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## **SYNTHESIS OF PILLARED CLAYS FOR USING THEM AS CARRIERS OF CATALYTIC SYSTEMS**

**Abstract.** Natural clays are of particular interest for their rational use as not only adsorbents, but also carriers of new highly selective catalysts. This article presents an overview of the application of pillared clays in catalytic chemistry as catalyst matrix. The physicochemical properties of the synthesized Al-, Zr-, Al / Zr-modified clays were studied by BET, XRF and elemental analysis. The elemental composition of montmorillonite and kaolinite clays was determined. Pillared clays with high specific surface (montmorillonite clay from 20 to 243 m<sup>2</sup>/g and kaolinite clay from 5 to 66 m<sup>2</sup>/g.) were obtained. The use of pillared clays in catalysis will help to solve the problems of the development of domestic production of catalysts and the replacement of expensive imported analogues.

**Key words:** natural clays; montmorillonite; kaolinite; mechanical activation; pillared clay; pillarization.

### **Introduction**

Cost-effective and environmentally friendly catalysts are always in demand for synthesis of valuable organic compounds. The main features of a highly efficient catalytic support are: 1) developed surface area for the location of catalytically active centers [1, 2], 2) high thermal stability to prevent sintering and abrasion of the catalyst [3, 4] 3) the presence of various functional groups responsible for stabilization and activation of the catalytically active phase [5, 6].

The presented requirements are fully met by natural clays with a high specific surface. Obtaining of pillared clays and their modification by various transition metal complexes lead to the formation of new porous structures with unique physicochemical properties [7]. In this regard, the urgent task is to develop catalysts based on pillared clay-matrix both for metals and for metal oxides deposited on the surface as catalytically active phases [8].

Therefore the goal of this study is to synthesize new pillared clay samples for the development of highly selective catalysts and to obtain high yields of industrially important gas and petrochemical products, as well as to study the physicochemical properties of columnar structures based on natural clays of the Tagan and Turgay deposits of the East Kazakhstan region.

### **Materials and methods**

Objects of study - synthesized columnar clays for use as a catalyst carrier. Natural clays of the Tagan and Turgay deposits of East Kazakhstan region were used in this work.

#### *Mechanical activation of natural clays*

To activate natural kaolinite clays, the AGO-2 high-voltage planetary mill with steel balls with a diameter of 8 mm and a total mass of 200 g, with 150 ml water-cooled steel drums was used. The ratio of the mass of the balls to the mass of the mixture (M) was 20:30. The rotational speed of the drums is 1200 rpm. To ensure a low level of powder contamination in the steel grinding medium, the natural lining of the working surface of the drums and balls, obtained by preliminary processing of a similar mixture, leading

to coating the surface of the balls and the inner surface of the drums with the processed composition [9], was used.

#### *Synthesis of pillared clays*

Natural clays pre-cleaned and ground to a particle size of 0.25 mm were incubated for 24 hours at room temperature for complete hydration. The aluminum and zirconium hydroxocomplexes obtained by hydrolysis of aqueous solutions of aluminum chloride (0.2 M) and zirconium (0.2 M) in an aqueous solution of NaOH (0.5 M) were used as intercalating solutions [7, 8, 10]. Pillarization was carried out by slowly adding an intercalating agent to clay samples and further washing from chlorine ions. The obtained columnar clays were dried for one day at room temperature and then calcined at a temperature of 500°C for 5 hours [11].

#### *Textural and physico-chemical properties of pillared clays*

The texture characteristics of pillared clays were studied via nitrogen adsorption and desorption isotherms using the BET method (Brauner-Emmett-Teller) on SORBTOMETR-M device (Russia). The change in the phase composition of columnar clays was monitored using x-ray phase analysis on a general-purpose diffractometer DRON-4-0.7 with CuK $\alpha$  radiation (Russia).

The elemental composition of the pillared clay samples was analyzed using an INCAENERGY energy dispersive spectrophotometer (OXFORDINSTRUMENTS, UK) combined with Superprobe 733 electron probe microanalyzer at an accelerating voltage of 25 kV and a probe current of 25 nA.

#### **Results and discussion**

Montmorillonite is known to be a clay composed of blocks of tetrahedral quartz sheets with a central octahedral aluminum oxide sheet with the chemical formula  $(\text{Si}_{7.8}\text{Al}_{0.2})^{\text{IV}}(\text{Al}_{3.4}\text{Mg}_{0.6})^{\text{VI}}\text{O}_{20}(\text{OH})_4$ , and the theoretical composition without intermediate material is SiO<sub>2</sub> 66.7%, Al<sub>2</sub>O<sub>3</sub> 28.3% and H<sub>2</sub>O 5%. Taking into account the speciation of various metals in this formula, the theoretical net surface charge on montmorillonite is 0.8 charge / element, which is responsible for the adsorption of cations [12].

Elemental analysis of the oxide composition of natural montmorillonite and kaolinite clays samples was carried out using quantitative X-ray spectral analysis. The results are presented in table 1.

Table 1 - Elemental composition of natural kaolinite and montmorillonite clay samples

| Element / Sample     | SiO <sub>2</sub>      | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | PS   |
|----------------------|-----------------------|--------------------------------|--------------------------------|------------------|------|------|------------------|-------------------|------|
| Montmorillonite Clay | Elementcontent, wt. % |                                |                                |                  |      |      |                  |                   |      |
|                      | 55,5                  | 19,38                          | 4,4                            | 0,3              | 1,98 | 2,18 | 1,5              | 1,14              | 9,5  |
| Element / Sample     | SiO <sub>2</sub>      | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | PS   |
| Kaolinite clay       | Elementcontent, wt. % |                                |                                |                  |      |      |                  |                   |      |
|                      | 39,33                 | 40,20                          | 17,80                          | 2,01             | n.e  | 0,16 | n.e              | 0,19              | 0,31 |

Note: PS –

The data presented in Table 1 indicate that the montmorillonite clay sample contains a large number of alkali and alkaline earth metal cations that can participate cation-exchange reactions, while Ca<sup>2+</sup> and K<sup>+</sup> ions are absent in the kaolinite clay sample and only small amounts of Mg<sup>2+</sup> and Na<sup>+</sup> are detected. The results obtained are consistent with published data [13, 14].

Kaolinite is a clay mineral from the group of aqueous aluminum silicates with a chemical composition: Al<sub>4</sub>[Si<sub>4</sub>O<sub>10</sub>](OH)<sub>8</sub>. It contains 39.5% Al<sub>2</sub>O<sub>3</sub>, 46.5% SiO<sub>2</sub> and 14% H<sub>2</sub>O. The crystal structure of kaolinite consists of two-layer packets containing one oxygen tetrahedral layer of the composition [Si<sub>2n</sub>O<sub>5n</sub>]<sup>2n+</sup> and one aluminum-hydroxyl octahedral layer of the composition [Al<sub>2n</sub>(OH)<sub>4n</sub>]<sup>2n+</sup>. Both layers are combined into a package through common oxygen-silicon-oxygen layer. These layers are interconnected by weak bonds, which determine the very perfect cleavage of kaolinite and the possibility of different overlays of one layer onto another.

Considering the speciation of various metals in this formula, the theoretical net surface charge on kaolinite is zero. However, kaolinite acquires a small total negative charge due to the fact that its surface is not completely inert [12-15].

Thus, mechanical activation of kaolinite clay (Turgay deposit, East Kazakhstan area) was carried out on a high-voltage planetary mill AGO-2. Spectra for natural and mechanically activated kaolinite clay, which are shown in Figures 1 and 2, were obtained by the method of diffraction of the total X-ray radiation (DRON-4-0.7).

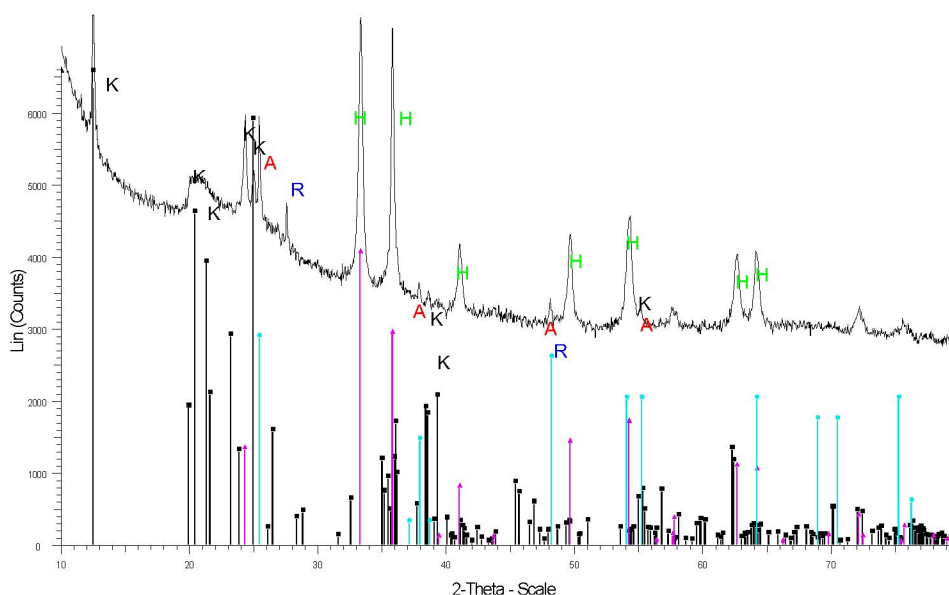


Figure 1 - Diffraction pattern of a sample of the original natural clay: K-kaolinite, A-anatase, R-rutile, H-hematite

When studying the spectrum of a sample of the original natural clay (Figure 1), kaolinite diffraction reflections were recorded (K, PDF-080-0885) with interplanar distances 7.12 ( $12.40^\circ 2\theta$ ), 4.38 ( $20.35^\circ$ ), 4.16 ( $21.34^\circ$ ), 3.56 ( $24.96^\circ$ ) Å; hematite ( $\alpha\text{-Fe}_2\text{O}_3$ , (PDF-089-8103) with interplanar distances 3.661( $24.30^\circ$ ), 2.69 ( $33.3^\circ$ ), 2.51 ( $35.78^\circ$ ), 2.198 ( $41.02^\circ$ ), 1.834 ( $49.66^\circ$ ), 1.688 ( $54.30^\circ$ ), 1.598 ( $57.64^\circ$ ), 1.481 ( $62.68^\circ$ ), 1.449 ( $64.18^\circ$ ), 1.308 ( $72.18^\circ$ ); ( $26.85^\circ 2\theta$ );  $\text{TiO}_2$  (anatase – 3.502 ( $25.41^\circ$ ), 2.373 ( $37.88^\circ$ ), 1.89 ( $49.09^\circ$ ), 1.664 ( $55.14^\circ$ );  $\text{TiO}_2$  (rutile – 3.240 ( $27.50^\circ$ ) Å ( $^\circ 2\theta$ )).

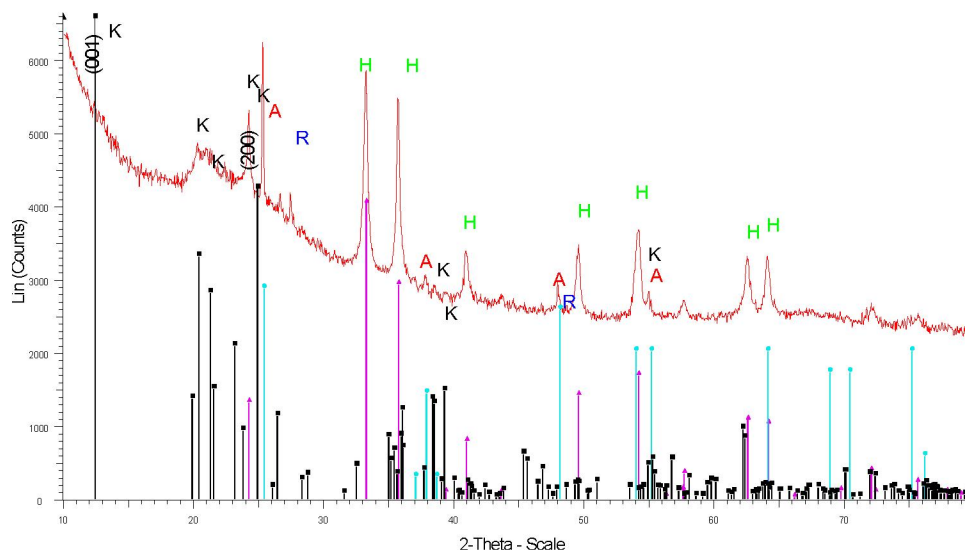


Figure 2 - Diffraction pattern of a sample of modified clay: K-kaolinite, A-anatase, R-rutile, H-hematite

Figure 2 shows the diffraction reflections of mechanically activated kaolinite clay.

According to the literature [15-19], the x-ray spectra of kaolinite clays have nine peaks in the range  $1-30^\circ (2\theta)$ :

- The basal distance is 7,27 Å ( $2\theta = 12,15^\circ$ ) with intensity 79,4% and tip width 0,20 ( $2\theta = 12,15^\circ$ );
- Calcined kaolinite gives 13 peaks in the same range 2. The basal distance is 7,15 Å ( $2\theta = 12,15^\circ$ ) with intensity 69,7% for kaolinite and tip width 0,10 ( $2\theta = 12,15^\circ$ );

- For acid activated kaolinite, the expansion of the basal gap is from 7,27 to 7,30 Å;  $2\theta = 12,14^\circ$ , and the peak intensity is from 23.14% to 21.32% [16].

According to the data obtained, it can be concluded that after mechanical activation, the phase and chemical composition of kaolinite clay has changed, since kaolinite reflections (001) with interplanar spacings of 7.12 Å ( $12.40^\circ 2\theta$ ) and (002) 3.56 Å ( $24.96^\circ 2\theta$ ) not detected. Hydrogen bonds between the octahedral layer and the oxygen of the tetrahedral layer can serve as a source of interlayer bonds in the structure of kaolinite. [19, 20].

Despite the fact that many works on the general structure of pillared clays have been published, the detailed structure of the columns and the type of connection of the columns with silicate layers are still poorly understood.

Natural clays, including kaolinite and montmorillonite, have a layered structure and high cation exchange capacity. The surface area values vary from 5 to 25 m<sup>2</sup>/g for kaolinite and 15.5–82.0 m<sup>2</sup>/g for montmorillonite depending on the particle size distribution, particle shape, and pore distribution in the clay material [20, 21].

Changes in the texture characteristics of pillared montmorillonite and kaolinite clays according to the isotherms of low-temperature nitrogen adsorption are presented in table 2.

Table 2 - Structural characteristics of pillared clays

| Type of montmorillonite pillared clay  | The content of the oxide columns, wt. % | Specific surface area $S_{BET}$ , m <sup>2</sup> /g | Type of kaolinite pillared clay   | The content of the oxide columns, wt. %                     | Specific surface area $S_{BET}$ , m <sup>2</sup> /g |
|--|---|---|---|---|---|
| MI-1-Zr/Ba   | ZrO <sub>2</sub> – 23%                  | 243   | KI-1-Zr   | ZrO <sub>2</sub> – 18%                                      | 66  |
| MI-2-Zr/Sr   | ZrO <sub>2</sub> – 22%                  | 240   | KI-2-Al   | Al <sub>2</sub> O <sub>3</sub> – 15%                        | 55  |
| MI-3-Zr/Ca   | ZrO <sub>2</sub> – 22.5%                | 240   | KI-3-Zr/Al  | Al <sub>2</sub> O <sub>3</sub> – 4%, ZrO <sub>2</sub> – 18% | 51  |
| Note: The specific area of natural montmorillonite clay is ~ 20 m <sup>2</sup> /g. |   |   | Note: The specific area of natural kaolinite clay is ~ 5 m <sup>2</sup> /g. |   |   |

The data in table 2 show that the specific surface area of the initial clay increases with pilling: in montmorillonite clay from 20 to 243 m<sup>2</sup>/g and in kaolinite clay from 5 to 66 m<sup>2</sup>/g, the content of zirconium reaches 18-23%, aluminum 4 -15%.

The obtained characteristics are in good agreement with the published data that montmorillonite and kaolinite can be used as starting material for modification with the introduction of aluminum and zirconium into the intermediate layers [12–15, 22–24].

The synthesized columnar clays are environmentally friendly and effective for use as carriers in the preparation of heterogeneous catalysts. Also, their use as adsorbents in the production of petrochemical and organic chemicals is not ruled out.

### Conclusion

The structure of natural and pillared clays was studied, the relationship between the structure of the pillars and the mechanism of their formation was determined, columnar clays having catalytic properties were obtained.

It is shown that pillared clays synthesized from natural clays of the Tagan and Turgay deposits of the East Kazakhstan region, the Republic of Kazakhstan, can be used as carriers for catalysts. Their specific surface area and catalytic activity are significantly increased by using the pilling process.

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### КАТАЛИТИКАЛЫҚ ЖҮЙЕЛЕРДІҢ ТАСЫМАЛДАУШЫСЫ РЕТІНДЕ ҚОЛДАНЫЛАТЫН БАҒАНАЛЫ САЗБАЛШЫҚТАРДЫ СИНТЕЗДЕУ

**Аннотация.** Табиғи сазбалшықтарды адсорбенттер ретінде ғана емес, сонымен қатар жаңа жоғары селективті катализаторлардың тасымалдаушылары ретінде де ұтымды қолдану үлкен қызығушылық тудырады. Бұл мақалада каталитикалық химия бағытында катализаторлардың тасымалдаушысы ретінде бағаналы сазбалшықтарды қолдануға шолу жасалған. Al-, Zr-, Al/Zr-модификацияланған сазбалшықтардың физика-химиялық қасиеттері элементтік талдау, БЭТ және РФА әдістері арқылы зерттелген.

Каолинитті сазбалшықты механикалық активтендіру (Торғай кен орны, Шығыс Қазақстан облысы) жоғары кернеулі АГО-2 планеталық диірменінде жүзеге асырылды. Жалпы рентген сәулесінің дифракциясы әдісімен (DRON-4-0.7) табиғи және механикалық активтендірілген каолинит сазбалшықтарына арналған спектрлер зерттелді.

Табиғи сазбалшықтан жасалған үлгінің спектрін зерттеу барысында, каолиниттің (K, PDF-080-0885) дифракциялық шағылыстары: 7.12 (12.40 ° 2 $\theta$ ), 4.38 (20.35), 4.16 (21.34), 3.56 (24.96) Å 3.661 (24.30), 2.69 (33.3), 2.51 (35.78), 2.198 (41.02), 1.834 (49.66), 1.688 (54.30), 1.598 (57.64), гематиттің ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, PDF-089-8103) аралық қабаты: 1.481 (62.68), 1.449 (64.18), 1.308 (72.18); кварц (26,85 ° 2 $\theta$ ); TiO<sub>2</sub> (анатаза - 3.502 (25.41), 2.373 (37.88), 1.89 (49.09), 1.664 (55.14); TiO<sub>2</sub> (рутил - 3.240 (27.50) Å (° 2 $\theta$ ) аралық қабаттары жазылды. Алынған мәліметтер негізінде сазбалшықтың фазалық құрамы туралы қорытынды жасауға болады. Каолинит сазбалшығының механикалық құрамы механикалық активацияға байланысты өзгерді, өйткені 7,12 Å (12.40 °2 $\theta$ ) және (002) 3.56 Å (24.96 °2 $\theta$ ) аралығындағы қабат кеңістігі бар каолинит (001) шағылыстары анықталмады.

Зерттеуге алынған каолинит және монтмориллонит сазбалшықтарының элементтік құрамдары анықталды. Нәтижесінде монтмориллонит үшін ~20-дан 243 м<sup>2</sup>/г, каолинит үшін ~5-тен 66 м<sup>2</sup>/г дейінгі меншікті беттік қабаты бар бағаналы сазбалшықтар алынды.

Алынған көрсеткіштер монтмориллонит пен каолинитті аралық қабаттарға алюминий мен цирконий енгізумен модификациялау үшін бастапқы материал ретінде қолдануға болатыны әдебиеттерде жақсы келісілген.

Осылайша, жоғарыда келтірілген ақпарат синтезделген бағаналы саздар экологиялық таза және гетерогенді катализаторлардың тасымалдаушысы ретінде пайдалану үшін тиімді екенін көрсетті. Катализде аталған бағаналы сазбалшықтарды қолдану катализаторлардың отандық өндірісін дамыту және қымбат импорттық аналогтарын алмастыру мәселесін шешуге септігін тигізеді.

**Түйін сөздер:** табиғи сазбалшықтар; монтмориллонит; каолинит; механикалық активтендіру; бағаналы сазбалшықтар; бағаналау.

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### СИНТЕЗ СТОЛБЧАТЫХ ГЛИН ДЛЯ ПРИМЕНЕНИЯ ЕГО В КАЧЕСТВЕ НОСИТЕЛЯ КАТАЛИТИЧЕСКИХ СИСТЕМ

**Аннотация.** Природные глины представляют особый интерес для их рационального использования в качестве не только адсорбентов, но и носителей новых высокоселективных катализаторов. В данной статье представлен обзор сведений использования столбчатых глин в области каталитической химии в качестве носителей катализаторов. Изучены физико-химические свойства синтезированных Al-, Zr-, Al/Zr-модифицированных глин методами БЭТ, РФА и элементного анализа.

Была проведена механическая активация каолиновой глины (Тургайское месторождение, ВКО) на высоконапряженной планетарной мельнице АГО-2. Методом дифракции общего излучения рентгеновских лучей (DRON-4-0.7) были изучены спектры для природной и механически активированной каолиновых глин.

При исследовании спектров образца исходной природной глины были зафиксированы дифракционные рефлексы каолинита (K, PDF-080-0885) с межплоскостными расстояниями 7.12 (12.40° 2 $\theta$ ), 4.38 (20.35), 4.16 (21.34), 3.56 (24.96) Å; гематита ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, PDF-089-8103) с межплоскостными расстояниями 3.661(24.30), 2.69 (33.3), 2.51 (35.78), 2.198 (41.02), 1.834 (49.66), 1.688 (54.30), 1.598 (57.64), 1.481 (62.68), 1.449 (64.18), 1.308 (72.18); кварца (26.85° 2 $\theta$ ); TiO<sub>2</sub> (анатаз – 3.502 (25.41), 2.373 (37.88), 1.89 (49.09), 1.664 (55.14); TiO<sub>2</sub> (рутил – 3.240 (27.50) Å (° 2 $\theta$ ). По полученным данным можно сделать выводы о том, что фазовый состав проведения механической активации химический состав каолиновой глины изменилась, так как, рефлексы каолинита (001) с межплоскостными расстояниями 7.12 Å (12.40° 2 $\theta$ ) и (002) 3.56 Å (24.96° 2 $\theta$ ) не обнаружены.

Определены химические элементные составы исследуемых монтмориллонитовой и каолиновой глины. В результате исследования получены столбчатые глины с высокой удельной поверхностью: у монтмориллонитовой глины от ~20 до 243 м<sup>2</sup>/г и у каолиновой глины от ~5 до 66 м<sup>2</sup>/г.

Полученные показатели вполне согласуются с литературными данными о том, что монтмориллонит и каолинит вполне могут быть использованы в качестве исходного материала для модификации с введением алюминия и циркония в промежуточные слои.

Таким образом, выше представленные сведения показали, что синтезированные столбчатые глины являются экологически чистыми и эффективными для применения их в качестве носителя гетерогенных катализаторов. Использование столбчатых глин в катализе поможет решить вопросы развития отечественного производства катализаторов и замены дорогих импортных аналогов.

**Ключевые слова:** природные глины; монтмориллонит; каолинит; механическая активация; столбчатые глины; пилларирование.

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