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Efficient production of hydrogen from natural gas steam reforming in palladium membrane reactor

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Abstract

Ultra-thin, high performance composite palladium membrane, developed via a novel electroless plating method, was applied to construct a membrane reactor for methane steam reforming reaction, which was investigated under the following working conditions: temperature 723–823 K, pressure 300–900 kPa, gas hourly space velocity (GHSV) 4000–8000 mL g_{cat}^{-1} h^{-1}, steam-to-carbon feed ratio (S/C, mol/mol) 2.5–3.5 and sweep ratio (defined as the ratio between flux of sweep gas to that of methane at the inlet of catalyst bed) 0–4.3. In contrast with previous investigations using commercial catalysts activated at lower temperatures, the catalyst applied in this work was a nickel-based one pre-reduced at 1023 K. The results indicated that selective removal of H_2 from reaction zone obtained methane conversion much higher than thermodynamic control ones and CO selectivity significantly lower than thermodynamic control values. For instance, 98.8% methane conversion, over 97.0% selectivity to CO_2 and over 95.0% H_2 recovery rate could be obtained under mild working conditions. The much higher performance of membrane reactor was attributed to the combination of hydrogen ultra-permeable Pd-based membrane, highly active catalyst for methane steam reforming with countercurrent sweep gas flux design. Further work on stability investigation may develop an efficient onsite route of hydrogen production for application to proton exchange membrane fuel cells.

Keywords: Hydrogen production; Methane steam reforming; Palladium membrane reactor; Nickel-based catalyst

1. Introduction

Hydrogen production from various fuel sources, particularly biomass-derived fuels through steam reforming, partial oxidation and aqueous phase reforming, etc. [1–10], has been the focus of investigation world wide. For the traditional natural gas (methane) steam reforming (MSR), which is currently carried out using multi-tubular fixed bed reactors to produce syngas (a mixture of H_2 and CO) or H_2. Renewed interesting in MSR has been increasing, due to the fact that improvement on MSR process promisingly offers lower cost of H_2 for PEMFC application. During MSR, the following reversible reactions occur.

$$CH_4 + H_2O = CO + 3H_2, \quad \Delta H_{298}^0 = 206\,\text{kJ/mol} \tag{1}$$

$$CO + H_2O = CO_2 + H_2, \quad \Delta H_{298}^0 = -41\,\text{kJ/mol} \tag{2}$$

$$CH_4 + 2H_2O = CO_2 + 4H_2, \quad \Delta H_{298}^0 = 165\,\text{kJ/mol} \tag{3}$$

Because of the high endothermicity of reactions (1) and (3), higher temperature favors forward reactions. Generally, methane conversion over 80.0% could be obtained over 1123 K. To improve energy efficiency, higher reaction pressure is also applied. To efficiently lower reaction temperature and achieve high methane conversion at the same time, equilibria for MSR reaction should be broken, due to the low methane conversion limited by thermodynamics at low temperatures. As the major products in MSR are H_2 and CO_2 at low reaction temperatures, selective removal of CO_2 or H_2 could meet the purpose [11,12]. Calculation performed by setting a residual H_2 ratio in

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equilibrium composition of MSR reaction showed that higher methane conversion could be obtained at lower temperatures [13]. For example, methane conversion of 94.0% was predicted when 90.0% of H_2 was removed from reaction zone at 773 K. Therefore, Pd membrane, whose mechanism is based on a H_2 solution-diffusion mechanism on perm-selective film, has been applied to construct membrane reactors to shift thermodynamic equilibrium limited reactions [12–17].

Advantages of membrane reactor over conventional fixed bed reactor (CFBR) for MSR reaction have been recognized, since Oertel et al. first disclosed improved reaction performances in membrane reactor based on a Pd disk of 100 μm [18]. However, due to the low H_2 permeance of membrane, reaction temperatures in the range of 973–1073 K were still necessary to achieve sufficient methane conversion. To improve H_2 permeance of Pd-based membranes, Kikuchi and co-workers [19,20] invented electroless plating method and prepared thin Pd composite membranes on porous glass substrate. This method was further developed and widely investigated, and some high performance Pd membranes were developed [21]. Using Pd composite membrane in MSR reaction, Kikuchi and co-workers [12] obtained methane conversion of 88.0% at 773 K. Shu et al. [13] investigated MSR reaction in membrane reactor using Pd or Pd-Ag/porous stainless steel composite membranes systematically. Higher reaction temperature, S/C or sweep ratio favored methane conversion, while higher reaction pressure may decrease or increase methane conversion, depending upon other operation parameters. Jorgensen et al. [22] investigated MSR in membrane reactor using a 100 μm thick 23 wt.% Pd-Ag membrane tube. Methane conversion of 51% was obtained at 773 K and 600 kPa, and it became 61% at 1000 kPa. Possible coke-free working conditions for MSR in membrane reactor were predicted. Lin et al. [23] investigated effect of incipient removal of H_2 through Pd membrane on methane conversion in MSR by experiment and modeling. They found that L/S (load-to-surface ratio, defined as inlet volumetric flux of methane relative to membrane area ($m^3\ m^{-2}\ h^{-1}$)) and space velocity had great influence on the performances of membrane reactor. Higher space velocity or higher L/S decreased methane conversion. Basile et al. [24] applied a cold-rolled Pd/Ag alloy membrane to construct membrane reactor for MSR. Influences of different kind of sweep gases such as nitrogen, air, steam, CO and O_2 on conversion were reported. By using O_2 sweep gas, methane conversion of 69.0% was obtained at 723 K. Very recently, Tong et al. [25] investigated MSR in membrane reactor using high performance Pd membrane supported on macro-porous stainless steel. Methane conversion of 96.9% and H_2 recovery rate of 90.4% were obtained at 823 K. They also investigated the influence of different kinds of steam reforming catalysts on the performances of membrane reactor [16]. It was found that catalytic performance impacted not only reaction rate but also H_2 flux across Pd membrane, thus separation efficiency of membrane.

Thus, renewed interest in developing catalysts suitable for MSR reaction at low temperatures was boosted. For instance, Matsumura and Nakamori [26] investigated catalytic performances of nickel-based catalysts for MSR at 773 K. Nickel catalyst supported on γ-alumina was not well reduced at 773 K and inactive for MSR. However, the catalyst reduced at 973 K was fairly active, while Ni^0 was partially oxidized during reaction. Among catalysts with similar nickel content, the one supported on zirconia was the most active. Kusakabe et al. [27] investigated nickel and precious metal catalysts supported on Ce-ZrO_2 solid solutions for MSR reaction. Supported Rh catalyst showed best performances among Ni, Pt, Ru and Rh. However, nickel catalysts were still the preferred choice, due to their wide availability and cheapness. Nickel supported on $Ce_{0.15}Zr_{0.85}O_2$ had obvious superiority over that on γ-alumina. Moreover, investigation by Aparicio et al. [28] on methane dry reforming over nickel catalysts in membrane reactor also suggested that $Ce_xZr_{1-x}O_2$ support, instead of γ-alumina, suppressed coke formation and deposition. The lower CO selectivity and decreased coke deposition may be ascribed to the highly mobile oxygen species, possibly generated through a redox cycle of Ce^{4+}/Ce^{3+}. Though impregnated nickel catalysts were not so active in MSR reaction, nickel-alumina based catalysts prepared via coprecipitation had shown high activity for higher hydrocarbons steam reforming or methanation reactions in 1980s [29,30], and these catalysts were still investigated on their application to biomass gasification recently [31]. Ross et al. [32] investigated different nickel/alumina catalysts prepared via coprecipitation or impregnation. Some evidence was found that two types of sites, metallic crystallites and those derived from surface nickel aluminate spinel, may exist on Al_2O_3 supported catalysts, both of which can participate in MSR and associated reactions. While for nickel/alumina catalysts prepared by coprecipitation, the well-dispersed Ni^0 species derived from surface aluminate may possess good activity for MSR. Our previous work showed that Ni/La-Al_2O_3 catalysts, prepared via coprecipitation, had good performances for higher hydrocarbons steam reforming [33]. In the process for preparation nickel/alumina catalysts by coprecipitation, precipitation process and calcination temperature were found to play an important role in determining nickel aluminate formation and its existence state [34].

Currently, although high methane conversion has been previously reported, generally, the reaction gas hourly space velocity (GHSV) was still small. Furthermore, high fluxes of sweep gases were applied. These working conditions were unpractical, for under most cases, pure H_2 was the desired product. But as suggested by Gallucci et al. [24], using steam as sweep gas at low sweep ratios may be a good choice for pure H_2 production due to the easy separation of steam by condensation. Thus, in a practical membrane reactor, it is vitally important to find the bottleneck in membrane reactor. Besides high performance membrane for H_2 separation, catalysts with high activity at temperatures around 773 K were also indispensable. But in previous studies [12–17,22–25,35–38], nickel-based commercial MSR catalysts activated at lower temperatures were applied. As we know, those catalysts were designed for MSR reaction at temperatures as high as 1123 K, their adaptability to MSR in membrane reactor at a much lower reaction temperature are still very unclear and needs further investigation. This work investigated the application of a