

## PHYSICOCHEMICAL PROCESSES AT THE INTERFACES

# Formation and Stability of Porous Structure of Pillared Clays

T. V. Kon'kova<sup>a,\*</sup>, M. B. Alekhina<sup>a</sup>, A. I. Vezentsev<sup>b</sup>, and P. V. Sokolovskii<sup>b</sup>

<sup>a</sup>Mendeleev Russian State Chemical Engineering University, Moscow, Russia

<sup>b</sup>Belgorod State National Research University, Belgorod, Russia

\*e-mail: kontat@list.ru

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**Abstract**—The relationship between calcination conditions and texture characteristics is established for pillared clays that were prepared from natural montmorillonite-containing feedstock. The instability of porous structure of pillared clays upon storage in humid air atmosphere is shown.

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### INTRODUCTION

Pillaring of native clay minerals is a method of modification that allows the directed adjustment of their porous structure and chemical composition. The main stages of the process involve the ionic exchange of interlayer (interstitial) alkali and alkaline-earth cations of clay by polynuclear hydroxo cations of multivalent metals and thermal treatment of the obtained material. As a result, oxide clusters (or columns) are formed between the clay layers, which hinder the interlayer space with the formation of slotlike micropores; in addition, they act as supports, which prevent the approach of layers. In pillared clays, the interstitial distance is increased as compared to the initial material. In the national literature, pillared clays are also referred to as “columnar” [1, 2].

During calcination of both initial and modified montmorillonite clay, dehydration and dehydroxylation of montmorillonite surface occur; in this case, the curves of differential thermal analysis have two endothermic effects: a low-temperature one (125–175°C) and a high-temperature one (560–575°C) [3]. Issues that are related to the formation of the porous structure of pillared clays and the effect of the calcination temperature of samples on their textural characteristics are still insufficiently investigated and are of scientific interest.

Columnar clays may serve as materials for the design of effective and relatively cheap adsorbents and catalysts for various processes in gas and liquid phases. One example of this is for adsorption purification and oxidative destruction of organic substances in waste water and gas phase [4–8], as well as cracking catalysts in petrochemistry and catalysts for hydrogenation and aromatization in organic synthesis [1, 9, 10]. The study of the catalytic and adsorption properties of pillared clays has developed within the last two decades,

which has been indicated by numerous publications; however, there exists no published information on the stability of the porous structure and properties of these materials during operation in gas and liquid media, as well as during storage.

The aim of this work was to modify native montmorillonite clay by pillaring and study the textural characteristics of the obtained materials depending on the thermal treatment and storage conditions.

### EXPERIMENTAL

The objects of study were samples of native clays of Tagansk deposit (Kazakhstan) with montmorillonite content of 90–95 wt %. In the work, samples of various horizon clays were used: initial horizon samples 1, 3, 5, and 6 were denoted as 1<sub>in</sub>, 3<sub>in</sub>, 5<sub>in</sub>, and 6<sub>in</sub>.

The elemental composition of samples was determined according to X-ray fluorescent method using an X-MAX INCA ENERGY analyzer (Oxford Instruments, United Kingdom) and the adapter to a JEOL JSM-6510 LV scanning electron microscope (JEOL, Japan) at the Mendeleev Center for Collective Use.

The procedure of clay pillaring is described in detail in [11]. During the preparation of samples 1 and 3, we used horizon clay 3. When preparing the pillaring solution, the ratio of OH<sup>-</sup>/Me<sup>n+</sup> (where Me<sup>n+</sup> is Al<sup>3+</sup>) was 2.32 and 2.0. In the synthesis of samples 2 and 4, horizons 1 and 6 were used, respectively, and the ratio of OH<sup>-</sup>/Me<sup>n+</sup> (where Me<sup>n+</sup> is the sum of Al<sup>3+</sup> and Co<sup>2+</sup>) was 2.2.

During the study of the properties of clays, the samples were taken both as a powder and molded by pelletizing under a pressure of 1500 kg/cm<sup>2</sup> using a Crush IR PIKE Technologies hydraulic press.

Calcination of clay samples was carried out in an SNOL laboratory furnace. The calcination tempera-

**Table 1.** Elemental composition of initial and modified clay samples (wt %)

| Sample no.      | O     | Al    | Si    | Na   | K    | Ca   | Mg   | Ti   | Fe   | Co   | Other |
|-----------------|-------|-------|-------|------|------|------|------|------|------|------|-------|
| 1 <sub>in</sub> | 59.41 | 9.69  | 22.35 | 1.10 | 0.24 | 1.53 | 1.81 | 0.11 | 1.26 | 0    | 2.50  |
| 3 <sub>in</sub> | 57.54 | 8.33  | 26.14 | 0.92 | 0.13 | 1.02 | 2.00 | 0.31 | 3.46 | 0    | 0.14  |
| 5 <sub>in</sub> | 55.92 | 9.38  | 26.89 | 0.64 | 0.03 | 1.34 | 2.10 | 0.03 | 3.10 | 0    | 0.57  |
| 6 <sub>in</sub> | 57.62 | 8.82  | 24.78 | 0.41 | 0.07 | 1.35 | 1.86 | 0.00 | 5.09 | 0    | 0     |
| 1               | 58.96 | 11.55 | 23.34 | 0.27 | 0    | 0.02 | 1.38 | 0.19 | 4.29 | 0    | 0     |
| 3               | 58.13 | 13.78 | 22.87 | 0.05 | 0.22 | 0.04 | 1.32 | 0.21 | 2.96 | 0    | 0.42  |
| 2               | 62.17 | 13.59 | 21.14 | 0.52 | 0.11 | 0    | 1.49 | 0.04 | 0.83 | 0.11 | 0     |
| 4               | 59.11 | 13.54 | 20.40 | 0.35 | 0.11 | 0.10 | 1.41 | 0.19 | 4.72 | 0.07 | 0     |

ture of initial and pillared samples varied in the range of 70–600°C, after which their textural characteristics were determined.

Textural characteristics of initial and modified samples were calculated based on nitrogen adsorption and desorption isotherms at a temperature of 77 K, which were recorded on a Nova 1200e volumetric setup (Quantachrome, United States). Prior to isotherm measurements, the samples were activated in the temperature range of 70–300°C and a residual pressure of 10<sup>-3</sup> mm Hg for 4 h. Specific surface  $S_{\text{specific}}$  of samples was calculated according to BET equation, whereas volume of micropores  $W_o$  and intrinsic adsorption energy  $E_0$  were determined via the Dubinin–Radushkevich equation. Overall sorption volume of meso- and micropores  $V_{\Sigma}$  was determined according to a nitrogen adsorption isotherm at a relative pressure of 0.99.

To study the moisture stability, modified samples were held in desiccant over distilled water up to equilibrium and, then, dehydrated at 300°C and textural characteristics were determined. This procedure was repeated for several cycles.

**Table 2.** Textural characteristics of initial clay sample 3<sub>in</sub> (powder sample) depending on the calcination temperature

| $T$ , °C | $S_{\text{specific}}$ , m <sup>2</sup> /g | $V_{\Sigma}$ , cm <sup>3</sup> /g | $W_o$ , cm <sup>3</sup> /g | $E_0$ , kJ/mol |
|----------|---|-----------------------------------|----------------------------|----------------|
| 70       | 65.2                                      | 0.062                             | 0.031                      | 12.74          |
| 100      | 64.1                                      | 0.064                             | 0.031                      | 13.38          |
| 150      | 72.1                                      | 0.061                             | 0.034                      | 13.09          |
| 400      | 73.8                                      | 0.072                             | 0.035                      | 12.44          |
| 500      | 65.8                                      | 0.063                             | 0.032                      | 11.72          |

## RESULTS AND DISCUSSION

It follows from estimating X-ray fluorescent data analysis (Table 1) that all the studied Tagansk clay samples contain titanium and iron along with silicon, aluminum, and alkali and alkaline-earth metals. The magnesium content varied little in samples, whereas they substantially differed from each other according to iron and titanium contents.

In the modified clay samples, there was a decrease in silicon, sodium, calcium, and magnesium contents as compared to the initial samples. The aluminum content increased, which indirectly confirms the formation of aluminum oxide columns. The iron content in pillared samples mainly decreased with the exception of sample 1.

In Tables 2 and 3, the results of the investigation of textural characteristics are given for initial clay sample 3<sub>in</sub> and modified sample 1 after pelletizing depending on the calcination temperature.

It is known from the literature [12] that heat treatment of initial clay, which is accompanied by the removal of interlayer water, leads to an irreversible collapse (adhesion) of layers and worsening of textural characteristics. However, as follows from the presented data, in the calcination temperature range of 70–500°C, no significant changes of the parameters of porous structure of samples of initial and modified clays were observed. The highest values of specific surface and pore volume were located in the samples of initial and modified clay that were calcined at 400°C.

According to thermal analysis, results of which are given in [11], all physically adsorbed water and a slight fraction of chemically bound water were removed from samples at 400°C. An increase in temperature up to 500°C leads to further dehydroxylation of the montmorillonite surface and, consequently, sintering of

**Table 3.** Textural characteristics of modified sample 1 (pelletized sample) depending on the calcination temperature

| $T$ ,<br>°C | $S_{\text{specific}}$ ,<br>m <sup>2</sup> /g | $V_{\Sigma}$ ,<br>cm <sup>3</sup> /g | $W_o$ ,<br>cm <sup>3</sup> /g | $E_0$ ,<br>kJ/mol |
|-------------|--|--------------------------------------|-------------------------------|-------------------|
| 150         | 127.6  | 0.082                                | 0.064                         | 15.63             |
| 250         | 172.7  | 0.098                                | 0.089                         | 16.85             |
| 350         | 182.6  | 0.100                                | 0.094                         | 16.79             |
| 400         | 187.3  | 0.116                                | 0.095                         | 16.49             |
| 450         | 168.1  | 0.110                                | 0.086                         | 16.28             |
| 500         | 143.6  | 0.096                                | 0.076                         | 17.18             |
| 550         | 107.5  | 0.075                                | 0.058                         | 15.60             |
| 600         | 101.4  | 0.070                                | 0.052                         | 15.94             |

material, which is accompanied by a decrease in the volume of interstitial slotlike pores.

For a modified sample, the dependence of micropore volume on the calcination temperature has a critical character with the maximum in the temperature range of 350–400°C. An increase in temperature to 600°C is accompanied by the more complete dehydroxylation of surface, as well as pore sintering. For the samples calcined at 550–600°C, the micropore volume was almost halved as compared to the maximum value.

Results also indicate that the intrinsic nitrogen adsorption energy on initial and modified samples almost does not depend on the calcination temperature.

It was determined during experiments that it is a fundamental drawback of pillared clays that their microporous structure is unstable in humid medium. The results of the study of the change of the characteristics of porous structure of samples are given in Fig. 1, and they are exemplified by the change in the specific surface of sample 1 (powder and pelletized) after several water vapor adsorption–desorption cycles.

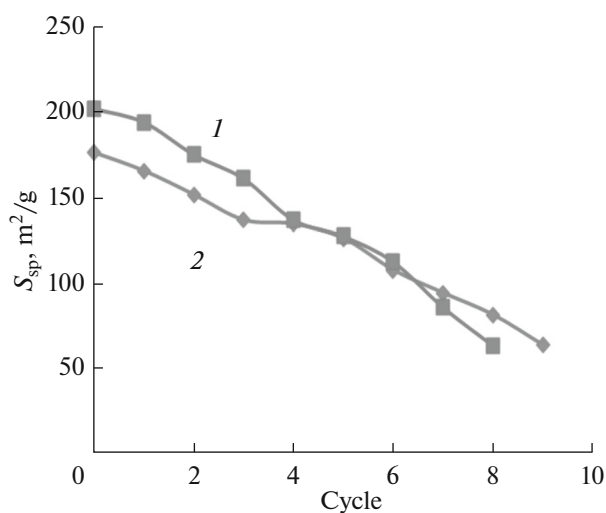
As follows from the figure, after eight or nine water vapor adsorption–desorption cycles, the specific surface of samples decreased by three times in the cases of both powder and pressed samples. The values of micropore volume also halved as compared to those of freshly prepared samples. It can be stated from this that the porous structure of pillared clay is unstable at humid atmosphere and it deteriorated. The adsorption value of water on pillared samples almost did not change with the number of cycles and took the values of 0.20–0.25 g/g clay.

We have recently shown [13] that the adsorption properties of ion-exchange forms of zeolite X are unstable and zeolites transform into stable modifications with time. The changes in the adsorption capacity of zeolites correlated with the growth of the parameter  $a$  of their crystal lattice. In addition, the retention of adsorption properties of zeolite without water in the system was noted. The textural studies of initial and modified samples of montmorillonite clay were performed after storage in closed weighing cups in air atmosphere; the experimental data are given in Table 4.

The results of investigations show that air atmosphere has an adverse effect on the characteristics of

**Table 4.** Textural characteristics of initial and modified clay samples depending on the storage period

| Sample              | $T_{\text{calc}}$ ,<br>°C | Storage period,<br>months | $S_{\text{specific}}$ ,<br>m <sup>2</sup> /g | $V_{\Sigma}$ ,<br>cm <sup>3</sup> /g | $W_o$ ,<br>cm <sup>3</sup> /g | $E_0$ ,<br>kJ/mol |
|---------------------|---------------------------|---------------------------|--|--------------------------------------|-------------------------------|-------------------|
| 5 <sub>in</sub>     | 550                       | 0                         | 68.4   | 0.072                                | 0.032                         | 10.62             |
| 5 <sub>in</sub>     | 550                       | 12                        | 65.3   | 0.069                                | 0.030                         | 12.46             |
| 6 <sub>in</sub>     | 550                       | 0                         | 65.7   | 0.074                                | 0.030                         | 11.6              |
| 6 <sub>in</sub>     | 550                       | 12                        | 59.7   | 0.060                                | 0.028                         | 12.10             |
| 2 <sub>powder</sub> | 550                       | 0                         | 156.3  | 0.088                                | 0.076                         | 15.80             |
| 2 <sub>powder</sub> | 550                       | 12                        | 82.7   | 0.066                                | 0.042                         | 16.79             |
| 4 <sub>powder</sub> | 450                       | 0                         | 146.8  | 0.090                                | 0.071                         | 14.13             |
| 4 <sub>powder</sub> | 450                       | 6                         | 100.4  | 0.070                                | 0.050                         | 14.86             |
| 4 <sub>powder</sub> | 450                       | 12                        | 82.5   | 0.064                                | 0.042                         | 15.96             |
| 1 <sub>pellet</sub> | 450                       | 6                         | 136.5  | 0.080                                | 0.070                         | 15.50             |
| 1 <sub>pellet</sub> | 350                       | 6                         | 161.9  | 0.096                                | 0.084                         | 15.81             |
| 3 <sub>pellet</sub> | 450                       | 0                         | 103.6  | 0.071                                | 0.052                         | 14.77             |
| 3 <sub>pellet</sub> | 450                       | 12                        | 73.9   | 0.062                                | 0.037                         | 14.38             |



Dependence of specific surface of modified clay (sample 1) on the adsorption–desorption cycles of water vapors: (1) powder sample; (2) pelletized sample.

the porous structure of layered aluminosilicates and the medium more strongly affects the modified samples. For example, during the storage of initial samples calcined at 550°C, the specific surface decreased by only 10% after 1-year storage. In modified samples (Tables 2, 3), this decrease is more considerable, corresponding on average to 20% for 6 months of storage and 50% after 1 year. To retain a porous structure of pillared clays, they should presumably be stored in dry atmosphere and sealed packing in analogy with modified zeolites.

## CONCLUSIONS

The effect of calcination temperature on the formation of the porous structure of pillared clays has been studied. Heat treatment of modified clays in the temperature range of 350–400°C yields a material

with a maximum volume of micropores. It has been determined that the porous structure of pillared clays is unstable in air atmosphere; their textural characteristics deteriorate upon storage in humid medium.

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