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EFFECTS OF γ-RADIATION ON THE THERMAL STABILITY OF COBALT OXIDES

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ABSTRACT

Pure cobaltic oxide, prepared by thermal decomposition of pure basic cobalt carbonate in air at 500°C, was subjected to different doses of γ-radiation varying between 5 and 50 M rad. The influence of γ-radiation on the thermal decomposition of cobaltic oxide to cobaltous oxide and the re-oxidation of CoO to Co_3O_4 was studied using DTA, with a controlled rate of heating and cooling. The effects of γ-radiation on the specific surface area (S_{BET}) and oxidation character of Co_3O_4 were also investigated.

The DTA investigation revealed that γ-radiation effectively decreased the thermal stability of cobaltic oxide to an extent proportional to the dose employed. The maximum decrease in the thermal stability of 60% was attained by exposing Co_3O_4 solid to 30 M rad. γ-Irradiation, however, exerted no detectable effect on the re-oxidation of CoO by O_2 to Co_3O_4.

The S_{BET} measurements showed that the small dose (5 M rad) of γ-radiation effected a decrease of 15% in the surface area of Co_3O_4, the higher doses (10–50 M rad) caused a further slight decrease of 18% in its surface area.

γ-Irradiation was found to decrease the oxidation character of Co_3O_4 to an extent proportional to the dose employed.

The decrease in the thermal stability of Co_3O_4 due to radiation is explained in terms of the decrease in the oxidation character of cobaltic oxide observed after subjecting the solid to γ-radiation.

INTRODUCTION

The effects of different types of radiation on surface, catalytic, structural, textural and semiconducting properties of a wide variety of solids have been studied by several authors [1–7]. It has been reported that neutrons in nuclear reactors exert no appreciable changes in surface properties of TiO_2 [1], whereas γ-irradiation effects important modifications in surface, catalytic and structural properties of various solids such as TiO_2 [2], silica gel, alumina gel [3], NaCl [4], In_2O_3 [6], NiO and Co_3O_4 [7].

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The effects of dissolution of small amounts of foreign ions having different valence states in Co_3O_4 on its thermal decomposition to CoO have been extensively studied in our previous investigations [8–10]. Most of the dopant ions, Li^+, Na^+, Al^{3+}, V^{5+} and Mo^{6+}, being dissolved in the cobaltic oxide lattice, effected an increase in its thermal stability. The observed increase in the thermal stability of Co_3O_4 due to doping has been attributed to the increase in the oxidation character of doped solids which act as barriers, opposing the reduction of Co_3O_4 to CoO. The effects of γ-radiation, to our knowledge, on thermal decomposition of cobaltic oxide have not been investigated.

In the present work, we studied the effects of γ-radiation on the thermal decomposition of Co_3O_4 and the reactivity of the produced cobaltous oxide towards oxidation by O_2 to Co_3O_4. The techniques employed in this investigation were DTA, with a controlled rate of heating and cooling, low temperature adsorption of nitrogen and iodometric determination of the oxidation character of various cobaltic oxide specimens.

EXPERIMENTAL

Materials

Cobaltic oxide samples were prepared by thermal decomposition of basic cobalt carbonate, 5 $CoCO_3$ $Co(OH)_2$, in air at 500°C for 4 h.

Techniques

Solid cobaltic oxide was subjected to different doses of γ-radiation using a ^{60}Co source. The doses were 5, 10, 20, 30 and 50 M rad and the solid samples were left for one week before the surface, thermal stability and oxidation character measurements were carried out. No special temperature control was attempted, but the irradiation temperatures were probably not above 150°C.

Differential thermal analysis (DTA) of unirradiated and γ-irradiated cobaltic oxide specimens was carried out using a DuPont 990 thermal analyser with a differential scanning calorimeter cell. Both the rate of heating and cooling were kept at 20°C min^{-1} and the sensitivity was 1 mV in^{-1}. A 30-mg sample of each solid was used in each run.

The specific surface areas (S_{BET}) of various Co_3O_4 solids were calculated from nitrogen adsorption isotherms determined at 77 K using a conventional volumetric apparatus (following the BET method). Before the measurements were carried out, the samples were degassed at 200°C under a reduced pressure of 10^{-5} Torr for 2 h.

The oxidation character of unirradiated and γ-irradiated Co_3O_4 was

determined by an iodometric method. A 20-mg sample of each solid was introduced into a 250-ml round-bottomed flask containing 30 ml 50% HCl and 20 ml 20% KI. The flask was then tightly closed and heated gently at about 70°C, until complete dissolution was obtained (15 min). The flask, with its contents, was cooled and the liberated iodine was titrated against approximately 0.02 N $Na_2S_2O_3$. A blank experiment was carried out to correct for the presence of free chlorine in the hydrochloric acid employed. The volume of $Na_2S_2O_3$ consumed in each case was estimated per gram of Co_3O_4 and taken as a measure for the oxidation character of the solid specimens.

RESULTS

Figure 1 represents the DTA of unirradiated and γ-irradiated Co_3O_4 prepared by thermal decomposition of basic cobalt carbonate at 500°C. A strong endothermic peak with its maximum at 920°C was observed in all cases which corresponds to the decomposition of Co_3O_4 to CoO. A strong exothermic peak was detected during the cooling of the thermal products of unirradiated and γ-irradiated cobalt oxide heated at 1000°C. The maxima of the recorded exothermic peaks were located at 770°C, in all cases, which indicates the oxidation of CoO to Co_3O_4.

Since a constant weight of unirradiated and γ-irradiated Co_3O_4 specimens was taken in each run, the area of the endothermic and exothermic peaks for each solid could be regarded as a measure of the amount of the solid that

TABLE 1

Effect of γ-radiation on the peak area of the DTA curves of the thermal decomposition of Co_3O_4 and oxidation of CoO

Solid	Radiation dose (M rad)	Peak area (arb. units)		Change [a] in area of endothermic peak (%)	Ratio between area of exothermic and endothermic peaks
		Endo thermic peak	Exo thermic peak		
Co_3O_4	0.0	23.44	18.30		0.78
Co_3O_4	5.0	26.76	21.48	−14.16	0.80
Co_3O_4	10.0	27.10	20.90	−15.61	0.77
Co_3O_4	20.0	29.10	23.48	−24.15	0.80
Co_3O_4	30.0	37.58	29.56	−60.32	0.79
Co_3O_4	50.0	30.20	23.98	−28.88	0.79

[a] The data in this column were obtained by subtracting the area of the endothermic peak for each solid from 23.44 (the value of unirradiated solid). The negative sign indicates a decrease in the thermal stability of Co_3O_4.

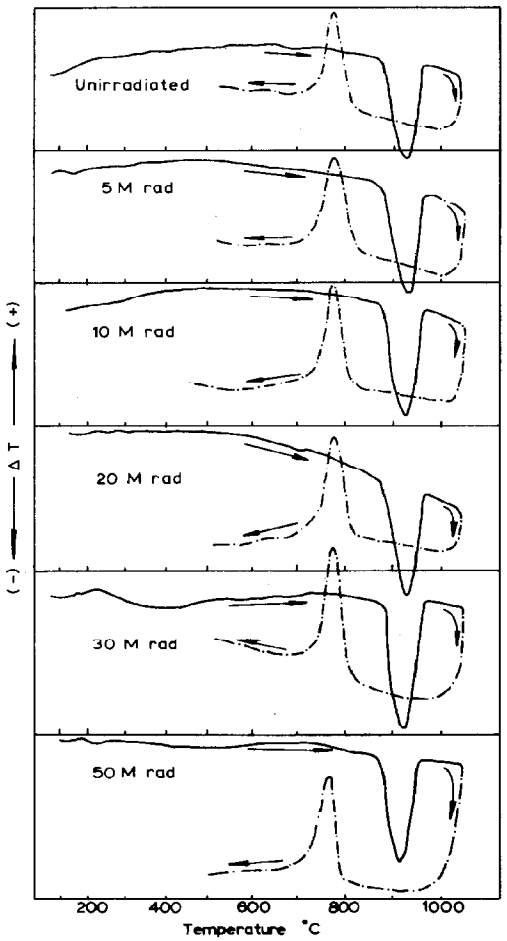

Fig. 1. DTA heating (————) and cooling (– · – · –) curves of unirradiated and irradiated cobalt oxide prepared by thermal decomposition of pure basic cobalt carbonate in air at 500°C.

undergoes a chemical change (decomposition, $Co_3O_4 \rightarrow CoO$, and oxidation, $CoO \rightarrow Co_3O_4$). The data of the endothermic and exothermic peaks, indicating the decomposition of cobaltic to cobaltous oxide and oxidation of cobaltous to cobaltic oxide, are given in Table 1 for unirradiated and γ-irradiated solids. This table also includes the percentage change in the area of the endothermic peak due to γ-irradiation and the ratio between the area of the exothermic and endothermic peaks. It can be seen from Table 1 that γ-irradiation of Co_3O_4 effected a decrease in its thermal stability to an extent proportional to the dose employed. A maximum decrease of 60% in the thermal stability of Co_3O_4 was attained when the dose reached 30 M rad;

increasing the dose to 50 M rad produced a decrease in the thermal stability from 60 to 29%. The ratio between the area of exothermic and endothermic peaks (Table 1, final column) is a measure of the ability of the CoO produced to undergo oxidation by O_2 to Co_3O_4. When this ratio reached unity, all the produced cobaltous oxide underwent oxidation to cobaltic oxide. The data of this ratio, obtained for various solids, are always smaller than unity, indicating an incomplete oxidation of CoO. It can be concluded from the results given in Table 1 that γ-irradiation of cobaltic oxide much enhanced its thermal decomposition to CoO and exerted no effect on the re-oxidation of cobaltous to cobaltic oxide.

Effects of γ-radiation on S_{BET} of cobaltic oxide

The specific surface areas of unirradiated and irradiated Co_3O_4 at 500°C were determined. The data obtained are 47 $m^2\ g^{-1}$ for unirradiated solid Co_3O_4 and 40, 39, 38, 38 and 37 $m^2\ g^{-1}$ for those samples subjected to 5, 10, 20, 30 and 50 M rad, respectively. The observed decrease in S_{BET} due to γ-irradiation could be attributed to pore widening. γ-Irradiation has been found to decrease the specific surface area of Fe_2O_3/Cr_2O_3 mixed oxide catalyst due to widening of its pores during the irradiation process [7].

Effect of γ-radiation on the oxidation character of cobaltic oxide

The volume of 0.02 N $Na_2S_2O_3$ solution consumed per gram of Co_3O_4

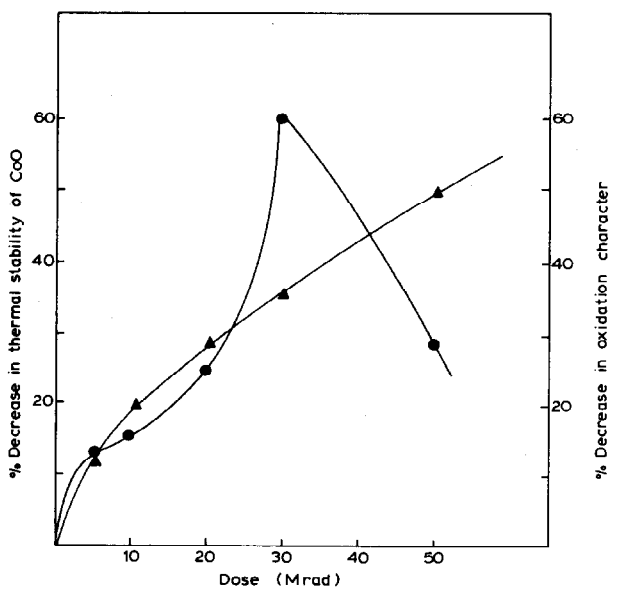

Fig. 2. Effects of γ-rays dose upon % decrease in thermal stability (●) and % decrease in oxidation character (▲) of Co_3O_4.

specimen was taken as a measure for the oxidation character of cobaltic oxide sample. The results obtained revealed that γ-irradiation effected a decrease in the oxidation character of Co_3O_4 at 500°C to an extent proportional to the dose employed. The percentage decrease in the oxidation character due to γ-irradiation as a function of the dose is represented graphically in Fig. 2. This figure also included the percentage decrease in the thermal stability as a function of the dose of γ-radiation. It can be seen from Fig. 2 that the decrease in the thermal stability of Co_3O_4 due to γ-irradiation runs parallel to the decrease in the oxidation character. However, the percentage decrease in the oxidation character, due to γ-irradiation, is directly proportional to the dose employed up to 50 M rad and the percentage decrease in the thermal stability of irradiated solid attains a maximum value at 30 M rad, then drops by increasing the dose from 30 to 50 M rad.

DISCUSSION

The DTA investigation of γ-irradiated cobaltic oxide clearly revealed that the irradiation process of the solid much enhanced its thermal decomposition to CoO and exerted no detectable effect upon the oxidation of the produced cobaltous oxide by O_2 giving Co_3O_4. The effects of doping on thermal decomposition of cobaltic oxide have been extensively studied in our previous investigations [8–10]. The ability of Co_3O_4 to undergo thermal decomposition to CoO has been found to be mainly dependent on the oxidation character of cobaltic oxide solid. Dissolution of some foreign ions as Li^+, Na^+ and Al^{3+} in the Co_3O_4 lattice much increased the oxidation character of the doped solid and made the process of its thermal decomposition to CoO very difficult, especially in the case of lithium-doping. The oxidation character of Co_3O_4, which can be readily modified by doping, is a measure for the deviation of cobaltic oxide from stoichiometry. The greater the deviation from stoichiometry, the greater will be the oxidation character of the solid and the greater will be its thermal stability, and vice versa. In other words, the oxidation character of cobaltic oxide is directly proportional to the extent of deviation from stoichiometry and by turns proportional to the concentration of lattice defects or charge carriers (Co^{3+} ions). The fact that γ-irradiation much decreased the thermal stability of cobaltic oxide might indicate that the irradiation process of the solid was accompanied by a decrease in its oxidation character. In fact, the oxidation character of Co_3O_4, determined iodometrically, was found to decrease monotonically by increasing the dose employed (Fig. 2).

The effects of γ-radiation on surface, catalytic and electrical properties of different solids have been studied by several investigators [1–7,11–13]. Spalaris et al. [11] have reported extensive changes in the surface properties

of irradiated synthetic graphite due to progressive blocking of its pores. The observed decrease in the specific surface area of Co_3O_4 due to γ-irradiation could not be attributed to blocking of pores simply because the nitrogen adsorption capacity of Co_3O_4 has been found to be increased by γ-irradiation [7]. The observed decrease in the S_{BET} of cobaltic oxide due to irradiation could result from widening of its pores. It has been reported by some workers [11–13] that γ-irradiation might produce some kind of lattice damage and modifications in the concentration of charge carriers of semiconductors. The lattice damage induced by γ-irradiation was generally not accompanied by changes in lattice parameters but involved creation of vacancies and interstitial atoms [13]. An important increase in the electrical conductivity of In_2O_3 (*n*-type semiconductor) has been reported [6]. The Co_3O_4 employed in this investigation is a *p*-type semiconductor [14,15] containing an excess of oxygen. The γ-radiation might thus decrease the extent of deviation from stoichiometry of Co_3O_4 by causing the oxygen to escape into the gaseous phase. γ-Irradiation of NiO (*p*-type semiconductor) has been found to decrease its excess O_2, i.e., decreased its oxidation character [7]. The effects of γ-irradiation of Co_3O_4 on its thermal stability could thus be understood.

It has been reported in our previous investigations [8–10] that doping of Co_3O_4 with some ions as Li^+, Na^+, Al^{3+}, V^{5+} and Mo^{6+} increased, differently, its thermal stability, while γ-irradiation exerted an opposite effect. It seems of interest to study the effects of γ-irradiation on the thermal stability of doped Co_3O_4 solids. This study will be the object of a forthcoming investigation.

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