[Letter]

**Low Carbon Deposition on CO₂ reforming of Methane
over Ni/Al₂O₃ Catalysts Prepared Using W/O Microemulsion**Hiroki Hayashi^{† 1)}, Seiichiro Murata^{† 2)}, Teruoki Tago^{† 2)}, Masahiro Kishida^{† 2)*}, and Katsuhiko Wakabayashi^{† 2)}^{† 1)} Research and Development Institute, Saibu Gas Co., Ltd., 421-4 Aoki, Imazyuku, Nishi-ku, Fukuoka 819-0162, JAPAN^{† 2)} Dept. of Materials Process Engineering, Graduate School of Engineering, Kyushu University,
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The catalytic activity and durability for the CO₂ reforming of methane was studied on an Ni/Al₂O₃ catalyst prepared using water-in-oil (w/o) microemulsion. The initial activity of the Ni/Al₂O₃ catalyst thus prepared was higher than that of an impregnated one. The impregnated catalyst deactivated with time-on-stream due to severe coking. In contrast, the catalyst prepared using w/o microemulsion kept its activity for 50 h and caused little coking at a CO₂/CH₄ molar ratio above 1.4. The carbon species deposited on the catalyst prepared using w/o microemulsion was less crystallized than that on the impregnated one. The superior resistance of the catalyst to carbon deposition is attributed to the generation of such a carbon species.

In recent years, considerable attention has been paid to global warming due to the greenhouse effect. The reduction and utilization of greenhouse gases such as carbon dioxide is, therefore, becoming more and more important. Catalytic reforming of methane with carbon dioxide to synthesis gas has been proposed as one of the most promising technologies for the utilization of carbon dioxide as carbon-containing materials¹⁾. The synthesis gas produced by this reaction has a high CO content which is favorable for the synthesis of valuable oxygenated chemicals^{2), 3)}.

There is no established industrial technology for the CO₂ reforming of methane, in spite of the fact that the economical and environmental benefits constitute an attractive incentive. The major problem lies in the catalyst deactivation caused by carbon deposition^{4)~6)}. The noble metals-supported catalysts are reported to be less sensitive to coking compared to the nickel-based catalysts in this reforming reaction^{7)~9)}. However, considering the high cost and limited availability of noble metals, it is more practical to develop anti-coking Ni-supported catalysts which exhibit stable activity for a long time.

Recently, we found that a Ni/Al₂O₃ catalyst prepared using water-in-oil (w/o) microemulsion was highly active and stable for the CO₂ reforming of methane. In this study, we investigated the catalytic activity and durability of the Ni/Al₂O₃ catalyst thus prepared during methane-CO₂ reforming.

Ni/Al₂O₃ catalysts were prepared in the following manner using w/o microemulsion. The Ni(OH)₂ nanoparticles were formed in a Ni(NO₃)₂aq. / Polyoxyethylene (*n*=10) -nonylphenyl ether / 1-hexanol microemulsion by adding tri-ethylamine directly to the microemulsion. Aluminium tri-isopropoxide (ATI), as a source of Al₂O₃ supports, was added to the microemulsion containing the Ni(OH)₂ nanoparticles, and then the hydrolysis of ATI was carried out for 30 min with vigorous stirring. The precipitate separated from the solution was dried at 353 K overnight and was calcined in air at 673 K for 5 h. The calcined powder was pressed into disks and ground through 18/26 mesh. The catalyst prepared in this manner was designated as the ME catalyst.

An impregnated catalyst, designated as an IMP catalyst, was used as a reference. The IMP catalyst was prepared by impregnating Al₂O₃, which was prepared in advance by the hydrolysis of ATI, with an aqueous Ni(NO₃)₂ solution.

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Table 1 Physical Properties of Ni/Al₂O₃ Catalysts

Catalyst	Ni cont. / wt%	Ni particle size ^{a)} / nm		S _{BET} ^{b)} / m ² g ⁻¹	S cont. / 10 ⁻⁵ wt%
		by TEM	by XRD		
ME	10	9.1	7.2	341	2.3
IMP	10	8.7	7.6	320	1.8

^{a)}Determined after 873 K 2 h H₂ reduction. ^{b)}BET surface area.

The CO₂ reforming of methane were conducted in a fixed-bed reactor of a quartz tube (8 mm i.d.). The test conditions were as follows: 973 K, CO₂/CH₄ molar ratio=1.0-2.0, SV=60000 h⁻¹. Gaseous reactants and products were passed through heated lines to gas chromatographs (Shimadzu GC-8A) for on-line analysis. The catalysts were reduced *in-situ* under H₂ flow at 873 K for 2 h prior to the tests.

The Ni particle size was determined by transmission electron microscopy (TEM, JEOL JEM-2000FX) and X-ray diffraction (XRD, Rigaku Rint2500). The S content was estimated based on JIS K 2301.

Physical properties and S content of the ME and IMP catalysts prepared in this work are shown in **Table 1**. Raman spectra of the carbon deposited on the Ni/Al₂O₃ catalysts were measured with the 514.5 nm line of an argon laser at room temperature by using a laser Raman spectrometer. **Figure 1** shows activity changes with time-on-stream for the ME and IMP catalysts at different CO₂/CH₄ molar ratio. **Table 2** shows the amount of carbon on both the catalysts before and after reactions.

At any CO₂/CH₄ molar ratio, the ME catalyst exhibited higher CH₄ conversion than the IMP catalyst in the initial period.

The decrease in CH₄ conversion of these two catalysts showed a similar tendency at a CO₂/CH₄ molar ratio of 1.0. The CH₄ conversion of these two catalysts decreased with time-on-stream. A considerable amount of carbon was deposited on these two catalysts after the reaction. This coking seemed to induce the deactivation of both the catalysts.

Reaction condition: 973 K, atmospheric pressure, SV=60000 h⁻¹.

Fig. 1 Activity Change with Time-on-stream for ME (closed symbols) and IMP (open symbols) Catalysts

Table 2 Carbon Amount on Ni/Al₂O₃ Catalysts before and after Reaction

Catalyst	Carbon / wt%			
	Fresh ^{a)}	Used ^{b)}		
		CO ₂ /CH ₄ =1.0	1.4	2.0
ME	0.27	14.5	0.47	0.44
IMP	0.11	18.3	15.3	13.6

^{a)}After 873 K 2 h H₂ reduction. ^{b)}After 50 h reaction.

Reaction conditions: 973 K, atmospheric pressure, GHSV=60000 h⁻¹.

At CO₂/CH₄ of 1.4 and 2.0, the deactivation behavior of these two catalysts was quite different. The ME catalyst kept its high CH₄ conversion for 50 h, whereas the IMP catalyst deactivated with time-on-stream. Similar to the result at a CO₂/CH₄ molar ratio of 1.0, a considerable amount of coke was deposited on the IMP catalyst after the reaction. In contrast, little carbon was deposited on the ME catalyst (below 0.5 wt%-carbon deposit after 50 h).

Rostrup-Nielsen reported that carbon deposition over Ni/Al₂O₃ catalyst was suppressed by partial poisoning of Ni by sulfur^(m). As can be seen from Table 1, the contents of sulfur in the ME and IMP catalysts were very low and substantially the same. It is therefore found that the superior resistance of the ME catalyst to carbon deposition was independent from the partial poisoning of Ni by sulfur.

Figure 2 shows the raman spectra of the carbon species deposited on the catalysts. With both the spectra, three bands were observed at 1340 cm⁻¹ (D band), 1580 cm⁻¹ (G band), and 1605 cm⁻¹ (D' band). The G band was attributed to the in-plane carbon-carbon stretching vibrations of graphite layers, and the D and D' bands were attributed to the disordered carbons (amorphous carbon)⁽ⁿ⁾. It is expected that the intensity ratio of D and D' bands to G band (I_D/I_G and $I_{D'}/I_G$) is higher when the degree of crystallization of the deposited carbon is higher. Figure 2 shows that ID'/IG ratio with the carbon species deposited on the ME catalyst is higher than that on the IMP catalyst. This observation indicates that the carbon species deposited on the ME catalyst was less crystallized than that on the IMP catalyst.

Fig. 2 Raman Spectra of Carbon Species Deposited on ME and IMP Catalysts

The reactivity of carbon species is well known to increase with decreasing the degree of crystallization of them. It is therefore considered that the carbon speices formed on the ME catalyst was gasified more easily by CO₂ than that on the IMP catalyst during the reaction, leading to the superior resistance of the ME catalyst to carbon deposition.

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Keywords

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