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LETTER

Synthesis, characterization and modification of DDR membranes grown on α-alumina supports

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Introduction

Zeolites are crystalline aluminosilicates with uniformly sized pores of molecular dimensions [1–3]. In recent years, considerable effort has been directed into synthesis of zeolite membranes, such as silicalite-1 [4–7] and ZSM-5 [8–11], for energy-efficient, simple, and compact gas separation processes where integration of separation with chemical reaction could improve reaction conversion or selectivity [12]. Hydrogen separation by zeolite membranes from products of coal gasification, steam reforming of natural gas, and water-gas-shift reaction, to yield high purity hydrogen fuel has attracted much recent attention due to current energy crisis [13, 14]. Moreover, zeolite membranes displaying high H_2 permselectivity will concentrate CO_2 from the above dilute streams, which is required for many CO_2 sequestration schemes proposed to curb the global warming effect of this greenhouse gas [15, 16]. However, no satisfactory hydrogen permselectivities have been obtained to date, especially at elevated temperatures because the kinetic diameters of H_2, CO, and CO_2 are smaller than the zeolitic pore diameter of the silicalite-1 and ZSM-5 [17]. High separation selectivity for zeolite membranes may be achieved through differences in adsorption or steric resistances between hydrogen and other gas molecules permeating through zeolitic pores [18]. Deca-dodecasil 3R (DDR) is a particularly promising membrane material for hydrogen separation from larger gas molecules due to its 8-membered ring pore aperture of 0.36×0.44 nm [18–25].

First examples of DDR membranes have been recently reported. Yajima et al. [26] reported the selectivity of H_2O/ethanol over 1,100 at 75 °C with a total flux of 0.85 kg $m^{-2}h^{-1}$ explained by the molecular sieving effect and hydrophobic nature of the DDR phase. Corcoran et al. [27], van den Bergh et al. [28], and Tomita et al. [29] reported very high CO_2/CH_4 selectivity (>100) for DDR membranes. However, to the best of our knowledge, hydrogen separation at elevated temperatures by DDR membranes has not been investigated.

We report here the hydrogen separation properties of DDR membranes obtained by in-situ crystallization, seeded secondary growth and chemical vapor deposition (CVD) of tetraethylorthosilicate (TEOS) employed to repair DDR membrane defects.

Experimental

DDR synthesis solution was prepared by the method of den Exter et al. [19]. The molar ratio of the final solution mixture was 47 1-adamantaneamine (1-ADA): 100 tetramethoxysilane (TMOS): 404 ethylenediamine (ED): 11240 water. The as-synthesized DDR was pulverized by agate mortar and pestle. Disk shaped α-alumina supports (diameter: 22 mm, thickness: 2 mm) were fabricated by pressing and calcining α-alumina powders (Mineral and Pigment Solutions, Inc. USA) according to a published procedure [30] and dip-coated twice with the suspension of DDR seeds for 5 s of contact time. The seeded membrane supports were placed vertically into the autoclave. Fresh synthesis solution was poured into the autoclave and kept at 160 °C to allow the DDR crystals in the seeded layer to grow into a continuous layer. After cooling down to room temperature, the membranes were removed from the

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autoclave and washed with DI water several times until the pH value of wash water was close to 7.0 and then dried in an oven at 40 °C at 40% relative humidity for 2 days. DDR membranes were also obtained by in-situ crystallization method. Defective DDR membranes were modified by CVD of TEOS at 550 °C for 6 days. TEOS was carried by N_2 gas with a flow rate of 72 mL min^{-1} at 80 °C to prevent TEOS condensation.

DDR membranes were characterized by X-ray diffraction (XRD) (Siemens D500, CuK_α) and Scanning Electron Microscopy (SEM) (Cambridge S-90) to study their phase composition and morphology. The unsteady-state gas permeation measurements were conducted according to Kumar et al. [30]. Single gas permeances were calculated from the rate of increase of the downstream pressure (the upstream pressure was fixed) which was monitored by pressure transducer and the permselectivity was calculated as the ratio of single gas permeances.

Results and discussion

The XRD patterns of DDR powders and membranes demonstrated the absence of crystalline or amorphous impurities (Fig. 1). Figure 2 shows SEM micrographs of DDR membranes prepared by in-situ crystallization and seeded secondary growth methods for the supports in the vertical orientation. Approximately 10 μm thick DDR membrane layer of highly intergrown DDR crystals was observed for DDR membranes obtained by seeded secondary growth after 2 days of hydrothermal synthesis as compared to ~15 μm thick DDR membrane layer obtained after 10 days of in-situ crystallization. The DDR crystallites in the membrane layer exhibited random orientation (Figs. 1 and 2). The DDR phase composition and its morphology in the membrane layer were not affected by CVD modification with TEOS at 550 °C for 6 days (Figs. 1e and 2c, respectively), which suggested that CVD technique is highly promising as a non-destructive method for membrane modification.

The H_2 and CO_2 single gas permeation studies were performed on DDR membranes. The as-synthesized DDR membranes on α-alumina supports were calcined at 450 °C for 6 h and further calcined at 700 °C for another 6 h (heating and cooling rate: 0.2 °C min^{-1}). The H_2 and CO_2 single gas permeances through calcined DDR membranes were measured at 25 and 550 °C under transmembrane pressure of 30 psi. Table 1 shows that M1 was a H_2-selective membrane possessing the H_2/CO_2 selectivity of 2.4 and 2.6 at 25 and 550 °C, respectively. However, M2 obtained by seeded secondary growth was CO_2-selective at 25 °C and became H_2-selective at 550 °C. The CO_2 adsorption capacity of DDR zeolite is greater than that of H_2 by a factor of 20 at ~25 °C [29]. Therefore, CO_2 showed the higher permeance than hydrogen at low temperatures for M2 due to high CO_2/H_2 solubility selectivity. The CO_2 adsorption decreased with increasing temperature resulting in the decrease of CO_2 permeance. M2 became H_2-selective at 550 °C because the H_2/CO_2 diffusivity selectivity became dominant at high temperatures. This also suggested that M2 was largely defect-free, while M1 contained larger defects than the DDR micropores.

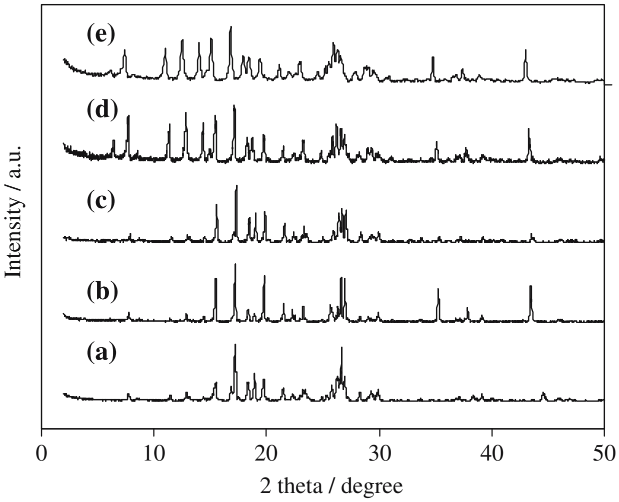

Fig. 1 XRD patterns of (**a**) DDR powder; (**b**) DDR membrane obtained by in-situ crystallization for 10 days at 160 °C (M1); (**c**) DDR membrane obtained by seeded secondary growth for 2 days at 160 °C (M2); (**d**) DDR membrane calcined at 700 °C for 6 h (M1); (**e**) DDR membrane after CVD modification at 550 °C for 6 days (M1-CVD)

The CVD technique was applied to modify the defective M1 membrane using TEOS as the silica source. The H_2 and CO_2 permeances decreased by nearly two orders of magnitude from $\sim10^{-6}$ mol m^{-2} s^{-1} Pa^{-1} to

Table 1 H_2 permeances and H_2/CO_2 permselectivity of the DDR membranes at transmembrane pressure of 30 psi

Membrane	Synthesis conditions	H_2 permeance (10^{-7} mol m^{-2} s^{-1} Pa^{-1})		$\alpha(H_2/CO_2)$	
	Method/Time	25 °C	550 °C	25 °C	550 °C
M1	In-situ/10 days	22.8 ± 0.1	9.0 ± 0.1	2.4	2.6
M1-CVD	In-situ/10 days	–	0.2	–	32.7 ± 0.1
M2	SG/2 days	0.3	0.5	0.7	4.4

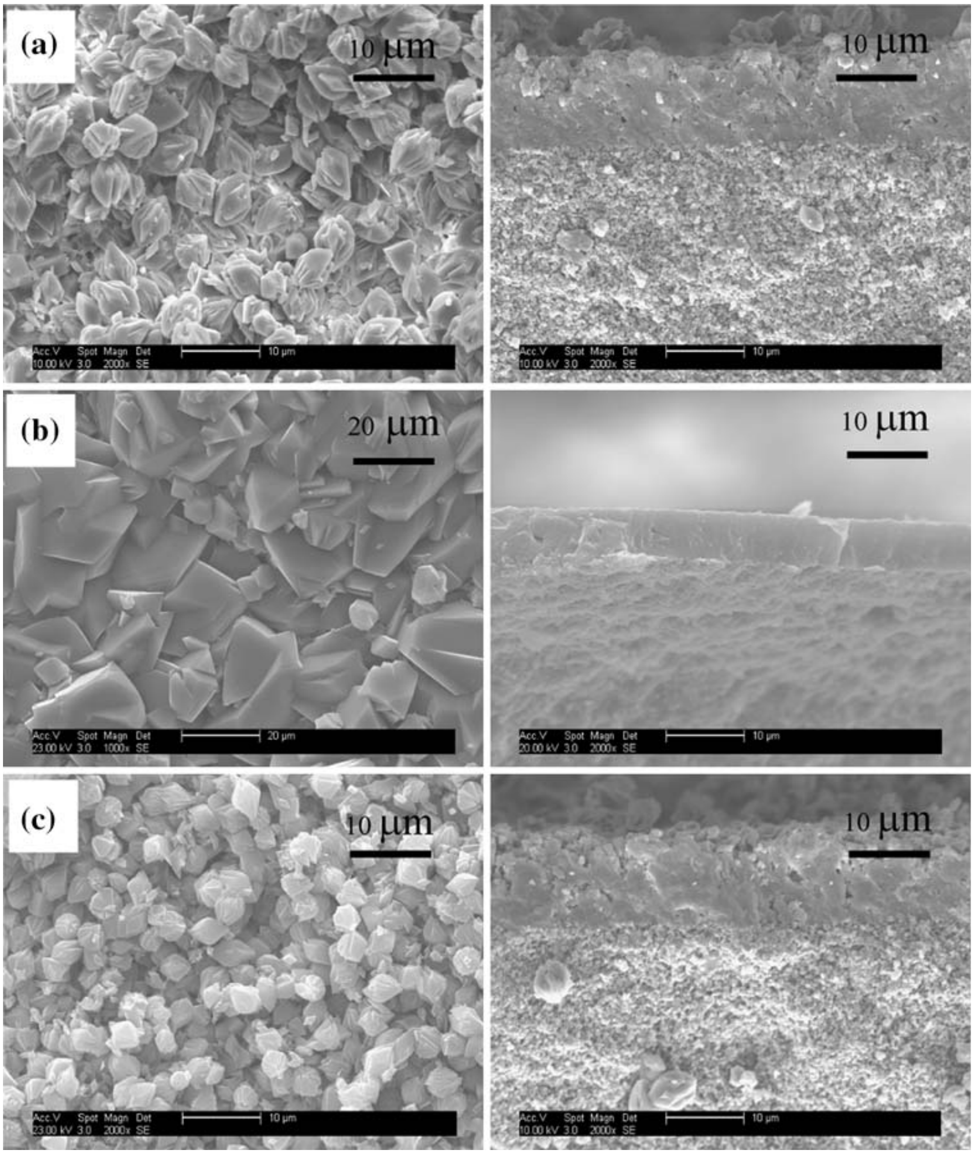

Fig. 2 SEM images of the DDR membranes obtained by (**a**) in-situ crystallization for 10 days (M1); (**b**) seeded secondary growth for 2 days at 160 °C (M2); (**c**) DDR membrane after CVD modification at 550 °C for 6 h (M1-CVD). (Left: surface view; Right: cross-section view)

$\sim 10^{-8}$ mol m^{-2} s^{-1} Pa^{-1} after CVD modification and became similar to those of M2 obtained by seeded secondary growth. Moreover, the H_2/CO_2 permselectivity of M1 increased from ~2.6 to 32.7 at 550 °C indicating that CVD modification was successful in repairing small membrane defects.

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