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ACTIVATION OF RARE EARTH OXIDE CATALYSTS*

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Summary

It has previously been shown that even the heaviest rare earth oxides undergo partial conversion to bulk hydroxycarbonates when exposed to air. However, when rare earth oxides are used as catalysts, activation temperatures lower than those necessary to achieve the complete removal of H_2O and CO_2 are often reported. To elucidate the actual active phases that operate in catalytic processes involving rare earth oxides, a systematic temperature-programmed desorption study of La_2O_3, Sm_2O_3 and Yb_2O_3 was carried out. Our results lend support to a particle structure for the activated powder "oxides" consisting of an oxycarbonate nucleus surrounded by an outer oxide layer.

1. Introduction

Even the heaviest rare earth sesquioxides undergo partial conversion to bulk hydroxycarbonates on exposure to air. According to the experimental results reported in ref. 1 the temperatures used in the activation of Ln_2O_3 ($Ln \equiv$ lanthanide) catalysts aged in air [2–5] are lower than those necessary for the complete removal of CO_2 and H_2O from these oxides. However, in refs. 2–5 the active phases were considered to be the corresponding oxides. The correctness of such an interpretation is discussed on the basis of the results reported here.

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2. Experimental methods

2.1. *Materials*

Lanthanum, samarium and ytterbium sesquioxides were selected for this study. Lanthanum and ytterbium hydroxycarbonates were precipitated from nitrate solutions by adding NH_3 at a rate of 5 cm^3 min^{-1}. The experiments were performed in air containing the normal CO_2 content at room temperature. La_2O_3 and Yb_2O_3 were finally prepared by calcining the precipitates in air at 873 K over a period of 5 h. This temperature is only appropriate for unaged precipitates. The Sm_2O_3 was a commercial AnalaR grade (Merck).

The thermal decomposition profile of oxide samples aged in air has been shown to be independent of the preparation method [1].

The samples studied here were characterized by X-ray diffraction, thermogravimetric analysis, differential thermal analysis, O 1s X-ray photoelectron spectroscopy, IR spectroscopy and pore size distribution.

2.2. *Apparatus*

Details of the temperature-programmed desorption (TPD) device are given in ref. 6. The gas chromatography (GC) and mass spectrometry (MS) analyses were performed using a Hewlett–Packard model 5830A gas chromatograph and a Hewlett–Packard model 5992A quadrupole mass spectrometer. All the experiments were carried out in a helium flow (30 ml min^{-1}) at a heating rate of 8 K min^{-1}.

Quantitative TPD calibrations of H_2O and CO_2 were performed by decomposing variable amounts of $CuSO_4 \cdot 5H_2O$ and $MnCO_3$ as reported in ref. 6. Because of the instability of the electron multiplier, the mass spectrometry determinations of the amount of gases evolved were always referred to recent calibrations.

3. Results and discussion

Figures 1 and 2 show TPD traces for oxides aged in air for more than 3 years. The identification of intermediate phases is beyond the scope of this paper. The total amounts of H_2O and CO_2 evolved agree with those reported in ref. 1 and are higher than would be expected for a surface reaction alone. The hydration and carbonation of these oxides require periods of time ranging from hours for La_2O_3 to months for Yb_2O_3.

After isothermal heating for 30 min at the upper temperature (1173 K) the amounts of evolved CO_2 are below our experimental detection limit of 0.2 molecules per square nanometre of the Brunauer–Emmett–Teller (BET) surface area of the sample. It can also be seen in Figs. 1 and 2 that the temperature at which dehydration occurs decreases as the polarizing power of the 4f ions increases.

Although TPD processes do not take place under true equilibrium conditions, Figs. 1 and 2 show the difficulty of obtaining pure oxide phases when,

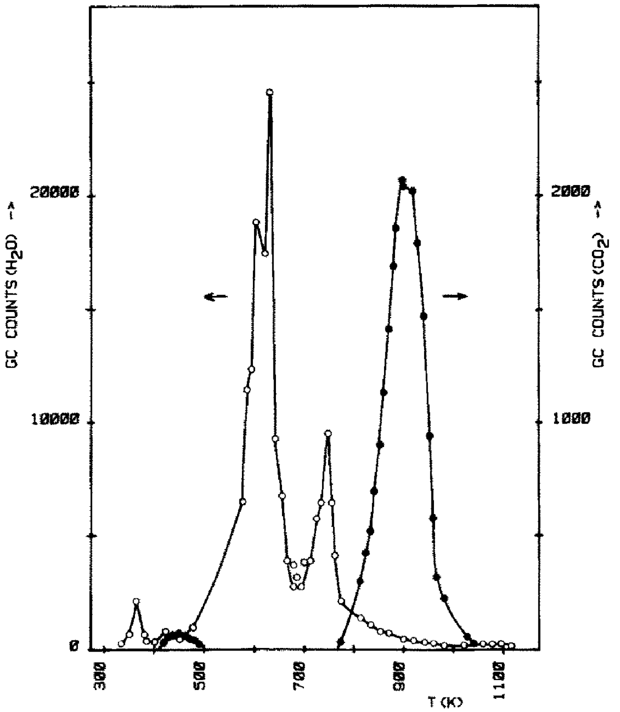

Fig. 1. TPD–GC diagrams of aged La_2O_3.

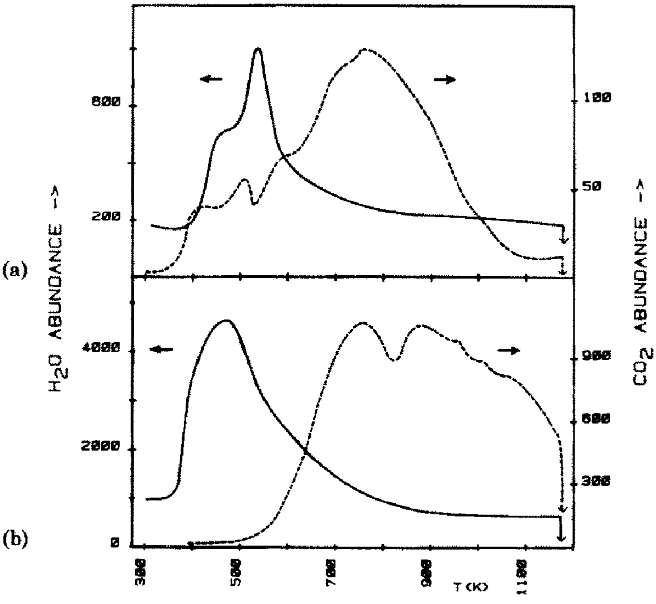

Fig. 2. TPD–MS diagrams of (a) aged Sm_2O_3 and (b) aged Yb_2O_3. The units on the ordinate are the MS counts.

as in refs. 2–5, the catalysts are activated at 773–823 K. Samples activated in this way should be partially carbonated.

The surface model proposed in ref. 7 predicts a different result for the hydration of pure Ln_2O_3 and of its carbonated phases. Therefore the behaviour of the hydration reaction of samples activated as described in refs. 2–5 and of samples free from H_2O and CO_2 has been compared. Samples which had been aged in air were further heated in a helium flow up to either 823 or 1173 K. The data for several H_2O pressures and time treatments of Sm_2O_3 and Yb_2O_3 show that the behaviour of these oxides is essentially the same for both activation temperatures when differences in the BET surface area are taken into account. Figure 3 shows representative results for Yb_2O_3.

Table 1 reports the amounts of H_2O evolved in addition to the activation temperature and the surface area of each sample. The H_2O evolved is in excess of 8 molecules H_2O nm^{-2} which is the maximum value estimated for a saturated surface monolayer [7]. A detailed discussion of the nature and the development of H_2O evolution with increasing pressure and time of hydration of the two forms of oxide observed here is beyond the scope of this paper and will be discussed elsewhere.

A model analogous to that previously proposed [8] to interpret the decomposition of 3d metal formates may account for the results given above. According to this model the oxide powder particles activated at 823 K consist of

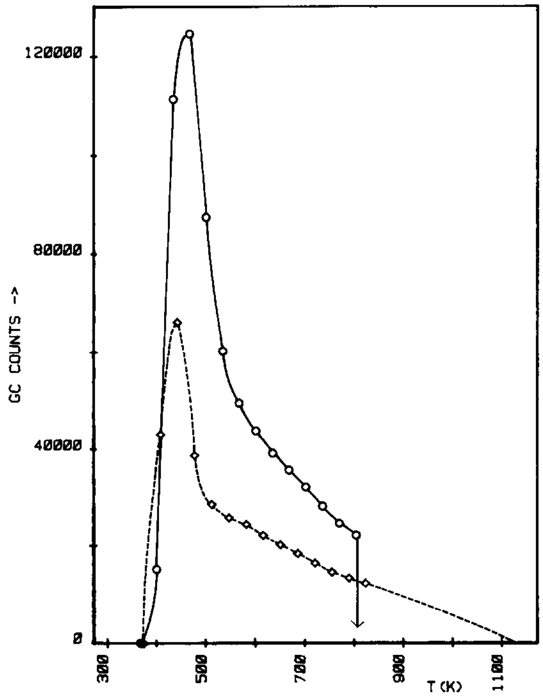

Fig. 3. TPD–GC diagrams of Yb_2O_3 hydrated at room temperature for 18 h at a final pressure of 15 Torr: ○, sample activated at 823 K; ◇, sample activated at 1173 K.

TABLE 1

Effect of the activation temperature on the H_2O content of hydrated oxides

Oxide	*T* (K)	S_{BET} ($m^2 g^{-1}$)	W_{H_2O} (molecules nm^{-2})
Sm_2O_3	823	5.3	17.5
Sm_2O_3	1173	5.2	17.3
Yb_2O_3	823	42.6	11.2
Yb_2O_3	1173	21.6	11.3

an oxycarbonate nucleus surrounded by an outer multilayer of the oxide phase. The very slow diffusion of CO_2 resulting from the decomposition of the carbonate phase would cause its exhaustion in the outer part of the particle. A decomposition mechanism of the Polanyi–Wigner type [9] would fulfil these requirements.

To obtain additional evidence supporting this model, the following experiments were carried out on aged Sm_2O_3 and Yb_2O_3: programmed heating up to 823 K, isothermal heating at this temperature until no evolution of H_2O and CO_2 was detected, cooling to room temperature and TPD from room temperature to 1173 K. The helium flow was maintained without interruption. Representative results corresponding to these experiments are shown in Fig. 4. It can be deduced from this figure that the samples activated at 823 K are not free from H_2O and CO_2; higher temperatures are necessary to achieve their complete

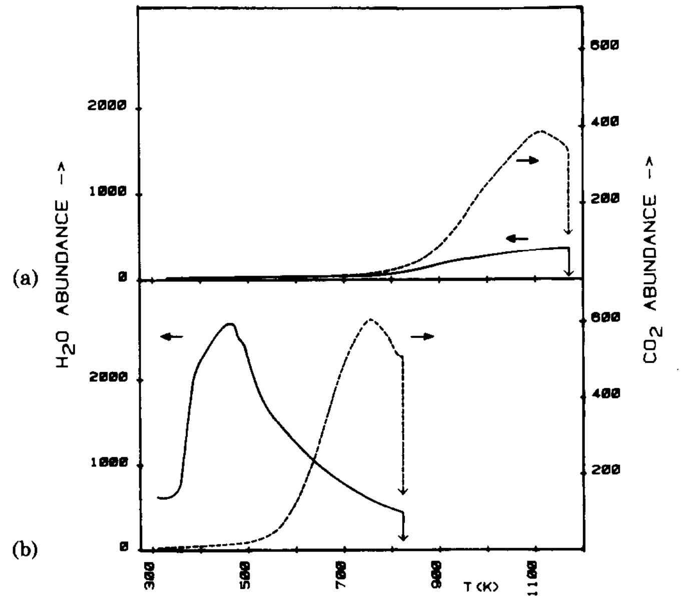

Fig. 4. TPD-MS diagrams of aged Yb_2O_3: (a) from room temperature to 1173 K; (b) from room temperature to 823 K. The units on the ordinate are the MS counts.

removal. Therefore it is notable that the evolution of H_2O and CO_2 begins at about 823 K during the final TPD experiment up to 1173 K.

4. Conclusions

La_2O_3, Sm_2O_3 and Yb_2O_3 undergo partial conversion to bulk hydroxycarbonates when exposed to air. When used as catalysts these oxides are usually activated at temperatures lower than those necessary to achieve complete removal of H_2O and CO_2. However, the results reported here lend support to a particle structure for the activated powdered "oxides" consisting of an oxycarbonate nucleus surrounded by an outer oxide layer which operates as the active phase.

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