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Influence of the method of preparation on Yb_2O_3 hydration

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Preliminary studies have shown that in order to achieve the complete removal of the uptaken CO_2 and H_2O from a ytterbium oxide aged in air, thermal activation up to 1173 K is required. Parallel studies have shown that bulk hydration of Yb_2O_3 does occur, the CO_2 acting as a kinetic inhibitor. The above results refer to a Yb_2O_3 prepared in our laboratory from hydroxicarbonate-like phases. In the present work, the influence of the preparation method on the hydration process is examined, by extending the study to two additional samples, a standard commercial one and another obtained by calcining a ytterbium oxalate. It is shown that the intensity of the hydration reaction depends strongly on the method of preparation. Certain applications of 4f oxides, such as their use as transition metal supports, involve thermochemical processes which may alter drastically the initial texture of the ytterbia from the oxalate. It makes this sample less useful although its initial specific surface area is high.

1. Introduction

Several papers dealing with the catalytic properties of 4f oxides [1] and their behaviour as transition metal supports [2], recently reported, have suggested that some important aspects of the chemistry of lanthanide oxides have not been thoroughly studied. One of these aspects is the reactivity of 4f oxides towards atmospheric H_2O and CO_2. Preliminary studies in our laboratory have shown that in order to achieve the complete removal of the uptaken CO_2 and H_2O from a ytterbium oxide aged in air, thermal activation up to 1173 K is required [3]. Parallel studies performed on the same sample, under controlled pressures and temperatures, have shown, on the other hand, that bulk hydration of Yb_2O_3 does occur, the carbon dioxide acting as a kinetic inhibitor of the hydration process [4, 5].

The above results refer to a ytterbium sesquioxide prepared in our laboratory from hydroxicarbonate-like phases. In the present work the influence of the preparation method is examined, by extending the study to two additional samples, prepared in different ways. The results now obtained and those previously reported [4] are compared. A notable influence of the sample origin and pretreatments on the catalytic properties of ytterbia towards alcohol decomposition has been recently reported [6].

2. Experimental details

2.1. Materials

The ytterbia samples studied here will be labelled Yb_2O_3-I, Yb_2O_3-II and Yb_2O_3-III. The first corresponds to a standard commercial sample, Merck AR grade. The second, oxide II, was prepared by calcining in air, at 873 K, the phase precipitated with ammonia from a nitrate aqueous solution. The Yb_2O_3-III was obtained by thermal decomposition of the corresponding oxalate. Details concerning the preparation of samples II and III have been reported elsewhere [3].

BET (Brunauer, Emmett and Teller) surface area, S_{BET}, and some isolated characterization data corresponding to samples I and III are given by Alvero *et al.* [3]. Data concerning Yb_2O_3-II, on the other hand, are included in [4].

2.2. Apparatus

X-ray powder diffraction diagrams were obtained

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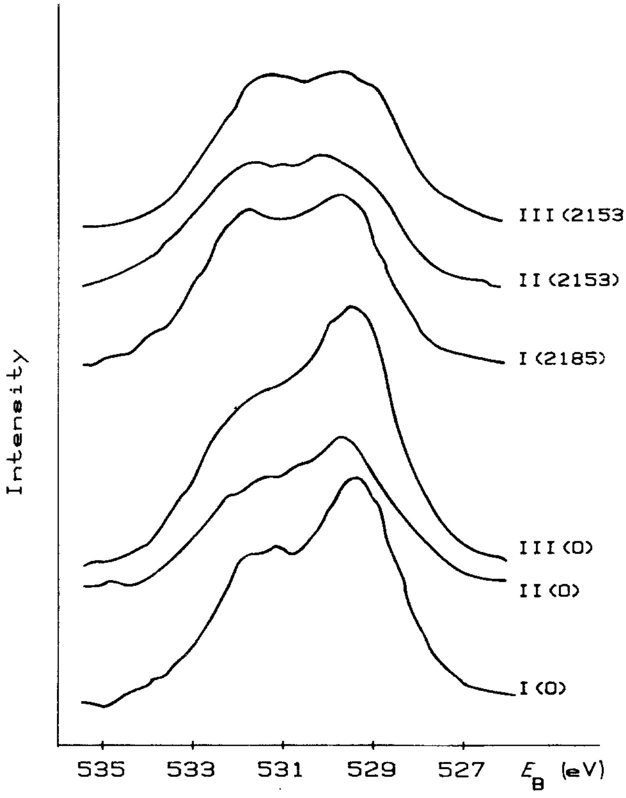

Figure 1 O(1 s) XP spectra of oxides I, II and III, aged in air during the hours shown in brackets.

with a Siemens Kristaloflex D-500 instrument, using Cu$K\alpha$ radiation and Ni filter. The X-ray photoelectron spectra were recorded on a Kratos XSAM 800 apparatus, with Mg$K\alpha$ radiation. The observed line positions were corrected by comparing the C(1s) signal of the sample to that of gold. According to a more precise correction, a certain shift of the peaks can be observed with reference to data in [3].

The description of systems and conditions for infrared spectra (ir) and temperature programmed decomposition or desorption (tpd) analyses are given elsewhere [7]. Quantitative tpd calibrations for H_2O and CO_2 were performed by decomposing variable amounts of $CuSO_4 \cdot 5H_2O$ and $MnCO_3$ as reported by Alvero *et al.* [8]. The amounts of evolved reaction products will be exposed as molecules per unity of surface area, although this process is not always restricted to the surface. As a consequence of the 4f oxides basicity, both H_2O adsorption and hydration in the bulk processes overlap. Amounts of evolved H_2O larger than that estimated in [9] for the surface monolayer will clearly show bulk hydration.

The S_{BET} measurements were made employing spectroscopically pure nitrogen at 77 K.

3. Results

The diffraction patterns for oxide I, and II-III recently prepared, show type C (cubic) structures. Exposure to water vapour or to air, for up to three years in the latter case, only causes the widening of the original peaks. From these results, it is noteworthy that several amorphous phases have been reported for binary and tertiary systems of composition Ln_2O_3–H_2O–CO_2 [10].

Thermograms in [3] for Yb_2O_3-I and Yb_2O_3-II exposed to air for two years show weight losses which must be interpreted as due to a bulk hydration and carbonation. In the case of oxide II, the XPS spectra for O(1 s) binding energy did lend support, indeed, to the occurrence of a bulk reaction with the components of the air, through the formation of a non-compacted layer. The ageing of oxides I and III show a similar evolution (Fig. 1). According to the literature and our previous results [3], the principal peaks at 8.48×10^{-17} J (530.4 eV) and 8.51×10^{-17} J (532.0 eV) correspond to oxide and hydroxide and/or carbonate species, respectively.

When used as catalysts, 4f oxides are often activated at temperatures up to ca. 800 K [11, 12], which is too low if one is trying to achieve the

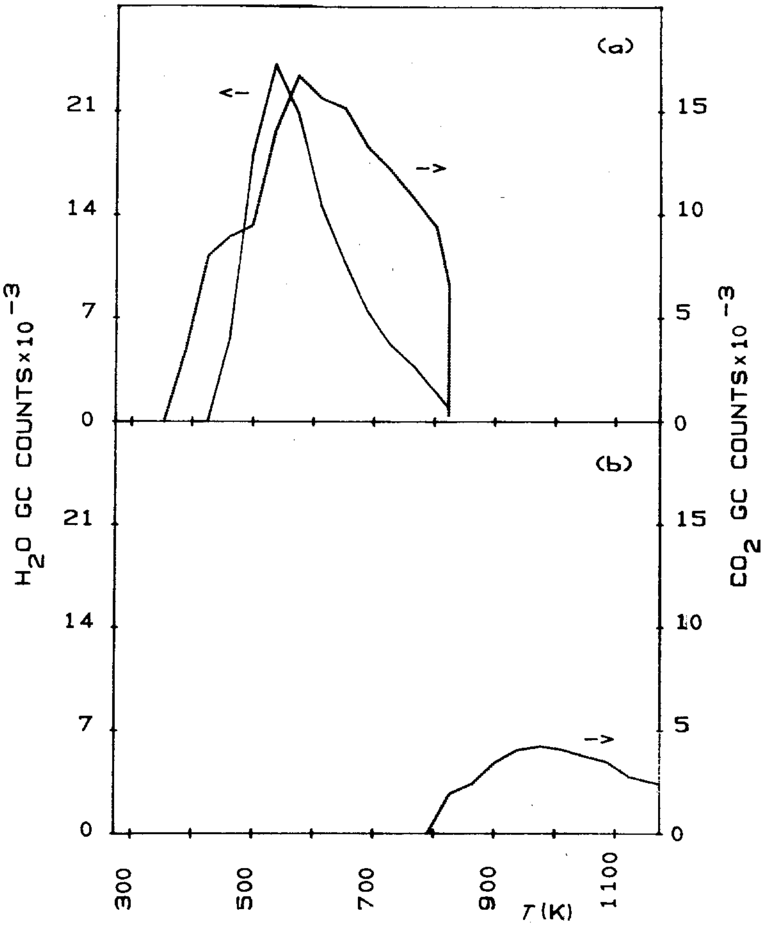

Figure 2 tpd diagrams of aged Yb_2O_3-I: (a) from RT to 823 K; (b) from RT to 1173 K after (a). The units on the ordinate are the gas-chromatograph, GC, counts.

complete elimination of H_2O and CO_2. Nevertheless, the results reported in [8] suggest a particle structure for the powdered oxide activated at 823 K, consisting of a carbonated nucleus surrounded by an outer oxide layer which operates as the actual active phase. In order to obtain some experimental evidence supporting the application of the model to Yb_2O_3-I and III, the thermograms plotted in Figs. 2 and 3 were obtained. Samples of both oxides aged in air for more than two years were heated up to 823 K, first tpd diagram, then isothermally decomposed until no evolution of H_2O–CO_2, cooled down to room temperature (RT) and, finally, heated up to 1173 K, second tpd diagram. The helium flow was maintained without interruption through the whole experiment. After activation at 823 K it is observed that the samples contain residual CO_2. However, its partial elimination at temperatures above 823 K appears to indicate a surface layer exhausted of carbonate, as was suggested for Yb_2O_3-II by Alvero *et al.* [8].

According to the above results and the observation that the S_{BET} of all the oxides decreases drastically with heating at temperatures higher than about 800 K, the activation temperatures of 823 and 1173 K have been selected. The profiles of the thermal diagrams for samples activated and then hydrated at RT up to periods of weeks are independent of the activation temperature.

Fig. 4 shows a few representative tpd diagrams for a sample of the oxide III activated at 823 K. After hydration, under the indicated conditions, evacuation at 330 K for 30 min was always carried out, previous to the tpd analyses. The thermal dehydration occurs through three steps. If the sample is not evacuated at 330 K, water evolution is observed around 390 K, which corresponds to a weakly adsorbed form, non-dissociate according to

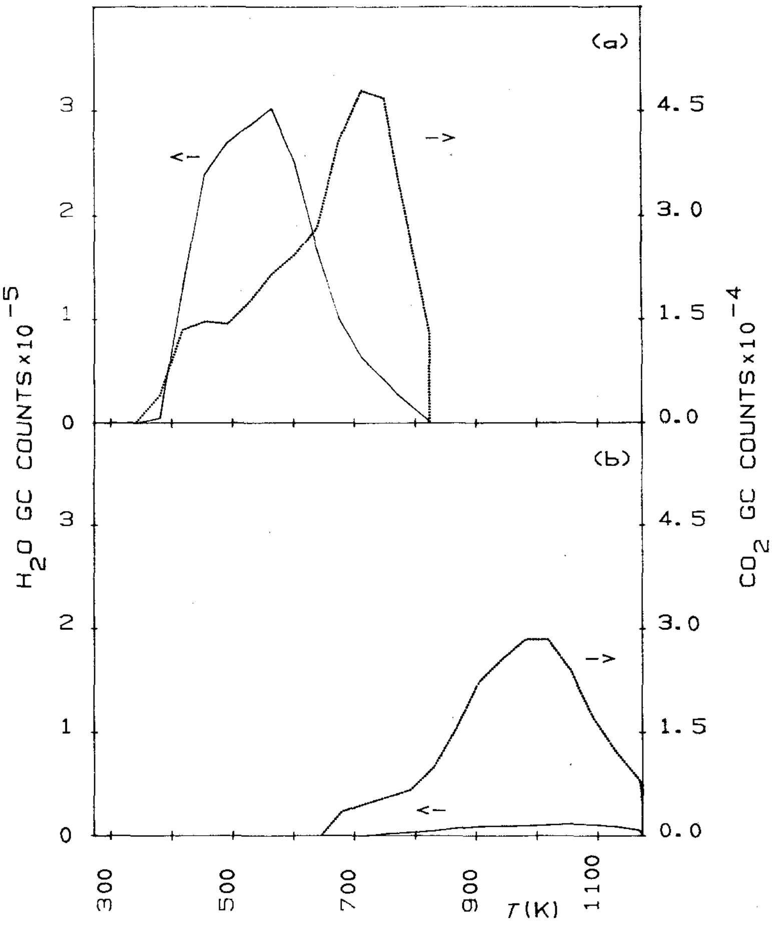

Figure 3 tpd diagrams of aged Yb_2O_3-III: (a) from RT to 823 K; (b) from RT to 1173 K after (a). The units on the ordinate are the gas-chromatograph, GC, counts.

the evolution observed of the ir band at 1630 cm^{-1}. When the hydration is carried out at pressures greater than 1060 Pa (8 torr), a well defined tpd peak is observed at 440 K, followed by a broad one from 600 K. Integration of the former gives amounts which increase with the time of oxide–water interaction and become larger than that corresponding to a surface monolayer [9]. This form of water must involve a previous process of bulk-hydration.

The amounts of water eliminated during the last stage of the tpd analyses are always lower than that estimated for a surface monolayer [9]. Additional observation of the ir band at 3650 to 3700 cm^{-1} seems to indicate that this form is originated by the condensation of isolated OH groups.

The bulk hydration of Yb_2O_3-III is peculiar in the sense that a sample activated at 823 K and successively hydrated–dehydrated at RT, shows a notable decrease in its S_{BET} and amounts of uptaken H_2O. Table I shows a series of experiments, separated chronologically by a further fifteeen.

The pattern of the Yb_2O_3 activated at 1173 K is qualitatively the same as that at 823 K, but the S_{BET} and capacity towards water uptake remain practically constant. The intensity of the hydration is shown in Table I, in the range of pressures where bulk hydration is favoured.

The profile of the tpd analysis after hydration for oxide I is the same as for oxide II [4] and III, at both activation temperatures, 823 and 1173 K. A series of representative diagrams are plotted in Fig. 5, a higher activation temperature being selected in order to complement Fig. 4. At 823 K the results are reproducible for this oxide. Some data are included in Table II.

Touret and Queyroux [13] have studied the reactivity towards H_2O of several lanthanide

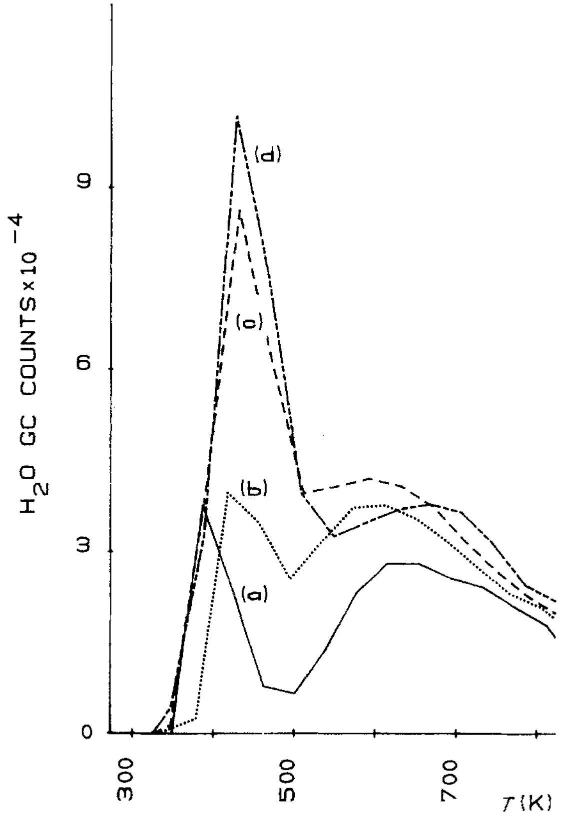

Figure 4 tpd diagrams of Yb_2O_3-III previously activated at 823 K and then hydrated at RT: at 493 Pa for 16 h; (b) at 2800 Pa for 4 h; (c) at 2800 Pa for 24 h; (d) at 2800 Pa for 72 h.

sesquioxides. In the case of ytterbia, they have found that bulk hydration is not favoured, even by soaking the oxide in boiling water. In connection with this conclusion, the influence of the temperature at which the hydration is carried out has been investigated here. Temperatures ranging from 298 K up to 400 K, at water vapour pressure of 2670 Pa have been studied. The residual H_2O vapour was always evacuated before carrying out the tpd analysis, at the same temperature of the reaction in order to avoid rehydration. According to the results obtained here, bulk hydration is only favoured at temperatures lower than 350 K.

TABLE I Effect on Yb_2O_3-III hydration at room temperature of activation temperature (T), pressure of H_2O vapour (P) and time of reaction (t)

T (K)	P (Pa)	t (h)	S_{BET} ($m^2\,g^{-1}$)	W_{H_2O} (mol nm^{-2})
823	2933	1/12	15.4	6.8
823	2800	4	12.8	17.2
823	2933	24	13.2	23.6
823	2800	72	12.1	26.5
823*	2800	1/12	7.7	5.2
823	2933	6	10.1	10.1
823	2666	17	9.7	15.0
823	2533	87	9.4	17.2
1173	2133	1/12	2.4	2.8
1173	2133	16	5.0	7.2
1173	2000	24	3.0	8.7
1173	2000	67	4.0	10.8
1173	2133	110	4.2	9.8

*After a series of fifteen hydration–thermal dehydration runs. 1 torr = 101325/760 Pa.

4. Discussion

The laboratory-prepared ytterbium sesquioxides and the commercial sample undergo partial conversion to bulk carbonate hydroxide when exposed to air. After two years of ageing, the intensity of

TABLE II Effect on Yb_2O_3-I hydration at room temperature of activation temperature (T), pressure of H_2O vapour (P) and time of reaction (t)

T (K)	P (Pa)	t (h)	S_{BET} ($m^2\,g^{-1}$)	W_{H_2O} (mol nm^{-2})
823	2133	1/12	7.6	0.8
823	2000	39	7.3	9.4
1173	2000	13	4.5	1.8
1173	2000	23	7.8	3.1
1173	2000	62	8.0	5.3
1173	2000	116	4.5	8.1

1 torr = 101325/760 Pa.

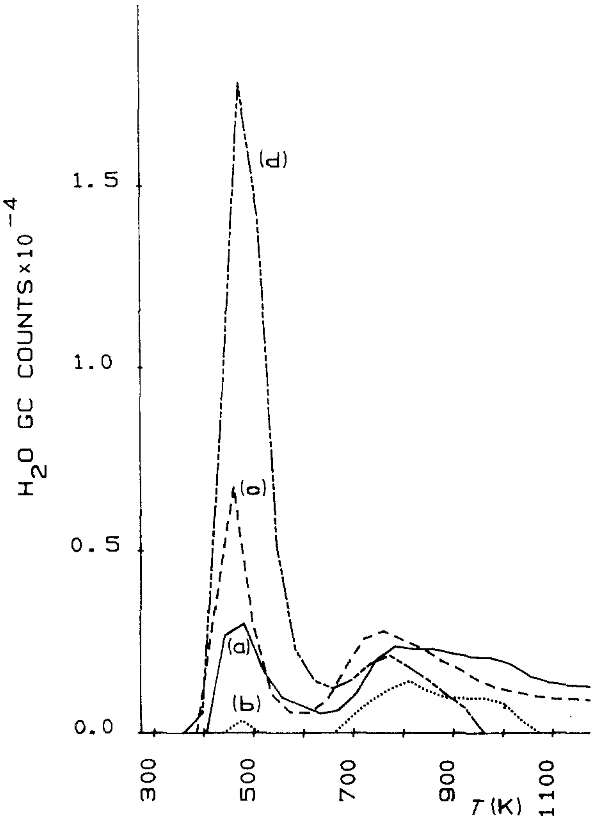

Figure 5 tpd diagrams of Yb_2O_3-I previously activated at 1173 K and then hydrated at RT: (a) at 800 Pa for 116 h; (b) at 2000 Pa for 5 min; (c) at 2000 Pa for 23 h; (d) at 2000 Pa for 116 h.

the reaction with the atmospheric H_2O and CO_2 is similar for the oxides from the oxalate and the hydroxicarbonate. Weight losses of 5.6%, as determined from Fig. 3, and 5.1%, from [3], respectively, have been found. The weight loss for Yb_2O_3-I, aged during an undetermined period of time, but larger than two years, is lower by a factor of 5, data calculated from Fig. 2. Accordingly, the final temperature of calcination of the oxides seems mainly to control this property. For Yb_2O_3-I a preparation temperature higher than 1300 K has been assumed.

The evolution of XPS spectra for O(1 s) binding energy indicates in the three oxides that the reaction does not occur through the advance of a compacted new phase. The intensity ratio of peaks at 8.51×10^{-17} J and 8.48×10^{-17} J after 1 h exposure to the air shows clear differences: Yb_2O_3-I (0.52), Yb_2O_3-II (0.67), Yb_2O_3-III (0.75). At ~ 24 h the intensity ratios reach values close to the unity, then evolving very slowly.

The finding by Alvero *et al.* [8] for the effects of activation at 823 K of Yb_2O_3-II is applicable to the others. With independence of the preparation method, the complete removal of H_2O is achieved at that temperature, but the CO_2 is only eliminated at 1173 K. The residual CO_2, after activation at 823 K, does not appear to influence the surface properties in relation to the hydration of the oxides.

Another general conclusion is that the method of preparation does not exert any influence on the range of pressures at which hydration is favoured at RT, $P > 1060$ Pa.

The values of S_{BET} and intensity of hydration depend strongly on the method of preparation. Nevertheless, data for the fresh samples do not seem to be representative of their further behaviour. The high initial S_{BET} values observed for Yb_2O_3-III decay rapidly, even at 823 K, a temperature lower than that used in its preparation. Certain applications of 4f oxides, such as their use as transition metal supports [2], involve thermo-chemical processes which may alter drastically the initial texture and chemical surface lability of the sample. With respect to this, attention must be paid to the expectations of preparation methods by means of which large S_{BET} values are obtained, for example hydrothermal ones. In the present case, Fig. 6 shows graphically this effect for the oxide from

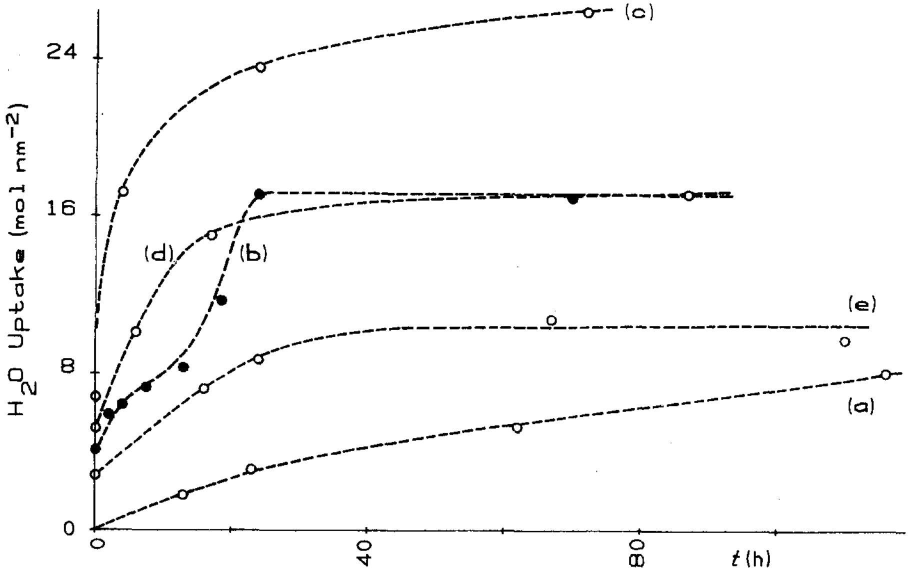

Figure 6 H_2O uptake by ytterbium sesquioxides activated at 823 K as a function of time of exposure to it, at RT and indicated pressures; (a) Yb_2O_3-I at ≈ 2800 Pa; (b) Yb_2O_3-II at ≈ 2000 Pa; (c), (d) and (e) Yb_2O_3-III at ≈ 2800 Pa.

the oxalate. The initial reactivity of Yb_2O_3-III, curve c, decays to values around those of Yb_2O_3-I, the less active one.

The method of preparation by calcining the phase precipitated with ammonia from a solution of the nitrate, under the conditions described elsewhere to avoid nitrate impurity [3], produces the most labile oxide after activation at 823 K.

The general acceptance that bulk hydration of 4f sesquioxides, under mild conditions, is only possible for the earlier members of the series, from lanthanum to gadolinium, must be definitively refused. Justification of the confusion appears to consist of a compromise between kinetically and thermodynamically favoured conditions. This is illustrated by the above observation of Queyroux *et al.* about Yb_2O_3 hydration; according to our results the reaction is favoured at temperatures lower than 350 K. In fact the bulk hydration of Yb_2O_3 occurs at a very low rate, even at the highest thermodynamically favoured temperature. However, after prolongued exposure to water vapour, at RT and pressures higher than 1060 Pa, bulk hydration of ytterbium sesquioxides must be taken into account. The intensity of the reaction depends on the method of preparation in the way discussed above.

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