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Study of some aspects of the reactivity of La_2O_3 with CO_2 and H_2O

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The behaviour of three different samples of La_2O_3 on exposure to atmoshperic CO_2 and H_2O and the influence of the origin is discussed. The thermal evolution of the samples, stabilized in air for months or even years, has been studied by TG, TPD, IR spectroscopy and X-ray diffraction. BET surface areas of the samples were determined from the corresponding nitrogen adsorption isotherms at 77 K. In all three samples, hydration and carbonation occur in bulk. In accordance with our results, lanthana samples stabilized in air would consist of lanthanum hydroxide, $La(OH)_3$, partially carbonated, $La_2(OH)_{6-3x}(CO_3)_x, (x \lesssim 1)$. When hexagonal phases of La_2O_3, obtained by calcining, at 1130 K, the samples stabilized in air were re-exposed, hydration and carbonation levels similar to those observed in the stabilized samples were reached after less than 24 h. Some lanthana samples were soaked in water, at 298 K, and then dried at 380 K. In this way, the evolution of the oxide when treated under similar conditions to those used in both impregnation and ion exchange techniques for preparation of supported metal phases, could be investigated.

1. Introduction

The ternary systems Ln_2O_3–H_2O–CO_2 have been studied by several authors, particularly under high temperature and pressure conditions [1–4]. Nevertheless, when the behaviour of 4*f* oxides as catalyst or transition metal supports is studied, the knowledge of hydration and carbonation phenomena undergone by these oxides at ambient pressure and temperature is very important. Information concerning the properties of the ternary system mentioned above under the latter conditions is, however, relatively scarce and much less systematic. In some cases, even contradictory results have been reported. Thus, Fullam and Roberts consider the influence of the simple exposure to the atmosphere on Nd_2O_3 and Sm_2O_3. According to these authors, no carbonation effects are observed on these oxides. Nevertheless the TG traces for the exposed oxides are quite similar to that previously determined [6] for a sample of La_2O_3, where carbonation effects were uniquivocally demonstrated by TPD, IR spectroscopy and X-ray diffraction measurements.

Other experiments carried out in our laboratory demonstrate that the preparation method of 4*f* oxides plays an important role in determining both their catalytic properties [7] and their reactivity towards atmospheric H_2O and CO_2 [8, 9].

For these reasons, in the present paper La_2O_3 samples from three different origins are studied: two of them are commercial samples and the third was prepared in our laboratory by calcining $La(OH)_3$. Some results for the latter sample have been reported in a previous paper [6].

Since some of the most usual methods of preparation of transition metal supported phases, impregnation [10] and ion exchange [11], imply a specific treatment of supports consisting of soaking them in an aqueous solution and drying them in air at about 380 K, the behaviour of some lanthana samples under these conditions has also been investigated.

2. Experimental details

Three different samples of La_2O_3, previously referred to as F, M and S, have been studied.

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Samples F and M were commercial oxides supplied, respectively by Fluka (99.98%) and Merck (99.9%). Lanthana S was prepared in our laboratory by calcining in air, at 873 K, a phase obtained by precipitation with ammonia from a nitrate solution. Additional details concerning the preparation of sample S are reported elsewhere [12].

2.2. Methods

The thermal evolution of the samples was studied by thermogravimetric analysis (TG) and temperature programmed decomposition (TPD). In both cases the experiments were carried out in flow of helium of 1 m sec^{-1}, at a heating rate of 0.1 K sec^{-1}, the initial weight of the samples being always 50 mg.

The thermobalance here used was Mettler, model BE-ME-21. The TPD experimental device was similar to that described by Cvetanovic and Amenomiya [13], the gas chromatography (GC) being used as analytical technique.

Infrared spectroscopy and X-ray diffraction techniques were applied to study the initial samples as well as those obtained after each of the steps of their thermal evolution. The intermediate phases were prepared by heating the original samples for 30 min at the selected temperature. The whole treatment was carried out in a flow of helium.

The IR spectra were recorded in a SP-300, Pye Unicam spectrometer. In order to protect the samples from the atmospheric CO_2 and H_2O they were prepared in KBr matrixes (90% KBr and 10% sample). In this way no alterations of the original spectrum could be observed after several runs. X-ray diffraction patterns were obtained with CuKα radiation and a nickel filter in a Siemens instrument, model D-500. Capillary tubes (0.3 mm diameter), sealed immediately after the introduction of the sample, were used.

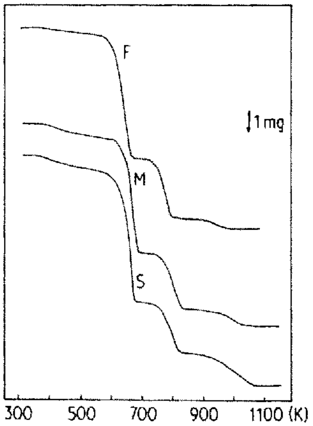

Figure 1 TG diagrams of samples F, M and S stabilized by exposure to the atmosphere.

Brunauer–Emmett–Teller surface areas were determined from the corresponding nitrogen adsorption isotherms at 77 K, obtained in a conventional vacuum system.

The exposures of the samples to the atmosphere were carried out under the following conditions: temperature 290 to 298 K, total pressure 100 to 102 KPa (750 to 770 torr) and relative humidity higher than 60%.

3. Results and discussion

3.1. Study of the samples F, M and S stabilized in air

Representative TG diagrams of samples F, M and S stabilized in the atmosphere are depicted in Fig. 1. The minimum exposure time was 6 months. For the three samples the thermal decomposition process occurs through three well-defined steps, the limit temperatures for them being 580 to 680, 740 to 820 and 900 to 1050 K, respectively. Below 500 K, an additional weight loss which is not well defined can also be observed.

Fig. 2 shows a typical TPD trace corresponding to a stabilized sample. As can be deduced from this figure, water is the only product emitted in the first two steps, CO_2 being generated, exclusively, in the third. At the lowest range of temperatures, small amounts of both CO_2 and H_2O are also emitted. Table I includes average results corresponding to the amounts of H_2O and CO_2 evolved during the three well defined steps of the thermal decomposition process. For the three samples the amounts of H_2O are similar to those

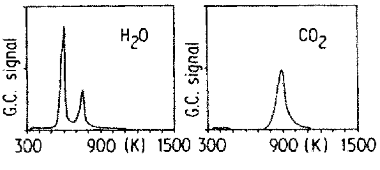

Figure 2 TPD traces for H_2O and CO_2 corresponding to the thermal decomposition of sample F stabilized in air.

TABLE I Average amounts of CO_2 and H_2O evolved from the samples F, M and S stabilized in air (data in mg/sample)

	F	M	S
H_2O	140	134	122
CO_2	9.5	13	24

associated to the decomposition of $La(OH)_3$ to La_2O_3 (142 mg/g $La(OH)_3$). On the other hand, according to Rosynek and Magnuson [14], this process, as in our case, takes place in two steps: $La(OH)_3 \rightarrow LaOOH \rightarrow La_2O_3$.

The X-ray diffraction patterns corresponding to the stabilized samples are also in good agreement with the existence of the hexagonal phase of $La(OH)_3$. No evidence for the existence of crystalline carbonated phases could be obtained from the X-ray diffraction data. After the first decomposition step, the X-ray diffraction diagrams obtained by us can be ascribed to the monoclinic phase of LaOOH.

The IR spectra of samples F, M and S, shown in Fig. 3. show adsorption bands at 3600 and 640 cm^{-1}. In accordance with the literature these two bands can, respectively, be interpreted as associated with OH stretching [14] and with La–OH bending [15] modes in the hydroxide.

In summary, as far as the hydration process is concerned, no significant structural differences are observed among the three lanthana samples here investigated, the results for samples M and F being in fairly good agreement with those previously found by us for La_2O_3–S [6].

In relation to the carbonation reaction, the data given in Table I demonstrates that the intensity of the process increases from sample F to M and to S. A parallel decrease of the hydration level is also observed. The values of the Brunauer–Emmett–Teller surface area are 3.4, 5.2, and 16.2 $m^2 g^{-1}$ for samples F, M and S, respectively. According to the surface model for the lanthanide oxides proposed by Bernal *et al.* [16] CO_2 amounts higher than 7 molecules per nm^2 allow one to exclude a simple surface process. In our case, values higher than 20 molecules per nm^2 were always found and, therefore bulk carbonation does occur.

The IR bands at 3440 cm^{-1}, as well as those appearing between 1600 and 1200 cm^{-1} for the stabilized samples, (Fig. 3) suggest the existence of an hydroxicarbonate phase, analogous to that reported by Caro *et al.* [17–19]. In effect, for the $Ln(OH)_3$ dispersed in water and exposed to a CO_2 pressure similar to atmospheric, Caro *et al.* have suggested the formation of phases $Ln_2(OH)_{6-2x}(CO_3)_x$, with x ranging from 1 for the last elements of the lanthanide series, to 2 in the case of $La(OH)_3$.

The thermal decomposition of the carbonated phase mentioned above might well take place through a dioxomonocarbonate-like intermediate species, as has been suggested for a number of lanthanide salts [20–22] including $Pr_2(OH)_{6-2x}(CO_3)_x$ (with $x = 2$) [2]. In fact, for sample S, the X-ray diffraction pattern obtained after the second step of its thermal decomposition can be adscribed to the hexagonal phase of $La_2O_2CO_3$ [6]. The IR spectra obtained after the second step of the thermal decomposition of samples F, M and S, (Fig. 5) are also consistent with those reported

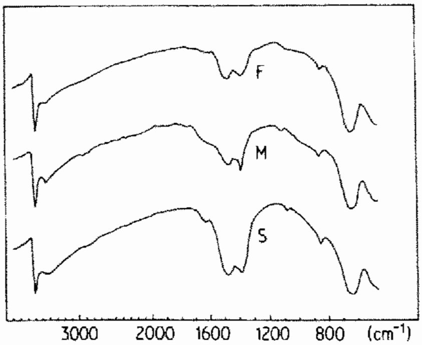

Figure 3 IR spectra of samples F, M and S stabilized in air.

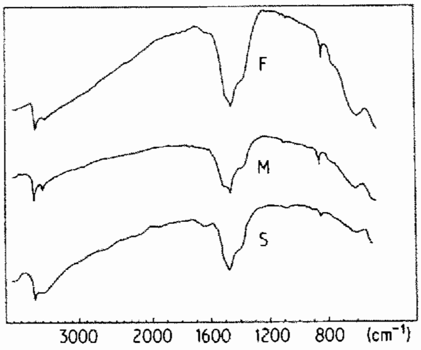

Figure 4 IR spectra of samples F, M and S after the first well-defined step of their thermal decomposition.

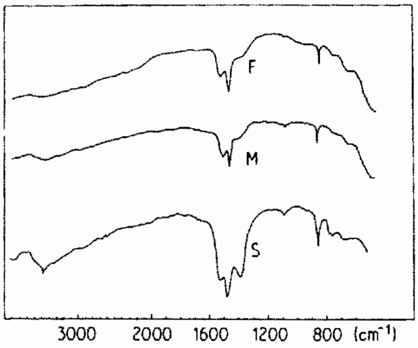

Figure 5 IR spectra of samples F, M and S after the second well-defined step of their thermal decomposition.

by Turcotte *et al.* [23] for the three known phases of the lanthanum dioxomonocarbonate.

Since CO_2 evolution occurs in a single step (3rd step) and the ratio of the amounts of water emitted in the first two steps was always slightly higher than 2, the theoretical value for the process:

$$2\,La(OH)_3 \xrightarrow[2\,H_2O]{\text{1st step}} 2\,LaOOH \xrightarrow[H_2O]{\text{2nd step}} La_2O_3$$

a tentative scheme for the decomposition of the carbonated phase could be:

$$La_2(OH)_{6-2x}(CO_3)_x \xrightarrow[2\,H_2O]{\text{1st step}} La_2O_2CO_3$$

$$\xrightarrow[CO_2]{\text{3rd step}} La_2O_3$$

where $x \simeq 1$.

If small deviations of x from the unit ($x < 1$) occur, residual amounts of hydroxide ions could be retained by the carbonated phase, which according to Caro *et al.* would account for the IR band at 3440 cm^{-1} observed after the first step of the decomposition process. Fig. 4.

In summary, the results discussed above suggest that, when stabilized in air, the three lanthana samples studied here consist of lanthanum hydroxide partially transformed into an hydroxicarbonate phase, $La_2(OH)_{6-2x}(CO_3)_x$ with $x \lesssim 1$. The intensity of the carbonation process seems to be related to the surface area of the samples. Although some of the samples were exposed to the atmospheric CO_2 for more than 3 years, no progress of the carbonation reaction was observed. In other words, contrary suggestions in the literature for the carbonation of $La(OH)_3$ under only slightly different conditions to ours [17], no complete transformation in hydroxycarbonate was observed. If it is taken into account that, under the reported above conditions [17], hydroxycarbonate phases are stable against the hydroxide, kinetic factors ought to be responsible for the results observed here. A particle model consisting of a nucleus of $La(OH)_3$ overcoated by the carbonated phase could reasonably account for the reported results.

3.2. Additional essays

In accordance with the data included in Fig. 1 in addition to those deduced from the study by TPD, X-ray diffraction and IR spectroscopy of the thermal evolution of samples, F, M and S, the regeneration of the oxide phase can be achieved by calcining the samples, stabilized in air, in a flow of helium, at 1130 K, and then cooling them down, also in a flow of inert gas.

When samples, regenerated as above, are re-exposed to the atmosphere, at room temperature hydration can be detected after 3 h.

As Fig. 6 shows, in effect, bands at 3600 and 640 cm^{-1}, characteristic features of lanthanum hydroxide phase, are clearly distinguishable. On the contrary, no carbonation effects could be observed after that period of time. In the case of lanthana proceeding from the regeneration of sample F, (depicted in Fig. 6) a period of 13 h was long enough to reproduce the original hydration and carbonation levels. After this period of time, X-ray diffraction lines corresponding to the oxide

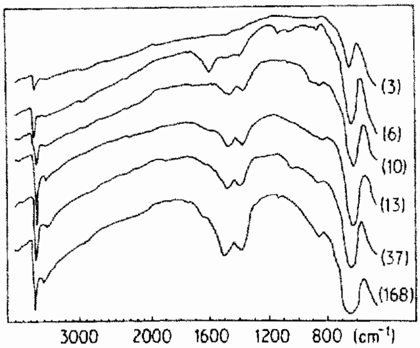

Figure 6 IR spectra corresponding to the evolution in air of an oxide phase obtained by calcination, at 1130 K, of sample F. (Exposure time, (h) is given on the right-hand side.)

phase completely disappeared, the $La(OH)_3$ pattern being the only one observable. Likewise, TG and TPD diagrams, as well as IR spectra, were similar to those previously obtained for sample F stabilized in air. The only notable difference was the amount of CO_2 picked up by the regenerated sample (16 mg/g sample), somewhat higher than that found for the original F sample (9.5 mg/g sample). This difference can be interpreted as being due to the Brunauer–Emmett–Teller surface area of the regenerated sample ($5.4\,m^2\,g^{-1}$), slightly higher than that corresponding to the original sample F ($3.4\,m_2\,g^{-1}$).

When the regenerated oxides produced from samples M and S, were exposed to atmospheric CO_2 and H_2O, hydration and carbonation processes, analogous to those previously described, occurred, the stabilization always being reached in less than 24 h.

Because of the increasing interest in lighter lanthanide oxides as transition metal supports [24–26], it seemed to us necessary to investigate the transformations undergone by these oxides when treated by the usual techniques for the preparation of supported metals: impregnation [10] and ionic exchange [11]. With this purpose, a sample of La_2O_3–F stabilized in air and a second sample consisting of the oxide phase produced from the regeneration of La_2O_3–F stabilized in air, were soaked in water at room temperature, for 2 h, and then dried in air, at 380 K, for 18 h. The phases obtained after this treatment were studied by means of the techniques mentioned above. The results were essentially the same for both samples, and no significant differences were found between the samples treated in this way and those stabilized by simple exposure to the air at room temperature.

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