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A highly active and stable catalyst for carbon dioxide reforming of methane: Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$

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A novel catalyst, Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ has been designed and examined in carbon dioxide reforming of methane. It gives synthesis gas with CH$_4$ conversion more than 97% at 800 °C and the activity was maintained during the reaction for longer than 40 h. The high stability of the catalyst is mainly ascribed to the beneficial precoating effect of Ce–ZrO$_2$ resulting in the existence of stable NiO$_x$ species, a strong interaction between Ni and the support, and an abundance of mobile oxygen species in itself. From TPR results, it has been confirmed that NiO$_x$ formation is more favorable than NiO or NiAl$_2$O$_4$ formation, resulting in strong interaction between Ni and the support.

KEY WORDS: θ-Al$_2$O$_3$; Ce–ZrO$_2$; CH$_4$; CO$_2$; Ni; reforming.

1. Introduction

In recent years, a renewable study on carbon dioxide reforming (CDR) of methane to produce synthesis gas has become an attractive and challenging subject for the chemical utilization of natural gas and carbon dioxide, which are substances intimately related to greenhouse effect and energy resources [1]. The major interest in CDR originates from the demand for the production of liquid hydrocarbons and oxygenates, *e.g.* acetic acid, formaldehyde and oxoalcohols, since this reaction gives synthesis gas with a low H$_2$/CO ratio [2]. However, there is no established commercial process for this reaction because of fatal coking on the reforming catalyst. For this reason, a number of studies have been focused on the development of a promising 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 from the industrial standpoint to develop Ni-based catalysts with high performance and high resistance to carbon deposition. Therefore, it is necessary to develop a new supported Ni catalyst having high activity and high stability suitable for CDR.

As a catalyst for the reforming reaction, Ni/γ-Al$_2$O$_3$ catalyst has been used [8,9]. However, Ni/γ-Al$_2$O$_3$ is usually unstable at high temperature (>700 °C) because of the thermal deterioration of the γ-Al$_2$O$_3$ support as well as phase transformation into α-Al$_2$O$_3$. Therefore, it is necessary to modify the γ-Al$_2$O$_3$ support in order to obtain a thermally stable support for the reforming reaction. In our recent studies, we have successfully performed partial oxidation of methane (POM) over Ni/θ-Al$_2$O$_3$ with high activity as well as high stability [10]. However, Ni/θ-Al$_2$O$_3$ was not stable in CDR. Thus, we aimed to modify θ-Al$_2$O$_3$ with suitable materials.

Lercher *et al.* [11] have recently reported that Pt/ZrO$_2$ showed excellent performance in CDR. However, they have failed to apply Ni/ZrO$_2$ with high Ni loading to the same reaction due to serious plugging of the reactor by coke formation. On the contrary, we have successfully performed CDR over Ni supported on ZrO$_2$ and modified ZrO$_2$ catalysts [12,13]. Moreover, Ni/Ce–ZrO$_2$ exhibited both high activity and stability in steam reforming of methane (SRM) [14,15], POM [16,17] and oxy-SRM (OSRM) [14,17], owing to the ability to make mobile oxygen species, easier reducibility of Ce–ZrO$_2$ and so on. Also, Montoya *et al.* [18] applied the Ni/Ce–ZrO$_2$ system to CDR. However, Ni/Ce–ZrO$_2$ is difficult to commercialize due to the high price of Ce–ZrO$_2$. Therefore, in this work, Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ has been designed and applied to CDR based on our previous results [12–17]. We report here that a novel catalyst, Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$, exhibited high catalytic performance in CDR.

2. Experimental

Support materials employed in this study were γ-Al$_2$O$_3$ ($S_{\mathrm{BET}} = 234\,\mathrm{m^2/g}$) and θ-Al$_2O_3$ ($S_{\mathrm{BET}} = 167\,\mathrm{m^2/g}$), which was prepared by calcining γ-Al$_2$O$_3$ at 900 °C for 6 h. Ce–ZrO$_2$-modified θ-Al$_2$O$_3$ support was prepared by the incipient wetness method (CeO$_2$: ZrO$_2$: Al$_2$O$_3$ = 1 : 4 : 95 w/w). Precursors used in this study were Zr–nitrate solution (20 wt% in ZrO$_2$ base, MEL Chemicals) and Ce–acetate (99%, Aldrich Chemicals).

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Supported Ni catalysts with various Ni loadings were prepared by impregnating appropriate amounts of $Ni(NO_3)_2 \cdot 6H_2O$ onto supports followed by drying at 100 °C and calcining at 550 °C for 6 h in air. Activity tests were carried out using a fixed-bed microreactor [14–17]. Reactant gas was composed of $CH_4 : CO_2 : N_2 = 1:1:3$. N_2 was employed as a reference gas for calculating both CH_4 and CO_2 conversions. Each catalyst was reduced in the reactor with 5% H_2/N_2 at 700 °C 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). The 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 −196 °C using a Micromeritics instrument (ASAP-2400). The Ni surface area was calculated according to ref. [19] by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom ($H/Ni_s = 1$). Temperature-programmed reduction (TPR) was carried out in a conventional apparatus [20] using 5% H_2/N_2 gas with a heating rate of 10 °C/min.

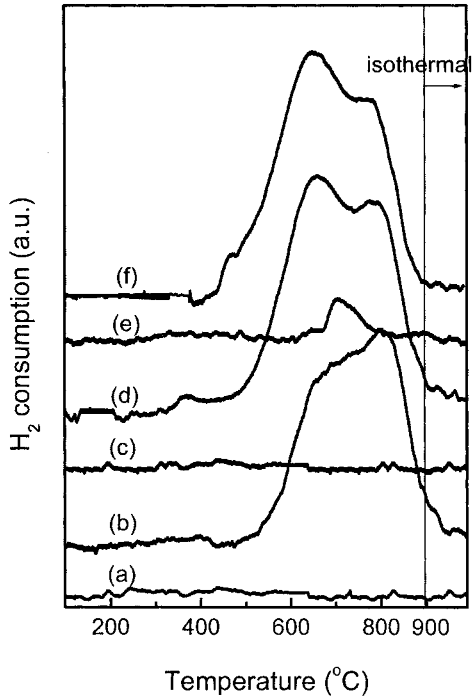

Figure 1. TPR patterns of supports and catalysts: (a) γ-Al_2O_3, (b) 3% Ni/γ-Al_2O_3, (c) θ-Al_2O_3, (d) 3% Ni/θ-Al_2O_3, (c) Ce–ZrO_2/θ-Al_2O_3 and (f) 3% Ni/Ce–ZrO_2/θ-Al_2O_3.

3. Results and discussion

From the industrial viewpoint, Al_2O_3-based supports are preferred because of their easier availability in the reforming processes. Therefore, Ni/Al_2O_3 and Ni/$MgAl_2O_4$ have been used as catalysts for steam reforming processes. However, they cannot be used as catalysts for CDR owing to the serious coke formation. As an alternative, Ni/γ-Al_2O_3 could be considered [8,9]. However, it is unstable at high temperature (>700 °C) because of the thermal deterioration of the γ-Al_2O_3 support that causes sintering and leads to pore closing and reduction in surface area as well as phase transformation into α-Al_2O_3, which changes an active surface layer and promotes a low surface area structure. Thus, we carefully changed γ-Al_2O_3 into θ-Al_2O_3 and successfully applied Ni/θ-Al_2O_3 in POM [10]. However, Ni/θ-Al_2O_3 is rather unstable in CDR. Therefore, we modified θ-Al_2O_3 with Ce–ZrO_2, resulting in its exhibiting high activity as well as stability in CDR.

Table 1 summarizes the BET specific surface areas and Ni surface areas of the catalysts employed in this study. The surface area of Ni/θ-Al_2O_3 (160 m^2/g) is lower than Ni/γ-Al_2O_3 (219 m^2/g) due to the careful heat treatment at 900 °C for 6 h. The surface area of Ni/Ce–ZrO_2/θ-Al_2O_3 is 150 m^2/g, which is the lowest among the catalysts. However, the trend of Ni surface area is opposite to that of BET surface area. This indicates that the degree of $NiAl_2O_4$ formation is in the order Ni/γ-Al_2O_3 >Ni/θ-Al_2O_3 >Ni/Ce–ZrO_2/θ-Al_2O_3.

TPR results confirm the precoating effect of Ce–ZrO_2 (figure 1). Generally, three peaks can be seen in the TPR curve of Ni/θ-Al_2O_3 [10]. One is assigned to free NiO species (peak maximum = 480 °C), another is complex NiO_x species (peak maximum = 640 °C), strongly interacting with the support, and the third is $NiAl_2O_4$ (peak maximum = 800 °C). Both γ-Al_2O_3 and θ-Al_2O_3 do not show any peak. By contrast, Ce–ZrO_2/θ-Al_2O_3 shows one peak at 700 °C assigned to the reduction of Ce–ZrO_2. According to our previous results [16], the reduction of Ce–ZrO_2 could be done at 640 °C, whereas CeO_2 reduction could be achieved at 880 °C and ZrO_2 reduction could not be detected. The high-temperature shift of the reduction peak is due to the strong interaction between Ce–ZrO_2 and θ-Al_2O_3.

Table 1
Surface areas of the supported Ni catalysts (Ni loading = 3%)

Catalyst	Ni/Ce–ZrO_2/θ-Al_2O_3	Ni/θ-Al_2O_3	Ni/γ-Al_2O_3
BET surface area (m^2/g) [a]	150	160	219
Ni surface area (m^2/g) [b]	0.44	0.25	0.19

[a] Estimated from N_2 adsorption at −196 °C.

[b] Estimated from H_2 adsorption at 50 °C.

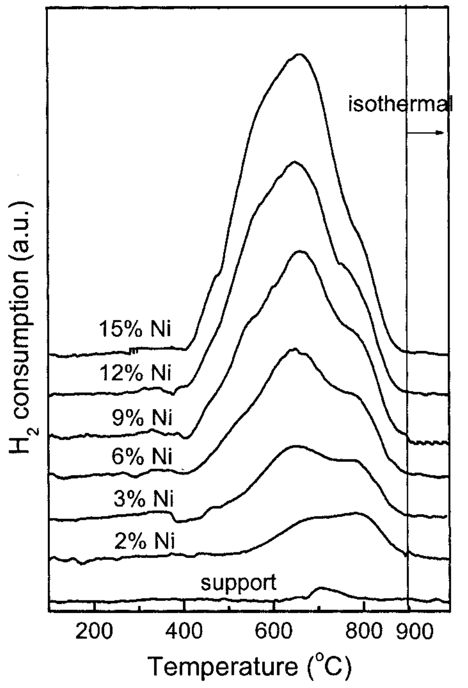

Figure 2. TPR patterns of Ni/Ce–ZrO_2/θ-Al_2O_3 catalysts with different nickel loadings.

Figure 2 describes the TPR patterns of Ni/Ce–ZrO_2/θ-Al_2O_3 depending on Ni loading. 2% Ni loading catalyst shows two reduction peaks assigned to NiO_x and $NiAl_2O_4$ respectively. Obvious NiO_x reduction peaks can be seen over the catalysts having more than 3% Ni loading. From 6 to 15% Ni loading, three peaks can be seen but the first and third peaks appear as shoulders.

Figure 3 presents the XRD patterns of used and reduced Ni/Ce–ZrO_2/θ-Al_2O_3 catalysts (Ni loading = 12 wt%). It is clear that there is no significant difference between used catalyst and reduced catalyst. The XRD patterns show metallic Ni peaks assigned at 44.5° and 51.8° and other peaks are consistent with the peaks originating from the support.

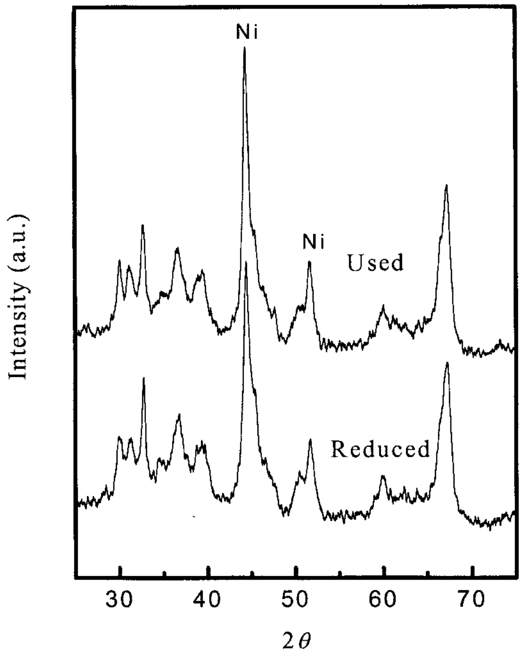

Figure 3. XRD patterns of used and reduced Ni/Ce–ZrO_2/θ-Al_2O_3 catalysts (Ni loading = 12%).

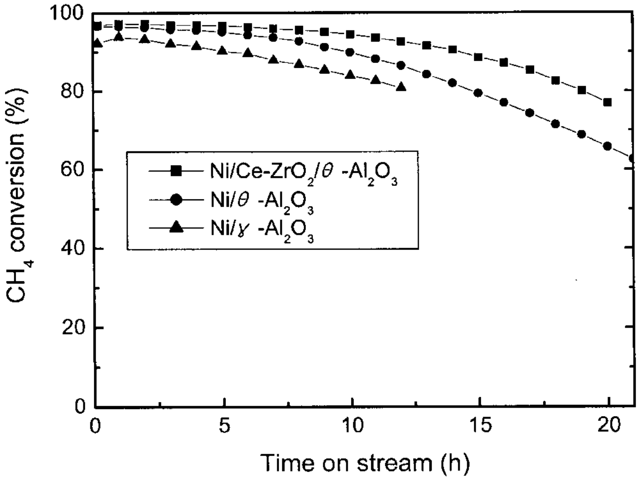

Figure 4. The effect of the support on CH_4 conversion with time on stream. (Reaction conditions: $CH_4 : CO_2 : N_2 = 1.0 : 1.0 : 3.0$, GHSV = 60 000 ml/h·g, $T = 800\,°C$, $P = 1$ atm).

Figure 4 shows CH_4 conversion with time on stream in CDR over various Al_2O_3-supported Ni catalysts (Ni loading = 3 wt%). All the catalysts deactivated with time on stream. However, the deactivation rate was dependent upon the support; that is, Ni/γ-Al_2O_3 deactivated quickly with time on stream owing to the phase transformation into $NiAl_2O_4$. This figure clearly shows that catalyst deactivation from the phase transformation is in the order Ni/γ-Al_2O_3 >Ni/θ-Al_2O_3 >Ni/Ce–ZrO_2/θ-Al_2O_3. Therefore, it can be said that Ce–ZrO_2 precoating effectively retards the phase transformation.

Figure 5 illustrates CH_4 conversion with time on stream over Ni/Ce–ZrO_2/θ-Al_2O_3 with various Ni loadings. For

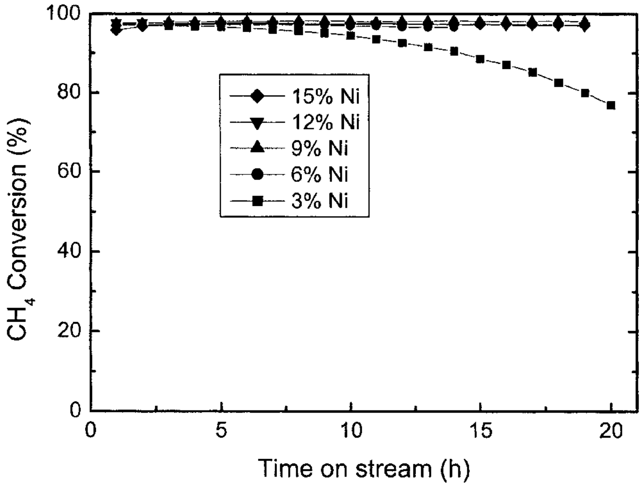

Figure 5. The effect of the Ni content on CH_4 conversion over Ni/Ce–ZrO_2/θ-Al_2O_3 catalysts. (Reaction conditions: $CH_4 : CO_2 : N_2 = 1.0 : 1.0 : 3.0$, GHSV = 60 000 ml/h·g, $T = 800\,°C$, $P = 1$ atm).

Table 2

Reaction results over Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ catalysts with different Ni loadings

Ni content (%)	CH_4 conversion (%)	CO_2 conversion (%)	H_2 yield (%)	CO yield (%)	H_2/CO ratio
6	97	98	95	100	0.96
9	98	99	97	101	0.97
12	97	98	96	100	0.96
15	97	98	96	99	0.96

Note: Reaction conditions: $CH_4:CO_2:N_2 = 1:1:3$, GHSV = 60 000 ml/h·g, $T = 800\,^\circ C$, $P = 1$ atm.

the catalysts with 6–15% Ni loading, CH_4 conversions were 97–98% without detectable catalyst deactivation. This is due to the beneficial effect of Ce–ZrO$_2$, which will be explained later. Table 2 summarizes reaction activities with Ni loading over Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$. Both CH_4 and CO_2 conversions were higher than 97% without regard to Ni loading. The trend of CO_2 conversion is closely similar to that of CH_4 conversion but CO_2 conversion is 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, the H_2/CO ratio is usually 0.96–0.97, which is very slightly lower than unity. Figure 6 shows CH_4 and CO_2 conversions over 9% Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ for 40 h. The catalyst exhibited almost the same activity even after 40 h, confirming its stability. During 40 h, CO_2 conversion was almost 1% higher than CH_4 conversion due to RWGS. According to the above results, a new catalyst, Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$, showed remarkable activity as well as stability in CDR. It should be noted that the catalyst having both high activity and stability with more than 5% Ni loading is very rare in CDR.

The fact that Ni supported on Ce–ZrO$_2$ precoated θ-Al$_2$O$_3$ showed high activity and stability can be explained as follows. First, Ce–ZrO$_2$ precoating inhibits the phase transformation into NiAl$_2$O$_4$. Second, mobile oxygen species can be supplied effectively resulting from high oxygen storage capacity (OSC) of Ce–ZrO$_2$ precoated onto θ-Al$_2$O$_3$. It is well known that CeO$_2$ has high OSC and, according to our earlier results [14], Ce–ZrO$_2$ has more mobile oxygen species than CeO$_2$, thus activating CO_2 molecules into CO and O* (active oxygen). Recently, we have reported that Ni/Ce–ZrO$_2$ showed remarkable activities as well as stabilities in SRM [14,15], POM [16,17] and OSRM [14,17] owing to the mobile oxygen species. Third, carbon formation can be prevented by the strong interaction between Ni and Ce–ZrO$_2$-precoated θ-Al$_2$O$_3$. That is, there is no obvious free NiO species responsible for carbon formation, which is confirmed by TPR (figure 2). It seems that metallic Ni sites reduced from free NiO species cause carbon formation during CDR. Fourth, the Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ system would rather form NiO$_x$ species, which are active for CDR, than form NiAl$_2$O$_4$, which are inactive. On the contrary, Ni/γ-Al$_2$O$_3$ favorably makes NiAl$_2$O$_4$. Even though Ni/θ-Al$_2$O$_3$ favors NiO$_x$ formation, it slowly transforms into NiAl$_2$O$_4$ during the reaction. According to the XRD analysis (figure 3), Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ did not show any detectable peak of NiAl$_2$O$_4$. Besides, TPR results confirm the precoating effect of Ce–ZrO$_2$ and the existence of NiO$_x$. Combined with the redox property of ZrO$_2$, it can be speculated that the reducibility of Ce–ZrO$_2$ could perform effective redox cycles during CDR. Based on the above results, it can be suggested that both Ni and Ce sites in Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ are partially oxidized under reforming conditions and the partially oxidized sites produce active oxygen species, which may react with the deposited carbon or prevent the carbon formation, and then are reoxidized with CO_2.

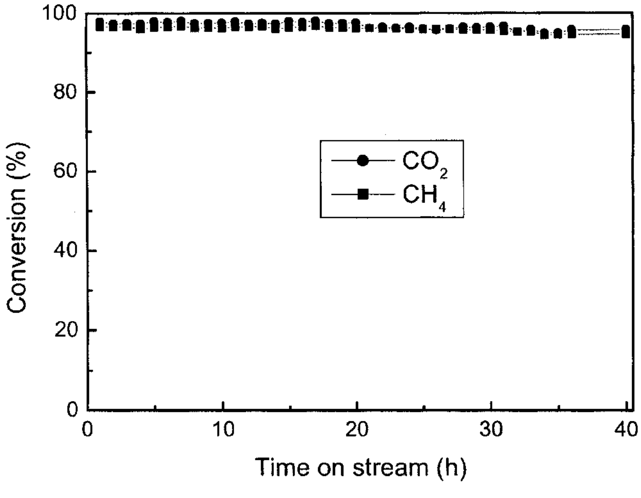

Figure 6. Stability test over 9% Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ catalyst.

4. Conclusions

Ni/Ce–ZrO$_2$/θ-Al$_2$O$_3$ catalyst reveals high activity as well as high stability in CDR. This is mainly ascribed to the beneficial precoating effect of Ce–ZrO$_2$, resulting in the existence of stable NiO$_x$ species, the strong interaction between Ni and the support, and abundance of highly-mobile oxygen species in itself.

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