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SHORT COMMUNICATION

Performance of Ni catalyst supported on La-hexaaluminate in CO_2 reforming of CH_4

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Abstract−CO_2 reforming of CH_4 was performed using Ni catalyst supported on La-hexaaluminate which has been an well-known material for high-temperature combustion. La-hexaaluminate was synthesized by sol-gel method at various conditions where different amount of Ni (5-20 wt%) was loaded. Ni/La-hexaaluminate experienced 72 h reaction and its catalytic activity was compared with that of Ni/Al_2O_3. Ni/La-hexaaluminate shows higher reforming activity and resistance to coke deposition compared to the Ni/Al_2O_3 model catalyst. Coke deposition increases proportionally to Ni content. Consequently, Ni(5)/La-hexaaluminate(700) is the most efficient catalyst among various Ni/La-hexaaluminate catalysts regarding the cost of Ni in Ni(X)/La-hexaaluminate catalysts. BET surface area, XRD, EA, TGA and TPO were performed for surface characterization.

Key words: CO_2 Reforming of CH_4, Ni, La-hexaaluminate, Al_2O_3, Coke Deposition

INTRODUCTION

CO_2 reforming of CH_4 has attracted our attention due to its potential significance as an alternative to the conventional steam reforming. The process is very useful for the conversion of two of the cheapest carbon containing molecules, both of which are green house gases, to the valuable ($CO+H_2$) mixture of great value [1]. CO_2 reforming of CH_4 is also an effective way of making the synthesis gas with a suitable H_2/CO ratio for Fischer-Tropsch synthesis. So far, precious metals such as Ru, Rh, Pd, Pt and Ir have showed high reforming activities, however the high price is an inhibiting factor for the industrial application. Accordingly, supported Ni catalyst has been preferred even though it suffers from serious deactivation due to carbon deposition, sintering of Ni particles and phase transformation.

For the enhancement of activity and durability of the reforming catalyst, Ni was supported on La-hexaaluminate which has been well known material for high-temperature catalytic combustion. Hexaaluminate are of interest due to the high thermal stability originated from their peculiar layered structure that consists of γ-Al_2O_3 spinel block intercalated by planes in which the largest cations (Ba, Ca, La, and Sr) are located [2,3]. It has been reported that La-hexaaluminate shows good resistance towards poisoning by sulfur compounds or carbonates and sintering [4].

The objective of this study is to investigate the performance of Ni/La-hexaaluminate catalyst in CO_2 reforming of CH_4. The catalytic activity of Ni/La-hexaaluminate was compared with that of Ni/Al_2O_3 model catalyst.

EXPERIMENTAL

La-hexaaluminate was synthesized by sol-gel method using cetyltrimethylammonium chloride (CTACl, 25 wt%, Aldrich), $La(CH_3COO)_2\cdot xH_2O$ (99%, Aldrich) and alumina sol (10% Al_2O_3, 10-100 nm, Nissan) as starting materials. As an example, 50 g alumina sol was added to a mixture of lanthanum acetate (1.47 g) and CTACl (20 g) at a rate of 5 g min^{-1} under vigorous stirring and it was further stirred for 6 h for complete mixing. After the mixture was aged at 100 °C for 24 h, the mixture was dried at 100 °C. The obtained powder was calcined at 550 °C for 6 h and further at 1,200 °C for 6 h. In this step, various calcination temperatures were used for the modification of the structure. Then, 5-20 wt% Ni was loaded on La-hexaaluminate by using $Ni(NO_3)_2\cdot 6H_2O$ (97%, Junsei) as precursor and by incipient-wetness method. For comparison with Ni/La-hexaaluminate, Ni/Al_2O_3 was also synthesized by wet-impregnation using γ-Al_2O_3 (97.7%, Strem) support and used as a model catalyst. Each catalyst was designated as Ni(X)/La-hexaaluminate(Y) or Ni(X)/Al_2O_3, where X means the amount of Ni loaded and Y is the calcination temperature in the calcination step. BET surface area and pore structure were observed by ASAP2010 (Micromeritics) and the structure of Ni particles was analyzed by X-ray diffraction (Rigaku Miniflex, Cu kα source, 15 mA).

The catalytic activity of the Ni/La-hexaaluminate for the CO_2 reforming of CH_4 was examined and was compared with that of Ni/Al_2O_3. The reaction gas consisted of CH_4 and CO_2 with a molar ratio of 1 : 1 and flow rate of 20 ml/min (72,000 GHSV). All the reactions were carried out at 700 °C and lasted for 72 h for the durability tests. The reaction products were on-line analyzed by using a gas chromatograph (GC, Donam instruments). Elemental analysis (EA, LECO), thermogravimetric analysis (TGA, TA system) and temperature programmed oxidation (TPO, Micromeritics) were carried out for the investigation of the carbonaceous deposit on the catalyst surface.

RESULTS AND DISCUSSION

1. Surface Characterization

BET surface area, pore volume and pore diameter of La-hexaaluminate synthesized at various conditions and γ-Al_2O_3 were meas-

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Table 1. BET surface area, pore volume and pore diameter

Catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
γ-Al_2O_3	207.2	0.50	9.7
La-hexaaluminate (1,200)	44.8	0.16	14.1
La-hexaaluminate (900)	118.4	0.88	29.8
La-hexaaluminate (700)	212.8	1.04	19.6

ured and the data are shown in Table 1. BET surface area of La-hexaaluminate(1,200) is much smaller than that of Al_2O_3 and which depends largely on the calcination temperature. As the calcination temperature decreases, the surface area and the pore volume of La-hexaaluminate significantly increase. That is, the surface area of La-hexaaluminate(700) is about five times larger than that of La-hexaaluminate(1,200).

Fig. 1 shows the XRD spectra of Al_2O_3 and those of La-hexaaluminate calcined at different temperatures. In this figure, the spectra of La-hexaaluminate(900) or La-hexaaluminate(700) are different from that of La-hexaaluminate(1,200). In fact, the XRD spectrum of La-hexaaluminate(900) or La-hexaaluminate(700) resembles that of Al_2O_3, which means that the surface structures of La-hexaaluminate(900) and La-hexaaluminate(700) are rather similar

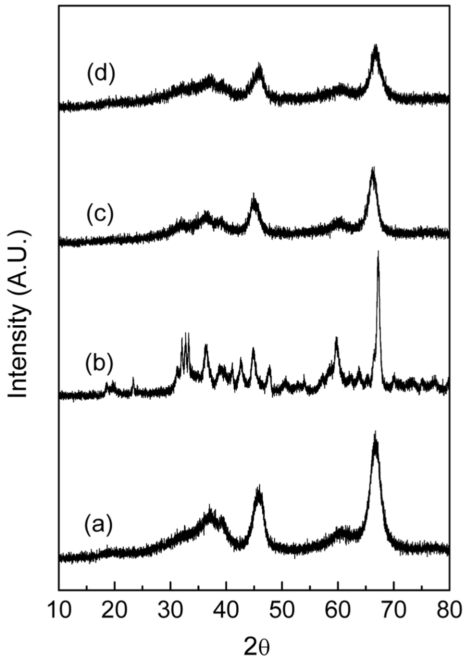
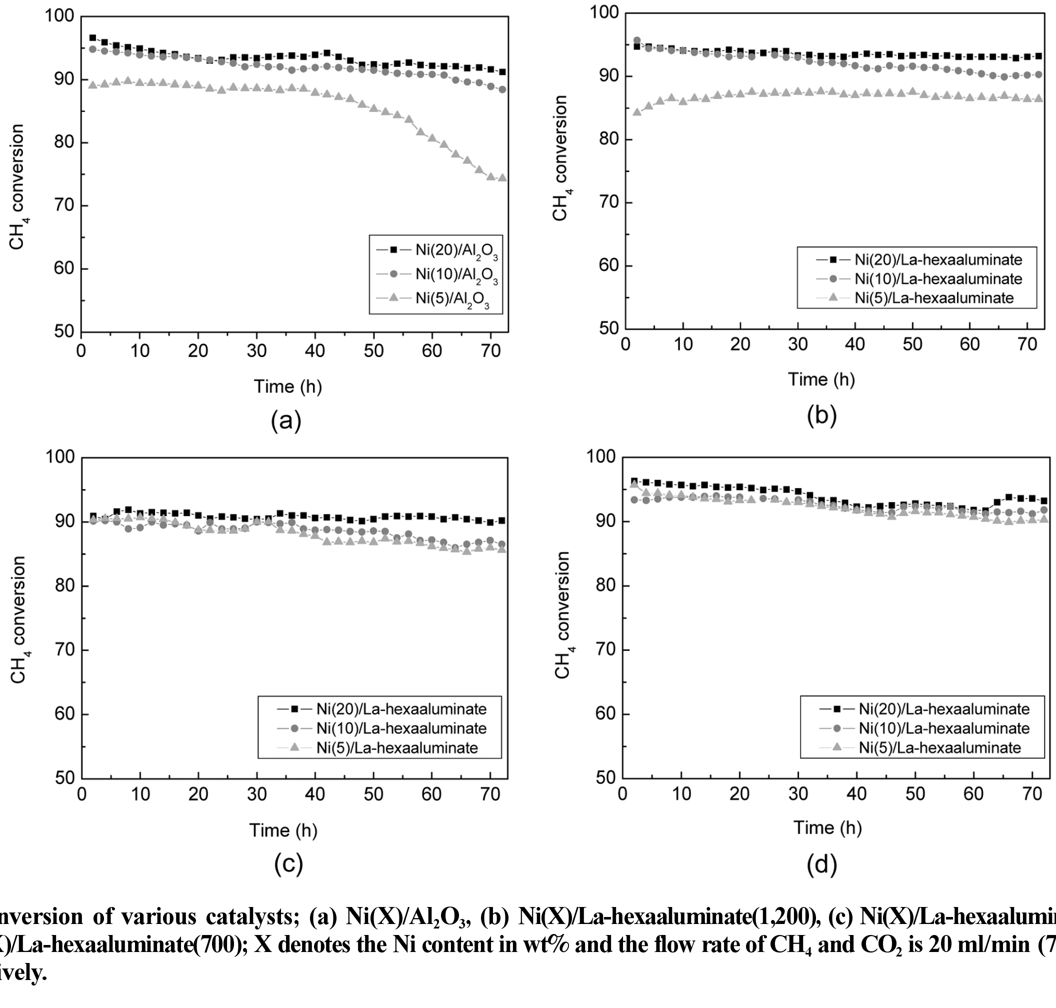


Fig. 1. XRD spectra of Al_2O_3 and La-hexaaluminate; (a) γ-Al_2O_3, (b) La-hexaaluminate(1,200), (c) La-hexaaluminate(900) and (d) La-hexaaluminate(700).



(a) (b) (c) (d)

Fig. 2. CH_4 conversion of various catalysts; (a) Ni(X)/Al_2O_3, (b) Ni(X)/La-hexaaluminate(1,200), (c) Ni(X)/La-hexaaluminate (900), and (d) Ni(X)/La-hexaaluminate(700); X denotes the Ni content in wt% and the flow rate of CH_4 and CO_2 is 20 ml/min (72,000 GHSV), respectively.

to that of Al_2O_3.

2. Reforming Activity

The reforming activities of Ni catalysts with various Ni loadings were examined and the results are indicated in Fig. 2. Comparing Fig. 2(a) with Fig. 2(b), CH_4 conversion of Ni(20)/Al_2O_3 at the beginning of the reaction is 97%, which is larger by about 2% than the case of Ni(20)/La-hexaaluminate(1,200). After 72 h reaction, the catalytic activity of Ni(20)/Al_2O_3 is somewhat decreased, but that of Ni(20)/La-hexaaluminate(1,200) is maintained almost unchanged. In the product distribution, each catalyst shows the relative ratio of the H_2 to CO in 1 : 1, though the amount of produced H_2 is somewhat greater than that of CO. Similar trends were observed in both cases of Ni(10) and Ni(5), with the exception of the differences of the catalytic activities between Ni(X)/Al_2O_3 and Ni(X)/La-hexaaluminate. In the case of Ni(5)/Al_2O_3, CH_4 conversion at the beginning of the reaction is somewhat larger than that of Ni(5)/La-hexaaluminate, but which significantly decreases with the lapse of reaction time. On the contrary, CH_4 conversion of Ni(5)/La-hexaaluminate(1,200) is almost unchanged even after 72 h reaction. CO/H_2 selectivity and H_2 yield show almost the same value irrespective of the catalyst used. For example, the selectivity of Ni(20)/La-hexaaluminate(700) and Ni(20)/Al_2O_3 are 1.08-1.09 and 1.06-1.13, respectively.

It is noteworthy that the reforming activity of Ni(X)/La-hexaaluminate(700) is similar or a little larger than that of Ni(X)/La-hexaaluminate(1,200), which is more significant at small Ni loading. That is, the catalytic activity of Ni(5)/La-hexaaluminate(700) is similar to that of Ni(20)/La-hexaaluminate(700). Moreover, its reforming activity is much larger than that of Ni(5)/La-hexaaluminate(1,200) or Ni(5)/La-hexaaluminate(900). The reason is that the surface area of La-hexaaluminate(1,200) is significantly decreased by the calcination at high temperature, as shown in Table 1, and the degree of Ni dispersion goes bad due to the decrease in surface area. In other words, the surface area of La-hexaaluminate(700) is rather larger than that of Al_2O_3; accordingly, the reforming activity is also better in the case of the former than the latter. In addition, the pore volume and the average pore diameter of La-hexaaluminate(700) are about twice larger than those of Al_2O_3, which is helpful for CH_4 reforming reaction. Consequently, the superior catalytic activity of Ni(5)/La-hexaaluminate is due to the large surface area of La-hexaaluminate(700) and the high dispersion of Ni particles.

3. Catalyst Deactivation

As illustrated in previous researches [5], the reforming activity of Ni catalyst in CO_2 reforming of CH_4 deteriorates mainly due to the coke deposition. Table 2 shows EA data of Ni catalysts supported on La-hexaaluminate(1,200) and Ni(X)/Al_2O_3 both of which have experienced 72 h reaction. It is noticeable that the carbon content increases proportionally to the Ni loaded amount, which is much larger in the case of Ni(X)/Al_2O_3 than in the case of Ni(X)/La-hexaaluminate(1,200). Accordingly, Ni/La-hexaaluminate is considered to be more resistant to coke deposition than Ni/Al_2O_3.

Table 2. EA data of Ni(X)/La-hexaaluminate(1,200) after the reforming reaction for 72 h

Catalyst	Carbon (wt%)
Ni(20)/La-hexaaluminate(1,200)	31.85
Ni(20)/Al_2O_3	69.15
Ni(10)/La-hexaaluminate(1,200)	10.58
Ni(10)/Al_2O_3	19.20
Ni(5)/La-hexaaluminate(1,200)	0.08
Ni(5)/Al_2O_3	0.66

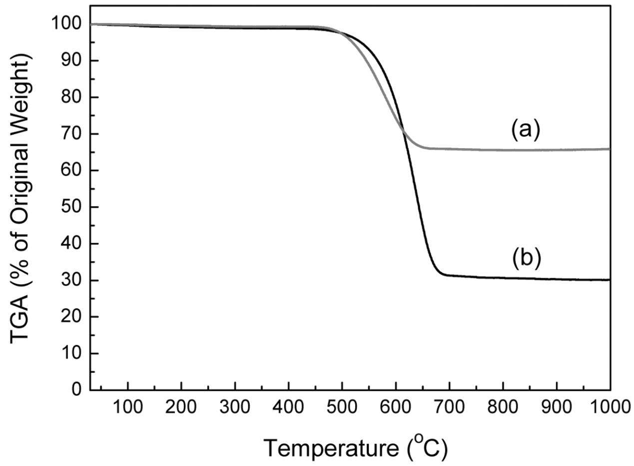


Fig. 3. TGA data of (a) Ni(20)/La-hexaaluminate(1,200) and (b) Ni(20)/Al_2O_3 after the reforming reaction for 72 h.

Fig. 3 shows the TGA results of Ni(20)/La-hexaaluminate(1,200) and Ni(20)/Al_2O_3 both of which experienced serious carbon deposition as shown in EA data (Table 2). It is remarkable that the amount of coke deposited on the catalyst surface is much smaller in the case of the former than the latter. The weight loss in TGA data is about 70% in the case of Ni(20)/Al_2O_3, while that is about 35% in the case of Ni(20)/La-hexaaluminate(1,200). In both cases, the oxidation of carbonaceous species begins at about 470 °C. However, the termination temperature in the case of Ni(20)/Al_2O_3 is somewhat higher than that in the case of Ni(20)/La-hexaaluminate(1,200). These above results mean that La-hexaaluminate facilitates the oxidation of the carbonaceous species on the catalyst surface and, accordingly, is more tolerant to coke deposition. Moreover, the carbonaceous spe-

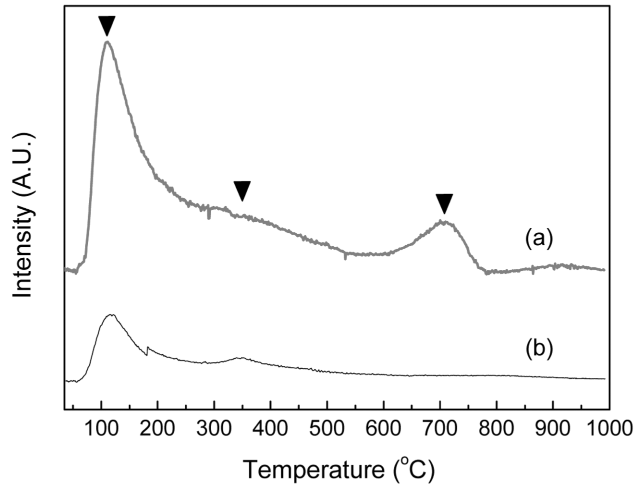


Fig. 4. TPO data of (a) Ni(20)/Al_2O_3 and (b) Ni(20)/La-hexaaluminate(1,200) after the reforming reaction for 72 h.

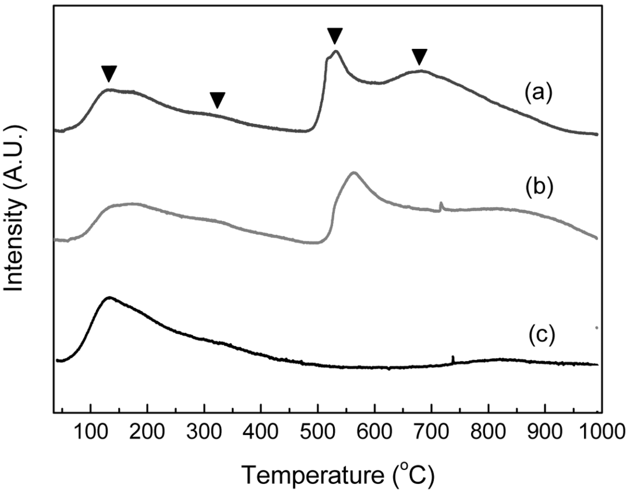


Fig. 5. TPO data of Ni(X)/La-hexaaluminate(700) after the reforming reaction for 72 h; (a) Ni(20)/La-hexaaluminate(700), (b) Ni(10)/La-hexaaluminate(700), and (c) Ni(5)/La-hexaaluminate (700).

cies is supposed to be more reactive on La-hexaaluminate(1,200) than on Al_2O_3. Therefore, La-hexaaluminate is preferable to Al_2O_3 as a support of reforming catalysts.

TPO was performed for the discrimination of the carbonaceous species on the catalyst surface. Fig. 4 shows the TPO spectra of Ni (20)/Al_2O_3 and that of Ni(20)/La-hexaaluminate(1,200). In both cases, there is a large peak at 110 °C (peak i) which is possibly due to the evaporation of moisture in micropores of catalyst surface. Another broad peak at 350 °C (peak ii) is supposed to be the surface carbon or the coke containing hydrogen (CH_x species) and the other one at 700 °C (peak iii) originates from carbon nanotubes [6]. This figure inidicates that the amount of coke deposited on Ni catalyst is much larger in the case of Ni(20)/Al_2O_3 than in the case of Ni(20)/La-hexaaluminate(1,200). Moreover, the last peak at 700 °C appears only in the case of Ni(20)/Al_2O_3. The reason is that La-hexaaluminate has essential advantages over the conventional Al_2O_3 support in resistance to carbon deposition [7].

The effect of Ni loading on coke deposition was investigated by TPO of Ni(X)/La-hexaaluminate(700), which shows excellent reforming activity and relatively small amount of carbonaceous deposits (Fig. 5). This figure shows that the amount of coke deposited on catalyst surface increases proportionally to Ni content. It is noteworthy that the oxidation peak at high temperature regions (>500 °C) increases at Ni(10), which is more significant in the case of Ni (20). In the case of Ni(20)/La-hexaaluminate(700), the coke that originated from carbon nanotubes greatly increases. The reason is that the reforming reaction is more vigorous on the catalyst of large Ni content and, therefore, it generates a large amount of carbonaceous deposit. Consequently, Ni(5)/La-hexaaluminate(700) is the most efficient catalyst in the reforming reaction considering the required amount of Ni.

Comparing the TPO results of Ni(20)/La-hexaaluminate(1,200) (Fig. 4(b)) and Ni(20)/La-hexaaluminate(700) (Fig. 5(a)), peak iii caused by carbon nanotubes appears only in the case of the latter though both catalysts show similar reforming activities as shown in Fig. 2. The reason is that the structure of La-hexaaluminate(700) is different from that of La-hexaaluminate(1,200), while it is very similar to that of Al_2O_3. In other words, La-hexaaluminate(1,200) shows superior coke resistance to La-hexaaluminate(700). These results can be proven by the decay of the reforming activity, which is more significant in the case of the latter catalyst.

CONCLUSION

In the CO_2 reforming of CH_4, Ni catalyst supported on La-hexaaluminate shows catalytic activity and resistance to coke deposition higher than Ni/Al_2O_3. The reason is that La-hexaaluminate promotes the oxidation of coke species on catalyst surface. Among the Ni catalysts supported on La-hexaaluminate, Ni(5)/La-hexaaluminate(700) is the predominant one. It shows a reforming activity similar to that of Ni(20)/Al_2O_3 or Ni(20)/La-hexaaluminate, despite the smaller Ni loading. Moreover, it shows the best resistance to coke deposition and the decay of reforming activity is insignificant even after 72 h reaction. Consequently, Ni(5)/La-hexaaluminate(700) is the most efficient catalyst in the reforming reaction considering the required cost of Ni.

REFERENCES

1. K. H. Kim, S. Y. Lee and K. J. Yoon, *Korean J. Chem. Eng.*, **23**, 356 (2006).
2. G. Groppi, C. Cristiani and P. Forzatti, *Appl. Catal. B*, **35**, 137 (2001).
3. K. S. Song, Y. S. Seo, H. K. Yoon and S. J. Cho, *Korean J. Chem. Eng.*, **20**, 471 (2003).
4. M. Johansson, Ph.D. Thesis, KTH Stockholm, Sweden (1998).
5. J. H. Edwards and A. M. Maitra, *Fuel Process. Technol.*, **42**, 269 (1995).
6. A. Djaidja, S. Lips, A. Kiennemann and A. Barama, *Catalysis Today*, **113**, 194 (2006).
7. Z. Xu, M. Zhen, Y. Bi and K. Zhen, *Appl. Catal. A*, **198**, 267 (2000).