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THE ROLE OF Ni^{2+} DIFFUSION ON THE REDUCIBILITY OF NiO/MgO SYSTEM: A COMBINED TRP-XPS STUDY

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The progressive dissolution of nickel ions in the lattice of MgO matrix, promoted by the calcination temperature, has been monitored using XPS. The reducibility of Ni/MgO catalysts is affected by the modification of the surface chemical composition. TPR peaks have been correlated with several NiO forms. Both XPS and TPR results indicate a different behaviour pattern for the supported and physically mixed NiO/MgO systems, and this has been attributed to the different available "contact area" between NiO and MgO. The formation of both "NiO rich" and "MgO rich" NiO-MgO solid solutions, with the tendency to evolve towards the "bulk" solid solution, has been invoked to explain the substantial changes in the TPR pattern of the different air calcined systems.

1. Introduction

The NiO/MgO system has been the subject of numerous papers dealing with its physico-chemical and catalytic properties [1–7]. In particular, the peculiarities of NiO-MgO solid solutions have been extensively investigated [6–7]. Several studies using temperature programmed reduction (TPR) have previously shown the influence of calcination temperature (T_C) on the reduction profile of NiO/MgO system [3,8–9]. In order to explain the complex interaction pattern, emerging from these TPR studies, the diffusion of Ni^{2+} ions on the surface and in the bulk of MgO matrix has been invoked [8–9]. Bond and Sarsam [9], studying the reduction of Ni/MgO catalysts, emphasized the influence of the Ni precursor and preparation method on the location and subsequent reduction of the Ni^{2+} ions. Although a great effort has been devoted to characterizing these systems, a systematic investigation dealing with the effects of calcination temper-

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ature on the diffusion of NiO is still lacking. Our aim is to assess, by means of a comparative TPR and XPS study, the role of Ni^{2+} diffusion on NiO reducibility in both supported and mechanically mixed NiO/MgO systems.

2. Experimental

The supported nickel catalyst was prepared by the incipient wetness method, according to the procedure described elsewhere [8], using MgO "smoke" powder (UBE Ind. Ltd., Japan, average particle size, 50 nm; S.A., 34 $m^2 \cdot g^{-1}$; pore volume, 0.023 $cm^3 \cdot g^{-1}$) as support. NiO-MgO physical mixture was prepared by mixing predetermined amounts of NiO (obtained by thermal decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ at 400 °C in an air-stream) and MgO UBE powder. The Ni/MgO catalyst (MPF 12) and the NiO-MgO physical mixture (PM) were dried overnight at 120 °C and then air-calcined for 16 h at temperature (T_C) ranging from 400 °C (MPF 12-4, PM-4) to 1000 °C (MPF 12-10, PM-10). Nickel contents of the MPF 12 and PM samples, determined by atomic adsorption spectroscopy (AAS), are respectively 18.0 and 13.3 wt%.

TPR tests were carried out in the temperature range 100–1000 °C by using a linear quartz gradientless microreactor and a 5.2% hydrogen in nitrogen mixture, flowing at 60 (STP) $ml \cdot min^{-1}$, with a heating rate of $10\,°C \cdot min^{-1}$. Sample weight was set in order to keep hydrogen consumption less than 5%, so to avoid mass-transfer limitations [10].

The samples for XPS measurements were prepared in form of pellets by pressing at 10 ton the original powders. XPS measurements were performed using a KRATOS ES 300 apparatus operating in Fixed Retarding Ratio mode (retard ratio 1/23). Unmonochromatized Al K_α radiation was used with 15 kV · 15 mA X-ray power. The residual pressure during the experiments was less than 10^{-9} Torr. The binding energy (B.E.) scale was calibrated in order to obtain 84.0 eV for the Au $4f_{7/2}$ peak on a clean Au foil. In these conditions the C 1s line, from "adventitious" carbon falls at 285.0 eV (B.E.). Peak intensities have been measured as integrated areas, after background removal. The Ni 3p peak intensities were corrected for the contribution of the overlapping Mg 2s satellite excited by Al $k_{\alpha 3,4}$ radiation. Quantitative compositions have been evaluated by considering that the peak intensity I_i is proportional to the atomic concentration n of the element considered:

$$I_i \propto A \cdot \sigma_i \cdot \lambda_{(E)} \cdot n$$

where σ_i is the theoretical [11] differential cross section, A an instrumental factor and $\lambda_{(E)}$ is the inelastic mean free path of the photoelectrons in the sample. The above relationship is valid for homogeneous materials. Dealing with an unknown depth distribution of an element into a matrix, n has to be interpreted as an average concentration over the sampled depth.

3. Results and discussion

TEMPERATURE PROGRAMMED REDUCTION

Since TPR is a powerful technique to investigate the solid state reactions involving a reducible oxide and an insulating support oxide, the TPR measurement have been performed in both quantitative and qualitative modes. Figure 1 shows the reduction profiles of (A) MPF 12 catalyst (Ni/MgO, 18.0 wt% Ni) and (B) PM samples (NiO-MgO, 13.3 wt% Ni) both air calcinated at various T_C. The notation used to identify the heat-treated samples, the temperature of TPR peak maxima (T_M) and NiO reducibility, as derived from hydrogen consumption up to 1000 ° C, are listed in table 1. Bulk NiO showed a single reduction peak with a maximum at 367 ° C, while magnesia support did not show any hydrogen consumption under our experimental conditions. Figure 1A clearly indicates the marked influence of T_C on the reduction pattern of Ni/MgO catalyst. Furthermore, two separate regions of hydrogen consumption can be distinguished: (1) a low temperature region (LTR) from 100 to 550 ° C and (2) a high temperature region (HTR) from 550 up to 1000 ° C. In particular, the following main features can be pointed out:

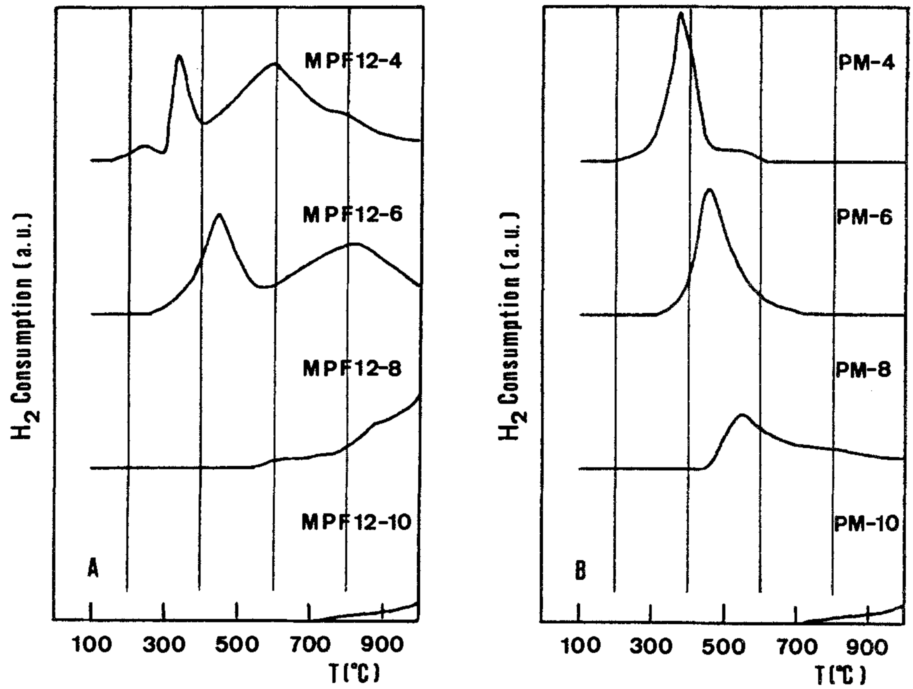

Fig. 1. TPR profiles of (A) MPF 12 catalyst (NiO/MgO, 18 wt% Ni) and (B) PM sample (NiO-MgO, 13.3 wt% Ni) air calcinated at different T_C. A: MPF 12-4 ($T_C = 400$ ° C); MPF 12-6 ($T_C = 600$ ° C); MPF 12-8 ($T_C = 800$ ° C); MPF 12-10 ($T_C = 1000$ ° C). B: PM-4 ($T_C = 400$ ° C); PM-6 ($T_C = 600$ ° C); PM-8 ($T_C = 800$ ° C); PM-10 ($T_C = 1000$ ° C).

Table 1
Temperature programmed reduction of NiO/MgO systems

Sample	T_C [a] (°C)	LTR		HTR		$NiO_{red.}$ [b] (%)
		T_{M1} (°C)	T_{M2} (°C)	T_{M3} (°C)	T_{M4} (°C)	
MPF 12-4	400	260	340	590	738	74
MPF 12-6	600	–	450	823	–	62
MPF 12-8	800	–	–	–	–	20
MPF 12-10	1000	–	–	–	–	3
PM-4	400	–	367	–	–	100
PM-6	600	–	425	–	–	100
PM-8	800	–	528	–	–	78
PM-10	1000	–	–	–	–	3

[a] All the samples were calcined at the listed temperature for 16 h.
[b] NiO reducibility as derived from hydrogen consumption up to 1000 °C.

(i) the reduction pattern of the sample MPF 12-4 is characterized by onset of four peaks (T_{M1}-T_{M4}) which have been attributed to different forms of NiO [12];

(ii) the T_{M1} peak at 260 °C disappears for any T_C higher than 400 °C;

(iii) the T_{M2} peak shifts to higher temperature and broadens upon increase of T_C from 400 to 600 °C;

(iv) NiO reducibility decreases monotonically from 74% for a T_C of 400 °C (MPF 12-4) to 3% for the sample calcined at 1000 °C (MPF 12-10).

The reduction pattern of the catalyst MPF 12-4 (fig. 1A) can be explained by invoking various states of NiO-MgO interaction leading to several "forms" of NiO on the surface and in the bulk of the MgO structure. Firstly, the T_{M1} peak is ascribable to the reduction of surface non-stoichiometric Ni^{3+} to Ni^{2+} [6] as undoubtedly denoted by the change in the colour from black to light-green. The occurrence of this peak is further correlated with the black "Ni_2O_3" clearly visible on the sample MPF 12-4 against the progressively paler green "NiO" observed for MPF 12-6, MPF 12-8 and MPF 12-10 catalysts. These evidences seem to indicate that at T_C higher than 400 °C Ni^{3+} decomposed to Ni^{2+} [9,13]. While the sharp peak at 340 °C (T_{M2}) of MPF 12-4 catalyst is due to the reduction of "unreacted" NiO on the surface, this NiO form being essentially uninfluenced by the MgO support [12]. The corresponding T_{M2} peak of MPF 12-6, centered at 450 °C, indicates for this sample the occurrence of some interaction between the "free" ("unreacted") NiO and the MgO support. This stronger interaction yields a NiO form that is more difficult to reduce. On the other hand, as MPF 12-8 and MPF 12-10 samples show a little, if any, hydrogen consumption in the LTR, we can conclude that, at any T_C higher than 600 °C, the most reactive forms of NiO have undergone a progressive diffusion into the MgO lattice, likely forming a "bulk" NiO-MgO solid solution.

Considering now the HTR on MPF 12-4 catalyst we note a substantial hydrogen consumption with a peak maximum at 590 ° C (T_{M3}). This peak, in accordance with the literature [7,9], can be assigned to the reduction of Ni^{2+} ions having square-pyramidal coordination in the outermost layer of the MgO structure. In addition, the less pronounced peak at 738 ° C (T_{M4}), appearing as a shoulder of the T_{M3} peak, indicates the reduction of Ni^{2+} ions located in the sub-surface layers of the MgO lattice [7]. The remaining fraction of NiO, reducible at T higher than 1000 ° C, is attributable to Ni^{2+} ions dissolved in the MgO matrix, forming a "bulk" NiO-MgO solid solution. Moreover, the enhanced NiO-MgO interaction induced by calcining at 600 ° C (MPF 12-6 sample) is apparent from the shift of the T_{M3} peak (823 ° C) in the HTR. Finally, the incipient slight consumption in the HTR of MPF 12-8 and MPF 12-10 is taken as evidence of the deep diffusion of Ni^{2+} ions into the MgO bulk, which renders very difficult their surface segregation and the consequent reduction [8].

For the NiO-MgO physical mixture (PM) it can be seen that as T_C is increased the reduction peak becomes progressively asymmetric and broad and the T_M shifts towards higher values. Since the reduction peak of PM-4 sample is analogous to that observed for the bulk NiO ($T_M = 367$ ° C), we can infer that a partial interaction between NiO and MgO, occurring for $T_C > 400$ ° C, is responsible for T_M increasing from 367 ° C (PM-4) to 425 ° C (PM-6). This interaction is likely to be related to the incipient diffusion of Ni^{2+} ions on the MgO surface, without alteration of the overall reducibility (100%). Indeed, the reduction pattern of PM-8 sample is characterized by a broad peak ($T_M = 528$ ° C), tailed towards higher T which denotes a reduction process evolving with a lower rate. This, together with the simultaneous decrease of NiO reducibility (see table 1) are a result of the partial formation of "bulk" NiO-MgO solid solution. The unreducible "ideal" solid solution is stabilized at 1000 ° C as indicated by the slight H_2 consumption of the PM-10 sample.

X-RAY PHOTOELECTRON SPECTROSCOPY

Air calcination of the supported system produces marked changes both in relative intensities and binding energies of XPS spectrum. We shall discuss these topics in the following. Figure 2 compared the Ni $2p_{3/2}$ photoelectron peaks of the MPF 12 catalysts along with that of a NiO sample (see experimental). We note a progressively change in the shape of the Ni $2p_{3/2}$ peak with a considerable sharpening as indicated by the FWHM decrease from ca. 3.9 eV for the "bulk" NiO and MPF 12-4 catalyst to 2.6 eV for MPF 12-10 sample ($T_C = 1000$ ° C), whose peak appears fairly symmetric. It is to note that the peak shape of the MPF 12-4 sample is still somewhat similar to that of the "bulk" NiO, the main difference being a more pronounced shoulder on the high B.E. side of the Ni 2p main peak; this should is at least attributable to $Ni(OH)_2$ and/or to Ni^{3+} defective sites on nickel oxide lattice [13-16]. In addition to the change in the

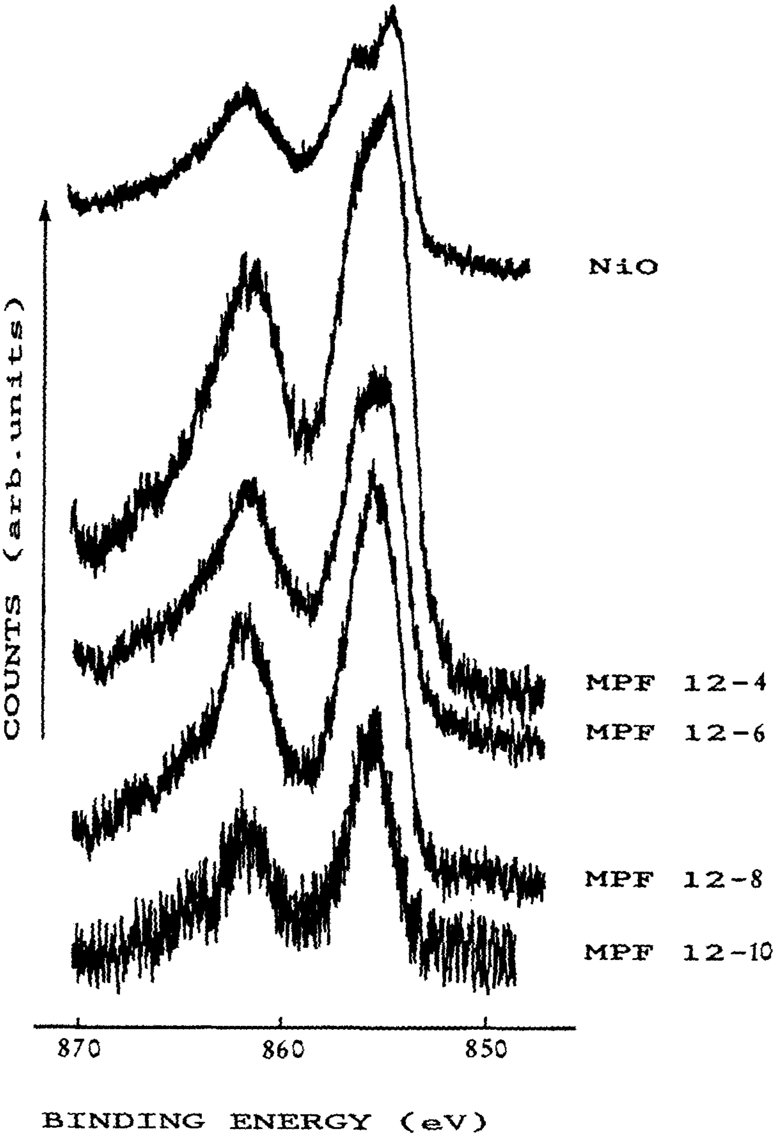

Fig. 2. XPS spectra of MPF 12 catalyst air calcined at different T_C and "bulk" NiO. Ni $2p_{3/2}$ region.

peak shape we observe a progressive B.E. shift in the Ni 2p peak, which amounts to 1.1 eV on going from MPF 12-4 to MPF 12-10 catalyst. Both the changes in the peak shape and B.E. can be interpreted by invoking the formation of a solid solution induced by the high temperature treatment. Indeed it is known [4] that the Ni 2p photoelectron spectra of $Ni_xMg_{(1-x)}O$ ($x < 0.5$) solid solutions do not exhibit the shoulder (B.E. 1.7 eV higher than that of the Ni 2p main peak) characteristic of the NiO [14–15]. In the same paper, however, no B.E. shift for the Ni 2p peak of the solid solution, with respect to the NiO, was reported [4]. By contrast, a more recent work [5] reports evidence for a B.E. value of Ni 2p main peak of NiO-MgO HSA solid solution higher than that found in NiO. Moreover the reported B.E. difference between the Ni 2p main peak and the "lattice component" of O 1s band (325.7 eV) [5] well agrees with the figure we find on the MPF 12-10 sample. All of this strongly suggests that the MPF 12-10 sample is a solid solution, whereas the MPF 12-4 catalyst mainly retains the features of a more or less defective NiO. The MPF 12-6 and MPF 12-8 samples represent intermediate surface situations, the former looking still similar to MPF 12-4 and the latter closely resembling to MPF 12-10 situation (fig. 2).

In the case of the PM samples, we observe a similar trend in the evolution of the XPS spectrum with T_C. However, the modification occurs at higher T_C: at 1000 °C, for instance, the Ni 2p FWHM is 3.0 eV and the B.E. shift amounts to 0.8 eV; these figures have to be compared respectively with 2.6 and 1.1 eV pertaining to the MPF 12-10 sample, which was calcined at the same T_C.

XPS has been also used to gain information on the changes in the depth distribution of Ni in the magnesia matrix owing to air calcination treatment. Because of the rough nature of the surfaces, no attempt was made to obtain concentration profiles by coupling XPS with ion etching. For this reason we tried to achieve information on the nickel profile over the sample depth of XPS technique.

Figure 3 reports the trend of the Ni 2p/Mg 2p atomic ratio with T_C for the supported (MPF 12 series) and physically mixed systems (PM series). In the case of MPF 12 samples the ratio decreases monotonically with T_C, till to reach at

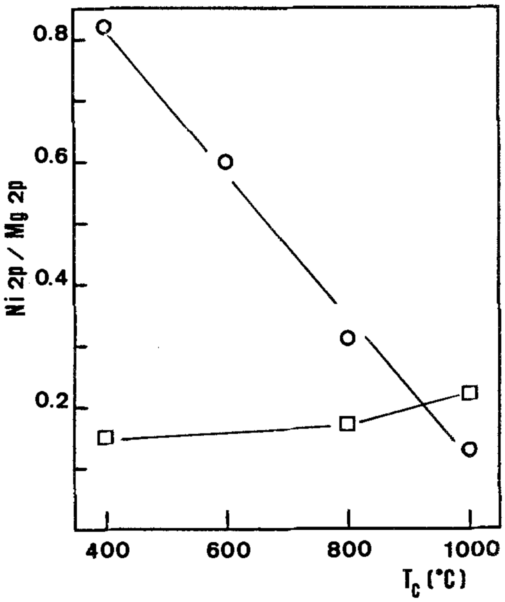

Fig. 3. Effect of T_C on the Ni 2p/Mg 2p atomic ratio (XPS) for: (○) MPF 12 catalyst and (□) PM sample.

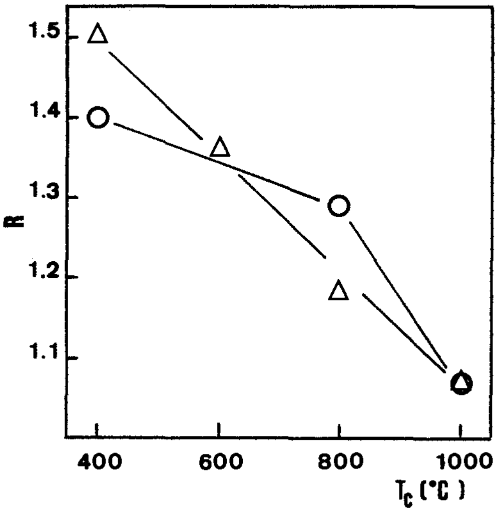

Fig. 4. Effect of T_C on the Ni 3p/Ni 2p photoelectron ratio (R) for: (△) MPF 12 catalyst and (○) PM sample.

1000 °C a value very close to that expected for a homogeneous NiO-MgO ideal mixture, having the nominal bulk composition of the MPF 12 sample (18.0 wt% Ni). The observed Ni depletion is consistent with an intermixing between NiO and MgO promoted by the thermal treatment, which leads to a progressively lower Ni concentration with respect to Mg in the sampled thickness. By contrast, in the PM samples T_C does not affect the Ni/Mg atomic ratio, which close to that expected for a homogeneous mixture (13.3 wt% Ni). Only a slight increase is observed at 1000 °C likely reflecting some incipient dispersion of NiO on the MgO surface.

Additional information can be extracted from XPS measurements by exploiting the different sampling depth of the Ni 2p and Ni 3p photoelectrons. Indeed, due to the different kinetic energy of Ni 2p and Ni 3p electrons (respectively 620 eV and ca. 1400 eV), it can be estimated that Ni 3p electrons have a sampling depth ca. 1.9 times higher than Ni 2p electrons. If in a given sample the Ni profile was flat throughout all the sampled thickness by the Ni 3p electrons, we should find identical values for the Ni atomic concentration independently of the Ni peak used for quantification. A concentration ratio $R = n\,(\text{Ni 2p})/n(\text{Ni 3p}) > 1$ indicates that the outermost surface layers are more Ni rich than the layers below, whereas a R value less than unity is diagnostic of a surface depletion. In fig. 4 the ratio R is plotted vs T_C for both the MPF 12 and PM samples. In the MPF 12 samples R decreases straightforwardly with the T_C accounting for the progressive diffusion of the Ni in the matrix and/or the Mg "migration" towards the surface with the consequent elimination of the initial concentration gradient; at 1000 °C (MPF 12-10) a value very close to unity is found, indicating a flat profile, likely connected with the formation of a homogeneous "bulk" solid solution.

In the PM series, on the other hand, T_C has a slight effect on R up to 800 ° C. Only above this temperature R significantly decreases. This behavior seems to confirm that the diffusion processes become valuable at high T_C and well agrees with TPR results showing a dramatic change in the PM samples calcined at T_C higher than 800 ° C.

FINAL REMARKS

Our experimental results show that the NiO/MgO system, air-calcinated at high temperature, exhibits the peculiarity to *intermix* up to 1000 ° C forming a "steady-state" corresponding to an "ideal" solid solution. The structural rearrangement renders the system progressively less reducible affecting substantially its reduction pattern. The correlation between the TPR reducibility (up to 1000 ° C) and the Ni 2p/Mg 2p peak intensity ratio, depicted in fig. 5, leads to the following conclusions:

- for a T_C increase from 400 to 600 ° C the Ni 2p/Mg 2p ratio steadily decreases and the reduction kinetics reflect an enhanced NiO/MgO interaction. Namely, the slight lowering in NiO reducibility with respect to the Ni 2p/Mg 2p decrease and also the shift of the T_{M2} peak (LTR) indicates the "transformation" of the "free" NiO form (MPF 12-4) in a surface that is "NiO rich" due to the diffusion of Mg^{2+} ions towards the surface NiO structure. Moreover the T_{M3} peak (HTR) of MPF 12-4, and its significantly shift for the MPF 12-6 sample, can be ascribed to the reduction of a surface "MgO rich" solid solution displaced from the surface to the sub-surface layers at higher T_C;

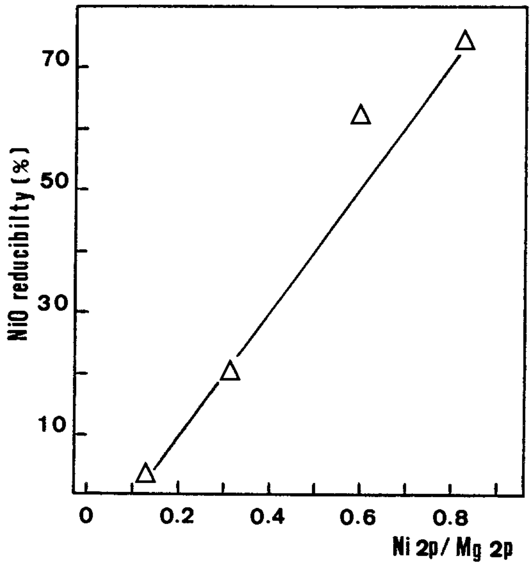

Fig. 5. Correlation between the NiO reducibility (TPR) and the Ni 2p/Mg 2p atomic ratio (XPS) of MPF 12 catalyst air calcined at different T_C.

– for T_C higher than 600 ° C surface NiO forms (LTR peaks) disappear, diffusing with the other forms (HTR peaks) in the bulk structure of magnesia. Accordingly, a dramatic decrease of the Ni 2p/Mg 2p ratio is found. Therefore, little if any hydrogen consumption in the LTR is observed for MPF 12-8 and MPF 12-10 catalysts and the incipient reduction in the HTR indicates the formation of a "bulk" NiO-MgO solid solution.

In contrast, the TPR profiles of PM samples, air calcined up to 800 ° C, show only a T_M peak shifted to higher T in the LTR and the absence of a well defined H_2 consumption in the HTR. This is attributed to the small "contact area" between NiO and MgO, which hinders a wide distribution of NiO into the MgO matrix, allowing the preferential formation of a surface "NiO rich" solid solution in the T_C range 600–800 ° C. Therefore the TPR patterns of the PM samples further strengthen our hypothesis concerning the role of T_C in stabilizing several kinds of NiO-MgO solid solutions: a) a surface "NiO rich" MgO-NiO solid solution reducible in the LTR; b) a surface "MgO rich" NiO-MgO solid solution reducible in the HTR; c) a "bulk" NiO-MgO solid solution, reducible at T higher than 1000 ° C.

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