Catalysis Letters 43 (1997) 71–77

The characterization of a highly effective NiO / MgO solid solution catalyst in the CO_2 reforming of CH_4

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Received 22 August 1996; accepted 5 November 1996

A NiO / MgO catalyst prepared by impregnation, which reduced in H_2 had very high CO yield and stability in CO_2 reforming of methane, was investigated by XPS, XRD, BET and pulse-MS response. This catalyst was compared to that obtained by mechanical mixing of powders of the two oxides. It was found that the entire NiO formed a solid solution with MgO in the former catalyst, while only a fraction of NiO formed a solid solution with MgO in the latter one. BET revealed that, in contrast to NiO and MgO, the NiO / MgO catalyst prepared by impregnation had a high stability to sintering, because its surface area hardly changed during calcination from 1.5 to 20 h at 800°C. In the same catalyst, a surface enrichment in MgO, which was greater after than before reduction, was detected. Compared to MgO or NiO, this catalyst had a lower Mg(2p) and a higher $Ni(2p_{3/2})$ binding energy. This indicates that electron transfer from NiO to MgO took place, which, increasing the binding between the two oxides, might be responsible for the resistance of the solid solution to sintering. Because of the interactions between Ni and Mg, the clustering of Ni, which stimulates carbon deposition is inhibited. This explains the high stability of the CO yield in the CO_2 reforming of methane over the NiO / MgO catalyst prepared by impregnation. The pulse-MS response suggested that the decompositions of CO_2 to CO and O and of CH_4 to C and H are involved in the reaction mechanism of CO_2 reforming of methane over the reduced NiO–MgO solid solution catalyst.

Keywords: NiO, MgO, solid solution, XPS, XRD, pulse-MS, CO_2 reforming of methane

1. Introduction

In recent years, renewed interest in the CO_2 reforming of methane to synthesis gas

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2\,, \quad \Delta H = 247\ \mathrm{kJ/mol}$$

has arisen [1–7]. While this pathway provides a high CO selectivity and a more suitable H_2/CO ratio for the Fischer–Tropsch or methanol syntheses, it could not be applied industrially because of the aging of the catalyst, caused mainly by carbon deposition. Ashcroft et al. [1] and Rostrup-Nielsen [8] observed that carbon deposition cannot be avoided over nickel-supported catalysts and for a CO_2/CH_4 molar ratio of 1 : 1. Ashcroft et al. [1] suppressed the carbon deposition in CO_2 reforming by replacing Ni with platinum-group catalysts. Rostrup-Nielsen [9] noted that carbon-free deposition in steam reforming of methane can be achieved by using a sulfur-passivated nickel catalyst. However, sulfur also reduces the activity of the catalyst. Zhang et al. found that Ni/La_2O_3 has high CO yield and stability in CO_2 reforming of methane [10], and we demonstrated that its stability depends on the preparation conditions and is enhanced by a small amount of chlorine in the catalyst [11]. Recently, we found that the reduced NiO / MgO catalyst prepared by impregnation has a rather high CO yield (94%) and excellent stability, since the carbon deposition is inhibited [12–14].

Because of similar structures, NiO and MgO are completely miscible and form an ideal solid solution [15]. The value of such solid solutions for catalysis was first recognized when trying to understand how electronic interactions between cations affect the catalytic action [16,17]. A number of physico-chemical properties of the NiO / MgO solid solution [18–26], such as the influence of Ni precursor and preparation conditions on the reducibility of magnesia-supported NiO and on the diffusion of Ni^{2+} ions into the MgO lattice [23], the effects of calcination temperature and treatment atmosphere on the phase composition of NiO-MgO solid solutions [22,24], and the interactions between small gas molecules (CO, CO_2 or CH_4) and the solid solution [19–21,25,26], were investigated.

Although the NiO / MgO catalyst was widely studied, it was considered inadequate for the reforming of methane, because it had a poor stability and a low activity [27]. We found, however, that its activity depends on the kind of MgO employed and conditions used in preparation [14]. The goal of this paper is to investigate the NiO / MgO catalyst, which has high CO yield and time stability in the CO_2 reforming of methane, by the XPS, XRD, pulse-MS response and BET techniques. A possible reaction mechanism is suggested.

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2. Experimental

2.1. *Catalyst preparation*

The catalyst was prepared by impregnating a MgO powder (Aldrich) 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. The prepared catalyst contained 20 g NiO per 100 g MgO, composition which provides the optimum activity [12,13].

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) reactor. The catalyst powder (weight: 0.02 g) was held on quartz wool. The molar ratio of the reactant gases, with a GHSV = 253500 $cm^3\ g^{-1}\ h^{-1}$, was $CO_2/CH_4 = 1:1$. The catalyst was reduced in a flow of H_2 (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, also in a flow of H_2 (20 ml/min). The analysis of the reactants/products mixtures was performed with an in situ gas chromatograph equipped with a Porapak Q column.

2.3. *BET surface area and pore size distribution measurements*

The surface area and the pore size distribution were determined using a Micromeritics ASAP 2000 instrument. The surface area was calculated by the BET method, while the pore size distribution curve was obtained by the BJH method [28]. The sample was degassed at 200°C in high vacuum before measurements.

2.4. *X-ray powder diffraction and ESCA*

X-ray powder diffraction (XRD) was carried out using a Nicolet X-ray diffraction instrument, equipped with a Cu K_α source, at 40 kV and 20 mA.

The ESCA analysis was carried out using a SSI model 100 small spot ESCA instrument, equipped with an Al K_α monochromatized X-ray source. The binding energies were referenced to the C(1s) level (285.0 eV).

2.5. *Pulse reaction and dynamic response*

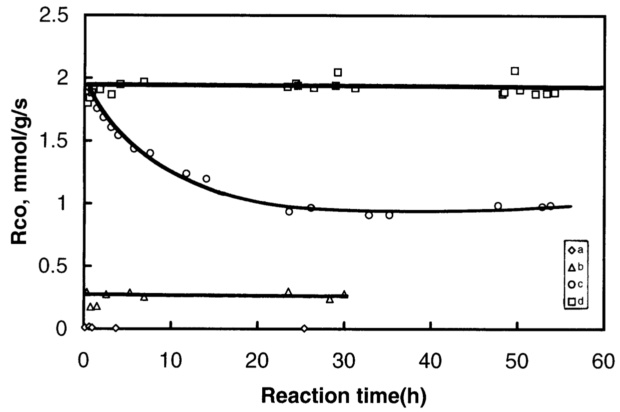

Fig. 1. Relationship between the rate of formation of CO and the reaction time over NiO/MgO catalysts: (a) catalyst obtained by mixing NiO and MgO powders (this is not followed by calcination); (b) catalyst obtained by mechanical mixing of NiO and MgO powders, followed by calcination in air at 800°C for 1.5 h; (c) catalyst obtained by mechanical mixing of NiO and MgO powders, followed by calcination in air at 800°C for 14 h; (d) catalyst prepared by impregnation, followed by calcination in air at 800°C for 1.5 h.

A quartz tube (2 mm inside diameter) was used as reactor and the catalyst powder (weight, 0.02 g; bed height, 2 mm) was held on quartz wool. Pulses of 45 μl were employed and ultra-high-purity helium was used as carrier gas, with a flow rate of 45 ml/min. The analysis of gases during transients was carried out with an on-line mass spectrometer (HP Quadrupole, 5971 series mass selective detector) equipped with a fast response inlet capillary system.

3. Results

3.1. *The CO_2 reforming reaction of methane*

As shown in fig. 1, the preparation conditions of the catalyst affect in a major way the CO_2 reforming of methane. For the reduced mechanical mixture of NiO and MgO which was not subsequently calcined, the rate of formation of CO is near zero (curve a of fig. 1). For the reduced mechanical mixture of NiO and MgO calcined for 1.5 h at 800°C, the rate of formation of CO is about 0.25 mmol $g^{-1}s^{-1}$. For the reduced mechanical mixture of NiO and MgO calcined for 14 h at 800°C, the

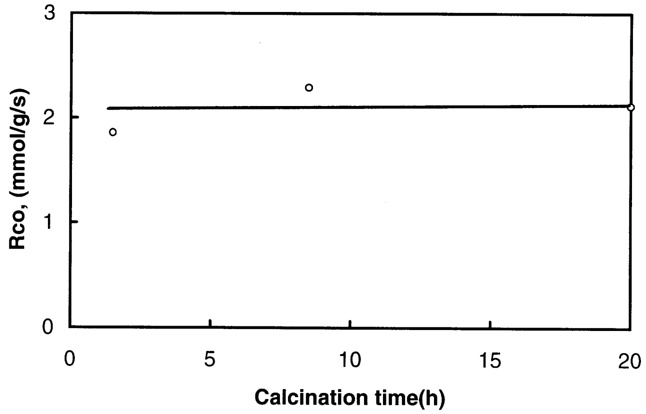

Fig. 2. Relationship between the rate of CO formation and calcination time over NiO/MgO catalysts prepared by impregnation, followed by calcination in air at 800°C.

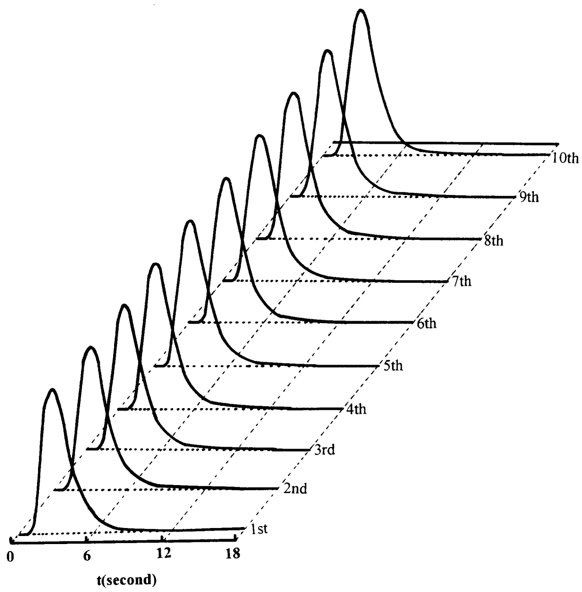

Fig. 3. Response to CH_4/CO_2 (1/1) pulses at 790°C over the unreduced NiO/MgO catalyst prepared by impregnation ((---) CO; (——) CO_2).

rate of formation of CO is initially 1.923 mmol g^{-1} s^{-1} and then decreases with reaction time. In contrast, the reduced NiO/MgO catalyst, prepared by impregnation followed by calcination in air at 800°C for 1.5 h, has the high rate of formation of CO of 1.9 mmol g^{-1} s^{-1}, which remains unchanged with reaction time. Fig. 2 shows that for the reduced NiO/MgO prepared by impregnation, the rate of formation of CO changes little with calcination time.

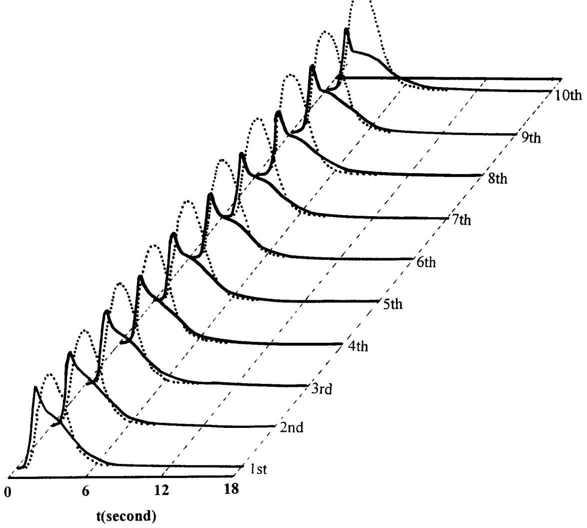

Fig. 4. Response to CH_4/CO_2 (1/1) pulses at 790°C over the reduced NiO/MgO catalyst prepared by impregnation ((---) CO; (——) CO_2).

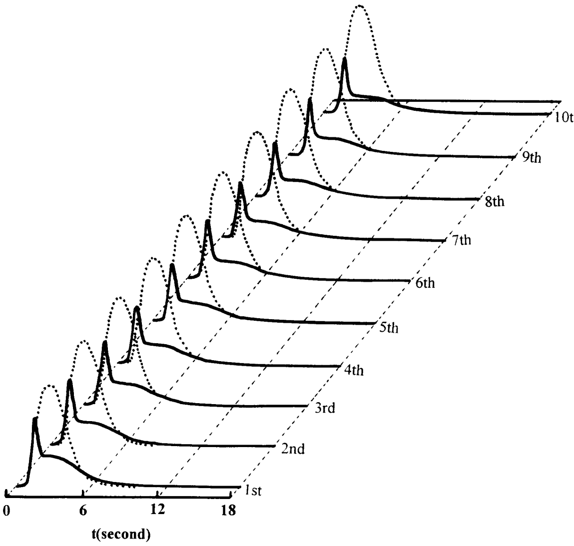

Fig. 5. Response to CH_4/CO_2 (1/1) pulses at 790°C over the NiO/MgO catalyst prepared by impregnation, reduced in H_2 and used for 2 h in the CO_2 reforming of methane ((---) CO; (——) CO_2).

3.2. *Pulse response of CO/CO_2 in CO_2 reforming of methane*

Fig. 3 shows that no CO is detected during ten CO_2/CH_4 (1/1) pulses over unreduced NiO/MgO catalyst prepared by impregnation. In contrast, over the reduced NiO/MgO catalyst, the CO concentration increases while that of CO_2 decreases with increasing number of pulses (fig. 4). For the reduced catalyst used for 2 h in the CO_2 reforming of methane, the results are similar to those over the reduced catalyst (fig. 5).

Over the reduced NiO/MgO used for 2 h in the CO_2 reforming of methane, CO and CO_2 are detected during CH_4 pulses, with concentrations which decrease with increasing number of pulses (fig. 6). Over the reduced

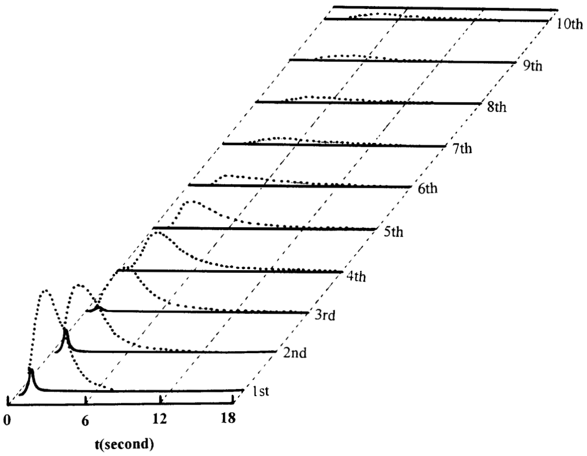

Fig. 6. Response to CH_4 pulses at 790°C over the reduced NiO/MgO catalyst prepared by impregnation, and employed for 2 h in the CO_2 reforming of methane ((---) CO; (——) CO_2).

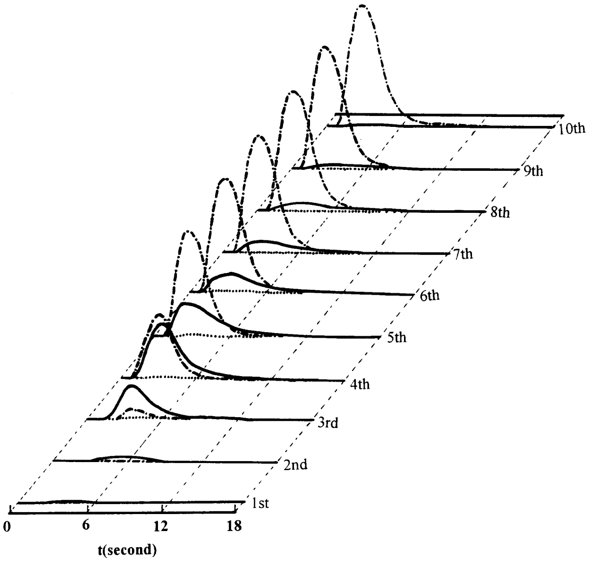

Fig. 7. Response to O_2 pulse at 790°C over the reduced NiO/MgO catalyst prepared by impregnation and employed for 2 h in the CO_2 reforming of methane ((- - -) CO; (——) CO_2; (– · –) O_2).

NiO/MgO previously used for 2 h in the CO_2 reforming of methane, a small amount of CO_2 is detected during the first O_2 pulse, the amount increases during the first four pulses and then decreases (fig. 7).

3.3. Surface area and pore size distribution

The BET measurements provide the values 54, 21, 50, 47 and 47 m^2/g for MgO without calcination, MgO calcined for 1.5 h, and for the NiO/MgO prepared by impregnation and calcined for 1.5, 8.5 or 20 h, at 800°C, respectively. This indicates that MgO sinters at 800°C, whereas NiO/MgO prepared by impregnation is stable to sintering at 800°C. Fig. 8 shows that there are two kinds of pores, with sizes in the ranges 10–100 Å and 200–1000 Å in the NiO/MgO catalysts prepared by impregnation. The 20 Å pores are more numerous in the NiO/MgO calcined for 20 h than in those calcined for 8.5 or 1.5 h

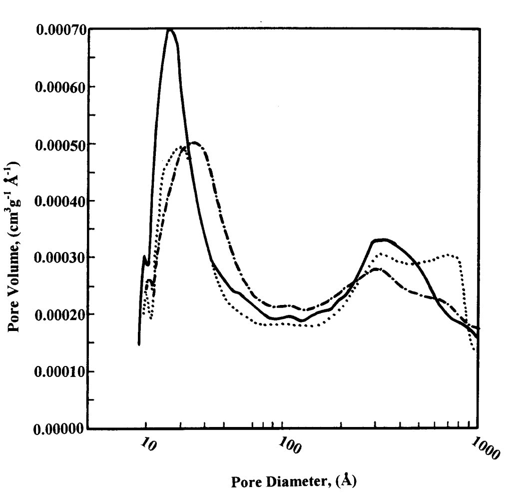

Fig. 8. Pore size distribution of NiO/MgO catalysts prepared by impregnation ((- - -) calcined at 800°C for 1.5 h; (– · –) calcined for 8.5 h; (——) calcined for 20 h).

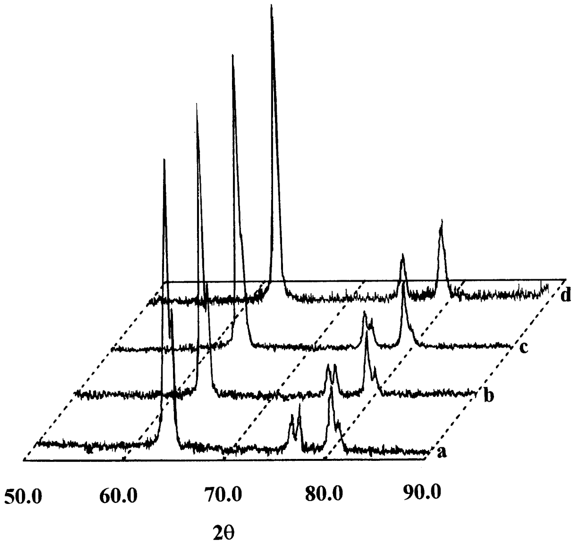

Fig. 9. XRD patterns of NiO/MgO: (a) mechanical mixture of NiO and MgO without calcination; (b) mechanical mixture of NiO and MgO calcined in air at 800°C for 1.5 h; (c) mechanical mixture of NiO and MgO calcined in air at 800°C for 14 h; (d) catalyst prepared by impregnation, followed by calcination in air at 800°C for 1.5 h.

3.4. Phase structure

The XRD patterns of mechanical mixtures of NiO and MgO and NiO/MgO prepared by impregnation are presented in fig. 9. As shown by this figure, three double peaks at 2θ of about 62.64, 75.00 and 79.00 are present for the mechanical mixtures. In contrast, the NiO/MgO catalyst prepared by impregnation and calcination has only three single peaks near the above 2θ values.

Although the XRD patterns of MgO are similar to those of NiO, there are some differences in their peak positions, by 0.6, 0.8 and 0.81° for $2\theta \approx 62.64$, 75.00 and 79.00, corresponding to the (220), (311) and (222) faces (the higher 2θ is for the NiO phase). The above three diffraction lines can be used to identify the formation of a solid solution. The NiO/MgO catalyst prepared by impregnation has three single peaks near the above 2θ values (fig. 9); this indicates that a solid solution was indeed formed. For the mechanical mixtures, the NiO peak in each of the double peaks decreases with increasing calcination time; this indicates that calcination leads to partial formation of a solid solution.

3.5. Surface composition and structure

The results of XPS analysis of three samples prepared by impregnation, but subjected to different treatments

Table 1
The binding energies of Mg(2p), Ni(2p) and O(1s)

Catalyst[a]	Binding energy (eV)		
	Mg(2p)	O(1s)	Ni($2p_{3/2}$)[b]
sample a	48.8	530.0, 532.2	856.0
sample b	49.4	529.8, 532.0	855.4
sample c	49.3	529.5, 531.6	855.3
NiO (ref. [29])	–	529.9	854.5
MgO (ref. [30])	50.5	530.5	–

[a] Samples a, b and c are the unreduced (a), reduced with H_2 (b), and both reduced and used in the CO_2 reforming of methane (c) catalysts, prepared by impregnation and calcined at 800°C for 1.5 h.

[b] The peak at about 861.5 eV is due to the charge-transfer multielectron excitation (electron shake-up).

(unreduced (a), reduced (b) and used in CO_2 reforming (c)), are summarized in table 1. There are two kinds of oxygen, with O(1s) binding energies of about 530 and 532 eV, respectively (fig. 10). The binding energy of Mg(2p) in sample a is 48.8 eV (fig. 11), which is lower than that in MgO (50.5 eV). The binding energy of Mg(2p) increases after reduction (sample b) and reaction (sample c). The binding energy of Ni($2p_{3/2}$) in sample a is 856.0 eV, which is higher than 854.5 eV in NiO, and the binding energy of Mg(2p) in samples b and c are larger than in sample a. The surface compositions of the samples are listed in table 2, which shows that the unreduced catalyst (sample a) has 5.1 / 100, the reduced one (sample b) has 2.1 / 100 and sample c 2.3 / 100 mol ratio Ni / Mg.

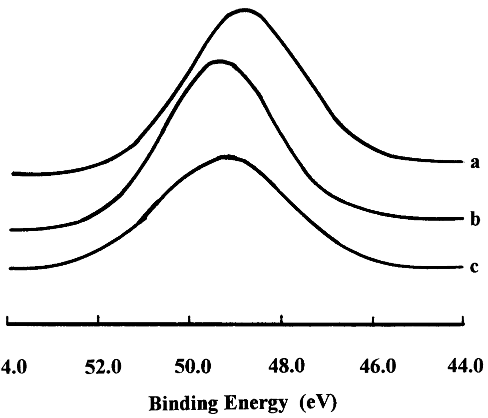

Fig. 11. XPS spectra of Mg(2p) for the NiO / MgO prepared by impregnation: (a) unreduced; (b) reduced; and (c) reduced and used for 2 h in the CO_2 reforming of methane.

4. Discussion

The XRD patterns indicate that, after calcination at 800°C for 1.5 h, the entire NiO in the NiO / MgO catalyst prepared by impregnation forms a solid solution with MgO (fig. 1). This catalyst has very high rate of CO formation and stability. Only a fraction of NiO forms a solid solution with MgO in the mechanical mixture, even when subjected to calcination at 800°C for 14 h (fig. 9). The amount of solid solution formed increases with increasing calcination time. In the CO_2 reforming of methane over the mechanical mixtures (fig. 1), the rate of CO formation is related to the calcination time; the longer the calcination time, the greater is the initial rate of formation of CO. Hence, the formation of a solid solution plays an important role in the generation of the active sites for the CO_2 reforming of methane. As pointed out by Parmaliana et al. [31], the first step in the formation of a NiO–MgO solid solution is the diffusion of NiO over the surface of MgO. This is followed by diffusion inside the MgO lattice. The longer the calcination time, the greater is the dispersion of NiO and for this reason the activity of the mechanical mixture of NiO and MgO increases with the calcination time. When the dispersion of NiO becomes sufficiently high, a large number of active sites is formed, and the initial activity is high. The activity decreases, however, with reaction time because of the clustering of the Ni atoms in particles. In contrast, for the NiO / MgO catalyst prepared by impregnation, even if the calcination time increases 13.3 times from 1.5 to 20 h, its surface area and the rate of CO formation in CO_2 reforming of methane do not change. This is because in the NiO / MgO catalyst the entire NiO is present in the solid solution, which stabilizes both oxides, and a greater calcination time does not affect the

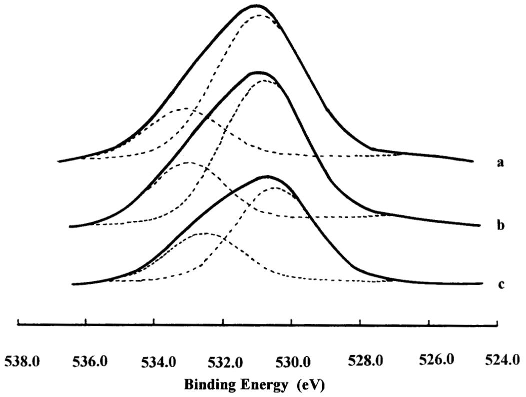

Fig. 10. XPS spectra of O(1s) for the NiO / MgO prepared by impregnation: (a) unreduced; (b) reduced; and (c) reduced and used for 2 h in the CO_2 reforming of methane.

Table 2
The Ni / Mg mol ratio of catalysts obtained by XPS

Catalyst[a]	Ni / Mg (mol. ratio)	
	total[b]	XPS
sample a	10.8 / 100	5.1 / 100
sample b	10.8 / 100	2.1 / 100
sample c	10.8 / 100	2.3 / 100

[a] The same as in table 1.

[b] Including the surface and bulk of the catalysts.

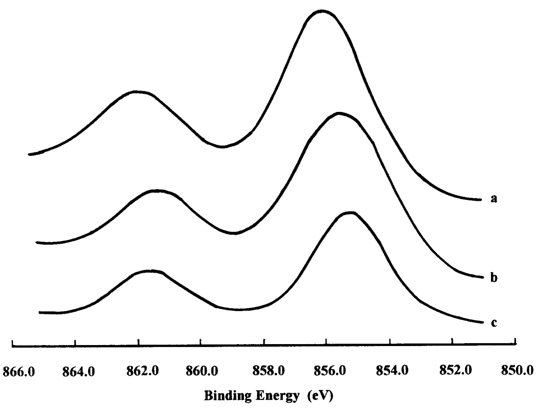

Fig. 12. XPS spectra of $Ni(2p_{3/2})$ for the NiO/MgO prepared by impregnation: (a) unreduced; (b) reduced; and (c) reduced and used for 2 h in the CO_2 reforming of methane.

structure. In addition, only the NiO in the surface layer of the NiO/MgO solid solution catalyst is reduced during reduction below 1093 K [20] and the Ni sites generated remain in close contact with MgO; this hinders their sintering.

As the XPS analysis indicates, there are two kinds of oxygen with binding energies of about 530 and 532 eV in the NiO/MgO prepared by impregnation. Since the O(1s) binding energy of O^{2-} is about 530 eV [29,30], the binding energy of about 530 eV corresponds to O^{2-} in either NiO or MgO. The binding energy of 532 eV might be due either to a peroxide species (O_2^{2-}) or to a hydroxy species [32], most likely to a hydroxy species generated by the exposure of MgO to air before the measurement. Compared to MgO or NiO, the MgO/NiO solid solution prepared by impregnation has a lower Mg(2p) and a higher $Ni(2p_{3/2})$ binding energy. Consequently, there is electron transfer from NiO to MgO. This increases the interactions between the two oxides and is probably responsible for the increased difficulty of reducing the NiO. Ni^0 was not detected in the reduced NiO/MgO, probably because the catalyst was reoxidized in air. However, since the $Ni(2p_{3/2})$ binding energy is decreased after reduction in H_2, it is clear that at least some reduction of NiO has taken place. This strong interaction between NiO and MgO is probably responsible for the inhibition of sintering in the solid solution NiO/MgO. While NiO and MgO sinter easily, their solid solution is almost free of sintering. In addition, the strong interactions inhibit coke deposition, probably because they inhibit the formation of the large clusters needed for coke generation [9]. This explains the time stability of the CO yield.

The XPS analysis also shows that, although the total mole ratio Ni/Mg in the catalyst is 0.1, its surface mole ratio is only 0.05 for the unreduced catalyst and even lower, 0.02, for the reduced one. This indicates that the surface is enriched in MgO. The enrichment is higher in the reduced case because the interfacial free energy of a metal is higher than that of its oxide. Interestingly, the surface concentration of Ni after reaction is almost equal to that before reaction (table 2), indicating that the surface composition of the reduced NiO/MgO catalyst prepared by impregnation is stable in the CO_2 reforming of methane.

The response to pulses of CH_4/CO_2 over the catalyst prepared by impregnation reveals that the reaction occurs only on the reduced catalyst, indicating that the active site is the reduced NiO. The CO and CO_2 were detected during the response to pulses of CH_4 over the catalyst already used in the CO_2 reforming of methane. This indicates that some of the Ni active sites, were oxidized by CO_2 during reaction. This means that CO_2 decomposes to CO and O. CO and CO_2 were also detected during the response of pulses of O_2 over the catalyst already employed in the CO_2 reforming of CH_4. This indicates that C species are formed during the reforming reaction; it is, therefore, possible that the reaction includes the CH_4 decomposition to C and H species. One can, therefore, propose the following mechanism:

$$CH_4 + Ni \rightarrow CH_{4(s)}$$

$$CH_{4(s)} + Ni \rightarrow \text{---} \rightarrow C_{(s)} + 4H_{(s)}$$

$$CO_2 + Ni\ (\text{or MgO}) \rightarrow CO_{2(s)}$$

$$CO_{2(s)} + Ni \rightarrow O_{(s)} + CO_{(s)}$$

$$O_{(s)} + C_{(s)} \rightarrow CO_{(s)}$$

$$CO_{(s)} \rightarrow CO_{(g)} + Ni$$

$$H_{(s)} + H_{(s)} \rightarrow H_{2(s)} \rightarrow H_{2(g)} + Ni$$

$$H_{(s)} + O_{(s)} \rightarrow OH_{(s)}$$

$$OH_{(s)} + H_{(s)} \rightarrow H_2O_{(s)} \rightarrow H_2O_{(g)}$$

5. Conclusions

The NiO/MgO catalyst prepared by impregnation, which has very high activity and stability in the CO_2 reforming of methane, was studied by XRD, XPS, BET and pulse-MS response and compared with the catalyst prepared by mechanical mixing of the two oxides. We found that a calcination time of 1.5 h was long enough for the entire NiO to form a solid solution with MgO in the catalyst prepared by impregnation. In contrast, only a fraction of NiO formed a solid solution with MgO in mechanical mixtures of powders of NiO and MgO, even after 14 h of calcination. In the latter case, the amount of solid solution increased with calcination time. The rate of formation of CO in the CO_2 reforming of methane depends on the amount of NiO–MgO solid solution present in the catalyst; the greater the amount of solid solution, the higher is the rate of CO formation. The NiO/MgO catalyst prepared by impregnation had high stability, since the surface area and CO yield did not change either when the calcination time was increased from 1.5 to 20 h or with reaction time. The XPS analysis indicated the existence of electron transfer from NiO to MgO and of a surface enrichment in MgO. Probably the strong interactions between Ni and Mg inhibited both the sintering of NiO and MgO and the formation of the large clusters of Ni needed for coke deposition. The pulse-MS investigations suggested a possible mechanism for the CO_2 reforming of methane.

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