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Effects of promoters and preparation procedures on reforming of methane with carbon dioxide over Ni/Al_2O_3 catalyst

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Abstract

Ni/Al_2O_3 catalysts promoted with alkaline earth (Mg and Ca) or lanthanide (La and Ce) oxides were prepared by co-impregnation or consecutive impregnation of nickel and promoter on γ-Al_2O_3 varying order. The reaction of reforming CH_4 with CO_2 was studied between 650 and 850°C at atmospheric pressure over these catalysts. It was found that both alkaline earth and lanthanide oxides exerted a promotion effect on the initial activity, but they likely behaved in different ways since the catalysts promoted with alkaline earth oxides were much more sensitive to the impregnation order of nickel than those promoted with lanthanide oxides.

Keywords: Methane; Carbon dioxide; Reforming; Lanthanide; Alkaline oxides

1. Introduction

The reforming of methane by carbon dioxide has recently received a revival of interest as it can generate syngas having a H_2/CO ratio around 1, suitable for specific synthesis processes such as the production of alcohols. Another reason for this renewed interest is environmental considerations since this reaction consumes carbon dioxide. The factor leading to increased environmental interest in this process is the endothermic nature of the reaction that makes it possible to store solar energy as synthesis gas.

It is well known that supported group VIII metals are good catalysts for this reforming reaction giving a high yield of synthesis gas. One serious problem is the catalyst deactivation by carbon deposition on the active surface. It has been well established that noble metals (Rh, Ru, Pt) do not suffer the carbon deposition while Co, Ni and Pd are very sensitive to deactivation by coking [1–13]. The expensive market prices of noble metals render their industrial application quite questionable. Thus, this leads to the investigation of supported catalysts consisting of non-noble metal and promoters, in order to obtain a catalyst having a high catalytic activity without suffering the coking deactivation.

Our work was aimed at investigating of the preparation of Ni/Al_2O_3 promoted with two groups of oxide, lanthanide (La and Ce) and alkaline earth metal (Mg and Ca) oxides, and their performance. The preliminary results on the effect of promoters and preparation methods on the reforming activity are reported in this paper.

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2. Experimental

2.1. Catalyst preparation

A series of Ni/Al_2O_3 catalysts were prepared by impregnating the support γ-Al_2O_3 with a solution containing a given concentration of metal nitrate salts. Different impregnation volume of the solution yielded different metal and/or oxide loading wt%, after evaporation-drying at 110°C overnight and calcination at 650°C in air for about 5 h. The γ-Al_2O_3 used is a commercial product with the following physical properties: $S_{BET} = 190\ m^2/g$, cylinder shape of $\phi = 2–3$ mm and length of 10–20 mm. It has been calcined at 650°C in air for 5 h prior to impregnation. The nitrate salts used are $Ni(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 4H_2O$, $Ce(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ of analytic grade. Three groups of catalysts were prepared according to the following detailed steps.

1. Co-impregnation of nickel oxide with promoter oxides.
2. Consecutive impregnation of nickel oxide and then promoter oxides.
3. Consecutive impregnation of promoter oxides and then nickel oxide.

In the case of consecutive impregnation, the first impregnation was carried out by impregnation of solution, evaporation, drying and calcination, and then the same operation was repeated for the second impregnation.

2.2. Reaction of CO_2 reforming CH_4

The reforming reaction was conducted in a fixed bed reactor of a stainless steel tube with inner diameter 8 mm at atmospheric pressure. The bar-shaped catalyst was cut into small size of 1–1.5 mm length and then packed in the reaction tube. The amount of 0.5 g catalyst resulted in a catalyst bed height of 30 mm, corresponding to a volume of 1.5 ml. The reactor tube (length 300 mm) was placed in a vertical tube furnace and connected to a supply of the reaction gas mixture preheated to about 200°C. A thermocouple was located outside the reactor tube wall at the position corresponding to the middle of the catalyst bed. The temperature measured was thus different from that inside of the catalyst bed; however, it was considered as the reaction temperature only for the purpose of comparison of the catalytic activity. The reactant gas, CH_4 (99.9%)/CO_2 (99.8%) = 1, passed over the catalyst at a flow rate of 280 ml/min, corresponding to a GHSV of $1.1 \times 10^4\ h^{-1}$. Before catalytic reaction, the catalyst was reduced at 650°C with a flow of 10% H_2 in N_2 at a rate of 240 ml/min for about 3 h. Afterwards, the reforming reaction was initiated from 650°C to 850°C and finished during 3 h.

Table 1
Method of catalyst preparation and metal (oxide) loading

Catalyst	Method	Metal (or oxide) loading wt.%
Pt/Al_2O_3	impregnation	1% Pt
Ni/Al_2O_3	impregnation	10% Ni
$Ni + CeO_2/Al_2O_3$	coimpregnation	10% Ni, 5% CeO_2
Ni-CeO_2/Al_2O_3	impregnation of NiO prior to CeO_2	10% Ni, 5% CeO_2
CeO_2-Ni/Al_2O_3	impregnation of CeO_2 prior to NiO	10% Ni, 5% CeO_2
$Ni + La_2O_3/Al_2O_3$	coimpregnation	10% Ni, 5% La_2O_3
Ni-La_2O_3/Al_2O_3	impregnation of NiO prior to La_2O_3	10% Ni, 5% La_2O_3
La_2O_3-Ni/Al_2O_3	impregnation of La_2O_3 prior to NiO	10% Ni, 5% La_2O_3
$Ni + MgO/Al_2O_3$	coimpregnation	10% Ni, 5% MgO
Ni-MgO/Al_2O_3	impregnation of NiO prior to MgO	10% Ni, 5% MgO
MgO-Ni/Al_2O_3	impregnation of MgO prior to NiO	10% Ni, 5% MgO
CaO-Ni/Al_2O_3	impregnation of CaO prior to NiO	10% Ni, 5% CaO

The reaction products were monitored using an on-line Varian 3400 gas chromatograph equipped with a thermal conductivity detector. The amount of water produced in the reforming reaction was too small to be considered in the calculation of product distribution.

3. Results

3.1. Prepared catalysts

The prepared catalysts are listed in Table 1.

Table 2
Concentration (mol%) of products for CO_2 reforming CH_4 over the catalysts

Catalyst/Al_2O_3	Products	650°C	700°C	750°C	800°C	850°C
Ni	$CO + H_2$	30	42	57	74	84
	CH_4	40	30	22	14	8.8
	CO_2	30	28	21	12	7.0
Pt	$CO + H_2$	33	45.3	53.6	64.6	73.3
	CH_4	37.8	30.7	26.5	20.4	16.2
	CO_2	29.2	23.9	19.9	14.8	10.5
Ni + CeO_2	$CO + H_2$	49	66.6	75.0	83.0	92.0
	CH_4	27.4	19.0	15.0	11.1	6.3
	CO_2	23.6	14.4	10.2	6.1	1.9
CeO_2-Ni	$CO + H_2$	55	65.4	76	89	94
	CH_4	25	19.3	14	6.7	3.7
	CO_2	20	15.2	10	3.9	1.7
Ni-CeO_2	$CO + H_2$	48.5	60.4	72.4	81.9	89.7
	CH_4	24.1	20.3	14.4	9.4	5.5
	CO_2	27.4	19.3	13.2	8.7	4.7
Ni + La_2O_3	$CO + H_2$	57.4	66.3	79.3	88.3	93.6
	CH_4	26	21	14.5	7.9	4.8
	CO_2	16.5	12.8	6.23	3.9	1.5
Ni-La_2O_3	$CO + H_2$	65.6	74.8	86.3	92.1	96.2
	CH_4	21.5	16.8	9.3	5.9	2.9
	CO_2	13.5	8.9	4.8	1.7	0.7
La_2O_3-Ni	$CO + H_2$	54.8	66.7	80	87.6	93.4
	CH_4	22.4	15.7	8.9	5.1	2.3
	CO_2	22.9	17.5	11.3	7.2	4.5
Ni + MgO	$CO + H_2$	37	50.2	63.8	80.4	90.0
	CH_4	32.7	26.1	21.4	11.5	6.5
	CO_2	30.3	23.7	14.8	8.1	3.5
Ni-MgO	$CO + H_2$	37.3	49	54	72.8	87.2
	CH_4	35.7	30.5	24.7	16.6	9.6
	CO_2	27.6	21	21.3	10.0	3.6
MgO-Ni	$CO + H_2$	63	74	85.6	92.2	96.2
	CH_4	20	14.6	8.5	5.2	2.8
	CO_2	17	11.4	5.9	2.6	1.0
CaO-Ni	$CO + H_2$	53	69	79.2	87.3	93.4
	CH_4	26	18.7	13	7.4	3.9
	CO_2	21	12.3	7.8	5.3	2.7

Thermodynamic equilibrium at 1 atm with $CH_4/CO_2 = 1$

	Products	650°C	700°C	750°C	800°C	850°C
	$CO + H_2$	72	85	91	94	96.5
	CH_4	14	7.0	4.5	3	2
	CO_2	9	4.5	2	2	1
	H_2O	5	3.5	2.5	1.0	0.5

3.2. Activity of CO_2 reforming CH_4

Over the catalysts in Table 1, the concentrations (mol%) of produced syngas ($CO + H_2$) and unconverted CH_4 and CO_2 are presented in Table 2, in comparison with those of thermodynamic equilibrium at the temperatures between 650 and 850°C [3]. The H_2/CO ratio in the product stream was found to be around 1 in any case.

The unpromoted catalyst 10% Ni/Al_2O_3 has the activity comparable with, and even higher than, the noble metal catalyst 1% Pt/Al_2O_3 at high temperatures 800–850°C. However, the concentration of syngas was still much less than that of thermodynamic equilibrium, even at temperature 850°C (Fig. 1).

When Ni/Al_2O_3 was promoted with lanthanide oxides such as CeO_2 or La_2O_3, the activity was greatly enhanced whatever the preparation methods were used: co- or successive impregnation, as is seen in Fig. 2a and Fig. 2b. At the temperature of 650°C, the syngas concentration was almost doubled, comparing with that over unpromoted Ni/Al_2O_3 catalyst. At the temperature of 850°C the syngas concentration was mostly over 90 mol% and close to the equilibrium limit 96.5 mol% (Table 2). It was demonstrated in Fig. 2a and Fig. 2b that the promotion effect of lanthanide oxide on the syngas production was slightly sensitive to the impregnation order of nickel and promoter onto alumina. In the case of CeO_2 (promoted catalyst), the impregnation of CeO_2 prior to nickel resulted in the best promotion effect on the syngas production (Fig. 2a); while in the case of La_2O_3 the impregnation of nickel prior to La_2O_3 gave the best promotion effect (Fig. 2b); and with these catalysts the syngas concentrations at 800–850°C were very close to the equilibrium

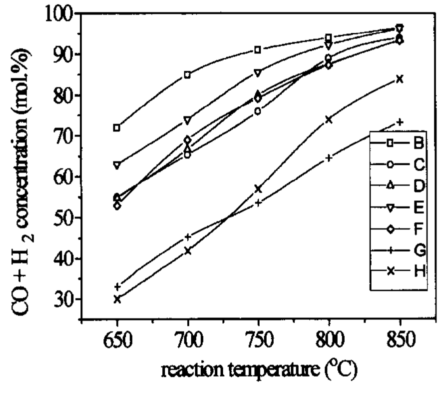

Fig. 1. Promoter effect on reforming methane with carbon dioxide over the catalysts Ni/Al_2O_3: B, thermodynamic equilibrium concentration; C, $Ce\text{-}Ni/Al_2O_3$; D, $La\text{-}Ni/Al_2O_3$; E, $Mg\text{-}Ni/Al_2O_3$; F, $Ca\text{-}Ni/Al_2O_3$; G, Pt/Al_2O_3; H, Ni/Al_2O_3.

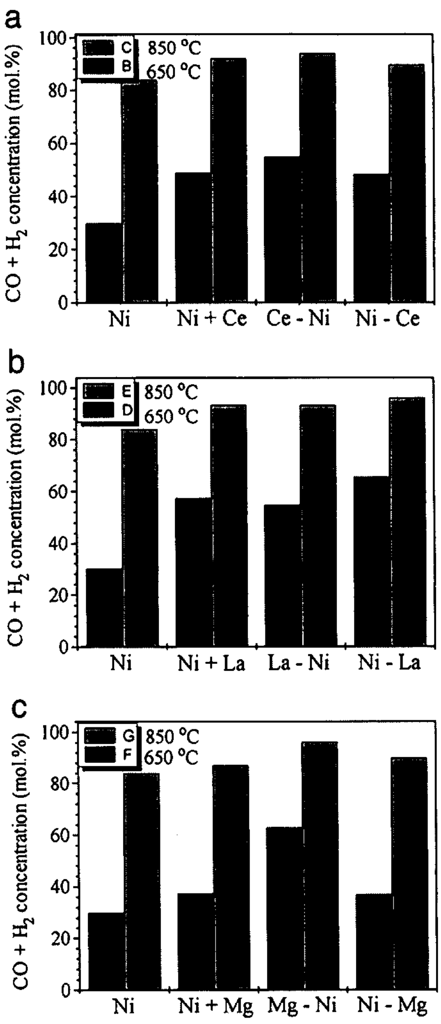

Fig. 2. (a) Influence of the impregnation order of nickel and promoter CeO_2 on the production of $CO + H_2$ at a temperature of (B) 650°C and (C) 850°C. (b) Influence of the impregnation order of nickel and promoter La_2O_3 on the production of $CO + H_2$ at a temperature of (D) 650°C and (E) 850°C. (c) Influence of the impregnation order of nickel and promoter MgO on the production of $CO + H_2$ at a temperature of (G) 650°C and (F) 850°C.

limit (Table 2 and Fig. 1). Additionally, the promotion effect of La_2O_3 was better than that of CeO_2.

The addition of alkaline earth metal oxides like MgO or CaO to Ni/Al_2O_3 also increased the syngas concentration (Table 2 and Fig. 1). However, the promotion effect by these metal oxides was very sensitive to the preparation methods, apparently being different from the behavior of lanthanide oxides, as shown in Fig. 2c. When the oxide MgO was impregnated onto NiO/Al_2O_3 the promotion effect on the syngas production was very small; while the impregnation of MgO or CaO prior to nickel resulted in a remarked increase of syngas production, the syngas concentration being close to the equilibrium limit at 850°C (Fig. 1). The effect of MgO was found to be greater than that of CaO.

In conclusion, the activity of these catalysts (Table 1), i.e. the syngas production (Table 2), decreased following the order:

Ni-La, Mg-Ni > Ce-Ni > Ca-Ni, La-Ni, Ni + La > Ni + Ce > Ni-Ce > Ni + Mg > Ni-Mg > Ni, Pt

4. Discussion

Let us mention that when Rh was supported on different carriers such as SiO_2, TiO_2, Al_2O_3, MgO, CeO_2, and Y_2O_3-ZrO_2 [14], the initial specific activity was found to be strongly depended on the carriers and also on the metallic particle size with the carriers of TiO_2 and SiO_2; for supported nickel catalyst, the strong support effect was revealed by Takyasu et al. [15], ultrafine single-crystal magnesium oxide used as support resulted in the best activity in comparison with the supports like SiO_2, γ-Al_2O_3 and MgO decomposed from $Mg(NO_3)_2$, and this seems to be related to the fact that the adsorbed species CH_X ($X > 2$) [16] on Ni/MgO involve a much higher amount of hydrogen in comparison with that on other catalysts and will not easily be transformed into kinds of coke; Martin and co-workers [17] showed that the initial activity was greatly influenced by the states of the metallic nickel phase such as reduction, dispersion and surface decoration. Obviously, several variables affect the catalytic activity of CO_2 reforming CH_4. Our experimental results are going to be discussed on the basis of the known literature data.

4.1. Interaction of nickel and promoter with alumina

It was reported that when nickel was supported on silica [18,19] or alumina [20], the nickel reducibility was strongly affected by nickel-support interaction and the metallic nickel dispersion was essentially determined by the dispersion of Ni(II) before being reduced.

It was experimentally established [21–23] that when a γ-alumina support is impregnated with Ni(II) ions and heated to a temperature of about 600°C, two reactions occur concurrently on the alumina surface; one produces a ''surface spinel'' somewhat like $NiAl_2O_4$ and the other gives segregation of free nickel oxide. The nickel oxide supported on alumina surface is in weak interaction with alumina surface and easily reducible at the temperatures between 350°C and 700°C, while the nickel surface compound like $NiAl_2O_4$ is in strong interaction with alumina and difficult to be reduced below 700°C in H_2. Additionally, the proportion of nickel surface compound to free nickel oxide increases with the increase of calcination temperature and might be lowered through an addition of other metal ions prior to Ni(II) on the alumina surface.

Similarly, a cation of promoter such as Mg(II), Ca(II), Ce(IV) and La(III) could also interact with alumina surface during a thermic treatment of the sample containing such metal nitrates, since metal oxide formed from decomposition has basic properties and will react with the acidic hydroxyl groups on alumina surface to produce a surface compound, as mentioned in reference [24,25]. With respect to Ni(II) ions, a cation of promoters such as Mg(II), Ca(II), Ce(IV) and La(III) could serve as a competitor to interact with alumina when they coexist at alumina surface, according to [23].

4.2. MgO and CaO as promoter

CaO was reported to have a promotion effect on the reforming methane with carbon dioxide over the Ni/CaO-Al_2O_3 catalyst prepared by the impregnation of CaO-modified alumina with nickel nitrate [26]. This promotion action of CaO was attributed to an enhanced reducibility of nickel as confirmed with TPR study and a chemisorption of H_2 showed that the nickel dispersion was nearly not influenced by the presence of CaO on alumina surface. For the catalysts in Table 1 promoted with alkaline earth oxides CaO and MgO, a large promotion action was found only when promoter was impregnated prior to nickel onto alumina surface like in MgO-Ni/Al_2O_3 and CaO-Ni/Al_2O_3; whereas little is observed for the catalysts like Ni-MgO/Al_2O_3 and Ni + MgO/Al_2O_3. This result is illustrated in Fig. 2c. Our results concerning the promotion action of alkaline earth oxides are in agreement with the authors [26]. Moreover, they tend to support the attribution of CaO promotion action in this reference [26]. In fact, these promoters were added in catalyst Ni/Al_2O_3 after impregnation of alumina with nickel and calcination as well, like in Ni-MgO/Al_2O_3, the cations such as Mg(II) and Ca(II) would not be possible to greatly lower the portion of nickel, which is in strong interaction with alumina, and to enhance the reducibility of impregnated nickel in a dispersed oxide state, since nickel already interacted with alumina surface before the introduction of Mg(II) or Ca(II) to alumina. It is worthwhile noticing here that the increase in the portion of Ni-Al_2O_3 interactions with the calcination temperature decreases the nickel reducibility, and causes a decrease in activity for the low temperature reaction between CO_2 and CH_4 [27].

4.3. La_2O_3 and CeO_2 as promoter

According to Blom et al. [24], the addition of La_2O_3 in Ni/Al_2O_3 resulted in a decrease of reforming activity. This does not agree with our results presented in Fig. 2b. This may be due to the difference in catalyst pretreatment. The temperature of calcination adopted by us in the preparation of catalysts (Table 1) is 650°C; while in the case of [24], the La_2O_3 modified alumina was calcined at 1350°C and the nickel containing sample was again calcined at 900°C; this resulted in a lowered reducibility of nickel as confirmed by TPR.

The metal catalysts promoted with lanthanide oxide have extensively been studied in the following two reactions: steam reforming of hydrocarbons and synthesizing methane or methanol from syngas. Ross and co-workers [28] prepared and characterized the coprecipitated Ni/Al_2O_3 promoted with the oxides of TiO_2, La_2O_3 and CeO_2 and studied these catalysts in methanation reaction. It was found that only La_2O_3 did vary nickel reducibility, and the reduction temperature of nickel decreased with increasing the amount of lanthanum; the decrease in nickel particle size on alumina surface was less than 30% whatever promoters were used. The impregnated Ni/Al_2O_3 catalysts promoted with lanthanide oxides were studied by the authors [29]. It is worthwhile to note that two opposite impregnation orders of nickel and promoter were adopted, as did in our catalyst preparation. When the promoter was impregnated prior to nickel, both the enhancement of reducibility of nickel and the decrease of nickel particle size were reported. However, the influence of promoter on nickel particle size was not observed when nickel was impregnated prior to promoter. These literature data seem to indicate that different ways to add a promoter into Ni/Al_2O_3, as the two opposite impregnation orders of nickel and promoters applied in the preparation of promoted catalysts in Table 1, would result in a possible difference in nickel reducibility and that in nickel dispersion. This could be speculated in term of the interactions of nickel and promoter with alumina surface, as discussed previously. When nickel was impregnated prior to promoter as in Ni-La_2O_3/Al_2O_3 and Ni-CeO_2/Al_2O_3 (Table 1), the promoter would be difficult to vary both nickel reducibility and nickel particle size since nickel had interacted with alumina surface; when promoter was impregnated prior to nickel as in La_2O_3-Ni/Al_2O_3 and CeO_2-Ni/Al_2O_3 (Table 1), the enhancement of nickel reducibility and the decrease of nickel particle size would occur as mentioned in reference [29]; when promoter and nickel were co-impregnated in alumina (Table 1), these two different metal ions would concurrently interact with alumina surface. However, these three different ways to introduce a promoter (La_2O_3 or CeO_2) in Ni/Al_2O_3 (Table 1) did not lead to a large difference of promotion action in reforming methane with carbon dioxide, and this is illustrated in Fig. 2a and Fig. 2b. This is remarkably different from the MgO-promoted catalyst as shown in Fig. 2c. These experimental results likely indicate that the observed promotion action of lanthanide in Fig. 2a and Fig. 2b could not be attributed to the possible variations of nickel reducibility and nickel dispersion caused by the different ways to add a promoter.

It was clearly shown that the impregnation of La_2O_3 after NiO in alumina resulted in the best promotion action (Fig. 2a). This leads us to the discussion about metal–lanthanide oxide interaction. The lanthanide oxide-promoted catalysts were found to have a higher activity for the reactions of $CO + H_2$ [28,30–36] and steam reforming [29] than do the unpromoted catalysts. This promotion action was successfully interpreted by metal–lanthanide oxide interaction. Bell and co-workers [30–36] have studied the catalysts of Pd/SiO_2, Pd/lanthanide oxide and lanthanide oxide promoted Pd/SiO_2 in methanation reaction. The introduction of different lanthanide oxides into the Pd/SiO_2 catalyst, just as the way to prepare the catalysts of Ni-La_2O_3/Al_2O_3 and Ni-CeO_2/Al_2O_3 (Table 1). It was experimentally confirmed that there exists a partial coverage of the Pd particles by promoter oxides. Upon the reduction of the catalysts, part of promoters in contact with Pd was also reduced. The partially reduced lanthanide oxide species covering the Pd particles reduced the amounts of H_2 and CO that could be adsorbed on the metal, but aided the dissociation of CO and raised thereby the activity for CH_4 production in comparison to that over Pd/SiO_2. After that, Ross and co-workers [28] have carried out the studies on coprecipitated catalysts Ni/Al_2O_3 promoted with TiO_2, La_2O_3 and CeO_2 and an increased activity in methanation was found. It was clearly demonstrated that the interaction of nickel with the partially reduced promoter oxides had to be kept in order to produce the promotion action. This promotion action was considered to be associated with the variation of CO and H_2 adsorption on nickel surface due to partially reduced promoter oxides interacting with nickel in the catalyst. A similar attribution of lanthanide-promotion action, named as lanthanide-embedment effect, was also made for the lanthanide oxide-promoted Ni/Al_2O_3 in steam reforming methane by the authors [29]. These literature results lead us to suggest that for the lanthanide promoted Ni/Al_2O_3 catalysts (Table 1), the observed promotion effect on CO_2 reforming CH_4 (Fig. 2a and Fig. 2b) may be attributed to the interaction between lanthanide oxide and nickel, which may likely cause a variation of CH_4 and CO_2 adsorption as well as their dissociation on active surface. Additionally, CeO_2 [37] and MnO_x-based [38] catalysts were reported to be also active in the reaction of CO_2 reforming CH_4, but with lower activity than the group VIII metals; over seventeen unsupported oxides including lanthanide [39], syngas $CO + H_2$ was found to be the dominant products in the reaction of CH_4 with CO_2 at 850°C. It is therefore difficult to exclude that the lanthanide oxide added in Ni/Al_2O_3 alone participates in reforming giving directly rise to the promotion effect on reforming. To further clarify the principles of promotion action of alkaline earth and lanthanide oxides, other experimental work is being done.

5. Conclusions

The addition of alkaline earth oxides (MgO and CaO) or lanthanide oxides (CeO_2 and La_2O_3) in Ni/Al_2O_3 catalyst was able to produce a promotion effect on the reaction of CO_2 reforming CH_4.

For alkaline earth oxides, the promotion effect observed is dramatically sensitive to the methods of catalyst preparation – co-impregnation and successive impregnation with varying the impregnation order of nickel and promoter. For lanthanide oxides it is, however, not too sensitive to the preparation methods. Very likely, these two oxides behave differently in promotion action.

The observed promotion action in reforming was interpreted on the basis of literature data. The promotion actions of alkaline earth and lanthanide oxides are not likely related to the possible variation of metal dispersion in Ni/Al_2O_3. The promotion action of alkaline earth oxide is probably associated with weakening the nickel–alumina interaction relative to the unpromoted Ni/Al_2O_3 catalyst and promotion effect of lanthanide oxide is probably related to the nickel–lanthanide oxide interaction in the promoted Ni/Al_2O_3 catalyst.

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