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The State of Nickel in Ni/SiO$_2$ and Ni/TiO$_2$-Calcined Catalysts

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Ni/TiO$_2$- and Ni/SiO$_2$-calcined catalysts prepared by an ion exchange method have been studied by TPR, UV visible spectroscopy, XPS, and EXAFS. In Ni/SiO$_2$ it is shown that Ni^{2+} cations exist in an octahedral coordination forming very stable nickel silicate structures. On the contrary, in Ni/TiO$_2$, the existence of Ni^{3+} is revealed by EXAFS (Ni–O distance at 1.841 Å) and UV visible (bands at 29400 and 24400 cm^{-1}). In this case Ni^{2+} together with Ni^{3+} cations exists in small patches of nickel oxide on the surface of the TiO$_2$. The formation of a Ni^{3+}–O$_2^{n-}$ complex at the surface is also likely.

INTRODUCTION

It is well established that the final state of a catalyst depends on the characteristics of its precursors, which, in turn, are closely related to the method used for the catalyst preparation (*1, 2*). In this context much work has been devoted to the characterization of catalyst precursors by different spectroscopic and thermal techniques (*3*). Recently, Ni/SiO$_2$-oxidized precursors prepared by homogeneous precipitation with urea (*4*) or by ion exchange (*5*) have been studied by EXAFS to determine the coordination of nickel. These studies have shown that the Ni^{2+} ions exist in an octaedral environment in a kind of nickel silicate structure.

Another interesting feature that has been widely studied with Ni catalysts is the possibility that nickel exists as Ni^{3+} species, which, in nonstoichiometric NiO, have been claimed to be responsible for the good performance of this material as a catalyst for oxidation reactions (*6, 7*). Stabilization of this oxidation state has been reported for Ni/SiO$_2$ (*8*), Ni/Al$_2$O$_3$ (*9*), and Ni/MgO (*10, 11*) catalysts from UV-visible spectra.

In the present work, TPR analysis and XPS and UV-visible and EXAFS spectroscopies have been combined to characterize the state of nickel in Ni/TiO$_2$- and Ni/SiO$_2$-calcined catalysts prepared by an ion exchange method. The differences observed between the two systems have been discussed in terms of the small solubility of TiO$_2$ in a basic aqueous solution and the ability of this support to form and stabilize O$_2^{n-}$ species.

EXPERIMENTAL

Materials

The Ni/SiO$_2$ and Ni/TiO$_2$ samples (1.8 and 1.0% of Ni by weight) were prepared by ion exchange from a NH$_4$OH solution of Ni^{2+} ions buffered at pH 9.5. SiO$_2$ (Aeorosil-200, S_{BET} = 200 m^2 g^{-1}) and TiO$_2$ (Anatase P-25, S_{BET} = 50 m^2 g^{-1}) supports had been previously washed with a NH$_4$OH solution, pH 11.5, at 298 K. A suspension of 15 g of the supports in 0.3 liters of the buffered solution at pH 11.5 was stirred for 120 h, and the solids were filtered off, dried in flowing N$_2$ (first at 298 K and then at 383 K for 15 h), and finally calcined in a flow of oxygen at 673 K for 1 h. At this point it is worth noting that the solution filtered from the silica suspension became turbid after several days at room temperature, which showed the existence of a floculation pro-

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cess. After these treatments the samples were green (Ni/SiO_2) and yellow (Ni/TiO_2) in color. The nickel oxide used as reference was prepared by thermal decomposition in air of $Ni(NO_3)_2 \cdot 6H_2O$ according to Houalla *et al.* (*12*).

Methods

UV-visible reflectance spectra of the two samples and the supports were recorded with a Perkin–Elmer (Model 554) instrument using a $BaSO_4$ sample as a reference. The spectra have been modified by the Schuster–Kubalka–Munk equation (*13*) to make comparable the spectra intensities of the different samples. XPS spectra were recorded on a Leybold LHS10 spectrometer using Al$K\alpha$ radiation as an excitation source. The electron energy analyzer was set in the pass energy constant mode at 50 eV. Binding energy (BE) was measured taking as reference the Ti($2p_{3/2}$) level at 458.5 eV. The NiO and Ni/SiO_2 samples were homogeneously mixed with small amounts of TiO_2 in an agata mortar to obtain an internal reference. The spectra were stored and handled mathematically in a H–P computer on line with the spectrometer.

X-ray absorption spectra at the Ni K-edge were recorded at the Frascati radiation facility. The monochromator was a channel-cut single crystal of Si(111) and the energy was scanned with 2-eV steps starting from 200 eV below the absorption edge of Ni (8331 eV). The samples consisted of pellets of the powdered catalysts in a boric acid matrix. Analysis of EXAFS spectra was performed with standard procedures for preedge and postedge background removal, extraction of the EXAFS signal, normalization of the edge absorption, and phase correction. Fitting analysis of the first and second coordination shells of Ni in Ni/TiO_2 and Ni/SiO_2 samples was done by comparison with NiO as a reference.

TPR spectra of samples were recorded according to the method given by Malet *et al.* (*14*), by passing a 5% mixture of H_2/Ar (10 ml min^{-1}) and with a heating ramp of 10 K min^{-1}.

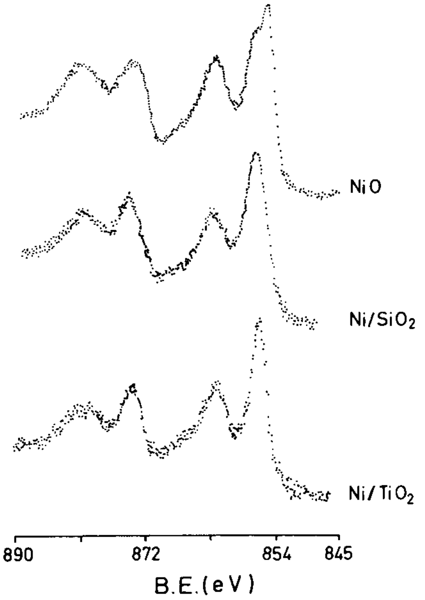

FIG. 1. Ni($2p$) photoelectron spectra of the samples.

RESULTS

The XPS spectra of the two catalyst samples and that of NiO included for comparison are shown in Fig. 1. It is interesting that, although the spectra of the two catalysts have similar shapes, they show slightly different Ni($2p_{3/2}$) BEs (856.0 and 855.6 eV for Ni/SiO_2 and Ni/TiO_2). The differences are greater when compared with the Ni($2p$) spectrum of NiO, which has a satellite peak at ca. 2.0 eV BE higher than the main one, a fact showing the presence of Ni^{3+} in NiO (*15, 16*).

Figure 2 shows the Fourier transforms obtained from the Ni K-edge EXAFS spectra of Ni/TiO_2, Ni/SiO_2, and NiO. These spectra reveal the existence of important differences in the coordination spheres of Ni in the three samples. In particular, for Ni/TiO_2 there are two peaks at $R < 2$ Å, which indicate the presence of two Ni–O bond distances in the first coordination shell. Fitting analysis of the first and second shell of

TABLE 1

EXAFS Fitting Parameters of the First and Second Coordination Shells of Nickel in Ni/TiO$_2$ and Ni/SiO$_2$

Coor. shell	Neighbor	N	d(Å)	ΔE(eV)	$\Delta\sigma \times 10^3$
		Ni/TiO$_2$			
First shell	O(I)	3.8	1.841	20.0	−1.0
	O(II)	3.2	2.170	−6.4	0.0
Second shell	Ni	4.1	2.955	1.1	3.7
		Ni/SiO$_2$			
First shell	O	5.9	2.076	−2.5	−0.1
Second shell	Ni	No reasonable fitting			

nickel in Ni/SiO$_2$ and Ni/TiO$_2$ was carried out taking the Ni–O and Ni–Ni shells of nickel in NiO as references. The fitting parameters are summarized in Table 1 and the results of this analysis for Ni/TiO$_2$ are shown in Fig. 3. However, as it is shown in Fig. 4, only the first shell of nickel in Ni/SiO$_2$ could be reproduced by assuming a Ni–O coordination, but not the second shell under the assumption of a pure Ni–Ni coordination.

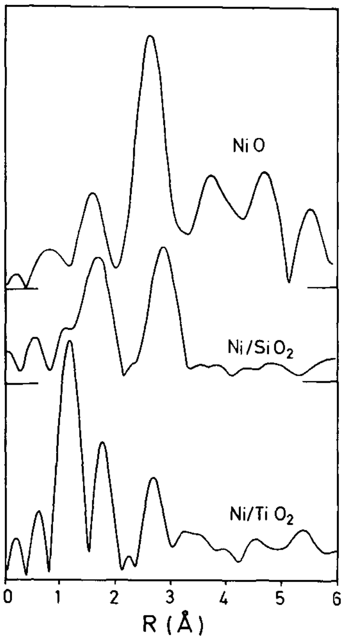

FIG. 2. Fourier transform spectra of the samples.

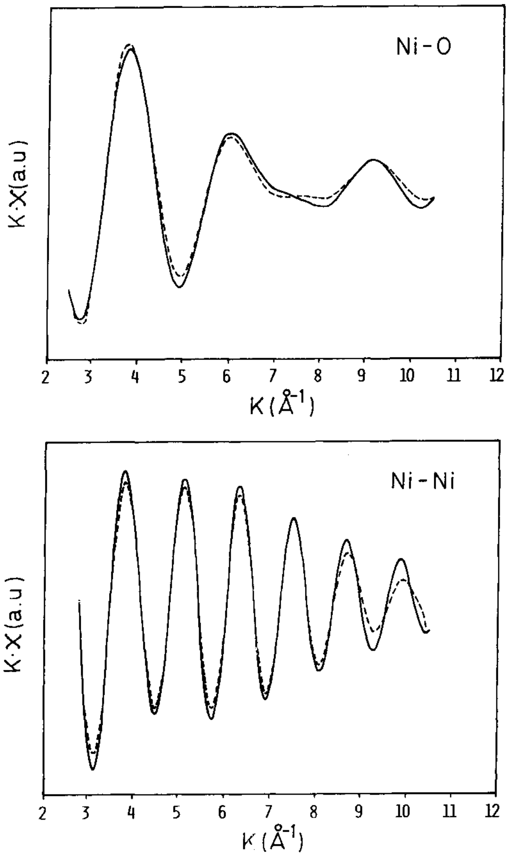

FIG. 3. Fitting analysis of the first and second coordination shells of Ni in the Ni/TiO$_2$ catalyst. Dashed line: fitted EXAFS functions.

The UV-visible reflectance spectra of the Ni/TiO_2, Ni/SiO_2, and NiO samples together with that of the TiO_2 support are shown in Fig. 5. The spectrum of the TiO_2 support has been used to calculate the difference spectrum also shown in the same figure. From this difference spectrum, it is clear that the most characteristic feature for Ni/TiO_2 is the appearance of two rather sharp bands at ca. 29400 and 24400 cm^{-1}, in a spectral region where Ni/SiO_2 only presents one weak peak, which is similar to that of Ni^{2+} in aqueous solution (i.e., Ni $(H_2O)_6^{+2}$, a d^8 system) (*17*). The UV-visible spectrum of NiO shows a complex pattern in the range 30000–20000 cm^{-1}, where the spectrum looks like the sum of the Ni/TiO_2 and Ni/SiO_2 spectra, while a strong band is also observed at ca. 15000 cm^{-1}.

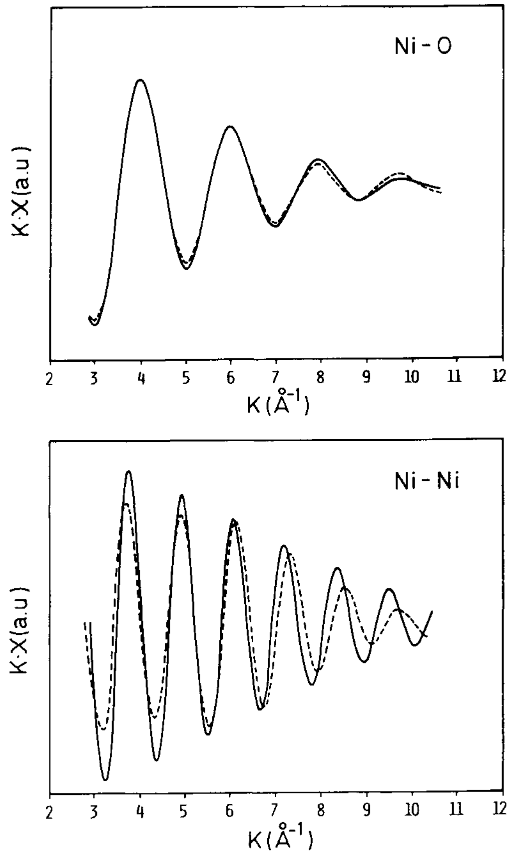

FIG. 4. Fitting analysis of the first and second coordination shells of Ni in the Ni/SiO_2 catalyst. Dashed line: fitted EXAFS function.

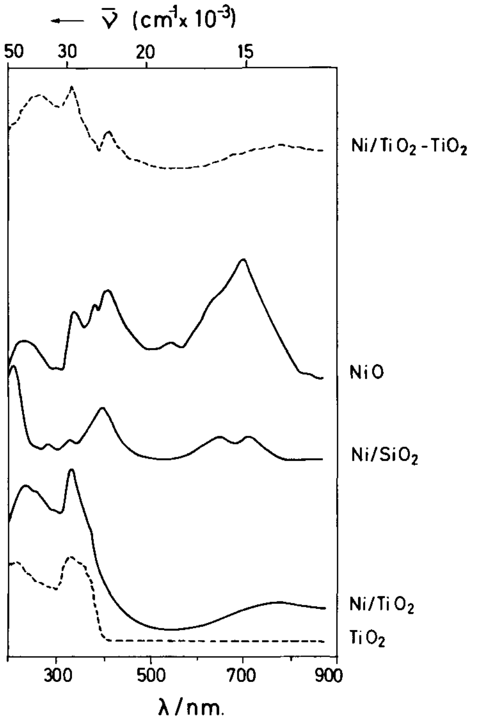

FIG. 5. UV-visible spectra of samples. Dashed line: spectra of the TiO_2 support and difference spectra between Ni/TiO_2 and TiO_2.

TPR analysis of the samples confirmed that nickel is in a different state in the Ni/TiO_2 and Ni/SiO_2 catalysts. The TPR spectra in Fig. 6 for the two catalysts and for the NiO reference show that the reduction of nickel in Ni/TiO_2 occurs in a temperature range similar to that of NiO with a peak at ca. 723 K. On the contrary, the reduction process begins in Ni/SiO_2 at about 773 K and progresses very slowly up to 1073 K with a broad maximum at 973 K.

DISCUSSION

The TPR and UV-visible results described above for the Ni/SiO_2 catalyst are similar to those reported previously in the literature for nickel/silica catalysts prepared by deposition–precipitation or ion exchange methods (*3, 18, 19*) and natural silicates (*20*).

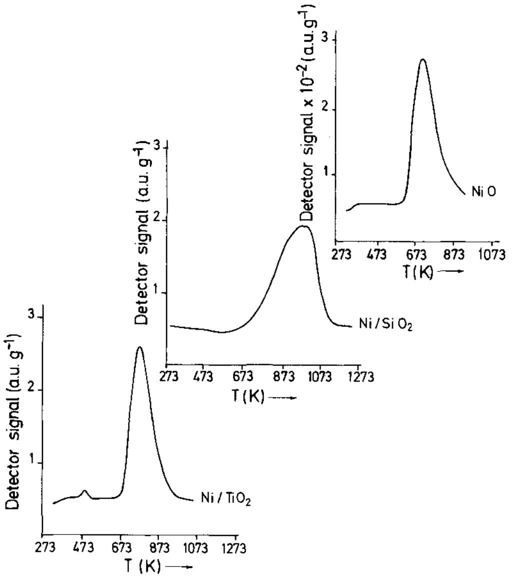

FIG. 6. TPR spectra of the samples.

Particularly interesting is that the results are similar to those obtained with the EURONi-1 catalyst (*18*) with 25% of Ni and where a nickel silicate structure has been determined by X-ray diffraction and TEM. Meanwhile the XPS spectrum is very similar to that found by Vedrine *et al.* (*21*) for Ni^{2+} in silicate or hydroxide compounds. So, the comparison with these previous works supports the fact that in our sample the nickel forms a kind of a nickel-silicate structure, where the Ni^{2+} ions are octahedrically coordinated by oxide ions in their first coordination shell. The same conclusion has been reached from EXAFS analysis by Tohji *et al.* (*22*) for coprecipitated Ni/SiO$_2$ samples and by Che and co-workers (*4, 5*) for Ni/SiO$_2$ catalysts prepared by an ion exchange method. However, the first authors propose that the second coordination shell consists of Si atoms (*22*), while Che and co-workers (*4, 5*) suggest that it is formed by a variable number of Si and Ni atoms, depending on the loading of nickel and small changes in the preparation methodology. In our case, the formation of such a phase is in agreement with the difficulty to get a good fitting for the second shell of nickel by means of the Ni–Ni phase shift and amplitude functions derived from NiO (Fig. 4). As recently proposed by Che and co-workers (*4, 5*) the formation of this nickel-silicate phase involves the partial solution of the silica during the preparation of the precursor, followed by its precipitation on the surface of the silica grains in the form of nickel silicate. Our observation of a floculation process during the preparation of the Ni/SiO$_2$ sample agrees with this hypothesis.

The XPS spectra of Ni/SiO$_2$ and Ni/TiO$_2$ present a main peak without the satellite appearing in NiO at ca. 2 eV higher BE. This satellite in the Ni(2*p*) spectrum of the NiO has been attributed to a final state effect (differences in the electronic configurations of the final state of the system after the photoemission process) due to a change in the ionic charge and coordination induced by the cation vacancies (*16*). In relation to our work, the absence of this satellite in the spectra of the two catalyst samples is a clear indication that the nickel ions do not form big nickel oxide aggregates in these two samples (*15, 16*). The same conclusion has been obtained by the analysis of the sputtering depth profiles of these two samples by a method recently proposed (*23, 24*). However, no clear inference on oxidation states of nickel (i.e., presence of Ni^{2+} or Ni^{3+} species; see below) can be made from the XPS spectra of the two samples because they have very similar BE.

The absence of big NiO aggregates in Ni/TiO$_2$ is confirmed by the Fourier spectra in Fig. 2 and the fitting analysis of the second coordination shell of nickel under the assumption of a Ni–O–Ni arrangement (Fig. 3 and Table 1). Attempts to include Ti in this shell always led to worse fittings. This could be due to the absence of this atom in the coordination shell or just to the cancelation of their contributions because of their heterogeneous distribution in this shell. The results of the fitting show that the second shell is formed by four nickel atoms. In principle, this result would suggest that in Ni/

TiO_2 nickel is in the form of very small, likely two-dimensional, patches of ca. 8–10 nickel–oxygen octahedra, a size for which the calculated average second-shell Ni–Ni coordination number (i.e., 4) would agree with the value of four determined by fitting (Table 1). However, the most remarkable point in the Fourier spectra in Fig. 2 is that the first coordination shell of nickel in Ni/TiO_2 is characterized by two Ni–O peaks in the Fourier spectrum, the first one at an unusually short distance. After back-Fourier transformation and fitting analysis it results in a Ni–O distance of 1.84 Å. Similar Ni–O distances have been reported by Dürr and Lenglet (*25*) for Ni^{3+} ions in a $Ni_2Co_2O_4$ spinel (Ni–O distance of 1.95 Å) and McBreen *et al.* (*26, 27*) in an "*in situ*" study by EXAFS of Ni electrodes (Ni–O distances from 1.86 to 2.06 Å depending on the number of voltametric cycles). Similary Tohji *et al.* (*28*), for Co/TiO_2 catalysts calcined at 723 K, have found a Co–O distance at ca. 1.9 Å, which has been attributed by these authors to the average distance of the Co^{3+}–O and Co^{2+}–O bonds existing in Co_3O_4 aggregates formed on the TiO_2 under their experimental conditions.

The existence of Ni^{3+} cations on the surface of the Ni/TiO_2 catalyst is confirmed by the UV-visible spectra. In fact, a comparison with the bands given in the literature for Ni^{3+} complexes (*2, 30*) shows a good agreement with those obtained here for our Ni/TiO_2 sample. In all cases two bands, centered between 37.000–31000 cm^{-1} and 24000–21000 cm^{-1}, characterize this oxidation state of nickel, the second band being responsible for the yellow color of these systems containing Ni^{3+} (*31*).

Formation of a Ni_3O_4 spinel phase at the surface of NiO during electron bombardment in a TEM microscope has been reported recently by Buckett and Marks (*32*). In Ni/TiO_2 it is possible that the active phase forms oxide patches at the surface of TiO_2 with a similar spinel-like structure. This kind of structure for the Ni_3O_4 patches would have more favorable crystal field stabilization energy than similar patches of Co_3O_4. This structure for the nickel oxide would also be in agreement with the EXAFS and TPR results. In the case of the TPR experiments, the similar shape and values of the reduction temperature of NiO and Ni/TiO_2 strongly suggest that the nickel is in the form of a kind of nickel oxide in this sample. However, the existence of nonstoichiometric NiO patches on the surface of Ni/TiO_2 (i.e., to account for the Ni^{3+} state) would be difficult to reconcile with its pale yellow color. In fact, highly nonstoichiometric nickel oxide samples present a black color which is associated with electronic transitions of the type Ni^{3+}–$O^{2-} \rightarrow Ni^{2+}$–$O^{-}$ (*33*). So, another possibility is that stoichiometric NiO patches coexist in Ni/TiO_2 with Ni^{3+} ions isolated on the surface of the TiO_2. However, this state cannot be ascertained by EXAFS, a technique by which only average coordination values can be obtained.

In a previous work Rives *et al.*(*34*) have postulated the formation of peroxo species on calcined Ni and other 3*d* metal ions supported on titania to account for a band at ca. 24400 cm^{-1} recorded for all their samples in their UV-visible spectra. Owing to the well-known ability of TiO_2 to form and stabilize O_2^{2-} species (*35, 36*), it is likely that this kind of oxygenated species might be also present in our calcined Ni/TiO_2 catalysts (note that the EXAFS fitting analysis of the first coordination shell of this sample would be compatible with the coordination of some or all the Ni^{3+} ions with a peroxo-like species). In that case, they would contribute to the stabilization of the Ni^{3+} species in a way similar to Ni^{3+}–O_2^{2-} complexes in solution (*29, 30*) or on the surface of a highly nonstoichiometric NiO sample as has been recently shown by XPS and factor analysis (*37*). In relation to other works the formation of such a type of species might explain why EPR spectroscopy either failed to detect signals due to Ni^{3+} (*8*) or did not account for the total amount of Ni^{3+} estimated by XPS (*11*), in previous studies on Ni supported on SiO_2 (*8*) or dispersed in MgO (*11*). Finally the appearance of just one main peak in the XPS spectrum of Ni/TiO$_2$ could be explained by the decomposition of such nickel-peroxo species in the UHV of the photoelectron spectrometer, in a way similar to that found for the peroxo species of a titanium hydroxyperoxide sample (*35*). In this way, the resulting Ni^{2+} ions anchored on the surface of TiO$_2$ (i.e., $Ni^{3+}–O_2^{2-} \rightarrow Ni^{2+}–O^{2-} + \frac{1}{2}O_2$) would have a BE similar to that of the nickel in the small NiO aggregates.

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