CO_2 reforming of CH_4 over Ni/Mg–Al oxide catalysts prepared by solid phase crystallization method from Mg–Al hydrotalcite-like precursors

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Ni supported catalysts were prepared by the solid phase crystallization (*spc*) method starting from hydrotalcite (HT) anionic clay based on $[Mg_6Al_2(OH)_{16}CO_3^{2-}]\cdot H_2O$ as the precursor. The precursors were prepared by the co-precipitation method from nitrates of the metal components, and then thermally decomposed, *in situ* reduced to form Ni supported catalysts (*spc*-Ni/Mg–Al) and used for the CO_2 reforming of CH_4 to synthesis gas. Ni^{2+} can well replace the Mg^{2+} site in the hydrotalcite, resulting in the formation of highly dispersed Ni metal particles on *spc*-Ni/Mg–Al. The *spc*-catalyst thus prepared showed higher activity than those prepared by the conventional impregnation (*imp*) method such as Ni/α-Al_2O_3 and Ni/MgO. When Ni was supported by impregnation of Mg–Al mixed oxide prepared from Mg–Al HT, the activity of *imp*-Ni/Mg–Al thus prepared was not so low as those of Ni/α-Al_2O_3 and Ni/MgO but close to that of *spc*-Ni/Mg–Al. The relatively high activity of *imp*-Ni/Mg–Al may be due to the regeneration of the Mg–Al HT phase from the mixed oxide during the preparation, resulting in an occurring of the incorporation of Ni^{2+} in the Mg^{2+} site in the HT as seen in the *spc*-method. Such an effect may give rise to the formation of highly dispersed Ni metal species and afford high activity on the *imp*-Ni/Mg–Al.

KEY WORDS: CO_2 reforming of CH_4; synthesis gas; hydrotalcite; Ni supported catalyst

1. Introduction

During the past decade the catalytic conversion of methane into more valuable synthesis gas has a great importance in chemical industry. The conversion of CH_4 to synthesis gas is usually carried out by its H_2O reforming:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{1}$$

The catalytic conversion of CO_2 into valuable products is also increasingly important. The CO_2 reforming of CH_4

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{2}$$

has been intensively studied since this process has several advantages over the H_2O reforming of CH_4 [1–8]. Since the replacement of H_2O by CO_2 results in a lower H_2/CO ratio in the product gas, the combination of these two reforming reactions widens the utility of synthesis gas, i.e., in methanol or acetic acid synthesis. Recently, this process has also received attention from an environmental viewpoint since the emission of CH_4 and CO_2 in the atmosphere brings about global warming by the greenhouse effect and these harmful gases can simultaneously be converted into useful synthesis gas. Ni or precious metals are reported to be active as catalysts for this reaction [1,4]; however, this reaction is frequently accompanied by coke formation, especially on Ni catalysts, leading to catalyst deactivation.

High dispersion of metal species over catalysts [8] or use of alkaline earth metal oxides in catalysts [9] may reduce coke formation. Metal supported catalysts are conventionally prepared by wet impregnation of different supports. This method is not fully reproducible and may give rise to some heterogeneity in the distribution of metal on the surface. A new concept of catalyst preparation, therefore, may be required. Use of precursors containing homogeneously distributed metal in the structure may, on further calcination and reduction, result in the formation of highly dispersed and stable metal particles on the surface. We named this method "solid phase crystallization (*spc*) method". This method was successfully applied to the preparation of Ni supported catalysts for the partial oxidation and CO_2 reforming of CH_4 to synthesis gas by using perovskite-type mixed oxides as the precursors [10]. The *spc* method may be generally applicable in the preparation of highly dispersed metal supported catalysts starting from many kinds of mixed metal oxide as the precursors. Use of hydrotalcite anionic clay as the precursor has been also tested in the literature, since all the cations are homogeneously distributed inside brucite-type sheets of the hydrotalcite anionic clay structure [11]. Extremely dispersed Pt catalysts (H/Pt = 1.1) were prepared from Pt(acac) and a Mg–Al mixed oxide prepared from a hydrotalcite-like precursor [12]. Ni supported catalysts were also prepared from a Mg–Al hydrotalcite precursor containing Ni^{2+} and were tested in hydrogenation of acetoni-

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trile [13]. Highly dispersed Rh or Ni supported catalysts were prepared from Mg–Al hydrotalcite anionic clay as precursor and used for the partial oxidation of methane [14,15]. We have already reported that Pd supported catalysts prepared from Mg–Cr and Mg–Al hydrotalcite-like precursors showed high activity for methanol decomposition [16,17].

Here we report high activity and sustainability of Ni supported catalysts prepared by the *spc* method from hydrotalcite-like precursors in the CO_2 reforming of CH_4.

2. Experimental

2.1. Catalysts preparation

The catalyst *spc*-Ni/Mg–Al was prepared by using a hydrotalcite anionic clay as the precursor. $[Mg_6Al_2(OH)_{16}CO_3^{2-}]\cdot 4H_2O$ (abbreviated as Mg_3Al-HT) was used as the HT and a part of Mg^{2+} was replaced by Ni^{2+} for preparing the precursor of the catalyst. The atomic ratio of Ni/Mg was fixed at 1.0/2.0. The HT precursor was prepared by co-precipitation at pH $= 10.0$ and at room temperature by adding slowly an aqueous solution containing the nitrates of the metal components to an aqueous solution containing NaOH and Na_2CO_3, followed by aging for 12 h at 383 K. The catalysts were obtained by calcining the HT precursors at 923 K for 14 h and 1123 K for 5 h in air. The *imp*-Ni/Mg–Al, *imp*-Ni/MgO and *imp*-Ni/Al_2O_3 catalysts were prepared by the impregnation method (*imp*) and finally calcined at 1123 K in air for 5 h. α-Al_2O_3 (Kanto) and MgO "smoke" powder (JRC-MgO-4) were used as supports and impregnated in Ni nitrate aqueous solution. In the case of *imp*-Ni/Mg–Al, Mg–Al mixed oxide (abbreviated as Mg_3Al) prepared from Mg_3Al-HT was used as the support. The loading amount of Ni was 25.1 wt% on each support.

2.2. Characterization of the catalysts

Surface area of the catalyst was measured by the BET method using N_2 at 77 K with a BEL Japan BELSORP18. X-ray diffraction (XRD) was performed on an X-ray diffractometer (Rigaku RINT2550VHF) using Cu Kα radiation ($\lambda = 1.5405$ Å). The dispersion of Ni on the Ni supported catalyst was measured by the H_2 pulse method at room temperature. 100 mg of catalyst was first reduced at 1073 K for 10 min in 20 vol% H_2 in N_2 stream (total flow rate 25 ml min^{-1}) and then used for the measurement.

2.3. CO_2 reforming of CH_4

CO_2 reforming of methane was carried out at an atmospheric pressure in a conventional flow reactor with a fixed-bed quartz tubular reactor (∅ 10 mm). The catalyst (0.1 g) was diluted by 1.0 g of quartz sand and was put between two quartz-wool plugs in the reactor. The feed gas compositions were controlled with a mass flow controller (Okura Riken, model MF1171). The space velocity changed from 51000 to 204000 ml h^{-1} g-cat^{-1}. The thermocouple was introduced from the top of the reactor, and placed in the middle of the catalyst bed. The reaction temperature monitored by the thermocouple increased from room temperature to 1073 K at the heating rate of 2.5 K min^{-1}. Moreover, the reactions were carried out at 1073 K for 6 h under the same conditions in order to check the sustainability. The products were analyzed by three on-line TCD gas chromatographs with Porapak-Q and Molecular Sieve 5A columns.

After 6 h of testing, the reactor was filled with nitrogen and cooled according to normal procedures. Finally, a temperature-programmed oxidation (TPO) experiment was performed by heating the reactor from room temperature to 1223 K at a rate of 2.5 K min^{-1}, in a mixture of O_2 (0.3 $dm^3\,h^{-1}$) and N_2 (2.1 $dm^3\,h^{-1}$). Off-gases were analyzed as usual and the amount of coke formed on the catalyst was estimated from the amount of CO_2 formed during TPO experiment.

3. Results and discussion

3.1. Structure of the Ni supported catalysts

The XRD pattern of the Ni-containing precursor after drying at 393 K (figure 1(a)) shows the diffraction lines of a well-crystallized HT phase (JCPDS 22-700) alone, suggesting that Ni^{2+} is incorporated in the Mg^{2+} site and dispersed uniformly in the brucite layer of HT structure. The intensities of the diffraction lines due to the HT phase slightly decreased by the addition of Ni cations, indicating that the crystallinity of the HT phase in the Ni-containing precursor is lower than that of the Mg–Al HT (Ni free).

After calcination at 1073 K, the XRD pattern of the *spc*-Ni/Mg–Al catalyst (figure 1(b)) shows the strong diffraction

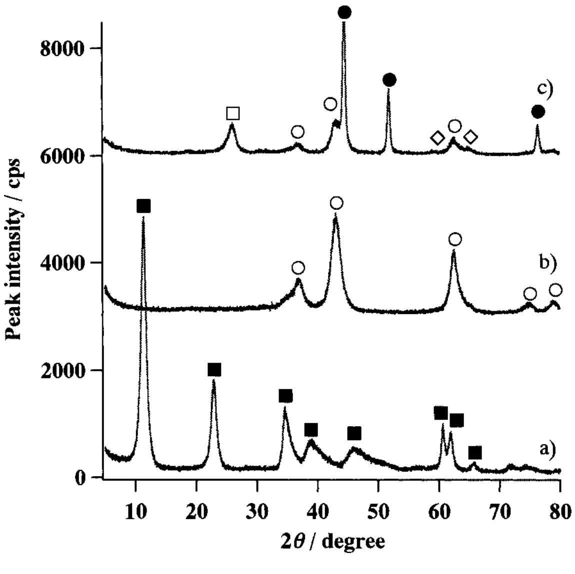

Figure 1. XRD patterns of *spc*-Ni/Mg–Al (a) dried at 383 K, (b) calcined at 1123 K and (c) after the reaction. (○) MgO, NiO; (●) Ni; (◇) $MgAl_2O_4$; (■) hydrotalcite; and (□) graphite.

Table 1
XRD parameters of Ni supported catalysts.

Catalyst	Temperature	XRD parameter *a* (nm)	
spc-Ni/Mg–Al	Calcined at 923 K	0.41774	
	Calcined at 1123 K	0.41866	
	After the catalytic test[a]	0.42128	
imp-Ni/Mg–Al	Calcined at 923 K	0.41998	
	Calcined at 1123 K	0.42010	
	After the catalytic test[a]	0.42108	
imp-Ni/Mg–O	Calcined at 1123 K	0.42070	
	Reduced at 1073 K	0.42090	
	After the catalytic test[a]	0.42108	
Mg_3Al	Calcined at 923 K	0.41960	
	Calcined at 1123 K	0.42090	
	Calcined at 1273 K	0.42166	
MgO		0.42112	JCPDS 45-0948
NiO		0.41771	JCPDS 47-1049
$Mg_{0.4}Ni_{0.6}O$		0.41900	JCPDS 34-0410
$Mg_{0.5}Ni_{0.5}O$		0.41926	JCPDS 24-0712

[a] After the CO_2 reforming of CH_4 at 1073 K for 6 h.

lines of MgO (JCPDS 45-948) and NiO (JCPDS 47-1049), which overlapped each other. The value of the lattice parameter *a* of the MgO cubic phase in the *spc*-Ni/Mg–Al calcined at 1073 K was smaller than that of pure MgO. This value was also smaller than that calculated for the Ni–Mg–O solid solution on the basis of Vegard's law, by linear interpolation of the values of the pure oxides (table 1). These results suggest the formation of a Ni–Mg–O solid solution as well as the presence of Al^{3+} ions in the Ni–Mg–O cubic lattice as reported by Puxley et al. [18] and Ross et al. [19]. Al^{3+} has smaller ionic radius than Mg^{2+} and Ni^{2+} [20]. Fornasari et al. [21] reported similar phenomena. After the reaction at 1073 K for 6 h, diffraction lines due to the MgO phase were weakened and a Ni metal phase was observed together with the MgO phase (figure 1(c)) and the lattice parameter *a* of the MgO cubic phase decreased. These results indicate that a part of NiO was reduced to Ni metal and segregated from the Ni–Mg–O cubic lattice during the reaction. Very weak diffraction lines due to a spinel phase ($MgAl_2O_4$; JCPDS 33-853) were also observed, indicating that the spinel phase was segregated during the reaction.

The XRD pattern of Mg–Al mixed oxide (figure 2(a)) shows the strong diffraction lines of MgO. However, the value of the lattice parameter *a* was smaller than that of pure MgO, again suggesting that Al^{3+} ions were incorporated in the oxide lattice of MgO. When the Mg–Al mixed oxide was impregnated in nickel nitrate solution, followed by drying at 383 K, the diffraction peaks due to MgO disappeared, and the XRD pattern shows a significant reconstruction of the HT structure (figure 2(b)). During the impregnation procedure, the hydrotalcite lattice might be regenerated by rehydration as reported by Richle [22]. This result suggests that a substantial part of Ni cations replaced Mg^{2+} and were dispersed in octahedral sites in brucite layers of the hydrotalcite phase. It is likely that, during the preparation, the circumstances around Ni species in the *imp*-Ni/Mg–Al catalyst are similar to that of *spc*-Ni/Mg–Al. After the calcination at 1073 K, the XRD pattern of *imp*-Ni/Mg–Al (figure 2(c)) shows the presence of MgO, NiO and $MgAl_2O_4$ phases. The value of the lattice parameter *a* of the MgO cubic lattice in *imp*-Ni/Mg-Al calcined at 1073 K was again smaller than that of pure MgO, suggesting the formation of a Ni–Mg–O solid solution including Al^{3+} ions in the oxide lattice. The intensities of the diffraction peaks of both MgO and spinel phase are stronger than those of *spc*-Ni/Mg–Al, indicating that the crystal sizes of both MgO cubic and $MgAl_2O_4$ phases in *imp*-Ni/Mg–Al are larger than those in *spc*-Ni/Mg–Al. After the reaction at 1073 K for 6 h, the intensities of diffraction lines due to the MgO phase decreased (figure 2(d)). In addition, new diffraction lines due to a Ni metal phase were observed together with the MgO phase, indicating that some of NiO was reduced and segregated from the MgO cubic lattice during the reaction.

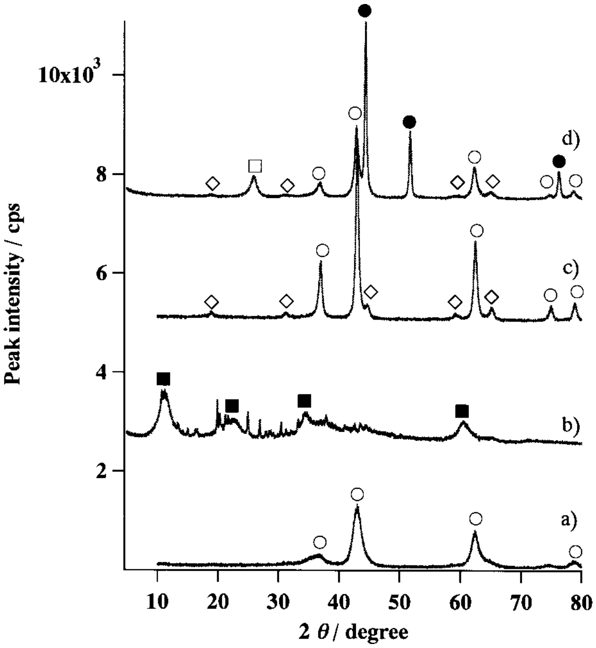

Figure 2. XRD patterns of *imp*-Ni/Mg–Al (a) before impregnation, (b) dried at 383 K, (c) calcined at 1123 K and (d) after the reaction. (○) MgO, NiO; (●) Ni; (◇) $MgAl_2O_4$; (■) hydrotalcite; and (□) graphite.

3.2. Catalytic activity of the Ni supported catalysts

The CH_4 conversions of the four catalysts, *spc*-Ni/Mg–Al, *imp*-Ni/Mg–Al, *imp*-Ni/MgO and *imp*-Ni/α-Al_2O_3, at various temperatures (during TPR) are shown in figure 3. After the TPR, the activities of these Ni catalysts were tested for 6 h at 1073 K at the space velocity of 51000 ml h^{-1} g-cat^{-1}, and time course of the reactions is shown in figure 4. The conversion of CO_2 over the catalysts showed a slightly higher value than that of CH_4. In the case of *spc*-Ni/Mg–Al catalyst, CH_4 conversion suddenly appeared at 1023 K, where Ni species may be reduced to Ni metal to afford highly active Ni supported catalyst, resulting in synthesis gas formation. The value of CH_4 conversion reached to

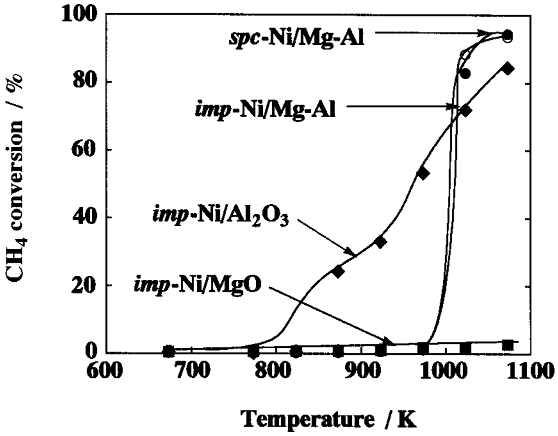

Figure 3. CO_2 reforming of CH_4 over Ni supported catalysts; $CH_4/CO_2/N_2 = 1/1/1.4$, GHSV = 54000 ml h^{-1}g-cat^{-1}.

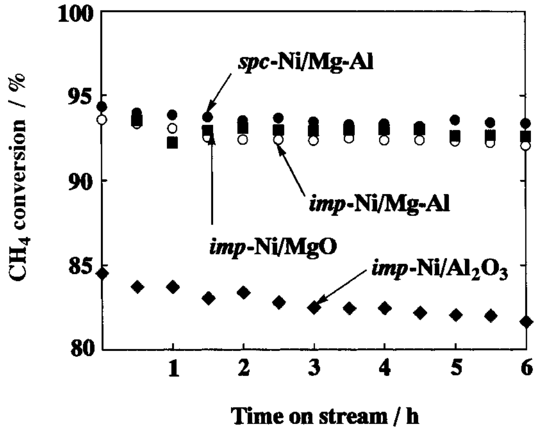

Figure 4. CO_2 reforming of CH_4 over Ni supported catalysts; $CH_4/CO_2/N_2 = 1/1/1.4$, GHSV = 54000 ml h^{-1} g-cat^{-1}, reaction temperature 1073 K.

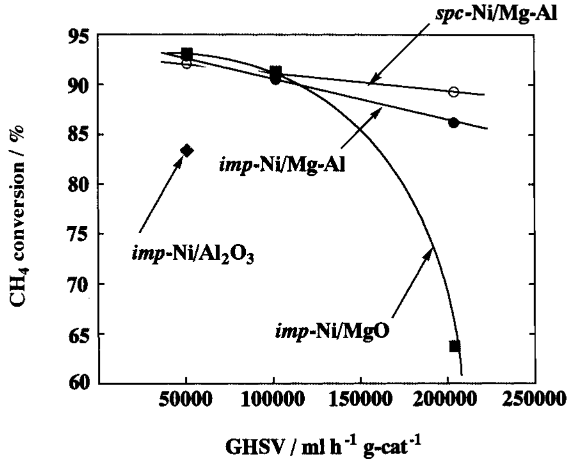

Figure 5. Effect of space velocity on CO_2 reforming of C_4; $CH_4/CO_2/N_2 = 1/1/1.4$, reaction temperature 1073 K.

94% at 1073 K, and the activity of *spc*-Ni/Mg–Al was stable during the reaction for 6 h at 1073 K, as shown in figure 4. *imp*-Ni/Mg–Al showed similar behavior to *spc*-Ni/Mg–Al, even though the CH_4 conversion was slightly lower than that of *spc*-Ni/Mg–Al at 1073 K. As for Ni/α-Al_2O_3, the activity appeared at 800 K and gradually increased with increasing temperature, but the CH_4 conversion at 1073 K was about 84%. This value is lower than those of both *spc*-Ni/Mg–Al and *imp*-Ni/Mg–Al mentioned above. *imp*-Ni/MgO did not show activity even at 1073 K. *imp*-Ni/MgO required a longer time of activation, and revealed the activity after keeping 1073 K for 0.5 h, as shown in figure 4. The activity of *imp*-Ni/MgO was higher and more stable than that of *imp*-Ni/α-Al_2O_3; the activity of *imp*-Ni/α-Al_2O_3 gradually decreased during the reaction. XRD measurements of *imp*-Ni/MgO showed the lines of MgO and NiO, which overlapped each other, suggesting the formation of a Ni–Mg–O solid solution. After the reaction at 1073 K, the lines of Ni metal were observed, though weakly, suggesting the formation of highly dispersed Ni metal particles. Parmaliana et al. [23–26] reported that the NiO–MgO system forms “ideal” solid solutions over the whole molecular fraction range and was successfully used as the catalyst for the steam reforming of CH_4. Ni^{2+} diffuses progressively into the MgO matrix during air calcination of a 19% Ni/MgO catalyst in the range 673–1273 K, resulting in the formation of a $Ni_xMg_{1-x}O$ solid solution [26]. Fujimoto and co-workers [9,27,28] reported that a solid solution $Ni_{0.03}Mg_{9.97}O$ (atomic ratio) was reduced at high temperature (>1073 K) to form an active and stable catalyst for steam or CO_2 reforming of CH_4. It is likely that the formation of a Ni–Mg–O solid solution is a key step for bestowing the high activity on the Ni/MgO catalyst and that this is the case also in the present catalyst system.

No significant difference was observed between the activities of the effective catalysts; i.e., *spc*-Ni/Mg–Al, *imp*-Ni/Mg–Al and *imp*-Ni/MgO, selected by screening at 1073 K for 6 h at the space velocity of 51000 ml h^{-1} g-cat^{-1}. This may be due to the fact that the thermodynamic equilibrium of reaction (2) was attained over these active catalysts in the reaction conditions. The activity was further tested under high space velocity (from 102000 to 204000 ml h^{-1} g-cat^{-1}). The results are shown in figure 5. At the higher space velocity, reaction (2) must be kinetically controlled on the catalyst surface, therefore, the catalytic activity may be compared more precisely. Upon increasing the space velocity, the catalysts prepared using HT as the support (both *spc*-Ni/Mg–Al and *imp*-Ni/Mg–Al), were still active enough, while *imp*-Ni/MgO lost its activity. The highest activity was observed over *spc*-Ni/Mg–Al. It is thus very likely that the *spc* method is quite effective for catalyst preparation. The high activity of the catalyst prepared by the *spc* method may be due to the formation of highly dispersed and stable Ni particles such as in the case of *spc*-Ni/perovskite catalyst [10] and Pd supported catalysts [16,17]. In the case of *imp*-Ni/Mg–Al, the hydrotalcite lattice might be regenerated during the impregnation procedure. This phenomenon suggests the formation of highly dispersed Ni metal particles also on *imp*-Ni/Mg–Al as seen in *spc*-Ni/Mg–Al.

Table 2
Amount of coke and H_2 adsorption over Ni supported catalysts.

Catalyst	BET surface area ($m^2\,g^{-1}$)	Amount of coke[a] (μmol g^{-1})	Amount of coke[a] (μmol m^{-2})	Amount of adsorbed H_2[b] (μmol g^{-1})	Dispersion (%)
spc-Ni/Mg–Al	181	541.7	29.9	299.3	7.0
imp-Ni/Mg–Al	102	408.3	40.0	205.5	4.8
imp-Ni/α-Al_2O_3	3	1266.7	4222.2	12.8	0.3
imp-Ni/MgO	24	316.7	131.9	29.9	0.7

[a] After the CO_2 reforming of CH_4 at 1073 K for 6 h.
[b] Reduced at 1073 K.

3.3. Coke formation over the catalysts

The amount of coke formed over the Ni catalysts after the reaction for 6 h at 1073 K was measured by TPO experiment and shown in table 2. BET surface areas are also shown in table 2. The amount of coke per gram of catalyst over *imp*-Ni/α-Al_2O_3 was the largest, followed by *spc*-Ni/Mg–Al, *imp*-Ni/Mg–Al and *imp*-Ni/MgO. The order of the amount of coke per surface area was as follows: *imp*-Ni/α-$Al_2O_3 \gg$ *imp*-Ni/MgO $>$ *imp*-Ni/Mg–Al $\geqslant$ *spc*-Ni/Mg–Al. This result clearly indicates that Mg–Al mixed oxide is an effective support for sustainability against coke formation. The decrease in the activity during the CO_2 reforming of CH_4 at 1073 K was observed with *imp*-Ni/α-Al_2O_3. This may be due to deposition of a large amount of coke on the catalyst surface; indeed, a large amount of coke was observed over *imp*-Ni/α-Al_2O_3. When the HT was used as the support (*spc*-Ni/Mg–Al and *imp*-Ni/Mg–Al), no significant difference was observed in the sustainability of the catalyst against coke formation.

3.4. Dispersion of Ni metal on the catalysts

The adsorption of H_2 on the Ni supported catalysts was measured by the H_2 pulse method and the dispersions of Ni metal on the catalysts were calculated (table 2). The amount of H_2 absorbed increased in the order of *imp*-Ni/α-$Al_2O_3 <$ *imp*-Ni/MgO $<<$ *imp*-Ni/Mg–Al $<$ *spc*-Ni/Mg–Al, and inevitably the dispersion of Ni metal on the catalyst can be put in the same order. This order well agrees with the catalytic activity except for *imp*-Ni/MgO. XRD analysis suggests the formation of a Ni–Mg–O solid solution in *imp*-Ni/MgO. The cubic structure of the Ni–Mg–O solid solution is very stable, resulting in a slow migration of Ni species from the bulk to the surface during the reaction, followed by the formation of highly dispersed Ni metal particles. The amount of surface Ni metal may be too small and most part of Ni species exist in the bulk under the reaction conditions. Despite the small amount of surface Ni metal species, the highly dispersed Ni metal particles on *imp*-Ni/MgO showed high catalytic activity for the CO_2 reforming of CH_4 and high sustainability against coke formation under the conventional conditions. However, the number of surface Ni metal species on *imp*-Ni/MgO is much smaller than those of both *spc*-Ni/Mg–Al and *imp*-Ni/Mg–Al catalysts, resulting in the decrease in activity at the high space velocity. In the case of *imp*-Ni/α-Al_2O_3, Ni metal exists exclusively on the surface and the size of Ni metal particles is much larger than that of the other catalysts. Such a large size of Ni metal particles may be responsible for the low activity and the large amount of coke deposition.

In the *spc* method starting from HT as the precursor, the resulting catalysts may contain Ni metal homogeneously in the bulk. During the *in situ* reduction of Ni species in the catalysts, a substantial part of Ni may migrate from the oxide structure to the surface to form highly dispersed and stable metal particles. Thus, it is likely that well dispersed and stable Ni metal particles were formed by the *spc* method, resulting in the high activity for the CO_2 reforming of CH_4 into synthesis gas. These results clearly suggest that the *spc* method is preferable for the preparation of highly dispersed metal supported catalysts. The relatively high catalytic activity of *imp*-Ni/Mg–Al may be due to the fact that a substantial part of Ni ions can be incorporated in the hydrotalcite phase during the preparation, resulting in the high dispersion of Ni metal. This phenomenon is exclusively due to the regeneration of the Mg–Al HT structure and seems to be important in the catalyst preparation.

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