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ALUMINA POWDER PROPERTIES OBTAINED BY NEUTRALIZATION PROCESS OF SODIUM ALUMINATE

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ABSTRACT

Today, the most production of alumina is used for aluminum production [1, 2] (metallurgy alumina), minor production of alumina is used for special purpose, as fire-resistant materials, electro porcelain and etc., and because this alumina are called special alumina. For production some types of special alumina, as activated alumina (alumina with good adsorption properties) Bayer process is not optimal. Aluminum-hydroxide (gibbsite) obtained with this procedure have small specific area, approximately ~10 m^2/g, and it was thermal treatment on 400-500°C given γ-Al_2O_3 with up specific area around 250 m^2/g. Some physical-chemistry properties (adsorption's properties) of obtained alumina under these conditions are unsatisfactory for requirement in last time. High specific area, and also good adsorption properties of activated alumina, can be reached by using different procedures of synthesis starting aluminum–hydroxide with adjusting synthesis conditions and later thermal treatment. The aim of this paper is research powder properties of aluminum hydroxide obtained by neutralization process of sodium aluminates.

KEYWORDS: Alumina, Bayer process, Specific area.

1. Introduction

For production some types of special alumina, like as activated alumina (alumina by good adsorption properties), Bayer process is not optimal method. Aluminum-hydroxide (gibbsite) obtained by this procedure has little specific area, approximately ~10 m^2/g, and it is thermal treatment on 400-500°C give γ-Al_2O_3 with up specific area 250 m^2/g [3]. Some physical-chemical properties (adsorption's properties) obtained alumina under these conditions is unsatisfactory for requirement in last time. A typical physical–chemistry characteristic of activated alumina was given in table 1.

High specific area and good adsorption properties of activated alumina can be reached by using different synthesis procedures of starting aluminum hydroxide with adjusting synthesis conditions and supplementary thermal treatment.

The broadest application for production of aluminum-hydroxide as starting raw material for obtaining activated alumina two procedures was found:

- Deposition from acid solutions salts of aluminum (sulfate, nitrate) with basic solution, as NH_3,
- Deposition from basic solution (aluminates) with acids as H_2SO_4, HNO_3, HCl.

Table 1. *Typical physical–chemistry characteristics of activated alumina*

Properties	Values
Specific area, (m^2/g)	~350
Middle diameter of pore, (A)	max. 100
Specific volume of pore, (cm^3/g)	around 0.5
XRD-phase of alumina	amorphous, γ
Statistic adsorption, (%) -at pH 60 - at pH 100	 22 43
Contents of Al_2O_3, (%)	93
Loss by heating, (250-1200°C)	6.5

In this paper for obtained aluminum hydroxide as starting raw material for obtained activated alumina, was used neutralization of sodium-aluminates solution with sulfuric acid. This process consists of two phase:

- First phase, neutralization free NaOH,
- Second phase, hydrolysis of sodium-aluminates, when we have deposition solid phase of aluminum - hydroxide.

Thermal activation this obtained aluminum–hydroxide is made activated alumina. In function from pH aluminates solution, in neutralization process of sodium-aluminates can be obtained three crystal phases [4-6]: boehmite, bayerite and gibbsite. In Bayer process are made gibbsite only. In this paper we have one aim, and it is to show how phases structure, size of primary and secondary particles influence to specific area of aluminum-hydroxide powder.

2. Experimental part

Sodium–aluminates with small and high caustic module and sulfuric acid with defined concentration were used for experimental research and results were presented in this paper. Sodium–aluminates solution with small and high caustic model was made in Factory "Birac" Zvornik (caustic module of aluminates solution are defined as mole ration caustic basic Na_2O_k and Al_2O_3 in alumina solution) have been used in these research. Starting aluminates solution had concentration 150-155 grams of $Na_2O_κ$/l, and then dilution to concentrate of 30 and 85 grams of $Na_2O_κ$/l. The temperature of neutralization aluminates solution has been 30 and 70°C, and dripping time sulfuric acid in aluminates solution were 30, 60 and 180 minute. Samples of synthesis powder were marked: $A,H^T{}_C$ - $S_τ$ и $A,M^T{}_C$- $S_τ$ where is:

A- Marked sample of aluminum – hydroxide powder,

M, H- marked small and high caustic model of aluminates solution,

C- Marked concentration of aluminates solution, [g $Na_2O_κ$/l],

T – Marked temperature neutralization of aluminates solution, [°C],

S- Marked neutralization of aluminates solution with sulfuric acid

τ -marked dripping time sulfuric acid, [min.].

Qualitative sample identification was performed on x-ray powder (XRD) type PHILIPS PW1729.

Estimation phase's structure in synthesis sample was performed using equation (1)

$$Fi = \frac{Ii \cdot Bi}{I_B \cdot B_B + I_{BAY} \cdot B_{BAY} + I_G \cdot B_G} \qquad (1)$$

Where are:

Fi –part of observed phase,

I_i- the highest intensity of peak,

B_i-broad on half of highest peak,

Roentgen analyze was used for calculating size of primary particle using Sheerer formula:

$$d = \frac{0,9 \cdot \lambda}{B \cdot \cos\theta} \qquad (2)$$

Where are:

d - size of primary particle [nm],

λ - wave length of X-ray (λ =0,154 nm),

B - broad highest peak on half, [rad]

Θ - half angle diffraction on highest peak, [°].

Calculation middle diameter size performed on apparatus COULTER COUNTER T A-II. Calculation specific area performed with BET method on apparatus type "FLOWSORB".

3. Results and discussion

In process neutralization aluminates solution by sulfuric acid can appear three crystal phases:

- Boehmite (marked B),
- Bayerite (marked with Bay),
- Gibbsite (marked with G).

In dependence (function) from neutralization condition can appear samples which consist all three crystal phases (fig. 2.), samples which consist only bayerite and gibbsite (fig. 3.), and sample which consist only boehmite phase (fig. 4).

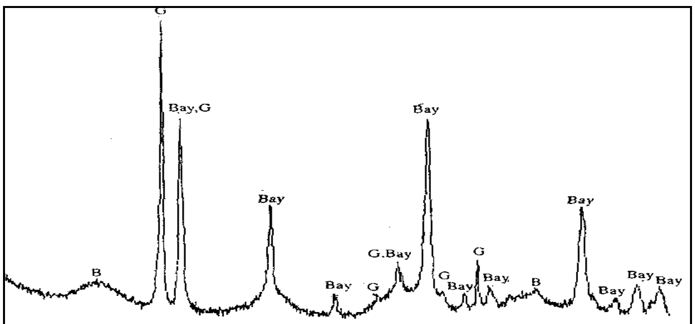

Fig. 2. *X-ray data for sample* $AM_{30}^{30}\_S_{180}$

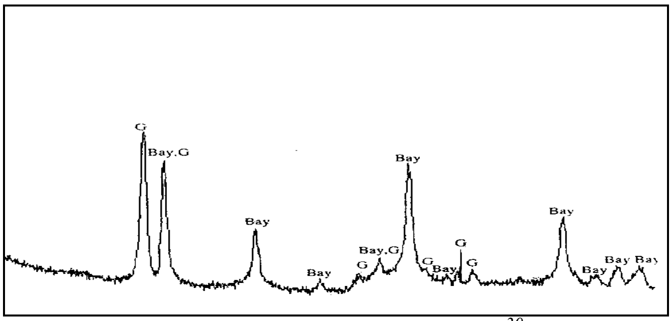

Fig. 3. *X-ray data for sample $AM_{85}^{30}\_S_{180}$*

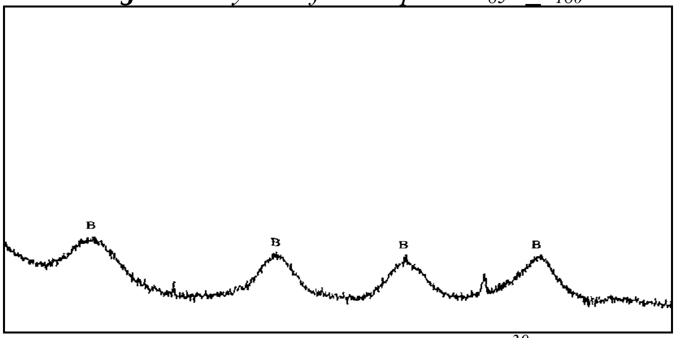

Fig. 4. *X-ray data for sample $AH_{30}^{30}\_S_{30}$*

Selected samples of aluminum–hydroxide powder are characteristic toward phase structure, size primary particle, size secondary particle and specific area. These results are given in Annex 1, and they describe the influence of phase's structure, size of primary particle and size of secondary particle on specific area of synthesis powder. From table 2 we can see that phase structure, size primary particle of bayerite and gibbsite and size secondary particle have important (significant) influence to specific area synthesis aluminum–hydroxide powder. Increasing portion in sample synthesis aluminum–hydroxide powder significantly increasing specific area of sample, because that primary particle boehmite (2-3 nm) are rapidly less then primary particle of bayerite and gibbsite (10-50 nm).

Also, decreasing size primary particle bayerite and gibbsite bring about to increasing specific area samples of synthesis powder. Further, samples of synthesis powder less secondary particle have higher specific area, and this fact can be explanation with less area contact between primary size(crystallite), and this provoke increasing specific area of synthesis powder samples.

4. Conclusion

Obtained results from performed experiments which refer to process neutralization aluminates solution by sulfuric acid given next conclusion:

- Neutralization aluminates solution with sulfuric acid can appear three crystal phase: boehmite, bayerite и gibbsite, but with Bayer procedure appear only gibbsite;
- Powder obtained by neutralization aluminates solution can have specific area to up 300 m^2/g, but aluminum–hydroxide powder (gibbsite) obtained with Bayer process have specific area less from 10 m^2/g;
- Specific area of synthesis alumina powder is in function of phase's structure, size primary particle (crystallite) and size of secondary particle, and with increasing portion of boehmite decreasing size crystallite bayerite and gibbsite, and decreasing size secondary particle bring about forming samples with high specific area. High specific area of synthesis powder are result higher portion of boehmite with primary particle 2-3 nm;

With changing processing condition neutralization of aluminates solution as: caustic model of aluminates solution, concentration of aluminates solution, temperature of neutralization, and time dripping sulfuric acid influence to characteristic of synthesis powder which are: phase structure, size of primary particle and size of secondary size.

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***Annex 1.** Specific area synthesis alumina powder in function phase structure, size primary and secondary size*

Sample	Phase structure [%] and size primary particle [nm]						Size of secondary particle	Specific area
	Boehmite		Bayerite		Gibbsite			
	Portion	ds	Portion	ds	Portion	ds		
	[%]	[nm]	[%]	[nm]	[%]	[nm]	[μm]	[m²/g]
$AM_{30}^{30}-S_{30}$	88	(2.8)	4.5	(24.7)	7.5	(23.5)	13.5	219.1
$AM_{30}^{30}-S_{60}$	-	-	-	-	-	-	15.3	166.7
$AM_{30}^{30}-S_{180}$	19.5	(2.5)	30.0	(29.6)	50.5	(31.3)	47.0	79.4
$AM_{30}^{70}-S_{30}$	19.0	(2.6)	34.0	(24.6)	46.0	(25.6)	12.5	56.5
$AM_{30}^{70}-S_{60}$	-	-	-	-	-	-	16.0	55.2
$AM_{30}^{70}-S_{180}$	16.0	(2.9)	20	(27.0)	64.0	(28.2)	37.0	34.1
$AM_{85}^{70}-S_{30}$	67.0	(2.8)	17.5	(22.8)	15.5	(28.1)	8.2	164.0
$AM_{85}^{30}-S_{60}$	-	-	-	-	-	-	10.5	33.1
$AM_{85}^{30}-S_{180}$	-	-	49.0	(21.2)	51.0	(25.6)	43.0	30.1
$AM_{85}^{70}-S_{30}$	23.0	(3.7)	58.0	(29.7)	19.0	(28.0)	13.5	58.2
$AM_{85}^{70}-S_{60}$	-	-	-	-	-	-	19.0	55.3
$AM_{85}^{70}-S_{180}$	-	-	14.0	(40.2)	86.0	(40.2)	39.0	16.8
$AH_{30}^{30}-S_{30}$	100	(2.2)	-	-	-	-	7.9	277.7
$AH_{30}^{30}-S_{60}$	-	-	-	-	-	-	8.2	274.8
$AH_{30}^{30}-S_{180}$	100	(2.4)	-	-	-	-	10.5	226.0
$AH_{30}^{70}-S_{30}$	89.0	(2.6)	5.5	(19.8)	5.5	(18.8)	12.0	284.0
$AH_{30}^{70}-S_{60}$	-	-	-	-	-	-	12.5	213.9
$AH_{30}^{70}-S_{180}$	15.0	(2.5)	35.0	(16.5)	50	(23.5)	13.5	79.1
$AH_{85}^{30}-S_{30}$	59.0	(3.0)	11.0	(14.8)	30.0	(11.3)	9.7	295.5
$AH_{85}^{30}-S_{60}$	-	-	-	-	-	-	10.7	245.4
$AH_{85}^{30}-S_{180}$	56.0	(2.8)	14.0	(16.5)	30.0	(12.8)	12.0	218.6
$AH_{85}^{70}-S_{30}$	42	(2.4)	29.0	(17.4)	29.0	(23.5)	10.0	212.5
$AH_{85}^{70}-S_{60}$	-	-	-	-	-	-	12.0	160.6
$AH_{85}^{70}-S_{180}$	28.0	(2.6)	41.0	(29.7)	31.0	(28.2)	13.0	98.7