Catalysis Communications 15 (2011) 60–63

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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

Short Communication

Highly enhanced ammonia decomposition in a bimodal catalytic membrane reactor for CO_x-free hydrogen production

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ARTICLE INFO

Article history:
Received 15 June 2011
Received in revised form 6 August 2011
Accepted 10 August 2011
Available online 18 August 2011

Keywords:
CO_x-free hydrogen
Ammonia decomposition
Bimodal catalytic membrane reactor
Silica membrane

ABSTRACT

Ammonia decomposition in a bimodal catalytic membrane reactor (BCMR) consisting of a Ru/γ-Al_2O_3/α-Al_2O_3 bimodal catalytic support and a hydrogen-selective silica membrane in a single unit was proposed for CO_x-free hydrogen production in the present study. The bimodal catalytic membrane showed a H_2 permeance of 6.2×10^{-7} mol/(m^2 s Pa) at 500 °C, with H_2/NH_3 and H_2/N_2 permeance ratios of 200 and 720, respectively. Ammonia conversion was surprisingly enhanced form 45 to 95% at 450 °C in the BCMR after selective H_2 extraction. The BCMR showed excellent stability with respect to both gas permeation properties and catalytic activities.

1. Introduction

With increasing concerns over gradual depletion of non-renewable fossil fuels and global warming, considerable attention has been paid to hydrogen for fuel cells in various applications owing to their zero emission and high efficiency [1]. A major challenge associated with the potential implementation of a H_2 economy is the issue of storage due to the low volumetric density of H_2, and this has triggered decades of efforts in the development of H_2 storage materials such as metal/complex hydrides [2], metal organic frameworks (MOFs) [3], and carbon [4], *etc.* Unfortunately, to date none of these H_2 storage materials has been capable of meeting all required properties for practical application.

Recently, NH_3 has been proposed as a H_2 carrier in a promising solution that would bypass the intractable issues related to H_2 storage and delivery [5–8], since NH_3 has a high hydrogen storage capacity of 17.6 wt.%, and can be easily stored and transported in liquid form under mild conditions. NH_3 decomposes to H_2, which produces only H_2O after combustion, and N_2, which is not a greenhouse gas, in other words, NH_3 is a CO_x-free H_2 carrier. Other H_2 carriers, such as methanol, *etc.*, inevitably cause end-user CO_2 emissions, since they are carbonaceous compounds and on-board CO_2 capture is not feasible. The advantages of NH_3 mentioned above make the NH_3-mediated hydrogen economy extremely attractive and promising.

For low-temperature fuel cell systems, such as proton exchange membrane fuel cells (PEMFCs), NH_3 must be decomposed to produce H_2 before it is fed to the fuel cell. Membrane reactors combining a catalytic reaction with the separation process into a single unit offer an ideal device to produce H_2 from NH_3 efficiently, where enhanced NH_3 conversion and high-purity CO_x-free H_2 can be simultaneously obtained by applying a hydrogen separation membrane. To date, only a few studies have reported membrane reactors for NH_3 decomposition. Collins and Way [9] and García-García *et al.* [10] reported NH_3 decomposition in a packed-bed Pd membrane reactor, and improved NH_3 conversion was obtained after H_2 extraction. However, the reaction was conducted at very low NH_3 feed concentrations. A packed-bed Pd membrane reactor was also applied to pure NH_3 by Zhang *et al.* [11], showing enhanced NH_3 decomposition compared with a conventional reactor.

In the present study, a bimodal catalytic membrane reactor (BCMR) was proposed for CO_x-free H_2 production *via* NH_3 decomposition. This new type of membrane reactor had a configuration that consisted of a silica separation layer and a bimodal catalytic support (Ru/γ-Al_2O_3/α-Al_2O_3), as illustrated in Fig. 1. The impregnation of γ-Al_2O_3 into a α-Al_2O_3 membrane support to form a bimodal support is expected to effectively improve catalytic membrane reactor performance, since the bimodal structure contains both mesopores and macropores, which results in improved catalytic activities by mesopores and high gas diffusivity by macropores [12,13]. Compared with a packed-bed Pd membrane reactor, the novel BCMR with a hydrogen-selective silica membrane will have the great advantages of compact configuration due to the catalytic membrane structure and much lower cost due to the silica separation layer.

2. Experimental

2.1. Preparation and characterization of bimodal catalytic membranes

Porous α-Al_2O_3 tubes (outer diameter: 10 mm; inner diameter: 8 mm; length: 10 cm; average pore size: ~1 μm; porosity: ~50%) were

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doi:10.1016/j.catcom.2011.08.011

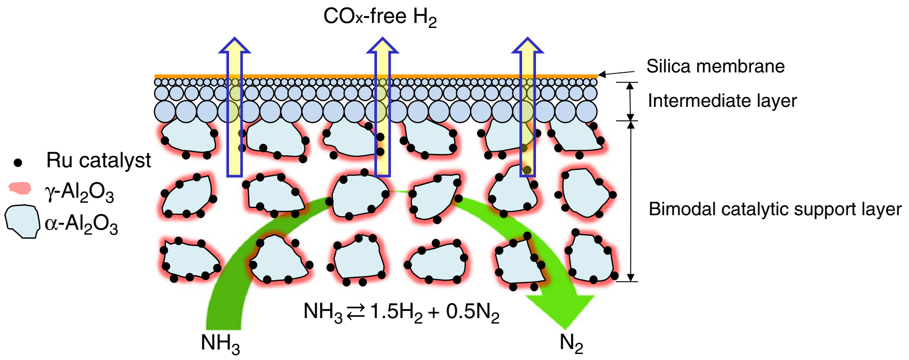

Fig. 1. Schematic diagram of the proposed bimodal catalytic membrane reactor for CO_x-free H_2 production *via* ammonia decomposition.

used as membrane supports. First, the support was soaked in a boehmite sol solution (Nissan Chemical Industries, Ltd., Japan) with a concentration of 10 wt.% for 1 h, followed by drying at room temperature and calcination at 550 °C in air to convert impregnated boehmite sols into γ-Al_2O_3, resulting in a bimodal support (γ-Al_2O_3/α-Al_2O_3). The catalysts were then impregnated into the bimodal support by soaking the support in a $Ru(NO)(NO_3)_3$ solution (1.5 wt.%, Sigma-Aldrich). After drying, the support was then calcined at 550 °C under an air flow of 50 ml/min for 1 h to obtain a bimodal catalytic support (Ru/γ-Al_2O_3/α-Al_2O_3). For comparison, a monomodal catalytic support (Ru/α-Al_2O_3) was prepared using the same procedures, with the exception of impregnation of γ-Al_2O_3.

A sol-gel method was used to prepare the H_2 separation layer. First, an α-Al_2O_3 particle and SiO_2–ZrO_2 intermediate layer was prepared on the outside surface of the bimodal catalytic support to reduce the pore size from ~1 μm to several nanometers [14]. Then, silica sols derived from polyhedral oligomeric silsesquioxane (POSS) were coated on the intermediate layer, followed by drying and calcining at 300 and 500 °C, respectively, in air for 30 min to obtain a homogeneous (HOMO)-POSS-derived silica membrane. Details of the preparation of HOMO-POSS-derived silica sols and membranes can be found in a previous study by this group [15]. The bimodal catalytic membrane was characterized by a scanning electron microscope (SEM), a transmission electron microscope (TEM), N_2 adsorption, and single-gas permeation tests.

2.2. NH_3 decomposition in bimodal catalytic membrane reactors

Catalytic decomposition of pure NH_3 was carried out in the BCMR at 450 °C at a NH_3 flow rate of 10 ml/min (GHSV: 500 h^{-1}, defined as $F_{NH_3}/V_{support}$ at 450 °C) with both retentate and permeate streams kept at atmospheric pressure. Prior to the reaction, the catalytic membrane was reduced *in situ* at 500 °C in pure H_2 under a flow rate of 50 ml/min for 3 h, and then purged with N_2 under a flow rate of 50 ml/min for 30 min to remove the residual H_2 from the experimental apparatus. N_2 sweep gas (SG) of 100 ml/min was applied to the permeate stream to provide a driving force for gas permeation through the membrane. Gas compositions of both permeate and retentate streams were analyzed by a gas chromatograph (GC) instrument.

3. Results and discussion

3.1. Bimodal catalytic supports

Fig. 2 shows the catalytic activities of the bimodal and monomodal catalytic supports using a NH_3 feed flow rate of 10 ml/min at 450 °C. NH_3 conversion gradually decreased from 28 to 22% during 28 h for the monomodal catalytic support, while the bimodal catalytic support showed a stable NH_3 conversion of 45%. Obviously, the bimodal catalytic support showed a higher NH_3 conversion and better stability, although the loadings of Ru were almost the same for the bimodal (3.33×10^{-2} g) and monomodal catalytic supports (3.34×10^{-2} g). Fig. 3(a, b) shows the TEM images of the bimodal and monomodal catalytic supports. γ-Al_2O_3 was successfully impregnated into the bimodal catalytic support, and the impregnated Ru particles were less than 40 nm in size. On the other hand, Ru particles with a size of more than 100 nm were observed on the monomodal support. This confirmed that the impregnation of γ-Al_2O_3 with mesopores ~5 nm efficiently improved Ru dispersion for the bimodal catalytic support due to a significant increase in the specific surface area (Table S1), which led to enhanced catalytic activity and stability for NH_3 decomposition, as reported for Ni impregnated bimodal catalytic supports in this group's previous study [12,13].

3.2. Bimodal catalytic membranes

Fig. 3(c) shows an SEM image of the bimodal catalytic membrane. The membrane consisted of graded structures; three typical layers could be distinguished clearly: a Ru/γ-Al_2O_3/α-Al_2O_3 bimodal catalytic support layer, a α-Al_2O_3 particle and SiO_2–ZrO_2 intermediate layer, and a SiO_2 separation layer. The thickness of the SiO_2 top layer for H_2 separation was less than 300 nm. It should be noted that most pores in the α-Al_2O_3 support were not blocked by the impregnated γ-Al_2O_3 and Ru, and were still available for gas permeation probably due to the large pore size, which ensured a high diffusivity of NH_3 and H_2 through the bimodal catalytic support.

Fig. 4 shows the kinetic diameter dependence of gas permeance for the bimodal catalytic membrane at 500 °C. The catalytic membrane showed a H_2 permeance of 6.2×10^{-7} mol/(m^2 s Pa) with a H_2/N_2 permeance ratio of more than 700. Moreover, the H_2/NH_3 permeance ratio was as high as 200, indicating NH_3 was much less permeable than H_2 that has a kinetic diameter of 0.289 nm. Previously, the kinetic diameter of NH_3 was inconsistently reported to be 0.26 [16] and 0.326 nm [17]. Since the adsorption of NH_3 on silica

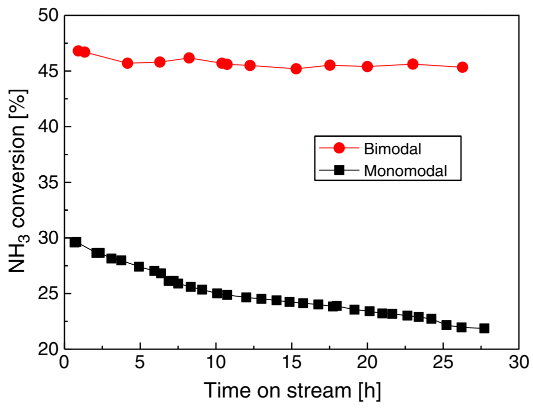

Fig. 2. Catalytic activities of the bimodal and monomodal catalytic supports at 450 °C.