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CHARACTERIZATION OF SAMARIA SAMPLES STABILIZED IN AIR*

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Summary

The reaction of three different Sm_2O_3 samples with atmospheric CO_2 and H_2O was studied by means of TGA, temperature-programmed decomposition, IR spectroscopy and X-ray diffraction. One of the samples showed a distinctly different behaviour, which was interpreted as a complete transformation to partially carbonated $Sm(OH)_3$. The other two samaria samples partially formed a hydroxycarbonate-like phase. This behaviour is discussed by comparison with other rare earth sesquioxides.

Introduction

According to some recent studies [1 - 6], a number of transition metal/4f oxides show quite singular catalytic properties towards the CO and CO_2 hydrogenation reactions. However, in most of these papers no detailed information concerning the characterization of the 4f-oxide-supported metal catalyst is given. Particularly, no studies on the actual state of the lanthanide oxides used as supports have been reported. This has prompted us to initiate a research program, the major objective of which is the characterization of both supported phases and supports.

In this initial investigation, the nature of the phases resulting from the stabilization in air at room temperature, of 4f oxides is studied. Data corresponding to La_2O_3 [7, 8] and Yb_2O_3 [9] have already been published by us. Here, results relating to samaria, Sm_2O_3, are reported.

Although studies on the ternary systems Ln_2O_3–H_2O–CO_2 under various experimental conditions have previously been reported [10 - 14], a systematic investigation of the hydration and carbonation processes occurring when 4f oxides are exposed to atmospheric CO_2 and H_2O, the usual storage and manipulation conditions, is, to our knowledge, lacking.

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In the present paper, data obtained by means of Thermogravimetric Analysis (TGA), Temperature-Programmed Desorption/Decomposition (TPD), IR spectroscopy and X-ray diffraction are reported. In order to check the influence of the origin of the oxide on its behaviour, three different samaria samples were investigated.

Experimental details

The three samaria powder samples studied here will be referred to as M, F and S. The first two samples were commercial 99.9%-pure oxides from Merck (M) and Fluka (F), respectively. The third, S, was prepared in our laboratory. Unfortunately, no information could be obtained either from Merck or Fluka concerning their oxides. Details of the preparation of sample S are given elsewhere [15].

From the corresponding nitrogen adsorption isotherms at 77 K, BET surface areas were estimated: 6.4 $m^2 g^{-1}$ (Sm_2O_3 - F); 8.2 $m^2 g^{-1}$ (Sm_2O_3 - M) and 14.9 $m^2 g^{-1}$ (Sm_2O_3 - S). These surface areas correspond to the samples stabilized in air.

The TGA experiments were carried out in a Mettler ME-21 microbalance. The flow of helium was $10^{-6} m^3 s^{-1}$ (60 $cm^3 min^{-1}$) and the heating rate 0.1 $K s^{-1}$.

The TPD experiments were recorded under the following conditions: flow of helium, $5.8 \times 10^{-7} m^3 s^{-1}$ (35 $cm^3 min^{-1}$); heating rate 0.1 $K s^{-1}$. The analysis of evolved gases was performed by gas chromatography. The amounts of evolved CO_2 and H_2O were determined from the corresponding calibration curves. The integration of experimental TPD traces was made with the help of a microcomputer Apple IIe.

The IR spectra were recorded with a Pye-Unicam, model SP3-300 instrument. The sample disks were prepared by pressing a mixture containing 2.5% of the oxide and 97.5% of KBr under 5×10^8 Pa.

The X-ray diffraction patterns reported here were obtained with a Siemens instrument, model D-500. The Debye–Scherrer camera was a Philips model PW 1024/30. The X-ray radiation was either Mo Kα (Sm_2O_3 - F) or Cu Kα (Sm_2O_3 - M and Sm_2O_3 - F).

Results

The oxide samples studied here were exposed to atmospheric CO_2 and H_2O for an extended period, minimum nine months (Sm_2O_3 - F). In the case of the M and S samples the exposure was very prolonged (2 - 3 years) but was not controlled from the beginning.

Table 1 reports data corresponding to the amounts of H_2O and CO_2 evolved from the three samples upon heating in an inert gas flow. These data were determined from the corresponding TG and TPD traces, and referred to

TABLE 1

Amounts of H_2O and CO_2 taken up by Sm_2O_3 samples M, F and S exposed to air up to stabilization

Sample	*H_2O*		*CO_2*	
	(mol/mol oxide)	(molecules/nm^2)	(mol/mol oxide)	(molecules/nm^2)
M	3.02	696	0.13	29
F	0.95	187	0.14	28
S	1.23	130	0.25	27

either mole of Sm_2O_3 or square meter of surface area. Good agreement was found between TG and TPD quantitative results.

According to Table 1, the amount of water taken up by the sample M is notably higher than that taken up by samples F and S, and corresponds to the formation of $Sm(OH)_3$.

The first difference between the samples M, F and S is confirmed when TPD traces (Fig. 1), IR spectra (Fig. 2) and X-ray diffraction patterns (Fig. 3), corresponding to the three samples stabilized in air, are compared. As far as Fig. 1 is concerned, in addition to the different ordinate scales used in either the F and S or M samples, Sm_2O_3 - M shows, in contrast to the F and S samples, two distinct, well resolved peaks for water evolution. The

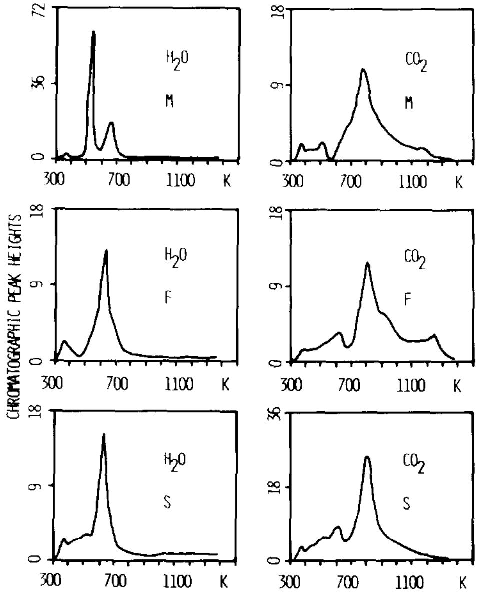


Fig. 1. TPD traces corresponding to the H_2O (left-hand side) and CO_2 evolved from samples M, F and S of Sm_2O_3. Chromatographic signals per gram of sample have been plotted.

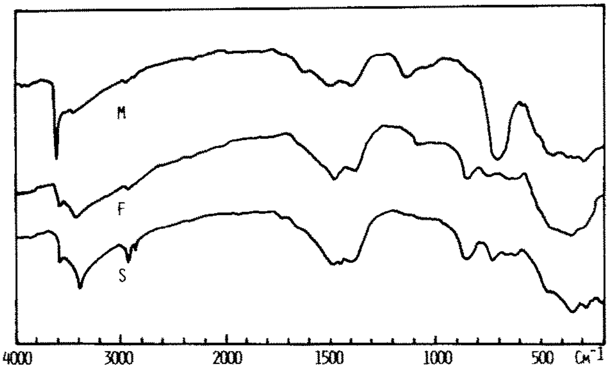
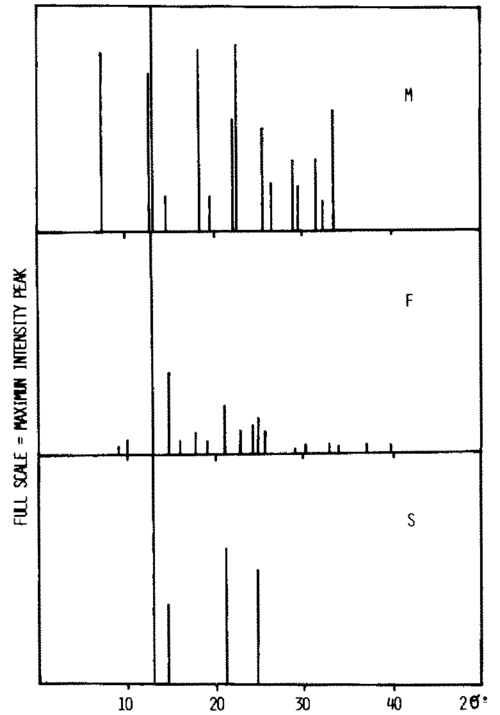


Fig. 2. IR spectra corresponding to M, F and S samaria samples stabilized in air.



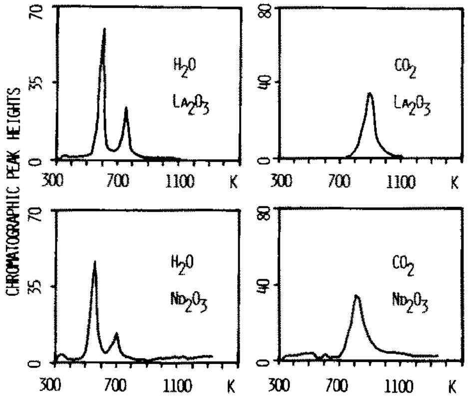


Fig. 3. X-ray diffraction patterns corresponding to samples M, F and S of samaria, stabilized in air. For comparison, the diagrams have been referred to Cu Kα radiation.

Fig. 4. TPD traces corresponding to the H_2O (left-hand side) and CO_2 evolved from La_2O_3 and Nd_2O_3 samples, stabilized in air. Chromatographic signals per gram of sample have been plotted.

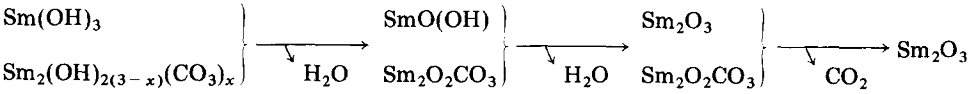
TPD trace for Sm_2O_3-M, is similar, on the other hand, to those previously found by us for La_2O_3 [7, 8] and Nd_2O_3(A) [16] stabilized in air, Fig. 4.

The analogy between the behaviour of La_2O_3 and Sm_2O_3-M may also be deduced from their corresponding IR spectra [7]. In this respect, we note the strong feature at 680 cm (630 cm^{-1} for lanthana) which is completely lacking in the spectra of samples F and S. According to the discussion of Beall *et al.* [17], the above mentioned feature might be ascribed to an IR-active deformation mode of $Ln(OH)_3$. The shifting of this vibration mode from 630 cm^{-1} to 680 cm^{-1} when one goes from La_2O_3 to Sm_2O_3-M, stabilized in air, is also consistent with that observed for the corresponding Raman-active mode of $La(OH)_3$ and $Sm(OH)_3$ in ref. 17.

Finally, the X-ray diffraction pattern (Fig. 3) also suggests that hexagonal samarium hydroxide is present in the Sm_2O_3-M sample stabilized in air.

In summary, the data reported above strongly support the fact that, upon aging in air, the samaria-M sample transforms into $Sm(OH)_3$. On the other hand, TPD and IR spectroscopic data demonstrate that this hydroxide is partially carbonated. As discussed in ref. 7, for La_2O_3 this carbonated phase might well be constituted by an hydroxycarbonate phase, $Sm_2(OH)_{2(3-x)}(CO_3)_x$, similar to those previously reported by Caro [18]. Contrary to the suggestion in ref. 18, however, no complete transformation of the hydroxide into the hydroxycarbonate phase occurs.

In accordance with the model previously suggested by us for lanthana aged in air [7], the thermal decomposition of hydrated and carbonated Sm_2O_3-M might well be described:



$$\left.\begin{matrix}\mathrm{Sm(OH)_3}\\ \mathrm{Sm_2(OH)_{2(3-x)}(CO_3)_x}\end{matrix}\right\} \xrightarrow[\mathrm{H_2O}]{} \left.\begin{matrix}\mathrm{SmO(OH)}\\ \mathrm{Sm_2O_2CO_3}\end{matrix}\right\} \xrightarrow[\mathrm{H_2O}]{} \left.\begin{matrix}\mathrm{Sm_2O_3}\\ \mathrm{Sm_2O_2CO_3}\end{matrix}\right\} \xrightarrow[\mathrm{CO_2}]{} \mathrm{Sm_2O_3}$$

According to this model, the thermal evolution of CO_2 occurs in a single step, which is confirmed by the TPD experiments (Fig. 1).

The behaviour of samples F and S towards atmospheric CO_2 and H_2O is notably different from that observed for Sm_2O_3-M. First, there is no evidence supporting the existence of $Sm(OH)_3$. A single peak is found in the corresponding TPD traces for water (Fig. 1). As depicted in Fig. 2, the IR spectra of samples F and S, in addition to the complete absence of the strong feature at 680 cm^{-1}, show band structures in the OH stretching region which are very similar to each other but quite different from that observed for Sm_2O_3-M. The IR spectra for samples F and S are, on the other hand, analogous to those previously reported [19, 20] for hydroxycarbonate-like phases. Similarly, the X-ray diffraction patterns of the F and S samples which were stabilized in air are in good agreement with that for cubic Sm_2O_3. This suggests that when the apparent stabilization of Sm_2O_3-F and S is reached a notable fraction of the original oxide remains unaltered.

Discussion

Our experiments show two, well-differentiated behaviours of Sm_2O_3 powder towards atmospheric CO_2 and H_2O. Sample M completely transforms in partially carbonated hydroxide, whereas for samples F and S the hydration and carbonation are only partial. In this latter case a single hydroxycarbonate-like phase is probably formed. It is worth mentioning in this respect that the H_2O/CO_2 mole ratio is rather similar for samples F (6.7) and S (5.0); values much lower than 23.0, that found for Sm_2O_3-M.

When the amounts of CO_2 taken up by the three samples are referred to the BET surface area (Table 1) *ca.* 28 molecules per nm^2 are found in every case, which suggests that the intensity of this process is directly related to the specific surface area. Taking into account that for these oxides the CO_2 surface monolayer corresponds to approximately 8 molecules per nm^2 [9, 21], bulk carbonation does occur. However, the above results seem to indicate that only a few layers of the oxide are involved in this process, suggesting that, when the outer layers of the solid are carbonated, the reaction becomes very slow and an apparent stabilization is reached.

In accordance with this tentative model, the differences observed between Sm_2O_3-M and samples F and S suggest that in the former case hydration would be a relatively fast process, followed by a carbonation reaction restricted to a few layers. On samples F and S, by contrast, hydration and carbonation reactions would take place in a parallel manner, the progression of both being determined by the latter process.

In the case of Sm_2O_3-F the aging process was followed by TPD from the onset. Results corresponding to variable exposure times from 0 days to 270 days were obtained. According to these, throughout the whole aging process, the H_2O/CO_2 mole ratio did not change greatly, ranging from 6.1 to 7.7, which supports the above interpretation of the manner in which hydration and carbonation of samples F and S occur.

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