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THERMAL EVOLUTION OF A SAMPLE OF La_2O_3 EXPOSED TO THE ATMOSPHERE

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ABSTRACT

Because the basic character of La_2O_3 carbonation and hydration of this oxide may strongly modify its catalytic behaviour, a study of the regeneration conditions of a sample of La_2O_3 exposed to atmospheric H_2O and CO_2 for a long period of time have been carried out.

TG–DTA data have shown that the thermal decomposition of La_2O_3 in a flow of helium takes place in three well-defined steps: evolution of water in the first two steps, and CO_2 in the third could be observed by TPD.

Stoichiometric calculations as well as IR spectroscopy and X-ray diffraction data corresponding to the initial sample and each of the phases formed after the three steps reported previously, suggest that exposure of lanthanum oxide to the air results in the formation of the hydroxide and an amorphous hydroxycarbonate phase. The regeneration of the hexagonal phase of La_2O_3 occurs above 1020 K, after the third step, which seems to correspond to the decomposition of a dioxomonocarbonate phase.

INTRODUCTION

Although the catalytic properties of 4*f* oxides have been increasingly studied over the past 10 years [1–3], the general properties of these oxides are not well known. In this sense, it is worth mentioning that some previous results, like those reported by Touret and Queyroux [4], have suggested that the intensity of hydration and carbonation of these oxides under ordinary atmospheric conditions would decrease from La_2O_3 to Lu_2O_3, so that at the end of the series only surface processes would occur. On the contrary, recent results from our laboratory have shown that, after prolonged atmospheric exposure, even Yb_2O_3 undergoes bulk hydration and carbonation [5]. This contradiction shows that studies concerning the behaviour of the 4*f* oxides under atmospheric H_2O and CO_2 are rather scarce. Because the catalytic properties might well be modified by hydration and carbonation phenomena, a systematic study of these phenomena on 4*f* oxides under the usual manipulation and storage conditions appears to be of interest.

The present work reports the results corresponding to a lanthanum oxide

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sample prepared in our laboratory. The thermal evolution of the phases formed after its stabilization in air have been studied by TG–DTA and TPD techniques. Likewise, IR spectra and X-ray diffraction patterns corresponding to each of the observed decomposition steps have been drawn. From these data the nature of the phases initially formed and their thermal evolution to the oxide are discussed.

EXPERIMENTAL METHODS

The lanthanum oxide under study was prepared 5 years ago by calcinating in air a phase obtained by precipitation with ammonia from a nitrate solution. Details concerning the preparation conditions and characterization of the sample are reported and discussed in ref. 6. After its preparation, the oxide was stored in air, at room temperature, without special precautions.

TG–DTA studies were made with a Mettler instrument, model TA-HE 20. Alumina calcined at 1373 K was used as reference. The experiments were carried out in a flow of helium at 10 K min^{-1}.

In the TPD experiments a device analogous to that described in ref. 7 was used. This device operates in a flow of helium. Analysis of the evolved gases was made using gas chromatography. The rate of heating was always 6 K min^{-1}.

Infrared spectroscopic studies were carried out with a Pye-Unicam instrument, model SP-300. Because all the spectra were recorded in air, a KBr matrix was used in order to protect the samples as much as possible from atmospheric CO_2 and H_2O.

X-Ray diffraction pattern were obtained with CuK_α radiation and Ni filter in a Siemens instrument, model D-500. Capillary tubes (0.3 mm diameter), sealed immediately after the introduction of the sample, were used.

In order to prepare the intermediate phases studied by IR spectroscopy and X-ray diffraction, the initial sample was heated as in TG experiments up to either 650 K (first step) or 800 K (second step), maintained at the upper temperature for 30 min, and finally cooled to room temperature. The whole treatment was carried out in a flow of helium.

RESULTS AND DISCUSSION

The sample of La_2O_3 used in the present work, stabilized in air by prolonged exposure to the atmosphere (hereafter referred to as the initial sample), was studied by TG–DTA techniques. In the first of these experiments the sample was heated up to 1273 K. No weight loss or thermal effects could be detected above 1073 K. Accordingly, 1123 K was selected as the standard upper limit for the remaining thermal treatments.

Figure 1 shows the TG–DTA diagrams corresponding to the initial sample. The nature of the evolved gases during the decomposition process was studied by TPD (Fig. 2).

No agreement was found for the temperature of the maxima in TG–DTA and TPD experiments. Differences in heating rates and the experimental devices may account for this effect.

According to thermogravimetric data, the total weight loss represents 15% of the initial weight, so it can be said that, after prolonged exposure of La_2O_3 to the atmosphere, bulk hydration and carbonation take place. Likewise, Fig. 1 shows that thermal decomposition of the initial sample occurs through three well-defined steps, associated with which thermal effects at 650, 800 and 1020 K can be reported. The average percentage weight loss for each of these three stages was 62% (first step), 22% (second step) and 16% (third step). On the other hand, it can be deduced from Fig. 2 that the first two steps correspond to the evolution of H_2O, whereas only CO_2 is formed in the third step.

In order to gain some additional information concerning the nature of the phases involved in the hydration and carbonation of the La_2O_3 sample and its thermal decomposition, X-ray diffraction and IR spectroscopic studies were also carried out. Data corresponding to the initial sample as well as the phases formed after each of the three steps of its thermal evolution have

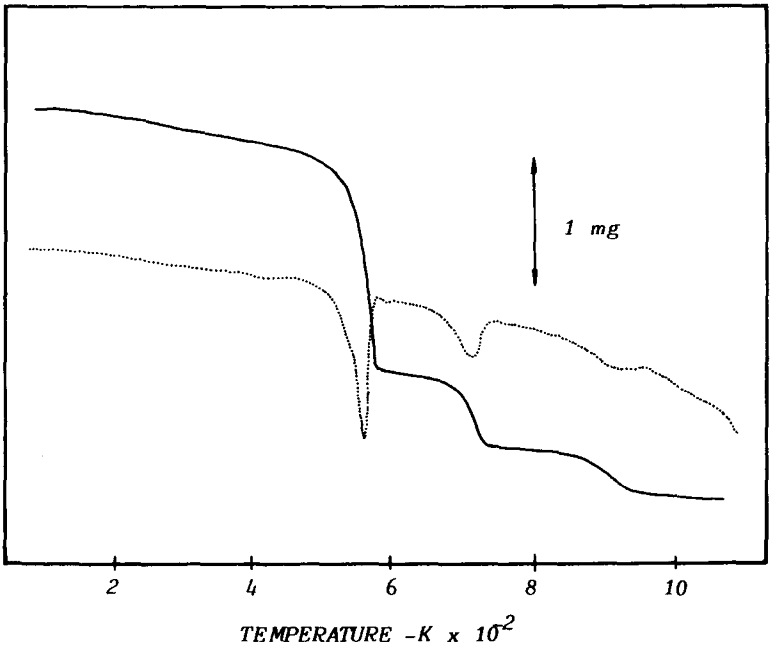

Fig. 1. TG–DTA diagram corresponding to 20 mg of the initial sample.

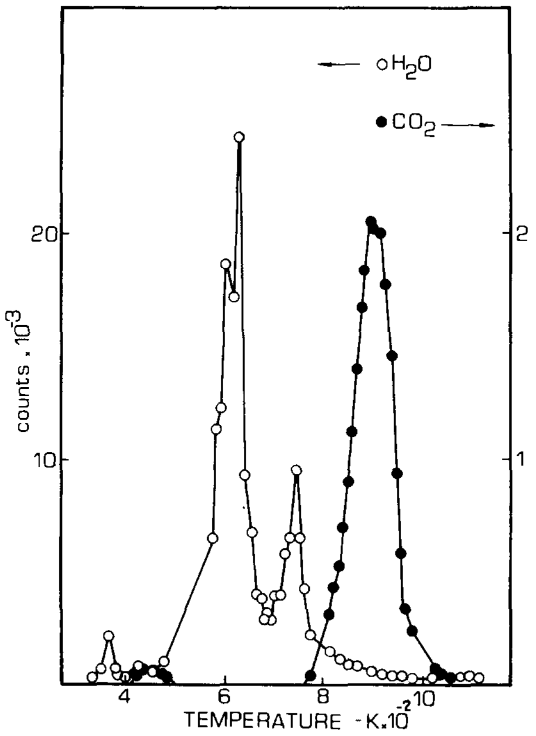

Fig. 2. TPD diagram of the initial sample.

been drawn. The samples to be studied were prepared as described in the previous section. In the IR study the spectra were recorded in air. Under these conditions some of the phases studied undergo chemical reactions. However, it was checked that the protective effect of the KBr matrix was efficient enough to prevent substantial modifications of the spectra during the recording time (20 min).

The IR spectrum of the initial sample (Fig. 3A) distinctly shows a narrow band at 3605 cm^{-1}, which may be ascribed to the stretching mode of hydroxide ions, and a second broader feature at 3430 cm^{-1}, corresponding to molecular water. Likewise, the band at 1620 cm^{-1}, due to the deformation mode of molecular water, and the strong one at 630 cm^{-1}, assigned by Chebotarev and co-workers [8] to the deformation mode of LaOH, suggest the existence of both hydroxide ions and molecular water in the initial sample. On the other hand, the strong bands centred around 1490 cm^{-1} and 1385 cm^{-1}, as well as those at 1060 cm^{-1} and 860 cm^{-1}, confirm the already reported carbonation of the sample.

As can be deduced from Fig. 3B, heating of the sample up to 650 K (first stage) causes the bands at 3605 cm^{-1} and 630 cm^{-1} to disappear, as well as a notable change in the carbonate region of the spectrum. At the same time,

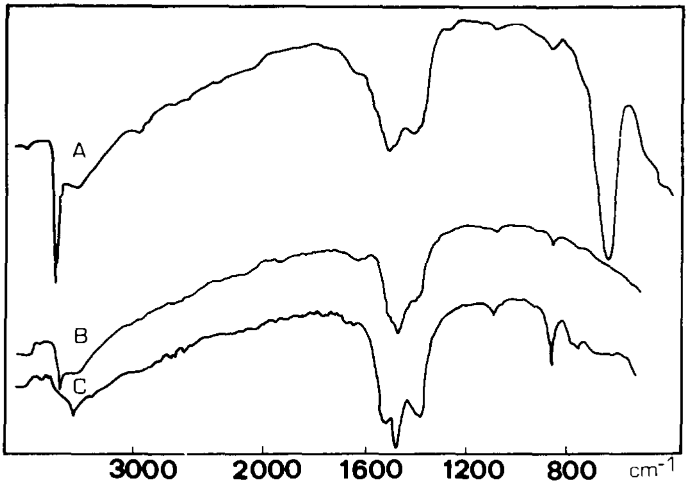

Fig. 3. IR Spectra corresponding to: the initial sample (A); and the sample after the first and second steps of the decomposition process (B and C).

the band at 3585 cm^{-1}, which may correspond in the initial sample to a masked shoulder observed at the low frequency side of the strong feature at 3605 cm^{-1}, now becomes apparent.

Rosynek and Magnuson [9] report that the IR spectrum of $La(OH)_3$ shows two characteristic features at 3610 cm^{-1} and 3590 cm^{-1} which they ascribe to the two different kinds of OH groups existing in the lattice of this hydroxide. These authors have also found that the thermal decomposition of $La(OH)_3$ to the oxyhydroxide implies removal of OH groups responsible for the highest frequency band. So, in our case, during the decomposition of $La(OH)_3$ to LaO(OH) (the first step) two well-known phases of the La_2O_3–H_2O system [10,11] may occur. Furthermore, associated with this first stage of the TG diagram a notable change of the carbonate spectrum can be observed. This spectrum, although poorly resolved, is similar to that observed after the second stage in the initial sample decomposition (Fig. 3C). This suggests that the carbonated phase distinctly observed after the second stage is already formed after the first one.

As is well known, the thermal decomposition of several lanthanide salts like formates [12], acetates [13], oxalates [14] and carbonates [15], takes place through the dioxomonocarbonate, $La_2O_2CO_3$, a well characterized species for which three different structural modifications have been established: tetragonal (I), hexagonal (II) and monoclinic (IA) [16]. In ref. 16 the IR spectra corresponding to these three phases are shown and discussed. According to Eyring and co-workers [16], phase IA shows the most complicated spectrum, the three observed bands around 850, 860, and 880 cm^{-1} being related to the three different kinds of carbonate ions existing in this structure. Because no such splitting of the corresponding carbonate vibration mode can de deduced from Fig. 3C, the existence of this phase in our case seems to be unlikely. Nevertheless, in the 1500–1300 cm^{-1} range bands at 1500, 1460 and 1370 cm^{-1} are found, whereas for phases I and II only two bands are reported. Taking into account that the stabilities of these two phases are rather similar [16], observation of the bands reported above might well be related to the coexistence of both phases I and II in our sample. After the third step the IR spectrum clearly shows the decomposition of the carbonated phase mentioned above.

The phases involved in the thermal decomposition process have also been studied by X-ray diffraction. Figure 4 accounts for the results obtained. As can be seen, notable structural changes take place during the thermal decomposition. For the initial sample (Fig. 4A) and the final product (Fig. 4D) a comparison with the ASTM index suggests the existence of hydroxide and hexagonal oxide phases, respectively. On the other hand, the diffraction patterns shown in Fig. 4B and C, although corresponding to more poorly crystallized phases, suggest the existence of the oxyhydroxide after the first step (Fig. 4B) and a phase II dioxomonocarbonate after the second one (Fig. 4C).

From TG experiments a weight loss ratio for the first two steps of 2.8 can be calculated which is larger than the theoretical value (2.0) corresponding to the case of a simple process of dehydration of $La(OH)_3$ to La_2O_3 throughout an intermediate phase LaO(OH). On the other hand, as TPD experiments show, CO_2 evolution can only be observed in the final step of the decomposition reaction. If the third step of the thermal process corresponds to the decomposition of a dioxomonocarbonate, $La_2O_2CO_3$, the above mentioned

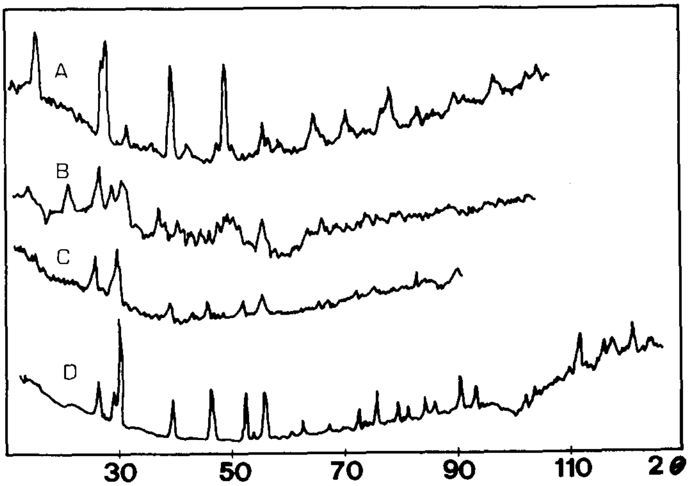

Fig. 4. X-Ray diffraction patterns of the initial sample (A); the sample after the first and second steps of the decomposition process (B and C); and the final state of the sample (D).

TPD result suggests that the stoichiometric CO_2–La_2O_3 ratio in $La_2O_2CO_3$ ought to be the same as that in the initial sample. Accordingly, some hydroxycarbonate phases like those reported by Caro and Lamaitre-Blaise [17] could be formed after the prolonged exposure of our La_2O_3 sample to the atmosphere. Contrary to the work reported in ref. 17, however, the phase found here seems to be amorphous.

In summary, the sample of La_2O_3 studied here, stabilized in the atmosphere for a number of years, underwent bulk hydration and carbonation, the hexagonal $La(OH)_3$ and amorphous hydroxycarbonate $La_2(OH)_4CO_3 \cdot n\,H_2O$ phases being formed. When heated in a flow of helium, the thermal decomposition of the sample takes place in three well-defined stages. A tentative reaction scheme for whose process is

$$\boxed{\begin{array}{c} La(OH)_3 \\ La_2(OH)_4CO_3 \cdot nH_2O \end{array}} \rightarrow \boxed{\begin{array}{c} LaO(OH) \\ La_2O_2CO_3 \end{array}} \rightarrow \boxed{\begin{array}{c} La_2O_3 \\ La_2O_2CO_3 \end{array}} \rightarrow La_2O_3$$

The temperature range at which the third decomposition step is observed suggests that thermal treatment at about 1100 K is necessary in order to regenerate the oxide phase.

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