

Articles

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/Ce-ZrO₂ exhibited high activity and stability in POM,⁸ SRM,⁹ 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_s = 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

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Table 1. Textural properties of SiO₂ and Ni/SiO₂

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

Table 2. H₂ pulse chemisorption results of Ni/SiO₂

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

elsewhere.¹² The conversion and selectivity were calculated on the basis of 100% carbon and oxygen balances. In the pulse study, CO, CO₂, CO*, and CO₂* selectivities were defined as follows.

$$\text{CO selectivity (\%)} = (\text{moles of CO formed} / \text{moles of CH}_4 \text{ converted}) \times 100\%$$

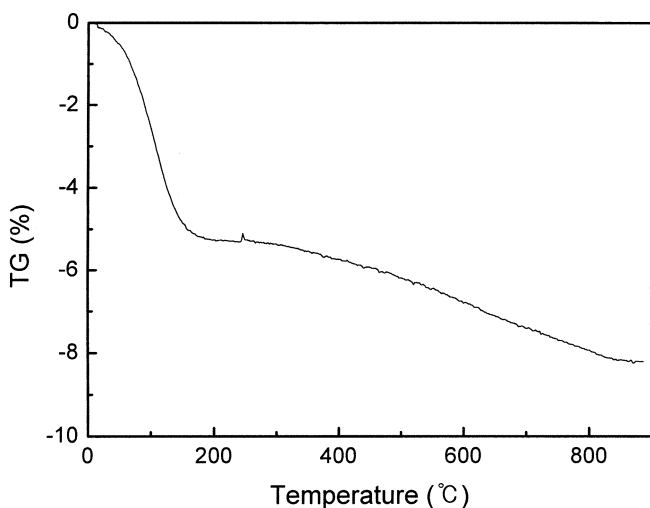
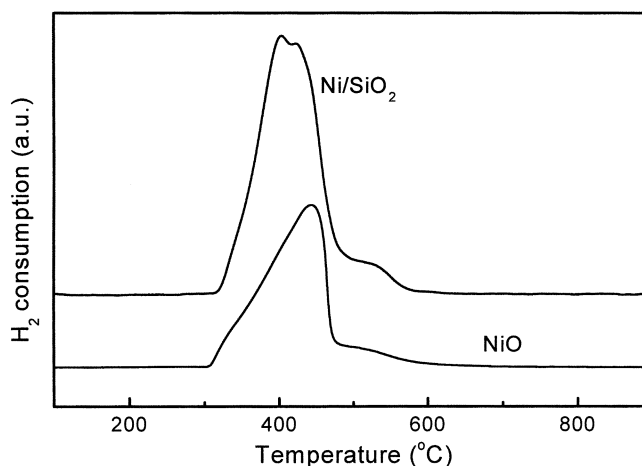
$$\text{CO}_2 \text{ selectivity (\%)} = (\text{moles of CO}_2 \text{ formed} / \text{moles of CH}_4 \text{ converted}) \times 100\%$$

$$\text{CO}^* \text{ selectivity (\%)} = (0.5 \times \text{moles of CO formed} / \text{moles of O}_2 \text{ converted}) \times 100\%$$

$$\text{CO}_2^* \text{ selectivity (\%)} = (\text{moles of CO}_2 \text{ formed} / \text{moles of O}_2 \text{ converted}) \times 100\%$$

Results and Discussion

Characterization. Table 1 summarizes the typical textural properties of SiO₂ and Ni/SiO₂. After SiO₂ was precalcined at 900 °C for 6 h, BET surface area decreased from 453 to 400 m²/g. This is the evidence of the dehydroxylation of SiO₂ during heat treatment. The BET surface area of Ni/SiO₂ is 262 m²/g. Table 2 presents H₂ pulse chemisorption results.

**Figure 1.** TGA curve of SiO₂.**Figure 2.** TPR patterns of NiO and Ni/SiO₂.

Ni surface area is 0.29 m²/g and the average particle diameter of nickel is 303 nm.

The TGA curve of SiO₂ is presented in Figure 1. SiO₂ 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 SiO₂ during precalcination process.

The TPR patterns of pure NiO and Ni/SiO₂ are illustrated in Figure 2. Bulk NiO shows a sharp reduction peak at about 450 °C followed by a small hump. Ni/SiO₂ 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,¹⁶ the TPR peaks are due to the reduction of NiO. No strong metal to support interaction (SMSI) is typical with silica.¹⁶

Pulse Reactions. Sequential pulse experiments (CH₄ → O₂ → CH₄) were performed over Ni/SiO₂ at 800 °C to investigate the CH₄ dehydrogenation activity and carbon elimination by O₂. In these experiments, five pulses of each gas were injected. The blank run in an empty tube and CH₄ pulses over only SiO₂ supports did not show detectable CH₄ conversion.

Figure 3 shows CH₄ (O₂) conversion, CO (CO*) and CO₂ (CO₂*) selectivities over Ni/SiO₂ catalyst during three sets of pulses. In the first CH₄ pulse, a large amount of H₂ and a very small amount of CO were detected, implying that CH₄ 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, CH₄ conversion rapidly decreased with increasing CH₄ pulse resulting from coke formation. There was no CO₂ detected during methane pulses. At the same time, the CO selectivity for the first pulse of methane was only 4.5%. Ni/SiO₂ exhibited 77% CH₄ conversion. According to our previous result,¹² Ni/MgO showed 39% CH₄ conversion. This is probably due to a

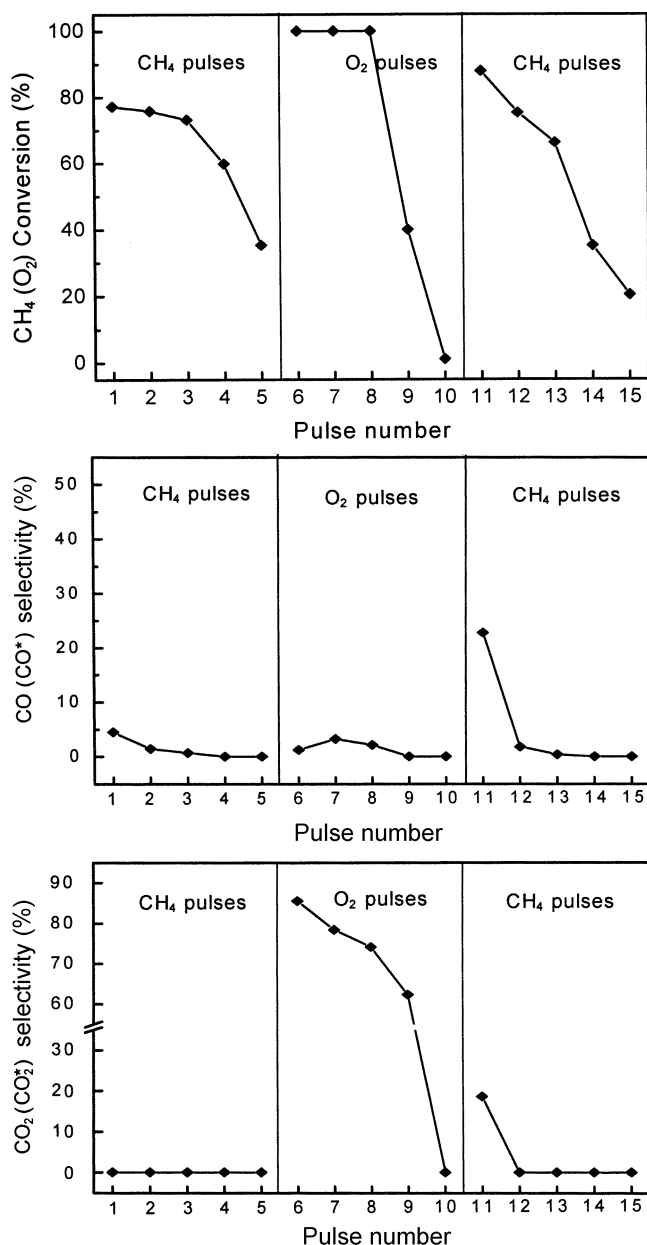


Figure 3. Sequential pulse reaction (CH₄ → O₂ → CH₄) over Ni/SiO₂ at 800 °C.

structural sensitive reaction, which is in agreement with the literature.¹⁷ Namely, Ni/SiO₂ has no SMSI, whereas Ni/MgO has the SMSI. With increasing CH₄ pulse, CH₄ conversion slowly decreased from 77.5% in the first pulse to 73.2% in the third CH₄ 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,¹² CH₄ conversion rapidly decreased with increasing CH₄ pulse. Compared with Ni/MgO, Ni/SiO₂ seems to be less sensitive to carbon accumulation. After five CH₄ pulses, the amount of carbon deposited on Ni/SiO₂ was 0.141 mmol (Table 3), which is 3 times higher than that on Ni/MgO, revealing that Ni/SiO₂ has higher capability to dissociate CH₄ than Ni/MgO. This is due to the fact that Ni/SiO₂ has no SMSI, whereas Ni/MgO has

Table 3. Pulse reaction results of Ni/SiO₂

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

(Condition: 5 CH₄ pulses followed by 5 O₂ 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_α). If there is an excess of C_α, then polymerization to C_β is possible. C_β is much less reactive than C_α. As a result, C_β may accumulate on the surface.¹⁸ During CH₄ pulses, because there is no gas phase oxygen species, the polymerization of C_α to C_β is favored especially on Ni/SiO₂ due to much larger Ni ensemble size than Ni/MgO.

To investigate the reaction between surface carbides and O₂, a step switch from CH₄ to O₂ flow was carried out after 5 CH₄ pulses. A large amount of CO or CO₂ was produced in the first O₂ pulse, indicating the carbon species could quickly react with surface O species to form CO or CO₂. Ni/SiO₂ generated a considerable amount of CO₂ until the fourth O₂ pulse. These results reveal that the carbon species on Ni/SiO₂ favors CO₂ formation. This is probably due to the fact that the bond strength between carbon species and the active metallic Ni surface on Ni/SiO₂ is very strong. The strong bond mode favors CO₂ formation, because carbon species can be easily oxidized further to CO₂ 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 CO₂ 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.¹⁹ Therefore, Ni/SiO₂ having the stronger bond strength between carbon species and the Ni surface favors CO₂ formation rather than CO. After five O₂ pulses, the amount of carbon residue was 0.013 mmol.

After O₂ pulses, some activated oxygen species still remained on the catalysts. In order to investigate the oxygen species involved in POM, CH₄ pulse was re-introduced after O₂ pulses. It was found that a considerable amount of CO and CO₂ was generated over Ni/SiO₂ in the first CH₄ pulse. CH₄ 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 CH₄ pulses. This indicates that the oxygen species adsorbed on the catalyst may enhance the conversion of CH₄. CO selectivity (23%) was slightly higher than CO₂ 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 CO₂.²⁰⁻²² After O₂ 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 CH₄ pulses. The oxygen with strong bond can oxidize carbon species easily to CO₂ due to

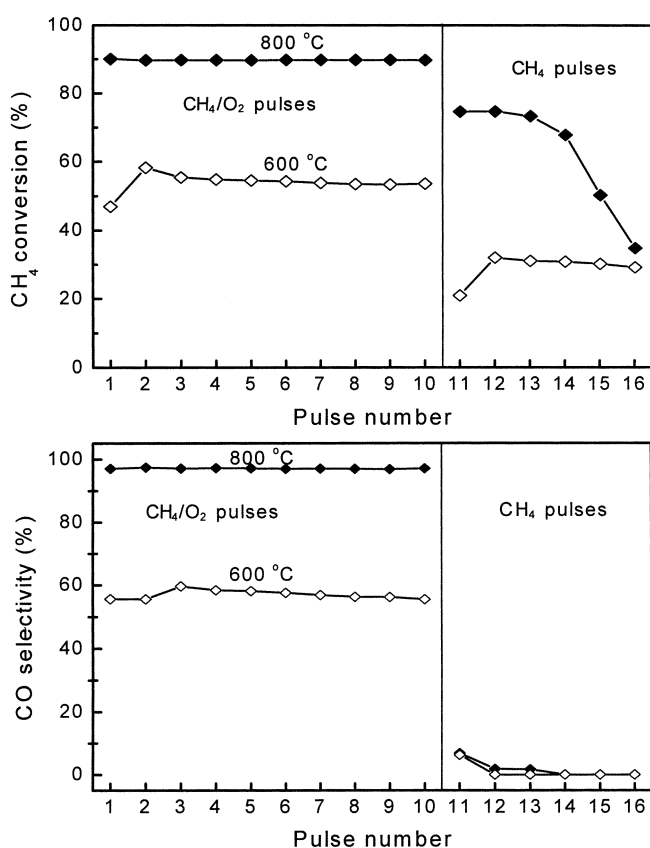


Figure 4. Pulse reaction of CH_4/O_2 (2/1) and CH_4 over Ni/SiO_2 .

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 SiO_2 support is so weak that a large amount of oxygen species having the strong bond strength is formed during O_2 pulses. Consequently, it results in better selectivity to CO_2 over Ni/SiO_2 .

The CH_4/O_2 (2/1) pulse reactions were performed over Ni/SiO_2 catalysts at 600 °C and 800 °C, respectively. The results are shown in Figure 4. During CH_4/O_2 pulses, O_2 was completely consumed. Ni/SiO_2 showed about 90% CH_4 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 (O_2 pulse after CH_4 pulses), it is clear that Ni/SiO_2 showed much higher CO selectivity (97%) in pulse reaction of CH_4/O_2 at 800 °C. This suggests that only highly reactive carbon species are formed on the catalyst surface by CH_4 dissociation to produce CO during the partial oxidation of mixed CH_4/O_2 . Comparing the pulse results at 800 °C with those at 600 °C, CO_2 selectivity decreased with increasing reaction temperature. This is probably due to the following reasons. Since the activation energy of $\text{CO}(\text{s})$ desorption is nearly double that of $\text{CO}(\text{s})$ oxidation over Ni surface, the increase of reaction temperature would favor $\text{CO}(\text{s})$ desorption, leading to the increase of CO selectivity.¹⁹

After 10 pulses of CH_4/O_2 , pure CH_4 was injected. In the first CH_4 pulse, a considerable amount of CO was produced without CO_2 formation. This indicates that some oxygen

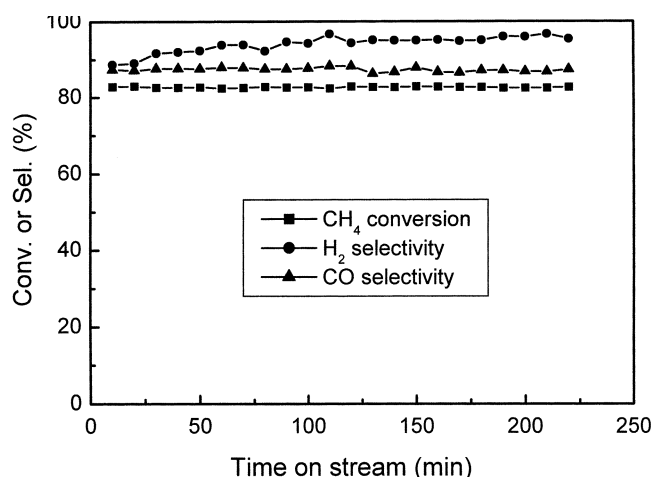


Figure 5. Steady state activities in POM over Ni/SiO_2 . (Reaction conditions: $T = 750$ °C, $\text{CH}_4/\text{O}_2 = 1.875$, $\text{GHSV} = 55,200$ mL/gh).

species were still present on the catalysts after CH_4/O_2 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_4 conversion increased from 21% in the first CH_4 pulse to 32% in the second pulse. The results suggest that Ni/SiO_2 is slightly oxidized at 600 °C. In the first CH_4 pulse, H_2 produced from CH_4 dissociation could reduce the Ni/SiO_2 catalyst, resulting in the increase of CH_4 dissociation in the second CH_4 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 CH_4 conversion with time on stream is presented in Figure 5. Ni/SiO_2 exhibited high activity as well as stability during the reaction. It exhibited 83% CH_4 conversion, 95% H_2 selectivity, 88% CO selectivity, and a H_2/CO ratio of 2.1, suggesting that Ni/SiO_2 is a fairly good POM catalyst compared with the references.^{8,12} According to our previous results,^{8,12} $\text{Ni}/\text{Ce-ZrO}_2$ and Ni/MgO showed 85% and 78% CH_4 conversion, respectively. Therefore, it can be suggested that Ni/SiO_2 can be a good candidate in POM. This result is different from Choudhary and co-workers' results.¹³ They reported that Ni/SiO_2 rapidly deactivated with time on stream. They explained that the deactivation of Ni/SiO_2 was not due to the carbon deposition but due to a strong chemical interaction between Ni and SiO_2 . However, in our case, the TPR pattern of Ni/SiO_2 showed no SMSI. This is mainly due to the de-hydroxylation of SiO_2 at 800 °C for 6 h. As a consequence, the defect sites of SiO_2 could be eliminated. Hadjiivanov *et al.*⁸ characterized Ni/SiO_2 and claimed that no SMSI is typical with Ni/SiO_2 prepared by the impregnation method.

The fact that Ni/SiO_2 shows good activity is in good agreement with the pulse results of methane revealing the high capability of Ni/SiO_2 to dissociate methane. Ni/SiO_2 maintained stability for several hours without catalyst deactivation. This is ascribed to the high ability to remove the carbon species deposited from CH_4 dissociation by adsorbed oxygen species. It is known that the active sites for POM are free NiO having the weak interaction with the

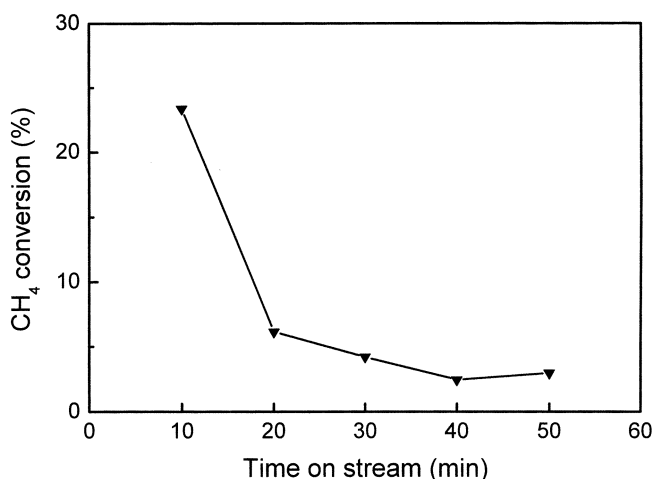


Figure 6. CH₄ conversion with time on stream in SRM over Ni/SiO₂. (Reaction conditions: T = 750 °C, H₂O/CH₄ = 3.0, GHSV = 144,000 mL/gh).

support and complex NiO_x having the strong interaction with the support.^{8,10,12,23} 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.⁸ 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.¹³ 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 NiAl₂O₄.²³ 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.²⁴ 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

- Peña, M. A.; Gómez, J. P.; Fierro, J. L. G. *Appl. Catal. A* **1996**, *144*, 7.
- Tsang, S. C.; Claridge, J. B.; Green, M. L. H. *Catal. Today* **1995**, *23*, 3.
- Armor, J. N. *Appl. Catal. A* **1999**, *176*, 159.
- Rostrup-Nielsen, J. R. In *Catalytic Steam Reforming Catalysis, Science & Technology*; Anderson, J. R.; Boudart, M., Eds.; Springer: Berlin, 1984; vol. 5.
- Padovani, C.; Franchetti, P. *Giron. Chem. Ind. Applicata* **1933**, *15*, 429.
- Prettre, M.; Eichner, C. H.; Perrin, M. *Trans. Faraday Soc.* **1946**, *43*, 335.
- Ashcroft, A. T.; Cheetham, A. K.; Foord, J. S.; Green, M. L. H.; Grey, C. P.; Murrell, A. J.; Vernon, P. D. F. *Nature* **1990**, *344*, 319.
- Roh, H.-S.; Dong, W.-S.; Jun, K.-W.; Park, S.-E. *Chem. Lett.* **2001**, 88.
- Roh, H.-S.; Jun, K.-W.; Dong, W.-S.; Park, S.-E.; Joe, Y.-I. *J. Mol. Catal. A* **2002**, *181*, 137.
- Roh, H.-S.; Jun, K.-W.; Dong, W.-S.; Park, S.-E.; Baek, Y.-S. *Catal. Lett.* **2001**, *74*, 31.
- Choudhary, V. R.; Mamman, A. S.; Sansare, D. *Angew. Chem. Int. Ed.* **1992**, *31*, 1189.
- Dong, W.-S.; Roh, H.-S.; Liu, Z.-W.; Jun, K.-W.; Park, S.-E. *Bull. Korean Chem. Soc.* **2001**, *22*, 1323.
- Choudhary, V. R.; Rajput, A. M.; Prabhakar, B.; Mamman, A. S. *Fuel* **1998**, *77*, 1803.
- Chang, J.-S.; Park, S.-E.; Chon, H. *Appl. Catal. A* **1996**, *145*, 111.
- Bartholomew, C. H.; Pannell, R. B. *J. Catal.* **1980**, *65*, 390.
- Hadjiivanov, K.; Mihaylov, M.; Klissurski, D.; Stefanov, P.; Abadjieva, N.; Vassileva, E.; Mintchev, L. *J. Catal.* **1999**, *185*, 314.
- Beebe, T. P. Jr.; Goodman, D. W.; Kay, B. D.; Yates, J. T. Jr. *J. Chem. Phys.* **1987**, *87*, 2305.
- Trimm, D. L. *Catal. Today* **1999**, *49*, 3.
- Au, C. T.; Wang, H. Y.; Wan, H. L. *J. Catal.* **1996**, *158*, 343.
- Shen, S.; Li, C.; Yu, C. *Stud. Surf. Sci. Catal.* **1998**, *119*, 765.
- Jin, R.; Chen, Y.; Li, W.; Cui, W.; Ji, Y.; Yu, C.; Jiang, Y. *Appl. Catal. A* **2000**, *201*, 71.
- Hu, Y. H.; Ruckenstein, E. *J. Catal.* **1996**, *158*, 260.
- Roh, H.-S.; Jun, K.-W.; Dong, W.-S.; Park, S.-E.; Joe, Y.-I. *Chem. Lett.* **2001**, 666.
- Kochloefl, K. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; VCH: Weinheim, 1997; vol. 4, p 1820.