Journal of Thermal Analysis, Vol. 367(1991) 267-275

KINETICS AND HYDROTHERMAL TRANSFORMATION OF GIBBSITE

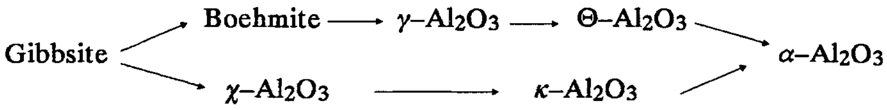
S. K. Mehta and A. Kalsotra

*REGIONAL RESEARCH LABORATORY, JAMMU - TAWI INDIA

(Received March 14, 1990; in revised form July 28, 1990)

The transformation of gibbsite have been studied under hydrothermal influence. Results of the X-ray diffraction analysis of the samples heated at different temperatures from 170°C to 265°C are also discussed in detail. The percentage of the boehmite phase formed, due to the transformation of the gibbsite, have been determined by comparing the intensity of the most strongest reflection of the boehmite phase with a fully transformed sample. The activation energy value calculated form X-ray diffractograms is almost comparable with the value calculated from main DTA endotherm of gibbsite.

The thermal transformation of aluminium hydroxide had been the subject of numerous investigator [1-8]. From all these studies it had been established that gibbsite transforms to α-alumina via boehmite and χ-alumina routes;



The possible explanation for the two way transformation has also been put forward by Goswami and Gupta [9]. Some of the authors have also reported [10-12] that submicron sized gibbsite transform to α-alumina via χ-alumina and κ-alumina routes. Presently the authors have studied the transformation of gibbsite under hydrothermal atmosphere. The percentage

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* RRL Contribution No. 2028.

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of the boehmite phase formed at different stages of heat treatment have also been reported. In this investigation a systematic study has been carried out and activation energy values of boehmite formed were calculated and compared with the values obtained from DTA endotherm.

Experimental

The gibbsite used in the present investigation was supplied by Messers Aluminium Corporation, Muri (Bihar). The raw sample was powdered and passed through 200 B. S. S. mesh. The powdered sample was subjected to hydrothermal treatment in an autoclave (Chas W. Cooks & Sons Birmingham). The temperature rise was maintained at the rate of 2 deg/min. The X-ray analysis was carried using Phillips Powder diffractometer (PW 1350) having microprocessor attachment (PW 1710). This microprocessor is the control unit of the diffractometry system. It also print out the output of the scan (peak angle 2Θ, dÅ value and peak intensities in term of counts per second). The scanning speed of the Goniometer was maintained at 1 degree in 2 Θ/min. The CuK$_\alpha$ radiation (40 kV, 20 mA) was used for all runs. The differential thermal analysis was carried using MOM derivatograph at a linear heating rate of 10 deg/min.

Result and discussion

Figure 1 represents the DTA curve of the gibbsite. The endotherm temperatures are in well agreement with the previous reported differential thermal curves of gibbsite. Table 1 includes the intensities and interplaner-spacings of gibbsite sample. The intensities of the lines are recorded interms of maximum number of counts per second. The dÅ values and intensities are in agreement with the standard ASTM data cards. As per the findings of Goswami and Gupta [9] this type of gibbsite can be indexed as well crystalline gibbsite.

For studying the hydrothermal transformations the sample of gibbsite has been heated in an autoclave at different temperatures ranging from 170° to 265°. After each stage the sample was taken out from the autoclave, filtered, dried in an electric oven at 60° and then subjected to X-ray diffraction analysis. Figure 2 represents the intensities of some of the basal spacings of gibbsite and boehmite phases at different temperatures. It is seen from the figure that intensity of (002) line of gibbsite (which is most prominent line of gibbsite) goes on decreasing where as the intensity of (020) line of boehmite (most strongest line of boehmite phase) goes on increasing with respect to temperature and attains a maximum value of 13000 counts/sec at 265^0 there is also a similar behaviour in intensities of other reflections of gibbsite and boehmite.

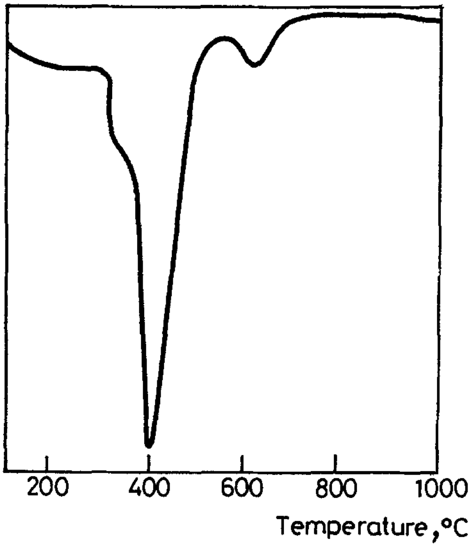

Fig. 1 Differential thermal analysis curve of gibbsite at normal atmosphere

The thermal transformation of gibbsite to α-alumina has been studied by many researchers [13-16] and a number of sequences of transformation were suggested. According to Goswami and Gupta [9] poorly crystalline transforms to α-alumina via χ-alumina sequence while the well crystalline gibbsite follows the following two way sequence of transformation;

$$\begin{tikzcd}
 & \chi\text{-}Al_2O_3 \arrow[rr] & & \kappa\text{-}Al_2O_3 \arrow[dr] & \\
\text{Gibbsite} \arrow[ur] \arrow[dr] & & & & \alpha\text{-}Al_2O_3 \\
 & \text{Boehmite} \arrow[r] & \gamma\text{-}Al_2O_3 \arrow[r] & \Theta\text{-}Al_2O_3 \arrow[ur] &
\end{tikzcd}$$

The possible explanation put forward by Lipens [17], for the two way transformation is; that in the presence of water vapour gibbsite transforms to boehmite while the absence of hydrothermal influence causes the gibbsite to transform to χ-Al_2O_3. De Boer *et al.* [18] showed that hydrargillite dehydrated to χ-alumina under normal condition of water vapour pressure and to boehmite under hydrothermal conditions. Sealfeld [19] concluded that large crystallites of hydrargillite follows the sequence boehmite, γ and Θ-aluminas under hydrothermal conditions and additionally the sequence χ, κ and α-aluminas during atmospheric heating. Further the formation of boehmite phase and microporous alumina during thermal decomposition of hydrargillite at low pressure was also examined by Rouquerol *et al.* [20]. Goswami and Gupta [9] reported that outer peri-pheri of large crystallite of gibbsite at 300^0 transform to χ-alumina and this χ-alumina builds up hydrothermal atmosphere inside the crystallite causing the inside core to transform to boehmite.

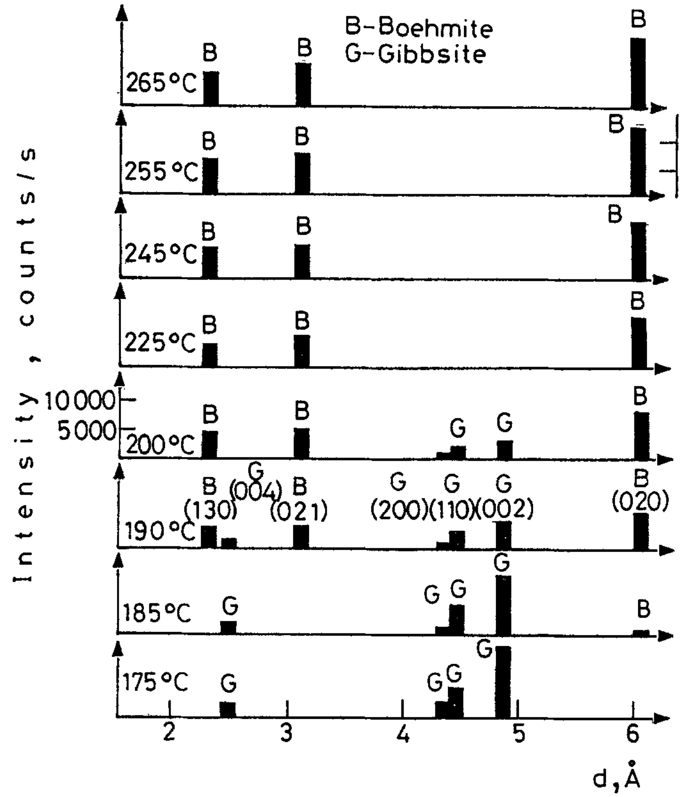

Fig. 2 Change in the intensities of some of the basal spacings of boehmite and gibbsite with the increase of temperature in hydrothermal atmosphere

Table 1 Interplaner spacings of gibbsite at room temperature

d, Å	*I*	*hkl*
4.83	13743	002
4.36	4993	110
4.31	2327	200
3.306	1200	112
3.177	995	$11\bar{2}$
3.108	488	
2.456	1642	021
2.4221	1069	004
2.3827	2382	$31\bar{1}$
2.288	582	312
2.243	838	022, $21\bar{3}$
2.162	952	$31\bar{2}$
2.61	694	
2.084	169	114
2.047	1642	313
1.993	1115	023
1.916	825	$41\bar{1}$
1.804	1295	$31\bar{4}$
1.751	1005	024
1.684	1011	314
1.658	320	$22\bar{4}$
1.592	270	224, $51\bar{1}$
1.597	291	422, 512

d, Å = Interplanar spacing
I = Intensities in counts / sec.
hkl = Miller indices

It is quite clear from Fig. 2 that at 175° the intensity of most prominent line of gibbsite (002) 4.85 Å is 11997 counts, at 200° it is 2437 counts and vanishes completely at 225°. There is no reflection of boehmite at 175° but at 190° the intensity of (020) reflection of boehmite phase is 6402 counts which increase gradually and becomes 11858 counts at 258°. This shows that after 190° boehmite phase is in the process of crystallisation and can be described on the lines put forward by Rao and Rao [21]. The well developed, and distinct, lines having pronounced intensities at 265° shows that there is complete growth of the boehmite phase. This may be conjectured that in hydrothermal atmosphere gibbsite transforms to boehmite at much lower temperature 190° as compared to gibbsite transforming to boehmite when heated at 300° in a normal atmosphere [9]. Figure 3 shows X-ray diffractogram of one of the gibbsite sample heated at 300^0 under normal atmosphere. It is observed from the figure that boehmite lines are very sharp and the values of intensities are in good agreement with the values of sample heated hydrothermally at 265^0, more over additional lines due to χ-Al_2O_3 have have also appeared in the diffractogram. So based on the observations the conclusion may be drawn that hydrothermal atmosphere is responsible for the complete decomposition of gibbsite to boehmite only. The DTA endotherm at 290^0 and 340^0 indicates the transformation of gibbsite to boehmite and χ-Al_2O_3. The diffrential curves was taken at normal atmosphere.

The kinetics of gibbsite has been reported by Eyraud and Gotam [22].

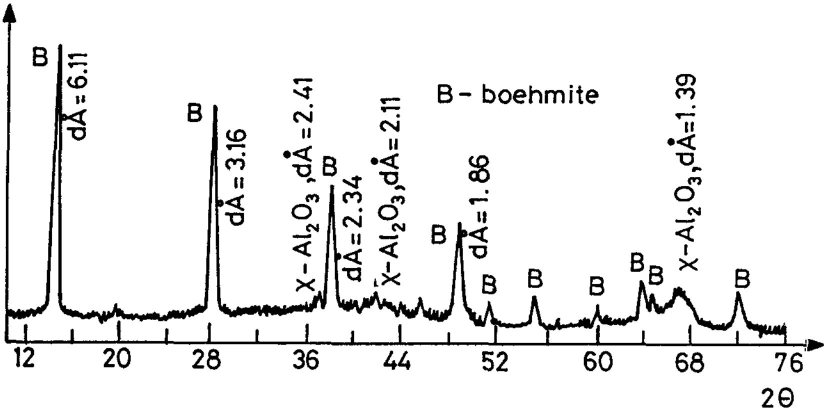

Fig. 3 X-ray diffractogram of gibbsite heated to 300°C at normal atmosphere

Goswami [12] *et al.* have studied the dehydration reactions of gibbsite and reported the activation energies calculated from DTA and TG curves. In the present investigation the kinetics have also been reported from X-ray diffraction results. All the samples were heated in an autoclave, using hydrothermal atmosphere, for selected interval of time at a particular temperature. After the required heat treatment the samples were analysed by X-ray diffraction technique. The amount of boehmite phase formed was calculated by comparing the intensity of basal spacing (020) of boehmite with the intensity of the same peak of a fully transformed sample (which has been heated hydrothermally at 265^0). The five X-ray measurements for each sample showed that the boehmite formed could be determined to an accuracy of ±5% (Gross and Martin [23]).

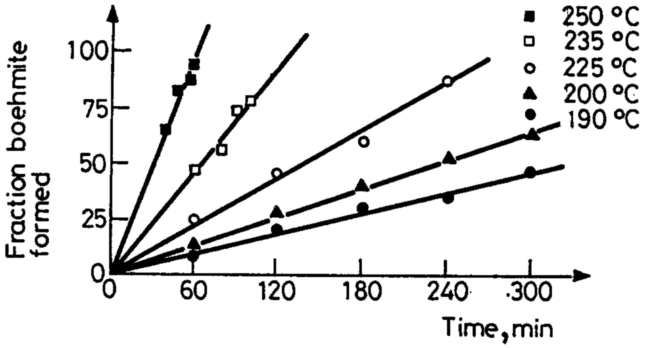

Fig. 4 Plot of the fraction of boehmite formed *vs.* time in the gibbsite to boehmite transformation, (hydrothermal atmosphere), for different temperatures

Figure 4 shows the linear dependence of the fraction of boehmite phase formed from gibbsite on hydrothermal treatment as a function of time, at various temperatures. The rate constant K can be calculated from;

$$\mathrm{d}c/\mathrm{d}t = K$$

where c is the fraction of boehmite formed at any time t. The values of K were calculated for all temperatures investigated. Figure 5 represents the semi log plot of K *vs.* the reciprocal of temperature (T). The scatter of points has been approximated to straight line and from the slope of the line the activation energy was calculated which comes out to be 16.579 Kcal/mole. This value is in agreement with the values reported by Goswami [12] *et al.* for well crystalline sample. To suppliment the results, the activation energy value has also been calculated from the main endothermic peak of DTA curve of Fig. 1 using Piloyans [24] method;

$$\log \Delta T = C - \frac{E}{23RT}$$

where ΔT is the deviation from base line. The activation energy value calculated from the slope of Fig. 6 is 17.49 Kcal/mole and this value is comparable with the value calculated from X-ray results.

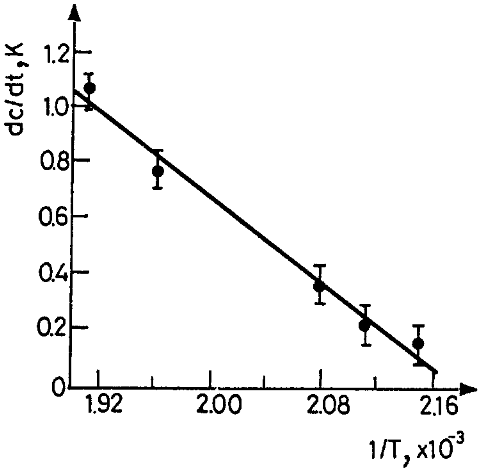

Fig. 5 Plot of rate constant *K* vs. inverse of temperature (*T*)

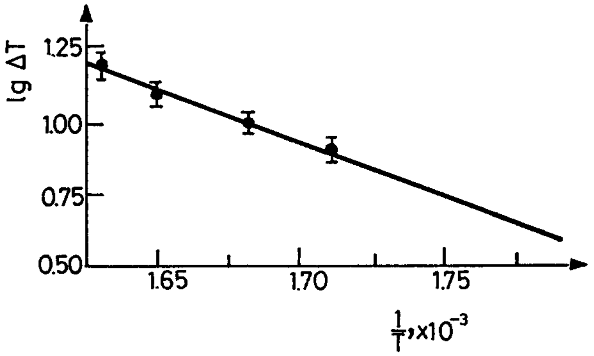

Fig. 6 Arrhenius plot using the Piloyan's[24] method

Conclusion

From the study of hydrothermal treatment of gibbsite the following conclusions can be drawn;

i) Gibbsite starts transforming to boehmite at 190° and completely transforms to boehmite at 250°.

ii) The activation energy values calculated from X-ray diffraction studies of boehmite phase formed are in well agreement with the previous reported results.

iii) Hydrothermal atmosphere is responsible to the transformation of gibbsite to boehmite structure only and not to χ-alumina.

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Authors are thankful to Director, Regional Research Laboratory, Jammu for his kind permission and encouragement to publish this paper. Thanks are also due to H. C. Gupta for typing the manuscript.

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Zusammenfassung — Es wurde die Umwandlung von Gibbsit unter hydrothermalem Einfluß untersucht. Weiterhin werden auch Ergebnisse der Röntgendiffraktionsanalyse an den bei verschiedenen Temperaturen zwischen 170°C und 265°C erhitzten Proben besprochen. Durch Vergleich der Intensität der stärksten Reflexion der Böhmitphase mit einer vollständig umgewandelten Probe wurde der prozentuelle Anteil der während der Umwandlung von Gibbsit gebildeten Böhmitphase bestimmt. Der Wert für die Aktivierungsenergie, berechnet aus den Röntgendiffraktogrammen ist annähernd vergleichbar mit dem aus der DTA von Gibbsit berechneten Wert.