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Physicochemical characterization of oxide Co–TiO$_2$ and Mn–TiO$_2$ systems

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The preparation and physicochemical characterization (specific surface area, X-ray diffraction, electronic spectra, and magnetic properties) of oxide Mn–TiO$_2$ and Co–TiO$_2$ (1–5% atomic ratio Mn/Ti or Co/Ti) systems are described. The samples were obtained from commercial TiO$_2$ and soluble manganese and cobalt salts, after treatment in an oxidizing atmosphere at 770 K. While the Mn–TiO$_2$ samples show a good dispersion of the supported phase irrespective of the manganese content, increasing amounts of cobalt content lead to formation of Co$_3$O$_4$.

1. Introduction

Solid solutions and surface-dispersed systems of transition metal ions in diamagnetic (usually main group) metal oxide lattices have received a lot of attention in the last few years, as they provide a way to investigate the oxidation states of the guest cations sometimes unstable outside the host lattice; they are also of interest in materials science problems, as well as in heterogeneous catalysis. Moreover, systems using TiO$_2$ as support have received increasing attention because of their role in the photochemical splitting of water and other photo-assisted processes [1–4], in order to extend the photo-response of unloaded TiO$_2$ towards the visible range to increase the quantum yield of such reactions; metal–support interactions with transition metal oxides supported on TiO$_2$ have been very recently discussed in the literature [5].

In the present paper, the preparation and physicochemical characterization of manganese- and cobalt-containing TiO$_2$ systems obtained from commercial TiO$_2$ are described, as are the differences observed in the behaviour of both series of samples with regards to the attained dispersion of the supported phase.

2. Experimental details

2.1. Samples preparation

The TiO$_2$ support (P-25, from Degussa, Frankfurt) was heated overnight at 670 K in order to eliminate any adsorbed organic residues; known amounts of TiO$_2$ (about 5 g) were impregnated with an aqueous solution (50 cm^3) of Mn(AcO)$_2 \cdot$4H$_2$O or Co(AcO)$_2 \cdot$4H$_2$O (Merck, pa) to yield final materials containing 1, 3, and 5% atomic ratio Mn/Ti (or Co/Ti). After stirring for 60 min, the solvent was slowly evaporated at 330 K and the solids then dried overnight at 380 K. The product thus obtained was manually ground in an agate mortar and heated for 3 h at 770 K in flowing oxygen (30 cm$^3_{\text{SPT}}$ min^{-1}) in a tubular Heraeus ROK 3/60 furnace, and then very slowly cooled to room temperature (16 h) in order to avoid any quenching effect. The samples were stored in a desiccator until use.

2.2. Apparatus and procedures

The specific surface areas of the samples were determined by the BET method from the nitrogen (from SCO, 99.995%) adsorption isotherms (77 K) of the samples, previously outgassed for 1 h at 423 K and 10^{-4} N m^{-2} in a conventional high vacuum system, with grease-free stopcocks and equipped with a MKS Baratron pressure transducer; the system was previously calibrated with helium (from SCO, 99.998%).

The X-ray diffraction patterns were recorded in a Philips PW 1030 instrument using Ni-filtered Cu$K\alpha$ ($\lambda = 0.15405$ nm) radiation and standard conditions, while sensitivity was set at 500 cps/fsd.

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TABLE I Monolayer volume (V_m) and specific surface area of Mn–TiO_2 and Co–TiO_2 samples

Sample	V_m (cm^3_{STP} g^{-1})	S_{BET} (m^2 g^{-1})
TiO_2	11.5	49.9
Mn1–TiO_2	11.1	48.4
Mn3–TiO_2	10.6	46.1
Mn5–TiO_2	10.2	44.5
Co1–TiO_2	10.7	46.9
Co3–TiO_2	10.3	44.9
Co5–TiO_2	10.7	46.7

The electronic spectra of the samples and of the precursors in the range 800–240 nm were obtained in a Shidmazu UV-240 spectrophotometer provided with a diffuse reflectance accessory and a Shidmazu PR-1 graphic printer, and using MgO or untreated TiO_2 as the reference.

Magnetic measurements were carried out at room temperature using a Stanton MC-5 Gouy balance equipped with a Newport C electromagnet and using Hg[Co(SCN)$_4$] as reference for calibrating the tube.

3. Results and discussion

3.1. Adsorption of nitrogen at 77 K

The monolayer volume (V_m) and specific surface area (S_{BET}) for both series of samples, as determined by nitrogen adsorption at 77 K, have been collected in Table I, together with the same data for the parent TiO_2. A slight decrease in the S_{BET} values is observed in the manganese- and cobalt-containing samples, probably as a result of sintering during preparation of the samples, but while for the Mn–TiO_2 samples the S_{BET} decreases on increasing manganese content, for Co–TiO_2 samples the S_{BET} value changes randomly; this decrease cannot be attributed to the anatase → rutile phase change transformation (see X-ray diffraction results below).

3.2. Mn–TiO_2 samples

3.2.1. X-ray diffraction diagrams

The X-ray diffraction diagrams of all three samples, shown in Fig. 1, exclusively show the peaks due to both the anatase and rutile forms of TiO_2. From the heights of the peaks at 0.352 nm, plane (1 0 1) of anatase, and 0.325 nm, plane (1 1 0) of rutile, and using the equation given by Criado and Real [6], the relative amounts of anatase and rutile were calculated. This was found to correspond to 45 ± 1% anatase, as in the original TiO_2 P-25 sample, thus indicating that the annealing treatment in oxygen at 770 K of the precursors containing the manganese salt does not catalyse the anatase–rutile phase change.

In order to check if the absence of MnO_x peaks was due to a failure of the method, due to the low manganese loading, mechanical mixtures of α-Mn_2O_3 and TiO_2 containing the same relative amounts of manganese as the samples under study

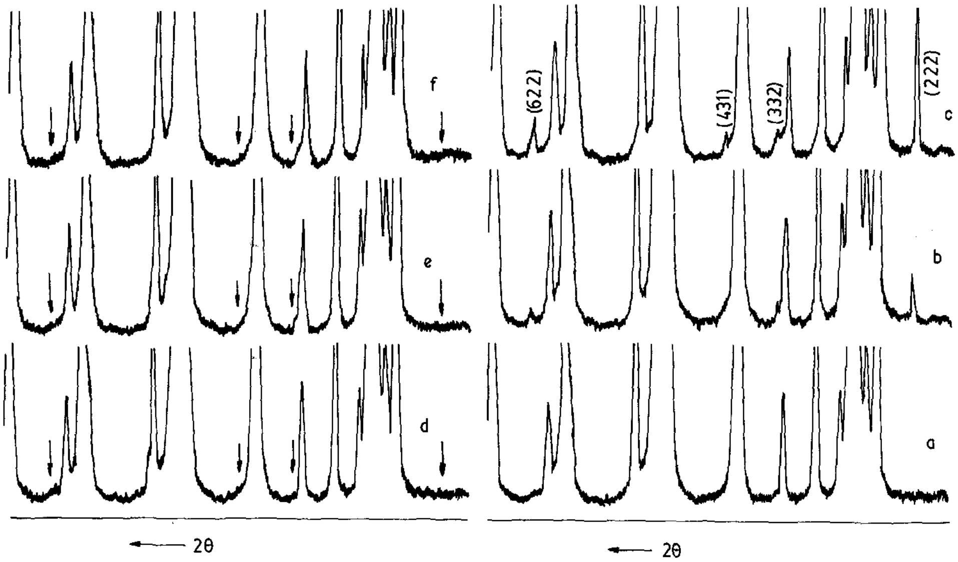

Figure 1 X-ray diffraction patterns of: (a) parent TiO_2, (b) 1% α-Mn_2O_3–TiO_2 mixture, (c) 5% α-Mn_2O_3–TiO_2 mixture, (d) Mn1–TiO_2, (e) Mn3–TiO_2, (f) Mn5–TiO_2. For clarity, only planes of α-Mn_2O_3 are indicated. Vertical arrows in patterns d, e and f correspond to the expected positions of the α-Mn_2O_3 main peaks.

were prepared by mixing TiO_2 and α-Mn_2O_3 obtained by heating $Mn(AcO)_2 \cdot 4H_2O$ at 820 K for 6 h in air [7]. In the X-ray diffraction diagrams of these samples (even in that containing 1% Mn/Ti atomic ratio, Fig. 1b), two peaks at 0.272 and 0.14191 nm, corresponding to planes (2 2 2) and (6 2 2) of α-Mn_2O_3 (partridgeite) were observed. Other peaks at 0.201 nm, plane (3 3 2), and 0.1845 nm, plane (4 3 1) (with relative intensities of 14% with respect to the most intense peak at 0.272 nm) were hardly recognized in the diagram of the low loaded mechanical mixture because of their nearness to major peaks of TiO_2. On the other hand, while Valigi and Cimino [8] have reported the presence of $MnTiO_3$ for high loaded Mn–TiO_2 samples fired at 1273 K, peaks due to ternary stoichiometric Mn–Ti–O compounds (e.g. Mn_2TiO_4, $MnTiO_3$) were not detected.

3.2.2. *Electronic spectra*

The solids are pale brown in colour, darkening as the manganese content is increased. Electronic spectra of the Mn–TiO_2 samples are shown in Fig. 2, where they have been displaced vertically for clarity. Below 400 nm, the TiO_2 support exhibits a charge transfer band, centred at about 300 nm, corresponding to the excitation of an electron from the valence band to the conduction band of the oxide, and all spectra show a large absorption extending all along the visible region. In spectra of samples Mn1–TiO_2 and Mn3–TiO_2 a weak band at 490 nm is recorded, while this band is absent in the spectrum of sample Mn5–TiO_2. The position of this band at 20 400 cm^{-1} is very close to the value of 10Dq (crystal field splitting energy) for the $[Mn(H_2O)_6]^{3+}$ species [9], which coincides with its only *d–d* spin-allowed transition. So, taking into account the vicinity of the oxide and the water ligands in the spectrochemical series, the presence of Mn^{3+} cations in these samples can be tentatively assumed from these spectra, althought the adsorption extending all along the visible region makes possible the existence of manganese ions in some other oxidation state(s) or environment (tetrahedral). It is worthy of note that if TiO_2 is used as reference instead of MgO, a maximum at 415–420 nm is recorded in the spectra of all samples containing manganese, as well as in those containing cobalt (see Fig. 3 below). This band has been previously observed in oxidized Cr–TiO_2 samples [10–13], and has been ascribed to a $M^{n+} \rightarrow Ti^{4+}$ charge transfer, i.e. the transition of an electron of the M^{n+} ion into the conduction band of TiO_2, which consists mainly of Ti 3*d* orbitals. Its presence in all the spectra, irrespective of the cation existing besides TiO_2, as well as its absence in the spectrum of the parent TiO_2, supports its ascription to a process involving both the guest cation and the TiO_2 host lattice, and not merely to a *d–d* transition in the guest cation.

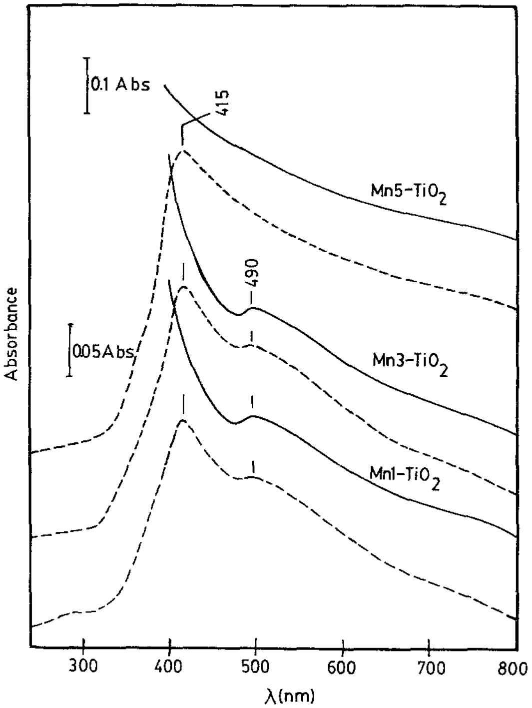

Figure 2 Electronic spectra of Mn–TiO_2 samples. Solid line: using MgO as reference; dotted line: using TiO_2 as reference. Note the change in the absorbance scale for samples Mn1–TiO_2 and Mn3–TiO_2 (0.05 Abs) and sample Mn5–TiO_2 (0.1 Abs).

3.2.3. *Magnetic susceptibilities*

These were measured at room temperature; the content of paramagnetic species was so low that diamagnetic corrections were carried out from the experimental diamagnetism of unloaded TiO_2. This is contrary to Valigi and Cimino's [8] results with quenched, high temperature (1273 K) synthetized Mn–TiO_2 samples, who reported a slight paramagnetism of TiO_2 obtained by hydrolysis and oxidation of $TiCl_3$ and ascribed this to the existence of Fe^{3+} paramagnetic impurities. TiO_2 P-25 exhibits a weight loss when placed in increasing magnetic fields.

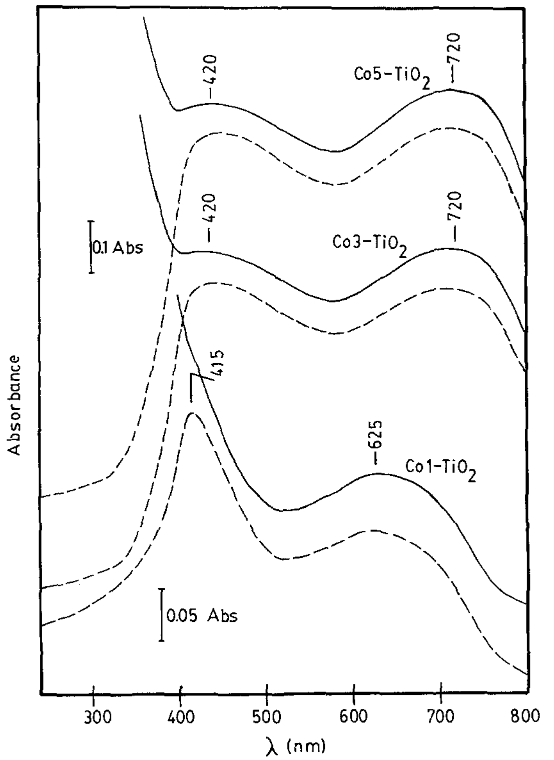

Figure 3 Electronic spectra of Co–TiO_2 samples. Solid line: using MgO as reference; dotted line: using TiO_2 as reference. Note the change in the absorbance scale for sample Co1–TiO_2 (0.05 Abs) and samples Co3–TiO_2 and Co5–TiO_2 (0.1 Abs).

For both Mn–TiO_2 and Co–TiO_2 samples, susceptibilities increased with decreasing field strength, showing the presence of ferromagnetism; plots of susceptibility against reciprocal field were linear and were extrapolated to infinite field to eliminate the effect of ferromagnetism [14]. From these extrapolated values, and taking into account the diamagnetic corrections, the values of effective magnetic moments were obtained and have been collected in Table II, where magnetic properties of some manganese model compounds have been also included. At first sight, it seems clear that manganese ions in more than one oxidation state should coexist in these samples. The predicted magnetic moments for isolated Mn^{2+} (d^5), Mn^{3+} (d^4), and Mn^{4+} (d^3) ions in an octahedral water molecule environment, corrected for spin-orbit coupling using Equation 1 are 5.73, 4.86, and 3.78 BM, respectively;

$$\mu_{\text{eff}} = \mu_{\text{so}}\left(1 - \frac{\alpha\lambda}{10\text{Dq}}\right) \qquad (1)$$

These values have been obtained taking into account a weak field situation, and $^6A_{1g}$, ^5E_g, and $^4A_{2g}$, respectively, for the ground states of these ions; the values of the α parameter and the λ spin-orbit coupling parameter are those reported by Mabbs and Machin [15], and the 10Dq values used are those reported by Dunn *et al.* [9] or calculated from the f and g parameters reported by Jørgensen [16], μ_{so} being the spin-only magnetic moment. So, while the μ_{eff} values for $K_2Mn(SO_4)_2 \cdot 6H_2O$ and $Mn(acac)_3$ fit very well with those predicted above for Mn^{2+} and Mn^{3+}, those for α-Mn_2O_3 and MnO_2 in Table II deviate strongly, as a result of magnetic exchange interactions in α-Mn_2O_3 and (antiferromagnetic) β-MnO_2 [17], a typical consequence of cooperative interactions in the lattices of these compounds. These cooperative effects should be absent in our samples, as the above X-ray diffraction results suggest that no differentiated MnO_x phase exists in the samples. Thus, the magnetic properties of our samples should be compared with those of materials where no cation–cation interaction exists. Bearing this in mind, it can be concluded that the decrease in the μ_{eff} values when the manganese content increases is due to an oxidation of well dispersed manganese cations, $Mn^{3+} \rightarrow Mn^{4+}$. Moreover, this interpretation agrees with the absence of the band at 490 nm (ascribed to a *d–d* transition in Mn^{3+} species) in the electronic spectrum of sample Mn5–TiO_2. The percentages of Mn^{3+} and Mn^{4+} species in the samples can be obtained from the expression

TABLE II Magnetic properties of some manganese compounds and of Mn–TiO_2 samples

Compound	Mn configuration	μ_{eff} (BM)	Reference
$K_2Mn(SO_4)_2 \cdot 6H_2O$	d^5	5.92	[24]
$Mn(acac)_3$	d^4	4.86	[24]
α-Mn_2O_3	d^4	3.5	[17]
β-MnO_2	d^3	5.90	[17]
Mn1–TiO_2		4.81	This work
Mn3–TiO_2		4.19	This work
Mn5–TiO_2		3.67	This work

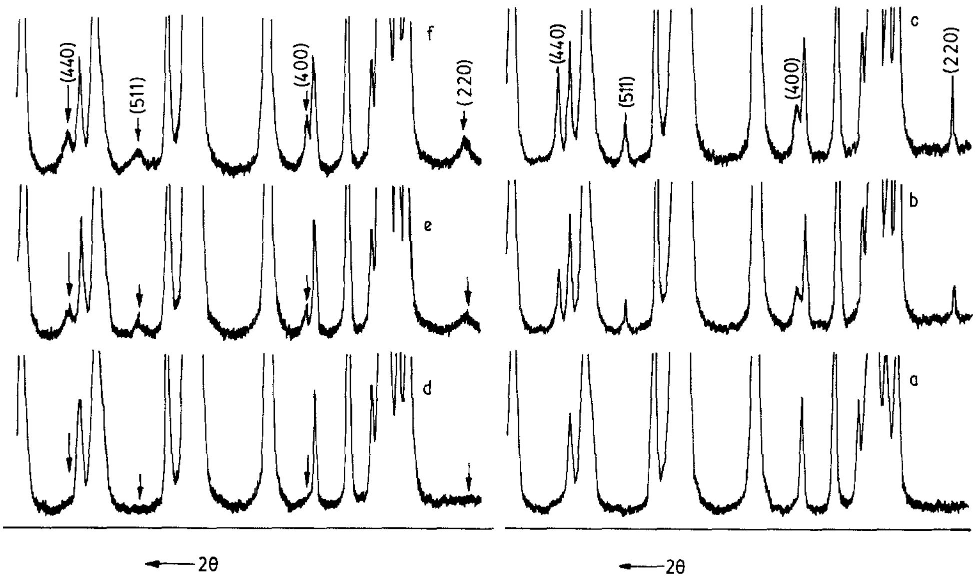

Figure 4 X-ray diffraction patterns of: (a) parent TiO_2, (b) 1% Co_3O_4–TiO_2 mixture, (c) 5% Co_3O_4–TiO_2 mixture, (d) Co1–TiO_2, (e) Co3–TiO_2, (f) Co5–TiO_2. For clarity, only planes of Co_3O_4 are indicated. Vertical arrows in patterns d, e and f correspond to the positions of the Co_3O_4 main peaks.

$$\mu^2_{\text{exptl}} = \mu^2_{\text{Mn}^{3+}}x + \mu^2_{\text{Mn}^{4+}}(1-x) \qquad (2)$$

modified from that used by Ashley and Mitchell [18] to calculate the percentages of octahedral and tetrahedral Co^{2+} cations containing these ions in both types of environments, and where x stands for the molar fraction of Mn^{3+} species. In this way, it may be concluded that in sample Mn1–TiO_2 all manganese ions exist as Mn^{3+}, and as Mn^{4+} in Mn5–TiO_2, while in Mn3–TiO_2 only 35% of the total manganese ions exist as Mn^{3+}.

3.3. Co–TiO_2 samples

3.3.1. *X-ray diffraction diagrams*

As with the Mn–TiO_2 samples, the sensitivity of the method was checked by recording the X-ray diffraction diagrams of Co_3O_4–TiO_2 mechanical mixtures containing the same relative amounts of cobalt and titanium as the samples under study, and the main peaks of Co_3O_4 (as described below and in Fig. 4) were easily recognized.

Contrary to the results obtained with the Mn–TiO_2 samples, where only TiO_2-peaks were detected, in the Co–TiO_2 samples some peaks due to diffraction by poorly crystallized Co_3O_4 (spinel) have been observed, Fig. 4, while no peaks corresponding to ternary Co–Ti–O stoichiometric compounds (e.g. $CoTiO_3$, $CoTi_2O_5$, Co_2TiO_4) could be detected. The most intense peaks of Co_3O_4 occur at 0.2438 nm (100% (3 1 1) plane), 0.1429 nm (45%, (4 4 0) plane), 0.2860 nm (40%, (2 2 0) plane), 0.15559 nm (35%, (5 1 1) plane), and 0.2021 nm (25%, (4 0 0) plane), but the first one coincides with that at 0.2431 nm corresponding to diffraction by the (1 0 3) planes to anatase. The other peaks can be undoubtedly distinguished in the X-ray diffraction patterns of Co3–TiO_2 and Co5–TiO_2, while they were absent in that of Co1–TiO_2 (Figs. 4e, f and d respectively).

Similar to the Mn–TiO_2 samples, the anatase–rutile content remains unchanged, 45 ± 1% anatase, in all three samples, thus indicating a lack of activity in catalysing the phase change transformation under the experimental conditions here used.

3.3.2. *Electronic spectra*

The Co–TiO_2 samples exhibit different colours, according to the cobalt content. Thus, while samples Co3–TiO_2 and Co5–TiO_2 are grey, the second one slightly darker, sample Co1–TiO_2 exhibits a light green colour, while all three precursors (dried at 380 K) were light blue.

The electronic spectra of these samples are shown in Fig. 3; the spectra have been vertically displaced for clarity. Sample Co1–TiO_2 shows a broad absorption centred at about 625 nm (16 000 cm^{-1}), together with the band at 415 nm men-

TABLE III Magnetic properties of some cobalt compounds and species and of Co–TiO_2 samples

Compound or species	Co configuration	Environment geometry*	μ_{eff} (BM)	Reference
Co^{2+}	d^7	O_h (HS)	4.7–5.2	[25]
Co^{2+}	d^7	O_h (LS)	1.8–2.0	[25]
Co^{2+}	d^7	T_d	4.2–4.8	[25]
Co^{3+}	d^6	O_h (LS)	0	–
Co_3O_4	d^7	T_d	2.78	[26]
Co_3O_4	d^6	O_h (LS)	2.78	[26]
Co1–TiO_2			4.53	This work
Co3–TiO_2			3.44	This work
Co5–TiO_2			2.99	This work

*O_h = octahedral; T_d = tetrahedral; HS = high spin; LS = low spin.

tioned above when TiO_2 is used as a reference, while for samples Co3–TiO_2 and Co5–TiO_2 their spectra show two broad bands at about 720 and 430 nm, the band at 415 nm being nearly unobservable if TiO_2 is used as a reference because of its overlap with that at 430 nm. The shape and position of the band at 625 nm are very similar to those for the better resolved triplet at 625, 580 and 520 nm shown in the spectra of the precursors; this triplet has been previously ascribed [18–21] to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition in tetrahedral Co^{2+} ions in several metal oxide host lattices, the band being split by spin-orbit coupling and distortion, but the maximum appears here shifted to lower wavelengths. Moreover, the presence of octahedral Co^{2+} species cannot be totally ruled out, since if tetrahedral Co^{2+} ions occur together with octahedral ones, the more intense bands of the former (partially Laporte-allowed by *p–d* mixing in a tetrahedral environment) will cover the weaker bands of the latter [18, 21, 22].

When the cobalt content is increased, the spectra develop an absorbance increase all along the visible region, although two maxima at 720 and 430 nm are clearly detected. This behaviour has been previously attributed to the formation of Co_3O_4 [18, 21, 22] as a result of a partial oxidation of Co^{2+} to Co^{3+} ions, and the simultaneous migration to octahedral sites, in good agreement with the X-ray diffraction results above.

3.3.3. Magnetic susceptibilities

Effective magnetic moments for Co–TiO_2 samples are shown in Table III, together with those for model compounds. As with the Mn–TiO_2 samples, diamagnetic corrections were performed from the experimental diamagnetism of unloaded TiO_2. Again, increasing susceptibilities were measured with decreasing field strength, and so the susceptibilties were plotted against reciprocal fields to obtain the corrected susceptibilities from the infinite-field intercepts.

The μ_{eff} value for sample Co1–TiO_2 very slightly exceeds that reported for Co^{2+} species in a tetrahedral oxide ion environment, thus suggesting the presence of very small amounts of octahedral Co^{2+} ions, undetected in the visible-UV spectrum due to the reasons given above. The percentage of tetrahedral Co^{2+} ions can be obtained from a expression similar to Equation 2, concluding that 94% of the Co^{2+} ions would exist in a tetrahedral environment.

The μ_{eff} values for samples Co3–TiO_2 and Co5–TiO_2 are much lower, and together with the results above, the presence of Co_3O_4 (μ_{eff} = 2.78 Bohr magnetons) can be concluded, as the presence of low spin Co^{2+} species is hardly to be expected in an octahedral oxide ion environment. This behaviour, i.e. the formation of Co_3O_4 when the cobalt content increases, has been previously observed [18, 21–23] in Co–Mo–Al_2O_3 and Co–Al_2O_3 systems, among others, and has been attributed to an increase in the number of low spin octahedral Co^{3+} species (ground term $^1A_{1g}$) by oxidation of Co^{2+} ions, preferently occupying octahedral sites.

4. Conclusion

Although both series of samples studied here show an increase in the oxidation state of the guest cation with its own content, as concluded from the electronic spectra and the magnetic measurements, the degree of dispersion of these cations is different, as deduced from the magnetic measurements and the X-ray diffraction data. While the manganese ions seem to keep well dispersed in all three samples, cobalt ions form a differentiated Co_3O_4 phase for cobalt contents equal or larger than 3% (atomic Co/Ti ratio).

Both anatase and rutile forms of TiO_2 consist of TiO_6 octahedra stacked in different ways along the *c*-axis. The temperature used here to obtain the samples is too low to lead to deep migration of the guest cations into the host lattice, and so formation of cobalt and manganese oxide layers on the surface of the TiO_2 (or located within the very external layers of the TiO_2 crystallites) may be concluded. Taking into account the specific surface area values in Table I and the manganese and cobalt contents in the samples, the manganese and cobalt surface densities can be calculated, and values ranging from $1.6\,nm^{-2}$ (1% samples) to $5\,nm^{-2}$ (3% samples) and $8\,nm^{-2}$ (5% samples) are obtained. These values are low enough to permit a good dispersion of the ions on the surface, as observed for the Mn–TiO_2 samples, but not in the Co–TiO_2 samples. This difference may be related to the decrease in the S_{BET} values in Table I, assuming that in the Mn–TiO_2 samples the increase in the dispersed manganese content on the surface of the TiO_2 crystallites favours sintering of the particles, thus leading to a steady surface area decrease when the manganese content increases. However, as the increase in the cobalt content leads to a change in the nature of the cobalt-containing species (well dispersed Co^{2+} ions in Co1–TiO_2, and Co_3O_4 in the other two samples) existing in the Co–TiO_2 samples as the Co_3O_4 aggregates content increases (on passing from Co3–TiO_2 to Co5–TiO_2), the sintering process decreases and a larger S_{BET} value is obtained. The value for Co3–TiO_2 seems to correspond to a compromising situation because of the presence of both well dispersed Co^{2+} ions and Co_3O_4 aggregates.

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