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Research Note

Preparation of extruded alumina with suitable crushing strength and good stability

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Abstract. The extruded alumina was prepared by the extrusion of a paste that contains boehmie, δ-alumina, polyethylene glycol 400 as an additive, and nitric acid as a peptizing agent. Porosity and crushing strength of the samples were carried out by means of N_2 adsorption-desorption isotherm and mechanical strength instrument, respectively. The calcined extruded alumina has the specific surface area of 168-240 m^2/g, pore volume of 0.37-0.5 cm^3/g, and pore diameter of 8.2-8.8 nm. More than 36% of pore volume belonged to the pore diameters larger than 10 nm. The lateral crushing strength was found to be 232-476 N/cm^2. The highest crushing strength of the prepared samples was 30% higher than that reported in the literature. The addition of aluminum nitrate to the paste increased 50% in the lateral crushing strength; hence, it reached the value of 622 N/cm^2. This was mainly the result of the binder functionality of aluminum nitrate that led to stronger connections between the particles. The extruded alumina did not show any deformation when introduced to the impregnation solution. This extruded alumina can be used as the catalyst support.

1. Introduction

Heterogeneous catalysts play a very important role in many industrial processes. Different kinds of materials such as alumina, zirconia, and alumina-silicates, which can be of a single phase or composites, can be used as a catalyst support [1]. Among these materials, alumina is the most widely used catalyst support because of its attractive mechanical properties, cheapness, intrinsic acid-base characteristics, reasonable stability, adjustable surface, and physicochemical properties. Alumina can provide, through its different phases, a wide range of surface areas and porosities that are suitable for many catalytic applications such as petrochemical and petroleum industries [2-4]. The catalyst should be formed into a suitable shape according to the reactor's essentials. Pressing and extrusion are two common methods of manufacturing shaped supports [1]. The miscibility of components, i.e. alumina source such as boehmite and different phases of alumina with different particle sizes, additives, and peptizing agent, is necessary, because if the components of the paste are not miscible, the liquid and solid phases may separate during the extrusion. The preparation of a paste with desirable viscosity is an important factor in the extrusion method because very viscous paste could not come out of the extruder and stick around the extruder helix. On the other hand, using low-viscosity paste will result in the phase separation. The boehmite powder is being mixed with suitable additives such as polymers, grease, graphite and peptized by

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the addition of acids or alkalis [1,3]. Binders are necessary for alumina supports extrusion. Polymer solutions, clay, boehmites, and pseudo boehmite, gelled by the addition of acids and alkalis, are used as a binder. The use of boehmite and pseudo boehmite species as a binder is beneficial, because they are transformed into the high-surface-area γ-alumina. The crushing strength, shape retention of extruded support, and textural properties, such as specific surface area, pore diameter, and pore volume, are the important characteristics of a suitable support.

In the present work, the alumina support was prepared using boehmite, δ-alumina, polyethylene glycol 400, and nitric acid as a peptizing agent. The extruded alumina with different boehmite/δ-alumina was prepared, and their crushing strength and textural characteristic were studied. The effect of aluminum nitrate addition on the porosity and crushing strength was also investigated.

2. Experimental analysis

2.1. Materials

Boehmite (surface area: 275 m^2/g, pore volume: 0.71 cm^3/g, and pore diameter: 10.34 nm are obtained from the Iranian Institute of Research and Development in Chemical Industries), γ-alumina (particle size < 0.063 mm of about 72%, Merck), polyethylene glycol 400 as an additive denoted as PEG-400 (Merck), nitric acid as a peptizing agent (Merck), aluminum nitrate nonahydrate ($Al(NO_3)_3.\ 9H_2O$, Merck), cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$, Merck), and distilled water were provided. All materials were used without further purification.

2.2. Characterization

2.2.1. Textural properties

The specific surface area, pore volume, and pore size distribution of extruded alumina were obtained from nitrogen adsorption-desorption isotherms, determined at -203°C with Belsorp II apparatus. The extruded alumina was degassed at 300°C for 5 h. The specific surface area of the samples was calculated according to Brunauer-Emmett-Teller (BET) method, and the pore size distribution and total pore volume were determined from the adsorption branches of the corresponding nitrogen isotherm by the Barrett-Joyner-Halenda (BJH) method.

2.2.2. Crushing strength

The crushing strength of extruded alumina was determined by measuring the breaking force for a sample compressed between two parallel plates using a Santam STM-20 (Iranian) machine. The Side Crushing Strength (SCS) was calculated from the following equation:

$$\text{SCS} = F/L, \tag{1}$$

where F is Force (N), and L is the length of extruded catalyst (mm). In the Lateral Crushing Strength (LCS) measurements, the cross-sectional area of the granule is taken to be $S = DL$, where D is the granule diameter (cm) and L is the granular length (cm):

$$\text{LCS} = F/S. \tag{2}$$

2.2.3. Paste preparation

The extruded alumina supports were prepared via the kneading and extrusion of a paste as follows: boehmite powder and δ-alumina (γ-alumina is calcined at 900°C) mixed thoroughly at different ratios. The nitric acid solution was added to this composite and kneaded using a mechanical paddle. Then, the aqueous solution of PEG 400 was added to the mixture and mixed. The prepared paste was extruded using an extruder with the cylindrical die of 2.5 mm. The extruded samples were dried at room temperature and, then, at 110°C for 12 h. The dried materials calcined at 550°C for 4 h in air. Calcined extruded alumina was broken into an appropriate length. Sample H was prepared in the presence of 3 wt% $Al(NO_3)_3$.

The image of extruded alumina is presented in Figure 1.

2.2.4. Impregnation

The sample prepared with 5% δ-alumina was impregnated with cobalt salt via incipient wetness impregnation method for 12 h at room temperature. After that, the samples were dried at 110°C for 12 h and calcined at 550°C for 5 h. The calcined samples contained 9% wt. Co.

3. Results and discussion

Calcination of γ-alumina at 900°C led to the formation

Figure 1. The image of extruded alumina after calcination.

Table 1. Textural characteristics of γ-alumina and δ-alumina.

Alumina	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
γ	139	5.4	0.27
δ	20	21.2	0.22

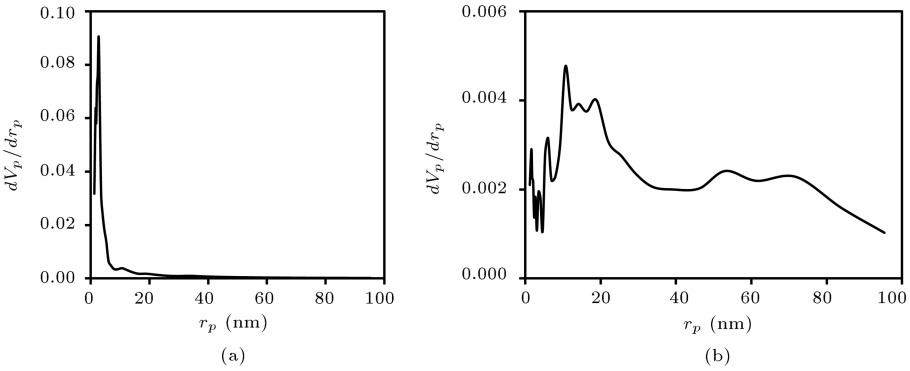

Figure 2. pore size distribution of (a) γ-alumina and (b) δ-alumina.

of δ-alumina [5]. This phase transition decreased specific surface area and increased pores diameter significantly. The result is presented in Table 1.

Pore size distributions of γ-alumina and δ-alumina are shown in Figure 2. Pore size distribution of δ-alumina is significantly broader than that of γ-alumina. These results showed that increasing calcination temperature led to the formation of meso and macro porosity in the alumina, which is in agreement with those reported in the literatures [5-7]. Because of the presence of large molecules in the hydrodesulphurization reactions, the presence of meso and macro pores in the support is necessary; therefore, the porosity of support must be tuned by calcination.

Table 2 shows the composition of paste and textural properties of extruded alumina. The paste prepared only with boehmite was highly viscous; hence, the paste could not come out of the extruder and stick around the helix. The addition of δ-alumina to the materials improved the extrudability of the paste. The absence of boehmite in the paste led to the separation of liquid and solid phase during the extrusion.

The specific surface area and pore volume decreased with increasing the amount of δ-alumina. The crushing strength of extruded alumina did not change so much in the presence of 5-25 %wt δ-alumina; however, the addition of 50% wt δ-alumina reduced the crushing strength from 9 N/mm to 5 N/mm which

Table 2. Composition of paste and properties of extruded alumina.

Sample	δ-Alumina (%w)	Bohmite (%w)	HNO_3 (%w)	PEG 400 (%w)	Surface area (m^2/g)	Pore diameter (nm)	Pore Volume (cm^3/g)	Side crushing strength (N/mm)	Lateral crushing strength (N/cm^2)	Ext.[a]	Paste viscosity
A	0	100	3	15	—	—	—	—	—	None	Very thick
B	5	95	3	15	240.5	8.4	0.51	8.94	420	Good	Good
C	10	90	3	15	240	8.4	0.50	9.5	426	Good	Good
D	15	85	3	15	226.5	8.2	0.46	8.92	476	Good	Good
E	25	75	3	15	188.5	8.6	0.40	9.6	432	Good	Good
F	50	50	3	15	168.2	8.8	0.37	5.17	232	Good	Good
G	100	0	3	15	—	—	—	—	—	None	Poor
H[b]	5	95	3	15	266	7.6	0.5	14	622	Good	Good

[a]Ext.: Extrudability; [b]Addition of $Al(NO_3)_3$.

Table 3. Distribution of pore volume in different pore diameters.

Sample	Pore volume in pores diameter of	0-3 nm	3-5 nm	5-10 nm	10-20 nm	20-30 nm	+30 nm	Total
B	cc/g	0.0229	0.0819	0.220	0.1135	0.0246	0.0476	0.5109
	%	4.48	16.03	43.14	22.2	4.82	9.31	
C	cc/g	0.0215	0.0788	0.217	0.117	0.0259	0.0445	0.5046
	%	4.26	15.62	43.00	23.17	5.12	8.82	
D	cc/g	0.0218	0.0753	0.2065	0.1017	0.0235	0.037	0.4658
	%	4.68	16.17	44.33	21.84	5.04	7.94	
E	cc/g	0.016	0.0654	0.1805	0.0915	0.0212	0.0371	0.4124
	%	3.98	15.87	43.79	22.21	5.15	9.00	
F	cc/g	0.013	0.0543	0.1622	0.0822	0.0206	0.0408	0.3731
	%	3.48	14.55	43.47	22.04	5.52	10.93	

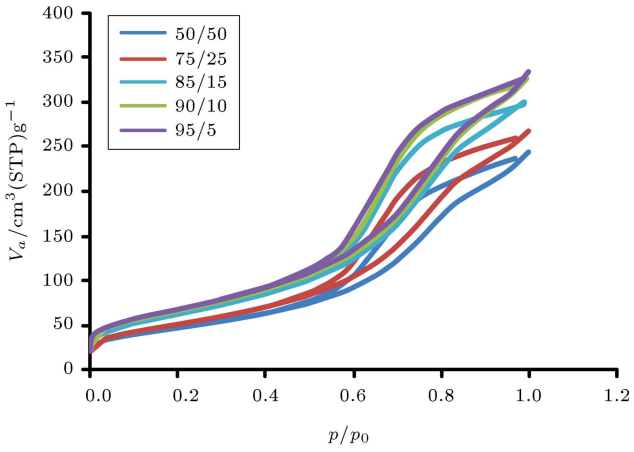

Figure 3. N_2 adsorption-desorption isotherms of samples with different Boehmite/δ-alumina ratios.

resulted from the higher percentage of δ-alumina with larger particles. The distribution of pore volume in different pore sizes is presented in Table 3. For instance, the pore volume of the pores with a diameter larger than 10 nm is 36.3 when applying 5% δ-alumina and 38.5 to the sample containing 50% δ-alumina, respectively.

N_2 adsorption-desorption isotherms of different Boehmite/δ-alumina samples are shown in Figure 3. These isotherms are of type IV and reveal a hysteresis loop of type H1, indicting the presence of mesopores [8].

Hysteresis loop of these isotherms tended to the larger P/P_0 at a lower Boehmite/δ-alumina ratio, which is due to the presence of larger pores in the sample. Increasing the amount of δ-alumina shifted the isotherms to the lower consumed gas and resulted in the reduction of specific surface area and pore volume.

Table 4. Crushing strength of samples prepared in this work and other researches.

Sample	Crushing strength $\mathrm{N/cm^2}$	References
Example 1	97	[9]
Example 1	360	[10]
S3	322	[11]
B	420	This work
H	622	This work

Lateral crushing strength of the sample with 5% wt δ-alumina was about 420 $\mathrm{N/cm^2}$. The comparison of crushing strength with the samples prepared in the other researches is presented in Table 4. Therefore, the samples prepared in this research showed higher crushing strength than the sample prepared in other research did.

The metals should be added to the extruded support in order to prepare the catalyst. The catalyst support may be deformed or shattered once added to

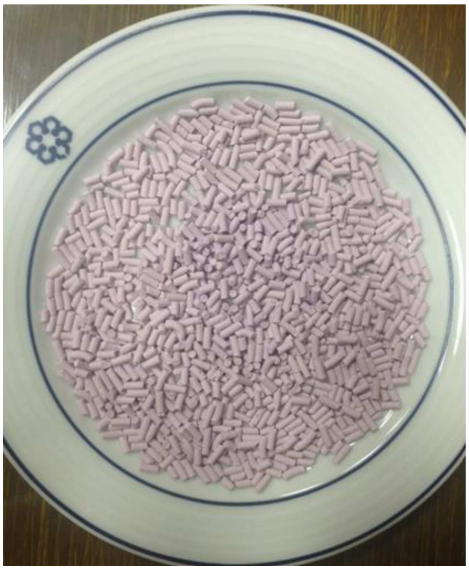

Figure 4. Image of extruded alumina after impregnation.

water. The preparation of extruded alumina, which can preserve their forms and shapes, is an important issue in the catalyst preparation. When the extruded alumina (sample B) was added to the aqueous cobalt impregnation solution, no deformation was observed after 12 h. The image of the impregnated sample is shown in Figure 4. The specific surface area (204 m^2/g) and pore volume (0.4 cm^3/g) decreased after impregnation, confirming the penetration of metal into the pores.

4. Conclusion

The extruded alumina was prepared using boehmite, δ-alumina, nitric acid as a peptizing agent, and PEG 400 as an additive. The calcined extruded alumina has the specific surface area of 168-240 m^2/g, pore volume of 0.37-0.5 cm^3/g, and pore diameter of 8.2-8.8 nm. More than 36% of pore volume belonged to the pore diameters larger than 10 nm. The crushing strength was found to be 232-476 N/cm^2. The addition of aluminum nitrate to the paste led to an increase in the crushing strength up to 622 N/cm^2. The crushing strength of extruded alumina is by far higher than the values reported in the literature. The extruded alumina did not show any deformation when introduced to the impregnation solution. This extruded alumina can be used as the catalysis support. Further works should be focused on the activity performance of these catalysts in the hydrodesulphurization of heavy hydrocarbons such as gasoil.

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