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THERMAL DECOMPOSITION OF BASIC COBALT AND COPPER CARBONATES
Thermal stability of the produced oxides as influenced by gamma-irradiation

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Abstract

Basic cobalt and copper carbonates were prepared by precipitation from solutions of their nitrates using $KHCO_3$ at room temperature in CO_2 atmosphere. The thermal decomposition of the prepared basic carbonates was studied by means of TG and DTA techniques and the phases produced were identified by XRD measurements. The products obtained at 400°C were subjected to different doses of gamma-rays (40–160 M rad) and the thermal stabilities of these solids were investigated.

The results obtained revealed that basic cobalt carbonate decomposed at 335°C to produce Co_3O_4 which remained stable up to 850° and then decomposed above this temperature giving CoO which transformed into Co_3O_4 on cooling to room temperature. Basic copper carbonate dissociated at 290°C yielding CuO which yielded Cu_2O and metallic copper at 1060 and 1150°C, respectively. However, the produced cuprous oxide and metallic copper solids were converted into CuO and Cu_2O, respectively by cooling in air to room temperature.

Gamma-irradiation decreased the thermal stability of Co_3O_4 to an extent proportional to the dose employed. On the other hand, this treatment increased the thermal stability of both CuO and Cu_2O.

Keywords: basic cobalt, gamma-irradiation, thermal stability

Introduction

Cobalt and copper-containing solids behave as active catalysts for oxidation-reduction reactions [1–6]. The activity and service life time of these catalysts are mainly dependent on the prehistory of parent materials, calcination conditions, doping with certain foreign oxides and subjecting to ionizing radiations [1, 3, 4, 6, 7]. It has been reported by one of the authors [8] that irradiation by

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gamma-rays of Co_3O_4/Al_2O_3 brought about a significant decrease in both the microstrain and lattice parameter of Co_3O_4 crystallites. These changes in structural characteristics of cobaltic oxide solid have been attributed to desorption of excess oxygen in non-stoichiometric Co_3O_4 with subsequent decrease in the concentration of lattice defects (Co^{3+} ions) and also to the splitting of Co_3O_4 crystallites. These changes were accompanied by a considerable increase in catalytic activity, in CO oxidation by O_2, of the treated solids [8]. The thermal treatment is expected also to modify some physicochemical and catalytic properties of cobalt and copper-containing solids.

The present work reports a study on the thermal behaviour of cobalt and copper carbonates and the thermal stability of the produced oxides being subjected to different doses of gamma rays using XRD, TG and DTA techniques.

Experimental

Materials

Pure basic cobalt and copper carbonates were prepared by precipitation from cobalt and copper nitrate solutions using $KHCO_3$ at room temperature and a *pH* of about 8. The obtained precipitates were carefully washed with distilled water till free from NO_3^- and K^+ ions, then dried at 100°C to a constant weight. The employed chemicals, $KHCO_3$, $Co(NO_3)_2{\cdot}9H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$, were analytical grade products supplied by Fluka.

Techniques

TG and DTA analyses of the prepared basic carbonates were carried out using a Netzsch-Gerätebau thermal analysis apparatus (STA 405, type 6.223). The rate of heating was kept at 10°C min^{-1}. A 50 mg sample was used in each case.

X-ray diffraction patterns of the thermal decomposition products of the prepared basic carbonates were obtained with a Philips diffractometer (type PW 1390). The patterns were run with iron-filtered cobalt radiation (λ= 1.790 Å) for the thermal decomposition products of cobalt carbonate, and nickel-filtered copper radiation (λ=1.5405 Å) for those of copper carbonate.

Results and discussion

X-ray investigation of the thermal decomposition products of cobalt and copper carbonates

XRD measurements were carried out on basic cobalt and copper carbonates preheated in air at 400, 600, 900, 1000 and 1100°C. The results obtained revealed that the thermal decomposition products obtained at 400, 600 and 900°C consisted of Co_3O_4 and CuO phases. The degree of crystallinity of the produced cobaltic oxide was found to increase with increasing heating temperature in the range of 400–900°C, and CuO obtained at 400–900°C exhibited an excellent degree of crystallinity. Inspection of X-ray diffractograms, not given here of the thermal decomposition products of basic cobalt and copper carbonates precalcined in air at 1000 and 1100°C showed the presence of diffraction lines of both Co_3O_4 and CoO in case of cobalt carbonate and the lines of CuO and Cu_2O in case of copper carbonate. However, the relative intensities of diffraction lines of each of CoO and CuO produced at 1000°C were relatively small, especially in the case of the cobalt containing sample indicating their presence in small amounts.

Exposure of Co_3O_4 and CuO obtained at 400°C to different doses of γ-rays up to 160 Mrad did not affect the degree of crystallinity of these two phases as indicated by the relative intensities of their diffraction lines. Different results have been reported in the case of Co_3O_4 supported on amorphous alumina [3]. The gamma-irradiation of Co_3O_4/Al_2O_3 brought about a decrease in the crystallinity of cobaltic oxide to an extent proportional to the dose employed due to the fragmentization of its crystallites [3].

Thermal behaviour of basic copper and cobalt carbonates

TG and DTA analyses were carried out on basic cobalt and copper carbonates. Figure 1 presents DTA curves of both basic carbonates. The DTA curve of the copper compound consists of three sharp and strong endothermic peaks with maxima at 290, 1060 and 1150°C. The first peak which was accompanied by a mass loss of 27.4% characterizes the thermal decomposition of basic copper carbonate into cupric oxide. The obtained percentage loss in mass of 27.4% suggests the formula of the prepared carbonate as $CuCO_3{\cdot}Cu(OH)_2$ which decomposed to produce cupric oxide according to:

$$CuCO_3{\cdot}Cu(OH)_2 \xrightarrow{290^\circ C} 2CuO + CO_2(g) + H_2O(g) \tag{1}$$

The second endothermic peak was followed by a mass loss of 9.7% which points to a complete conversion of CuO into Cu_2O according to:

$$2CuO \xrightarrow{1060^\circ C} Cu_2O + 1/2O_2(g) \tag{2}$$

X-ray investigation, perviously given, showed the presence of a small amount of Cu_2O phase beside CuO in basic copper carbonate preheated in air at 1000°C. The existence of CuO as a major constituent indicates the reoxidation of the produced Cu_2O by atmospheric oxygen during its cooling to room temperature. The third peak was accompanied by a mass loss of 9.7% which corresponds to dissociation of most of the produced Cu_2O (about 87%) to yield metallic copper according to:

$$Cu_2O \xrightarrow{1150^\circ C} 2Cu + 1/2O_2(g) \tag{3}$$

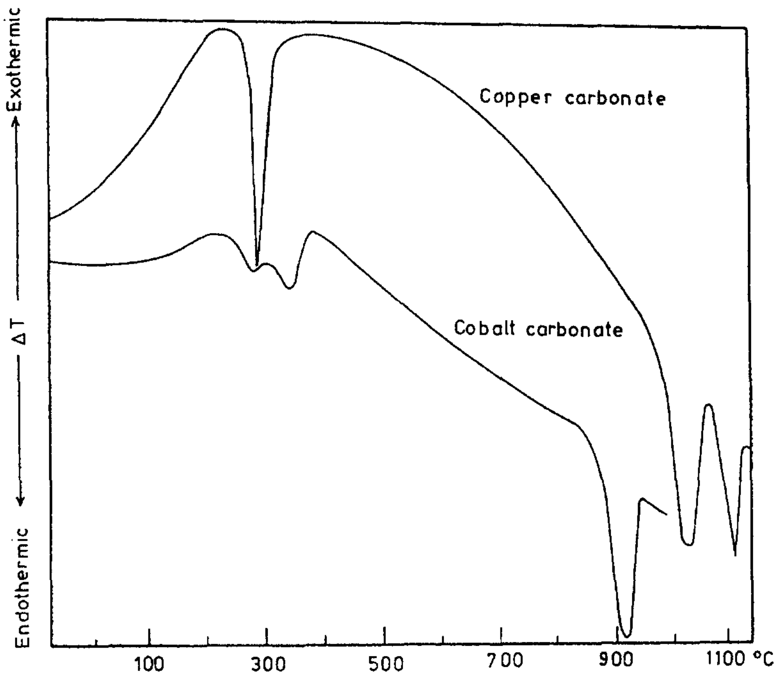

Fig. 1 DTA curves of basic copper and cobalt carbonates

The absence of the diffraction lines of metallic copper in the X-ray pattern of the solid copper specimen preheated in air at 1100°C showed its oxidation to Cu_2O by atmospheric oxygen during the cooling process to room temperature which was susceptible to partial oxidation by atmospheric oxygen to a CuO phase.

The DTA curve (Fig. 1) of the prepared cobalt carbonate includes four endothermic peaks, the first being broad extending between 50 and 200°C, while the other three peaks sharp and strong, especially the last one. The first, second and third peaks were accompanied by mass losses of 4.2, 9.3 and 20.3%, respectively. The first peak indicates the departure of physically sorbed water, the second and third peaks, with maxima at 250 and 350°C correspond to the loss of water of constitution and decomposition of $CoCO_3$ to Co_3O_4 [9]. The departure of water of constitution and CO_2 from the basic cobalt carbonate occurs successively over the temperature range of 225–375°C and is followed by a mass loss of 29.6%. This value corresponds to the reaction:

$$5CoCO_3 \cdot Co(OH)_2 + O_2(g) \xrightarrow{225-375^\circ C} 2Co_3O_4 + 5CO_2(g) + H_2O(g) \quad (4)$$

The produced cobaltic oxide remains stable up to 850°C, above which it undergoes decomposition into CoO [10]. The last endothermic peak at 940°C, which was accompanied by a 6.5% loss in mass corresponds to a complete conversion of Co_3O_4 into CoO according to:

$$Co_3O_4 \xrightarrow{850-980^\circ C} 3CoO + 1/2O_2(g) \qquad (5)$$

The previously cited XRD investigations showed the presence of a very small amount of CoO phase in a cobalt oxide solid preheated in air at 1000°C. These findings clearly indicate the tendency of the produced cobaltous oxide solid to reoxidation by atmospheric oxygen to Co_3O_4 on cooling to room temperature.

The thermal stabilities of Co_3O_4 and CuO could be modified by doping with small amounts of certain foreign oxides and also by treating with gamma-rays. The effects of doping with Li_2O, Na_2O, BeO, MgO, Al_2O_3, ZrO_2, ThO_2, V_2O_5, Ta_2O_5 and MoO_3 on the thermal stability of Co_3O_4 was the subject of investigations carried out by one of the authors [10, 11]. It has been reported that doping with 3 mole% Li_2O completely prevented conversion of Co_3O_4 into CoO even by heating at 1100°C [10] while the other dopant oxides modified the thermal stability of Co_3O_4 in different manners, depending mainly on both the oxidation state of the dopant oxide ions and their size.

Thermal stability of Co_3O_4 subjected to gamma-rays

A cobaltic oxide sample (Co_3O_4) obtained by thermal decomposition of basic cobalt carbonate in air at 400°C was exposed to different doses (40, 80 and 160 Mrad) of gamma-irradiation. The effect of this treatment on the thermal stability of Co_3O_4 was studied by DTA investigation of the various irradiated solids.

Figure 2 presents DTA curves of various treated solids. It is suggested by this Figure that gamma-rays resulted in a slight shift in the position of the endothermic peak from 925 to 910°C by exposure to different doses varying between 40 to 160 Mrad. This small decrease in the temperature of decomposition of Co_3O_4 into CoO due to gamma-irradiation may be taken as an indication for an induced decrease in the thermal stability of cobaltic oxide solid. However, the thermal stability of Co_3O_4 is better reflected by the area of the endothermic peak corresponding to the decomposition of cobaltic into cobaltous oxide. This has been done by taking a constant mass of Co_3O_4 solid (200 mg) in each DTA measurement and the area of the endothermic peak for each solid was taken as a measure of the amount of the solid that undergoes a chemical change (decomposition, $Co_3O_4 \rightarrow CoO$) [10, 11].

The areas of the endothermic peaks corresponding to conversion of cobaltic oxide into CoO are given in Table 1.

It can be seen from Table 1 that gamma-rays decreased the thermal stability of Co_3O_4 to an extent proportional to the dose employed. However, a maximum decrease of 40.7% in the thermal stability was obtained by treatment with a dose of 80 Mrad.

Co_3O_4 preheated in air at temperatures as high as 750°C still contains a slight excess of oxygen with respect to it stoichiometric composition [12]. It has been

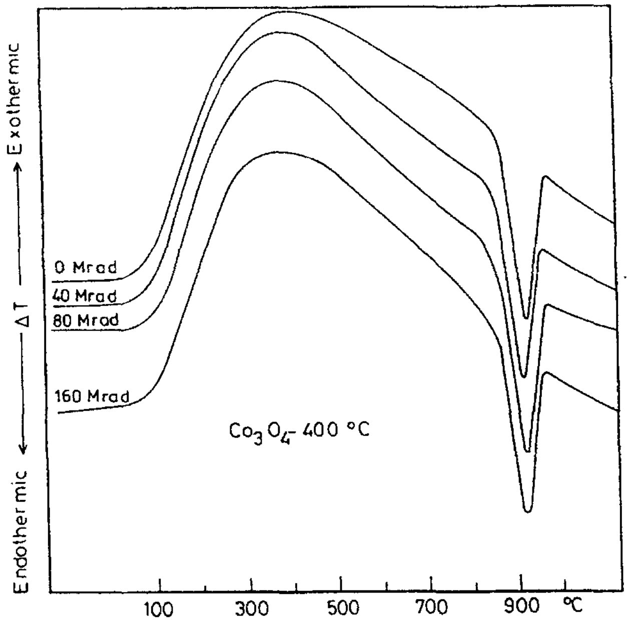

Fig. 2 DTA curves of different gamma-irradiated cobalt oxide

postulated by one of the authors [12] that the excess oxygen in the Co_3O_4 lattice, which gives rise to trivalent cobalt ions, acts as an energy barrier opposing its reduction into CoO. Once cobaltic oxide attains its stoichiometric composition via removal of the last traces of excess oxygen it starts to undergo the change $Co_3O_4 \rightarrow CoO$. Gamma-irradiation is expected to remove the excess chemisorbed oxygen, especially from the outermost surface layers of the treated oxide. So, gamma-rays can be regarded as an effective force destroying the energy barrier responsible for the thermal stability of Co_3O_4 via removal if surface excess oxygen. This effect attains its maximum potentiality at a dose of 80 Mrad.

Table 1 Effect of gamma-irradiation on the peak area of the DTA curves of the thermal decomposition of Co_3O_4

Dose/ M rad	Peak area/ Arbitrary unit	Increase in the area of endothermic peak*/%
0	10.8	0.00
40	12.0	11.10
80	15.2	40.74
160	13.0	20.40

* The data of this coulumn were obtained by subtracting the area of the endothermic peak of the unirriadiated specimen (10.8) from the peak area of each treated specimen.

Thermal stability of copper oxide

The thermal stability of cupric oxide was investigated by DTA measurements of CuO obtained by thermal decomposition of copper carbonate in air at 400°C, and subjected to different doses of gamma-rays, namely 20, 40, 80 and 160 Mrad.

A 100 mg sample of CuO obtained at 400°C was taken in each DTA measurement. Figure 3 presents DTA curves of the different irradiated solids. The areas of the first and second endothermic peaks were taken as a measure for the changes CuO → Cu_2O → Cu, respectively. The areas of those endothermic peaks are given in Table 2 showing that the treatment of cupric oxide with different doses of gamma-rays brought about a measurable increase in the thermal stability of both CuO and Cu_2O. The gained thermal stability of CuO due to gamma-irradiation runs parallel to the dose employed and the dose of 160 Mrad brought about 31.2% increase in the thermal stability of CuO. The thermal stability of Cu_2O increased by increasing the dose to 40 Mrad (17.5%) and remained unchanged by increasing the dose up to 160 Mrad.

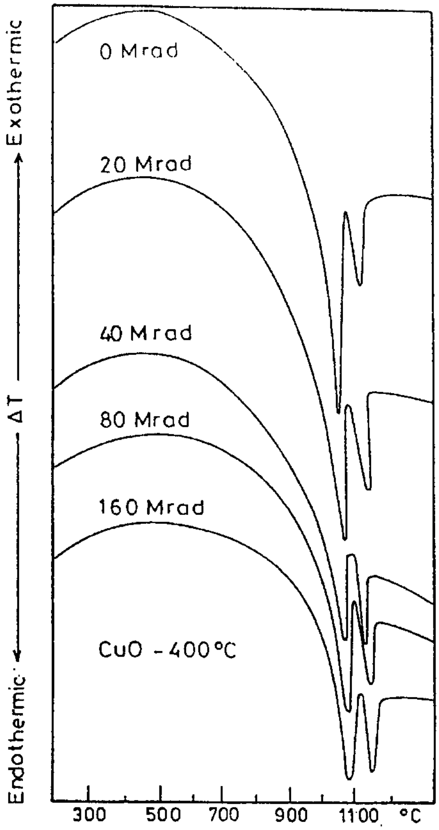

Fig. 3 DTA curves of gamma-irradiated copper oxide

Table 2 The effect of gamma-irradiation on the thermal stability of cuppric and cupprous oxide

Dose/ M rad	First endothermic peak		Second endothermic peak	
	Peak area/ Arbitrary unit	Decrease in the area of endothermic peak/%	Peak area/ Arbitrary unit	Decrease in the area of endothermic peak*/%
0	15.62	0.0	9.50	0.0
20	13.20	15.5	8.67	8.8
40	11.20	28.7	7.83	17.5
80	11.20	28.7	7.83	17.5
160	10.88	31.2	7.83	17.5

*The data of this coulumn were obtained by subtracting the area of the endothermic peak for each irradiated specimen from the peak area of un-irradiated sample (15, 62).

Cupric oxide behaves as an electric insulator but cuprous oxide acts as a *p*-type semiconductor [13, 14]. Cu_2O chemisorbs oxygen in an ionic form [13, 14]. The chemisorption process is expected to increase the oxidation state of cuprous oxide solid. Gamma-rays might remove the chemisorbed oxygen. If the chemisorbed oxygen acted as an energetic barrier opposing reduction into copper metal it might be expected that gamma-rays decreased thermal stability. Opposite results have been obtained since an increase in the thermal stability was observed (cf. Table 2). It might be expected that other parameters rather than the oxidation state of the copper species in the cuprous oxide lattice control its reduction into copper metal, among these parameters the particle size and textural characteristics can be cited. On this basis, the effect of gamma-rays in modifying the thermal stability of cupric and cuprous oxides could not be directly correlated to the oxidation state of the copper ion in cupric and cuprous oxide lattices.

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