Steam reforming of CH_4 over Ni-Ru catalysts supported on Mg-Al mixed oxide

Running title: CH_4 Reforming over Ni-Ru/Mg(Al)O Catalysts

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Abstract

$Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst prepared from hydrotalcite precursors showed high and stable activity in the CH_4 steam reforming, but was severely deactivated in the daily start-up and shut-down (DSS) operation under steam purging. The addition of Ru drastically improved the behavior of $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst for the DSS operation. During the wet Ru loading on the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst, the reconstitution of hydrotalcite took place by “memory effect,” resulting in the formation of Ru-Ni alloy as well as the strong interaction between Ru and Ni after the calcination followed by reduction. This provided the catalyst with high sustainability probably by suppressing the oxidation of Ni metal by steam by hydrogen spillover from Ru. Only 0.05 wt% of Ru loading was enough to effectively suppress the deactivation.

Key words: steam reforming; CH_4; H_2 production; Ru-Ni/Mg(Al)O catalyst

1. Introduction

Hydrogen production for polymer electrolyte fuel cell (PEFC) is an emergent research area 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] and still requires further advancement in the preparation of prominent reforming catalysts. The authors have reported the preparation of highly dispersed and stable Ni supported catalyst starting from hydrotalcite-like compounds as the precursors; Ni/Mg(Al)O catalysts were prepared starting from Mg-Al hydrotalcite containing Ni at the Mg sites, and were successfully applied for steam reforming of CH_4 [2,3].

In contrast to the large-scale use of reformers in the industry under typical operating conditions, temperature varied frequently at startup and shutdown, i.e. daily startup and shutdown (DSS), for the operation in hydrogen production for PEFC in domestic use. Between shutdown and startup in each DSS operation, catalyst bed in the reformer must be purged by sufficiently inert and economically available gas for keeping the safety. Thus, the catalyst must withstand multiple cycles under such unusual transient conditions without deterioration. Deactivations of Ni-loaded catalysts caused by coking, sintering or oxidation of active metal species have been frequently reported [4,5]. 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 [6].

In this contribution, we report the catalytic behavior of Ni/Mg(Al)O in DSS operation for steam reforming of CH_4. Effects of the (Mg+Ni)/Al ratios on physicochemical properties and catalytic behaviors of Ni/Mg(Al)O have been discussed in connection with the effect of steam purging on the sustainability of Ni/Mg(Al)O catalysts. Finally, we report an enormously improved behavior of $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst in the DSS operation of steam reforming of CH_4.

2. Experimental

2.1. Catalyst preparation

Mg(Al,Ni)O periclases were prepared by co-precipitation of nitrates of each metal component, followed by calcination [2,3] 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(Ni)-Al hydrotalcites with varying Mg/Al ratio were obtained as precipitate, dried at 100 ºC, and calcined by increasing the temperature from ambient temperature to 900 ºC, to form Mg(Al,Ni)O periclase as the precursor of Ni/Mg(Al)O catalysts. Ni loading was fixed and determined as 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 100 ºC and finally calcined at 900 ºC, to form the precursor of $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts with varying Ru loading.

2.2. Characterization of catalyst

The structure of the catalyst 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% of H_2/Ar as reducing gas after passing through a 13X molecular sieve trap to remove water. The N_2 adsorption (-196 ºC) study was used to examine the BET surface area of the catalyst. 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. 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 at a rate of 20 ºC min^{-1} 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 at a rate of 20 ºC min^{-1} still under the purging conditions. 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 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.

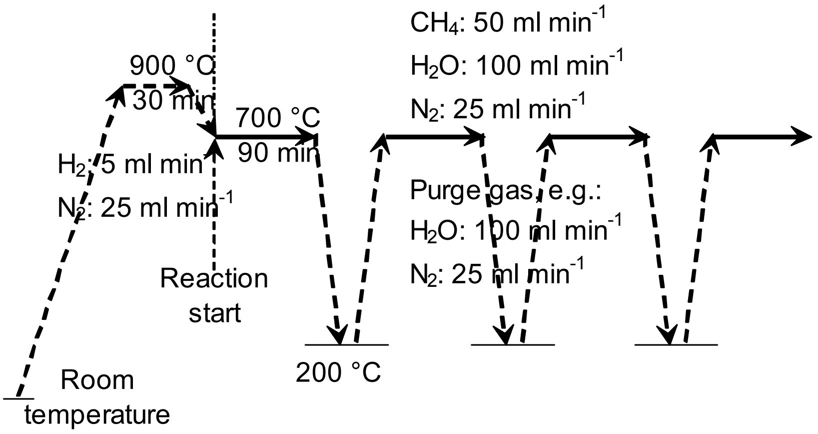

Fig. 1 DSS mode of the CH_4 steam reforming

3. Results and discussion

3.1. DSS operation over Ni/Mg(Al)O catalysts

The results of the DSS operation with the Ni/Mg(Al)O catalysts in steam reforming of CH_4 are shown in Fig. 2. H_2O/N_2 (100/25 ml min^{-1}) mixed gas was used for steam purging. Among the Ni/Mg(Al)O catalysts tested, $Ni_{0.5}/Mg_{2.5}(Al)O$ and $Ni_{0.62}/Mg_{3.38}(Al)O$ showed clear decrease in the activity, whereas $Ni_{0.85}/Mg_{5.15}(Al)O$ showed no significant deactivation during the DSS operation. Notable deactivation was observed for Ni/MgO, whereas Ni/Al_2O_3 showed stable activity. The sustainability of the Ni/Mg(Al)O catalysts varied depending on the (Mg+Ni)/Al ratio. It must be emphasized that the Ni/Mg(Al)O catalysts were most severely deactivated at the ratio of 3/1, which was the most active and sustainable in the steady state reforming of CH_4 [2,3].

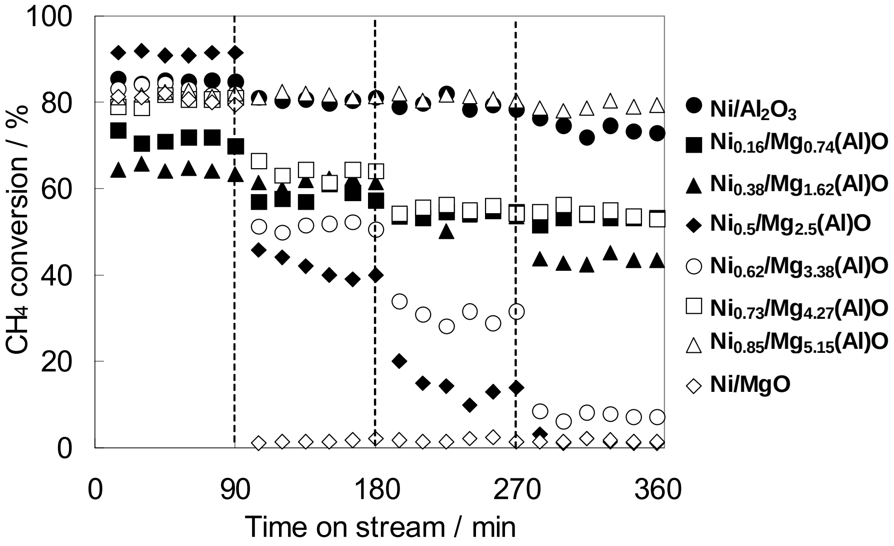

Fig. 2 Steam-purged DSS opearion in the CH_4 reforming over the Ni/Mg(Al)O catalysts

3.2. Oxidation of Ni on Ni/Mg(Al)O catalysts during DSS operation

XRD patterns of the Ni/Mg(Al)O catalysts after the steam-purged DSS operation are shown in Fig. 3. For the Al rich catalysts, the reflection lines of $MgAl_2O_4$ and $NiAl_2O_4$ spinels were observed, while those of Mg(Ni,Al)O periclase were observed for the Mg rich catalysts. As reported previously [2,3], fresh catalysts showed mainly the reflection lines of Mg(Ni,Al)O periclase; Ni^{2+} ions in the periclase were reduced to Ni metal during the pre-reduction treatment and showed activity for the CH_4 reforming. After the DSS operation for 4 cycles, the reflection lines of Ni metal were observed for the catalysts which showed no deactivation in Fig. 2. The line intensities of Ni metal did not well coincide with the sustainability of the catalyst; the sustainability was higher for $Ni_{0.85}/Mg_{5.15}(Al)O$ than for Ni/Al_2O_3 although the line intensity was stronger for the latter than for the former. This suggests that finely dispersed Ni metal particles were formed on the $Ni_{0.85}/Mg_{5.15}(Al)O$ catalyst, resulting in the higher activity than the Ni/Al_2O_3 catalyst with larger-sized Ni metal particles.

It is most likely that MgO on the Ni/MgO catalyst must be converted to $Mg(OH)_2$ brucite at low temperature during the DSS operation, since $Mg(OH)_2$ is thermodynamically more stable than MgO [7], which probably induced the Ni oxidation, resulting in the deactivation. Although no reflection line of Mg-Al hydrotalcite was detected in the XRD pattern of the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst after the DSS operation, it is possible that the catalyst surface was changed to hydrotalcite-like structure as supposed in the formation of $Mg(OH)_2$ brucite on Ni/MgO. It is concluded that the $Ni/Mg_{0.5}(Al_{2.5})O$ catalyst was most severely deactivated by Ni oxidation in steam purged DSS operation, although it showed the highest activity as well as the highest stability during the steady state operation.

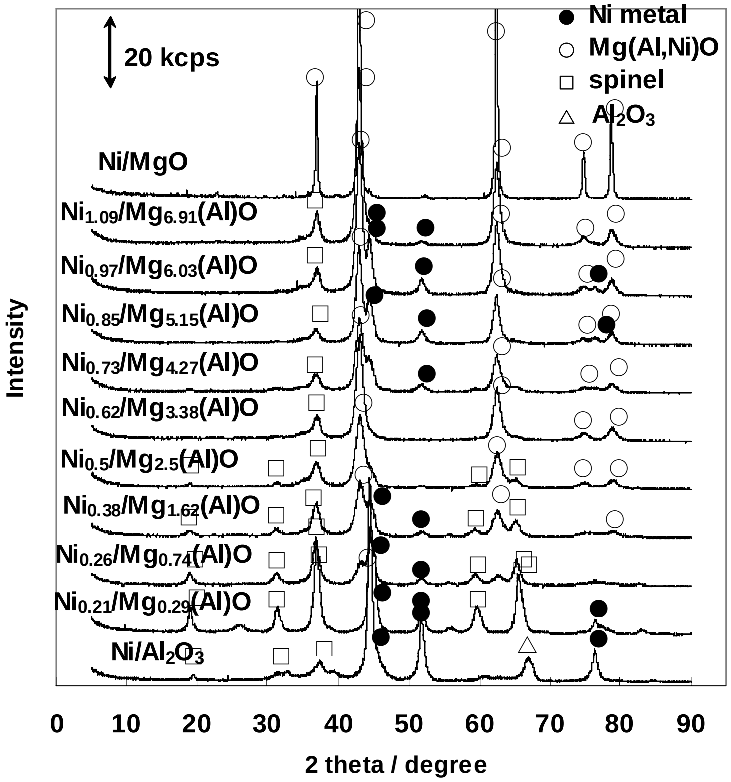

Fig. 3 XRD patterns of Ni/Mg(Al)O catalysts after the steam-purged DSS operation

3.3. Sustainability of the $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts during the DSS-like operation.

XRD patterns of the samples during the preparation of the Ru(0.1 wt%)-$Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts showed the reflection lines of $Mg_{2.5}(Ni_{0.5})$-Al hydrotalcite as deposited by coprecipitation and those of $Mg_{2.5}(Al,Ni_{0.5})O$ periclase appeared after the calcination at 900 ºC. 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. The dipping treatment was followed by 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 proceeds by the hydration of MgO. After the calcination of the hydrotalcite reconstituted at 900 ºC for 5 h, the lines of periclase again appeared together with those of $MgAl_2O_4$ or $NiAl_2O_4$ spinel. The lines of Ni metal appeared after the reduction of the calcined sample at 900 ºC for 1h. It is noticeable that the lines of Ni metal remained even after the 4 cycled DSS operation.

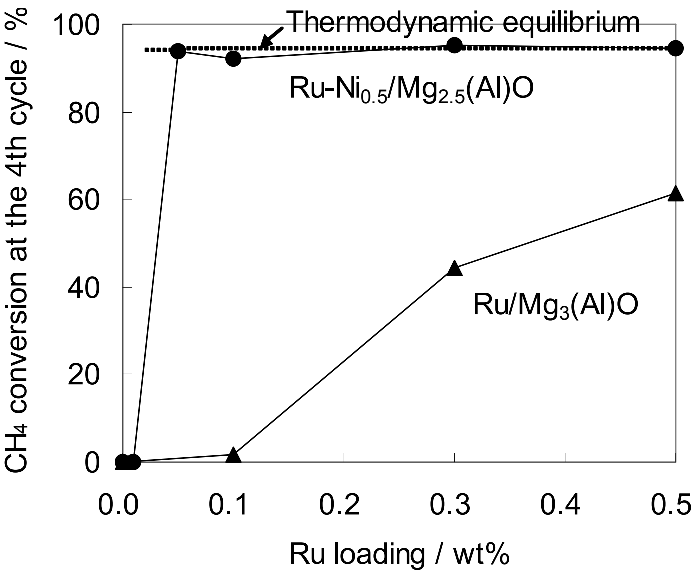

Fig. 4 Steam-purged DSS operation in the CH_4 reforming over the supported Ru catalysts.

The results of DSS operation over the supported Ru catalysts are shown in Fig. 4. The $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst showed a clear deactivation during the DSS operation (Fig. 2), indicating that Ni metal was quickly oxidized by steam. The addition of Ru on the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst was quite effective for preserving the activity during the 4 cycled DSS operation; even when the Ru loading decreased from 0.5 wt% to 0.05 wt%. With the Ru loading of 0.01 wt%, however, the catalyst was totally deactivated after the 3rd cycle. In the absence of Ni, the activity of the $Ru/Mg_3(Al)O$ 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 loading.

TPR measurements of the catalysts (data are not shown) showed that the reduction of Ni appeared at 895 ºC for the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst and the reduction temperature gradually decreased with increasing the Ru loading amount. No Ru reduction peak was observed. 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 $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts. H_2 uptakes determined by the H_2 pulse method for the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst drastically changed by the Ru loading; even with 0.05 wt% of the Ru loading, H_2 uptake enormously increased although the surface area of the catalysts rather decreased. All $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts showed higher values of the H_2 uptake compared with the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst. This indicates an occurring of synergetic effect between Ru and Ni metals. Even after the 4th cycled DSS 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 and the CH_4 conversion reached the value of thermodynamic equilibrium (Fig. 4). According to the XRD measurements, the average diameter of Ni metal particles decreased from 9 nm for $Ni_{0.5}/Mg_{2.5}(Al)O$ to 4 nm for 0.5 wt%Ru-$Ni_{0.5}/Mg_{2.5}(Al)O$ after the reduction. Moreover, XANES measurements (data are not shown) suggest that Ni-Ru bonding takes place on the $Ru\text{-}Ni_{0.5}/Mg_{2.5}(Al)O$. It is likely that Ru and Ni metals were finely dispersed and strongly interacted each other or that both Ru metal and Ni metal partially formed alloy; Ru protects Ni metal against the oxidation by supplying hydrogen to the surface of Ni metal particles by spillover.

4. Conclusion

The Ni/Mg(Al)O catalysts have been prepared from hydrotalcite precursors and tested for the CH_4 steam reforming. The $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst showed high and stable activity but was significantly deactivated in the daily start-up and shut-down

(DSS) operation under steam purging. The addition of Ru drastically improved the behavior of the $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst for the DSS operation. The Ru loaded $Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts were prepared by adopting “memory effect” of 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, 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 resulted in a decrease in the reduction temperature of Ni in TPR and an increase in the amount of H_2 uptake on Ni on the catalyst In H2 pulse measurement, suggesting the formation of Ru-Ni alloy as well as the strong interaction between Ru and Ni. The Ru-$Ni_{0.5}/Mg_{2.5}(Al)O$ catalysts showed high sustainability during the DSS 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.

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