



Ni nanosheet-coated monolith catalyst with high performance for hydrogen production via natural gas steam reforming



Kee Young Koo, Hyun Ji Eom, Un Ho Jung, Wang Lai Yoon*

Hydrogen Laboratory, Korea Institute of Energy Research (KIER), 152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

ARTICLE INFO

Article history:

Received 11 April 2016

Received in revised form 17 July 2016

Accepted 18 July 2016

Available online 19 July 2016

Keywords:

Ni nanosheet

Catalyst coating

Monolith

Steam reforming

Hydrogen production

ABSTRACT

A Ni nanosheet-coated FeCrAlloy monolith catalyst was successfully prepared using a deposition-precipitation-based “Korea Institute of Energy Research” (KIER) coating method, which provides a uniform coating of highly dispersive Ni catalyst on the metal substrate. The newly developed monolith catalyst showed a higher Ni dispersion and surface area on the substrate as compared to a washcoated monolith catalyst. The Ni nanosheet-coated monolith catalyst exhibited high activity and long-lasting stability at a high space velocity of GHSV = 15,000 h⁻¹ during a natural gas steam reforming reaction for H₂ production. This is mainly attributed to the fact that the uniform and highly dispersed Ni nanosheet catalyst improves the availability of surface active metal sites on the metal substrate.

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1. Introduction

Most chemical processes are accompanied by the evolution or absorption of reaction heat. Natural gas steam reforming (NGSR) for hydrogen production in a fuel reformer is strongly endothermic and, hence, requires a large amount of reaction heat [1]. A conventional packed bed reactor that uses a ceramic pellet catalyst is inefficient owing to the low thermal conductivity and mass transfer limitations, resulting in the disadvantage of unnecessarily large reactor volume [2]. According to a study by Xu and Froment [3], the effectiveness factor of the steam reforming catalyst is around 0.03; thus, only active sites on the outer surface of the pellet catalyst participate in the reaction. From the perspective of reaction kinetics, the diffusion of a gaseous reactant to the surface of the catalyst becomes the rate-limiting step owing to a rapid surface reaction at temperatures above 700 °C. Therefore, it is imperative to develop a new reactor technology to address various drawbacks such as channeling, pressure drop, low thermal conductivity, and slow systemic response in existing fixed bed reactors that are packed with ceramic pellet catalysts [4–6].

A structured catalyst is a very useful core technology in reactions that exhibit a rate-limiting diffusion of gaseous reactants toward the catalyst surface [2,7]. The main advantage of a metallic structured catalytic reactor is that it can increase the heat transfer rate

per unit volume (US/V, intensification factor), while providing a large geometrical reaction surface to reaction volume ratio (S/V, compacity factor) [8]. In addition, highly regular reactor channels can provide a uniform fluid flow to minimize systemic pressure drop, as well as concentration and temperature radial gradients [9,10].

In particular, metal monolith catalysts have attracted a great deal of attention as alternatives to conventional pellet catalysts. According to a previous study by Roh et al. [11], a stainless steel-supported (SUS) Ni catalyst monolith showed higher activity compared to a pellet catalyst during an NGSR reaction owing to its higher heat transfer efficiency. Moreover, Bobadilla et al. [12] showed that a Ni-Sn/MgO-CeO₂/Al₂O₃-coated metal monolith used in glycerol steam reforming had superior activity and stability compared to conventional powder and spherical pellet catalysts. Unlike the case of a packed bed reactor, reactants easily flow through the channels of a monolith catalyst, thereby mitigating pressure drop and channeling problems [13,14]. In addition, a metal monolith reactor provides a more compact and lighter reaction system owing to its improved heat and mass transfer capabilities, which in turn increases the reactor throughput as a result of the higher capacity per unit reactor volume and hour [15–17].

However, in order to commercialize this technology, the catalyst of choice has to be deposited stably, and should be highly dispersed on the surface of a metallic substrate to afford high activity and long-term stability. Therefore, it is necessary to devise a proper coating method using a highly dispersed catalyst to maximize the number of exposed active sites, which are responsible for the fast

* Corresponding author.

E-mail address: wlyoon@kier.re.kr (W.L. Yoon).

surface reaction at high space velocity, and to prevent the sintering of the catalyst particles at high temperatures [18,19]. In particular, a monolith in the shape of a long-channel honeycomb makes it difficult to achieve an even catalyst coating within the channel owing to capillary forces. As such, it is essential to develop an efficient coating strategy to afford a highly dispersed deposition of the catalyst in order to improve the activity and stability of the metal monolith catalyst [20]. Some previous studies have reviewed the different coating methods used in depositing the catalyst of interest on metallic structured substrates, and conventional coating methods such as impregnation and washcoating (slurry coating) are typically the main choices [5,21,22]. As reported in previous works, the impregnation method results in minimal catalyst deposition and has difficulties in controlling the catalyst dispersion, while it is challenging to control the thickness of the coating layer using the washcoating method, especially when it comes to achieving an even layer of catalyst coating [23]. Benito et al. [24] have highlighted the problem of non-uniformity in metal dispersion on a structured catalyst when the impregnation method is used and emphasized the necessity to achieve a highly dispersed active metal deposition on the surface of the structured support. An electrosynthesis procedure was used to coat Rh/Mg/Al hydrotalcite-type compounds on FeCrAlloy foams for the catalytic partial oxidation of CH₄. However, the ability to control the composition of the deposited catalyst, which affects the metallic particle size and adhesion of the film, remains an unresolved issue. According to Fukuhara et al. [25], a honeycomb-type Ni-based catalyst was prepared by using a combination of the sol-gel and electroless plating methods on a stainless steel substrate. In other words, the structured catalyst consisted of a porous alumina layer formed by the sol-gel method, whereas the nickel component was deposited via electroless plating. They reported that the monolith structure that was washcoated with a commercial catalyst showed lower activity compared to the prepared honeycomb catalyst in a methane dry reforming reaction. Therefore, the present study focuses on developing a new coating technique (named the Korea Institute of Energy Research (KIER) technique), based on a general deposition-precipitation method, to provide an effective control of catalyst deposition and to achieve a high dispersion of the Ni catalyst particles. The results obtained using the newly developed catalyst system were compared to the activity of a metal monolith catalyst, which was prepared using a conventional washcoating method, via an NGRS reaction.

2. Experimental

2.1. Catalyst preparation

A FeCrAlloy (Goodfellow, Fe: 72.8, Cr: 22, Al: 5, Y: 0.1, Zr: 0.1 wt%) monolith (used as a metal structured carrier) was manufactured by rolling flat and corrugated metal strips into the shape of a cylinder. The diameter of the cylinder was 22 mm, the height was 20 mm, and the cell density was 690 cpi (cells/in²). The metal monolith catalyst was prepared by the following process. Firstly, the metal surface was rinsed with acetone in an ultrasonic bath for 0.5 h and subsequently, electrochemically treated with aqueous HF solution at an electrical voltage of 5 eV. After the preliminary treatment of the metal surface, it was calcined at 900 °C for 6 h. We previously showed that the Al₂O₃ layer formed on the pre-treated surface of a FeCrAlloy substrate enhanced the adherence between the metal substrate and the coated catalyst layer, thus resulting in a more stable catalytic performance compared to a system that had only undergone a conventional thermal oxidation treatment (900 °C, 6 h) [19]. The pre-calcined monolith was repeatedly washcoated with a 10 wt% Al₂O₃ sol solution until a sufficient Al₂O₃ amount was loaded onto the metal monolith, after which the Al₂O₃-coated

monolith was re-calcined at 900 °C for 6 h. A 10 wt% Al₂O₃ sol solution was prepared by dissolving boehmite (Disperal P2, Sasol) in distilled water. The viscosity of the Al₂O₃ sol solution was kept constant by maintaining the solution's pH at 4.5. In order to use Ni as the main active metal of the catalytic system, nickel nitrate (97%, Junsei) was used as the catalyst precursor in a proprietary KIER coating technique based on a general deposition-precipitation method, along with the addition of an ammonia solution (28%, Junsei) as a precipitating agent to control the pH of the coating solution at 13.0 [26]. After the loading of Ni, the monolith was calcined at 700 °C for 2 h. To compare different coating methods, the monolith catalyst was also prepared via washcoating using a 15 wt% Ni/MgAl₂O₄ catalyst slurry, which is a mixture of 15 wt% Ni/MgAl₂O₄ catalyst powder, Al₂O₃ sol, and distilled water in the ratio of 1:1:4. We prepared the powder catalyst by grinding the 15 wt% Ni/MgAl₂O₄ pellet catalyst finely. The washcoated monolith was calcined at 600 °C for 3 h. Meanwhile, a 15 wt% Ni/MgAl₂O₄ pellet catalyst (Brunauer-Emmett-Teller (BET) surface area = 22 m²/g, Ni dispersion = 1.9% and Ni surface area = 13 m²/g) was prepared via an impregnation method using a nickel nitrate solution on a MgAl₂O₄ spinel (1-hole, Sasol) pellet. The pellet catalyst was calcined at 700 °C for 2 h.

The Ni coating amount per unit area of monolith catalyst was calculated according to Eq. (1).

$$\text{Nicoating amount (g/cm}^2\text{)} = (W_1 - W) / A \quad (1)$$

Where W is the metal monolith's weight (g), W₁ is the coated metal monolith's weight (g), and A is the surface area of the metal monolith (cm²).

2.2. Catalyst characterization

The N₂ adsorption-desorption isotherm and BET surface area of the monolith catalyst were measured using a BELSORP-Max instrument (BEL Japan, Inc.). To measure a whole monolith sample, a homemade cell was used. Before the analysis, the sample was treated at 200 °C for 3 h in vacuum, followed by a N₂ adsorption at -196 °C. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method. H₂-chemisorption was performed to identify the metal surface area and metallic dispersion using the BEL-METAL-3 instrument (BEL Japan, Inc.). A 0.3 g sample which was prepared by cutting the coated monolith in a proper size was reduced under a H₂ gas flow at 700 °C for 3 h. The sample was then purged at 700 °C for 1 h under a He gas flow and subsequently cooled to 50 °C. A H₂ pulse (20 vol.% H₂/Ar) was then injected into the catalyst. The adsorbed H₂ amount, obtained by assuming the adsorption stoichiometry of one hydrogen atom per nickel atom on the surface (H/Ni_{surface} = 1), was used to estimate the Ni dispersion and surface area. The surface morphology of the monolith catalyst, the shape of the coated catalyst particle, and the composition of the metal substrate were observed using scanning electron microscopy (SEM; S-4700, Hitachi, Japan) and energy dispersive X-ray spectroscopy (EDS; EMAX 7200-H, Horiba, Japan).

2.3. Catalyst reaction

Fig. 1 shows the schematic diagram of the experimental apparatus used for the NGRS reaction system. The test reaction was performed at 700 °C under atmospheric pressure in a one-inch diameter Inconel tubular reactor (O.D. = 25.4 mm, I.D. = 22.1 mm), and the thermocouple was located at the bottom center of the monolith. Prior to the reaction, the catalyst was reduced at 700 °C for 3 h in 20 vol.% H₂/N₂ balance. Reactants were fed with a steam-to-carbon (S/C) ratio of 3 (mol/mol), and the gas hourly space velocity (GHSV) was 6000–15,000 h⁻¹. The effluent was passed through a trap to condense residual water and analyzed with an

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