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Deuterium/hydrogen permeation through different molecular sieve membranes: ZIF, LDH, zeolite

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ABSTRACT

Different molecular sieve membranes have been evaluated in the separation of deuterium (D_2)/hydrogen (H_2) mixtures. Both the single gases and the binary D_2/H_2 mixture have been permeated at room temperature through supported Metal Organic Framework (MOF) membranes (ZIF-8 and ZIF-90) as well as through supported zeolite (SOD, LTA, FAU) and layered double hydroxide (LDH) membranes. Also the D_2/H_2 permeation through the non-coated bare α-Al_2O_3 supports, and pressed graphite discs has been studied. Since the molecular mass of D_2 is twice the mass of H_2, and D_2 is slightly smaller than H_2, D_2 should show higher single component permeability than H_2 because of its favored adsorption and diffusion compared with H_2. For the MOF membranes (ZIF-8 and ZIF-90) as well as the LDH membrane, the single gas D_2 permeabilities are indeed by the factor of 3 larger than those of H_2 at room temperature. However, due to strong molecular interaction, no separation is found for the equimolar D_2/H_2 mixture. For comparison, we also studied the permeation of He/D_2. Since these mixture components are of the same molecular mass and almost the same size, no separation can be expected and no separation has been found.

1. Introduction

The stable hydrogen isotope deuterium (D_2) is used in a variety of applications like nuclear fusion or isotopic tracing. Based on the limited availability [1] on earth and the versatile applicability of D_2 it is necessary to develop low-cost separation processes. However, in consequence of the almost same size and the similar physical and chemical behavior of the hydrogen isotopes, D_2/H_2 separation becomes a challenging task. Therefore, just a few methods, namely cryogenic distillation or electrolysis of water, are qualified at present for large scale hydrogen isotope separation. However, the main disadvantage of these methods is their expensiveness due to their low separation factors (1.5 in distillation and 2.3 in electrolysis) [2]. Another interesting principle for the isotope separation is the adsorptive quantum sieving (QS) effect at temperatures around 70 K and lower [3,4]. This effect occurs when the difference between molecular size and the pore diameter is in the range of the de-Broglie wavelength of hydrogen. If these conditions are fulfilled, the lighter isotope H_2 will be impeded more than the heavier D_2 in the pore system due to the differences between their zero point energy (ZPE). The lower the temperature gets, the higher are the differences between the diffusion coefficients of the isotopes. This effect results in a separation of the isotopes what was already investigated by different groups such as Beenakker et al. [4] or Heine et al. [5]. Nevertheless, the drawback with this method is the stringent necessity of the cooling to low temperatures. Otherwise the effect of QS cannot be obtained.

Here we present another separation concept based on the different diffusion and adsorption behavior of D_2 and H_2 at room temperature. On the one hand, D_2 is slightly smaller than H_2. As a result of this, the D_2 diffusion coefficient should be higher than the H_2 diffusion coefficient. On the other hand, D_2 is twice heavier than H_2, which affects the adsorption selectivity resulting in a higher adsorbed amount of D_2. This adsorption concept was followed in previous quantum sieving experiments at much lower temperature [6]. The two effects, better D_2 adsorption and higher D_2 diffusivity, should cooperate in the case of membrane permeation. As a rough estimate for membrane selectivity, we can assume that.

Membrane selectivity ≈ diffusion selectivity × adsorption selectivity [7,8]. (1)

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Following this concept of different adsorption and diffusion behavior of the hydrogen isotopes, we can expect a permeative separation of a D_2/H_2 mixture even at room temperature with D_2 as the preferentially permeated component.

For the evaluation of this concept, we selected several nanoporous membranes with proven molecular sieve separation ability developed in our group: Metal Organic Framework (MOF) materials of type ZIF (zeolitic imidazolate framework), zeolites, layered double hydroxide (LDH) and pressed graphite. Especially MOFs are promising membrane materials because of their property to tune their adsorption properties (pore size [9], linker functionalization [10], specific gas adsorption [11]). Based on their very high porosity, MOFs show enormous specific surface areas which can be used for gas storage by physisorption [12]. Teufel et al. demonstrated the potential of MOF's in adsorptive hydrogen isotope separation [13].

The pressed graphite membranes should also show interesting separation behavior due to a different D_2/H_2 adsorption selectivity. For instance, Jiao et al. [14] and Zhang et al. [15] studied the adsorptive hydrogen isotope separation on carbon materials based on quantum sieving with a favored adsorption selectivity of D_2. The gas transport through a graphite membrane proceeds through the grain boundaries as shown in Ref. [16]. Therefore, the pressed graphite membrane is a good candidate to investigate separation behavior independent of a molecular sieve pore system.

However, zeolites with their rigid pore system separate gases by molecular sieving rather than by adsorptive interactions. Since D_2 is only slightly smaller than H_2, we expect that most of the zeolite membranes will not separate the D_2/H_2 mixture since their pore size is not exact at 2.9 Å. As a proof of our concept, also the permeation of the hydrogen isotopes through the neat α-Al_2O_3 support has been studied. Whereas for the MOF and zeolite membranes a more or less pronounced D_2 over H_2 selectivity is anticipated, for the macroporous support a separation in the range of the Knudsen factor

$$\alpha(D_2/H_2) \approx \sqrt{\frac{M(H_2)}{M(D_2)}} \approx \sqrt{0.5} \approx 0.7$$

is expected. This behavior occurs if the pores are bigger than the diameter of the gases and if there are no special interactions with the pore system. In this case collisions with the walls of the pore system appear more frequently than collisions between the gas molecules, and the lighter gas should pass the pore system easier [17,18].

2. Experimental

2.1. Preparation of supported ZIF-90, ZIF-8 and LDH membranes

For hydrogen isotope permeation, different types of membranes were prepared. The syntheses of these membranes were done following recipes reported elsewhere (ZIF-90 [19], ZIF-8 [20], LDH [21,22], pressed graphite [16], FAU [23], SOD [24], LTA [23,25]). Here, we give only a short description of the three most promising membranes according to the single component tests. All supported membranes were prepared on α-alumina supports (70 nm pores in top layer, Fraunhofer IKTS, former Hermsdorfer HITK, Germany).

2.1.1. Synthesis of ZIF-90 membrane

The α-Al_2O_3 supports were functionalized with 0.46 g APTES (3-aminopropyltriethoxysilane, Sigma Aldrich) in 10 mL toluene at 110 °C for 2 h, followed by several washing steps with toluene. Afterward the disks were placed horizontally in a Teflon lined autoclave. A solution of 0.43 g $Zn(NO_3)\cdot 4H_2O$ and 0.23 g imidazole-2-carboxyaldehyde (Sigma Aldrich) in 24 mL DMF was then filled into a vessel and sealed. Then the autoclave was heated to 100 °C in a convection oven for 18 h. After the synthesis the membrane was washed with DMF and dried at 60 °C overnight.

2.1.2. Synthesis of ZIF-8 membrane

The ZIF-8 membranes were produced by the secondary growth method. Therefore a solution of 0.12 g sodium hydrogen carbonate, 1.20 g polyethyleneimine (Sigma Aldrich, ~50% in water, 4 wt.%), 0.80 g ZIF-8 nanoparticles in 30 mL water was prepared. This solution was used to produce a layer of seeding crystals on top of the supports by dip coating. The dipping parameters were set as following: up speed = 200 mm min^{-1}, down speed = 300 mm min^{-1}, lower delay = 10 s, and upper delay = 3 min. After the coating process the supports were dried overnight at room temperature. For the secondary growth process, 0.54 g $ZnCl_2$ (3.94 mmol, 1 eq.), 0.49 g 2-methylimidazole (5.92 mmol, 1.5 eq.) and 0.27 g sodium formate (3.94 mmol, 1 eq.) (Sigma Aldrich) were solved in 80 mL methanol. This solution was filled in a 200 mL Teflon lined autoclave and one of the seeded supports was put vertically in the solution. The autoclave was heated in the microwave oven with a heating rate of 7.5 °C min^{-1} at 100 °C for 1.5 h. After the autoclave was cooled down to room temperature, the membrane was washed with 20 mL methanol and dried overnight at room temperature.

2.1.3. Synthesis of LDH membrane

The precursor solution was prepared by adding 5.8 g $Ni(NO_3)_2\cdot 6H_2O$ (98.0 wt. %, Merke) and 4.8 g NH_4NO_3 (Aldrich, 98.0 wt.%) into 100 mL CO_2-saturated water (Vitalitasia Classic, containing saturated CO_2). Consequently 10 mL 1 wt.% $NH_3\cdot H_2O$ (Aldrich, 28 wt.%) was added dropwise into the aqueous solution and stirred in an ice bath for 10 min. After that a γ-Al_2O_3-modified α-alumina support was vertically placed into a 50 mL Teflon-lined stainless vessel. Then 35 mL of aqueous solution was poured into the vessel and sealed. The vessel was put into convective oven with the temperature pre-heated to 85 °C. After an elapsed time of 40 h, it was taken out and cooled to room temperature in air. Finally the membrane was taken out and washed with copious of DDI water. Before gas separation measurement, the membrane was dried in a convective oven at 60 °C for 12 h.

2.2. Electron microscopy

The Scanning Electron Microscopy (SEM) studies of the membranes were done with a field-emission electron microscope (JEOL JSM-6700F). The accelerating voltage was set to 2 kV and the working distance was 8 mm.

2.3. Gas permeation measurements

Our assumptions of the permeation properties are evaluated by single gas and mixed gas separation measurements. The membranes were sealed in the permeation cell with Viton O-rings (FKM 70 Vi 370). In single gas measurements gas chromatography (Agilent Technologies 7890B) was applied. Mixed gas separation analysis was done by mass spectrometry (OMNISTAR GSD QMS 200 Quadrupol). Some membranes were tested with vacuum on the permeate side to minimize the effect of counter diffusion which can take place in Wicke-Kallenbach measurements (cf. the influence of the pressure difference Δp over the membrane in Table 1). In this case, the permeate side was evacuated by a vacuum pump (Pfeiffer MVP 015-4). Fig. 1 shows the measurement setup for both single and mixed gas permeation. For mixed gas permeation, the