Promoting effect of Ru on Ni/Mg(Al)O catalysts in DSS-like operation of CH$_4$ steam reforming

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Abstract

Effects of Ru addition on the activity and the sustainability of Ni/Mg(Al)O catalysts were investigated in the daily start-up and shut-down (DSS) operation of the steam reforming of CH_4. $Mg_{2.5}(Ni_{0.5})$-Al hydrotalcite was prepared by coprecipitation and calcined to form $Mg_{2.5}(Al,Ni_{0.5})O$ periclase. When the powders of the periclase were dipped in an aqueous solution of Ru(III) nitrate, the hydrotaclite was reconstituted on the surface of $Mg_{2.5}(Al,Ni_{0.5})O$ particles, resulting in the formation of highly dispersed Ru/Ni bimetal supported catalysts after the calcination, followed by the reduction. The addition of Ru on Ni caused a decrease in the reduction temperature of Ni and an increase in the amount of H_2 uptake on the Ni over the catalyst. Formation of Ru-Ni alloy or strong interaction between Ru and Ni was also suggested. When $Ru-Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts were tested in the DSS-like operation under steam purging, the deactivation due to the oxidation of Ni metal by steam was effectively suppressed by hydrogen spillover. Moreover, only 0.05 wt% of Ru loading was enough to effectively suppress the deactivation during the DSS-like operation.

Key Words: CH_4 reforming, H_2 production, DSS operation, Ni/Mg(Al)O catalyst, Ru addition, memory effect.

1. Introduction

Hydrogen production for polymer electrolyte fuel cell (PEFC) is a research area of an urgent necessity for solving global warming in the world. Steam reforming of hydrocarbons, especially of CH_4, is the largest and generally the most economical way to make H_2 [1]. This process still requires a further advancement in the preparation of superior reforming catalysts. The authors have reported the preparation of highly dispersed and stable metal supported catalyst starting hydrotalcite-like compounds; Ni/Mg(Al)O catalysts were prepared starting from Mg-Al hydrotalcite containing Ni at the Mg sites as the precursors, and were successfully applied in CH_4 steam reforming [2-4].

In contrast to the large-scale use of reformers in the industry under stationary operating conditions, temperature varied frequently by daily start-up and shut-down (DSS) in the operation for hydrogen production of PEFC in domestic use. Between shut-down and start-up in the DSS operation, catalyst bed in the reformer is certainly purged by steam for securing the safety. Thus, catalyst must be tolerable to multiple cycles under such unusual transient conditions without deterioration. Deactivations of Ni-loaded catalysts caused by coking, sintering or oxidation of the active metal species have been frequently reported [5-8]. Ni metal can be oxidized not only by gaseous oxygen but also even in the presence of steam as reported for lanthanide-promoted sol-gel Ni/Al_2O_3 catalyst in propane steam reforming [8].

We have reported that Ru supported on Ni/Mg(Al)O catalysts showed high and stable activity for dry reforming of CH_4 [9]. In this contribution, we report an improved behavior of Ru-Ni/Mg(Al)O catalyst in the DSS operation of steam reforming of CH_4.

Effects of the addition of small amount Ru on Ni/Mg(Al)O periclase have been investigated.

2. Experimental

2.1. Catalyst preparation

Mg$_{2.5}$(Al,Ni$_{0.5}$)O periclase was prepared by co-precipitation of nitrates of each metal component, followed by calcination [2-4,9] as follows: an aqueous solution containing the nitrates of Mg(II), Ni(II) and Al(III) was added slowly into an aqueous solution of sodium carbonate at the pH of 10. Mg$_{2.5}$(Ni$_{0.5}$)-Al hydrotalcite was obtained as precipitate, dried at 105 ºC, and calcined by increasing the temperature from ambient temperature to 900 ºC, to form Mg$_{2.5}$(Al,Ni$_{0.5}$)O periclase as the precursor of Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts. Ni loading was 13.5 wt% by ICP analyses after calcining at 900 ºC.

Ru loading has been done by adopting "memory effect" as follows: the powders of Mg$_{2.5}$(Al,Ni$_{0.5}$)O periclase were dipped in an aqueous solution of Ru(III) nitrate, dried at 105 ºC and finally calcined at 900 ºC, to form the precursor of Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts.

2.2. Characterization of catalyst

The structure of the catalysts was studied by using XRD, ICP, TPR, N$_2$ and H$_2$ adsorption method. Powder X-ray diffraction was recorded on a Rigaku powder diffraction unit, RINT 2250VHF, with mono-chromatized Cu Kα radiation (λ = 0.154

nm) at 40 kV and 300 mA. The diffraction pattern was identified by comparing with those included in the JCPDS data base (Joint Committee of Powder Diffraction Standards). The ICP measurement was carried out using a Perkin-Elmer OPTIMA 3000 spectrometer. The content of metal component was determined after the sample was completely dissolved using diluted hydrochloric acid and a small amount of hydrofluoric acid. The TPR of the catalyst was performed at a heating rate of 10 ºC min^{-1} using a mixture of 3 vol% H_2/Ar as reducing gas after passing through a 13X molecular sieve trap to remove water. A U-shaped quartz tube reactor, the inner diameter of which was 6 mm, equipped with a TCD for monitoring the H_2 consumption was used. Prior to the TPR measurements, the sample was calcined at 300 ºC for 2 h in 20 vol% O_2/N_2 gas. The N_2 adsorption (-196 ºC) study was used to examine the BET surface area of the Mg(Al)O periclase. The measurement was carried out on a Bell Japan Belsorp 18SP equipment (volumetric), and all samples were pretreated in vacuum at 200 ºC for 12 h before the measurements. The H_2 adsorption was carried out by static equilibrium method at ambient temperature using the pulse method. A 20 mg of the catalyst was reduced in a H_2/N_2 (5/25 ml min^{-1}) mixed gas at 900 ºC for 1 h and used for the measurement. During the pulse experiment, the amount of H_2 was monitored by a TCD-gas chromatograph.

2.3. Catalytic testing

Steam reforming of CH_4 was conducted using a fixed bed flow reactor in a CH_4/H_2O/N_2 (50/100/25 ml min^{-1}) mixed gas at 700 ºC over 50 mg of the catalyst in a DSS-like mode (Fig. 1). The catalyst was used as the powders dispersed in quartz sand.

U-shaped quartz reactor was used, with the catalyst bed near the bottom. N_2 was used as an internal standard for calculating the CH_4 conversion and the yields of products. After pre-reduction of the catalyst in a H_2/N_2 (5/25 ml min^{-1}) mixed gas at 900 ºC for 30 min, the reaction was started at 700 ºC. After the reaction for 90 min at 700 ºC, the reactor was cooled to 200 ºC under purging with a H_2O/N_2 (100/25 ml min^{-1}) mixed gas. After keeping the reactor at 200 ºC for 30 min, the temperature was again increased to 700 ºC still under the steam purging. When the temperature reached to 700 ºC, the reaction was started by adding CH_4 (50 ml min^{-1}) gas, carried out at 700 ºC for 90 min, and followed by the steam purging; the cycle reaction was repeated 4 times to perform the DSS-like operation. The thermocouple to control the reaction temperature was placed at the center of the catalyst bed. Product gases were analyzed by online TCD-gas chromatography.

3. Results and discussion

3.1. Reconstitution of hydrotalcite during the Ru catalyst preparation

XRD patterns of the samples during the preparation of Ru(0.1 wt%)-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts are shown in Fig. 2. The reflection lines of Mg$_{2.5}$(Ni$_{0.5}$)-Al hydrotalcite were observed for the sample as deposited by coprecipitation (Fig. 2a) and those of Mg$_{2.5}$(Al,Ni$_{0.5}$)O periclase appeared after the calcination at 900 ºC (Fig. 2b). After dipping the powders of Mg$_{2.5}$(Al,Ni$_{0.5}$)O periclase in aqueous solution of Ru(III) nitrate, Mg(Ni)-Al hydrotalcite was reconstituted together with Mg(OH)$_2$ brucite (Fig. 2c). The dipping treatment was followed by the

drying using water bath at 100 ºC, during which the reconstitution of hydrotalcite was completed by "memory effect" and no line of the periclase was observed. The formation of $Mg(OH)_2$ brucite suggests that the reconstitution of hydrotalcite from the periclase proceeded by the hydration of MgO, since MgO is thermodynamically unstable compared with $Mg(OH)_2$ [10]. MgO reacts very easily even with moisture in the air, especially at low coordination atomic site, to form $Mg(OH)_2$ brucite. The formation of $Mg(OH)_2$ implies segregation of MgO from periclase, i.e., destruction of original periclase. However, $Mg(OH)_2$ disappeared and the periclase phase regenerated after the calcination at 900 ºC for 5 h (Fig. 2d). Moreover, the formation of $Mg(OH)_2$ was suppressed by shortening the dipping time or by decreasing the amount of aqueous solution of Ru(III) nitrate. The formations of MgA_2O_4 or $NiAl_2O_4$ spinels are probably due to the repeated heating treatments. It must be noticed that Ru(III) was included in the hydrotalcite phase after the reconstitution although the detailed structure was not precisely determined. The lines of Ni metal appeared after the reduction of the calcined sample at 900 ºC for 1h (Fig. 2e) and noticeably remained after the 1st step of DSS-like operation (Fig. 2f). Interestingly after the 4th step of the DSS-like operation, the reflections of Ni metal were observed more intensively than those after the reduction and after the 1st step DSS-like operation (Fig. 2g).

3.2. Sustainability of Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts during the DSS-like operation.

The results of DSS-like operation over the supported Ru catalysts are shown in Fig. 3. The Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst showed a clear deactivation just after the 1st steam purging, indicating that Ni metal was immediately oxidized by steam. The Ni oxidation

was confirmed by XRD analyses, where no reflection line of Ni metal was observed. The Ni(13.5 wt%)/γ-Al$_2$O$_3$ catalyst showed also a similar behavior (data are not shown). By the addition of Ru(0.5 wt%) on Ni(13.5 wt%)/γ-Al$_2$O$_3$, the catalytic behavior was improved, but the catalyst was slowly deactivated in the 2nd and 3rd runs and the activity was lost totally after the 3rd steam purging in the DSS-like operation. Such drastic deactivation is certainly due to the oxidation of Ni metal. The addition of Ru on the Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst was quite effective for maintaining the activity during the 4 cycled DSS-like operation; even when the Ru loading decreased from 0.5 wt% to a very small value of 0.05 wt%. With the Ru loading of 0.01 wt%, however, the catalyst was totally deactivated after the 3rd cycle (data are not shown). Usually supported metal catalysts have been prepared by incipient wetness method using an aqueous solution, the volume of which corresponds to pore volume of the support materials. The Ru(0.1 wt%)-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst prepared by the incipient wetness method showed a clear deactivation after the 2 cycled DSS operation (data are not shown). No hydrotaclite reflection was observed in the XRD patterns of this catalyst, indicating that "memory effect" plays important role in the present catalyst preparation. In the absence of Ni, the activity of Ru(0.1~0.5 wt%)/Mg$_3$(Al)O catalysts gradually decreased during the reaction independently on the cycle number, suggesting that the deactivation was not due to the Ru oxidation but probably due to the sintering or the coking on the catalyst. It must be emphasized that Ru alone was not enough active with such small loadings and the activity of the Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts depended mainly upon the Ni species.

3.3. Reducibility of Ni and Ru species on Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts.

TPR profiles of the supported Ru catalysts are shown in Fig. 4. In the absence of Ni, no distinct H$_2$ consumption was observed for Ru(0.1 wt%)/Mg$_3$(Al)O and Ru(0.3 wt%)/Mg$_3$(Al)O (Fig. 4B a and b). A weak peak was observed around 500 ºC for both Ru(0.3 wt%)/Mg$_3$(Al)O and Ru(0.5 wt%)/Mg$_3$(Al)O with increasing intensity with increasing Ru loading (Fig. 4Bc) and is assigned to the reduction of RuO$_2$ to Ru metal. Ru replaces neither Mg^{2+} sites nor Al^{3+} sites in Mg-Al hydrotalcite reconstituted by the "memory effect" and separately exists in the layered structure of the hydrotalcite. It is likely that isolated Ru exists as RuO$_2$, since no other stable ruthenium oxides are known to exist in the solid state [11,12]. The TPR of Ru/Al$_2$O$_3$ and Ru/MgO catalysts showed the Ru reduction peak around 250 ºC and 235 ºC, respectively [13,14]. However, a strong metal-support interaction was frequently observed on the catalyst having well-dispersed Ru particles, causing an increase in the reduction temperature.

The reduction peak of Ni was observed at 895 ºC for the Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst (Fig. 4A d), and shifted to lower temperature even with a small Ru loading of 0.01 wt% (Fig. 4A e); the reduction temperature gradually decreased with further increasing the Ru loading on Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst (Fig. 4A f-h). This strongly suggests that a Ru-Ni alloy was formed or a strong interaction worked between Ru and Ni, resulting in an easy reduction of Ni on the Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts. On the other hand, only for Ru(0.5 wt%)-Ni$_{0.5}$/Mg$_{2.5}$(Al)O, a peak was observed around 400 ºC and is assigned to the reduction of RuO$_2$ to Ru metal (*vide infra*) (Fig. 4B i); the peak temperature was lower than 500 ºC observed for the Ru/Mg$_3$(Al)O catalysts, suggesting that Ru has interaction not only with Mg(Al)O support but also with Ni on the catalysts.

3.4. Active Ni species on Ru-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts.

H$_2$ uptakes were determined by the H$_2$ pulse method and reduction degrees were calculated from TPR peak area of Ni reduction for the supported Ni-Ru catalysts, and the results are shown in Table 1 together with the BET surface areas. The reduction degree of the Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst (88 %) was close to the value (87 %) reported for 1.9 wt% Ni/Mg(Al)O hydrotalcite-derived catalyst [15] and was lower than those observed for Ni/Al$_2$O$_3$ (106 %) and Ni/TiO$_2$ (97 %) catalysts prepared by incipient wetness method [16]. This is certainly due to the fact that a part of Ni was still incorporated as Ni^{2+} in Mg(Al,Ni)O periclase-solid solutions even after the reduction [15]. Ru loading of 0.05 wt% brought a significant increase in the H$_2$ uptake, while a decrease in the reduction degree, on the Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst; this may be due to an appearance of strong synergy between Ni metal and Ru metal. However, further increase in the Ru loading (0.1 and 0.3 wt%) caused a decrease in the H$_2$ uptake and oppositely an increase in the reduction degree. On both Ru(0.1 wt%)- and Ru(0.3 wt%)-Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalysts, RuO$_2$ separated from Ru-Ni bimetallic system exist as fine particles, which were well dispersed on the catalyst surface and probably showed a reduction peak overlapping on the Ni reduction in the TPR. Such RuO$_2$ was reduced during the TPR and assisted the reduction of Ni in Mg(Ni)O periclase by hydrogen spillover as observed in a decrease of Ni reduction temperature (Fig. 4A g and h). Moreover, such Ru species are likely to suppress the H$_2$ uptake on Ni metal probably by decreasing the Ni dispersion. Balint et al. [12] reported that the equilibrium exists between RuO$_2$ and Ru metal around 450 ºC on 12 wt%Ru/Al$_2$O$_3$ catalyst. In fact, Ru(0.5 wt%)-Ni$_{0.5}$/Mg$_{2.5}$(Al)O showed a peak around 400 ºC assigned to the reduction

of RuO_2 to Ru metal (Fig. 4B i), suggesting that excess Ru forms particulates of RuO_2 as a separate phase. This is also supported by the fact that no decrease was observed in the Ni reduction temperature by increasing Ru loading from Ru(0.3 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O to Ru(0.5 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O (Fig. 4A h and i); the excess Ru did not play a role for assisting the Ni reduction any more. However, after the H_2 reduction at 900 ºC before the H_2 pulse measurements, such Ru species became to have a contact with Ni and assisted to form Ni fine particles resulting in an increase in the H_2 uptake.

All Ru-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts showed higher values of the H_2 uptake compared with the $Ni_{0.5}$/$Mg_{2.5}$(Al)O catalyst. The contribution of Ru metal itself in the H_2 uptake on the Ru-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts must be small, since H_2 uptakes were extremely small on the Ru/Mg_3(Al)O catalysts compared with those on the Ru-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts of the same Ru loading. This strongly suggests an occurring of synergetic effect between Ru and Ni metals. Even after the 4th cycled DSS-like operation under steam purging, XRD pattern of the Ru(0.1 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalyst still showed reflection lines of Ni metal (Fig. 2f) and the CH_4 conversion reached the value of thermodynamic equilibrium (Fig. 3). The procedure of Ru loading by adopting "memory effect" of Mg-Al hydrotalcite seems to be important in preparing the active and sustainable Ni catalysts, since both Ru(0.1 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O (*vide supra*) and Ru(0.5 wt%)-Ni(13 wt%)/γ-Al_2O_3 prepared by incipient wetness showed a clear deactivation (Fig. 3). It is likely that Ru metal was finely dispersed on Ni metal particles or that both Ru metal and Ni metal partially

formed alloy; Ru metal protects Ni metal against the oxidation or promotes the reduction of NiO by suppling hydrogen to the surface of Ni metal particles by spillover.

4. Conclusion

The addition of Ru drastically improved the behavior of Ni/Mg(Al)O catalysts in the steam-purged daily start-up and shut-down (DSS) operation in the steam reforming of CH_4. The Ru loaded $Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts were prepared by adopting "memory effect" of $Mg_{2.5}$($Ni_{0.5}$)-Al hydrotalcite. When the powders of $Mg_{2.5}$(Al,$Ni_{0.5}$)O periclase prepared from the hydrotalcite were dipped in an aqueous solution of Ru(III) nitrate, the hydrotaclite structure was reconstituted on the surface of $Mg_{2.5}$(Al,$Ni_{0.5}$)O particles and included Ru species, resulting in the formation of highly dispersed Ru/Ni bimetal supported catalysts after the reduction. The addition of Ru on Ni resulted in a decrease in the reduction temperature of Ni and an increase in the amount of H_2 uptake on Ni on the catalyst. It is suggested that Ru-Ni alloy was formed or strong interaction worked between Ru and Ni. Ru-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts showed high sustainability during the DSS-like operation under steam purging, since the oxidation of Ni metal by steam was effectively suppressed by hydrogen spillover from Ru. Moreover, only 0.05 wt% of Ru loading was enough to effectively suppress the deactivation during the DSS-like operation.

References

1   J.R. Rostrup-Nielsen, Catal. Today 71 (2002) 243.

2   K. Takehira, T. Shishido, P. Wang, T. Kosaka and K. Takaki, J. Catal. 221 (2004) 43.

3   T. Shishido, P. Wang, T. Kosaka, K. Takehira, Chem. Lett. (2002) 752.

4   K. Takehira, T. Shishido, P. Wang, T. Kosaka, K. Takaki, Phys. Chem. Chem. Phys. 5 (2003) 3801.

5   S. Wang, H.Y. Zhu, G.Q. Lu, J. Colloid Interface Sci. 204 (1998) 128.

6   V.A. Tsipouriari, Z. Zhang, X.E. Verykios, J. Catal. 179 (1998) 283.

7   H.S. Bengaard, J.K. Nørskov, J. Sehested, B.S. Clausen, L.P. Nielsen, A.M. Molenbroek, J.R. Rostrup-Nielsen, J. Catal. 209 (2002) 365.

8   S. Natesakhawat, R.B. Watson, X. Wang, U.S. Ozkan, J. Catal. 234 (2005) 496.

9   A.I. Tsyganok, M. Inaba, T. Tsunoda, K. Uchida, K. Suzuki, K. Takehira, T. Hayakawa, Appl. Catal. A 292 (2005) 328.

10   J.H. Eun, J.H. Lee, S.G. Kim, M.Y. Um, S.Y. Park, H.J. Kim, Thin Solid Films 435 (2003) 199.

11   H. Madhavaram, H. Idriss, S. Wendt, Y.D. Kim, M. Knapp, H. Over, J. Aβmann, E. Löffler, M. Muhler, J. Catal. 202 (2001) 296.

12   I. Balint, A. Miyazaki, K. Aika, J. Catal. 220 (2003) 74.

13   S.-F. Yin, Q.-H. Zhang, B.-Q. Xu, W.-X. Zhu, C.-F. Ng, C.-T. Au, J. Catal. 224 (2004) 384.

14 C. Elmasides, D.I. Kondarides, W. Grünert, X.E. Verykios, J. Phys. Chem. B 103 (1999) 99.

15 A. Olafsen, Å. Slagtern, I.M. Dahl, U. Olsbye, Y. Schuurman, C. Mirodatos, J. Catal. 229 (2005) 163.

16 T. Miyazawa, T. Kimurea, J. Nishikawa, S. Kado, K. Kunimori, K. Tomishige, Catal. Today 115 (2006) 254.

Table 1. Surface area, H_2 uptake and reduction degree of supported Ni-Ru catalysts

Catalyst	BET surface area / $m^2\ g_{cat}^{-1}$	H_2 uptake[a] / $\mu mol\ g_{cat}^{-1}$	Reduction degree[b] / %
$Ni_{0.5}/Mg_{2.5}(Al)O$	189	118	88
$Ru(0.05\ wt\%)$-$Ni_{0.5}/Mg_{2.5}(Al)O$	149	196	77
$Ru(0.1\ wt\%)$-$Ni_{0.5}/Mg_{2.5}(Al)O$	149	172	85
$Ru(0.3\ wt\%)$-$Ni_{0.5}/Mg_{2.5}(Al)O$	148	172	80
$Ru(0.5\ wt\%)$-$Ni_{0.5}/Mg_{2.5}(Al)O$	146	202	77
$Ru(0.1\ wt\%)/Mg_3(Al)O$	146	1	-
$Ru(0.3\ wt\%)/Mg_3(Al)O$	140	4	-
$Ru(0.5\ wt\%)/Mg_3(Al)O$	144	2	-

a) Determined by the H_2 pulse method.
b) Determined by TPR.

Figure captions

Figure 1. DSS operation mode in the steam reforming of CH_4.

Figure 2. XRD patterns during the preparation of Ru(0.1 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O catalysts.

a) $Mg_{2.5}(Ni_{0.5})$-Al hydrotalcite; b) after calcination of a) at 900 °C for 5 h (0.83 °C min^{-1}) ; c) after dipping b) in an aqueous solution of Ru(III) nitrate, followed by drying; d) after calcination of c) at 900 °C for 5 h (1.7 °C min^{-1}); e) after reduction of d) at 900 °C for 1 h (H_2/N_2 = 1/5); f) after using e) in the 1st step of DSS operation followed by decreasing temperature to 200 °C under steam purge; g) after using e) in the 4 cycled DSS operation followed by decreasing temperature to 200 °C under N_2 purge.

●, Mg(Ni)-Al hydrotalcite; ■, Mg(Al,Ni)O periclase; ▲, $Mg(OH)_2$ brucite; □, $MgAl_2O_4$ or $NiAl_2O_4$ spinel; ○, Ni metal.

Figure 3. The results of DSS operation under steam purging in the steam reforming of CH_4.

+, $Ni_{0.5}$/$Mg_{2.5}$(Al)O; ◊, Ru(0.5 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; Δ, Ru(0.3 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; □, Ru(0.1 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; ○, Ru(0.05 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; *, Ru(0.5 wt%)-Ni(13.5 wt%)/γ-Al_2O_3; ●, Ru(0.5 wt%)/Mg_3(Al)O; ▲, Ru(0.3 wt%)/Mg_3(Al)O; ■, Ru(0.1 wt%)/Mg_3(Al)O.

Figure 4. TPR profiles of supported Ru catalysts.

a) Ru(0.1 wt%)/Mg_3(Al)O; b) Ru(0.3 wt%)/Mg_3(Al)O; c) Ru(0.5 wt%)/Mg_3(Al)O; d) $Ni_{0.5}$/$Mg_{2.5}$(Al)O; e) Ru(0.01 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; f) Ru(0.05 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; g) Ru(0.1 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; h) Ru(0.3 wt%)-$Ni_{0.5}$/$Mg_{2.5}$(Al)O; i) (0.5 wt%)Ru-$Ni_{0.5}$/$Mg_{2.5}$(Al)O.

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CH$_4$: 50 ml min^{-1}

H$_2$O: 100 ml min^{-1}

N$_2$: 25 ml min^{-1}

900 °C
30 min

700 °C
90 min

H$_2$: 5 ml min^{-1}

N$_2$: 25 ml min^{-1}

Purge gas,

H$_2$O: 100 ml min^{-1}

N$_2$: 25 ml min^{-1}

Reaction
start
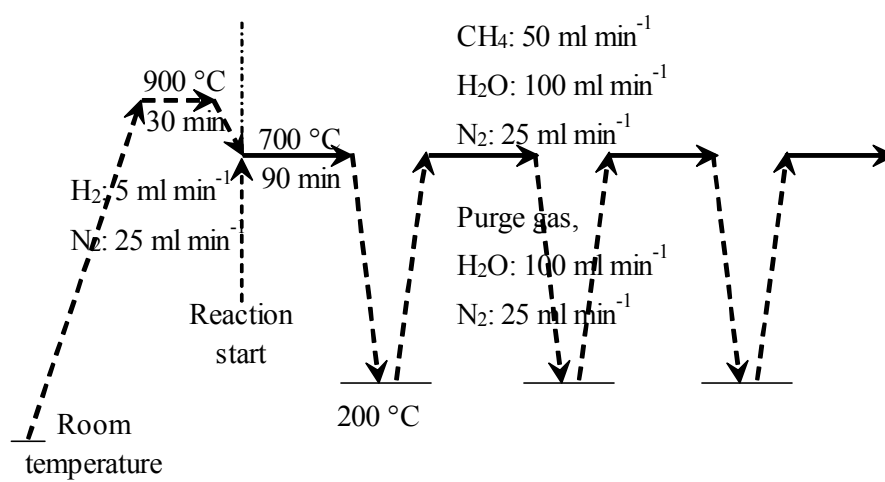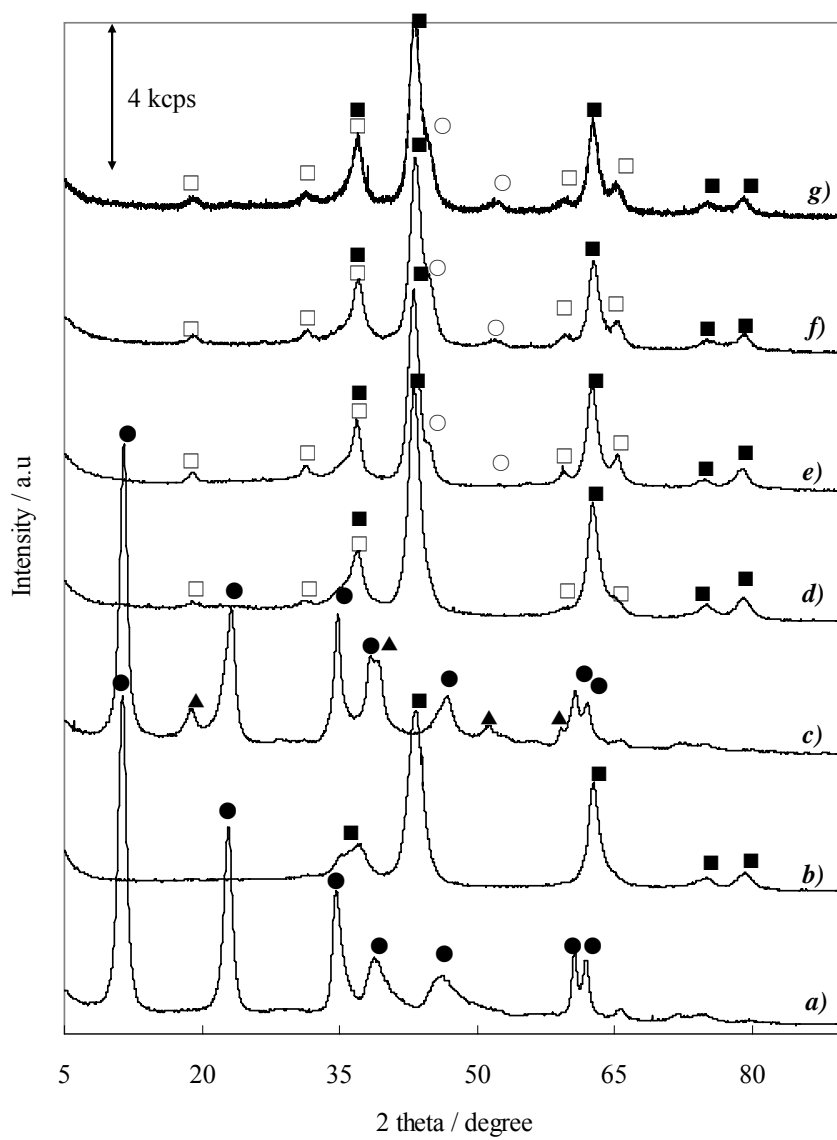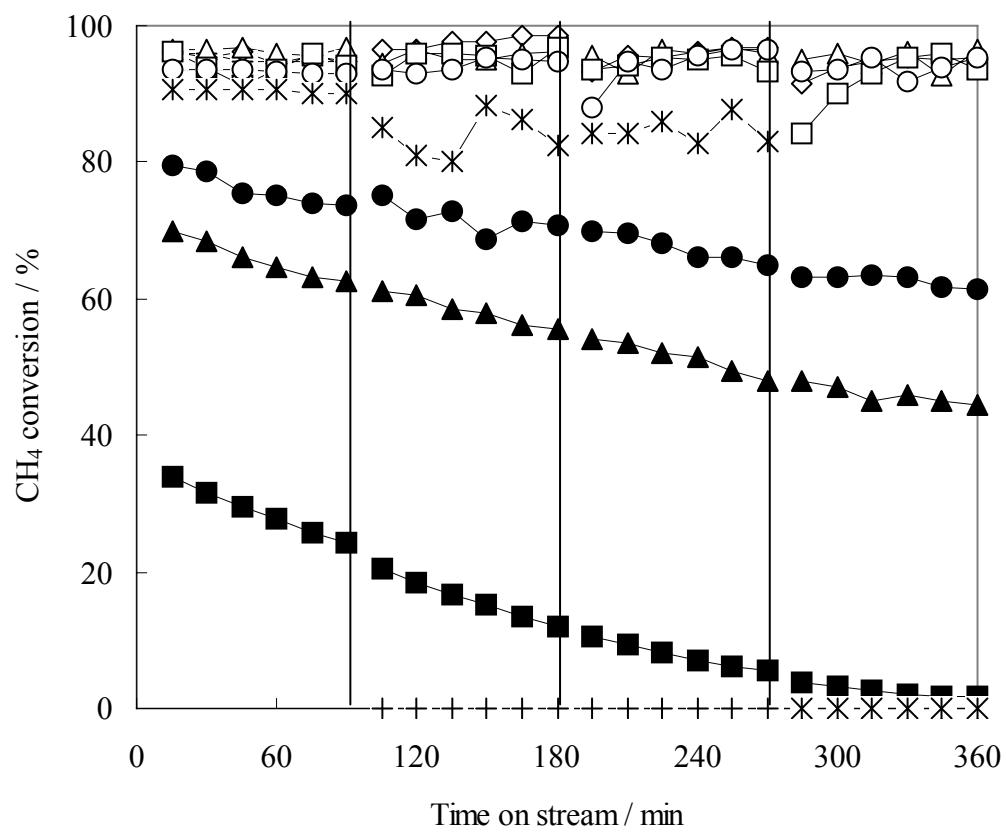
200 °C

Room
temperature

Figure 2. K. Takehira et al.

Figure 3.   K. Takehira et al.

Figure 4.   K. Takehira et al.