Methane-Steam Reforming over Ni/Al_2O_3 Catalyst Prepared Using W/O Microemulsion

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The catalytic activity and durability of methane-steam reforming under a low H_2O/CH_4 molar ratio was studied on an Ni/Al_2O_3 catalyst prepared using water-in-oil (w/o) microemulsion. The initial activity of the prepared Ni/Al_2O_3 catalyst was higher than that of an impregnated one. The impregnated catalyst deactivated rapidly and lost its activity at a time-on-stream of 15 h due to severe coking (> 30 wt%-carbon after 20 h). In contrast, the catalyst prepared using w/o microemulsion sustained its activity for 40 h, and gave little coke (<0.3 wt%-carbon after 40 h) on the catalyst.

Methane-steam reforming (eq [1]) is a typical process for syngas production.[1] This process is usually conducted under an H_2O/CH_4 molar ratio over 1.4. This is because the carbon deposition[2] causing catalytic deactivation is promoted under an H_2O/CH_4 molar ratio below 1.4.[3,4]

$$CH_4+H_2O = CO+3H_2 \qquad [1]$$
$$H_2O+CO = CO_2+H_2 \qquad [2]$$

Under a high H_2O/CH_4 molar ratio (>1.4), however, the following drawbacks exist: (a) The equilibrium of the water-gas shift reaction (eq [2]) will move toward the right. As a result, the H_2/CO molar ratio in the product will be high, which is unsuitable for the subsequent processes such as methanol and Fischer–Tropsch synthesis; (b) an enormous amount of energy will be consumed in the production of steam.

Therefore, the development of an anti-coking catalyst, one that sustains its activity even under a low H_2O/CH_4 molar ratio, is desirable.

Recently, we found that the Ni/Al_2O_3 catalyst prepared using water-in-oil (w/o) microemulsion was highly active and stable for methane-steam reforming even under an H_2O/CH_4 molar ratio of 1.0. In this report, we investigated the catalytic activity and durability of the Ni/Al_2O_3 catalyst prepared using w/o microemulsion during methane-steam reforming under an H_2O/CH_4 molar ratio of 1.0.

Ni/Al_2O_3 catalysts were prepared in the following manner using w/o microemulsion. The $Ni(OH)_2$ nanoparticles were formed by adding triethylamine directly to the $Ni(NO_3)_2$aq/polyoxyethylene (n=10) nonylphenyl ether/1-hexanol microemulsion. Alminium triisopropoxide (ATI), as a source of Al_2O_3 supports, was added to the microemulsion containing the $Ni(OH)_2$ nanoparticles, 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 sample was pressed into disks and ground through 18/26 mesh. The catalyst prepared in this manner is designated as the ME catalyst.

The impregnated catalyst, designated as the IMP catalyst, was used as a reference. The IMP catalyst was prepared by impregnating Al_2O_3, which was prepared in advance by the hydrolysis of ATI, with an aqueous $Ni(NO_3)_2$ solution.

The catalytic activity and durability tests were conducted in a fixed-bed reactor of a quartz tube (8 mm i.d.). 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 H_2 flow at 873 K for 2 h before the reaction.

The Ni particle size was determined by transmission electron microscopy (TEM, Nihon Denshi JEM-2000FX) and X-ray diffraction (XRD, Rigaku Rint 2500). The suface composition of the catalyst was estimated by X-ray photoelectron spectroscopy (XPS, Shimadzu/Kratos Axis-165).

Temperature-programmed reduction (TPR) was carried out using a 5% H_2/N_2 gas as a reductant. A reductant flow rate of 40 mL/min and a temperature ramp of 10K/min from 373 K to 1173 K were used in the experiments. The consumption of H_2 was measured with a TCD.

Figure 1 shows the activity changes with time on stream for the ME and IMP catalysts. Physical properties and the amount of coke on both catalysts are summarized in Table 1.

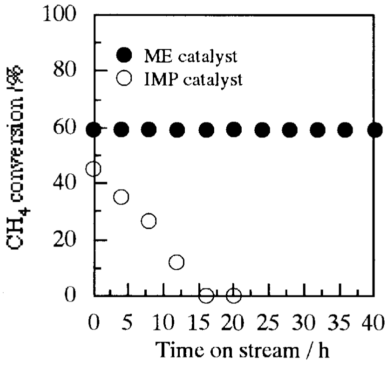

Figure 1. Activity change of Ni/Al_2O_3 catalysts with time on stream during steam reforming of methane. Reaction conditions: 873 K, atmospheric pressure, H_2O/CH_4=1.0, GHSV=35000 h^{-1}.

In the initial period of the reaction, the ME catalyst exhibited higher activity (as CH_4 conversion of 59%) than the IMP catalyst (43%). The ME catalyst sustained its high activity for 40 h, whereas the IMP catalyst deactivated rapidly and lost its activity at a time-on-stream of 15 h. A considerable amount of coke was deposited on the IMP catalyst after the reaction (>30 wt%-carbon/g-cat. after 20 h). This coking seemed to induce the rapid deactivation of the IMP catalyst. In contrast, little

Table 1. Physical properties and the amount of coke for the Ni/Al_2O_3 catalysts

Catalyst	Ni cont. / wt%	Ni particle size[a] / nm		S_{BET} [b] / $m^2\ g^{-1}$	Surface composition Rs = Ni / (Ni+Al)	Coke / wt%	
		by TEM	by XRD			Fresh[c]	Used[d]
ME	10	9.1	11.2	341	0.108	0.27	0.30
IMP	10	8.7	11.6	320	0.137	0.11	30.3

[a] Determined after 873 K 2 h H_2 reduction. [b] BET surface area. [c] After 873 K 2 h H_2 reduction. [d] At a time on stream of 20 h for IMP catalyst, and 40 h for ME catalyst. Reaction conditions: 873 K, atmospheric pressure, H_2O/CH_4=1.0, GHSV=35000 h^{-1}.

coke was deposited on the ME catalyst (<0.3 wt%-carbon/g-cat. after 40 h).

Several works[5,6] reported the carbon-forming tendency of supported Ni catalysts might have a close relationship with the Ni particle size. However, the carbon-forming tendency was much different between the ME and IMP catalysts with the same Ni particle size. This observation indicates that the other factor which influences the carbon deposition exsits.

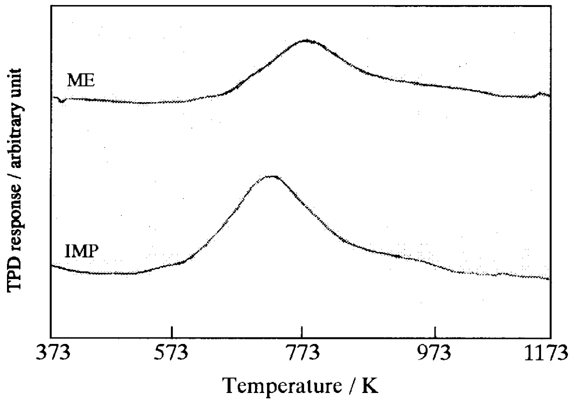

Figure 2. TPR profiles of Ni/Al_2O_3 catalysts. Experiment conditions : reductant; 5% H_2/N_2 gas, reductant flow rate; 40 mL/min,temperature ramp; 10 K/min from 373 K to 1173 K.

TPR profiles of both the catalysts are shown in Figure 2. For both catalysts, a reduction peak corresponding to (NiO → Ni) was observed. As can be seen from this figure, the reduction peak of the ME catalyst was much higher than that of the IMP catalyst, indicating that the reduction of Ni particles is hard in the ME catalyst. The surface composition Ni/(Ni + Al) of the ME catalyst was lower than that of the IMP catalyst with the same Ni loading. This indicates Ni particles were partially covered with Al_2O_3 in the ME catalyst. Therefore, in the ME catalyst, Ni particles were much more strongly influenced by Al_2O_3 which is electron-attractive to Ni, leading to the generation of stable $Ni^{\delta+}$ species. This is considered to be the reason why the reduction of Ni particles was hard in the ME catalyst. Similar behavior was observed over Pd/SiO_2 catalyst prepared by the ME method.[7] Wang et al.[8] reported that the strong interaction between metal and support made catalysts more resistant to coking during CO_2 reforming of methane. The superior resistance to coking of the Ni/Al_2O_3 catalyst prepared using microemulsion is attributed to the strong interaction between Ni particles and Al_2O_3.

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