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Preparation of a novel bimodal catalytic membrane reactor and its application to ammonia decomposition for CO_x-free hydrogen production

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ABSTRACT

A novel bimodal catalytic membrane reactor (BCMR) consisting of a Ru/ γ -Al₂O₃/ α -Al₂O₃ bimodal catalytic support and a silica separation layer was proposed. The catalytic activity of the support was successfully improved due to enhanced Ru dispersion by the increased specific surface area for the γ -Al₂O₃/ α -Al₂O₃ bimodal structure. The silica separation layer was prepared via a sol–gel process, showing a H₂ permeance of 2.6×10^{-7} mol Pa⁻¹ m⁻² s⁻¹, with H₂/NH₃ and H₂/N₂ permeance ratios of 120 and 180 at 500 °C. The BCMR was applied to NH₃ decomposition for CO_x-free hydrogen production. When the reaction was carried out with a NH₃ feed flow rate of 40 ml min⁻¹ at 450 °C and the reaction pressure was increased from 0.1 to 0.3 MPa, NH₃ conversion decreased from 50.8 to 35.5% without H₂ extraction mainly due to the increased H₂ inhibition effect. With H₂ extraction, however, NH₃ conversion increased from 68.8 to 74.4% due to the enhanced driving force for H₂ permeation through the membrane.

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1. Introduction

Membrane reactors integrating both reaction and separation processes into a single unit have attracted much attention, as there is great potential for application to thermodynamically limited reactions owing to an equilibrium shift by the selective permeation of reaction products. An ever-increasing demand for clean and renewable energy to cope with the depletion of fossil fuels and climate change has driven this type of research significantly in recent years, and an extensive amount of studies have concentrated on hydrogen production from hydrocarbons via various processes, such as methane steam reforming [1–5], dehydrogenation of cyclohexane [6–9], etc., using hydrogen-selective membrane reactors in an attempt to

obtain improved conversion and purification of hydrogen. However, less attention has been paid to NH₃ decomposition in membrane reactors for CO_x-free hydrogen production [10–14], although the high hydrogen volumetric density, CO_x-free feature and feasible storage and transportation of hydrogen confer great advantages to liquid NH₃ over the traditional carbonaceous compound as a hydrogen carrier [15–17].

Most studies use a packed-bed membrane reactor (PBMR) for hydrogen production [4–12]. PBMRs consist of a packed catalyst in the membrane module for catalytic reactions, and an inert membrane that is used only for separation. To achieve a larger ratio of permeation area to reactor volume for practical application, a membrane tube with a small diameter, such as hollow fibers, is usually much more favorable from

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the viewpoint of membrane-packing density. However, this poses a problem in that catalyst packing is very difficult in a PBMR. However, catalytic membrane reactors (CMRs) with a configuration that allows the membrane itself to act as a catalyst, or with a catalyst impregnated into it [18], have aroused increasing interest due to the quality of compactness [1–3,13,14]. With a CMR, catalytic reaction and gas separation can be accomplished using only the membrane, and the catalyst packing in the reactor can thus be avoided. In addition, a concentration polarization effect, which results in a decrease in both the membrane flux and selectivity due to the formation of boundary layer with enriched less-permeable species after the depletion of preferentially permeating species near the membrane surface, is expected to be reduced, because the diffusion length of permeating species from the catalyst to membrane surface is greatly shortened in the CMR [13,14].

Previously [1], our research group reported the steam reforming of methane for hydrogen production in a CMR, which consisted of a Ni/ α -Al₂O₃ catalytic support and a hydrogen-selective silica separation layer, and resulted in a conversion that was much higher than the equilibrium after hydrogen extraction. In order to further improve the catalytic performance of a CMR, a bimodal catalytic membrane reactor (BCMR) was proposed with a Ni/ γ -Al₂O₃/ α -Al₂O₃ bimodal catalytic support and a silica layer for hydrogen separation [2,3]. Since the bimodal structure provided both mesopores by γ -Al₂O₃ for high catalyst dispersion and macropores by α -Al₂O₃ for high gas diffusivity through the support, enhanced membrane reactor performance was successfully realized. This concept was recently applied to prepare a novel BCMR with a Ru/ γ -Al₂O₃/ α -Al₂O₃ bimodal catalytic support for NH₃ decomposition to produce CO_x-free hydrogen. This BCMR showed higher catalytic activity and better stability compared with monomodal catalytic membrane reactors, which had no impregnation with γ -Al₂O₃ in the support [13,14].

In order to gain insight into the role of a bimodal catalytic structure in the BCMR and to obtain the optimal preparation conditions for the BCMR, in this paper, the bimodal catalytic supports with different γ -Al₂O₃ loadings were prepared, and the impregnation effect of γ -Al₂O₃ on the gas permeation, pore structure and catalytic activity of the bimodal catalytic supports was discussed in detail. Moreover, the application of the BCMR to NH₃ decomposition for CO_x-free hydrogen production under a pressurized system without using sweep gas was investigated.

2. Experimental

2.1. Preparation and characterization of the bimodal catalytic support and membrane

The preparation procedure for the bimodal catalytic membranes is shown in Fig. 1. Porous α -Al₂O₃ tubes (average pore size: 1 μ m, length: 8 cm, outer diameter: 10 mm, porosity: ~50%) were used as supports for the bimodal catalytic membrane preparation. First, the support was sealed at both ends using glass tubes, and one end was sealed

as a dead-end. A boehmite sol solution was then fed inside the support to fill the macropores of α -Al₂O₃. After removing the excess solution and drying at room temperature, the support was calcined at 550 °C for 30 min to form a γ -Al₂O₃/ α -Al₂O₃ bimodal support. Differing γ -Al₂O₃ loading amounts were obtained by varying the impregnation times using the above procedure. To obtain a catalytic activity for the bimodal support, a Ru(NO)(NO₃)₃ solution (1.5 wt.% based on Ru, Sigma–Aldrich) was then impregnated into the bimodal support, followed by drying at room temperature and calcination at 500 °C, resulting in a Ru/ γ -Al₂O₃/ α -Al₂O₃ bimodal catalytic support. This process was repeated twice to achieve a catalyst loading of around 0.45 wt.%. For comparison, the Ru/ α -Al₂O₃ monomodal catalytic support was prepared using the same procedure described above with the exception of the impregnation with γ -Al₂O₃. After preparation of a SiO₂–ZrO₂ intermediate layer on the outside surface of the bimodal catalytic support, a sol–gel method was applied to prepare a homogenous polyhedral oligomeric silsesquioxane (HOMO-POSS)-derived silica layer on the support for H₂ separation. The details of the experimental procedure can be found in a previous study [19].

Hg-intrusion porosimetry (Autopore 9520, Shimadzu) and CO adsorption analyses (BELCAT, Bell Japan Inc.) for both monomodal and bimodal catalytic supports were conducted to study the pore structure and Ru catalyst dispersion, respectively, using the samples prepared by grinding the corresponding catalytic supports into powders. The morphology of the BCMR was examined using a scanning electron microscope (SEM) (JCM-5700, JEOL) and a transmission electron microscope (TEM) (JEM-2011, JEOL). The permeation properties of the BCMR were evaluated by a single gas permeation test conducted at 100–500 °C, using He, H₂, N₂, and NH₃, with feed and permeate pressures kept at 0.2 and 0.1 MPa, respectively. The permeation flow rate of He, H₂ and N₂ through the BCMR was measured using a bubble flow meter. For the NH₃ permeation test, 20 ml min⁻¹ sweep gas was applied to the permeate side, and the gas composition was analyzed using a gas chromatography (GC) instrument (GC-14B, Shimadzu) equipped with a thermal conductivity detector (TCD) and a Porapak N column using N₂ as a carrier gas. The experimental apparatus for a single gas permeation test and NH₃ decomposition is shown in Fig. 2.

2.2. Ammonia decomposition in the bimodal catalytic membrane reactor

NH₃ decomposition in the BCMR was carried out at 400 or 450 °C under a NH₃ flow rate of 10 or 40 ml min⁻¹. The feed side was maintained at atmospheric pressure, while the permeate side was kept under vacuum conditions at a pressure of 5 kPa using no sweep gas in order to obtain purified H₂. Prior to the membrane reaction, the BCMR was reduced *in-situ* in the membrane module under a H₂ flow of 50 ml min⁻¹ for 3 h at 500 °C, and the experimental apparatus was then purged with a N₂ flow of 50 ml min⁻¹ for 30 min. The gas compositions of the retentate and permeate streams were analyzed by GC, and the flow rates of both streams were measured by a bubble flow meter after leading a 1.0 M HCl aqueous solution.

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