Characterization of Cobalt Oxides Transformations with Temperature at Different Atmospheres

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Abstract

Cobalt is a transition metal with many oxidation states, which results in the formation of different oxides, such as CoO, CoO_2, Co_2O_3, Co_3O_4, etc. Their exceptional properties generate a great interest in optic, catalysis and ceramic industries, so the deep study of the cobalt oxide transformations with temperature in different atmospheres is the key to improve the industrial processes.

The aim of the work was to devise the transformations of the cobalt oxides by undergoing different heating cycles in three atmospheres (air, nitrogen/hydrogen and oxygen) and to carry out a complete characterization of each compound obtained from the treatments.

Different materials based on cobalt compounds, such as $Co(OH)_2$, Co°, CoO and Co_3O_4, have been treated in different atmospheres (air, nitrogen/hydrogen and oxygen), and temperature conditions. The formation of Co_3O_4 as a product of the treatment of $Co(OH)_2$ under an oxidative atmosphere, the obtaining of CoO and Co° from the thermal treatment of Co_3O_4 in a reductive atmosphere and the production of Co_3O_4 from the oxidation of Co° and CoO were studied. All the materials were characterized by determining the cobalt content by WD-XRF, the oxygen concentration by an elemental analyzer and the crystalline phases by XRD and FT-IR.

Keywords: Cobalt oxide; Phase transformation; Thermal treatment; Oxidation; Reduction

Introduction

Cobalt is a transition metal with many oxidation states, which results in the formation of different oxides [1]. According to Tang et al., five species of cobalt oxide have been reported (CoO_2, Co_2O_3, $CoO(OH)$, Co_3O_4 and CoO) although other authors sustain that the existence of only three of them is certain: CoO, Co_3O_4 and Co_2O_3 [2,3].

The great interest in cobalt oxides and the derived compounds is due to their exceptional physical and chemical properties, which make them promising materials widely applied in different fields [4,5], such as ceramics, optics or catalysis. Regarding ceramic industry, cobalt (II, III) oxide Co_3O_4 is an important metal oxide because its spinel structure with cobalt existing in both Co (II) and Co(III) valence states turns it a versatile material and a stable pigment [1-3, 6-9]. Concerning catalyst field, cobalt has similar properties to platinum, and it is considered to be the first catalyst made from nonprecious metals which might allow to get cheaper and more durable hydrogen fuel cells [10]. Finally, other industries use cobalt oxide as gas sensor, anode material for rechargeable ion-Li batteries or in high-temperature solar absorbers.

Cobalt oxide decomposition has been studied by thermogravimetric analysis in different atmospheres and have characterized the product obtained by different techniques by many authors, never reaching a complete characterization. Haenen et al. applied thermogravimetric analysis to study the course of the decomposition of cobalt nitrate as a function of temperature, which results in the spinel oxide Co_3O_4 [11]. Pejova et al. studied the decomposition of Co_3O_4 to CoO in air and vacuum [12], while El Baydi et al. sustain that cobalt oxide CoO is likely to be an intermediate in the synthesis of Co_3O_4 [11,13]. Other authors, such as Maslennikova and Tang et al., found that the lower cobalt oxide is transformed into higher oxides: Co_3O_4 and Co_2O_3. Under elevated temperatures, these oxides dissociate into oxygen and a lower cobalt oxide [2,3]. Furthermore, other authors, such as Wang et al., chose the in situ thermogravimetry-temperature programmed reduction (STG-TPR) method so as to prepare a series of pure cobalt oxide and understand the degree of reduction of cobalt oxides [5]. Even so, the cobalt oxide species found by these authors, were not completely characterized.

The cobalt oxides studied by the authors mentioned above, were analyzed by powder X-Ray diffraction analysis (XRD), Fourier-transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA) [1,12], while other authors added Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman and UV-Vis to the earlier analytical techniques [4,5,7,10]. Sharifi et al. characterized the cobalt oxides by XRD, FT-IR and SEM [6], but none of them were giving quantitative results, that should be achieved by measuring cobalt and oxygen content.

About the results obtained in the literature, Garavaglia et al. found evidences that the TGA gives non-equilibrium data, and that cooling the samples to room temperature may lead to reabsorption of oxygen [8].

Some literature reported special methods to obtain higher valence cobalt oxides, such as Co_2O_3 and CoO_2. However, these methods always end up with either a mixture of CoO and Co_2O_3 or a mixture of Co_2O_3 and CoO_2. Lin et al. determined the ratio of each cobalt oxide species in CoO_x from the consumption of hydrogen in TPR [14].

As it can be seen, each author has run the experimental procedure using different conditions and then, they have brought about different conclusions. According to the consulted literature, different studies have been carried out focused on cobalt oxide characterization and the phase transformation that they undergo after thermal treatments in different atmospheres and most of them concluded that more research is needed. The results obtained have been interpreted qualitatively or semi-quantitative so, the oxygen determination would confirm the different cobalt oxide transformation in the different conditions applied.

Thus, the present work will study the phase transformation that undergoes the cobalt oxides with different thermal treatment under certain atmosphere conditions. The species formed will be characterized by determining the cobalt concentration by WD-XRF, the crystalline phases by XRD and FT-IR; and oxygen determination by an oxygen elemental analyzer.

Materials and Methods

A LECO model TC-436 Oxygen Elemental Analyzer was used to determine the Oxygen content. The technique consists on heating the sample in an inert atmosphere to turn it into gas, which passes through the carbon dioxide converter where oxygen reacts with carbon, forming CO_2 and is measured by infrared absorption.

The preparation of the fused beads for WD-XRF analysis was carried out in an EQUILAB model F2 Induction Fluxer instrument, using a Pt-Au crucible and dish from EQUILAB. WD-XRF analysis was conducted using a PANalytical model AXIOS spectrometer with a Rh target tube and 4-kW power.

The crystalline structures were identified by XRD using a Bruker Theta-Theta model D8 Advance diffractometer.

Cobalt oxides were identified by a NICOLET 6700 Fourier-transform Infrared Spectrometer (FTIR) from THERMO. Pellets were prepared using KBr. Measurement conditions used were: nº of scans of 32 and scan speed of 0.6329 cm/s.

The thermal treatments of the cobalt oxides were carried out in a CARBOLITE HST 12/400 tubular furnace from CARBOLITE in all the three atmospheres (air, oxygen and a 5% H_2/95% N_2).

A Mettler-Toledo model XS105 balance with a sensibility of 0.01 mg was used for preparing all the working standards and samples.

A vacuum device from JATA was used to store the samples and standards in vacuum atmosphere to avoid undesirable changes in the studied materials and they were kept in a Star-Auto desiccator from SICCO.

Studied materials

Different reagents with different chemical and physical composition, were selected to undergo the study. The materials were labelled as following:

- R1: Cobalt (II) hydroxide, (Sigma Aldrich)

- R2: Cobalt (II, III) Oxide (Alfa-Aesar)

- R3: Cobalt (II) Oxide (Alfa-Aesar)

- R4: Cobalt powder (Merck)

Experimental Procedure

### Thermal treatments in different atmospheres

Different thermal treatments were designed in three atmospheres (air, hydrogen/nitrogen and oxygen) to study the cobalt transformations experienced with the different thermal treatments, in order to know the transformation that the cobalt materials experience.

Thermal treatment in an air atmospheres

Thermal treatment in air atmosphere was carried out by heating the materials at different temperatures.

Pejova et al., transformed the $Co(OH)_2$ to Co_3O_4 upon 350℃ in air, characterizing the obtained product by XRD and FTIR [12], although, the phase obtained was not quantified.

The process would follow the next reaction:

$$3Co(OH)_2 + \frac{1}{2}O_2 \rightarrow Co_3O_4 + 3H_2O \qquad (1)$$
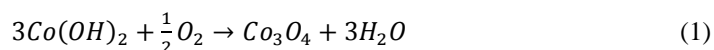
Furthermore, according to Haenen et al., the spinel oxide Co_3O_4 decomposes to CoO at 900℃, as indicated by the weight loss observed in a TGA curve [11]. However, the weight loss just indicates that some transformation is occurring, but it does not quantify or identify the exact compound, contrary to other techniques such as XRD, WD-XRF and oxygen determination do.

So, two experiments were designed (at 350℃ and 900℃), in order to completely characterize the products obtained, identifying and quantifying the phases formed by different analytical techniques (XRD, FTIR, WD-XRF and oxygen elemental determination). The thermal treatments conditions and the materials studied are shown in TABLE 1.

TABLE 1. **Thermal treatment conditions in air atmosphere.**

Experiment	Studied material	Tmax (ºC)	Heating rate (ºC/min)	Dwell time (at Tmax) (min)
1	R1	350	3	50
2	R2	900	3	30

Thermal treatment in a N_2/H_2 atmosphere

In accordance to the consulted literature, Cobalt (II, III) oxide, Co_3O_4, is reduced to metallic cobalt, Co°, after undergoing a thermal treatment at 350℃ in a H_2 atmosphere [5,14]. According to Wang et al., who set out reaction (2), cobalt (II, III) oxide (Co_3O_4) is reduced to cobalt (II) oxide (CoO) at 200℃ and to metallic cobalt (Co°) at 350℃.

$$(in\ H_2\ atm) \qquad Co_3O_4 \xrightarrow{200ºC} CoO \xrightarrow{350ºC} Co^0 \qquad (2)$$
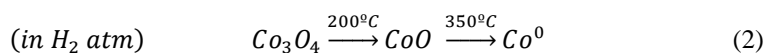
As said by Lin et al., cobalt (II, III) oxide is reduced to cobalt (II) oxide at 260℃, and then to metallic cobalt at 425℃, following the next reactions [14]:

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \qquad (3)$$

$$CoO + H_2 \rightarrow Co + H_2O \qquad (4)$$
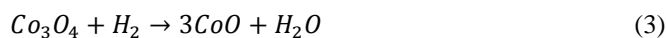
Thus, these experiments were reproduced in a CARBOLITE tubular furnace with a 95% N_2/5% H_2 atmosphere, starting by trying to reduce Co_3O_4 to Co° at 350℃ in a reducing atmosphere. The oxygen content was determined, and the results obtained in the experiment 3 were not the expected ones for metallic cobalt. So, experiment 4 was designed by raising the final temperature to 600℃ to help reducing the starter material and to eliminate the possible water traces that could remain in the sample (as it is shown in reaction 3 and 4)

The experiment conditions are detailed in TABLE 2.

TABLE 2. **Thermal treatment conditions in N$_2$/H$_2$ atmosphere.**

Experiment	Studied material	Temperature (ºC)	Heating rate (ºC/min)	Dwell time (min)
3	R2	350	3	120
4	R2	600	3	60

Thermal treatment in an O$_2$ atmosphere

Wang et al. realized a range of experiments to observe the reduction/oxidation of the cobalt oxide CoO, characterizing the products obtained by TEM, XRD and FTIR. They stated that CoO was oxidized to Co$_3$O$_4$ over 500℃, and that this oxide was decomposed back to CoO at 1000℃. Experiment 5 was designed in accordance to literature so, Cobalt (II) Oxide was treated in an oxidative atmosphere (O$_2$) using the CARBOLITE tubular furnace at 900℃ to transform it into Cobalt (II, III) Oxide [2, 5]. In addition, metallic cobalt underwent a thermal treatment at 600℃ in an oxygen-rich atmosphere. None oxidation experimentation from metallic cobalt was found in the literature. Experiments 5 and 6 follow the reaction (5):

$$Co^0 \xrightarrow{600ºC, O_2} CoO \xrightarrow{900ºC, O_2} Co_3O_4 \tag{5}$$

Thermal treatment conditions are shown in TABLE 3.

TABLE 3. **Thermal treatment conditions in an O$_2$ atmosphere.**

Experiment	Studied material	Temperature (ºC)	Heating rate (ºC/min)	Dwell time (min)
5	R3	900	3	40
6	R4	600	3	40

Complete characterization

Materials were characterized by different analytical techniques such as WD-XRF, XRD, FTIR and oxygen determination by the elemental analyzer TC-436, before and after undergoing the thermal treatments in the different atmospheres.

Chemical characterization by WD-XRF

Materials were analyzed by the program UNIQUANT, a program based on fundamental parameters, to determine minor elements and traces. The concentration obtained of Si, Al, Fe, Ca, Mg, Na, K, Ti, Zn, P, Mn, Cr, Ni and Cu was lower than 0.05% w/w. Thus, Cobalt content was determined by preparing a calibration curve in the SuperQ program in WD-XRF; using LiF200 as crystal analyzer, Kα line, a collimator of 150 μm and a Flow detector.

For WD-XRF analysis, the sample was prepared in the form of beads. A 50:50 mixture of LiBO$_2$:Li$_2$B$_4$O$_7$ was used as flux and a 250 g·L^{-1} solution of LiI from Merck was used as bead-releasing agent.

Crystalline phases characterization by XRD

Crystalline phases were determined by XRD, giving information about the oxides and crystalline phases that might be present in the sample. The mineralogical species present were identified using the ICDD files for pure crystalline phases [15-18].

A refinement Rietveld protocol was performed using the specific software DIFFRACplus TOPAS (version 4.2). The agreement indices, as defined in Topas, were: Rwp (R-weighted pattern)=0.80 and GOF (Goodness of fit)=1.02.

Phase determination by Fourier-Transform Infrared Spectra (FTIR)

Fourier transformed infrared spectrometry (FTIR) has been carried out by many authors to identify the cobalt oxides phases formed, combined with XRD. According to Fahardi et al., two weak bands of the spinel-type Co_3O_4 structure should appear at about 660 and 560 cm^{-1} [7].

Determination of oxygen by TC-436 elemental analyzer

Oxygen content was determined by the TC-436 Elemental Analyzer after preparing the corresponding calibration curves. The amount of sample introduced on the piece of equipment was optimized on a previous work [19].

The aim of the Oxygen determination was to confirm all the theoretical assumptions made about the species present in each sample from the results obtained by the other techniques used, i.e. XRD and FTIR.

Results and Discussion

Oxidation and reduction treatments

Thermal treatment in an air atmosphere: Materials R1 and R2 were characterized before and after the thermal treatment. Starter material of R1 was $Co(OH)_2$, while starter material of R2 was Co_3O_4, as XRD and oxygen determination confirms. The results obtained are shown in TABLE 4.

TABLE 4. **Complete characterization of R1 and R2 before and after the thermal treatment in air atmosphere.**

Experiment	Studied material	Crystalline phases	Co content	Experimental oxygen	Calculated oxygen
-	R1 (original)	$Co(OH)_2$	63.40%	34.43%	34.41%
1	R1 (treated)	Co_3O_4	73.30%	26.80%	26.58%
-	R2 (original)	Co_3O_4	73.60%	26.40%	26.58%
2	R2 (treated)	CoO (major)+ Co_3O_4 (minor)	77.00%	23.00%	-

As it can be seen in TABLE 4, experiment 1 consisted in R1 being oxidized from $Co(OH)_2$ to Co_3O_4, as expected from Pejova's et al. work [12], who considered this oxidation at the temperature of 350℃ following the reaction (1). The oxygen values obtained confirmed the existence of the crystalline phases identified by XRD, as significative differences were not found between the experimental values and the calculated ones from the cobalt oxide phases identified.

Regarding experiment 2, R2 was mostly reduced from Co_3O_4 to CoO after 2h at 900℃, as the XRD and the oxygen content showed. However, part of the Co_3O_4 was left, as some peaks corresponding to Co_3O_4 crystalline phase were still remaining in the diffractogram, apart from the well-defined CoO peaks. The values obtained in cobalt and oxygen determination confirmed the crystalline phases identified, since the oxygen values obtained were slightly higher than the stoichiometric values for CoO, which might be contributed by the presence of Co_3O_4.

In addition, the original material R2 was also characterized by undergoing FT-IR. Two bands at 568 and 666 cm^{-1} were obtained. According to literature, two bands around 560 and 660 cm^{-1} correspond to Co_3O_4 [6,7,12,14,20-23]. Thus, the results obtained coincided with the ones shown in TABLE 4, so it was concluded that the starter material was Co_3O_4.

Thermal treatment in a N_2/H_2 atmosphere: Material R2 underwent a complete characterization before and after being treated in a 95%N_2/5%H_2 atmosphere. The results obtained are shown in TABLE 5.

TABLE 5. **Complete characterization of R2 before and after the thermal treatment in 95%N_2/5%H_2 atmosphere.**

Experiment	Studied material	Crystalline phases	Co content	Experimental oxygen	Calculated oxygen
-	R2 (original)	Co_3O_4	73.60%	26.40%	26.58%
3	R2 (treated)	-	81.5	18.00%	-
4	R2 (treated)	Co°+ CoO (trace level)	96.8	3.06%	-

After running experiment 3, the oxygen value obtained was still too high, as much as low was the cobalt value, so it was considered that other cobalt species with oxygen were present in addition to metallic cobalt.

According to Wang et al., Co_3O_4 should be reduced to Co° at 350℃ in a reductive atmosphere [5], but the oxygen determination to the material that was submitted to the thermal treatment was showing that the material was not completely reduced. Thus, maximum temperature was then raised to 600℃ in experiment 4 to eliminate the water formed as a by-product of the reactions (3) and (4) formulated by Lin et al. [14]. The cobalt and oxygen determination, and the XRD obtained in experiment 4, showed that the cobalt oxide was reduced to metallic cobalt with CoO traces.

Thermal treatment in an Oxygen atmosphere: Materials R3 and R4 were characterized before and after undergoing the thermal treatment in an oxygen atmosphere at 900℃. The results obtained are in TABLE 6:

TABLE 6. **Complete characterization of R3 and R4 before and after the thermal treatment in O_2 atmosphere.**

Experiment	Studied material	Crystalline phases	Co content	Experimental oxygen	Calculated oxygen
5	R3 (original)	CoO (64%)+Co₃O₄ (36%)	76.70%	23.30%	23.22%(1)
	R3 (treated)	Co₃O₄	73.80%	26.00%	26.58%
6	R4 (original)	CoO(2)	99.10%	0.80%	-
	R4 (treated)	CoO	78.00%	21.82%	21.35%

(1) This value was calculated with the ratio of crystalline phases determined by Rietveld and the calculated oxygen of each compound.

(2) Metallic cobalt was the only phase shown in XRD but, according to cobalt and oxygen quantification, cobalt oxide (CoO) might be present at trace levels

The characterization of the original R3 material showed that it had CoO and Co_3O_4 phases in its composition, so Rietveld refinement was carried out to determine the phases concentration in order to achieve a complete knowledge of the starter material. Thus, although the certificate of analysis of the reagent stated that the material was entirely CoO, the quantification of the crystalline phases pointed out that the Co_3O_4 phase was also present in a 36% (w/w). The oxygen was calculated taking into account the phases concentration obtained by Rietveld refinement. The oxygen content determined was very similar to the calculated one so, the analysis was validated.

The values obtained for oxygen concentration and the XRD in the treated materials showed that the compounds were oxidized to the next oxide form according to reaction (5). Experiment 5 consisted on the oxidation of CoO to Co_3O_4 at 900℃, which agrees with Tang's et al. work [2], while experiment 6 transformed Co° to CoO at 600℃ in an oxygen atmosphere.

Conclusions

The experiments realized in the three atmospheres and at different temperatures have allowed to perform a quantitative study about the cobalt oxide transformations at each condition.

Cobalt (II, III) oxide (Co_3O_4) was obtained after treating the cobalt hydroxide ($Co(OH)_2$) at 350℃ in an air atmosphere. Furthermore, Co_3O_4 treated at 900℃ in air atmosphere for 30 min gave major phase CoO and minor Co_3O_4.

About the thermal treatment of Co_3O_4 in a 95%N_2/5%H_2, the only successful results were obtained after treating the material at 600℃, as the starting material was reduced to metallic cobalt.

Regarding the thermal treatments carried out in an oxygen atmosphere, metallic cobalt was oxidized to CoO at 600℃ and this cobalt oxide was transformed into Co_3O_4 at 900℃.

The quantification of oxygen concentration made possible to get a quantitative information about the different cobalt species.

The study has demonstrated the need of carrying out a complete characterization of the reagents bought that claim a 100% of purity in a cobalt oxide specie, such as CoO. As it was proved in the characterizations that underwent the original reagent R3 (before any thermal treatment), some of them were showing a mix of cobalt oxides (64% CoO+36% Co_3O_4), although the

certificate of analysis was ensuring a 95% of purity of CoO. This fact brings about important errors about the cobalt concentration value, if it is being calculated from the compound formula.

Acknowledgement

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