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Interactions with the support in Co/TiO_2 and Co_3O_4/TiO_2 systems

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TiO_2-supported cobalt systems have been studied both in the oxidized and in the reduced state. After high temperature (770 K) reduction no hydrogen adsorption is observed, indicating the occurrence of strong interactions with the support. Oxidation at room temperature is not observed, but after 770 K oxidation, Co_3O_4 particles are detected, decreasing the dispersion of the supported phase and the extent of their interaction with the support.

1. Introduction

Although known since the 1950s, strong metal-support interactions (SMSI) have deserved a great deal of attention [1, 2] since the work by Tauster *et al.* [3] on high temperature reduced Pt/TiO_2 systems. Such interactions lead to a lack of hydrogen and carbon monoxide adsorption capacity and to unexpected catalytic properties, if compared to those of the same metal supported on conventional supports (SiO_2, Al_2O_3, zeolites). These studies have usually been performed on TiO_2-supported noble metals, but it has been recently shown that such SMSI also exist when first series transition metals are supported on semiconducting oxides, such as TiO_2 [4–11].

In the present paper, evidence is provided on the existence of SMSI in TiO_2-supported cobalt, a catalytic system very scarcely studied in the literature [10–12].

2. Experimental details

2.1. Samples preparation

The preparation of the samples has been described elsewhere [13]. The composition corresponds to 2.5% atomic ratio Co:Ti. The precursor (TiO_2 Degussa P-25 impregnated with an aqueous solution of $Co(AcO)_2 \cdot 4H_2O$ and dried overnight at 380 K) was manually ground in an agate mortar and oxidized (in oxygen, 99.95% from Sociedad Castellana del Oxigeno, SCO) or reduced (in hydrogen, 99.998% from SCO) at 770 K for 2 h, in a dynamic system ($50\,ml_{STP}\,min^{-1}$) or in a static one (gas pressure $27\,kN\,m^{-2}$), and in this case a cold trap (77 K) was located by the reaction chamber to withdraw the gases/vapours evolved during the reaction. No significant difference was observed between samples obtained in both ways. When naming the samples, the letters O and R stand for samples oxidized or reduced as described above.

2.2. Apparatus and procedures

Physicochemical procedures for characterizing the samples were the same as described elsewhere [13]. Hydrogen/oxygen titrations were carried out as follows: a known amount of sample was heated in oxygen at 770 K for 5 h and outgassed at $10^{-4}\,N\,m^{-2}$ and 770 K for 3 h. A pressure of $27\,kN\,m^{-2}$ of hydrogen was admitted in the reaction chamber and the sample heated at 770 K for 2 h; a cold trap (77 K) was located by the sample to condense the water vapour evolved during the reaction (thus avoiding readsorption) and that was measured after removing the hydrogen and isolating the sample, to know the extent of the reaction 1

$$Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O \qquad (1)$$

A specially built quartz cell was used to record the visible–ultraviolet/diffuse reflectance spectra of samples in the absence of air.

3. Results and discussion

3.1. X-ray diffraction diagrams

The percentage of anatase in the parent TiO_2 and in all samples here studied was 53 ± 1% (a batch different to that used in [13] was used), as determined from the intensities of the main lines of rutile, (1 1 0) planes at 325 pm, and of anatase, (1 0 1) planes at 352 pm, and using the equation given by Criado and Real [14]. Anatase–rutile phase change takes place above 970 K [10] in the presence of cobalt. No peak due to ternary Co–Ti–O phases was observed.

Peaks corresponding to diffraction by the (2 2 0), (4 0 0), (5 1 1) and (4 4 0) planes of Co_3O_4 were hardly detected in sample Co–O, but were intensified in the diagram of sample Co–ORO, indicating that the three thermal treatments given to this sample at 770 K (oxidation, reduction, oxidation) have increased the sintering of Co_3O_4 particles. On the contrary, the diagram of sample Co–ROR (also after three thermal treatments) shows no peak of metallic cobalt (nor peak of Co_3O_4), suggesting that if the precursor is reduced before oxidation the dispersion of the supported phase increases, and sintering is delayed.

3.2. Adsorption measurements

The 770 K reduced samples show a complete lack of ability for hydrogen adsorption at room temperature; taking into account that cobalt is included by Bond in group B_1 [15], i.e. metals showing ability for hydrogen

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TABLE I Specific surface areas (S_{BET}, $m^2 g^{-1}$) for some Co/TiO_2 samples after different treatments

Sample	S_{BET} ($m^2 g^{-1}$)
TiO_2	51.5
Co–O	45.6
Co–ROR	40.3

chemisorption, this behaviour can be seen as a result of strong interactions with the support.

Adsorption of nitrogen at 77 K on samples outgassed at 420 K, 2 h was performed to determine the specific surface areas (S_{BET}) of the samples. These are included in Table I. A steady decrease of the S_{BET} value is observed when the number of thermal treatments is increased, as a result of the sintering of the crystallites.

3.3. Electronic spectra

The oxidation/reduction treatments deeply change the colour of the samples. While the precursor is pale blue, the reduced samples are grey and the oxidized ones are dark brown.

The spectra are displayed in Fig. 1, and vertically displaced for clarity. Parent TiO_2, Fig. 1a, shows only a very intense band at ~300 nm, ascribed to a $O^{2-} \rightarrow Ti^{4+}$ charge transfer process, i.e. excitation of an electron from the valence band (mainly formed by oxygen 2p orbitals) into the conduction band (titanium 3d orbitals) [16]. As this band is observed for all samples, parent TiO_2 was used as reference to record the spectra of the cobalt-containing samples.

The precursor shows a band at 625 nm with a shoulder at 545 nm, Fig. 1b; this split band corresponds to a $^4A_2(F) \rightarrow {}^4T_1(P)$ transition in tetrahedral Co(II) (d^7) species, as described elsewhere [13, 17–19], although the presence of octahedral Co(II) species cannot be undoubtedly discarded.

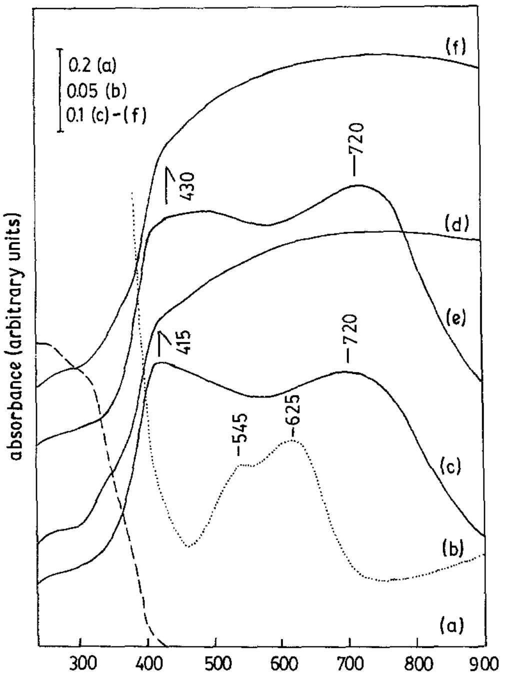

Figure 1 Electronic spectra (diffuse reflectance) of the samples. (a) Parent TiO_2, (b) precursor $Co(II)/TiO_2$, (c) sample Co–O, oxidized in oxygen at 770 K, (d) sample Co–OR, reduced in hydrogen at 770 K, (e) sample Co–ORO, oxidized in oxygen at 770 K, (f) sample Co–OROR, reduced in hydrogen at 770 K. Reference: spectra (a) and (b): MgO; spectra (c) to (f): TiO_2.

When heated in oxygen at 770 K, Fig. 1c, sample Co–O, two maxima at 720 and 415 nm, with a shoulder at 430 nm, are observed. The maxima at 720 and 430 nm have been previously ascribed to the formation of Co_3O_4 species, as confirmed by the X-ray diffraction data above, as a result of a partial $Co(II) \rightarrow Co(III)$ oxidation process and simultaneous migration of the Co(III) species to octahedral holes of the lattice.

The origin of the band at 415 nm has been discussed in the literature, and it has been ascribed to a $M^{n+} \rightarrow Ti^{4+}$ process, i.e. a process implying both the support and the guest cation, thus being a consequence of an interaction between both [13, 20–24]. However, its real origin needs to be further confirmed as, although its occurrence in the spectra of samples containing transition cations supported on TiO_2 (but not in pure TiO_2) suggests the above ascription, the fact that its position remains the same whichever the supported cation (manganese, chromium, cobalt and copper) seems to indicate that it does not merely correspond to the excitation into the conduction band of TiO_2 of an electron from discrete *d* orbitals of the guest cations, as the energy position of these orbitals will depend on the nature and oxidation state of the cation. Nevertheless, the band is not recorded in the spectra of pure TiO_2, nor in those of mechanical mixtures MO_x/TiO_2 (M = manganese, chromium, cobalt and copper), and it can then be used as a guide to the existence of metal oxide–TiO_2 interactions.

When the sample is reduced at 770 K, Fig. 1d, sample Co–OR, a flat spectrum, the sample absorbing all along the visible range, is observed. The reduced sample is stable in air at room temperature, but after oxidation in oxygen at 770 K, sample Cu–ORO, Fig. 1e, the two maxima at 720 and 430 nm, but with significant changes in the shape of the spectrum around 400 nm, are recovered.

If Figs 1c and e are compared, it can be observed that the maximum close to 400 nm has been shifted from 415 to 430 nm, or it can be said that the maximum at 415 nm has disappeared. Taking into account that the reduced samples are not reoxidized by exposure to air at room temperature, it can be assumed that the successive thermal treatments in sample Co–ORO have sintered the Co_3O_4 particles, decreasing their dispersion and their interaction with the support, responsible for the band at 415 nm.

Finally, Fig. 1f, corresponding to the reduced Co–OROR sample, coincides with that of sample Co–OR.

3.4. Hydrogen/oxygen treatments

A sample of parent TiO_2 gave rise to 35 μmol $H_2O\ g^{-1}$ TiO_2 when reduced in hydrogen at 770 K for 2 h. This amount agrees fairly well with previous results by Delk and Vavere [9], as determined by temperature programmed reduction. This value remains the same after successive oxidation/reduction cycles, indicating that oxidation at 770 K for 5 h in oxygen recovers the original state of TiO_2, as indicated by Iwaki and Mihura [25].

Before studying the reduction of Co_3O_4/TiO_2 systems and in order to check if reduction in hydrogen at 770 K for 2 h is enough to reduce quantitatively all Co_3O_4 to metallic cobalt, such a reaction was studied on Co_3O_4/Al_2O_3 (obtained similarly to those here studied and with a Co : Al atomic ratio 2.5), where interactions with the support are not expected to occur. The amount of water formed by the thermodynamically favoured Reaction 1 corresponds to reduction of 98 $\pm$ 1% of the total cobalt content, indicating that, in the absence of SMSI, treatment in hydrogen at 770 K for 2 h is powerful enough to reduce quantitatively Co_3O_4 to cobalt.

Consumption of hydrogen for the Co_3O_4/TiO_2 samples was 540 μmol $H_2\,g^{-1}$, while 417.2 μmol $H_2\,g^{-1}$ are expected to be consumed for a 100% reduction of the cobalt. Even taking into account the amount consumed during reduction of the support (35 μmol $H_2\,g^{-1}$), the value experimentally obtained is too high, well above the experimental error. Bearing in mind that consumption of hydrogen is not measured from the amount of hydrogen withdrawn from the gas phase during reaction, but from the amount of water formed, the excess in hydrogen consumption cannot be due to diffusion into the support nor the metallic phase, but to a further reduction of the support, catalysed by the presence of cobalt, similar to previous results in Cu/TiO_2 systems [9, 24].

According to our diffuse reflectance data, the reduction process is reversible after oxidation at 770 K, as for the pure support, and this was confirmed by repeated measurements of the H_2/O_2 treatments on the same portion of sample.

However, although successive oxidation/reduction treatments lead to maintained SMSI (lacking in hydrogen adsorption capacity) in the reduced state, the oxidized samples are actually modified, favouring the formation of Co_3O_4 particles, as observed in the X-ray diffraction diagrams, and decreasing the metallic oxide–support interactions, as deduced from the absence of the 415 nm band. This effect is not observed in Cu/TiO_2 systems [24], despite the favourable thermodynamics for both oxides ($-86\,kJ\,mol^{-1}$ and $-613\,kJ\,mol^{-1}$ for CuO and Co_3O_4, respectively) and may be due therefore to kinetic effects.

4. Conclusions

According to the results above, it can be concluded that the final state of Co/TiO_2 and Co_3O_4/TiO_2 systems does not depend only on the thermal treatments given, but on the sequence of such treatments as well. If the precursor is initially reduced, the interactions of the metal with the support "help" to keep a high degree of dispersion, delaying the sintering of the supported phase. On the contrary, if the precursor is initially oxidized, although interactions with the support exist (and the band at 415 nm develops) and the Co_3O_4 phase is well dispersed, further thermal treatments are enough to cancel such interactions with the support, thus allowing an increase in the size of the Co_3O_4 crystallites.

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