Short communication

Single-stage temperature-controllable water gas shift reactor with catalytic nickel plates

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HIGHLIGHTS

- A new single-stage temperature-controllable reactor was developed for the exothermic WGS reaction.
- CO conversion increased to its equilibrium value at 375 °C with a CH_4 selectivity of <0.5%.
- The heat generated from the WGS reaction was sufficiently controlled with the coolant flow rate.

ARTICLE INFO

ABSTRACT

In this study, a microstructured reactor with catalytic nickel plates is newly designed and developed for proper heat management in an exothermic water gas shift WGS reaction. The reactor is designed to increase the reactor capacity simply by numbering-up a set of a catalyst layers and heat exchanger layers. The WGS reactor is built up with two sets of a catalyst layers and heat exchanger layers. The performance of the reactor is verified by WGS testing with the variation of the furnace temperatures, gas hourly space velocity (GHSV) and coolant (N_2) flow rate. At a GHSV of 10,000 h^{-1}, CO conversion reaches the equilibrium value with a CH_4 selectivity of $\leq$0.5% at the furnace temperature of $\geq$375 °C. At high GHSV (40,000 h^{-1}), CO conversion decreases considerably because of the heat from the exothermic WGS reaction at a large reactants mass. By increasing the coolant flow rate, the heat from the WGS reaction is properly managed, leading an increase of the CO conversion to the equilibrium value at GHSV of 40,000 h^{-1}.

1. Introduction

The growing energy demand has caused the depletion of oil reserves and an increase in CO_2 emission. Consequently, the need for the development of clean energy technologies has increased. Hydrogen is considered a promising clean energy carrier, and the environment-friendly hydrogen production technologies from coal and natural gas have been developed in the last decade. At present, the annual world hydrogen production is approximately 45–50 million tonnes, corresponding to approximately 2% of the primary energy demand [1,2]. The largest consumption of hydrogen is in petroleum refining and petrochemical industries for ammonia and methanol synthesis [3]. Most of the hydrogen ($\sim$96%) is produced by steam reforming of natural gas and gasification of coal and biomass [4,5]. In the case of the use of fossil fuels as hydrogen sources, carbon dioxide capture and storage is an important issue in the hydrogen production route. The stream that is emitted by a reformer or gasifier contains 10–60% CO (dry basis), which can be further converted to CO_2 and H_2 through the water gas shift (WGS) reaction (Eq. (1)). Then, CO_2 capture and high purity H_2 production is simultaneously accomplished by H_2/CO_2 separation through liquid phase solvents for which both physical solvents (e.g., Selexol) [6], chemical solvents (e.g., amines) [7] and hydrogen selective membranes [8] are used.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ KJ mol}^{-1} \tag{1}$$
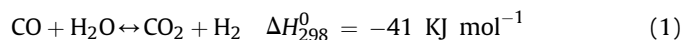
In traditional applications, the CO conversion process has multi-stage WGS reactors. The first of these reactors is a high-

temperature shift (HTS) reactor that is operated at high temperature (350–400 °C) under a Fe–Cr based catalyst [9–11], and the second one is a low-temperature shift (LTS) reactor that is operated at a low temperature (∼200–300 °C) under a Cu–Zn based catalyst [12–14]. Like other chemical reactors, proper heat management is a key issue in the WGS reactor for efficient use of catalyst. This reaction is exothermic and reversible, and there is no variation of the mole number. Therefore, CO conversion is thermodynamically favoured at low temperatures, and the pressure does not affect the conversion in traditional reactors. Because the exothermal WGS reaction causes the reactor temperature to rise, integrated heat removal is needed to maintain the isothermal operation and thus, high CO conversion. In typical industrial applications, the multi-bed adiabatic reactors with interstage cooling for exothermal reversible reactions are suggested to ensure sufficiently high CO conversion [6,15,16]. There are new designs for compacting the WGS reactor by applying active heat exchange or heat distribution in monolith or micro-structured reactors [17–20]. These reactors are composed of metallic thin plates and allow for isothermal operation or operation with a minimised temperature gradient.

Recently, we developed a novel catalytic nickel plate for the production of synthetic natural gas [21] and steam reforming of methane [22]. The advantages of the catalytic nickel plate are: i) a hydrogen selective membrane effect that allows the system to surpass the equilibrium conversion, ii) a super mass transfer through the sub-micron channel formed in the membrane structure, and iii) a super heat transfer and re-distribution throughout the thin metal plate. Hwang et al. modified the catalytic nickel plate with potassium and showed a good performance in the HTS reaction [23].

In this study, a newly designed microstructured reactor with catalytic nickel plates was developed for proper heat management in an exothermal reaction. The HTS reaction test was carried out under very severe experimental conditions (GHSV = 40,000 h^{-1}) with the variation of coolant flow rate to manage the heat from the exothermal WGS reaction.

2. Experimental

2.1. Catalytic nickel plate and reactor design

The catalytic nickel plate was made using the sintered metal method developed by KIER [21,22] and modified with potassium for a good performance of the WGS reaction, as shown in the previous study [23]. The reactor was newly designed to control the temperature of the catalyst bed on a single stage because the WGS reaction is exothermic and can generate a great amount of heat causing catalyst deactivation and side reactions, such as methanation. As shown in Fig. 1, the designed MCR consists of cover plate, catalyst layers, reactant distribution layers, product collection layers and heat exchanger layers. The reactor capacity of the WGS reaction can be increased by numbering up a set of layers that includes a catalyst layer, a reactant distribution layer, a product collection layer and a heat exchanger layer. All of the layers are made of metal sheets. The catalyst layer is composed of a catalyst holding plate and a catalytic nickel membrane. Several micron-sized channels are patterned on the product collection plates and heat exchanger plates. To distribute the reactant in the catalytic nickel membrane, 3-D channels are formed on the reactant distribution layer. The reactant inlet and the coolant outlet tubes and the coolant inlet and product outlet tubes are welded onto the cover and the bottom plates, respectively. Each plate is stacked alternately and then bonded by diffusion bonding method.
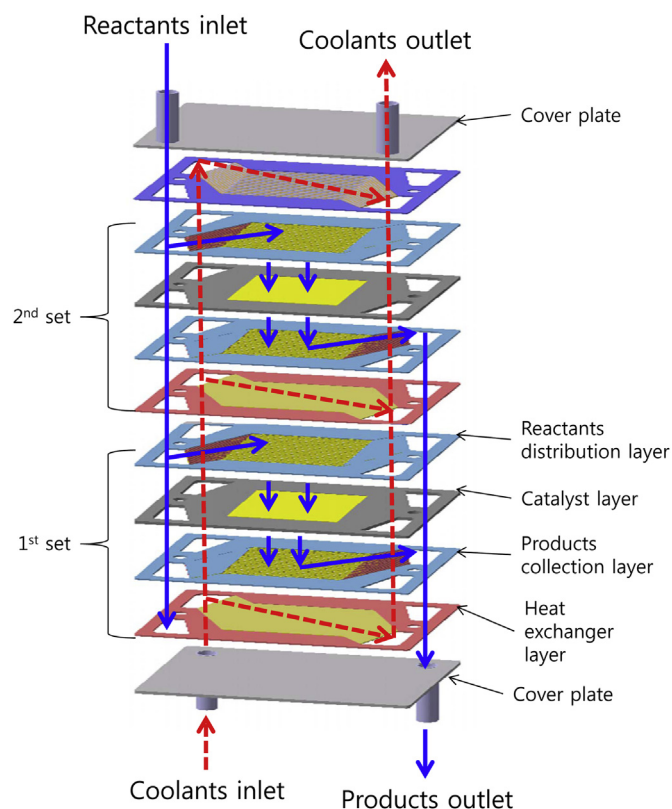

Fig. 1. The schematic representation of the newly designed single-stage temperature-controllable reactor and flow paths. Blue solid line: reactant and product flow path; Red solid line: coolant flow path. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. WGS test

The schematic of the WGS test is shown in Fig. 2. The WGS reactor was heated in an electric furnace equipped with a programmable temperature controller. The temperature of the furnace was controlled by a K-type thermocouple placed on the outside of the reactor, and the temperatures in the reactant inlet, product outlet, coolant inlet and coolant outlet were monitored. Nitrogen was supplied by a mass flow controller into the coolant inlet tube. As reactants, hydrogen and carbon monoxide were supplied by a mass flow controller (MFC, Brooks 5850 series), and liquid water was supplied by a micro liquid pump (NS, MINICHEMI PUMP). The WGS test was performed with a 60 vol.%CO + 40 vol.%H$_2$ mixture of gas with an H$_2$O/CO molar ratio of 3. The feed gas composition is similar to the gas composition of the coal gasifier [24], which is a more severe condition compared with the reformate gas that arises from the steam reforming of methane [22]. The effect of temperature on the CO conversion was investigated at the temperature range of 300–450 °C with gas hourly space velocity (GHSV) of 10,000 h^{-1}. During the test of the temperature effect on CO conversion, N$_2$ of 0.12 Nm^3 h^{-1} was introduced. To see the reactor capacity, the GHSV was verified from 5000 to 40,000 h^{-1} at a furnace temperature of 375 °C. The reactor temperature is expected to rise under high GHSV because the WGS reaction is exothermic. The effect of the coolant's flow rate was performed under GHSV of 40,000 h^{-1} at 375 °C to verify the performance of the newly designed WGS reactor for proper heat management. The product gases were analysed by a gas chromatograph (Agilent 6890N) equipped with HP-MOLSIV and HAYESEP D columns and thermal conductivity detectors (TCD). The surplus water in the products was separated by a cold trap before analysing the product gases.