Mechanical strength of alumina supports synthesized using residues

E A Belopukhov\textsuperscript{1,2}, V Yu Tregubenko\textsuperscript{1,2,*} and A S Belyi\textsuperscript{1,2}
\textsuperscript{1}Institute of Hydrocarbons Processing SB RAS, Neftezavodskaya str. 54, 644040 Omsk, Russia
\textsuperscript{2}Omsk State Technical University, 11, Mira Ave., Omsk, 644050, Russia
*Corresponding author: kalinina_ihcp1@mail.ru

Abstract. The study elucidates the effect exerted by the composition of alumina support with the addition of milled aluminum hydroxide/oxide residues on its textural and strength characteristics and catalytic properties of Pt, Re-containing systems with these supports in n-heptane reforming. The introduction of milled dried residues was shown to increase the support strength. The content of residues in the catalyst can be increased up to 100 wt.% without a detrimental effect on the target characteristics of the catalyst performance in reforming. According to experimental data, a high (from 50 to 100 wt.%) content of such residues in the support increases the mechanical strength factor of the support to 30 abs.%, which may be related to remodification of the aluminum hydroxide structure during its “resynthesis”. It was demonstrated that 1-2 wt.% of milled residues of the calcined support can be used in the synthesis because this amount only slightly changes the mechanical strength factor and does not affect the catalyst performance. This approach is based on dilution of the initial pseudoboehmite with calcined Al\textsubscript{2}O\textsubscript{3} at the peptization step.

1. Introduction
Alumina is widely used as a support of catalysts for oil refining processes (hydrotreatment, hydrocracking, reforming, isomerization, and others) [1]. General regularities in the formation of the alumina pore structure from reprecipitated hydroxide and its strength characteristics have been revealed [2, 3].
Industrial production of the alumina supports for catalysts gives up to 6 wt.% of wastes represented by chips and dust. To minimize industrial wastes, a small amount of milled residues of the dried supports (actually aluminum hydroxide) can be mixed with aluminum hydroxide powder at the peptization step. However, there are no data concerning the effect of such additives on the textural and strength characteristics of the resulting supports. There are no studies on the regularities in the formation of the structure of such supports. It is unclear also how will the mechanical strength of the support depend on the introduction of powdered residues of the calcined support (actually aluminum oxide), which will serve as a “filler” rather than a binder upon remixing.
This work is aimed to investigate the strength, physicochemical and catalytic properties of such composite supports with different composition and the related catalysts. Results of the study can be used to minimize losses in the production of commercial catalysts.

2. Experimental
2.1. Synthesis of composites
A powder of non-peptized aluminum hydroxide with the pseudoboehmite structure (Sasol Germany GmbH) was used as the initial component of the support. The initial aluminum hydroxide dried at 120°C had a specific surface area of 268 m²/g and a pore volume of 0.47 cm³/g. Aluminum hydroxide was peptized with a solution of organic acids. The resulting slurry was extruded as grains with the diameter of 1.8 mm. The extruded aluminum hydroxide samples were dried in air at room temperature for ca. 12 h, and then at 120°C for 2-3 h. Thus prepared samples were used to obtain two types of composite supports.

A part of the dried support was milled, and then a powder fraction with the size below 0.05 mm was screened. This powder was further used in the synthesis of composite supports of SD (Support Dried) series by adding to powdered aluminum hydroxide at the peptization step by the method reported above. The content of the milled dried support in the composite supports was varied from 0 to 100 wt.%. Thus synthesized composite supports were calcined at 620°C for 2 h.

Another part of the dried support was first calcined at 620°C for 2 h and then milled to screen a powder fraction with the size less than 0.05 mm. A powder of the calcined support was then used in the synthesis of composite supports of SC (Support Calcined) series by adding to powdered aluminum hydroxide at the peptization step. The content of the milled calcined support in the composite supports was varied from 0 to 60 wt.%. Thus obtained composite supports were also calcined at 620°C for 2 h. For comparative testing, a sample of the initial aluminum hydroxide was subjected to similar drying and thermal treatment.

The reforming catalysts were represented by a system of 0.25 wt.% Pt and 0.3 wt.% Re on γ-Al₂O₃. The catalysts synthesized by impregnation of alumina with H₂PtCl₆ and HReO₄ solutions were dried at 120°C, calcined in flowing air at 500°C, and reduced in a hydrogen flow at 500°C with simultaneous sulfidizing. The composition and synthesis conditions of the supports and catalysts under consideration are close to conventional commercial ones.

The following designations were used. For supports: SD – synthesized using the dried milled support, SC – synthesized using the calcined milled support; for catalysts: CSD-X (Catalyst on Support Dried), CSC-X (Catalyst on Support Calcined), where X is the percentage of the milled support. S is the reference sample – the support prepared without the introduction of milled residues.

2.2. Mechanical strength

The strength of the synthesized composites was measured on a Lintel PK-21 strength meter under static conditions by cross-section method. Each sample was tested 48 times; statistical absolute measurement error for forces in a range from 10 to 100 N did not exceed 1 N. The strength factor was calculated using a truncated sample of load measurements excluding four maximum and four minimum values. The average strength factor (kg/mm) for the truncated sample was calculated by the formula:

\[ M = \frac{\sum_{i=1}^{n} F_i (d_i)^2}{n} \]  

where \( M \) is the strength factor, \( F_i \) is the measured load for the destruction of \( i \)-th grain, \( n \) is the number of load measurements in the truncated sample, \( d_i \) is the diameter of \( i \)-th grain, and \( g \) is the free fall acceleration (9.81 m/s²).

2.3. Textural characteristics

Textural characteristics of the samples precalcined at 620°C were studied on a Sorptomatic-1900 (CarloErbo) instrument using nitrogen adsorption-desorption isotherms at 77.4 K. Prior to measurements, the samples were treated in a vacuum at 300°C for 6 h. The BET specific surface area (\( S_{BET} \)) was calculated in a range of equilibrium relative nitrogen vapor pressure \( P/P_0 \) = 0.05-0.33 from the adsorption isotherm. The adsorption pore volume (\( V_{ads} \)) was determined from nitrogen adsorption at \( P/P_0 = 0.990 \).

2.4. n-Heptane reforming

The catalysts were tested in the model reaction of n-heptane reforming using an isothermal flow reactor at temperatures between 460 and 520°C, pressure 1.0 MPa, feed space velocity (FSV) from 8.2
to 14 h⁻¹, and hydrogen to hydrocarbon molar ratio 5:1. Compositions of the obtained mixtures of hydrocarbon products were analyzed online using a gas chromatograph equipped with capillary column and flame ionization detector.

3. Results and discussion

3.1. Textural characteristics

Table 1 lists the main textural characteristics of the supports calcined at 620°C, which were obtained from the analysis of adsorption isotherms.

| Sample | \( S_{\text{BET}} \), m²/g | \( V_{\text{ads}} \), cm³/g | \( D^* \), Å |
|--------|-----------------|-----------------|--------|
| S      | 265             | 0.52            | 78     |
| SD-20  | 288             | 0.54            | 75     |
| SD-30  | 283             | 0.59            | 83     |
| SD-60  | 286             | 0.58            | 81     |
| SD-100 | 288             | 0.53            | 74     |

\( *D = 4V_{\text{ads}}/S_{\text{BET}} \)

Data of Table 1 indicate that all the supports have a developed pore structure typical of \( \gamma \)-\( \mathrm{Al}_2\mathrm{O}_3 \). Therewith, the samples synthesized with 20 – 100 wt.% of milled aluminum hydroxide have higher specific surface area and pore volume as compared to the reference sample.

Table 2. Main textural characteristics of composite supports ‘alumina – milled alumina’ calcined at 620°C

| Sample | \( S_{\text{BET}} \), m²/g | \( V_{\text{ads}} \), cm³/g | \( D^* \), Å |
|--------|-----------------|-----------------|--------|
| S      | 265             | 0.52            | 78     |
| SC-10  | 294             | 0.56            | 76.5   |
| SC-20  | 292             | 0.56            | 76     |
| SC-30  | 284             | 0.56            | 79     |
| SC-60  | 287             | 0.56            | 78     |

\( *D = 4V_{\text{ads}}/S_{\text{BET}} \)

According to the data of Table 2, the samples synthesized using 10 – 60 wt.% of milled alumina have higher specific surface area and pore volume than the reference sample. This may be related to the contribution of \( \gamma \)-\( \mathrm{Al}_2\mathrm{O}_3 \), which has its own high porosity, to the formation of the pore space of the composites [4].

When the catalysts are synthesized by impregnation of the supports with platinum and rhenium solutions, porosity of the samples does not show significant changes.
3.2. Mechanical strength

Fig. 1 displays dependences of the average strength factor of extrudates on the content of milled aluminum hydroxide and alumina. According to experimental data, a high (from 60 to 100 wt.%) content of the milled aluminum hydroxide dried at 120°C in the composite increases mechanical strength of the support from 7 to 30 abs.%, respectively, which may be related to remodification of the aluminum hydroxide structure during its reincorporation into support or “resynthesis.” Supposedly, the increase in strength with increasing the content of the milled support dried at 120°C in the samples is caused by an additional peptizing action of organic acids on aluminum hydroxide aggregates during the synthesis of composites. Indeed, organic acids introduced at the first step of the synthesis remain in the support after drying: one part of the acids forms organic salts of aluminum, while another part remains unreacted (adsorbed on the support) and can serve as a peptizer upon addition to the initial aluminum hydroxide. During the acidic peptization, surface electrostatic interactions with aluminum hydroxide aggregates may result in the destruction of the latter ones. Thus, the action of peptizing acids leads to the structural rearrangement primarily of brittle large particles (aggregates) of aluminum hydroxide [5]. During a further transformation of the system under the action of high temperatures, organic salts of aluminum and organic acids are removed as CO, CO₂, and H₂O; this leads to the formation of the composition “alumina – milled aluminum hydroxide”, which is less mesoporous than unmodified alumina. Certainly, this will affect the strength characteristics of the tested materials.

Another approach is based on dilution of the initial pseudoboehmite with calcined Al₂O₃ at the peptization step. When the milled calcined residue is involved in the support synthesis, the mechanical strength expectedly drops (Fig. 1). The introduction of a greater amount (according to the plot on Fig. 1, above 5 wt.%) of the milled calcined alumina decreases the mechanical strength factor from 1.2 to 0.4 kg/mm. At a 60 wt.% content of such milled residue, the strength is so low that the support grains do not retain their shape. This occurs because calcined alumina is not involved in the peptization process; in this case, the particles are connected only by Van der Waals forces. However, the introduction of a small (1-2 wt.%) amount of calcined alumina may exert only a slight effect on the mechanical strength factor.
The production of commercial reforming catalysts shows that impregnation of supports with active metals and subsequent calcination of the synthesized catalysts commonly lead to a small increase in the grain strength. A comparison of the strength factors of laboratory samples of the supports and related catalysts is illustrated on Fig. 2. One can see that a higher content of the milled residue in the support increases the strength factor of the catalysts. Therewith, the average strength factor of the catalyst with the 30 wt.% content of milled residue and the catalyst supported on the reference sample is slightly (by 0.1 kg/mm) lower as compared to the average strength factors of the corresponding supports.

3.3. n-Heptane reforming

The results of testing of alumina-platinum-rhenium catalysts in n-heptane reforming are illustrated on Figs. 3 and 4. Activity and selectivity of the tested samples correspond to the modern level of reforming catalysts. It is seen that the content of the milled support dried at 120°C in the catalyst can be increased up to 100 wt.% without a detrimental effect on the target characteristics of the catalyst.
performance. The introduction of 10-30 wt.% of milled alumina does not affect the aromatization activity and selectivity of the reforming catalysts.

4. Conclusions
The study demonstrated that residues of the dried and calcined support can be involved in the synthesis of catalyst support. The content of milled dried support in the catalyst can be increased up to 100 wt.% without a detrimental effect on the target characteristics of the catalyst operation in reforming. A high (from 50 to 100 wt.%) content of such residues in the support increases the mechanical strength of support to 30 abs.%, which is related to structural remodification of aluminum hydroxide during its “resynthesis”.

The involvement of 1-2 wt.% of the milled calcined residues in the support synthesis exerts virtually no effect on the mechanical strength factor and does not change the catalyst activity and selectivity. The proposed approach is based on dilution of the initial pseudoboehmite with calcined Al₂O₃ at the peptization step, which is a new method not earlier reported in the literature.

5. References
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Acknowledgements
The study was supported by the Russian Foundation for Basic Research (Project No. 18-33-00791).