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Separation dynamics of hydrogen isotope gas in mesoporous and microporous adsorbent beds at 77 K: SBA-15 and zeolites 5A, Y, 10X

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ABSTRACT

The separation of a hydrogen isotope mixture on porous materials was studied using equilibrium and breakthrough experiments. The adsorption equilibria of H_2 and D_2 on SBA-15 with mesopores and molecular sieves 5A, Y, and 10X with micropores were measured at 77 K using the volumetric method. The breakthrough experiments of a H_2 and D_2 mixture in each adsorbent bed were carried out at various conditions of flow rate and pressure. The equilibrium ratio of D_2 to H_2 on mesoporous molecular sieves was larger than the ratio on microporous molecular sieves (SBA-15 > 10X > Y > 5A), but the difference among the adsorbents decreased with increases in pressure. On the other hand, the order of breakthrough separation factor showed the opposite result (SBA-15 < 10X < Y < 5A). The breakthrough separation factors for zeolite 10X was approximately equal to the equilibrium ratio of D_2 to H_2 at the corresponding partial pressures, whereas zeolites 5A and Y showed higher breakthrough separation factors than their equilibrium ratios. In SBA-15, the separation factors from breakthrough results were even smaller than the corresponding equilibrium ratio. In the microporous adsorbent with a limited pore size (zeolite 5A in the study), the diffusion mechanism contributed to the separation of hydrogen isotope gases as one of key factors.

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1. Introduction

Deuterium, a heavy isotope of hydrogen, is an important material in the nuclear industry and its demand is expected to continuously increase. Also, deuterium is widely used in organic chemistry and biochemistry as a tracer [1,2], pharmaceutical technology and the analysis of materials in ^{2}H NMR [3–5]. Moreover, since less than 10% of the deuterium and tritium used are consumed in nuclear fusion reactors, the separation of hydrogen isotopes is crucial for the reuse of deuterium [6]. However, it is difficult to separate hydrogen isotopes because of their similar physical properties. At present, the separation of hydrogen isotopes is carried out using commercialized separation methods such as cryogenic distillation, laser, and thermal diffusion [7–9]. Since these separation processes involve high energy consumption or complex equipment, the demands for more energy-saving and lower-cost processes are continuously increasing. Although adsorptive separation is known to be highly efficient [10–12], few experimental studies have reported using this method for hydrogen isotope separation [13–16].

It has been reported that the separation of a hydrogen isotope mixture does not rely on steric effects because of the similarity in molecular size. Most studies have applied microporous adsorbents for the separation of hydrogen isotopes [9,13–15]. And the cryogenic condition was applied to the adsorptive separation to enhance the adsorption capacity of hydrogen isotope gas on microporous adsorbents [9,14]. In zeolites, the equilibrium capacity will directly vary with the cation density. However, it was reported that, above their supercritical temperatures, the surface properties of adsorbents are not important for hydrogen adsorption capacity because of the law of monolayer adsorption [17–19]. In addition, the specific surface areas of the adsorbents only affect the adsorption amount of hydrogen isotopes [17,18,20,21]. It has also been shown that the surface area of the adsorbents is not a crucial factor for hydrogen isotope separation [20–23]. In terms of the influence of the surface characteristics of adsorbents, it was also reported that palladium did not affect the hydrogen storage capacity at 77 K and 1.6 MPa compared with the undoped materials, even though palladium activity was much higher than the other adsorbents examined [24,25]. Recently, a difference in the mechanism separating H_2 and D_2 by using carbon materials and zeolites was reported. It has also been suggested that zeolites have high selectivity due to kinetic quantum molecular sieving [15,16].

At low temperatures and pore dimensions on the order of de Broglie wavelengths, kinetic quantum effects are significant [15,16,26–29]. Despite the importance of adsorbents in determining the feasibility and cost of isotope separation, few experiments have compared isotope separation among various molecular sieve adsorbents. It is also necessary to explore the effects of pore size on hydrogen isotope separation using different molecular sieve adsorbents and adsorption equilibrium.

In this study, the equilibrium and dynamic adsorption behaviors of H_2 and D_2 on SBA-15 with mesopores and zeolites 5A, Y, and 10X with micropores were investigated using the volumetric method and breakthrough experiments at 77 K using liquid nitrogen. Instead of using zeolite powder, commercial zeolite pellets were packed to the bed after they were ground. In the breakthrough experiments, a mixture of H_2, D_2, and He (3.49:4.36:92.15 vol.%) was used as a feed. The contributions of equilibrium and dynamic separation to isotope separation were compared among adsorbents. Understanding the separation behaviors and mechanisms of these isotopes on different microporous or mesoporous adsorbent beds can contribute to designing and developing adsorbents for the efficient separation of isotopes.

2. Experimental section

2.1. Materials and instruments

SBA-15, a mesoporous silica with two-dimensional ordered channels, was synthesized under acidic conditions. A nonionic oligomeric alky-ethylene oxide surfactant (Pluronic P123) was used as the structure-directing agent, and analytical-grade tetraethyl orthosilicate was used as the silica source. Details of the synthesis were reported previously [30,31]. The pelletized molecular sieves zeolites 5A, Y, and 10X were provided by the Jin-Zhong Molecular Sieve Factory, Shanghai. Adsorbents with particle sizes of 0.4–0.5 mm were used after grinding the pellets. The specific surface area and pore size of the adsorbents were measured by the BET method (SA-3100 Plus analyzer, Beckman Coulter, USA). Their physical properties are listed in Table 1. Hydrogen with higher than 99.999% purity was supplied by Liu-Fang High-Tech Co., China. Deuterium with greater than 99.9% purity was provided by the Hai-Pu Gas Industry Co., Beijing, with a detectable impurity of hydrogen by gas chromatography (GC).

Table 1 – BET surface area, average pore size, saturated adsorption capacity (q_s) and adsorption affinity coefficient (b) of H_2 and D_2 on different adsorbents.

Adsorbents	S_{BET} m^2/g	Average pore size nm	Adsorbates	q_s (mol kg^{-1})	b (kPa^{-1})
5A	436	0.5	H_2	5.23	0.115
			D_2	5.35	0.193
Y	367	0.7	H_2	5.94	0.0317
			D_2	6.08	0.0455
10X	474	0.8	H_2	5.09	0.0820
			D_2	5.53	0.106
SBA-15	653	5.1	H_2	3.82	0.0375
			D_2	4.02	0.0538