

HYDROUS ALUMINIUM-OXIDES PREPARED BY HOMOGENEOUS PRECIPITATION FROM ALUMINIUM(III)SULPHATE WITH UREA

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Easily filtrated alumina-oxides spherical precursors were prepared by homogenous precipitation from aluminium(III) sulphate with urea. Urea was employed as precipitation agent. X-Ray powder diffraction (XRD) spectra identified three different phases, namely: α -boehmite, boehmite and hydrobasaluminite. The morphology of prepared samples was observing by SEM (scanning electron microscopy) equipped with EDX (energy dispersive analysis by X-rays). The spherical clusters were examined at small concentration and the hydrobasaluminite islands were observed at the largest concentration of reagents. The microstructure characteristics were obtained by BET (Brunauer-Emmett-Teller) and BJH (Barret-Joyner-Halanda) methods. BET in wide range from 6 to 142 m²/g and the all kinds of porous distribution were acquired, respectively. These methods showed that relationship between phase structures and microstructure exists.

INTRODUCTION

De A.A. Soler-Illia et al. [1] have presented in detail the urea method as an adequate way to synthesize both amorphous and crystalline uniform metal(hydrous)-oxide particles from aqueous media. The decomposition of urea (CH₄N₂O) in aqueous is accompanied by slow and controlled supply of ammonia (NH₃) and carbon dioxide (CO₂) into solution. The smooth pH increase was obtained by the degradation of urea in synchrony with the active release of OH⁻ and CO₃²⁻ ions, usually lead to precipitation of metal hydrous-oxide particles of controlled particle morphology. All microstructural parameters such as particle shape and size, specific surface area and porosity are quite sensitive towards pH, metal ion concentration, temperature and aging time.

Ramanathan et al. [2,3] studied the role of the process conditions on the formation of submicrometre size boehmite powders by aqueous aluminium chloride-urea reaction at 373 K [2]. They prepared boehmite powders with size (0.3 to 0.8 μ m) having elongated fibrillar bundle morphology and also precursor powders for alumina by aluminium nitrate-urea and aluminium sulphate-urea reactions. Aluminium nitrate-urea reactions resulted in an amorphous gel that upon prolonged refluxing at a higher pH crystallized into boehmite powders of 0.3-0.8 μ m size. Aluminium sulphate-urea reactions resulted in the direct formation of amorphous powders of 2-7 μ m size which were agglomerates of spherical particles [3].

Sarikaya et al. [4,5] have presented homogeneous precipitation of aluminium sulphate (0.010-0200 M Al³⁺) with urea in boiling aqueous solution. A reaction between aluminium sulphate and urea at presence of the hydro peroxide and follow up by ultrasound treatment lead to again create of the non-uniform particles of boehmite [4,5]. These particles possess morphology corresponding to products obtained by means of heterogeneous precipitation [6]. Studies on low-temperature synthesis of α -alumina from concentrated solutions of aluminium salts and urea at low temperature are reported in [7]. Using aluminium salts: (i) particles with low-density alumina (0.2-0.4 g/cm) could be formed; (ii) low-temperature synthesis of α -alumina could be possible; (iii) alumina hydrate with d₅₀ varying from 16 to 19 μ m could be prepared. Also, keeping d₅₀ constant powders with different particle size range could be prepared. The sample with 10% of the particles lie below 3.11 μ m could also be prepared with different processing condition.

The aim of this work was to show that at low concentration of reagents is α -boehmit formed. Hence, if concentration of reagents in rises, continuously hydrobasaluminite was discovered. The resulted precipitated are very badly washed. These oxides could be successfully applied as catalysts in degradation of chemical war fore agents. This fact was publicized earlier [8]. Further, the primary goal of this study was to investigate the properties, such as specific surface area, porosity and morphology prepared of precursors. Therefore, relationship between formed phases, specific surface area, pore size distribution and morphology of porous samples is investigated.

EXPERIMENTAL

Experimental method

Aqueous solutions of aluminium sulphate and urea in concentration ranges of 0.4-120 g/l and 10-240 g/l, respectively were used in the experiments (see table 1. the samples with signification Alk1 - Alk12). The solutions were prepared from of pure $\text{Al}_2(\text{SO}_4)_3$, urea and distilled water. The experiments were carried out in 5 l stirred glass vessel at temperature of 98°C. The precipitation was stopped, when all Al^{3+} ions were coagulated.

The precipitate was filtered, washed with distilled water and dried at temperature of 105°C approximately 12 h.

Characterization methods

X-ray powder diffractions were performed with a Siemens D5005 using Cu $K\alpha$ radiation (40 kV, 30 mA) and diffracted beam monochromator, using a step scan mode with the step of $0.02^\circ 2\theta$ and 2.4 s per step. Qualitative analysis performed with Diffract Plus EVA Application V.8.0 and JCPDS PDF-2 database [9].

Table 1. Initial concentrations of reactants at which all precipitates (Alk1-Alk12) were obtained.

Sample	Alk1	Alk2	Alk3	Alk4	Alk5	Alk6	Alk7	Alk8	Alk9	Alk10	Alk 11	Alk12
$\text{Al}_2(\text{SO}_4)_3$ (g/l)	0.4	1	2	4	10	14	16	20	28	36	40	120
urea (g)	10	10	20	40	80	120	160	200	200	200	200	240

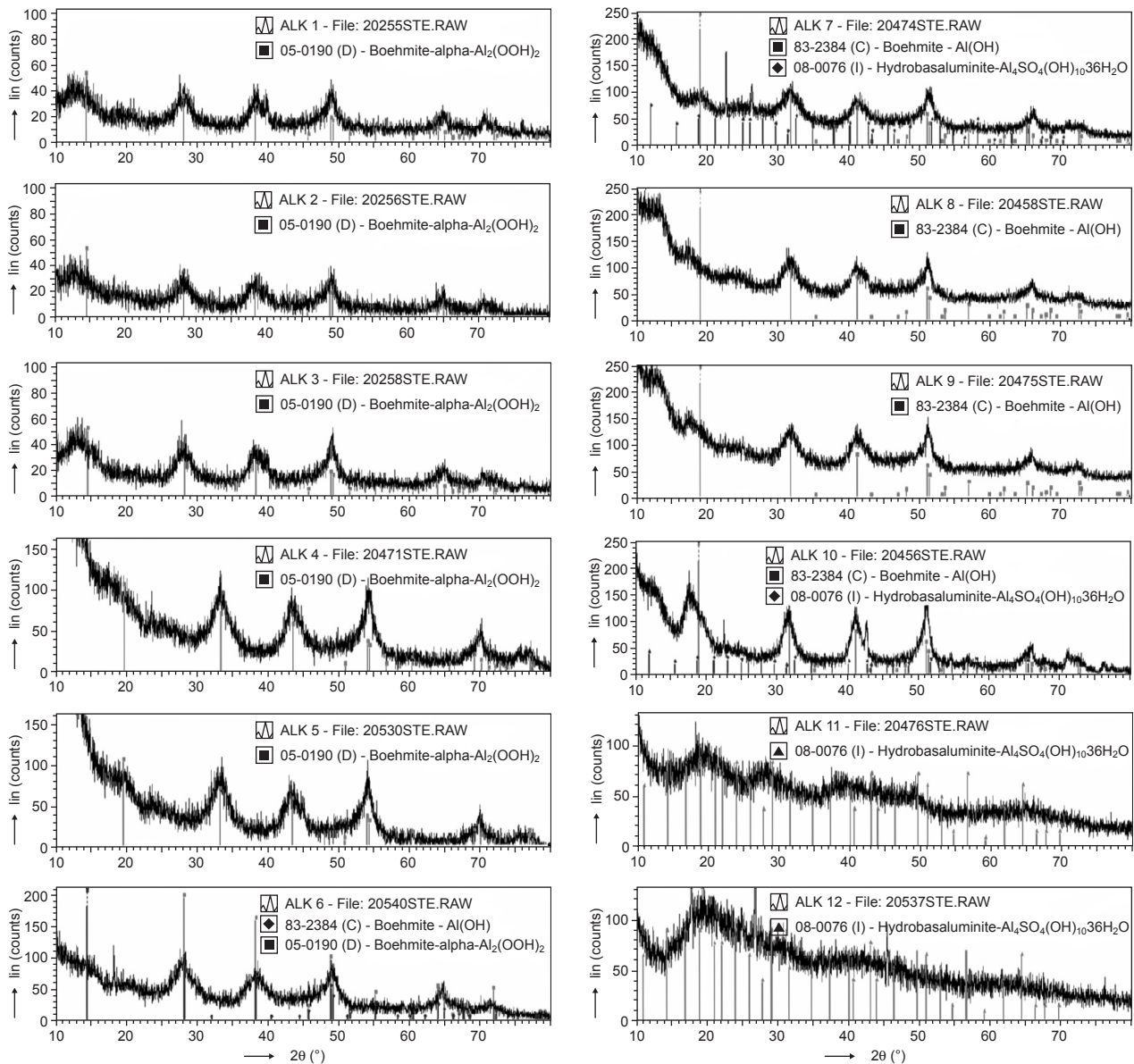


Figure 1. X-ray powder diffraction patterns of Alk1-Alk12 samples.

The SEM studies were performed using a XL30 Philips CP microscope equipped with EDX (semiquantitative analyze), Robinson, SE and BSE detectors. The EDX information was believed to be correct to about $\pm 3\%$.

The specific surface area of the samples was determined by nitrogen adsorption-desorption isotherms at liquid nitrogen temperature using the Coulter SA 3100 instrument with outgas 15 min. on 120°C. The specific surface area was calculated by the BET method, while pore size distributions (pore diameter and pore volume) by the BJH method.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD)

X-ray powder diffraction patterns for samples Alk1-Alk5 have diffraction lines characteristic for boehmite, $\alpha\text{-Al}_2\text{O}_3\cdot x\text{H}_2\text{O}$, ICDD PDF 05-0190 [9] (see figure 1). The intensity of diffraction lines increases with growth concentration of aluminium sulphate and urea in reaction mixture. The samples Alk6-Alk10 without the sample Alk7 include the diffraction lines for boehmite $\text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O}$, ICDD PDF 83-2384 [9] (see figure 1). Nevertheless, the samples of Alk7 and Alk10

Table 2. The residual content of sulphur.

Sample	Alk1	Alk2	Alk3	Alk4	Alk5	Alk6	Alk7	Alk8	Alk9	Alk10	Alk 11	Alk12
S (wt.%)	2.19	1.71	1.37	1.58	1.53	3.27	4.91	0.88	0.75	2.21	5.87	7.37

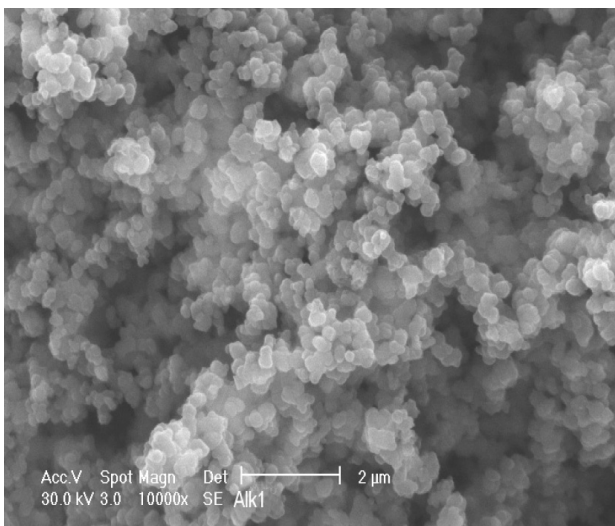


Figure 2. SEM morphology of sample Alk1.

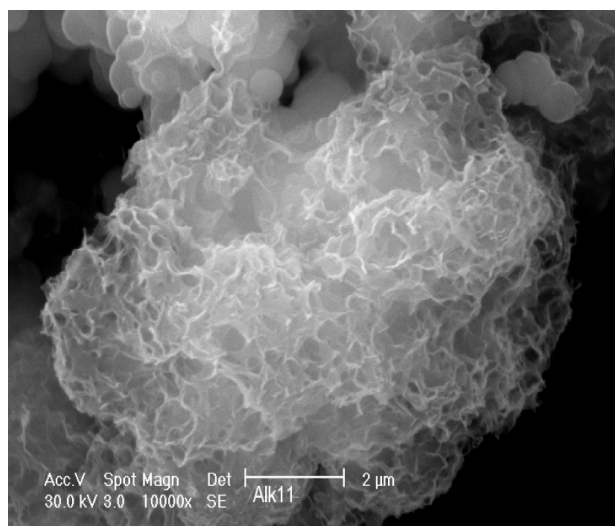


Figure 4. SEM morphology of sample Alk11.

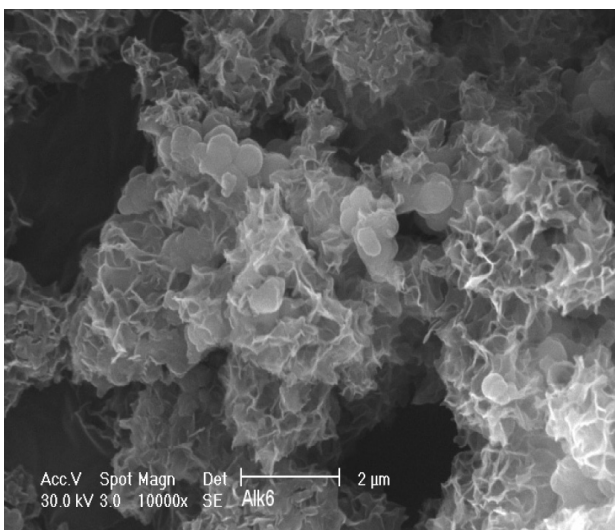


Figure 3. SEM morphology of sample Alk6.

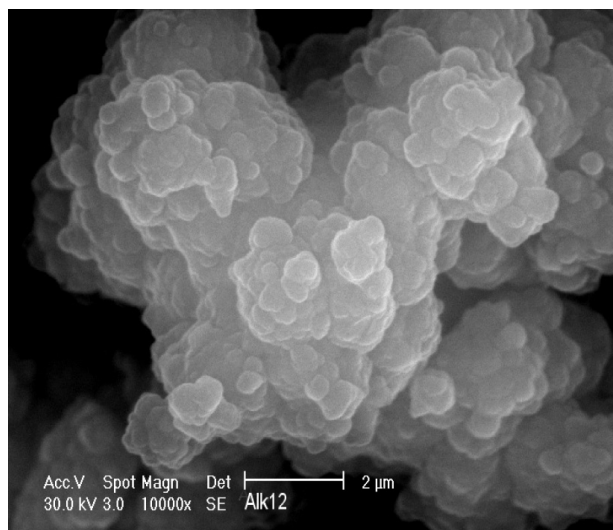


Figure 5. SEM morphology of sample Alk12.

are specific, because besides boehmite peaks, hydrobasaluminite phase was discovered. Accordingly, at the sample of Alk6 was appearance peak of else phase, consequently with α -boehmit phase exists boehmit phase. The samples of Alk11 and Alk12, were prepared with high concentration of alumina sulphate and urea, have all diffraction lines identical with hydrobasaluminite, $\text{Al}_2\text{SO}_4(\text{OH})_{10}\cdot 36\text{H}_2\text{O}$, ICDD PDF 08-0076 [9] (see figure 2). Detected hydrobasaluminite showed the high value of residual sulphur content (see table 2). In conclusion, hydrobasaluminite was observed at the samples from Alk10 to Alk12, while boehmie structure at the all other samples was observed. It seems, that between individual phases a transition exists dependence.

Scanning electron microscopy (SEM)

As it has been shown earlier [10], the urea precipitation method leads (at the reaction condition used) to colloid $\text{AlO}(\text{OH})$ nanoparticles assemblage into $1\mu\text{m}$ porous spherical clusters (see figure 2 as sample Alk1). At different concentration of both $\text{Al}_2(\text{SO}_4)_3$ and urea solutions, the size and shape of the spherical particles were changed. Figure 3, shows the SEM image of sample Alk6, with difficult shape characterization, recovered from precipitation of 14 g/l $\text{Al}_2(\text{SO}_4)_3$ and 120 g/l urea. The particles in some regions of the agglomerates are presented as submicron-scale balls, consisting of soundly packed smaller particles. These spherical agglomerates are disappeared when the concentration of reagents increases to 40g/l $\text{Al}_2(\text{SO}_4)_3$ and 200 g/l urea (see figure 4 as sample Alk11). The figure 5 reveals hydrobasaluminite "islands" obtained at the highest concentration of reagents (120 g/l $\text{Al}_2(\text{SO}_4)_3$ and 240 g/l urea) which are not accurate spheres in shape and not

very uniform in size (sample Alk12). On the other hand, each "island" consists of many spherical particles with narrow size distribution.

Specific surface area and porosity

Values of BET, Total Pore Volume V_p of prepared samples are shown in table 3. Pore Size Distribution (%) of samples Alk1-Alk12 is shown in tables 3 and 4. It is well know, that micropores have pore sizes in range from 0.3 to 2 nm. Mesopores substances have pore sizes from 2 up to 50 nm and macropores range from widths of 50 nm up to about 10^5 nm [11]. The porosity of samples was changed from mesopores to macropores with increasing concentration of urea and aluminium sulphate. It seems, that three fields of porous distribution in the samples exist. First field was occurred in the samples of Alk1-Alk5 where macropores are dominant, micropores are not practically there. Second field, the samples of Alk6-Alk10 have together dominantly mesopores and macropores. In this case, the micropores have larger representation as previous group. Third field, the samples of Alk11-Alk12 have the same ratio of the all kind of pore distribution. The total pore volume of fields decrease in following sequence: first (Alk1-Alk5), second (Alk6-Alk10) and three (Alk11-Alk12). Generally, if changes in phase composition are occurred, the changes in microstructural parameters are also presented. Therefore, to three phases (two different of boehmite phases and hydrobasaluminite phase) three fields of porous distribution correspond. However, the sample of Alk7 is exemption, because this sample contents boemite and hydrobasaluminite phases and there are mesopores and macropores dominant.

Table 3. Characteristic of porous of samples, BET and Total Pore Volume (V_p).

Sample	Alk1	Alk2	Alk3	Alk4	Alk5	Alk6	Alk7	Alk8	Alk9	Alk10	Alk 11	Alk12
BET (m^2/g)	13.5	102.3	141.8	128.3	91.8	54.4	57.5	66.4	61.7	90.1	71.9	6.4
V_p (cm^3/g)	0.492	0.481	0.475	0.462	0.456	0.272	0.297	0.256	0.224	0.187	0.159	0.146

Table 4. Pore Size Distribution (%) of ALK1-ALK12 samples.

Pore diameter (nm)	Alk1	Alk2	Alk3	Alk4	Alk5	Alk6	Alk7	Alk8	Alk9	Alk10	Alk 11	Alk12
< 6	4.12	4.46	4.07	3.38	4.72	18.31	15.09	14.34	13.55	11.45	29.79	30.69
6-8	2.27	2.55	2.40	1.89	6.57	4.80	3.48	7.97	3.95	8.22	19.98	6.99
8-10	1.52	1.75	1.68	1.30	4.44	3.94	2.02	5.55	3.28	5.65	6.40	3.51
10-12	1.91	2.31	2.09	1.79	6.02	5.48	3.07	6.62	4.25	7.03	2.80	3.84
12-16	2.60	3.45	2.86	2.71	7.79	6.76	4.13	6.13	3.94	6.22	0.00	4.62
16-20	3.66	5.24	4.04	3.79	6.47	6.47	7.71	6.16	4.52	4.52	0.00	3.05
20-80	39.62	45.40	38.76	37.19	24.02	25.98	51.08	29.43	36.79	31.50	20.43	27.36
> 80	44.31	34.83	44.11	47.95	39.97	28.27	13.41	23.79	29.72	25.40	20.61	19.94

CONCLUSION

Three different phases have been successfully prepared by homogenous precipitation from aluminium (III) sulphate-urea reaction at 98°C. The following conclusion can be drawn:

- (i) X-ray powder diffraction showed three different phases: α -boehmit, boehmit and hydrobasaluminite.
- (ii) Scanning electron microscopy showed that the samples have different morphology. The irregular shape of particles was prevailing, when the content of reagents increased.
- (iii) BET surface area of the samples showed very wide range (from 6 to 142 m²/g).
- (iv) The BJH measurements showed that the samples have very large porous distribution: α -boehmit is dominantly macroporous, mesoporous and macroporous exist together in boehmit. Micro, meso and macroporous are occurred in hydrobasaluminite samples. Hence, we can to say, that if changes in phase composition are occurred, the changes in microstructural parameters are also occurred.

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OXIDY HLINITÉ PŘIPRAVENÉ HOMOGENNÍM SRÁŽENÍM $Al_2(SO_4)_3$ S MOČOVINOU VE VODNÉM PROSTŘEDÍ

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Snadno filtrovatelné sférické prekurzory oxidu hliníku byli připraveny homogenním srážením $Al_2(SO_4)_3$ s močovinou ve vodném prostředí. Močovina se využívá jako precipitační činidlo. Produkt byl charakterizován práškovou rtg. difrakcí. Byly získané tři následující fáze: α -boehmite, boehmite a hydrobasaluminite. Morfologie byla pozorována pomocí skenovacího elektronového mikroskopu. Mikrostrukturní charakteristiky byly získány metodami BET a BJH. S rostoucí obsahem koncentrace reakčních látek se měnili nejenom fáze, ale také docházelo ke zvyšování iregularity morfologie. U α -boehmitu byly objeveny makropóry. V boehmitu byly objeveny mezopóry s makropóry a u hydrobasaluminitu byly všechny tři druhy pórů na stejné úrovni.