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CeO_2 Promoted Ni/Al_2O_3 Catalyst in Combined Steam and Carbon Dioxide Reforming of Methane for Gas to Liquid (GTL) Process

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Abstract The effect of ceria promotion over Ni/Al_2O_3 catalysts on the catalytic activity and coke formation was investigated in combined steam and carbon dioxide reforming of methane (CSCRM) to produce synthesis gas ($H_2/CO = 2$) for gas to liquid (GTL) process. Ce-promoted Ni/Al_2O_3 catalysts were prepared by co-impregnation method. It has been found that the Ce promotion over Ni/Al_2O_3 catalyst is beneficial to catalytic activity and coke resistance. As a result, the catalyst promoted with 6 wt% Ce exhibits the highest activity as well as high coke resistance due to the improvement of Ni dispersion and high oxygen storage capacity of CeO_2.

Keywords Combined steam and carbon dioxide reforming of methane · $Ni\text{-}Ce/Al_2O_3$ · Coke resistance · Gas to liquid (GTL)

1 Introduction

Recently, the conversion process of natural gas into liquid fuels (gas to liquids: GTL) has been considered as a clean and alternative process in an environmental respect. Syngas, a mixture of H_2 and CO is a major feedstock for methanol, ammonia and Fischer–Tropsch (F–T) synthesis [1, 2]. It is very important to adjust a H_2/CO ratio for these processes. In conventional reforming process such as steam reforming of methane (SRM) and carbon dioxide reforming of methane (CRM), the additional process is required to meet the appropriate H_2/CO ratio [3, 4]. In addition, partial oxidation of methane (POM) which is an exothermic reforming process makes it difficult to control the temperature due to the hot spot [5]. On the other hand, combined steam and carbon dioxide reforming of methane (CSCRM) is a suitable process for the direct control of the H_2/CO ratio without additional process by regulating the H_2O/CO_2 feed ratio [6, 7].

Ni-based catalysts are preferred to the commercial reforming processes because they are economical compared to noble metal-based catalysts. However, commercial Ni catalysts are faced with a fatal problem of deactivation resulting from the coke formation under severe conditions ($(H_2O + CO_2)/CH_4 < 1.5$). As a consequence, it is necessary to optimize catalysts with high coke resistance for CSCRM [8–10]. In general, coke formation is caused by methane decomposition ($CH_4 \Leftrightarrow C + 2H_2$) and Boudouard reaction ($2CO \Leftrightarrow C + CO_2$) [11, 12]. It has been reported that CeO_2 plays an important role as a carrier of active oxygen species which oxidize the coke over catalyst surface and increases strong metal to support interaction (SMSI) [13–15]. Especially, ceria promoting schemes are as follows [16–18]. These schemes indicate that reduced ceria (CeO_{2-x}) enhances the dissociation of CO_2 and H_2O and adsorbed oxygen species react with the surface carbon to form CO, CO_2, and H_2. Due to the above-mentioned advantages, CeO_2 has been employed as a support or a promoter in methane reforming reactions [19–25].

$$CeO_2 + xCH_4 \rightarrow CeO_{2-x} + xCO + 2xH_2 \quad (1)$$

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$$CeO_{2-x} + xCO_2 = CeO_2 + xCO \tag{2}$$

$$CeO_{2-x} + xH_2O = CeO_2 + xH_2 \tag{3}$$

Our objectives are to study the CeO_2 effect on coke formation over Ce-modified Ni/Al_2O_3 catalyst by monitoring the SEM image of used catalysts and to determine the adequate Ce content in Ni–Ce/Al_2O_3 catalysts with high activity and coke resistance in CSCRM.

2 Experimental

2.1 Catalyst Preparation

Ce-modified Ni/Al_2O_3 catalysts were prepared by co-impregnation of the mixture of $Ce(NO_3)_3 \cdot 6H_2O$ (99%, Aldrich) and $Ni(NO_3)_2 \cdot 6H_2O$ (97%, Junsei) solution on α-Al_2O_3 (99.9%, High Purity Chem.). The loading amount of Ni was fixed at 12 wt% and the Ce content was varied from 0 to 24 wt%. After the supports were pre-calcined in air at 800 °C for 6 h, the Ni and Ce were co-impregnated. The catalysts were calcined in air at 800 °C for 6 h.

2.2 Characterization

The crystal structure and compositional homogeneity of the prepared catalysts were examined by X-ray diffraction (XRD, Rigaku D/Max-III C, CuKα radiation), and the NiO crystallite size was estimated by using the Scherrer equation. The surface area of catalysts was measured by BET (Micromeritics, ASAP 2000) through the nitrogen adsorption at −196 °C. H_2-chemisorption was performed by using pulse technique to identify the metallic dispersion and metal surface area in BEL-METAL-3 (BEL Japan, Inc.). The sample of 50 mg was reduced in H_2 flow at 700 °C for 1 h. The sample was purged at 700 °C for 1 h in He flow and cooled to 50 °C. A hydrogen pulse (20% H_2/Ar) was injected into the catalyst. The adsorbed H_2 amount obtained by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom ($H/Ni_{surface} = 1$) was used to estimate Ni dispersion and surface area. Temperature programmed reduction (TPR, Micromeritics, Autochem 2910) was carried out to identify the reduction temperature and H_2 consumption of catalysts. The sample of 0.1 g in a quartz reactor was pre-treated with He gas at 250 °C for 1 h, then cooled down to 50 °C, and then re-heated by an electrical furnace at a heating rate of 20 °C/min from 100 to 1,000 °C under 10% H_2 in Ar gas. The sensitivity of the detector was calibrated by reducing known weight of NiO. The morphology of used catalysts and coke formation were examined by scanning electron microscopy (SEM, Philips XL30SREG).

2.3 Catalyst Reaction

The combined steam and carbon dioxide reforming of methane was carried out at 800 °C for 20 h using 10 mg catalysts diluted with 100 mg $MgAl_2O_4$ in a fixed-bed quartz reactor (I.D. = 4 mm) after the catalysts were reduced at 700 °C for 1 h under a mixture of 10% H_2 in N_2. The reaction temperature was controlled by thermocouple placed at the center of the catalyst bed. The reactant feed ratio of $(H_2O + CO_2)/CH_4$ was 1.2 and the space velocity was 265,000 ml/g_{cat}-h. The ratio of H_2O/CO_2 was fixed at 2 to get syngas with a H_2/CO ratio of 2 based on our previous works [8]. Steam was fed by vaporizing deionized water at 150 °C upstream of the reactor. The effect of reforming temperature on catalytic activity was investigated at 750 and 700 °C, respectively. The effluent was passed through a trap to condensate residual water and then analyzed by an on-line micro gas chromatography (Agilent 3000) equipped with a TCD detector.

3 Results and Discussion

3.1 Catalyst Characterization

Figure 1 presents the XRD patterns of Ni-Ce/Al_2O_3 catalysts with various Ce content. To see the effect of Ce content, Ni content was fixed at 12 wt%. CeO_2 shows characteristic peaks corresponding to cubic phase with (111), (200), (220), (311), (222) and (400) planes [19]. All characteristic reflections of NiO are present at 2θ values equal to 37.28, 43.36, 62.90 and 75.49 degrees. XRD diffraction peak at $2\theta = 62.90^{o}$ was used to calculate the NiO crystallite size in Table 1. The peak intensity of NiO is

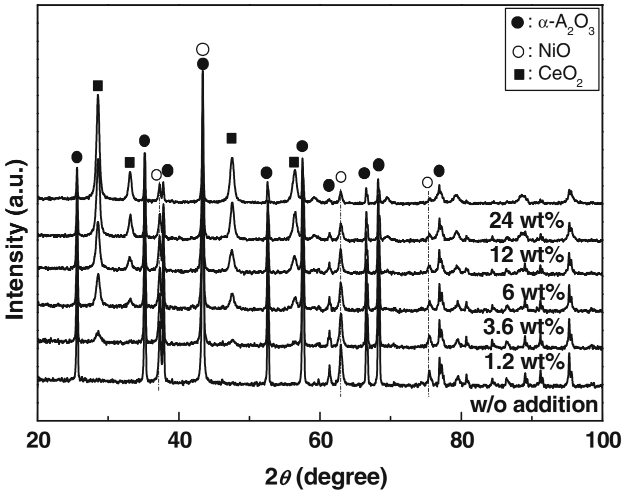

Fig. 1 XRD patterns of Ni–Ce/Al_2O_3 catalysts with various Ce content

Table 1 Characteristics of Ni–Ce/Al_2O_3 catalysts with various Ce content

Ce (wt%)	0	1.2	3.6	6	12	24
NiO size (nm)	32	29	30	24	21	28
BET surface area (m^2/g)	2.4	4.6	5.5	9.4	8.8	6.7
Ni surface area (m^2/g)	0.72	0.76	0.88	0.99	0.78	0.37
Ni dispersion (%)	0.90	0.96	1.1	1.2	0.97	0.47

dependent on the Ce content. It is interesting to note that as the Ce content increases, the intensity of NiO peak decreases. This XRD result implies that ceria promotion improves the dispersion of NiO.

H_2-TPR patterns of 12% Ni–Ce/Al_2O_3 catalysts with various Ce content are shown in Fig. 2. In the case of the Ni/Al_2O_3 catalyst without Ce promotion, reduction peaks with maxima at about 460 and 560 °C are observed. It is known that the lower temperature peaks can be assigned to the reduction of the relatively free NiO species, while the higher temperature peaks can be attributed to the reduction of complex NiO_x species, which strongly interact with the support [3]. As the Ce content increases, the reduction peak of free NiO species shifts toward high temperature due to a strong Ni to support interaction, resulting from the highly dispersed NiO particles. Wrobel et al. [26] reported that the reduction peak appearing at 630 °C can be ascribed to the strong interaction between NiO and Ni–CeO_2 solid solution. By the way, at Ce 12 and 24 wt%, there is a weak reduction peak at 830 °C. This peak is attributed to the reduction of segregated CeO_2 [27].

Table 1 summarizes the NiO crystallite size, BET surface area, Ni surface area, and metal dispersion of the Ce-modified Ni/Al_2O_3 catalysts with different Ce content. Ni/Al_2O_3 catalyst without ceria addition shows the largest NiO size. As Ce content increases up to 6 wt%, NiO size decreases while Ni surface area and metal dispersion increase. It is clear that the promotion of ceria in the Ni/Al_2O_3 catalysts improves the Ni dispersion on the support. On the contrary, 12 wt% Ce has negative effect on Ni dispersion. It is possible that the decrease of Ni dispersion and surface area is ascribed to agglomeration of Ni particles. In general, highly dispersed and small Ni crystallites have a strong metal to support interaction (SMSI) [28]. In Table 1, Ni/Al_2O_3 catalyst with 6 wt% Ce has the highest metal dispersion (1.2%) due to a strong metal to support interaction. The Ni surface area of the catalyst with 6 wt% Ce is higher than that of the catalyst with 12 wt% Ce. As expected from the TPR results (Fig. 2), the Ni surface area decreases due to agglomeration of Ni particles and the formation of a Ni–CeO_2 solid solution above 12 wt% Ce. It has been reported that it is difficult to reduce Ni^{2+} in Ni–CeO_2 solid solution [29].

3.2 Catalytic Test in CSCRM

The catalytic activities of Ce-modified Ni/Al_2O_3 catalysts are shown as CH_4 conversion with time on stream (TOS) in Fig. 3. The catalysts promoted with 6–12 wt% Ce reached the thermodynamic equilibrium state at 800 °C at a GHSV of 265,000 ml/h-g_{cat}, while the catalyst without Ce promotion showed the lowest CH_4 conversion. It can be explained that Ce promotion improves the catalytic activity owing to the supply of active oxygen species which results in preventing coke formation. Especially, it is noted that the catalyst promoted with 24 wt% Ce deactivates gradually and leads to the final CH_4 conversion of Ni/Al_2O_3 catalyst. This reaction result supports that the optimum Ce

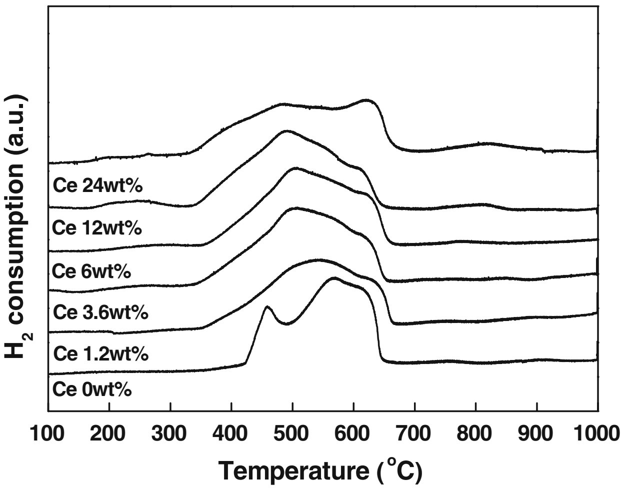

Fig. 2 TPR patterns of Ni–Ce/Al_2O_3 catalysts with various Ce content

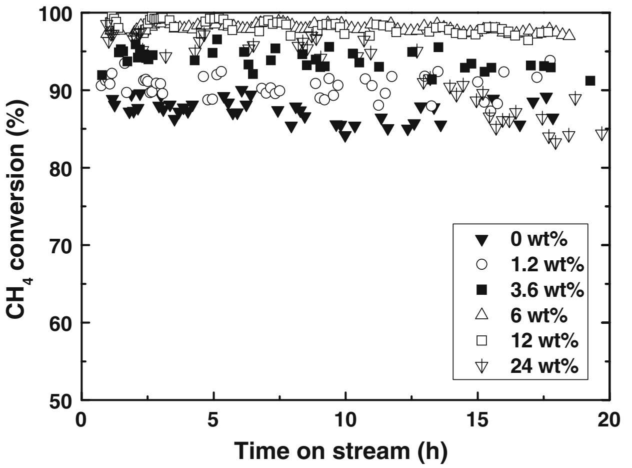

Fig. 3 Reaction data over Ni–Ce/Al_2O_3 catalysts with various Ce content (Reaction conditions: $T = 800$ °C, $P = 1$ atm, GHSV $=$ 265,000 ml/h-g_{cat})

Table 2 Comparison of reaction results over Ni–Ce/Al_2O_3 catalysts

Ce (wt%)	CH_4 conversion		CO_2 conversion	
	750 °C	700 °C	750 °C	700 °C
3.6	74	49	59	33
6	89	76	73	54
12	71	45	57	28
Theoretical equilibrium	92	86	72	52

All the data were obtained at the time on stream (TOS) of 15 h

content is required for the good catalytic performance and high coke resistance in Ce-modified Ni/Al_2O_3. To clearly identify the effect of Ce-modification on Ni/Al_2O_3 catalyst, reforming tests were carried out at 750 and 700 °C, respectively. It is known that coke formation is favorable at low temperatures [30]. The reaction results are summarized in Table 2. The catalyst modified with 6 wt% Ce exhibits the highest CH_4 and CO_2 conversion, while 12 wt% Ce shows the lowest conversion among the catalysts. The difference in catalytic performance appears to be related with the Ni surface area and Ni dispersion [27]. The catalyst promoted with 6 wt% Ce has the largest Ni surface area and Ni dispersion. As pointed out previously, this implies that Ce content of 6 wt% is optimal to obtain highly dispersed Ni particles on the support surface. As the reaction temperature decreases from 750 to 700 °C, both CH_4 and CO_2 conversion decreases.

The difference of catalytic activity with respect to coke formation was investigated by using SEM (Fig. 4). The used catalysts were collected after reforming reaction. It is evident that the degree of coke formation is related to the Ce content. There are a lot of filamentous carbon species on the surface of used Ni/Al_2O_3 catalyst with 3.6 wt% Ce. In the case of 12 wt % Ce, filamentous coke was scattered all over the catalyst particles. To show coke clearly, the magnified image of coke was inserted in Fig. 4c. In the contrary, the degree of coke formation was not severe at 6 wt% Ce. These results confirm that 6 wt% Ce is an optimum content to suppress coke formation. It means that catalyst with 6 wt% Ce has high coke resistance due to highly dispersed Ni particles with SMSI.

In summary, Ce-modified catalysts show high activity in CSCRM. Ceria can effectively produce active oxygen species from H_2O and CO_2. In addition, the optimum Ce content can make the highly dispersed Ni particles with strong metal to support interaction, resulting in high coke resistance.

Table 3 summarizes the H_2/CO ratio over Ni–Ce/Al_2O_3 catalysts with various Ce content in CSCRM. It has been confirmed that the optimum H_2/CO ratio (=2) is achieved, which is suitable for the F–T synthesis in GTL.

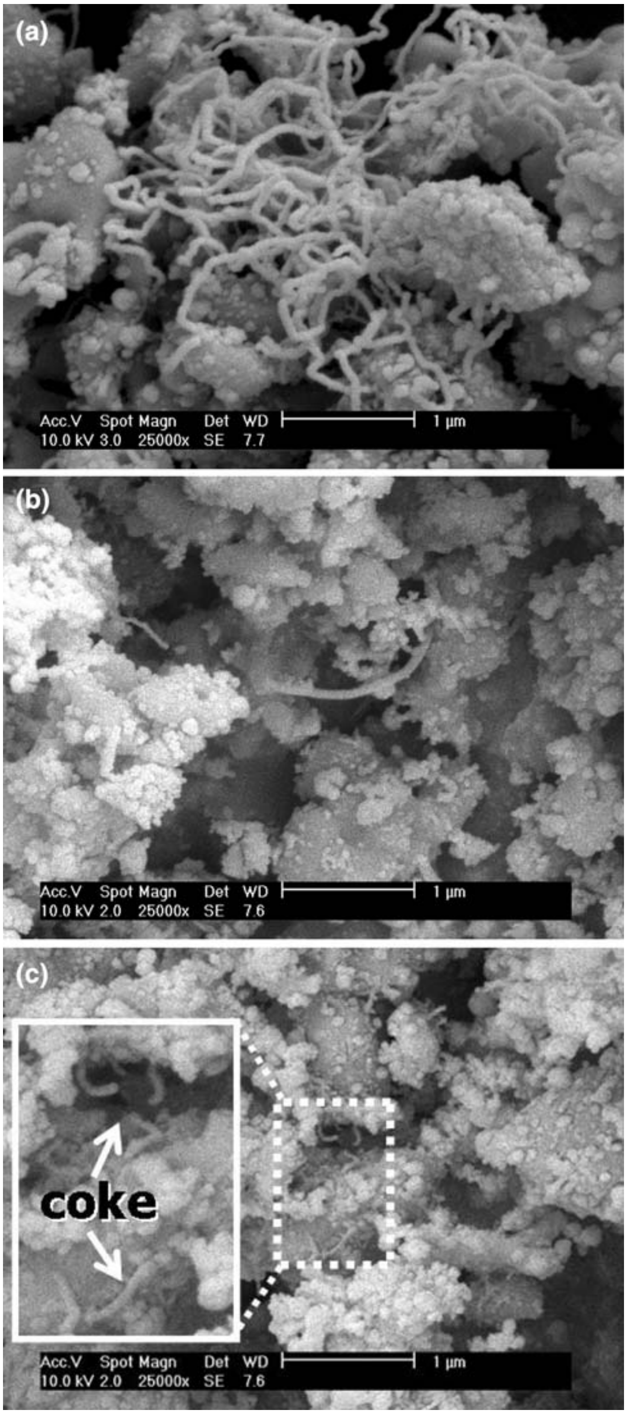

Fig. 4 SEM images of used Ni-Ce/Al_2O_3 catalysts with **a** 3.6 wt% Ce, **b** 6 wt% Ce and **c** 12 wt% Ce

Table 3 H_2/CO ratio over Ni–Ce/Al_2O_3 catalysts with various Ce content at 800 °C

Ce (wt%)	0	1.2	3.6	6	12	24
H_2/CO	2.0	1.9	2.0	2.0	2.0	2.0

4 Conclusion

The promotion of ceria on Ni/Al_2O_3 catalysts for CSCRM effectively suppresses the coke formation. As the Ce content is increased, NiO crystallite size decreases, because ceria improves Ni dispersion on the surface. In addition, ceria which has the high oxygen storage capacity provides the active oxygen species, resulting in suppressing coke formation. When catalysts are prepared with high Ce content, i.e., above 12 wt%, the catalytic activity decreases because of the agglomeration of Ni particles and segregation of CeO_2. The catalyst with 6 wt% Ce exhibits the highest catalytic activity as well as high coke resistance in CSCRM due to the effective oxygen transfer during the reaction and SMSI.

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