Comparative study of propane steam reforming in vanadium based catalytic membrane reactor with nickel-based catalysts

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ABSTRACT

The performance of catalytic membrane reactor with Pd-coated V membrane was examined for steam reforming of propane. The long term reforming experiment confirmed the stability of the V membrane with high hydrogen selectivity and permeability. The effect of types of hydrogen permeable membranes on the performance of the catalytic membrane reactor was studied by comparing Pd-coated V, Pd–23Ag, and Pd–10Ag membranes. The types of hydrogen separation membranes (i.e. hydrogen removal rates) did not have a marked effect on the propane conversion rates, while the product compositions were largely influenced by the hydrogen removal rate. Varying metal oxide supports of Ni-catalysts resulted in significant differences in the product compositions. Further, the evaluation of various catalyst-support systems (9wt%Ni–1wt%M/CeO$_2$, M = Co, Pt, Ag, Ru) revealed that hydrogen yield was the highest when 1wt%Ag was added to Ni/CeO$_2$. However, it was also found that excessive secondary metal additions can have negative impact on the catalytic behaviour of parent catalysts.

Introduction

Natural gas is one of the well-known sources of hydrogen along with water and biomass. The well-established distribution system of natural gas makes it suitable for domestic fuel cell applications or distributed hydrogen refuelling stations with on-site hydrogen generation [1]. Depending on the availability and price of natural gas, higher hydrocarbons, such as Liquefied Petroleum Gas (LPG) can become a more preferred source of hydrogen [2]. LPG is readily available commercially, and has a higher caloric value than natural gas. It liquefies under relatively low pressures at ambient temperature, which allows convenient and safe storage and transport [1]. Propane is the main component of LPG. The conversion of propane to hydrogen is typically carried out by steam reforming [3–8], partial oxidation [3,4,7–12], or autothermal reforming [5,7,8,13–20]. Steam reforming is the most economical method in terms of hydrogen yield, as the steam can also be the source of hydrogen [2], and can produce high

concentrations of hydrogen [21]. The overall steam reforming of propane is written as [2]:

$$C_3H_8 + 6H_2O = 3CO_2 + 10H_2 \tag{1}$$

This overall reaction typically consists of the following main, but not limited to, three sub reactions [22]:

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{3}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{4}$$

Propane is readily converted to CO and H_2 at moderate temperatures through the reaction (2), followed by the main successive reactions (3) and (4) [22]. The water gas shift (WGS) reaction (3) produces H_2, while the methanation reaction (4) (alternatively called reverse steam reforming of CH_4) consumes product H_2. The efficiency of the overall conversion of propane is largely affected by this negative reverse CH_4 steam reforming reaction (4). The use of a membrane reactor allows the removal of H_2 from reaction site, which shifts the equilibrium of WGS reaction (3) to the product side and suppress the methanation reaction (4) [2,22]. Moreover, high CO_2 and CO contents can affect on the efficiency in fuel cell applications, especially in proton exchange membranes fuel cells system [23]. The use of catalytic membrane reactor allows the production of high purity hydrogen from the permeate side of the reactor, which can be directly utilised in fuel cells. Many past studies explored the applications of catalytic membrane reactors for hydrogen production from CH_4 [24–33] and syngas [34–39], however only a few were based on propane or LPG [2,40].

The ability of hydrogen separation membranes to selectively remove hydrogen from reaction site, as well as to withstand variable operating conditions are important characteristics of a catalytic membrane reactor system. The degradations of membrane materials can adversely influence the hydrogen selectivity of the membranes, reducing the purity of hydrogen produced. Palladium (Pd) based membranes have been by far the most studied hydrogen separation membranes in catalytic membrane reactor applications [2,24–33,35–39]. It is well-known that Pd-based membranes are suitable for hydrogen separation process, due to their excellent hydrogen dissociation property and high hydrogen permeability. However, the very high cost of Pd and instability of Pd against hydrogen embrittlement unfortunately necessitate the development of non-Pd alloy membranes with high hydrogen selectivity, permeability, and stability [41]. There have been many studies on non-Pd alloy hydrogen separation membranes [41], and vanadium (V) based membranes are one of the most promising alternative hydrogen permeable membranes [42–47]. However, there has been no study on the actual examination of V based membranes in a catalytic membrane reactor system for the reforming of methane or other gaseous hydrocarbons. Our previous study [48]

examined a V-based membrane reactor system to produce hydrogen from methane, and showed a great potential of V-based membranes as the alternative. It also compared the stability of Pd–23Ag and V-based membranes under the direct exposure to Fe in a hydrogen atmosphere. The study showed that the V-based membrane was less reactive with Fe than the Pd–23Ag sample, confirming good stability against Fe in the hydrogen containing atmosphere. This present study undertakes the application of V-based membrane for propane steam reforming using a catalytic membrane reactor system. The performance and long-term stability of the membrane and the overall catalytic membrane reactor, as well as the effects of various process components on the performance of catalytic membrane reactor system are to be described.

Experimental

Catalyst preparation and characterisation

The catalyst supports examined in this study were CeO_2, SiO_2, and Al_2O_3. Commercially available SiO_2 (AEROSIL®) and Al_2O_3 (AEROSIL®) were directly utilised as the support materials, while CeO_2 was prepared by thermal decomposition of the nitrate precursor. $Ce(NO_3)_3 \cdot 6H_2O$ (Kishida Chemical Co., Ltd.) was stirred in distilled water on a heated magnetic stirrer until dry, followed by the calcination at 773 K in air for 3 h. 10wt% Ni/SiO_2, 10wt%Ni/Al_2O_3 and 10wt%Ni/CeO_2 catalysts were prepared by the conventional wet process. An appropriate amount of support material (i.e. SiO_2, Al_2O_3, or CeO_2) and $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd.) were mixed in distilled water on a heated magnetic stirrer until dry, and calcined at 673 K in air for 2 h. The calcined powders were uni-axially pressed into disks at 183 MPa. The disks were then crushed and sieved through 14–30 mesh, and treated in dry hydrogen (40 ml min^{-1}) at 873 K for 3 h with the heating and cooling rates of 10 K min^{-1} in dry hydrogen. The same procedure was adapted for the preparation of other various catalyst-support systems, with $Co(NO_3)_2 \cdot 6H_2O$ (Kishida Chemical Co., Ltd.), $Pt(NH_3)_4(NO_3)_2$ (Aldrich), $AgNO_3$ (Wako Pure Chemical Industries, Ltd.), or $RuCl_3 \cdot nH_2O$ ($n = 1$–3, Kishida Chemical Co., Ltd.) as metal source. Phase crystallographic structures of the catalysts were determined by x-ray diffraction analysis (XRD) using Cu-Kα radiation (40 kV, 80 mA) (RINT 2500HLR+, Rigaku Corporation). Raman spectroscopy analysis was performed at ambient conditions using a Raman spectrometer (Horiba LabRAM HR800, 648 nm). The specific surface area of the catalysts were analysed by using a BET surface area analyser (BEL-mini, Bell Japan Inc.). The samples were treated in nitrogen at 773 K for 3 h prior to the surface area analysis.

Propane steam reforming

Steam reforming of propane was performed in a catalytic membrane reactor as illustrated in Fig. 1. Pd-coated V membrane (Pd/V/Pd) was prepared by coating both sides of V membrane (100 μm) with 1 μm-thick Pd using DC magnetron sputtering. The hydrogen permeable membrane was placed at the centre of the reactor between two outer tubes, and the