

Surface and Structural Features of Co-Fe Oxide Nanoparticles Deposited on a Silica Substrate

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Mono- and dimetallic cobalt- and iron oxide nanoparticles deposited on the surface of a silica substrate have been prepared by an impregnation technique. Both the bulk and surface structures of these particles have been characterised by different physical and chemical techniques. The results provided by X-ray diffraction, Mössbauer and X-ray photoelectron spectroscopy show the formation of separate Co_3O_4 and Fe_2O_3 nanoparticles in oxide samples, but in no case were cobalt-iron mixed oxides detected. Quantitative data also showed that the dispersion degree of cobalt- and iron oxides is rather low. It was also observed that pretreatment of the supported metal oxide nanoparticles under a hydrogen atmosphere does not promote the formation of a metal-support

interaction, although a cobalt-iron interaction is observed in the dimetallic systems. The diffraction patterns and photoelectron and Mössbauer spectra of these dimetallic samples provide conclusive proof for the formation of both metallic Co^0 and iron-cobalt (Co_7Fe_3) alloy phases in the hydrogen-reduced samples. It was also found that the crystallite size of the alloyed Co_7Fe_3 phase increases with increasing iron content, i.e. 11 and 23 nm for samples containing 1 % and 5 % Fe added to the base Co sample, respectively, while that of Co^0 was constant (10 nm).

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Introduction

Nowadays, composite materials give rise to numerous studies with a view to improving their mechanical, thermal, optical and other properties, which hold promise for novel technological applications. Transition metal oxides are being widely used, and Fe-Co materials are of particular interest in catalytic reactions such as the Fischer-Tropsch synthesis (FTS),^[1–6] methanol decomposition,^[7–9] NH_3 synthesis,^[10] carbon nanotube synthesis.^[11–13] Furthermore, their interesting magnetic properties^[14] suggest that they will have many applications in magneto-optical recording media, displays and devices such as wave-guides, insulators, modulators and switches.^[15–17]

This fact has provoked several reports in which these mixtures are prepared by different synthetic methods such as sol-gel,^[18,19] co-precipitation,^[20] plasma coating,^[21] sintering^[22] and thermal decomposition.^[23] Co- and/or Fe-supported systems prepared by wetness- or incipient wet-

ness impregnation methods from nitrate precursors have also been reported.^[6,14] Dimetallic catalysts prepared by the incipient wetness method show reactivities different from that of equivalent Fe- or Co single-metal catalysts, thus indicating that the intimate interaction between Fe and Co is important.^[24,25] A synthesis of iron-cobalt nanoparticles dispersed in a silica matrix has also been reported, and the authors noted the formation of magnetic cobalt ferrite nanocomposites, Co_3O_4 and ferrihydrite or Co-Fe alloys, depending on the Fe and Co precursors.^[19] Fe/Co catalyst mixtures have been prepared on several supports, including alumina,^[24] carbon,^[26,27] zirconia^[28] and titania.^[14,25,29,30]

A viable methodology that has been developed for controlling the property of a metal is that of alloying.^[31–35] Three structures have been found for the metal in the iron-cobalt alloy, depending on the synthesis temperature and the subsequent thermal treatment: a bcc structure, an α -Mn-like structure and a fcc structure that appears after thermal treatment.^[36,37] The bcc and fcc structures are classical structures for iron- and cobalt-based alloys. These alloys exhibit outstanding properties, particularly the cobalt-enriched composites. Indeed, these latter are active in the FTS and favour the formation of olefins without producing high amounts of CO_2 ^[4,38] and alcohol production.^[6]

A large body of work has been developed over the past decades on the performance of supported cobalt catalysts, especially with regard to the effect of promoters,^[39–43] sup-

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ports^[44–46] and preparation^[47–52] methods. Cobalt catalysts produce high yields of long-chain alkenes in the FTS. They are also characterised by a low ability to yield oxygenates. In addition, cobalt catalysts exhibit considerable stability in the metallic state.

Iron is the other active phase that is most often used in the hydrogenation reactions of carbon oxides. It is known that several forms of iron (iron, iron carbides, iron oxide) exist in iron-based catalysts when subjected to FTS, and there are many studies dealing with the role of iron phases in the FTS.^[53–55] Iron catalysts used in CO hydrogenation are usually promoted to obtain a high stability and catalytic activity. These systems produce higher yields of oxygenated products and can perform the water gas-shift reaction. The incorporation of cobalt and iron phases onto a support substrate results in substantial changes in both activity and product distribution as, when used together, they do not simply give the additive properties (activity, selectivity) expected from knowledge of the properties of the individual metals. These dimetallic CoFe catalysts proved to be much more attractive in terms of alcohol formation and give rise to the production of ethanol and propanol, depending on the iron content.^[6] Taking this into account, the possible interaction of cobalt and iron, in the form of cobalt ferrite or alloys, when used together as active phases for catalytic reactions such as FTS or as a possible magnetic composite should be studied by different characterisation techniques.

In light of the above, the present work was undertaken with the aim of analysing the effect of the incorporation of both cobalt and iron species supported on a silica matrix on the structural, textural and morphological characteristics relative to the properties shown by the monometallic systems. In particular, emphasis is placed on the formation of CoFe intermetallic compounds after catalyst activation. Some clues to the nature of the bulk and surface structures generated on the silica-supported cobalt-iron catalysts were obtained by XRD, X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy and temperature-programmed reduction (TPR). The synergism between cobalt and iron, two FT active metals, will be explored in a subsequent work that will consider whether the above metals, when used together, give the additive properties (activity and selectivity) expected of the individual metals or not.

Results and Discussion

Chemical Composition and Textural Properties

The chemical composition of the oxide samples was determined by ICP-AES; results are compiled in Table 1. These results indicate that cobalt- and/or iron loadings are close to the nominal values. The BET specific areas and pore volumes of the fresh metal oxide loaded samples and the bare SiO₂ support, also summarised in Table 1, indicate that incorporation of cobalt and/or iron onto the SiO₂ substrate leads to a drop in both specific area and pore volume. A decrease in the BET area of around 20–30% is found upon incorporation of iron and cobalt, and a similar drop is found for the other two dimetallic (CoFe10/1-c and CoFe10/5-c) samples. The pore-size distributions of the metal-oxide-loaded samples and SiO₂ reference are displayed in Figure 1. The pore-size distributions of the samples do not change upon incorporation of cobalt- and/or iron oxides during the preparation step. The simultaneous drop in BET area and pore volume and the almost unchanged pore distribution of the metal-oxide-loaded sam-

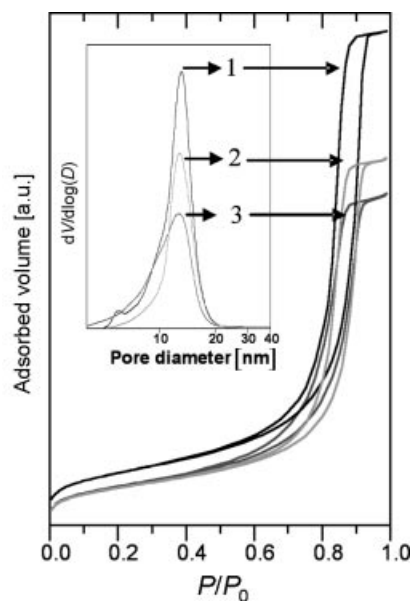


Figure 1. Pore distribution for the (1) support, (2) CoFe10/5-c and (3) Co10-c.

Table 1. Elemental analysis and textural characteristics of the CoFe/SiO₂ system.

Catalyst	Elemental analysis				N ₂ adsorption	
	Metal loading (% Co)		Metal loading (% Fe)		S_{BET} [m ² g ⁻¹]	V_{ads} [cm ³ g ⁻¹]
	nominal	ICP	nominal	ICP		
SiO ₂	–	–	–	–	289	1.19
SiO ₂ -c	–	–	–	–	300	1.18
Co10-c	10	10.2	–	–	219	0.80
Fe10-c	–	–	10	10.2	216	0.93
CoFe10/5c	10	9.3	5	5.1	221	0.96
CoFe10/1c	10	9.4	1	0.9	210	0.88

ples point to a preferential location of big cobalt- and/or iron oxide particles in the interparticle voids between silica particles. Thus, the decrease in the pore volume as a result of pore locking does not change the pore-size distribution and is in accordance with the greater decrease in pore volume, which is higher than the weight fraction of deposited metal phases. However, deposition of very small metal oxide particles within the smallest pores of silica, and more specifically for the Co10-c sample, cannot be ruled out.

Crystalline Structure

Calcined Samples

The crystal structures of the supported cobalt and iron phases of oxide samples were determined by X-ray diffraction (Figure 2A). The monometallic Co10-c sample displays sharp and narrow diffraction lines that fit very well with that of Co_3O_4 spinel (JCPDS card 78-1970).^[56] The obtained lattice parameter for this phase is $a = 8.088 \text{ \AA}$, which is similar to that obtained for the cobalt oxide spinel phase. A broad band centred at about $22^\circ 2\theta$ belongs to the amorphous structure of silica. A detailed examination of the spectrum was done to ensure that no other crystalline Co-containing phases, such as Co_2SiO_4 , had developed. As Co_3O_4 and CoSiO_4 species have similar interplanar distances, differentiation between both compounds is not easy unless they are very well crystallised. It should be emphasised that formation of a crystalline Co_2SiO_4 phase is only possible upon calcination of the impregnate at temperatures substantially higher than that (773 K) employed in this work.^[57] Note that the formation of a cobalt-oxide-silica interacting layer cannot be ruled out from this XRD pattern.

The diffraction pattern of the calcined Fe10-c sample shows all the lines of crystalline Fe_2O_3 ^[58,59] (JCPDS card 85-0599), together with the broad feature of silica at about $22^\circ 2\theta$ (see above). No peaks of any other iron-containing compound are observed.

The XRD patterns of calcined CoFe10/5-c and CoFe10/1-c samples are also included in Figure 2A. Both samples show diffraction lines that correspond to the Fe_2O_3 phase; these lines, as expected, are more intense in the sample with a higher Fe loading (CoFe10/5-c). Some of the Fe_2O_3 lines are overlapped by those of the Co_3O_4 spinel,^[58,60] and the rather low intensity of the lines corresponding to Fe_2O_3 indicates the low crystallinity of the Fe_2O_3 particles. A weak interaction between Fe_2O_3 and Co_3O_4 phases is possible and could affect the crystallinity of the iron oxide particles without producing any modification in the structure of the oxides. These results indicate that the two oxides remain as separate phases at the scale of the XRD technique, which is above $3\text{--}4 \text{ nm}$. The lattice parameters found for the bimetallic systems CoFe10/5-c and CoFe10/1-c are $a = 8.090$ and $8.089 \text{ \AA}$, respectively, and are very similar to that of Co_3O_4 , which indicates that a CoFe mixed composite has not been formed. The presence of a mixed cobalt-iron oxide phase would give a higher value of the lattice parameter.

The mean particle size of the supported cobalt- and/or iron oxides was calculated from the Scherrer equation by selecting the most intense diffraction line for each oxide — the crystal planes (311) for Co_3O_4 and (220) for Fe_2O_3 — and by assuming a spherical geometry for the oxide particles. The results compiled in Table 2 reveal that the larger size corresponds to Co_3O_4 particles in the monometallic catalyst (21 nm), while it is slightly reduced (17 nm) for the parent Fe10-c sample. It can also be seen that the size of the Co_3O_4 particles decreases upon adding iron, and this drop is even more marked for sample CoFe10/5-c. Finally,

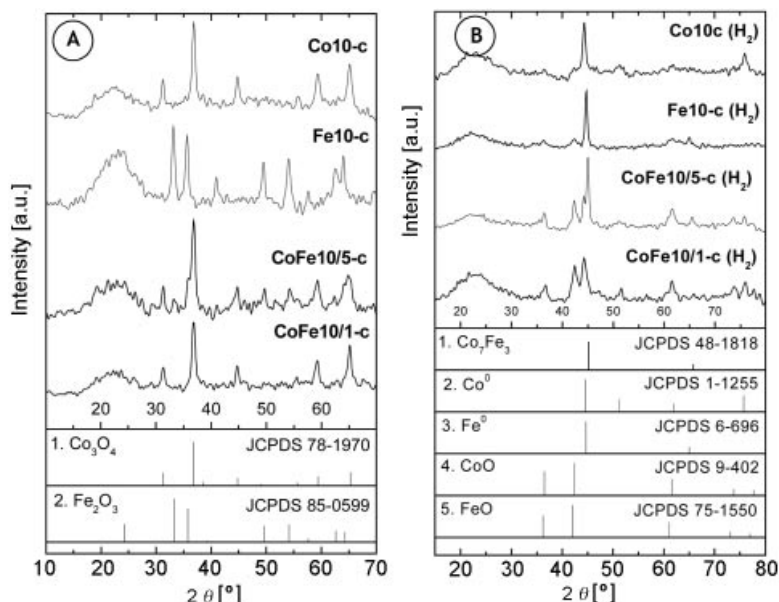


Figure 2. X-ray diffraction pattern of Co/Fe(SiO_2): (A) calcined, (B) after H_2 reduction at 773 K .

no attempt was made to calculate the size of the iron oxide particles in the CoFe10/1-c sample because of the extreme broadening of the Fe_2O_3 diffraction lines. This fact indicates that the particle size should be below 5 nm, which is the limit for applying the Scherrer equation.

Table 2. Crystallite size of supported nanoparticles for the calcined and reduced systems.

Sample	XRD phases	2θ [°]	Crystal size [nm]
Co10-c	Co_3O_4	44.38	21
Fe10-c	Fe_2O_3	44.75	18
CoFe10/5-c	Co_3O_4	44.22	14
	Fe_2O_3	45.03	14
CoFe10/1-c	Co_3O_4	44.33	17
	Fe_2O_3	42.49	—
Co10-c (H_2)	Co^0	44.38	17
Fe10-c (H_2)	Fe^0	44.75	22
CoFe10/5-c (H_2)	Co^0	44.22	10
	Fe_3Co_7	45.03	23
CoFe10/1-c (H_2)	Co^0	44.33	10
	Fe_3Co_7	42.49	11

Reduced Samples

The pattern of the Co10-c sample reduced in H_2 at 773 K shows diffraction lines belonging to the (111), (220) and (311) planes of the fcc Co^0 crystallites (JCPDS card 1-1255). The lattice parameter found for cubic Co^0 is $a = 3.541 \text{ \AA}$. No hexagonal structure is observed because the reduction temperature is too high to achieve this type of crystal structure. The diffraction lines of CoO are still observed, which indicates that the cobalt phase has not been reduced completely, although their intensity is lower than that of the oxide sample. A broad feature at about $22^\circ 2\theta$ arising from the amorphous silica substrate is also found.

The reduction profile of the Fe10-c sample is shown in Figure 2B. Diffraction lines of metallic α -Fe (JCPDS card 6-696) and FeO (JCPDS card 75-1150) are observed, although the intensity of the peaks of the latter phase is weak. The absence of hematite (Fe_2O_3) or magnetite (Fe_3O_4) phases indicates that the reduction is in the final stage. The lattice parameter found for this species is $a = 2.863 \text{ \AA}$.

The diffraction profiles of the dimetallic CoFe10/5-c and CoFe10/1-c samples are also displayed in Figure 2B. Besides the species found in the monometallic samples, new diffraction lines belonging to a FeCo phase are observed. These new peaks — the most intense one in both diffraction patterns occurs at $2\theta \approx 45^\circ$ — correspond to the (110) plane of the Co_7Fe_3 alloy (JCPDS card 48-1818) with a bcc crystal structure. This indicates that most of the cobalt and iron phases are involved in this alloy. Some additional peaks observed in both reduced samples can be indexed to metallic Co and cobalt oxide, although apparently no lines for a metallic iron phase are present. This fact could be due to an overlapping of these lines with those assigned to cobalt and to the Co_7Fe_3 alloy, since the ionic radii are very similar. The intensity of the main diffraction line characteristic of the alloy in the reduced CoFe10/1-c sample is lower than that of metallic Co^0 , which contrasts with the proportion

obtained for the reduced CoFe10/5-c sample and is in accordance with the relative proportions of Co and Fe in this sample. Both metallic species found in the dimetallic systems present very similar lattice parameters. The following lattice parameters are found for both systems: $a = 2.842 \text{ \AA}$, which corresponds to Co^0 , and $a = 3.541 \text{ \AA}$, which corresponds to the CoFe alloy.

The mean particle size was determined by X-ray line broadening according to the Scherrer equation (Table 2). For this calculation, the (111) plane of metallic Co, the (110) plane for metallic Fe and the (110) plane for the Co-Fe alloy phases were selected. A comparison of the crystallite sizes for both reduced and calcined samples shows an increase in crystallite phase during the reduction because of sintering of the metal phase. In addition, the extent of sintering is higher in Fe10-c than in Co10-c. For the dimetallic catalysts, an increase in alloy particle size is observed in CoFe10/5-c. Finally, the crystallite size of Co^0 in both dimetallic samples is similar but lower than for Co10-c, which suggests that alloy formation inhibits the sintering of Co^0 particles.

Morphology and Phase Distribution

Calcined Samples

The morphology of the samples was studied by electron microscopy and line profile analysis (LPA). The LPA technique allows the determination of the catalyst surface topology as well as the active-phase disposition, the metallic particle size and the surface state of the support. Figures 3A and 3C show SEM micrographs of cobalt, while Figures 3B and 3D display micrographs of monometallic silica-supported samples taken at two different magnifications. No differences were found for these two types of samples. The surface is made up of particles of irregular shape and size ranging from 2 to $25 \mu\text{m}$. The particles are delimited by well-defined faces formed by laminar exfoliation (A and B). Higher magnification images (C and D) indicate

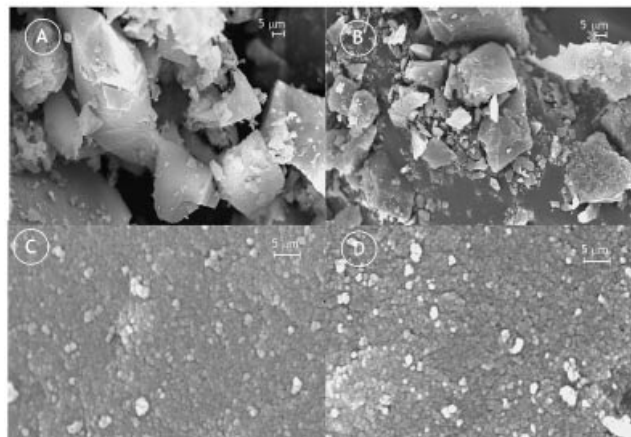


Figure 3. SEM images of calcined Co10-c (A and C) and Fe10-c (B and D).

the presence of uniformly developed spherical particles, about $0.2\ \mu\text{m}$ in size, with compact packing. The SEM micrographs of the dimetallic samples do not show any differences with respect to those of the monometallic samples.

The LPA analysis indicates a very irregular profile for silicon, with holes and protuberances of different sizes, depths and heights. However, the profile belonging to cobalt is more homogeneous and is consistent with a well-dispersed phase. Similarly, LPA analysis of the monometallic Fe10-c sample shows a silicon profile resembling that of the cobalt counterpart (Co10-c), although the iron profile reflects a wider size distribution of the iron oxide particles. In addition, the LPA profiles for the dimetallic CoFe10/5-c and CoFe10/1-c samples indicate that both cobalt and iron profiles are more homogeneous than in the monometallic ones, thereby suggesting a better distribution of the Co_3O_4 and Fe_2O_3 phases across the surface.

The cobalt and iron mono- and dimetallic systems were also analysed by TEM with the aim of determining the form, shape and distribution of the particles on the silica

support. The TEM images of Co10-c show spherical particles with non-uniform sizes within each SiO_2 particle. The same is true for other SiO_2 particles. The size of the cobalt oxide particles falls between 0.1 and $1\ \mu\text{m}$ (Figure 4A). Riva et al.^[61] have performed a TEM analysis of silica-supported cobalt oxides and found that metal oxide particles form spherical aggregates both inside and on the surface of silica particles, with non-uniform sizes and a mean diameter of between 0.3 and $0.5\ \mu\text{m}$. On the contrary, the micrograph of Fe10-c shows that iron oxide particles are not spherical as in the case of Co10-c (Figure 4B). In addition, non-uniform aggregates, with sizes ranging from 0.1 to $1\ \mu\text{m}$, are formed on each silica particle. Elemental analysis was also performed on individual particles, and the results indicated that they are mainly made up of iron and oxygen. XRD, XPS and Mössbauer spectroscopy revealed Fe_2O_3 to be the only phase present. Finally, the TEM images of CoFe10/5-c and CoFe10/1-c revealed that the particle size diminishes with respect to the monometallic samples, which is in good agreement with the Mössbauer data.

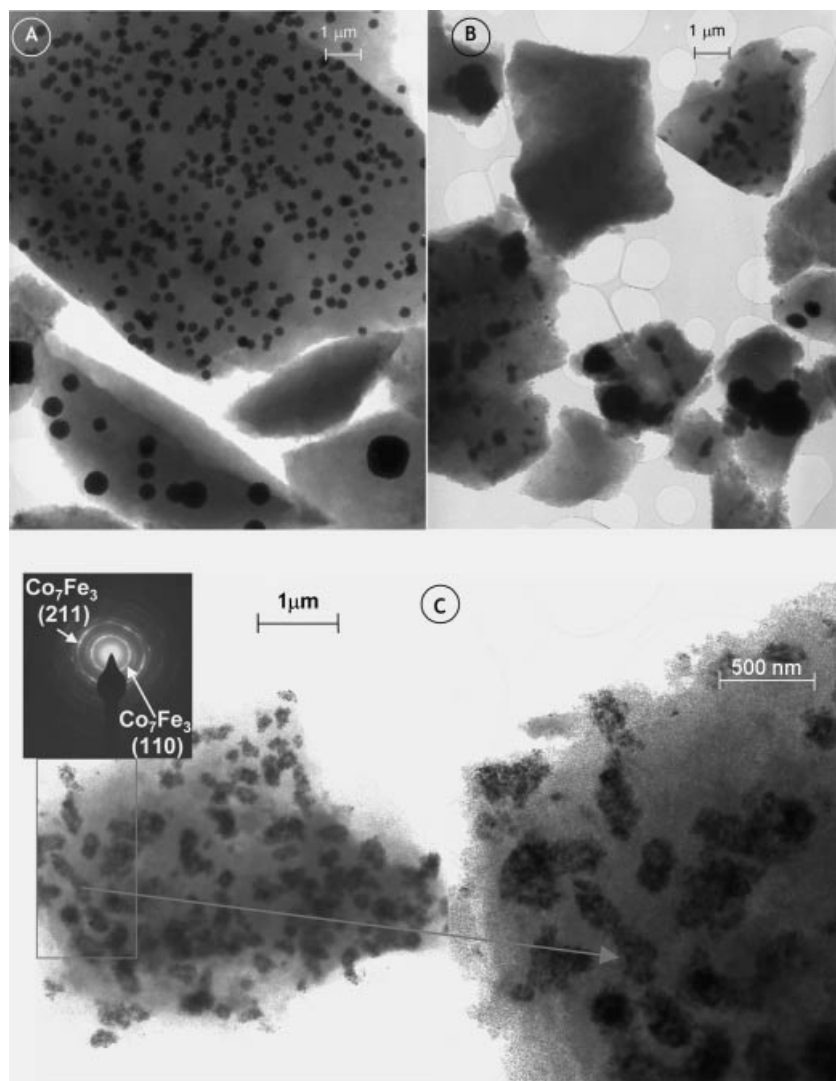


Figure 4. TEM images of (A) Co10-c and (B) Fe10-c; (C) TEM images of CoFe10/5-c reduced in H_2 at $773\ \text{K}$, with a high resolution image on the right. Inset: the electron diffraction pattern.

Reduced Samples

Co10-c, Fe10-c and dimetallic samples reduced in hydrogen at 773 K were analysed by TEM with the aim of comparing the size, shape and distribution of the metal particles with respect to the fresh counterparts. The TEM images of Co10-c show that the size and shape of some particles remain unchanged upon reduction. In addition, a certain fraction of particles lose their spherical form and form other non-uniform aggregates. The reduced Fe10-c sample behaves similarly. The TEM image of reduced CoFe10/5-c displayed in Figure 4B reveals that the particles present an irregular shape and appear better dispersed on the silica substrate. Electron nanodiffraction taken on a large particle (Figure 4B) confirms the formation of an iron-cobalt alloy. This phase was also confirmed by XRD, XPS and Mössbauer spectroscopy.

Bulk Structures of Iron-Containing Catalysts (Mössbauer Spectroscopy)

Oxide Samples

The bulk structure of iron-containing catalysts was revealed by Mössbauer spectroscopy, and both the chemical state and relative abundance of iron and cobalt at the cata-

lyst surface was determined by photoelectron spectroscopy. The iron-containing samples were characterised by Mössbauer spectroscopy with the aim of determining the local environment of the iron species and their concentration. Only the two calcined Fe10-c and CoFe10/5-c samples were analysed by this technique. The other dimetallic sample (CoFe10/1-c), which contains a much lower amount of iron (1 wt.-%), was not studied since its signal is too weak to get reliable information. Figure 5A displays the Mössbauer spectrum of sample Fe10-c. It includes two components: a paramagnetic doublet assigned to highly dispersed Fe^{3+} and a magnetic sextet related to iron(III) oxide particles with a particle size larger than that responsible for the doublet. The hyperfine field corresponding to the sextet (50.4 T) is lower than that of bulk $\alpha\text{-Fe}_2\text{O}_3$ (51.5 T).^[62,63] This fact points to the presence of small $\alpha\text{-Fe}_2\text{O}_3$ particles with a diameter of between 7 and 12 nm.^[64] $\alpha\text{-Fe}_2\text{O}_3$ species are the only species detected by Mössbauer analysis of the calcined Fe10-c sample, in agreement with the XRD pattern analysis presented above. The isomer shift (δ), quadrupolar shift (QS), quadrupolar magnetic field (H_{hf}) and weight concentration of each species were measured and are reported in Table 3. It can be seen that $\alpha\text{-Fe}_2\text{O}_3$ crystallites form the major phase (71%), while the proportion of Fe^{3+} nanoparticles is substantially lower (29%). In addition, these results indicate that the dispersion degree of the major phase ($\alpha\text{-Fe}_2\text{O}_3$) is rather low.

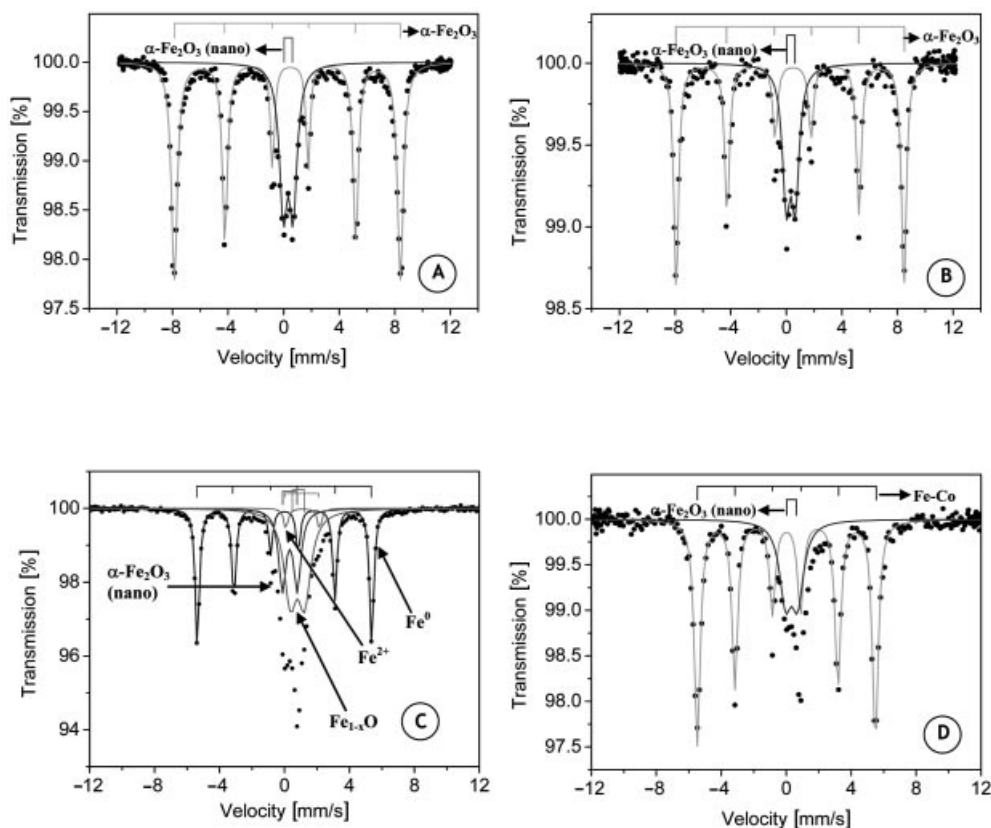


Figure 5. Mössbauer spectra of calcined (A) Fe10-c and (B) CoFe10/5-c; Mössbauer spectra of (C) Fe10-c and (D) CoFe10/5-c reduced in H_2 at 773 K.

Table 3. Mössbauer parameters for the systems Fe10-c and CoFe10/5-c calcined and reduced with H₂ at 773 K.

Sample	Components	δ [mm s ⁻¹]	QS [mm s ⁻¹]	H_{hf} [T]	%
Fe10-c	α -Fe ₂ O ₃	0.37	0.21	50.4	71
	α -Fe ₂ O ₃ (nano-size)	0.33	0.71	–	29
CoFe10/5-c	α -Fe ₂ O ₃	0.37	0.21	50.7	69
	α -Fe ₂ O ₃ (nano-size)	0.32	0.71	–	31
Fe10-c (H ₂)	α -Fe	0.00	0.01	33.2	39
	α -Fe ₂ O ₃ (nano-size)	0.33	0.92	–	20
	Fe _{1-x} O	0.79	0.87	–	38
	Fe ²⁺ (Fe ₂ SiO ₄)	1.12	2.07	–	3
CoFe10/5-c (H ₂)	Co-Fe	0.01	0.01	33.9	76
	α -Fe ₂ O ₃ (nano-size)	0.32	0.71	–	24

The Mössbauer spectrum of the calcined CoFe10/5-c sample (Figure 5B) is quite similar to that of the monometallic Fe10-c sample. The appearance of a sextet suggests the presence of ferromagnetic particles that correspond to iron(III) oxide, while the doublet ($\delta = 0.32 \text{ mm s}^{-1}$, $QS = 0.71 \text{ mm s}^{-1}$) is characteristic of highly dispersed Fe³⁺ ions, thus revealing the existence of nanometre-sized particles (5–10 nm). From the data collected in Table 3, it can be inferred that the proportion of α -Fe₂O₃ and nano-sized Fe^{III} oxide particles in the calcined CoFe10/5-c sample is similar to that found in monometallic Fe10-c.

Reduced Samples

The local environment of the iron atoms in H₂-reduced iron-containing samples was revealed by Mössbauer spectroscopy. The Mössbauer spectrum of Fe10-c after reduction with hydrogen at 773 K for 2 h is displayed in Figure 5C. This spectrum can be fitted by four components: (i) a magnetic sextet that corresponds to α -Fe, (ii) a paramagnetic doublet due to small iron oxide particles (α -Fe₂O₃) similar to the one found in the calcined sample, and (iii) two paramagnetic doublets corresponding to Fe²⁺ species. It should be emphasised that one of these latter doublets has a low isomer shift, which suggests that the Fe²⁺ ions have a low coordination number (tetrahedral coordination), while the other doublet has an isomer shift characteristic of octahedral coordination.^[65,66] No magnetic component belonging to Fe₃O₄ was found after hydrogen reduction. This observation agrees with previous studies by Yuen et al.^[67] and Weilers et al.^[68] Thus, for hydrogen-reduced silica-supported iron samples, Yuen et al.^[54] observed the presence of two doublets corresponding to Fe²⁺ species with different coordination environments: an inner doublet attributed to low-coordinate cations strongly interacting with the substrate and an external doublet assigned to high-coordinate Fe²⁺ cations present in highly dispersed iron oxide particles. A somewhat different interpretation of these two doublets was proposed by Bjerne et al.^[69] These authors suggested that both components correspond to superficial iron silicates with different symmetry (tetrahedral and octahedral environment). The Mössbauer parameters found

in the H₂-reduced Fe10-c sample are collected in Table 3 and are similar to the ones reported by these authors. The assignment of the parameters was done on the basis of studies by Cagnoli et al.^[70] and Hobson et al.,^[66] in which the doublet with $\delta = 0.76 \text{ mm s}^{-1}$ and $\Delta QS = 0.98 \text{ mm s}^{-1}$ was assigned to small FeO crystallites supported on the SiO₂ substrate. For the second doublet, the large differences between the obtained quadrupole shift and the one reported in the literature for Fe_{1-x}O species suggests the existence of Fe²⁺ particles interacting strongly with the support. The quadrupole shift of this second doublet is similar to that reported in the literature for different Fe₂SiO₄ species.^[71,72] Indeed, the reduction of these iron silicate species to iron metal [Equation (1)] is extremely difficult and hence requires high temperatures.

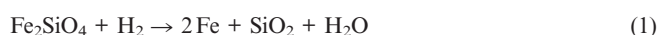


Figure 5D depicts the Mössbauer spectrum of the CoFe10/5-c sample reduced under hydrogen at 773 K for 2 h. The Mössbauer spectrum of this sample arises from the convolution of a magnetic sextet and a paramagnetic doublet. The values of the hyperfine field (H) obtained for the sextet points to the appearance of the CoFe alloy. Johnson et al.^[73] have collected a sequence of values for different CoFe alloys between 34.6 and 35.6 T. The value of the hyperfine field (33.9 T) found for the H₂-reduced CoFe10/5-c sample is similar to that reported by other authors.^[74,75] The paramagnetic doublet can be assigned to small Fe₂O₃ particles highly dispersed on the silica surface. In favour of this assignment is the work of Huang et al.,^[76] who proposed that this paramagnetic doublet arises from iron(III) particles exchanged with the silica, which are, indeed, very difficult to reduce.

Surface Structures

Oxide Samples

The chemical state and relative abundance of cobalt- and/or iron oxides at the silica surface were determined by photoelectron spectroscopy. Figure 6A shows the energy region corresponding to the Co 2p_{3/2} core levels in calcined Co10-c. This peak can be resolved, after curve-fitting procedures, into two components belonging to the Co²⁺ and Co³⁺ ions present in the two samples. From this comparison, it is evident that the Co₃O₄ spinel phase is present in the sample Co10-c. The first peak at 780.0 eV can be ascribed to Co³⁺ in an octahedral environment, while that at 782.5 eV can be assigned to Co²⁺ ions in a tetrahedral environment.^[57] Similarly, the XP spectrum of the Fe 2p_{3/2} core level of calcined Fe10-c is displayed in Figure 6B. This suggests that hematite (Fe₂O₃) is the only species present in the calcined Fe10-c sample.

Figures 6C and 6D show the energy regions corresponding to the Co 2p_{3/2} and Fe 2p_{3/2} core-levels of the calcined CoFe10/5-c sample. The similarity between the peak posi-

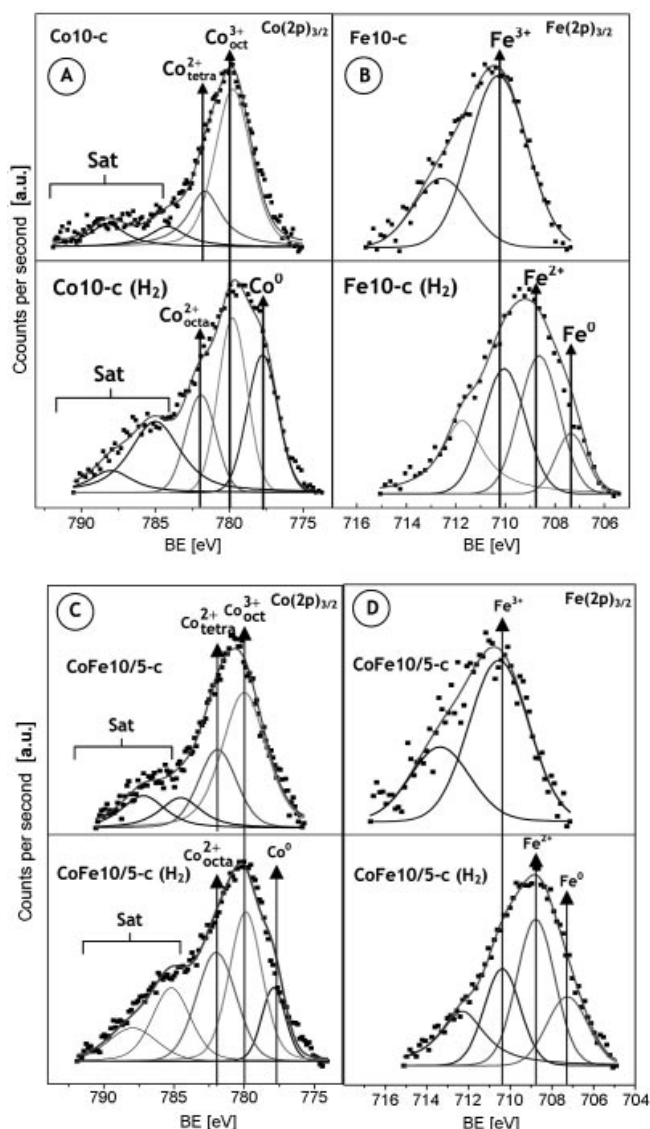


Figure 6. XPS profiles of (A) Co10-c, (B) Fe10-c and (C and D) CoFe10/5-c calcined and reduced with H_2 at 773 K.

tions and line profiles in the Co $2p_{3/2}$ and Fe $2p_{3/2}$ regions for the calcined CoFe10/5-c sample and those of the respective Co10-c and Fe10-c monometallic samples is an indication that the cobalt- and iron oxide phases are the same as in the monometallic systems, that is, Co_3O_4 and Fe_2O_3 are the only phases detected. As is the case with Co10-c, a shift in the binding energy of the Co $2p_{3/2}$ peak of CoFe10/5 is observed relative to bulk Co_3O_4 because of the presence of metal–substrate interactions. As the binding energies of the Co $2p_{3/2}$ and Fe $2p_{3/2}$ levels for CoFe10/5-c are practically the same as those found for the monometallic samples, it can be inferred that the Co–Fe interaction in the calcined sample, if any, is very weak. Finally, it should be emphasised that both CoFe10/5-c and CoFe10/1-c were analysed but the signal-to-noise ratio in the Fe $2p_{3/2}$ region for the latter sample was too low to be measured accurately and hence no further attention was paid to this level.

Reduced Samples

The chemical state of the elements and their relative abundances on the catalyst surface after reduction were revealed by photoelectron spectroscopy. Figure 6A depicts the Co $2p_{3/2}$ peaks of Co10-c after reduction. The calcined Co10-c sample shows two components: one associated with Co^{3+} in an octahedral position and the other assigned to Co^{2+} in the tetrahedral position of the Co_3O_4 spinel.^[77,78] Upon reduction with H_2 , three components are observed: octahedral Co^{3+} ions present in an unreduced Co_3O_4 phase,^[57,77] octahedral Co^{2+} ions in CoO^[79–81] and Co^0 .^[81–83] Figure 6B shows the Fe $2p_{3/2}$ core-level spectrum of Fe10-c after reduction. The fresh sample exhibits one component assigned to Fe^{3+} (Fe_2O_3), whereas the reduced sample displays three components, one due to Fe^{3+} in a non-reduced Fe_2O_3 ^[84] phase, the second due to Fe^{2+} (FeO),^[85,86] and the third due to metallic iron.^[84,87]

Figure 6C shows the Co $2p_{3/2}$ and Fe $2p_{3/2}$ regions of CoFe10/5-c. Some differences are observed for the reduced samples. Although the profiles of the dimetallic and monometallic samples are similar, the binding energies of the Co^0 and Fe^0 species are different, which suggests that a Co–Fe alloy is formed in the dimetallic samples. It is apparent from the binding energies that the reduction of iron oxide is facilitated in the presence of cobalt,^[88] while the reduction of cobalt oxide in close interaction with iron oxide is partly inhibited. This observation agrees with the results reported in the literature^[89] and is consistent with the TPR data. Table 4 shows the metal/support surface ratios. An increase in the amount of surface metallic phase is observed for the dimetallic catalyst after reduction.

Table 4. Surface metal/Si ratios obtained by XPS.

Sample	Oxide		H_2 reduced (773 K)	
	Co/Si	Fe/Si	Co/Si	Fe/Si
Co10-c	0.01	–	0.01	–
Fe10-c	–	0.01	–	0.01
CoFe10/5-c	0.01	0.01	0.02	0.02

Redox Properties

An insight into the structure of the supported metal oxide phase can be derived from programmed reduction experiments. The reduction profile of Co10-c and a bulk Co_3O_4 reference are shown in Figure 7A. The reduction profile of Co10-c shows two peaks that are similar to those observed in the bulk Co_3O_4 oxide. These profiles point to a two-step reduction process: the first one involving low H_2 consumption starts at about 475 K and overlaps with the more intense second one whose maximum is placed at about 630 K. Thus, the reduction of Co_3O_4 can be described by the reduction of Co^{3+} ions present in the spinel structure to Co^{2+} [Equation (2)], with the subsequent structural change to CoO, followed by the reduction of CoO to metallic cobalt [Equation (3)].^[90–92]

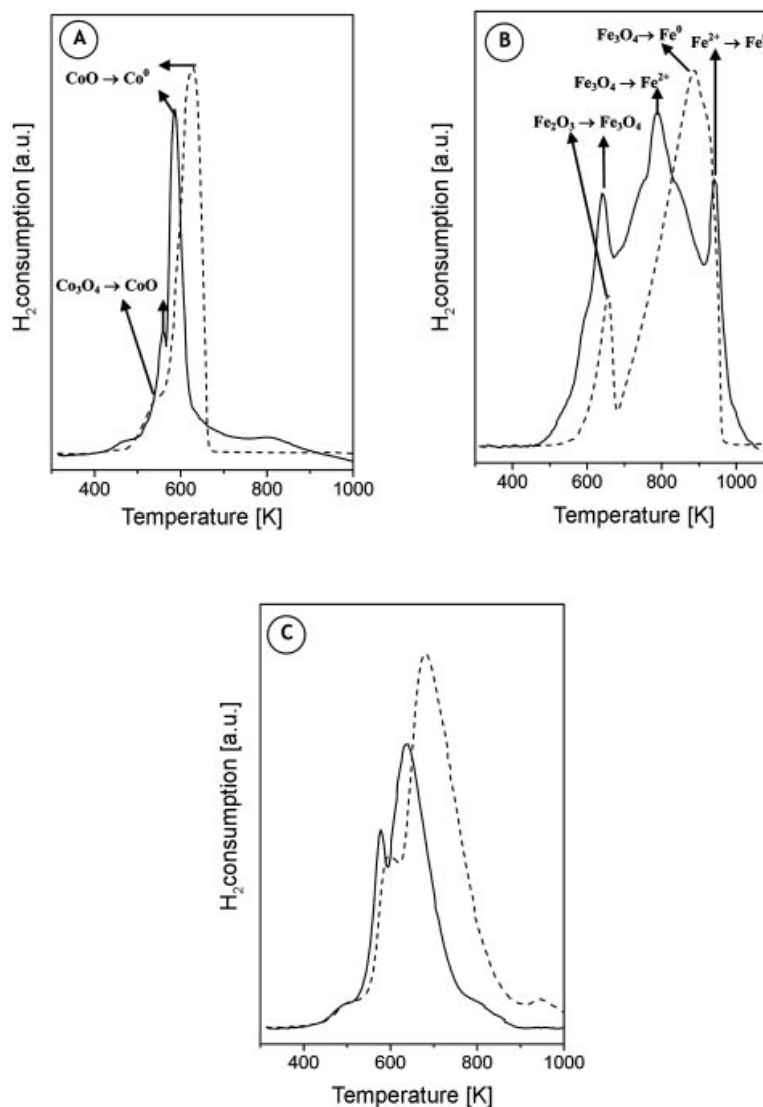


Figure 7. A comparison of the TPR profiles: (A) Co_3O_4 (dashed line) vs. Co_{10-c} (solid line); (B) Fe_2O_3 (dashed line) vs. Fe_{10-c} (solid line); (C) $CoFe_{101/5-c}$ (dashed line) and $CoFe_{101/c}$ (solid line).



The reduction profile of Co_{10-c} shows a very intense peak, which includes contributions at 558 and 587 K, associated to the two reduction steps found in bulk Co_3O_4 , although shifted to lower temperatures as a consequence of lower crystallite sizes of supported phase. Deconvolution of the reduction peak into two components reveals that the ratio between the hydrogen consumption for the first peak and the second peak is 1:3, which is consistent with the two-step reduction depicted in Equations (2) and (3) and agrees with literature findings.^[93–98] H_2 consumption still continues in the range 770–1000 K, and then tends to increase again at higher temperature. The broad H_2 consumption peak in the range 770–1000 K could reasonably be attributed to the reduction of cobalt species placed in the in-

ternal cavities of the support, where the reduction process should be limited by H_2O diffusion through the pores.^[90,93] This interpretation is supported by the XPS results, which point to a low surface concentration of Co^{2+} . The hydrogen consumption between 950 and 1000 K could be due to the reduction of a cobalt silicate phase, which could not be detected by other techniques. Therefore, the similarity of the reduction profiles for Co_{10-c} and bulk Co_3O_4 up to 770 K can be taken as an indication that most of the cobalt oxide species in Co_{10-c} interact weakly with the silica substrate.

Figure 7B shows the reduction profiles of calcined Fe_{10-c} and bulk Fe_2O_3 as reference. The reduction of bulk hematite ($\alpha-Fe_2O_3$) occurs via magnetite (Fe_3O_4) and wustite (FeO) to zero-valent metallic iron.^[99,100] FeO formation is not observed as wustite is a metastable phase below 843 K^[99,100] and disproportionates into Fe_3O_4 and Fe^0 . Two well-defined peaks are observed in the Fe_2O_3 reduction profile: the first is narrow, with a maximum at 654 K, and the

second is wider and asymmetric, with a maximum at 886 K. Thus, the two-stage reduction of Fe_2O_3 can be described by Equations (4) and (5).



FeO formation is not detected under the reduction conditions employed in this work. However, the reduction profile of Fe10-c exhibits three peaks arising from the reduction of iron species through the consecutive steps $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}^0$ according to Equations (6), (7) and (8).^[99]



The similarity in reduction temperatures for both bulk Fe_2O_3 and Fe10-c suggests a weak metal–support interaction in the first reduction stage, as for Co10-c. The only major difference between them is the absence of the reduction stage of magnetite to wustite.

The reduction profiles of mono- and dimetallic cobalt samples were also recorded and are compared in Figure 7C. Quantitative analysis of these reduction profiles is difficult because the iron oxide reduction steps are overshadowed by the cobalt oxide ones. Nevertheless an interaction between both oxides can be inferred from the changes in the reduction of both iron- and cobalt oxides. It appears that the cobalt oxide reduction is inhibited by iron oxide — this is more evident for CoFe10/5-c — while the iron oxide reduction is favoured by the presence of cobalt oxide. As can be seen by Mössbauer spectroscopy, a CoFe alloy is formed in this sample upon reduction. Thus, it is likely that this interaction between both metal oxides is responsible for alloy formation.

An important observation for all reduction profiles is that H_2 consumption continues above 1100 K. As mentioned above, the species that are reduced at high temperature could be metallic silicates, i.e. Co_2SiO_4 and Fe_2SiO_4 , or ionic species placed inside the support cavities.

Conclusions

A detailed analysis of the data derived from mono- and dimetallic silica-supported cobalt-iron systems has allowed us to draw the following conclusions: (i) the textural properties of the supported oxide phases are not influenced by the calcination of the oxide precursors; (ii) the results obtained by XRD, XPS and Mössbauer spectroscopy do not show the development of a cobalt–iron interaction in the calcined oxides — the dimetallic systems only show separate Co_3O_4 and Fe_2O_3 phases and in no case are cobalt–iron mixed oxides detected. The quantitative data also show that the dispersion degree of the cobalt- and iron oxides is very low; (iii) pre-treatment of the supported cobalt oxide nanopar-

ticles under a hydrogen atmosphere does not promote the formation of a metal–support interaction; (iv) a cobalt–iron interaction is observed in dimetallic systems after reduction, and as a result of this interaction, the reducibility of cobalt oxide is partly inhibited while that of iron oxide follows an opposite trend. The XRD patterns and photoelectron and Mössbauer spectra are conclusive for the formation of an iron-cobalt alloy in the hydrogen-reduced samples.

Experimental Section

Catalyst Preparation: Silica-supported cobalt- and/or iron oxides were prepared by the wetness impregnation method on a silica carrier (Grace Davison; specific surface area of $310 \text{ m}^2 \text{ g}^{-1}$, pore volume of $1.22 \text{ m}^3 \text{ g}^{-1}$) with aqueous solutions of cobalt nitrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Merck reagent grade] and iron nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Merck reagent grade]. Monometallic cobalt and iron catalysts were prepared by the appropriate concentration of the above salts to achieve a final metal amount of 10 wt.-%. These samples are labelled Co10-c and Fe10-c, respectively. Two dimetallic FeCo-supported catalysts containing a fixed amount of cobalt (10 wt.-%) and different amounts of Fe (1 and 5 wt.-%, labelled CoFe10/1-c and CoFe10-5c, respectively) were prepared by simultaneous impregnation with a solution containing both cobalt and iron salts. All impregnates were dried at 393 K overnight and calcined at 773 K under flowing air for 2 h.

Catalyst Characterisation: The cobalt content of the catalyst was determined by the ICP technique using a Perkin–Elmer Optima 3300 DV apparatus. Specific areas were calculated using the BET method from the nitrogen adsorption isotherms, recorded at the temperature of liquid nitrogen using a Micromeritics apparatus (model ASAP-2000) with a value of 0.162 nm^2 for the cross-sectional area of the N_2 molecule adsorbed at 77 K. Samples were degassed at 423 K prior to adsorption measurements.

The powder XRD patterns of the precursor and calcined samples were recorded with a Seifert 3000 P diffractometer using nickel-filtered $\text{Cu-K}\alpha_1$ ($\lambda = 0.15406 \text{ nm}$) radiation. A scanning step of 0.02° was taken between 5 and 80° Bragg angles.

Temperature-programmed reduction (TPR) experiments were carried out with a Micromeritics TPD/TPR 2900 apparatus equipped with a thermal conductivity detector. Reduction profiles were obtained by passing a 10% H_2/Ar flow at a rate of 50 mL (STP) per minute through the sample (weight about 30 mg). The temperature was increased from 300 to 1273 K at a rate of 10 K min^{-1} , and the amount of hydrogen consumed was determined as a function of temperature. Under these conditions, the line profile and peak position can be measured accurately. The effluent gas was passed through a cold trap placed before the TCD in order to remove water from the exit stream of the reactor.

SEM images were recorded with an ISI DS-130 microscope coupled to a solid-state Si/Li Kevex detector and a SUN SparcStation 5 for acquiring and processing energy-dispersive X-ray (EDX) spectra. Powder samples were converted into flat pellets and coated with a thin graphite layer to prevent the accumulation of static charge derived from the electron beam. Transmission electron micrographs were recorded with a Fei Tecnai G30 microscope. The acceleration voltage was set at 200 kV. The powdered sample was first suspended in acetone, after which a drop of the suspension was deposited on a copper grid covered with a fine carbon film evaporated under vacuum.

Surface analysis was carried out with a VG Escalab 200R electron spectrometer equipped with an Mg- K_{α} X-ray source and a hemispherical electron analyser. The powder samples were pressed in 8-mm-diameter copper troughs and then mounted on a sample rod placed in a pre-treatment chamber and heated under vacuum at 373 K for 1 h prior to being moved into the analysis chamber. The base pressure in the analysis chamber was maintained below 4×10^{-9} mbar during data acquisition. The area under analysis was about 2.4 mm², and the pass energy of the analyser was set at 50 eV, for which the resolution as measured by the full width at half maximum (FWHM) of the Au 4f_{7/2} core level was 1.7 eV. The binding energies were referenced to the C 1s peak at 284.9 eV due to adventitious carbon. Data processing was performed with the XPS peak program, the spectra were decomposed with the least-squares fitting routine provided with the software with Gaussian/Lorentzian (90/10) product function and after subtracting a Shirley background. Atomic fractions were calculated using peak areas normalised on the basis of sensitivity factors.^[10]

Mössbauer spectra were recorded in a sinusoidal mode using a transmission spectrometer with a ⁵⁷Co/Rh source. Spectral analyses were performed by non-linear fit using the NORMOS^[10] program, and energy calibrations were accomplished with an α -Fe (6 μ m) foil.

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