Partial Oxidation of Methane over Ni/SiO₂

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Ni catalyst (Ni: 15 wt%) supported on precalcined SiO₂ has been investigated in reforming reactions of methane to synthesis gas. The catalyst exhibited fairly good activity and stability in partial oxidation of methane (POM), whereas it deactivated in steam reforming of methane (SRM). Pulse reaction results of CH₄, O₂, and CH₄/O₂ revealed that Ni/SiO₂ has high capability to dissociate methane. The results also revealed that both CH₄ and O₂ are activated on the surface of metallic Ni, and then surface carbon species react with adsorbed oxygen to produce CO and CO₂ depending on the bond strength of the oxygen species on the catalyst surface.

Keywords : Methane, Ni/SiO₂, POM, Pulse reaction, Reforming.

Introduction

Catalytic partial oxidation of methane (POM) is of great practical importance in producing hydrogen or synthesis gas by using natural gas.1-3 Compared with the conventional highly endothermic catalytic steam reforming of methane (SRM),4 which is the established process for converting hydrocarbons into hydrogen or synthesis gas in industry, the catalytic POM offers the alternatively greatest potential for fast, efficient and economical conversion of methane to hydrogen or synthesis gas, due to the mild exothermicity, high conversion, high selectivity, suitable H₂/CO ratio for C₁ chemistry, and the very short residence time. Consequently, catalytic POM is estimated to be more economical than SRM.1 Therefore, it is necessary to develop the effective catalyst.

POM was first investigated in the 30’s and 40’s.5,6 But, coke formation occurred on the metal catalysts at the stoichiometric CH₄/O₂ ratio. Such undesirable carbon formation cannot be avoided by increasing the O₂/CH₄ ratio or by increasing the operating temperature without also increasing the potential explosion hazards, separation problems, and decreased synthesis gas selectivities. Catalytic POM has thus been virtually ignored for the last 50 years. In 1990, Green and co-workers7 reported that some noble metals could catalyze POM to the thermodynamic equilibrium composition of product gases. This observation reawakened industrial and academic interest in POM. Very recently, we reported that Ni/Co-ZrO₂ exhibited high activity and stability in POM, SRM, and oxy-steam reforming of methane (OSRM).10 Since Choudhary and co-workers11 reported that Ni/MgO showed good activity and selectivity in the reaction, Ni/MgO has been considered as one of the best candidate for POM.12 They also applied Ni/SiO₂ to POM, but failed to obtain stable activity.13 As a consequence, Ni/ SiO₂ has not been considered as a promising catalyst for POM. However, in this work, we found that Ni supported on de-hydroxylated SiO₂, which was precalcined at 800 °C for 6 h, showed fairly good activity corresponding to Ni/MgO in POM.

Experimental Section

Catalyst Preparation and Characteristics. The SiO₂ support (99%, PQ Corp.) employed in this study was precalcined at 800 °C for 6 h in order to improve stability at high temperature. 15 wt% Ni/SiO₂ catalyst was prepared by the molten-salt method as described elsewhere.14 The BET specific surface area and pore volume of the sample were measured by N₂ adsorption at -196 °C (Micromeritics, ASAP-2400). TPR was carried out in a conventional apparatus using 5% H₂/N₂ gas with a heating rate of 10 °C/min. Pulse chemisorptions were performed in a multifunction apparatus.12 The metal dispersion, surface area and average crystallite diameter were calculated based on the methods described in the reference15 by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

Reactions. Continuous flow activity tests were carried out under atmospheric pressure in a quartz micro-reactor with an inner diameter of 4 mm. The detailed procedures were described elsewhere.12 Pulse experiments using CH₄, O₂ and CH₄/O₂ mixed gas (CH₄/O₂=2) were performed under atmospheric pressure in a quartz micro-reactor with an inner diameter of 4 mm (1 mL pulse). 50 mg catalysts were loaded into the reactor. The detailed procedures were described...
The conversion and selectivity were calculated on the basis of 100% carbon and oxygen balances. In the pulse study, CO, CO$_2$, CO*, and CO$_2*$ selectivities were defined as follows.

$$\text{CO selectivity (\%)} = \left( \frac{\text{moles of CO formed}}{\text{moles of CH}_4 \text{ converted}} \right) \times 100\%$$
$$\text{CO}_2 \text{ selectivity (\%)} = \left( \frac{\text{moles of CO}_2 \text{ formed}}{\text{moles of CH}_4 \text{ converted}} \right) \times 100\%$$
$$\text{CO}^* \text{ selectivity (\%)} = \left( 0.5 \times \frac{\text{moles of CO formed}}{\text{moles of O}_2 \text{ converted}} \right) \times 100\%$$
$$\text{CO}_2^* \text{ selectivity (\%)} = \left( \frac{\text{moles of CO}_2 \text{ formed}}{\text{moles of O}_2 \text{ converted}} \right) \times 100\%$$

**Results and Discussion**

**Characterization.** Table 1 summarizes the typical textural properties of SiO$_2$ and Ni/SiO$_2$. After SiO$_2$ was precalcined at 900 °C for 6 h, BET surface area decreased from 453 to 400 m$^2$/g. This is the evidence of the dehydroxylation of SiO$_2$ during heat treatment. The BET surface area of Ni/SiO$_2$ is 262 m$^2$/g. Table 2 presents H$_2$ pulse chemisorption results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume (mL/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (untreated)</td>
<td>453</td>
<td>3.2</td>
<td>281</td>
</tr>
<tr>
<td>SiO$_2$ (treated)</td>
<td>400</td>
<td>3.0</td>
<td>300</td>
</tr>
<tr>
<td>Ni/SiO$_2$</td>
<td>262</td>
<td>1.6</td>
<td>244</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>H$_2$ uptake (µmol/g cat)</th>
<th>Dispersion (%)</th>
<th>Ni surface area (m$^2$/g)</th>
<th>Average particle diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.59</td>
<td>0.32</td>
<td>0.29</td>
<td>303</td>
</tr>
</tbody>
</table>

Ni surface area is 0.29 m$^2$/g and the average particle diameter of nickel is 303 nm.

The TGA curve of SiO$_2$ is presented in Figure 1. SiO$_2$ shows two distinct stages of weight loss, which are interpreted to be mainly due to removal of water. A first step up to 180 °C, assigned to the desorption of water, and a second step above 180 °C, related to condensation of silanol groups to form siloxane bonds, are clearly visible. This is another evidence of the dehydroxylation of SiO$_2$ during precalcination process.

The TPR patterns of pure NiO and Ni/SiO$_2$ are illustrated in Figure 2. Bulk NiO shows a sharp reduction peak at about 450 °C followed by a small hump. Ni/SiO$_2$ shows a peak consisting of two components with maxima at 400 and 420 °C. This evidences some inhomogeneity of supported Ni. According to the data from the literature, the TPR peaks are due to the reduction of NiO. No strong metal to support interaction (SMSI) is typical with silica.

**Pulse Reactions.** Sequential pulse experiments (CH$_4$ → O$_2$ → CH$_4$) were performed over Ni/SiO$_2$ at 800 °C to investigate the CH$_4$ dehydrogenation activity and carbon elimination by O$_2$. In these experiments, five pulses of each gas were injected. The blank run in an empty tube and CH$_4$ pulses over only SiO$_2$ supports did not show detectable CH$_4$ conversion.

Figure 3 shows CH$_4$ (O$_2$) conversion, CO (CO*) and CO$_2$ (CO$_2*$) selectivities over Ni/SiO$_2$ catalyst during three sets of pulses. In the first CH$_4$ pulse, a large amount of H$_2$ and a very small amount of CO were detected, implying that CH$_4$ is effectively dissociated to form carbon species. Since there was no gas-phase oxygen species present in the system after the prereduction at 700 °C for 3 h, the oxygen species may originate from the support. However, because reducible oxygen species were very scarce, CH$_2$ conversion rapidly decreased with increasing CH$_4$ pulse resulting from coke formation. There was no CO$_2$ detected during methane pulses. At the same time, the CO selectivity for the first pulse of methane was only 4.5%. Ni/SiO$_2$ exhibited 77% CH$_4$ conversion. According to our previous result, Ni/MgO showed 39% CH$_4$ conversion. This is probably due to a
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The reaction is a structural sensitive reaction, which is in agreement with the literature. Namely, Ni/SiO$_2$ has no SMSI, whereas Ni/MgO has the SMSI. With increasing CH$_4$ pulse, CH$_4$ conversion slowly decreased from 77.5% in the first pulse to 73.2% in the third CH$_4$ pulse, and then sharply decreased, suggesting that only when the amount of carbon accumulation on the catalyst is higher than a critical value, the catalyst would be deactivated. In the case of Ni/MgO, CH$_4$ conversion rapidly decreased with increasing CH$_4$ pulse. Compared with Ni/MgO, Ni/SiO$_2$ seems to be less sensitive to carbon accumulation. After five CH$_4$ pulses, the amount of carbon deposited on Ni/SiO$_2$ was 0.141 mmol (Table 3), which is 3 times higher than that on Ni/MgO, revealing that Ni/SiO$_2$ has higher capability to dissociate CH$_4$ than Ni/MgO. This is due to the fact that Ni/SiO$_2$ has no SMSI, whereas Ni/MgO has the strong interaction between NiO and MgO. The detailed explanation is as follows. It is believed that hydrocarbon should dissociate to produce highly reactive monatomic carbon (C$_\alpha$). If there is an excess of C$_\alpha$, then polymerization to C$_\beta$ is possible. C$_\beta$ is much less reactive than C$_\alpha$. As a result, C$_\beta$ may accumulate on the surface. During CH$_4$ pulses, because there is no gas phase oxygen species, the polymerization of C$_\alpha$ to C$_\beta$ is favored especially on Ni/SiO$_2$ due to much larger Ni ensemble size than Ni/MgO.

To investigate the reaction between surface carbides and O$_2$, a step switch from CH$_4$ to O$_2$ flow was carried out after 5 CH$_4$ pulses. A large amount of CO or CO$_2$ was produced in the first O$_2$ pulse, indicating the carbon species could quickly react with surface O species to form CO or CO$_2$. Ni/SiO$_2$ generated a considerable amount of CO$_2$ until the fourth O$_2$ pulse. These results reveal that the carbon species on Ni/SiO$_2$ favors CO$_2$ formation. This is probably due to the fact that the bond strength between carbon species and the active metallic Ni surface on Ni/SiO$_2$ is very strong. The strong bond mode favors CO$_2$ formation, because carbon species can be easily oxidized further to CO$_2$ by adsorbed O species. This is due to the reason that the selectivity to CO is governed mainly by two parallel steps, namely the oxidation of CO(s) to give CO$_2$ and the desorption of CO(s) to CO(g). The activation energy of CO(s) desorption is nearly double that of CO(s) oxidation over Ni. Therefore, Ni/SiO$_2$ having the stronger bond strength between carbon species and the Ni surface favors CO$_2$ formation rather than CO. After five O$_2$ pulses, the amount of carbon residue was 0.013 mmol. After O$_2$ pulses, some activated oxygen species still remained on the catalysts. In order to investigate the oxygen species involved in POM, CH$_4$ pulse was reintroduced after O$_2$ pulses. It was found that a considerable amount of CO and CO$_2$ was generated over Ni/SiO$_2$ in the first CH$_4$ pulse. CH$_4$ conversions over the partially oxidized catalysts in the third set of pulses were higher than those over the freshly reduced catalysts in the first set of CH$_4$ pulses. This indicates that the oxygen species adsorbed on the catalyst may enhance the conversion of CH$_4$. CO selectivity (23%) was slightly higher than CO$_2$ selectivity (19%). It is reported that the relative concentration of adsorbed oxygen to carbon species on the catalyst surface as well as the strength of O species bound to the catalyst is the crucial factor to determine the selectivity to CO and CO$_2$. After O$_2$ pulses, two types of adsorbed O species could be formed over the catalyst. One is the strong bond mode and the other is the relatively weak bond mode. These two O species show different performance with CH$_4$ pulses. The oxygen with strong bond can oxidize carbon species easily to CO$_2$ due to the strong interaction between NiO and MgO. The detailed explanation is as follows. It is believed that hydrocarbon should dissociate to produce highly reactive monatomic carbon (C$_\alpha$). If there is an excess of C$_\alpha$, then polymerization to C$_\beta$ is possible. C$_\beta$ is much less reactive than C$_\alpha$. As a result, C$_\beta$ may accumulate on the surface.

![Figure 3](image-url) Sequential pulse reaction (CH$_4$ → O$_2$ → CH$_4$) over Ni/SiO$_2$ at 800°C.

<table>
<thead>
<tr>
<th>CH$_4$ pulse</th>
<th>O$_2$ pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{\text{deposited}}$ (mmol)</td>
<td>C$_{\text{removed}}$ (mmol)</td>
</tr>
<tr>
<td>0.141</td>
<td>0.128</td>
</tr>
</tbody>
</table>

(Condition: 5 CH$_4$ pulses followed by 5 O$_2$ pulses).

Table 3. Pulse reaction results of Ni/SiO$_2$
its strong oxidation ability; while the oxygen with relatively weak bond reacts with carbon species to form CO. Since the interaction between Ni crystallite and SiO2 support is so weak that a large amount of oxygen species having the strong bond strength is formed during O2 pulses. Consequently, it results in better selectivity to CO2 over Ni/SiO2.

The CH4/O2 (2/1) pulse reactions were performed over Ni/SiO2 catalysts at 600 °C and 800 °C, respectively. The results are shown in Figure 4. During CH4/O2 pulses, O2 was completely consumed. Ni/SiO2 showed about 90% CH4 conversions and 97% CO selectivity at 800 °C, which is almost similar to those of Ni/MgO.12 Comparing with the results in the second set of sequential pulse reaction (O2 pulse after CH4 pulses), it is clear that Ni/SiO2 showed much higher CO selectivity (97%) in pulse reaction of CH4/O2 at 800 °C. This suggests that only highly reactive carbon species are formed on the catalyst surface by CH4 dissociation to produce CO during the partial oxidation of mixed CH4/O2. Comparing the pulse results at 800 °C with those at 600 °C, CO2 selectivity decreased with increasing reaction temperature. This is probably due to the following reasons. Since the activation energy of CO(s) desorption is nearly double that of CO(s) oxidation over Ni surface, the increase of reaction temperature would favor CO(s) desorption, leading to the increase of CO selectivity.19

After 10 pulses of CH4/O2, pure CH4 was injected. In the first CH4 pulse, a considerable amount of CO was produced without CO2 formation. This indicates that some oxygen species were still present on the catalysts after CH4/O2 pulses, resulting in CO formation. Thus, it can be reasonably considered that the adsorbed oxygen species play a role as the reaction intermediates in POM. At 600 °C, CH4 conversion increased from 21% in the first CH4 pulse to 32% in the second pulse. The results suggest that Ni/SiO2 is slightly oxidized at 600°C. In the first CH4 pulse, H2 produced from CH4 dissociation could reduce the Ni/SiO2 catalyst, resulting in the increase of CH4 dissociation in the second CH4 pulse.

**Steady State Activity in POM**

Continuous POM reaction was tested at 750 °C and space velocity of 55,200 mL/h·g cat, and the change in CH4 conversion with time on stream is presented in Figure 5. Ni/SiO2 exhibited high activity as well as stability during the reaction. It exhibited 83% CH4 conversion, 95% H2 selectivity, 88% CO selectivity, and a H2/CO ratio of 2.1, suggesting that Ni/SiO2 is a fairly good POM catalyst compared with the references.8,12 According to our previous results,8,12 Ni/Co-ZrO2 and Ni/MgO showed 85% and 78% CH4 conversion, respectively. Therefore, it can be suggested that Ni/SiO2 can be a good candidate in POM. This result is different from Choudhary and co-workers’ results.13 They reported that Ni/SiO2 rapidly deactivated with time on stream. They explained that the deactivation of Ni/SiO2 was not due to the carbon deposition but due to a strong chemical interaction between Ni and SiO2. However, in our case, the TPR pattern of Ni/SiO2 showed no SMSI. This is mainly due to the de-hydroxylation of SiO2 at 800 °C for 6 h. As a consequence, the defect sites of SiO2 could be eliminated. Hadjiivanov et al.3 characterized Ni/SiO2 and claimed that no SMSI is typical with Ni/SiO2 prepared by the impregnation method.

The fact that Ni/SiO2 shows good activity is in good agreement with the pulse results of methane revealing the high capability of Ni/SiO2 to dissociate methane. Ni/SiO2 maintained stability for several hours without catalyst deactivation. This is ascribed to the high ability to remove the carbon species deposited from CH4 dissociation by adsorbed oxygen species. It is known that the active sites for POM are free NiO having the weak interaction with the
support and complex NiO, having the strong interaction with the support. Usually, the catalysts having only NiO are suspected to be sensitive to carbon formation in reforming reactions. Actually, Ni/α-Al₂O₃ deactivated with time on stream. However, Ni/SiO₂ having no SMSI showed stable activity, resulting from the high capability of Ni/SiO₂ to eliminate the carbon deposited from CH₄ decomposition by adsorbed oxygen species. Whereas, Ni/SiO₂ having a chemical interaction did not show stability. It may be due to the deactivation of Ni resulting from the change of physical properties. Likewise, Ni/γ-Al₂O₃ would deactivate in POM as it changes into NiAl₂O₄. Thus, in the case of Ni/SiO₂, a strong chemical interaction between Ni and support should be prevented to obtain stability in POM.

**Steady State Activity in SRM.** Steam reforming of methane (SRM) over Ni/SiO₂ was conducted with a H₂O/CH₄ ratio of 3 at 750 °C. As shown in Figure 6, Ni/SiO₂ showed very low initial activity (23% CH₄ conversion) and it dramatically deactivated with time on stream. The main reason is that SiO₂ is volatile at high steam partial pressure and temperature above 700 °C. So, the structure of Ni/SiO₂ was collapsed by the evaporation of the hydrated silica (Si(OH)₄). Therefore, it was confirmed that Ni/SiO₂ is not suitable in SRM.

**Conclusions**

Ni supported on de-hydroxylated SiO₂ exhibits high activity as well as stability in POM, whereas deactivates in SRM. The high catalytic activity and stability in POM is ascribed to the stabilization of the SiO₂ support and the high capability to dissociate CH₄ and the ability to eliminate the carbon species by adsorbed O species.

**References**