

Distinctive cobalt ferrites prepared by the thermal-transformation alkoxide route

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Abstract

Cobalt ferrites (inverse spinel structures) were prepared by progressive heat treatments (270–600–1000°C) in air of synthetic Fe : Co alkoxides of glycerol having different Fe : Co ratios. The XRD examination indicates that the crystallization of the cobalt ferrites is initiated at 270°C and, thereafter, it strongly increases between 600 and 1000°C. Moreover, at 1000°C, XRD and chemical analyses show a shift of the resulting cobalt ferrite *d*-spacings to lower values when the ferrite contains more cobalt, suggesting that cobalt partially replaces iron in the spinel structure. At 1000°C, the XRD lines of some co-products like hematite and Co₃O₄ previously formed at 600°C, either strongly decrease or disappear. The surface areas of cobalt ferrites range from 131 to 165 m²/g. Such high values are unusual for spinel oxides obtained by calcination at 1000°C. © 1998 Elsevier Science B.V.

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1. Introduction

Iron–cobalt oxide compounds may find useful applications, i.e. in the change of thermoelectric power of cobalt ferrite in the hydrogen–deuterium exchange reaction [1] or as catalysts for the hydrogen peroxide decomposition [2].

Procedures for the preparation of cobalt ferrite spinels of variable compositions were carried out either by calcination at 1050°C of mixtures of cobalt carbonate plus iron oxide (ceramic route) [1], or by co-precipitation of iron and cobalt oxalates (oxalate route) [2] or else by co-precipitation of metal hydroxides from chloride solutions followed by decomposition at 1000°C (hydroxide route) [3]. The latter yields

more homogeneous products and ones of higher catalytic activity. The catalytic activity depends on factors like surface areas of the ferrites, the spinel chemical composition, cations structural distribution, electronic structure, etc.

Another route for preparing multi-metallic oxide structures, employed in our laboratory, is based on the synthesis of metallic alkoxides of glycerol followed by their thermal transformations at different temperatures in air. This is called the thermal-transformation alkoxide route. By these procedures, Al-bearing hematite [4] and finely divided iron and manganese spinel oxides of variable composition [5] have been obtained. The present study deals with the comparative thermal transformations of Fe–Co alkoxides of variable compositions and characterization of the transformation products, mostly by X-ray diffraction (XRD), chemical analysis and sorptometry.

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2. Experimental

Synthetic iron–cobalt alkoxides of glycerol (brownish solids) with different Fe : Co ratios, namely 2.27 : 1, 1.16 : 1 and 1 : 1.49, were prepared by a method similar to the synthesis of iron–manganese alkoxides [6], using cobalt carbonate as the cobalt source. Hereafter, the Fe : Co alkoxides will be referred to in the text as samples I, II and III, respectively. The detailed synthesis of Fe–Co alkoxides of glycerol will be described elsewhere. Each of the Fe–Co alkoxides was progressively heated in a furnace under static air atmosphere at ~270, 600 and 1000°C, since at these temperatures some relevant transformations were observed. Hereafter, the transformation products, being related to the alkoxide precursors, resulting at these temperatures will be called thermoproducts.

After each heating interval, the transformation products were examined by X-ray diffraction (XRD) as random powders, with a Philips 1730 diffractometer, at a scanning rate of $1^\circ (=2\theta)/\text{min}$ using FeK_α radiation. Identical instrumental settings were employed for the examination of each product.

Chemical analysis of both, total cobalt and iron were made upon dissolution of the samples in hot 6 M HCl, followed by atomic absorption spectroscopy (AAS) determinations with a Varian Techtron 1200 spectrophotometer. Fe^{2+} was assessed by dichromatometry and by the Microquant 14759 (Merck) test. Co^{2+} was again determined by AAS, previous precipitation and separation of Co^{3+} from the HCl dissolution by $\text{NH}_4\text{VI}-\text{NH}_4\text{OH}$ [7]. Co^{3+} was calculated from the difference. Surface areas (BET) of the product, resulting from the heat treatments, were determined with a Quantachrome apparatus employing nitrogen as adsorbate.

3. Results and discussion

Fig. 1(a) displays the X-ray pattern of sample I with a very strong and sharp, single peak at 8.063 Å, characteristic of a single-phase Fe–Co alkoxide of glycerol. All the other peaks exhibited in this pattern (Fig. 1(a)) belong as well to the Fe : Co alkoxides of glycerol. In Fig. 1(b), the pattern of this precursor alkoxide can be seen after heating at 270°C. At this

stage, a complete structural transformation of the precursor takes place, as no Fe–Co alkoxide peaks were detected. The positions of the broad reflections appearing in Fig. 1(b) suggest that the transformation product at 270°C has a disordered, poorly crystalline spinel structure, presumably a defect cobalt ferrite. The XRD patterns recorded after heating samples II and III at 270°C (not shown here) are similar to the pattern of the thermoproduct of sample I shown in Fig. 1(b). A more complete study of the thermoproducts, resulting at 270°C, related to their precursors is in progress in our laboratory.

The X-ray diffractogram after progressive heating at 600°C is exhibited in Fig. 1(c). It can be seen that the X-ray lines of the 270°C thermoproduct increase in sharpness and intensity, and their maxima appear at 2.526 (most intense line) 2.964, 2.096 and 4.827 Å. This pattern matches the JCPDS 3-0864 file identifying cobalt ferrite, CoFe_2O_4 . This may be interpreted as an evolution of the spinel disordered structure, resulting at 270°C, to a more crystalline thermoproduct at 600°C. Additional lines (mainly at 3.677 and 2.208 Å) in the diffractogram, shown in Fig. 1(c), are assigned to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 13-534), implying that hematite is also formed at 600°C.

Heating at 1000°C, the thermoproduct obtained at 600°C results in a further crystallization of the cobalt-ferrite structure, as can be inferred from the pattern displayed in Fig. 1(d), where the characteristic lines of the ferrite have strongly increased in intensity. There are no appreciable shifts in the positions of the cobalt ferrite lines during this heating sequence. Other features observed during this sequence include the hematite lines appearing at 600°C, but decreasing in intensity after heating at 1000°C (Fig. 1(c and d)). Similar results were observed by direct (not progressive) heating treatments of the Fe–Co alkoxides at the above temperatures.

Fig. 2 displays the comparative XRD patterns of the three precursor alkoxides, each heated until 600°C. The respective patterns show that a cobalt-ferrite structure is always formed and developed, regardless of the Fe : Co ratio in the precursor alkoxide. Fig. 2 also indicates that another crystalline spinel structure, Co_3O_4 , is formed at 600°C, mostly in thermoproducts II and III (Fig. 2(a and b)). Co_3O_4 was identified by the lines at 2.456, 2.873 and 4.700 Å, matching the JCPDS file 9-418. The same figure shows an inverse

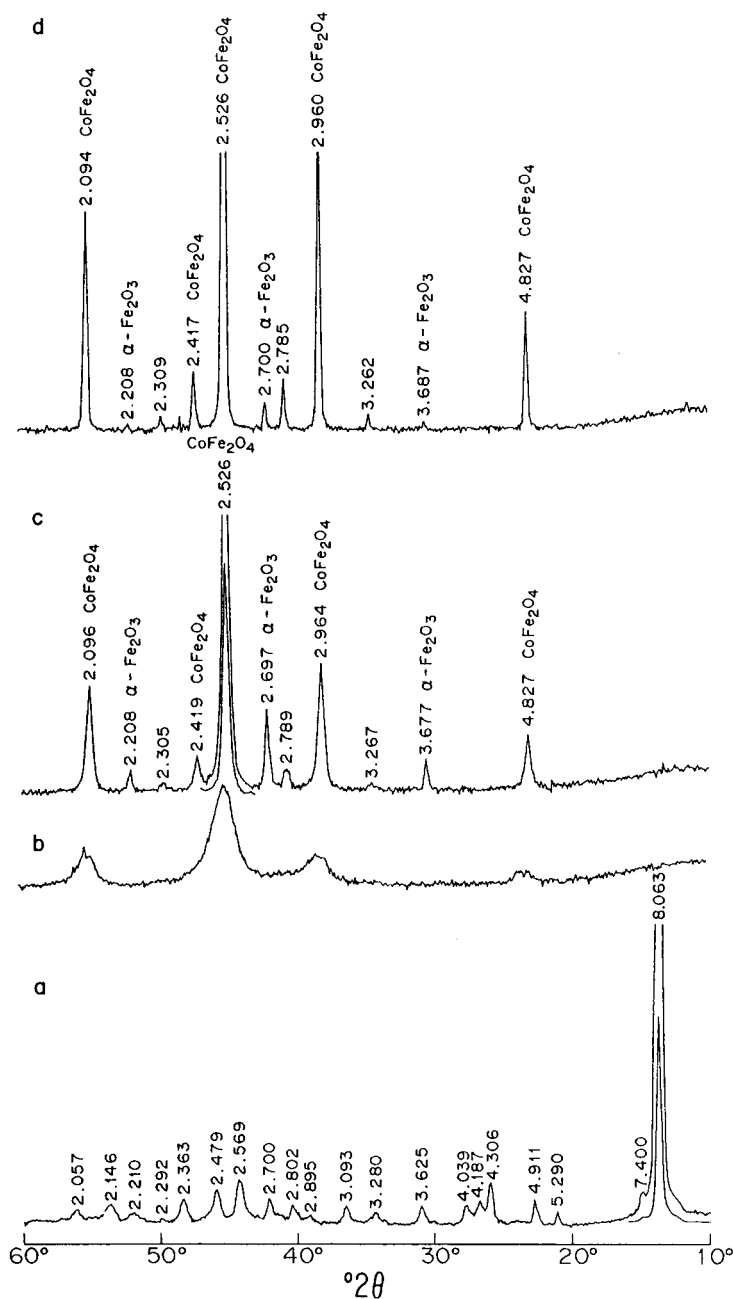


Fig. 1. X-ray diffraction patterns of (a) Fe:Co alkoxide in the 2.27:1 ratio; (b) sample (a) heated at 270°C ; (c) sample (b) heated at 600°C ; and (d) sample (c) heated at 1000°C . Spacings in Å.

relationship between the amounts of Co_3O_4 and CoFe_2O_4 produced at 600°C , as inferred from the intensities of the main diagnostic lines at 2.45 (Co_3O_4) and 2.52 Å (CoFe_2O_4) in thermoproducts II

and III. This means that the formation of Co_3O_4 at 600°C , which is abundantly detected in the thermoproduct III is favored by an increasing content of Co in the precursor alkoxide. With high Fe–Co ratios, as in

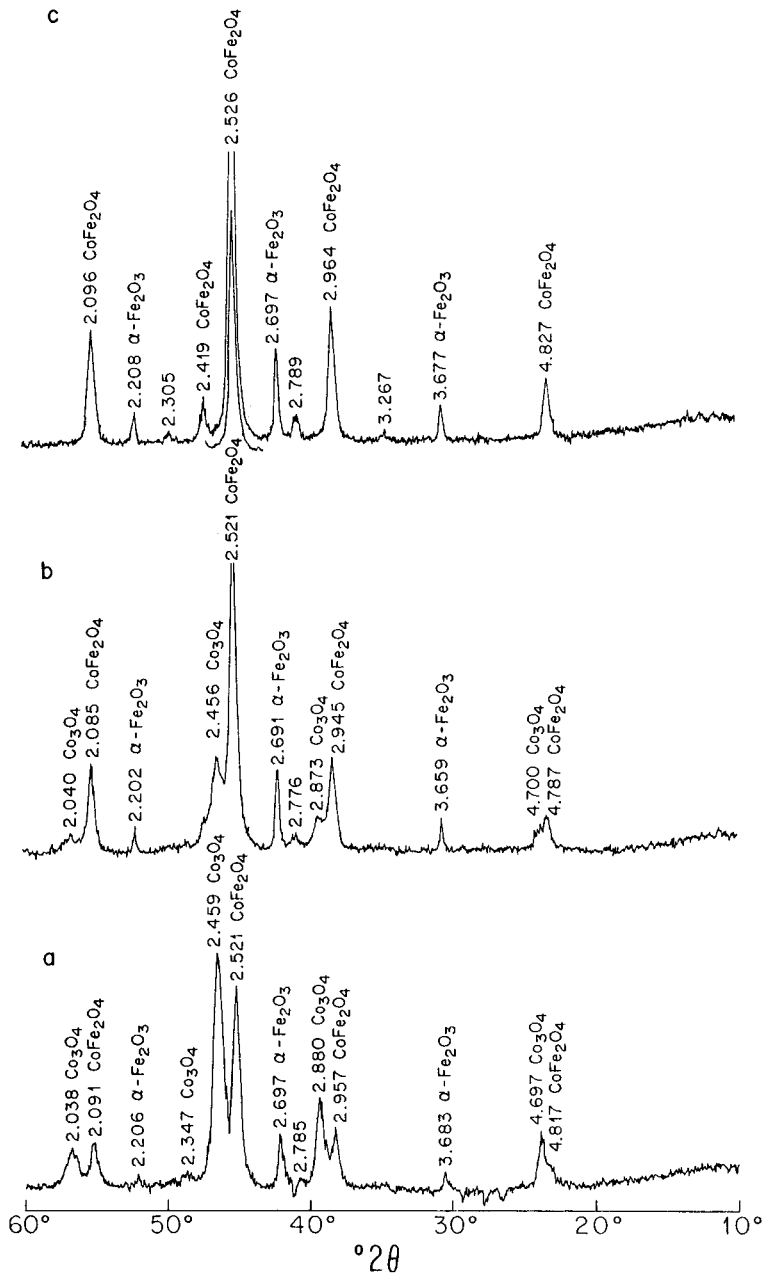


Fig. 2. X-ray diffraction patterns after heating treatments, at 600°C , of Fe:Co alkoxides with the following Fe:Co ratios: (a) 1:1.49; (b) 1.16:1; and (c) 2.27:1. Spacings in \AA .

the thermoproduct I, the opposite effect is observed where CoFe_2O_4 is the predominant structure (Fig. 2(c)). The weak reflections at ca. 2.79, 2.30 and 3.27 \AA have not been identified.

A comparative XRD examination of the Fe-Co transformation products at 1000°C from I, II and III is shown in Table 1. Following the initial Fe-Co order, it can be seen that an appreciable and coherent

Table 1
Comparative X-ray diffraction maxima (*d*-spacings) of Fe–Co alkoxides heated at 1000°C

(Fe : Co) ratios in alkoxide precursors								
2.27 : 1(I)			1.16 : 1(II)			1 : 1.49 (III)		
<i>d</i> (Å)	products	relative intensity	<i>d</i> (Å)	products	relative intensity	<i>d</i> (Å)	products	relative intensity
4.827	CoFe ₂ O ₄	m ^a	4.817	CoFe ₂ O ₄	m ^a	4.797	CoFe ₂ O ₄	m ^a
						4.678	Co ₃ O ₄	w ^a
3.683	α-Fe ₂ O ₃	w ^a						
3.262	n.i. ^a	w ^a	3.257	n.i. ^a	w ^a	3.230	n.i. ^a	w ^a
2.960	CoFe ₂ O ₄	vs ^a	2.953	CoFe ₂ O ₄	s ^a	2.938	CoFe ₂ O ₄	m ^a
						2.866	Co ₃ O ₄	m ^a
2.785	n.i. ^a	m ^a	2.782	n.i. ^a	w ^a	2.763	n.i. ^a	w ^a
2.700	α-Fe ₂ O ₃	w–m ^a						
2.526	CoFe ₂ O ₄	vs ^a	2.515	CoFe ₂ O ₄	vs ^a	2.505	CoFe ₂ O ₄	vs ^a
						2.449	Co ₃ O ₄	w–m ^a
2.417	CoFe ₂ O ₄	m ^a	2.412	CoFe ₂ O ₄	m ^a	2.400	CoFe ₂ O ₄	w ^a
2.309	n.i. ^a	w ^a						
2.094	CoFe ₂ O ₄	s ^a	2.087	CoFe ₂ O ₄	s ^a	2.079	CoFe ₂ O ₄	m ^a
						2.030	CoFe ₂ O ₄	w ^a

^a Key: m, medium; w, weak; v, very; s, strong; and n.i., non identified.

shift of the *d*-spacings of the corresponding cobalt ferrites to lower values occurs. This means that, as more cobalt is redistributed in the ferrite spinel structure, the unit cell becomes smaller. Table 1 also indicates that the Co₃O₄ and α-Fe₂O₃ lines, which were quite prominent at 600°C (Fig. 2), strongly decreased or are not detected at 1000°C.

Table 2 gives the chemical analysis of the products, resulting from heating at 100°C, for each Fe–Co alkoxide. It can be seen from this table that the Fe : Co ratios found in the precursor alkoxides are close to the Fe : Co ratios of the thermoproducts resulting at 1000°C, as calculated from the elemental analysis.

The XRD results show that lines due to both, hematite and Co₃O₄ at 600°C strongly decrease or are no longer detectable at 1000°C. This means that

at 1000°C, when the high amounts of cobalt ferrite are crystallized, the presence of other separate phases, such as hematite or Co₃O₄, is negligible. The XRD results have shown as well that cobalt ferrite is either the sole phase, or the predominant phase resulting at 1000°C in the thermoproducts II and I, respectively. On this basis, the experimental molecular formulas derived from the chemical compositions given in Table 2 for the thermoproducts I and II, respectively, are: Co_{0.77}²⁺Co_{0.07}³⁺Fe_{2.02}³⁺O_{3.91} and Co_{1.23}²⁺Co_{0.10}³⁺Fe_{1.68}³⁺O_{3.90}. The structural location of Co³⁺ is generally associated with the presence of Fe²⁺ (both cations have a similar 3*d*-electron configuration). As only traces of Fe²⁺ are detected (Table 2), the small amount of Co³⁺ is probably not incorporated in the ferrite structure. According to the XRD results,

Table 2
Chemical analysis and surface areas (*S*₀) of Fe–Co alkoxides heated at 1000°C

Fe : Co ratios found in alkoxides	Total iron (%)	Fe ²⁺ (%)	Total cobalt (%)	Co ²⁺ (%)	Co ³⁺ (%)	Fe : Co ratios after heating	<i>S</i> ₀ (m ² /g)
2.7 : 1	48.75	tr ^a	21.06	19.25	1.81	2.31:1	131.6
1.16 : 1	40.50	tr ^a	33.25	30.88	2.37	1.22:1	163.3
1 : 1.49	27.50	tr ^a	43.25	36.31	6.49	1:1.57	159.3

^a traces.

the above-derived formulas correspond to the inverse spinel structure of cobalt ferrite whose ideal structure is: $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$. When $x=1$, Co^{2+} shares the octahedral sites with one-half of Fe^{3+} , whereas the remaining one-half of Fe^{3+} is located in the tetrahedral sites. The calculations derived from chemical analysis show that the oxygen fraction is around 3.90 in the molecular formula of both thermoproducts I and II at 1000°C , which can be attributed to oxygen-deficient structures.

The stoichiometric differences in the formulas are consistent with the deviations in the d -spacings of the resulting cobalt ferrites (Table 1), suggesting that cobalt partially replaces iron in the spinel. The formula of the thermoproduct III cannot be calculated as another phase, Co_3O_4 , ($\text{CoO}\cdot\text{Co}_2\text{O}_3$), is also formed in this thermoproduct (Table 1), accounting for most of the Co^{3+} found in its composition (Table 2).

The surface areas (BET) of the strongly magnetic thermoproducts resulting at 1000°C are also given in Table 2. There are no important differences in the surface areas of the different Fe–Co products, which range from ~ 131 to $165\text{ m}^2/\text{g}$. The surface areas of the transformation products at 600°C are slightly lower. The minor phases, Co_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$, eventually formed with CoFe_2O_4 in the above-mentioned thermoproducts, do not affect their surface areas significantly. The surface areas of the Fe–Co thermoproducts (Table 2) are higher than those reported for cobalt ferrites synthesized by other methods, i.e. by the hydroxide route ($60\text{--}130\text{ m}^2/\text{g}$) [2].

Generally, metallic oxide products obtained by calcination of precursors (starting materials) at high temperatures ($\sim 1000^\circ\text{C}$) have low surface areas. This is valid for ferrites prepared by the ceramic route as well as for manganese ferrites prepared by the thermal-transformation alkoxide route. The latter method, i.e. preparation of spinel products by calcination at 1000°C of Fe–Mn alkoxides of glycerol, is reported to result in thermoproducts whose surface areas were around $1\text{ m}^2/\text{g}$ [5]. Therefore, the high surface areas of the cobalt ferrites prepared in this study by calcination of Fe–Co alkoxides at 1000°C is considered to be a distinctive feature.

This, and other characteristics could be an indicator that the cobalt ferrites produced by the thermal-transformation alkoxide route may find promising applications in catalysis or in other fields and should be further investigated.

4. Conclusions

Cobalt ferrites (inverse spinel structures) were identified by XRD as the major phases resulting from the progressive thermal transformation of synthetic iron–cobalt alkoxides of glycerol with different Fe : Co ratios. The crystallization of cobalt ferrites, which starts at 270°C , is strongly improved between 600 and 1000°C . At 1000°C , a coherent shift of the cobalt ferrite d -spacing is observed, which is related to the Fe and Co contents (Fe : Co ratios) in the respective thermoproducts. Typical formulas of the latter (as derived from their chemical compositions) are: $\text{Co}_{0.77}\text{Fe}_{2.02}\text{O}_{3.91}$ and $\text{Co}_{1.23}\text{Fe}_{1.65}\text{O}_{3.90}$, both corresponding to oxygen-deficient cobalt ferrite structures.

These cobalt ferrite products obtained by the thermal-transformation alkoxide route, whose preparation includes calcination of precursor Fe–Co alkoxides at 1000°C , have unusually high surface areas ($131\text{--}1645\text{ m}^2/\text{g}$).

References

- [1] R.G. Squires, G. Paravano, *J. Catal.* 2 (1963) 324.
- [2] J.R. Goldstein, C.C. Tseung, *J. Catal.* 32 (1974) 452.
- [3] R. Rajaram, P.A. Sermon, *J. Chem. Soc., Faraday Trans.* 81 (1985) 2577.
- [4] E. Mendelovici, A. Sagarzazu, R. Villalba, *Thermochim. Acta* 107 (1986) 75.
- [5] E. Mendelovici, A. Sagarzazu, R. Villalba, *J. Thermal. Anal.* 40 (1993) 1115.
- [6] E. Mendelovici, R. Villalba, A. Sagarzazu, *J. Mater. Sci. Lett.* 9 (1990) 28.
- [7] L.J. Curtman, *Análisis Químico Cualitativo*, M. Marin y Co., Madrid, 1959, p. 223.