Separation and Purification Technology 140 (2015) 1–5

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Comparative study on the influence of toluene and methylcyclohexane on the performance of dimethoxydiphenylsilane-derived silica membranes prepared by chemical vapor deposition

Masahiro Seshimo [a,1], Kazuki Akamatsu [a,*], Satoshi Furuta [b], Shin-ichi Nakao [a]

[a] *Department of Environmental and Energy Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji-shi, Tokyo 192-0015, Japan*
[b] *Hydrogen & New Energy Research Laboratory, JX Nippon Oil & Energy Corporation, 8, Chidori-cho, Naka-ku, Yokohama 231-0815, Japan*

ARTICLE INFO

Article history:
Received 26 August 2014
Received in revised form 11 November 2014
Accepted 14 November 2014
Available online 21 November 2014

Keywords:
Methylcyclohexane
Toluene
Silica membrane
Dimethoxydiphenylsilane
Chemical vapor deposition

ABSTRACT

The influence of toluene (TOL) and methylcyclohexane (MCH) on the performance of dimethoxydiphenylsilane-derived silica membranes prepared by chemical vapor deposition was investigated. The presence of TOL decreased the H_2 and N_2 permeances. These decreases were more pronounced at higher TOL concentration and lower temperature. This was attributed to the adsorption of TOL, and permeance was largely recovered by regeneration in H_2. The recovery of N_2 permeance was less satisfactory than that of H_2 permeance. The presence of MCH had a much smaller effect on membrane performance, though N_2 permeance was mildly affected. The difference in the effects of TOL and MCH on membrane performance reflected the differing physical interactions of these molecules with the membrane. The interaction between TOL and silica was stronger and adsorption therefore more favorable, than that between MCH and silica. Thus, TOL was more difficult to remove from the membrane surface and pores.

1. Introduction

Obtaining hydrogen from organic chemical hydrides has been the subject of increasing recent attention, and developing feasible hydrogen purification technologies is of significant importance. Organic chemical hydrides such as methylcyclohexane (MCH) offer many advantages over other hydrogen carriers. Organic chemical hydrides are ideally dehydrogenated to yield hydrogen, which must then be separated from reactants and unreacted hydride before use.

Various membranes can be used to purify hydrogen from organic chemical hydrides and/or their reactants. Palladium and its alloyed membranes [1–3] typically exhibit excellent hydrogen selectivity. Zeolite membranes [4–10] with uniform pores are good candidates for hydrogen separation from organic chemical hydrides. Carbon membranes [11–14] also have potential. Microporous silica membranes prepared by sol–gel methods [15–17] or chemical vapor deposition (CVD) [18–25] also exhibit excellent hydrogen selectivity. Membrane reactors and catalytic membranes, which simultaneously dehydrogenate MCH and purify hydrogen, have been reported [26–30]. However, there are few studies investigating the effects of MCH and toluene (TOL) on membrane performance, regardless of membrane type. Swesi et al. investigated the effect of TOL on the hydrogen purification of palladium and zeolite membranes [31]. Hydrogen diffusion was reportedly hindered by TOL adsorption on the zeolite membrane micropores and palladium membrane film. The diffusion of TOL on the zeolite membrane surface also affected the purification performance. The high cost of palladium is a major barrier for its use in industry. There are no reports of favorable hydrogen purification from organic chemical hydrides by zeolite membranes. Carbon membranes exhibit much lower hydrogen permeances than other membranes.

Silica membranes have a low production cost, and their hydrogen permeance is relatively high. We previously prepared silica membranes by CVD using dimethoxydiphenylsilane (DMDPS) as a precursor. The membranes exhibited excellent performance in the separation of hydrogen from a H_2/TOL mixture [32], providing hydrogen of purity >99.99%. The membranes high performance lasted for >1000 h [33]. These results only considered TOL at low

---

Abbreviations: DMDPS, dimethoxydiphenylsilane; CVD, chemical vapor deposition; TOL, toluene; MCH, methylcyclohexane.

[*] Corresponding author. Tel.: +81 42 628 4584; fax: +81 42 628 4542.
E-mail address: akamatsu@cc.kogakuin.ac.jp (K. Akamatsu).

[1] Present address: Department of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan.

http://dx.doi.org/10.1016/j.seppur.2014.11.006
1383-5866/

concentrations (0.5–2.0%). Further investigation is necessary to better understand the effects of TOL and MCH on silica membrane performance.

The current study investigates the effects of TOL and MCH on the performance of silica membranes prepared from DMDPS by CVD. Permeation tests of H_2/TOL and H_2/MCH mixtures were conducted on the DMDPS-derived membranes. The TOL and MCH concentrations of the H_2 feed gas ranged from 5.0% to 20%, and 1.0% to 10%, respectively. The regeneration of membranes in H_2 was investigated in attempt to recover the decreased membrane performance.

2. Experimental

2.1. Preparation of DMDPS-derived silica membranes and evaluation of their performance

A porous α-alumina tube of length 100 mm and outer diameter 6.3 mm was used as the membrane support. The effective membrane area was 1.36×10^{-3} m^2 at the center of the membrane support, and the remaining membrane regions were sealed with glass. A γ-alumina layer was coated on the α-alumina support by the sol–gel method, to reduce its pore size from 70 to ~4 nm [32]. An amorphous silica layer derived from DMDPS (Shin-Etsu Chemical Co. Ltd., Japan) was deposited in pores and on the surface of the γ-alumina by counter-diffusion CVD. DMDPS saturated vapor was supplied in a carrier gas (N_2, 200 mL min^{-1}) from outside of the γ-alumina coated membrane support. O_2 was supplied from inside of the support, at a rate of 200 mL min^{-1}. The CVD reaction temperature and time were 873 K and 60 min, respectively. The performance of the DMDPS-derived silica membranes was evaluated at 573, 473 and 373 K, using single-component gases of H_2, N_2 and SF_6. H_2 and N_2 permeances were measured using a bubble flow meter (SF 1U, Horiba Co., Japan), and the SF_6 permeance was determined using the pressure difference method.

2.2. Permeation tests under H_2/TOL and H_2/MCH mixtures

Two membranes (denoted Membrane-1 and Membrane-2) were prepared for testing. Membrane-1 and Membrane-2 were employed for the H_2/TOL and H_2/MCH tests, respectively. The schematic diagram of the test apparatus is available elsewhere [32]. In the gas permeation tests for the H_2/TOL and H_2/MCH mixtures, the membrane temperature was 573, 473 or 373 K, and the transmembrane pressure was 0.20 MPa. TOL or MCH was introduced through a vaporizer using a microfeeder (NRX-01, Nihon Seimitsu Kagaku Co. Ltd.), and was carried in H_2 to outside of the membrane. For the H_2/TOL mixture, the H_2 flow rate was 400 mL min^{-1}, and the TOL concentration was 5.0%, 10% and 20%. For the H_2/MCH mixture, the H_2 flow rate was 500 mL min^{-1}, and the MCH concentration was 1.0%, 5.0% and 10%.

2.3. Regenerations of membranes

Membranes were placed in a H_2 atmosphere at 573 K for 5 h, in attempt to flush TOL and MCH molecules onto the membrane surface and inside the pores effectively and to recover their performance. H_2 gas was fed from outside of the membrane, at a rate of 500 mL min^{-1}. The transmembrane pressure was 0.20 MPa. For each membrane, the regeneration procedure was conducted after each permeation test (i.e. after 5.0%, 10% and 20% TOL, and 1.0%, 5.0% and 10% MCH). After each regeneration procedure, membrane performance was evaluated at 573, 473 and 373 K using the single-component gases H_2, N_2 and SF_6.

3. Results and discussion

3.1. Effect of TOL concentration

Fig. 1 shows the temperature dependence of gas permeation through Membrane-1 at 573–373 K, in the absence and presence of 5.0%, 10% and 20% TOL. In the absence of TOL, the H_2, N_2 and SF_6 permeances were largely independent of temperature. This tendency and the measured gas permeances were comparable with those reported previously [32].

The effect of TOL concentration on H_2 permeance is shown in Fig. 1(a). H_2 permeance decreased in the presence of TOL. At 573 K, H_2 permeance in the absence of TOL was 9.62×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and in the presence of 5.0%, 10% and 20% TOL were 9.12×10^{-7}, 8.85×10^{-7} and 7.11×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, respectively. This decreasing H_2 permeance with increasing TOL concentration was more pronounced at lower temperatures. At 5.0% TOL, the H_2 permeances at 573, 473 and 373 K were 9.12×10^{-7}, 7.56×10^{-7} and 4.99×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, respectively. H_2 permeance in the absence of TOL did not exhibit temperature dependency. Thus, the presence TOL resulted in the temperature dependence of H_2 permeation, which was more pronounced at higher TOL concentration. The effect of TOL concentration on N_2 permeance is shown in Fig. 1(b). The trend was similar to that of H_2 permeance. N_2 permeance decreased in the presence of TOL, which was more pronounced at lower temperature and higher TOL concentration. The effect of TOL on N_2 permeance was larger than that on H_2 permeance. The susceptibility of the DMDPS-derived membranes N_2 permeance to TOL was previously observed for lower TOL concentrations (0.5–2.0%) [32]. The same tendency was observed for higher TOL concentrations (5.0–20%) in the current study. This is probably because TOL molecules tend to be stably into the pores of the silica membrane through which only N_2 can permeate [32]. The effect of TOL concentration on SF_6 permeance is shown in Fig. 1(c). A slight decrease in SF_6 permeance was observed in the presence of TOL. A different trend in temperature dependence was observed to that in Fig. 1(a) and (b). SF_6 permeance exhibited minimal temperature dependence at 573–373 K. The effect of low TOL concentrations

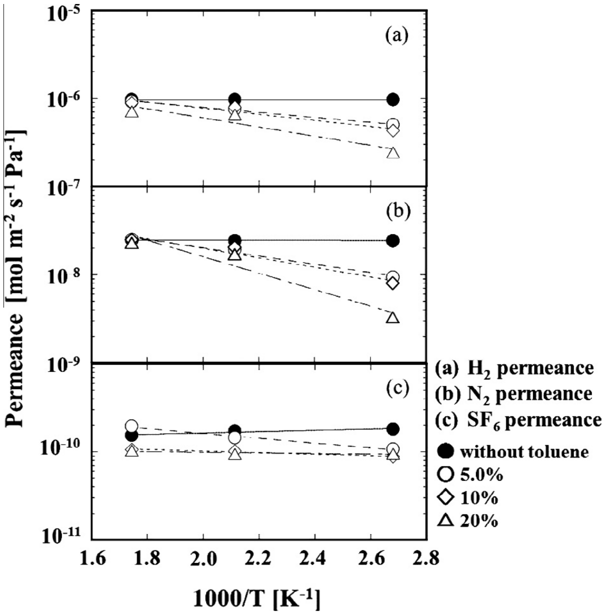

Fig. 1. Temperature dependence of gas permeation through Membrane-1 at 573–373 K, in the absence and presence of 5.0%, 10% and 20% TOL.