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Pore size control of microporous carbon membranes by post-synthesis activation and their use in a membrane reactor for dehydrogenation of methylcyclohexane

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ABSTRACT

Hydrogen-permselective carbon membranes were prepared by a vapor-phase synthesis using furfuryl alcohol as a carbon source. Their pore sizes were evaluated from the molecular sieving properties by single gas permeations of H₂, CO₂, CH₄ and CF₄. The pore size of the carbon membranes was increased by a post-synthesis activation using various gases and vapors such as H₂, CO₂, O₂ and steam. The activation using H₂ was the most effective for improving both the H₂ permeance and permselectivity because the molecular size of H₂ is smaller than the pore size of the carbon membrane and can react with the inner surface of the carbon membrane. After the activation using H₂ at 973 K, the pore size of the carbon membrane was increased from 0.30 to 0.45 nm, and the permeance of H₂ was increased from 3.6×10^{-9} to 1.6×10^{-8} mol m⁻² s⁻¹ Pa⁻¹. The activated carbon membrane was used in a membrane reactor for dehydrogenation of methylcyclohexane and showed potential for application in the dehydrogenation of chemical hydrides in membrane reactors.

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1. Introduction

In order to meet the ever increasing energy demand without causing further damage to the environment, zero carbon emission fuel such as H₂ is required. However, there are many difficulties in storing and transporting H₂. A system that has a low potential risk for H₂ storage and transportation is needed to be established, since it has an explosive combustion rate and very high combustion temperature. Organic chemical hydrides, which means hydrogenated aromatic compounds (like cyclohexane, methylcyclohexane and decaline) offer many advantages [1]. First of all, their H₂ content is very attractive (e.g. 7.2 wt% of cyclohexane) compared with metal hydrides (at most 3 wt%). Secondary, the transporting system of petroleum products like gasoline can be used as that of organic chemical hydrides. Moreover, the dehydrogenated products can be reversibly hydrogenated and reused. All these are technically important factors for establishing a H₂ storage and transmission system.

The dehydrogenation reactions of organic chemical hydrides are endothermic and equilibrium reactions. Noble metal such as particularly Pt and bimetallic Pt-M (M=second metal) have been well reported as a catalyst for highly selective dehydrogenation of

organic chemical hydrides, especially cycloalkanes, and the reaction was mainly conducted at various temperature conditions ranging from 473 to 573 K. Biniwale et al. reviewed the dehydrogenation reactions of cycloalkanes in detail [1]. In the dehydrogenation reactions of organic chemical hydrides, equilibrium conversion is limited by thermodynamics and increases with temperature. So far, the application of membrane reactors to the dehydrogenation reactions of organic chemical hydrides have been discussed, since H₂ extraction from the reaction mixture would lead to conversion enhancement and simultaneous H₂ production in lower temperature. Various H₂ separation membranes, including palladium membranes [2–8], zeolite membranes [9], γ -alumina membranes [10] and amorphous silica membranes [11–13] have been applied to the membrane reactor.

The objective of this study is to develop microporous carbon membranes whose pore sizes are tuned for the H₂ separation in a dehydrogenation membrane reactor. Microporous carbon membranes have been widely studied in gas separation processes such as natural gas processing, hydrocarbon separation, air separation, and H₂ separation [14–39]. However, there are a few reports which deal with applications of carbon membrane to membrane reactors [34–39]. In this study, carbon membrane was applied, for the first time, to the membrane reactor for dehydrogenation of organic chemical hydrides. In our previous paper, H₂-permeable carbon membranes were prepared on a porous α -alumina plate support from furfuryl alcohol (FFA) by a vapor-phase synthesis [14].

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The FFA carbon membrane carbonized at 1073 K had uniform pores with a size of 0.30 nm, and showed very high separation factors for H₂/CO₂, H₂/N₂ and H₂/CO binary gas mixtures. On the other hand, for the separation of H₂/methylcyclohexane and H₂/toluene (dehydrogenated chemical of methylcyclohexane), larger pore sizes are favorable for improving a H₂ permeance but should be less than 0.6 nm since the kinetic diameters of methylcyclohexane and toluene are about 0.60 nm. In most cases, the pore dimensions and distribution in carbon membranes have been finely adjusted by a simple thermochemical treatment to meet different separation needs and objectives [15]. So far, various post-synthesis treatments have been applied to control pore size and to improve separation properties of carbon membranes, including activation (oxidation) [16–22], chemical vapor deposition [23–25], pyrolysis [26] and coating [15,27]. Activation is a favorite treatment used to alter the pore size of carbon membranes. Kusakabe et al. showed that the activation of a polyimide carbon membrane in a mixture of O₂–N₂ increased its permeability to CO₂ and O₂ without damaging its permselectivity [16]. Other activating agents, including pure O₂ [16], CO₂ [19,20], NH₃ [21] and KOH [22] were also used for the activation of carbon membranes.

In this study, the pore size of the FFA carbon membranes was increased by a post-synthesis activation using various gases and vapors such as H₂, CO₂, O₂ and steam (H₂O). Effect of the activation treatments using different gas/vapors at different temperatures on the pore size and morphology of the FFA carbon membranes was discussed. Their pore sizes were evaluated from the molecular sieving properties by single gas permeations of H₂, CO₂, CH₄ and CF₄. The activated FFA carbon membrane was applied to the dehydrogenation of methylcyclohexane in a membrane reactor.

2. Experimental

2.1. Membrane preparation and characterization

A porous α -alumina tube (o.d. 10 mm, i.d. 8 mm and 30 mm length) with an average pore size of 0.1 μ m (NGK Insulators, Ltd.) was used as a support. A sulfuric acid solution was prepared from sulfuric acid (H₂SO₄aq., 2 mol L⁻¹), ethanol (EtOH), and deionized water with mass ratios of 2 H₂SO₄aq.: 1 H₂O: 2 EtOH and stirred at 298 K for 60 min. Sulfuric acid acts as a catalyst for the polymerization of FFA. All chemicals were purchased from Wako Pure Chemical Industries. The solution was deposited on the alumina support by dip-coating, and then the support was dried at 363 K for 30 min.

The H₂SO₄/alumina support was exposed to a FFA vapor at 453 K for 24 h by the following method. The support and a small vessel filled with FFA were separately put into a closed vessel. The closed vessel was placed in an oven at 453 K. After cooling to room temperature, the product was dried at 363 K for 24 h to promote polymerization. The membrane was then carbonized at 1073 K for 2 h under N₂ atmosphere with heating rate of 1 K min⁻¹. Hereafter, obtained FFA carbon membranes are described as “as-made” membranes.

The obtained FFA carbon membranes were activated under gas and vapor atmosphere for 1 h at 573–1073 K with a heating rate of 5 K min⁻¹. Various gas/vapors such as H₂, CO₂, O₂ and steam (H₂O) were used as activating agents. Hereafter, activated membrane samples are written as “activating agent–activating temperature”, for example “H₂O–773 K”.

The morphology of the membranes was observed with a scanning electron microscope (SEM; Hitachi S-2250).

2.2. Gas and vapor permeation tests

Single gas permeances of H₂, CO₂, methane (CH₄) and tetrafluoromethane (CF₄) were measured at 293 K. The feed side

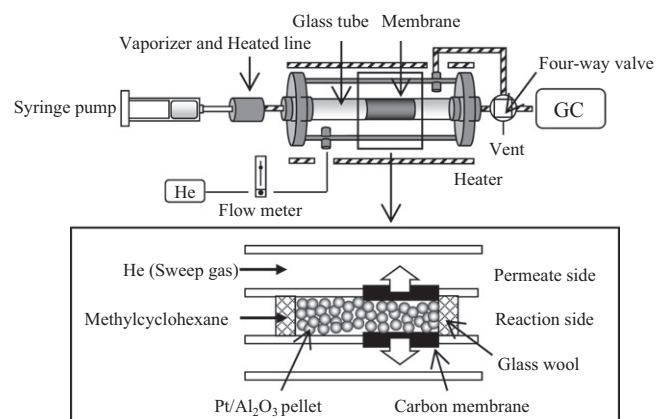


Fig. 1. Schematic diagram of the membrane reactor apparatus.

pressure was 0.3 MPa, and permeate side pressure was 0.1 MPa. The flow rate was measured using a soap meter and the detection limit of single gas permeation test was 10⁻¹¹ mol m⁻² s⁻¹ Pa⁻¹.

Separation of H₂/condensable vapor binary mixture through the carbon membranes was conducted. Water, methanol and toluene were used as condensable vapor. The H₂/condensable vapor binary mixture was fed into a feed side of the membrane. Argon as a sweep gas was fed into a permeate side of the membrane. Permeate stream was analyzed to measure the permeance of H₂, using a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC-8A). The total pressure on the feed side and the permeate side was kept at 0.1 MPa. The relative vapor pressure to saturated vapor pressure (p/p_{sat}) was stepwise increased from 0 to 1 by adjusting a flow rate of H₂. All measurements were performed at 293 K.

2.3. Membrane reactor to dehydrogenate methylcyclohexane

A schematic diagram of the membrane reactor apparatus is shown in Fig. 1. Platinum-supported alumina pellets (0.5 wt% Pt/Al₂O₃) purchased from N. E. CHEMCAT Corporation were used as catalyst. The catalyst was reduced in hydrogen at 673 K before reaction. As a feed material, methylcyclohexane was sent to a vaporizer and carried to the membrane. The product stream was analyzed with a gas chromatograph equipped with a flame ionization detector (Shimadzu GC-2014) using Xylene Master column (Shinwa Chemical Industries, Ltd.) and the conversion of methylcyclohexane was determined from the concentration ratios of unreacted methylcyclohexane.

First, the dehydrogenation of methylcyclohexane in a fixed-bed reactor was examined to determine equilibrium conversion at each reaction temperature. The $W_{\text{cat}}/F_{\text{MCH}}$ [mass of the catalyst (g) divided by the feed rate of methylcyclohexane (mol h⁻¹)] were 0.32. Experimental temperatures ranged from 473 to 533 K, and the experimental pressure was 0.1 MPa.

Second, the dehydrogenation of methylcyclohexane in a membrane reactor using He sweep gas was carried out. The $W_{\text{cat}}/F_{\text{MCH}}$ value and experimental pressure were same as those of the fixed-bed reactor. The reaction temperatures were 473 and 493 K. The purity of H₂ obtained from the permeation side was measured by the gas chromatograph.

3. Results and discussions

3.1. Single gas permeability

Single gas permeances through the FFA carbon membranes were plotted in Fig. 2 as a function of kinetic diameter (d). Only H₂

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