TPD-MS STUDY OF CARBONATION AND HYDRATION OF Yb_2O_3(C)

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A TPD-MS study of the behaviour of Yb_2O_3(C) against atmospheric environment has been carried out. Contrary to suggestions in the literature, the results show that that after prolonged atmospheric exposure (3 years) bulk hydration and carbonation of ytterbia take place. If this sample, previously regenerated by calcination in helium flow at 870 K, is exposed to the atmosphere up to 80 hours, only surface reactions seem to occur. The present study, in which several CO_2 and H_2O treatments have been included, suggests that over Yb_2O_3, the hydration and carbonation reactions are related to each other, the amount and thermal stability of adsorbed CO_2 being determined by the surface water content. The discussion of the results is based on a surface model of Yb_2O_3.

The lanthanide sesquioxides are generally considered to be basic oxides[1]. Therefore, bulk hydration and carbonation of them might well occur by simple atmospheric exposure. These reactions may strongly modify the general and surface properties of 4f oxides, particularly their catalytic behaviour, increasingly studied in recent years[1-4]. A few studies have dealt with these processes at similar conditions to those existing at atmospheric ambient[5-7].

In order to initiate a systematic study of the behaviour of 4f oxides against atmosphere, the ytterbium oxide has been selected, the cubic structure of which is stable [8] up to 2 300 K. Thermal programmed desorption (TPD) has been used as the experimental technique. The quantitative analysis of evolved gases was carried out by mass spectrometry (MS).

According to the current literature[7,6], minor effects ought to be expected from atmospheric exposure of Yb_2O_3. Thus, Queyroux and coworkers[7] who have studied the reactivity towards water of several lanthanide sesquioxides, have reported that the greater the atomic weight of the element the smaller the hydration effect on the corresponding oxide. Particularly, for Yb_2O_3 they have found that hydration is not possible even by soaking the oxide in boiling water. Likewise, Fullam and coworkers[6] have not observed significant carbonation of Nd_2O_3, Pm_2O_3 and Sm_2O_3 when exposed to atmosphere.

Nevertheless, preliminary studies carried out by us suggested that, after prolonged exposure, both bulk hydration and carbonation of Yb_2O_3 (one of the less basic oxides within the lanthanide series) take place. Accordingly, several experiments, including different CO_2 and H_2O treatments of ytterbia, have been performed in order to analyse the behaviour of this oxide at the above mentioned conditions. The results will be discussed on the basis of a surface model of Yb_2O_3.

EXPERIMENTAL

The ytterbium sesquioxide here used was prepared in our laboratory by calcination in air, at 873 K, from the corresponding hydrated phase. The oxide was characterized by X-ray diffraction, and surface and pore size distribution were measured[9]. For this sample a cubic or C type structure has been found. The surface areas was 40 $m^2 g^{-1}$ and pore radius ranging 1·6 nm to 4 nm have been observed.

The experimental device for TPD studies has been described in a previous paper[10]. This system, which operates at normal pressure, allows quantitative analysis of evolved gases by mass spectrometry (MS). The experiments have been carried out under the following conditions: helium flow throughout the reactor $5{\cdot}5 \,.\, 10^{-1}$ $cm^3 s^{-1}$ (33 $cm^3 min^{-1}$); flow throughout the analytical device: $5{\cdot}5 \,.\, 10^{-2}$ $cm^3 s^{-1}$ (3·3 $cm^3 min^{-1}$); total pressure at the ionization chamber of MS: $1{\cdot}01 \,.\, 10^{-3}$ Pa ($7{\cdot}6 \,.\, 10^{-6}$ Torr), and heating rate: 0·16 K s^{-1} (10 K min^{-1}).

RESULTS

The present study of hydration and carbonation phenomena over Yb_2O_3 includes four series of TPD experiments which we describe as: *A*) hydration, *B*) carbonation, *C*) atmospheric exposures and *D*) carbonation after hydration of the sample.

When the oxide used, prepared three years earlier, was studied by TPD (Fig. 1), the desorbed amounts of CO_2 and H_2O were 14 and 48 molecules.nm^{-2}, respectively. As we shall discuss later, these results are singular in relation to both those obtained here and those reported in the literature[6,8].

After several heating cycles up to 870 K, the sample showed a repetitive behaviour. Then, the four mentioned series of experiments were carried out, being alternatively performed in order to test the reproducibility of the results.

Fig. 2*a*, shows a TPD diagram corresponding to series *A*. The sample was treated at 400 K in a nitrogen stream which was previously bubbled through boiling water. Before starting the TPD experiment, dry helium flowed for some time through the reactor at 330 K. Besides small amounts of CO_2 desorbed at temperatures higher than 600 K, a broad single peak corresponding to water evolution has been found. The amount of desorbed water was 6·7 molecules . nm^{-2}. Between 2·5 and 72 hours no influence of the treatment time on water spectrum has been observed.

For series *B*, a stream of CO_2 containing less than 0·5% of water was passed over the sample at 298 K. Table I reports the quantitative results and Fig. 2*b* shows a representative TPD spectrum. Several aspects ought to be pointed out concerning these experiments. Firstly, the lowest surface coverage has been found. On the other hand, in spite of the above finding, the desorption of both CO_2 and H_2O takes place at a rather low temperature. No significant influence of the treatment time on the results could be observed within a period of 12 hours.

According to the results reported in Table I,' in series *C* (at 297 K and a relative humidity of 70%) the amount of desorbed CO_2 is higher than that found in series *B*. Further, the data seem to indicate that the hydration and carbonation reactions, after an initial step in which they occur with measurable rates, must become very

TABLE I

Average results (molecules nm^{-2}) corresponding to different series of experiments

Series	H_2O	CO_2
A	6·7	—
B	2·9	1·9
C	7·0	2·4
D	8·5	3·5

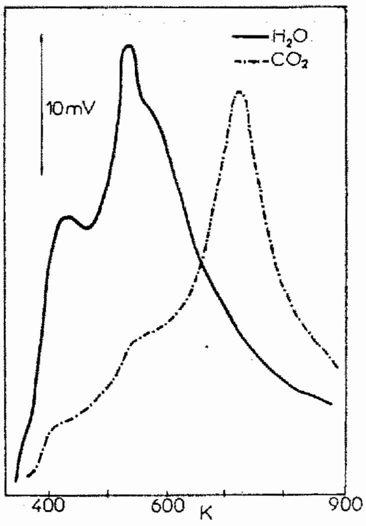


FIG. 1

TPD diagram of Yb_2O_3 three years after its preparation

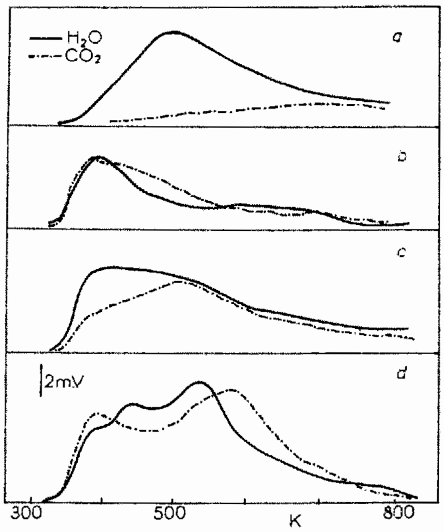


FIG. 2

TPD diagrams of representative experiments corresponding to series *a*, *b*, *c* and *d* slow, because no progress of these phenomena were observed from 19 to 55 hours of exposure. Concerning the shape of TPD spectra (Fig. 2*c*), two maxima could be reported for CO_2 desorption. The second one, a broad peak centered at 500 K, was not observed in previous experiments.

The highest amounts of desorbed CO_2 and H_2O have been found in experiments of series *D*. In this case, Yb_2O_3, hydrated like in series *A* experiments, was treated with flowing CO_2 at 298 K. As can be seen in Fig. 2*d*, CO_2 evolution shows two distinct peaks, the highest one appearing at 580 K. Water desorption seeems to occur at rather higher temperature than those previously found.

DISCUSSION

From crystallographic data reported in the literature[11–12] for cubic Yb_2O_3, a tridimensional model of its structure has been built. The analysis of this model has allowed us to establish that the surface unit cell, drawn in Fig. 3, represents the surface of maximum packing for the afore mentioned structure. This surface unit cell has 1·53 nm^2, being constituted by 8 cations (5·2 per nm^2) and 12 anions (7·8 per nm^2). Four Yb^{3+} ions have two vacancies in their first coordination sphere and the remaining four cations only one vacancy. Dotted circles indicate the position of these vacant sites. Concerning the anions, every surface O^{2-} would be coordinated by three Yb^{3+}, therefore having one vacancy in their coordination sphere.

In accordance with other authors[13,14] who have developed surface models for

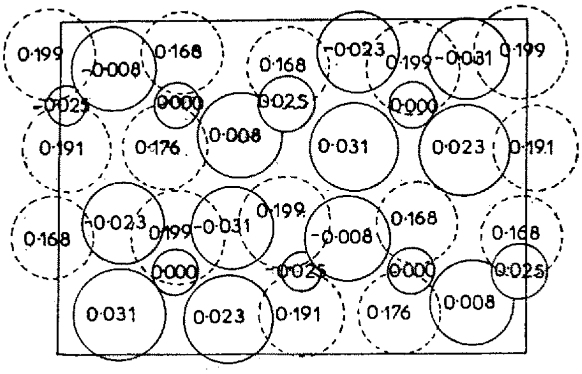


Fig. 3

Unit cell for the surface of Yb_2O_3(C). Full line circles represent the ions of the surface; of them the smaller are associated to Yb^{3+} and the greater ones to O^{2-}. Dotted circles are associated to vacants in the Yb^{3+} coordination spheres. Numerical data in the figure indicate heights (in nm) relative to the plane defined by the four Yb^{3+} at 0·000 positions different metal oxides, the maximum packing criterion is adequate for the determination of the surface preferentially exposed. In any case, it may constitute a good reference in ordeı to estimate the limits for surface adsorption of CO_2 and H_2O. Thus, our results corresponding to experiments carried out with the starting sample (Fig. 1), cannot be interpreted as surface processes, it being neccesary to assume that hydration and carbonation phenomena have occurred in bulk. Accordingly, the former results suggest that prolonged atmospheric exposures of the oxide here studied. Yb_2O_3(C), may introduce severe modifications of its structure and properties. In order to obtain new insight in these processes, X-ray difraction studies of the initial sample have been performed. No evidence of bulk hydration or carbonation could be drawn. However, it is worth mentioning that Caro and coworkers[5] have found that amorphous phases are obtained when carbonation of hydrated phases of some 4*f* oxides is carried out at low CO_2 pressure.

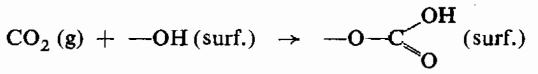
When the above results are compared with the following ones, they must be considered unique. The amounts of desorbed H_2O and CO_2 are far higher, and the structure of TPD spectra is different. Fig. 1 shows a maximum for CO_2 desorption at 725 K not observed in any other experiment, which ought to be ascribed to some bulk carbonate form.

The results of series *A*, *B*, *C* and *D*, contrary to the above discussed, may be satisfactorily interpreted in terms of surface reactions even in those cases in wich the sample has been treated at drastic conditions (series *A*). For series *A*, the amount of desorbed water, about 7 molecules . nm^{-2}, is a little lower than the maximum which, according to the surface model, could be directly coordinated to cations. The broadness of these spectra might well be related to the surface heterogeneity, also suggested by this model. On the other hand, the results of these experiments seem to indicate that at 400 K thermodynamic rather than kinetic factors control the progess of hydration into bulk. In spite of the treatment conditions, no evidence of bulk hydration can be reported. This contrasts with results found after prolonged atmospheric exposures (Fig. 1).

In remaining experiments, broad TPD spectra have been generally obtained, suggesting that desorption processes are by no means simple. Nevertheless, some striking aspects of these results ought to be pointed out. Firstly, according to Table I, the amount of CO_2 adsorbed in series *C* experiments is higher than that reported for series *B*, in spite of the different CO_2 pressure used in both experiments (higher in series *B*). Moreover, the analysis of Table I demonstrates that a correlation exists between surface contents of H_2O and CO_2, the amounts of them increasing parallely. On the other hand, from the comparison of figures 2*b*,2*c* and 2*d* it can be deduced that thermal stability of adsorbed CO_2 depends on the surface water content.

In summary, the obtained results suggest that the surface hydration and carbonation of Yb_2O_3 are closely related in such a way that water determined the amount and thermal stability of adsorbed CO_2.

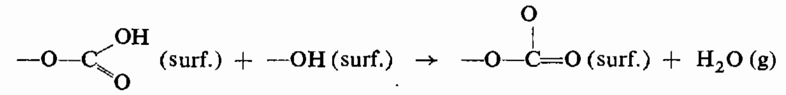
Concerning the likely existence of a relationship between both hydration and carbonation reactions over metal oxides, several authors[15,16] have found that hydration prevents or at least introduces severe restriction in CO_2 adsorption. However, Ramsay[17] studing these reactions over magnesia, has found that previous hydration may have opposite effects depending on the conditions in wich MgO was prepared. According to this author[17], the reported differences ought to be related to relaxation phenomena, which would determine the chemical activity of surface anions; it is suggested that the least relaxed surface would have Mg^{2+} strongly exposed, a previous process of surface hydration being necessary in order to generate the active center for CO_2 adsorption. In this case, hydration would allow carbonation, which would occur throughout an initial step, implying the formation of surface hydrogen carbonate species.



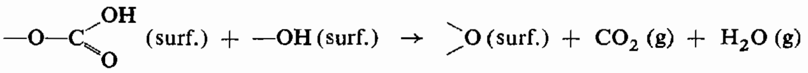
$$\mathrm{CO_2\,(g) + {-OH}\,(surf.) \rightarrow {-O-C}\Big\langle\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O}\end{smallmatrix}\,(surf.)} \qquad (1)$$

Over TiO_2, Boehm[18] has also suggested this type of carbonation. Several studies concerning adsorption over γ-Al_2O_3(ref.[19]), TiO_2 (ref.[20]) and MgO (ref.[21] have dealt with the existence of HCO_3^- species too.

In our case, the interdependence between both hydration and carbonation reactions might well be interpreted in terms of a mechanism rather similar to the one proposed in the literature[17,18]. According to the surface model formerly suggested, two distinct kinds of surface hydroxyls ought to be generated by the hydration process: on the one hand, vacancies on the coordination sphere of single ions Yb^{3+}, occupied by —OH; on the other hand, the hydration would give rise to —OH groups within the surface. This second kind, coordinated to three cations, ought to be the less accesible and more acidic of the two. Therefore, in the initial step of the carbonation of Yb_2O_3, the first kind of —OH groups, ought to be primarily involved. The hydrogen carbonate species so formed could then evolve in one of the following two ways:



$$\mathrm{{-O-C}\Big\langle\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O}\end{smallmatrix}\,(surf.) + {-OH}\,(surf.) \rightarrow {-O-}\overset{\mathrm{O}}{\overset{|}{\mathrm{C}}}{=O}\,(surf.) + H_2O\,(g)} \qquad (2)$$



$$\mathrm{{-O-C}\Big\langle\begin{smallmatrix}\mathrm{OH}\\ \mathrm{O}\end{smallmatrix}\,(surf.) + {-OH}\,(surf.) \rightarrow {>}O\,(surf.) + CO_2\,(g) + H_2O\,(g)} \qquad (3)$$

Reaction (2) which implies the existence of basic —OH groups besides bicarbonates —HCO_3, ought to be favoured for strongly hydrated surfaces. On the other hand, over surfaces with low water content, the second reaction seems to be more likely, because adsorption of water ought to generate pairs of isolated —OH groups with rather different acid-base character.

A scheme like the one formerly discussed might well account for TPD results corresponding to experiments of series *B*, *C* and *D*. Thus, the amounts and thermal stability of CO_2 adsorbed in experiments of series *B* may be asociated with the surface water content (the lowest found here) and the operation of reaction (*3*).

Likewise, the increasing amount of adsorbed water could favour reaction (*2*), allowing the formation of adsorbed carbonate species, the decomposition of which would take place at a higher temperature. This could account for the second maxima observed for CO_2 desorption in experiments corresponding to series *C* and *D*. Otherwise, the greater thermal stability of adsorbed CO_2 in series *D* could also be related to the surface water content, which might stabilized the surface carbonate by means of cooperative-like effect rather analogous to that proposed by Knözinger and coworkers[22].

According to our TPD-MS study of the hydration and carbonation of Yb_2O_3 exposed to the atmosphere, these reactions are complex processes. Nevertheless, some conclusions are possible. Following a step which might be well related to surface phenomena the progression into bulk of these reactions seems to be very slow. However, contrary to literature, after long air exposure bulk hydration and carbonation of ytterbia do occur. Concerning Yb_2O_3–H_2O–CO_2 surface interactions, our results show that the greater the amount of adsorbed H_2O the greater the thermal stability and amount of adsorbed CO_2. Accordingly, a mechanism for CO_2 adsorption which implies the previous Yb_2O_3–H_2O interaction is suggested. Lastly, a suitable interpretation of the catalytic behaviour of 4*f* oxides, even in the cases of the heaviest members of the lanthanide series, ought to take into account that bulk hydration and carbonation of these oxides may occur at the usual storage and manipulation conditions.

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