[Review Paper]

Production and Utilization of Hydrogen Carriers by Using Supported Nickel Catalysts

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Utilization of hydrogen carriers is an important method for the storage and transportation of hydrogen energy. We have investigated supported nickel catalysts for methane production from hydrogen and carbon dioxide, and hydrogen production from ammonia. In the methane production, methane yield was drastically enhanced at 225-250 °C and reached maximum at 300-350 °C for most catalysts tested. CO₂ desorption behavior over the catalysts indicated that moderate basic sites should positively affect the catalytic activity for the reaction. According to the infrared spectroscopic analyses, CO₂ methanation over Ni/Al₂O₃ proceeded via the formation of CO intermediate, whereas the formate adsorbate would be the main intermediate over Ni/Y₂O₃. For the hydrogen production from ammonia, rare-earth oxide-supported catalysts showed relatively high performance despite the low surface area of the support materials. Ammonia conversion over Ni/Y₂O₃ reached 87 % at 550 °C. Rare-earth components were also effective as additives for the Ni/Al₂O₃ catalyst. These results were derived from the alleviation of hydrogen inhibition by rare-earth materials.

Keywords
Hydrogen carrier, Nickel catalyst, Carbon dioxide methanation, Ammonia decomposition, Rare-earth element, Basic property

1. Introduction

The Industrial Revolution improved both productivity and living standards, and fossil fuels have been used as the essential energy sources for human society. However, the resultant enormous consumption has induced serious environmental and energy issues. An increase in world population and an economic growth of developing countries have accelerated the consumption of the resources. Consequently, a new energy system independent of fossil fuels must be urgently developed.

Hydrogen has been widely considered as an alternative energy source since the commercialization of fuel cells. Hydrogen is presently produced by the reforming of fossil fuels. Thus, application of renewable energy to hydrogen production is required for the reduction of the dependence on fossil fuels. However, areas optimum for solar and wind energy production are often far from energy consumption areas, although present policies depend greatly on renewable energy for the realization of a low-carbon society. Therefore, conversion of these renewable energies to hydrogen is also desirable in terms of utilization on a large scale.

Hydrogen has low boiling point and volumetric energy density, leading to great difficulties in the liquefaction and compression processes. Therefore, hydrogen carrier, compounds containing hydrogen, are possible solutions for the storage and transportation of hydrogen fuel. Such hydrogen carriers can be delivered to energy consumption areas, and reformed or decomposed to produce hydrogen.

Ammonia, methylcyclohexane, and methane are all potential candidates for hydrogen carriers because of the high hydrogen content, suitability for mass production, and ease in storage and transportation. We have focused on methane synthesis from CO₂ and hydrogen, and hydrogen production by ammonia decomposition. This review mainly introduces our recent research on these reactions using supported Ni catalysts.

2. Methane Production from Carbon Dioxide and Hydrogen

2.1. CO₂ Methanation
Methane is one of the most important chemical feedstocks, and is also a major component of natural gas, so infrastructures for storage and transportation are already
available. The CO₂ methanation reaction, also called the Sabatier reaction, proceeds as follows.

\[ \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \]  

(1)

This process is an exothermic reaction and thermodynamically proceeds at lower temperatures. However, a catalyst is required to achieve a sufficient reaction rate. Various catalysts have been developed based on metals such as Ru, Rh, Pd, and Ni as the active species, and metal oxides (Al₂O₃, SiO₂, zeolite, TiO₂, CeO₂, CeO₂-ZrO₂, etc.) as the support materials. Ru and Rh catalysts possess high activity, but Ni catalysts are more suitable for practical application due to low material cost, and superior selectivity to methane³.

Many studies have been conducted to elucidate the reaction mechanism of CO₂ methanation but no clear conclusion has been reached. At present, the proposed reaction mechanisms can be classified into two main types⁴. In one mechanism, CO intermediate is formed from CO₂ and then hydrogenated to methane. In the other mechanism, carbon dioxide is directly hydrogenated to formate species as an intermediate, which is converted to methane and water.

We have investigated Ni catalysts supported on various metal oxides and evaluated their activity for CO₂ methanation. Moreover, the chemical species formed on the catalyst surface during the reaction were examined by in-situ infrared spectroscopy⁵.

2.2. Development of Metal Oxide-supported Ni Catalyst

The metal oxides of Al₂O₃, Y₂O₃, ZrO₂, La₂O₃, CeO₂, and Sm₂O₃ were selected as the support materials. Supported Ni catalyst was prepared by an impregnation method and subsequent calcination at 600 °C for 2 h⁵).

The catalytic activity test for CO₂ methanation was conducted after reduction at 600 °C. The methane yield was significantly enhanced in the temperature range of 200-300 °C for all catalysts as shown in Fig. 1. The yield gradually decreased from the maximum with higher temperatures along the equilibrium curve. The selectivity to methane was extremely high at low temperatures, but the CO yield exceeded 1 % above ca. 300 °C because the reverse water gas shift reaction \((\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O})\) tends to predominate at higher temperature. Overall, the Ni/Y₂O₃ catalyst showed superior performance in CO₂ methanation.

CO₂ desorption behavior was evaluated for the catalysts as shown in Fig. 2. After reduction at 600 °C and exposure to CO₂ at 50 °C, the catalyst was heated at 10 °C min⁻¹ in He. Desorbed CO₂ was scarcely detected for Ni/ZrO₂, indicating a very small number of basic sites. The profile of Ni/CeO₂ showed a specific desorption peak at ca. 110 °C. Only weak basic sites were widespread on the catalyst. For Ni/Al₂O₃, the high surface area of Al₂O₃ support (141 m² g⁻¹) induced a large amount of desorbed CO₂. Desorption was notable at 400-500 °C for Ni/La₂O₃, which implied that carbon dioxide was strongly adsorbed on the basic sites.
Because the adsorbed CO\textsubscript{2} species have to be converted in CO\textsubscript{2} methanation, the reaction would not be readily accelerated over Ni/La\textsubscript{2}O\textsubscript{3} catalyst as shown in Fig. 1. On the other hand, most of adsorbed CO\textsubscript{2} on Ni/Y\textsubscript{2}O\textsubscript{3} and Ni/Sm\textsubscript{2}O\textsubscript{3} was desorbed in the temperature range of 200-400 °C where the CO\textsubscript{2} methanation reaction proceeds. Medium basic sites were important in the high catalytic activity of Ni/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{26}). In this study, therefore, the high activity of Ni/Y\textsubscript{2}O\textsubscript{3} and Ni/Sm\textsubscript{2}O\textsubscript{3} at low temperatures would be related to the high ratio of CO\textsubscript{2} desorbed in the medium temperature region.

Adsorbates formed on the relatively low active Ni/Al\textsubscript{2}O\textsubscript{3} and the highly active Ni/Y\textsubscript{2}O\textsubscript{3} catalysts in CO\textsubscript{2} methanation were analyzed by \textit{in-situ} diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. \textbf{Figure 3} shows the infrared spectra of adsorbates formed on Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/Y\textsubscript{2}O\textsubscript{3} at 200 °C after holding in the CO\textsubscript{2}-N\textsubscript{2} atmosphere for 30 min and in the CO\textsubscript{2}-H\textsubscript{2}-N\textsubscript{2} atmosphere for 30 min.

Because the adsorbed CO\textsubscript{2} species have to be converted in CO\textsubscript{2} methanation, the reaction would not be readily accelerated over Ni/La\textsubscript{2}O\textsubscript{3} catalyst as shown in Fig. 1. On the other hand, most of adsorbed CO\textsubscript{2} on Ni/Y\textsubscript{2}O\textsubscript{3} and Ni/Sm\textsubscript{2}O\textsubscript{3} was desorbed in the temperature range of 200-400 °C where the CO\textsubscript{2} methanation reaction proceeds. Medium basic sites were important in the high catalytic activity of Ni/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{26}). In this study, therefore, the high activity of Ni/Y\textsubscript{2}O\textsubscript{3} and Ni/Sm\textsubscript{2}O\textsubscript{3} at low temperatures would be related to the high ratio of CO\textsubscript{2} desorbed in the medium temperature region.

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The carbonyl hydride consists of CO and H species at the same adsorption site of the metal catalyst. The hydrogen atom donates its electron to the metal or the carbon atom, resulting in the weakened C-O bond. As a result, the corresponding band appears at a lower wavenumber compared with CO adsorbate\textsuperscript{9,10)}. Therefore, the absorption bands at 1832, 1907, 2021, and 2052 cm\textsuperscript{-1} can be assigned to the bridged nickel carbonyl hydride and/or formyl adsorbate, bridged CO adsorbate, linear nickel carbonyl hydride adsorbate, and linear CO adsorbate, respectively. Broad bands for Ni/Y\textsubscript{2}O\textsubscript{3} were mainly confirmed at 1200-1700 cm\textsuperscript{-1} under the CO\textsubscript{2} atmosphere, attributable to various adsorption states of carbonate and hydrogen carbonate over Y\textsubscript{2}O\textsubscript{3}. The bands of hydrogen carbonate adsorbate (1219 cm\textsuperscript{-1} and 1672 cm\textsuperscript{-1}) disappeared after holding in CO\textsubscript{2}-H\textsubscript{2} accompanied by the emergence of strong bands of formate adsorbate (1383, 1369, and 1595 cm\textsuperscript{-1}). Adsorption bands of CO-related species were slightly observed at 1800-1900 cm\textsuperscript{-1}.

Subsequently, the change in the adsorbates formed in CO\textsubscript{2}-H\textsubscript{2} was examined by exposure to H\textsubscript{2} for 2 h. The infrared spectra of species formed on Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/Y\textsubscript{2}O\textsubscript{3} in the H\textsubscript{2}-N\textsubscript{2} atmosphere are shown in \textbf{Fig. 4}. Two adsorption bands of formate adsorbate were confirmed at 2906 cm\textsuperscript{-1} and 2767 cm\textsuperscript{-1} for Ni/Al\textsubscript{2}O\textsubscript{3} and at 2852 cm\textsuperscript{-1} and 2728 cm\textsuperscript{-1} for Ni/Y\textsubscript{2}O\textsubscript{3} in addition to the wavenumber range in \textbf{Fig. 3}. The bands of CO-related adsorbates in Ni/Al\textsubscript{2}O\textsubscript{3} disappeared within 20 min from changing the atmosphere, implying desorption and/or conversion of these species in H\textsubscript{2}. In contrast, the band intensity of formate adsorbate slowly decreased and then remained almost constant. According to the previous literatures, the CO species serves as an intermediate for CO\textsubscript{2} methanation over Ni/Al\textsubscript{2}O\textsubscript{3}. CO species on the Ni surface is dissociated into carbon and oxygen species, which are converted to CH\textsubscript{4} and water, respectively, by hydrogenation\textsuperscript{7,11)}. The change in the band intensity of formate adsorbate suggests that the contribution of this adsorbate to the reaction was not significant.

The spectra for Ni/Y\textsubscript{2}O\textsubscript{3} showed the band intensities of formate adsorbate rapidly decreased with time. The weak adsorption bands of CO-related adsorbates disappeared within 20 min as for Ni/Al\textsubscript{2}O\textsubscript{3}. Ni catalysts supported on CeO\textsubscript{2} and CeO\textsubscript{2}-ZrO\textsubscript{2} showed high catalytic activity for CO\textsubscript{2} methanation because the formate intermediate was readily decomposed\textsuperscript{6,12,13)}.

![Fig. 3 Infrared Spectra of Species Formed on (A) Ni/Al\textsubscript{2}O\textsubscript{3} and (B) Ni/Y\textsubscript{2}O\textsubscript{3} at 200 °C after Holding (a) in the CO\textsubscript{2}-N\textsubscript{2} Atmosphere for 30 min and (b) in the CO\textsubscript{2}-H\textsubscript{2}-N\textsubscript{2} Atmosphere for 30 min. Reproduced from Muroyama et al. (2016)\textsuperscript{5)}](image-url)

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\textsuperscript{5)} Muroyama, K., et al. (2016). "Infrared Spectra of Species Formed on Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/Y\textsubscript{2}O\textsubscript{3} in the H\textsubscript{2}-N\textsubscript{2} Atmosphere at 200 °C after Holding 30 min in the CO\textsubscript{2} Atmosphere: The Influence of Medium Basic Sites on the Catalytic Activity of Ni/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}." J. Jpn. Petrol. Inst., 64(3), pp. 125-132.
fore, we concluded that the formate adsorbate was the main intermediate for the highly active Ni/Y$_2$O$_3$ catalyst. Accordingly, the Y$_2$O$_3$ support is effective for the formation of formate intermediate and its hydrogenation to methane.

**Figure 5** shows the plausible main reaction routes for Ni/Al$_2$O$_3$ and Ni/Y$_2$O$_3$. For Ni/Al$_2$O$_3$, carbon dioxide is dissociatively adsorbed on the Ni surface to form CO adsorbate. Some CO adsorbate should be converted to formyl and/or nickel carbonyl hydride adsorbates. Then, CO and these CO-related adsorbates are hydrogenated to form CH$_4$ and H$_2$O. For Ni/Y$_2$O$_3$, carbon dioxide is adsorbed as carbonate on the Y$_2$O$_3$ support, and the resulting adsorbate is hydrogenated to hydrogen carbonate. Formate adsorbate originates from the hydrogenation of the hydrogen carbonate by hydrogen species activated over Ni. Then, sequential hydrogenation of the formate adsorbate by the activated hydrogen species forms CH$_4$ and H$_2$O.

### 3. Hydrogen Production from Ammonia

#### 3.1. Ammonia Decomposition

Ammonia has higher hydrogen weight ratio than methylcyclohexane and can be liquefied under mild conditions (−33.3 °C at atmospheric pressure or 8.46 atm at 20 °C) due to its relatively high boiling point. The handling and transport systems are well established worldwide since ammonia is one of the most fundamental industrial chemicals. Hydrogen can be produced by an endothermic process as follows.

$$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$$

Ammonia conversion thermodynamically achieves ca. 99% at 400 °C under atmospheric pressure. Catalytic ammonia decomposition consists of adsorption of ammonia, stepwise hydrogen dissociation of the adsorbed ammonia, and combinative desorptions of nitrogen and hydrogen atoms. The reaction mechanism has been extensively investigated so far. Nitrogen desorption is widely accepted to be kinetically important in the reaction. Hydrogen dissociation of ammonia is also regarded as the slow step. In addition,
hydrogen inhibits the reaction, especially at low temperatures or low ammonia partial pressures.

Ammonia decomposition catalysts have been strenuously investigated. Ru catalysts show the highest activity due to the moderate nitrogen bonding energy of Ru metal for both adsorption of ammonia molecules and desorption of nitrogen atoms\(^ {22}\). Furthermore, modification of the electronic state of Ru metal is key for enhancement of the activity. However, considering the limited availability and cost of precious metals, development of catalysts consisting of base metals is desirable.

Therefore, we have investigated Ni catalysts supported on various metal oxides for ammonia decomposition. The previous study found that lanthanum oxide is effective as a support material despite its low surface area\(^ {23}\). Furthermore, addition of La and Ce components to Ni catalysts improved the activity\(^ {24,25}\). Therefore, we considered that rare-earth components would enhance the activity of Ni catalysts. Ni catalysts were fabricated using various rare-earth oxides as supports or additive components, and were studied to characterize the dispersion of Ni particles, activity for ammonia decomposition, and behavior of reactant and products during the reaction\(^ {26,27}\).

### 3.2. Development of Ni Catalyst Supported on Rare-earth Oxide

Several rare-earth oxides, Y\(_2\)O\(_3\), La\(_2\)O\(_3\), CeO\(_2\), Sm\(_2\)O\(_3\), and Gd\(_2\)O\(_3\), were selected as the support materials of the Ni catalyst for ammonia decomposition. The catalyst was prepared by an impregnation method and subsequent calcination at 600 °C for 5 h\(^ {26}\).

The specific surface area of the support was measured by N\(_2\) adsorption with the BET method. Ni surface area for the catalysts reduced at 600 °C was estimated with the CO pulse method assuming mono-molecular adsorption of CO on each Ni atom over the catalyst surface. The results are summarized in Table 1. The specific surface areas of the rare-earth oxides was much smaller than that of Al\(_2\)O\(_3\). Generally, support materials with high surface area are desirable for dispersion of the metal catalyst. However, some rare-earth oxide-supported catalysts exhibited relatively high Ni surface area. In particular, the value for the Ni/Y\(_2\)O\(_3\) catalyst was comparable to that of Ni/Al\(_2\)O\(_3\), suggesting that the Y\(_2\)O\(_3\) support was effective for dispersion of the Ni particles.

![Fig. 6](image.png)

**Fig. 6** XRD Patterns of (a) Fresh Y\(_2\)O\(_3\), (b) Acid-treated Y\(_2\)O\(_3\) before the Calcination, and (c) Acid-treated Y\(_2\)O\(_3\) after the Calcination

Reproduced from Okura et al. (2016)\(^ {26}\).

### Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area of support ([\text{m}^2 \text{g}^{-1}])</th>
<th>Ni surface area ([\text{m}^2 \text{g}^{-1}])</th>
<th>Reaction order (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Y(_2)O(_3)</td>
<td>7</td>
<td>1.62</td>
<td>0.77</td>
</tr>
<tr>
<td>Ni/La(_2)O(_3)</td>
<td>5</td>
<td>0.42</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni/CeO(_2)</td>
<td>4</td>
<td>0.18</td>
<td>0.74</td>
</tr>
<tr>
<td>Ni/Sm(_2)O(_3)</td>
<td>9</td>
<td>0.74</td>
<td>0.98</td>
</tr>
<tr>
<td>Ni/Gd(_2)O(_3)</td>
<td>4</td>
<td>1.06</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni/Al(_2)O(_3)</td>
<td>201</td>
<td>1.88</td>
<td>0.37</td>
</tr>
</tbody>
</table>

\(a\) Reaction temperature: 450 °C, SV: 10,000 l kg\(^{-1}\) h\(^{-1}\), Reaction gas: NH\(_3\)_H\(_2\)_Ar (NH\(_3\): 10-30 %, H\(_2\): 10-30 %, and Ar balance).
treatment. In response, the specific surface area of Y2O3 was expanded to 50 m2 g1. Accordingly, the high Ni dispersion for the Ni/Y2O3 catalyst could be attributable to the microstructural change of Y2O3 support after the impregnation process.

Activities of the catalysts for ammonia decomposition were evaluated. The catalyst sample was reduced at 600 °C for 2 h prior to the test. Figure 7 shows ammonia conversion over the catalysts. Ammonia conversion started to increase from 350 °C for all catalysts. The catalysts of Ni/Y2O3, Ni/Sm2O3, Ni/Gd2O3, and Ni/Al2O3 showed higher performance than Ni/Al2O3. Considering the highest Ni surface area for Ni/Al2O3, rare-earth oxide supports of these catalysts had positive effects on the activity of Ni catalysts. Ammonia conversion over Ni/Y2O3 achieved 87 % at 550 °C. The high Ni surface area is presumably one reason for its high performance compared with the other rare-earth oxide-supported catalysts. Some researchers indicated the importance of Ni particle size for activity in ammonia decomposition28,29. Li et al. reported that catalytic activity was enhanced with decreasing the Ni particle size up to 3 nm28. In the present study, therefore, small particles over the Y2O3 support would contributed to the high catalytic activity of Ni/Y2O3.

Ammonia decomposition over the Ni catalysts was kinetically analyzed to clarify the effect of the support material. The reaction rate (r) was defined by using the partial pressures of ammonia (PNH3) and hydrogen (PH2) as follows.

\[ r = k P_{NH3}^α P_{H2}^γ \]  

where k is the reaction rate constant, and α and γ are reaction orders. Ammonia decomposition rate is independent of the partial pressure of nitrogen14. Then, the catalytic reaction test was carried out at 450 °C by supplying gaseous mixtures with various ammonia and hydrogen concentrations. The reaction orders are also summarized in Table 1. The order for ammonia partial pressure was positive for all catalysts. The dependence on hydrogen partial pressure was negative, indicating that ammonia decomposition was inhibited by hydrogen. Because both ammonia and the produced hydrogen are competitively adsorbed on the active sites in ammonia decomposition, their partial pressures should influence the reaction rate. The previous study reported that a large negative value of γ corresponds to a significant inhibition of reaction by hydrogen14,30. In the present study, the absolute value was much larger for Ni/CeO2 and Ni/Al2O3 than for the other catalysts. Thus, the low catalytic activity of these two samples can be ascribed to inhibition by the produced hydrogen.

In contrast, hydrogen had a less effect on ammonia decomposition over Ni/La2O3, Ni/Gd2O3, and Ni/Y2O3. Previous study of the Ru surface found that the presence of Cs species strongly decreased the sticking coefficient of hydrogen11. Thus, the basic property of rare-earth oxide supports may prevent hydrogen adsorption over these Ni catalysts. Consequently, the high activity of rare-earth oxide-supported catalyst was partially derived from suppression of hydrogen inhibition.

The behavior of reactant and products desorbed from the surface of Al2O3, Y2O3, Ni/Al2O3, and Ni/Y2O3 were examined by ammonia temperature programmed surface reaction (NH3-TPSR). The sample was treated at 600 °C for 2 h in H2, and then exposed to NH3 at 50 °C. The desorption behavior of ammonia, hydrogen, and nitrogen were monitored by a mass spectrometer during heating at 5 °C min1 in Ar. The hydrogen desorption profiles are shown in Fig. 8. No nitrogen production was confirmed for both support materials, indicating that ammonia decomposition did not proceed under this condition. Hydrogen was detected above ca. 300 °C, mainly derived from the hydrogen atoms strongly-adsorbed on the surface during pretreatment in H2. The profile of the Ni catalyst was different from that of the corresponding support material for both systems. New hydrogen desorption was observed at 90-290 °C and 320-500 °C for Ni/Al2O3, whereas hydrogen desorption newly occurred only at 90-290 °C for Ni/Y2O3. These desorption processes were attributed to the hydrogen atoms generated by ammonia dissociation over both Ni catalysts. Considering the desorption process at high temperatures over Ni/Al2O3, dehydrogenation of NHx (x = 1-3) and subsequent hydrogen desorption would be promoted more readily over the Ni particles.
supported on Y₂O₃. Consequently, the Y₂O₃ support effectively alleviated hydrogen inhibition, leading to the high catalytic activity of Ni/Y₂O₃.

### 3.3. Additive Effects of Rare-earth Component on Catalytic Activity of Ni/Al₂O₃

In the previous section, rare-earth oxide supports were effective for suppression of hydrogen inhibition in ammonia decomposition. In contrast, the Ni/Al₂O₃ catalyst showed low activity due to severe hydrogen inhibition. Therefore, we focused on the addition of rare-earth components to Ni/Al₂O₃ to improve its catalytic activity for ammonia decomposition. The Ni/Al₂O₃ catalysts with rare-earth components (Y, La, Ce, Sm, Gd) were prepared by an impregnation method and subsequent calcination at 500 °C for 5 h²⁷).

The Ni surface areas for the catalysts reduced at 600 °C were estimated by the CO pulse chemisorption measurement as shown in Table 2. The surface area was slightly dropped by the additives other than La component. Addition of rare-earth components was found to enlarge the Ni surface area²⁴,³². In these cases, the Ni particle size of unmodified catalysts was ca. 5 nm. In this study, the particle size was ca. 30 nm. Thus, enlargement of Ni surface area by rare-earth modification would depend on the Ni particle size of the unmodified catalyst.

The catalytic performance for ammonia decomposition was studied after reduction at 600 °C. The ammonia conversion and hydrogen reaction order (γ) at 450 °C are shown in Table 2. The dependence of reaction rate on hydrogen partial pressure was evaluated based on Eq. (3), as explained previously. Addition of rare-earth components dramatically improved ammonia conversion and reduced the absolute value of the hydrogen reaction order. Combined with the slight difference in Ni surface area among the prepared samples, the reaction rate on one active site was significantly enhanced by the alleviation of hydrogen inhibition.

The hydrogen desorption behavior during ammonia decomposition was examined by NH₃-TPSR measurement. Figure 9 shows the hydrogen desorption profiles for the catalysts reduced at 600 °C. Two specific desorption peaks were confirmed at ca. 170 °C and 390 °C for Ni/Al₂O₃. For the modified catalysts, hydrogen was desorbed in the lower temperature region as for the unmodified one, while only the gradual increase in the signal was observed above ca. 300 °C. Comparison of the ratio of desorption amount above 300 °C to that at lower temperatures showed that the value was much higher for the unmodified sample than for the modified ones. This indicated that addition of a rare-earth component suppressed the strong adsorption of hydrogen species over the catalyst. This result was consistent with the tendency of hydrogen reaction order among the catalysts.

Previous studies suggested that part of the additives is located at the metal-support interface and prevents spillover of hydrogen from the metal surface to the support surface. In this study, the specific hydrogen desorption process in the high temperature region was confirmed only for the unmodified Ni/Al₂O₃ catalyst. Thus, hydrogen species would strongly adsorbed on Ni

![Fig. 8 Desorption Profiles of Hydrogen (m/z = 2) for Al₂O₃, 40 wt% Ni/Al₂O₃, Y₂O₃, and 40 wt% Ni/Y₂O₃ Obtained by NH₃-TPSR in Ar Flow at a Heating Rate of 5 °C min⁻¹ Reproduced from Okura et al. (2016)²⁶).

<table>
<thead>
<tr>
<th>Additive</th>
<th>Ni surface area [m² g⁻¹]</th>
<th>NH₃ conversion [%]</th>
<th>Hydrogen reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>1.99</td>
<td>18.8</td>
<td>-0.74</td>
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<tr>
<td>La</td>
<td>2.09</td>
<td>20.2</td>
<td>-0.72</td>
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<tr>
<td>Ce</td>
<td>2.01</td>
<td>15.4</td>
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<td>Sm</td>
<td>1.80</td>
<td>18.2</td>
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<tr>
<td>Gd</td>
<td>2.02</td>
<td>15.8</td>
<td>-0.87</td>
</tr>
<tr>
<td>None</td>
<td>2.05</td>
<td>10.0</td>
<td>-0.97</td>
</tr>
</tbody>
</table>

a) Ni loading amount: 9 wt% (modified catalyst), 10 wt% (unmodified catalyst); loading amount of additive: 12 wt%.
b) Reaction temperature: 450 °C, SV: 6000 l kg⁻¹ h⁻¹, Reaction gas: 100 % NH₃.
c) Reaction temperature: 450 °C, SV: 10,000 l kg⁻¹ h⁻¹, Reaction gas: 30 % NH₃-x % H₂-(70 - x) % Ar (x = 10-30).
in the vicinity of the interface with Al₂O₃. The formation of such species was suppressed by the additives, resulting in significant decrease in the ratio of hydrogen desorbed at high temperatures.

The catalytic performance test and NH₃-TPSR measurement revealed that the enhancement of catalytic activity by the rare-earth component was derived from the alleviation of hydrogen inhibition for ammonia decomposition.

4. Summary

This review introduced CO₂ methanation and ammonia decomposition over supported Ni catalysts. Basic strength and adsorption strength of CO₂ were the important factors determining the activity of catalysts for CO₂ methanation. DRIFT spectroscopy indicated that the main intermediate was different between Ni/Al₂O₃ and Ni/Y₂O₃. Promotion of the hydrogenation of formate adsorbate by Ni/Y₂O₃ would result in high catalytic activity. For ammonia decomposition, supports and additives with rare-earth components provided high performance for nickel catalysts. Hydrogen inhibition was alleviated by the rare-earth components. However, the activity of developed nickel catalysts for these reactions was not sufficient compared to precious metal catalysts. Therefore, further extensive investigation needs to be carried out.

Large-scale utilization of renewable energy is desirable in terms of current issues of resources, energy, and environment. Storage and transportation of energy with chemical substances are important challenges, and new related technologies will be developed and put into practical applications.

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References


要　旨

金属酸化物担持ニッケル触媒を使用した水素キャリアの製造・利用

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水素エネルギーを貯蔵・輸送するための手段として、水素キャリアの利用が注目されている。本稿では水素キャリアに関連する技術として、担持ニッケル触媒を使用したCO2メタン化反応およびアンモニア分解反応について紹介した。CO2メタン化反応では、多くの触媒でメタン収率が225 〜 250 ℃で大幅に向上し、300 〜 350 ℃で最大値に達した。触媒上でのCO2脱離挙動は、中程度の強度を有する塩基性サイトが触媒の反応活性に影響を与えることを示した。赤外分光分析によると、Ni/Al2O3上のCO2メタン化反応は、CO中間体の形成を経て進行する一方、Ni/Y2O3上ではジ酸種が主な中間体であることが示唆された。アンモニア分解反応において、希土類酸化物担持触媒は、触媒材料の表面積が小さいにもかかわらず、高い活性を示し、Ni/Y2O3触媒において550 ℃で87 %のアンモニア転化率を達成した。希土類成分はNi/Al2O3触媒の添加物としても有効であった。これらの結果は、希土類成分が水素による反応の阻害を緩和することに起因した。

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