

INFLUENCE OF ADDITIVES AND WATER VAPOUR ON THE TRANSFORMATION OF TRANSITION ALUMINAS INTO ALPHA ALUMINA.

M. PIJOLAT, M. DAUZAT and M. SOUSTELLE

Laboratoire de Chimie - Physique des Processus Industriels, Ecole Nationale Supérieure des Mines, 158 Cours Fauriel, 42023 Saint-Etienne Cedex 02 (France).

ABSTRACT

Addition of magnesium cations to gamma (and delta) alumina enhances its rate of transformation into alpha alumina, whereas addition of zirconium cations inhibits it. The effect of adding both magnesium and zirconium cations at various concentrations from 0.5 to 5% to aluminium ions has been studied. The kinetic curves of transformation into alpha alumina at 1373 K are reported. The effects observed are in agreement with the D.T.A. measurements. Changes in surface area accompanying the phase transformation have also been measured. A synergy effect may occur between magnesium and zirconium behaviours, since maximum stabilization of the surface area is found with a particular co-doped product ($Mg^{2+}(1\%)-Zr^{4+}(0.5\%)$).

In the case of pure alumina, the influence of water vapour in the range 1-20 torr has also been investigated with the same methods. The results show that water vapour enhances the rate of transformation into alpha.

INTRODUCTION

Transition aluminas are widely used as a catalyst support in the chemical industry. At reaction temperatures higher than 1273 K, their initially high surface area drops rapidly, and they are transformed into alpha alumina (corundum). The efficiency of the catalyst is therefore irreversibly lost. These phenomenas are greatly influenced by the presence of impurities and the nature of the gazeous atmosphere (refs. 1-4). In previous studies we have shown the influence of several added cations on the rate of transformation into alpha alumina and interpreted their effects by means of two distinct parameters: ionic radius and charge (refs.1,2). In this paper we describe the effect of simultaneous addition of magnesium (accelerator) and zirconium (inhibitor) ions. The influence of water vapour is also investigated.

METHODS

Alumina (purity 99.8%) provided by the Rhône-Poulenc company, consisted of ϕ 2-4 mm balls. After annealing for one hour at 1173 K, it contains a mixture of gamma and delta phases. Co-doping was performed by a dry

impregnation method with the appropriate solution of nitrates (same nitrate content for all samples). The concentrations given below are ionic percentages referred to aluminium ions.

After drying, subsequent calcination at 873 K to remove the nitrate ions, the balls were calcined at 1378 K in a Netsch 417/1 furnace. Calcinations under fixed water vapour pressure were performed at 1403 K in a cylindrical furnace equipped with an alumina tube connected to a pumping unit and a refrigerated source.

The alpha alumina percentage was obtained by X-ray diffraction analysis.

The specific surface areas were measured by the B.E.T. method for nitrogen adsorption at 77 K.

Differential thermal analysis was performed on a Perkin-Elmer D.T.A. 1700 under flowing argon by raising the temperature at a rate of 20 K.min⁻¹.

RESULTS AND DISCUSSION

Influence of Mg²⁺ and Zr⁴⁺ co-doping

The transformation into alpha alumina as a function of calcination time of the pure, doped and co-doped samples is illustrated in Fig. 1. The addition of 1.5% zirconium has a very important inhibitor effect, since no alpha alumina is detected after 30 hours and the corresponding curve is lost in the abscissa scale. Magnesium (1.5%) accelerates the transformation. In the case of co-doped products, if the zirconium ion content is kept at 0.5%, the overall effect is greatly dependent on the magnesium content. Even at 5% Mg²⁺, however, it is still inhibitor.

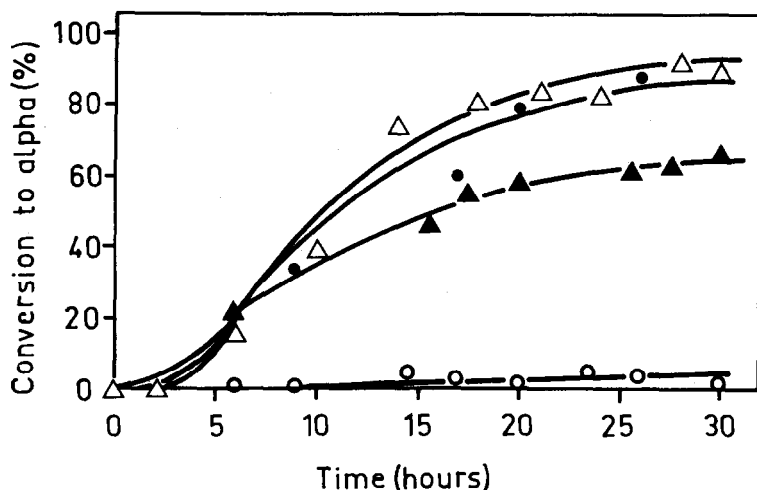


Fig. 1. Conversion to alpha alumina (%) as a function of calcination time at 1378 K: ● pure sample, △ Mg²⁺(1.5%), ▲ Mg²⁺(5%)-Zr⁴⁺(0.5%) and ○ Mg²⁺(1%)-Zr⁴⁺(0.5%) doped samples.

Figure 2 illustrates the specific surface area diminution of these samples as a function of calcination time. Two groups can be distinguished: those whose diminution is substantial until about $20 \text{ m}^2 \cdot \text{g}^{-1}$ (pure solid, $\text{Mg}^{2+}(1.5\%)$, $\text{Mg}^{2+}(5\%)-\text{Zr}^{4+}(0.5\%)$), and with rapid stabilization at more than $50 \text{ m}^2 \cdot \text{g}^{-1}$ ($\text{Zr}^{4+}(1.5\%)$ and $\text{Mg}^{2+}(1\%)-\text{Zr}^{4+}(0.5\%)$). It is worth noting that the co-doped solid has the greater surface area, i.e. $60 \text{ m}^2 \cdot \text{g}^{-1}$ after 30 hours, versus $50 \text{ m}^2 \cdot \text{g}^{-1}$ for the Zr^{4+} doped solid, for which, however, no trace of alpha formation could be detected. This result may thus be described in terms of an effect of synergy between the two cations (see Fig. 3).

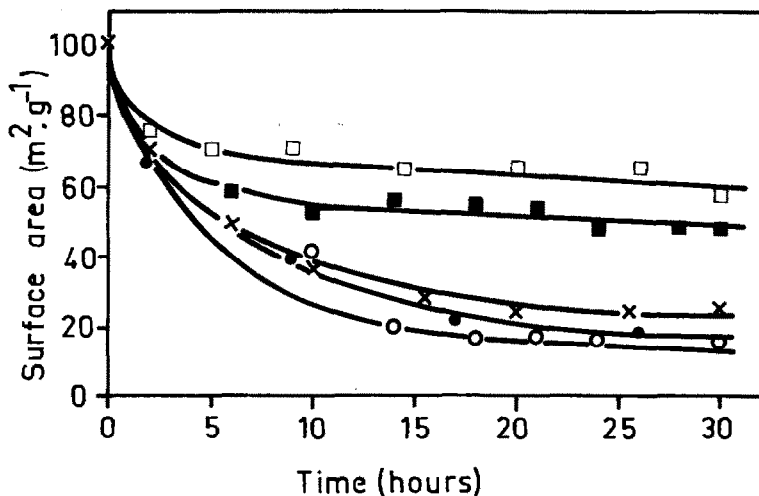


Fig. 2. Surface area as a function of calcination time at 1378 K: ● pure sample, ○ $\text{Mg}^{2+}(1.5\%)$, ■ $\text{Zr}^{4+}(1.5\%)$, □ $\text{Mg}^{2+}(1\%)-\text{Zr}^{4+}(0.5\%)$ and × $\text{Mg}^{2+}(5\%)-\text{Zr}^{4+}(0.5\%)$ doped samples.

The D.T.A. curves (Fig.4) show a substantial exothermic peak corresponding to the transformation into alpha alumina. Its maximum is shifted according to the added cation(s), as seen in the Table.

TABLE

Peak temperature from D.T.A. experiments for pure and doped alumina samples.

sample	pure	$\text{Mg}^{2+}(1.5\%)$	$\text{Mg}^{2+}(1\%)-\text{Zr}^{4+}(0.5\%)$	$\text{Zr}^{4+}(1.5\%)$
temperature	1554 K	1549 K	1599 K	1623 K

We also observed a second exothermic phenomenon represented by a small and broad peak at a lower temperature. It appears more distinctly in the case of the $\text{Zr}^{4+}(1.5\%)$ sample, i.e. when the transformation into corundum

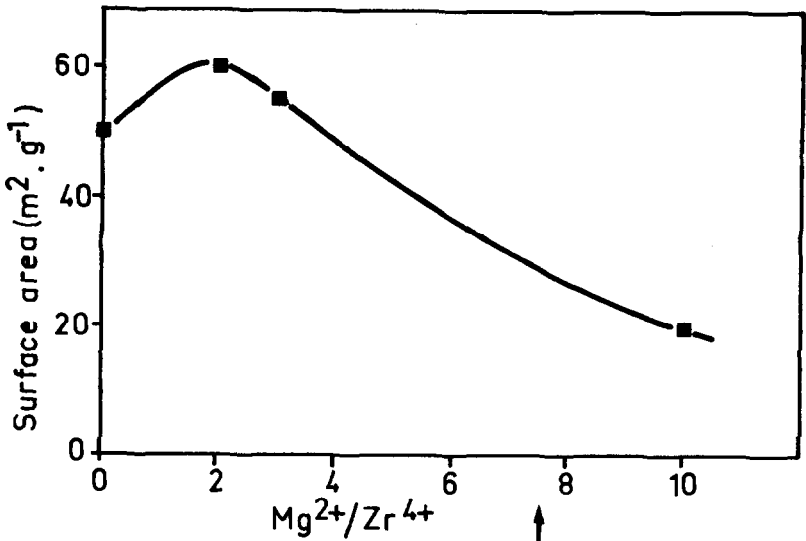


Fig. 3. Stabilized surface area after 30 hours at 1378 K for Zr⁴⁺(0.5%) co-doped aluminas as a function of Mg²⁺ content.

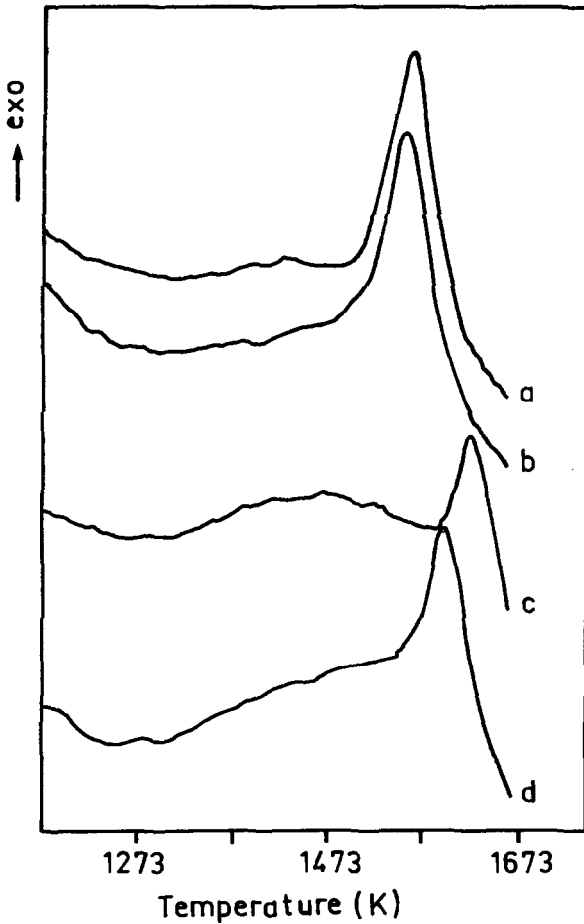


Fig. 4. D.T.A. curves obtained for :
 (a) pure alumina,
 (b) Mg²⁺(1.5%),
 (c) Zr⁴⁺(1.5%) and
 (d) Mg²⁺(1%)-Zr⁴⁺(0.5%) doped aluminas.

takes place at much higher temperatures. Its origin is now being investigated.

The results can be discussed with the help of the theoretical model of the influence of the dopes described in reference 1. The transformation of transition aluminas into alpha alumina was depicted as the annihilation of the cationic and anionic vacancies of the spinel-like structure. The influence of dopes on the kinetics of transformation could be theoretically predicted from the charge and the ionic radius of the inserted cation. Our present findings for Mg^{2+} and Zr^{4+} doped alumina are in agreement with the predictions of this model for all the samples, except for $Mg^{2+}(1.5\%)-Zr^{4+}(0.5\%)$ and $Mg^{2+}(5\%)-Zr^{4+}(0.5\%)$ (observed effect: inhibitor; predicted: none and accelerator respectively). This disagreement points out the problem of the range of validity of the model for which the initial alumina had to be nearly dehydroxylated.

It is well known that gamma alumina transforms into alpha alumina through the sequence $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$. Of these, θ -alumina corresponds to the most dehydroxylated form. The results suggest that dopes may also influence the transformation of the transition alumina before $\theta \rightarrow \alpha$. Indeed, using detailed characterization by X-ray diffraction we observed, for a constant rate of transformation into alpha alumina, that the mixtures of the remaining aluminas were different for each doped alumina. Since the decrease in surface area is due to the overlapping of two successive phenomena ($\gamma \rightarrow \theta$ and $\theta \rightarrow \alpha$ transformations), the maximum observed on Fig.3 may come from the effects of the Mg^{2+} and Zr^{4+} cations on the $\gamma \rightarrow \theta$ transformation. Current studies are being developed to obtain a complete description of these phenomena.

Influence of water vapour pressure

The curves for the transformation into alpha alumina at 1403 K of the pure sample under various water vapour pressures are shown in Fig.5. The highest transformation rate is observed under 15 torr of air (curve 4) though the slowest is obtained when calcination is performed under 10^{-2} torr vacuum (curve 1). When the calcination tube is first evacuated and water vapour admitted at 1 and 15 torr, the transformation takes place at an intermediate rate, that increases with the water vapour pressure (curves 2 and 3). The difference between the curves 4 and 3 may be due to water vapour diffusion when the reaction is performed in air.

Our D.T.A. experiments under dry and humid argon showed that the peak attributed to the transformation into alpha alumina is 6 (± 1) K lower with humid argon. This is in agreement with the accelerator effect of water vapour. Water vapour also had the same influence with regards to the change in surface area.

Some studies have reported the accelerator effect of water vapour in the initial sintering of oxides, such as MgO (ref.5). During their evolution to alpha, transition aluminas initially undergo a substantial decrease in

surface area, that most probably corresponds to transformation to θ phase (ref.1). Moreover, in their study of $\theta \rightarrow \alpha$ transformation, Wynnyckyj and Morris (ref.6) proposed that θ crystallite size increase was the rate determining step.

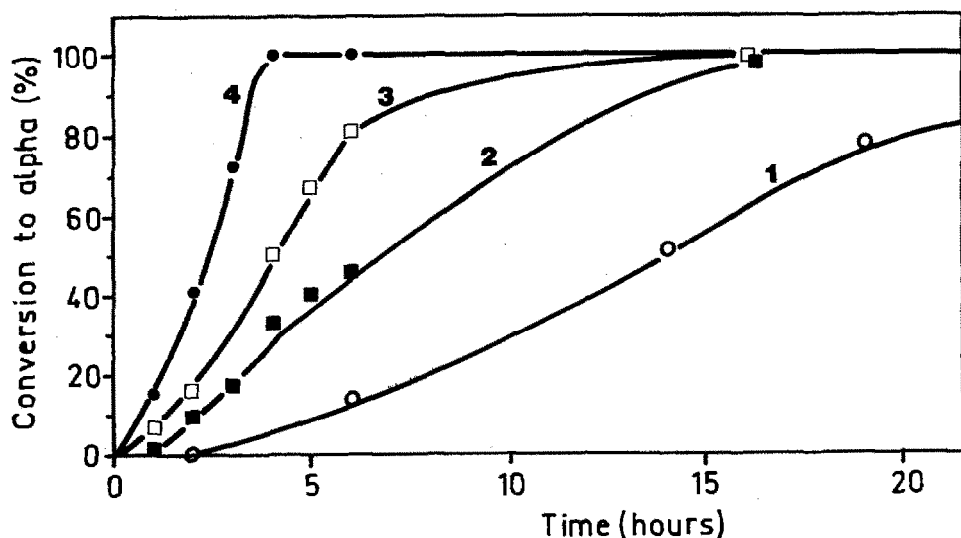


Fig. 5. Conversion to alpha alumina at 1403 K as a function of calcination time under vacuum (○), 1 torr (■) and 15 torr (□) of water vapour, and under static air at atmospheric pressure with 15 torr water vapour (●).

The influence of water vapour illustrated in Fig.5 can thus be interpreted as an accelerator effect on the transformations occurring before the structural rearrangement of oxygen and aluminium sublattices corresponding to alpha formation. The mechanisms of the interaction of water vapour throughout these transformations would also provide an interesting subject for closer investigation.

CONCLUSIONS

This study has brought out the effect of co-doping on the transformation of transition aluminas into alpha alumina. The behaviour of a particular $Mg^{2+}-Zr^{4+}$ co-doped sample was interesting, mainly on account of the stabilization of high surface area transition alumina. Moreover, the accelerating effect of water vapour has been shown. Further studies devoted to the understanding of these effects will pay special attention to the influence of dopes and water vapour on formation of the intermediate phases through the sequence $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$.

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