Novel Preparation of Uniform Heterogeneous Catalysts Derived from Hydrotalcites

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Several heterogeneous catalysts were prepared starting from Mg–Al and Zn–Al hydrotalcites (HTs) and evaluated for oxidation, ozonation, dehydrogenation and reforming of hydrocarbons, and the CO shift reaction. All catalysts exhibited unique and excellent activities in these reactions. Fe/Mg/Al oxide catalysts prepared from Mg–Al(Fe) HT exhibited high activity for Baeyer-Villiger oxidation of various ketones and dehydrogenation of ethylbenzene. Ozonation activity of Cu/Mg/Al oxide catalysts similarly prepared from Mg(Cu)–Al HT was enhanced by the ‘memory effect,’ as reconstituted HT on the catalyst surface adsorbed oxalic acid and assisted in complete oxidation. Ni/Mg(Al)O catalysts prepared from Mg(Ni)–Al HT exhibited high and stable activity in steam reforming and oxidative reforming of methane and propane. Moreover, the activity of the Ni catalysts was improved by doping a trace amount of noble metals by adopting the ‘memory effect.’ Use of these catalysts in the production of hydrogen for the PEMCs under daily start-up and shut-down operation showed that the catalysts were self-activated and the active Ni metal particles were self-regenerated during the reaction, resulting in high and sustainable activity. CO shift activity of Cu/Zn(Al)O catalysts was also improved by doping a trace Pt or Mg by adopting the memory effect of Zn(Cu)–Al HT in the precursor, resulting in the high sustainability.

Keywords
Hydrotalcite derived catalyst, Oxidation, Dehydrogenation, Reforming, Shift reaction, Memory effect

1. Introduction

Hydrotalcite-like compounds (HTs) can be described by the general formula: [\(\text{M}^{2+}\text{L}_{1-x}\text{M}^{3+}(\text{OH})_2\text{L}^+\text{A}^{n-}\text{mH}_2\text{O}\)], and contain various cations (\(\text{M}^{2+}\) and \(\text{M}^{3+}\)) and the anion (\(\text{A}^{n-}\)), with the most common HT combining Mg and Al. The structure of HT is basically that of brucite, Mg(OH)\(_2\), in which octahedral Mg\(^{2+}\) ions (6-fold coordinated to OH\(^-\)) share edges to form infinite sheets. These sheets are stacked and held together by hydrogen bonding (Fig. 1\(^2\)). If the Mg\(^{2+}\) ions are replaced with a trivalent ion with an ionic radius not too different from that of Mg\(^{2+}\) (such as Fe\(^{3+}\) and Al\(^{3+}\) for pyroaurite and HT, respectively), a positive charge is generated in the hydroxy sheet. This net positive charge is balanced by CO\(_2\)\(^{2-}\) anions, which lie in the interlayer region between two brucite sheets. Water of crystallization is also located in the free space of this interlayer region. Therefore, the main features of HT structures are determined by the nature of the brucite-like sheets, by the position of anions and water in the interlayer region, and by the type of stacking of the brucite sheets. The sheets containing cations are arranged as in brucite, and the cations randomly occupy the octahedral holes in the close-packed configuration of the OH\(^-\) ions. Generally M\(^{2+}\) and M\(^{3+}\) ions can be accommodated within these octahedral holes as far as allowed by the ionic radii and the valence states.

HTs have been mainly used as catalysts after calcina-

$$[\text{M}^{(\text{II})}_{1-x}\text{M}^{(\text{III})}_x\text{(OH)}_2]^{+}\text{A}^{n-}\text{mH}_2\text{O}$$

ex) $$[\text{Mg}_{1-x}\text{Ni}_x\text{(OH)}_2]_1/2\text{CO}_2\text{H}_2O$$

![Fig. 1 Structure of HT](image)

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tion because the resultant oxides possess interesting properties such as high surface area and basic properties. Calcination results in the formation of homogeneous mixtures of oxides with very small crystal size, and stable to thermal treatments, which further form small and thermally stable metal crystallites by reduction\(^6\). Moreover, the calcined oxides show a unique property, the 'memory effect,' which allows the reconstitution of the original HT structure contacting the oxides after calcination with aqueous solutions containing various anions. Thermal decomposition of these materials by calcination results in the formation of mixed oxides with high thermal stability and large surface area. In addition, high dispersion of metallic particles is obtained after reduction\(^5\). Moreover the structure can accommodate a wide range of different metals, leading to many different catalytic properties. The HT-derived oxides are well characterized base catalysts and have already been reviewed\(^9\).

This study focused on our recent investigations into catalyst preparation derived from the Mg-Al HT obtained by introducing Fe and Ni as the active species for oxidation, ozonation, dehydrogenation and reforming. The Zn(Cu)-Al HT as a precursor of the Cu/Zn(Al)O catalysts has been evaluated for the CO shift reaction. Such results are discussed in connection with the new catalyst preparation technologies\(^6\).

2. Mixed Metal Oxides Catalysts for Various Reactions

2.1. Fe/Mg/Al Oxide Catalysts for Baeyer-Villiger Oxidation

Fe/Mg/Al oxide catalyst prepared by impregnation of Fe into Mg(Al)O periclase and activating by the 'memory effect' showed high activity for the Baeyer-Villiger oxidation of cyclic ketones to the corresponding lactones using O\(_2\)/benzaldehyde as the oxidizing agent (1) (Table 1)\(^7\).

\[
\begin{array}{c}
\text{PhCHO} + \text{O}_2 \\
\text{Fe/Mg(Al)O} \\
\rightarrow \text{R}_1\text{R}_2 \text{O} \rightarrow \text{R}_1\text{R}_2\text{O} (1)
\end{array}
\]

Use of Fe(NH\(_2\))\(_2\)(SO\(_4\))\(_2\)·6H\(_2\)O was uniquely effective as the metal salt in the impregnation; Fe\(^{3+}\)-O-Fe\(^{3+}\) cluster-type compounds were formed as the active species on the surface of Mg(Al)O particles during the reconstitution of HT by the 'memory effect,' resulting in the highest activity at about 6% Fe loading. The reconstitution of the HT was clearly observed by X-ray diffraction (XRD). During the reconstitution of HT by the 'memory effect,' Fe\(^{2+}\) cations from Fe(NH\(_2\))\(_2\)(SO\(_4\))\(_2\)·6H\(_2\)O were probably incorporated into the HT reconstituted on the particles of Mg(Al)O periclase. The combination of Mg\(^{2+}\)-Fe\(^{3+}\) formed HT layered structure by coprecipitation starting from the nitrates of Mg\(^{2+}\) and Fe\(^{3+}\)\(^8\). The iron species observed in the Fe/Mg(Al)O catalyst occurred as Fe\(^{3+}\) although the Mg(Al)O was immersed in an aqueous solution of Fe(NH\(_2\))\(_2\)(SO\(_4\))\(_2\)·6H\(_2\)O containing Fe\(^{2+}\). The Mössbauer (Table 2) UV-vis and Fe K-edge X-ray absorption fine structure (XAFS) spectra suggested that the Fe species occurred as Fe\(^{3+}\), were mainly octahedrally coordinated, and formed Fe-O-Fe cluster-type structures on the Mg(Al)O periclase. Therefore, the Fe\(^{3+}\)-O-Fe\(^{3+}\) cluster-type compounds are probably more active for the Baeyer-Villiger oxidation than the well dispersed Fe\(^{3+}\) species formed on the HT prepared by coprecipitation\(^7\).

2.2. Cu/Mg/Al Oxide Catalysts for Ozonation

In the treatment of waste water, catalysis combined with ozonation processes (catalytic ozonation) can improve the oxidation and degradation of organic contaminants, especially small carboxylic acids that cannot be easily attacked by conventional oxidation processes. Cu/Mg/Al oxide catalysts prepared from Mg(Cu)-Al HT exhibited high activity in the aqueous-phase ozonation of phenol and oxalic acid (2);
Table 2 Mössbauer Parameters of the Supported Fe Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Isomer shift [mm s(^{-1})]</th>
<th>Quadrupole splitting [mm s(^{-1})]</th>
<th>Line-width [mm s(^{-1})]</th>
<th>Spectral contribution [%]</th>
<th>Phases by XRD and UV-Vis</th>
</tr>
</thead>
<tbody>
<tr>
<td>cp-7.9 wt% Fe/e</td>
<td>0.41</td>
<td>0.74</td>
<td>0.37</td>
<td>59</td>
<td>HT</td>
</tr>
<tr>
<td>Mg(_2)AlO(_x)</td>
<td>0.24</td>
<td>0.76</td>
<td>0.37</td>
<td>41</td>
<td>HT</td>
</tr>
<tr>
<td>m-3.5 wt% Fe/e</td>
<td>0.32</td>
<td>0.63</td>
<td>0.62</td>
<td>68</td>
<td>HT</td>
</tr>
<tr>
<td>Mg(_2)AlO(_x)</td>
<td>0.21</td>
<td>0.86</td>
<td>0.62</td>
<td>32</td>
<td>—</td>
</tr>
<tr>
<td>m-6.1 wt% Fe/e</td>
<td>0.34</td>
<td>0.69</td>
<td>0.58</td>
<td>94</td>
<td>HT</td>
</tr>
<tr>
<td>Mg(_3)Al(_2)O(_x)</td>
<td>0.46</td>
<td>1.24</td>
<td>0.58</td>
<td>6</td>
<td>Fe(^{3+}) clusters</td>
</tr>
</tbody>
</table>

a) Prepared by coprecipitation.
b) Prepared by adopting the ‘memory effect.’

The combination of ozone and the Cu/Mg/Al oxide catalyst was effective for the reduction of total organic carbon (TOC)\(^b\). Leaching of Cu, probably due to the chelation of metals by oxalic acid, was significant at the beginning of reaction. However, the Cu leaching disappeared at the end of the reaction, possibly due to total consumption of the oxalic acid during the reaction. The best result for oxalic acid mineralization was observed over Cu/Mg/Al calcined at 600\(^\circ\)C, which was associated with the least Cu leaching. Moreover, the ‘memory effect’ of HT accelerated the mineralization of oxalic acid over the Cu/Mg/Al catalyst; as oxalate anions were captured and decomposed in the reconstituted HT interlayer space on the surface of the Cu/Mg/Al, resulting in remarkable enhancement of the catalytic activity of ozonation\(^b\).

The Mg\(_{2.77}\)/Cu\(_{0.23}\)/Al system forms ternary Mg(Cu)-Al HTG\(^6\) and produces periclase Mg(Al,Cu)O after calcination above 400\(^\circ\)C. The Mg(Cu)Al\(_2\)O\(_4\) spinel phase appears after calcination above 850\(^\circ\)C, as the periclase Mg(Al,Cu)O is converted to pure MgO and the spinel. The effects of the calcination temperature of Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide on the activity, the reconstitution of HT (A) and the Cu leaching (B) are shown in Fig. 2. The rate constant (k\(_t\) /min\(^{-1}\)) of the ozonation of oxalic acid over Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide was calculated from the time course of ln(C/C\(_0\)), where C is the concentration of oxalic acid, and was plotted against the calcination temperature (Fig. 2A), assuming that the reaction is quasi-first order with respect to oxalic acid. The XRD patterns of the Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide clearly showed HT reconstitution after the reaction, if the catalyst was calcined at 400, 600 and 850\(^\circ\)C. The intensity of the reflection by basal plane (003) of the HT formed on the catalysts was plotted against the calcination temperature (Fig. 2A). Both peak intensity and first order rate constant showed maximum values at 600\(^\circ\)C; so a good correlation was observed between peak intensity and rate constant against the calcination temperature. This suggests that the catalytic activity was enhanced by the reconstitution of HT on the Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide; oxalate anions were incorporated and compensated for the positively charged layers; as observed in the infrared spectra of the material during the reaction (Fig. 3). The Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide before calcination had the Mg\(_{2.77}\)(Cu\(_{0.23}\))-Al HT structure, so the following assignments are possible: hydroxyls attached to Al and Mg: 3500 cm\(^{-1}\)\(^{10\text{)}}\); hydrogen bonding between interlayer water and interlayer carbonate: 3000 cm\(^{-1}\)\(^{1\text{)}}\); H\(_2\)O bending vibration: 1650 cm\(^{-1}\) and interlayer carbonate anion: 1380 cm\(^{-1}\)\(^{1\text{)}}\). All these bands were weakened after calcination at 600\(^\circ\)C, (Fig. 3-b). If Cu\(_{0.23}\)/Mg\(_{2.77}\)/Al oxide was used in the reaction for 15 min, the bands around 3500 and
1650 cm⁻¹ were intensified, whereas the band at 1380 cm⁻¹ was not, suggesting that the interlayer space was filled with water molecules, and simultaneously the brucite phase was regenerated (Fig. 3-c). The band at 1640 cm⁻¹ and the shoulder at 1320 cm⁻¹ can probably be assigned to interlayer oxalate, since these absorptions also appeared when the sample was dipped in an aqueous solution of oxalic acid.

XRD measurements also confirmed intercalation by oxalate anions (Table 3). Interlayer distance was calculated assuming that the thickness of the brucite-like layer is 0.48 nm[12]. When Cu₀.25/Mg₂.77/Al oxide calcined at 600°C was dipped in distilled water (Table 3, Sample I), the basal interlayer spacing of reconstituted HT was calculated as 0.757 nm, which is close to the value reported for the Mg-Al carbonate HT[13]. After reaction for 15 min (Table 3, Sample II), the basal spacing slightly increased to 0.778 nm. The sample was further dipped in an aqueous solution of oxalic acid (Table 3, Sample III) as a reference, and showed the basal spacing of 0.782 nm. The basal spacing is 0.960 nm for the Mg-Al oxalate HT[14]. The intercalation by oxalate anions was unlikely to be completed in the present samples after the reaction or after the dipping in oxalic acid solution, due to the rapid decomposition of oxalate in the interlayer space of the catalysts. Actually both the band around 1640 cm⁻¹ and the shoulder around 1320 cm⁻¹ observed in the infrared spectra disappeared after the reaction for 240 min, indicating that the oxalate anions were completely consumed by the mineralization reaction with ozone (Fig. 3-d). Therefore, the oxalate anions were probably localized in the positively charged layers of the HT and were effectively oxidized to carbon dioxide, which was released into the solution due to the inadequate charge balance.

2.3. Fe/Mg/Al Oxide Catalysts for Dehydrogenation

Styrene, an important basic chemical and raw material for polymers, is produced commercially by the dehydrogenation of ethylbenzene over a typical Fe-K-Cr oxide-based catalyst in the presence of a large quantity of steam at 600-700°C, just below the temperature at which thermal cracking becomes significant. The commercial catalysts are very active and selective, but have some disadvantages. The active oxidation state is unstable as hematite (α-Fe₂O₃) is preferred for styrene production, but tends to form lower oxides and even elemental iron, both of which catalyze coke formation and dealkylation. The catalysts have low surface area, and are deactivated with time, because of the susceptibility to poisoning by halides and residual organic chloride impurities. The most serious deactivation is caused by the loss of potassium promoter, which migrates as the catalyst ages. The catalysts also contain chromium compounds which are toxic to humans and to the environment. Therefore, new catalyst systems with high surface areas and stabilized active state of iron, in the absence of potassium, are greatly in demand.

We prepared supported iron catalyst from Mg-Fe-Al HTs as precursors, which exhibited high activity in the ethylbenzene dehydrogenation to styrene[15]. The iron-substituted HTs were converted by calcination to mixed oxides with high surface area as well as mesoporous character, and the XRD analysis indicated the formation of periclase Mg(Fe,Al)O as the main phase (Fig. 4). Catalytic tests of the Fe/Mg₂/Al₁₋ₓ catalysts showed

![Infrared Spectra of Cu₀.25/Mg₂.77/Al Oxide during the Reaction](image)

**Fig. 3** Infrared Spectra of Cu₀.25/Mg₂.77/Al Oxide during the Reaction

**Table 3** Basal Spacing and Interlayer Distance of HT Reconstituted on the Cu₀.25/Mg₂.77/Al Oxide Catalyst Calcined at 600°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>2 theta [degree]</th>
<th>d [nm]</th>
<th>Interlayer distance [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I[a]</td>
<td>11.68</td>
<td>0.757</td>
<td>0.277</td>
</tr>
<tr>
<td>II[b]</td>
<td>11.36</td>
<td>0.778</td>
<td>0.298</td>
</tr>
<tr>
<td>III[c]</td>
<td>11.30</td>
<td>0.782</td>
<td>0.302</td>
</tr>
</tbody>
</table>

Calculated from the data of 2 theta = 11° ascribed to diffraction by the basal planes (003). All samples, I, II and III, were vacuum-dried for 1 night after the treatment.

a) Dipped in distilled water at 20°C for 15 min.
b) After the reaction for 15 min.
c) Dipped in aqueous solution of oxalic acid (8.0 mM/400 ml) at 20°C for 15 min. 1 M=1 mol·dm⁻³.

that styrene conversion increased with higher iron content up to \( x = 0.75 \) and then decreased, and the selectivity was the highest at \( x = 0.25 \). The optimum temperature for the reaction was 550°C, which was lower than that used in the commercial process. Although ethylbenzene dehydrogenation has been carried out over Fe/Mg/Al catalysts under a CO₂ atmosphere\(^{(16)}\), no favorable effect of the addition of CO₂ or O₂ in the reaction medium was observed. In fact, pretreatment with H₂ resulted in increased activity at the beginning of the reaction as well as stable activity during the reaction. Typical results are shown in Table 4. Ethylbenzene conversion of 60% and styrene selectivity of 95% were maintained for 3 h over the Fe₀.₅/Mg₀.₅(Al₂₃)O catalysts at 550°C (Fig. 10 in Ref. 15). The iron species on the catalyst were partially reduced to the valence state between Fe²⁺ and Fe³⁺ after the reaction for 3 h. The good catalytic performance can probably be attributed to the formation of partially reduced iron oxides on the surface of catalyst, and to the high surface area connected with the porous structure, which originated from the precursor Mg–Fe–Al HT structure.

3. Ni/Mg(Al)O Catalysts for Reforming

Hydrogen production for use in polymer electrolyte fuel cells (PEFCs) is an important research area in the urgent search for solutions to global warming. Steam reforming of hydrocarbons, especially of CH₄, is the most widely used and generally most economical method to produce H₂ (3).

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

However, this process still requires further advances in the preparation of superior reforming catalysts. We previously reviewed the preparation of highly dispersed and stable Ni-supported catalysts starting from precursor perovskites and HTs\(^{(17)}\). Further development of the supported Ni catalysts derived from HTs is reported here.

3.1. Ni/Mg(Al)O Catalysts

Ni/Mg(Al)O catalysts can be prepared by thermal treatment followed by reduction of ternary Mg(Ni)–Al HT with various Mg/Al ratios\(^{(18–22)}\) and successfully applied to partial oxidation\(^{(20)}\), steam reforming\(^{(21)}\), dry reforming\(^{(18)}\) and autothermal reforming of CH₂\(^{(22)}\). The high and stable activity of these catalysts can be attributed to the stable and well-dispersed Ni metal particles evolved from Mg(Ni,Al)O periclase; Ni²⁺ in the Mg(Ni,Al)O periclase is reduced to Ni⁰ and migrates to the periclase surface to form fine metallic Ni particles by reduction. Partial oxidation of CH₄ over Ni/Mg(Al)O catalyst proceeds via combustion (4), followed by steam reforming (SR) (3) and dry reforming (5).

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]  

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2
\]  

Among the Ni/Mg(Al)O catalysts prepared, Ni₀.₅/Mg₀.₅(Al₂₃)O exhibited the highest activity; CH₂ conversion reached thermodynamic equilibrium even at the enormously high space velocity of \( 9 \times 10^6 \text{ m}^3/\text{h} \cdot \text{m}^{-1} \cdot \text{g}_{\text{cat}}^{-1} \) (Fig. 5-a)\(^{(22)}\). Ni catalysts were frequently deactivated during partial oxidation, due to the surface oxidation of the Ni particles, usually accompanied by drastic decreases in CH₂ conversion as seen for the commercial 12 wt% Ni/α-Al₂O₃ catalyst (FCR from Süd Chemie

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of ethylbenzene [%]</th>
<th>Selectivity [%]</th>
<th>Hydrogen [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene</td>
<td>Benzene</td>
</tr>
<tr>
<td>Fe₀.₅/Mg₀.₅(Al₂₃)O</td>
<td>58.5</td>
<td>91.2</td>
<td>5.0</td>
</tr>
<tr>
<td>imp-Fe/Fe²⁺/Al₂O₃</td>
<td>34.0</td>
<td>92.8</td>
<td>4.6</td>
</tr>
<tr>
<td>imp-Fe/MgO</td>
<td>36.9</td>
<td>92.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\( \text{a) Reaction conditions: catalyst, 150 mg; reaction temperature, 550°C; reaction time, 1 h; N}_2/\text{Ar, 10/30 m}^3/\text{min}^{-1}; \text{ethylbenzene, 1.5 mmol} \cdot \text{h}^{-1}; \text{b) Calculated based on the stoichiometry of ethylbenzene dehydrogenation to styrene.} \)
Preparation of NiO/Mg₂₋₃(Al)O catalyst by co-precipitation from the nitrates of Ni²⁺, Mg²⁺ and Al¹⁺ resulted in homogeneous distribution of all Ni species in the catalyst particles, so the Ni species located deeply inside the particles cannot act as active species. Temperature-programmed reduction (TPR) measurements of the NiO/Mg₂₋₃(Al)O catalyst indicated that the reduction degree was ca. 85% (23), indicating that much of the Ni remains as Ni²⁺ within the MgNi₃(Al)O periclase particles even after reduction. Preferential Ni loading in the outer layer of the catalyst particles, i.e., eggshell-type Ni loading on the Mg(Al)O periclase particles, can be achieved by adopting the 'memory effect' of Mg-Al HT. Active Ni metal particles were effectively concentrated in the surface layer of the catalyst particles by controlling the preparation conditions (24). Moreover the activity per unit amount of Ni was enhanced due to the surface concentration of active Ni species; as confirmed by measurements of the effectiveness factor of the Ni/Mg(Al)O catalyst (24). The eggshell-type Ni loaded catalyst exhibited high activity for both steam reforming (25) and autothermal reforming (26) of CH₄.

### 3.2 Improvement of Ni/Mg(Al)O Catalyst by Noble Metal-doping

Large-scale reformers in continuous industrial use operate under stable conditions, whereas hydrogen production for PEFCs in domestic use will require daily start-up and shut-down (DSS) operations with variations in temperature. Between shut-down and start-up, the catalyst bed in the reformer is purged with steam to enhance safety. Therefore, the catalyst must be able to tolerate multiple cycles under such unusual transient conditions without deterioration. Deactivation of Ni-loaded catalysts has been frequently reported, caused by coking, sintering, or oxidation of the active metal species. Use of Ni/Mg(Al)O catalysts in the DSS operation of SR of CH₄ (Fig. 7) resulted in severe deactivation (27) although this catalyst has high and stable activity in steady state CH₄ reforming (Figs. 5 and 6) (21,22). Ni/Mg(Al)O catalysts with various (Mg + Ni)/Al ratios were tested in the DSS SR of CH₄ using three purging gases, i.e., steam, air and spent gas, together with the commercial catalysts, RUA and FCR, and the
catalysts prepared by impregnation\(^{27}\). RUA is a commercial 2 wt% Ru/Al\(_2\)O\(_3\) catalyst supplied by Süd Chemie Co. The most severe damage to all supported Ni catalysts was caused by O\(_2\) in air. MgO-supported Ni catalysts were completely deactivated by both steam and spent gas, whereas Al\(_2\)O\(_3\)-supported Ni catalysts retained stable activity. The stability of the Ni/Mg(Al)O catalysts depended on the (Mg + Ni)/Al ratio. XRD observations indicated that the deactivation proceeded rapidly due to oxidation of Ni\(^{2+}\) to Ni\(^{3+}\), which is incorporated into Mg(Ni,Al)O periclase, as the Ni reflections disappeared and those of Mg(Ni,Al)O periclase increased after the deactivation. Ni oxidation probably occurred through direct interaction with O\(_2\) or H\(_2\)O, 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\(^{28}\).

Ni can also be incorporated as anion into the interlayer of the Mg\(^{2+}\)-Al HT\(^{29-33}\); Ni\(^{2+}\) reacts with the anionic chelating agent of EDTA\(^{4-}\) to form the stable anionic species [Ni(EDTA)]\(^{4-}\). Ni/Mg\(_2\)Al\(_2\)O\(_4\) catalyst prepared by coprecipitation of Mg and Al nitrates with presynthesized nickel chelate showed the highest catalytic activity in the steam reforming of CH\(_4\) to H\(_2\) with high yield\(^{29}\), because of optimum distribution of the active phase established by reconstitution of HT by the ‘memory effect.’ Rh, Ru and Pt prechelated with EDTA\(^{4-}\) were also supported on Mg(Al)O by adopting the ‘memory effect,’ and the loading could be lowered from 2.0 to 0.1 wt% without any decrease in catalytic activity in the CO\(_2\) reforming of CH\(_4\)\(^{31}\). Ru–Ni bimetallic catalyst was also prepared by this method\(^{22}\).

Noble metals can be doped on Ni/Mg(Al)O catalysts simply by dipping Mg(Ni,Al)O periclase particles in aqueous solutions of noble metal nitrates. Noble metal–Ni/Mg(Al)O catalysts can be prepared by calcination followed by reduction of the obtained particles, and successively applied in the DSS SR of CH\(_4\)\(^{32,33}\).

Trace amounts of the noble metals, Rh, Pt and Ru, effectively suppressed the oxidative deactivation of the Ni\(_{0.5}\)/Mg\(_2\)Al\(_2\)O\(_4\) catalyst during the DSS SR of CH\(_4\). During preparation of the noble metals–Ni\(_{0.5}\)/Mg\(_2\)Al\(_2\)O\(_4\) catalysts, reconstitution of HT was observed; the XRD patterns of the samples during preparation of Ru(0.1 wt%–Ni\(_{0.5}\)/Mg\(_2\)Al\(_2\)O\(_4\) catalysts are shown in Fig. 8\(^{33}\). The reflection lines of Mg\(_2\)Al\(_{5}\)N\(_{10}\)–Al HT were observed after coprecipitation (Fig. 8-a) and the reflection lines of Mg\(_2\)Al\(_{10}\)Ni\(_{0.5}\)O periclase appeared after calcination at 900°C (Fig. 8-b). After drying powders of Mg\(_2\)Al\(_{5}\)N\(_{10}\)O periclase in aqueous solution of Ru\(^{3+}\) nitrate, Mg(Ni–Al)–Al HT was reconstituted together with Mg(OH)\(_2\) brucite (Fig. 8-c). The formation of Mg(OH)\(_2\) brucite suggests that the reconstitution of HT from the periclase proceeds via hydration of MgO, since MgO is thermodynamically unstable compared with Mg(OH)\(_2\)\(^{28}\). MgO reacts very easily, even with moisture in the air, especially at low coordination atomic sites, to form Mg(OH)\(_2\) brucite. After calcination at 900°C for 5 h, Mg(OH)\(_2\) disappeared, the periclase phase was regenerated (Fig. 8-d) and the Ni metal reflection line appeared after reduction at 900°C for 1 h (Fig. 8-e). However, the Ni metal reflection lines were still quite intense even after the fourth step (Fig. 8-f)\(^{33}\).

3.3. Noble Metal–Ni/Mg(Al)O Catalysts for DSS Operation

The results of DSS-like operation of CH\(_4\) SR over supported Ru–Ni/Mg(Al)O catalysts are shown in Fig. 9\(^{33}\). The Ni\(_{0.5}\)/Mg\(_2\)Al\(_2\)O\(_4\) catalyst showed a clear deactivation just after the first steam purging, indicating that Ni was quickly oxidized by steam. The Ni oxidation was confirmed by XRD analyses; neither Ni metal nor NiO reflection was observed, whereas Mg(Ni,Al)O periclase reflections were intensified, suggesting that Ni was oxidized to Ni\(^{2+}\) and was incorporated into the periclase. The 13.5 wt% Ni/γ-Al\(_2\)O\(_3\) catalyst also showed deactivation during DSS operation. Addition of 0.5 wt% Ru to 13.5 wt% Ni/γ-Al\(_2\)O\(_3\) improved the catalytic behavior, but catalyst activity was slowly and finally totally lost due to Ni oxidation after the third steam purging. Ru doping of Ni\(_{0.5}\)/Mg\(_2\)Al\(_2\)O\(_4\) was quite effective for maintaining high activity during the four-cycled operation; even if Ru doping was decreased from 0.5 wt% to 0.05 wt% (Fig. 9). However, with Ru loading of 0.01 wt%, the catalyst was totally deactivated after the third cycle.

In the catalyst preparation using the ‘memory effect,’ 1.0 g of Mg$_2$S$_x$(Al,Ni)$_{15}$O periclase powder was dispersed in 5 ml of Ru(III) nitrate aqueous solution. 0.1 wt% Ru-doping was carried out by the incipient wetness method using a small volume of Ru(III) nitrate aqueous solution, but the catalyst obtained exhibited clear deactivation after the second steam purging. No HT reflection was observed in the XRD patterns of this catalyst, indicating that the ‘memory effect’ is important in the catalyst preparation. In the absence of Ni, the activity of 0.1-0.5 wt% Ru/Mg$_2$O($\gamma$-Al)$_2$O catalysts drastically decreased during the reaction independent of steam purging, suggesting that the deactivation was due to slow surface change of Ru, or sintering or coking on the catalyst. It must be emphasized that the Ru was not sufficiently active at such small loadings, and the activity of the Ru–Ni$_6$s/Mg$_2$S$_x$(Al)O catalysts depended mainly on the Ni species (Fig. 9).

The effects of Ru, Rh, Pd and Pt doping on the activity retention of Ni$_6$s/Mg$_2$S$_x$(Al)O catalyst were tested in the DSS SR of CH$_4$ with steam-purging$^{21,33}$. As noted previously, Ni$_6$s/Mg$_2$S$_x$(Al)O catalyst was severely deactivated by Ni oxidation just after the first steam purging$^{22}$. Doping of a small amount (0.05 wt%) of Ru, Rh and Pt considerably increased the stability of this catalyst by suppressing Ni oxidation, whereas simple loading of the noble metal on Mg$_2$O periclase had little effect. XRD of 0.5 wt% Ru–Ni$_6$s/Mg$_2$S$_x$(Al)O catalysts during the DSS SR of CH$_4$ suggested that Ni was included in Mg$_2$S$_x$(Al,Ni)$_{15}$O periclase as Ni$^{2+}$ ions just after dipping, followed by calcination. Ru was first physically trapped in the layered structure of MgNi–Al HT reconstituted after dipping, and then converted to fine particles of RuO$_2$ after calcination. After reduction, Ni$^{2+}$ ions in Mg$_2$S$_x$(Al,Ni)$_{15}$O periclase were reduced to Ni$^0$ located on the surface of the periclase particles and reacted with Ru to form alloy. Interestingly, XRD detected such Ni metal species throughout the DSS operation, although the intensity varied depending on the atmosphere. Ni was probably partly oxidized by steam, but partly persisted in the reduced state during steam purging, and the oxidized Ni$^{2+}$ was reoxidized during the steam reforming reaction at 700°C. In the absence of noble metal, Ni$_6$s/Mg$_2$S$_x$(Al)O was completely deactivated and XRD showed no Ni metal reflection after the first steam purging$^{33}$. All these findings indicate that the active species is Ni metal, even on noble metal doped Ni$_6$s/Mg$_2$S$_x$(Al)O catalysts, and the noble metal, such as Ru, Rh and Pt, suppresses the oxidation of Ni, probably through hydrogen spillover from the noble metal$^{33,34}$.

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

The specific surface areas, H$_2$ uptakes, Ni dispersion and Ni particle sizes on the Ru, Rh and Pt–Ni$_6$s/Mg$_2$S$_x$(Al)O catalysts are shown in Table 5$^{35}$. Specific surface area significantly decreased, whereas H$_2$ uptake drastically increased with noble metal doping; H$_2$ uptake was enhanced even with only 0.01 wt% of Ru doping. The contribution of the noble metal to the H$_2$ uptake must be small, because 0.1 wt% Ru/Mg$_2$O showed extremely small H$_2$ uptake. Therefore, strong synergy probably occurs between the noble metal and Ni on the catalysts, leading to enhanced H$_2$ uptake due to the formation of bimetallic systems such as alloy.

The TPR profiles of Ru–Ni$_6$s/Mg$_2$S$_x$(Al)O with varying Ru dopings showed that Ni$_6$s/Mg$_2$S$_x$(Al)O exhibited a single and intense peak at 895°C due to Ni reduction. The peak shifted toward lower temperatures with increasing Ru doping and, additionally, a weak and broad peak appeared around 400°C for the 0.5 wt% Ru-doped catalyst. The decrease in the reduction temperature of Ni suggests a formation of RuNi alloy. The peak observed around 400°C catalyst can be ascribed to the reduction of RuO$_2$ to Ru metal, because no other stable ruthenium oxides are known to exist in the solid state$^{36,37}$. The RuO$_2$ separated from the Ru–Ni bimetallic system probably exists as fine particles on the catalyst surface.

3.5. Role of Noble Metals in the Bimetallic Active Species

XRD patterns of Ru–Ni$_6$s/Mg$_2$S$_x$(Al)O after reduction are shown in Fig. 10. Ni$_6$s/Mg$_2$S$_x$(Al)O showed rather sharp and intensive reflections of Ni metal (Fig. 10A-a), which were broadened and slightly shifted to lower angles with increasing Ru doping as seen in the reflection of Ni (200) at 2θ = 52.5° (Fig. 10B-a, b and c)$^{35}$. Rh is reported to be completely soluble in Mg(Al)O periclase, whereas Ru is not soluble and re-

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Table 5 Physicochemical Properties and TOF of Noble Metal-Ni Supported Catalysts before and after Steaming Treatment, and after Further Followed by DSS SR of CH₄

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area [m²·g⁻¹]</th>
<th>Dispersion [%]</th>
<th>Ni particle size [nm]</th>
<th>TOF [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before</td>
<td>after</td>
<td>after DSS</td>
<td>before</td>
</tr>
<tr>
<td>Ni₉₆Mg₂₆Al₃O₉⁴</td>
<td>173.6</td>
<td>56.8</td>
<td>76.5</td>
<td>11.0</td>
</tr>
<tr>
<td>0.1 Ru Ni₉₆Mg₂₆Al₃O₉⁴</td>
<td>128.7</td>
<td>56.4</td>
<td>71.8</td>
<td>20.3</td>
</tr>
<tr>
<td>0.1 Rh Ni₉₆Mg₂₆Al₃O₉⁴</td>
<td>133.1</td>
<td>59.5</td>
<td>83.5</td>
<td>15.3</td>
</tr>
<tr>
<td>0.1 Pt Ni₉₆Mg₂₆Al₃O₉⁴</td>
<td>141.2</td>
<td>56.9</td>
<td>76.1</td>
<td>20.6</td>
</tr>
<tr>
<td>13.5 wt% Ni₉₆Mg₂₆Al₃O₉⁴</td>
<td>106.8</td>
<td>61.0</td>
<td>67.7</td>
<td>6.4</td>
</tr>
<tr>
<td>FCR³</td>
<td>12.3</td>
<td>11.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>RUA³</td>
<td>11.4</td>
<td>10.6</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Steaming treatment was carried out at 900°C for 10 h in H₂/H₂O/N₂ (20/100/25 mL·min⁻¹).
SRM (steam reforming of methane) was carried out for evaluating TOF at 900°C in CH₄/H₂O/N₂ (88.8/177.6/44.4 mL·min⁻¹) at GHSV = 1.6 × 10⁵ [b] and 3.6 × 10⁵ [c] mL·g⁻¹·h⁻¹. TOF-4 means TOF value per total Ni on the catalyst.

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Figure 10 XRD Patterns of Supported Ru-Ni-Bimetallic Catalysts after Reduction

- Ru(0.05)/Ni(0.5)/Mg₉₆Al₃O₉⁴ (left)
- Ru(0.1)/Ni(0.5)/Mg₉₆Al₃O₉⁴ (middle)
- Ru(0.1)/Ni(0.5)/Mg₉₆Al₃O₉⁴ (right)
3.6. Self-regenerative Activity of Noble Metal-doped Ni/Mg(Al)O Catalysts

Ru-, Rh-, or Pt-doped Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O exhibited self-regenerative activity during SR of CH<sub>4</sub> in steam-purged DSS operation<sup>39,40,42</sup>. CH<sub>4</sub> conversion decreased after each steam purging and gradually increased during the reaction, suggesting that the Ni was partly oxidized by steam purging, then re-oxidized during the reaction (Fig. 9).

TEM images of 0.10 wt% Pt-Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O passivated by steam treatment, followed by DSS SR of CH<sub>4</sub>, are depicted in Fig. 11. After steam treatment at 900°C, the catalyst was severely passivated and the Ni particles were heavily sintered (Fig. 11A), but these sintered Ni particles were redispersed to the original sizes during the DSS SR in the presence of Pt (Fig. 11B). XRD and H<sub>2</sub> pulse measurements also clearly observed this redispersion of sintered Ni particles after DSS SR (Table 5). Judging from the TOF-t values before and after steaming (Table 5), noble metal-doped Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O catalysts still exhibited high activity for SR of CH<sub>4</sub> even after steaming, although the other supported Ni catalysts, Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O, 13.5 wt% Ni/γ-Al<sub>2</sub>O<sub>3</sub> and FCR, were substantially deactivated. This catalytic sustainability strongly suggests that Ni redispersion takes place not only during DSS SR but also during stationary SR of CH<sub>4</sub>, i.e., sintered Ni particles are redispersed in the reaction atmosphere of SR. The sintered Ni particles must be oxidized to Ni<sup>2+</sup> by steam and possibly incorporated into Mg(Ni,Al)O periclase. In turn, the Ni<sup>2+</sup> in Mg(Ni,Al)O periclase is quickly reduced assisted by hydrogen-spillover from Pt metal or Pt-Ni alloy. Such reversible reduction-oxidation between Ni<sup>0</sup> and Ni<sup>2+</sup> on/in Mg(Ni,Al)O periclase effectively promotes both self-activation and self-regeneration of activity on Pt-doped Ni/Mg(Al)O during DSS operation (Fig. 12). XAFS analyses of 0.50 wt% Pt-Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O showed that Pt formed Pt-Ni alloy located in the surface layer of the fine Ni metal particles, based on the formation of Pt-Ni bonds and the coordination number of Pt, respectively<sup>59</sup>.

Similar phenomena were also observed for 0.10 wt% Ru-Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O<sup>59</sup> and 0.10 wt% Rh-Ni<sub>10</sub>/Mg<sub>2.5</sub>(Al)O<sup>42</sup> before and after steam treatment, followed by DSS SR of CH<sub>4</sub>.

4. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalysts for the CO Shift Reaction

Hydrogen fuel for PEFCs can be supplied by steam reforming of hydrocarbons such as CH<sub>4</sub>, CH<sub>3</sub>H<sub>2</sub> and kerosene. The reformed gas contains 1-10% CO which hinders the electrochemical reaction at the Pt electrode in the PEFCs. Therefore, the CO level must be reduced to less than 10-20 ppm in the reformed gases. The CO shift reaction (6)

\[
CO + H_2O \rightarrow CO_2 + H_2
\]

is desirable for removal of a large amount of CO because it is moderately exothermic reaction and the reaction temperature is easy to control. Ternary Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been widely employed in the CO shift reaction. The catalyst was usually prepared by coprecipitation, resulting in higher Cu metal dispersion in the resulting catalyst and so higher catalytic activity.
4.1. Effects of Pt-doping on Cu/ZnO/Al₂O₃ Catalysts

Cu/ZnO/Al₂O₃ catalysts were doped with trace amounts of noble metals and tested in the CO shift reaction. Ternary Cu/ZnO/Al₂O₃ mixed oxides were prepared as the catalyst precursors by coprecipitation (cp) of metal nitrates; auriichalcite (AC), (Cu,Zn)₆(CO₃)₆(OH)₁₂, was formed as the main product and HT, (Cu,Zn)₆Al₁₂(OH)₁₆CO₃·4H₂O, appeared with increasing Al content after coprecipitation. Noble metal-doping was conducted by dipping the precursor calcined at 300°C in aqueous solutions of the noble metal nitrates; HT was reconstituted by the ‘memory effect’ and noble metals were simultaneously incorporated. XRD patterns of 0.05 wt% Pt doped Cu/ZnO/Al₂O₃ obtained during the preparations are depicted in Fig. 13 for the cp-Cu/Zn/Al(45/45/10) precursor, containing mainly AC together with a small amount of HT (Fig. 13-a). When the precursor after calcination was doped with Pt, HT was reconstituted and formed amor-

phous phases together with AC after calcination (Fig. 13-b, c and d)⁴⁴.

To assess the activity and sustainability of the catalysts, the CO shift reaction was carried out at 250°C for 30 h. The [CO conversion] extrapolated to reaction time = 0 was designated as the index of the catalytic activity, whereas the [−dCO/dt] estimated from the decline in CO conversion per unit time and unit amount of the catalyst was designated as the index of catalyst deactivation. Among the noble metals, Pt was the most effective for stabilizing the catalytic activity, although slight deactivation due to Cu sintering occurred. The [CO conversion] and [−dCO/dt] over 0.05 wt% Pt-doped cp-Cu/Zn/Al(45/45/10) exceeded the values obtained over a commercial Cu/Zn/Al catalyst, MDC-7, supplied by Süd Chemie Co.⁴⁵. This finding may be partly due to the higher activity of the AC-derived Cu/ ZnO phase; according to the results previously reported for Cu/ZnO catalysts prepared by homogeneous precipitation using urea, AC is a potential precursor for the preparation of potential CO shift catalyst⁴⁵,⁴⁶.

In-situ observation of Cu LMM Auger electron spectra of the Cu/ZnO catalyst clearly indicated oxidation of Cu⁰ to Cu⁺ during steam treatment, suggesting that the shift reaction proceeds via the reduction-oxidation mechanism expressed by Eqs. (7) and (8)⁴⁷:

\[ 2Cu + H₂O \rightarrow Cu₂O + H₂ \]  
\[ Cu₂O + CO \rightarrow 2Cu + CO₂ \]  

(7)  
(8)

The cationic Cu⁺ sites probably chemisorb CO as the first step of the reaction, followed by reduction to Cu⁰, which in turn catalyzes H₂O dissociation as well as O-H bond cleavage, resulting in acceleration of the surface oxidation-reduction reactions (7) and (8). Cu metal surface areas of Pt-doped Cu/ZnO/Al₂O₃ catalysts obtained by the N₂O decomposition method and TOF calculated from CO conversions at 150°C and 250°C are shown in Table 6⁴⁷. Surface areas of Cu metal were significantly decreased by Pt-doping, indicating that Cu metal particles were sintered. During noble metal-doping, Cu once dissolved in an aqueous solution cannot be reincorporated into HT due to the Jahn-Teller

![Fig. 13 XRD Patterns of 0.05 wt% Pt-doped Cu/Zn/Al (45/45/10) Catalyst during Preparation](image)
Effect on the Cu sintering on the surface of the catalyst particles. The TOF values per exposed copper sites were increased by Pt-doping on cp-Cu/Zn/Al(45/45/10) at both 150°C and 250°C, indicating the intrinsic promoting effect of Pt. The TOF values were the highest at 0.05 wt% with Pt-doping on cp-Cu/Zn/Al(45/45/10). These results indicate that hydrogen-spillover from metallic Pt particles to active metallic Cu particles improves the catalytic activity, although the promoting effect of Pt was apparently masked by the decrease in the metallic Cu active sites.

4.2. Effects of Mg-doping on Cu/ZnO/Al₂O₃ Catalysts

Mg-doping was also effective for enhancing both activity and sustainability of cp-Cu/Zn/Al(45/45/10) derived from a mixture of Zn(Cu)-Al ternary HT and Cu/Zn binary AC. Trace amounts of Mg were doped on cp-Cu/Zn/Al(45/45/10) precursor after calcination by adopting the ‘memory effect’ (m) of HT. When the precursor was dipped in an aqueous solution of Mg(II) nitrate, HT was reconstituted by the ‘memory effect.’ During this procedure, the catalyst particle surface was modified, leading to high sustainability as well as increased intrinsic activity of m-Mg-Cu/Zn/Al(45/45/10). In contrast, cp-Mg/Cu/Zn/Al(45/45/10) prepared by co-precipitation of nitrates of Mg, Cu, Zn, and Al as a control exhibited high activity but low sustainability compared with m-Mg-Cu/Zn/Al(45/45/10).

The activity and sustainability of m-Mg-Cu/Zn/Al (45/45/10) and cp-Mg/Cu/Zn/Al(45/45/10) are summarized in Fig. 14. The activity exhibited by the [CO conversion] was far higher on cp-Mg-added catalysts than on m-Mg-doped catalysts. In contrast, the rate of deactivation exhibited by \([-\frac{d\text{CO}}{dt}]\) was substantially lower on m-Mg-doped catalysts than on cp-Mg-added catalysts, indicating that the sustainability was more efficiently enhanced by m-Mg doping than by cp-Mg addition.

![Graph showing the effect of Mg-doping on Cu/ZnO/Al₂O₃ Catalysts](image)

*Fig. 15* Turnover Frequency of m-Mg-Cu/Zn/Al (45/45/10) and cp-Mg/Cu/Zn/Al (45/45/10) Catalysts in the CO Shift Reaction.
Mg-doped catalysts than \textit{cp}-Mg-added catalysts. MgO probably acts as electron donor to the Cu active species, resulting in enhanced stability of Cu species against oxidative sintering as well as enhanced catalytic activity via the reduction-oxidation cycle between Cu\textsuperscript{0} and Cu\textsuperscript{+} [45,47,50]. Although the activity was apparently masked by the decrease in metallic Cu surface area due to sintering, the sustainability was effectively enhanced on m-Mg–Cu/Zn/Al(45/45/10) by the Mg doping.

5. Conclusion

HTs after heat treatment formed 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 can be reconstituted in the product mixed oxide. Such HTs allow fine modification of the surface structure of mixed oxides, provoking a unique catalytic activity in the various reactions.

Fe/Mg(Al)O catalyst exhibited high activity for Baeyer-Villiger oxidation of cyclic ketones as well as for ethylbenzene dehydrogenation to styrene. Cu/Mg/Al mixed oxide catalyst showed high activity for the mineralization of oxalic acid by O\textsubscript{2}, and the ‘memory effect’ of HT accelerated the mineralization by capturing oxalic acid in the reconstituted HT interlayer space of the catalyst.

Ni/Mg(Al)O catalysts exhibited high and stable activity in the reforming of CH\textsubscript{4}, because of the formation of stable and well-dispersed Ni metal particles produced from Mg(Ni,Al)O periclase as solid solutions obtained by calcination of the Mg(Ni)–Al HT. Trace amounts of noble metals were doped in the surface layer of the Mg(Ni,Al)O periclase by adopting the ‘memory effect,’ resulting in the formation of efficient bimetallic catalysts for H\textsubscript{2} fuel production for PEMCs. The noble metal-doped Ni/Mg(Al)O catalysts exhibited self-activation as well as self-regeneration during the reforming reactions.

Cu/Zn/Al mixed oxide catalysts prepared from a mixture of AC and HT precursors exhibited high and sustainable activity in the CO shift reaction; the former catalyst formed highly dispersed Cu metal species and the latter catalyst formed Pt- or Mg-doped Cu species. Pt or Mg doping was effective for stabilizing the active Cu species against oxidative sintering, and accelerated the CO shift reaction by enhancing the reduction-oxidation between Cu\textsuperscript{0} and Cu\textsuperscript{+}, by hydrogen spillover from Pt to Cu or electron donation from Mg to Cu, respectively.

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References


要 旨

ハイドロタルサイトを出発原料とするユニフォーム固体触媒の新規製造法

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Mg-Al および Zn-Al 系ハイドロタルサイト（HT）前躯体から各種の不均一系触媒を調製して、酸化、オゾン分解、脱水素、炭化水素改質および CO シフト反応に用いた。Mg-Al(Fe)HT から調製した Fe/MgAl 酸化物触媒は、種々のケトンのパイ ヤー・ビリーア酸化のみならず、エチルベンゼンの脱水素に活性を示した。同様に、Mg(Cu)–Al HT から調製した Cu/MgAl 酸化物触媒は、水溶液中でその "メモリー効果" により触媒粒子表面に HT 相を再生して、難分解性のメチル酸を効果的に取り込んで完全に酸化分解した。Mg(Ni)–Al HT から調製した Ni/Mg(Al)O 触媒はメタンおよびプロパンの水蒸気改質や酸化改質に高い活性と耐久性を示した。また、この Ni 触媒の活性は "メモリー効果" を利用して触媒粒子表面に膜貫通の装置をドープすることにより飛躍的に改善され、家庭用固体高分子形燃料電池への水素供給に必須の "daily start-up and shutdown (DSS)" 条件下でも Ni は酸化されず高耐久性を示した。この時、活性 Ni 粒子は反応中に自己再生され、高活性ならびに耐久性が得られた。さらに、Zn(Cu)–Al HT の "メモリー効果" を利用して粒子表面に膜貫通の Pt あるいは Mg をドープした Cu/Zn(Al)O 触媒は CO シフト反応に高い耐久性を示した。