Organosilica functionalized zeolitic imidazolate framework ZIF-90 membrane for CO2/CH4 separation postprint

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Abstract

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Full Text

Preamble

Organosilica functionalized zeolitic imidazolate framework ZIF-90 membrane for CO_2/CH_4 separation

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The separation of CO_2/CH_4 is reported by using 3-aminopropyltriethoxysilane (APTES) modified zeolitic imidazolate framework ZIF-90 membrane. The as-prepared ZIF-90 membrane was modified by APTES based on an imine condensation reaction between the free aldehyde groups of the ZIF-90 frameworks and the amino groups of APTES. After APTES modification, the morphology, purity and crystallinity of the ZIF-90 membrane keep unchanged. Attributing to both pore mouth narrowing and sealing of invisible intercrystalline defects of the polycrystalline ZIF-90 layer, the separation performances of the APTES-modified ZIF-90 membrane are remarkably enhanced. For the separation of equimolar CO_2/CH_4 mixture at 225°C and 1 bar, a CO_2 permeance of 1.26×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and a CO_2/CH_4 selectivity of 4.7 are obtained, which shows promise for potential applications in CO_2 separation and removal.

1. Introduction

CO_2 is an undesirable impurity in many natural gas wells; therefore, the separation and removal of CO_2 from natural gas are highly important from the perspective of energy effectiveness. In comparison with conventional separation methods like pressure swing adsorption (PSA), membrane-based separation has been considered to be the most promising alternative because of its low energy consumption, ease of operation, and cost effectiveness [1]. Since organic polymer membranes usually suffer from instability problems at high temperatures or in contact with solvents, inorganic zeolite membranes are more promising under harsh separation conditions [2]. So far, CO_2-permselective zeolite membranes such as DDR [3], zeolite T [4], and SAPO-34 [5,6] have been developed for the separation of CO_2 from CH_4. These zeolite membranes display high CO_2/CH_4 selectivities due to the interplay of adsorption and diffusion. However, it is usually necessary to use organic template for the preparation of zeolite membranes. The thermal burning of the organic template may result in the formation of cracks due to a compression stress within the zeolite layer during the cooling step [7,8], which is detrimental to the separation selectivity.

Due to their well-defined, adjustable and highly porous framework structures, metal–organic frameworks (MOFs) are of high potential application in gas adsorption and storage, molecular separation, drug delivery, and catalysis [9-23]. Among the reported MOFs, the subfamily zeolitic imidazolate frameworks (ZIFs), which are based on transition metals (Zn, Co) and imidazolates as linkers [24–26], have emerged as a novel type of crystalline porous material for the fabrication of molecular sieve membranes attributed to their zeolite-like properties such as permanent porosity, uniform pore size, exceptional thermal and chemical stability. So far, a series of supported ZIF membranes, such as ZIF-7 [27], ZIF-8 [28–32], ZIF-22 [33], ZIF-69 [34], ZIF-71 [35], ZIF-90 [36–39], and ZIF-95 [40] have been reported for single gas permeation or mixture gas separation. These ZIF membranes have shown promising H_2 selectivity, but there are only a few reports of highly CO_2-permselective ZIF membranes [28,34].

Sodalite (SOD) ZIF-90, reported by Yaghi and co-workers [41], is of high interest for the fabrication of molecular sieve membranes. ZIF-90 not only shows a high stability, but also a permanent microporosity with a narrow pore window of 0.35 nm (Fig. 1a [Figure 1: see original paper]), which is in between the molecular size of CO_2 (0.33 nm) and CH_4 (0.38 nm), thus it is expected to exclude CH_4 from CO_2/CH_4 mixtures through molecular sieving. Further, the carbonyl group in ZIF-90 frameworks has a favorable chemical non-covalent interaction with CO_2 [42]. However, according to the previous report [36,39], for the separation of CO_2/CH_4 mixture, the as-prepared ZIF-90 membrane shows a rather ordinary CO_2/CH_4 selectivity due to lattice flexibility of MOFs. Recently, we have developed a novel post-functionalization method for the preparation of highly permselective ZIF-90 molecular sieve membranes through an imine condensation reaction by using the organosilica APTES (Fig. 1b). With APTES-functionalization, the gas separation selectivity is enhanced due to the sealing of invisible intercrystalline defects of the polycrystalline ZIF-90 layer [38]. It can be expected, therefore, that the APTES-modified ZIF-90 membrane could display high CO_2 permselectivity. In the present work, we report the separation of CO_2/CH_4 by using the APTES-modified ZIF-90 membrane.

2. Experimental

2.1. Materials

Chemicals were used as received: zinc nitrate tetrahydrate (>99%, Merck), imidazolate-2-carboxyaldehyde (ICA > 99%, Alfa Aesar), 3-aminopropyltriethoxysilane (APTES, 98%, Abcr), toluene (Acros), N,N-dimethylformamide (DMF, water <50 ppm, Acros). Porous α-Al_2O_3 disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as supports.

2.2. Synthesis of ZIF-90 membranes

The ZIF-90 membranes were synthesized as the preparation procedure reported previously [30,34]. Porous α-Al_2O_3 disks were treated with APTES (0.2 mM in 10 mL toluene) at 110°C for 1 h under argon [43,44], leading to an APTES monolayer deposited on the supports surface. The APTES-treated α-Al_2O_3 supports were placed horizontally in a Teflon-lined stainless steel autoclave which was filled with synthesis solution. After solvothermal reaction at 100°C in an air-circulating oven for 18 h, the ZIF-90 membranes were washed with DMF several times, and then dried in air at 60°C overnight.

2.3. Covalent functionalization of ZIF-90 membranes

The ZIF-90 membranes were covalently functionalized with APTES according to the procedure reported previously [38]. The as-prepared ZIF-90 membranes were immersed in methanol and APTES solution, and refluxed at 110°C for 0.5 h. After reaction, the APTES-functionalized ZIF-90 membranes were washed with methanol several times to remove unreacted APTES, and then dried in air at room temperature overnight for next characterization and permeation measurement.

2.4. Characterization of ZIF-90 membranes

The morphology and thickness of the as-prepared and APTES-functionalized ZIF-90 membranes were characterized by field emission scanning electron microscopy (FESEM). FESEM micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 A. The phase purity and crystallinity of the as-prepared as well as APTES-functionalized ZIF-90 membranes were confirmed by X-ray diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuKα radiation at 40 kV and 40 mA.

2.5. Evaluation of single gas permeation and mixture gas separation

For the single gas permeation and mixture gas separation, the APTES-functionalized ZIF-90 membranes were sealed in a permeation module with silicone O-rings. Before single gas permeation and mixture gas separation, the ZIF-90 membranes were on-stream activated to remove guest molecule methanol at 225°C with a heating rate of 0.2°C min^{-1} by using an equimolar H_2/CO_2 mixture in the Wicke-Kallenbach permeation apparatus [36,37]. The sweep gas N_2 was fed on the permeate side to keep the concentration of permeating gas as low as possible thus providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. The fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromatograph (HP6890) was used to measure the gas concentrations. The separation factor a , of a binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the retentate, as shown in Eq. (1).

a , = (y ,Perm / y ,Perm) / (y ,Ret / y ,Ret)

3. Results and discussion

3.1. Membrane preparation and characterization

Fig. 2 [Figure 2: see original paper] shows the FESEM images of the as-prepared and APTES-functionalized ZIF-90 membrane. It can be seen that the surface of the alumina support has been completely covered with well intergrown and randomly oriented rhombic dodecahedrons, and no cracks, pinholes or other defects are observed in the as-prepared ZIF-90 layer (Fig. 2a). From the cross-section view, it can be seen that a compact ZIF-90 layer with a thickness of about 20 m has formed on the surface of the alumina support (Fig. 2b). The XRD pattern shows that a pure ZIF-90 layer with high crystallinity is formed on the surface of the alumina support (Fig. 3a [Figure 3: see original paper]), and all peaks match well with those of ZIF-90 reported previously besides the Al_2O_3 signals from the support [41].

After APTES-functionalization, no remarkable difference in the membrane morphology is found between the as-prepared and APTES-functionalized ZIF-90 membranes (Fig. 2c), and a well intergrown ZIF-90 layer with a thickness of about 20 m was observed on the porous alumina support (Fig. 2d), which is in good agreement with our previous report [39]. The XRD pattern shows the ZIF-90 membrane keeps unchanged after APTES modification and all XRD peaks of the APTES-functionalized ZIF-90 membrane match well with those of the as-prepared ZIF-90 membrane (Fig. 3b), indicating the high crystallinity of the ZIF-90 membrane is maintained.

3.2. Single gas permeation and mixed gas separation

Before single gas permeation and mixture gas separation, the APTES-functionalized ZIF-90 membranes were on-stream activated at 225°C with a heating rate of 0.2°C min^{-1} by using an equimolar H_2/CO_2 mixture in the Wicke-Kallenbach permeation apparatus. Fig. 4 shows the variation of the H_2 and CO_2 permeances as well as the H_2/CO_2 selectivity from its binary mixture during the on-stream activation. Whereas the H_2 permeance remarkably increases with increasing temperature from 25 to 225°C, the CO_2 permeance only slightly increases, resulting in a remarkable enhancement of H_2/CO_2 selectivity from 7 to 21. Similar to the previous report [37,38], the APTES-functionalized ZIF-90 membrane is more easily activated than the as-prepared ZIF-90 membrane since the difficulty of removing the guest molecule DMF has been exchanged by the more volatile methanol during the covalent post-functionalization. After on-stream activation at 225°C for 60 h, the APTES-functionalized ZIF-90 membrane shows a constant H_2 permeance of about 2.83×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a H_2/CO_2 selectivity of about 21.

After on-stream activation, the volumetric flow rates of the single gases H_2, CO_2, CH_4, C_2H_6 and C_3H_8 through the APTES-functionalized ZIF-90 membrane were measured by using the Wicke-Kallenbach technique, and the C_4H_{10} permeance was determined by soap bubble. Fig. 5 [Figure 5: see original paper] shows the permeances of the single gases through the APTES-functionalized ZIF-90 membranes at 225°C and 1 bar as a function of the kinetic diameters of the permeating molecules. As shown in Fig. 5, the permeances clearly depend on the molecular size of the gases, and the H_2 permeance of 2.85×10^{-7} mol m^{-2} s^{-1} Pa^{-1} is much higher than those of the other larger gases, resulting in a clear cut-off between H_2 and the other larger gases. Compared with the as-prepared ZIF-90 membrane [36], the H_2 permeance of the APTES-functionalized ZIF-90 membrane keeps almost unchanged although all other gas permeances decrease, indicating that the window of the ZIF-90 channel was not blocked by APTES modification since the bulky APTES molecules are restricted to enter the interior of the ZIF-90 layer in a short time, thus avoiding remarkable reduction of the H_2 permeance.

At 225°C and 1 bar, the ideal separation factors of H_2 over CO_2, CH_4, C_2H_6, C_3H_8 and C_4H_{10} are 21, 77, 254, 456 and 1370, which by far exceed the corresponding Knudsen coefficients (4.7, 2.8, 3.9, 4.7 and 5.4) and those of the as-prepared ZIF-90 membrane [36]. These results are in good agreement with our previous report [38], suggesting the hydrogen selectivity of the ZIF-90 membrane can be enhanced through APTES functionalization by eliminating the intercrystalline defects.

There are a few reports about separation of mixtures on MOF membranes, and most of them are H_2 selective rather than CO_2 selective (Table 1). Carreon and colleague reported a CO_2 selective ZIF-8 membrane with CO_2/CH_4 selectivity of about 4.8 [28]. Lai and colleagues reported a CO_2 selective ZIF-69 membrane with CO_2/CH_4 selectivity of about 4.6 [34]. ZIF-90 has a small pore window of 0.35 nm, which is in between the molecular size of CO_2 (0.33 nm) and CH_4 (0.38 nm), thus it is expected that CO_2 can be easily separated from a CO_2/CH_4 mixture through molecular sieving. However, according to our previous report [36], for the separation of a CO_2/CH_4 mixture, the separation performance of the as-prepared ZIF-90 membrane falls short of our expectations with CO_2/CH_4 selectivity of about 1.6 due to the well-known fact of lattice flexibility of MOFs, which allows large molecules like CH_4 to pass the small pore window of the ZIF-90 membrane. Recently, Nair and colleagues prepared a continuous polycrystalline ZIF-90 membrane on polymeric hollow fiber, and a similar CO_2/CH_4 selectivity of about 1.5 was obtained [39].

Through the covalent linkages between the free aldehyde groups of the ZIF-90 and the amino group of APTES, both narrowing of pore mouth and sealing of intercrystalline defects of the polycrystalline ZIF-90 layer took place [38], thus it is expected to enhance CO_2/CH_4 selectivity of the APTES-functionalized ZIF-90 membrane. The molecular sieve performance of APTES-functionalized ZIF-90 membrane was confirmed by the separation of equimolar CO_2/CH_4 mixtures at different operating temperatures. As shown in Fig. 6 [Figure 6: see original paper], with increase of the operating temperature from 25°C to 225°C, the CO_2 permeance increases from 6.87×10^{-9} to 1.26×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, but the CH_4 permeance slightly increases from 1.71×10^{-9} to 2.66×10^{-9} mol m^{-2} s^{-1} Pa^{-1}, thus the CO_2/CH_4 mixture separation factor rises from 4.0 to 4.7, which are higher than the corresponding Knudsen coefficient of 0.6. Comparing with literature data of the gas separation of MOF membranes for CO_2/CH_4 mixture (Table 1), the APTES-functionalized ZIF-90 membrane developed in this study is among those with high separation performances.

More work is in process to decrease the membrane thickness, thus to increase the CO_2 permeance. Further, similar to our previous report, the APTES-functionalized membranes show a very good stability in the separation of CO_2/CH_4, and both CO_2 permeance and CO_2/CH_4 selectivity are unchanged for 24 h (Fig. 7 [Figure 7: see original paper]). This hydrothermal stability combined with a high CO_2/CH_4 selectivity recommends the APTES-functionalized ZIF-90 membrane as a good candidate for CO_2 separation and removal.

4. Conclusion

In conclusion, pure and compact ZIF-90 membranes are prepared on the porous Al_2O_3 supports. Through the covalent post-functionalization of the ZIF-90 membrane by using the organosilica APTES, the separation performances of ZIF-90 membranes are remarkably enhanced. For the separation of an equimolar CO_2/CH_4 mixture at 225°C and 1 bar, a CO_2 permeance of 1.26×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and a CO_2/CH_4 selectivity of 4.7 is obtained, which is among the developed MOF membranes with high separation performances. In addition, the APTES-functionalized ZIF-90 membranes show a very good stability in the long-term separation of CO_2/CH_4. This hydrothermal stability combined with high CO_2/CH_4 selectivity is promising for a potential application in the CO_2 separation and removal.

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