase from 1.32×10^{-7} to 2.85×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and the H_2/CH_4 mixture separation factor rises from 7.0 to 16.4 (Figure S5). This phenomenon can be explained by the adsorption-diffusion model. At low temperature, mainly CH_4 is adsorbed in the ZIF-90 pores thus blocking the diffusion of the rarely adsorbed and highly mobile H_2. As temperature increases, less CH_4 is adsorbed and thus more H_2 can diffuse in the resulting free volume, leading to a large enhancement of H_2 permeance. Furthermore, the ZIF-90 membrane shows completely reversible separation behavior between 25 and 225 °C. The permeances measured with decreasing temperature are well consistent with those with increasing temperature. The ZIF-90 membrane can keep its high H_2 permselectivity when the H_2 partial pressure increases from 0.5 to 1.5 bar (Figure S6). Development of steam-stable molecular sieve membranes is highly desired since water is usually present in traces in every gas. To evaluate its hydrothermal stability, the ZIF-90 membrane was tested to separate an equimolar H_2/CH_4 mixture containing 3 mol % steam at 200 °C and 1 bar.[26] The ZIF-90 membranes show a very good stability in the presence of steam, and both H_2 permeance and H_2/CH_4 selectivity are unchanged for 24 h (Figure S7), which shows that the ZIF-90 pore volume is not blocked by adsorbed water. This hydrothermal stability combined with its high thermal stability recommends the ZIF-90 membrane to be used for H_2 separation/purification at high temperature.

In conclusion, via an imine condensation reaction, we have developed a novel seeding-free approach to prepare reproducible ZIF-90 molecular sieve membranes with high H_2 permselectivity by using APTES as a covalent linker to promote the nucleation and growth of ZIF-90. The ZIF-90 molecular sieve membranes displayed high thermal and hydrothermal stabilities. These properties recommend the ZIF-90 membrane as a promising candidate for both hydrogen production and purification.

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Supporting Information Available: Experimental details; SEM image and XRD of the ZIF-90 membrane; measurement equipment of gas permeation; separation performances of the ZIF-90 membrane as a function of operating conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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