

## **THE KINETICS OF $\text{Ln}_2\text{O}_3$ HYDRATION UNDER MILD CONDITIONS**

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The kinetics of  $\text{Ln}_2\text{O}_3$  hydration ( $\text{Ln} = \text{Sm}, \text{Ho}, \text{Yb}, \text{Lu}$ ) have been studied at room temperature and atmospheric pressure, as have the influence of the activation temperature and the method of preparation of the oxides.

The best correlation coefficients are obtained for a diffusion mechanism. If a structural relationship between the  $\text{C}-\text{Ln}_2\text{O}_3$  and their precursors is considered, the possibility arises of the existence of defect planes in the oxides prepared from the hydroxide and carbonate. This facilitates the hydration process through a diffusion mechanism in the case of the rare earth sesquioxides prepared from the above precursors.

Recent papers dealing with the hydration of rare earth oxides have pointed out the existence of a correlation between the method of preparation of the oxide and the degree of hydration [1, 2]. A structural relationship between the prepared oxide and the precursor salt can favour the hydration of the oxide; thus, oxides obtained by calcining hydroxide or carbonate species are more reactive than those from oxalate precursors [2]. Likewise, an increase in the calcination temperature of the oxide causes an enhancement of oxide inertness towards the hydration reaction.

The bulk hydration of rare earth oxides on exposure to air, even in the case of the heavy ones, is a process thermodynamically favoured, as shown in [2]; therefore, the degree of hydration as a function of the oxide preparation method should be related to kinetic factors.

In this paper, hydration degree data referring to cubic samarium, holmium, ytterbium and lutetium sesquioxides are analysed on the basis of reaction rate laws for isothermal conditions, in order to establish a structural relationship between the oxide and the hydrated phase formed.

## Experimental

Samaria and ytterbia (Merck A. R. grade), holmia (Kola-Light Lab.) and lutetia (Sigma Chemical Co.) samples, nominally 99.9% pure, were studied. Some ytterbium and lutetium sesquioxides prepared by calcining hydroxide, carbonate and oxalate precursors, as previously described [3, 4], were also used. The samples will be denoted by the sesquioxide formula, followed by the temperature of activation on the Kelvin scale and, in the case of laboratory prepared ones, by the precursor symbol in brackets (*hy* = hydroxide; *ca* = carbonate; *ox* = oxalate).

The influence of the activation temperature on the actual hydration degree of the initial sample has been examined in [5].

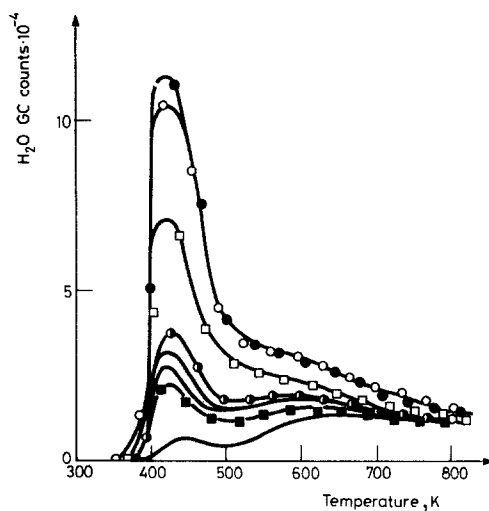
The hydration of  $\text{Ln}_2\text{O}_3$  samples was studied by means of temperature-programmed decomposition (TPD) of the phases formed upon the reaction of  $\text{Ln}_2\text{O}_3$  with water at pressures within the range of atmospheric conditions and at room temperature. The evolved water was analysed using a Hewlett-Packard 5834A gas chromatograph. All the experiments were carried out in a helium flow ( $30 \text{ ml} \cdot \text{min}^{-1}$ ) at a heating rate of  $8 \text{ deg} \cdot \text{min}^{-1}$ . Quantitative TPD calibrations of  $\text{H}_2\text{O}$  were performed by decomposing variable amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

## Results and discussion

The studied C- $\text{Ln}_2\text{O}_3$  samples ( $\text{Ln} = \text{Sm}, \text{Ho}, \text{Yb}, \text{Lu}$ ) undergo bulk hydration when hydrated at room temperature at a water pressure of ca. 20 torr. After hydration for periods ranging between some minutes and a hundred hours, the water evolved was analysed by means of TPD diagrams. In order to determine the bulk water contents of the oxides, the hydrated samples were evacuated for 30 minutes at room temperature before the TPD run, this treatment ensuring the elimination of weakly adsorbed water [6]. Figure 1 shows a sequence of TPD experiments performed on  $\text{Yb}_2\text{O}_3$ -1173(hy) samples, hydrated for different periods under the above-mentioned conditions.

The  $\alpha$  value is calculated as the degree of conversion of the pure oxide into hydroxide, according to the following reaction:  $\text{Ln}_2\text{O}_3 + 3 \text{H}_2\text{O} = 2 \text{Ln}(\text{OH})_3$ . Table I shows representative hydration degree data for the studied sesquioxides as a function of time, precursor salt and activation temperature. The hydration degree of each oxide sample has been examined up to  $\alpha$  values which do not increase appreciably within additional periods of ca. 10 hours.

The preparation method and the activation temperature of each oxide exert such an influence on the  $\alpha$  values for the hydration process that  $\alpha$  for a constant period of time cannot be expected to show a smooth variation with the basic character of the



**Fig. 1** TPD of  $\text{Yb}_2\text{O}_3$ -1173(hy) hydrated at 298 K and 20 torr for 1/12, 2, 4, 7.5, 13, 18.5, 24 and 70 hours, respectively, on going from the lowest curve to the top one

**Table 1** Hydration degree of  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{Sm}, \text{Ho}, \text{Yb}, \text{Lu}$ )

|                                   |              |       |       |       |
|-----------------------------------|--------------|-------|-------|-------|
| $\text{Sm}_2\text{O}_3$ -1173     | $t(h)$       | 5     | 20    | 71    |
|                                   | $\alpha$ (%) | 1.728 | 1.830 | 2.906 |
| $\text{Sm}_2\text{O}_3$ -823      | $t(h)$       | 5     | 22    | 137   |
|                                   | $\alpha$ (%) | 1.340 | 3.137 | 7.853 |
| $\text{Ho}_2\text{O}_3$ -823      | $t(h)$       | 1/12  | 22    | 95    |
|                                   | $\alpha$ (%) | 0.355 | 2.639 | 3.538 |
| $\text{Yb}_2\text{O}_3$ -1173     | $t(h)$       | 13    | 23    | 62    |
|                                   | $\alpha$ (%) | 0.177 | 0.525 | 0.924 |
| $\text{Yb}_2\text{O}_3$ -1173(hy) | $t(h)$       | 4     | 13    | 24    |
|                                   | $\alpha$ (%) | 1.130 | 2.024 | 6.638 |
| $\text{Yb}_2\text{O}_3$ -1173(ox) | $t(h)$       | 16    | 24    | 67    |
|                                   | $\alpha$ (%) | 0.349 | 0.281 | 0.576 |
| $\text{Lu}_2\text{O}_3$ -823(hy)  | $t(h)$       | 1/12  | 8     | 60    |
|                                   | $\alpha$ (%) | 7.894 | 19.13 | 22.73 |
| $\text{Lu}_2\text{O}_3$ -823(ca)  | $t(h)$       | 1/12  | 5     | 173   |
|                                   | $\alpha$ (%) | 5.749 | 8.992 | 20.42 |

4f sesquioxides through the series. Thus, a  $\text{Lu}_2\text{O}_3$ -823(hy) sample is able to rehydrate up to 22% of the maximum value, whereas a commercial samaria sample attains only an 8% hydration degree for the same period of time. However, independently of the  $\alpha$  value reached, all the studied sesquioxides undergo a rapid hydration, followed by a decay in the hydration rate between 24 and 70 hours. Figure 2 shows the influence of the activation temperature on the variation of the hydration degree for  $\text{Lu}_2\text{O}_3$  samples obtained by calcining hydroxide precursor and subsequently activated at 823 and 1173 K.

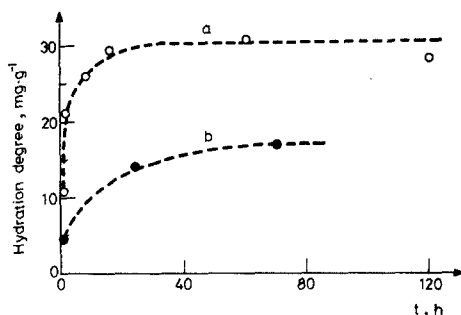


Fig. 2 Hydration degree vs. time of reaction for  $\text{Lu}_2\text{O}_3$ (hy) samples activated at: a) 823 K; b) 1173 K

The mechanism for a solid-state reaction is usually determined by means of the best correlation coefficient of the  $g(\alpha)$  integral function vs. time straight line among those obtained for all the possible mechanisms. The usual rate law equations for isothermal conditions are well known.

Table 2 shows the correlation coefficients of the straight lines obtained when the different rate laws are applied to  $\text{Lu}_2\text{O}_3$  samples activated at both 823 and 1173 K,

Table 2 Correlation coefficients from the usual rate law equations for the shown  $\text{Lu}_2\text{O}_3$  samples

| Mechanism* | $\text{Lu}_2\text{O}_3$ -823<br>(hy) | $\text{Lu}_2\text{O}_3$ -1173<br>(hy) | $\text{Lu}_2\text{O}_3$ -823<br>(ca) | $\text{Lu}_2\text{O}_3$ -1173<br>(ca) |
|------------|--------------------------------------|---------------------------------------|--------------------------------------|---------------------------------------|
| $R_1$      | 0.670                                | 0.751                                 | 0.940                                | 0.954                                 |
| $R_2$      | 0.750                                | 0.756                                 | 0.945                                | 0.955                                 |
| $R_3$      | 0.680                                | 0.757                                 | 0.946                                | 0.955                                 |
| $A_2$      | 0.644                                | 0.717                                 | 0.909                                | 0.936                                 |
| $A_3$      | 0.630                                | 0.693                                 | 0.893                                | 0.929                                 |
| $F_1$      | 0.684                                | 0.760                                 | 0.950                                | 0.956                                 |
| $D_1$      | 0.738                                | 0.821                                 | 0.985                                | 0.985                                 |
| $D_2$      | 0.743                                | 0.847                                 | 0.986                                | 0.985                                 |
| $D_3$      | 0.749                                | 0.851                                 | 0.987                                | 0.986                                 |
| $D_4$      | 0.745                                | 0.849                                 | 0.987                                | 0.986                                 |

\* Notation from J. H. Sharp and S. A. Wentworth, *Anal. Chem.*, 41 (1969) 2060.

and prepared by calcining hydroxide and carbonate precursors. The best coefficients are systematically obtained for diffusion mechanisms. Diffusion mechanisms are also obtained for the remaining sesquioxides, as shown in Table 3. In the case of the commercial samples obtained at temperatures higher than 1300 K, the correlation coefficients are close to unity. The better agreement in these

**Table 3** Correlation coefficients from the diffusion rate law equations for the shown  $\text{Ln}_2\text{O}_3$  samples

|                                   | $D_1$ | $D_2$ | $D_3$ | $D_4$ |
|-----------------------------------|-------|-------|-------|-------|
| $\text{Sm}_2\text{O}_3$ -1173     | 0.957 | 0.957 | 0.958 | 0.957 |
| $\text{Sm}_2\text{O}_3$ -823      | 0.999 | 0.999 | 0.999 | 0.999 |
| $\text{Ho}_2\text{O}_3$ -823      | 0.908 | 0.909 | 0.910 | 0.910 |
| $\text{Yb}_2\text{O}_3$ -1173     | 0.995 | 0.995 | 0.995 | 0.995 |
| $\text{Yb}_2\text{O}_3$ -1173(hy) | 0.829 | 0.829 | 0.829 | 0.829 |
| $\text{Yb}_2\text{O}_3$ -1173(ox) | 0.934 | 0.934 | 0.934 | 0.934 |

samples may be explained by the sintering process undergone by them, which lowers their surface free energies and leads to a higher textural stability. On the other hand, it is worth pointing out that the successive hydration-dehydration runs cause an important modification in the  $S_{\text{BET}}$  and pore size distribution of prepared  $\text{Lu}_2\text{O}_3$  samples activated at 823 K [4]; thus, conversion of the hydroxide into the oxide gives rise to a sample whose specific surface area varies from 60 to ca.  $40 \text{ m}^2 \cdot \text{g}^{-1}$ , whereas the  $S_{\text{BET}}$  of a sample from the carbonate changes from 20 to ca.  $40 \text{ m}^2 \cdot \text{g}^{-1}$  under the same conditions. These variations in  $S_{\text{BET}}$  explain the differences found in the correlation coefficients when comparing commercial samples (hardly porous and with high surface stability) with the prepared ones, which are very porous and have a surface area dependent on the treatment.

While studying the hydration of A- $\text{Nd}_2\text{O}_3$  samples, Lejus et al. [7] found the existence of a cleavage plane, suitable for the hydration reaction, which preserves  $|\text{LnO}|_n^{n+}$  entities. A- $\text{Ln}_2\text{O}_3$  can be considered formally as a layered structure which contains  $|\text{LnO}|_n^{n+}$  entities formed by the linkage of  $\text{OLn}_4$  tetrahedra sharing four over six edges. This formalism can be extended to cubic sesquioxides, considering a tridimensional framework [8]. However, if we consider the structural relationship between the hydroxide, the carbonate and the corresponding oxide, taking into account that the calcination temperature of the oxides, 873–973 K, is very far from the Tamman temperature, it is possible to assume defect planes which let water diffuse into the oxide structure. The observed changes in the textural characteristics of successively rehydrated lutetia samples, which even show microporosity, indirectly confirm the assumption about the existence of defect planes.

When a diffusion mechanism is considered, the slope ( $m$ ) of the straight line

obtained by plotting  $g(\alpha)$  vs.  $t$  is expressed by  $k/r^2$ , where  $k$  is the diffusion coefficient and  $r$  the effective radius for the diffusion process. Considering the relation between inertness towards the hydration reaction and textural properties, previously reported [1], it can be assumed that the effective radius for the diffusion process is related to the mean pore radius of the sample; on this basis, if the diffusion coefficient is supposed to be only a function of the nature of the ion, the following relationship may be written:

$$\sqrt{\frac{m(\text{precursor A})}{m(\text{precursor B})}} = \frac{\bar{r}_p(\text{precursor B})}{\bar{r}_p(\text{precursor A})} \quad (1)$$

Table 4 shows the data corresponding to both the left and the right hand side of this equation for lutetia samples activated at 823 and 1173 K, respectively. The textural variations described above are responsible for the oscillations in the mean pore radius ratio shown in this Table.

**Table 4** Application of Equation 1 to  $\text{Lu}_2\text{O}_3$  samples activated at 823 and 1173 K and prepared from the hydroxide and carbonate

|      | $\sqrt{\frac{m(\text{hy})}{m(\text{ca})}}$ | $\frac{\bar{r}_p(\text{ca})}{\bar{r}_p(\text{hy})}$ |
|------|--|---|
| 823  | 1.6  | 1.1-2.2   |
| 1173 | 1.1  | 1.2   |

The agreement found between the kinetic parameters and the textural ones in the studied cubic sesquioxides justifies the assumption that precursor salts which can decompose to oxide through a topotactic process, e.g. the carbonate or the hydroxide, create sufficient structure defect planes in the oxide to facilitate the hydration process through a diffusion mechanism. Moreover, an increase in the calcination temperature diminishes the number of defects, increasing the inertness of the oxide.

The indirect evidence provided by the kinetic results for the defect plane assumption, in addition to the previous ones reported in [1, 4], has led to the elaboration of the proposed model, which can successfully explain the different reactivities in the ternary system  $\text{Ln}_2\text{O}_3\text{--H}_2\text{O--CO}_2$  as a function of the sesquioxide preparation method [1, 2].

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**Zusammenfassung** — Die Kinetik der Hydratisierung von  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{Sm}, \text{Ho}, \text{Yb}, \text{Lu}$ ) wurde bei Raumtemperatur und atmosphärischem Druck bezüglich des Einflusses der Aktivierungstemperatur und der Art der Darstellung der Oxide untersucht. Die besten Korrelationskoeffizienten werden für einen Diffusionsmechanismus erhalten. Wenn die strukturelle Beziehung zwischen den  $\text{C}-\text{Ln}_2\text{O}_3$  in Betracht gezogen wird, so ergibt sich die Möglichkeit der Existenz von defekten Gitterebenen in den aus Hydroxiden und Carbonaten hergestellten Oxiden. Dies erleichtert den Hydratisierungsprozeß durch einen Diffusionsmechanismus im Falle von aus den oben genannten Vorstufen hergestellten Sesquioxiden der Seltenen Erdmetalle.

**Резюме** — При комнатной температуре и атмосферном давлении изучена кинетика гидратации  $\text{Ln}_2\text{O}_3$ , где  $\text{Ln} = \text{Sm}, \text{Ho}, \text{Yb}, \text{Lu}$ , в зависимости от температуры активации и метода получения окислов. Наилучшие коэффициенты корреляции были получены для диффузионного механизма. При рассмотрении структурной взаимосвязи между кристаллическими окислами лантанидов и исходными веществами для их получения, установлена возможность существования нарушенных плоскостей в окислах, полученных из гидроокисей и карбонатов. В этом случае наличие таких дефектов облегчает процесс гидратации посредством диффузионного механизма.