

# Development of a Structured Catalyst for Microchannel Natural-Gas Steam Reformers

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A high-performance Rh structured catalyst with an applicable low-pressure drop was developed for use with compact high-efficiency microchannel natural-gas steam reformers. When this catalyst is used, it is possible to steam-reform methane with a very low-pressure drop ( $< 15$  kPa) even at a higher space velocity ( $30\,000\text{ h}^{-1}$ ) than that used with conventional reformers. The catalyst was confirmed to be chemically and physically stable throughout the course of a continuous test that was conducted for approximately 1 000 hours. The Damkohler number ( $Da$ ) was calculated to predict the performance characteristics that would be obtained in commercial steam reformers. It was found that the catalyst could be operated without a gas diffusion limitation across the entire reactor.

## 1. Introduction

Synthesis gas, which consists chiefly of hydrogen and carbon monoxide produced by reforming natural gas, is commonly used as raw material for chemical substances such as methanol, ammonia, and oxo alcohol<sup>(1), (2)</sup>. In recent years, with the globally increasing demand for methanol and ammonia, it is expected that, going forward, there will be an increase in plans for the construction and expansion of synthesis gas production facilities.

At the same time, there is a growing trend, mainly in North America, toward construction and expansion of chemical plants which use low-cost gas, such as shale gas, and small and medium-sized petrochemical plants which use shale oil as raw material, so that relatively small synthesis gas production facilities are attracting attention. In addition, with the increasingly strict restrictions on flare gas, which is the associated gas produced in the course of natural gas extraction<sup>(3)</sup>, there is an increasing need for steam reforming facilities that can treat associated gas economically even on a small scale.

The steam reforming reaction for natural gas, using its chief component methane, is represented by the following Equation (1). The catalyst used is generally nickel (Ni) based but, in addition to Ni, platinum group elements such as platinum (Pt) also help activate this reaction<sup>(4)</sup>.



Since methane steam reforming is an endothermic reaction, reaction heat must be supplied from the outside of the catalyst bed in order for the reaction to proceed. In general,

steam reformers use multi-tubular reactors. Tubes of 100 to 200 mm in diameter and 10 to 13 m in length are arranged vertically, and so steam reforming facilities need to be larger than the tube length. In addition, the reaction heat needed for the reaction is supplied by burners installed around each reaction tube, so it is necessary to install refractory material to protect the facilities, which results in increased facility size.

However, in recent years, increasing attention is being paid to technologies that drastically reduce the size and enhance the controllability of the reactor by utilizing a microchannel reactor, which uses micro channels as the reaction fields<sup>(5)</sup>. Microchannels are small reaction channels of a few tens of micrometers to a few millimeters in width, and the fluid flowing in a reactor that uses microchannels generally is laminar flow. Considering reaction using a solid catalyst, since the reaction occurs on the surface of the catalyst that is in contact with the fluid, it is desirable for the channels in the reactor to have a large surface area. If the characteristic length of a channel where the reaction occurs is  $L$ , then the surface area corresponds to  $L^2$  and the volume to  $L^3$ , so that the surface area per unit volume is represented by  $L^{-1}$ . If a characteristic channel length of 1 m is taken as the reference, then the surface area per unit volume becomes large, i.e.,  $10^6$ , when the characteristic channel length is 1  $\mu\text{m}$ , and is as high as  $10^3$  even when the characteristic channel length is 1 mm. Hence, by reducing channel size, it is possible to achieve the large internal surface area needed for the catalyst reaction even with the same reactor volume. Stated alternatively, the surface area necessary for the reaction can

be achieved with a smaller reactor, allowing a drastic reduction in reactor size.

Taking advantage of the effects of microchannels, IHI is developing compact reactors that can be utilized not only in the synthesis gas production process using steam reforming of natural gas, but also various chemical synthesis for petrochemical industry<sup>(6)</sup>. Compact reactors use so-called structured catalyst in which porous catalyst is uniformly coated on the surface of a structure formed of refractory metal foil that can be installed inside and removed from the microchannels. This allows enhancement of the catalytic reaction, and diffusion of reactants and heat supply.

This paper reports on the performance and durability of a structured catalyst developed for the steam reforming reaction. It also describes the application availability obtained when the developed catalyst was used in an actual steam methane reformer.

## 2. Experiment

### 2.1 Catalysts

First, we determined catalyst formulation by conducting an activity test on powdered catalyst samples. In particular, in order to determine optimal catalyst formulation, we focused on the type of active metal, preparation method, amount of active metal supported, and type of catalytic support. As a result of this examination, it was confirmed that rhodium (Rh) is desirable as the active metal, and the structured catalyst was prototyped by coating metal foil with catalyst powder having the identified optimal formulation.

Catalyst performance for both the prepared powdered Rh catalyst and structured catalyst made by coating metal foil with the catalyst powder was evaluated.

### 2.2 Catalyst performance evaluation

**Table 1** shows the catalyst performance test conditions. For the powdered catalyst, evaluation was performed after filling a quartz glass tube of inside diameter approximately 4 mm with catalyst. For the structured catalyst, evaluation was performed after inserting a sample made by coating metal foil with the catalyst into a rectangular channel with an opening size of 4 × 10 mm.

For both the powdered and structured catalyst, the temperature was measured by inserting thermocouples upstream and downstream of the catalyst bed. After sampling the gas at the outlet of the catalyst bed and removing excess

moisture, gas chromatography was used to analyze the concentrations of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>, together with that of N<sub>2</sub>, a small quantity of which was added for analysis purposes. The reforming rate of methane (CH<sub>4</sub>) (CH<sub>4</sub> conversion) was defined by the following Equation (2):

$$CH_4 \text{ conversion} = [F_{CH_4}^{in} - F_{CH_4}^{out}] / F_{CH_4}^{in} \times 100. \quad (2)$$

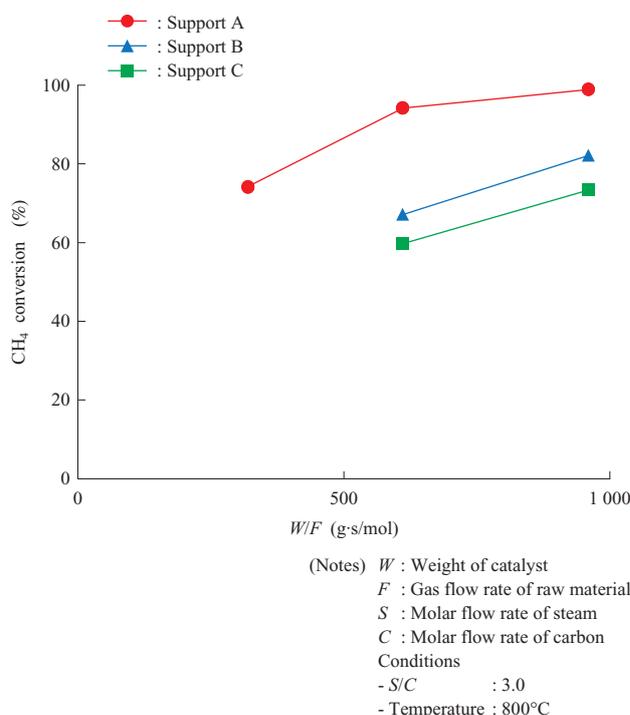
In this equation,  $F_{CH_4}^{in}$  and  $F_{CH_4}^{out}$  represent the molar flow rates of methane at the inlet and outlet of the catalyst bed.

In addition, interface and adhesion of coated structured catalyst were evaluated. The condition at the interface of the coated structured catalyst was observed using a scanning electron microscope (SEM). The adhesion between the catalyst bed and metal foil was evaluated by the following method. A structured catalyst sample was immersed in petroleum ether and subjected to ultrasonic vibration for 0.5 hours. The sample was then taken out of the petroleum ether, dried, and its mass measured. The adhesion was evaluated based on the change in the mass of the sample before and after ultrasonic treatment.

## 3. Results and discussion

### 3.1 Catalyst support

Different oxide catalytic supports A, B, and C supporting Rh, an active metal, at a level of 1 wt% were prepared as the catalyst samples. **Figure 1** shows the relationship between CH<sub>4</sub> conversion and  $W/F$  for the powdered catalyst. For all samples, the larger the value of  $W/F$ , the higher the CH<sub>4</sub> conversion is. With a  $W/F$  value of 600, support A, which showed the highest activity, gave a CH<sub>4</sub> conversion of 95%. On the other hand, supports B and C at  $W/F = 600$  gave CH<sub>4</sub> conversions of 66% and 60%, respectively. The BET



**Fig. 1** Relationship between CH<sub>4</sub> conversion and  $W/F$  for powder catalysts

**Table 1** Reaction conditions for the catalyst performance test

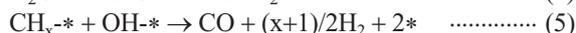
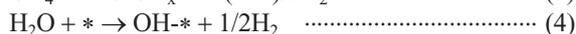
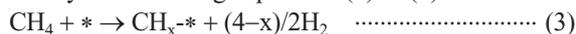
Item	Unit	Powdered catalyst	Structured catalyst
Temperature	°C	800	500 to 800
Pressure	—	Atmospheric pressure	Atmospheric pressure
Raw material	—	CH <sub>4</sub>	CH <sub>4</sub>
$S/C$ <sup>*1</sup>	—	3	3
$W/F$ <sup>*2</sup>	g-s/mol	320 to 960	—
space velocity ( $SV$ ) <sup>*3</sup>	h <sup>-1</sup>	—	15 000 to 45 000

(Notes) \*1 : Molar flow rate of steam/molar flow rate of carbon

\*2 : Weight of catalyst/gas flow rate of raw material

\*3 : Flow rate of raw material (Nm<sup>3</sup>/h)/Volume of reactor (m<sup>3</sup>)

(Brunauer-Emmett-Teller) surface areas of supports A, B, and C were 130, 176, and 72 m<sup>2</sup>/g, respectively. In general, a support with a larger BET surface area is expected to show higher catalytic activity due to better dispersion of the supported Rh. These results, however, show no correlation between conversion and the BET surface area of the support. It is therefore presumed that the activity of this catalyst depends not on dispersion of the supported Rh but on the chemical action of each support. The CH<sub>4</sub> steam reforming reaction proceeds through adsorbed methane, and hydroxide (OH) groups that are activated at the catalyst surface<sup>(7)</sup>, as expressed by the following Equations (3) to (5).

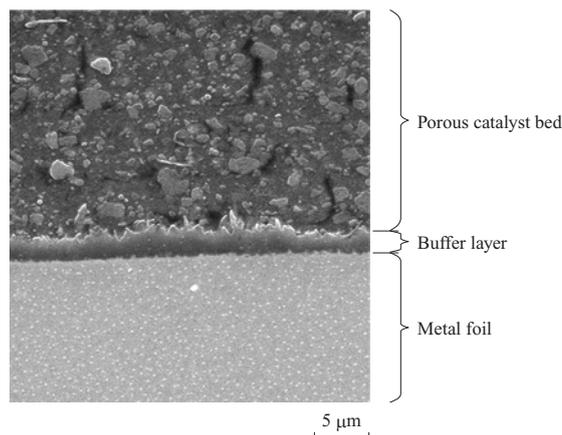


In these equations, the asterisk (\*) represents an active site on the catalyst surface. CH<sub>4</sub> is adsorbed on the active site, is activated, and then reacts with an activated OH group. It is presumed that, unlike CH<sub>4</sub>, which is activated at the adsorption point, steam is often activated at the support surface<sup>(7)</sup>, with supports A, B, and C showing different degrees of steam activation. More specifically, it is presumed that the OH group is activated more easily on support A than on support B or C. From the above results, we concluded that high methane reforming performance can be achieved by combining support A, which exhibits the highest activity for steam activation, with Rh.

### 3.2 Interface of Rh structured catalyst

In the steam reforming reaction, the catalyst is used at high temperatures higher than 800°C, and exposed to a wide range of temperatures, from low to high, each time the plant is started or stopped. Because the catalyst support is made of oxide-based material, its thermal expansion coefficient is of the order of 10<sup>-6</sup> K<sup>-1</sup>. However, the thermal expansion coefficient of the metal foil used as the substrate is of the order of 10<sup>-5</sup> K<sup>-1</sup>, i.e., higher than that of the oxides commonly used in catalysts. Therefore, a strong interface structure is required to prevent the coated catalyst bed from separating due to thermal stress generated at the interface between the catalyst and metal foil when the plant is started or stopped, and during operating.

**Figure 2** shows an SEM image of the interface between the metal foil and porous catalyst bed in the developed Rh structured catalyst. This shows that a porous catalyst bed has formed on the metal foil. In addition, a buffer layer has formed between the metal foil and porous catalyst bed, improving the adhesion of the catalyst bed. We evaluated the adhesion of the catalyst and confirmed that it exhibits a high adhesion of 98% or more even after exposure to intense ultrasonic vibration. It is presumed that the adhesion between the two different materials, which have different thermal expansion coefficients, is improved by the buffer layer's high affinity for both the metal foil and catalyst bed. By creating a buffer layer, it is possible to achieve a structured catalyst with a stable interface structure that can withstand the thermal stress generated when the plant is started or stopped.

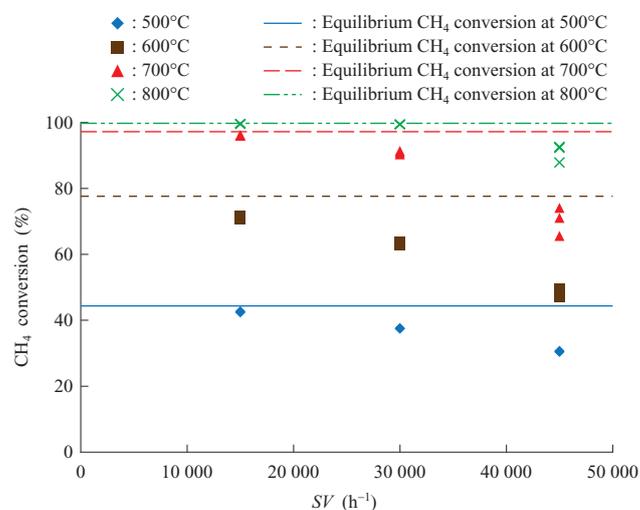


**Fig. 2** SEM image of the interface between the porous catalyst layer and the metal foil in the Rh structured catalyst

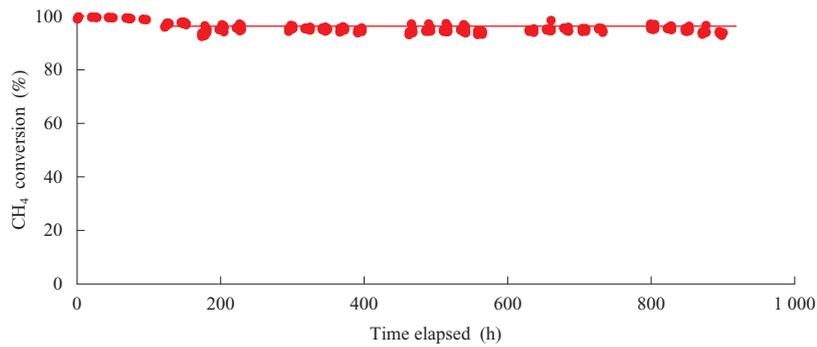
### 3.3 Performance and durability of Rh structured catalyst

**Figure 3** shows the relationship between CH<sub>4</sub> conversion of the Rh structured catalyst and space velocity (*SV*). *SV* can be obtained by dividing the flow rate by the volume of the catalyst. As reaction temperature increases, conversion also increases, together with equilibrium conversion. As *SV* increases, conversion decreases slightly, but is almost equal to the equilibrium value even at *SV* = 30 000 h<sup>-1</sup>. At *SV* = 30 000 h<sup>-1</sup>, pressure drop is 15 kPa or less, which is extremely low given that the feed gas is supplied at high flow rate. This suggests that plants with a structured catalyst enable operation at extremely high *SV* compared to conventional multi-tubular steam reforming plants, which generally operate at an *SV* of a few thousand h<sup>-1</sup>. From the above results, it can be said that the developed Rh structured catalyst enables operation at high *SV* with low pressure drop, and makes it possible to drastically reduce the size of steam reformers.

**Figure 4** shows life test results for the Rh structured catalyst. CH<sub>4</sub> conversion is stable for approximately



**Fig. 3** Relationship between CH<sub>4</sub> conversion and space velocity (*SV*) at different temperatures



(Note) Conditions  
 - S/C : 3.0  
 - Temperature : 800°C

Fig. 4 Results of the life test conducted for the Rh structured catalyst

1 000 hours. It was confirmed that the Rh structured catalyst can operate stably under reaction conditions without carbon deposition or sintering<sup>(8)</sup>, which are problems when using conventional Ni catalyst, and without structural problems such as catalyst detachment due to separation from metal foils, etc.

### 3.4 Application to steam reformers

The application availability of the developed Rh structured catalyst in an actual methane steam reformer was considered. The methane steam reforming reaction in the reaction channels is dominated by the reaction rate at the catalyst surface, and the rate of diffusion of methane — the reacting molecule — to the catalyst surface. Damkohler number  $Da$  is a dimensionless number defined by the following Equation (6), and is expressed by the ratio of the reaction rate at the catalyst surface and diffusion rate of the reactant (methane). When the Damkohler number is less than 1, the diffusion rate of the reactant is sufficiently high, and the reaction at the catalyst surface is the rate-limiting step. When the Damkohler number is higher than 1, the diffusion rate of the reactant is lower than the reaction rate at the catalyst surface, and diffusion of the reactant molecules is the rate-limiting step of the reforming reaction.

$$Da = \frac{r_{SMR}}{N_{CH_4}} \dots\dots\dots (6)$$

In this equation,  $r_{SMR}$  is the reaction rate at the catalyst surface and  $N_{CH_4}$  is the diffusion rate of methane in the gas phase. It was experimentally confirmed that the apparent reaction rate for the structured catalyst is expressed by the following Equation (7):

$$r_{SMR} = \alpha P_t^{-2} \exp(-\beta / RT) P_{CH_4} P_{H_2O} \left( 1 - \frac{P_{H_2}^3 P_{CO}}{K_{eq} P_{CH_4} P_{H_2O}} \right) \dots\dots\dots (7)$$

In this equation,  $P$  indicates the partial pressure of each component,  $K_{eq}$  is the equilibrium constant of the steam reforming reaction,  $P_t$  is the total pressure,  $R$  is the gas constant, and  $T$  is the temperature. In addition,  $\alpha$  and  $\beta$  are values specific to the Rh structured catalyst used in the test.

Table 2 shows the reformer reaction conditions used to

Table 2 Reactor conditions for calculating the Damkohler number

Item	Unit	Reformer inlet	Reformer outlet
Temperature	°C	490	850
Pressure	MPa	1.9	1.9
space velocity (SV) <sup>*1</sup>	h <sup>-1</sup>	30 000	30 000

(Note) \*1 : Flow rate of raw material (Nm<sup>3</sup>/h) / Volume of reactor (m<sup>3</sup>)

calculate the Damkohler number. In an actual reformer, the feed gas is introduced to the reactor inlet at low temperature, heated gradually by heat supplied from outside, reformed at high temperature, and then discharged outside the reformer. It was assumed that the inlet and outlet temperatures of the reformer were 490°C and 850°C, respectively. Since the gas composition is different at the reformer's inlet and outlet, the Damkohler number was calculated for both the inlet and outlet conditions of the reformer. In addition, the calculation takes account of the distance that the gas diffuses in the structured catalyst formed from metal foil. Figure 5 shows the calculation results. At the inlet of the reformer, the Damkohler number is as small as 0.016, showing that the gas diffusion rate is sufficiently high compared to the reaction rate.

At the outlet of the reformer, the Damkohler number is 0.54, and although the diffusion has a greater influence on the reaction than that at the inlet of the reformer, the diffusion rate of the reactant is still higher than the reaction rate.

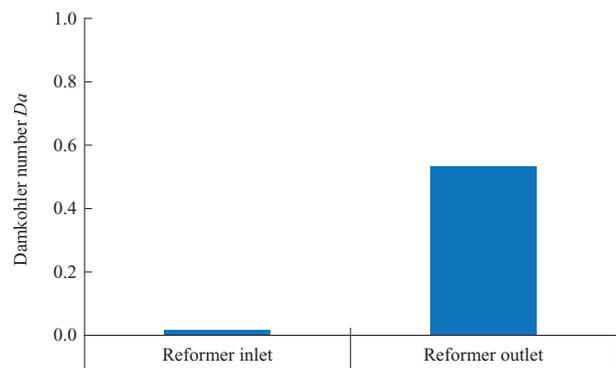


Fig. 5 The Damkohler number for the steam reformer

Hence, it was found that the reaction at the catalyst surface is the rate-limiting step throughout the reformer, with the highly active catalyst being fully utilized, and with no hindrance to diffusion of the reactant. From the above results, it was confirmed that using the developed Rh structured catalyst with the microchannel configuration makes it possible to drastically reduce the size of the reactor with low pressure drop.

#### 4. Conclusion

Using the advantages of microchannels, we developed a structured catalyst with low pressure drop and high performance that can be utilized in natural-gas steam reformers. Reformers with the developed Rh structured catalyst enable methane steam reforming with much lower pressure drop than conventional reformers, even at high space velocities. As a result of approximately 1 000 hours of continuous operational testing, it was confirmed that the catalyst functions stably with stable interface structure.

Through calculation of the Damkohler number under the actual operating conditions of a steam reformer, it was confirmed that steam reformers with the developed catalyst allow the reactant in the gas to diffuse throughout the reactor, enabling effective utilization of the catalyst.

Going forward, we will work to develop a compact reactor-type high-efficiency steam reformer that uses this catalyst, and investigate the application of the structured catalysts to various chemical synthesis processes.

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