

# Articles

## Partial Oxidation of Methane over Ni/SiO<sub>2</sub>

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Ni catalyst (Ni: 15 wt%) supported on precalcined SiO<sub>2</sub> 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 CH<sub>4</sub>, O<sub>2</sub>, and CH<sub>4</sub>/O<sub>2</sub> revealed that Ni/SiO<sub>2</sub> has high capability to dissociate methane. The results also revealed that both CH<sub>4</sub> and O<sub>2</sub> are activated on the surface of metallic Ni, and then surface carbon species react with adsorbed oxygen to produce CO and CO<sub>2</sub> depending on the bond strength of the oxygen species on the catalyst surface.

**Keywords :** Methane, Ni/SiO<sub>2</sub>, 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.<sup>1-3</sup> Compared with the conventional highly endothermic catalytic steam reforming of methane (SRM),<sup>4</sup> 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 H<sub>2</sub>/CO ratio for C<sub>1</sub> chemistry, and the very short residence time. Consequently, catalytic POM is estimated to be more economical than SRM.<sup>1</sup> Therefore, it is necessary to develop the effective catalyst.

POM was first investigated in the 30's and 40's.<sup>5,6</sup> But, coke formation occurred on the metal catalysts at the stoichiometric CH<sub>4</sub>/O<sub>2</sub> ratio. Such undesirable carbon formation cannot be avoided by increasing the O<sub>2</sub>/CH<sub>4</sub> 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-workers<sup>7</sup> 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/Ce-ZrO<sub>2</sub> exhibited high activity and stability in POM,<sup>8</sup> SRM,<sup>9</sup> and oxy-steam reforming of methane

(OSRM).<sup>10</sup> Since Choudhary and co-workers<sup>11</sup> 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.<sup>12</sup> They also applied Ni/SiO<sub>2</sub> to POM, but failed to obtain stable activity.<sup>13</sup> As a consequence, Ni/SiO<sub>2</sub> has not been considered as a promising catalyst for POM. However, in this work, we found that Ni supported on de-hydroxylated SiO<sub>2</sub>, 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 SiO<sub>2</sub> 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/SiO<sub>2</sub> catalyst was prepared by the molten-salt method as described elsewhere.<sup>14</sup> The BET specific surface area and pore volume of the sample were measured by N<sub>2</sub> adsorption at -196 °C (Micromeritics, ASAP-2400). TPR was carried out in a conventional apparatus using 5% H<sub>2</sub>/N<sub>2</sub> gas with a heating rate of 10 °C/min. Pulse chemisorptions were performed in a multifunction apparatus.<sup>12</sup> The metal dispersion, surface area and average crystallite diameter were calculated based on the methods described in the reference<sup>15</sup> by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni<sub>s</sub> = 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.<sup>12</sup> Pulse experiments using CH<sub>4</sub>, O<sub>2</sub> and CH<sub>4</sub>/O<sub>2</sub> mixed gas (CH<sub>4</sub>/O<sub>2</sub>=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

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**Table 1.** Textural properties of SiO<sub>2</sub> and Ni/SiO<sub>2</sub>

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (mL/g)	Average pore diameter (Å)
SiO <sub>2</sub> (untreated)	453	3.2	281
SiO <sub>2</sub> (treated)	400	3.0	300
Ni/SiO <sub>2</sub>	262	1.6	244

**Table 2.** H<sub>2</sub> pulse chemisorption results of Ni/SiO<sub>2</sub>

H <sub>2</sub> uptake (μmol/g cat)	Dispersion (%)	Ni surface area (m <sup>2</sup> /g)	Average particle diameter (nm)
3.59	0.32	0.29	303

elsewhere.<sup>12</sup> The conversion and selectivity were calculated on the basis of 100% carbon and oxygen balances. In the pulse study, CO, CO<sub>2</sub>, CO\*, and CO<sub>2</sub>\* selectivities were defined as follows.

CO selectivity (%) = (moles of CO formed / moles of CH<sub>4</sub> converted) × 100%

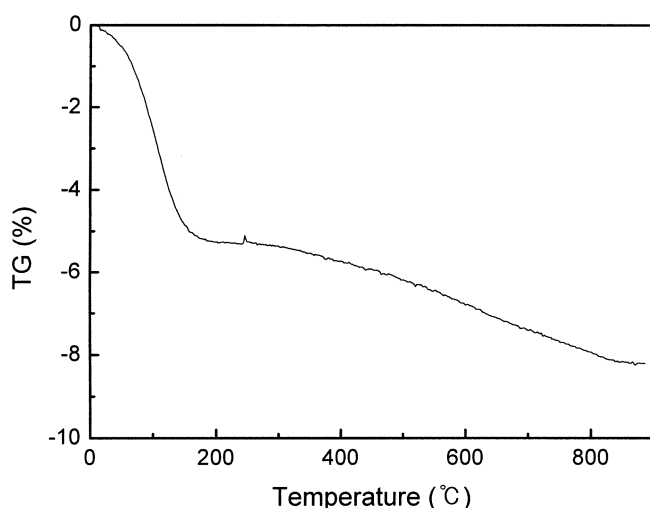
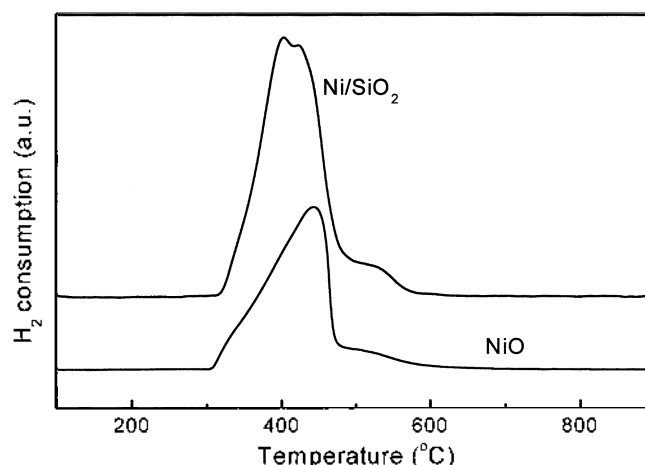
CO<sub>2</sub> selectivity (%) = (moles of CO<sub>2</sub> formed / moles of CH<sub>4</sub> converted) × 100%

CO\* selectivity (%) = (0.5 × moles of CO formed / moles of O<sub>2</sub> converted) × 100%

CO<sub>2</sub>\* selectivity (%) = (moles of CO<sub>2</sub> formed / moles of O<sub>2</sub> converted) × 100%

## Results and Discussion

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

**Figure 1.** TGA curve of SiO<sub>2</sub>.**Figure 2.** TPR patterns of NiO and Ni/SiO<sub>2</sub>.

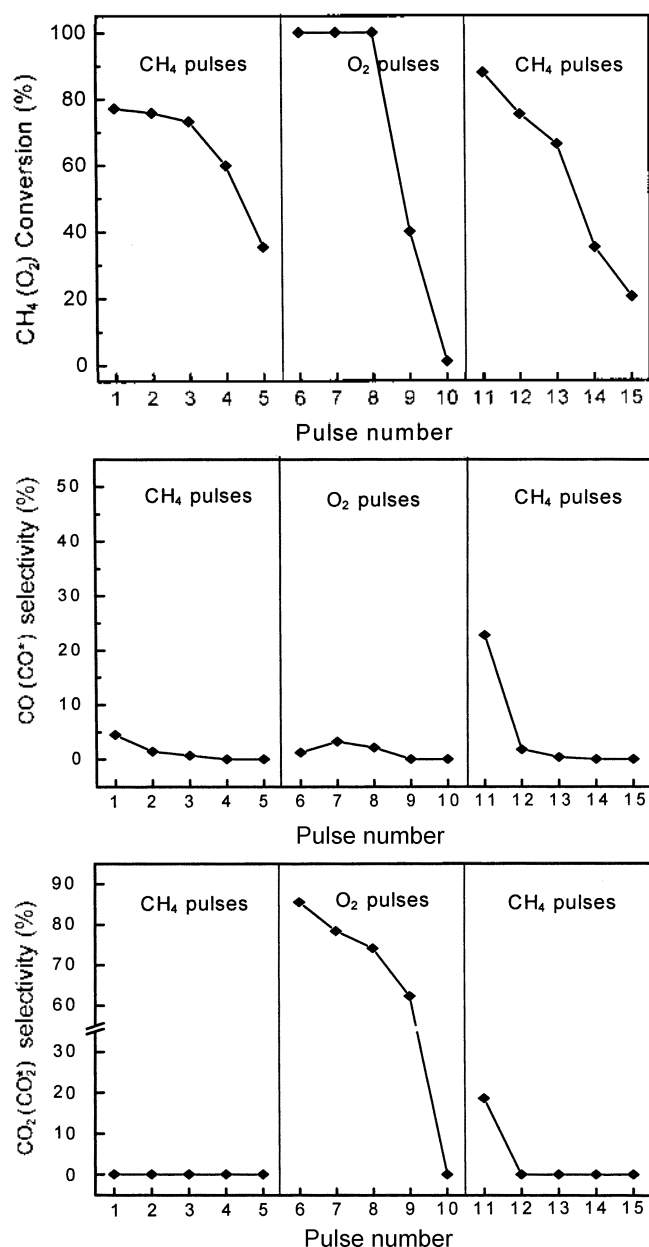
Ni surface area is 0.29 m<sup>2</sup>/g and the average particle diameter of nickel is 303 nm.

The TGA curve of SiO<sub>2</sub> is presented in Figure 1. SiO<sub>2</sub> 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<sub>2</sub> during precalcination process.

The TPR patterns of pure NiO and Ni/SiO<sub>2</sub> are illustrated in Figure 2. Bulk NiO shows a sharp reduction peak at about 450 °C followed by a small hump. Ni/SiO<sub>2</sub> 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,<sup>16</sup> the TPR peaks are due to the reduction of NiO. No strong metal to support interaction (SMSI) is typical with silica.<sup>16</sup>

**Pulse Reactions.** Sequential pulse experiments (CH<sub>4</sub> → O<sub>2</sub> → CH<sub>4</sub>) were performed over Ni/SiO<sub>2</sub> at 800 °C to investigate the CH<sub>4</sub> dehydrogenation activity and carbon elimination by O<sub>2</sub>. In these experiments, five pulses of each gas were injected. The blank run in an empty tube and CH<sub>4</sub> pulses over only SiO<sub>2</sub> supports did not show detectable CH<sub>4</sub> conversion.

Figure 3 shows CH<sub>4</sub> (O<sub>2</sub>) conversion, CO (CO\*) and CO<sub>2</sub> (CO<sub>2</sub>\*) selectivities over Ni/SiO<sub>2</sub> catalyst during three sets of pulses. In the first CH<sub>4</sub> pulse, a large amount of H<sub>2</sub> and a very small amount of CO were detected, implying that CH<sub>4</sub> is effectively dissociated to form carbon species. Since there was no gas-phase oxygen species present in the system after the pre-reduction at 700 °C for 3 h, the oxygen species may originate from the support. However, because reducible oxygen species were very scarce, CH<sub>4</sub> conversion rapidly decreased with increasing CH<sub>4</sub> pulse resulting from coke formation. There was no CO<sub>2</sub> detected during methane pulses. At the same time, the CO selectivity for the first pulse of methane was only 4.5%. Ni/SiO<sub>2</sub> exhibited 77% CH<sub>4</sub> conversion. According to our previous result,<sup>12</sup> Ni/MgO showed 39% CH<sub>4</sub> conversion. This is probably due to a



**Figure 3.** Sequential pulse reaction (CH<sub>4</sub> → O<sub>2</sub> → CH<sub>4</sub>) over Ni/SiO<sub>2</sub> at 800 °C.

structural sensitive reaction, which is in agreement with the literature.<sup>17</sup> Namely, Ni/SiO<sub>2</sub> has no SMSI, whereas Ni/MgO has the SMSI. With increasing CH<sub>4</sub> pulse, CH<sub>4</sub> conversion slowly decreased from 77.5% in the first pulse to 73.2% in the third CH<sub>4</sub> 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,<sup>12</sup> CH<sub>4</sub> conversion rapidly decreased with increasing CH<sub>4</sub> pulse. Compared with Ni/MgO, Ni/SiO<sub>2</sub> seems to be less sensitive to carbon accumulation. After five CH<sub>4</sub> pulses, the amount of carbon deposited on Ni/SiO<sub>2</sub> was 0.141 mmol (Table 3), which is 3 times higher than that on Ni/MgO, revealing that Ni/SiO<sub>2</sub> has higher capability to dissociate CH<sub>4</sub> than Ni/MgO. This is due to the fact that Ni/SiO<sub>2</sub> has no SMSI, whereas Ni/MgO has

**Table 3.** Pulse reaction results of Ni/SiO<sub>2</sub>

CH <sub>4</sub> pulse		O <sub>2</sub> pulse	
C deposited (mmol)	C removed (mmol)	C residue (mmol)	O adsorbed (mmol)
0.141	0.128	0.013	0.0629

(Condition: 5 CH<sub>4</sub> pulses followed by 5 O<sub>2</sub> pulses).

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<sub>α</sub>). If there is an excess of C<sub>α</sub>, then polymerization to C<sub>β</sub> is possible. C<sub>β</sub> is much less reactive than C<sub>α</sub>. As a result, C<sub>β</sub> may accumulate on the surface.<sup>18</sup> During CH<sub>4</sub> pulses, because there is no gas phase oxygen species, the polymerization of C<sub>α</sub> to C<sub>β</sub> is favored especially on Ni/SiO<sub>2</sub> due to much larger Ni ensemble size than Ni/MgO.

To investigate the reaction between surface carbides and O<sub>2</sub>, a step switch from CH<sub>4</sub> to O<sub>2</sub> flow was carried out after 5 CH<sub>4</sub> pulses. A large amount of CO or CO<sub>2</sub> was produced in the first O<sub>2</sub> pulse, indicating the carbon species could quickly react with surface O species to form CO or CO<sub>2</sub>. Ni/SiO<sub>2</sub> generated a considerable amount of CO<sub>2</sub> until the fourth O<sub>2</sub> pulse. These results reveal that the carbon species on Ni/SiO<sub>2</sub> favors CO<sub>2</sub> formation. This is probably due to the fact that the bond strength between carbon species and the active metallic Ni surface on Ni/SiO<sub>2</sub> is very strong. The strong bond mode favors CO<sub>2</sub> formation, because carbon species can be easily oxidized further to CO<sub>2</sub> 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<sub>2</sub> 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.<sup>19</sup> Therefore, Ni/SiO<sub>2</sub> having the stronger bond strength between carbon species and the Ni surface favors CO<sub>2</sub> formation rather than CO. After five O<sub>2</sub> pulses, the amount of carbon residue was 0.013 mmol.

After O<sub>2</sub> pulses, some activated oxygen species still remained on the catalysts. In order to investigate the oxygen species involved in POM, CH<sub>4</sub> pulse was re-introduced after O<sub>2</sub> pulses. It was found that a considerable amount of CO and CO<sub>2</sub> was generated over Ni/SiO<sub>2</sub> in the first CH<sub>4</sub> pulse. CH<sub>4</sub> 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<sub>4</sub> pulses. This indicates that the oxygen species adsorbed on the catalyst may enhance the conversion of CH<sub>4</sub>. CO selectivity (23%) was slightly higher than CO<sub>2</sub> 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<sub>2</sub>.<sup>20-22</sup> After O<sub>2</sub> 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<sub>4</sub> pulses. The oxygen with strong bond can oxidize carbon species easily to CO<sub>2</sub> due to

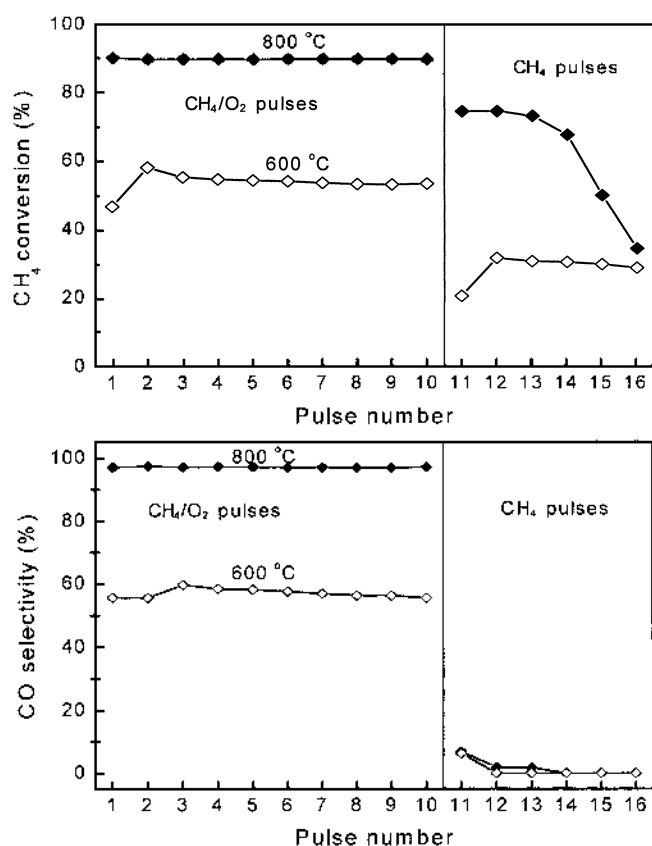


Figure 4. Pulse reaction of CH<sub>4</sub>/O<sub>2</sub> (2/1) and CH<sub>4</sub> over Ni/SiO<sub>2</sub>.

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 SiO<sub>2</sub> support is so weak that a large amount of oxygen species having the strong bond strength is formed during O<sub>2</sub> pulses. Consequently, it results in better selectivity to CO<sub>2</sub> over Ni/SiO<sub>2</sub>.

The CH<sub>4</sub>/O<sub>2</sub> (2/1) pulse reactions were performed over Ni/SiO<sub>2</sub> catalysts at 600 °C and 800 °C, respectively. The results are shown in Figure 4. During CH<sub>4</sub>/O<sub>2</sub> pulses, O<sub>2</sub> was completely consumed. Ni/SiO<sub>2</sub> showed about 90% CH<sub>4</sub> conversions and 97% CO selectivity at 800 °C, which is almost similar to those of Ni/MgO.<sup>12</sup> Comparing with the results in the second set of sequential pulse reaction (O<sub>2</sub> pulse after CH<sub>4</sub> pulses), it is clear that Ni/SiO<sub>2</sub> showed much higher CO selectivity (97%) in pulse reaction of CH<sub>4</sub>/O<sub>2</sub> at 800 °C. This suggests that only highly reactive carbon species are formed on the catalyst surface by CH<sub>4</sub> dissociation to produce CO during the partial oxidation of mixed CH<sub>4</sub>/O<sub>2</sub>. Comparing the pulse results at 800 °C with those at 600 °C, CO<sub>2</sub> 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.<sup>19</sup>

After 10 pulses of CH<sub>4</sub>/O<sub>2</sub>, pure CH<sub>4</sub> was injected. In the first CH<sub>4</sub> pulse, a considerable amount of CO was produced without CO<sub>2</sub> formation. This indicates that some oxygen

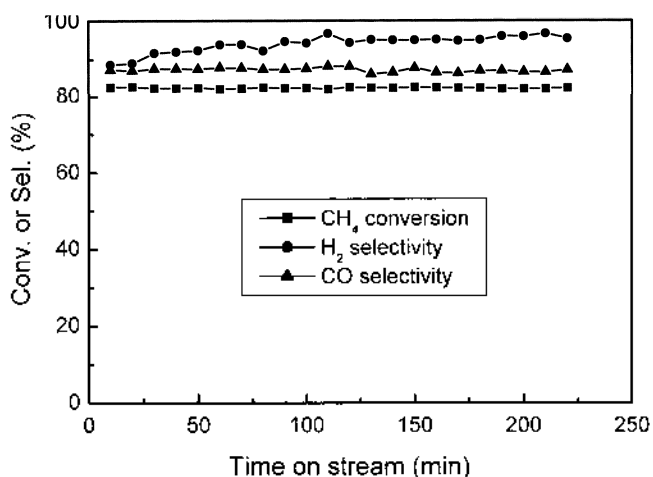
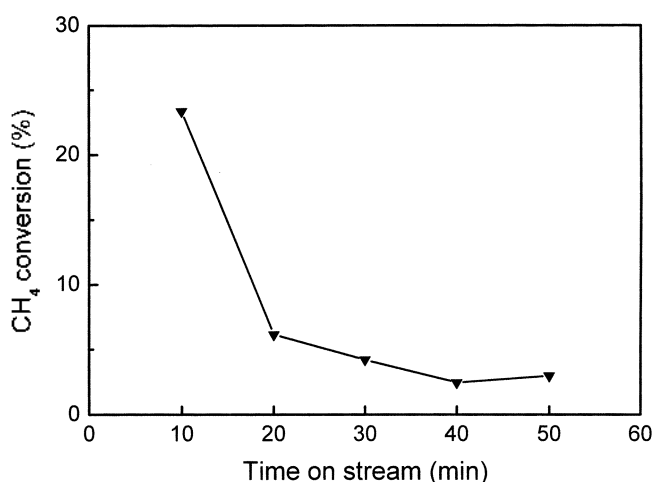


Figure 5. Steady state activities in POM over Ni/SiO<sub>2</sub>. (Reaction conditions: T = 750 °C, CH<sub>4</sub>/O<sub>2</sub> = 1.875, GHSV = 55,200 ml./gh).

species were still present on the catalysts after CH<sub>4</sub>/O<sub>2</sub> 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, CH<sub>4</sub> conversion increased from 21% in the first CH<sub>4</sub> pulse to 32% in the second pulse. The results suggest that Ni/SiO<sub>2</sub> is slightly oxidized at 600 °C. In the first CH<sub>4</sub> pulse, H<sub>2</sub> produced from CH<sub>4</sub> dissociation could reduce the Ni/SiO<sub>2</sub> catalyst, resulting in the increase of CH<sub>4</sub> dissociation in the second CH<sub>4</sub> pulse.

**Steady State Activity in POM.** Continuous POM reaction was tested at 750 °C and space velocity of 55,200 ml./h<sub>cat</sub>, and the change in CH<sub>4</sub> conversion with time on stream is presented in Figure 5. Ni/SiO<sub>2</sub> exhibited high activity as well as stability during the reaction. It exhibited 83% CH<sub>4</sub> conversion, 95% H<sub>2</sub> selectivity, 88% CO selectivity, and a H<sub>2</sub>/CO ratio of 2.1, suggesting that Ni/SiO<sub>2</sub> is a fairly good POM catalyst compared with the references.<sup>8,12</sup> According to our previous results,<sup>8,12</sup> Ni/Ce-ZrO<sub>2</sub> and Ni/MgO showed 85% and 78% CH<sub>4</sub> conversion, respectively. Therefore, it can be suggested that Ni/SiO<sub>2</sub> can be a good candidate in POM. This result is different from Choudhary and co-workers' results.<sup>13</sup> They reported that Ni/SiO<sub>2</sub> rapidly deactivated with time on stream. They explained that the deactivation of Ni/SiO<sub>2</sub> was not due to the carbon deposition but due to a strong chemical interaction between Ni and SiO<sub>2</sub>. However, in our case, the TPR pattern of Ni/SiO<sub>2</sub> showed no SMSI. This is mainly due to the de-hydroxylation of SiO<sub>2</sub> at 800 °C for 6 h. As a consequence, the defect sites of SiO<sub>2</sub> could be eliminated. Hadjiivanov *et al.*<sup>8</sup> characterized Ni/SiO<sub>2</sub> and claimed that no SMSI is typical with Ni/SiO<sub>2</sub> prepared by the impregnation method.

The fact that Ni/SiO<sub>2</sub> shows good activity is in good agreement with the pulse results of methane revealing the high capability of Ni/SiO<sub>2</sub> to dissociate methane. Ni/SiO<sub>2</sub> maintained stability for several hours without catalyst deactivation. This is ascribed to the high ability to remove the carbon species deposited from CH<sub>4</sub> dissociation by adsorbed oxygen species. It is known that the active sites for POM are free NiO having the weak interaction with the



**Figure 6.** CH<sub>4</sub> conversion with time on stream in SRM over Ni/SiO<sub>2</sub>. (Reaction conditions: T = 750 °C, H<sub>2</sub>O/CH<sub>4</sub> = 3.0, GHSV = 144,000 ml/gh).

support and complex NiO<sub>x</sub> having the strong interaction with the support.<sup>8,10,12,23</sup> Usually, the catalysts having only NiO are suspected to be sensitive to carbon formation in reforming reactions. Actually, Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> deactivated with time on stream.<sup>8</sup> However, Ni/SiO<sub>2</sub> having no SMSI showed stable activity, resulting from the high capability of Ni/SiO<sub>2</sub> to eliminate the carbon deposited from CH<sub>4</sub> decomposition by adsorbed oxygen species. Whereas, Ni/SiO<sub>2</sub> having a chemical interaction did not show stability.<sup>13</sup> It may be due to the deactivation of Ni resulting from the change of physical properties. Likewise, Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> would deactivate in POM as it changes into NiAl<sub>2</sub>O<sub>4</sub>.<sup>23</sup> Thus, in the case of Ni/SiO<sub>2</sub>, 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/SiO<sub>2</sub> was conducted with a H<sub>2</sub>O/CH<sub>4</sub> ratio of 3 at 750 °C. As shown in Figure 6, Ni/SiO<sub>2</sub> showed very low initial activity (23% CH<sub>4</sub> conversion) and it dramatically deactivated with time on stream. The main reason is that SiO<sub>2</sub> is volatile at high steam partial pressure and temperature above 700 °C.<sup>24</sup> So, the structure of Ni/SiO<sub>2</sub> was collapsed by the evaporation of the hydrated silica (Si(OH)<sub>4</sub>). Therefore, it was confirmed that Ni/SiO<sub>2</sub> is not suitable in SRM.

### Conclusions

Ni supported on de-hydroxylated SiO<sub>2</sub> 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 SiO<sub>2</sub> support and the high capability to dissociate CH<sub>4</sub> and the ability to eliminate the carbon species by adsorbed O species.

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