Temperature-Programmed Desorption of CO Adsorbed on NiO/MgO

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The temperature-programmed desorption (TPD) of CO adsorbed on unreduced and reduced NiO/MgO solid solution catalysts was investigated. For the unreduced NiO/MgO, two peaks were observed: one for CO and another one for CO_2. The CO_2 peak is a result of the reaction between NiO and adsorbed CO. The CO_2 thus generated is adsorbed on the MgO sites, whereas CO is adsorbed on the Ni generated through the reduction of NiO by CO. For the H_2 reduced NiO/MgO, two temperature ranges for CO TPD were identified: (a) A low temperature range (50–200°C), with two overlapped CO peaks, whose temperatures are independent of the catalyst composition, and no peak for CO_2. (The two overlapped CO peaks are attributed to CO molecularly adsorbed on Ni.) (b) A high temperature range (400–700°C), with peaks for both CO and CO_2, whose temperatures depend on the composition of the catalyst. They are attributed to CO species dissociatively adsorbed on Ni. A fraction of these dissociatively adsorbed species of CO are converted to CO_2 via the reaction $2CO \rightarrow 2C + 2O \rightarrow CO_2 + C$ and the reduction of some of the NiO that remained unreduced in H_2. The CO_2 generated is adsorbed on MgO sites. The other fraction of CO dissociatively adsorbed desorbs as CO.   © 1996 Academic Press, Inc.

1. INTRODUCTION

Because of their very similar structures, NiO and MgO are completely miscible over the entire molar fraction range and form an ideal solid solution (1). The properties of Ni^{2+} ions located in substitutional positions of the guest MgO matrix (2–4), and the relationship between the properties of the NiO/MgO and the calcination temperature were investigated (5, 6). The interactions of the solid with CO were studied via IR spectroscopy (3, 4). Recently, the NiO/MgO solid solution was found to be an excellent catalyst for the CO_2 reforming of methane (7, 8).

The temperature-programmed desorption (TPD) of a species adsorbed on a catalyst can provide some information about the surface active sites. In the present paper, the interactions between CO and both unreduced and reduced NiO/MgO were investigated by TPD, and their dependence on the composition of NiO–MgO solid solution was examined.

2. EXPERIMENT

2.1. Catalyst Preparation

The catalyst was prepared by the impregnation of a MgO powder (Aldrich, 325 mesh, BET surface area = 54 m²/g without additional treatment and 21 m²/g after calcination at 800°C) with an aqueous solution of nickel nitrate (Alfa Chemicals), followed by drying at room temperature in air and finally by calcination at 800°C in air for 1.5 h.

2.2. X-Ray Powder Diffraction and BET Surface Area Measurements

X-ray powder diffraction (XRD) was carried out using a NICOLET X-ray diffraction instrument, equipped with a CuK_α source, at 40 kV and 20 mA. The surface areas of the catalysts, listed in Table 1, were determined via nitrogen adsorption, using a Micromeritics ASAP2000 instrument, after the sample was degassed at 200°C for 3 h in high vacuum.

2.3. CO and CO_2 Temperature-Programmed Desorption

The chemisorption of CO and CO_2 on NiO/MgO was carried out in a vertical quartz tube (6 mm inside diameter), at room temperature and atmospheric pressure, the catalyst powder (weight: 0.250 g) being held on quartz wool. The reduction of the catalyst was carried out at 500°C and atmospheric pressure, with 45 ml/min hydrogen flowing through the quartz tube for 12 h. Then, under the same hydrogen flow, the temperature was increased to 790°C, at a rate of 20°C/min and maintained at 790°C for 10 min. The reduced catalyst was purged with high purity He (45 ml/min, 99.995% purity containing 10 ppm O_2) for 10 min at 790°C. After cooling at room temperature, successive pulses of CO (or CO_2) (0.13 ml, each; 99.995% purity) were injected at room temperature, using He (45 ml/min) as the carrier gas, until no change in the CO (or CO_2) concentration was detected. Then, the TPD experiment was carried out at a constant heating rate of 10°C/min, using ultra high purity helium as the carrier gas, at a flow rate of 45 ml/min. The

TABLE 1

The XRD Data for NiO/MgO

Catalyst mol% NiO	d (Å)		
	220	311	222
0 (MgO)	1.489	1.270	1.216
2.6	1.486	1.268	1.214
5.1	1.486	1.268	1.214
13.9	1.486	1.268	1.214
17.7	1.484	1.264	1.210
35.0	1.490	1.271	1.215
100 (NiO)	1.476	1.259	1.206

analysis of gases during the CO adsorption and desorption 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 unreduced catalysts, the TPD experiments were carried out after degassing the samples at 800°C for 2 h in a He flow (45 ml/min).

2.4. Carbon Deposition Determination

The amount of carbon deposited during TPD was obtained via combution at 800°C with oxygen pulses, by determining the CO and CO_2 with the on-line mass spectrometer.

3. RESULTS

3.1. XRD Pattern

Figure 1 presents the XRD patterns when the amount of NiO was varied between 2.63 and 35.05 mol%. The d values of the (220), (311), and (222) faces are listed in Table 1. Table 1 shows that the d values are very near those of MgO, and that only small differences exist when compared to those of NiO. The BET areas of NiO/MgO catalysts are listed in Table 2.

3.2. The Effect of Catalyst Composition on the CO TPD over Unreduced NiO/MgO Catalysts

Figure 2 shows that the CO TPD curves for the unreduced NiO/MgO catalysts have a single CO peak at about 80°C and a single CO_2 peak above 400°C. The CO peak first increases with increasing NiO loading upto 21.25 mol% NiO and then decreases, while the CO_2 peak increases with increasing NiO loading. The pure MgO has only a very small CO_2 peak.

3.3. The Effect of the Catalyst Composition on CO TPD over Reduced NiO/MgO Catalysts

Figure 3 shows that there are two groups of desorption peaks for CO and a single group for CO_2 in the CO TPD curves of the reduced NiO/MgO catalysts. At low temper-
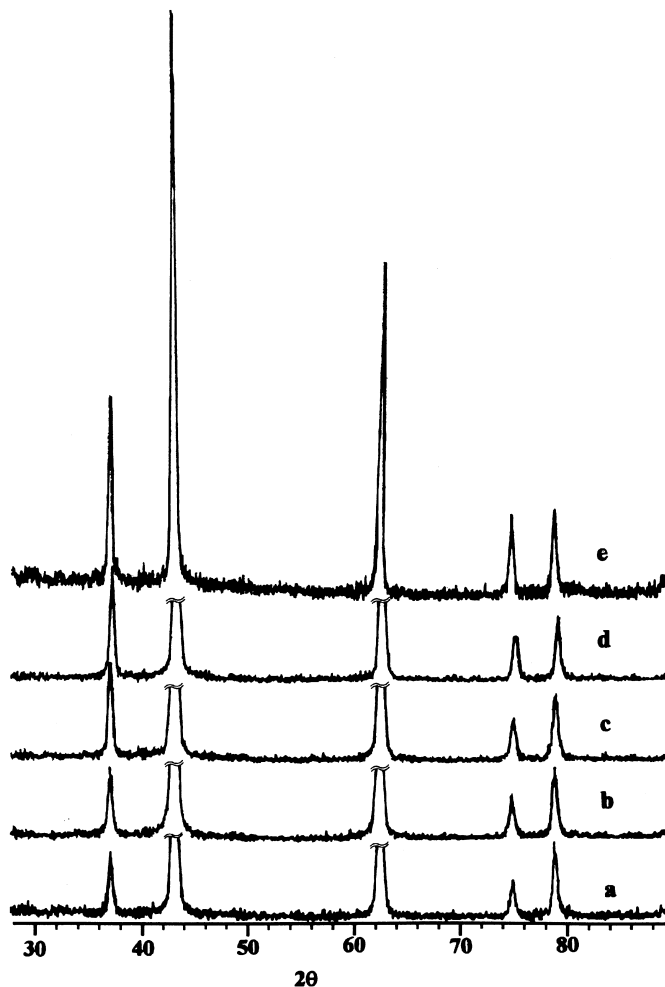

FIG. 1. X-ray diffraction patterns of NiO/MgO catalysts prepared by impregnation: (a) 2.6 mol% NiO, (b) 5.1 mol% NiO, (c) 13.9 mol% NiO, (d) 17.7 mol% NiO, (e) 35.0 mol% NiO.

atures, there are two CO peaks at about 80 and 150°C, temperatures independent of the NiO/MgO catalyst composition. At low compositions (2.63 mol% NiO), there is another CO peak at about 280°C. However, at temperatures higher than 350°C, there are several CO and CO_2 peaks

TABLE 2

BET Surface of NiO/MgO Catalysts

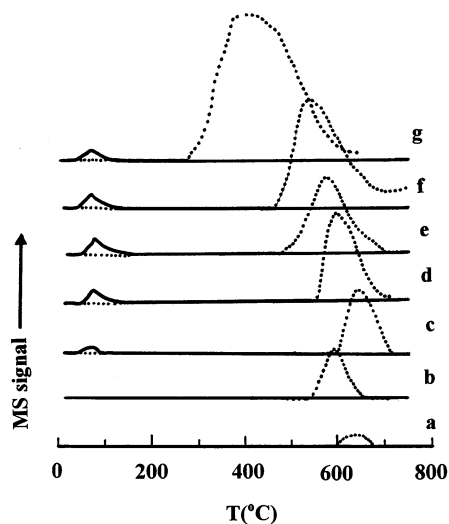| NiO (mol%)	BET surface area (m²/g)
0 (MgO)[a]	21
2.6	37
5.1	45
13.9	31
17.7	28
21.2	24
35.0	20

[a] MgO was calcined at 800°C for 1.5 h.

FIG. 2. The temperature-programmed desorption curves of CO adsorbed at room temperature at saturation on unreduced NiO/MgO: (a) pure MgO, (b) 2.6 mol% NiO, (c) 5.1 mol% NiO, (d) 13.9 mol% NiO, (e) 17.7 mol% NiO, (f) 21.25 mol% NiO, (g) 35.0 mol% NiO.

whose positions depend on the catalyst composition. The 2.63 mol% NiO has one very small CO peak at about 560°C and one CO_2 peak at 620°C. The 5.12 mol% NiO has two CO peaks at 490 and 570°C, and a single CO_2 peak at 620°C. The 13.93 mol% NiO has a single CO peak at about 480°C and two overlapped CO_2 peaks at about 480 and 620°C. The 17.75 mol% NiO has a single CO peak at about 420°C, and a broad CO_2 peak around 520°C. The 21.25 mol% NiO has
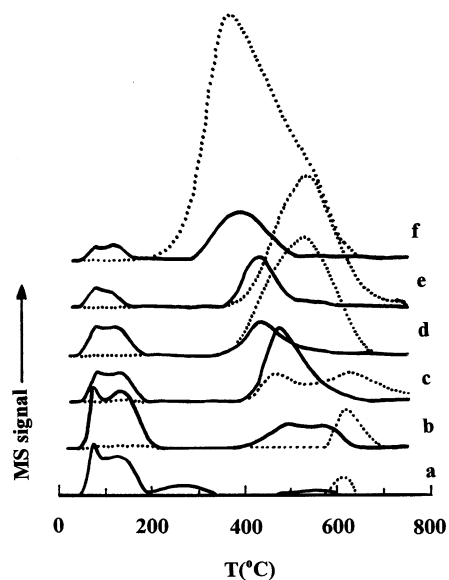

FIG. 3. The temperature-programmed desorption curves of CO adsorbed at room temperature at saturation on the NiO/MgO reduced with H_2: (a) 2.6 ml% NiO, (b) 5.1 mol% NiO, (c) 13.9 mol% NiO, (d) 17.7 mol% NiO, (e) 21.25 mol% NiO, (f) 35.0 mol% NiO
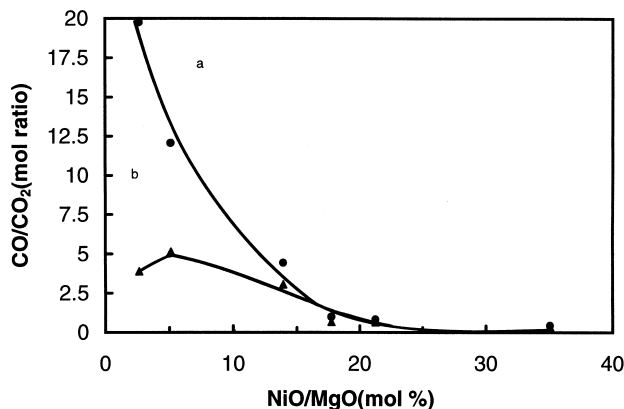

FIG. 4. The molar ratio of CO/CO_2 as a function of the composition of the catalyst in CO TPD, for CO adsorbed under the conditions of Fig. 3 (a) total, (b) at high temperatures $>350°C$.

a single CO peak at about 420°C, and one broad CO_2 peak around 520°C. The 35.05 mol% NiO has a single CO peak at about 380°C, and two broad overlapped CO_2 peaks at about 380 and 520°C. As shown in Fig. 4, the ratio CO/CO_2 decreases with increasing NiO loading.

3.4. Effect of CO_2 and O_2 on the CO TPD over Reduced NiO/MgO

When a small amount of CO_2 was adsorbed at room temperature on the 5.1 mol% NiO sample before CO adsorption, the TPD curve (Fig. 5) still showed two groups of CO peaks and a single CO_2 peak, as for the case free of CO_2 preadsorption.

When the 5.1 mol% NiO sample on which CO was adsorbed was treated with a single pulse of 0.045 ml of O_2 at room temperature, the CO peaks decreased, with a greater decrease for those at low temperatures (Fig. 6). However, only a single peak remained, namely a CO_2 peak, after the 5.1 mol% NiO was treated at room temperature with a large number of O_2 pulses until no adsorption of O_2 was detected (Fig. 6).
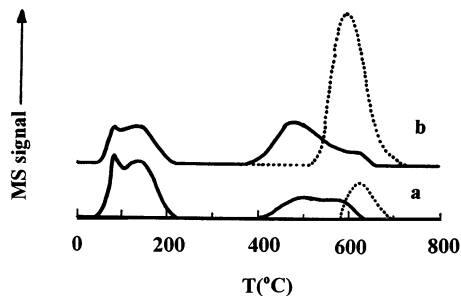

FIG. 5. The temperature-programmed desorption curves of CO adsorbed at saturation at room temperature on the 5.1 mol% NiO reduced with H_2: (a) no CO_2 preadsorbed, (b) 0.008 mmol/g of CO_2 were preadsorbed before CO was adsorbed.
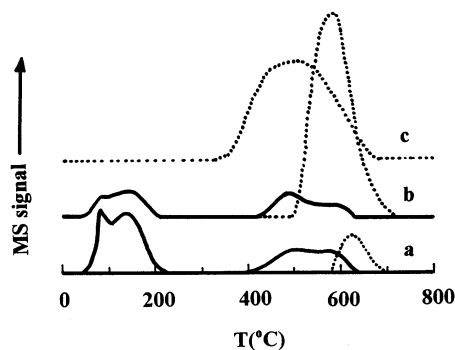
FIG. 6. The temperature-programmed desorption curves of CO adsorbed on the 5.1 mol% NiO reduced with H_2: (a) no oxygen was adsorbed on the sample after CO was adsorbed. (b) 0.002 mmol of O_2 was adsorbed on the sample after CO was adsorbed, at room temperature; (c) after CO was adsorbed the sample was saturated with oxygen at room temperature.

3.5. Effect of the Amount of Adsorbed CO on CO TPD over Reduced NiO/MgO

When only a single pulse of CO (0.045 ml) was adsorbed on the 5.1 mol% NiO sample, a single CO peak at 80°C and a single CO_2 peak at 620°C were present (Fig. 7). When, subsequently, on the same sample two pulses were adsorbed, an additional small CO peak at a high temperature was detected (Fig. 7).

3.6. CO_2 TPD over MgO and Unreduced NiO/MgO

The unreduced NiO/MgO catalysts have CO_2 TPD curves similar to that of MgO, namely, overlapped CO_2 peaks which cover a broad area between 80 and about 650°C (Fig. 8). When only a small amount of CO_2 (0.045 ml) was employed, the CO_2 was adsorbed only on the stronger active sites and had a high desorption temperature (Fig. 9).

4. DISCUSSION

The XRD patterns reveal cubic phases for all compositions, very similar to that of MgO. This indicates that NiO
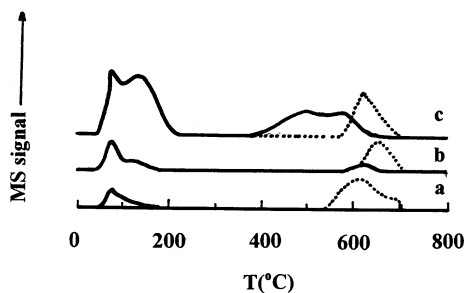

FIG. 7. The temperature-programmed desorption curves of CO adsorbed on the 5.1 mol% NiO reduced with H_2: (a) CO was adsorbed by introducing a single pulse (0.002 mmol) of CO at room temperature; (b) CO was adsorbed by introducing two pulses (0.002 mmol each) of CO at room temperature; (c) CO was adsorbed at saturation at room temperature.
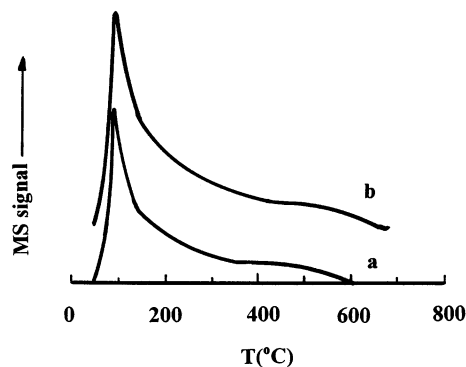

FIG. 8. The temperature-programmed desorption curves of CO_2 adsorbed at saturation at room temperature on (a) MgO and (b) 5.1 mol% NiO/MgO.

and MgO form solid solutions. Evidence for the formation of solid solutions between NiO and MgO was also brought in Refs. (5) and (6).

There is a very small CO_2 peak in the CO TPD of pure MgO (Fig. 2), indicating that a very small amount of CO is adsorbed on MgO. The absence of a CO peak indicates that CO was converted to CO_2 before desorption. Zecchina *et al.* (3, 4) suggested that CO adsorbed on MgO is transformed into CO_3^{2+} even at room temperature. The CO_2 TPD shows that there are various active sites for the CO_2 adsorption at saturation at room temperature on MgO (Fig. 8). However, when only a single small pulse of CO_2 is employed (Fig. 9), CO_2 is adsorbed only on the strong active sites and the desorption temperature is high. Consequently, the small amount of CO_2 generated through the conversion of CO adsorbed on MgO should desorb at a high temperature and this indeed happens. Our results differ from those of Hattori *et al.* (9, 10), who found several CO peaks for MgO. This might be due to the different kinds of MgO employed, since the surface properties of MgO strongly depend on the precursor used in its preparation (11).

The unreduced NiO/MgO catalysts have a small CO peak at 80°C and a large CO_2 peak above 400°C in the CO TPD
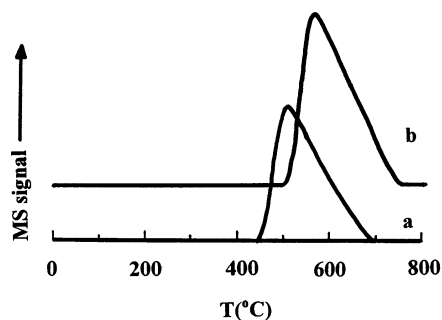

FIG. 9. The temperature-programmed desorption curves of CO_2 on (a) MgO and (b) 5.1 mol% NiO (in both cases the amount adsorbed was 0.008 mmol/gcatalyst at room temperature).
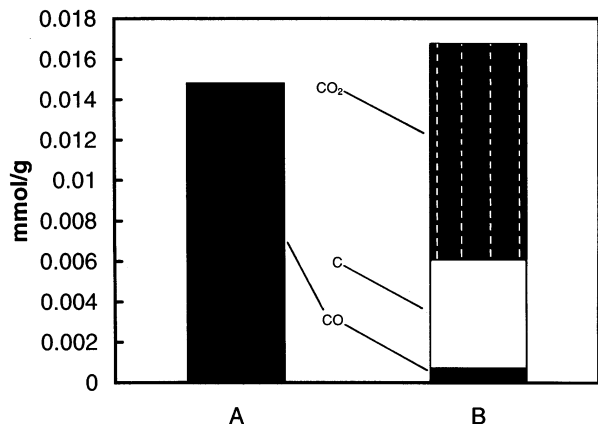
FIG. 10. Carbon balance during the TPD of the reduced 35 mol% NiO/MgO catalyst (A) CO adsorbed; (B) CO and CO_2 desorbed and carbon deposited during TPD.

curves (Fig. 2). The small CO peak increases first and then decreases with increasing NiO content, whereas the CO_2 peak increases with increasing NiO content. Figure 2 shows that the increase in the NiO content results in increased CO adsorption. A large CO peak, located as for the unreduced catalysts at 80°C, was detected for the reduced NiO/MgO as well. This indicates that this CO peak of the unreduced catalyst is due to the desorption of CO adsorbed on Ni. As suggested by Zecchina *et al.* (3, 4), this is a result of the reduction of Ni^{2+} by CO at low temperatures, followed by the adsorption of CO on Ni. The amount of adsorbed CO which reduces NiO is expected to increase with increasing NiO content. This explains why the CO_2 peak increases with increasing NiO content. The CO peak has the tendency to increase with the amount of Ni generated via the reduction of NiO by the adsorbed CO, but also to decrease because CO is employed to generate Ni. This explains why for the unreduced NiO/MgO the CO peak first increases and then decreases with increasing NiO content.

For the reduced 5.1 mol% NiO sample, the CO TPD curve for saturated CO adsorption exhibits two groups of CO peaks: one at low temperatures with two peaks, which will be attributed to what we call α sites and another one at high temperatures with also two peaks, which will be attributed to β sites. The curve also exhibits a single CO_2 peak in the high-temperature range. When, however, only a single small pulse of CO was adsorbed, only a single CO peak at 80°C and two overlapped CO_2 peaks, a larger one at 620°C and a much smaller one at 690°C, were present. This indicates that the CO_2 peak has its origin in the transformation of the CO species present on the β sites. Comparing the curves of Fig. 7, one can also conclude that the frequently used principle that the stronger adsorption sites are first occupied is violated. Indeed, the molar amount of CO plus CO_2 corresponding to CO adsorption at saturation (Fig. 7, curve c), in the high-temperature range, is 4.4 times larger

than that present, in the same range, when a small amount of CO is adsorbed (Fig. 7a). According to the above principle, the low-temperature range sites, when only a small amount of CO is adsorbed, should not be occupied at all. This indicates that the molecules which land on the surface can remain in metastable potential minima for long times, being separated from the deepest minimum by relatively high potential barriers.

For the reduced NiO/MgO, the areas of the low temperature range CO peaks decrease with increasing NiO content, whereas those of the high temperature range CO peaks increase. Hence, the number of β sites increases with increasing NiO content. The preadsorption of CO_2 did not affect the CO peaks. This means that the CO_2 and CO have different adsorption sites. The CO_2 TPD curves (Fig. 8) show that MgO and NiO/MgO have very similar CO_2 TPD curves. One can therefore conclude that CO_2 is adsorbed on MgO sites of the NiO/MgO catalysts, and that the CO peaks are associated with Ni. Investigations regarding the thermal-desorption curve of CO adsorbed on Ni found one CO peak at low temperatures (below 200°C) for smooth Ni crystal planes (α sites) and another one, only for stepped Ni surfaces (β sites), at high temperatures (around 550°C) (12, 13). The low-temperature peak was attributed to the molecularly adsorbed CO, while the high-temperature peak was attributed to the dissociative adsorption of CO followed by associative desorption (12, 13). It is, therefore, likely that for the reduced NiO/MgO, the low-temperature range CO peaks are associated with the molecularly adsorbed CO on α Ni sites, whereas the high-temperature CO peaks are due to the dissociative adsorption of CO on β Ni sites followed by associative desorption.

Zecchina *et al.* (4) reported that the NiO/MgO solid solutions are reduced by H_2 in two different ways: in the temperature range 398–820°C, mainly the Ni^{2+} ions located on the surface are reduced, while at temperatures higher than 820°C those located in the bulk are reduced as well. In the present work, the reduction was carried out at temperatures <820°C. Consequently, only the NiO located on the surface could be reduced by H_2. However, because CO is a stronger reductant than H_2, some NiO, which was not reduced during H_2 reduction, can be reduced by CO at high temperatures. Hence, in the CO TPD of reduced NiO/MgO, the formation of CO_2 can be due to the reaction between the CO species adsorbed dissociatively on β sites and the NiO which was not reduced by H_2. In addition, CO_2 can be generated via the reaction $2CO \rightarrow 2C + 2O \rightarrow CO_2 + C$, which also leads to carbon deposition on the surface of the catalyst. Indeed, the presence of carbon was detected by its combustion after TPD at 800°C with oxygen pulses. Figure 10 provides the combustion results obtained for the 35 mol% NiO. The total amount of carbon provided by the combustion experiment (0.0054 mmol/gcatalyst) being smaller than that provided by CO TPD CO_2 (0.0106 mmol/

gcatalyst), a fraction of CO_2 is generated via the reduction of NiO by CO. The carbon balance between the adsorbed CO, the CO and CO_2 of the CO TPD, and the CO and CO_2 of combustion after the TPD is satisfied with an error of 13%.

5. CONCLUSION

In the CO TPD of the unreduced NiO/MgO solid solution catalysts a single CO peak and a single CO_2 peak were found; the former is due to the CO adsorbed on Ni, while the latter is due to the CO_2 (adsorbed on MgO) which was generated via the reduction of NiO and the CO conversion to CO_2. In the CO TPD of the reduced catalysts, two groups of desorption peaks were found; one at low temperatures (50–200°C) and another one at high temperatures (400–700°C). In the low-temperature range, there are two overlapped CO peaks at temperatures independent of the catalyst composition and no peak for CO_2. In the high-temperature range, there are both CO and CO_2 peaks, whose temperatures depend on the composition of the catalyst. In the reduced catalysts, CO_2 is generated by two mechanisms: the reaction of $2CO \rightarrow 2C + 2O \rightarrow CO_2 + C$ and the reduction of NiO (remained unreduced after the H_2 reduction) by CO.

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