

Highly Active and Stable All-Round Catalyst for Methane Reforming Reactions: Ni/Ce-ZrO₂/θ-Al₂O₃

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Received November 23, 2001

Keywords : θ-Al₂O₃, Ce-ZrO₂, Methane, Ni, Reforming.

Methane reforming reactions are important routes to produce H₂ or synthesis gas. Three kinds of methane reforming reactions attracting research interests are steam reforming of methane (SRM), oxy-reforming of methane (ORM), and CO₂ reforming of methane (CDR).¹⁻⁴ So far, specific catalyst has been reported as a candidate for each reforming reaction. However, each reaction has its own disadvantages such as excess steam, explosive dangers, high endothermicity, and so on. Thus, the combination of each reforming reaction can be more desirable. Besides, in the case of a compact fuel cell system, simultaneous exothermic ORM and endothermic SRM (OSRM) can give a lot of merits such as a fast start-up, high efficiency, cost save, and so on.⁵ Consequently, it is necessary to develop highly active and stable all-round catalyst for all the reforming reactions.

Although Ni/γ-Al₂O₃ catalyst has been used as a reforming catalyst,⁶ it is necessary to modify the γ-Al₂O₃ support in order to obtain a thermally stable support for the reforming reaction. In our recent studies, we have successfully performed ORM over Ni/θ-Al₂O₃ with high activity as well as high stability.⁷ However, Ni/θ-Al₂O₃ was not stable in SRM, OSRM, and CDR. We have also developed modified zirconia supported Ni catalysts for CDR.⁸ In addition, we have shown that Ni/Ce-ZrO₂ is highly active and stable in ORM,⁹ SRM,⁵ and OSRM.⁵ However, this system is difficult to commercialize due to the high price of Ce-ZrO₂. Therefore, in this work, we tried to precoat Ce-ZrO₂ onto a commercially available Al₂O₃ support before impregnating Ni in order to decrease the Ce-ZrO₂ content and modify the θ-Al₂O₃ support. As a result, we have successfully developed Ni catalysts supported on Ce-ZrO₂ precoated Al₂O₃. We report here that a novel catalyst, Ni/Ce-ZrO₂/θ-Al₂O₃, exhibited high catalytic performances in all the reforming reactions.

Support materials employed in this study were γ-Al₂O₃ (S_{BET} = 234 m²/g) and θ-Al₂O₃ (S_{BET} = 167 m²/g), which was prepared by calcining γ-Al₂O₃ at 900 °C for 6 h.⁷ Ce-ZrO₂ modified θ-Al₂O₃ support was prepared by the incipient wetness method (CeO₂ : ZrO₂ : Al₂O₃ = 1 : 4 : 95 w/w). Supported Ni catalysts (3 wt% Ni) were prepared by the impregnation method using appropriate amounts of Ni(NO₃)₂·6H₂O 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.^{5,9} All the reforming reactions except OSRM were executed with stoichiometric feed ratio. For example, in the case of SRM, we did not use excess steam. OSRM was tested with molar ratio of O₂ : H₂O : CH₄ = 1 : 2 : 2. All the catalysts were reduced in the reactor with 5% H₂/N₂ at 700 °C for 2 h prior to the reaction.

According to our previous results,^{5,9} Ni/Ce-ZrO₂ exhibited the highest activity in ORM, SRM, and OSRM among the tested catalysts including Ni/MgO and Ni/MgAl₂O₄ which have been considered as the best catalyst in ORM and SRM, respectively. Table 1 summarizes the reaction activities of ORM, SRM and OSRM over Ni/Ce-ZrO₂ and Ni/Ce-ZrO₂/θ-Al₂O₃ catalysts at 750 °C. Comparison between Ni/Ce-ZrO₂ and Ni/Ce-ZrO₂/θ-Al₂O₃ reveals that both catalysts have similar catalytic activity for SRM and OSRM. Besides, for ORM, Ni/Ce-ZrO₂/θ-Al₂O₃ showed even higher activity than Ni/Ce-ZrO₂. Therefore, the results in this work suggest that Ni/Ce-ZrO₂/θ-Al₂O₃ is a promising catalyst for methane reforming reactions even though most part of Ce-ZrO₂ is replaced by θ-Al₂O₃. It should be noted that the catalyst having both high activity and stability in all the stoichiometric reforming reactions is very rare. Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst presented a H₂/CO ratio of 2 with slight formation of H₂O and CO₂ in the case of ORM. In SRM, H₂/CO ratio was 3.3 resulting from the water gas shift (WGS) reaction. In the case of OSRM, H₂/CO and H₂/CO_x ratio were 3.3 and 2.2, respectively, indicating that ORM and WGS are dominant.

Figure 1 shows CH₄ conversion with time on stream in CDR at 800 °C. Ni/Ce-ZrO₂/θ-Al₂O₃ showed the highest activity as well as stability. CH₄ and CO₂ conversion were 97 and 98%, respectively, with a H₂/CO ratio was 0.96, resulting from reverse WGS. But, both Ni/θ-Al₂O₃ and Ni/γ-Al₂O₃ deactivated with time on stream owing to the phase

Table 1. Comparison of the activities between 3% Ni/Ce-ZrO₂ (A) and 3% Ni/Ce-ZrO₂/θ-Al₂O₃ (B) depending on reaction type

Reaction	CH ₄ conv. (%)		H ₂ yield (%)		CO yield (%)		H ₂ /CO ratio	
	A	B	A	B	A	B	A	B
ORM	78	89	73	85	72	85	2.0	2.0
SRM	70	71	74	74	62	63	3.5	3.3
OSRM	89	93	102*	103*	55	62	3.8	3.3

*Calculated based on considering only ORM

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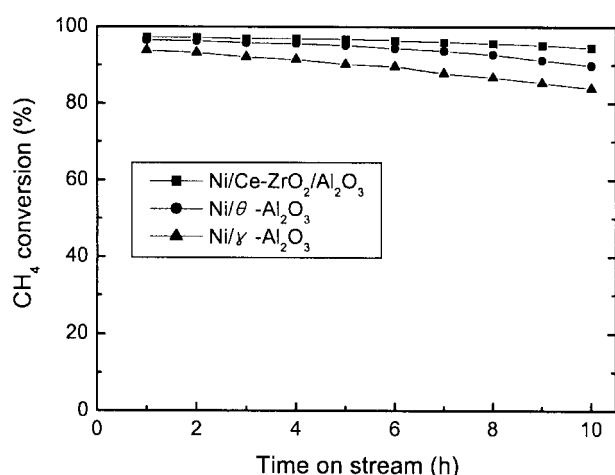


Figure 1. CH₄ conversion with time on stream in CDR. (Reaction conditions: CH₄/CO₂/N₂ = 1/1/3, GHSV = 60,000 mL/h·g, T = 800 °C, P = 1 atm).

transformation.

To compare Ni/Ce-ZrO₂/θ-Al₂O₃ and Ni/Ce-ZrO₂, XRD patterns of the supports and catalysts are illustrated in Figure 2. In order to see clear difference for both catalysts, 15 wt% Ni loading was chosen. As for 3% Ni catalysts, NiO peak could not be seen resulting from high dispersion of Ni. The XRD pattern of Ni/Ce-ZrO₂ shows 5 characteristic peaks of tetragonal phase and NiO peaks. Ni/Ce-ZrO₂/θ-Al₂O₃ also shows peaks identified as a tetragonal phase and NiO peaks, confirming the existence of Ce-ZrO₂ layer on the surface. According to the XRD patterns of used and reduced Ni/Ce-ZrO₂/θ-Al₂O₃ catalysts, there is no significant difference between used catalyst and reduced catalyst.

This fact that Ni supported on Ce-ZrO₂ precoated θ-Al₂O₃ showed high activity and stability can be explained as follows. Firstly, Ce-ZrO₂ precoating inhibits phase transformation of θ-Al₂O₃ into α-Al₂O₃. Secondly, mobile oxygen species can be supplied effectively resulting from the high oxygen storage capacity (OSC) of Ce-ZrO₂ precoated onto θ-Al₂O₃. Thirdly, carbon formation can be prevented by the strong interaction between Ni and Ce-ZrO₂ precoated θ-Al₂O₃. Fourthly, Ni/Ce-ZrO₂/θ-Al₂O₃ system would rather form NiO_x species, which are active for methane reforming reactions, than form NiAl₂O₄, which are inactive for methane reforming reactions. It is most likely that the interlayer of Ce-ZrO₂ can prevent a chemical interaction between Ni and θ-Al₂O₃ from forming NiAl₂O₄. On the contrary, Ni/γ-Al₂O₃ favorably makes NiAl₂O₄. Even though Ni/θ-Al₂O₃ favors NiO_x formation,⁷ it is more easily transformed into NiAl₂O₄ in the presence of steam, resulting in the negligible activities in both SRM and OSRM. This is confirmed by XRD analysis of used Ni/θ-Al₂O₃. In contrast to Ni/θ-Al₂O₃, Ni/Ce-ZrO₂/θ-Al₂O₃ did not show clear peak of NiAl₂O₄ in XRD analysis. Combined with the redox property of ZrO₂, the reducibility of Ce-ZrO₂ could perform effective redox cycles during the reforming reactions. Ni/Ce-ZrO₂/θ-Al₂O₃ showed

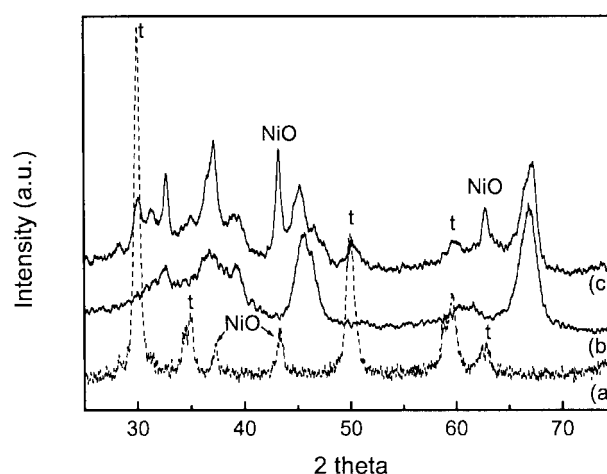


Figure 2. XRD patterns of 15% Ni/Ce-ZrO₂ (a), θ-Al₂O₃ (b) and 15% Ni/Ce-ZrO₂/θ-Al₂O₃ (c) (t denotes tetragonal phase of Ce-ZrO₂).

relatively large NiO_x peak compared with Ni/θ-Al₂O₃. Besides, NiO_x species were not transformed into NiAl₂O₄ even in the presence of steam, resulting in high activities as well as high stabilities in both SRM and OSRM. Based on the above results, it can be suggested that Ni/Ce-ZrO₂/θ-Al₂O₃ is partially oxidized under each reforming condition and the partially oxidized sites produce active oxygen species, which may react with the deposited carbon or prevent the carbon formation, and then is reoxidized with oxygen-containing molecules from each reactant gas.

In summary, novel Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst reveals high activity as well as high stability in all types of the reforming reactions even under stoichiometric feed composition. These results are mainly ascribed to the beneficial precoating effect of Ce-ZrO₂ resulting in the existence of stable NiO_x species, preventing the formation of NiAl₂O₄, and high mobile oxygen species in itself.

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