Support and Catalyst for the alkylation of benzene by ethylene process

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Abstract

A method for preparation of a spherical alumina support with preset porous structure for a catalyst of benzene alkylation with ethylene has been developed. The process of the support manufacture has been adjusted in a pilot installation, and an industrial installation for production of alumina support for the alkylation catalyst has been designed and built at the Shevchenko Plastics Plant (Aktau, Kazakhstan).

Introduction

The process of benzene alkylation with ethylene in the presence of spherical catalyst «boron fluoride on alumina» was originally realized by UOP. In the 70s, in Kazakhstan the Shevchenko Plastics Plant was built, with a shop for ethylbenzene production based on catalyst imported from the USA.

A domestic catalyst designed for the replacement of the imported one had to fit in with the operating regimes of the existing installation. Therefore, in addition to sufficient activity and selectivity, the new catalyst had to meet the requirements of heat and hydrodynamic regimes of the operating installation. Consequently, it had to have physicochemical characteristics similar to those of the USA catalyst. These characteristics depend mostly on alumina support properties and can be regulated by the selection of alumina preparation conditions.

Results

A comparative study of the properties of aluminas of different types, both of domestic and foreign origin, and the imported catalyst (Table 1) showed that the latter has a rather high value of the pore volume (0.75 cm^3/g) with a high fraction of pores with a radius over 100Å (0.44 cm^3/g). The domestic support with the closest characteristics is the alumina A-64M, and the Japanese alumina even surpasses the catalyst in these indices. As to the

crushing strength, the imported catalyst proved to be much stronger than all alumina types studies, with the Japanese alumina ACBW-1 having the least crushing strength value. The contents of Na$_2$O and Fe$_2$O$_3$ admixtures in aluminas are on the whole close to the ones in the imported catalyst, with the exception that the ACBW-1 alumina has an elevated content of sodium oxide and the SKTB-4 alumina has a higher content of ferric oxide, while Rhone-Poulenc alumina contains no Na$_2$O at all. In addition, the commercial catalyst of USA, type A-2, contains up to 8 wt.% of boron fluoride. Apparently, the introduction of this compound into alumina can change its properties, and the direct comparison of the physicochemical characteristics of the catalyst and aluminas should not be considered entirely correct. However, basing on the results described in [1, 2], the catalyst preparation can be performed directly in the reactor for alkylation process, by alumina support saturation with boron fluoride. Thus, it was assumed that the replacement of the imported catalyst could be achieved by development of alumina with similar properties.

To specify requirements to the support in order to provide its further transformation to the active and stable alkylation catalyst, a research of the surface acid properties of various supports (aluminas) of domestic and foreign origin different in physicochemical properties was carried out (Table 1). As the process of benzene alkylation with ethylene proceeds via the formation of intermediate carbonium ion on the catalyst Lewis acid sites, it was important to compare the strength and the

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Table 1
Properties of pilot batches of alumina supports.

Parameters	Alumina types						
	A-2 (USA), Catalyst	SKTB-2 (OTK-22)	SKTB-3 (OTK-94)	SKTB-4 (OTK-118)	A64k (Angarsk)	ACBW-1 (Japan)	Rhone-Poulenc (France)
Granule diameter, mm length, mm	1.4-2.0 -	1.4-2.0 -	1.4-2.0 -	1.4-2.0 -	2.0-3.0 3.5-7.0	2.0-5.0 -	1.4-2.0 -
Pore volume, cm^3/g	0.75	0.60	0.60	0.60	0.65	0.93	0.55
Volume of pores with r>100 Å, cm^3/g	0.40	0.10	0.04	0.06	0.24	0.50	0.02
R_{eff}, Å	90	60	50	80	90	r_1=50 r_2=400	40
S_{BET}, m^2/g	150	220	150	220	160	203	233
Bulk density, g/cm^3	0.55	0.60	0.61	0.70	-	0.50	0.65
P_{av}, MPa : Spherical granule Cylindrical gran. -forming side	23.0 -	4.2 -	8,0 -	16.5 -	- 4.7	2,1 -	15.5 -
Na_2O, %	0.01	0.02	0.02	0.008	0.02	0.05	absent.
Fe_2O_3, %	0.04	.01	0.021	0.064	0.05	0.04	0.03
BF_3, %	8,0	-	-	-	-	-	-

number of these sites in the samples studied. The acidity of the samples was determined by the adsorption of CO probe-molecules, studied in IR spectrometer UR-20 at 110 K according to the technique developed at Boreskov Institute of Catalysis [3].

The number of Lewis sites on the surface was estimated from the formula:

$$C_s = A/A_o \bullet \rho \bullet 10^{-3}, \mu mole /g, \quad (I)$$

where A is the observed integral absorbance of a band calculated as $\int lgT_o/T \bullet \partial \nu$; A_o is the integral intensity for 1 µmole of the compound adsorbed, ρ is the density of the tablet.

The Lewis site strength was determined by the formula:

$$Q = 10.5 + 0.5 \, \Delta \nu_{co} , kJ/mole \quad (II)$$

where $\Delta \nu_{co} = \nu^{ads}_{co} - 2143 \, cm^{-1}$; 2143 cm^{-1} taken as a value of ν^{gas}_{co}.

The results obtained are shown in Table 2. It can be seen that all supports, independent on the preparation method or the type of the initial aluminum hydroxide, have only one type of Lewis acid sites ($\nu \sim 2190 \, cm^{-1}$) of medium strength (Q=34-36.5 kJ/mole), and the number of these sites is roughly the same.

After BF_3 deposition on alumina (samples 7 and 8) new sites ($\nu = 2220$ and $2210 \, cm^{-1}$) with higher strength (Q=49 kJ/mole) appear with simultaneous reduction in the number of the sites at $\nu = 2195 cm^{-1}$. The total number of Lewis acid sites in the catalyst is approximately the same as in the initial aluminas. Therefore, the acidities of the supports studied and the commercial catalyst are practically the same.

Since the liquid-phase process of benzene alkylation with ethylene proceeds under inner diffusion limited regime [2], the catalyst pore structure should have a significant effect on the catalyst activity and selectivity. Tests of the supports studied in an experimental alkylation reactor at the Shevchenko Plastics Plant, performed

under conditions of the catalyst formation by support treatment with boron fluoride before testing, showed that actually the highest ethylene conversion and the highest selectivity (ethylbenzene yield) were observed on the catalyst Alcar-2 having the highest specific volume of the transport pores (>100Å), the medium pore radius in

this catalyst being ~90Å. Sufficiently high selectivity and conversion were observed also on the catalysts prepared from the aluminas A64k and ACBW-1 (See Table 1). At the same time, the catalysts prepared from the supports SKTB-2, SKTB-3 and SKTB-4 had the lowest values of the activity and selectivity.

Table 2.
Acid properties of alumina.

N	Type of Al_2O_3	ν^{ads}_{co}, cm^{-1}	$\Delta\nu_{co}$, cm^{-1}	Q, kJ/mole	A_o, cm/µmole	A, cm^{-1}	ρ, mg/cm^2	C_s, µmole /g	C_s, µmole/m^2
1	ACBW-1	2195	52	36.5	0.80	6.6	10.5	780	3.9
2	SKTB-2	2190	47	34	0.75	5.0	15.7	600	2.6
3	SKTB-3	2190	47	34	0.75	5.3	10.7	660	3.1
4	SKTB-4	2190	47	34	0.75	4.8	10.7	560	2.5
5	A-64k	2195	52	36.5	0.80	5.7	13.5	560	2.5
6	Rhone- Poulenc	2190	47	34	0.75	6.1	11.0	690	3.4
7	A-2	2190	47	34	0.75	1.5	-	150	1
	(USA)	2210	67	44	1.00	1.7	12.8	130	0.86
	(Fresh catalyst)	2220	77	49	1.15	2.1	-	140	0.93
8	A-2	2190	47	34	0.75	1.2	-	140	1.35
	(USA)	2210	67	44	1.00	1.6	11.5	130	1.26
	(after reaction)	2220	77	49	1.15	1.7	-	125	1.21

Thus, it can be concluded that the main parameter affecting the performance of the catalyst is the alumina pore structure.
It is necessary that large pores (>100Å) are present in the support, taking up no less than 0.2 cm³/g, with the effective pore radius being at least 70Å.

For regulation of the support pore structure two methods can be used [4, 5]. The first one is the introduction of burn-out additives, such as lignin, starch or wood flour, which decompose upon aluminum hydroxide thermal treatment, leading to the formation of large pores. The second method consists in the doping of the placticized aluminum hydroxide mass with coarse-dispersion powder material. One can use for this purpose the product of gibbsite thermal decomposition (PTD). The method of PTD preparation and its properties are described in [5, 6]. The main problem was to develop a method of preparation of spherical alumina granules with required pore structure, based on the technology of PTD production and reprocessing.

As shown in [5, 6], the preparation of spherical γ-Al₂O₃ from PTD includes the following main stages (see Fig.1):

- gibbsite reprocessing to PTD in catalytic heat generator;
- PTD milling;
- washing out soluble admixtures (Na₂O) from the PTD milled;
- preparation of aluminum hydroxide of pseudoboehmite structure in autoclave (plasticized mass);
- preparation of spherical aluminum hydroxide granules by the method of hydrocarbon-ammonia molding;
- drying and calcination producing spherical γ-Al₂O₃ granules.

This scheme is adopted in the manufacture of the spherical alumina support for combustion catalysts used in catalytic heat generators, with high mechanical strength and monodisperse pore radius distribution in the region of 50-60Å.

For the preparation of the alkylation catalyst support it was necessary to synthesize alumina with required pore structure characteristics in the framework of this technology.

Table 3 shows the properties of spherical alumina supports in relation to the amount of added PTD.
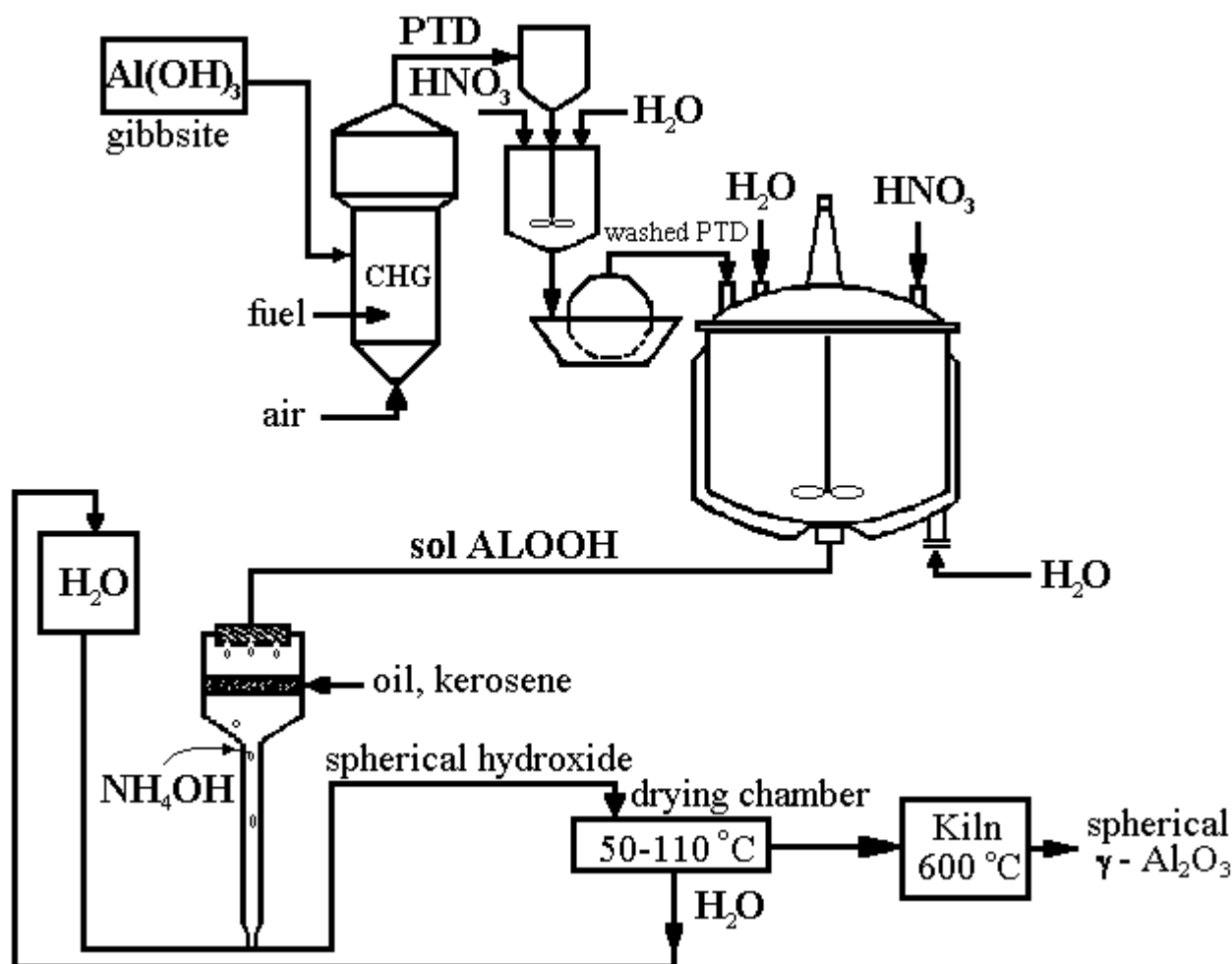
Fig.1. Scheme of spherical γ-Al2O3 production based on the method of gibbsite decomposition
in Catalytic Heat Generator (CHG).

Table 3
Properties of pilot alumina batches.

No of batch	1/0	1/1	1/2	2/0	2/1	2/2
Non milled amount of PTD (as Al_2O_3), %	0	30	40	0	40	60
Total pore volume , $V\Sigma$, cm^3/g	0,40	0,43	0,46	0,42	0,48	0,52
Effective pore radius, r_{eff}, Å	45	60	60	50	65	60
Volume of pores with r>100Å, cm^3/g	0,03	0,10	0,15	0,01	0,14	0,21
Volume of pores with r<60Å cm^3/g	0,32	0,15	0,12	0,35	0,20	0,18
S_{BET}, m^2/g	205	220	250	195	230	210
Mech. strength,P_{av}, MPa	17,0	10	4 ,8	26,1	15	4,0

As can be seen, at the chosen calcination conditions (550°C, 8 h), the preparation of alumina with required volume of large pores is possible only when about 60% of PTD (calculated on alumina basis) is introduced into the plasticized mass. In this case the volume of pores with a radius over 100Å attains 0.21 cm^3/g. With less amount of PTD (30-40%) the large pores volume does not

exceed 0.15 cm³/g. However the introduction of large amount of PTD into the plasticized mass results in degradation of the alumina strength. Thus, while the pure alumina without PTD has a crushing strength in the range of 17-26 MPa, the one with 30% of PTD has much less strength - about 10 MPa, and the further addition of PTD to 60% content results in the reduction of the crushing strength to 4 MPa. The introduction of PTD provides the increase of the volume occupied by pores with radius over 100Å, however the effective pore radius does not exceed 65Å. As can be seen from Table 3, the alumina obtained at 550°C has rather high volume of pores with a radius below 60 Å, even after 60% addition of PTD this value amounts to 0.18 cm³/g. Since the process of liquid-phase benzene alkylation with ethylene proceeds under inner diffusion limited regime, the presence of small pores in the catalyst worsens its performance.

To reduce the volume of fine pores and increase the effective pore radius it was considered necessary to select conditions of alumina thermal treatment providing sintering of fine pores.

Table 4
Alumina properties as function of the calcination conditions.

No of samples	2/0	2/1	2/2	2/0	2/1	2/2	2/0	2/1	2/2
Calcination conditions	Mode 1			Mode 2			Mode 3		
V_Σ , cm³ /g	0,51	0,61	0,61	0,50	0,56	0,56	0,50	0,58	0,64
R_{eff}, Å	80	80	80	75	80	78	80	80	78
Volume of pores with r>100 Å, cm³ /g	0,015	0,27	0,21	0,02	0,26	0,25	0,015	0,28	0,22
Volume of pores with r<60 Å, cm³ /g	0,06	0,05	0,05	0,08	0,06	0,05	0,10	0,06	0,05
$S_{BET.}$, m² /g	157	144	150	167	131	148	143	150	145
$P_{av.}$, MPa	24,6	13,8	4,8	28,4	13,4	8,7	22,3	14,5	10,0

Effect of thermal treatment conditions on γ-Al₂O₃ pore structure

The effective pore radius in alumina is known to increase with temperature only in the temperature range below 750°C [4, 5]. The further increase of the temperature, although accelerating sintering, is inexpendient because it leads to phase transformations of γ-Al₂O₃ to high temperature alumina modifications.

Three methods of alumina calcination were studied.

1. The dried alumina granules were placed in a cold tubular electric furnace, and the temperature was increased to 750°C at a rate of 100°/h. The air flow rate during the temperature rise and in the course of initial 2 hours of calcination was 100-200 h⁻¹. Then the air flow was stopped and the sample was calcined for 14 hours without air supply. This procedure will be referred to as the Mode 1.

2. The possibility of decreasing the duration of alumina samples calcination was examined by conducting the thermal treatment without air flow for 8-12 h at a constant temperature of 750 °C (alumina samples were placed into the furnace preheated to 750°C). Mode 2.

3. The calcination was also performed without air flow, under conditions close to Mode 1, with a constant temperature (750°C) heat time of 8-12 h. Mode 3.

The results obtained are given in Table 4. The data in the Table show that at 750°C the sintering of fine pores occurs in all alumina samples and that the mode of thermal treatment has no noticeable effect on the resulting pore structure. However the calcination in Mode 3 results in the highest mechanical strength of the samples.

Taking into account these results, the following calcination mode was selected to provide maximum process efficiency:

• temperature increase from room temperature to 750°C at a rate of 100°/h;

• calcination at 750°C for 8 h without forced removal of the compounds formed with air flow.

Table 5
Properties of pilot spherical alumina batch OTK-166

Parameter	Value
Granule diameter, mm	1.4-2.0
Bulk density, g/cm^3	0.60
S_{BET}, m^2/g	150
Pore volume, cm^3/g	0.66
P_{av}, MPa	11.0
Admixture, %	
Na_2O	0.05
Fe_2O_3	0.01
Volume of pores with r>100 Å, cm^3/g	0,25
r_{eff}, Å	78

On the basis of the data of Tables 3 and 4, suggesting that the addition of 40% of PTD and the selection of the above-mentioned calcination procedure provides the formation of the required pore structure in alumina, at the same time retaining sufficient granule strength for stable process performance, it was recommended to introduce PTD as a pore-forming additive in an amount of 40%.

Adjustment of the technology for production of supports with required pore structure

The adjustment of the technology for production of support for the alkylation catalyst was performed in a pilot-scale installation at the «Katalizator» Stock Company in Novosibirsk. Two pilot catalyst batches (OTK-164, OTK-166), 50 kg each were produced.

During the technology adjustment the conditions of individual process stages: washing, filtration, autoclaving, etc. were optimized.

Since the introduction of insufficiently washed PTD into the plasticized mass resulted in an elevated Na_2O content in the final product, the need for more meticulous washing of the milled PTD became apparent. The PTD washing was carried out in three repulpings, each for 20 min, at 55-70° C. The filtration was performed in a drum vacuum filter of BOK-1 type working at rarefication 0.4-0.6 atm provided by a vacuum pump.

The residual Na_2O content in PTD after 3 repulpings was 0.02 wt. %.

In the process of the technology adjustment the conditions of preparation of the plasticized mass in

autoclave were selected, an optimum concentration of Al_2O_3 in the mass (250 g/kg) was determined, and the optimum duration of autoclaving was found.

Before molding non milled and unwashed PTD was introduced into the plasticized mass in an amount of 40% (calculated as Al_2O_3). The parameters ascertained were the mass of PTD portions added at a time to the mass, frequency and duration of the stirring of the resulting mixture.

During the manufacture of alumina experimental batches, all technological parameters of the proposed method of preparation of support for the catalyst of benzene alkylation with ethylene were examined. The properties of the alumina support (batch OTK-166) are given in Table 5.

This batch (50 kg) was shipped to the Shevchenko Plastics Plant (Aktau city) for testing in the experimental-industrial reactor of benzene alkylation with ethylene.

Before that, the alumina OTK-166 had been preliminarily tested in a pilot installation of Krasnodar Polytechnical Institute under the following conditions:

- temperature   180°C;
- pressure   3 MPa;
- space velocity with respect to benzene   30 h^{-1};
- molar ratio benzene/ethylene   2.8:1;
- duration of testing   6 hours.

Under these conditions the alkylation catalysts based on the alumina OTK-166 exhibited the activity and selectivity comparable or superior to those of the imported catalyst, type A-2 (USA).

The testing of the alumina OTK-166 at the Shevchenko Plastics Plant was carried out in the experimental reactor placed in parallel with the industrial reactor. The support loading was 30 l. Before loading into the reactor, the alumina had been in contact with air for 3 days.

The drying of the support loaded into the reactor was carried out in two stages. First, the support was treated with hot dry nitrogen flow directed downward at 230-250°C and normal pressure for three days, then the treatment with hot dry benzene was conducted for 3 days under the following conditions:

- benzene mass flow   200-250 kg/h;
- pressure   20 kg/cm^2;
- temperature   180-200°C.

The heating of the system was accomplished by the supply of a heat-carrier into the reactor jacket.

After stopping the heat carrier supply and the change of the direction of the benzene flow, the saturation of the support with boron fluoride fed to the lower part of the reactor was performed. This process was conducted at 80-90°C for 150 h. The saturation degree control was performed by monitoring the content of boron fluoride in benzene. The saturation was considered complete when the concentrations of boron fluoride at the reactor inlet and outlet became equal. After the complete support saturation with BF_3 the catalyst was conditioned by gradually increasing the ethylene load from 12-16 Nm^3/h to 30-32 Nm^3/h.

The tests of the pilot batch of the support were carried out under the following operating parameters:

- ethylene flow rate   30-36 m^3/h;
- benzene mass flow rate   310-350 kg/h;
- mass flow rate of the recycled alkylate   1200-1300 kg/h;
- boron fluoride flow rate   3.0 m^3/h;
- pressure   28 kg/cm^2;
- temperature   170-180°C;
- molar ratio benzene/ethylene   (3.0-2.8)/1.

The operation of the experimental reactor was stable for sufficiently long time. During all testing period (over 100 days) the ethylene conversion was practically 100% with the process selectivity to ethylbenzene 50-60%.

Thus, the data presented show that the aljylation catalyst based on the alumina OTK-166 has the performance characteristics: activity and selectivity comparable and superior to those of the imported catalyst of USA (type A-2).

Conclusions

A method for preparation of support with required pore structure for the alkylation catalyst has been developed.

Based on the research results, an a «Addendum» to the «Initial Data Set» for the design of an industrial installation for production of the alumina support of the alkylation catalyst has been prepared.

On the basis of the «Initial Data Set with Addendum» the industrial installation for production of the alumina support of the alkylation catalyst has been designed and constructed at the Shevchenko Plastics Plant (Kazakhstan, Aktau).

The methods of preparation of the alumina support and the alkylation catalyst have been patented in Russia [7-11].

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