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Investigation of CH_4 reforming with CO_2 on meso-porous Al_2O_3-supported Ni catalyst

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Meso-porous Al_2O_3-supported Ni catalysts exhibited the highest activity, stability and excellent coke-resistance ability for CH_4 reforming with CO_2 among several oxide-supported Ni catalysts (meso-porous Al_2O_3 (Yas1-2, Yas3-8), γ-Al_2O_3, α-Al_2O_3, SiO_2, MgO, La_2O_3, CeO_2 and ZrO_2). The properties of deposited carbons depended on the properties of the supports, and on the meso-porous Al_2O_3-supported Ni catalyst, only the intermediate carbon of the reforming reaction formed. XRD and H_2-TPR analysis found that mainly spinel $NiAl_2O_4$ formed in meso-porous Al_2O_3 and γ-Al_2O_3-supported catalysts, while only NiO was detected in α-Al_2O_3, SiO_2, CeO_2, La_2O_3 and ZrO_2 supports. The strong interaction between Ni and meso-porous Al_2O_3 improved the dispersion of Ni, retarded its sintering and improved the activated adsorption of CO_2. The coking reaction via CH_4 temperature-programed decomposition indicated that meso-porous Al_2O_3-supported Ni catalysts were less active for carbon formation by CH_4 decomposition than Ni/γ-Al_2O_3 and Ni/α-Al_2O_3.

KEY WORDS: methane; dry reforming; meso-porous Al_2O_3; TPR; TPD; TPO.

1. Introduction

Methane reforming with CO_2 obtained much attention in the past 20 years for the lower H_2/CO ratio in the production gas, and from the point of environmental protection since both CO_2 and CH_4 are greenhouse gases. Supported Ni catalyst was popularly used in methane reforming with CO_2 for its lower price and high activity, but it deactivated easily because of carbon deposition and metal sintering.

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

$$CH_4 \longrightarrow C + 2H_2 \ (\Delta G = -127.66\,\mathrm{kJ\,mol^{-1}},\ 1100\,\mathrm{K}) \tag{2}$$

$$2CO \longrightarrow C + CO_2 \ (\Delta G = +22.90\,\mathrm{kJ\,mol^{-1}},\ 1100\,\mathrm{K}) \tag{3}$$

Earlier studies found that coke formation is a structure-sensitive process, and it depends on the surface Ni species, particle size and electron density [1–4]. Many kinds of oxides, combined oxides, zeolites, carbon and SiC were tried as the support for Ni catalysts [3]. While most earlier papers were concerned mainly with the chemical properties of the support, limited attention was paid to its structures.

Recently, it was found that the structures of the support possess an important influence on the catalytic activity of Ni in methane reforming with CO_2 [5–7]. Wei *et al.* reported that Ni supported on nano-sized ZrO_2 (15–25 nm), MgO (10–20 nm) and γ-Al_2O_3 (5–19 nm) were highly active and stable [8–12]. Hwang *et al.* reported that meso-porous clay-supported Ni exhibited high catalytic activity and a long lifetime of catalyst stability [13].

In order to investigate the effect of the support and its structure, Ni catalysts on several oxide supports (meso-porous Al_2O_3 (Yas1-2, Yas3-8), γ-Al_2O_3, α-Al_2O_3, SiO_2, MgO, La_2O_3, CeO_2 and ZrO_2) were prepared and used for CH_4 reforming with CO_2 in this study, and temperature-programed techniques were tried to detect the properties of deposited carbons, the activation of CO_2 and coke formation via CH_4 decomposition.

2. Experiments

2.1. Catalyst preparation and test

Meso-porous Al_2O_3 (Yas1-2, Yas3-8) was kindly supplied by the Development Center of Chiyoda Chemical Co. (Japan). γ-Al_2O_3 and α-Al_2O_3 were kindly supplied by Basic Chemicals Research Laboratory of Sumitomo Chemical Co. (Japan). SiO_2, MgO, La_2O_3, CeO_2 and ZrO_2 were purchased from Wako Pure Chemicals (Japan). The catalysts used in this research were prepared by wet impregnation methods. $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemicals, Japan) was

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dissolved in water, then each support was added into the solution, dried at 120 °C for 12 h and finally calcined at 800 °C for 3 h. The loading amount of Ni is 10 wt% of the support. The experiments were carried out in a continuous flow system. Each catalyst (50 mg) was reduced in H_2 at 800 °C for 1 h, purged by Ar and tested in a quartz reactor (6 mm i.d.). The reforming reaction was carried out in a reaction gas mixed at the stoichiometric ratio (1 : 1) of CH_4 (99.99%) and CO_2 (99.99%) without dilution. The outlet gas was cooled by ice water and analyzed by an on-line gas chromatography (Yanaco G2800, Japan) automatically every 30 min. After reaction, each used catalyst was characterized by TG-DTA (Rigaku TAS-200, Japan) in air from 25 to 700 °C, in order to detect the amount of coke formed during the reaction. The properties of formed carbons during the reforming reaction were characterized by the O_2-TPO experiment in 10% O_2 (He in balance, 50 mL min^{-1}) at 10 °C min^{-1} to 750 °C.

2.2. Characterizations

Pore structures of the supported Ni catalysts were detected in a Belsorp 28 system (Belsorp, Japan) by N_2 adsorption at 77 K. Before analysis, all samples were pretreated in high vacuum at 250 °C for 4 h. The pore size, pore volume and relative surface area were calculated from the adsorption isotherm.

X-ray diffraction was carried out in a RINT2000 system (Rigaku, Japan). Anode Cu Kα (40 kV, 40 mA) was used as the X-ray source. The mean size of nickel crystallites was calculated from the broadening of the Ni (200) peak, according to the Scherrer–Warren equation [14,15].

2.3. H_2-*TPR*, CO_2-*TPD and coking reaction characterizations*

The reducibility of Ni catalysts on different supports was investigated by temperature-programed reduction (H_2-TPR) under 5% H_2 in He, in a TPD51 system equipped with an on-line mass spectrometer (Belsorp, Japan). Each catalyst (100 mg) was pretreated in He at 500 °C for 30 min. Analysis conditions: gas flow rate 50 mL/min, heating rate 15 °C/ min and from 100 to 950 °C.

CO_2 temperature-programed desorption (CO_2-TPD) was carried out according to the following steps: the sample was first reduced at 800 °C in H_2 for 1 h, cooled to room temperature and then exposed to 10% CO_2 (He in balance) for 20 min. The sample was purged in He for 30 min and then heated linearly at 20 °C/ min to 850 °C in 50-mL/min He. CO_2 ($m/e = 44$) and CO ($m/e = 28$) in effluent were measured by a mass spectrometer and recorded as functions of temperature.

Coke formation via CH_4 temperature-programed decomposition was carried out as follows: the catalyst (100 mg) was reduced at 800 °C in H_2, cooled to 100 °C in He, shifted to 10% CH_4 (50 mL/min, He in balance) and then the temperature was increased linearly to 900 °C at 10 °C/ min. CH_4 ($m/e = 16$), H_2 ($m/e = 2$), CO ($m/e = 28$), CH_3CH_3 ($m/e = 30$) and H_2O ($m/e = 18$) in effluent were detected and recorded as functions of temperature. The carbon deposited on the catalyst was detected by CO_2-TPO under 10% CO_2/He.

2.4. FE-SEM characterization

In order to identify the property of formed carbons, the used Ni/SiO_2 catalyst was characterized with field emission scanning electron microscopy (FE-SEM, Hitachi S-4000, Japan).

3. Results and discussions

3.1. Physicochemical properties of Ni catalysts on different supports

The structure of meso-porous Al_2O_3 supports (Yas1-2 and Yas3-8) and supported Ni catalysts are listed in table 1. Pure meso-porous Al_2O_3 (Yas1-2 and Yas3-8) possessed unique meso-pore, big pore volume and large surface area. The catalysts showed similar patterns of porous structure as the supports and the appreciable decrease in surface area and pore volume was due to the loading of nickel. The thermal stability of Ni/Yas3-8 was investigated at 800 °C for 200 h. The porosity data indicated that the surface area of Ni/Yas3-8 decreased slightly because of the damage at high temperature, while its meso-pore structure remained (table 1 and figure 1).

Table 2 summarizes the physicochemical properties of Ni catalysts on different supports. Compared to the meso-porous Al_2O_3, a wide-ranged pore distribution and lower surface area were detected in γ-Al_2O_3, α-Al_2O_3, SiO_2, MgO, La_2O_3, CeO_2 and ZrO_2-supported Ni catalysts. XRD analysis of the above catalysts indicated that the surface state of Ni depended on the properties of supports. In meso-porous Al_2O_3 (Yas1-2, Yas3-8) and γ-Al_2O_3-supported catalysts, $NiAl_2O_4$ was mainly detected. Only NiO formed on α-Al_2O_3, SiO_2, ZrO_2, La_2O_3 and CeO_2 supports, which indicated that the interaction between these supports and Ni is poor compared to that in meso-porous Al_2O_3-supported Ni catalysts. In Ni/MgO, solid solution Ni-Mg-O formed as reported [16–18]. The mean Ni particle size of the fresh and used catalysts indicated that Ni dispersed highly on the surface of meso-porous Al_2O_3 supports (less than 10.5 nm in both Ni/Yas1-2 and Ni/Yas3-8), and also that the sintering of Ni was retarded. Ni existed in bigger particles on the supports such as α-Al_2O_3, SiO_2,

Table 1
Pore structure of meso-porous Al_2O_3 and meso-porous Al_2O_3-supported Ni catalyst

	Meso-porous Al_2O_3[a]			Meso-porous Al_2O_3-supported Ni (10 wt%) catalysts					
				Fresh catalysts[a]			Aged catalysts[b]		
	P. volume ($cm^3 g^{-1}$)	S. area ($m^2 g^{-1}$)	P. size (nm)	P. volume ($cm^3 g^{-1}$)	S. area ($m^2 g^{-1}$)	P. size (nm)	P. volume ($cm^3 g^{-1}$)	S. area ($m^2 g^{-1}$)	P. size (nm)
Yas1-2	0.607	241.7	7.0	0.512	207.8	6.2	–	–	–
Yas3-8	0.773	205.9	11.7	0.659	184.7	11.7	0.587	161.1	11.7

[a] Samples were calcined at 800 °C in air for 3 h.
[b] Sample was calcined at 800 °C in air for 200 h.

La_2O_3 and CeO_2. Seriously sintering of Ni was detected in used Ni/La_2O_3. These results indicate that the dispersion of Ni depended on both the chemical properties of the support and its structure. On the higher surface area of meso-porous Al_2O_3 supports, the strong interaction between Ni and Al_2O_3 improved the dispersion of Ni and hindered its sintering.

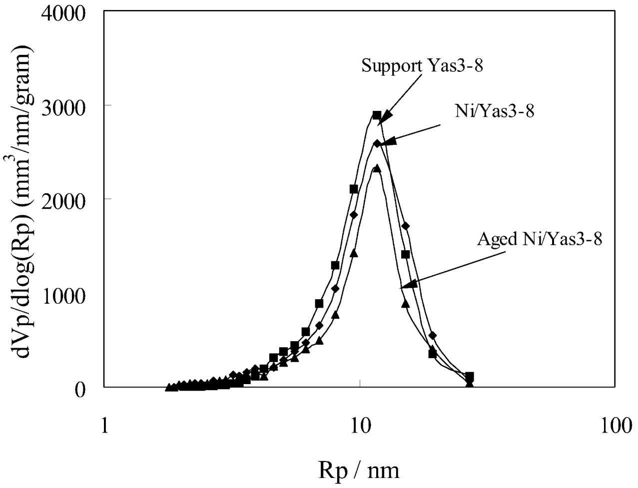

Figure 1. Pore distribution of Yas3-8, Ni/Yas3-8.

3.2. *Catalytic activity for* CH_4 *reforming with* CO_2

Meso-porous Al_2O_3-supported (Yas1-2 and Yas3-8) Ni catalysts exhibited highest reforming activity, stability and lower coke formation rate (table 3). Ni catalysts on other supports showed a middle reforming activity except Ni/ZrO_2. The coke formation rate was strongly affected by the properties of the supports. No carbon

Table 2
Physicochemical properties of Ni catalysts on different supports

Support	Pore structure[a]			Mean Ni particles[b]		Crystal phases[a]
	P. volume (cm^3g^{-1})	S. area ($m^2 g^{-1}$)	P. size (nm)	Fresh[c] (nm)	Used[d] (nm)	
Yas 1-2[e]	0.512	207.8	6.2^{MPD}	< 10.0	12.1	γ-Al_2O_3 (+++), $NiAl_2O_4$ (++)
Yas 3-8[e]	0.659	184.7	11.7^{MPD}	< 10.0	10.5	γ-Al_2O_3 (+++), $NiAl_2O_4$ (++)
γ-Al_2O_3 [f]	0.335	114.7	6.2^{APD}	10.6	18.3	γ-Al_2O_3 (+++), $NiAl_2O_4$ (++)
α-Al_2O_3 [f]	0.019	8.4	19.3^{APD}	54.3	72.5	α-Al_2O_3 (+++), NiO (++)
SiO_2 [g]	0.411	157.2	19.3^{APD}	48.8	59.1	NiO (+++)
MgO[g]	0.081	42.7	15.2^{APD}	< 10.0	< 10.0	$Ni_XMg_{1\text{-}X}O$, solid solution (+++)
La_2O_3 [g]	0.023	12.0	15.2^{APD}	79.1	> 100.0	La_2O_3 (+++), NiO (+)
CeO_2 [g]	0.014	5.7	15.2^{APD}	87.5	94.5	CeO_2 (+++), NiO (++)
ZrO_2 [g]	0.016	6.0	19.3^{APD}	ND	ND	ZrO_2 (+++), NiO (++)

Note: MPD: meso-pore diameter; APD: average pore diameter; ND: no data available because of the overlapping peaks of Ni with those of ZrO_2.
[a] Samples were calcined at 800 °C in air for 3 h, Ni loading 10 wt%. XRD analysis conditions: 10–85 ° min^{-1}, step 0.02° min^{-1} and 1.5° min^{-1} (+) weak intensity, (++) medium intensity, (+++) strong intensity.
[b] XRD analysis conditions: 50.0–54.0° min^{-1}, step 0.01° min^{-1} and 0.1° min^{-1}.
[c] Samples were reduced in H_2, 800 °C, 1 h.
[d] Samples of 4 h on stream, 800 °C except Ni/La_2O_3 (1 h on stream).
[e] Supplied by Development Center, Chiyoda Chemical Co. Ltd, Japan.
[f] Supplied by Basic Chemicals Research Laboratory, Sumitomo Chemical Co. Ltd, Japan.
[g] Wako Pure Chemicals, Japan.

Table 3
Activity of Ni on different supports for CH_4 reforming with CO_2

Support	Reactivity						
	Initial conv. (mol%)[a]		Final conv. (mol%)[b]		Coke[c]		Stability[d]
	CH_4	CO_2	CH_4	CO_2q	mg/gcat· h	Ni/C	
Yas 1-2	85.6	86.8	84.4	85.7	1.5	9.73	−1.4
Yas 3-8	85.8	86.6	85.0	86.0	5.2	2.81	−1.0
γ-Al_2O_3	78.2	81.6	76.5	80.6	20.2	0.72	−2.2
α-Al_2O_3	71.5	77.1	67.4	73.7	24.0	0.61	−5.74
SiO_2	69.4	72.7	61.5	68.6	93.1	0.16	−11.3
MgO	67.8	75.1	65.2	72.7	0.0	–	−3.9
La_2O_3 [e]	66.1	66.2	56.7	63.4	1410.0	0.01	−16.1
CeO_2	62.5	69.8	51.6	63.0	47.4	0.31	−17.4
ZrO_2	9.7	15.2	9.8	15.2	0.0	–	+0.5

Note: Reaction conditions: 800 °C, CH_4 25 mL (STP)/min, CO_2 25 mL (STP)/min and catalyst 50 mg.
[a] 30 min on stream.
[b] 4 h on stream.
[c] Average data during 4 h on stream.
[d] Defined as (final conv. of CH_4 - initial conv. of CH_4)/initial conv. of CH_4 × 100%.
[e] 1 h on stream.

was detected on Ni/MgO because of the formation of solid solution $Ni_XMg_{1-X}O$, while its activity was lower than that of meso-porous supported Ni catalysts. The Ni/La_2O_3 catalyst produced large amounts of coke and deactivated quickly owing to carbon deposition and seriously sintering of Ni (from 79.1 nm to more than 100 nm in 1 h on stream, see table 2). Ni/SiO_2 and Ni/CeO_2 catalysts produced a middle amount of carbon and showed a poor catalytic stability.

The properties of deposited carbons on these catalysts during the reforming reaction were detected by temperature-programed oxidation (TPO) with 10% O_2, and the produced CO_2 was recorded and compared for the property of formed carbon (figure 2). Three kinds of carbons were detected on these catalysts. According to the published papers [7,15,19,20], the highly reactive carbon detected at 380 °C (C_α) was popularly accepted as the monatomic carbon; it is the active intermediate in the reforming reaction. The second peak at 520 °C or 580 °C (C_β) was assigned as whisker carbon formed on or close to Ni particles. The most stable carbon at 680 ± 20 °C (C_γ) was the graphite coke formed on the support. Because Ni can catalyze the carbon combustion by oxygen spillover [21–24], carbon formed on and near the metal could be burned at lower temperature than the carbon formed on the support. Mainly, the highly reactive carbon and trace amount of C_β formed on the Ni/Yas3-8. And the calculated mol ratio between Ni and C_α is quite close to Ni_3C (see table 2), which was confirmed as an intermediate in the reforming reaction [20]. Only the second kind of carbon formed on α-Al_2O_3-, SiO_2-, La_2O_3-supported Ni catalysts and three kinds of carbon formed on Ni/γ-Al_2O_3. The TPO profiles of Ni/α-Al_2O_3 and Ni/SiO_2 fit well with published data [25–27]. FE-SEM analysis confirmed that the carbons formed on Ni/SiO_2 were mainly tube whisker carbons (20–60 nm) with Ni metals on their top (figure 3). These results inferred that both the property and amount of deposited carbon depended on the properties of the support and the Ni particles. C_β and C_γ are more stable than the intermediate C_α, whose scavenge is difficult, and they accumulate easily during the reforming process. The catalyst covered by deposited

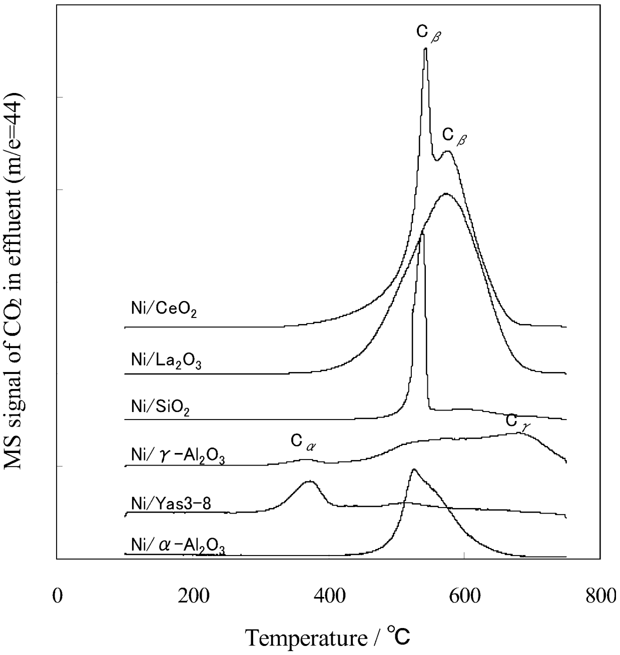

Figure 2. O_2-TPO profile of used catalysts.

Figure 3. SEM images of carbon formed on Ni/SiO_2.

C_β and C_γ is easily deactivated as the deposited carbon hinders the access to the reactant on the Ni surface. On meso-porous Al_2O_3-supported Ni catalysts, deposition of C_β and C_γ was suppressed and then exhibited a high activity and stability.

3.3. TPR characterization

Figure 4 shows the H_2-TPR profiles of Ni catalysts on different supports. In Ni/La_2O_3, Ni/CeO_2, Ni/SiO_2 and Ni/α-Al_2O_3 catalysts, the reduction peaks were detected below 770 °C. On the other hand, the reduction peaks at 870 ± 20 °C were detected in Ni/Yas1-2, Ni/Yas3-8 and Ni/γ-Al_2O_3 catalysts. According to the published data [28–31], the different reduction temperature regions were due to the interaction strength between Ni and supports. Two reduction peaks were detected in Ni/La_2O_3. The first peak at 415 °C was quite close to the reduction temperature of bulk NiO [31], which indicated that this kind of Ni showed no interaction with the support. The second peak at 580 °C was assigned as the reduction of NiO contacted with the support. And the broadening reduction peaks in Ni/CeO_2 (400660 °C), Ni/SiO_2 (440700 °C) and Ni/α-Al_2O_3 (470770 °C) were assigned as NiO contacted with supports. The Ni species reduced at 870 ± 20 °C in Ni/Yas1-2, Ni/Yas3-8 and Ni/γ-Al_2O_3 were assigned as spinel $NiAl_2O_4$. No clear reduction peak of Ni/MgO was detected because of the formation of $Ni_XMg_{1-X}O$ solid solution. These results inferred that the properties of the support played an important role on the nature of surface Ni. Ni contacted strongly with the meso-porous Al_2O_3 and γ-Al_2O_3 as $NiAl_2O_4$ formed mainly. This strong interaction improved the dispersion of Ni and hindered its sintering during the reforming reaction [32,33].

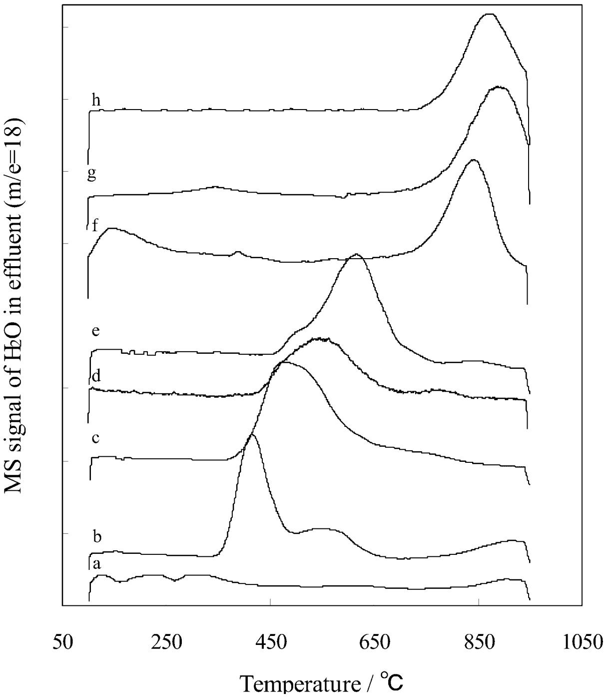

Figure 4. H_2-TPR of Ni catalysts on different supports.(a) Ni/MgO, (b) Ni/La_2O_3, (c) Ni/CeO_2, (d) Ni/SiO_2, (e) Ni/α-Al_2O_3, (f) Ni/γ-Al_2O_3, (g) Ni/Yas3-8 and (h) Ni/Yas1-2. Analysis conditions: 5% H_2 (He in balance) and 15 °C min^{-1}.

3.4. CO_2-TPD

CO_2 was mainly adsorbed physically on Ni/α-Al_2O_3 (desorbed at 95 °C) (figure 5). On Ni/γ-Al_2O_3, the main desorption peak of CO_2 shifted to 125 °C and a small peak at 480 °C was detected. On meso-porous Al_2O_3-

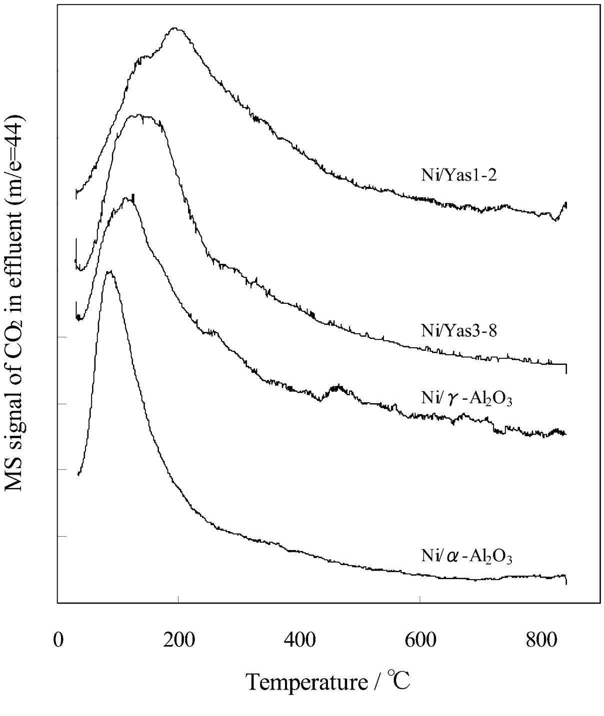

Figure 5. CO_2-TPD profile of Ni on different supports.

supported Ni catalysts, the desorption peak of CO_2 shifted to 210 °C and its tail extended to around 500 °C. It was confirmed that the detected CO_2 species above 200 °C in effluent were from the dissociated adsorbed $CO_2^{\delta-}$ or CO [34]. This kind of adsorbed $CO_2^{\delta-}$ is stable and could have enough lifetime to react with the intermediate carbons formed from CH_4. These results indicated that the dissociated adsorption of CO_2 was improved on meso-porous Al_2O_3-supported Ni catalysts and Ni/γ-Al_2O_3.

3.5. *Coking reaction*

Coking reaction via CH_4 temperature-programed decomposition on Ni/Yas1-2 is shown in figure 6. Two separate consumption peaks of CH_4 were detected at 600 °C and 830 °C. In product gas, mainly H_2 was detected at 600 °C, while at 830 °C corresponding amounts of CH_3CH_3 and CO were also detected. On the basis of these products, we think that the first consumption peak of CH_4 was its decomposition to carbon and hydrogen on the active Ni surface. On the other hand, the second consumption peak at 830 °C was due to the dehydrogenation of CH_4 to CH_3CH_3 catalyzed by the support material. This suggestion was further confirmed on pure support (Yas1-2). The second consumption peak of CH_4 was also detected on Ni/Yas3-8 catalyst, while only the first consumption peak was detected on Ni/α-Al_2O_3 and Ni/γ-Al_2O_3 (figure 7). From the comparison of produced H_2 in effluent, it could be found that the ignited decomposition temperature increased on the surface of meso-porous Al_2O_3-supported Ni catalysts and the amount of produced H_2 decreased. Carbons formed during the CH_4 decomposition were detected by CO_2-TPO, as shown in figure 8. These carbons could be gasified completely by CO_2 below 750 °C, and the produced amount of CO fit well with that of H_2 (in figure 7). These results inferred that the decomposition of CH_4 to carbon was mainly carried out on the surface of metallic Ni. Meso-porous Al_2O_3-supported Ni catalysts (Ni/Yas1-2, Ni/Yas3-8) were less active for carbon formation via CH_4 decomposition. Thermodynamic calculations (equations (1)–(3) in introduction) indicated that CH_4 decomposition would be the main source for deposited carbon (equation (2)) in

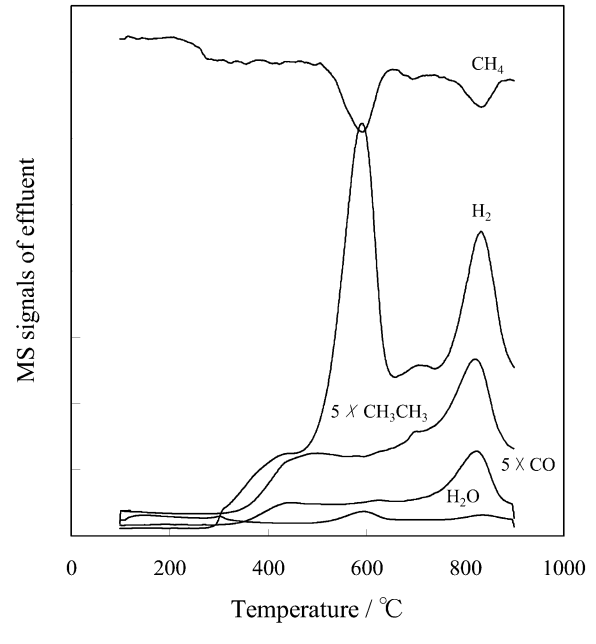

Figure 6. MS[AQ6] signal of effluent of CH_4 decomposition on Ni/Yas1-2. Analysis condition: 10% CH_4 (He in balance) and 10 °C/ min.

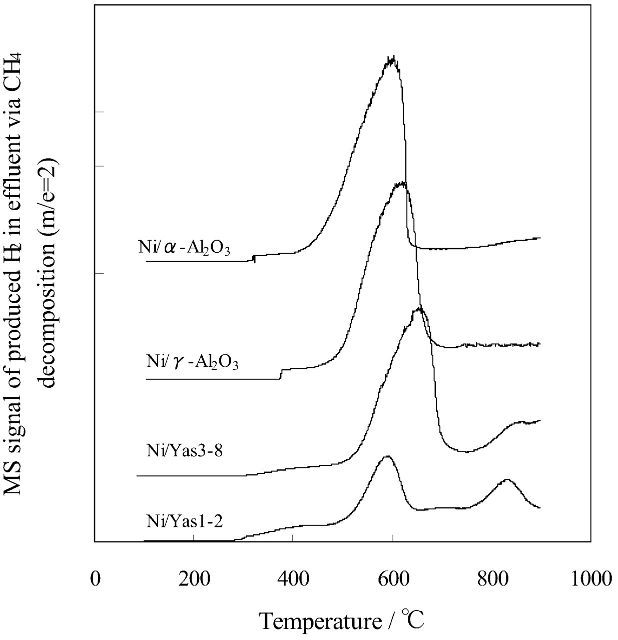

Figure 7. H_2 production via CH_4 decomposition.

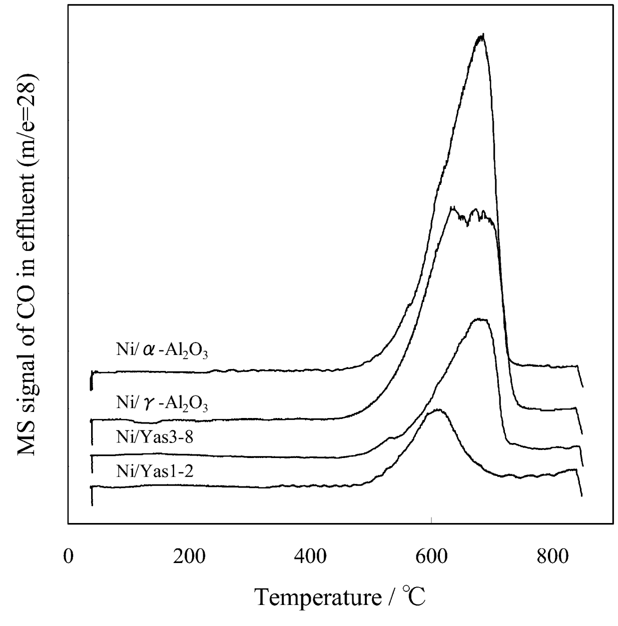

Figure 8. CO_2-TPO of formed carbon via CH_4 decomposition.

these research conditions. The higher activity of meso-porous Al_2O_3-supported Ni catalysts was also due to the activation of CH_4 by the support itself at higher temperature.

4. Conclusions

On the basis of reforming activity, XRD, H_2-TPR and coking reaction characterizations, it can be found that the property of supports played an important role on the nature of Ni species, Ni dispersion and carbon deposition. Meso-porous Al_2O_3 is a good support for Ni catalysts in the following areas:

The strong interaction between Ni and meso-porous Al_2O_3 improved the dispersion of Ni and retarded its sintering. And the highly dispersed Ni was highly active for the reforming reaction, improved the active adsorption of CO_2 and was less active for carbon deposition via CH_4 decomposition. Another reason for the higher activity of meso-porous supported Ni catalysts was due to the direct activation of CH_4 on the surface of supported materials.

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