



# Catalytic properties of pure Ni honeycomb catalysts for methane steam reforming

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## ARTICLE INFO

### Article history:

Received 12 May 2015

Received in revised form 15 July 2015

Accepted 30 September 2015

Available online 9 October 2015

### Keywords:

Hydrogen production

Metallic honeycomb catalyst

Cell density

Geometric surface area

Temperature profile

## ABSTRACT

Honeycomb catalysts were assembled, using only 30  $\mu\text{m}$ -thick Ni foils, to develop genuine monolithic catalysts for hydrogen production via methane steam reforming. A high cell density (900 cps) and geometric surface area ( $59.4 \text{ cm}^2/\text{cm}^3$ ) were achieved on the honeycomb catalyst. The catalyst exhibited high  $\text{CH}_4$  conversion (over 97%) at 1073 K for a long period of up to 8321.1 h under low steam-to-carbon ratio (1.34) and space velocity ( $335 \text{ h}^{-1}$ ) conditions. A  $\text{H}_2$  production rate of 74.2 ml/min was achieved, and carbon deposition was hardly detected in spite of the low steam-to-carbon ratio. The catalyst was gradually deactivated due to the oxidation of Ni, but was repeatedly regenerated by reduction in flowing hydrogen. These findings proved the high potential of the Ni honeycomb catalyst for application to a small-scale hydrogen production system. Monitoring the temperature profile along the axial direction showed good heat transfer between the catalyst and the surrounding gas, which was attributed to the high thermal conductivity of Ni and to the high cell density of the catalyst. The high geometric surface area and good heat transfer are considered responsible for the good performance of the catalyst.

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## 1. Introduction

Efficient, low-cost, and small-scale hydrogen production is essential for the widespread use of automobile and household fuel cells [1–3]. High-performance catalysts are constantly required for hydrogen production. Honeycomb catalysts, which consist of narrow, straight, parallel channels separated by thin walls, are highly promising compared with conventional pelleted catalysts. The greater potential of honeycomb catalysts is ascribed to the low pressure drop in the channels, because of the laminar reactant gas flow [4], and to the high heat transfer rate in the channels because of the high geometric surface area [4–9].

Honeycomb catalysts have been developed mainly for cleaning automotive exhaust gases. In the meantime, attempts have been made for applications to other chemical processes [10], such as oxidative dehydrogenation of paraffins to the corresponding olefins, partial oxidation of methane and higher hydrocarbons to synthesis gas, and steam reforming of *n*-hexane to hydrogen, car-

bon monoxide, and carbon dioxide. These pioneering works have demonstrated the high potential of honeycomb catalysts for chemical processes other than exhaust gas cleaning. However, despite their unique characteristics the use of honeycomb catalysts is still very limited, and further studies are required in terms of a wide range of fundamental and technological aspects.

Honeycomb catalysts are classified into two types depending on the substrate substance. Metallic honeycomb catalysts have advantages of high thermal conductivity and geometric surface area compared with ceramic honeycomb catalysts, leading to high heat and mass transfer rates [9]. In view of these advantages, in this study we have directed our efforts towards the application of metallic honeycomb catalysts in hydrogen production via methane steam reforming, which has rarely been investigated.

Metallic honeycomb catalysts have mostly been made from the foils of heat-resistant ferritic steel, FeCrAlloy [9]. FeCrAlloy foils are not catalytically active but can be used as a structural substrate for supporting catalytically active species. A thin porous  $\gamma$ -alumina layer is wash-coated on the foil surface in order to ensure a high surface area, and active species, commonly noble metals such as Pt, Pd, and Rh, are then dispersed on the  $\gamma$ -alumina layer; that is, metallic honeycomb catalysts are designed based on the concept that structural and catalytic functions are separated from each other [9]. Therefore, they are referred to as incorporated monolithic catalysts [4]. Although this fabrication technique has been well established,

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there still remain some issues to be addressed. First, the use of noble metals inevitably leads to high costs. Second, the wash-coating and dispersing processes usually followed by calcination also lead to increased costs. Third, the dispersed active species and the porous  $\gamma$ -alumina layer cause a concern of potential break away from the substrate, which can lower the catalyst's durability.

The challenge in this study is to develop honeycomb catalysts using only pure Ni foils, and without using noble metals and porous  $\gamma$ -alumina, i.e., we aim to develop genuine monolithic catalysts, which are different from the incorporated monolithic catalysts. Specifically, in our design, pure Ni foils accomplish both structural and catalytic functions. Ni is a heat-resistant structural metal, but the concern is whether the catalytic activity of pure Ni foils is sufficiently high. To date, Ni foils are known to have a level of catalytic activity adequate for methane steam reforming. Indeed, the reaction kinetics for methane steam reforming [11,12] and carbon dioxide reforming [13] have been studied using Ni foils. However, the level of the catalytic activity remains unknown. Because of the lack of noble metals and low surface area, technologically attractive activity was hardly expected for bulk Ni foils. We suggest that this issue can be overcome by increasing the cell density of the honeycomb. On the other hand, compared with other honeycomb substrate materials, pure Ni has the advantage of high thermal conductivity: at room temperature, the thermal conductivity of Ni is 90.7 W/mK [14], which is much higher than that of FeCrAlloy (16 W/mK) [15] and Cordierite (0.3–5 W/mK) [16,17]. This advantage could promote the catalytic performance of Ni honeycomb catalysts. In this study, high cell density honeycomb catalysts were assembled using only pure Ni foils, and the catalytic properties for methane steam reforming were examined over a long period of time (8000 h).

A few studies related to genuine monolithic catalysts have been reported previously. Fichtner et al. developed a microstructured honeycomb catalyst made from only rhodium foils [18], thus achieving a high catalytic performance for the partial oxidation of methane due to the high thermal conductivity of rhodium; however, a noble metal was employed. We have previously disclosed that heat-resistant  $\text{Ni}_3\text{Al}$  intermetallic compound foils show high catalytic activity for methanol decomposition [19,20]. This activity was attributed to the spontaneous formation of fine Ni particles on the surface during the reaction, i.e., the  $\text{Ni}_3\text{Al}$  foils served as precursors of the active species.

## 2. Experimental

### 2.1. Ni foils

Flat pure Ni foils with 30  $\mu\text{m}$  thickness were used for assembling honeycomb catalysts. The foils were fabricated by cold rolling of commercially available pure Ni ingots. Table 1 lists the concentration of impurity elements, the texture, and the BET (Brunauer–Emmett–Teller) specific surface area of the foils that could affect their catalytic properties. The concentrations of carbon and other elements were analyzed by infrared absorption method of combustion gas and inductively coupled plasma method, respectively. The texture was measured on the foil surface by the X-ray Schultz back reflection method. The BET specific surface area of the foils was measured by krypton adsorption using a surface area analyzer (Micrometrics model ASAP 2020).

### 2.2. Assembling Ni honeycomb catalysts

The Ni foils ( $10 \times 265 \times 0.03$  mm) were tightly corrugated in a sinusoidal wave form (0.8 mm in height and 2 mm in spacing), and they were spirally wound with flat foils ( $10 \times 330 \times 0.03$  mm)

**Table 1**  
Specifications of the Ni foils used.

Impurities	(wt%)
C	0.018
Mn	0.1
Al	0.013
Cu, Co, Fe, Sn, Mo, W, Cr, Mg, Si, Zn, Au	<0.005
Ag	<0.05
Pt, Pd, Rh, Ru, Ir	<0.05 <sup>a</sup>
Texture	(001)<100>
BET specific surface area ( $\text{m}^2/\text{g}$ )	0.0083
BET surface area/geometrical surface area	1.08

<sup>a</sup> Below detection limit.

**Table 2**  
Geometry of the foils, honeycomb and honeycomb catalyst.

Honeycomb	
Type	Spirally wound
Number of turn	10
Dimension	
Diameter $\times$ Height (mm)	16 $\times$ 10
Geometric surface area ( $\text{cm}^2$ )	119
Volume ( $\text{cm}^3$ )	119
Geometric surface area/volume ( $\text{cm}^2/\text{cm}^3$ )	59.2
Weight (g)	1.9
Bulk density ( $\text{g}/\text{cm}^3$ )	0.945
Cell geometry	
Cell shape	Sinusoidal
Height $\times$ Spacing (mm)	0.8 $\times$ 2
Wall thickness (mm)	0.03
Cell density (cpsi)	900
Five-stacked honeycomb catalyst	
Geometric surface area ( $\text{cm}^2$ )	595
Volume ( $\text{cm}^3$ )	10.05
Weight (g)	9.5

to assemble the honeycomb structure with straight parallel cells (10 mm in length). The Ni honeycomb is shown in Fig. 1(a). Neither porous  $\gamma$ -alumina nor noble metals were coated on the surface. Table 2 lists the geometry of the corrugated foils, of the flat foils, and of the assembled honeycomb. Five pieces of the honeycomb were vertically stacked to form the honeycomb catalyst. The specifications of the five-stack honeycomb catalyst are also listed in Table 2.

### 2.3. Catalytic reaction

Methane steam reforming was carried out over the five-stack honeycomb catalyst in quartz reaction tubes in a flow reactor. A mixture of reactant gases was introduced from the top of the honeycomb catalyst. The honeycombs were numbered from the top (HC-1 to HC-5) and the temperatures of each honeycomb were monitored in their bottom center using a sheathed Chromel–Alumel (1 mm in diameter) thermocouple as schematically shown in Fig. 1b. The gas temperature was maintained constant along the axial direction of flow over 50 mm using the same thermocouple positioned at 2.5 mm below the center of HC-5.

Prior to the reaction, the honeycomb catalyst was reduced at 1073 K for 1 h by flowing pure hydrogen. Next, hydrogen was switched to feed gas mixtures to start long-term catalytic reaction tests up to 8321.1 h at 1073 K. In the first 6500 h, the reaction tests were performed mainly under conditions of low steam-to-carbon ratio (S/C) and space velocity (SV) (Feed-A, Table 3). The Reynolds number in the honeycomb channel was calculated to be about 0.1; thus, the flow was in the laminar range. When  $\text{CH}_4$  conversion decreased to a specific level, Feed-A was switched to pure hydrogen in order to regenerate the catalytic activity. The

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