

Effect of calcination on the structure of Ni/MgO catalyst: An X-ray diffraction study

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The progressive diffusion of Ni²⁺ ions into the MgO matrix, with the consequent formation of an Ni_xMg_(1-x)O solid solution, occurring during the air calcination of a 19% Ni/MgO catalyst in the range 400–1000 °C, has been monitored by X-ray diffraction (XRD) measurements using monochromatized non-doublet synchrotron radiation. A solid-state reaction model accounting for the NiO–MgO interaction in supported and mechanically mixed systems is discussed.

The solid-state reactions occurring between active phase and support during calcination generally determine the surface and structural properties and the reactivity of supported oxide catalysts. When the matrix of the support is able to incorporate transition-metal ions in solid solutions the rationalisation of such interaction becomes rather complicated. In this respect, the NiO–MgO system constitutes a very interesting model since NiO and MgO form ‘ideal’ solid solutions over the whole molar fraction range and have singular catalytic properties.^{1–4} In our previous papers we have ascertained the effects of the calcination and reduction temperature on the reducibility,^{5,6} metal dispersion⁷ and surface chemical properties⁸ of MgO-supported Ni catalysts. Moreover, from an X-ray photoelectron spectroscopy (XPS) study of an 18% Ni/MgO catalyst air-calcined in the temperature range 400–1000 °C the progressive diffusion of Ni²⁺ ions across the MgO lattice has been monitored.^{6,7} On the basis of those findings, it was claimed that, at 1000 °C, such a diffusion process leads to the formation of an irreducible Ni_xMg_(1-x)O solid solution.⁶

The suitability of the Ni/MgO system as a real catalyst in the CH₄ steam-reforming process has also been assessed.^{6,7} We showed that the preparation method, the Ni loading, the calcination and reduction treatments are crucial for inhibiting the dissolution of NiO into the MgO lattice which limits the reducibility of NiO and the availability of the active Ni phase.^{6–9} Such unique features of the title system, giving rise to Ni/MgO catalysts having a wide range of metal dispersion (i.e. 1–90%),⁶ allowed us also to demonstrate the structure sensitive character of the CH₄ steam-reforming reaction.⁷

This XRD study aims to provide additional insights into the structure modifications induced by the calcination treatment in a ‘real’ Ni/MgO catalyst.

Experimental

Supported nickel on magnesia catalyst (MPF 12) was prepared by the incipient wetness impregnation method, according to the procedure described elsewhere,⁵ using a toluene solution of Ni acetylacetonate and MgO ‘smoke’ powder [UBE Ind. Ltd, Japan, average particle size 50 nm; pore volume, 0.023 cm³ g^{−1}; surface area (BET), 34 m² g^{−1}] as support. After impregnation and drying of the MPF 12 sample several aliquots were calcined in air flow for 16 h at 400 (MPF 12-4), 600 (MPF 12-6), 700 (MPF 12-7), 800 (MPF 12-8) and 1000 °C (MPF 12-10).

NiO–MgO physical mixture (PM) was prepared by mechanical mixing of the ‘smoke’ powder MgO and NiO powder

(obtained by thermal decomposition of the Ni(NO₃)₂·6H₂O at 400 °C under an air stream). The PM sample was then air calcined at 400 °C for 16 h (PM-4). The nickel content of the MPF 12 and PM samples is 18.0 and 13.3 wt.%, respectively.

XRD measurements were carried out at the Siberian Synchrotron Radiation Centre using a high-resolution powder diffractometer¹⁰ with monochromatized non-doublet synchrotron radiation, wavelength $\lambda = 1.7188$ Å. The lattice parameters of MgO and NiO were calculated from the relative (420) reflections. The calibration of their position, the precise determination of the wavelength and instrumental broadening were made using the (531) reflection of silicon as internal standard. The instrumental broadening for $2\theta = 130$ – 135° was as much as $\Delta(2\theta) \approx 0.12^\circ$. The estimate of the extent of Ni²⁺ dissolved into the MgO lattice was calculated on the basis of the value of the MgO lattice parameter (a) from the equation:

$$a = \sqrt{(h^2 + k^2 + l^2)} \frac{\lambda}{2 \sin \theta} \quad (1)$$

assuming a linear variation of a between the values of 4.212 and 4.1769 Å, corresponding to pure MgO and NiO, respectively. The XRD spectra were analysed by the Pearson VII function using a least-square method. The R -value for all the measurements was at least 3–4%. Under the adopted conditions the lattice parameter of MgO was determined with an accuracy better than 0.0001 Å. No attempt was made to calculate the extent of Mg²⁺ dissolved into the NiO lattice, as the lattice parameter of NiO depends strongly on both the calcination temperature¹¹ and the presence of residual traces of anions within the structure.¹²

Results and Discussion

XRD spectra in the range $2\theta = 130$ – 135° of (a) the PM-4 sample and (b)–(f) MPF 12 catalyst, air calcined in the range 400–1000 °C, are shown in Fig. 1. The values of the MgO and NiO peak position (2θ /degrees), lattice parameters (a /Å) and full width at half maximum (FWHM/degrees) together with the relative composition of the MgO-based NiO–MgO solid solution are summarised in Table 1. It can be seen that the PM-4 sample [Fig. 1(a)] shows two well resolved XRD peaks at 131.71 and 133.6° (2θ) ascribable to MgO and NiO lattice reflections, respectively. The value of the MgO lattice parameter of this sample (see Table 1), corresponding to that of the pure MgO (4.2120 Å), rules out the occurrence of any interaction between Ni²⁺ ions and the MgO lattice.^{6,8} By contrast, the MPF 12-4 catalyst displays an XRD peak, relative to the

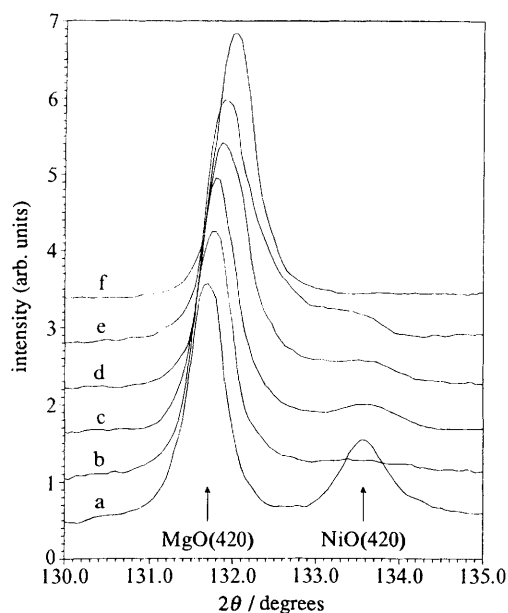


Fig. 1 XRD patterns of (a) PM-4 sample air calcined at 400 °C and MPF 12 catalyst air-calcined at (b) 400 °C (MPF 12-4); (c) 600 °C (MPF 12-6); (d) 700 °C (MPF 12-7); (e) 800 °C (MPF 12-8) and (f) 1000 °C (MPF 12-10)

MgO lattice reflection, slightly shifted to a higher 2θ value with respect to that of the pure MgO (131.73°) while no peak connected with the presence of NiO crystals ($2\theta = 133.5^\circ$) is detected [Fig. 1(b)]. Therefore, according to our previous characterisation findings,⁶ such XRD features further account for the differences in the morphological properties of MPF 12-4 and PM-4 systems linked with their different preparation methods. Indeed, the presence of a well resolved NiO peak in the XRD spectrum of the PM-4 sample [Fig. 1(a)], as well as the negligible H_2 chemisorption capacity of this system with respect to that of the MPF 12-4 catalyst,⁶ undoubtedly signal the presence of highly sintered crystalline NiO particles (*ca.* 10^3 Å) formed during the thermal decomposition of the NiO precursor [*i.e.* $Ni(NO_3)_2 \cdot 6H_2O$]. These results evidently contradict the statements of Narayanan and Sreekanth which, invoking the experimental difficulties in distinguishing between MgO and NiO peaks in their XRD patterns of the Ni/MgO system,¹³ concluded that the poor H_2 uptake of the NiO–MgO PM system arises from the fact that reduced Ni clusters are buried in the bulk of MgO lattice rather than from the very low metal dispersion of large Ni particles ‘available’ on the surface of the MgO matrix.¹³ On the other hand, the good agreement between transmission electron microscopy (TEM) and H_2 chemisorption estimates of the surface average Ni particle size in Ni/MgO catalysts⁷ leads us to exclude the occurrence of any geometric effect induced by the support on the reduced metal phase. Moreover, the absence of any NiO peak in the XRD spectrum of the MPF 12-4 system [Fig. 1(b)] confirms that the NiO phase is spread on the surface of the MgO support in an amorphous and highly dispersed form, which exhibits a rather high H_2 chemi-

sorption capacity after reduction at low temperature (300–400 °C).⁶

The progressive shift of the MgO peak position towards higher 2θ values and the consequent decrease in the MgO lattice parameter with T_c observed for the MPF 12 sample (Table 1) strengthens our previous hypotheses on the diffusion of Ni^{2+} ions across the MgO lattice.^{5–7} In fact, upon increase of T_c from 400 to 600 °C [Fig. 1(c)], the MgO XRD peak moves further to higher 2θ values, accounting for the formation of higher extents of MgO-based NiO–MgO solid solution on the MPF 12-6 catalyst (Table 1). Whereas, the appearance of a small peak at 133.7° , characteristic of the presence of NiO, signals the occurrence of a sintering process during calcination at 600 °C which, in competition with the diffusion of the Ni^{2+} ions into the MgO lattice, affects the morphology of the surface NiO.^{6,8,9} At $T_c > 600$ °C [Fig. 1(d) and (e)], the MgO and NiO XRD peaks shift to higher and lower 2θ values, respectively, demonstrating the increasing mutual dissolution of Ni^{2+} and Mg^{2+} ions into MgO and NiO lattices, respectively. These results account for the formation of two kinds of solid solutions according to our previous temperature-programmed reduction (TPR)–XPS evidence;⁶ namely an ‘easily reducible’ NiO-based MgO–NiO solid solution and a ‘hardly reducible’ MgO-based NiO–MgO solid solution.^{6–9} Finally, at $T_c = 1000$ °C [Fig. 1(f)] both MgO and NiO XRD peaks disappear and one single peak in an intermediate position ($2\theta = 132.09^\circ$) is diagnostic of the formation of the substitutional $Ni_xMg_{1-x}O$ solid solution^{8,9} with the atomic composition $Ni_{0.20}Mg_{0.80}O$ (Table 1). Such an experimental composition, slightly larger than the theoretical one ($Ni_{0.14}Mg_{0.86}O$) of the MPF 12 catalyst indicates a slight Ni^{2+} enrichment of the substitutional solid solution likely due to a residual depth profile in the Ni^{2+} concentration across the MgO particles. Further, the larger FWHM value of the MgO reflection peak in the MPF 12 catalysts with respect to that of the PM-4 sample indicates that the crystalline habit of the MgO support is perturbed by the addition of the Ni precursor. In fact, the diffusion of Ni^{2+} in the MgO lattice, mainly at lower T_c (≤ 800 °C), should imply concentration inhomogeneities and local defects in the MgO structure which overlap sintering effects generally resulting in a sharpening of the XRD reflex peak. At $T_c > 700$ °C, the increasing diffusion rate of Ni^{2+} towards the core of the MgO particles tends to stabilize an ideal solid solution having a progressively more homogeneous composition accounting then for the decrease in the FWHM value (see Table 1). However, the considerations based on the analysis of FWHMs of the MgO peak are qualitative since only the (420) reflection was analysed. No comments can be made about the FWHM variations of NiO peak with T_c (Table 1) because of the weak intensity of such XRD peaks (Fig. 1) and the consequent high uncertainty in the determination of this parameter.

Therefore, the above results allow us to propose the comprehensive solid-state model, shown in Fig. 2, for the NiO–MgO physical mixture (a) and Ni/MgO catalyst air calcined at T_c ranging between (b) 400 and (e) 1000 °C. In particular, the poor metal dispersion of the PM-4 sample [Fig. 2(a)], showing NiO crystallites with a size comparable with

Table 1 XRD characterisation of the 13.3% NiO–MgO physical mixture (PM) and 18% Ni/MgO catalyst (MPF 12) air-calcined at different T_c

sample	$T_c/^\circ C$	MgO XRD parameters			NiO XRD parameters			composition of MgO-based NiO–MgO solid solution
		$2\theta/\text{degrees}$	$a/\text{\AA}$	FWHM/degrees	$2\theta/\text{degrees}$	$a/\text{\AA}$	FWHM/degrees	
PM-4	400	131.70	4.2120	0.497	133.61	4.1814	0.671	MgO
MPF 12-4	400	131.73	4.2114	0.525	—	—	—	$Ni_{0.03}Mg_{0.97}O$
MPF 12-6	600	131.79	4.2105	0.514	133.77	4.1791	0.77	$Ni_{0.05}Mg_{0.95}O$
MPF 12-7	700	131.87	4.2093	0.581	133.50	4.1831	0.82	$Ni_{0.09}Mg_{0.91}O$
MPF 12-8	800	131.90	4.2088	0.562	133.31	4.1861	0.96	$Ni_{0.10}Mg_{0.90}O$
MPF 12-10	1000	132.10	4.2054	0.523	—	—	—	$Ni_{0.20}Mg_{0.80}O$

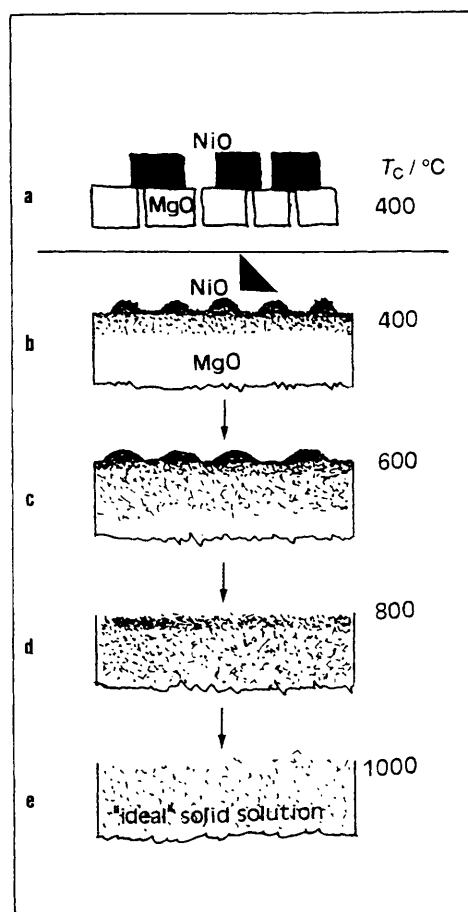


Fig. 2 Solid-state reaction model of (a) PM sample air-calcined at 400 °C and the MPF 12 catalyst air-calcined at (b) 400 °C (MPF 12-4); (c) 600 °C (MPF 12-6); (d) 800 °C (MPF 12-8) and (e) 1000 °C (MPF 12-10)

that of the MgO support (10^3 Å), in contrast with the supported MPF 12-4 system [Fig. 2(b)], characterised by the presence of small NiO clusters highly spread on the MgO

surface, should be noted. At $T_c \leq 800$ °C [Fig. 2(c) and (d)] the competition between sintering and the dissolution of the Ni^{2+} ions into the MgO matrix leads to a progressive decrease in the availability of the NiO phase.⁷ Finally, at 1000 °C [Fig. 2(e)] the Ni/MgO system reaches a stationary condition resulting in the formation of irreducible $\text{Ni}_x\text{Mg}_{(1-x)}\text{O}$ solid solution.

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References

- 1 A. Zecchina, G. Spoto, S. Coluccia and E. Guglielminotti, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1891.
- 2 A. P. Hagan, M. G. Lofthouse, F. S. Stone and M. A. Trevethan, in *Preparation of Catalysts II*, ed. B. Delmon, P. Grange and G. Poncelet, Elsevier, Amsterdam, 1979, p. 417.
- 3 J. G. Highfield, A. Bossi and F. S. Stone, in *Preparation of Catalysts III*, ed. G. Poncelet, P. Grange and P. A. Jacobs, Elsevier, Amsterdam, 1983, p. 181.
- 4 T. Borowiecki, *Appl. Catal.*, 1984, **10**, 273.
- 5 A. Parmaliana, F. Arena, F. Frusteri and N. Giordano, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2663.
- 6 F. Arena, A. Licciardello and A. Parmaliana, *Catal. Lett.*, 1990, **6**, 131.
- 7 F. Arena, B. A. Horrell, D. L. Cocke, A. Parmaliana and N. Giordano, *J. Catal.*, 1991, **132**, 58.
- 8 F. Arena, A. Parmaliana, N. Mondello, F. Frusteri and N. Giordano, *Langmuir*, 1991, **7**, 1555.
- 9 A. Parmaliana, F. Arena, F. Frusteri, S. Coluccia, L. Marchese, G. Martra and A. L. Chuvilin, *J. Catal.*, 1993, **141**, 34.
- 10 A. N. Shmakov, *Mater. Sci. Forum*, 1993, **133–136**, 361.
- 11 T. A. Krieger, L. M. Plyasova, T. M. Yurieva, T. P. Minyukova and A. V. Shkarin, *Izvest. Acad. Nauk. SSSR, Seria Khim.*, 1988, **19**, 76.
- 12 G. Chembar, P. Gregoire, P. Azon and P. Bastien, *C. R. Acad. Sci. Series C*, 1971, **272**, 226.
- 13 S. Narayanan and G. Sreekanth, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 943.

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