Application of Porous Metal Celmet to Catalyst Support Materials

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Development of new catalysts is progressing rapidly toward the construction of chemical processes with lower environmental impact. Celmet is a porous metal with a three-dimensional network structure having over 90% of porosity, and therefore is expected to be used as a support material for catalysts with low pressure loss and high deformability. The Celmet support also has the advantage that it can be heated directly by an electrical heating means. This paper revealed that a catalyst coated with CeO_2 powder loaded with fine Ru particles on Ni Celmet exhibited practical propane steam reforming performance comparable to commercially available Ru spherical catalysts. Furthermore, NiCr Celmet electrically heated at 500°C was estimated to have long-term durability based on the time-course change in electrical resistance, suggesting that it can contribute to the construction of compact and energy-efficient reactors.

1. Introduction

Catalysts, which can increase the rate of chemical reactions, are indispensable for chemical syntheses, and the development of new catalysts is progressing rapidly toward the construction of chemical processes with lower environmental impact. In general, solid catalysts exhibit high activity when they are composed of fine particles with a large specific surface. However, when finely particulate solid catalysts are used directly, they may increase the pressure loss in the reaction system and their activity may also be degraded due to agglomeration and sintering of the particles. As a preventive measure, chemically stable porous materials having a large surface area, such as alumina, silica, and ceria, are used as support materials. A catalyst with high reaction efficiency and durability is realized by stably dispersing fine catalyst particles over the surface of these support materials. The shape of support materials is selected mainly from granular, pellet, and honeycomb shapes (pressure loss decreases in this order), depending on the allowable pressure loss. The production cost of catalysts increases as their shape becomes more complex.

Celmet, manufactured by Sumitomo Electric Toyama Co., Ltd., is a porous metal with a three-dimensional network structure and a porosity of more than 90%. Celmet has been used as a current collector*[1] for nickel-hydrogen batteries and various fuel cells because of its excellent electrical conductivity, machinability, and fluid permeability.[1]–[4] Due to the above excellent characteristics, Celmet is also expected to be an unprecedented support material that combines low pressure loss and high deformability comparable to those of a honeycomb. In addition, due to the advantage of directly heating the catalyst (chemical reaction field) electrically, Celmet is expected to enable the construction of compact reactors with low energy consumption.

The authors fabricated a photocatalyst by coating titanium dioxide particles on Celmet and confirmed that this catalyst has a good acetaldehyde decomposition property.[5] However, when fine metallic particles, which are usually used at high temperatures, are used as catalysts, the surface area of Celmet is not large enough to suppress the agglomeration and sintering of the particles as described above, and there is also a risk of reaction between the fine metallic particles and Celmet. To avoid the risk, it is necessary to support the fine metallic particles on the surface of chemically stable particles with a large surface area, such as alumina, silica, or ceria, and then coat them on Celmet.

From the above viewpoint, we fabricated a catalyst by coating Ni Celmet with CeO_2 powder loaded with fine Ru particles, and evaluated the catalytic performance. In addition, we predicted the long-term durability of solid NiCr Celmet by electrically heating it and measuring the change in resistance.

This paper discusses the usefulness of Celmet as a catalyst support material based on the results of the above evaluation and prediction.

2. Experiment Method

2-1 Fabrication of catalyst

Deionized water and CeO_2 (reference catalyst of Catalysis Society of Japan: JRC-CEO-5, median diameter:*[2] 4.70 μm, specific surface area: 92 $m^2 \cdot g^{-1}$, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) were put into a glass container and degassed with a vacuum pump while stirring. A Ru $(NO_3)_3$ solution (50 $g \cdot L^{-1}$, Tanaka Kikinzoku Kogyo K.K.) was further added to the container, stirred, and then heated to remove water to prepare CeO_2 (Ru/CeO_2) powder supporting 10 wt% fine Ru particles. Subsequently, a Ru/CeO_2-coated Ni Celmet catalyst with a Ru-supporting amount of approximately 24 $mg \cdot cm^{-3}$ (hereinafter referred to as "Celmet catalyst") was fabricated. In the fabrication, a slurry prepared by mixing Ru/CeO_2 powder, water, dispersant, and binder was baked after being dip-coated*[3] on 5

cm square Ni Celmet (part #: 2, coating weight: 1,860 g·m^{-2}, thinned from 5 mm to 2 mm by rolling). The morphology of the fabricated Celmet catalyst was observed under an optical microscope and SEM.[*4]

2-2 Evaluation of catalyst performance

Using a fixed-bed flow reactor,[*5] the propane-steam reforming characteristics of the Celmet catalyst fabricated in the preceding section were evaluated. As shown in Photo 1, five small pieces of the Celmet catalyst cut to 16 mm in diameter were sandwiched between quartz wool and fixed in a quartz reaction tube. The steam-to-carbon ratio (S/C)[*6] of the reaction gas (a mixture of propane and steam) was kept constant at 2.5, and the reaction temperature and space velocity (SV)[*7] were varied in the range of 400 to 700°C and 1,000 to 7,000 h^{-1}, respectively. The concentrations and flow rates of the components (H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8) of the gas produced by removing moisture were measured using a gas chromatograph and soap film flow meter, respectively.
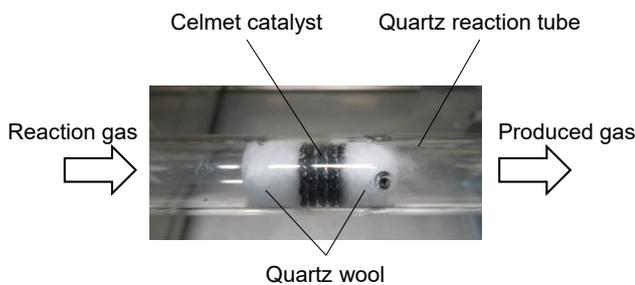
Photo 1. Sample for Celmet catalyst performance evaluation

2-3 Electrical heating test

The time-course change in the electrical resistance of Celmet due to electrical heating[*8] in the atmosphere was measured using the experimental system shown in Fig. 1. NiCr Celmet (part #: 7, coating weight: 750 g·m^{-2}) having excellent electrical resistance and thermal oxidation resistance was used as the test sample. A two-ply NiCr Celmet sample was connected to stainless steel electrode plates with bolts at both ends (sample width: 1 cm, distance between electrodes: 4 cm), and a thermocouple was
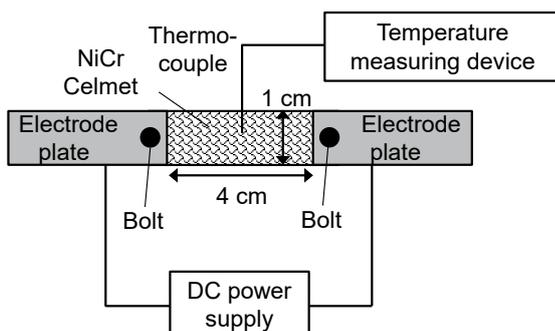
Fig. 1. Experimental system for electrical heating test

inserted between the NiCr Celmet sample components. Using a DC power supply, a voltage was applied to the electrode plates to maintain the sample temperature at approximately 500°C. The electric current was continuously fed to the Celmet sample for 1,000 hours at this voltage.

3. Test Results and Their Analysis

3-1 Celmet catalyst

As described in Section 2-1, Ni Celmet with a thickness compression ratio of 60% was used to fabricate the Celmet catalyst. The objective was to increase the fine Ru particle-supporting density in the Celmet catalyst. Other possible means would be to coat Ru/CeO_2 powder more thickly or to increase the Ru-supporting amount of Ru/CeO_2 powder. However, the former would make the Ru/CeO_2 powder fall off more easily and the latter would promote the agglomeration and sintering of the fine Ru particles. Since the change in porosity due to the compression of thickness is modest (decrease from 96% to 90%) and does not significantly affect the pressure drop, the means used in this study is considered to be the most appropriate.

As can be understood from the optical microscope image shown in Photo 2, clear metallic shines were observed on the surface of Ni Celmet (a), but the color of the surface changed to glossless black after the surface was coated with Ru/CeO_2 powder (b). However, in the areas having large Celmet framework curvatures, some spots were still left uncoated with Ru/CeO_2 powder. Surface modification of Ni Celmet, as well as the optimization of slurry formulation and coating conditions, will become necessary in the future. A 16 mm diameter test sample was used to evaluate the catalytic performance as described in Section 2-2. The amount of Ru/CeO_2 powder separated from the Celmet catalyst when cutting out the test sample was not so large as to affect the test results.
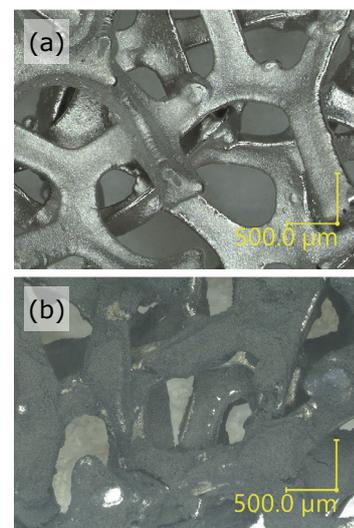
Photo 2. Optical microscope images
((a) Ni Celmet, (b) Celmet catalyst)

As the SEM backscattered electron image in Photo 3 (a) shows, the surface of the Celmet catalyst was an agglomerate mainly composed of particles with a diameter of approximately 5 μm, which was close to the median diameter of CeO_2 used to fabricate the catalyst. As a result of careful observation of Photo 3 (b), which is a further enlargement of the above backscattered electron image, many small spots (white dots) were recognized on all the particles, including those with a diameter of 1 μm or less, suggesting the presence of fine Ru particles. The above results suggested that the Ru/CeO_2 powder preparation process described in Section 2-1 was appropriate.
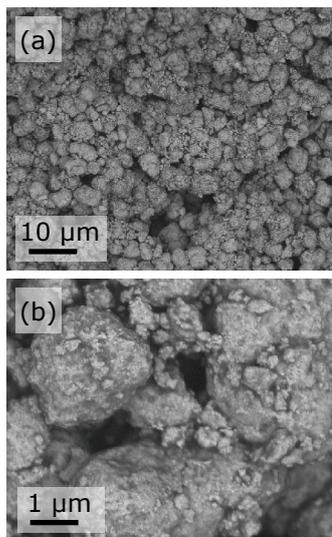
Photo 3. SEM backscattered electron image of Celmet catalyst surface
((a) 1,000 magnifications, (b) 10,000 magnifications)

3-2 Propane-steam reforming characteristics

Sumitomo Electric Industries, Ltd. is developing a proton-conductive ceramic cell that can operate as a fuel cell in the medium-temperature range of around 600°C.[6] Propane-steam reforming, which can supply hydrogen at this operating temperature, is expected to be applicable to a hydrogen production system (reformer) that uses waste heat from a medium-temperature fuel cell.

Figure 2 shows the reaction temperature dependence of the concentration of the components in the produced gas and the amount of H_2 production at SV = 1,000 h^{-1}. The solid symbols represent the concentration of each component of the produced gas (left axis), and the empty symbols with a solid line through them represent the amount of H_2 produced per 1 cm^3 of the Celmet catalyst (right axis). Each symbol represents a measured value and the solid line is an interpolation between the measurement points. Under the above SV condition, the concentration of C_3H_8 in the produced gas was below the detection limit at a reaction temperature of 400°C or more, suggesting that the total amount of C_3H_8 fed was consumed for the reaction with water. Although not plotted in the figure, the concentrations of C_2H_4 and C_2H_6 were also below the detection limit, verifying that these components were not produced by the reaction. The concentration of H_2 in the produced gas increased as the reaction temperature increased, reaching approximately 72% at 700°C. The amount of H_2 produced also increased approximately fivefold when the reaction temperature rose from 400°C to 700°C. Contrary to the behavior of H_2, the concentration of CH_4, which accounted for roughly half of the produced gas at 400°C, decreased to approximately 1% at 700°C. The above results suggest that the increase in the concentration and production amount of H_2 with a rise in reaction temperature is mainly attributable to the decomposition of CH_4. CO and CO_2 also exhibited contradictory behaviors: a gradual decrease and increase in concentration, respectively, with an increase in reaction temperature. A comparative evaluation was also performed in the same way for a similar volume of a commercial spherical catalyst (with pressure loss approximately three times that of the Celmet catalyst) supporting approximately the same amount of fine Ru particles. As a result, the propane-steam reforming characteristics test results for the Celmet catalyst were confirmed to agree with the comparative evaluation results within the range of measurement error.

The reaction between propane and steam is complicated, making it difficult to calculate the equilibrium concentration of each component using equilibrium constants. However, if the following reaction formula is assumed to be true based on the above analysis results, the concentration x_i of each component at equilibrium can be calculated by the minimum free energy method.[7],[8]

$$x_1 C_3H_8 + x_2 H_2O \leftrightarrow x_3 H_2 + x_4 CH_4 + x_5 CO + x_6 CO_2 + x_7 H_2O \cdots (1)$$
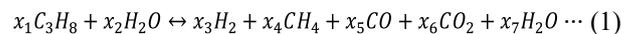
The calculation values (Calc.) of the concentration of individual components at equilibrium, which are represented by dotted lines in Fig. 2, agreed well with the measured values. This verified that, under the conditions of this test, the Celmet catalyst accelerates the reaction to reach equilibrium even at such a low temperature as 400°C.
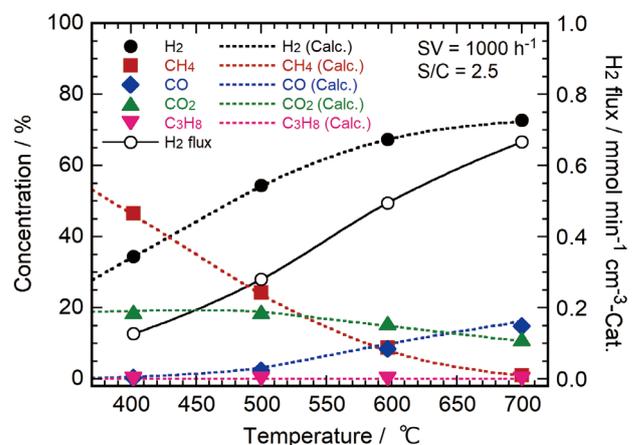
Fig. 2. Reaction temperature dependence of the concentration of the components in produced gas and the amount of H_2 production

Figure 3 shows the SV-dependence of the concentration of produced gas components and the amount of H_2 production at a reaction temperature of 600°C. In this figure, the solid symbols represent the concentration of each component in the produced gas (left axis), and the empty symbols represent the amount of H_2 production per 1 cm^3 of Celmet catalyst (right axis). The solid lines are interpolations. The concentrations of H_2 and CH_4 decreased or increased moderately with an increase in SV. C_3H_8 was below the detection limit in this range of SV. CO decreased slightly, while CO_2 remained virtually unchanged. The amount of H_2 production did not exceed 4.7 times even when SV was increased from 1,000 h^{-1} to 7,000 h^{-1}, suggesting that the decrease in H_2 production efficiency with increasing raw material feed rate is due to the rate-limited decomposition reaction of CH_4, an intermediate product. For comparison, a commercial spherical catalyst was also tested under the same conditions. In the test, the amount of H_2 produced on the Celmet catalyst at SV = 7,000 h^{-1} was approximately 5% less than that produced on the commercial catalyst, but both catalysts exhibited nearly the same catalytic performance.

The electrical resistance increased relatively rapidly up to about 100 hours after the start of current supply, but the increase rate decreased thereafter. Although it was difficult in this test to logically derive the relationship between the growth rate of the oxide film of NiCr Celmet and ΔR, it was confirmed from Fig. 4 (b) that ΔR is highly correlated with the logarithmic value of the elapsed time. The values of ΔR after 10,000 and 100,000 hours, predicted expediently using the regression line in red in the figure, were calculated to be 1.8 and 2.2%, respectively. Although further long-term tests are needed to improve the reliability, NiCr Celmet is considered to have very long-term durability as long as it is heated electrically at around 500°C.

Photo 4. Electrically heated NiCr Celmet

Fig. 3. SV-dependence of the concentration of the components in produced gas and the amount of H_2 production
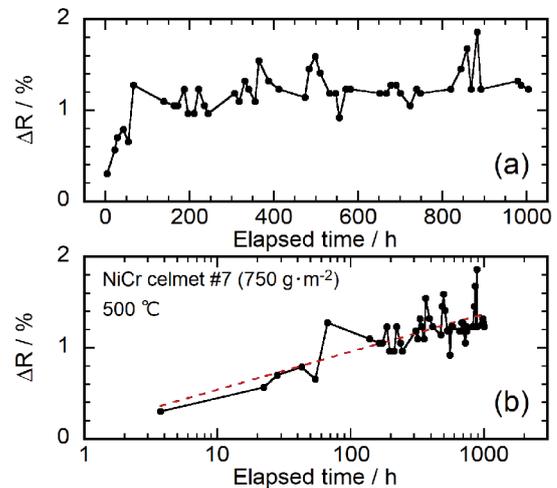
Fig. 4. Time-course change in the resistance increase rate of NiCr Celmet ((a) linear scale for horizontal axis, (b) logarithmic scale for horizontal axis)

Although it will be necessary in the future to further improve the catalytic performance of the Celmet catalyst by optimizing the fabrication conditions and to evaluate its durability, catalysts using Celmet as a support material have been verified to be promising for future use. The Celmet catalyst fabricated in this study is also applicable to the decomposition of ammonia, which has recently been attracting attention as a hydrogen carrier. We will also evaluate the performance of Celmet as a hydrogen carrier.

3-3 High-temperature conducting durability of NiCr Celmet

When heated electrically, NiCr Celmet became red hot and its relatively low-temperature periphery was discolored to brown due to the oxidation of Celmet, as shown in Photo 4.

Figure 4 (a) is a line graph showing the time-course change in the resistance increase rate (ΔR) of NiCr Celmet.

As described at the beginning of this paper, constructing a reactor using a catalyst supported with NiCr Celmet and electrically heating the catalyst will make it possible to downsize a conventional reactor by eliminating the need for a heater. Further, the new reactor will dramatically reduce energy consumption since it is enough to directly heat the catalyst only. In the future, we will prototype a reactor provided with a catalyst using NiCr Celmet as a support material and evaluate the performance of the reactor.

4. Conclusion

The Celmet catalysts fabricated in this study exhibited propane steam reforming performance comparable to that of a commercial catalyst. In addition, we predicted from the time-course change in resistance increase rate that NiCr Celmet will demonstrate good long-term durability when it is electrically heated at 500°C. We also showed that Celmet catalyst is promising for practical use and enables the construction of more compact reactors with lower energy consumption.

• Celmet is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

Technical Terms

*1 Current collector: A device for efficiently taking electricity out of the electrodes of a battery.

*2 Median diameter: The particle diameter at which one-half the total number of particles are larger and one-half are smaller.

*3 Dip coating: A method for coating a substrate after dipping in a coating agent.

*4 SEM: An abbreviation for scanning electron microscope, which is used to observe the surface of a sample by irradiating the sample with electron beams and detecting the emitted secondary electrons and reflection electrons.

*5 Fixed-bed flow reactor: A device for inducing a reaction by flowing a reaction gas on a catalyst fixed inside a reaction tube.

*6 Steam-to-carbon ratio (S/C): The molar ratio between water and carbon fed as raw materials.

*7 Space velocity (SV): The value obtained by dividing the hourly volume of a gas passing through a catalyst by its volume.

*8 Electrical heating: A method for heating a conductive material by passing an electric current through the material and thus generating Joule heat due to the internal resistance of the material.

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