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High-Temperature Steam Reforming of Hydrocarbons over Nickel/Hexaaluminate Catalysts

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Hexaaluminate supports effectively suppressed the sintering of supported Ni particles and the carbon deposition in the steam reforming reaction. These prominent features result from a large surface area of the hexaaluminate support in the presence of high-temperature water vapor.

Steam reforming reactions of hydrocarbons are widely used for production of city gas, synthesis gas and hydrogen.[1] Recently, the production of hydrogen has been attracted much attention in association with the fuel cell technology.[2] For high temperature fuel cells such as solid oxide fuel cells, especially, catalysts for the steam reforming reaction requires the extremely high heat resistance in order to retain a large surface area at around 1000 °C in the presence of water vapor. However, such a heat resistance can not be attained by conventional support materials such as γ-Al_2O_3. We have been developing hexaaluminate compounds as a heat resistant catalyst material.[3-5] The hexaaluminates can retain the large surface area (ca. 20 m^2/g) above 1300 °C, which is quite useful for catalytic combustion operated above 1200 °C. In this communication, we report the excellent catalytic properties of hexaalumiante catalysts for the high-temperature steam reforming of hydrocarbons. It has become evident that the hexaaluminate support is quite effective not only in suppressing sintering of Ni particles but also in inhibiting carbon deposition during the steam reforming reaction.

Three hexaaluminate compounds, $BaAl_{12}O_{19}$, $SrAl_{12}O_{19}$, and $CaAl_{12}O_{19}$, were prepared by calcining the corresponding hydrolyzed alkoxides at 1200 °C. Nickel acetate was impregnated onto the hexaaluminate and the sample thus obtained was calcined at 1200 °C (Ni-impregnated hexaaluminate). On the other hand, Ni-substituted hexaaluminate ($BaNi_{1.65}Al_{10.35}O_{19}$) was prepared by calcining of hydrolyzed alkoxides at 1200 °C in air. Heat

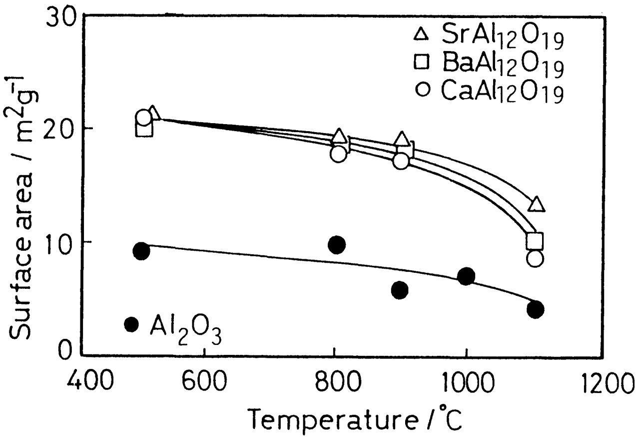

Fig. 1. Surface area of hexaaluminate and alumina after steam treatment for 10 h. H_2O:54 vol%, N_2:46 vol%

resistance and catalytic property of the hexaaluminate were compared to those of conventional catalysts such as 12wt%Ni/Al_2O_3 and a commercial catalyst (16wt%Ni/CaO-Al_2O_3). Heat resistance of the catalyst was evaluated by measuring the surface area after treatment in water vapor flow at 500-1000 °C. Steam reforming reaction of hydrocarbons was carried out in a conventional flow system at an atmospheric pressure (H_2O/C=1.0-5.0,(H_2O/C:molar ratio of water to carbon in hydrocarbons)). Catalysts were reduced in a H_2 flow at 600-1000 °C prior to the catalytic reaction. An amount of carbon deposition during steam reforming reaction was estimated by measuring the weight loss of the used catalyst due to combustion of the carbon deposits.

Figure 1 shows the surface area of the hexaaluminates and alumina after heating in the presence of water vapor (54 vol% H_2O, 46 vol% N_2). When the samples were calcined at 1200 °C in dry air prior to the steam treatment, hexaaluminate retained the surface area about twice larger than that of alumina. Heat resistance of hexaaluminate is obviously high even in the presence of high-temperature water vapor. Figure 1 shows that the decrease in the surface area of supports in the presence of water vapor is larger than in dry air. This rapid sintering appears to result from an accelerated mass transfer and/or a solution-precipitation process in the presence of water vapor. Among the three hexaaluminates, $SrAl_{12}O_{19}$ showed the highest heat resistance in high-temperature water vapor.

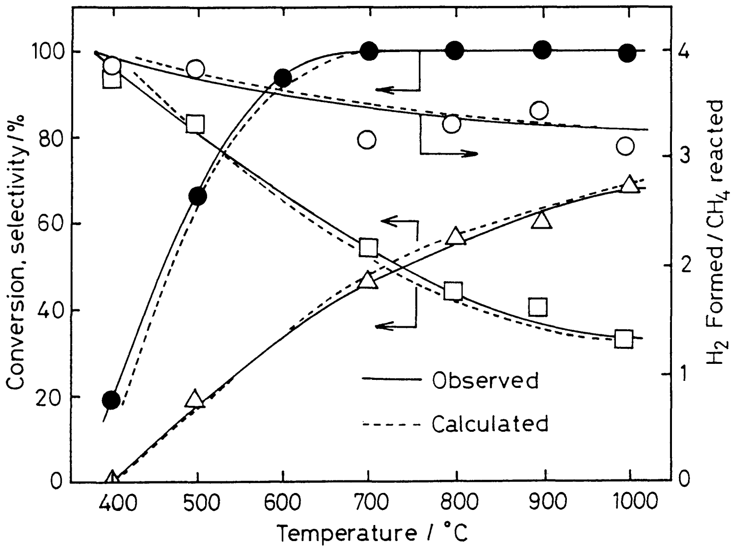

Fig. 2. Methane steam reforming over 12 wt% Ni/$BaAl_{12}O_{19}$.
CH_4:10.5 vol%, N_2:42.2 vol%, H_2O:47 vol%
S.V.=7100 h^{-1},
● CH_4 Conversion, selectivities to ○ H_2, △ CO, □ CO_2

Steam reforming of hydrocarbons was carried out over Ni catalysts supported on the four types of oxides (impregnated and substituted $BaAl_{12}O_{19}$, Al_2O_3, and $CaO-Al_2O_3$). Figure 2 shows the result of methane steam reforming over $12wt\%Ni/BaAl_{12}O_{19}$ at 400-1000 °C. The conversion of methane and selectivities to CO, CO_2, and H_2 agreed well with those expected from the thermodynamic equilibrium of following reactions.

$$CH_4 + H_2O \longrightarrow CO + 3\ H_2 \qquad CO + H_2O \longrightarrow CO_2 + H_2$$

Although the reaction was carried out at $1.0 < H_2O/C < 5.0$, at $7000\ h^{-1} < S.V. < 40000\ h^{-1}$, and at 400-1000 °C, the differences in the catalytic activity and the selectivities were scarcely observed among the four types catalysts. The most remarkable difference was observed in an amount of carbon deposition during the reaction.

In the steam reforming reaction, carbon is deposited on the catalyst surface or in the micropores via disproportionation of CO, decomposition of hydrocarbons and/or dehydrogenation of adsorbed hydrocarbons. Figure 3 shows the selectivity to carbon, which was calculated from the deposition amount during 5 h of steam reforming reaction. While the selectivity to carbon over the $Ni/CaO-Al_2O_3$ catalyst increased with decreasing H_2O/C ratio and reached to ca. 5% at $H_2O/C = 1.0$ (Fig. 3a), carbon deposition was scarcely detected over the other catalysts. Carbon deposition was more significant in the steam reforming of C_6H_{14} (Fig. 3b), in which the selectivity to carbon was extremely high for $Ni/CaO-Al_2O_3$ and Ni/Al_2O_3 catalysts at $1.0 < H_2O/C < 5.0$. However, in the reaction over hexaaluminate catalyst, especially derived from $BaNi_{1.65}Al_{10.35}O_{19}$, the amount of carbon deposition was negligibly low as well as in the methane steam reforming. The Ni surface area and overall surface area of the four types of catalysts were compared in Table 1. The Ni surface area was determined from the H_2 adsorption isotherms. It is apparent that the Ni surface area depends on the heat resistance of the oxide support. For the $Ni/CaO-Al_2O_3$ catalyst, which showed the largest amount of carbon deposition, large agglomerates of Ni parti-

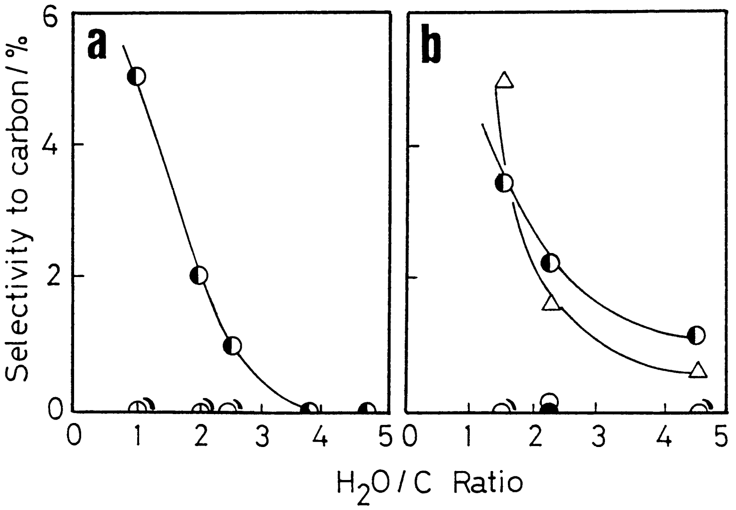

Fig. 3. Carbon deposition in steam reforming of a) methane (CH_4:10.5 vol%, SV=7100 h^{-1}) and b) hexane (C_6H_{14}:2.5 vol%, S.V.= 7100 h^{-1}) at 600 °C. Selectivity was calculated from the amount of carbon deposition during 5 h of the reaction.
○ $12wt\%Ni/BaAl_{12}O_{19}$, ● $BaNi_{1.65}Al_{10.35}O_{19}$
△ $12wt\%Ni/Al_2O_3$, ◐ $16wt\%Ni/CaO-Al_2O_3$

cle appears to result in small surface area (ca. 0.1 m^2/g). The Ni/Al_2O_3 catalyst showed a larger Ni surface area than $Ni/CaO-Al_2O_3$ even though alumina support sintered significantly. The largest Ni surface area was attained by the catalysts derived from both impregnated and substituted hexaaluminates with the large overall surface area. These results indicate that Ni particles as well as oxide supports need to have a large surface area for the suppression of the carbon deposition. Large surface area of Ni and oxide supports seems to be necessary to promote the adsorption of hydrocarbons and H_2O, respectively. In the hexaaluminate catalyst, barium ions in the lattice may also affect the basicity of support and thus suppress the carbon deposition. It is well known that an addition of alkali or alkaline earth element is effective in suppressing the carbon deposition over supported Ni catalysts.6-8) This effect is due to enhanced steam adsorption and neutralization of acid sites on the support in the presence of these additives.8) The Ni/hexaaluminate catalyst is believed to be suitable for the use in the high-temperature steam reforming operated around 1000 °C, which is strongly required to the fuel cell technology.

Table 1. Overall surface area and Ni surface area of steam reforming catalysts

Catalyst	Overall surface area / m^2g^{-1}	Ni surface area /m^2g^{-1}
$BaNi_{1.65}Al_{10.35}O_{19}$	8.9	0.9 a)
$12wt\%Ni/BaAl_{12}O_{19}$	19.6	1.1 b)
$12wt\%Ni/Al_2O_3$	1.9	0.6 b)
$16wt\%Ni/CaO-Al_2O_3$	6.5	0.1 b)

Catalysts were calcined at 1200 °C.
a) Reduced in H_2 flow at 1000 °C.
b) Reduced in H_2 flow at 600 °C.

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