Carbon Dioxide Reforming of Methane over Ni/θ-Al_2O_3 Catalysts: Effect of Ni Content

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Recently, carbon dioxide reforming of methane (CDR) to produce synthesis gas attracts many researchers for the chemical utilization of natural gas and carbon dioxide, which are suspected to be greenhouse gases.[1] The major interest in CDR originates from the demand of the production of liquid hydrocarbons and oxygenates, *e.g.* acetic acid, formaldehyde, and oxoalcohols since this reaction gives synthesis gas with a H_2/CO ratio of about 1.[2] However, this reaction has a disadvantage of serious coking on the reforming catalyst. For this reason, a number of studies have been focused on the development of a coke-resistant catalyst for CDR.[1-7] The catalysts based on noble metals have been found to be less sensitive to carbon deposition.[7] However, considering the high cost and limited availability of noble metals, it is more practical in industrial standpoint to develop Ni-based catalysts with high performance and high resistance to carbon deposition.

As a catalyst for CDR, Ni/γ-Al_2O_3 catalyst has been used.[8] However, Ni/γ-Al_2O_3 is usually unstable at high temperature (>1000 K) because of the thermal deterioration of the γ-Al_2O_3 support as well as phase transformation into α-Al_2O_3. Therefore, it is necessary to modify the γ-Al_2O_3 support in order to obtain thermally stable support. Xiong and coworkers[9] modified Ni/γ-Al_2O_3 with alkali metal oxide and rare earth metal oxide, and reported high performance with excellent stability. We attempted to prepare a stable Ni/θ-Al_2O_3 catalyst which overcomes the demerits of Ni/γ-Al_2O_3 catalyst without further modification, and successfully performed partial oxidation of methane (POM) over Ni/θ-Al_2O_3 with high activity as well as high stability.[10] We also applied Ni/θ-Al_2O_3 to steam reforming of methane (SRM) and oxy-SRM (OSRM) resulting in high activity and high stability.[11] We report here as a note that Ni/θ-Al_2O_3 exhibited also a good catalytic performance in CDR.

Experimental Section

Support materials employed in this study were γ-Al_2O_3 (S_{BET} = 234 m^2/g) and θ-Al_2O_3 (S_{BET} = 167 m^2/g), which was prepared by calcining γ-Al_2O_3 at 1173 K for 6 h. Supported Ni catalysts with various Ni loading were prepared by impregnating appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$ onto supports followed by drying at 373 K and calcining at 823 K for 6 h in air. Ni/$MgAl_2O_4$ (S_{BET} = 18 m^2/g), which has been used as a commercial SRM catalyst, was also employed for CDR as comparison. Activity tests were carried out using a fixed-bed quartz reactor.[10-16] Reactant gas was composed of CH_4:CO_2:N_2 = 1:1:3. The activity tests were carried out at 1073 K and 60,000 mL/g_{cat}·h. N_2 was employed as a reference gas for calculating both CH_4 and CO_2 conversion. Each catalyst was reduced in the reactor with 5% H_2/N_2 at 973 K for 2 h prior to each catalytic measurement. Effluent gases from the reactor were analyzed by a gas chromatograph (Chrompack CP9001) equipped with a thermal conductivity detector (TCD). GC column used in this study was a Fused Silica capillary column (CarboPLOT P7). The BET specific surface areas were measured by nitrogen adsorption at 77 K using a Micromeritics instrument (ASAP-2400). The Ni surface area was calculated according to the reference[17] by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni_s=1).

Results and Discussion

BET surface areas of 3-15% NiO/θ-Al_2O_3 catalysts are in the range of 160-138 m^2/g. Generally, the BET surface area decreases with increasing Ni content. These values are smaller than those of NiO/γ-Al_2O_3 by about 50 owing to the heat treatment at 1173 K for 6 h. As a result, it can be expected that Ni/θ-Al_2O_3 catalysts are more stable than Ni/γ-Al_2O_3 catalysts during CDR. Ni surface areas of 3, 6, 12, 15% NiO/θ-Al_2O_3 catalysts are 0.25, 1.02, 2.45 and 3.35 m^2/g, respectively. Average crystallite diameters are about 20 nm above 6% Ni loading, indicating that Ni is well dispersed on the support. The detailed characterization results were reported in an earlier publication.[11]

TPR patterns of NiO/θ-Al_2O_3 with various Ni loadings have three distinct peaks.[11] One (peak maximum = 753 K) is the free NiO species, the second peak (peak maximum = 913 K) can be assigned to the complex NiO_x species having the strong interaction with θ-Al_2O_3, and the third peak (peak maximum = 1073 K) is highly dispersed $NiAl_2O_4$ species. NiO/θ-Al_2O_3 catalysts having more than 6 wt% Ni show both NiO and NiO_x species. This indicates that Ni was deposited on the thermally stable θ-Al_2O_3, so that NiO_x species are formed rather than $NiAl_2O_4$. Comparison of TPR patterns between NiO/θ-Al_2O_3 and NiO/γ-Al_2O_3 catalysts revealed that the Ni-support interaction is stronger in NiO/

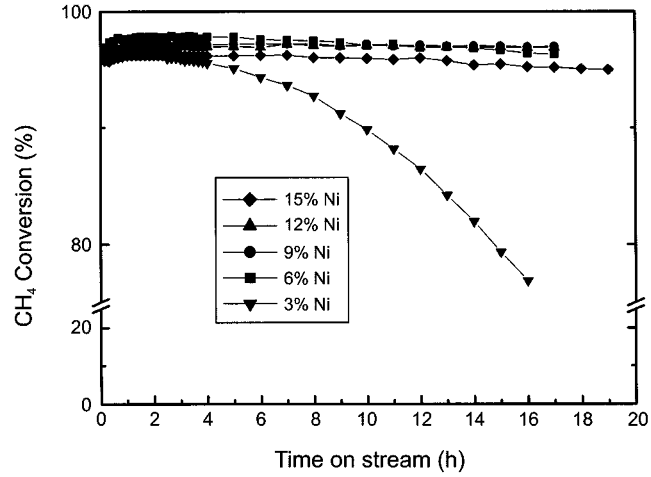

Figure 1. CH_4 conversion with time on stream over Ni/θ-Al_2O_3 catalysts in CDR (Reaction conditions: P = 1 atm, T = 1073 K, $CH_4/CO_2/N_2$ = 1/1/3, GHSV = 60,000 mL/g_{cat}·h).

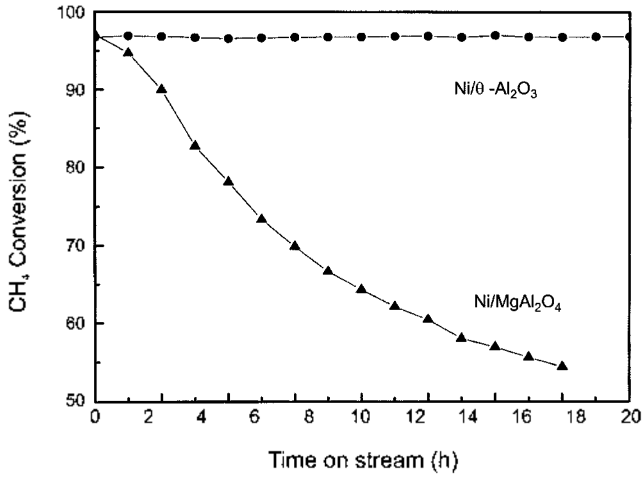

Figure 2. Comparison of CDR activity between 12% Ni/θ-Al_2O_3 catalyst and 12% Ni/$MgAl_2O_4$ catalyst (Reaction conditions: P = 1 atm, T = 1073 K, $CH_4/CO_2/N_2$ = 1/1/3, GHSV = 60,000 mL/g_{cat}·h).

γ-Al_2O_3. Thus, the temperature assigned to NiO_x peak of NiO/θ-Al_2O_3 is 50 K lower than that of NiO/γ-Al_2O_3. In the case of NiO/γ-Al_2O_3 catalysts, two peaks can be separated and there is no free NiO species. NiO_x species (peak maximum = 963 K) and highly dispersed $NiAl_2O_4$ species (peak maximum = 1073 K) appear. Since, it is well known that a chemical interaction between Ni and γ-Al_2O_3 leads to the formation of spinel $NiAl_2O_4$ having almost negligible activity in the reforming reaction,[10,11,16] it can be strongly expected that NiO_x species over Ni/θ-Al_2O_3 are more stable and effective in CDR than those over Ni/γ-Al_2O_3.

Figure 1 describes the Ni content effect on CH_4 conversion over Ni/θ-Al_2O_3 catalysts. 3% Ni catalyst deactivated with time on stream due to the phase transformation into inactive $NiAl_2O_4$. After the reaction, $NiAl_2O_4$ formation was confirmed from the color change of the used catalyst from black to blue. In the case of 6% Ni catalyst, initial CH_4 conversion was 97% but it slightly decreased to 96% after 17 h. For the catalysts with 9-12% Ni loading, however, CH_4 conversions were 97% without catalyst deactivation. Thus, it is likely that optimum Ni content is about 9-12%. In the case of 15% Ni loading, CH_4 conversion was initially 96% and it slowly decreased to 95% after 20 h. This is due to coke formation during CDR resulting from Ni sintering. This result is in good agreement with catalytic performances in POM, SRM, OSRM over the same catalyst.[11] According to the TPR pattern of 15% Ni/θ-Al_2O_3 catalyst,[11] this catalyst has a considerable amount of free NiO species which resulted in Ni sintering during the reforming reactions. Even though, due to too small amount of the catalyst employed, the amount of carbon deposition was not measured quantitatively over 15% Ni/θ-Al_2O_3 in CDR, carbon deposition on the quartz reactor was clearly observed after the reaction of 20 h. Except 15% catalyst, carbon was not seen over Ni/θ-Al_2O_3 catalysts having less than 15% Ni loading.

Table 1. Ni content effect on CH_4 conversion, CO_2 conversion, H_2 yield, CO yield and H_2/CO ratio over Ni/θ-Al_2O_3 catalysts in CDR

Ni content (%)	X_{CH4} (%)	X_{CO2} (%)	Y_{H2} (%)	Y_{CO} (%)	H_2/CO ratio
6	96	97	94	99	0.96
9	97	98	96	100	0.96
12	97	98	96	100	0.96
15	95	96	94	97	0.97

(Reaction conditions: P = 1 atm, T = 1073 K, $CH_4/CO_2/N_2$ = 1/1/3, GHSV = 60,000 mL/g_{cat}·h).

Table 1 summarizes CH_4 conversion, CO_2 conversion, H_2 yield, CO yield and H_2/CO ratio over Ni/θ-Al_2O_3 catalysts. The trend of CO_2 conversion was closely similar to that of CH_4 conversion but CO_2 conversion was 1% higher than CH_4 conversion. Besides, H_2 yield is slightly lower than CH_4 conversion but CO yield is slightly higher than CH_4 conversion. This suggests that there is reverse water gas shift reaction (RWGS: $H_2 + CO_2 \rightarrow H_2O + CO$) during CDR. Thus, H_2/CO ratio is usually 0.96-0.97, which is just slightly lower than unity.

In order to evaluate catalytic activity and stability of Ni/θ-Al_2O_3 catalyst, the performance of 12% Ni catalyst was compared with 12% Ni/$MgAl_2O_4$, which is a commercially available SRM catalyst. Figure 2 illustrates the comparison result. Ni/$MgAl_2O_4$ rapidly deactivated with time on stream owing to the carbon formation during the reaction. Ni/θ-Al_2O_3 catalyst, however, showed stable activity during 20 h. Thus, it was confirmed that Ni/θ-Al_2O_3 catalyst is more active and stable in CDR.

In summary, stable Ni/θ-Al_2O_3 catalyst can be prepared by heat treatment of γ-Al_2O_3 at 1173 K for 6 h and can be used for CDR. Low Ni loading catalysts deactivated with time on stream due to the transformation into inactive $NiAl_2O_4$ during the reaction, high Ni loading catalyst (15%) deactivated due to carbon formation, and 9-12% Ni loading is considered as the optimum value in CDR.

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