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THERMAL STABILITY OF CROSS-LINKED MONTMORILLONITE OBTAINED BY TREATING WITH FLUORO-HYDROXY- -ALUMINIUM AND HYDROXY-ALUMINIUM COMPLEXES

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Abstract. Fluoro-hydroxy-aluminium and hydroxy-aluminium polycations were synthesized and subsequently introduced into interlayer spaces of montmorillonite, separated from bentonite of the Chmielnik deposit. The complexes thus obtained were examined using X-ray study to determine their thermal stability by annealing at different temperatures. The measurements were carried out using high-temperature camera by analyzing the change of interplanar spacing of basal 001 reflexions of montmorillonite complexes with increasing calcination temperature. Fluoro-hydroxy-aluminium complex was found to be slightly more thermally resistant than the hydroxy-aluminium one. Their decomposition temperatures are about 550°C and 500°C respectively. It is supposed that this is due to higher thermal stability of (OH, F) groups when compared with (OH, OH) ones. These groups play the structural role of bridges linking adjacent Al^{3+} ions within complex polycations.

INTRODUCTION

In the last years several methods were proposed to obtain pillared forms of swelling clay minerals. They consist in introducing some complex inorganic polycations into the interlayer spacings of these minerals. The pillared porous structures thus obtained display the properties of molecular sieves, resembling in this respect zeolites. Consequently, they can be widely used in various branches of technology, especially as selective sorbents and catalysts.

Till now, aluminium hydroxy-cations (Brindley, Sempels 1977), as well as hydroxy-complexes of Cr, Ni, Co, Fe, Ti and Cu (Shabtai 1979) were applied as cross-linking elements, pillaring smectite layers.

In this paper, the authors present the results of studies of cross-linked complexes of montmorillonite from Chmielnik, pillared by introducing poly-hydroxy- and poly-fluoro-hydroxy-aluminium cations into exchange positions. The essential scope of this study was to compare the thermal stability of these both cross-linked montmorillonite complexes on the ground of X-ray analysis by using high-temperature camera.

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METHODS

The complexes studied were obtained from Na-form of the Chmielnik montmorillonite (fraction below 10 μm). Complex aluminium polycations were synthesized by reaction in aqueous solution, in which the proportion of Al/OH and $\text{Al}/(\text{OH}+\text{F})$ was maintained as 1 : 2. Montmorillonite suspension was subsequently introduced into the solution containing complex polycations and intensely stirred for 8 hours. The resulting complex compound, after washing from salt, was dried at 105°C. X-ray studies of initial samples, as well as of the products of their annealing in laboratory furnace and in high-temperature camera was carried out using X-ray diffractometer DRON 3 by applying filtered $\text{CuK}\alpha$ radiation and high-temperature GPWT-1500 camera.

RESULTS

In different stages of calcination, gradual change of the position of basal 001 reflexions of montmorillonite complexes was observed (Tab. 1). For comparison purposes, thermal behaviour of Na-form of montmorillonite from Chmielnik is also presented. The changes of the shape and intensity of this reflection with increasing temperature for hydroxy-aluminium sample (symbol X-M) is presented in Fig. 1, whilst for the fluoro-hydroxy-aluminium one — in Fig. 2.

Calcination of the samples studied in high-temperature X-ray camera, accompanied by simultaneous recording of X-ray diffraction pattern of selected samples, allowed to determine the temperature intervals, within which the reactions deciding on thermal stability of complex polycations take place. The first changes in position of the 001 reflection appear

Table 1

The positions of the basal 001 reflexions of the prepared samples at different temperatures

| Temperatures of calcination °C | The basal spacing 001 of the prepared samples before and after heat-treatment | | |
|--------------------------------|---|-------------|--------|
| | X-M Å | XF-M Å | Na-M Å |
| 20 | 18.03 | 18.03—19.21 | 12.45 |
| 100 | 14.73 | 15.78 | 9.825 |
| 300 | 14.73 | 15.78 | 9.825 |
| 400 | 14.03 | 15.50 | |
| 500 | 14.03 | 14.98 | |
| 550 | 13.192 | 14.98 | |
| 600 | 13.192 | | |
| 650 | 13.192 | | |
| 450/R* | 18.03 | 14.03 | 9.825 |
| 500/R* | | 18.03 | |
| | | 16.99 | |

* — Symbol R means that the samples have been submitted to rehydration after the heat-treatment.

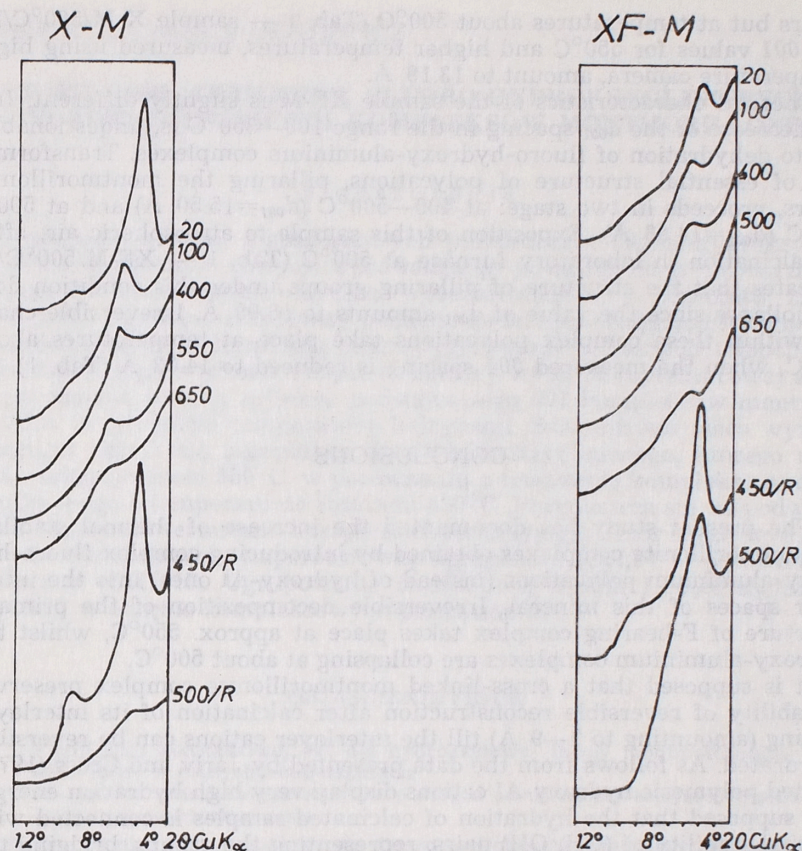


Fig. 1. The shape of basal 001 reflexion for hydroxy-aluminium form of montmorillonite calcinated at different temperatures

R — indicates the samples subjected to rehydration in air after preliminary calcination in an laboratory furnace for 2 hours

Fig. 2. The shape of basal 001 reflexion for fluoro-hydroxy-aluminium form of montmorillonite calcinated at different temperatures

R — indicates the samples subjected to rehydration in air after preliminary calcination in an laboratory furnace for 2 hours

already at the early stage of calcination. At 100°C this position for samples X-M and XF-M corresponds to 14.73 and 15.78 Å respectively and these values remain constant till about 350°C. Further calcination results in structural transformation of hydroxy-aluminium polycation (at 400—500°C) what is accompanied by successive decrease of the d_{001} spacing to 14.03 Å. It is interesting that the calcination of the complex in question at 450°C does not cause yet any irreversible changes in the structure of hydroxy-aluminium cation. As follows from the data, presented in table 1 and Fig. 1 (X-M/450°C/R), a complete reconstruction of initial value of the basal 001 reflection takes place, if the sample annealed at 450°C for 2 hours in an laboratory furnace is left in atmospheric air at 20°C. Irreversible collapse of the structure of complexes pillaring the montmorillonite layers,

occurs but at temperatures about 500°C (Tab. 1 — sample X-M/500°C/R). The 001 values for 550°C and higher temperatures, measured using high-temperature camera, amount to 13.19 Å.

Thermal characteristics of the sample XF-M is slightly different. Initial decrease of the d_{001} spacing in the range 100—350°C is, unquestionably, due to dehydration of fluoro-hydroxy-aluminium complexes. Transformation of essential structure of polycations, pillaring the montmorillonite layers, proceeds in two stage: at 400—500°C (d_{001} =15.50 Å) and at 500—550°C (d_{001} =14.98 Å). Exposition of this sample to atmospheric air, after its calcination in laboratory furnace at 500°C (Tab. 1 — XF-M/500°C/R) indicates that the structure of pillaring groups under this condition does not collapse since the value of d_{001} amounts to 16.99 Å. Irreversible changes within these complex polycations take place at temperatures above 550°C, when the measured 001 spacing is reduced to 14.03 Å (Tab. 1).

CONCLUSIONS

The present study has documented the increase of thermal stability of montmorillonite complexes obtained by introducing complex fluoro-hydroxy-aluminium polycations (instead of hydroxy-Al ones) into the interlayer spaces of this mineral. Irreversible decomposition of the primary structure of F-bearing complex takes place at approx. 550°C, whilst the hydroxy-aluminium complexes are collapsing at about 500°C.

It is supposed that a cross-linked montmorillonite complex preserves the ability of reversible reconstruction after calcination of its interlayer spacing (amounting to 7—9 Å) till the interlayer cations can be reversibly rehydrated. As follows from the data presented by Jariv and Cross (1979), sheeted polymeric hydroxy-Al cations display very high hydration energy. It is supposed that the hydration of calcinated samples is connected with thermal stability of (OH, OH) pairs, representing the groups, bridging the adjacent Al^{3+} ions within the complex cations in question. Partial substitution of bridging hydroxyls by F can result in increased thermal stability of complex fluoro-hydroxy-aluminium cation. This problem, however, needs further studies to explain the mechanism of the process under consideration.

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STABILNOŚĆ TERMICZNA FLURO-HYDROKSYGLINOWYCH I HYDROKSYGLINOWYCH KOMPLEKSÓW MONTMORILLONITU

Streszczenie

Wykonano syntezę kompleksowych polikationów fluoro-hydroksyglinowych i hydroksyglinowych wprowadzając je następnie w przestrzenie międzypakietowe montmorillonitu wyseparowanego z bentonitu złoża Chmielnik. Uzyskane kompleksy poddano badaniom rentgenowskim określając ich stabilność termiczną przez wygrzewanie w różnych temperaturach. Pomiary prowadzono z użyciem kamery wysokotemperaturowej analizując zmianę pozycji refleksu podstawowego 001 kompleksów montmorillonitu ze wzrostem temperatury kalcynacji. Stwierdzono nieco wyższą odporność termiczną kompleksu fluoro-hydroksyglinowego, którego rozkład następuje około 550°C, w porównaniu z trwałością kompleksu hydroksyglinowego o temperaturze rozkładu 500°C. Przypuszcza się, że podwyższona odporność termiczna kompleksu zawierającego fluor może wynikać z wyższej stabilności temperaturowej ugrupowań (OH,F) w porównaniu z grupami (OH,OH). Ugrupowania te stanowią mostki łączące sąsiednie jony Al^{3+} w obrębie kompleksowych polikationów.

OBJAŚNIENIE FIGUR

- Fig. 1. Profil linii podstawowej 001 dla hydroksylowej formy montmorillonitu kalcynowanej w różnych temperaturach
R — próbki poddane rehydratacji na powietrzu po uprzedniej kalcynacji przez 2 godziny w piecu laboratoryjnym
Fig. 2. Profil linii podstawowej 001 dla fluoro-hydroksyglinowej formy montmorillonitu kalcynowanej w różnych temperaturach
R — próbki poddane rehydratacji na powietrzu po uprzedniej kalcynacji przez 2 godziny w piecu laboratoryjnym

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ТЕРМИЧЕСКАЯ УСТОЙЧИВОСТЬ ФТОР-ГИДРОКСИАЛЮМИНИЕВЫХ И ГИДРОКСИАЛЮМИНИЕВЫХ КОМПЛЕКСОВ МОНТМОРИЛЛОНИТА

Резюме

Проведен синтез комплексных фтор-гидроксиалюминиевых и гидроксиалюминиевых поликатионов, которые затем вводились в межпакетное пространство монтмориллонита, выделенного из бентонита месторождения Хмельник. Полученные комплексы подверглись рентгеновским исследованиям,

с определением их термической устойчивости путем прогревания в различных температурах. Измерения проводились с применением высокотемпературной камеры, проводя анализ изменения положения базального отражения 001 комплексов монтмориллонита с увеличением температуры прокаливания. Обнаружено немного повышенную термическую стабильность фтор-гидроксилалюминиевого комплекса, разложение которого происходит в температуре около 550°C, по сравнению с устойчивостью гидроксилалюминиевого комплекса с температурой разложения 500°C. Предполагается, что повышенная термическая стойкость фторсодержащего комплекса может быть обусловлена высшей температурной стабильностью групп (ОН, F) по сравнению с группами (ОН, ОН). Эти группировки представляют мостки, соединяющие смежные ионы Al^{3+} внутри комплексных поликатионов.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Профиль базальной линии 001 для гидроксилалюминиевого вида монтмориллонита, прокаливаемого в различных температурах

R — образцы, подверженные регидратации в воздухе после предварительной кальцинации в течение 2 часов в лабораторной печи

Фиг. 2. Профиль базальной линии 001 для фтор-гидроксилалюминиевого вида монтмориллонита, прокаливаемого в различных температурах

R — образцы, подверженные регидратации в воздухе после предварительной кальцинации в течение 2 часов в лабораторной печи