C₂+ OXYGENATES SYNTHESIS
FROM CARBON DIOXIDE AND NATURAL GAS
OVER CATALYSTS PREPARED USING W/O MICROEMULSION

Hiroki Hayashi, Research & Development Institute, Saibu Gas Co., Ltd.

1. INTRODUCTION

1.1. CO₂ Reforming of Natural Gas (Conversion of CO₂ and Natural Gas to Syngas)

In recent years, considerable attention has been paid to global warming due to the greenhouse effect. The reduction and utilization of greenhouse gases such as carbon dioxide is, therefore, becoming more and more important. Catalytic reforming of natural gas (methane) with carbon dioxide, reaction (1), to syngas has been proposed as one of the most promising technologies for the utilization of carbon dioxide as carbon-containing materials [1]. The syngas produced by this reforming has a high CO content which is favorable for the synthesis of valuable oxygenated chemicals [2, 3].

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad (1)
\]

There is no established industrial technology for the CO₂ reforming of methane, in spite of the fact that the economical and environmental benefits constitute an attractive incentive. The major problem lies in the catalyst deactivation caused by carbon deposition [4-6]. Supported noble metal catalysts are reported to be less sensitive to coking compared to the nickel-based catalysts in this reforming reaction [7-9]. However, considering the high cost and limited availability of noble metals, it is more practical to develop anti-coke nickel-based catalysts.

Recently, we found that a Ni/Al₂O₃ catalyst prepared using water-in-oil (w/o) microemulsion was highly active and stable for the CO₂ reforming of methane. In this study, we investigated the catalytic activity and durability of the Ni/Al₂O₃ catalyst thus prepared during methane-CO₂ reforming and discuss the causes of their superior catalytic behavior.

1.2. C₂+ Oxygenates Synthesis from Syngas

As a fuel alternative and an additive to gasoline, C₂+ oxygenates provide many advantages, including lower production of hydrocarbons, NOx, and CO in the exhaust stream due to a more complete combustion, and improvement of volatility due to high octane number [10]. Apart from their use in the fuel industry, C₂+ oxygenates can also be utilized: 1) as precursors for synthesis of other organic chemicals; 2) for alkylation and solubilization of coal; 3) for combined cycle peak electric power generation; 4) as a substitute for propane in liquefied petroleum gas (LPG) applications; 5) as a transportation medium for coal in slurry pipelines; and 6) as general solvents.

At present, most C₂+ oxygenates are produced by the hydration of ethylene and propylene derived from naphtha in petroleum. However, the world’s petroleum supply will be exhausted in the near future. Therefore, a fundamental alteration of the feedstock for C₂+ oxygenates is needed.

Numerous works have been performed on utilization of syngas as feedstock for C₂+ oxygenates. Rh catalysts are well known to be highly active for the synthesis of C₂+ oxygenates from syngas [11-13]. However, considering the limited availability of Rh, it would be preferable to accomplish such synthesis using active catalysts composed of inexpensive metals. Great strides have been made in improving the activity of catalysts composed of inexpensive metals such as Fe [14-17], Co [18-20] and Cu [21, 22] for the synthesis of C₂+ oxygenates from syngas, but there still remain some drawbacks such as low selectivity to C₂+ oxygenates.

Recently, we found that Fe/SiO₂ catalysts prepared using w/o microemulsions were highly active for C₂+ oxygenates synthesis from syngas. The Fe/SiO₂ catalysts exhibited more than twice the level of CO conversion realized by the conventional impregnation catalyst, and also exhibited a much higher selectivity to C₂+ oxygenates of >40C-mol%. We therefore report the catalytic behavior of the Fe/SiO₂ catalysts in C₂+ oxygenates synthesis from syngas and discuss the causes of their superior catalysis.
2. EXPERIMENTAL

2.1. Preparation of Catalysts

Ni/Al$_2$O$_3$ and Fe/SiO$_2$ catalysts were prepared by using w/o microemulsion. The preparation procedures are shown in Figure 1. The procedures for Ni/Al$_2$O$_3$ catalyst preparation will be described as follows.

The surfactant (Polyoxyethylene-p-nonylphenylether ether (n=20), Tokyo Kasei) concentration in an organic solvent (1-hexanol, Kanto Chemical) and the Ni(NO$_3$)$_2$ (Kanto Chemical 98.0% min.) concentration in an aqueous solution were 0.3 and 0.25 mol/l, respectively. The microemulsion solution was prepared by adding a 20ml aqueous solution of Ni(NO$_3$)$_2$ to a 300ml surfactant/organic solvent mixture in all the microemulsion systems. Ni(OH)$_2$ nanoparticles were formed in the microemulsion solution by adding 3g of tri-ethylamine (TMA, Kanto Chemical 99.0% min.) directly. Aluminium tri-isopropoxide (ATI, Kanto Chemical 99.9% min.), as a source of Al$_2$O$_3$ supports, was added to the microemulsion containing the Ni(OH)$_2$ nanoparticles, and then the hydrolysis of ATI was carried out at 323K for 1h with vigorous stirring. Ni loading was controlled by changing an amount of ATI added. The precipitate separated from the solution was dried at 353 K overnight, and was calcined in air at 723 K for 5 h. The calcined powder was pressed into disks and ground through 18/26 mesh. The catalyst prepared in this manner is designated as the ME catalyst.

As references, impregnated Ni/Al$_2$O$_3$ catalysts, designated as IMP catalysts, were also prepared by impregnating Al$_2$O$_3$, which was prepared in advance by the hydrolysis of ATI in the NP-20/1-hexanol microemulsion, with an aqueous solution of Ni(NO$_3$)$_2$. The IMP catalyst was calcined and ground under the same conditions as the ME catalyst.

In the ME method, a precursor of supports is an alkoxide, and the hydrolysis and polycondensation of the alkoxide occurred around metal complex particles or metal hydroxide particles formed beforehand in microemulsion. Therefore, it can be easily considered that an interaction between metal particles and supports in the ME catalysts will be strong as compared to conventional impregnation (IMP) catalysts which are prepared by impregnating ready-made supports with aqueous solution of metal salts.

2.2. Apparatus and reaction condition

-CO$_2$ Reforming of Methane-

CO$_2$ reforming of methane were conducted in a fixed-bed reactor with a quartz tube (8 mm i.d.). Reaction temperature was controlled using a thermocouple protected by a quartz thermo-well inserted in the center of the catalyst bed. Temperature differences from 15K to 50K existed during the reactions between the center of catalyst bed and the reactor wall. Commercially available methane (purity > 99.9%) was used without further purification. The amount of catalyst was 0.2g. The catalysts were reduced in-situ under H$_2$ flow at 873 K for 2 h prior to the reaction. The reaction conditions were as follows: 973K, CO$_2$/CH$_4$ molar ratio=1.0-2.0, SV=60000 h$^{-1}$. Gaseous reactants and products were passed through heated lines to gas chromatographs (Shimadzu GC-8A) for on-line analysis. The catalysts were reduced in-situ under H$_2$ flow at 873 K for 2 h prior to the tests.

-CO$_2$ Oxygenates Synthesis from Syngas (CO Hydrogenation)-

CO hydrogenations were performed in a continuous flow system with a fixed-bed quartz reactor (11mm i.d.) using 1.0 g of catalyst. All catalysts were reduced in-situ under an H$_2$ flow prior to the reaction. The standard reaction condition was 533K and 4.0 MPa of total pressure with H$_2$:CO:Ar
Table 1: Physical Properties of Ni/Al₂O₃ Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ni cont. / wt%</th>
<th>Ni particle size / nm</th>
<th>BET surface area / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>10</td>
<td>9.1 x TEM, 7.2 by XRD</td>
<td>341</td>
</tr>
<tr>
<td>IMP</td>
<td>10</td>
<td>8.7</td>
<td>320</td>
</tr>
</tbody>
</table>

(6:3:1 Vol.) and an SV of 2000 h⁻¹. Gaseous reactants and products were passed through heated lines to two gas chromatographs (Shimadzu GC-8AIF and GC-8AIT) for on-line analysis.

Major compounds produced as C₂⁺ oxygenates were C₂⁻C₅ linear, primary alcohols and C₂⁻C₄ aldehydes in this study.

2.3. Catalyst Characterization

BET surface area was determined by nitrogen adsorption-desorption at 77K using a Shimadzu ASAP 2010 instrument. The Ni particle size was determined by means of Transmission electron microscopy (TEM) using a JOEL JEM 2000FX.

Temperature-programmed reduction (TPR) was carried out using a 5vol% H₂/Ar gas as a reductant. A reductant flow rate of 30 ml/min and a temperature ramp of 10K/min from 373 K to 1173 K were used in the experiments. The consumption of H₂ was measured using a TCD gaschromatograph (Shimadzu GC-8A).

The surface composition of the catalyst was estimated by means of X-ray photoelectron spectroscopy (XPS) using a Shimadzu/Kratos Axis-165.

3. RESULT AND DISCUSSION

3.1. CO₂ Reforming of Methane

Pyshical properties of the ME and IMP catalysts prepared in this work are shown in Table 1. Figure 2 shows activity changes with time-on-stream for the ME and IMP catalysts at different CO₂/CH₄ molar ratio. Table 2 shows the amount of carbon on both the catalysts before and after reactions.

At any CO₂/CH₄ molar ratio, the ME catalyst exhibited higher CH₄ conversion than the IMP catalyst in the initial period.

The decrease in CH₄ conversion of these two catalysts showed a similar tendency at a CO₂/CH₄ molar ratio of 1.0. The CH₄ conversion of these two catalysts decreased with time-on-stream. A considerable amount of carbon was deposited on these two catalysts after the reaction. This coking seemed to induce the deactivation of both the catalysts.

At CO₂/CH₄ of 1.4 and 2.0, the deactivation behavior of these two catalysts was quite different. The ME catalyst kept its high CH₄ conversion for 50 h, whereas the IMP catalyst deactivated with time-on-stream. Similar to the result at a CO₂/CH₄ molar ratio of 1.0, a considerable amount of coke was deposited on the IMP catalyst after the reaction. In contrast, little carbon was deposited on the ME catalyst (below 0.5 wt%-carbon deposit after 50 h).

We considered the catalytic property leading to the superior resistance to carbon deposition of the ME catalysts. The carbon deposition on supported Ni catalysts has been reported to be closely related to Ni particle size [23]. However, a correlation between the amount of carbon deposited and Ni particle size was not observed for the ME catalysts. This result indicates that the Ni particle size itself is not a key catalytic property to a superior resistance to carbon deposition.

Figure 2  Activity changes with time-on-stream for the ME (closed symbols) and IMP (open symbols) catalysts at CO₂/CH₄ molar ratio of 1.0, [23]. However, a correlation between the amount of carbon deposited and Ni particle size was not observed for the ME catalysts. This result indicates that the Ni particle size itself is not a key catalytic property to a superior resistance to carbon deposition.
Table 2: Carbon Amount on Ni/Al₂O₃ Catalysts before and after Reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fresh</th>
<th>After 50h reaction</th>
<th>CO₂/CH₄=1.0</th>
<th>1.4</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>0.27</td>
<td>14.5</td>
<td>0.47</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>IMP</td>
<td>0.11</td>
<td>18.3</td>
<td>15.3</td>
<td>13.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Amount of deposited carbon and eliminated carbon

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Deposited C by CH₄ pulse</th>
<th>Eliminated C by CO₂ pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>/ 10⁻⁵mol</td>
<td>/ 10⁻⁵mol</td>
</tr>
<tr>
<td>ME</td>
<td>3.14</td>
<td>2.01</td>
</tr>
<tr>
<td>IMP</td>
<td>1.93</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Most of the coking-resistant Ni-based catalysts reported previously, e.g., NiO-MgO solid solutions [24, 25], had Ni species with low oxidation states. A key catalytic property necessary to a superior resistance to carbon deposition may be the oxidation state of Ni atoms.

From the TPR experiments, the Ni particles in the ME catalysts were more difficult to reduce than those in the IMP catalysts, and a considerable amount of Ni oxides existed in the ME catalysts even after H₂ reduction at 873K for 2h. In the CH₄-CO₂ reforming, CH₄ decomposition is known to be a rate-limiting step under various conditions, and the driving force of the step is an interaction between the Ni unfilled d orbits and the s electron pairs in the C-H bond of CH₄. Therefore, it is concluded that the Ni particles in the ME catalysts are more active than those in the IMP catalysts due to the difficulty in the reduction of Ni particles and thus the existence of Ni\(^{2+}\) species in the ME catalysts.

The effect of the electronic state of Ni metals on stability to carbon deposition was investigated. The ME catalysts exhibited a high stability to carbon deposition even under 973K and an CO₂/CH₄ molar ratio of 1.4. The consideration is possible that the carbon species formed on the ME catalysts during reaction may react more easily with CO₂ and are gasified more easily than those on the IMP catalysts. The reactivity of the carbon species formed by CH₄ decomposition on the ME catalyst was thus compared to that on the IMP catalyst by means of CO₂ pulse experiments. The results are shown in Table 3. As can be seen from this table, the amount of carbon removed by a pulse of CO₂ was larger with the ME catalyst than with the IMP catalyst. This result indicates that the carbon species formed on the ME catalyst reacted more easily with CO₂ and were removed more easily during reaction than those on the IMP catalyst.

Figure 3 shows the Raman spectra of the carbon species formed on the ME and IMP catalysts by CH₄ decomposition. Three bands were observed with both of the catalysts at 1340 cm⁻¹ (D band), 1580 cm⁻¹ (G band), and 1605 cm⁻¹ (D’ band). The G band was attributed to the in-plane carbon-carbon stretching vibrations of graphite layers, and the D and D’ bands were arose from disordered carbons [26]. It is shown from Figure 3 that the intensity ratio of D and D’ bands to G band was larger with the carbon species formed on the ME catalyst than with those on the IMP catalyst. Consequently, the crystallization order of the carbon species formed on the ME catalyst was lower than that on the IMP catalyst. This result means that crystallization order was dependent upon the electronic state of Ni metals. The reactivity of carbon species is well known to be higher with decreasing the crystallization order. Therefore, it can be concluded that the carbon species formed on the ME catalyst was more reactive than that on the IMP catalyst and that the ME catalyst thus had a strong resistance to carbon deposition.

Figure 3  Raman spectra of carbon species deposited on the ME and IMP catalysts after CH₄ decomposition test.
Catalyst & Fe cont. & Fe particle size & BET surface area
--- & --- & --- & ---
ME-1 & 2 & 4.8 & 186
ME-2 & 5 & 5.2 & 176
ME-3 & 10 & 5.1 & 189
ME-4 & 10 & 8.1 & 193
ME-5 & 10 & 13.2 & 201
IMP-1 & 2 & 5.6 & 284
IMP-2 & 5 & 8.2 & 275
IMP-3 & 10 & 14.2 & 260

Table 4: Physical properties of the Fe/SiO₂ catalyst

3.2. C₂⁺ Oxygenates Synthesis from Syngas

It is well known that supported Fe catalysts are active for FT synthesis and produce hydrocarbons in large quantities in the CO hydrogenation [27, 28]. However, the Fe/SiO₂ catalysts prepared by the ME method exhibited a very interesting catalytic performance, that is, a selectivity to oxygenates as high as 45%. The oxygenates were composed mainly of 25% C₁-C₅ alcohols and 15% aldehydes. The catalytic performance of the ME catalysts are demonstrated in Figure 4 with those of the IMP catalysts. The catalytic properties of these catalysts are shown in Table 4. The ME catalysts exhibited higher conversions of CO than the IMP catalysts in spite of the same Fe loading. As mentioned above, the ME catalysts produced oxygenates in a selectivity as high as 45%, and kept the selectivity for 50h or more.

The electronic state of Fe metals was then evaluated by means of XPS, but only a peak corresponding to Fe³⁺ was observed with all the catalysts because the samples were exposed to air before analysis. Accordingly, the reducibility of Fe particles was evaluated by means of TPR measurements. TPR profiles of the ME and IMP catalysts are shown in Figure 5. Three peaks, corresponding to 1) Fe₂O₃ ⊂ Fe₃O₄, 2) Fe₃O₄ ⊂ FeO and 3) FeO ⊂ Fe, can be observed with all the profiles, in accordance with the result reported by Chen et al. [29]. The reduction peaks of the ME catalysts were at higher temperatures than those of the IMP catalysts. This result indicates that the Fe particles of the ME catalysts were more difficult to reduce than those of the IMP catalysts.

TPR measurements were also conducted over the catalysts after H₂ reduction at 873K for 10h in order to investigate the difference in the reducibility. A reduction peak corresponding to FeO ⊂ Fe was observed with all the profiles. The temperature and area of reduction peak of the ME catalysts were higher and larger than that of the IMP catalysts, respectively. This result indicates that FeO was more difficult to reduce and existed in larger amounts in the ME catalysts than that in the IMP catalysts.
The ability of Fe to chemisorb CO is dependent upon the electronic state of Fe and thus becomes weak as the electron density on Fe particles decreases [30]. Fe particles chemisorb CO strongly on the IMP catalyst in which Fe metals exist as Fe$^0$, leading to little H$_2$ adsorption. On the other hand, Fe particles chemisorb H$_2$ enough to promote the surface reaction with CO on the ME catalyst in which Fe exists as Fe$^{2+}$. This promotion of the surface reaction may result in a high activity of the ME catalyst for the CO hydrogenation. The insertion of CO into alkyl group on Fe metals is known to be promoted as the electron density on Fe metals decreased. Therefore, it is understandable that the ME catalyst promoted the insertion of CO into alkyl group and yielded oxygenates in a high selectivity.

4. CONCLUSION

1) An interaction between metals and supports was stronger in the catalyst (ME catalyst) prepared by using microemulsion than that in the catalyst (IMP catalyst) prepared by the impregnation method, and the electronic state of metals in the ME catalysts was more oxidative than that in the IMP catalyst.

2) Supported Ni and Fe catalysts exhibited a superior catalysis in the CO$_2$ reforming of methane and in the hydrogenation of carbon monoxide. This catalytic behavior is elucidated by the existence of M$^{2+}$ species in the ME catalysts.

REFERENCES