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Morphological and phase changes of transition aluminas during their rehydration

Z. JAWORSKA-GALAS, S. JANIAK, W. MIŠTA, J. WRZYSZCZ, M. ZAWADZKI
Department of Catalysis, W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wrocław, Poland

Transition aluminas (TA), obtained by fast (0.5–1 s) calcination of gibbsite in the temperature range 375–600 °C, were rehydrated at 20, 70 and 90 °C. The rehydration process was investigated using transmission electron microscopy, X-ray, and thermogravimetric–differential thermal analysis. During rehydration, the TAs react yielding aluminium hydroxides: pseudoboehmite, boehmite, and bayerite. The phase-composition changes are accompanied by changes in particle morphology. Using transmission electron microscopy, six stages of rehydration were found, with characteristic morphological changes occurring. The changes are responsible for connecting the particles into stable grains during the process of obtaining catalyst carriers or adsorbents from TA.

1. Introduction

Transition aluminas, obtained by fast calcination of gibbsite in the temperature range 360–800 °C, with the general composition $Al_2O_3xH_2O$ (where $0.2 < x < 1.0$), are increasingly being used in the production of adsorbents and catalyst carriers [1–5]. As a result of fast calcination, carried out in a time less than 3 s (usually 0.5 s), a highly amorphous product is obtained, which is a mixture of oxides, containing such phases as ρ-, χ-, γ-Al_2O_3, and boehmite. These products can be easily rehydrated with simultaneous changes in particle morphology and phase composition. Such changes are responsible for aggregation of the particles and the formation of stable granules during formation [6, 7].

The present work investigated the influence of the conditions of fast calcination of gibbsite on the reactivity of its products, as well as the influence of rehydration parameters (in particular temperature and time) on morphological changes of the particles of transition aluminas.

2. Experimental procedure

The morphological investigations and estimation of the size of particles of transition aluminium oxides, as well as of their products of rehydration, were carried out using transmission electron microscopy (TEM) TESLA BS-500. The phase composition was estimated using a diffractometer DRON-3, with Cu*K*α radiation and a nickel filter. The thermogravimetric–differential thermal analysis was made using a MOM-Budapest derivatograph, which worked in the system described by Paulik *et al.* [8]. The specific surface was measured using a Perkin-Elmer 212D sorptometer, with nitrogen as the adsorbate and calculated using the BET method.

The transition aluminas (TA) were obtained from technical gibbsite from the Groszowice cement plant. The gibbsite contained ~0.5% Na_2O. The average size of particles was 40 μm and the specific surface BET was 0.5 $m^2 g^{-1}$. The gibbsite was calcined in a rotary pipe furnace, made from stainless steel, and heated electrically. Calcination was carried out in the temperature range 375–600 °C, for times of 0.5–1 s. The most important properties of the TAs obtained are given in Table I, where the phase compositions of the samples were estimated using X-ray diffraction (XRD) and thermogravimetric–differential thermal analysis (TG–DTA).

With increasing temperature of gibbsite calcination, products containing less gibbsite and boehmite were obtained, together with amorphous ρ- and χ-Al_2O_3 phases. Consequently, at 600 °C the only phase found using XRD was defective γ-Al_2O_3. The products of dehydration, with increasing temperature of gibbsite calcination, contained less water and their specific surfaces decreased.

Samples of aluminium oxides were also prepared by calcination of gibbsite for 5 min. These samples contained less water compared with the samples calcined for less than 1 s, and their diffractograms showed that they were less defective. In Table I the properties of this sample, obtained at 500 °C, are given.

TABLE I The properties of samples investigated

Temperature of calcination of gibbsite (°C)	Phase composition	Weight loss (1000 °C) (%)	S_{BET} ($m^2 g^{-1}$)
TA-375	Trace of gibbsite, ~ 10% boehmite	9.5	220
TA-500	Trace of boehmite	8.7	185
TA-600	Defective γ-Al_2O_3	4.9	145
Al_2O_3-500[a]	γ-Al_2O_3	4.0	250

[a] This sample was calcined for 5 min.

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Rehydration of TAs was carried out by forming spheroids by granulating with the addition of water. At the same time, rehydration of the powders in a 10% aqueous suspension was carried out. The rehydration process was controlled in time by measuring some physico-chemical properties. It should be stressed that rehydration of aqueous powder suspensions was most useful in monitoring the changes in the morphology of particles using TEM. The average size of TA particles was 0.3 μm.

The TAs and aluminium oxides obtained by 5 min calcination were rehydrated at 20, 70, and 90 °C.

3. Results and discussion

The particles of TAs, obtained at 375, 500, and 600 °C, and those of aluminium oxide obtained by 5 min calcination at 500 °C, are similar in shape and size and give identical microscope pictures as shown in Fig. 1.

Fig. 2 shows the changes of TA particle morphology during rehydration at 70 °C. Although they concern the TA obtained at 500 °C, they are typical and can also represent those obtained under other conditions, showing all the observed stages of rehydration:

1. The formation of a layer of gel on the particle surface, as a result of the contact of water and an increase in pH on the borders of particles caused by the diffusion of sodium from TA (Fig. 2a);
2. the transformation of gel to boehmite and pseudoboehmite, manifested in the micrograph (Fig. 2b) in such a manner that the edges of the particles become washed out and ragged, and some appendages can be seen on them;
3. intensive growth of pseudoboehmite forming needles and plates (Fig. 2c);
4. connection of needles and plates of pseudoboehmite into bridges, which join particles thus forming aggregates (Fig. 2d);
5. partial decomposition of bridges, formation of crystallites of boehmite and bayerite (Fig. 2e); and
6. recrystallization of bayerite (Fig. 2f).

These stages of rehydration of TA are observed irrespective of the temperature at which they were obtained. Only for the TA obtained from gibbsite at 375 °C were the needles and appendages of the boehmite formed in the third stage short and poorly grown. The XRD and TGA showed that rehydration of TAs at 20 °C proceeds slowly. During the first 5–10 h no presence of defined phases was seen. Not until 20 h hydration in Sample TA-375 was the presence of about 10% bayerite recorded. In the samples obtained at higher (i.e. 500 and 600 °C) temperatures, bayerite does not appear before 48 h and its content is ~ 3%. The amount of boehmite and pseudoboehmite formed under those conditions was 25%–30%.

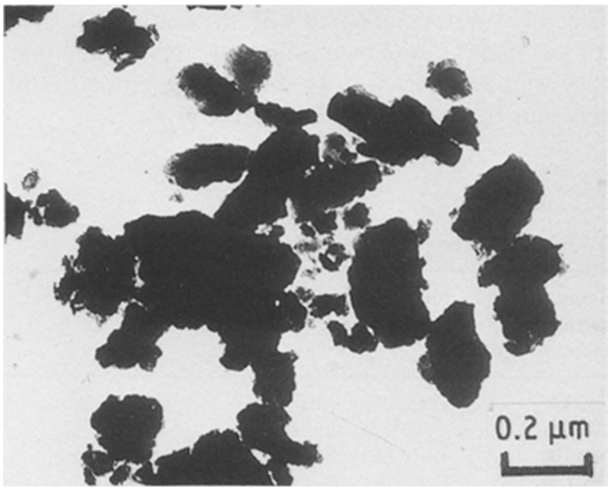

Figure 1 Transmission electron micrograph of TA-500 particles before rehydration.

The processes of rehydration, and consequently changes in phase composition and particle morphology, proceed slowly at 20 °C. Transformation, beginning from the first and ending with the fifth stage of rehydration takes 10–20 h at this temperature.

Increasing the temperature of rehydration to 70 or 90 °C considerably increases the rate of the rehydration process; also, changes in particle morphology are greater. The appendages formed on the particle surface (Fig. 2b) transform into much longer needles and plates of boehmite even after 0.5–3 h (depending on the TA), and the bridges connecting the particles in the grains appear after 3–5 h (Fig. 2d). When the temperature of rehydration is higher, bayerite is also formed much sooner, especially in the products of rehydration of TA-375 (12% after 1 h at 70 and 90 °C). The TAs obtained at 500 and 600 °C were more reactive compared with TA-375; 70% boehmite can be obtained from them, but from TA-375 under the same conditions, only 50% is obtained.

In general, it can be concluded that rehydration of TAs occurs faster when the temperature of rehydration is increased, and the reactivity of TAs increases with the temperature of calcination in the range 375–600 °C.

Aluminium oxide obtained by 5 min calcination of gibbsite can also be rehydrated. At room temperature, as well as at higher temperatures, mainly bayerite was obtained (up to 25%). During rehydration carried out at 20 and 90 °C, in the transmission electron micrographs, no second, third or fourth stages were found, i.e. the stages of formation of boehmite needles and/or plates. Attempts to form granules from these aluminium oxides were not successful. After drying and calcination, their mechanical strength was very low. Also, in the case of TA-375, which during rehydration forms only a few rather short appendages, the granules obtained were not strong enough. In an attempt to obtain extrudates or granules with greater mechanical strength, TAs obtained at temperatures above 375 °C should be used, whose particles undergo specific morphological changes during rehydration, thus making possible aggregation by the formation of bridges. This condition was fulfilled by samples TA-500 and TA-600. The stability of the bridges connecting the particles was also conserved during drying and calcination up to 1100 °C. Fig. 3 shows the particles of aluminium oxide obtained from TA-600, rehydrated at 70 °C (2 h) and calcined. After calcination at 600 °C (Fig. 3a), the particles still have their appendages and needles, as well as the bridges aggregating them. Not

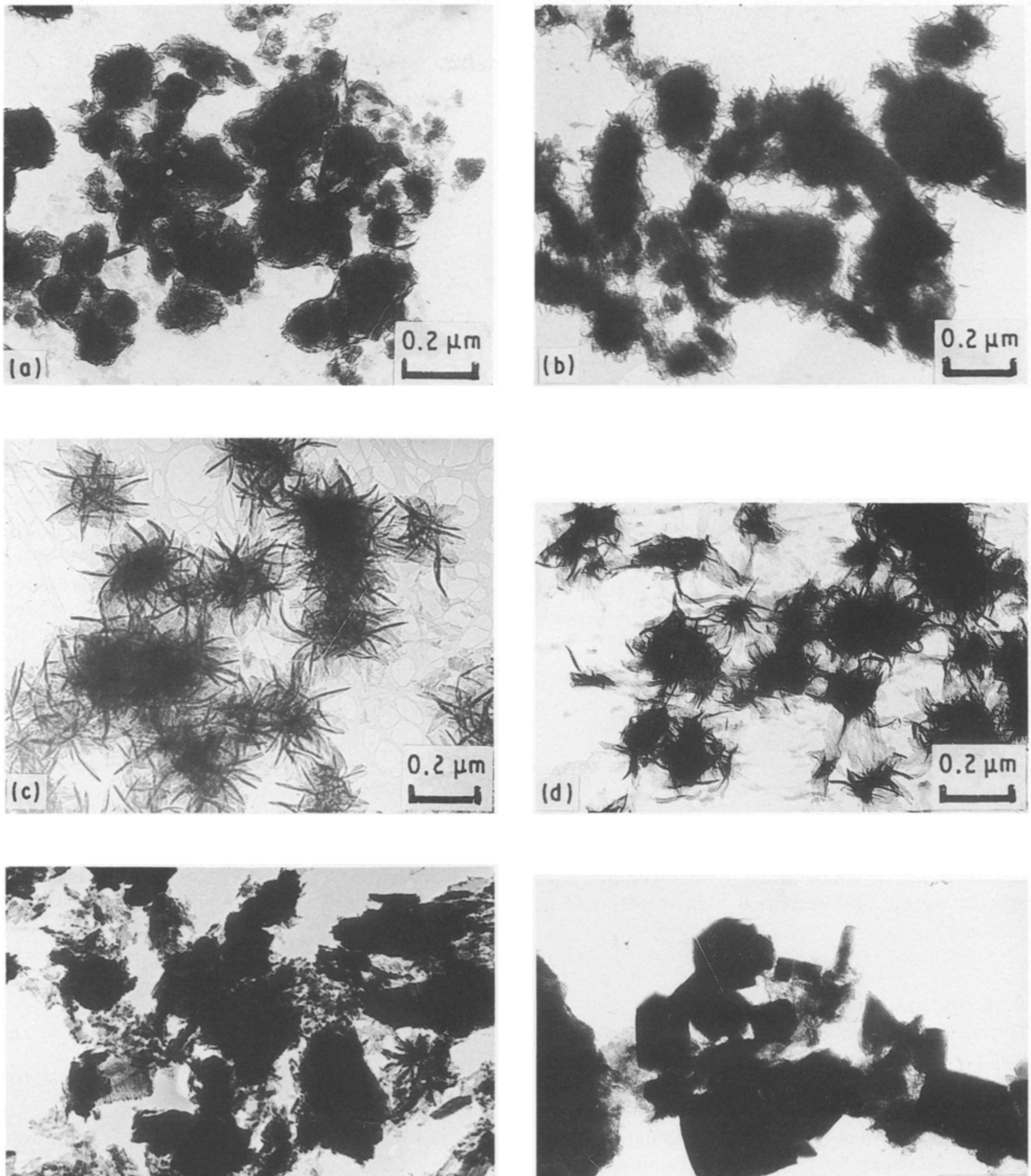

Figure 2 The changes in morphology of TA-500 particles, obtained during rehydration at 70 °C after (a) 0.5 h (b) 1 h (c) 3 h (d) 5 h (e) 10 h (f) 20 h.

until after the calcination at 1200 °C (2 h) can it be seen from Fig. 3b, that during the phase change γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$ and as a result of coalescence, the fibrous and bridge structures were destroyed.

Our investigations show that, by selecting appropriate rehydration parameters, i.e. temperature and time, hydroxides of different phase composition and different particle structure can be obtained, which after calcination should give aluminium oxides with different textures. Table II gives the properties of aluminium oxides obtained by calcination of the products of rehydration of TA-500. Prior to measurement of their specific surface and bulk density, the products of rehydration were calcined at 500 °C for 2 h. In the last column of Table II, the figures corresponding to the samples after rehydration are given.

By rehydrating, drying and calcining a TA, an active γ-Al_2O_3 can be obtained. Carrying out the rehy-

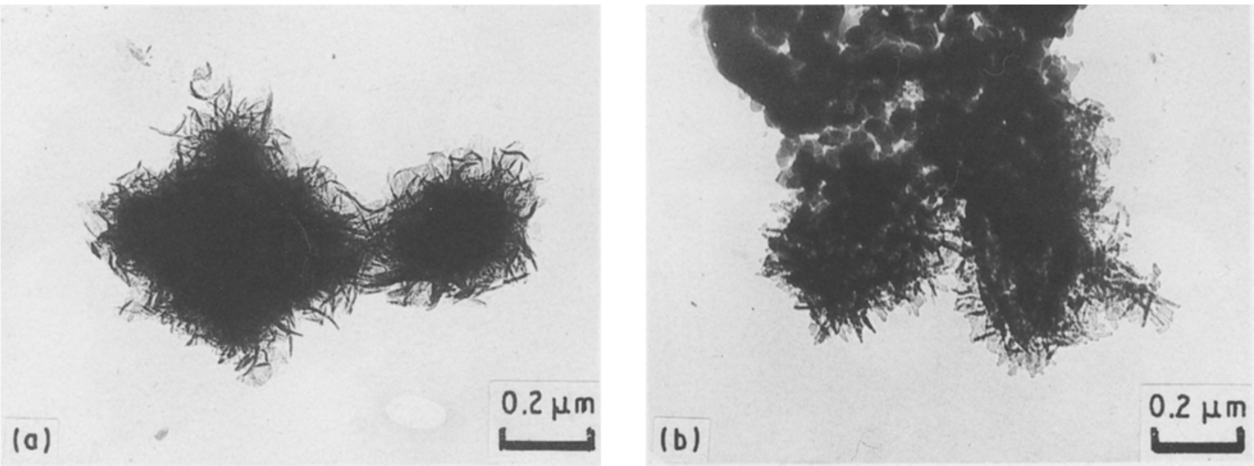

Figure 3 Al_2O_3 particles obtained after rehydration of TA-600 at 70 °C and calcination for 2 h at (a) 600 °C (b) 1200 °C.

TABLE II The specific surface areas of aluminium oxides obtained by calcination the products of rehydration of TA-500

Temperature of rehydration °C	Time (h)	S_{BET} ($m^2 g^{-1}$)	d^a ($g cm^{-3}$)	Figure
Before rehydration	0	185	0.63	1
20	1	185	0.66	2a
20	5	202	0.55	2b
20	20	220	0.35	2b
80	3	430	0.30	2c
90	5	260	0.31	2d

[a] Apparent bulk density.

dration at higher temperatures, oxides with increased specific surface and decreased bulk density can be produced.

4. Conclusion

During rehydration, transition aluminas react with water yielding aluminium hydroxides: pseudoboehmite, boehmite, and bayerite. The ratio of these phases in the rehydrated products depends on the rehydration conditions, mainly on temperature and time. The changes in phase composition are accompanied by changes in particle morphology, which is a precondition for aggregation of particles into stable grains or granules when they are formed. The stability of the bindings created between particles during rehydration is conserved after calcination, i.e. after transformation of aluminium hydroxides into its active oxides. By changing the parameters of rehydration reaction, one can control not only phase composition of the obtained carriers, but also their texture.

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