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A novel KCaNi/α-Al_2O_3 catalyst for CH_4 reforming with CO_2

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A potassium and calcium co-promoted nickel catalyst (KCaNi/α-Al_2O_3) prepared by a direct impregnation method possessed a high activity, high stability and excellent coke resistance properties in CH_4 reforming with CO_2. XRD, XPS and H_2-TPR characterizations indicated that (i) Ca and K strengthened the interaction between Ni and α-Al_2O_3 and promoted the formation of a unique $NiAl_2O_4$ phase on the surface of the catalyst and (ii) Ca and K increased the dispersion of Ni and retarded its sintering. Coking reactions (CH_4 temperature-programmed decomposition and O_2-TPO) disclosed that K reduced carbon formation via CH_4 decomposition.

KEY WORDS: CH_4; dry reforming; KCaNi catalyst; TPR; TPSR; XPS.

1. Introduction

CH_4 reforming with CO_2 has attracted much attention in the past 20 years for its low H_2/CO ratio in the product gas and its utilization of these two greenhouse gases:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad (\Delta G = -150.56\,\mathrm{kJ/mol},\ 1100\,\mathrm{K}). \tag{1}$$

A supported Ni catalyst was popular for use in this reaction for its high activity and low price; however, Ni deactivated easily due to coke deposition and metal sintering. Many kinds of promoters and promotion methods were tried toward the improvement of the Ni catalyst, but it was difficult to retain both the activity and the stability at high levels [1]. At the same time, mechanism studies indicated that the reforming activity and coke resistance of the catalyst depend on the nature of surface Ni species since the activation of CH_4 and CO_2 are structure-sensitive processes [2,3]. On supported Ni catalysts, CH_x ($1 \leq x \leq 3$) fragments form via stepwise decomposition of CH_4, and the retained amount of H atoms (x value) depends strongly on the surface Ni particles and the properties of the supports [4,5]. Deep dehydrogenation of CH_4 needs a large ensemble of metal atoms because the intermediate CH_x requires a concomitant occupation of higher coordination sites [6–8]. It is generally accepted that CO_2 chemisorption and dissociation on Ni is dominated by electron transfer and requires the formation of an anionic CO_2^- precursor [2,3]. Further studies indicated that stronger chemisorption of CO_2 and weaker chemisorption of CH_4 are helpful for the reduction of carbon deposition [9].

Alkali and alkaline earth metals (such as K, Na, Ca and Mg) possess the potential to have several kinds of effects on the physicochemical properties of Ni catalysts in reforming reaction: (a) influence on the electronic properties of the Ni clusters as well as their dimensions, (b) modification of the acidity of the support surface and (c) surface enrichment of CO_2 through stabilization of surface carbonate species [10–13]. In published papers, Ca was popularly used as a modification of support materials, but the coke resistance of these modified material-supported Ni catalysts was not good enough [14–17]. In previous studies on Ca-promoted Ni/α-Al_2O_3 catalysts, it was found that a small amount of Ca (Ca/Ni < 0.1, mole ratio) strengthened the interaction between Ni and support and increased the reforming activity and the stability. However, a greater amount of Ca occupied the limited surface of α-Al_2O_3 and bulk NiO without interaction with the Al_2O_3, which in turn enhanced coke deposition and accelerated deactivation [18]. The addition of K to Ni/Al_2O_3 catalysts resulted in the reduction of not only the coke formation but also the reforming activity [12,19]. It was found that K could divide the nickel surface into smaller ensembles, while the covering of the surface of the Ni particles with K reduced the reforming activity. Walter *et al.* have provided evidence that surface OH groups preferentially react with the surface CH_x species rather than surface O [20], which means that the addition of K would increase the amount of surface OH due to its strong basicity and increase the gasification of the intermediate CH_x fragment. Chang *et al.* have reported that a zeolite-supported KNiCa catalyst prepared by the molten salt ion-exchange method showed a stable activity in CH_4 reforming with CO_2 [21,22]. However, the preparation method of this zeolite-supported catalyst was quite complex and the thermal stability of the ZSM-5 support also limited its application.

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For potential applications, promotion of Ni/α-Al_2O_3 is more practical. The investigation of the promotion effect of K and Ca on the surface of Ni particles is important for designing more effective and stable catalysts. In this research, K and Ca co-promoted Ni catalysts were prepared by a direct impregnation method and used in CH_4 reforming with CO_2. The promoted catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction with H_2 (H_2-TPR). In order to study the activation process of CH_4, a coking reaction via CH_4 decomposition was carried out. A synergetic effect of K and Ca was revealed by these characterizations.

2. Experimental

The catalysts were prepared by a co-impregnation method. α-Al_2O_3 (kindly supplied by Basic Chemicals Research Laboratory, Sumitomo Chemical Co. Ltd, Japan; BET surface area, 9.0 m^2/g) was impregnated in a mixed solution of KNO_3, $Ca(NO_3)_2 \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemicals, Japan), dried at 120 °C for 12 h and finally calcined at 800 °C in stagnant air for 3 h. Each catalyst (50 mg) was reduced in H_2 at 800 °C for 1 h in a fixed-bed reactor (quartz, 6 mm inner diameter) purged by Ar and the reforming reaction was carried out under a stoichiometric CH_4 and CO_2 (1 : 1) mixture without dilution. After reaction, each catalyst was analyzed by TG-DTA (TAS 200, Japan) from 25 to 700 °C at 5 °C/min in air for the measurement of the coke formed during the reaction.

XRD was carried out using a RINT2000 system (Rigaku, Japan). An anode of CuKα (40 kV, 40 mA) was used as the X-ray source. The mean size of nickel crystallites was determined from the broadening of the Ni(111), according to the Scherrer–Warren equation [23–25]. XPS analysis was carried out using an ESCA 3200 (Shimadzu, Japan) spectrometer, which was equipped with a concentric hemispherical analyzer. An MgKα (1253.6 eV) X-ray source was used for excitation. The spectrometer was operated under a base pressure of 3×10^{-6} Pa in a chamber. Samples were pretreated in a vacuum at 300 °C for 2 h. Besides Ni $2p_{3/2}$ electrons, O 1s, Al $2p_{3/2}$, Ca $2p_{3/2}$ and K $2p_{3/2}$ levels were detected at the same time as the reference for analysis. The binding energies (BEs) were calibrated with respect to the Al $2p_{3/2}$ value of 74.93 eV [26–28].

H_2 temperature-programmed reduction (H_2-TPR) and the coking reaction via CH_4 temperature-programmed decomposition were carried out using a TPD 51 system (Belsorp, Japan), which was equipped with an online mass analysis system. In the H_2-TPR analysis, each catalyst (100 mg) was reduced from 50 to 950 °C at 15 °C/min in a reducing H_2/He mixture (5% H_2, total 50 ml/min). The H_2O produced ($m/e = 18$) was recorded as a function of temperature because the consumption of H_2 ($m/e = 2$) was a negative peak. In the coking reaction, each catalyst (100 mg) was initially reduced in H_2 at 800 °C for 1 h; after cooling in He, the sample was then tested from 50 to 830 °C at 10 °C/min under 10% CH_4 in He (total 50 ml/min). CH_4 ($m/e = 16$) and the H_2 ($m/e = 2$), CO ($m/e = 28$) and H_2O ($m/e = 18$) produced were recorded as functions of temperature. After CH_4 decomposition, the carbon formed on the surface of each catalyst was characterized by O_2 or CO_2 temperature-programmed oxidation (O_2-TPO or CO_2-TPO) under 10% O_2 or CO_2 (He in balance) from 100 to 850 °C at 10 °C/min.

3. Results and discussion

The activities of pure Ni/α-Al_2O_3, $Ca_{0.1}$Ni/α-Al_2O_3, $K_{0.5}$Ni/α-Al_2O_3 and K–Ca co-promoted $K_{0.5}Ca_{0.1}$Ni/α-Al_2O_3 catalysts in CH_4 reforming with CO_2 are summarized in table 1. It was found that the stability of the pure Ni/α-Al_2O_3 catalyst was lower compared with the promoted samples. K and Ca showed different effects on the activity of Ni in each of the promoted catalysts. $Ca_{0.1}$Ni/α-Al_2O_3 showed a higher reforming

Table 1
Activity of promoted Ni/α-Al_2O_3 for CH_4 reforming with CO_2

Ca/Ni (mol)	Initial conversion [a] (%)		Final conversion [b] (%)		Coke [c] (mg/g-cat/h)	Stability [d] (%)
	CH_4	CO_2	CH_4	CO_2		
Ni/α-Al_2O_3	71.5	77.1	67.4	73.7	24.0	−5.74
$Ca_{0.1}$Ni/α-Al_2O_3	84.1	84.9	83.1	84.8	73.0	−1.19
$K_{0.5}$Ni/α-Al_2O_3	64.1	71.9	63.6	71.5	0.0	−0.78
$K_{0.5}Ca_{0.1}$Ni/α-Al_2O_3	74.4	79.3	75.0	80.0	0.0	+0.08

Note: Rection conditions: 800 °C; CH_4, 25 ml(STP)/min; CO_2, 25 ml(STP)/min; catalyst, 50 mg; space velocity, 60 000 ml/(g-cat h).

[a] 30 min on stream.

[b] 240 min on stream.

[c] Average data during 240 min on stream.

[d] Defined as: (final conv. of CH_4 – initial conv. of CH_4)/initial conv. of $CH_4 \times 100\%$.

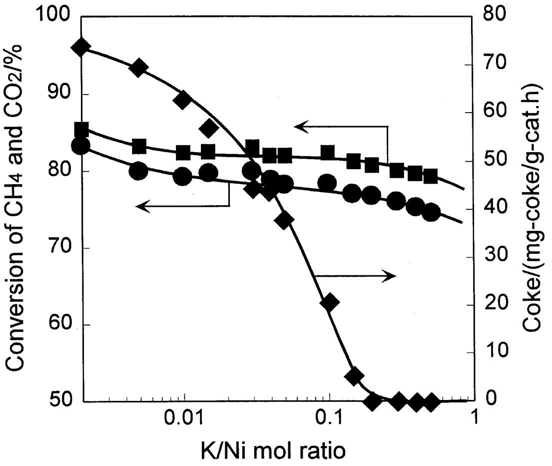

Figure 1. Effect of the amount of K added on the activity of $K_xCa_{0.1}Ni/\alpha$-Al_2O_3: (■) conversion of CO_2, (●) conversion of CH_4, (◆) coke formation rate. Reaction conditions: 800 °C; catalyst, 50 mg; CH_4, 25 ml/min; CO_2, 25 ml/min; space velocity, 60 000 ml/(g-cat/h).

activity and higher coke formation rate. On the other hand, $K_{0.5}Ni/\alpha$-Al_2O_3 showed a lower reforming activity and reduced coke formation. $K_{0.5}Ca_{0.1}Ni/\alpha$-Al_2O_3 exhibited the highest stability, high activity and excellent coke resistance. These results indicated that K and Ca had synergetic effects in the co-promoted sample. The advantages of K and Ca were retained and combined, while their negative influences were overcome.

Figure 1 shows the effects of different amounts of K on the activity of $K_xCa_{0.1}Ni/\alpha$-Al_2O_3. With the addition of K, the coke formation rate decreased quickly from 73.0 mg-coke/g-cat/h for $Ca_{0.1}Ni/\alpha$-Al_2O_3 or 24.0 mg-coke/g-cat/h for Ni/α-Al_2O_3 to zero, while the reforming activity decreased slightly. A stable, coke-free reforming process proceeded on the surface of $K_xCa_{0.1}Ni/\alpha$-Al_2O_3 catalysts when the amount of K added was higher than 0.2 ($x \geq 0.2$, mole ratio of K/Ni). Both the activity and the stability of $K_{0.2}Ca_{0.1}Ni/\alpha$-Al_2O_3 were higher than those of pure Ni/α-Al_2O_3.

Table 2
Ni crystallite size detected by XRD

Catalyst	Ni crystallite size (nm)[a]	
	Fresh[b]	Used[c]
Ni/α-Al_2O_3	54.3	72.5
$Ca_{0.1}Ni/\alpha$-Al_2O_3	45.8	50.7
$K_{0.05}Ca_{0.1}Ni/\alpha$-$Al_2O_3$	44.7	48.8
$K_{0.1}Ca_{0.1}Ni/\alpha$-Al_2O_3	44.3	50.3
$K_{0.15}Ca_{0.1}Ni/\alpha$-$Al_2O_3$	43.2	51.8
$K_{0.2}Ca_{0.1}Ni/\alpha$-Al_2O_3	42.0	48.7
$K_{0.3}Ca_{0.1}Ni/\alpha$-Al_2O_3	38.4	48.4
$K_{0.4}Ca_{0.1}Ni/\alpha$-Al_2O_3	37.5	46.1
$K_{0.5}Ca_{0.1}Ni/\alpha$-Al_2O_3	36.6	42.9
$K_{0.2}Ni/\alpha$-Al_2O_3	44.1	51.6

[a] Analysis conditions: 43–46°, at 0.1°/min and step 0.02°.
[b] Samples were reduced in H_2, 800 °C, 1 h.
[c] 240 min on stream, at 800 °C.

Table 3
XPS analysis results of K–Ca co-promoted Ni/α-Al_2O_3

Sample	O 1s	Al 2p	Ca 2p	Ni $2p_{3/2}$	K $2p_{3/2}$
Ni/α-Al_2O_3	531.23	74.93	–	855.07	–
$Ca_{0.1}Ni/\alpha$-Al_2O_3	531.42	74.93	346.90	856.00	–
$K_{0.05}Ca_{0.1}Ni/\alpha$-$Al_2O_3$	531.68	74.93	346.87	856.25	–
$K_{0.1}Ca_{0.1}Ni/\alpha$-Al_2O_3	531.78	74.93	346.90	856.18	293.9
$K_{0.2}Ca_{0.1}Ni/\alpha$-Al_2O_3	532.00	74.93	346.90	856.16	293.9
$K_{0.5}Ca_{0.1}Ni/\alpha$-Al_2O_3	532.10	74.93	347.00	856.23	293.9

The mean sizes of nickel crystallites in fresh and used catalysts are listed in table 2. In the case of fresh samples, the mean Ni particle size decreased with the amount of K added, and the smallest Ni particles were detected in $K_{0.5}Ca_{0.1}Ni/\alpha$-Al_2O_3 (36.6 nm). The mean size of Ni particles in the used catalysts also decreased from 72.5 nm (in Ni/α-Al_2O_3) to 42.9 nm (in $K_{0.5}Ca_{0.1}Ni/\alpha$-Al_2O_3). These results suggest that K increases the dispersion of Ni and retards its sintering during the reaction. As deep dehydrogenation of CH_4 needs large ensembles of Ni [6–8], in this case smaller Ni particles would be less sensitive for deep dehydrogenation and helpful in reducing coke deposition.

The XPS analysis results are summarized in table 3. Addition of Ca to Ni/α-Al_2O_3 increased the binding energy of the Ni $2p_{3/2}$ from 855.07 to 856.00 eV, while in K and Ca co-promoted catalysts the detected Ni

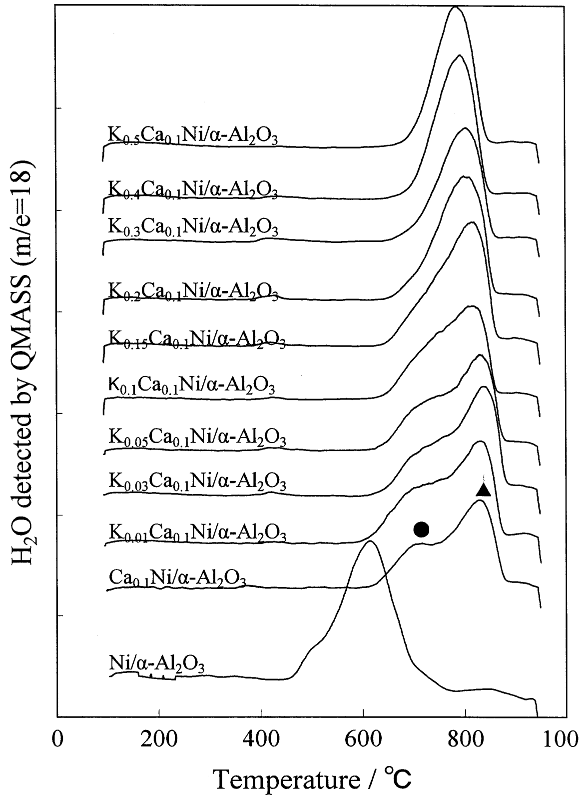

Figure 2. H_2-TPR profile of $K_xCa_{0.1}Ni/\alpha$-Al_2O_3: (●) NiO strong contact with α-Al_2O_3, (▲) $NiAl_2O_4$. Analysis conditions: catalyst, 100 mg; 5%H_2 in He; feed, 50 ml/min; rate 15 °C/min.

$2p_{3/2}$ levels were around 856.20 eV, and there was no clear relation between the binding energy and the amount of K added. According to Moulder [29] and an online database (http://srdata.nist.gov/XPS), the Ni species in Ni/α-Al_2O_3 can be assigned to NiO. On the other hand, the Ni species in K and Ca co-promoted catalysts could be attributed to $NiAl_2O_4$. Also, the detected Ca $2p_{3/2}$ levels (about 346.90 eV) suggested that Ca would exist in a state as $CaAl_2O_4$ [21,30]. The K $2p_{3/2}$ level (293.90 eV) is quite close to that of KOH (293.8 eV) [31]. These OH groups would be helpful in the gasification of intermediate CH_x fragments and also the strong basicity of KOH could improve the chemisorption of CO_2 through the formation of surface carbonates and then reduce carbon deposition [22].

Figure 2 shows the H_2-TPR profiles of CaNi/α-Al_2O_3 catalysts with different amounts of K. In the case of pure Ni/α-Al_2O_3, one peak attributed to the reduction of NiO was observed at 620 °C. $Ca_{0.1}$Ni/α-Al_2O_3 showed two reduction peaks at 695 and 870 °C. The first one was assigned as the NiO strong contact with α-Al_2O_3, and the second one was assigned as the spinel $NiAl_2O_4$ [18,32]. In K and Ca co-promoted catalysts, the peak at lower temperature (695 °C) decreased continuously with the amount of K added and totally disappeared when the amount of K was higher than 0.2 ($x \geq 0.2$, mole ratio of K/Ni). These results indicated that the progressive transformation of NiO to $NiAl_2O_4$ would occur with increasing K. It is suggested that K strengthened the interaction between Ni and α-Al_2O_3. A previous study found that a small amount of Ca could strengthen this interaction, but larger amounts of Ca (Ca/Ni > 0.1, mole ratio) occupied the limited surface of α-Al_2O_3 (9.0 m^2/g) and bulk NiO without interaction with α-Al_2O_3 [18]. Addition of K partially substituted for Ca and induced the formation of mainly $NiAl_2O_4$. Spinel $NiAl_2O_4$ forms easily in Ni/γ-Al_2O_3 [33,34], while the formation of $NiAl_2O_4$ on α-Al_2O_3 support is difficult at higher Ni loading and lower calcination temperature because of the stability of α-Al_2O_3 [33,35–37]. The

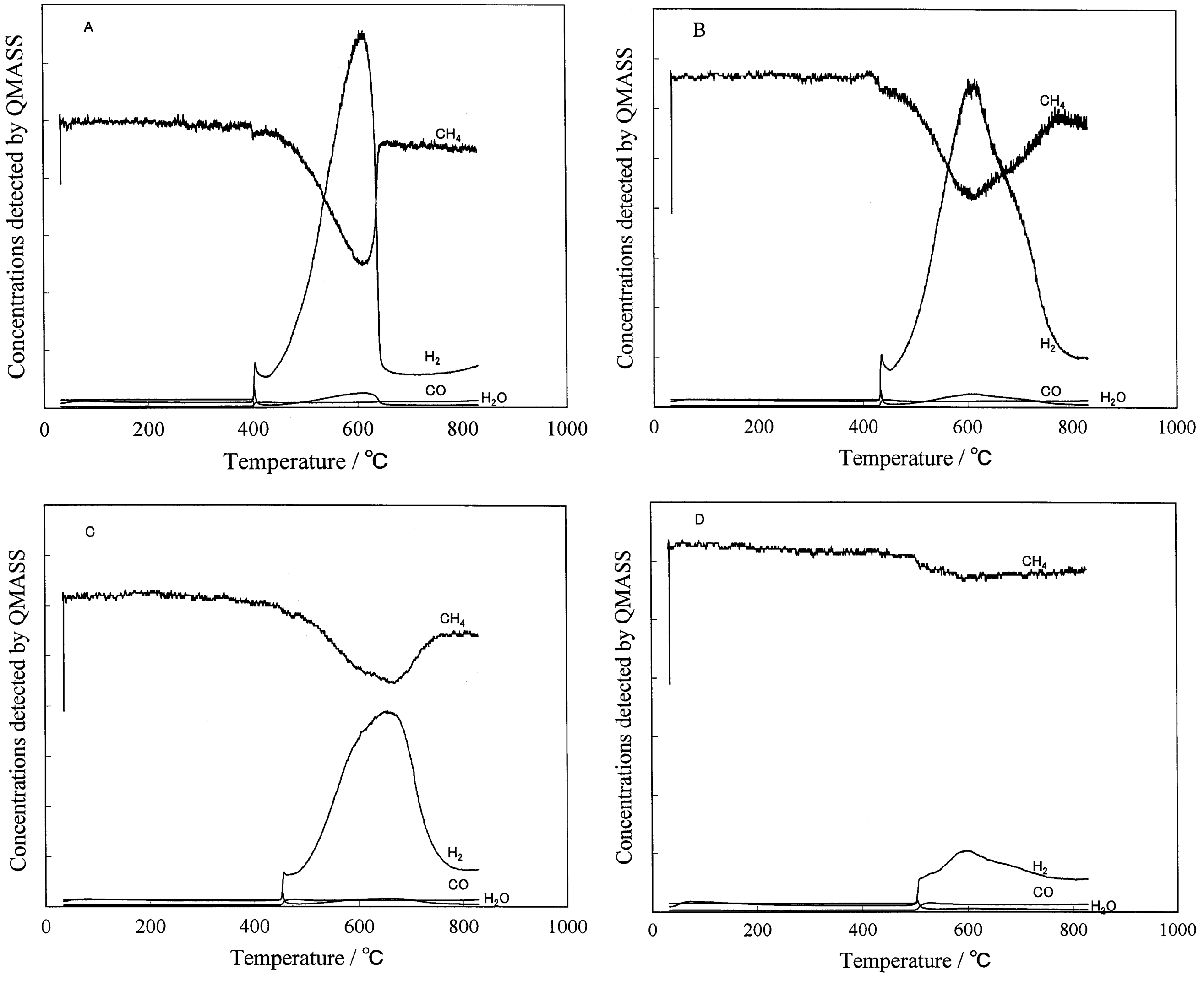

Figure 3. MS signal of effluent gas in CH_4 temperature-programmed decomposition: (A) Ni/α-Al_2O_3, (B) $Ca_{0.1}$Ni/α-Al_2O_3, (C) $K_{0.05}Ca_{0.1}$Ni/α-Al_2O_3, (D) $K_{0.5}Ca_{0.1}$Ni/α-Al_2O_3. Analysis conditions: catalyst, 100 mg; CH_4/He (50 ml/min, 10% of CH_4); 10 °C/min.

stable reforming activity of the co-promoted catalysts is in part due to the strong interaction between Ni and support, which hindered the sintering of surface Ni particles.

Figures 3(A)–(D) show the MS signal of effluent gas in the coking reaction via CH_4 temperature-programmed decomposition on Ni/α-Al_2O_3, $Ca_{0.1}$Ni/α-Al_2O_3, $K_{0.05}Ca_{0.1}$Ni/α-Al_2O_3 and $K_{0.5}Ca_{0.1}$Ni/α-Al_2O_3, respectively. The carbon deposited on these catalysts during CH_4 decomposition was detected by O_2-TPO and is summarized in figure 4. On Ni/α-Al_2O_3, CH_4 decomposition started at 420 °C and a large amount of H_2 was produced at the same time, but the catalyst deactivated quickly above 620 °C due to carbon deposition (figure 3(A)). The addition of Ca increased the ignition temperature of CH_4 decomposition (figure 3(B)). In this catalyst, the two kinds of Ni species with different activity (see figure 2) enhanced the decomposition of CH_4. On the surface of K–Ca co-promoted catalysts, small amounts of H_2 were detected in the effluent gas (figures 3(C) and (D)). Only one kind of carbon formed during CH_4 decomposition and it can be removed by oxygen below 650 °C, while the amount of carbon formed on K–Ca co-promoted catalysts decreased with the amount of K added (figure 4). Coking reactions also disclosed that (i) the ignited decomposition temperature of CH_4 increased slightly on the K-promoted catalysts, and (ii) the amount of H_2 and carbon produced via CH_4 decomposition decreased continuously with the amount of K added. A comparison O_2-TPO and CO_2-TPO of carbon formed on $K_{0.05}Ca_{0.1}$Ni/α-Al_2O_3 is summarized in figure 5. Carbon deposited on this catalyst can be gasified by CO_2 below 740 °C, which means that it is an active intermediate at the higher reforming temperature. These results revealed that K hindered the deep dehydrogenation of CH_4, and then reduced the coke deposition via CH_4 decomposition as suggested previously [9].

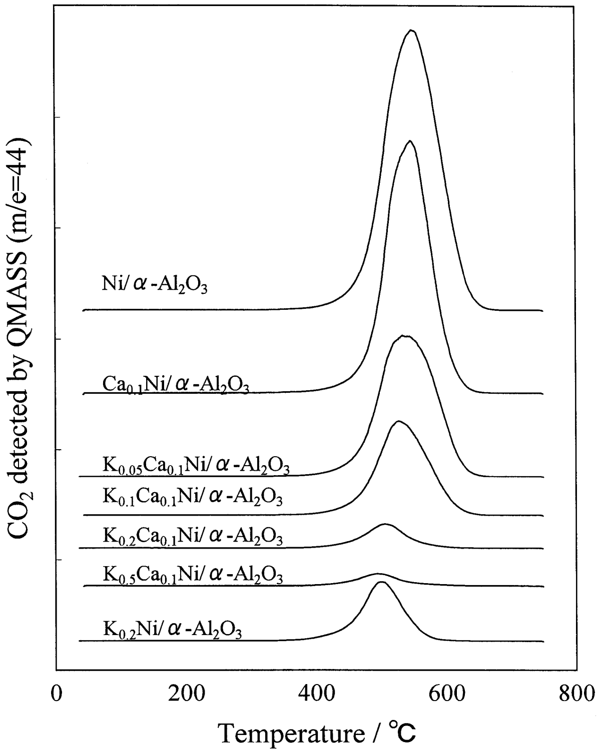

Figure 4. O_2-TPO profiles of $K_xCa_{0.1}$Ni /α-Al_2O_3 after CH_4 decomposition. Analysis conditions: O_2/He (50 ml/min, 10% of O_2); 10 °C/min.

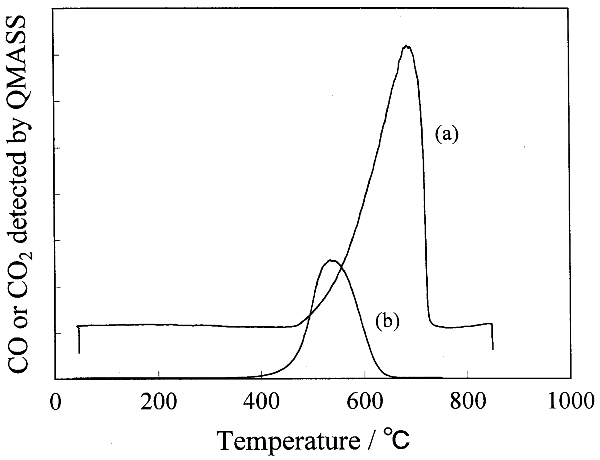

Figure 5. O_2-TPO and CO_2-TPO profiles of carbon formed on $K_{0.05}Ca_{0.1}$Ni/α-Al_2O_3: (a) CO_2 detected in O_2-TPO and (b) CO detected in CO_2-TPO. Analysis conditions: O_2/He or CO_2/He (50 ml/min, 10% of O_2 or CO_2); 10 °C/min.

4. Conclusions

$K_xCa_{0.1}$Ni/α-Al_2O_3 ($x \geq 0.2$) catalysts were stable, highly active and coke free in CH_4 reforming with CO_2. Smaller Ni particles detected in both fresh and used $K_xCa_{0.1}$Ni/α-Al_2O_3 catalysts indicated that K and Ca increased the dispersion of Ni and retarded its sintering during the reaction. H_2-TPR and XPS analysis disclosed that the addition of K and Ca strengthened the interaction between Ni and α-Al_2O_3, and promoted the formation of a unique $NiAl_2O_4$ phase on the surface of the catalyst. Coking reactions showed that K reduced carbon deposition via CH_4 decomposition.

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