Short Communication

Equilibrium shift of methylcyclohexane dehydrogenation in a thermally stable organosilica membrane reactor for high-purity hydrogen production

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ABSTRACT

A high-performance organosilica membrane was prepared *via* sol–gel processing for use in methylcyclohexane (MCH) dehydrogenation to produce high-purity hydrogen. The membrane showed a high H_2 permeance of 1.29×10^{-6} mol m^{-2} s^{-1} Pa^{-1}, with extremely high H_2/C_3H_8 and H_2/SF_6 selectivities of 6680 and 48,900, respectively, at 200 °C. The extraction of hydrogen from the membrane reactor led to the MCH conversion higher than the thermodynamic equilibrium, with almost pure hydrogen obtained in the permeate stream without considering the effect of carrier gas and sweep gas in the membrane reactor, and the organosilica membrane reactor was very stable under the reaction conditions employed.

1. Introduction

The ever-increasing use of hydrogen instead of fossil fuels in the pursuit of a sustainable society has prompted a tremendous amount of scientific and technical interest in hydrogen storage, because the volumetric density of gaseous hydrogen is too low for practical use. The chemical storage of hydrogen in liquid organic hydrides holds the significant advantages of high storage capacity and the possibility of using existing energy infrastructure, which makes it a very promising method based on both technical and economical feasibility. Among a variety of liquid organic hydrides, hydrogen allows very efficient storage in toluene (TOL) in the form of methylcyclohexane (MCH) [1,2], which is a liquid under a wide spectrum of temperatures. Therefore, the catalytic decomposition of MCH must be conducted in order to release hydrogen when it is needed. Since the dehydrogenation of MCH is limited by thermodynamic equilibrium, MCH
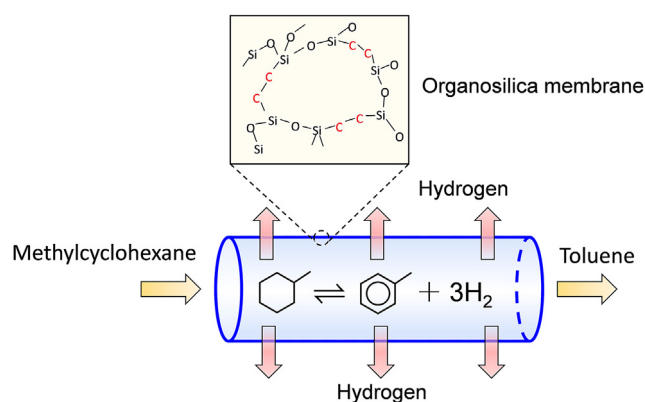
dehydrogenation in membrane reactors with a hydrogen-selective membrane is expected to allow MCH conversion that exceeds equilibrium at relatively low temperatures due to the effect of selective hydrogen extraction, which is particularly attractive for industrial hydrogen production from MCH.

A membrane reactor performance greatly depends on the membrane permeation characteristics, and both the permeation flux and selectivity are key factors. Therefore, a hydrogen-permeable membrane with both high flux and high selectivity would be an ideal candidate for MCH dehydrogenation from the viewpoint of selective hydrogen extraction. Unfortunately, even though great progress has been made in this area, there appears to be a trade-off between flux and selectivity for most hydrogen separation membranes. On the other hand, organosilica materials with organic–inorganic hybrid structures have generated great interest in recent years, due to their excellent hydrothermal stability and an easily tunable network size by comparison with conventional silica, which opens a new field in membrane development for highly permeable and hydrothermally stable organosilica membranes. Currently, research on organosilica membrane application has been focused mainly on pervaporation [3,4] and gas separation [5–7]. To the best of our knowledge, however, no studies have yet reported a membrane reactor application based on organosilica materials.

In the present study, a catalytic membrane reactor with a high flux and high selectivity organosilica membrane was developed for MCH dehydrogenation in hydrogen production, as shown in Fig. 1. Herein, the gas permeation properties of the organosilica membrane are discussed and compared with those of other typical inorganic hydrogen separation membranes, and the hydrogen extraction effect on MCH dehydrogenation in the membrane reactor also is investigated.

2. Experimental

Organosilica sols were prepared *via* the hydrolysis and condensation of 1,2-bis(triethoxysilyl)ethane (BTESE) (Sigma-–Aldrich) in a mixture of water and ethanol with HCl as a catalyst. Briefly, BTESE was added to a water and ethanol mixture at room temperature under stirring, followed by the addition of HCl, which resulted in a mixture with a molar ratio of BTESE : ethanol : H_2O : HCl = 1 : 52 : 240 : 0.1. Then, the mixture was stirred at room temperature for 2 h, which resulted in BTESE-derived organosilica sols.

An α-Al_2O_3 tube (average pore size: 1 μm; porosity: ~50%; length: 10 cm; outer diameter: 1 cm) was used as the support for membrane preparation. First, in order to increase the surface area for catalyst impregnation into the α-Al_2O_3 support, γ-Al_2O_3 was impregnated into the macropores of the α-Al_2O_3 support, as described previously [8–10]. The Pt catalyst was impregnated into the support by immersing the support into a H_2PtCl (Sigma–Aldrich) solution (25 wt%), which was then calcined at 500 °C for 3 h to form a catalytic support. An α-Al_2O_3 particle layer with SiO_2–ZrO_2 as the binder was coated onto the outside surface of the support, followed by deposition of a SiO_2–ZrO_2 layer, which resulted in a pore size of several nanometers for the support [5,7]. Finally, BTESE-derived organosilica sols were coated onto the support, followed by calcination at 300 °C for 30 min in air to form a catalytic membrane.

BTESE-derived organosilica sols were characterized by Fourier transform infrared (FT-IR) spectroscopy and by the water contact angle. The samples for measurement were prepared by coating the sols onto a KBr plate and a slide glass, respectively, followed by calcination at 300 °C in air to form a thin film. The gas permeation properties of the membrane were evaluated *via* single gas permeation tests at 200 °C using He, H_2, N_2, CH_4, C_3H_8, and SF_6. MCH dehydrogenation in the membrane reactor was conducted at 230 °C after the catalytic membrane was reduced in a H_2 flow at 300 °C. MCH was fed inside the membrane by bubbling the liquid at 50 °C (vapor pressure: 18 kPa) using Ar as a carrier gas with a flow rate of 10 ml min^{-1}. Ar sweep gas was applied to the permeate side to remove the hydrogen permeated through the membrane in the reactor. The gas flow rates and compositions of the retentate and permeate streams were measured using a film flow meter (Horiba Co. Ltd., Japan) and gas chromatography (GC) (GC-14B, Shimadzu), respectively. The membrane morphology and thickness were examined using a scanning electron microscope (SEM) (JCM-5700, JEOL) at an accelerating voltage of 20 kV. H_2 purity obtained in the membrane reactor was calculated without considering the effects of carrier gas and sweep gas introduced into the system.

3. Results and discussion

Fig. 2(a) shows the FT-IR spectrum of a BTESE-derived organosilica film. The characteristic peak at 3000–3700 cm^{-1} was attributed to the vibration of the O–H groups from the adsorbed water in the organosilica gel [11], and the peak centered at ~1050 cm^{-1} was ascribed to the Si–O asymmetric stretching vibration in the organosilica networks [12]. The peak between 2800 and 3000 cm^{-1} and the peak centered at 1412 cm^{-1} corresponding to the C–H vibrations [11,12], together with the peak centered at 1276 cm^{-1} corresponding to Si–C vibration [12], revealed the presence of thermally stable Si–C–C–Si bonding in the organosilica networks under calcination at 300 °C in an air atmosphere. This result is consistent with that obtained from the contact angle. As

Fig. 1 – A schematic diagram of MCH dehydrogenation in an organosilica membrane reactor for hydrogen production.