

Role of Support in CO₂ Reforming of CH₄ to Syngas over Ni Catalysts

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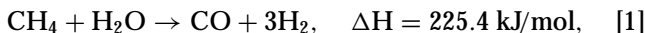
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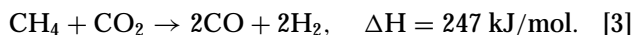
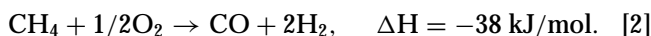
The dynamic changes in activity and selectivity for the CO₂ reforming of CH₄ over unsupported and supported Ni catalysts were investigated. The reduced NiO has low initial conversions of CH₄ and CO₂, which decrease rapidly with time. The mixture of powders of NiO and Al₂O₃ has low initial conversions of CH₄ and CO₂ and a low yield to CO, which, however, increase with reaction time, due most likely to Ni migration to Al₂O₃. In contrast, the reduced 1 wt% Ni/Al₂O₃ catalyst (reduced from NiO/Al₂O₃) has high initial conversions and CO yield, which slowly decrease with time due to carbon deposition. The reduced 13.6 wt% Ni/Al₂O₃ catalyst has high initial conversions and CO yield, but, because of carbon deposition, the reactor was completely plugged in 6 h. The reduced 1 wt% Ni/SiO₂ catalyst has moderate initial activity and CO yield, which decay fast with reaction time. The reduced 13.6 wt% Ni/SiO₂ has a high initial activity and CO yield, which decay slowly with reaction time. The reduced 13.6 wt% Ni/TiO₂ has a moderate initial activity and CO yield, which decay with reaction time. Carbon deposition was found to occur over all these catalysts, and the sequence of carbon deposition was: 13.6 wt% Ni/Al₂O₃ > 13.6 wt% Ni/SiO₂ > the reduced mixture of NiO and Al₂O₃ (13.6 wt% Ni) > 13.6 wt% Ni/TiO₂ > 1 wt% Ni/Al₂O₃ > 1 wt% Ni/SiO₂. © 1996 Academic Press, Inc.

1. INTRODUCTION

Syngas constitutes a very important feed in petrochemistry. While the dominant commercial method employed to produce synthesis gas is the steam reforming of methane,



this process has poor selectivity for CO and a too high H₂/CO product ratio, unsuitable for the methanol and the Fischer–Tropsch syntheses. Two other processes, namely, the catalytic partial oxidation of methane (1–7) and CO₂ reforming (8–14) can be employed to produce syngas from methane:



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Reaction [3] provides a high CO selectivity and a more suitable H₂/CO ratio. In the CO₂ reforming of CH₄, the carbon deposition sequence for various metals, reported by Rostrup–Nielsen (15), is: Ni ≫ Pt > Ru. Ashcroft *et al.* (8) and Rostrup–Nielsen (16) demonstrated that, over nickel-supported catalysts and for a CO₂/CH₄ molar ratio of 1 : 1, carbon deposition cannot be avoided. The effect of the support on carbon deposition was also investigated by Tang *et al.* (17). Ashcroft *et al.* (8) suppressed the carbon deposition in CO₂ reforming by replacing Ni with platinum-group catalysts; this provided a CO yield between 69% for Ru and 89% for Ir from a stoichiometric feed of CO₂ and CH₄. It is, however, worthwhile to develop improved stable and effective nickel-based catalysts because of the high cost of the noble metals. Rostrup–Nielsen (18) noted that carbon-free steam reforming of methane can be achieved using a partly sulfur-passivated nickel catalyst. However, although sulfur inhibits carbon formation, it also reduces the activity of the catalyst. Recently, we found that the reduced NiO/MgO catalysts have high activities and selectivities, as well as excellent stability (19, 20). In those cases the support (MgO), with which NiO forms a solid solution, inhibits carbon deposition.

In this article, we present a number of observations regarding the dynamic changes in activity and CO yield, during the CO₂ reforming of methane over Ni unsupported and supported catalysts with the emphasis on the effect of the nature of the support.

2. EXPERIMENT

2.1. Catalyst Preparation

NiO catalyst preparation. NiO was prepared by the decomposition of Ni nitrate in air at 800°C for 1.5 h.

NiO-supported catalyst preparation. NiO/Al₂O₃ and NiO/SiO₂ (containing after reduction 1 wt% Ni) and NiO/Al₂O₃, NiO/SiO₂, and NiO/TiO₂ (containing after reduction 13.6 wt% Ni) catalysts were prepared by impregnating the support with an aqueous solution of nickel nitrate. The obtained paste was dried at room temperature in air, then decomposed and calcined at 800°C in air for 1.5 h.

2.2. Catalytic Reaction

The catalytic reaction was carried out under atmospheric pressure, at 790°C, in a flow system, using a vertical quartz tube (2 mm inside diameter) as reactor. The catalyst powder (weight: 0.02 g) was held on quartz wool. The molar ratio of the reactant gases, with a GHSV = 60000 cm³/g/h, was CO₂/CH₄ = 1 : 1. The catalyst was reduced in H₂ (20 ml/min) at 500°C for 14 h, followed by an increase in temperature to 790°C at a rate of 20°C/min, and also in H₂ (20 ml/min). The analysis of the reactants/products mixtures was performed, with an *in situ* gas chromatograph equipped with a Porapak Q column. The yield to CO was calculated from the expression: $[\text{CO}/(\text{CO} + \text{CO}_2 + \text{CH}_4)] \times 100\%$.

2.3. CO Chemisorption and Temperature-Programmed Desorption (TPD)

The exposed Ni metal surface area and hence the dispersion of the catalyst were measured by CO pulse adsorption at room temperature, assuming a stoichiometry of 1/1. The catalyst (0.25 g), held on quartz wool in a vertical quartz tube (6 mm inside diameter), was reduced in H₂ (40 ml/min) at 500°C for 3 h, followed by an increase in temperature to 790°C at a rate of 20°C/min, also in H₂ (40 ml/min). At 790°C, the reduced catalyst was purged with He (40 ml/min) for 20 min. Then, the catalyst was allowed to cool at room temperature. The analysis of gases during the adsorption of CO at room temperature was carried out with an on-line mass spectrometer (HP Quadrupole, 5971 series mass selective detector) equipped with a fast-response inlet capillary system. For the mechanical mixture of NiO and Al₂O₃, the dispersion was measured both before and after the CO₂ reforming reaction of CH₄.

After the CO adsorption, a TPD experiment was carried out at a rate of 10°C/min. The analysis of gases during the desorption of CO was performed continuously with the on-line mass spectrometer.

2.4. BET Surface Area and Pore Size Distribution Measurements

The surface area and the pore-size distribution were determined by nitrogen adsorption, using a Micromeritics ASAP 2000 instrument. The surface area was calculated using the BET method, while the pore-size distribution curve was obtained from the adsorption branch of the N₂ isotherm by the BJH method (21). The sample was degassed at 200°C in high vacuum before measurements.

2.5. The Determination of Carbon Deposition

The deposited carbon was determined by O₂ pulse-MS. The catalyst (0.02 g) was reduced in H₂ and the reaction carried out for 6 h, both as described in Section 2.2. Then, the catalyst was purged with He at 790°C for 1 h. The analy-

sis of gases during the O₂ pulses at 790°C was carried out with an on-line mass spectrometer. The amount of carbon deposited was calculated from the amount of CO and CO₂ produced.

3. RESULTS

3.1. CO₂ Reforming Reaction of CH₄ over Unsupported NiO Catalysts

Figure 1 shows that the reduced NiO provides very low initial conversions and CO yield, which decrease rapidly with time. The unreduced NiO has high initial conversion and CO yield, which decrease catastrophically with time.

The reduced mixture of powders of NiO and γ -alumina (0.2 wt ratio NiO/Al₂O₃) has very low initial conversions of CH₄ (15%) and CO₂ (19%) and a low yield to CO (17%) (Fig. 2). As the reaction time increases, the conversions and yield increase. After 10 h, they reach maximum values (about 45, 42, and 40%), which do not change at longer times (Fig. 2).

In contrast, the unreduced NiO catalyst has higher initial conversions of CH₄ and CO₂ yield to CO, which first rapidly decrease and then increase somewhat with time (Fig. 2).

3.2. CO₂ Reforming of CH₄ over 1 wt% Ni/Al₂O₃ and 1 wt% Ni/SiO₂ Catalysts

Figure 3 shows that the reduced 1 wt% Ni/Al₂O₃ catalyst has high initial conversions of CH₄ and CO₂ (78 and 90%) and yield to CO (84%), which decrease slowly as the reaction time increases. After about 7 h, the conversions of CH₄ and CO₂ and the yield of CO become 73, 90, and 81%, respectively; after about 30 h, they decrease to 60, 75, and 70%, respectively. Compared with the 1 wt% Ni/Al₂O₃, the reduced 1 wt% Ni/SiO₂ has lower initial conversions of CH₄ and CO₂ (52 and 72%) and yield to CO (62%). The conversions and the yield to CO decrease with time. After 7 h, they become 35, 40, 37%, respectively. As shown in Fig. 3, the deactivation of the 1 wt% Ni/SiO₂ is faster than that of the 1 wt% Ni/Al₂O₃.

The unreduced 1 wt% Ni/Al₂O₃ and 1 wt% Ni/SiO₂ catalysts provide initial conversions of CH₄ and CO₂ and yield to CO of about 10%, which increase with time, the increase being faster for the 1 wt% Ni/Al₂O₃ catalyst than for the 1 wt% Ni/SiO₂ catalyst (Fig. 4).

3.3. CO₂ Reforming of CH₄ over Reduced 13.6 wt% Ni Supported Catalysts

The 13.6% Ni/Al₂O₃ reduced catalyst has very high initial conversions of CH₄ and CO₂ (91 and 98%) and yield to CO (95%) (Table 1). It was, however, impossible to obtain the relationship between the CO yield and reaction time due to the difficulty of maintaining constant feed flow. This happened because the pressure drop in reactor increased, due

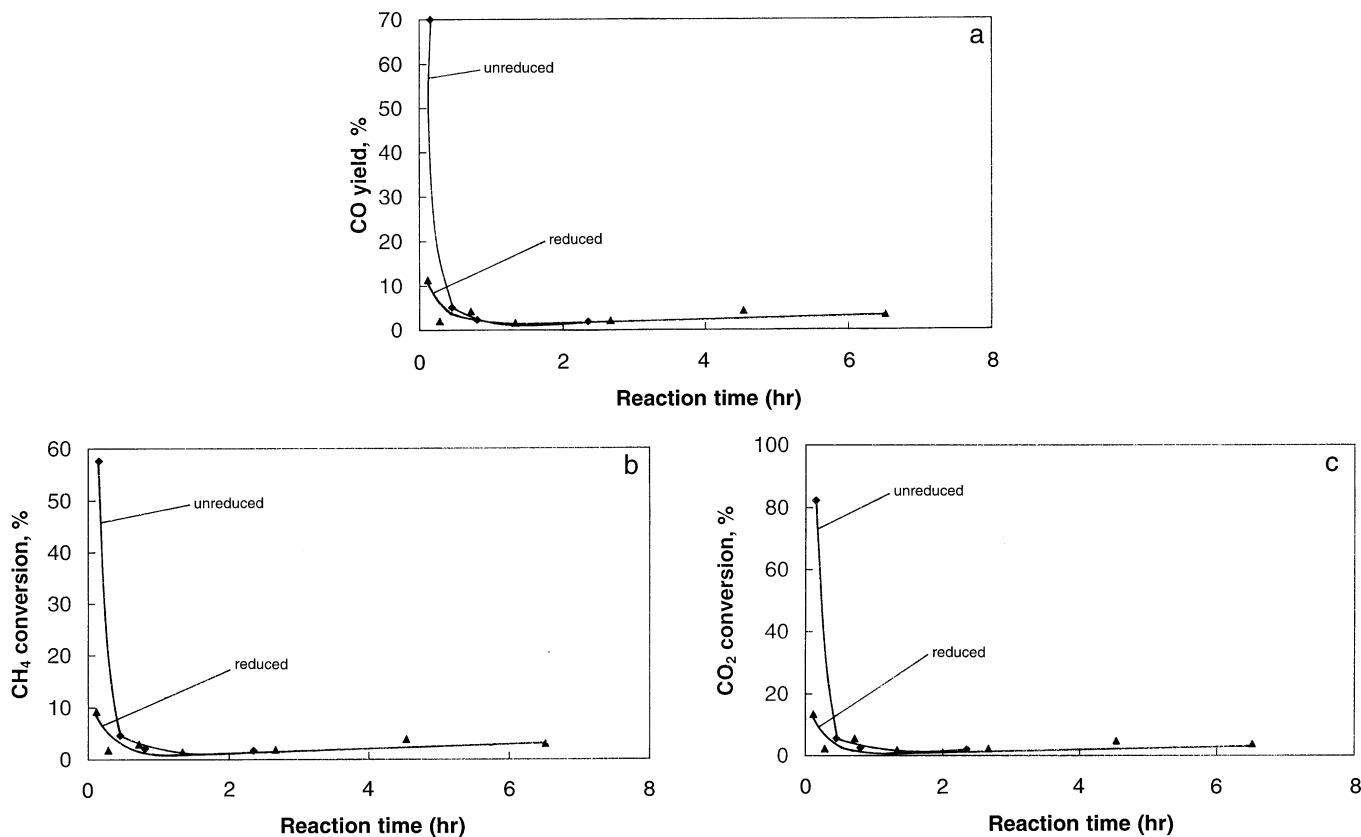


FIG. 1. The relationship between reaction time and (a) CO yield, (b) CH₄ conversion, and (c) CO₂ conversion over NiO. Reaction conditions: total pressure, 1 atm; $T = 790^{\circ}\text{C}$; CH₄/CO₂ = 1 : 1; GHSV = 60000 cm³/g/h.

to the fast carbon deposition, with reaction time. After 6 h, the reactor was completely plugged. In contrast, this did not occur over the reduced 13.6 wt% Ni/SiO₂ or Ni/TiO₂. The Ni/SiO₂ provides very high initial conversions of CH₄ and CO₂ (89 and 97%) and yield to CO (93%) (Table 1), which decrease slowly with reaction time (Fig. 5). The Ni/TiO₂ catalyst has relatively low initial conversions of CH₄ and CO₂ (41 and 67%) and yield to CO (53%) (Table 1), which decrease with reaction time faster than for the Ni/SiO₂ catalyst (Fig. 5).

3.4. BET Surface Area and Pore Size Distribution

The surface areas of the unreduced catalysts are listed in Table 1. The 1 wt% and 13.6 wt% Ni/SiO₂ have the high surface areas of 447 and 362 m²/g, respectively, the 1 and 13.6 wt% Ni/Al₂O₃ catalysts have the intermediate surface areas of 75 and 63 m²/g, respectively, and the 13.6 wt% NiO/TiO₂ and pure NiO catalysts have the very low surface areas of 6 and 3 m²/g, respectively. The pore size varied for 13.6 wt% Ni/SiO₂ between 20 and 150 Å with an average of 52 Å and for 13.6 wt% Ni/Al₂O₃ between 20 and 1000 Å with an average of 130 Å. NiO and 13.6 wt% Ni/TiO₂ have very few pores (Fig. 6).

3.5. CO Turnover Number and Amount of Carbon Deposited

The initial CO turnover numbers (TON) are listed in Table 1. The 1 wt% Ni/SiO₂ has the very high initial turnover number of 1721 s⁻¹. (Because the amount of CO chemisorbed is very small, there is, however, a large error in the determination of the number of active sites.) The sequence of TON is: 1 wt% Ni/SiO₂ > 1 wt% Ni/Al₂O₃ > 13.6 wt% Ni/TiO₂ > 13.6 wt% Ni/SiO₂ > 13.6 wt% Ni/Al₂O₃.

Both the 1 wt% Ni/Al₂O₃ and Ni/SiO₂ catalysts exhibit low carbon depositions (Table 1). For 13.6 wt% Ni-based catalysts, the sequence of carbon deposition is: Ni/Al₂O₃ > Ni/SiO₂ > Ni/TiO₂ (Table 1).

3.6. CO TPD on Reduced Ni Unsupported and Supported Catalysts

Figure 7 shows that the reduced mixture of NiO and Al₂O₃ (0.2 wt ratio NiO/Al₂O₃) has a sharp CO peak at 80°C and two wide CO overlapped peaks around 300°C. At about 420°C, a CO₂ peak appears. The reduced 1 wt% Ni/Al₂O₃ catalyst has a similar TPD curve: one sharp CO peak at 80°C and two wide CO overlapped peaks at a temperature over 150°C; no CO₂ peak was, however, detected

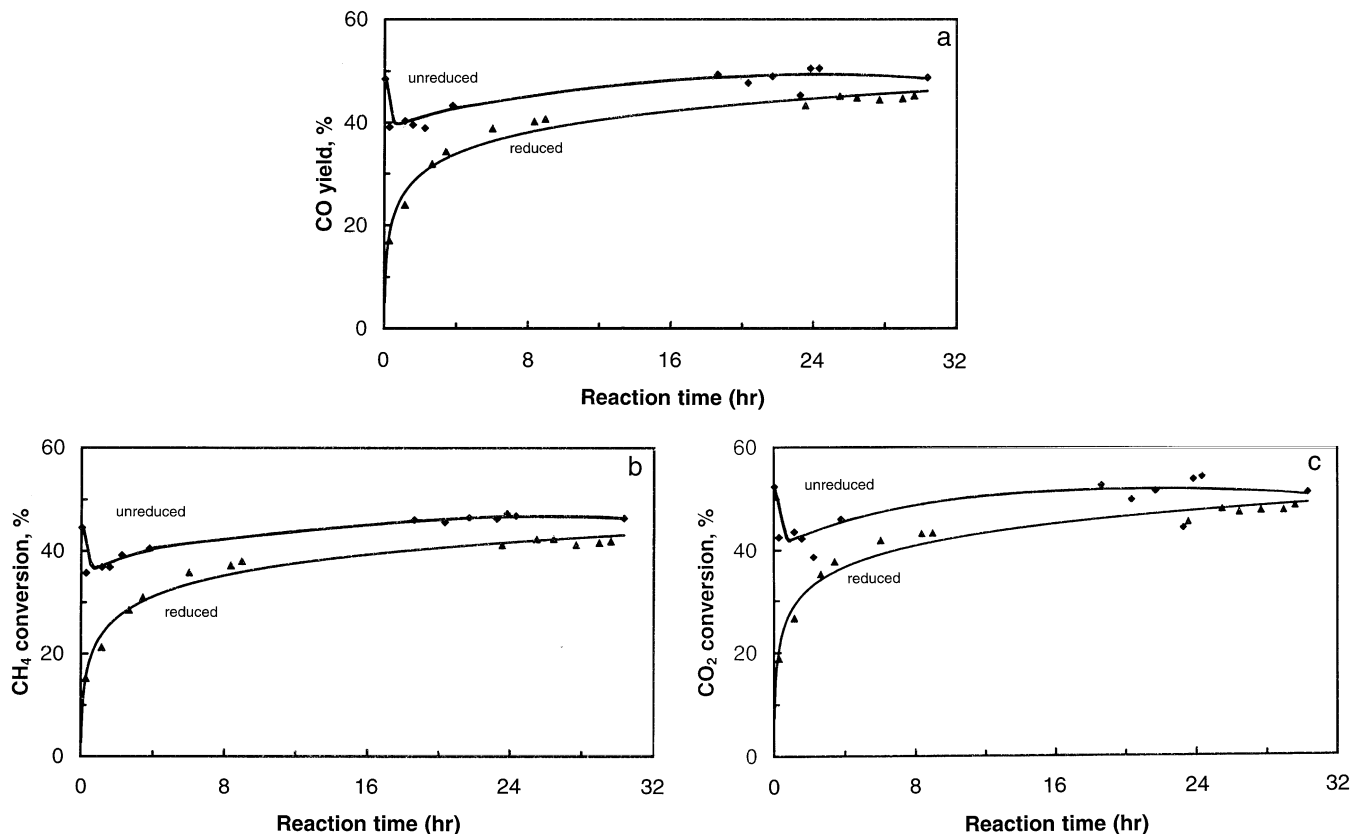


FIG. 2. The relationship between reaction time and (a) CO yield, (b) CH₄ conversion, and (c) CO₂ conversion over NiO catalyst diluted with Al₂O₃ via mechanical mixing (0.2 wt ratio NiO/Al₂O₃). Reaction conditions: total pressure, 1 atm; $T = 790^{\circ}\text{C}$; CH₄/CO₂ = 1 : 1; GHSV = 60000 cm³/g/h.

(Fig. 7). In contrast, very small amounts of CO and CO₂ were detected for the 1 wt% Ni/SiO₂ catalyst (Fig. 7). The TPD results also show that the curves for CO desorption from 13.6 wt% Ni/Al₂O₃ and 13.6 wt% Ni/SiO₂ (Figs. 8 and 9) are very different from those for 1 wt% Ni/Al₂O₃ and 1 wt% Ni/SiO₂. There are five overlapping CO peaks and four overlapping CO₂ peaks in the TPD curves for the 13.6 wt% Ni/Al₂O₃. This indicates that the increase in Ni content results in the increase of the CO disproportionation. The 13.6 wt% Ni/SiO₂ catalyst has a TPD curve similar to that of Ni/Al₂O₃. The TPD curve of the 13.6 wt% Ni/TiO₂ catalyst has two CO peaks at 98 and 200°C, respectively, and one CO₂ peak at 240°C (Fig. 10).

4. DISCUSSION

4.1. Effect of Al₂O₃ in Mechanical Mixture with NiO on CO₂ Reforming of CH₄

For the reduced mixture of NiO and Al₂O₃, the initial conversions of CH₄ and CO₂ and yield to CO are very low; however, they increase fast with reaction time, attain maximum values, and then remain constant (Fig. 1). The number of Ni sites increased after the reforming reaction. Before

reaction, but after reduction, the dispersion was 0.065%, while after reaction it was 0.18%. The increase in activity with reaction time is obviously due to the increase in the number of active sites. Two explanations are possible: either new sites, which consist of Ni and C, are generated during reaction (22), or Ni atoms are migrating to the surface of Al₂O₃ particles. Because the experiments carried out with reduced NiO particles alone (Fig. 1) show that the activity decreases with time, the second explanation is the more likely one. It is possible that the carbon deposited on Ni during reaction stimulates the migration of Ni atoms to the Al₂O₃ surface. Indeed, the deposited carbon has the tendency to diffuse into the bulk of NiO (23), thus weakening the bonds among the Ni atoms and making the latter more mobile.

For both the unreduced pure NiO and the unreduced mixture of NiO and Al₂O₃, the initial conversions of CH₄ and CO₂ and yield to CO are high; they first decrease fast and then slowly with time (Figs. 1 and 2). This can be explained as follows: The reduction of NiO by CH₄ provides Ni⁰ active sites for the reforming process. For this reason, the initial activity is high. The rapid sintering decreases, however, the number of active sites, and hence the activity decreases with time. A more rapid sintering occurs at

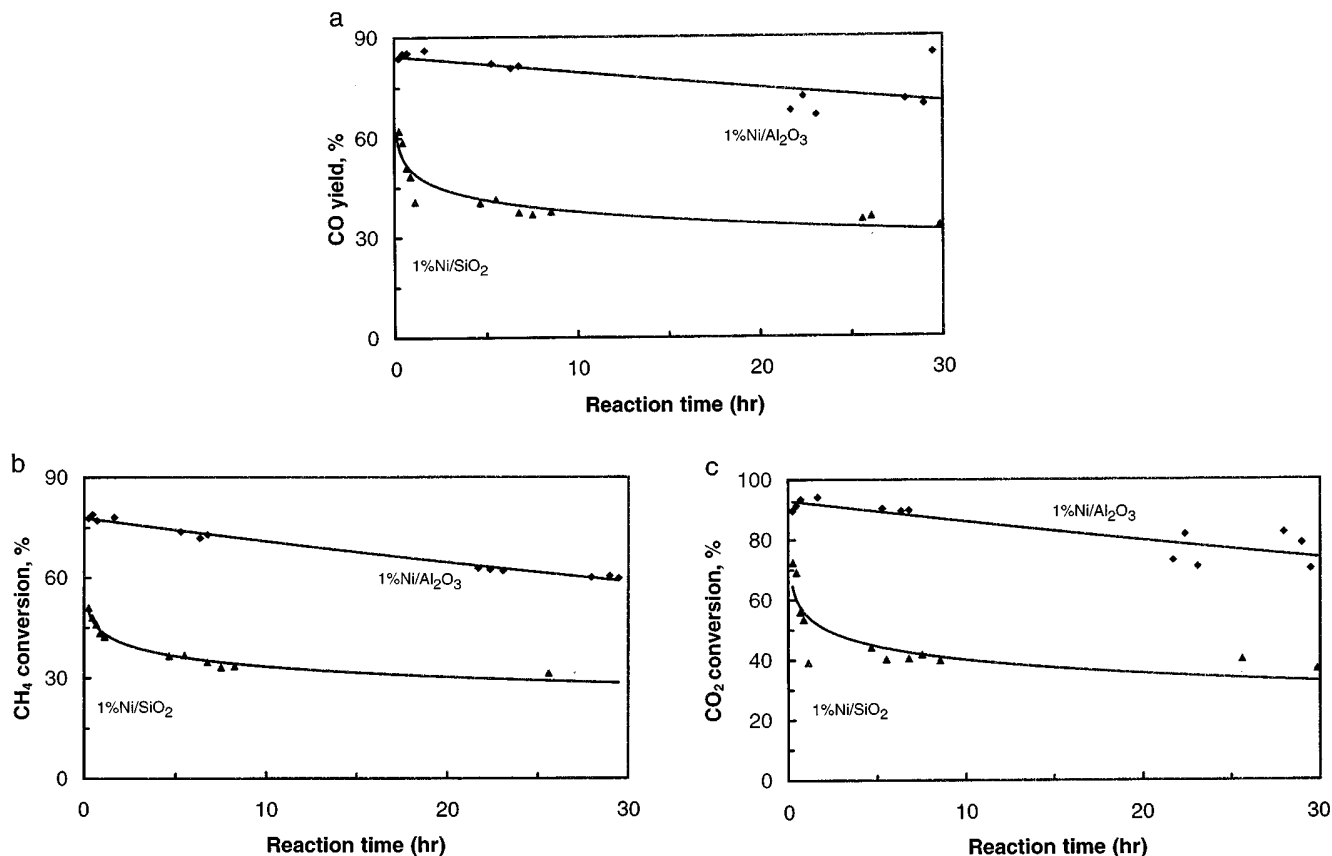


FIG. 3. The relationship between reaction time and (a) CO yields, (b) CH₄ conversion, and (c) CO₂ conversion over reduced 1% Ni/Al₂O₃ and 1% Ni/SiO₂ catalysts. Reaction conditions: total pressure, 1 atm; $T = 790^\circ\text{C}$; CH₄/CO₂ = 1 : 1; GHSV = 60000 cm³/g/h.

shorter times because then the Ni particles are smaller; this explains the rapid decay of activity at shorter times.

4.2. The Interactions between NiO and Al₂O₃ or SiO₂ Support

In contrast to the mechanical mixture of NiO and Al₂O₃, the unreduced 1 wt% Ni/Al₂O₃ catalyst has low initial activity, which increases slowly with reaction time (Fig. 4). This occurs because, during reaction, the unreduced 1 wt% Ni/Al₂O₃ is reduced by CH₄, and the number of Ni⁰ active sites increases. Comparing Figs. 1, 2, and 4, one can conclude that the alumina-supported NiO catalyst is reduced during reaction with greater difficulty than the unsupported one. This can be attributed to the formation of a nickel aluminate (24).

While the initial activities are comparable, the increase of activity is much slower over the unreduced 1 wt% Ni/SiO₂ catalyst than over the unreduced 1 wt% Ni/Al₂O₃ (Fig. 4). This indicates that the reduction of NiO is more difficult over 1 wt% Ni/SiO₂ than over 1 wt% Ni/Al₂O₃. Although the BET measurements show that the unreduced 1 wt% Ni/SiO₂ has a surface area (447 m²/g) much larger than the unreduced 1 wt% Ni/Al₂O₃ (71 m²/g), the CO chemisorp-

tion indicates that the reduced 1 wt% Ni/SiO₂ has a much smaller Ni metal surface area (0.01 m²/g) than the reduced 1 wt% Ni/Al₂O₃ (0.11 m²/g) (Table 1). This suggests that chemical interactions occur between NiO and SiO₂ in the NiO/SiO₂ (containing 1 wt% Ni) calcined at high temperatures. de Lange and Vissar (25) suggested as early as 1946 that chemical interactions between silica support and NiO, with the formation of silicate, is the reason for the difficult reducibility of silica-supported NiO catalysts. This was later supported by several investigations (26–28). The small number of active sites in 1 wt% Ni/SiO₂ catalyst can be explained as follows: SiO₂ has a very high surface area over which a small amount of NiO is dispersed. As a result, many of the NiO molecules are in direct contact with SiO₂. The high temperature (800°C) employed during the catalyst preparation leads to the reaction between the two, with the generation of a nickel silicate, which is difficult to reduce. This hinders the reduction of Ni²⁺ to Ni⁰. When the NiO content increases, large NiO particles are formed, and the fraction of NiO that does not contact SiO₂ can be reduced easily to Ni. Indeed, the Ni metal surface area of the 13.6 wt% Ni/SiO₂ is much greater than that of 1 wt% Ni/SiO₂ (Table 1).

Table 1 shows that the reduced 1 wt% Ni/SiO₂ has a very high turnover number (1721 s⁻¹), much larger than that

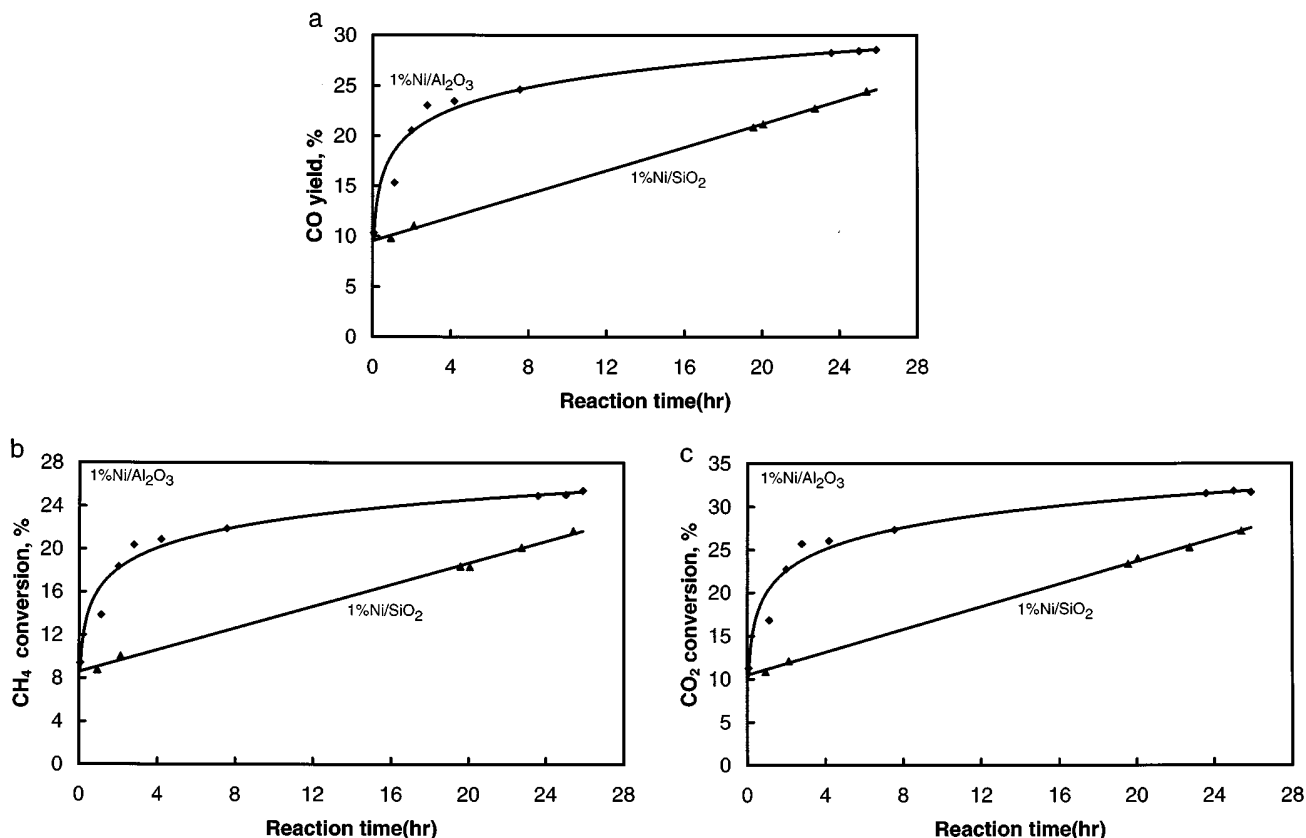


FIG. 4. The relationship between reaction time and (a) CO yield, (b) CH₄ conversion, and (c) CO₂ conversion over unreduced 1% Ni/Al₂O₃ and 1% Ni/SiO₂ catalysts. Reaction conditions: total pressure, 1 atm; $T = 790^{\circ}\text{C}$; CH₄/CO₂ = 1 : 1; GHSV = 60000 cm³/g/h.

of 1 wt% Ni/Al₂O₃ (230 s⁻¹). Because the reduced 1 wt% Ni/SiO₂ has a very small number of active sites with very high turnover number, a small decrease in their number during reaction, due to carbon deposition or sintering, results in large decrease in activity. This explains why the deactivation is faster over the reduced 1 wt% Ni/SiO₂ than over the reduced 1 wt% Ni/Al₂O₃ catalyst, although the carbon

deposition is greater over 1 wt% Ni/Al₂O₃ than over 1 wt% Ni/SiO₂.

4.3. Effect of Ni Content on the Activity of Ni-Supported Catalysts for CO₂ Reforming of CH₄

The reduced 1 wt% Ni/Al₂O₃ catalyst has high initial conversions of CH₄ and CO₂ and yield to CO, which decrease

TABLE 1

The Surface Area, Carbon Deposition, CO Yield, and CO TON of Various Catalysts

Catalyst	BET surface area (m ² /g)	Average pore diameter (Å)	Ni surface area (m ² /g)	CH ₄ initial conver. (%)	CO ₂ initial conver. (%)	CO initial yield ^a (%)	CO TON ^b (s ⁻¹)	C ^c (g/gcat)
Ni + Al ₂ O ₃ ^d	—	—	0.06	15	18	17	83	3.3×10^{-3}
1% Ni/SiO ₂	447	53	0.01 ^e	52	72	62	1721 ^e	2.3×10^{-4}
1% Ni/Al ₂ O ₃	75	130	0.11	78	90	84	230	3.9×10^{-4}
13.6% Ni/Al ₂ O ₃	63	129	1.76	91	98	95	15	^f
13.6% Ni/SiO ₂	362	52	1.57	89	97	93	18	1.9×10^{-1}
13.6% Ni/TiO ₂	8	—	0.19	41	67	53	80	8.0×10^{-4}

^a The initial yield for GHSV = 60,000 cm³/g/h, $T = 790^{\circ}\text{C}$, CH₄/CO₂ = 1 : 1.

^b CO turnover number.

^c Amount of carbon deposited over the catalyst during CO₂ reforming of methane at 790°C for 6 h.

^d The mixture of NiO and Al₂O₃ (containing 13.6 wt% Ni).

^e The error is very large because the amount of CO chemisorbed is extremely small.

^f The carbon deposition was so fast that the reactor was completely plugged in 6 h.

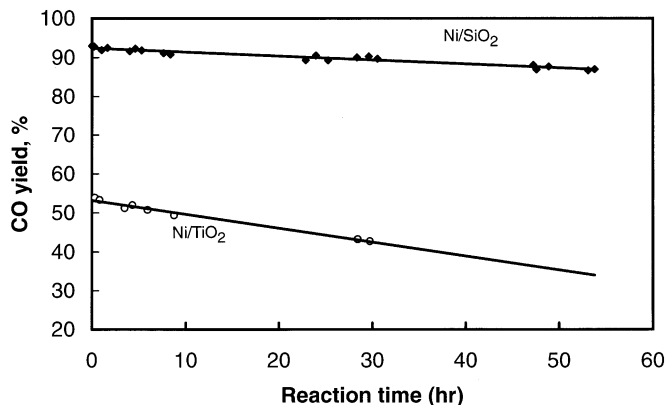


FIG. 5. The relationship between reaction time and CO yield over reduced 13.6% Ni/SiO₂ and Ni/TiO₂ catalysts. Reaction conditions: total pressure, 1 atm; $T = 790^{\circ}\text{C}$; CH₄/CO₂ = 1 : 1; GHSV = 60000 cm³/g/h.

slowly with reaction time (Fig. 3). The relatively small amount of carbon deposited during reaction (Table 1) may explain the slow decrease in activity with time. Instead, over the reduced 13.6 wt% Ni/Al₂O₃ catalyst, the carbon deposition was so fast that the reactor was plugged in 6 h. As shown by the TPD curves, the decomposition of CO to CO₂ is much higher over the reduced 13.6 wt% Ni/Al₂O₃ than over the reduced 1 wt% Ni/Al₂O₃ (Figs. 7 and 8). Therefore, the increase of CO disproportionation is partly responsible for the increase in carbon deposition with the increase of Ni content in Ni/Al₂O₃ catalysts. In addition, the increase of Ni content also increases the decomposition of CH₄, resulting in an increase in carbon deposition. As shown later, the latter mechanism is the main one at 790°C.

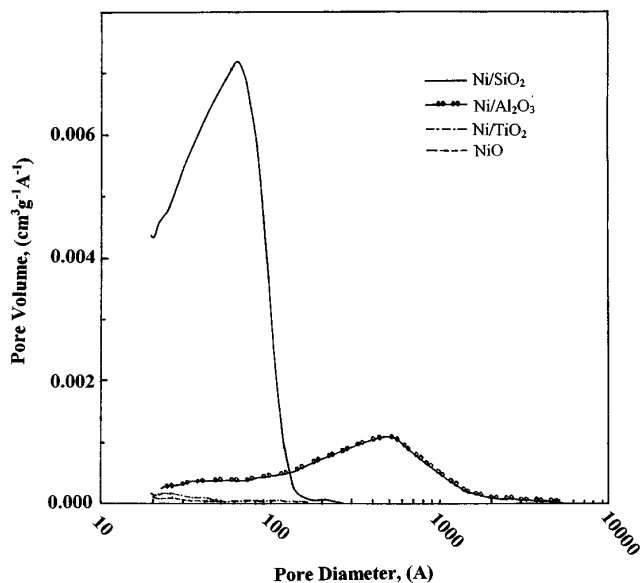


FIG. 6. The pore size distribution of 13.6 wt% Ni-based catalysts Ni/SiO₂, Ni/Al₂O₃, and Ni/TiO₂.

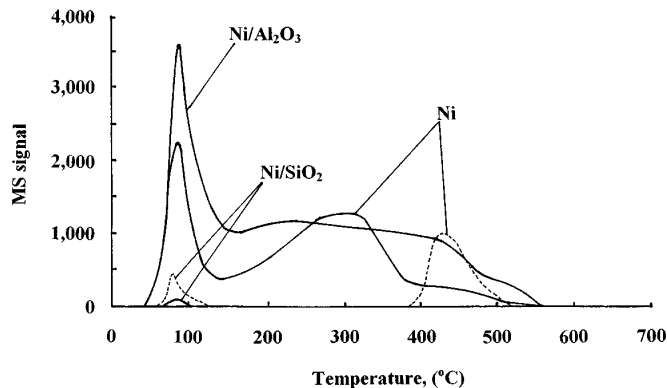


FIG. 7. Temperature-programmed desorption spectrum of CO over Ni from the reduced mixture of NiO and Al₂O₃, reduced 1 wt% Ni/Al₂O₃, and Ni/SiO₂ catalysts (—) CO, (---) CO₂.

Even though sintering occurs with some ease, the large amount of Ni present in the reduced 13.6 wt% Ni/SiO₂ provides a larger number of Ni sites than the 1 wt% Ni/SiO₂ catalyst. Indeed, both the CO chemisorption and TPD curve show that the 13.6 wt% Ni/SiO₂ adsorbs a much larger amount of CO than the 1 wt% Ni/SiO₂ (Figs. 7 and 9). Similar to the 13.6 wt% Ni/Al₂O₃ catalyst, the 13.6 wt% Ni/SiO₂ catalyst exhibits a much higher carbon deposition than the 1 wt% Ni/SiO₂ (Table 1). The activity of the 13.6 wt% Ni/SiO₂ catalyst does not decay, however, as fast as that of the 1 wt% Ni/SiO₂ catalyst. This happens probably because the initial number of sites is much larger for the 13.6 wt% catalyst, and the large amount of carbon deposited partially inhibits sintering.

Although the TPD CO curves show that the reduced 13.6 wt% Ni/Al₂O₃ and 13.6 wt% Ni/SiO₂ have comparable CO disproportionation abilities, the former catalyst exhibits at 790°C a much higher carbon deposition than the latter. This indicates that the CO disproportionation does not constitute the main mechanism for carbon deposition on Ni-based catalysts at 790°C. This observation

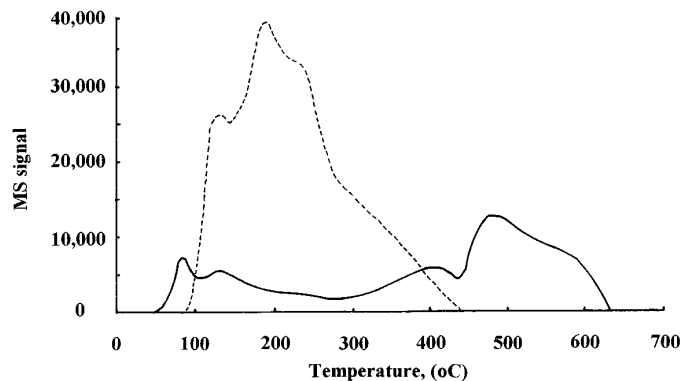


FIG. 8. Temperature-programmed desorption spectrum of CO over the reduced 13.6 wt% Ni/Al₂O₃ catalyst (—) CO, (---) CO₂.

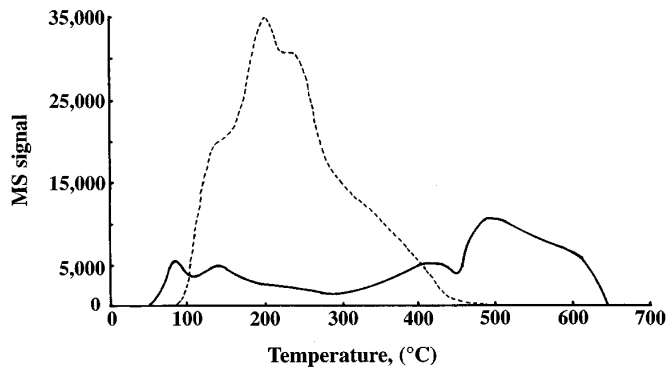


FIG. 9. Temperature-programmed desorption spectrum of CO over the reduced 13.6 wt% Ni/SiO₂ catalyst (—) CO, (---) CO₂.

is consistent with the thermodynamic conclusion of Claridge *et al.* (29), regarding the partial oxidation of methane, that, at low temperatures (<600°C), the CO disproportionation is the main mechanism of carbon deposition, while at high temperatures (>600°C) the CH₄ dissociation constitutes the main mechanism.

4.4. Ni/TiO₂

The CO yield is relatively small initially and decreases quickly with time over the reduced 13.6 wt% Ni/TiO₂ catalyst (Fig. 5). The initial yield is relatively small because, during reduction, TiO_x molecules migrate over the surface of Ni particles (30). This migration occurs because it leads to a decrease of the surface free energy of the system. This phenomenon was called “strong metal support interactions” (30), and, indeed, the strong interactions between TiO_x and Ni are responsible for the decrease of the free energy of the system (31). The decay of the yield with time is mostly due to carbon deposition. Indeed, carbon deposition was detected for this catalyst (Table 1).

4.5. CO Turnover Number for the CO₂ Reforming of CH₄

As shown in Table 1, the sequence of initial turnover numbers is 1 wt% Ni/SiO₂ > 1 wt% Ni/Al₂O₃ > the re-

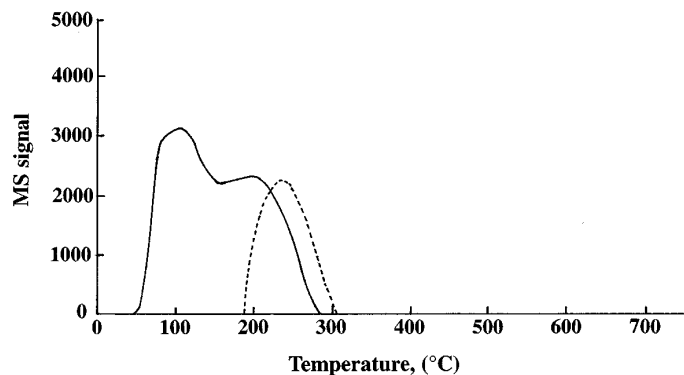


FIG. 10. Temperature-programmed desorption spectrum of CO over the reduced 13.6 wt% Ni/TiO₂ catalyst (—) CO, (---) CO₂.

duced mixture of NiO and Al₂O₃ (13.6 wt% Ni) > 13.6 wt% Ni/TiO₂ > 13.6 wt% Ni/SiO₂ ≈ 13.6 wt% Ni/Al₂O₃. The turnover number is much smaller for the catalysts containing a larger amount of Ni. Comparing the Ni/Al₂O₃ or Ni/SiO₂ catalysts for different Ni loadings, one can conclude that the reaction occurs more readily on the smaller crystallites, which are more likely to be present in the catalysts that contain smaller amounts of Ni. The crowding of Ni sites appears to affect negatively the CO turnover number for the CO₂ reforming of CH₄.

5. CONCLUSION

The CO₂ reforming of CH₄ over Ni-supported catalysts is profoundly affected by the nature of the support. SiO₂, Al₂O₃, and TiO₂ have been used as supports and the activities and CO yields compared. For completeness, the unsupported NiO catalyst and the unsupported NiO catalyst mixed mechanically with Al₂O₃ were also investigated. While the reduced 1 wt% Ni/Al₂O₃ has high initial activity and selectivity, which decay slowly with reaction time, the reduced 13.6 wt% Ni/Al₂O₃ catalyst has high initial activity and selectivity, but the fast carbon deposition plugs the reactor in about 6 h. In contrast, 1 wt% Ni/SiO₂ has a moderate initial activity and selectivity, which decay rapidly with reaction time, while the 13.6 wt% Ni/SiO₂ has high initial activity and selectivity, which decay slowly with reaction time. The sequence of the initial CO yields of various supports (all containing 13.6 wt% Ni and prepared via the reduction of supported NiO) is: Ni/Al₂O₃ > Ni/SiO₂ > Ni/TiO₂. In most catalysts, the CO yield decreases with reaction time. However, interestingly, the activity and selectivity of the reduced NiO catalyst mixed mechanically with Al₂O₃ increase rapidly with time at the beginning and moderately later. The behavior of these catalysts is explained in terms of sintering, carbon deposition, metal-support interactions, and, in the case of NiO mixed mechanically with Al₂O₃, Ni migration to Al₂O₃.

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