Partial Oxidation of Methane to Syngas Over Rh and Ni Catalysts Impregnated on CeO₂, SiO₂, and Al₂O₃

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Abstract: The partial oxidation of methane (POM) to syngas was investigated over Rh(5) and Ni(5) catalysts impregnated on CeO₂, SiO₂, and Al₂O₃ in a fixed bed flow reactor under atmospheric conditions. The catalysts were analyzed by TEM, EDS, XPS, BET, and XRD. The CeO₂ carrier exhibited a slightly higher initial catalytic activity than did the SiO₂ and Al₂O₃ carriers for both the Rh(5) and Ni(5) catalysts. The stability of the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts remained constant for this first 30 hr. The TEM and EDS analyses showed that the nanoparticles of Rh and Ni, as well as ceria, were located on the catalyst surface prior to the reaction. XPS spectra of the O 1s core electron levels for the reduced Rh(5)/CeO₂ showed the highest intensity of lattice oxygen, O²⁻, at 528.65 eV; that of Ni(5)/CeO₂ was shifted slightly to a higher binding energy. The XPS spectra of the Ce 3d core electron level for the reduced Rh(5)/CeO₂ and the Ni(5)/CeO₂ catalyst showed Ce⁴⁺ and Ce³⁺ ions. The high syngas yields over both the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts suggest that important roles are played by CeO₂₃₄⁻, caused by formation of the lattice oxygen, O²⁻, and the oxygen vacancy due to the redox reaction between Ce⁴⁺ and Ce³⁺.

Keywords: partial oxidation of methane, carrier (CeO₂, SiO₂, Al₂O₃), Rh, Ni, redox reaction

Introduction

Technologies for the conversion of natural gas to syngas have received attention in recent years for the preparation of feedstocks, such as methanol, dimethyl-ether, and ethylene [1-4]. Methane, the main component of natural gas, is currently a promising energy resource [3]. Conversion of methane to syngas, CO, and H₂, is achieved through steam reforming, dry reforming, and partial oxidation. These reactions are accompanied by the water gas shift reaction [3].

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta \text{H}^{\circ} \text{298} = -41 \text{ kJ/mol} \quad (1) \]

Partial oxidation of methane to syngas is a promising method because of the suitable H₂/CO ratio and exothermicity [3].

\[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta \text{H}^{\circ} \text{298} = -36 \text{ kJ/mol} \quad (2) \]

Takehira and coworkers [5] suggested that spc-Niₓ/Mgₓ-Al should display a high and stable activity for the autothermal reforming of CH₄ in the copresence of O₂ and H₂O. Yan and coworkers [6] reported that methane conversion and selectivity to both H₂ and CO were higher over Rh/SiO₂ than over Ru/SiO₂ in the POM reaction. Takeguch and coworkers [7] reported that the addition of Ru and Pt to Ni-Y₂O₃ stabilizes zirconia cerments, promoted the steam reforming of CH₄, and suppressed coke deposition. Balint and coworkers [8] suggested that the mechanism of the partial oxidation of methane over 12 % Ru/Al₂O₃ catalyst should be related to the morphology (size) and chemical state of the supported Ru nanoparticles, as well as to the nature of the oxidizing agent (i.e., O₂ and NO). Jun and coworkers [9] reported that nickel-calcium phosphate/hydroxyapatite catalysts exhibited high activity and selectivity in the partial oxidation of methane. Takehira and coworkers [10] showed that

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Ni/SrTiO$_3$ prepared by solid phase crystallization (spc) had the highest activity as well as the highest sustain-
ability against both coke formation and reoxidation of Ni
prepared by the impregnation method. Studies of the
reaction between methane and promoted cerium oxide
showed that the selectivity to syngas depended on the
degree of reduction of the cerium oxide [11]. Rucken-
stein and Wang [12] reported that the activity of the POM
to syngas increased in the sequence MgO $\geq$ γ-Al$_2$O$_3$ >
La$_2$O$_3$ among these irreducible oxides when supporting
Rh.

Fajardie and coworkers [13] reported that a fraction of
the CO adsorbed on Rh particles supported on partially
reduced CeO$_2$ single-crystal surfaces was stabilized; it
desorbed at a temperature 100 K higher than that for CO
adsorbed on bulk Rh because of the presence of Ce$^{3+}$
ions on the surface of the CeO$_2$ (111) and CeO$_2$ (100)
supports. He and coworkers [14] suggested that by in-
corporating Y$^{3+}$ ions into Ce$_{0.95}$Zr$_{0.05}$O$_2$ and loading Pd, Pt,
or Rh onto Ce$_{0.8}$Zr$_{0.2}$Y$_{0.05}$O$_2$ (CYZ), one could enhance
(i) the lattice oxygen mobility, (ii) the Ce$^{3+}$ ion concen-
tration, and (iii) the oxygen uptake capacity of the CYZ
solid solution, generating a class of materials suitable for
use in automotive catalytic converters. However, many
problems, such as those related to coke formation, ther-
mal stability, and activity, should be solved for the POM.
Catalytic materials based on ceria have shown great
potential in applications such as environmental catalysis
[15]. Ceria, among all the metal oxides, is a particularly
excellent support or promoter because of its reduct
properties and oxygen storage capacity [16-17]. It was
predicted that high catalytic activity and stability of the
POM to syngas would occur when using CeO$_2$ as the
carrier.

In this study we investigated the conversion of methane
to syngas over rhodium and nickel catalysts supported on
SiO$_2$, Al$_2$O$_3$, and CeO$_2$ by conducting catalytic activity
experiments; we also investigated the active sites of the
best catalyst among the tested catalysts through TEM,
EDS, XPS, BET, and XRD analyses.

**Experimental**

**Catalyst Preparation**

Commercial Rh(5) catalysts supported on Al$_2$O$_3$ (Aldrich)
were used in this study. The number in parenthesis is the
degree of impregnation in weight percent. In addition, the
SiO$_2$ (Aldrich) catalyst impregnated with RhCl$_3$ ·
6H$_2$O (Aldrich) was prepared as described in a previous
study [18]. Rh(5)/CeO$_2$ and Ni(5)/CeO$_2$ catalysts was
prepared using the coprecipitation method. All reagents
were of extra-pure grade. The Ce(NO$_3$)$_3$ · 6H$_2$O (Junsei
chemicals) carrier and the RhCl$_3$ · 6H$_2$O (Aldrich) and
Ni(NO$_3$)$_2$ · 6H$_2$O precursors, respectively, were mixed
homogeneously with deionized water through stirring
and then precipitated by the addition of 0.1 N NH$_4$OH.
The solution was filtered and the precipitate was dried
completely at 393 K in a oven for 24 hr, followed by calcu-
lation in an electric furnace (Eyela, TMF-1000) under
air for 5 hr at 1023 K. The product was then ground to a
size between 150 and 200 mesh.

**Catalyst Characterization**

The morphologies of the catalysts were observed using a
TEM (Jeol, Jem-2000FxII) operated at 1.33 × 10$^7$ kPa
and 200 keV. EDS peaks were obtained by a Si(Li)
detector using an Oxford Elx-II apparatus. X-Ray powder
diffraction was performed on a Rikagu X-ray diffraction
instrument (D/Max Ultima III) operated at 40 kV and 40
mA and using CuK$_\alpha$ radiation. The BET surface area
was obtained by nitrogen adsorption at 77.2 K using a
Micromeritics ASAP 2020 instrument. The sample was
degassed at 1.34 × 10$^7$ kPa prior to measurement. The
XPS spectra were recorded using a VG-Scientific
ESCALAB 250 spectrometer and a monochromatized Al
K$_\alpha$ X-ray source (1486 eV).

**Reaction Procedure**

The catalytic reaction was performed under atmospheric
pressure in a fixed bed flow reactor. A quartz tube (6 ×
10$^{-3}$ m inner diameter) was used as the reactor. The
catalyst powder (3 × 10$^5$ kg) was held on quartz wool.
The CH$_4$/O$_2$ molar ratio, temperature, and contact time of
reactant gas were 1:1, 1023 K, and 6.01 × 10 kg-cat ·
sec/m$^2$, respectively. The reactor was maintained at the
desired temperature with an accuracy of ±1 K by using a
K-type thermocouple and a PID-controller. The reactants
were purged with a pressure regulator attached to each
gas cylinder and then the composition of the reactants
was controlled using each mass flow meter. The effluent
was analyzed using an on-line G.C. (Shimadzu Co.,
Model 14B, Japan) equipped with a thermal conductivity
detector; Porapak Q and Molecular sieve 5A columns
were used in parallel. The fresh catalyst was reduced in a
hydrogen flow of 0.4 mL/sec at 773 K for 5 hr, and then
the temperature was increased to 1023 K at a rate of 4.88
K/sec before being exposed to the reactant gases. We
analyzed the activity of the catalysts as follows:

conversion of methane (%) = (converted moles of
methane to product/input moles of methane) × 100,
yield of carbon monoxide (%) = (moles of carbon
monoxide product/input moles of methane) × 100,
yield of hydrogen (%) = [moles of hydrogen product /(2
× input moles of methane)] × 100.
Figure 1. CH$_4$ conversion vs. time on stream over Rh and Ni catalysts impregnated on CeO$_2$, SiO$_2$, and Al$_2$O$_3$: T, 1023 K; CH$_4$/O$_2$ molar ratio, 1:1; W/F, 6.01×10$^3$ kg-cat.sec/m$^3$.

Figure 2. CO yield vs. time on stream over Rh and Ni catalysts, impregnated on CeO$_2$, SiO$_2$, and Al$_2$O$_3$: T, 1023 K; CH$_4$/O$_2$ molar ratio, 1:1; W/F, 6.01×10$^3$ kg-cat.sec/m$^3$.

Figure 3. H$_2$ yield vs. time on stream over Rh, Ru, and Ni catalysts, impregnated on CeO$_2$, SiO$_2$, and Al$_2$O$_3$: T, 1023 K; CH$_4$/O$_2$ molar ratio, 1:1; W/F, 6.01×10$^3$ kg-cat.sec/m$^3$.

Figure 4. TEM images of the (A) Rh(5)/CeO$_2$ and (B) Ni(5)/CeO$_2$ catalysts prior to reaction.

Results and Discussion

Figure 1 displays the conversion of the POM over Rh(5) and Ni(5) catalysts impregnated on SiO$_2$, Al$_2$O$_3$, and CeO$_2$. High activities (99.10 ~ 99.98 %) were observed at 1023 K. Figures 2 and 3 show the yields of the POM to syngas over the Rh(5) and Ni(5) catalysts impregnated on SiO$_2$, Al$_2$O$_3$, and CeO$_2$. The activities of the Rh(5)/CeO$_2$ and Ni(5)/CeO$_2$ catalysts, based on the syngas yield, were almost identical: 91.19 and 90.66 %, respectively, at 1023 K. The CeO$_2$ carrier had a slightly higher
initial catalytic activity than did the SiO₂ and Al₂O₃ carriers for the Rh(5) and Ni(5) catalysts; the stability for the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts remained constant for the first 30 hr. TEM images of the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts prior to the reaction are presented in Figure 4; the EDS analysis is presented in Figure 5. We observed that the nanoparticles of Rh and Ni, as well as ceria, were present on the surface of the catalyst prior to their reaction. Figure 6 shows the XRD spectra of the Rh(5)/CeO₂ catalyst before and after its reaction. All of the XRD peaks, except for the Rh(111) plane observed after the reaction at 2θ = 41.1°, are typical of CeO₂. It is possible that the peak for Rh did not appear prior to the reaction because it was dispersed well in the CeO₂ matrix, but after the reaction it appeared as a result of sintering. Figure 7 shows the XRD spectra of the Ni(5)/CeO₂ catalyst before and after its reaction. Apart from the Ni(011) plane at 2θ = 44.4°, the diffraction peaks are typical of CeO₂. The width and intensity of the XRD diffraction peaks before the reaction were narrower and stronger than those observed after the reaction. These patterns suggest that particles were smaller before the reaction, and that no crystalline materials formed by interaction of transition metals (Rh, Ni) and CeO₂ should exist on the catalyst surface under experimental conditions. The BET surface areas of Rh(5) and Ni(5) catalysts impregnated on CeO₂ and SiO₂ prior to the reaction are presented in Table 1. The catalytic activity did not correlate with the BET surface area. Figure 8 shows XPS spectra of the Ce 3d core electron levels for the reduced Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts. As shown in Figure 8, the two main 3d₅/₂ features at 899.25 and 902.35 eV for Rh(5)/CeO₂ correspond to Ce⁴⁺ and Ce³⁺ components [19-21], respectively. The 3d₅/₂ features at 880.40, 883.75, and 896.85 eV for Rh(5)/CeO₂ correspond to Ce⁴⁺, Ce³⁺, and Ce³⁺ components [18-20], respectively. The 3d₅/₂ features of Ni(5)/CeO₂ were shifted slightly to a higher binding energy, but they are similar to those of Rh(5)/CeO₂. The XPS spectra of the O 1s core electron levels for reduced Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts are shown in Figure 9. Two different oxygen components of Rh(5)/CeO₂ were found at 528.65
Figure 7. XRD patterns of the Ni(5)/CeO₂ catalyst before (A) and after (B) the reaction: a, CeO₂ (111); b, CeO₂ (200); c, Ni (011); d, CeO₂ (220); e, CeO₂ (311); f, CeO₂ (222); g, CeO₂ (400); h, CeO₂ (331); i, CeO₂ (420); j, CeO₂ (422); k, CeO₂ (511).

Figure 8. XPS spectra of the Ce 3d core electron levels for the reduced Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts.

Figure 9. XPS spectra of the O 1s core electron levels for the reduced Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts.

Figure 10. XPS spectra of the Rh 3d core electron levels for the reduced Rh(5)/CeO₂ catalyst.

Figure 11. XPS spectra of the Ni 2p core electron levels for the reduced Ni(5)/CeO₂ catalyst.

and 529.10 eV. The main peak at 528.65 eV can be assigned to lattice oxygen, O²⁻ [22]. The shoulder peak at 529.10 eV is assigned to OH groups [23]. The O 1s core electron levels of Ni(5)/CeO₂ were also shifted to a
Table 2. Redox Cycle of the Rh(5)/CeO₂ and Ni(5)/CeO₂ Catalysts

<table>
<thead>
<tr>
<th>Rh(5)/CeO₂</th>
<th>Ni(5)/CeO₂</th>
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<tbody>
<tr>
<td>( \frac{1}{2} \text{O}_2 + 2\text{Ce}^{3+} \rightarrow 2\text{Ce}^{4+} + \text{O}^2^- ) (3)</td>
<td>( \frac{1}{2} \text{O}_2 + 2\text{Ce}^{3+} \rightarrow 2\text{Ce}^{4+} + \text{O}^2^- ) (7)</td>
</tr>
<tr>
<td>2OH → H₂O + O²⁻ + □ (4)</td>
<td>2OH → H₂O + O²⁻ + □ (8)</td>
</tr>
<tr>
<td>2Ce⁴⁺ + O²⁻ + H₂ → 2Ce³⁺ + H₂O + □ (5)</td>
<td>2Ce⁴⁺ + O²⁻ + H₂ → 2Ce³⁺ + H₂O + □ (9)</td>
</tr>
<tr>
<td>2Rh³⁺ + O²⁻ + H₂ → 2Rh²⁺ + H₂O + □ (6)</td>
<td>Ni²⁺ + O²⁻ + H₂ → Ni²⁺H₂O + □ (10)</td>
</tr>
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□: Oxygen vacancy site.

slightly higher binding energy, but otherwise they appeared similar to those of Rh(5)/CeO₂. Figure 10 shows XPS spectra of the Rh 3d core electron levels for the reduced Rh(5)/CeO₂ catalyst. The Rh 3ds/2 and Rh 3d₅/₂ peaks appear at 308.00 and 312.50 eV, respectively. The peak at 308.00 eV is assigned to Rh³⁺ ions [24], and that at 312.50 eV to Rh⁵⁺ ions [25,26]. Figure 11 shows the XPS spectra of the Ni 2p core electron levels for the reduced Ni(5)/CeO₂ catalyst. A broad Ni 2p₃/₂ peak appears between 851.7 and 854.2 eV. The peaks at 851.7 eV are assigned to Ni⁰ elements [27], and those at 854.2 eV to Ni²⁺ ions [27]. These findings suggest that the catalysts of the POM to syngas should proceed through the Redox cycle in Table 2. In addition, we believe that the oxygen defects of CeO₂ₓ play an important role in affecting the oxygen storage capacity and the surface oxygen mobility [28].

Conclusions

The partial oxidation of methane (POM) to syngas was conducted using Rh(5) and Ni(5) catalysts impregnated on CeO₂, SiO₂, and Al₂O₃ in a fixed bed flow reactor under the atmospheric conditions. The CeO₂ carrier displayed a slightly higher initial catalytic activity than did the SiO₂ and Al₂O₃ carriers for the Rh(5) and Ni(5) catalysts. The stabilities of the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts remained constant for the first 30 hr. The activities of the Rh(5)/CeO₂ and Ni(5)/CeO₂ catalysts, based on syngas yield, were 91.19 and 90.66 %, respectively at 1023 K. Our findings suggest that the presence of CeO₂ₓ and the oxygen vacancy should enhance the catalytic activity and stability. Moreover, CeO₂ₓ plays important roles in both the oxygen storage capacity and the surface oxygen mobility. Yield of the methane to syngas conversion did not correlate with the BET surface area.

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References