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Rehydration of transition aluminas obtained by flash calcination of gibbsite

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Abstract

Thermokinetics of heat evolution during the rehydration of transition aluminas using an isothermal differential microcalorimeter is presented. The transition aluminas have been prepared by flash calcination of gibbsite. The results obtained are discussed in relation to phase transitions connected with the crystallization of amorphous aluminum gels that are formed during the contact of water with the surface of transition aluminas. During rehydration they transform into more orderly pseudoboehmite gels. The final stage of the hydration, especially at $pH \geq 10$, is crystalline $Al(OH)_3$, mainly bayerite.

Keywords: Transition aluminas; Alumina carriers; Rehydration process; Flash calcination; Calorimetry

1. Introduction

Transition aluminas (TA) obtained from gibbsite by flash calcination are commonly used for production of catalyst carriers and adsorbents. By heating gibbsite at 400–800°C for less than 1 s, quasi-amorphous products with the general composition $Al_2O_3{*}xH_2O$ (where $0.2 \leq x \leq 1$), are obtained. The TAs obtained in this way are fundamentally different from products obtained by gradual calcination of gibbsite. They are strongly defective, have increased surface energy, and exhibit higher chemical reactivity [1–12]. During contact with water they rehydrate, transforming partly into sols and gels, and further they crystallize with the formation of phases of aluminum hydroxides. Those reactions are exothermic. During rehydration, particles of TAs undergo deep morphological transformations [13]. In general, depending on temperature, time and pH of the environment, the following transformations occur [14,15]:

$$\begin{aligned}\mathrm{TA} + \mathrm{H_2O} &\rightarrow \text{amorphous gel}\\ &\rightarrow \text{pseudoboehmite} \rightarrow \text{boehmite}\\ &\rightarrow \text{bayerite}[\mathrm{Al(OH)_3}]\end{aligned}$$

In the literature, there are several reports about phenomena that occur during the rehydration of TAs, yet they are limited to a description of changes in the phase composition and morphology of particles [16–20]. Only Huang and Kono [21] have studied the kinetics of heat emission during the rehydration, but this investigation was carried out only during the preliminary period below 1 h. It was interesting to study the kinetics of that reaction using an isothermal calorimeter and to demonstrate whether this method might be useful in monitoring or controlling the process of rehydration.

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2. Experimental

2.1. Materials

A gibbsite from the Groszowice (Poland) cement plant was the raw material. TA samples were obtained by flash calcination of the gibbsite in a laboratory rotary pipe furnace at 500°C and 700°C (samples TA-500 and TA-700, respectively) with a residence time of 1 s in the heated zone. The TA were ground without access of moisture reaching an average size of grains of about 10 μm [22].

2.2. Method.

The kinetics of heat emission during the rehydration of active aluminum oxides were measured on a computerized isothermal calorimeter. The calorimeter consists of a two-part body that makes it possible to close samples hermetically. Because of the capability of achieving greater accuracy, measurement in the differential configuration was applied, using quartz sand as a standard. For maintaining the calorimeter at constant temperatures a water thermostat was used that kept the temperature with the accuracy of 0.01°C. The construction details of the calorimeter have been published [23]. The phase composition of rehydrated products was determined on a DRON-3 X-ray diffractometer, using Cu K_α radiation. Thermal analysis was done on a Q-Derivatograph MOM-Budapest instrument. The contents of bayerite in the samples during rehydration were determined by thermogravimetry (TG). Changes in the morphology of particles during rehydration were observed using transmission electron microscopy (TEM) TESLA BS-500.

3. Results and discussion

The curves of the heat evolution rate and the cumulative amount of heat evolved as a function of the time of rehydration of TA-500 and TA-700 sam-

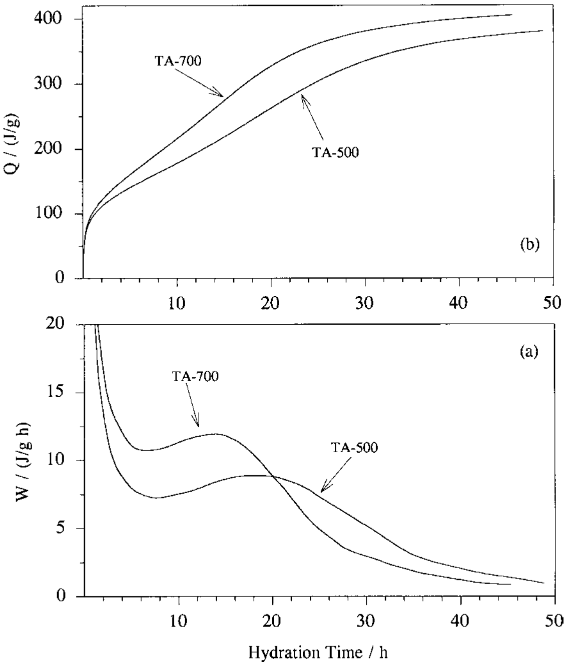

Fig. 1. Rehydration heat emitted in isothermal differential calorimetry for TA-500 and TA-700 samples, hydrated at 25°C with powder–water mass ratio (P/W)=1: (a) heat evolution rate as a function of hydration time; (b) integral heat evolution as a function of hydration time.

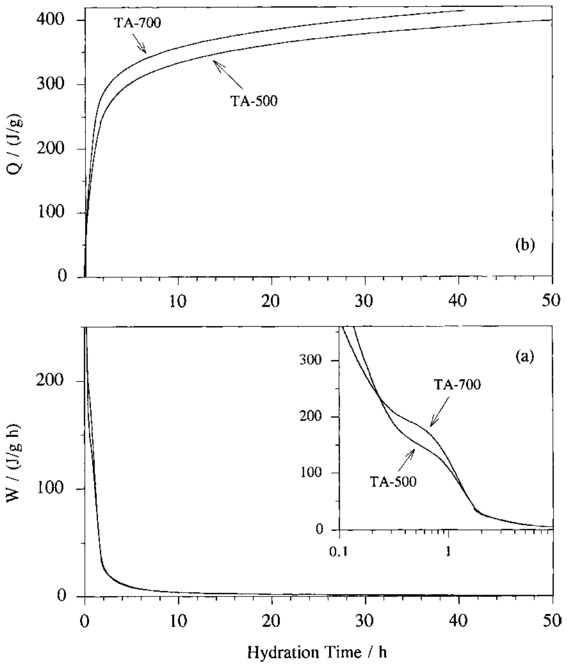

Fig. 2. Rehydration heat emitted in isothermal differential calorimetry for TA-500 and TA-700 samples, hydrated at 50°C with powder–water mass ratio (P/W)=1: (a) heat evolution rate as a function of hydration time; (b) integral heat evolution as a function of hydration time.

ples, with the powder–water mass ratio (P/W)=1 and the initial pH=10, are presented in Fig. 1 for the rehydration temperatures of 25°C and in Fig. 2 for 50°C. The process of heat emission during the rehydration at 25°C may be divided into four periods, similar to those proposed for the rehydration of inorganic binders and cements [24,25]. The first is a period of short-lived, intensive hydration, called the preliminary or pre-induction period. It is accompanied by a short, but very intense thermal effect. This is the result of the contact of TA with water. It represents the heat of wetting and heat of solution of a small number of surface layers of TA particles. As a result of this, an amorphous hydrate is formed in the form of a thin shell of gel on the external surface of particles and in their macropores. Morphological changes of the TA-700 particles that are occurring at the same time are illustrated in Fig. 3(a)–(d). In Fig. 3(b), small amounts of the gel formed on the surface of the particles are visible. This period lasts up to several

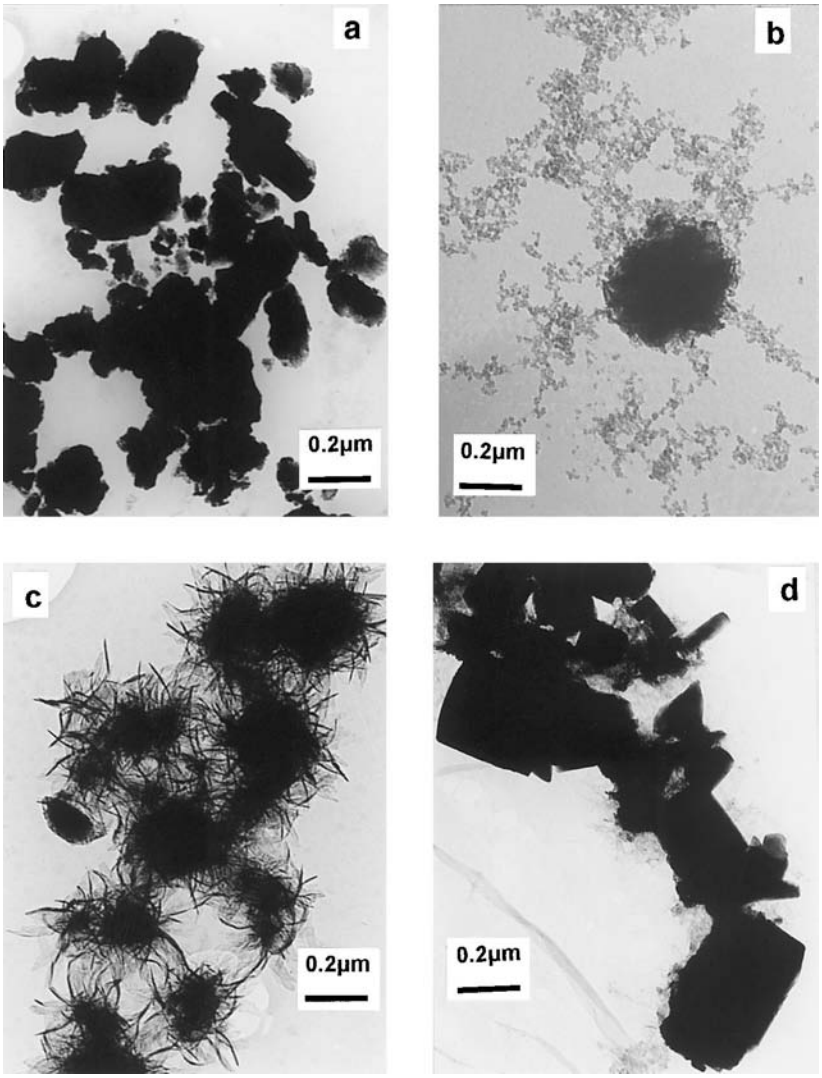

Fig. 3. TEM images of the raw TA-700 sample and rehydrated products from the TA-700 sample: (a) raw TA-700; (b) after 0.5 h rehydration at 25°C; (c) after 20 h rehydration at 25°C; (d) after 100 h rehydration at 25°C.

tens of minutes, and as was demonstrated by Huang and Kono [21], its length is connected with the size of TA grains. The second period, characterized by a low heat evolution rate, is called the induction period. The slowing down of the process of hydration is connected with a thin layer of gel hydrates formed around the grains of TA. At this stage that layer is so thick and dense that the possibility of diffusion of water molecules into deeper layers is strongly limited. The acceleratory period, begins after about 7 h and extends, depending on the temperature of the calcination of TA, up to 16–20 h. At this time, the speed of the rehydration increases, which is a result of breaking of the gel layer around the grains by osmotic pressure or as a result of syneresis [26]. As a result of this, the amount of gel formed in the external area increases, which favors a change of the morphology of particles into a system of fibrous needles growing radially out from the original TA particles. This phenomenon is illustrated in Fig. 3(c), where TA-700 particles are shown after 20 h of rehydration at 25°C. The maximum heat evolution rate during the third period occurs, in the case of TA-700, on 15 h, and in the case of TA-500, on 20 h. During the fourth stage, a systematic decrease of the rate of heat emission is observed. During this time the particles of needle morphology disappear and bigger $Al(OH)_3$ agglomerates are formed, which are presented in Fig. 3(d).

The course of rehydration of the same samples at 50°C is presented in Fig. 2. In principle, the process has the same course, but all the periods undergo significant shortening. The acceleratory period that

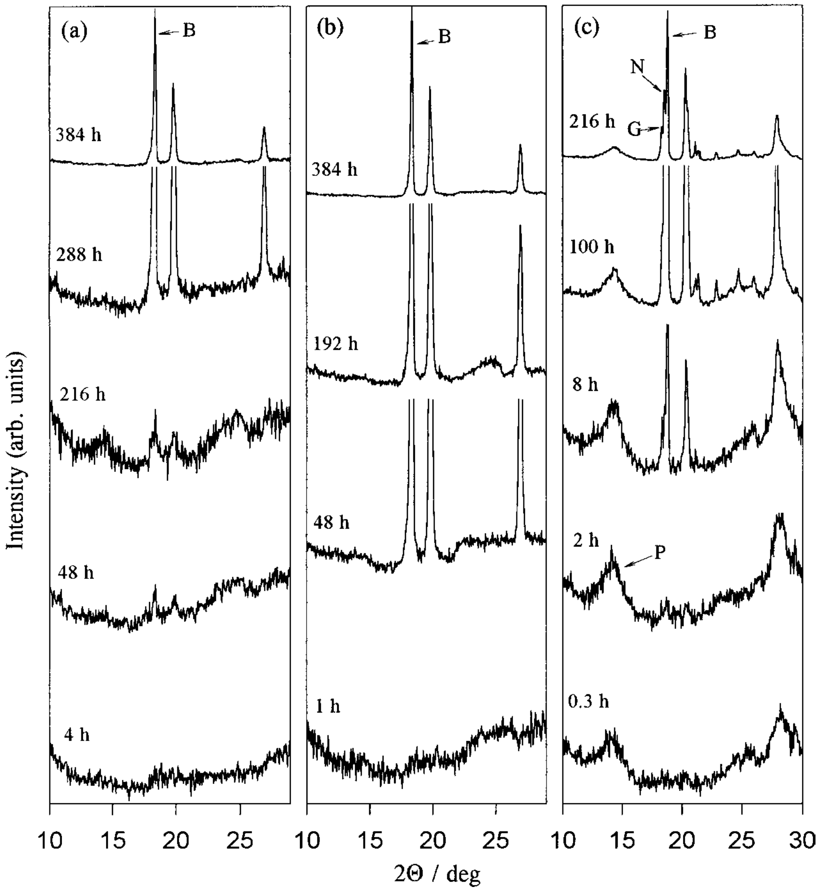

Fig. 4. XRD patterns of rehydrated products from TA-700 sample as a function of time for temperatures: (a) 5°C, (b) 25°C, (c) 50°C. B stands for bayerite, N for nordstrandite, G for gibbsite, and P for pseudoboehmite.

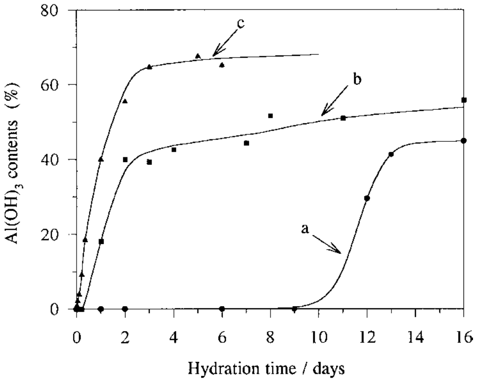

Fig. 5. Crystallization of $Al(OH)_3$ polymorphs during rehydration of TA-700 sample as a function of time for hydration temperatures: (a) 5°C; (b) 25°C; (c) 50°C.

follows the induction period reaches its maximum after about 35 min for the TA-700 sample, and 45 min for the TA-500 sample. An increase of the temperature of rehydration accelerates the reactions occurring to a great extent. The TA-700 sample is more active in rehydration and the total amount of heat evolved equals 402 and 410 J/g for 25°C and 50°C, and for TA-500, 381 and 393 J/g, respectively.

Changes in the phase composition, that proceed during rehydration, as a function of time at different temperatures have been presented for the TA-700 sample in Fig. 4. X-ray diffractograms illustrate well the transformations of amorphous gels that transform into pseudoboehmite gels, and then into $Al(OH)_3$, mainly bayerite. The formation of a stable pseudoboehmite phase is observed only for rehydration at 50°C. After a long time of rehydration at 50°C, the formation of small amounts of nordstandite and gibbsite (Fig. 4(c)) can be observed.

In Fig. 5, the content of bayerite in the product of rehydration at three different temperatures is presented as a function of time for the TA-700 sample. A significant influence of the decrease of rehydration temperature on the increase of induction time for the crystallization of bayerite at 5°C is worth noticing. In that case, this phase appears only after about 9 days. At 25°C, bayerite forms after about 20 h. This correlates well with the thermokinetics of heat emission where beginning of appearance of bayerite phase is connected with presence of maximum on heat evolution curve during the third period of rehydration.

The measurement of kinetics of heat emission by isothermal calorimetry may be a useful method for monitoring the progress of rehydration, steering its course towards the obtaining of desirable phases, as well as serving the purpose of assessing the activity and suitability of TA in the production of alumina carriers and adsorbents.

4. Conclusions

The hydration process may be divided into four stages: an intensive period of preliminary hydration; the induction period; the acceleratory period, passing through the maximum of speed of the evolving heat; and the final period of asymptotically vanishing amount of the evolving heat. The phase compositions of the samples obtained by X-ray diffraction show that the period of accelerated heat emission is connected with the crystallization of amorphous aluminum gels and the formation of bayerite. This period is also characterized by great changes in the morphology of the grains. With an increase of temperature, a shortening of the induction period for crystallization of bayerite is observed.

Acknowledgements

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