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Some physicochemical properties of aluminium oxides obtained from basic aluminium sulphates

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Abstract

Eight different kinds of aluminium oxide were obtained by thermal decomposition of isomorphous alunite compounds, namely, basic aluminium ammonium sulphate (BAAS) and basic aluminium potassium sulphate (BAPS). The thermal decomposition of the basic salts was performed in an atmosphere of air, in vacuum, in an atmosphere of hydrogen, and in an environment of carbon and water vapour. The Particle size distribution, phase composition, specific surface area (adsorption of benzene vapour), and the Na_2O and K_2O contents were determined in the aluminium oxide samples obtained.

INTRODUCTION

X-Ray diffraction (XRD) investigations were made to characterize many forms of aluminium oxide. The crystal lattices of all forms of aluminium oxide have been found to be ionic lattices [1,2].

Two ways of classifying the intermediate oxides have been applied [1,3]. The first is based on the reactivity of the oxides in relation to their temperatures of formation. According to Lippens [3] the so-called low temperature forms of aluminium oxide (in other words the reactive oxides), i.e. χ, ρ, η and γ forms, frequently referred to as the γ group, may be obtained during dehydration of the hydroxide below 873 K. Their formula is $Al_2O_3 \cdot nH_2O$ where $0 \leqslant n \leqslant 0.6$. The reactivity of these oxides depends on several factors, primarily on crystal structure, pore structure and surface properties.

Higher temperature non-hydrated aluminium oxides, referred to as the δ group (κ, θ and δ), may be obtained by dehydration at 1173–1273 K.

The second way of classifying the aluminium oxides is based on their structure [4]. Except for α-alumina all other forms have the spinel struc-

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ture; oxygen ions are arranged in the framework of a cubic close-packed (c.c.p.) structure while aluminium ions occupy some of the octahedral or tetrahedral positions.

The spinel-like aluminas differ from each other in the degree of cation ordering in their occupation sites, being less ordered in the lower temperature forms (γ, χ, η, and ρ) and more ordered in the higher temperature forms such as κ, θ and δ. α-Al_2O_3 has rhombohedral close packing (rh.c.p.), with all cations in octahedral sites. This form is the final product of the thermal transformations.

This work is concerned with the lower temperature forms of aluminium oxides obtained by thermal decomposition of basic aluminium sulphates under reducing conditions, in vacuum and in air.

The methods used for obtaining the appropriate oxides were determined in the light of previous investigations of the thermal decomposition of basic salts under different conditions [5–15]. The applications of aluminium oxide are correlated to its specific physicochemical properties, which may be regulated, i.e. particle size, specific surface area, porosity, sorption power, surface activity etc.

In this work, the influence of the conditions under which the oxides are obtained i.e. pressure and composition of gaseous phase, temperature and time, on some physicochemical properties of the oxides was investigated.

EXPERIMENTAL

Physicochemical properties of samples of the starting aluminium sulphates, i.e. aluminium ammonium sulphate (BAAS) and aluminium potassium sulphate (BAPS) (see Table 1), and of the products of their partial decomposition during 2 h under different conditions were determined.

In all the cases investigated the products of thermal decomposition of BAPS are mixtures of aluminium oxide and potassium sulphate (see

TABLE 1

The naming of the samples and the conditions under which they were prepared

BAAS/1273/A	BAAS heated in air at 1273 K
BAAS/973/C	BAAS heated with carbon (94 wt.% BAAS, 6 wt.% C) in an atmosphere of nitrogen and water vapour (45 vol.%) at 973 K
BAAS/973/H_2	BAAS heated in a hydrogen atmosphere at 973 K
BAAS/1273/V	BAAS heated in vacuum (about 10^{-3} hPa) at 1273 K
BAPS/1273/A	BAPS heated in air at 1273 K
BAPS/923/ C	BAPS heated with carbon (94 wt.% BAPS, 6 wt.% C) in an atmosphere of nitrogen and water vapour (45 vol.%) at 923 K
BAPS/ 873/H_2	BAPS heated in a hydrogen atmosphere at 873 K
BAPS/1273/V	BAPS heated in vacuum (about 10^{-3} hPa) at 1273 K

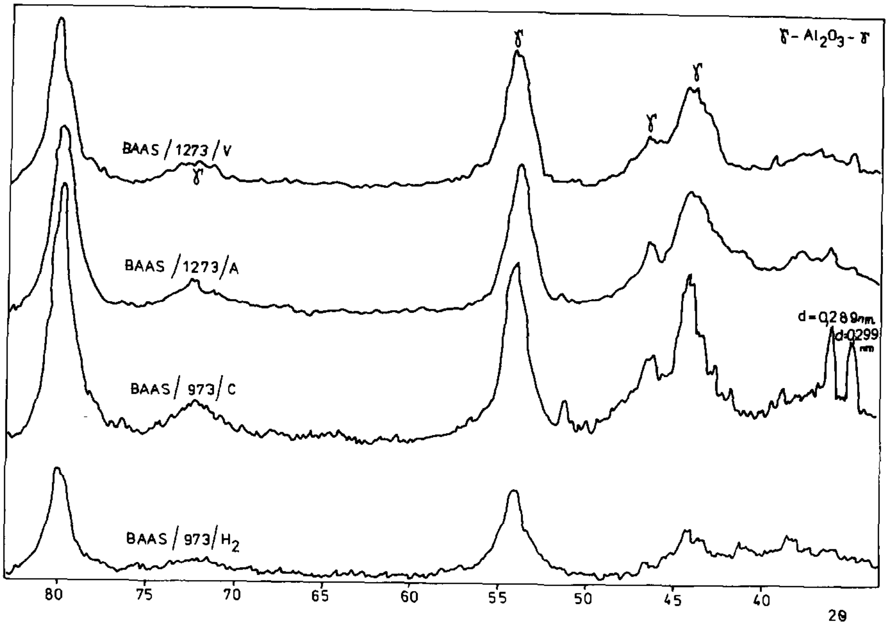

Fig. 1. X-ray diffraction patterns for the intermediate products of the decomposition of BAAS.

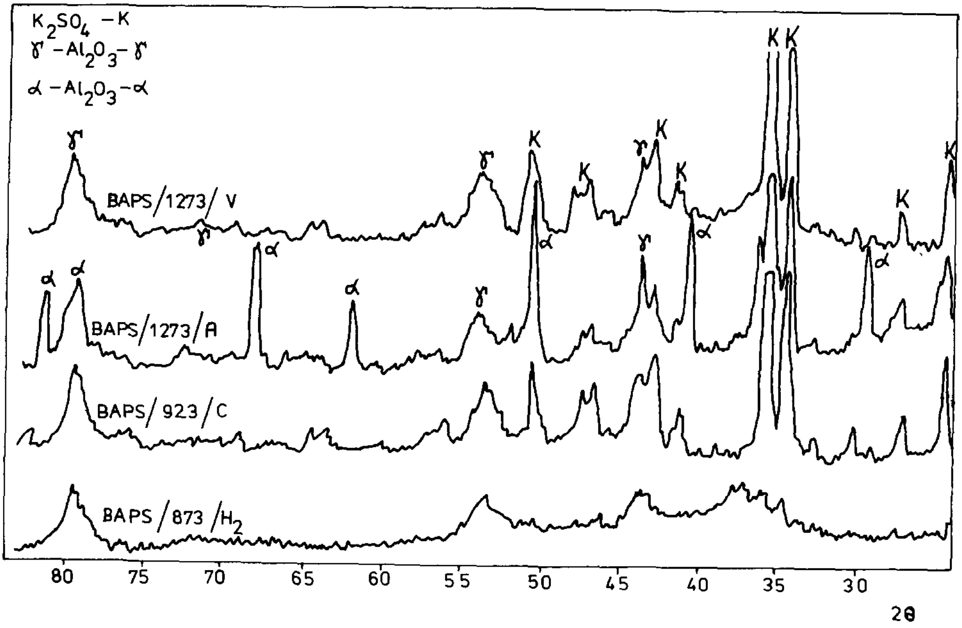

Fig. 2. X-ray diffraction patterns for the intermediate products of the decomposition of BAPS.

diffractograms in Fig. 2 and IR spectra in Fig. 7). In the samples BAPS/1273/V, BAPS/923/C and BAPS/873/H_2 a wide absorption band in the range 400–1000 cm^{-1}, characteristic of γ-Al_2O_3, and absorption peaks at 1120, 985 and 622 cm^{-1}, characteristic of K_2SO_4 were observed. In the sample BAPS/1273/A, however, one can observe absorption bands characteristic of K_2SO_4 and peaks at 465 and 506 cm^{-1} associated with Al–O vibrations in the AlO_6 octahedral units for α-Al_2O_3).

The physicochemical investigations were made on samples of BAPS directly after decomposition (mixture of Al_2O_3 and K_2SO_4) and furthermore on samples washed to remove the potassium sulphate as follows: 1 g of the sample in 100 ml of demineralized water was heated at 343 K for 0.5 h and continuously stirred. The washing process was repeated. The precipitate was dried at 378 K for 3 h. A capital letter "W" is added to the symbol of the washed samples.

In the samples investigated the following properties were determined.

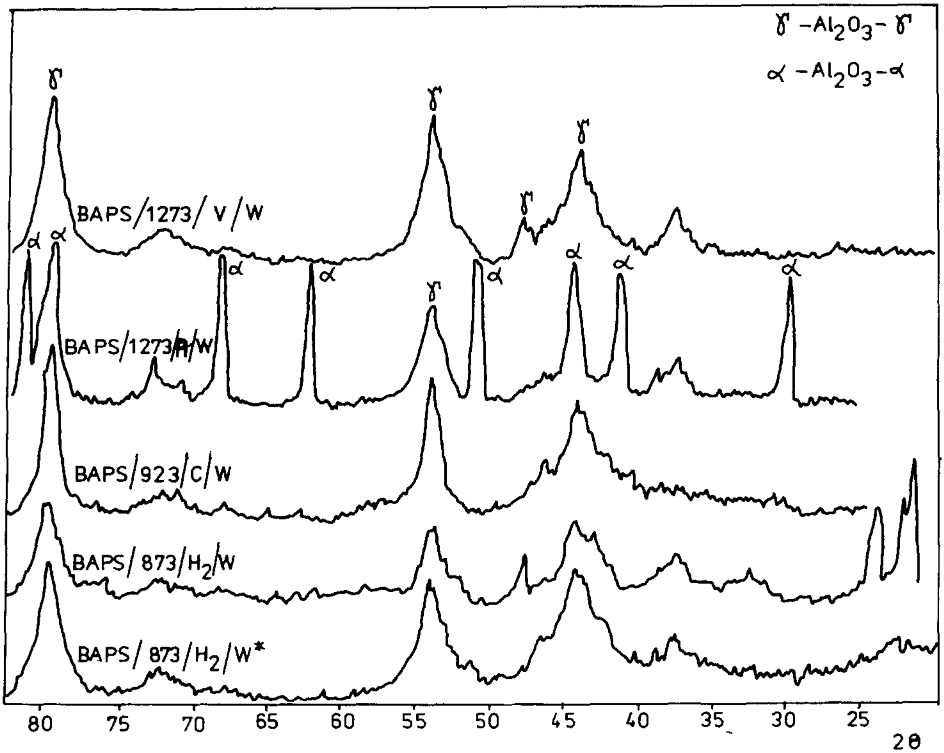

Fig. 3. X-ray diffraction patterns for the intermediate products of the decomposition of BAPS washed to remove potassium sulphate. An asterisk denotes the sample after washing and heating at 623 K for 2 h.

The phase composition was determined by the XRD method. X-Ray phase analyses were carried out with an HZG-4C diffractometer (made in Germany) using Co Kα radiation.

The particle size distribution was found by the sedimentation method using a Simadzu particle size analyser (made in Japan).

The specific surface, S_{BET}, was found from the isotherms of sorption of benzene vapour; the value for the settling surface of the benzene molecule was taken as $w = 0.40$ nm^2 [20]. To prepare the samples for measurements,

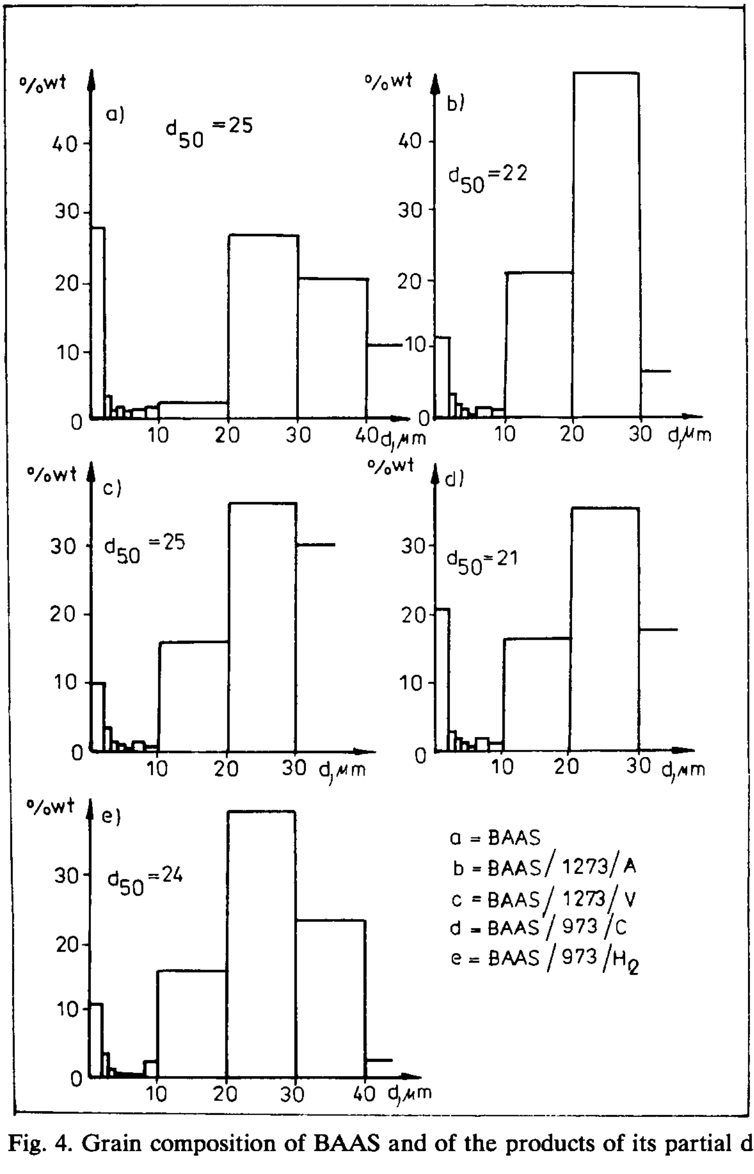

Fig. 4. Grain composition of BAAS and of the products of its partial decomposition.

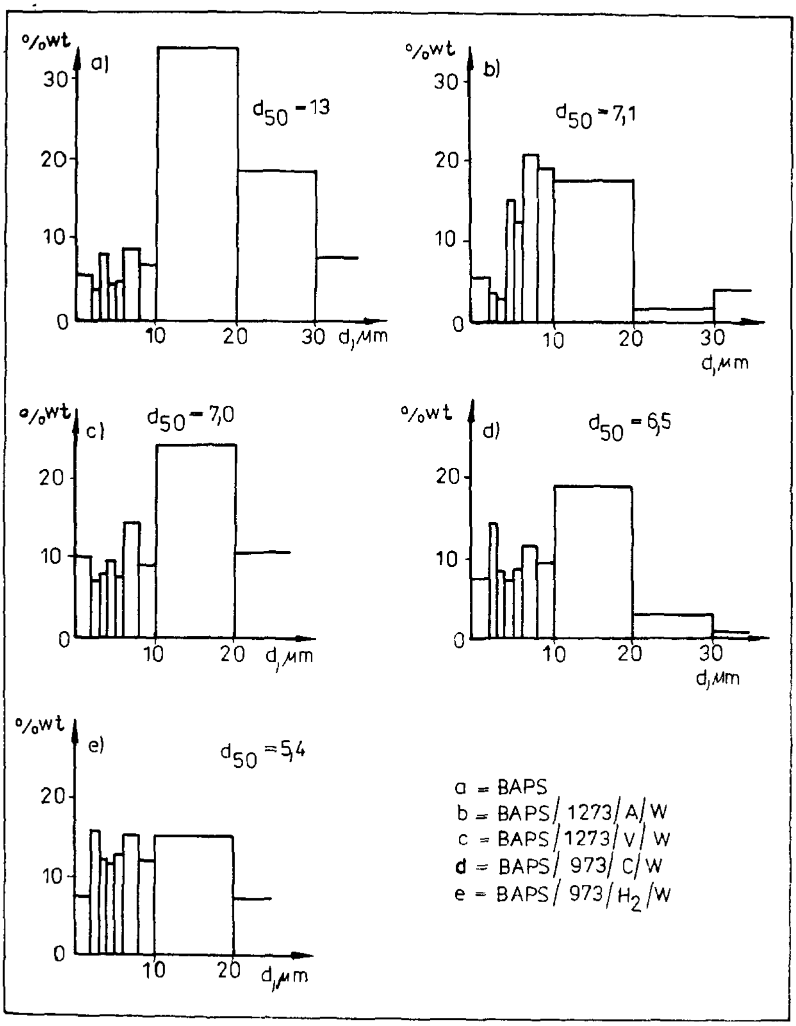

Fig. 5. Grain composition of BAPS and of the products of its partial decomposition.

TABLE 2

Physicochemical properties of BAAS and of the products of its partial decomposition under different conditions

Compound	Phase composition	S_{BET} ($m^2 g^{-1}$)	K_2O (wt.%)	Na_2O (wt.%)	D_{50} (µm)
BAAS	Alunite	6			25
BAAS/1273/V	γ-Al_2O_3	75	0.343	0.287	25
BAAS/1273/A	γ-Al_2O_3	34	0.232	0.334	22
BAAS/973/C	γ-Al_2O_3	87	0.329	0.435	21
BAAS/973/H_2	γ-Al_2O_3	101	0.307	0.337	24

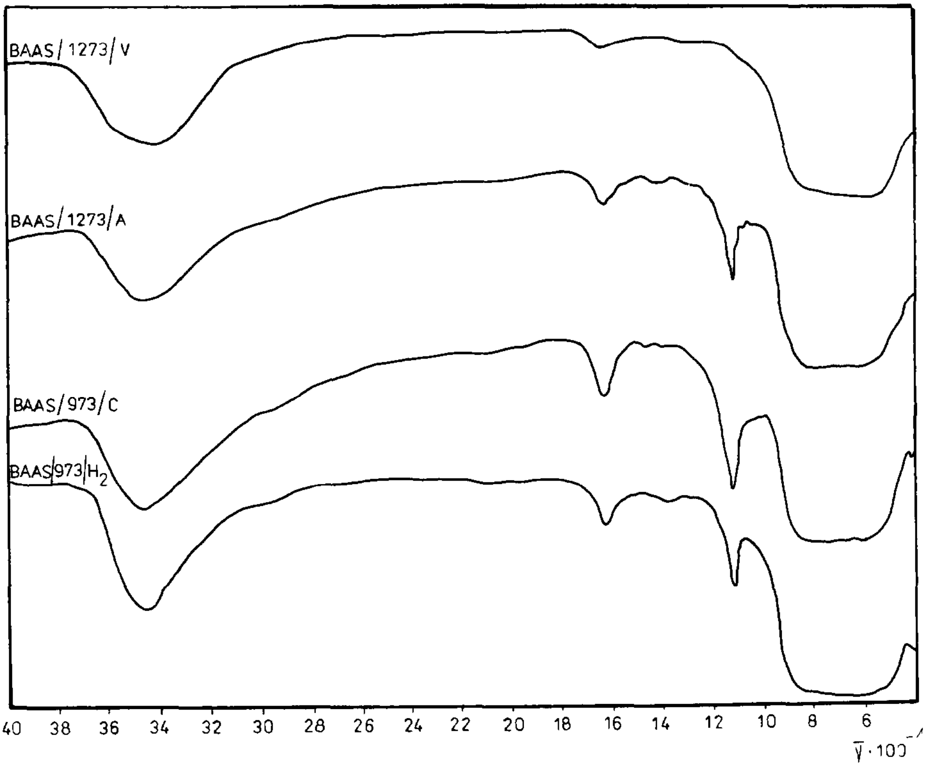

Fig. 6. IR spectra of the intermediate products of the decomposition of BAAS.

the samples of the initial materials were heated at 383 K and the partially decomposed samples were heated at 623 K.

The contents of K_2O and Na_2O were determined by atomic absorption spectroscopy.

TABLE 3

Physicochemical properties of BAPS and of the products of its partial decomposition under different conditions

Compound	Phase composition	S_{BET} (m^2 g^{-1})	K_2O (wt.%)	Na_2O (wt.%)	D_{50} (μm)
BAPS	Alunite	3			13
BAPS/1273/V	γ-Al_2O_3, K_2SO_4				
BAPS/1273/V/W	γ-Al_2O_3	226	0.153	0.174	7
BAPS/1273/A	α-Al_2O_3, K_2SO_4	28			
BAPS/1273/A/W	α-Al_2O_3	63	0.061	0.058	7.1
BAPS/923/C	γ-Al_2O_3, K_2SO_4	27			
BAPS/923/C/W	γ-Al_2O_3	92	0.079	0.035	6.5
BAPS/873/H_2	γ-Al_2O_3, K_2SO_4	21			
BAPS/873/H_2/W	γ-Al_2O_3	252	0.170	0.300	5.4

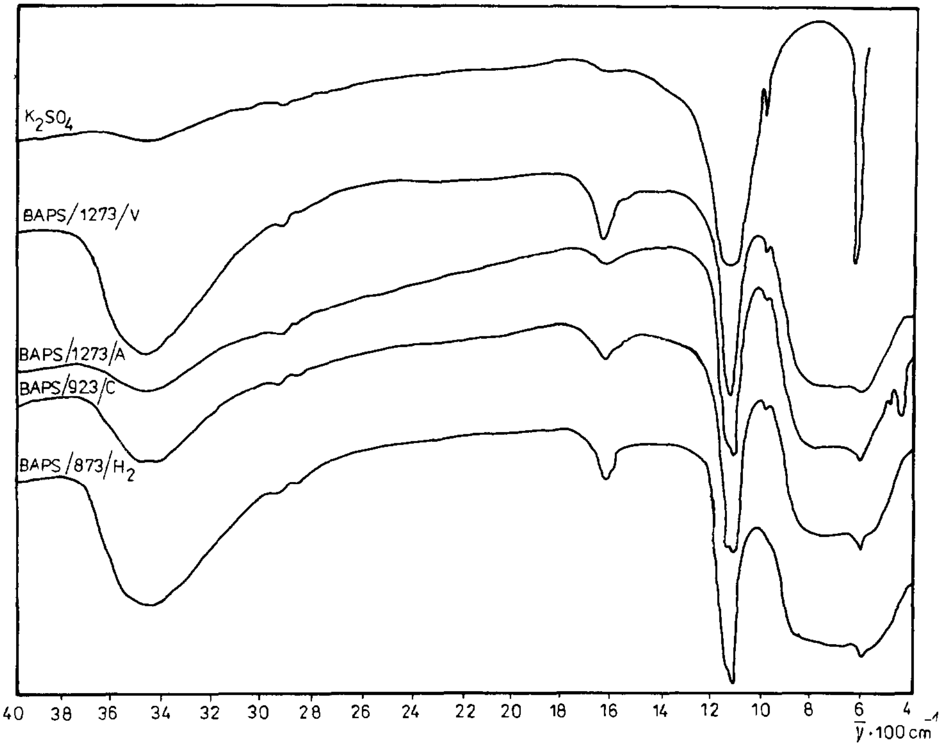

Fig. 7. IR spectra of the intermediate products of the decomposition of BAPS.

The IR spectra of the samples were recorded with a Specord 75 IR spectrometer (Carl Zeiss, Jena). The samples were pressed into tablets with KBr. Scanning electron microscopy (SEM) micrographs of the oxides were also taken.

Thermogravimetric curves of the oxides were recorded using a Derivatograph C (Hungarian).

The results of the investigations are presented in Figs. 1–12 and in Tables 2 and 3.

RESULTS AND DISCUSSION

An analysis of the results leads to the conclusion that the nature of the initial material influences the physicochemical properties of the oxides investigated. The aluminium oxides obtained from BAAS, independently of the conditions of the process, have the γ-Al_2O_3 structure (Figs. 1 and 6), and a similar particle size distribution which is also similar to that of the initial material (Fig. 4 and Table 2). The total alkali content ($K_2O + Na_2O$) in particular samples is not higher than 0.8 wt.% (Table 2).

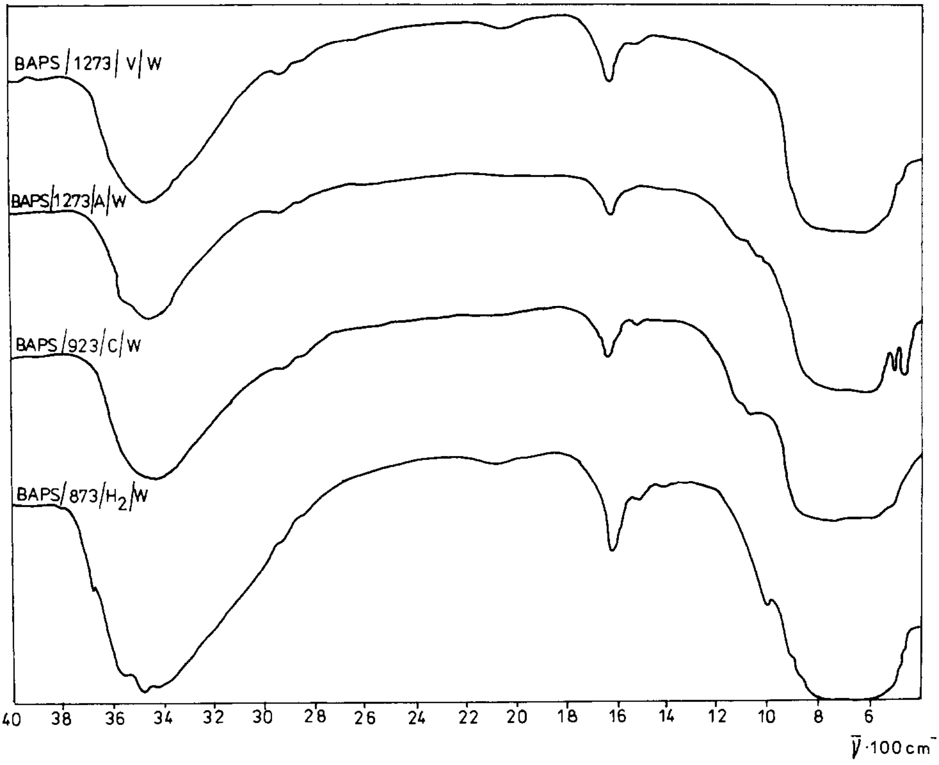

Fig. 8. IR spectra of the intermediate products of the decomposition of BAPS washed to remove potassium sulphate.

The S_{BET} values of the aluminium oxide samples differ. The samples obtained in air have the lowest values of S_{BET} (34 m^2 g^{-1}); the remaining three preparations are characterized by similar values of S_{BET} in the range 75–101 m^2 g^{-1} (Table 2).

The temperature, pressure and gaseous phase composition in the calcination process influence the S_{BET} value. The S_{BET} value of Al_2O_3 decreases with the temperature of decomposition and reaches its minimum for α-Al_2O_3 samples [1,16]. However, the elimination of gaseous calcination products from the environment of the reaction (which takes place when the process occurs in vacuum or under reducing conditions) enables products characterized by large S_{BET} values to be obtained.

Changes in the hygroscopic character of the investigated preparations (Fig. 9) occur in the same direction as changes in the specific surface value.

The aluminium oxide obtained by decomposition of BAAS in vacuum does not contain sulphur compounds; the other three oxides contain only traces of SO_3, probably as a solid solution of SO_3 in Al_2O_3 (absorption bands at 1120 cm^{-1} (Fig. 6)). This is consistent with previous observations

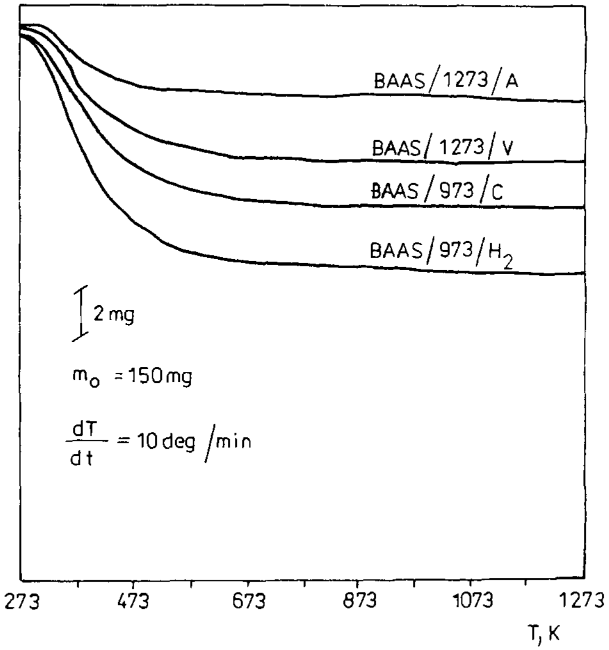

Fig. 9. Thermogravimetric curves of the intermediate products of the decomposition of BAAS.

of the persistence of sulphate in alumina to temperatures above 1379 K [17–19].

The aluminium oxides obtained from BAPS have a different phase composition in relation to the parameters of the decomposition process.

A mixture of γ-Al_2O_3 and K_2SO_4 is the product of BAPS decomposition in vacuum at 1273 K, in a hydrogen atmosphere at 873 K, and in an environment of carbon and water vapour at 923 K. However, a mixture of α-Al_2O_3 and K_2SO_4 is the product of calcination of BAPS in air at 1273 K (Figs. 2 and 7).

The specific surface area of the decomposition products is not very large and oscillates between 20 and 30 $m^2\ g^{-1}$. Washing out of the potassium sulphate causes both a several-fold increase in and a differentiation of the S_{BET} values of the oxides. Two preparations from the decomposition of BAPS in vacuum and in a reducing hydrogen atmosphere have especially high S_{BET} values of above 200 $m^2\ g^{-1}$. These oxides are reactive, as can be observed during the washing-out process of the K_2SO_4 from the BAPS/873/H_2 sample, the γ-Al_2O_3 combining with the water chemically during this operation (Figs. 3 and 10). The increase in hygroscopic character of the samples investigated is in agreement with the increase in their S_{BET} values (Table 3 and Fig. 10).

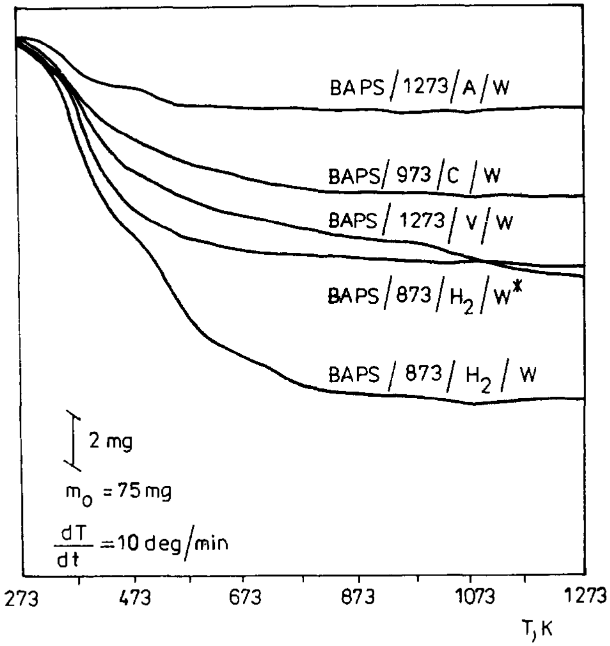

Fig. 10. Thermogravimetric curves of the intermediate products of the decomposition of BAPS. An asterisk denotes the sample after washing and heating at 623 K for 2 h.

The grain composition of the oxides produced under different conditions is similar, but it differs from the particle size distribution of the starting material, characterized by being twice that of the particle size distribution (Table 3).

For the eight samples of oxide considered the nature of starting material has a greater influence than changes in the conditions of the decomposition process (Tables 2 and 3).

The above considerations are valid not only with regard to grain composition but also with regard to the morphology of the oxides obtained (Figs. 11 and 12).

CONCLUSIONS

(1) The influence of the starting material on the physicochemical properties is considerable.

(2) The morphology and grain composition of the oxides obtained from the thermal dissociation of BAAS and BAPS are different.

(3) Reduction of pressure in the calcination process causes an increase in S_{BET} values of the oxides obtained.

(4) Under reducing conditions the calcination process of basic salts causes an increase in the specific surface area of the oxides produced.

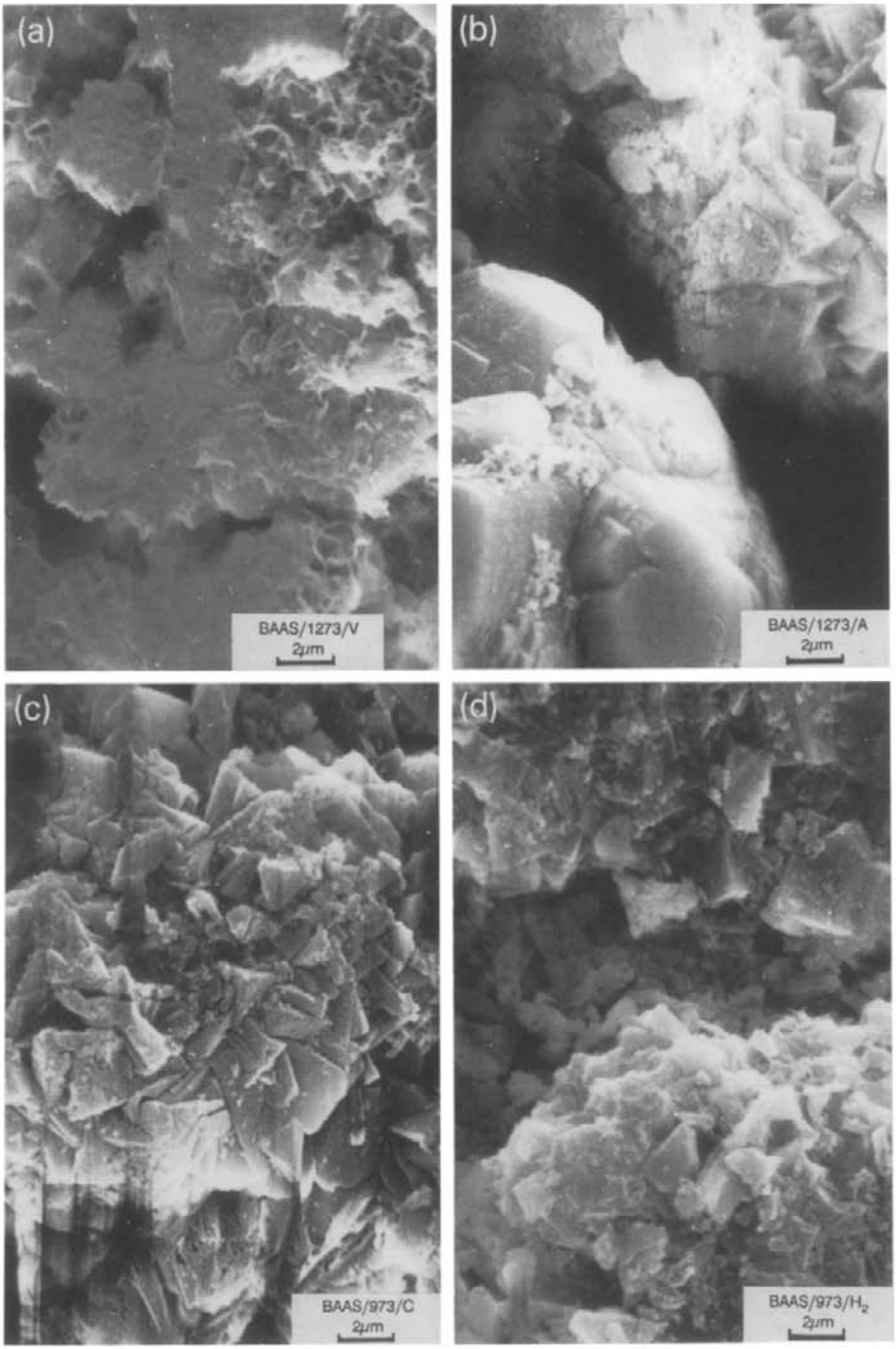

Fig. 11. SEM pictures of the intermediate products of BAAS decomposition.

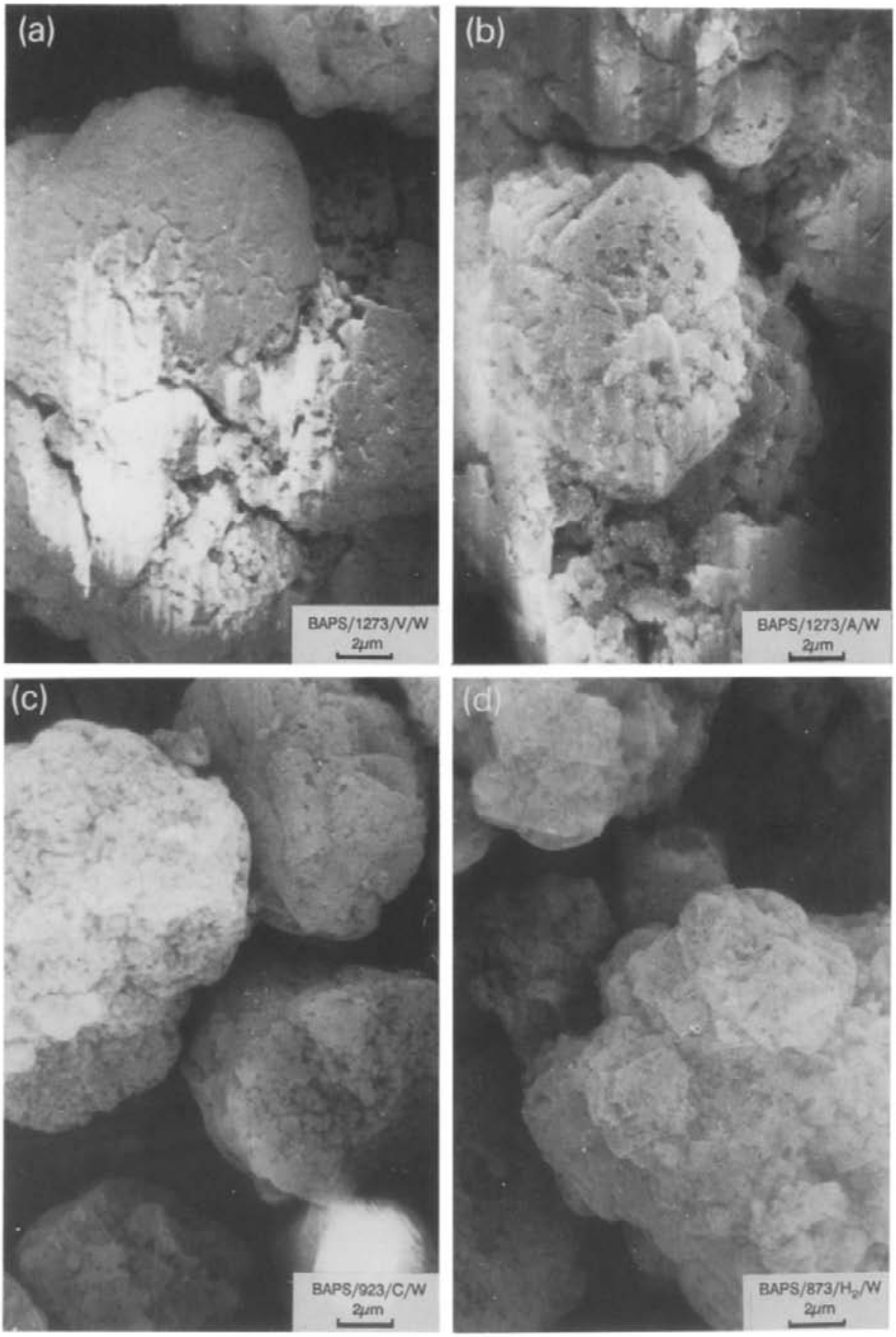

Fig. 12. SEM pictures of the intermediate products of BAPS decomposition after washing to remove potassium sulphate.

(5) Aluminium oxides obtained from the calcination of BAPS in vacuum or in a reducing atmosphere of hydrogen have the largest S_{BET} values. They have applications in catalysis or in sorptive processes.

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