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Combined pre-reformer/reformer system utilizing monolith catalysts for hydrogen production

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ABSTRACT

The pre-reforming of higher hydrocarbon, propane, was performed to generate hydrogen from LPG without carbon deposition on the catalysts. A Ru/Ni/MgAl₂O₄ metallic monolith catalyst was employed to minimize the pressure drop over the catalyst bed. The propane pre-reforming reaction conditions for the complete conversion of propane with no carbon formation were identified to be the following: space velocities over 2400 h⁻¹ and temperatures between 400 and 450 °C with a H₂O/C₁ ratio of 3. The combined pre-reformer and the main reformer system with the Ru/Ni/MgAl₂O₄ metallic monolith catalyst was employed to test the conversion propane to syngas where the reaction heat was provided by catalytic combustors. Propane was converted in the pre-reformer to 52.5% H₂, 27.0% CH₄, 17.5% CO, and 3.0% CO₂ with a 331 °C inlet temperature and a 482 °C catalyst outlet temperature. The main steam reforming reactor converted the methane from the pre-reformer with a conversion of higher than 99.0% with a 366 °C inlet temperature and an 824 °C catalyst outlet temperature. With a total of 912 cc of the Ru/Ni/MgAl₂O₄ metallic monolith catalyst in the main reformer, the H₂ production from the propane reached an average of 3.25 Nm³h⁻¹ when the propane was fed at 0.4 Nm³h⁻¹.

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1. Introduction

Pre-reforming technology has been used for many years as the first stage in the steam reforming of heavy hydrocarbons, e.g. LPG or naphtha, to synthesize gas or H₂ [1]. This process is a valuable tool for improving the efficiency and solving problems related to the conventional tubular steam reforming process (main reforming) [2]. During

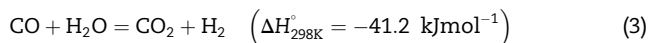
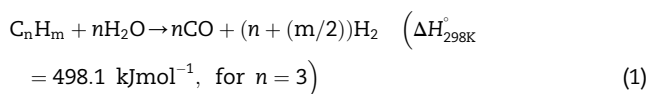
pre-reforming, heavy hydrocarbons are first converted to methane and carbon oxides (CO, CO₂) at relatively low temperatures, typically from 400 to 550 °C, and finally H₂-rich streams are produced in the main reforming process at higher temperatures of >800 °C [3–5]. Pre-reforming operated at low temperatures is an inevitable process because the steam reforming of higher hydrocarbons, which generally occurs at high temperatures, easily results in

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coke deposition on the walls of the reformer and catalyst surface [6].

The pre-reforming process can be expressed with the following reactions [7].



First, a mixture of CO and H₂ is produced from irreversible steam reforming (1) of higher hydrocarbons ($n > 1$). CH₄ and CO₂ are also formed by the subsequent methanation reaction (2) and water-gas shift reaction (3), respectively. The recently introduced steam reforming process is generally composed of 2 stages, main steam reformer and pre-reformer, due to the many benefits of using an additional pre-reformer [8,9]. Significant energy savings can be obtained by reducing the steam-to-carbon ratio. Moreover, carbon formation caused by the cracking of higher hydrocarbons in the top of the reformer tubes is avoided by the installation of a pre-reformer [2].

A nickel containing steam reforming catalyst can also be used in the pre-reforming process. However, a nickel based catalyst is easily deactivated during reforming processes, especially due to poisoning of the catalyst surface by coke deposition (coking), when the operations are performed at low steam-to-carbon ratios and high temperatures. To alleviate the coking problem, the addition of noble metals to the Ni catalysts, such as Ru, have resulted in significant improvements in both the activity and coke-resisting ability of silica supported Ni catalysts in the CO₂ reforming reaction [10]. The steam reforming reaction over pelletized Ni catalysts is a well-known heat-transfer limited reaction [11]. We washcoated Ru-doped Ni catalyst powders on metallic monoliths and they had an enhanced heat-transfer capability.

There are increased needs for small-scale hydrogen production units, especially for hydrogen refueling stations [12,13]. When the feed for the hydrogen product is LPG or naphtha, compact pre-reformer/reformer combination units are necessary [3]. Therefore, we developed a novel self-sustaining 5 kWe-class LPG reformer, which mainly consists of a very active metallic monolith catalyst in a highly endothermic reforming reaction, a combined compact system of a pre-reformer/reformer, and a catalytic combustor to supply the endothermic reaction heat. That is, there are three new ideas in this work. Firstly, we investigated the behavior of a Ru-doped Ni/MgAl₂O₄ catalyst washcoated on the metallic monolith for both the propane pre-reforming reaction and the main steam reforming reaction. Secondly, a combined unit of a pre-reformer/reformer at a pilot scale was developed for the LPG-fed hydrogen production unit. Finally, the endothermic reaction heat was supplied by a combustion reactor equipped with Pd catalysts that were supported on the ceramic monolith.

2. Experimental

2.1. Catalyst preparation

The commercial Ni-based steam reforming catalyst ($S_{BET} = 19.2 \text{ m}^2\text{g}^{-1}$) was washcoated on the metallic monolith. The preparation procedure can be found elsewhere [14]. Fecralloy plate (Fe 72.8%/Cr 22%/Al 5%/Y 0.1%/Zr 0.1%, Goodfellow Co.) was used to make the monolith (640 cpi) with dimensions of 2.2 cm (diameter) × 2 cm (height). Once the washcoating of the Ni catalysts was completed, a small amount of noble metal (0.12 wt.% Ru) was doped into the Ni catalyst to serve as both the reduction-enhancing agent and the coke-resisting agent. RuCl₃ (RuCl₃·xH₂O, Aldrich Chem. Co.) was used as a noble metal precursor and the wet impregnation method was used.

2.2. Catalyst characterization

The surface area, pore size, and pore volume of the catalyst were measured by N₂ adsorption–desorption isotherms using a BELSORP mini-II (BEL Japan Inc.) apparatus. Before measurements, the samples were degassed in a vacuum at 573 K for 6 h.

XRD data of the sample was collected in a Rigaku D-Max 2500 (18 kW) diffractometer with Cu K α radiation. The step-scans were taken over the range of 2 θ from 20° to 80° in steps of 0.02°/s.

For the TPR experiments, the catalyst sample was purged with 50 ml/min of Ar for 1 h at 500 °C, and then cooled to room temperature. The level of hydrogen consumption was measured using a BELCAT Catalyst Analyzer (BEL Japan Inc.) by heating the sample from ambient temperature to 1000 °C with a heating rate of 10 °C/min in a flow of 5% H₂/Ar at 30 ml/min.

The real content of Ru was measured in the samples by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), with a PolyScan 60E (Hewlett Packard, USA).

The metal (Ni, MgO, Al₂O₃) loading amounts of the samples were measured by a MiniPal2 energy dispersive X-ray fluorescence (EDXRF) spectrometer.

The carbon formation on the catalyst after the pre-reforming reaction was investigated by Cs-corrected STEM using a JEOL microscope that was operated at 200 kV (National Nanofeb Center, Korea). The samples were prepared by putting a few drops of the corresponding colloidal solutions on carbon coated copper grids (Ted Pellar, Inc.).

2.3. Catalytic reaction and pre-reformer/reformer system

To evaluate the behavior of the Ru-doped Ni/MgAl₂O₄ catalyst washcoated on the metallic monolith for the pre-reforming reaction, steam reforming of propane was performed in a tubular stainless steel reactor (inside diameter of 2.22 cm) operated at atmospheric pressure. Propane was supplied from a cylinder of C₃H₈ (99.999%) by a mass flow controller (Brooks, 5850E). Steam was supplied by a steam generator. One cylindrical metallic monolith catalyst (2.2 cm diameter and 2 cm

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