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XPS STUDY OF PHASE MOBILITY IN Ni/TiO$_2$ SYSTEMS

G. MUNUERA, A.R. GONZÁLEZ-ELIPE and J.P. ESPINÓS

Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad Sevilla) and Departamento Química Inorgánica, P.O. Box 1115, 41071 Sevilla, Spain

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The surface structure of the solid resulting from a partial reduction with H_2 at 873 K of polycrystalline $NiTiO_3$ has been examined by XPS in relation to the study of the strong metal support interaction (SMSI) in Ni/TiO$_2$ catalysts. The H_2-decomposed surface region consists of big Ni particles (~ 35 nm) encapsulated in a thick TiO_2 matrix. By Ar^+ etching the Ni particles become exposed at the surface, while a thin layer of the TiO_2 matrix is deeply reduced with formation of Ti^{3+} and Ti^{2+} species (O/Ti ratio ~ 1.7). Heating in UHV at 773 K leads to oxygen rearrangements between the bulk and this thin layer, a process that is greatly enhanced by heating the etched sample in the presence of H_2 (O/Ti ratio ~ 1.9). In addition, this treatment leads to nickel diffusion through the defective titanium oxide layer. The role of hydrogen in mobilizing the Ni and TiO_x phases is discussed.

1. Introduction

The interaction of group 8–10 metals (Ni, Pt, Rh, etc.) with reducible oxide supports such as TiO_2 has been a very active area of research in catalysis during the last ten years, owing to the generation of a strong metal support interaction (SMSI) when these systems are reduced at 773 K in hydrogen [1]. The existence of an "electronic interaction" [2] or the "decoration" of the surface of the metallic particles by TiO_x ($x < 2$) moieties [3–5] have been invoked to explain this SMSI state.

Recently, using a real polycrystalline Rh/TiO$_2$ catalyst, we have shown that hydrogen is essential to generate SMSI by enhancing the mobility within the reduced support [6]. For this process, formation of a H–TiO$_x$ phase by incorporation of hydrogen into the reduced TiO_x was found to be the keystone to produce migrating H–TiO$_x$ species onto the big Rh particles (~ 5 nm), while the presence of traces of water vapour seems to favour the diffusion, even at relatively low temperatures, of small Rh clusters in the bulk of the TiO_2 support [7].

In the present work, we have studied the factors controlling the mobilities of nickel and titanium oxide phases in a composite material formed by big Ni particles in a TiO_2 matrix (Ti/Ni atomic ratio ~ 1). The role of hydrogen in

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the diffusional processes has been examined using Ar^+ etched samples to deeply reduce the TiO_2 matrix [8] in the absence of hydrogen. Meanwhile, owing to the structure of the resulting material, any diffusional effect due to local electric fields can be ruled out. This is important since it has been recently shown by Ferrer et al. [9], using TiO_2 grown on a titanium foil, that electrostatic effects (i.e. the generation of a Mott–Cabrera capacitor) can be responsible for the diffusion of evaporated Pt or Au toward the TiO_2/Ti interface in this type of systems.

2. Experimental

Ventron GMBH (no. 53103) $NiTiO_3$ was used in this work as received. XRD spectra of the original sample and of the sample reduced in flowing H_2 (100 ml/min) at 873 K for 1 h were recorded with a Phillips diffractometer (model PW 1760) using Ni filtered copper radiation.

XPS spectra were recorded with a Leybold–Heraeus LHS-10 spectrometer working with constant pass energy at 50 eV and using the Al Kα radiation as excitation source. Binding energy (BE) reference was taken at the C(1s) line at 284.6 eV. A Shirley type [10] background subtraction was used for peak area calculation. The samples, in the form of pellets, were placed on a molybdenum holder that could be heated resistively while controlling the temperature by a thermocouple placed at its rear. Before any other treatment the sample was always outgassed at 773 K for 30 min to remove water and other volatile contaminants from the surface. Treatments in vacuo ($P < 10^{-8}$ Torr) or in H_2 (10 Torr) were performed “in situ” in the preparation chamber of the spectrometer where Ar^+ etching experiments could be carried out using an ion penning source working at 3.5 kV (estimated path length ~ 1.5 nm [11]).

3. Results

3.1. Hydrogen reduction of $NiTiO_3$

The XPS wide scan spectrum of the original $NiTiO_3$ material shows the existence of Ni, O and Ti ions in an almost stoichiometric composition, while signals due to C and K indicate the presence of these two elements as impurities.

Reduction with flowing H_2 of this material at increasing temperatures up to 873 K occurs according to the reaction:

$$NiTiO_3 + H_2 \rightarrow Ni + TiO_2 + H_2O, \qquad (1)$$

so that the XRD pattern after 1 h at 873 K shows a decrease by ~ 20% in the intensity of the original diffraction lines of the $NiTiO_3$ (illmenite) and the rise of new lines corresponding to metallic Ni and TiO_2 (rutile). The average particle size for the nickel particles, determined by the Scherrer method [12] from the width of the Ni(111) diffraction line, gives a value of ~ 35 nm.

Simultaneous XPS analysis of the reduced sample shows changes in the Ni(2p) and Ti(2p) peaks indicating a progressive reduction of nickel at the surface region from N^{2+} to Ni(0) (BE $\approx$ 855.6 and 851.9 eV) and a shift of the original Ti(2p) peak from 458.1 to 458.5 eV, corresponding to the rearrangement of the Ti^{4+} ions in the new TiO_2 phase at a thick surface layer of the reduced $NiTiO_3$. Meanwhile, the valence band spectrum of the reduced sample shows a displacement of the Ni(3d) density of states toward the Fermi level, thus confirming the decomposition of the outermost layers of the original sample in a Ni–TiO_2 composite material (estimated mean free path between 2.1 and 3.7 nm for electrons with ~ 1486 eV of kinetic energy [13]).

It is noteworthy that when the reduced sample is heated in UHV at $T > 573$ K, desorption of H_2 occurs indicating incorporation of hydrogen in the titanium oxide during the reduction step, as previously found for Rh/TiO_2 catalysts [6].

3.2. Ar^+-etching of reduced and unreduced $NiTiO_3$

Values for the I_{Ti}/I_{Ni} ratios (I intensities for the Ti(2p) and Ni(2p) peaks) recorded during the preparation of the Ni–TiO_2 material have been plotted in

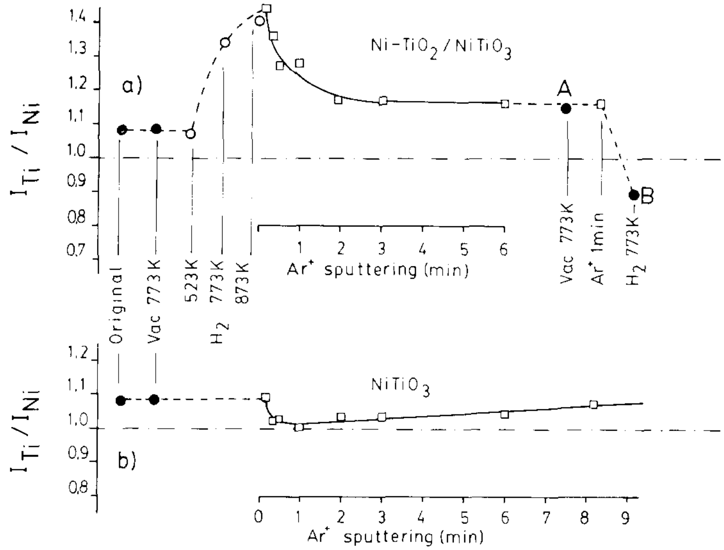

Fig. 1. Representation of the Ti/Ni intensities ratio for the $NiTiO_3$ sample: (a) reduced in H_2 at 523–873 K and then submitted to the indicated treatments; (b) directly submitted to Ar^+ etching.

fig. 1 together with those obtained after different Ar^+ etching and thermal treatments of this sample. In principle, the initial increase in the I_{Ti}/I_{Ni} values upon progressive H_2 reduction can be related to aggregation of the nickel to give big metallic particles, though encapsulation of these metallic particles by the segregated TiO_2 phase cannot be ruled out. In fact, Ar^+ etching experiments confirm that the Ni particles have become burried in the TiO_2 matrix during reduction, so that removal of the outermost layers leads to exposure of Ni particles. Once Ar^+ etching steady-state I_{Ti}/I_{Ni} values have been reached (after 6 min), heating under UHV at 773 K for 10 min does not modify this ratio (point A in fig. 1), while the same treatment in 10 Torr of H_2 produces an increase in the Ni(2p) intensity leading to a strong decrease of that parameter (point B) which is now even lower than in the original $NiTiO_3$ material where "atomic dispersion" of the Ni ions should be expected. For comparison, the effect of Ar^+ etching on the original $NiTiO_3$ material indicates a small Ti enrichment at the originial surface that is readily removed by sputtering. However, for longer periods of time a small but progressive increase in the I_{Ti}/I_{Ni} ratio occurs probably due to differential sputtering and/or segregation of the reduced phases. Total reduction of the nickel was

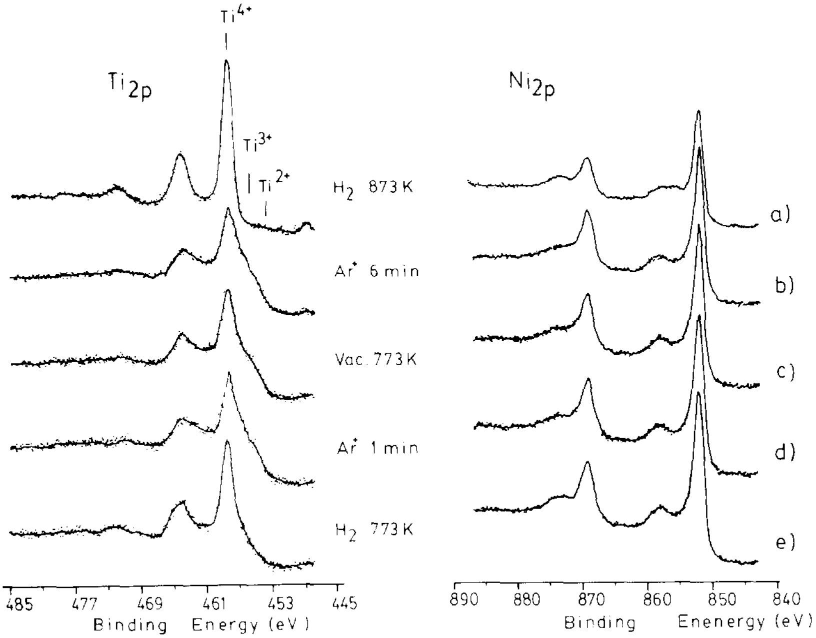

Fig. 2. Ni(2p) and Ti(2p) spectra of: (a) original sample reduced in H_2 at 873 K for 60 min; (b) submitted to Ar^+ etching for 6 min; (c) annealed at 773 K for 10 min; (d) submitted to Ar^+ etching for 1 min; (e) heated in H_2 at 773 K for 10 min.

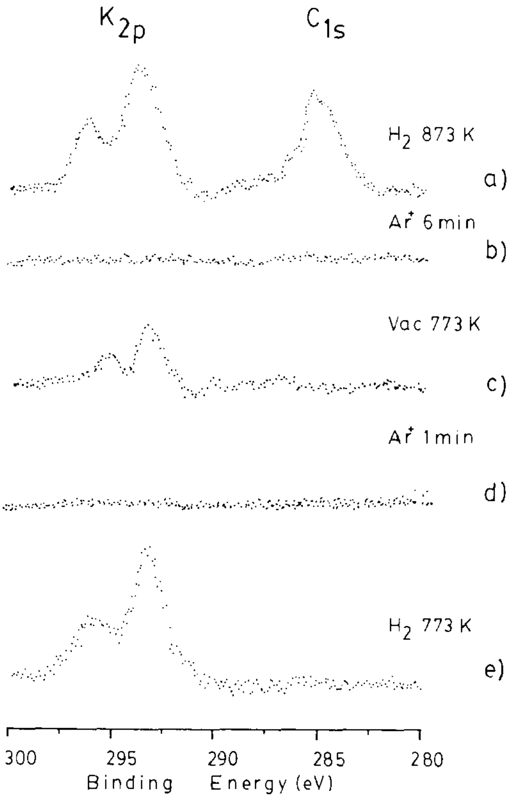

Fig. 3. C(1s) and K(2p) spectra of the sample submited to the same treatments as in fig. 1.

obtained after 6 min sputtering, what contrasts with Ar$^+$ etching data for NiO [14] where only partial reduction to metallic nickel occurs at 298 K under similar conditions.

In agreement with previous works [8,15], XPS spectra in fig. 2 for the H$_2$-reduced Ni–TiO$_2$ sample show that Ar$^+$ etching leads to a deep reduction of the TiO$_2$ matrix (O/Ti ratio ~ 1.7) with formation of Ti^{3+}/Ti^{2+} ions. A small decay in the concentration of these two species occurs by annealing at 773 K (O/Ti ratio ~ 1.8), and much more effectively by heating at the same temperature in 10 Torr of H$_2$ (O/Ti ratio ~ 1.9). These changes suggest the existence of diffusional processes between the deeply reduced surface thin layer of the TiO$_2$ and the bulk. Evidence of such diffusional processes can also be obtained from the XPS spectra of the K$^+$ impurities present in the original sample that can be used as a "probe" of ionic mobility within the titanium oxide lattice. As shown in fig. 3 the Ni–TiO$_2$ thick layer also contains K (and C) impurities, which are completely removed after Ar$^+$ etching. However,

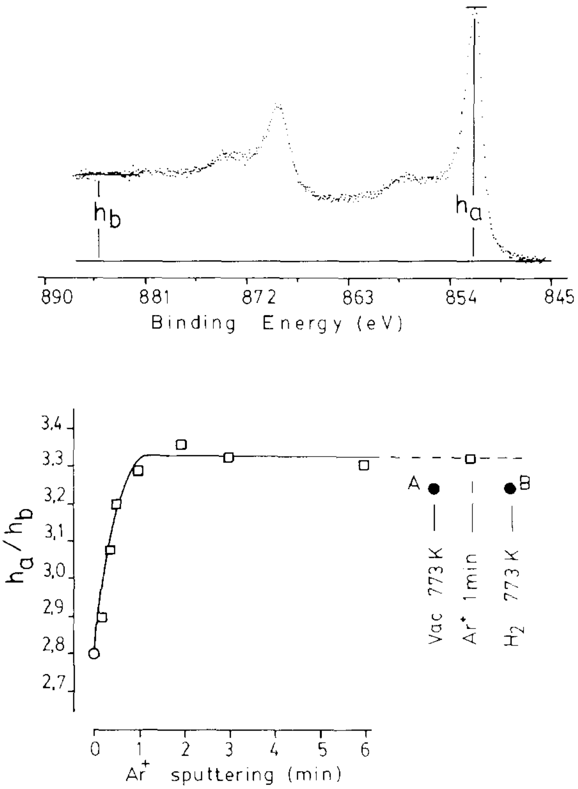

Fig. 4. Ni(2p) spectrum showing h_a and h_b parameters and plot of the h_a/h_b ratios for the sample submitted to the indicated treatments.

heating at 773 K under UHV produces a small new K(2p) signal, that after the treatment at 773 K in 10 Torr of H_2 recovers almost completely its original intensity, thus indicating an enhanced mobility of the "K^+ probe" in the presence of H_2. This effect is parallel to a strong decrease in the I_{Ti}/I_{Ni} ratio in fig. 1, corresponding to a net increase in the intensity of the Ni(2p) peaks in fig. 2, though, in principle, both phenomena might be not necessarily related.

To get more insight into the changes occurring in the Ni–TiO$_2$ thick layer during the different treatments, a detailed assessment of the Ni(2p) spectra has been made by measuring the height of the Ni(2p$_{3/2}$) peak and that of the backgrond at ~ 40 eV higher BE, as shown in fig. 4. According to Tougaard [16] the h_a/h_b ratios plotted in this figure can be taken as a measure of the in-depth nickel distribution. Indeed, Ni(2p) photoelectrons coming deep from the solid are more likely to lose part of their original energy by inelastic collisions and, therefore, contribute to the background tail below the elastic photoelectron peaks. In this way, for photoelectron peaks with similar signal to background ratios the same in-depth distribution of nickel should be expected, whatever the actual concentration (or aggregation, see below) of this element in the sample depth examined by XPS.

4. Discussion

According to the XRD and XPS/Ar$^+$ etching data for the H$_2$-decomposed NiTiO$_3$ sample, a thick layer of a composite material formed by a TiO$_2$ matrix and Ni in a 1 : 1 ratio with metal particles of ~ 35 nm average size is formed upon reduction in H$_2$ at 873 K. Fig. 5 represents the situation of this material where the big nickel particles formed during the reduction are completely "burried" in the TiO$_2$ matrix. Ar$^+$ etching progressively removes the TiO$_2$ layer covering the particles, which become exposed at the surface while a thin layer of the TiO$_2$ matrix is deeply reduced in their neighbourhood (i.e. forming a TiO$_x$ phase, $x < 2$).

The set of XPS spectra in fig. 3 shows that after the removal by sputtering of the K$^+$ ions at the outermost TiO$_x$ reduced layers a certain amount of K$^+$ appears again by annealing at 773 K. In addition, annealing of the sputtered sample produces an apparent oxidation of the upper TiO$_x$ phase as detected by a small decrease in the concentration of Ti^{3+}/Ti^{2+} species. Both facts are enhanced by heating in the presence of H$_2$ and suggest the existence of rearrangements between the outermost, deeply reduced, TiO$_x$ region and the bulk of the TiO$_2$ matrix. Diffusion of oxygen in defective titanium oxide has been previously observed by Heinrich et al. [15] for TiO$_2$ single crystals submitted to sputtering and then annealed at 773 K. In our case, though K$^+$ can contribute to a higher ionic mobility due to the lower Hüttig temperature of K$_2$TiO$_3$ (~ 543 K compared with 700 K for TiO$_2$/TiO [17]), the presence of hydrogen at 773 K is, by far, the most important factor to enhance the ionic mobility of the TiO$_x$/TiO$_2$ lattice components. This result agrees with our

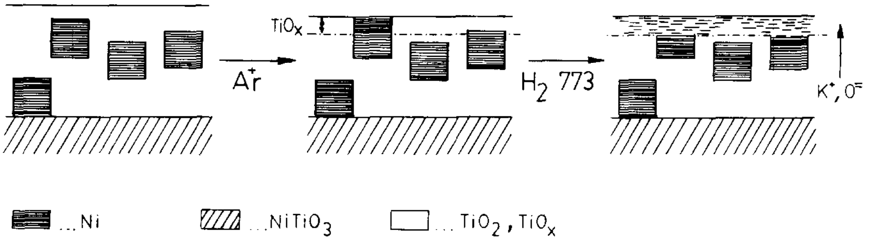

Fig. 5. Idealized picture of the Ni/TiO$_2$ thick layer: left, original layer generated by H$_2$ reduction at 873 K; middle, reduced by Ar$^+$ etching; right, nickel redispersion by H$_2$ treatment at 773 K after Ar$^+$ etching.

previous observations with Rh/TiO_2 catalysts [6] where incorporation of hydrogen in the reduced (Ar^+ etched) support occurs generating a $H-TiO_x$ phase, which readily diffuses to "decorate", and finally "encapsulate", the metallic particles. The existence of hydride-like species in TiO_2 has been postulated by Göpel et al. [18] in reduced TiO_2 (rutile) single crystals exposed to hydrogen and studied by us in these Rh/TiO_2 catalysts [19].

However, in the $Ni-TiO_2$ composite material studied here, diffusion of nickel in the reduced TiO_x thin layer must also take place during the heating in H_2. In fact, if hydrogen only contributes to increase the mobility within the bulk and the TiO_x upper layers of the titanium oxide, an increase or a constant value for the I_{Ti}/I_{Ni} ratio would be expected in fig. 1 for the etched sample heated in H_2 at 773 K (point B), in a similar way to that observed for the original $NiTiO_3$ after its reduction in H_2 at 773 or 873 K. On the contrary, by heating in H_2 at 773 K a decay in this ratio occurs for the Ar^+ etched sample. This must be ascribed to hydrogen-induced redispersion of nickel troughout the reduced TiO_x upper layers (or to a change in the shape of the nickel particles). Such redispersion is supported by data in fig. 4, where the low values of the h_a/h_b ratio for the initial $Ni-TiO_2$ material and its sharp increase upon Ar^+ etching confirm the removal of the TiO_2 overlayer covering the nickel particles. The final, almost constant, steady-state value only decreases very slightly by heating at 773 K, either in UHV or H_2, indicating that the Ni distribution in the outermost layers examined by XPS has not changed significatively after these treatments. This result, can be conciliated with the increase in the Ni(2p) intensity upon heating in H_2 the sputtered sample (see fig. 2 and the value of the I_{Ti}/I_{Ni} ratio for point B in fig. 1) only if a redispersion of the big nickel particles has occurred throughout the thin TiO_x defective layer (~ 1.5 nm thick for the energy of the Ar^+ ions used for sputtering [11]). This process would not substantially modify the in-depth Ni distribution through the whole sample thickness examined by XPS (mean free path of Ni(2p) photoelectron between ~ 1.5 and 2.7 nm [13]), although it would give rise to a more intense Ni(2p) spectrum.

Evidence of metal phase mobility under reduction conditions have been previously reported by Ruckenstein et al. [20] and by Baker et al. [21] for Ni/TiO_2 and Pt/TiO_2, and by ourselves [7] for Rh/TiO_2. Moreover, in an early work Kao et al. [22] have found by XPS that metallic nickel diffuses into a TiO_2 single crystal by annealing at $T > 573$ K. However, we like to stress here that the presence of hydrogen greatly enhances the mobility between the TiO_x/TiO_2 phases and that of the metallic nickel through defective titanium oxide layers. This fact suggests the generation of a strong interaction between nickel and the reduced titanium oxide where the hydrogen, incorporated in this latter, seems to play an important role [19]. Recent results of Jiang et al. [23] with Ni/TiO_2 catalysts (12% by weight) are also in favour of an active role of hydrogen in the $Ni-TiO_2$ interaction. These authors observe the formation of a new, unidentified phase, only stable in H_2 atmosphere, when this catalyst is heated in H_2 at 773 K. Under these conditions the XRD lines due to the TiO_2 support vanish, but they appear again upon exposure to air for a few minutes. In a recent work we have also reported [24] that removal of hydrogen from the support of a Ni/TiO_2 catalyst by outgassing at 773 K leads to an increase of 35% in the intensity of the ferromagnetic resonant (FMR) signal due to the nickel particles. This result suggests the existence of a direct Ni–H–TiO_x interaction, which is lost upon removal of hydrogen by outgassing at elevated temperatures and which must be responsible for the enhancement of Ni mobility found in the present work. In this context, it is also noteworthy that Ni–Ti alloys are known to absorb considerable amounts of hydrogen, while according to Aoki et al. [25] segregation of $TiNi_3$ and TiH_2 phases occurs by heating in H_2 at $T > 573$ K a $Ti_{67}Ni_{33}$ amorphous alloy, thus stressing the importance of hydrogen in mobilizing both elements.

Acknowledgments

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