



# A metal-honeycomb-type structured catalyst for steam reforming of methane: Effect of preparation condition change on reforming performance



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## ABSTRACT

In order to construct a structured steam reforming system, a honeycomb-type nickel-based catalyst was prepared by the combined technique of a sol-gel method and electroless plating on a stainless steel substrate. The type of the reducing agent used in the plating process influenced not only the forming rate of the nickel particles, but also the methane steam reforming (MSR) property of the prepared catalyst. The catalyst prepared using  $\text{NaBH}_4$  demonstrated a higher performance for MSR than the commercial catalyst, indicating that the catalyst degradation was quite low even under the severe  $\text{H}_2\text{O}/\text{CH}_4$  condition. The plating time of the nickel plating process also significantly influenced the reforming property. When using the  $\text{NaBH}_4$  reducing agent, the plating time of about 3 min provided the highest performance. The chloride and the sulfate were suitable for the anion species of the nickel reagent used in the plating. Based on the XPS measurement, the electron state of the nickel, which was prepared using the chloride and the sulfate was thought to be a state that is appropriate for the formation of the  $\text{CH}_x$  species and the formation of  $\text{O}^*$  species in the reforming mechanism. Adding a promoter component to the aluminum sol solution was effective for improving the reforming performance. Especially, the reforming property of the catalyst that adds the Ce component was improved. The combination technique developed in this study is a useful and expandable method for preparing the structured catalyst with a high performance on the stainless steel substrate.

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## 1. Introduction

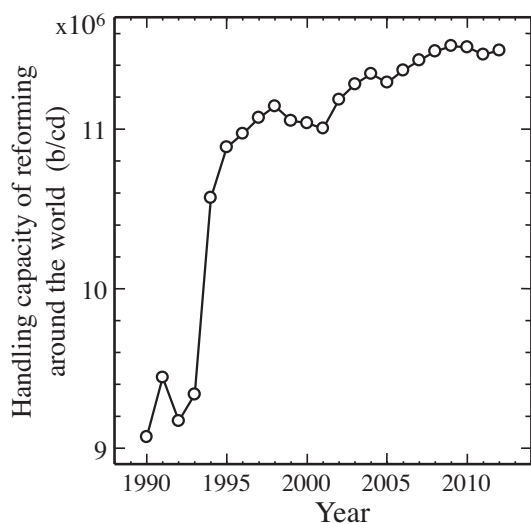
The steam reforming process of hydrocarbons for a hydrogen production system has been continuously improved for years by developing a high performance catalyst and improving the system efficiency. The reforming process that is currently operating in industry is thought to be a high perfection process as the reactive system. The large-scale steam reforming process with the hydrogen manufacturing ability of a maximum of  $100,000 \text{ Nm}^3/\text{h}$  is industrially operating [1]. Fig. 1 shows the secular change in the handling capacity of the catalytic reforming process in oil refinery fields around the world [2]. The change in the handling capacity, which is associated with the amount of hydrogen production, shows a remarkable increase in 1994, and shows the tendency that keeps increasing afterwards. Assuming a society based on hydrogen, the

amount of hydrogen manufacturing in the large-scale reforming process will significantly increase in the future.

On the other hand, in the case of the decentralized hydrogen manufacturing process like the on-site type hydrogen station, development of a novel reforming system, which has some unique properties not found in the large-scale reforming system, would be strongly needed. That is, such unique properties of the reaction system are (1) DSS operation ability, (2) rapid response to load fluctuation, (3) compactness of device, and (4) excellent thermal exchange. The fixed-bed reaction system adopted in the large-scale hydrogen manufacturing process cannot satisfy such properties. Therefore, the development of a novel reforming system based on a different concept from the fixed-bed reaction system is necessary.

The structured reaction system which integrates the chemical property (catalytic activity and selectivity) and the physical properties (enhancement of heat-transfer, rectifying property of flow and lower pressure drop) by depositing a catalytic component onto a metallic substrate, which composes the reactor, is a reactive system that satisfies the previous properties. We have investigated the

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**Fig. 1.** Secular change in handling capacity of reforming in oil refinery fields around the world. (b/cd: barrel per calendar day).

operating performance of such a structured reaction system from the experimental and theoretical viewpoints [3–6]. It was subsequently found that this reaction system enables a rapid response to load fluctuations, effective exchange of heat energy and downsizing of reactor dimensions. The development of the reforming system in which the structured reaction system was adopted would produce an advantage in the construction of a decentralized hydrogen production infrastructure like the on-site type hydrogen station.

A common method of preparing the plate-type catalyst and the fin-type catalyst for the structured reaction system is a wash-coat method and a sol-gel method as described in Meille's review [7]. We have focused our attention on an electroless plating technique for easily and uniformly depositing a catalytic component onto a metallic surface [8]. We also have separately prepared a nickel-based catalyst [9–12], a copper-based catalyst [13–16] and a palladium-based catalyst [17] on an aluminum substrate, and investigated their catalytic performances. However, the steam reforming of methane requires the high heat energy of about 600–900 °C, and the use of a stainless steel substrate is requested from the viewpoint of heat resistance. When preparing the structured catalyst on a stainless steel substrate, some ideas for the electroless plating are necessary. Because the standard electrode potential of iron is four times nobler than that of aluminum, the deposition of the metallic component having a strong adhesion on a stainless steel substrate is difficult using only the electroless plating technique.

We have developed the following novel method for preparing a stainless-honeycomb-type Ni/Al<sub>2</sub>O<sub>3</sub> catalyst; first the formation of an oxide layer on a stainless steel substrate by a sol-gel method, second, a seeding of elemental palladium as a catalyst nuclide for anodic oxidation of reducing agent, and finally the deposition of a nickel component onto the substrate by electroless plating [18]. The prepared honeycomb-type catalyst showed a high performance of methane-steam reforming (MSR), which was almost equal to the equilibrium, and high hydrogen manufacturing ability under the severe condition of 0.6 s or less residence time (S.V. based on the net volume of the catalyst layer: 301,500 h<sup>-1</sup>). These results demonstrated that the preparation method developed in our study is effective for preparing a structured catalyst having a high performance for steam reforming. Such a technique for preparing a structured catalyst by the combination of the sol-gel method and the electroless plating is a unique technique from the viewpoint of the catalyst preparation. By optimizing the operating

conditions of the electroless plating and the sol-gel method, a further active honeycomb-type catalyst might be prepared. In addition, the degrees-of-freedom of the oxide layer formed by the sol-gel method and that of the metal ion in the electroless plating suggest an attractive application of this combination method to prepare other kinds of structured catalysts.

In this study, the MSR performance of the structured Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was initially compared to that of the commercial reforming catalyst under the same reaction conditions in order to clarify the effectiveness of the combination technique of the sol-gel method and the electroless plating. Second, the effects of the plating condition change (kinds of reducing agent, kinds of counter anion of nickel, plating time) and the addition of the promoter element into the structured catalyst were investigated to enhance the reforming performance. It was then found that the structured Ni/Al<sub>2</sub>O<sub>3</sub> catalyst had a higher performance than the commercial catalyst and that the difference in the plating conditions profoundly influenced the reforming property. The construction of the structured reforming system would be realized by using the honeycomb-type catalyst developed in this study.

## 2. Experimental

### 2.1. Preparation of metal-honeycomb-type nickel-based catalyst

The preparation procedure of the honeycomb-type Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was shown in Fig. 2 [18]. The outline of the preparation procedure is as follows. A ferrite-type stainless honeycomb fin (18 mmφ × 45 mm length, cell density 100 cpsi, apparent surface area 250 cm<sup>2</sup>, fin thickness 0.1 mm) was used as the metallic honeycomb substrate. After washing and activating with a 6M-HCl solution, the fin substrate was immersed in the aluminum-triisopropoxide sol solution (Al[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>: 12 g, HNO<sub>3</sub> aq.: 6 mL, HCHO: 4 mL, H<sub>2</sub>O: 80 mL). To uniformly coat the fin surface by the sol, the immersed substrate was slowly raised and was rotated with about 170 rpm. After the rotation, the substrate was calcined at 500 °C. The coating and calcination were repeated with three times. In the third calcination, the temperature was at 800 °C (ramping time: 1.0 h, holding time: 2.0 h) to form a γ-alumina layer on its surface. After that, the Pd-Sn alternate plating was performed to deposit the Pd nuclide on the fin surface, which was a catalyst component for the electroless nickel plating on the oxide substrate. The fin substrate was alternately immersed 20 times in the activation liquid (PdCl<sub>2</sub>: 1.4 × 10<sup>-3</sup> mol/L, HCl aq.: 5.7 × 10<sup>-3</sup> mol/L, 35 °C) and the sensitization liquid (SnCl<sub>2</sub>·2H<sub>2</sub>O: 1.1 × 10<sup>-3</sup> mol/L, HCl aq.: 5.7 × 10<sup>-3</sup> mol/L, 35 °C), thus depositing the Pd nuclide on the fin surface. The nuclide was reduced by 3M-hydrazine. Finally, the substrate was immersed in the nickel plating bath at 55 °C to deposit the nickel component onto its surface. Three kinds of nickel plating baths with different reducing agents were used; i.e., a sodium borohydride bath (NiCl<sub>2</sub>·6H<sub>2</sub>O: 45 g/L, NaBH<sub>4</sub>: 0.6 g/L, NaOH: 20 g/L, NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>: 60 mL/L, 55 °C), a trimethylamineborane bath (NiCl<sub>2</sub>·6H<sub>2</sub>O: 45 g/L, (CH<sub>3</sub>)<sub>3</sub>NBH<sub>3</sub>: 3 g/L, NaOH: 5 g/L, C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O: 60 g/L, 55 °C) and a sodium hypophosphite monohydrate bath (NiCl<sub>2</sub>·6H<sub>2</sub>O: 45 g/L, NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O: 50 g/L, NaOH: 5 g/L, C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O: 60 g/L, 55 °C). The maximum plating time of each nickel bath was 60 min. In addition, other structured catalysts were prepared by changing NiCl<sub>2</sub>·6H<sub>2</sub>O to NiSO<sub>4</sub>·6H<sub>2</sub>O (50 g/L) and/or Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (55 g/L) in the sodium borohydride bath.

### 2.2. Performance test of methane steam reforming

The methane-steam reforming over the prepared catalyst was conducted at atmospheric pressure using a conventional flow

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