SYNTHESIS AND CHARACTERIZATION OF Co-ZnO COMPOSITE[1]

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ABSTRACT

The paper describes the preparation of composite Co-ZnO by preferential reduction with hydrogen. Initially we developed a thermodynamic assessment of the main reactions to the process such as pyrolysis of nitrates of cobalt and zinc, responsible for obtaining the respective oxides, and the reduction of hydrogen. The experimental study was performed to evaluate the effect of important variables (temperature and partial pressure of the reacting gas) on the kinetics of reduction reactions. There was the feasibility of establishing conditions occur where the preferential reduction of cobalt oxide in relation to zinc oxide. As an example may be mentioned that in the temperature range of the experiments of reduction of cobalt oxide (590K - 790K) were obtained from 20 conversions and 80% within an interval of time between 1 and 15 minutes using a hydrogen flow of 0.18 L / min. In turn, the composite can be obtained in the test conducted at a temperature of 590K by the time of 30 minutes kept the same flow. The properties of materials were carried out by X-ray diffraction, SEM / EDS and transmission electron microscopy, it is possible to identify relatively pure oxides and Co-ZnO composite very homogeneous and consists of particles on the nanometer scale, these features are desirable for such materials.

***KEY WORDS**: hydrogen reduction, Co-ZnO, characterization, nanocomposite.*

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1. INTRODUCTION

The composites are characterized by combining properties of different materials. They consist of two or more components, where each individual contributes to the final characteristic of the desired product. Examples are both the metal or ceramic matrix composites while the latter has, normally, a transition metal dispersed in its composition and has extensive applications in the electronics industry (Jimenez-Gonzalez, 1997; Modine, 1998 ; Puchert, 1996). The composites can be prepared by different methods such as precipitation, implantation and chemical vapor deposition (Hartmann, 1996, Joseph, 1999).

So, this work is dedicated to the synthesis and characterization of the Co-ZnO composite which presents some interest in the varistors segment. Also, in order to meet the expectations of the composite having nano particles in its structure, the process is based on the preparation of a precursor, consisting of the Co ans Zn oxides in the form of a solid solution, followed by the cobalt preferential hydrogen reduction.

The objectives of this work are directed to a thermodynamic approach (theoretical) of the main reactions of the process (nitrates dissociation and oxides hydrogen reduction) as well as to a kinetic study (experimental) of the reduction step. The materials obtained experimentally (oxides, co-precipitated oxides, metal and composite) were characterized by different methods (XRD, SEM, TEM) in order to evaluate the proposed process by an assessment of their most striking structural features, including the nano-particles presence.

2. BASIC THEORETICAL BACKGROUND

The nitrates of cobalt and zinc when subjected to relatively low temperatures can be dissocited through the following reactions:

$$Zn\ (NO_3)\ 2.6H_2O \rightarrow ZnO + 2NO_2\ (g) + 6H_2O\ (g) + ½\ O_2\ (g) \qquad (1)$$

$$3Co\ (NO_3)\ _2.\ Co_3O_4 \rightarrow 6H_2O + 6NO_2\ (g) + 18H_2O\ (g) + O_2\ (g) \qquad (2)$$

Figure 1 illustrates these dissociations free energy variation as function the temperature.

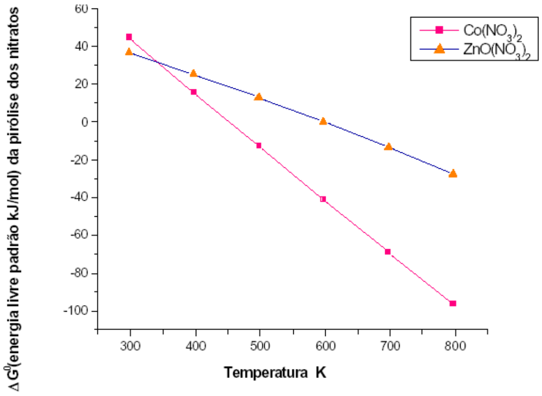

Figure 1 – ΔG°(standard free energy of the nitrates pyrolysis) X temperature (K).

It is observed that while the Co nitrate can be dissociated, in open reaction systems, at about 400K the Co one requires higher temperatures such as 600K.

The thermodynamic feasibility of the Co and Zn hydrogen reduction reactions can be appreciated by means of a predominance type diagram, as illustrated in Figure 2. It shows the stable phases areas as function of temperature and H_2 percentage in a mixture with water. Of course, the curves represent the equilibrium for the following reactions, considering the total pressure equal to 1 atm.

$$Co_3O_4 + 4H_2 (g) = 3Co + 4H_2O (g) \quad (3)$$

$$ZnO + H_2 (g) + H_2O = Zn (g) \qquad (4)$$

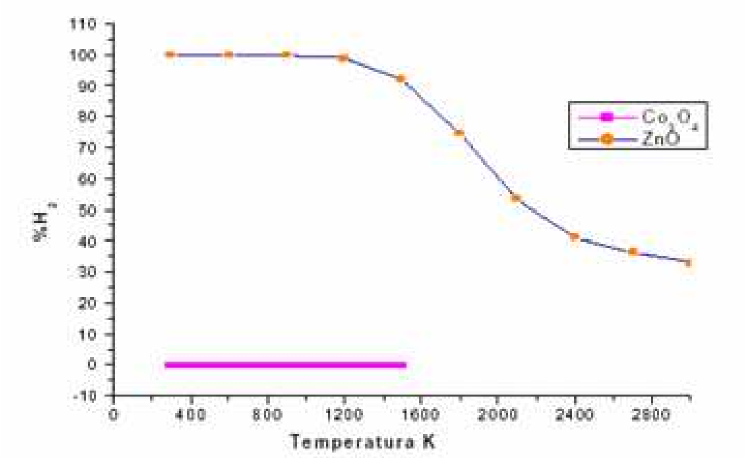

Figure 2 – H_2 percentage versus temperature (K).

It can be seen that, thermodynamically, very small H_2 partial pressures is enough to reduce the Co_3O_4 to Co. However, in the ZnO case, partial pressures smaller than something close to 100% are only viable for the reduction taking place above1200K. Thus, a compound of these oxides reactinh with hydrogen in the range between 600K and 800K, used in this study, would produce cobalt and ZnO.

These facts predict the feasibility of obtaining the Co-ZnO composite through the overall reaction represented below. Considering also that the oxides were obtained through a co-precipitation, it is possible to have a high dispersion degree of the Co and ZnO phases, making the obtained material very homogeneous.

$$Co_3O_4 (s) + ZnO (s) + 4H_2 (g) \rightarrow 3Co + ZnO (s) + 4H_2O (g) \quad (5)$$

3. EXPERIMENTAL METHODOLOGY

Cobalt and zinc nitrates, alone or mixed in appropriate proportion, were dissolved in a minimum amount of deionized water and subjected to a temperature rise up to 700K for about 40 minutes, during which a gaseous detachment was clearly observed.

Samples of the solid obtained material were subjected to reduction under an atmosphere containing hydrogen gas. The effects of temperature (590 to 790K) and hydrogen partial pressure (0.1 to 1.0) were studied with respect to the cobalt oxide reduction under a hydrogen flow kept at 0.18 L / min. The reduction reactions were performed by placing samples of known weight in navicular alumina which was positioned within a tubular reactor. After certain reaction times, the navicular were cooled under inert atmosphere and the conversions calculated from the mass differences. Such tests were also carried out with both zinc oxide and co-precipitated oxides, under specified conditions.

Oxides obtained from the nitrates pyrolysis were analyzed by X-ray diffraction and the composite produced from the partial reduction of co-precipitated oxides was characterized not only by this technique but also by SEM / EDS and TEM.

4. RESULTS AND DISCUSSION

Regarding the Co and Zn nitrates dissociation, the theory (Figure 1) was confirmed, as the product characterization by X-ray diffraction, as shown in Figure 3, indicates the presence of both oxides, Co3O4 (JCPDS No. 42-1467) and ZnO (No. 36-1451).

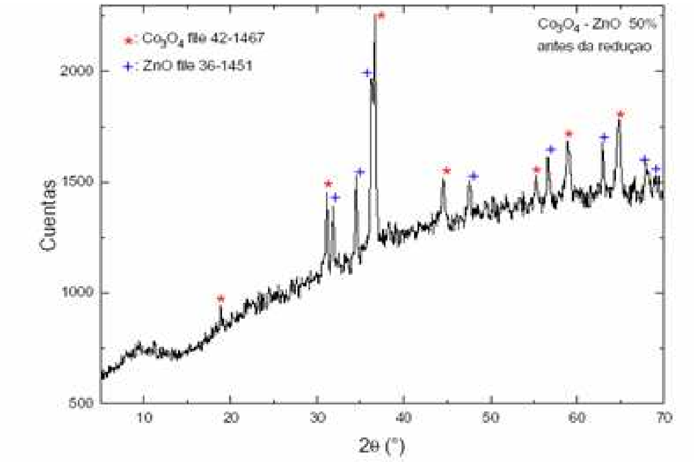

Figure 3 - Diffractogram of the precipitated from the nitrates pyrolysis (before hydrogen reduction).

In order to better stablish the conditions for obtaining the Co-ZnO composite, it was carried out individual studies on the hydrogen reduction of both oxides (Co_3O_4 and ZnO). In this cases, the effects of temperature and hydrogen partial pressure on the metal oxides conversion levels were assessed.

The temperature effect on the kinetics of the Co_3O_4 reduction was evaluated in the range 590K-790K and the results can be seen in Figure 4.

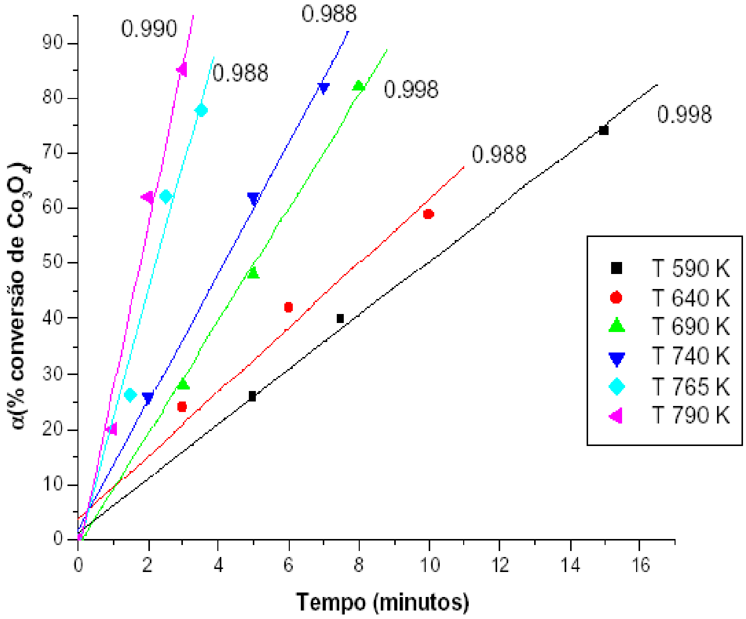

Figure 4 - Conversion of Co_3O_4 versus time (minutes).

It is observed that, at all tested temperatures, the conversion is proportional to the reaction time [α(%) = kt] and the increase in temperature is responsible for greater conversions. From the slope of the Figure 4 straight lines the values of k for different temperatures are obtained. It is then applied to the Arrhenius equation ($k = Ae^{-Ea/RT}$) obtaining the graph ln k versus 1 / T (Figure 5).

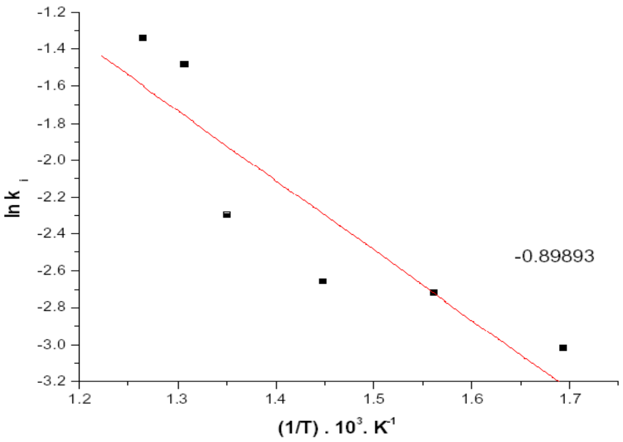

Figure 5 – ln k versus 1 / T (K)

Figure 5 illustrates the temperature effect on the rate constant of the Co_3O_4 reduction, which allows to estimate an apparent activation energy of about 33 kJ/mol for this reaction.

As noted in Figure 4, the whole reduction reaction occurs in a relatively short time and the conversion rate is sensitive to temperature increase. Thus, for the subsequent evaluation of the partial pressure, it was used the temperature of 590K, in which test the full conversion time is relatively larger, enabling a better system operational control. The reductions were carried out under different hydrogen partial pressures and the obtained results are shown in Figure 6.

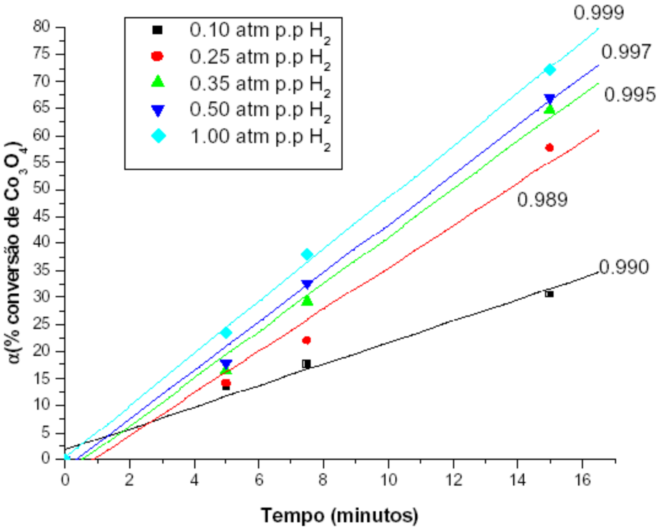

Figure 6 - Effect of hydrogen partial pressure on the Co_3O_4 reduction.

In all tests (10, 25, 35, 50 and 100% hydrogen pp) it was possible to keep the hydrogen flow of 0.18 L/m. Besides noting that increasing the reducing gas partial pressure it will increase the conversion level at any reaction time one can, also, see that very high Co3O4 conversion is attained even at dilute reducing atmospheres in a relatively short time.

In the order hand, as seen in Figure 2, the ZnO hydrogen reduction has not the same thermodynamic feasibility. This account was confirmed by carrying out three tests on the temperature of 590K, in a hydrogen 100% atmosphere, admitted to the reactor with the same flow, for a time of 15 minutes. As expected, it was not detected any traces of conversion in all three tests.

Therefore, the individualized studies on the Co and Zn oxides reduction, confirm that the former one can be implemented on a preferential basis in relation to the latter.

So, the co-precipitated oxides reduction were performed in order to obtain the Co-ZnO composite. A typical test at 590K (Gonçalves, 2005) indicated that high cobalt oxide conversion can be satisfactory reached in about 30 minutes.

Then, the characterization of the obtained material samples were submitted to X-ray diffraction and electronic microscopy. The diffractogram is shown in Figure 7. It clearly indicates the presence of ZnO phase, being also possible to note that the respective peaks remain virtually unchanged as compared to Figure 3. Moreover, as might be expected, the peaks indicative of Co3O4 suffered a significant change, although some seems to remain as seen in Figure 3. This reinforces the prediction for the occurrence of reduction of cobalt oxide by hydrogen and at the same time, gives nuances to the system in question. Among these, it may be mentioned that, possibly, the cobalt is either founded upon a very tiny crystallites or the detection of its peaks was not possible due to equipment operational conditions. In fact, the diffractogram increasingly shape indicates a strong sample fluorescence, enhanced by the cobalt presence and, therefore, deserves further evaluation under different analysis conditions (ex:radiation wavelength).

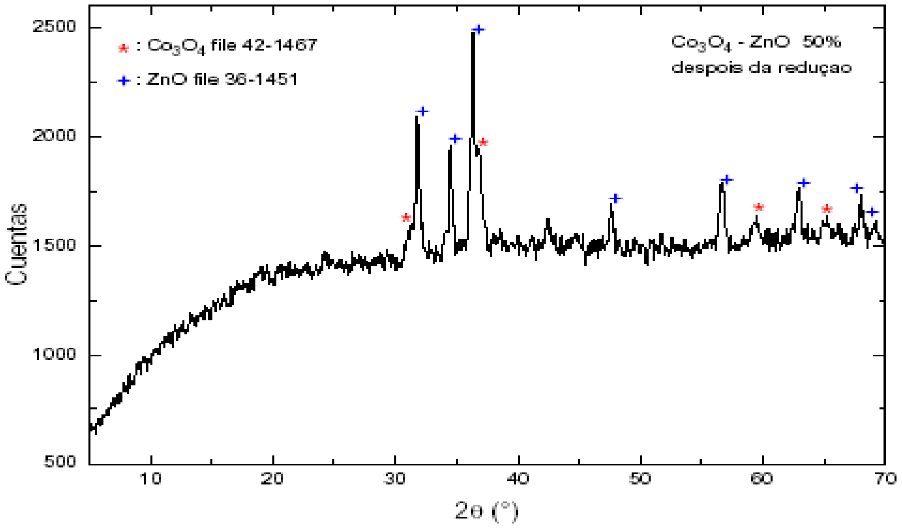

Figure 7 - Diffractogram of the material after hydrogen reduction.

With that in mind, an additional test has been carried out in order to better evaluate the characteristics of the obtained material. Using the same reduction methodology described, two navicular were loaded in the furnace, one (A) containing Co oxide and the other (B) with a sample of the Co and Zn co-formed oxides compound. This experiment was performed at 690K for 20 minutes using a 0.18L/min H_2 flow. It was observed that in the navicula A the cobalt metal was present as it has been readily verified its ferromagnetism feature. With the aid of a permanent magnet it was easily confirmed its behavior within a magnetic field. In the other hand, the obtained material in the navicula B, though showing the weight difference correspondent to cobalt oxide reduction, was not sensitive against the magnetic field. These facts would suggest that the compound is formed not only in terms of physical association between ZnO and Co but also from a chemical interaction between the elements involved. Confirmation of such a possibility can be found in other studies (Jedrecy, 2004; Kolesnik, 2004).

An observation conducted in the SEM / EDS (Figure 8) indicates the existence of a very homogeneous material and confirms the presence of those metals (Co and Zn), without taking into account its associations.

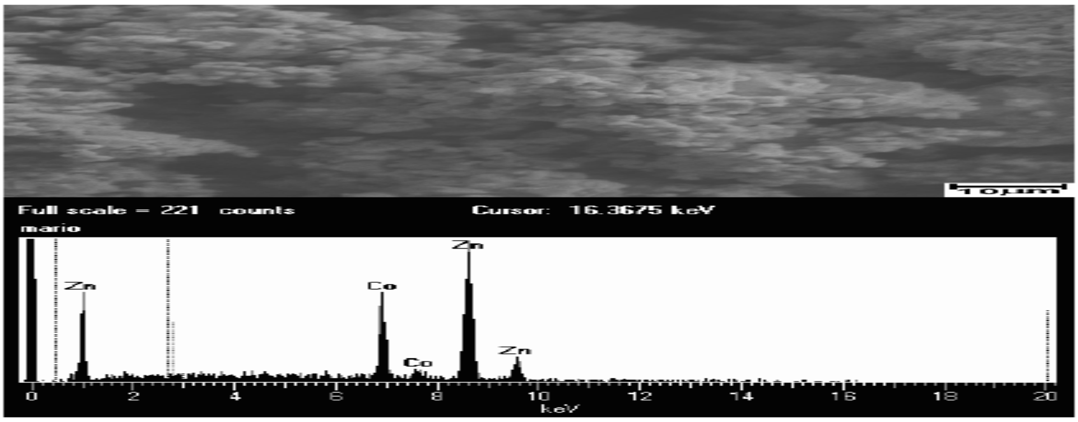

Figure 8 - Characterization SEM / EDS (after hydrogen reduction)

In order to give a greater consistency to the obtained material characterization it was carried out a further investigation by TEM (Figure 9). Samples of the synthesized powder were allocated in a copper grid supported by a carbon film and observed in a transmission electron microscope with accelerating voltage of 200 kV. Accordingly, one can see a very homogeneous distribution of particles having an average size of 30nm. It has been identified a material nominal composition of ZnO-0.9.Co-0.1.

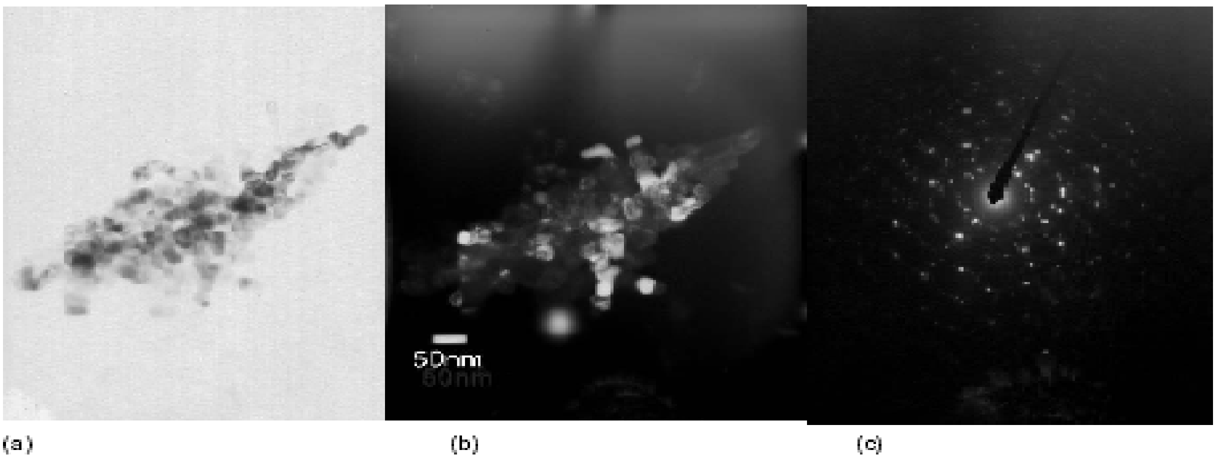

Figure 9 – TEM bright field (a) and dark field (b) .Cluster of Co-ZnO particles. Homogeneous dispersion of 30nm average size. Corresponding diffraction figure in a selected area (c).

5. CONCLUSIONS

As thermodynamically estimated the cobalt and zinc nitrates dissociation will take place satisfactorily at relatively low temperatures (500-600K). Under these conditions the individual oxides were obtained individually (Co_3O_4 and ZnO) as well as the compound consisted of both (co-precipitated).

The oxides reductions were carried out using hydrogen gas as reductant. It was experimentally confirmed that the Co_3O_4 and ZnO hydrogen reductions are feasible in the temperature range 590-790K and that, as expected, the conversions increase with increasing temperature. The temperature effect on the Co_3O_4 reduction was quantitatively assessed by means of kinetics curves and the apparent activation energy was found to be about 33 kJ / mol. This fact indicates that the reaction system is not characterized by a marked physical limitation (diffusion) and is therefore more dependent on the stage associated with the chemical reaction. In practical terms, it was observed that cobalt oxide can be 100% reduced at, for example, 690K for 20 minutes, using a rich hydrogen atmosphere.

Based on thermodynamics evaluation, the experiments focused on the ZnO reduction were carried out, deliberately, in unfavorable experimental conditions to its occurrence. The results has confirmed this fact, making possible the Co-ZnO composite formation through the implementation of a selective reduction. For example, a Co_3O_4-ZnO compound hydrogen reduction taking place at 590K and 30 minutes implies in high levels of a preferential cobalt oxide reduction.

Several characterization techniques were implemented to identify some of the obtained products. The Co_3O_4 and ZnO formations, resulting from the nitrates pyrolysis, were confirmed by X-ray diffraction as well as the existence of nano-sized particles in a ZnO-0.9.Co-0.1 composite, which was produced by hydrogen selective reaction. The obtained composite showed to be very homogeneous, a desirable feature for such materials. Further studies should be conducted in order to detail the synthesis and sintering conditions and, also, to provide a more detailed characterizarion of the composite produced by the studied method.

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