Journal of Thermal Analysis, Vol. 43 (1995) 103-112

Lectures

PHYSICOCHEMICAL PROPERTIES OF THE PRODUCTS OF BASIC ALUMINIUM-POTASSIUM SULFATE DECOMPOSITION IN HYDROGEN ATMOSPHERE

Barbara Pacewska, T. Zmijewski and Maria Mioduska

Institute of Chemistry, Technical University of Warsaw, Branch at Płock, Poland

Abstract

Low-temperature modifications of aluminium oxide were obtained by thermal decomposition of basic aluminium-potassium sulfate at temperatures 550, 600, and 650°C. Physicochemical properties of the obtained oxides were studied with particular consideration to phase composition and porous structure. It has been shown how the decomposition parameters of the basic salt used determine the porous structure of the obtained oxides.

Keywords: aluminium–potassium sulfate, hydrogen atmosphere

Introduction

All applications of aluminium oxide – except the metallurgy of aluminium – are tightly bound with its specific, controllable chemical properties, such as the phase composition, grain size, specific surface area, porous structure, activity, etc. The oxides of aluminium are most frequently obtained by thermal decomposition of aluminium hydroxides and aluminium salts. The properties of the products obtained in such processes depend strongly on many factors, in particular on the kind of raw material used and the conditions of the decomposition process [1].

In our earlier reports [2–4] we have pointed out the possibility of obtaining low-temperature modifications of aluminium oxide by thermal decomposition of basic aluminium sulfates under reducing conditions. The aim of using reducing

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

agents was to lower the temperature of desulfuration process in order to enable the manufacture of active aluminium oxides of high specific surface.

The decomposition of basic aluminium-potassium sulfate on heating at 530–670°C in hydrogen atmosphere results in desulfuration of aluminium salts to obtain, in the solid reaction products, a mixture of γ-Al_2O_3 and K_2SO_4. The latter may easily be washed out to obtain the low-temperature modification of aluminium oxide. The aim of the present work was to study the effect of conditions of desulfuration in hydrogen atmosphere on the properties of the oxides thus obtained.

Experimental

The raw material used for obtaining aluminium oxides was basic aluminium-potassium sulfate, isomorphous with alunite, obtained under laboratory conditions by hydrolysis of analytical grade aluminium-potassium alum of the following compositions (in wt%): Al_2O_3 – 30.9, K_2O – 10.6, SO_3 – 41.7, and H_2O – 16.8. The specific surface of that material, as determined from benzene adsorption isotherm, was 3 m^2/g. The granulometric composition of the raw material has been shown in Fig. 1.

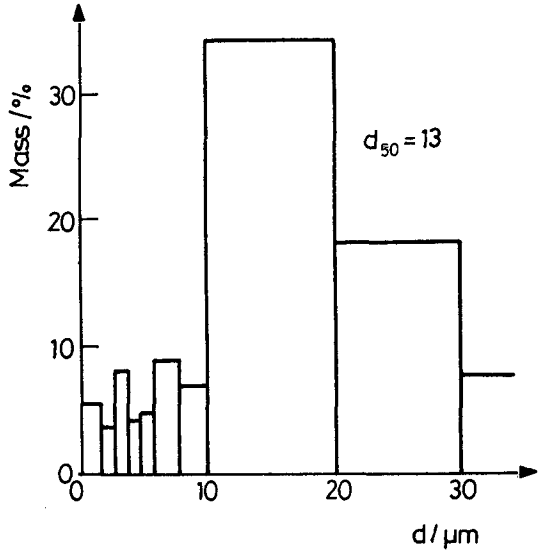


Fig. 1 Granulometric composition of the material used

Thermal decomposition of the basic aluminium-potassium sulfate was carried out, in a tubular reactor in hydrogen stream, for 2 h at temperature 550, 600, or 650°C. The decomposition products were denoted as P/550/H_2, P/600/H_2, and P/650/H_2, respectively. Potassium compounds were then leached from the samples in the following way: demineralized water (100 ml per 1 g) was added to the solid sample and the whole was heated for 30 min at 70°C under continuous stirring. The process of leaching was repeated twice. The solid residue was dried for 3 h at 105°C. The symbol of the washed samples was supplemented by adding a letter 'W' at the end (e.g. P/600/H_2/W). Samples P/600/H_2/W and P/650/H_2/W were heated isothermally for 2 h at 350°C in vacuum. The heated samples were denoted as P/600/H_2/W/350 and P/650/H_2/W/350, respectively.

The samples were subjected to determination of:

– phase composition by X-ray diffraction method; the X-ray patterns were recorded by means of HZG-4C apparatus produced by Carl Zeiss, Jena, using CoK_{α} radiation;

– specific surface S_{BET} and distribution of pore surface and volume *vs.* their radii, basing on low-temperature nitrogen adsorption isotherms.

Samples prepared for adsorption studies were heated under reduced pressure of 10^{-4} hPa for 2 h at 350°C.

Besides, IR absorption spectra of the samples were recorded in a Specord 75 IR device (in the form of tablets with KBr), and thermogravimetric curves were obtained with Derivatograph C device made in Hungary.

Results and discussion

The results of the studies have been presented in Figs 2–7 and in Table 1. Analysis of thermogravimetric curve of the sample P/550/H_2 (Fig. 2) obtained by decomposition of basic aluminium-potassium sulfate at 550°C in hydrogen atmosphere shows that only about 50% sulfur combined with aluminium has been removed. The X-ray pattern of the sample contains the reflexes both due to $KAl(SO_4)_2$ and K_2SO_4 formed in the decomposition of aluminium-potassium sulfate. Aluminium oxide forms an amorphous phase (Fig. 3a). For the assumed 2 h roasting the temperature of 550°C has been too low for obtaining, in the solid reaction products, the mixture of only aluminium oxide and K_2SO_4 suitable as semi-product for manufacture of active aluminium oxide.

Thermal decomposition of alunite carried out at 600 and 650°C results in formation of γ-Al_2O_3 and K_2SO_4, as evidenced by the study of TG, DTG, X-ray diffraction, and IR absorption curves (Figs 2, 3a, and 4a). Thermogravimetric curves of these samples show only the loss of water adsorbed on γ-Al_2O_3; there is no K_2SO_4 decomposition in this temperature range.

The X-ray diffraction patterns of these samples (Fig. 3a) comprise the reflexes due to K_2SO_4 and diffuse reflexes due to γ-Al_2O_3 that give account to its

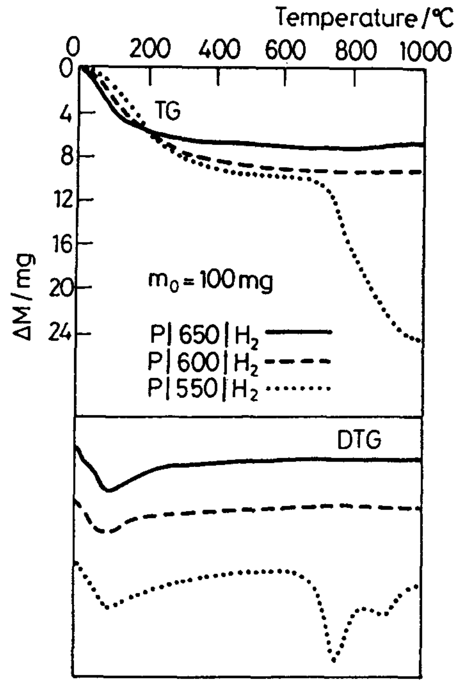


Fig. 2 The TG and DTG curves of basic aluminium-potassium sulfate decomposition products in hydrogen atmosphere

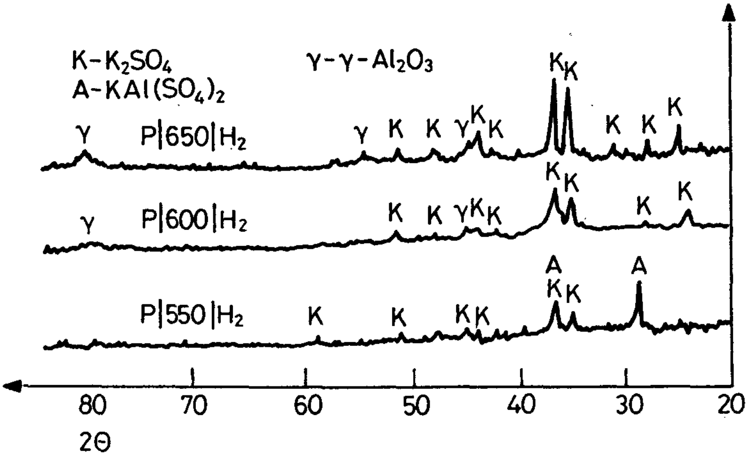


Fig. 3a X-ray diffraction patterns of basic aluminium-potassium sulfate decomposition products in hydrogen atmosphere

poorely crystalline structure. The IR absorption spectrum of the sample P/650/H_2 (Fig. 4) comprises absorption bands at wavelengths 1120, 622, and 985 cm^{-1} characteristic for K_2SO_4 and a broad band in the range 400–1000 cm^{-1} due to the presence of γ-Al_2O_3 [5].

Table 1 Parameters of porous structure of aluminium oxides

Sample	P-600/H_2	P/600/H_2/W/350	P/650/H_2/W/350
Specific surface S_{BET} [m^2/g]	32	333	228
Surface of pores [m^2/g] having the radius r [Å]			
within 100–60	6.0	30.4	10.6
60–30	5.9	95.4	26.1
30–16	8.9	114.1	44.1
16–10	9.2	87.0	103.0
100–10	30.0	326.9	183.8
Volume of pores $V_{0.92}^{*}$ [cm^3/g]	0.070	0.500	0.222
Volume of pores [cm^3/g] having the radius r [Å]			
within 100–60	0.025	0.115	0.041
60–30	0.013	0.199	0.054
30–16	0.010	0.126	0.047
16–10	0.006	0.058	0.063
100–10	0.054	0.498	0.205

* Volume of pores filled with liquid nitrogen under relative pressure $p/p_0 = 0.92$

It has been stated that samples obtained in decomposition of basic aluminium-potassium sulfate heated for 2 h at 600 and 650°C in hydrogen atmosphere may serve as an intermediate products for obtaining active aluminium oxides.

The sample roasted at 600°C was found to bind chemically water on washing out K_2SO_4. The X-ray diffraction pattern of that sample was found to comprise, in addition to reflexes due to γ-Al_2O_3, also some reflexes characteristic for pseudoboehmite (Fig. 3b). Absorption bands characteristic for these compounds are present also in the IR spectrum (Fig. 4).

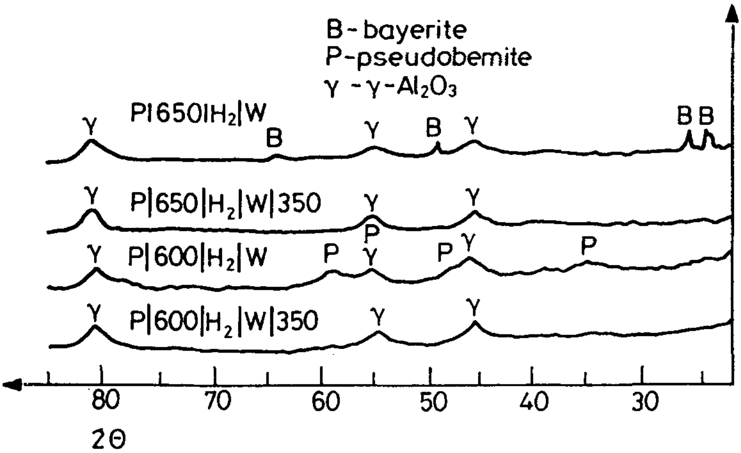


Fig. 3b X-ray diffraction patterns of basic aluminium-potassium sulfate decomposition products after washing out the potassium compounds

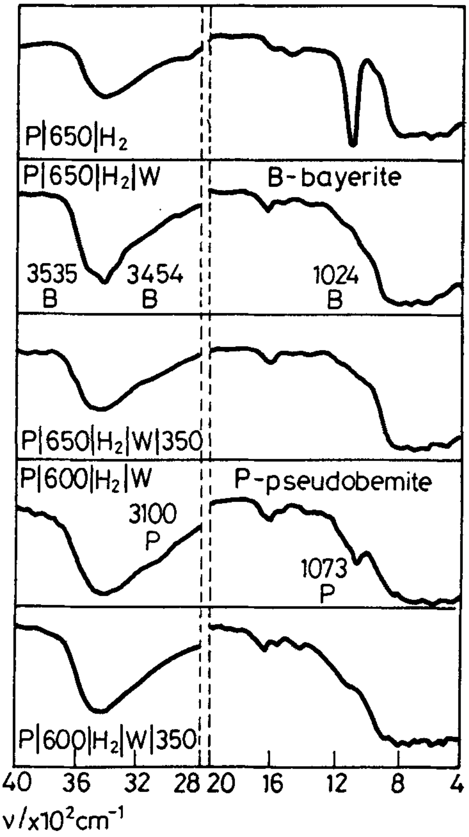


Fig. 4 Infrared absorption spectra of aluminium oxides roasted under various conditions

The TG and DTG curves exhibit, in addition to the stage of elimination of physically bound water, also a dehydration of pseudoboehmite, effected at temperature range 250–550°C (Fig. 5). Also the sample heated at 650°C was found to bind chemically water in the course of leaching the potassium compounds.

The X-ray diffraction pattern of that sample (Fig. 3b) comprises peaks characteristic for γ-Al_2O_3 and bayerite. Absorption bands corresponding to these compounds are present in the IR spectrum (Fig. 4). The presence of bayerite in the leaching products is also confirmed by the shape of thermogravimetric curves (Fig. 5).

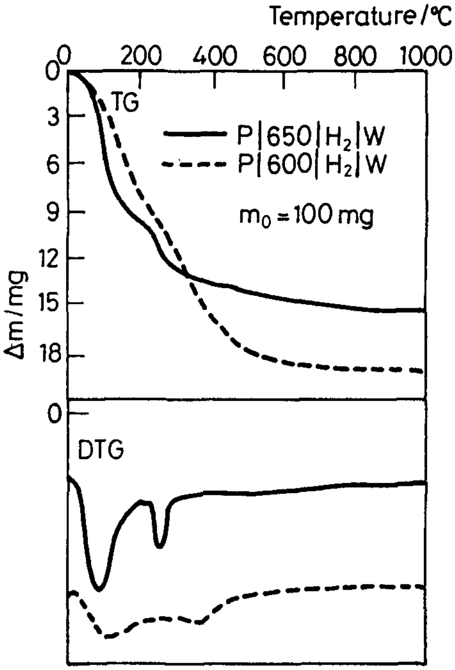
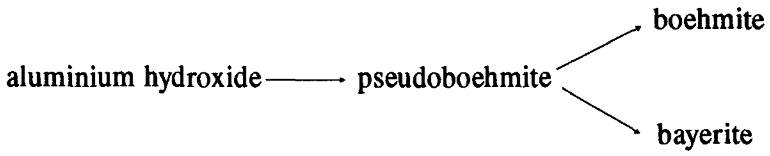


Fig. 5 The TG and DTG curves of the products of basic aluminium-potassium roasting after washing out the potassium compounds

The process of leaching the potassium salts is accompanied by some processes of rehydratation, and eventually ageing, of almost amorphous aluminium oxides, at least at the surface of the particles. These processes may lead to chemical binding of water molecules by the oxide and, consequently, to formation of hydrous aluminium oxides, and even of X-ray distiguishable phases of pseudoboehmite and bayerite.

Conforming to the results published by other authors [6] the processes occurring during ageing of aluminium hydroxides may be represented as follows:



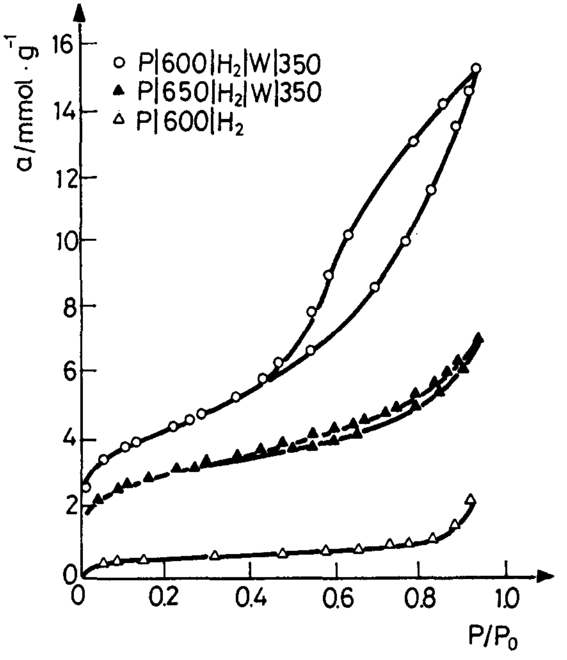


Fig. 6 Nitrogen adsorption and desorption isotherms

The formation of pseudobemite or bayerite in the leaching process depends on *pH* of the solution, temperature, and time of ageing. At lower *pH* values pseudoboehmite is formed in most cases, whereas in alkaline solutions the formation of bayerite is mostly observed. The formation of pseudoboehmite during the leaching of $P/600/H_2$ sample may be due to the presence of trace amounts of non-decomposed aluminium-potassium sulfate. The hydrolysis of that salt results in slight acidification of the solution. In the $P/650/H_2$ sample, fully decomposed, *pH* of the leaching solution is about 9 and thus the formation of bayerite is favorized.

Figure 6 represents the nitrogen adsorption isotherms for the samples $P/600/H_2$, $P/600/H_2/W$ and $P/650/H_2/W$, and Table 1 gives the results of calculations of specific surface by BET method, distribution of pore volume and pore surface with respect to their radii using the Dollimore and Heal method with assumption of cylindrical pore shape closed from one end (for that model good conformity was obtained between the BET surface and pore surface calculated from pore distribution).

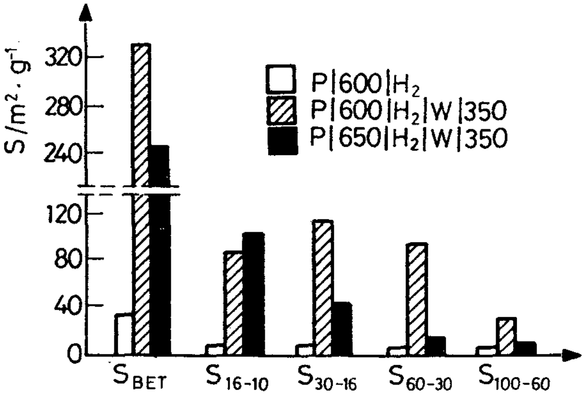


Fig. 7 Pore surface distribution with respect to their radii

The distribution of pore surface with respect to their radii has been presented in Fig. 7. The non-washed sample P/600/H$_2$ (Table 1) has a small specific surface equal 32 m^2/g.

Leaching of potassium salts followed by heating in vacuum in the adsorption apparatus at temperature 350°C results in multiplication of the specific surface and pore volume (Table 1). Similar trend of the changes was observed for the sample P/650/H$_2$, but the specific surface after leaching was smaller by about 100 m^2/g.

Calculation of the pore volume and surface shows (Fig. 7 and Table 1) that the sample P/600/H$_2$/W has the pore structure more strongly developed in the range of pore radii 16–100 Å. In the sample P/650/H$_2$/W most of the pores have the radii below 16 Å (micropores).

The above observations are in good agreement with the results of earlier works concerning the porosity of aluminium oxides obtained by decomposition of pseudoboehmite or bayerite [7]. The decomposition of trihydroxides leads mostly to formation of microporous products, whereas the decomposition of pseudoboehmite gives products of more developed mesopore structure.

Conclusions

The results of the studies performed have lead to the following conclusions:

1. The decomposition of basic aluminium-potassium sulfate should not be carried out below 600°C.

2. Increase of the decomposition temperature results in decrease of specific surface of the aluminium oxides formed.

3. Process parameters applied in manufacture of the oxides are decisive for their pore structure.

* * *

This work, sponsored by The Committee of Scientific Research, was carried out in the frame of the research project No. 7 7806 91 02.

References

1 E. Ingier-Stocka, Cz. Mazanek, L. Rycerz and R. Wojciechowska 'Aluminium hydroxides and oxides. The properties and technology of obtaining', Wrocław,, 1984.
2 B. Pacewska and J. Physiak, Thermochim. Acta, 179 (1991) 187.
3 B. Pacewska, J. Thermal Anal., 36 (1990) 2021.
4 B. Pacewska, Thermochim. Acta, 200 (1992) 887.
5 R. J. Ziniuk, A. G. Bałykow, J. B. Gawrylenko and A. M. Szczełakow, Chimija, Leningrad 1983.
6 V. A. Dzisko, A. S. Ivanova and G. P. Wisniakova, Kinet. i katal., 17 (1976) 483.
7 B. C. Lippens and J. J. Steggerda in 'Physical and chemical aspects of adsorbents and catalysts', ed. B. G. Linsen, Academic Press, London, 1970, p. 170.

Zusammenfassung — Durch thermische Zersetzung von basischem Aluminiumkaliumsulfat bei Temperaturen von 550, 600 und 650°C wurden Niedrigtemperaturmodifizierungen von Aluminiumoxid hergestellt. Die physikochemischen Eigenschaften der erhaltenen Oxide wurden in besonderer Hinsicht auf Phasenzusammensetzung und Porenstruktur untersucht. Es wurde gezeigt, wie die Parameter der Zersetzung des eingesetzten basischen Salzes die Porenstruktur der erhaltenen Oxide beeinflussen.