Role of Hydrogen in the Mobility of Phases in Ni–TiO$_x$ Systems

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The role of hydrogen in the mobility of Ni and titanium suboxide phases in Ni–TiO$_x$ systems has been investigated by means of XPS and ISS. Two different systems have been examined, a composite Ni–TiO$_x$ material formed by large Ni particles (ca. 35 nm) embedded in a nonstoichiometric titanium oxide matrix and a Ni foil with evaporated TiO$_x$ species. Heating at 773 K leads to diffusion of the TiO$_x$ species into the Ni foil, a process which is strongly enhanced in the presence of H$_2$. In a similar way, heating the Ni–TiO$_x$ composite in H$_2$ at the same temperature results in a redistribution of the Ni atoms through the defective titanium oxide lattice. This hydrogen-enhanced diffusion of the TiO$_x$ and Ni species is discussed in relation to the SMSI state and other related phenomena occurring during the activation in H$_2$ of Ni/TiO$_2$ catalysts. © 1991 Academic Press, Inc.

INTRODUCTION

The most widely accepted interpretation of the SMSI state in M/TiO$_2$ (M = Rh, Pt, Ni, etc.) catalysts (*1*) is perhaps the "decoration model," which assumes the decoration of the metal particles by TiO$_x$ moieties (*1, 2*). In addition, existence of long-range electronic interactions (*1, 3*) and partial alloying at the particle interface (*4*) have been claimed to contribute to the SMSI state. However, although there is agreement on the general properties of the SMSI interaction, its mechanism, i.e., the characteristics of the diffusional phenomena which, affecting the TiO$_x$ and probably also the metal phase, bring the systems from a non-SMSI state to a deep SMSI situation, remains unknown. In this context an alternative interpretation of the decoration/encapsulation of metal particles by the support has been proposed by Sánchez and Gásquez (*5*). For the early stages of SMSI generation the model proposed by these authors assumes the anchoring of some metallic atoms or clusters in oxygen vacancies at the surface of the support, whose progressive reduction would lead to the burial of these metal particles as the concentration of oxygen vacanc-

ies around them increased. This view suggests that in some cases the SMSI state may involve a mechanism more complex than the mere encapsulation of well-defined metallic particles by the reduced support (*6*). In this regard, Fiang *et al.* (*7*), in an *in situ* study by XRD of Ni/TiO$_2$, observed the suppression of the XRD patterns of Ni and the TiO$_2$ support when the catalyst was heated in H$_2$ at 773 K and the recovery of these patterns when the sample was exposed to air. These results suggest the existence in this system of important structural changes, and therefore diffusional phenomena, during the reduction step. In a similar direction, in some studies with model systems it has been found that the metal may diffuse through the titanium dioxide (and the TiO$_x$ species through the metal), under conditions similar to those giving the SMSI state (*8, 9*). Moreover, for a Ni–TiO$_2$ system, we have recently shown by XPS that hydrogen, incorporated into the titanium oxide in the form of hydride-like species, results in enhancement of the mobility of the components of a TiO$_x$ defective lattice, as well as diffusion through this lattice of atoms of the metallic phase (*10*).

In the present work we have studied the

nature of the diffusional processes occurring in Ni–TiO$_2$ systems when they are heated in H$_2$ at 773 K. For this purpose we have used the XPS and ISS and two different systems. The first one consists of a Ni–TiO$_2$ composite material formed by large (ca. 35 nm) nickel particles in a TiO$_2$ matrix. With this system we have aimed to check the diffusibility of Ni atoms through a titanium oxide lattice. The second one, chosen to simulate the possible phenomena occurring at the surface of Ni particles decorated by TiO$_x$ species, consists of a Ni foil where TiO$_x$ species were deposited by evaporation of Ti.

EXPERIMENTAL

The Ni–TiO$_2$ composite material was prepared in the pretreatment chamber of the XPS spectrometer by heating a pressed pellet of nickel titanate (NiTiO$_3$, Ventron Gmbh, u.53103) in H$_2$ (10 Torr) at 873 K for 1 h. XRD of this sample revealed the formation of TiO$_2$ with the rutile structure, in agreement with a previous work by Shannon (11), and nickel particles with a size of ca. 35 nm as estimated by the method of Scherrer from the (111) reflexion of Ni (12). The resulting material was sequentially submitted to ion etching for 6 min (using a Penning source supplied with Ar and working at 3.5 kV), annealing at 773 K for 10 min, ion etching for 1 min, and heating in H$_2$ (10 Torr) at 773 K for 10 min. The Ar$^+$ sputtering treatment results in deep reduction of the titanium oxide lattice by preferential etching of oxygen (13). In our case, the estimated stoichiometry of the external layers submitted to sputtering was TiO$_{1.7}$ (10). Heating of the sample was achieved resistively with a Mo foil on which the pellet was placed. The temperature was controlled with a thermocouple spotwelded at the rear of the foil.

The nickel foil (Goodfellow) was cleaned in the analysis chamber of the spectrometer (base pressure 2 × 10^{-10} Torr) by sequential Ar$^+$ etching (500 eV)/annealing cycles (up to 973 K by heating the foil resistively). With this sample all the experiments were carried out in this chamber. Evaporation from a heated Ti filament under 10^{-8} Torr of oxygen was used to deposit TiO$_x$ species on this foil.

DTP experiments were carried out after exposure of the Ni foil covered by different amounts of evaporated titanium (i.e., TiO$_x$ species) to H$_2$ up to saturation (10^{-5} Torr for 10 min). The desorbed H$_2$ was monitored by mass spectrometry while applying a heating ramp of 5 K s^{-1}.

XPS and ISS spectra were recorded on the same LHS-10 spectrometer (from Leybold). Photoelectron spectra were recorded in the pass energy constant mode at 50 eV. For the Ni–TiO$_2$ composite sample, the $C(1s)$ spectrum of the spurious carbon was used as a binding energy (BE) reference at 284.6 eV. With the Ni foil, where carbon impurities were practically nonexistent after the cleaning procedure, the Ni($2p_{3/2}$) peak was taken as an energy reference for the Ti($2p$) spectra of the deposited TiO$_x$ species. Peak intensities were calculated by integration of the peak areas after background subtraction using the method of Shirley (14). Ion-scattering spectra were recorded in the retardation ratio constant mode with a value of 3, and with the electron energy analyzer polarized to detect positive charges. The ion gun, an extractor ion source (IQE 12/38 from Leybold) supplied with helium and working with an acceleration voltage of 1 kV, was sweeping a surface of 2 × 2 mm to prevent extensive etching of the sample.

The mathematical procedure of factor analysis (15) was used to analyze the ISS spectra of the Ni foil with different coverages of TiO$_x$. These calculations allow a rather accurate estimation of the relative percentages of Ni and Ti atoms exposed at the surface of the Ni foil after the different treatments. The spectra of the clean Ni foil and that of a partially oxidized Ti foil were used as references for these calculations.

RESULTS

Ni–TiO$_2$ Composite

Figure 1 shows the ISS spectra of the Ni–TiO$_2$ sample submitted to Ar$^+$ bombard-
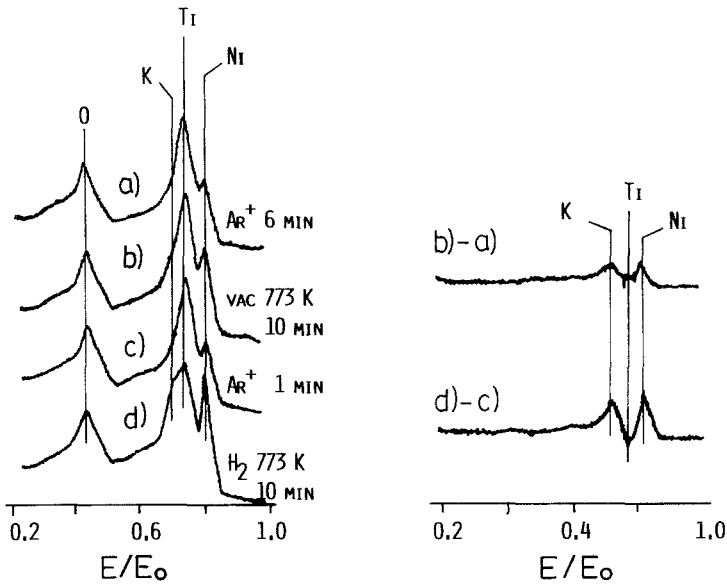
FIG. 1. Left: ISS spectra of the Ni–TiO$_2$ composite sample submitted to the indicated treatments. Right: Difference spectra b − a and d − c.

ment to create a defective titanium oxide overlayer [and therefore high concentrations of Ti^{3+} and Ti^{2+} species (10, 13)], annealing at 773 K, new Ar$^+$ bombardment to restore the previous situation, and heating in H$_2$ at 773 K. These spectra show peaks due to O, K, Ti, and Ni. The potassium was present as an impurity in the original NiTiO$_3$ material used to prepare the Ni–TiO$_2$ sample (10) and, according to the difference spectra in Fig. 1, it segregates to the surface by annealing the sputtered sample at 773 K or, to a much greater extent, by heating in H$_2$ at the same temperature.

According to the difference spectra shown in Fig. 1, heating of the sample *in vacuo* or in H$_2$ also produces a net increase in the intensity of the Ni peak and a decrease in that of the Ti peak. To assess in more detail these changes the values of the $h_{(Ni)}/h_{(Ti)}$ ratio (h = height of the ISS peaks) are shown in Fig. 2 as a function of the different treatments. For comparison, values of the I_{Ni}/I_{Ti} ratio (I = intensity of the photoelectron peaks) calculated from the corresponding photoelectron spectra reported in Ref. (10) have been plotted in the same figure.

For both, the XPS and ISS ratios, this figure shows an increase in the relative intensity of the Ni peaks upon heating at 773 K, particularly after heating in H$_2$ at this temperature. It is also worth noting that heating in
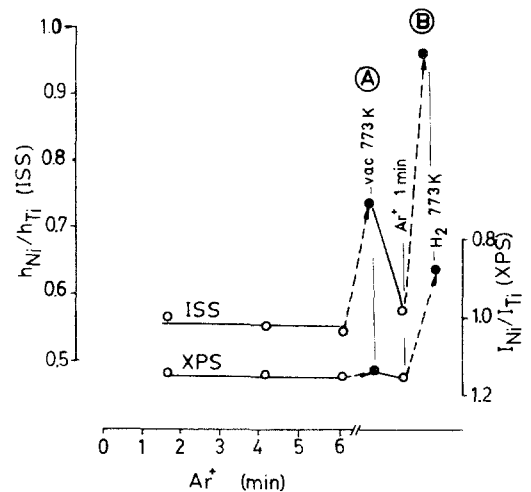

FIG. 2. Representation of the XPS and ISS Ni/Ti intensity ratios for the Ni–TiO$_2$ composite sample submitted to sputtering, heated *in vacuo* at 773 K, submitted again to sputtering to restore the previous situation, and heated in H$_2$ at 773 K.
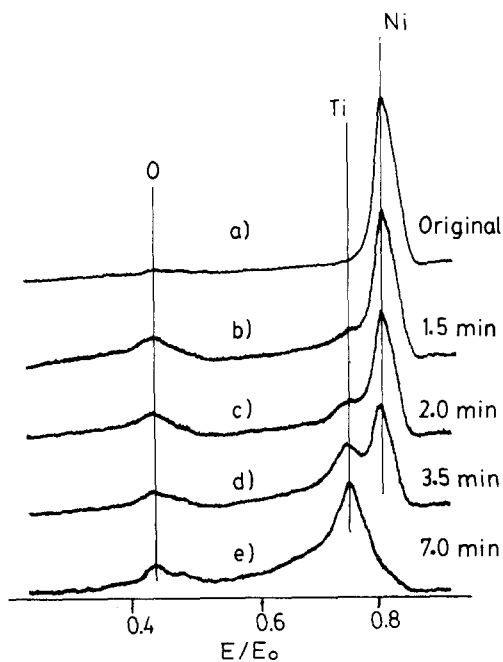
FIG. 3. ISS spectra of the nickel foil with TiO$_x$ species for increasing evaporation times up to 7 min.

ultrahigh vacuum the Ni–TiO$_2$ sample previously heated in H$_2$ at 773 K leads to considerable desorption of H$_2$. This desorption was continuously monitored by mass spectrometry for more than 5 min.

TiO$_x$ on Ni Foil

Figure 3 shows ISS spectra of the Ni foil after the evaporation of titanium under 10^{-8} Torr O$_2$ for increasing periods up to 7 min. For this evaporation time the Ni peak practically disappears, substituted by a peak due to titanium and a second feature due to oxygen. Figure 4 shows the spectra obtained when the covered foil is subsequently submitted to the following treatments: heating at 773 K for 10 min, first under vacuum and then under hydrogen (10^{-6} Torr); exposure to oxygen (10^{-6} Torr) at 298 K for 3 and 30 min and at 573 K for 30 min. As deduced from the changes in the intensity of the Ti and Ni peaks, it is clear that the degree of coverage of nickel by the TiO$_x$ species changes with the different treatments.

Quantitative estimates of these changes have been plotted in Fig. 5 where atomic percentages of Ni and Ti at the surface, calculated by factor analysis from the intensities of the Ni and Ti ISS peaks, are given as a function of the evaporation time and of the different treatments to which the fully covered sample was submitted. From this figure it is interesting that while heating *in vacuo,* and even more in H$_2$ at 773 K, results in a net decrease in the degree of coverage of Ni by TiO$_x$, exposure to oxygen at 298 K partially restores this effect, while a similar treatment with O$_2$ at 573 K leads to a decrease in the degree of TiO$_x$ coverage of the Ni foil. As shown in Fig. 6 these changes in the relative percentage of Ni and Ti atoms exposed at the surface are accompanied by changes in the oxidation state of Ti as indicated by an XPS shift in the Ti2$p_{3/2}$ B.E. from 455.9 eV, for the fresh TiO$_x$ deposits, to 459.0 eV after treatment in O$_2$ at 573 K. This shift occurs together with a net increase in the intensity of the O(1s) spectrum. It is also worth noting that the Ni(2$p3/2$) XPS spectrum did not show any significant oxida-
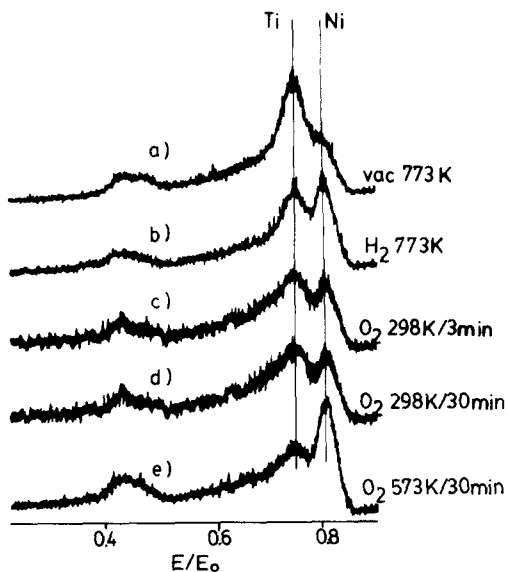

FIG. 4. ISS spectra of the nickel foil with TiO$_x$ evaporated for 7 min and then submitted to the indicated treatments (for details, see text).
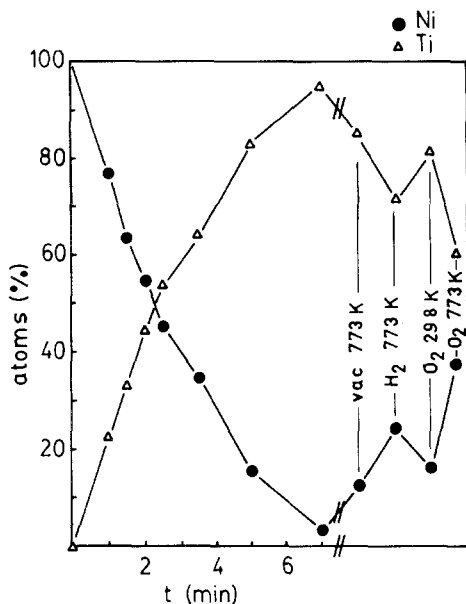
FIG. 5. Percentages of Ni and Ti atoms at the surface of the Ni foil as a function of the evaporation time and the indicated treatments *in vacuo*, in H$_2$ and in O$_2$.

sively present when the Ni foil is fully covered by TiO$_x$ species.

DISCUSSION

Diffusion of Ni through Defective Titanium Oxide

Previous works on Ni–TiO$_2$ model systems have shown that Ni^0 may diffuse through a titanium oxide lattice. Thus, in an early work, Kao *et al.* (8) found by UPS and XPS that depletion of the amount of Ni evaporated onto a TiO$_2$ single crystal occurs after annealing in UHV at 573 K. More recently, Bourgeois *et al.* (17), using AES and SIMS, observed the same phenomenon at room temperature when evaporating Ni on a TiO$_2$ (100) surface previously submitted to Ar$^+$ etching. A common characteristic of our present results by XPS and ISS and these previous works on model systems is that this diffusion is favored by the existence of oxygen vacancies in the TiO$_2$ lattice. This suggests that nickel atoms tend to occupy these vacancies, moving through them as

tion of the nickel even after heating in excess of O$_2$ at 573 K. This fact contrasts with the deep oxidation of nickel observed after a similar treatment on a clean foil, thus suggesting a specific interaction of the TiO$_x$ deposits that seems to prevent oxidation of the Ni substrate even when it is not fully covered by TiO$_x$.

Since our results above, either with the Ni–TiO$_2$ composite or with the Ni foil covered by TiO$_x$, show that heating in H$_2$ leads to changes in the Ni/Ti relative ISS intensities, it seems interesting to check the formation of new forms of adsorbed hydrogen that could be involved in enhancing the mobility of the components of the system. The TPD spectra in Fig. 7 were obtained after exposure of the Ni foil covered with different amounts of TiO$_x$ (from $\theta = 0$ to $\theta = 1$) to 10^{-5} Torr of H$_2$ at 298 K for 10 min to saturate the surface. The set of spectra clearly shows an evolution from a form of hydrogen desorbing at ca. 413 K and characteristic of a clean Ni foil (16), to a new form which desorbs at $T \geq 550$ K and which is exclu-
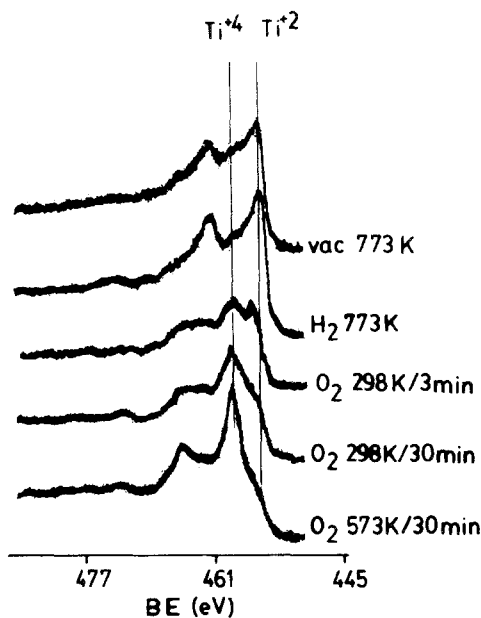

FIG. 6. Ti(2p) photoelectron spectra of the TiO$_x$ species covering the Ni foil submitted to the treatments described in Fig. 4.

θ=1.0

e)

θ=0.9

d)

θ=0.8

c)

θ=0.5

b)

a)

θ=0.0

373   473   573   673
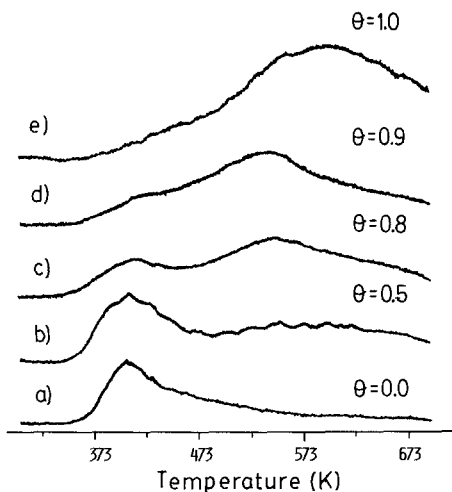Temperature (K)

FIG. 7. H$_2$ TPD spectra from the Ni foil with increasing TiO$_x$ coverage after saturation with hydrogen.

their concentration and/or the temperature increase. In comparison with other metal atoms such as Pt and Rh, also showing the SMSI state when supported on TiO$_2$, Ni has a smaller metal radius (1.246 Å vs 1.345 or 1.387 Å for Rh and Pt, respectively) and a lower Tamman temperature (525 K vs 680 and 746 K for Rh and Pt), which would favor the mobility of atoms of this metal through a defective titanium oxide lattice.

The results obtained with our Ni–TiO$_2$ composite suggest that diffusion of Ni occurs through the defective titanium oxide and that this process is enhanced in the presence of hydrogen. Difference ISS spectra in Fig. 1 show that annealing at 773 K of the sputtered composite system induces Ni (and K) enrichment of the outermost external layer of the composite material. K enrichment of the topmost layers of this system was reported on the basis of a XPS study in a previous work and attributed to the mobilization of the ionic components of the titanium oxide lattice (10). In addition, as shown in Fig. 2, the present XPS and ISS results reveal a redispersion of the large Ni particles (ca. 35 nm in size) existing in the original composite material through the defective titanium oxide lattice. This redisper-

sion is much more important at the topmost layer, as indicated in Fig. 2 by the comparatively much greater increase in the ISS intensity of the Ni signal upon UHV annealing or particularly after heating of the system in H$_2$ at 773 K. It is worth noting that with respect to real catalysts, where decoration/encapsulation of the metallic particles is assumed upon heating in H$_2$ at 773 K [decoration model of SMSI (2)], our results with the model system seem to show the opposite behavior characterized by an increase in the metal concentration at the surface. However, this is only an apparent contradiction related to the structure of our system where, after sputtering up to the steady state, the nickel, in the form of large particles, is homogeneously distributed within the TiO$_x$ matrix. This is not the case for real Ni/TiO$_2$ catalysts where the nickel is located at the surface of the support grains, so that the disappearance of nickel from the surface observed in the SMSI state can also be attributed to the disruption of the Ni particles within the reduced support beneath them.

The idea that the SMSI state may involve the diffusion of metal atoms through a defective metal oxide lattice, rather than a simple decoration of the metallic particles by migrating TiO$_x$ moieties, has been previously assumed by Sánchez and Gázquez (5). The model proposed by these authors, conceived in principle for reducible oxides with fluorite structure, gives a phenomenological explanation of the SMSI state in terms of a "burial" of the metallic particles in the support. In this process, the mechanism consists of the filling with metal atoms of the oxygen vacancies progressively generated upon reduction of the oxide. However, it must be pointed out that this is not exactly the experimental situation in the present work or in that of Bourgeois et al. (17) where the defective lattice (generated by Ar$^+$ etching) existed before diffusion of the metal. This difference is important in relation to the nature of the driving force leading to diffusion through the oxygen vacancies. According to Sánchez and Gázquez (5) the

metal particles are "drilling" their own hole into the support by spillover of hydrogen and elimination of oxygen of the anionic sublattice around them. However in the experiments above, when carried out in the absence of hydrogen [i.e., point A in Fig. 2 and also in those performed by Bourgeois *et al.* (*17*) and in some of Kao *et al.* (*8*)], a positive interaction between nickel and the cationic sublattice (i.e., Ti^{3+} or Ti^{2+}) of the titanium oxide should be invoked to enable diffusion of the nickel. This implies the formation of a certain bond between the metal and the titanium. The possibility of this interaction has been predicted by SCF-X calculations (*18*) and its existence has been shown experimentally by UPS by Fischer *et al.* (*18*) for a Ni$_3$Ti alloy and by EXAFS by Sankar *et al.* (*19*) for real Ni/TiO$_2$ catalysts. Recently (*20*) we have shown by XPS that Ni evaporated on a TiO$_x$ substrate interacts electronically with it, especially after being heated at 773 K under vacuum, an effect which is accompanied by a certain diffusion of nickel into the bulk.

The point that we would like to stress from our results is that the presence of hydrogen enhances the mobility of Ni (point B in Fig. 2) through the titanium suboxide layer deeply reduced by Ar$^+$ sputtering. With respect to this effect it is worth noting that NiTi alloys are used for storage of hydrogen (*21*) and that in this or in other similar Ti alloys [i.e., FeTi (*22*)] heating in H$_2$ (but not *in vacuo*) leads to the segregation of Ni (Fe) and the formation of titanium hydrides (*21, 22*). In a similar way, in real Rh/TiO$_2$ (*23*) or model Pt/TiO$_2$ catalysts (*24*), it has been shown the existence of a net effect of the hydrogen in mobilizing the TiO$_x$ moieties to decorate (or encapsulate) the metallic particles. Related phenomena for Ni–TiO$_2$ systems had previously been reported by Ruckenstein and Lee (*4*) and Baker *et al.* (*25*), who observed by TEM changes in the form of Ni crystallites associated with their extension and contraction when Ni–TiO$_2$ model catalysts were heated in H$_2$ at 773 K. However, in these works on nickel the observed effects were attributed to the reduction of the TiO$_2$, without considering a specific effect of hydrogen in the mobilization phenomenon. In previous works on Pt/TiO$_2$ (*26*) and Rh/TiO$_2$ catalysts (*23, 27, 28*) we investigated specifically this role of the hydrogen, showing that it is incorporated into oxygen vacancies at the reduced support, forming hydride-like species [i.e., (Ti–H)$^{3+}$] that may be responsible for this enhancement of the mobility. Under the experimental conditions used in the present work, incorporation of hydrogen into the reduced support is also shown by the observed desorption of H$_2$ during heating *in vacuo* the Ni–TiO$_2$ system previously heated in H$_2$. This suggests that the mobilization phenomenon observed in our system when heating in H$_2$ can be influenced by the formation in the reduced support of similar species of hydrogen. However, it is still unclear how these species contribute to the mobility of Ni. One possibility is the existence of a strong electronic interaction of the type Ti–H–Ni. Another is that the incorporation of hydrogen into the defective TiO$_x$ lattice might produce a weakening in their cohesion forces, thus decreasing the constraints for the diffusion of the nickel atoms. Further work is necessary to clarify these questions.

Diffusion of TiO$_x$ through Nickel

ISS spectra in Fig. 3 show a steady increase in TiO$_x$ coverage for progressive Ti evaporation times. The representation in Fig. 5 of the ISS relative intensities of Ni and Ti reveals that up to a coverage of half a monolayer (i.e., evaporation for ca 2.5 min), the TiO$_x$ islands grow only as a bidimensional phase, as can be deduced from the linear relationship with evaporation time. However, for greater coverages (i.e., evaporation for more than 2.5 min), there must be a certain agglomeration of the TiO$_x$ deposits as indicated by the decrease in the slope in this plot. This is in contrast with previous results for other similar systems studied by Somorjai and colleagues (*29*) and

Lambert and co-workers (9). Following by AES the growth of TiO_x species evaporated on Rh foil and Ru (0001) crystal, respectively, these authors report a layer-by-layer growth mode for the TiO_x deposits. However, differences in surface energies between TiO_x and the different metallic substrates, or the different surface sensitivities of ISS and AES, might be some of the reasons for this different behavior.

Changes in the relative percentages of Ni and Ti in Fig. 5 when the Ni foil, almost fully covered by TiO_x, is heated under different atmospheres indicate the existence of diffusion phenomena affecting the TiO_x species. The decrease in the relative percentage of Ti upon heating *in vacuo* or in hydrogen at 773 K can be explained by the agglomeration of the TiO_x species and/or their solution into the bulk of Ni. However, the partial recovery of the initial coverage by exposure to O_2 at 298 K is more consistent with a back-migration of the TiO_x species to the surface rather than with their redispersion on it. A similar diffusion of TiO_x species deposited into a metal has previously been reported by Lambert *et al.* (9) for a TiO_x/Ru (0001) model system heated in UHV at 800 K and by Ko *et al.* (30) for TiO_x/Pt heated at 700–900 K. By this migration a separate diffusion of titanium and oxygen species must occur rather than that of TiO_x ensembles. In this sense it is interesting that upon exposure of Ni to a few langmuirs of oxygen at room temperature, it not only remains adsorbed at the external layer, but distributes through the first three monolayers (31), thus revealing a great relative mobility in the oxygen–nickel system. The migration of titanium into the Ni is further confirmed by the decrease in the coverage observed after exposure of the sample to O_2 at 573 K, which must be associated with agglomeration of the TiO_x deposits, once they are oxidized up to TiO_2. This is confirmed by the XPS data in Fig. 6, showing that after evaporation and heating *in vacuo* or in H_2 at 773 K, Ti^{2+} species with a B.E. of 455.9 eV (32) constitute the majority in the system, while expo-

sure to O_2 at either 298 or 573 K leads to a progressive oxidation to Ti^{3+} (B.E. at ca 457.5 eV) and then to Ti^{4+} (B.E. at ca 459.0 eV) (32).

The most interesting result in our experiment is that the diffusion of the decorating TiO_x species into the metal is further enhanced by heating in hydrogen. The TPD spectra in Fig. 7 show the formation of a new state of adsorbed hydrogen when TiO_x species are covering the Ni, in a way similar to that found by Raupp and Dumesic (16) for TiO_x deposited on Ni foil or by Lambert and co-workers (33) for Ti deposited on a Ru (0001) single crystal. This new form must result from modification of the hydrogen adsorption sites on Ni by the deposited TiO_x species. It is probable that this new species is responsible for the enhancement of the diffusion of TiO_x species through the nickel.

The previous results with the TiO_x–Ni foil system together with those on the Ni–TiO_2 composite show a very complex situation in relation to SMSI in Ni/TiO_2 catalysts. According to these results it should be expected that in real catalysts there are similar phenomena of Ni^0 diffusion through the defective titanium oxide support, as well as diffusion of reduced TiO_x species through the Ni particles; in both cases, participation of new forms of active hydrogen enhances these diffusional processes. It is also likely that this kind of process may have led to the situation reported by Fiang *et al.* (7) for a Ni/TiO_2 catalyst (ca. 14% Ni by weight) heated in H_2 at 773 K, where the XRD patterns due to TiO_2 and Ni were lost on this treatment, although they were later recovered by exposure of the sample to the air.

CONCLUSIONS

From the previous results on a Ni–TiO_2 composite and a TiO_x–Ni model system we can deduce that hydrogen has a positive effect in enhancing the diffusion of TiO_x species into metallic nickel, as well as that of Ni atoms through a defective TiO_x lattice. These processes are particularly interesting in relation to generation of the SMSI state

in real Ni/TiO$_2$ catalysts and point to a very complex situation characterized by diffusion of Ni into the support, decoration of the Ni particles by TiO$_x$ species, and diffusion of these species into the nickel.

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