

## Highly Active and Stable All-Round Catalyst for Methane Reforming Reactions: Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>

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Received November 23, 2001

**Keywords :**  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, Ce-ZrO<sub>2</sub>, Methane, Ni, Reforming.

Methane reforming reactions are important routes to produce H<sub>2</sub> or synthesis gas. Three kinds of methane reforming reactions attracting research interests are steam reforming of methane (SRM), oxy-reforming of methane (ORM), and CO<sub>2</sub> reforming of methane (CDR).<sup>1-4</sup> 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.<sup>5</sup> Consequently, it is necessary to develop highly active and stable all-round catalyst for all the reforming reactions.

Although Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has been used as a reforming catalyst,<sup>6</sup> it is necessary to modify the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support in order to obtain a thermally stable support for the reforming reaction. In our recent studies, we have successfully performed ORM over Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> with high activity as well as high stability.<sup>7</sup> However, Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> was not stable in SRM, OSRM, and CDR. We have also developed modified zirconia supported Ni catalysts for CDR.<sup>8</sup> In addition, we have shown that Ni/Ce-ZrO<sub>2</sub> is highly active and stable in ORM,<sup>9</sup> SRM,<sup>5</sup> and OSRM.<sup>5</sup> However, this system is difficult to commercialize due to the high price of Ce-ZrO<sub>2</sub>. Therefore, in this work, we tried to precoat Ce-ZrO<sub>2</sub> onto a commercially available Al<sub>2</sub>O<sub>3</sub> support before impregnating Ni in order to decrease the Ce-ZrO<sub>2</sub> content and modify the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> support. As a result, we have successfully developed Ni catalysts supported on Ce-ZrO<sub>2</sub> precoated Al<sub>2</sub>O<sub>3</sub>. We report here that a novel catalyst, Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>, exhibited high catalytic performances in all the reforming reactions.

Support materials employed in this study were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub> = 234 m<sup>2</sup>/g) and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub> = 167 m<sup>2</sup>/g), which was prepared by calcining  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 900 °C for 6 h.<sup>7</sup> Ce-ZrO<sub>2</sub> modified  $\theta$ -Al<sub>2</sub>O<sub>3</sub> support was prepared by the incipient wetness method (CeO<sub>2</sub> : ZrO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> = 1 : 4 : 95 w/w). Supported Ni catalysts (3 wt% Ni) were prepared by the impregnation method using appropriate amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 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.<sup>5,9</sup> 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 O<sub>2</sub> : H<sub>2</sub>O : CH<sub>4</sub> = 1 : 2 : 2. All the catalysts were reduced in the reactor with 5% H<sub>2</sub>/N<sub>2</sub> at 700 °C for 2 h prior to the reaction.

According to our previous results,<sup>5,9</sup> Ni/Ce-ZrO<sub>2</sub> exhibited the highest activity in ORM, SRM, and OSRM among the tested catalysts including Ni/MgO and Ni/MgAl<sub>2</sub>O<sub>4</sub> 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-ZrO<sub>2</sub> and Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts at 750 °C. Comparison between Ni/Ce-ZrO<sub>2</sub> and Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> reveals that both catalysts have similar catalytic activity for SRM and OSRM. Besides, for ORM, Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> showed even higher activity than Ni/Ce-ZrO<sub>2</sub>. Therefore, the results in this work suggest that Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> is a promising catalyst for methane reforming reactions even though most part of Ce-ZrO<sub>2</sub> is replaced by  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. It should be noted that the catalyst having both high activity and stability in all the stoichiometric reforming reactions is very rare. Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst presented a H<sub>2</sub>/CO ratio of 2 with slight formation of H<sub>2</sub>O and CO<sub>2</sub> in the case of ORM. In SRM, H<sub>2</sub>/CO ratio was 3.3 resulting from the water gas shift (WGS) reaction. In the case of OSRM, H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>x</sub> ratio were 3.3 and 2.2, respectively, indicating that ORM and WGS are dominant.

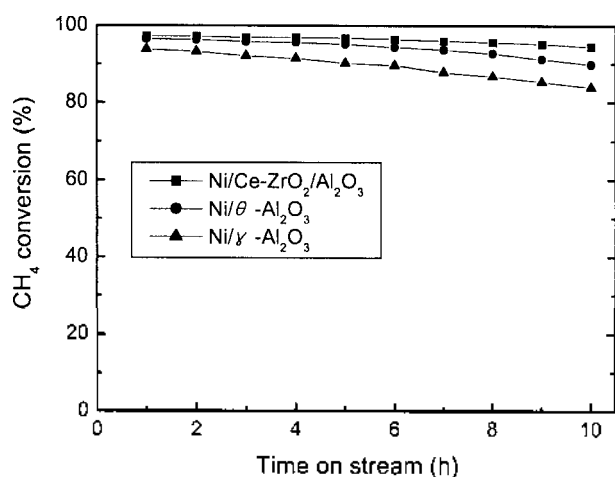
Figure 1 shows CH<sub>4</sub> conversion with time on stream in CDR at 800 °C. Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> showed the highest activity as well as stability. CH<sub>4</sub> and CO<sub>2</sub> conversion were 97 and 98%, respectively, with a H<sub>2</sub>/CO ratio was 0.96, resulting from reverse WGS. But, both Ni/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> deactivated with time on stream owing to the phase

**Table 1.** Comparison of the activities between 3% Ni/Ce-ZrO<sub>2</sub> (A) and 3% Ni/Ce-ZrO<sub>2</sub>/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> (B) depending on reaction type

Reaction	CH <sub>4</sub> conv. (%)		H <sub>2</sub> yield (%)		CO yield (%)		H <sub>2</sub> /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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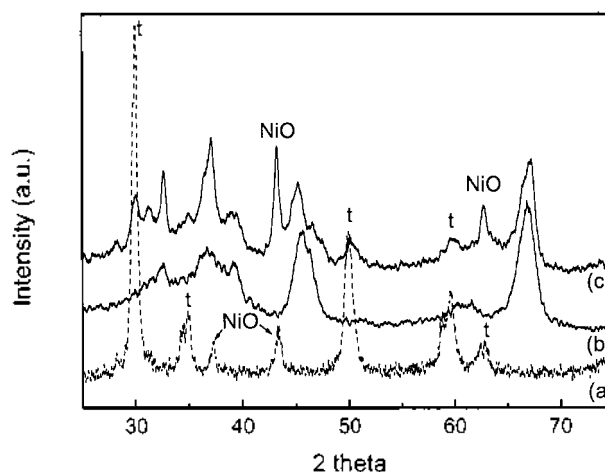


**Figure 1.** CH<sub>4</sub> conversion with time on stream in CDR. (Reaction conditions: CH<sub>4</sub>/CO<sub>2</sub>/N<sub>2</sub> = 1/1/3, GHSV = 60,000 mL/h·g, T = 800 °C, P = 1 atm).

transformation.

To compare Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> and Ni/Ce-ZrO<sub>2</sub>, 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-ZrO<sub>2</sub> shows 5 characteristic peaks of tetragonal phase and NiO peaks. Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> also shows peaks identified as a tetragonal phase and NiO peaks, confirming the existence of Ce-ZrO<sub>2</sub> layer on the surface. According to the XRD patterns of used and reduced Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> catalysts, there is no significant difference between used catalyst and reduced catalyst.

This fact that Ni supported on Ce-ZrO<sub>2</sub> precoated θ-Al<sub>2</sub>O<sub>3</sub> showed high activity and stability can be explained as follows. Firstly, Ce-ZrO<sub>2</sub> precoating inhibits phase transformation of θ-Al<sub>2</sub>O<sub>3</sub> into α-Al<sub>2</sub>O<sub>3</sub>. Secondly, mobile oxygen species can be supplied effectively resulting from the high oxygen storage capacity (OSC) of Ce-ZrO<sub>2</sub> precoated onto θ-Al<sub>2</sub>O<sub>3</sub>. Thirdly, carbon formation can be prevented by the strong interaction between Ni and Ce-ZrO<sub>2</sub> precoated θ-Al<sub>2</sub>O<sub>3</sub>. Fourthly, Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> system would rather form NiO<sub>x</sub> species, which are active for methane reforming reactions, than form NiAl<sub>2</sub>O<sub>4</sub>, which are inactive for methane reforming reactions. It is most likely that the interlayer of Ce-ZrO<sub>2</sub> can prevent a chemical interaction between Ni and θ-Al<sub>2</sub>O<sub>3</sub> from forming NiAl<sub>2</sub>O<sub>4</sub>. On the contrary, Ni/γ-Al<sub>2</sub>O<sub>3</sub> favorably makes NiAl<sub>2</sub>O<sub>4</sub>. Even though Ni/θ-Al<sub>2</sub>O<sub>3</sub> favors NiO<sub>x</sub> formation,<sup>7</sup> it is more easily transformed into NiAl<sub>2</sub>O<sub>4</sub> 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-Al<sub>2</sub>O<sub>3</sub>. In contrast to Ni/θ-Al<sub>2</sub>O<sub>3</sub>, Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> did not show clear peak of NiAl<sub>2</sub>O<sub>4</sub> in XRD analysis. Combined with the redox property of ZrO<sub>2</sub>, the reducibility of Ce-ZrO<sub>2</sub> could perform effective redox cycles during the reforming reactions. Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> showed



**Figure 2.** XRD patterns of 15% Ni/Ce-ZrO<sub>2</sub> (a), θ-Al<sub>2</sub>O<sub>3</sub> (b) and 15% Ni/Ce-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> (c) (t denotes tetragonal phase of Ce-ZrO<sub>2</sub>).

relatively large NiO<sub>x</sub> peak compared with Ni/θ-Al<sub>2</sub>O<sub>3</sub>. Besides, NiO<sub>x</sub> species were not transformed into NiAl<sub>2</sub>O<sub>4</sub> 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-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> 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-ZrO<sub>2</sub>/θ-Al<sub>2</sub>O<sub>3</sub> 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-ZrO<sub>2</sub> resulting in the existence of stable NiO<sub>x</sub> species, preventing the formation of NiAl<sub>2</sub>O<sub>4</sub>, and high mobile oxygen species in itself.

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