Thermochimica Acta, 62 (1983) 341–348
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

DEHYDRATION KINETICS OF BAYERITE PREPARED IN THE PRESENCE AND ABSENCE OF GUM TRAGACANTH

R. KARIMIAN and D. DOLLIMORE *

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (Gt. Britain)

(Received 10 September 1982)

ABSTRACT

The kinetics of the dehydration of two samples of bayerite which were prepared in the presence and absence of gum tragacanth has been studied by isothermal mass loss method. The isothermal decomposition data carried out at five different temperatures in the range between 176 and 205°C fitted a Gurstling and Brounshtein equation. It is found that the presence of gum tragacanth has no influence on the form of the kinetic equation. An activation energy of about 120 kJ mole^{-1} has been found for the dehydration of the sample prepared in the presence of the gum and 88 kJ mole^{-1} for the dehydration of the sample prepared in the absence of the gum.

INTRODUCTION

The adsorptive and catalytic properties of alumina have been the subject of numerous fundamental studies. It is known [1] that the important variables for the adsorptive and catalytic activities such as crystal structure, pore texture and the chemical nature of the surface are largely determined by minute procedural differences in the preparation of the alumina. In particular, it has been reported that the presence of organic materials during preparation may influence the nature of the product [2–4]. The initial product is usually a hydrated oxide. The aluminas are then produced by a calcination process from either a crystalline hydroxide or an amorphous or poorly crystalline gel [4–6].

The influence of gum tragacanth on the nature of the products in alumina preparation, crystallinity, thermal stability, specific surface area and pore size distribution of the product, has been described previously [7].

In the present work, an attempt has been made to study systematically the influence of the preparation conditions of bayerite on the kinetics of dehydration.

---

* Present address: Department of Chemistry, University of Toledo, OH 43606, U.S.A.

0040-6031/83/0000–0000/$03.00

EXPERIMENTAL

Preparation of the samples

Precipitates were obtained by bubbling carbon dioxide through sodium aluminate solutions under conditions of constant concentration, pH and gas flow rate. Solution A was prepared by dissolving the appropriate amount (60 g) of sodium aluminate in 500 ml of freshly prepared gum tragacanth (250 p.p.m.) solution. Samples prepared using this solution are designated A. Solution B was prepared by dissolving the appropriate amount (60 g) of sodium aluminate in 500 ml of distilled water only. Samples prepared using this solution are designated B. An atmosphere of carbon dioxide was then passed through the solutions at a flow rate of 30 ml min^{-1}. Bubbling of carbon dioxide was stopped when the solution reached pH = 9.5. The resulting precipitates were filtered, washed and then dried overnight at 120°C. The precipitates were crushed and sieved to 45–75 μm.

Identification and characterization of the samples

The X-ray diffraction data for the samples were obtained using a Philips generator, type PW1010. The *d* spacings were calculated using the Bragg equation. Identification of samples was made by reference to the data given by Lippens and Steggerda [1] for aluminium hydroxides.

The adsorption isotherms were obtained by measuring the volume of nitrogen adsorbed by the samples at a series of equilibrium pressures. The volumetric adsorption apparatus was based on that described by Faeth [8] with slight modifications.

The thermal dehydration of the samples was observed in terms of mass loss by using a Stanton Redcroft Thermobalance, model TG 750. An atmosphere of dry air was passed into the furnace at a flow rate of 50 ml min^{-1}.

Both the thermogravimetric (TG) experiments and the isothermal heat treatments involved weighing the sample into a crucible which was placed on the thermobalance. In the TG experiments, the furnace was raised, the balance mechanism was released, and after allowing 15 min for air to purge the system, the temperature was increased to 1000°C at a rate of 5°C min^{-1}. In the isothermal experiments, the temperature was raised by 5°C min^{-1} and then kept constant for 30 min at the appropriate temperature. The mass loss was then recorded by reference back to the mass loss at the end of the plateau representing the loss of sorbed water.

RESULTS AND DISCUSSION

X-Ray diffraction examination of the samples prepared in the presence and absence of gum tragacanth was carried out in order to identify the form

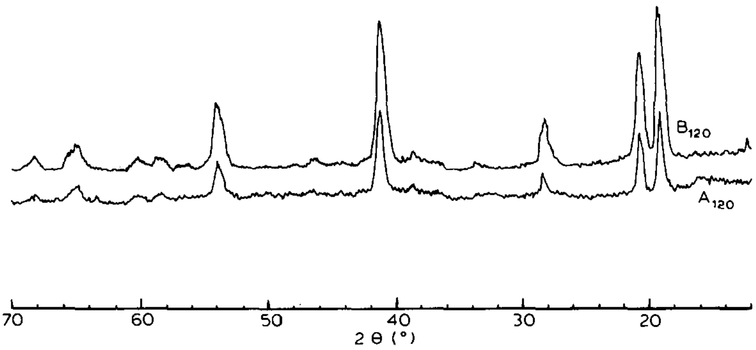
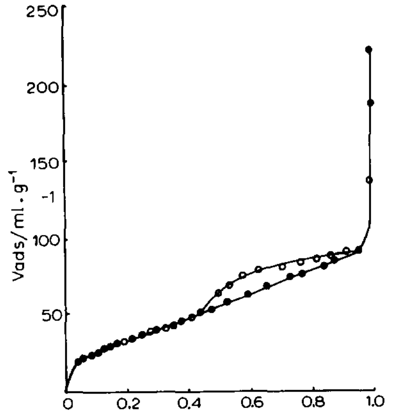


Fig. 1. X-Ray diffraction patterns obtained for precipitates A and B.

of the prepared aluminas. The X-ray diffraction patterns for the two precipitates are shown in Fig. 1. A comparison of the corresponding *d* spacings and intensities for the samples with the data given by Lippens and Steggerda [1] suggests that the precipitated aluminium hydroxides are bayerite modifications. Figure 1, however, shows that the diffraction lines for bayerite sample B, which was prepared in the absence of the gum, are sharp and this suggests a good crystallinity, whereas for sample A, which was prepared in the presence of the gum, the diffraction lines become more diffuse and of lower intensity, probably due to poor crystallinity.

The adsorption isotherms of nitrogen obtained for samples A and B are shown in Figs. 2 and 3, respectively. Sample B appears to be reversible so that hysteresis is absent. The adsorption isotherm obtained for sample A, however, is reversible only at low relative pressures (< ca. 0.42) and a hysteresis loop is present over the whole of the higher relative pressure range



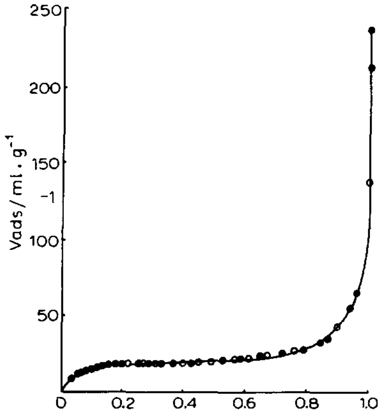


Fig. 2. Nitrogen adsorption isotherm on sample A.

Fig. 3. Nitrogen adsorption isotherm on sample B.

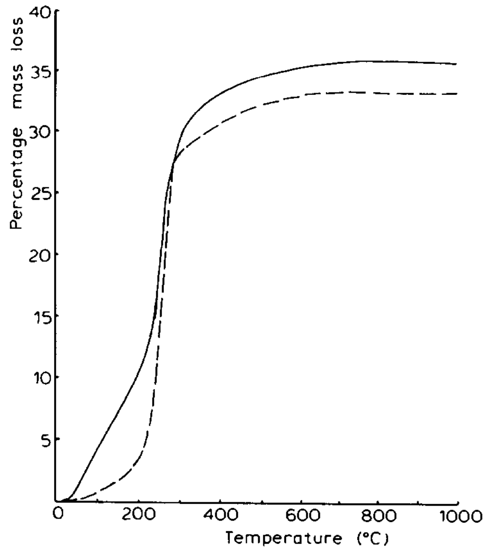


Fig. 4. Thermogravimetric curve of samples A (———) and B (- - - - -).

up to 0.98. The appearance of the hysteresis in the adsorption isotherm obtained on sample A may be attributable to either the existence of the pores in the gum present in the sample, or the appearance of pores produced due to the evaporation of the weakly bonded water content of the sample by both evacuation and heating at 120°C overnight.

The thermal behaviour of the samples A and B was observed in terms of mass loss against temperature. Typical thermogravimetric curves for the decomposition of the samples are shown in Fig. 4 as percentage mass loss against temperature. There is a mass loss of 12% for sample A and 4% for B. This loss is attributable to the evaporation of sorbed water from the samples. Such significant difference in the water content of the samples is probably due to the presence of gum tragacanth in the structure of sample A which, in turn, absorbs large quantities of water. The second and the major mass loss begins at 230°C for both samples in which aluminium hydroxide (bayerite) decomposes to η-Al_2O_3. This corresponded to about 23 and 29% of the initial sample mass for A and B, respectively.

Kinetics of dehydration

Isothermal mass change determinations were carried out in dry air at temperatures between 167 and 205°C. The results of the experiments for samples A and B are shown in Figs. 5 and 6, respectively, as percentage mass loss against time of heating.

The technique, already outlined, of bringing the samples to an appropriate temperature at a rate of 5°C min^{-1}, keeping it constant for 30 min and then

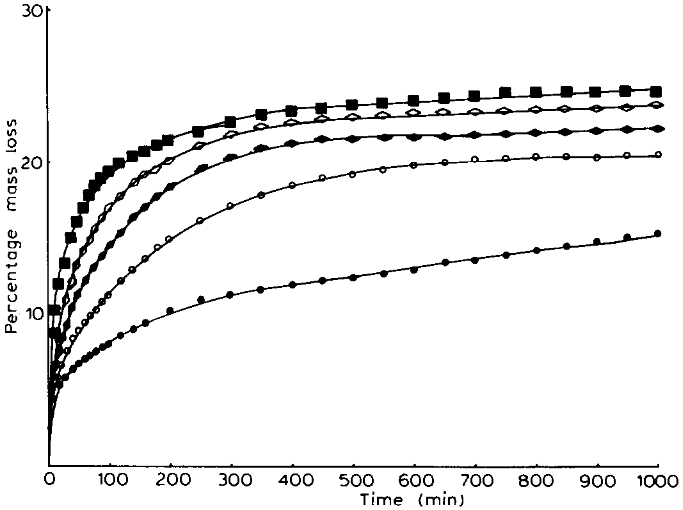


Fig. 5. Plots of mass loss against time for the isothermal dehydration of A in dry air. ●, 176°C; ○, 186°C; ◆, 190°C; ◇, 197°C; ■, 205°C.

raising it very quickly to the desired temperature was used for the isothermal experiments. It was found that an appropriate temperature was 140°C. This meant that the sorbed water forming the first mass loss in the TG curves (Fig. 4) was eliminated and the second mass loss region is the only stage remaining to be studied. The total percentage mass loss (M_t) in this second stage at any temperature was determined by allowing the run to continue for over 16 h and constructing a graph of mass loss against reciprocal time, extrapolating it to $1/t = 0$ in order to estimate M_t.

The isothermal data for each sample were plotted in the standard kinetic

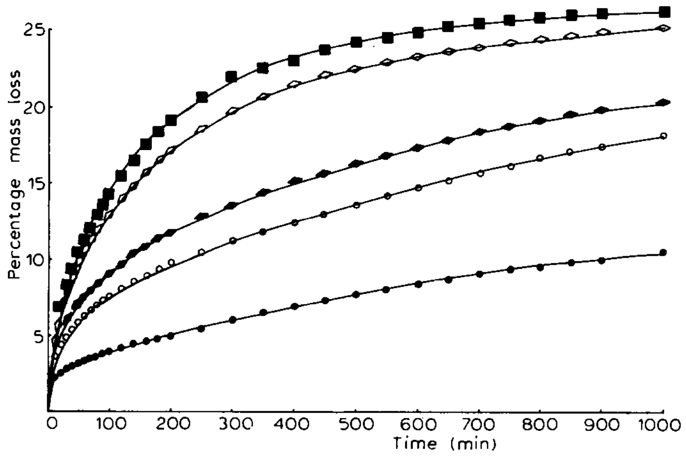


Fig. 6. Plots of mass loss against time for the isothermal dehydration of B in dry air. ●, 170°C; ○, 179°C; ◆, 186°C; ◇, 192°C; ■ 199°C.

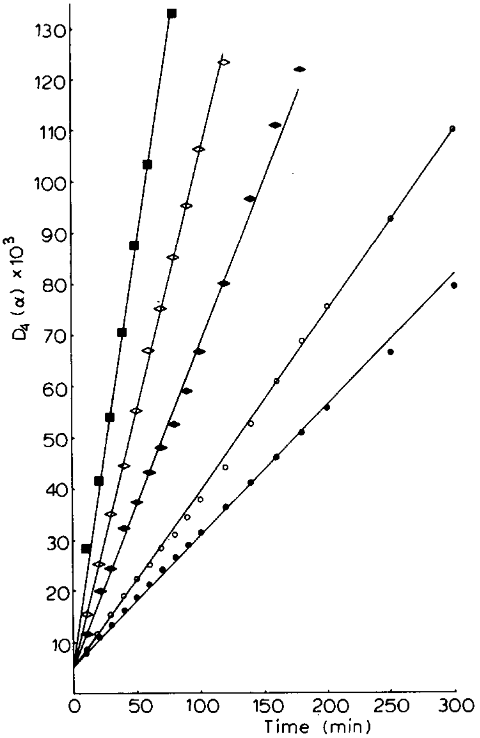


Fig. 7. Plots of $D_4(\alpha)$ against time for isothermal dehydration of A in dry air. ●, 176°C; ○, 186°C; ◆, 190°C; ◇, 197°C; ■ 205°C.

form [9] as degree of decomposition, α, against reduced time $t/t_{0.5}$, where α is the mass loss at time t divided by total mass loss and $t_{0.5}$ is the time when $\alpha = 0.5$. When plotted in this way, the data fitted a common curve at any temperature.

Analysis of the kinetic data shows that the data fit the Ginstling and Brounshtein equation of diffusion control, D_4 (α).

$$D_4(\alpha) = \left(1 - \tfrac{2}{3}\alpha\right) - (1 - \alpha)^{2/3} = Kt \qquad (1)$$

Figures 7 and 8 show that the derived plots of $D_4(\alpha)$ against time, in every case investigated, give straight lines, the slopes of which represent K.

The fact that the preparation conditions did not affect the diffusion control mechanism for the dehydration of the samples is of particular interest. However, the data obtained for the dehydration of A showed higher values for the rate of dehydration than those obtained for B.

The application of the Arrhenius equation, i.e.

$$K = A \exp(-E/RT)$$

where K = the rate constant, E = the activation energy, R = the gas constant, and T = the isothermal temperature in degrees Kelvin, allows the activation

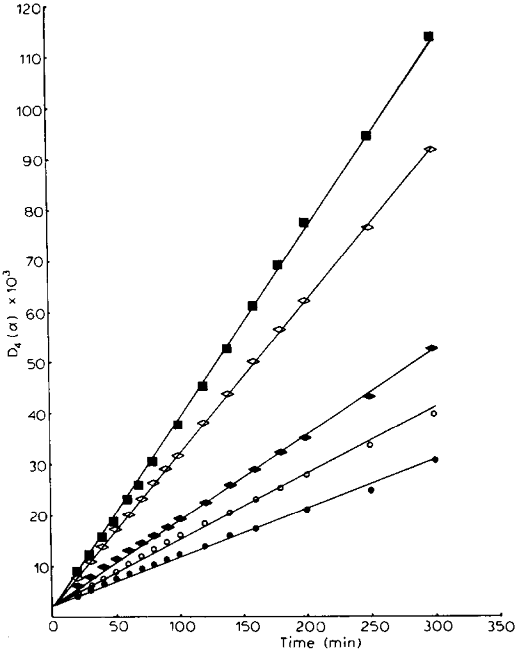


Fig. 8. Plots of $D_4(\alpha)$ against time for isothermal dehydration of B in dry air. ●, 170°C; ○, 179°C; ◆, 186°C; ◇, 192°C; ■ 199°C.

energy to be calculated. Plots of ln K against $1/T$ are linear and shown in Fig. 9.

The values of the activation energy calculated from the slopes of the plots presented in Figs. 7 and 8 are 120.4 and 88.7 kJ mole^{-1} for samples A and B, respectively.

As stated before, although the presence of the gum (in the course of preparation of sample A) did not influence the diffusion-controlled mecha-

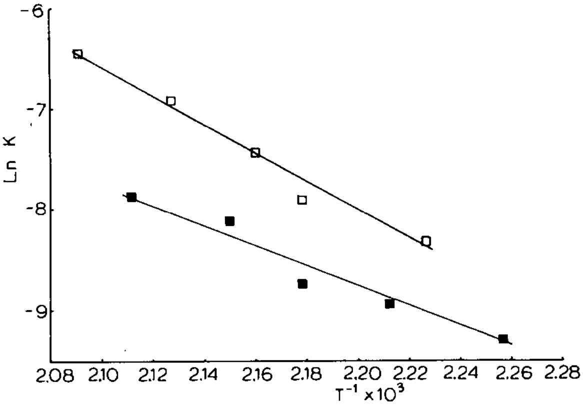


Fig. 9. Arrhenius plots for the dehydration of A (■) and B (□) in dry air.

nism, a significant difference in the activation energy obtained for A and B is observed.

REFERENCES

1 B.G. Linsen (Ed.), Physical and Chemical Aspects of Adsorbents and Catalysts, Academic Press, London, New York 1970.
2 G.C. Bye and J.G. Robinson, J. Appl. Chem., 17 (1967) 138.
3 D. Aldcroft and G.C. Bye, Proc. Br. Ceram. Soc., 13 (1969) 125.
4 D. Aldcroft, G.C. Bye, J.G. Robinson and K.S.W. Sing, J. Appl. Chem., 18 (1968) 301.
5 J.H. de Boer and B.C. Lippens, 2nd Int. Congr. Surf. Activity, Butterworths, London, 1957, p. 93.
6 J.H. de Boer and B.C. Lippens, J. Catal., 3 (1964) 38.
7 R. Karimian, Ph. D. thesis, University of Salford, 1982.
8 P.A. Faeth, Adsorption and Vacuum Techniques, Institute of Science and Technology, The University of Michigan, Oct. 1962, 58 pp.
9 J.H. Sharp, G.W. Brindley and B.N.N. Achar, J. Am. Ceram. Soc., 49 (1966) 379.