Preparation of Highly Dispersed Ni Catalysts for H₂ Production for Polymer Electrolyte Fuel Cells

Tetsuya Shishido¹ 1), ² and Katsuomi Takehira³)

¹ ¹Dept. of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Minami-Osawa 1-1, Hachioji, Tokyo 192-0397, JAPAN
² ²Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, JAPAN
³ ³Dept. of Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima, Hiroshima 739-8527, JAPAN

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Reforming of methane and propane with supported Ni catalysts was investigated for the production of hydrogen for polymer electrolyte fuel cells (PEFCs). Supported Ni catalysts were prepared from Mg(Ni)₃Al hydrotalcite-like compounds (HTlcs) as the precursor. The precursors were prepared by the co-precipitation method from nitrates of the metal components, thermally decomposed, and then in-situ reduced to form supported Ni catalysts. Ni²⁺ can effectively replace the Mg²⁺ site in the HTlcs, resulting in the formation of highly dispersed and stable Ni metal particles on supported Ni catalysts. Supported Ni catalysts prepared by this method showed higher activity than catalysts prepared by the conventional impregnation method such as Ni/α-Al₂O₃ and Ni/MgO. Moreover, the activity and stability of supported Ni catalysts were improved by combining a small amount of noble metals by adopting the “memory effect.” which allows the reconstitution of the original hydrotalcite-like structure, and were effective for the production of hydrogen under the daily start-up and shut-down operations.

Keywords
Hydrotalcite-like compound, Supported nickel catalyst, Reforming, Hydrocarbon, Hydrogen production, Memory effect

1. Introduction

Hydrogen production for use in polymer electrolyte fuel cells (PEFCs) is an important emerging research area for solving the global problems caused by global warming. Steam reforming of hydrocarbons, especially of CH₄, is the most common and generally the most economical way to make H₂ (Eq. (1))¹).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

However, the small units for providing hydrogen for fuel cell in vehicles or domestic supplies require the reformer to be far smaller and cheaper than the designs used in conventional steam reforming. Furthermore, the operating temperature will vary frequently at daily start-up and shut-down (DSS) in the reformers for domestic use, in contrast to the constant operating conditions for large-scale reformers in industrial use. The catalyst bed in the reformer requires purging with steam for safety reasons between shut-down and start-up in DSS operation. Therefore, the catalyst must tolerate multiple cycles under such unusual transient conditions without deterioration.

Deactivations of supported Ni catalysts is frequently caused by coking, sintering or oxidation of the active metal species²⁻⁻³). Ni metal is oxidized not only by gaseous oxygen but also by steam as found for lanthanide-promoted sol-gel Ni/Al₂O₃ catalyst in propane steam reforming⁴). Therefore, this process requires further developments in the preparation of suitable reforming Ni-based catalysts, which must have far higher activity as well as stability compared to those catalysts used for synthesis gas production for methanol or Fischer-Tropsch synthesis.

Highly dispersed metal particles over catalysts⁶) or use of alkaline earth metal oxides in catalysts⁷) may reduce coke formation and improve the catalyst sustainability. Supported metal catalysts are conventionally prepared by wet impregnation of different supports. This method is not fully reproducible and may result in some heterogeneity in the distribution of metal on the surface. Therefore, a new concept of catalyst preparation is required. Use of precursors with structures containing homogeneously distributed metal may, on
further calcination and reduction, result in the formation of highly dispersed and stable metal particles on the surface. This method may be generally applicable in the preparation of highly dispersed metal supported catalysts starting from many types of mixed metal oxide as the precursors.

We have developed a preparation method for highly dispersed and stable supported Ni catalysts (Ni/Mg(Al)O catalysts) derived from hydrotalcite-like compounds (HTlcs) as the precursors. Supported Ni catalysts (Ni/Mg(Al)O catalysts) were prepared by thermal treatment followed by reduction of ternary Mg(Ni)-Al HT with varying Mg/Al ratios8) 

Hydrotalcite-like compounds (HTlcs) can be represented by the general formula: \[ [\text{M}(\text{II})^{1-x}\text{M}(\text{III})^x(\text{OH})_2]^x(\text{A}^n_{-x/n})_{\text{m}}\text{H}_2\text{O} \], and contain various cations (M(II) and M(III)) and the anion (A\text{n}–)16). The structure of HTlcs is basically consists of brucite, Mg(OH)\text{2}, in which the octahedral of Mg\text{2}\text{+} (6-fold coordinated to OH–) share edges to form infinite sheets. These sheets are stacked on top of each other and are held together by hydrogen bonding (Fig. 1)\text{17}). Substitution of Mg\text{2}\text{+} ions with a trivalent ion with a similar radius to that of Mg\text{2}\text{+} (such as Fe\text{3}\text{+} and Al\text{3}\text{+} for pyroaurite and hydrotalcite, respectively), generates a positive charge in the hydroxyl sheets. This net positive charge is balanced by CO\text{3}\text{2}– anions, which lie in the interlayer region between two brucite sheets. Water of crystallization is also located in this free interlayer space.

The main features of HTlcs structures are determined by the nature of the brucite sheets, by the position of anions and water in the interlayer region, and by the type of stacking of the brucite sheets. The brucite sheets containing cations are arranged in the brucite structure, in which the cations randomly occupy the octahedral holes in the close-packed configuration of the OH– ions. Generally, M(II) and M(III) ions can be accommodated in the holes within the close packed configuration of OH groups in the brucite layers, as allowed by the ionic radii and the valence states.

HTlcs can be directly used as catalysts since the various transition metal cations act as active species and are well dispersed on the basic support materials. Mixed oxides derived from HTlcs are also potential catalysts since calcination forms mixed oxides with very small crystal size, and stable to thermal treatment. The mixed oxides possess interesting properties such as high surface area, basicity, and reduction forms small and thermally stable metal crystallites. Moreover, the mixed oxides show the unique property of the “memory effect,” which allows the reconstitution of the original hydrotalcite structure\text{18),19}). The most common HTlcs consist of the Mg–Al system, in which various metal cations can substitute at both sites of Mg(II) and Al(III) depending on the valence state and ionic radii\text{17),18}). Ni(II) substituted at the Mg(II) sites of Mg–Al hydrotalcite will be highly dispersed and octahedrally coordinated with oxygen.

The present study describes the high activity and sustainability of supported Ni catalysts prepared from Mg(Ni)–Al HTlcs for the reforming of CH\text{4} and propane. Catalysis by supported Ni catalysts was improved by adding a small amount of noble metals by adopting the “memory effect,” and used in the production of hydrogen under DSS operation.

2. Ni/Mg(Al)/O Catalysts Prepared from HTlcs for the Reforming of Hydrocarbons

Ni/Mg(Al)O catalysts were prepared by thermal treatment followed by reduction of ternary Mg(Ni)–Al HT with varying Mg/Al ratios \(\text{Scheme 1}^{8-15}\) and were successfully applied for the partial oxidation, the dry reforming of CH\text{4} (CO\text{2} reforming), the steam reforming of CH\text{4} and the autothermal reforming. Ni/ Ca(Al)O catalyst was also prepared and used for the partial oxidation of CH\text{2}\text{O}\text{19}).

The high and stable activity of these catalysts can be attributed to the formation of stable and well-dispersed
Mixed gas of CH₄/O₂/N₂ (1/2/1) was passed at 800 °C over 50 mg and 5 mg of the catalyst diluted by quartz beads at the low (dotted line) and the high (full line) space velocities, respectively.

Fig. 2 Partial Oxidation of CH₄ over Supported Ni Catalysts

Ni metal particles generated from Mg(Ni,Al)O periclase in solid solutions obtained by calcination of Mg(Ni)–Al HT. Mg(Ni,Al)O periclase was reduced in-situ to form fine Ni metal particles on the catalysts and showed activity for dry reforming of CH₄. After the pre-reduction treatment, the Ni/Mg(Al)O catalysts showed activity for partial oxidation of CH₄, in which the reaction proceeds via combustion (Eq. (2)), followed by steam reforming (Eq. (3)).

CH₄ + 2O₂ → CO₂ + 2H₂O (2)
CH₄ + CO₂ → 2CO + 2H₂ (3)

The Ni₀.₅/Mg₂.₅(Al)O catalyst prepared from Mg(Ni)–Al HT (Mg₂.₅Niₐ.₅(Al(III))ₐ(OH)₉·2H₂O, M(II)/M(III) = 3/1) showed the highest activity; as CH₄ conversion at the thermodynamic equilibrium was obtained even at the enormously high space velocity of 9 × 10⁵ mL h⁻¹ g cath⁻¹ (Fig. 2)¹². This excellent value of space velocity exceeded the value of 7 × 10⁴ mL h⁻¹ g cath⁻¹ obtained in CH₄ partial oxidation over the 0.1 wt% Rh/MgO catalyst previously reported.¹¹ Ni catalysts for partial oxidation were frequently deactivated due to the surface oxidation of Ni metal particles, which was usually accompanied by drastic decrease in the CH₄ conversion as seen for the commercial Niα–Al₂O₃ catalyst (FCR, Süd Chemie Co.) (Fig. 2). This FCR catalyst has been used in the steam reforming of CH₄ in the industrial scale. Ni₀.₅/Mg₂.₅(Al)O catalyst showed higher sustainability than FCR catalyst in steam reforming of CH₄ (Fig. 3)¹¹; the reaction was carried out using 20 cm³ of Ni₀.₅/Mg₂.₅(Al)O and FCR at 800 °C, steam to carbon ratio (S/C) = 1.6 and space velocity (SV) = 2500 h⁻¹ for 600 h, during which SV was increased to 10,000 h⁻¹ for precisely evaluating deactivation of the catalyst. Under the latter conditions, the reaction temperature inevitably decreased to 660 °C due to the endothermic reaction. Ni₀.₅/Mg₂.₅(Al)O always maintained CH₄ conversion at the thermodynamic equilibrium of steam reforming, whereas FCR showed clear decrease in CH₄ conversion during the 600 h of reaction.

Ni₀.₅/Mg₂.₅(Al)O prepared by co-precipitation from nitrates of Ni(II), Mg(II) and Al(III) was characterized by all Ni species distributed homogenously in the catalyst particles, so Ni species located inside the particles could not act as the active species. The reduction degree obtained from the temperature-programmed reduction (TPR) measurements of Ni₀.₅/Mg₂.₅(Al)O was 88 %, indicating clearly that some Ni remains as Ni²⁺ in Mg(Ni,Al)O periclase particles even after the reduction. Effective Ni loading in the outer layer of the catalyst particles is preferable; such eggshell-type Ni loading on the Mg(Al)O periclase was achieved by adopting the “memory effect” of Mg–Al HT (Scheme 2). Active Ni metal particles were effectively enriched in the surface layer of the catalyst particles by controlling the preparation conditions. The mechanism of reconstitution of Mg–Al HT leading to eggshell-type Ni loading on Mg(Al)O periclase was investigated.¹⁵ The reconstitution of HT by the “memory effect” proceeded in the micro-porous phase and formed “worm” like structures in the Mg(Al)O particles. Calculation of Mg–Al HT under mild conditions resulted in rapid formation of the “worm” like structures on the surface of Mg(Al)O particles and finally formed a dense
layer which perfectly covered the surface of the particles (Fig. 4 a, c) and e). This dense layer hindered a further penetration of Ni$^{2+}$ ions into the cores of the particles, resulting in the eggshell-type Ni loading. In contrast, high temperature calcination caused formation of MgAl$_2$O$_4$ spinel on the particles, which proceeded slowly throughout the particles and simultaneously Ni$^{2+}$ penetrated into the cores of the particles (Fig. 4 b, d and f). The balance between the rate of reconstitution of Mg-Al HT and the rate of penetration of aqueous solution of nickel nitrate determined the loading type of Ni. Moreover, the enhanced activity per unit of Ni due to the surface enrichment of active Ni species was successfully explained by the measurements of the effectiveness factor of the Ni/Mg(Al)O catalyst (Fig. 5). The eggshell-type Ni loaded catalyst was active not only for the steam reforming but also for autothermal reforming of CH$_4$. Such eggshell-type metal loading technique would be effective for the preparation of noble metal loaded catalysts on Mg(Al)O (vide infra).

3. Improvement of Stability of Ni/Mg(Al)O Catalysts by the Addition of a Small Amounts of Noble Metals

Application of Ni/Mg(Al)O catalysts to the DSS operation of the steam reforming of CH$_4$ (Fig. 6) found that the Ni$_{0.5}$/Mg$_{2.5}$(Al)O catalyst was severely deactivated although this catalyst showed high and stable activity in steady state CH$_4$ reforming (Figs. 2 and 3). The results obtained with the Ni/Mg(Al)O catalysts with various (Mg + Ni)/Al ratios together with commercial catalysts and catalysts prepared by impregnation for three purge gases, i.e., steam, air and spent gas, are shown in Fig. 7. RUA is a commercial Ru/α-Al$_2$O$_3$ catalyst and FCR is a Ni/α-Al$_2$O$_3$ catalyst, both supplied by Süd Chemie Co. O$_2$ in air most severely damaged all supported Ni catalysts. MgO-supported Ni catalysts were completely deactivated, whereas Al$_2$O$_3$-supported Ni catalysts showed stable...
activity using both steam and spent gas. The stability of the Ni/Mg(Al)O catalysts varied depending on the (Mg+Ni)/Al ratio. Ni catalysts are frequently deactivated by sintering or coking during the long term reaction. However, such deactivation was not significant in the present DSS operation. The deactivation apparently proceeded rapidly due to the oxidation of Ni metal to NiO, which transformed back into Mg(Ni,Al)O periclase, judging from the X-ray diffraction (XRD) observations indicating that the reflection lines of Ni metal disappeared and those of Mg(Ni,Al)O periclase increased after the deactivation. Ni oxidation probably occurred directly due to oxidation by O2 or H2O or was possibly induced by hydration of MgO to Mg(OH)2 brucite, since Mg(OH)2 is thermodynamically more stable than MgO under the present conditions (vide infra).

Noble metals, such as Rh, Ru and Pt, are also used as the active species in catalysts prepared from Mg–Al HT as the precursors. Rh/Mg2(Al12)O catalyst showed high and stable activity in the partial oxidation of CH4 under severe conditions. The structure of Rh dissolved in a Mg and Al matrix is responsible for the highly dispersed and active Rh catalyst obtained after reduction. The catalytic activity of Rh and Ru supported on Mg(Al)O was studied by changing the Mg/Al ratio in the precursors; high Mg/Al ratio depressed the formation of MgAl2O4 spinel and enhanced the formation of Mg(Al)O periclase, leading to a narrow distribution of particle size of both Rh and Ru metals, resulting in the high activity. Usually, Mg–Al HT is obtained with carbonate as the interlayer anion starting from metal nitrates, since a NaOH/Na2CO3 mixture is used as precipitating agent. Various anions can replace carbonates in the interlayer of Mg–Al HT. Starting from ternary Mg–Al(Rh) HT containing silicates as the interlayer anions, new active and stable nanostructured catalysts were prepared by the calcination followed by the reduction. The activity of these catalysts for the partial oxidation of CH4 was higher than those prepared from conventional carbonate methods. Synergy was observed in the partial oxidation of CH4 over Rh–Ni bimetallic catalysts prepared from quaternary Mg(Ni)–Al(Rh) HT precursors obtained by co-precipitation. Reactions at with very short residence times over Rh–Ni bimetallic catalyst under conditions in which O2 was not totally converted found high activity of the Rh/Ni catalyst due to the maintenance of Ni in the reduced state by the Rh. Rh–Ni bimetallic catalysts derived from HTlc's precursors were successfully tested in the autothermal reforming of CH4 in the presence of small amounts of ethane. Rh–Ni/Mg(Al)O catalyst showed stable activity whereas Ni/Mg(Al)O
catalyst was deactivated at very high space velocities (1.2 × 10^7 mL h^-1 gcat^-1) through oxidation of metallic Ni. The enhanced stability of 25 wt% Ni-1 wt% Rh/Mg(Al)O catalyst against oxidation is attributed to H2 spillover from Rh in the NiRh alloy as well as to its high activity.

4. Improvement of Activity and Stability of Ni/Mg(Al)O Catalysts by Adopting the "Memory Effect"

Ni can also be incorporated as anion into the interlayer of Mg-Al HT by using nickel chelate, since Ni(II) can react with the anionic chelating agent of EDTA^4-, producing the highly stable species [Ni(EDTA)]^2-. We studied on the effects of the preparation methods of the precursors as follows: A) co-precipitation of Ni, Mg and Al nitrates with carbonate; B) co-precipitation of Mg and Al nitrates with pre-synthesized nickel chelate; and C) anion exchange of NO3- of HT with nickel chelate. Ni/Mg(Al)O catalyst prepared by method A was the most active for converting CH4, with a high H2 yield in the steam reforming of CH4 probe. The amount of noble metals could be reduced from 2.0 to 0.1 wt% of support without decreases in catalytic activity or selectivity for synthesis gas product in CO2 reforming of CH4.

The synthesis strategy applied for preparing noble metal catalysts supported on Mg(Al)O, is summarized in Scheme 3. Calcining synthetic HT in air at 500 °C produced Mg(Al)O (step 1). The layered structure of HT was then reconstituted by the "memory effect," resulting in incorporation of negatively charged chelates of noble metals (MY-) into the HT matrix (step 2). Calcination in air at 1000 °C converted HT to mixed metal oxide, mainly consisting of Mg(Al)O periclase and of MgAl2O4 spinel (step 3). The introduced metal presumably occurred as fine oxide clusters (MOx) bound to the surface of the support. Such surface-bound metal oxide clusters transformed into metallic species (M°) under the reaction conditions (step 4), resulting in highly active and selective catalysts with low coking capacity. Ru(0.1 wt%)-Ni(5.0 wt%)/Mg(Al)O catalyst had the highest activity and selectivity for synthesis gas, a stable durability and a low coking capacity in the CO2 reforming of CH4.

Noble metals could be loaded on Ni/Mg(Al)O catalysts more simply by dipping the Mg(Ni,Al)O periclase particles in aqueous solution of noble metal nitrates. Calcination followed by reduction of the resultant particles prepared noble metal-Ni/Mg(Al)O catalysts which were successfully applied in the DSS operation of steam reforming of CH4. Small amounts of noble metals, Rh, Pt and Ru, effectively suppressed the deactivation of Ni0.5/Mg2.5(Al)O catalyst during the DSS operation of CH4 steam reforming. During the preparation of noble metals-Ni0.5/Mg2.5(Al)O catalysts, reconstitution of HT was clearly observed; the XRD patterns of samples during the preparation of Ru(0.1 wt%)-Ni0.5/Mg2.5(Al)O periclase appeared after calcination at 900 °C.

The reflection lines of Mg2.5(Ni0.5)O-Al HT were observed for the sample as deposited by co-precipitation (Fig. 8a)) and the lines of Mg2.5(AlNi0.5)O periclase appeared after calcination at 900 °C (Fig. 8a)). After dipping the Mg2.5(AlNi0.5)O periclase powder in aqueous solution of Ru(III) nitrate, Mg(Ni)-Al HT was reconstituted together with Mg(OH)2 (Fig. 8c)). The dipping treatment was followed by drying in a water bath at 100 °C, during which the reconstitution of HT was completed by the "memory effect" and no reflection line of periclase was observed. The formation of Mg(OH)2 suggests that reconstitution of HT from the periclase proceeds via hydration of MgO, since MgO is thermodynamically unstable compared with Mg(OH)2. MgO reacts very easily even with moisture in the air, especially at low coordination atomic sites, to form Mg(OH)2. The formation of Mg(OH)2 implies segregation of MgO from periclase, i.e., destruction of the original periclase. However, Mg(OH)2 disappeared and the periclase phase regenerated after calcination at 900 °C for 5 h (Fig. 8)
Noble Metal–Ni/Mg(Al)O Catalysts for the DSS Operation

2nd and 3rd runs, and activity was totally lost after the 3rd steam purging in the DSS-like operation. Such drastic deactivation is certainly due to the oxidation of Ni metal. Addition of Ru to Ni0.5/Mg2.5(Al)O catalyst was quite effective for maintaining high activity during the 4-cycled DSS-like operation; even with decreased Ru loading from 0.5 wt% to the very low 0.05 wt%. However, Ru loading of 0.01 wt% resulted in total deactivation after the 3rd cycle.

Supported metal catalysts are usually prepared by the incipient wetness method using an aqueous solution, with equal volume to the pore volume of the support materials. 0.1 wt% Ru–Ni0.5/Mg2.5(Al)O catalyst prepared by the incipient wetness method showed clear deactivation after 2-cycle DSS operation. No distinct HT reflection was observed in the XRD patterns of this catalyst, indicating that the “memory effect” was important in the catalyst preparation. In the absence of Ni, the activity of 0.1-0.5 wt% Ru/Mg3(Al)O catalysts gradually decreased during the reaction independent of the cycle number, suggesting that the deactivation was not due to Ru oxidation but probably due to sintering or coking on the catalyst. Only addition of Ru alone was not sufficiently active with such low loadings and the activity of the Ru–Ni0.5/Mg2.5(Al)O catalysts depended mainly on the Ni species.

The effects of Ru, Rh, Pd and Pt loading on the sustainability of the Ni0.5/Mg2.5(Al)O catalyst in CH4 steam reforming under DSS-like operation conditions with steam purging are shown in Fig. 10(37,38). As noted previously, Ni0.5/Mg2.5(Al)O catalyst was severely de-
activated by oxidation of Ni metal just after the 1st steam purging in the DSS operation. Loading of a small amount (0.05 wt\%) of Ru, Rh and Pt increased stability on this catalyst, probably by suppressing Ni oxidation with steam, whereas simple loading of the noble metal on MgAlO periclase resulted in only low activity. XRD patterns of 0.5 wt\% RuNi0.5/Mg2.5(Al)O catalysts during the DSS operation in steam reforming of CH4 showed that Ni was included as Ni2+ ions in the Mg2.5(Al,Ni0.5)O periclase just after dipping, followed by calcination. Ru was first trapped in the reconstituted layered structure of Mg(Ni)Al HT and then converted to the fine particles of RuO2 by calcination, which were not observed in the XRD pattern. After reduction, the Ni2+ ions in the Mg2.5(Al,Ni0.5)O periclase were reduced to Ni metal present on the surface of the periclase particles. Interestingly, such Ni metal species was still observed by XRD throughout the DSS operation although the reflection line intensity varied depending on the atmosphere. Ni metal was probably partly oxidized by steam and partly remained in the reduced state during steam purging, and the oxidized Ni2+ was re-reduced during the steam reforming reaction at 700 °C. In the absence of noble metal, Ni0.5/Mg2.5(Al)O was completely deactivated and showed no reflection line of Ni metal after the 1st DSS operation. All these results indicate that the active species is Ni metal, even on the noble metal loaded Ni0.5/Mg2.5(Al)O catalysts, and the noble metals, such as Ru, Rh and Pt, suppress the oxidation of Ni metal probably due to hydrogen spillover from the noble metal (vide infra). We have found improved activity of Ru, Rh, Pd, Ir and Pt-Ni0.5/Mg2.5(Al)O bimetallic catalysts in the partial oxidation of propane even under accelerated deactivation conditions.

6. Physico-chemical Property of Noble Metal–Ni/Mg(Al)O Catalysts

BET surface areas, H2 uptakes, metal dispersion and Ni metal particle sizes of the Ru, Rh, Pd, Ir and Pd-Ni0.5/Mg2.5(Al)O catalysts are shown in Table 1. The surface area of Ni0.5/Mg2.5(Al)O was significantly decreased by loading of noble metals. In contrast, H2 uptake of the Ni0.5/Mg2.5(Al)O catalyst was drastically enhanced by the loading of noble metals; H2 uptake increased even with 0.01 wt\% of Ru loading. At 0.1 wt\% of noble metal loading, the Ru-, Rh- and Ir-Ni0.5/Mg2.5(Al)O catalysts showed higher values of H2 uptake than the Pd- and Pt-Ni0.5/Mg2.5(Al)O catalysts. The contribution of the noble metal to the H2 uptake on noble metal-supported Ni0.5/Mg2.5(Al)O catalysts must be small, since 0.1 wt\% Ru/MgAlO catalyst showed an extremely small low H2 uptake. High synergy between noble metal and Ni metal is likely to occur on the catalysts, leading to enhanced H2 uptake due to the formation of bimetallic systems such as alloys, etc.

TFR profiles of the Ru-Ni0.5/Mg2.5(Al)O catalysts with various Ru loadings are shown in Fig. 11. In the absence of Ru, i.e., for the Ni0.5/Mg2.5(Al)O catalyst, a single and intense peak appeared at 895 °C. The Ni reduction peak shifted toward lower temperature with Ru loading, and was more significant with increasing Ru loading on the Ni0.5/Mg2.5(Al)O catalyst, and an additional weak and broad peak appeared around 400 °C for the 0.5 wt\% Ru-Ni0.5/Mg2.5(Al)O catalyst. The decrease in the reduction temperature of Ni suggests either a formation of RuNi alloy or at least strong interaction between Ru and Ni. The weak and broad peak observed around 400 °C for 0.5 wt\% Ru-Ni0.5/Mg2.5(Al)O catalyst can be ascribed to the reduction of...
RuO₂ to Ru metal, since no other stable ruthenium oxides are known to exist in the solid state⁴²,⁴³. This observation indicates that a part of the Ru separated during preparation. TPR of Ru/Al₂O₃ and Ru/MgO catalysts showed the Ru reduction peak occurred around 250 °C and 234 °C, respectively⁴⁴,⁴⁵. However, strong metal-support interaction was frequently observed for catalysts with well-dispersed Ru particles, resulting in higher reduction temperature. In contrast to TiO₂, Al₂O₃ apparently has a tendency to stabilize ruthenium in the ionic state and the reduction temperature sometimes exceeds 700 °C⁴⁵. RuO₂ separated from the Rh-Ni bimetallic system probably exists as fine particles on the catalyst surface and has a reduction peak around 400 °C.

### Involvement of Noble Metals in Bimetallic Active Species

XRD patterns of both 0.1 wt% and 0.5 wt% Ru-Ni₀.₅/Mg₂.₅(Al)O catalysts after the reduction are shown in Fig. 12, together with that of Ni₀.₅/Mg₂.₅(Al)O catalyst as a control. Ni₀.₅/Mg₂.₅(Al)O catalyst showed rather sharp and intense reflection lines of Ni metal (Fig. 12A), which were broadened and shifted toward lower reflection angles by the addition of 0.1 wt% Ru (Fig. 12B). Both line broadening and lower angle became significant with higher Ru loading up to 0.5 wt% (Fig. 12C) and were more clearly observed for the reflection of Ni(200) at 2 theta = 52.5° with higher Ru loading (Fig. 12C). RuNi alloy was presumably formed and/or the size of Ni metal particles decreased while maintaining the strong interaction with the support with Ru loading on the Ru-Ni₀.₅/Mg₂.₅(Al)O catalysts. Rh is completely soluble in the Mg(Al)O periclase phase, whereas Ru is not soluble in Mg(Al)O periclase and remains as a separate phase, if both were incorporated into HTls precursors with a large Mg/Al ratio⁵⁹. Such Ru species separated from the periclase reacted with Ni species liberated from Mg₂.₅(Al,Ni₀.₅)O periclase during the reduction, resulting in the formation of RuNi alloy and/or well dispersed Ni metal parti-

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area</th>
<th>H₂ uptake</th>
<th>Dispersion</th>
<th>Particle size of Ni metal [nm]</th>
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<tbody>
<tr>
<td>Ni₀.₅/Mg₂.₅(Al)O</td>
<td>158.0</td>
<td>120.7</td>
<td>13.1</td>
<td>6.9</td>
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<tr>
<td>i) 13.5 wt% Ni/γ-Al₂O₃</td>
<td>106.3</td>
<td>74.4</td>
<td>6.5</td>
<td>10.0</td>
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<tr>
<td>0.1 wt% Ru/Mg₅(Al)O</td>
<td>121.5</td>
<td>0.56</td>
<td>-</td>
<td>-</td>
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<tr>
<td>0.1 wt% Ru-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>146.7</td>
<td>221.9</td>
<td>24.0</td>
<td>5.2</td>
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<tr>
<td>0.1 wt% Rh-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>148.4</td>
<td>184.0</td>
<td>19.9</td>
<td>5.7</td>
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<tr>
<td>0.1 wt% Pd-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>134.9</td>
<td>148.8</td>
<td>16.1</td>
<td>5.8</td>
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<tr>
<td>0.1 wt% Ir-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>140.0</td>
<td>204.2</td>
<td>22.1</td>
<td>5.3</td>
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<tr>
<td>0.1 wt% Pt-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>134.9</td>
<td>225.3</td>
<td>24.4</td>
<td>5.5</td>
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<td>0.5 wt% Ru-Ni₀.₅/Mg₂.₅(Al)O</td>
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<td>261.4</td>
<td>28.3</td>
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<td>0.05 wt% Ru-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>138.3</td>
<td>187.2</td>
<td>20.3</td>
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<tr>
<td>0.01 wt% Ru-Ni₀.₅/Mg₂.₅(Al)O</td>
<td>137.7</td>
<td>183.5</td>
<td>19.9</td>
<td>5.7</td>
</tr>
</tbody>
</table>

a) Metal loading was carried out by dipping 1.0 g of the powder of Ni₀.₅/Mg₂.₅(Al)O in 5 mL of aqueous solution of the nitrates of noble metals for 1 h at room temperature.
b) Calcined at 900 °C for 5 h.
c) Determined by the H₂ pulse method.
d) Calculated from the H₂ uptake assuming reduction of 80 % for hydrotalcite derived catalyst and 100 % for impregnated catalyst⁵⁹.
e) Calculated from the full width at half maximum of the reflection of the Ni(200) plane in XRD using the Scherrer equation.

Fig. 11  TPR Profiles of Supported Ru Catalysts

![Fig. 11 TPR Profiles of Supported Ru Catalysts](image-url)

Link: [J. Jpn. Petrol. Inst., Vol. 58, No. 6, 2015](https://example.com/journal-article-url)
H₂ uptake was drastically enhanced by Ru loading on Ni₀.₅/Mg₂.₅(Al)O catalyst as shown in Table 1. Particle sizes of Ni metal on the catalysts were calculated from the data of both XRD and H₂ uptake. In both cases, the Ni particle size decreased and the H₂ uptake increased with higher Ru loading. These findings are consistent with the dependency of H₂ uptake on the metal particle size. The highest activity as well as the highest sustainability in partial oxidation of propane was obtained with the 0.1 wt% Ru–Ni₀.₅/Mg₂.₅(Al)O catalyst.  

The involvement of Ru in H₂ uptake on the Ru–Ni₀.₅/Mg₂.₅(Al)O catalysts must be small, since the H₂ uptake was significantly low on the 0.1 wt% Ru/Mg₂.₅(Al)O catalyst. The reforming activity of Rh–Ni bimetallic catalysts is mainly due to the presence of Ni metal on the catalysts surfaces, since the selectivity to H₂ was remarkably low on 0.1 wt% Ru/Mg₂.₅(Al)O catalyst at 700 °C [40,41]. X-ray absorption fine structure (XAFS) analyses of both Ru and Ni in 0.5 wt% Ru–Ni₀.₅/Mg₂.₅(Al)O catalysts suggest that Ru metal species were finely dispersed on or in the surface layer of the Ni metal particles[46]. Similarly, surface modification of Ni catalysts with trace Pt was much more efficiently achieved by the sequential impregnation method (Pt/Ni) than the co-impregnation method (Pt + Ni) on γ-Al₂O₃ in the oxidative reforming of CH₄[47]. Therefore, the catalytic property of Ni metal was enhanced by the loading of noble metal, probably mainly due to the formation of finely dispersed Ni metal particles and also to the synergy between Ni metal and noble metal on the surface of fine Ni metal particles.

Self-activation of 0.1 wt% Ru, Rh or Pt–Ni₀.₅/Mg₂.₅(Al)O catalysts was tested in the steam reforming of CH₄; the catalysts were used as calcined at 900 °C, i.e., without pre-reduction treatment with H₂. Pt-containing catalyst was the most effective, followed by Rh, and Ru was not effective. However, both the Pt–Ni and Rh–Ni systems and the Rh–Ni system as calcined at 900 °C catalyzed the partial oxidation of propane, suggesting that noble metals catalyzed C–H bond fission and liberated hydrogen atoms on the catalyst surface. Noble metals quickly dissociate the C–H bond of methane or propane to form H atoms which rapidly migrate to the Ni surface by spillover, reduce the oxidized Ni, and maintain the Ni species in the reduced and active state during the reaction.

8. Conclusion

The structure of HTlcs basically consists of brucite-like layers and anions, which can incorporate various metal cations or metal-containing anions. These metal species are randomly distributed in the brucite phase and potentially have catalytic activity for various types of reaction. HTlcs after the heat treatment incorporated oxides with very small crystal size, stable to thermal treatments, which can be applied as catalysts with high surface area, basic properties and thermally stable metal crystallites after reduction. Moreover, by adopting the “memory effect,” the HT structure was reconstituted in the mixed oxide derived from HTlcs. Such HTlcs finely modify the surface of mixed oxides and have unique catalytic activity in the various reactions.

Ni/Mg(Al)O catalysts derived from Mg(Ni)–Al HT were successfully applied for the reforming of CH₄. The high and stable activity of these catalysts was attributed to the formation of stable and well-dispersed Ni metal particles produced from Mg(Ni,Al)O periclase as solid solutions obtained by calcination of Mg(Ni)–Al HT. Noble metals were incorporated in the surface layer of the Mg(Ni,Al)O periclase by adopting the “memory effect,” resulting in the creation of efficient bimetallic catalysts for the H₂ production for PEFCs. Noble metal–Ni/Mg(Al)O catalysts showed high activity and stability for the reforming of methane and propane.

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References

要 目

燃料電池用水素製造のための高分散担持 Ni 触媒の調製

穴戸 哲也†1,†2，竹平 勝臣†3)

†1 首都大学東京大学学院都市環境科学研究所分子応用化学系, 192-0397 東京都八王子市南大沢1-1
†2 京都大学触媒・電池元素戦略ユニット, 615-8245 京都市西京区御陵大原1-30
†3 広島大学大学院工学研究科応用化学専攻, 739-8527 広島県東広島市鏡山1-4-1

活性金属種を構造中に均質に含有する前躯体を調製し、これ
を焼成・還元して構造中の活性金属種を安定に表面に析出させ
ることを特徴とする汎用性の高い触媒調製法により各種高分散
担持金属触媒の調製を行った。ハイドロカルサイト前躯体と
して調製した高分散担持 Ni 触媒は、天然ガス改質による水素
製造反応に対し優れた活性・安定性を示した。さらに、ハイド
ロタルサイト特有の Memory Effect の利用により Eggshell 型担
持 Ni 触媒の創製や活性サイト表面での合金形成を行った。こ
のように調製した担持 Ni 触媒は、酸化剤間に暴露した後に
還元処理を行うことなしに還元ガス雰囲気下で自己再生的に活
性化する機能を実現するなど、触媒の安定性向上した。これ
ら調製した Ni 触媒の高い活性・耐久性の要因は、高分散、か
つ安定な Ni 金属粒子の生成にあることを明らかとした。