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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

EMANATION THERMAL ANALYSIS OF INTERCALATED MONTMORILLONITIC CLAY

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Abstract

Emanation Thermal Analysis (ETA), based on the measurement of the release of radon from previously labelled samples, has been used for 'in-situ' characterisation of the morphology changes of intercalated montmorillonitic clay. The thermal behaviour of hydroxyaluminium intercalated montmorillonite was monitored in course of the preparation of alumina pillared montmorillonite, making possible to determine optimal temperature for the isothermal treatment of the intermediate product. Moreover, the thermal stability of alumina pillared montmorillonite porous structure was determined from the ETA data. A good agreement of ETA data and surface area, XRD patterns, DTA, and TG results was found.

Keywords: alumina pillared montmorillonite, emanation thermal analysis, pillared clays

Introduction

Thermogravimetry and differential thermal analysis have been traditionally used in the characterisation of thermal behaviour of clay minerals, including montmorillonitic clay and its intercalates [1–12]. For the characterisation of the interaction products of montmorillonite with various compounds and polymers morphology and surface area changes taking place as the result of these interactions should be monitored. We have proposed to use Emanation Thermal Analysis (ETA) for this purpose [13, 14].

The ETA [15] is based in the measurement of the release rate of inert gas atoms from the solids previously labelled by traces of inert gas (radon). In this paper we present the ETA results of characterising morphology changes of hydroxyaluminium intercalated montmorillonite (MMT) and alumina pillared MMT at 'in-situ' conditions of their heat treatment.

Experimental

Preparation of samples

The bentonite (locality Jelšovsky Potok, Slovak Republic) was wetted and suspended in water to approximately 5% solids. The solution used for pillaring

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was prepared separately: a 0.2 M solution of $AlCl_3 \cdot 6H_2O$ titrated to pH 4.5 and stirred overnight. An NMR spectrum for ^{27}Al showed the presence of a single peak at +60.2 ppm. This peak represents the tetrahedral Al in the Aluminium Keggin ion and shows that the species in solution is largely $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]$. This solution was then mixed with portions of the clay suspension in different ratios and held at 80°C for 4–10 h. The solids were then filtered off with distilled water and dried at 80°C [16]. This is the intermediate product of the alumina pillared MMT preparation. In order to prepare the final alumina pillared MMT the intermediate product is calcined at temperatures between 480–550°C for several hours. The temperature of the thermal treatment was determined from the results of ETA.

Methods

In the ETA the radon atoms were used as microstructural probe of the solids investigated. Adding the trace amounts of radionuclides of ^{228}Th and ^{224}Ra into the clay suspension before the intercalation process started enabled us to label the sample in volume. We can suppose that the atoms of radionulides were introduced uniformly into the sample. The specific activity of the sample was 10^4 Bq g^{-1}. The sample prepared at Texas A and M University [16] was labelled by impregnation with the acetone solution containing ^{228}Th and ^{228}Ra, the atoms of ^{220}Rn being introduced into the surface layers of the solid grains by recoil energy.

The ETA measurements were carried out using Netzsch Type 404 Device. The samples were heated and cooled in air at the rate of 2.5 K min^{-1}, being overflowed by a constant flow of air (40 ml min^{-1}) which carried the released radon atoms into the radioactivity detection chamber.

The XRD pattern were obtained using Philips Device, Ni filtered, CuK_α radiation. Surface area and porosity measurements were carried out by sorption/desorption of nitrogen using Sorptomat 1 800°C (Carlo Erba).

Results

Hydrated hydroxyaluminium ions (called Keggin ions) when intercalated into the MMT layered structure give rise to an intermediate product, which can be transferred by heat treatment to the alumina pillared MMT [16]. The alumina pillared MMT possesses an increased porosity, the enlarged pore size system (typical d_{001} based spacing being 1.82 nm), the high surface area (approx. 300 m^2 g^{-1}) and contains highly reactive alumina situated as 'pillars' in the interlayer space of the MMT.

The alumina pillared MMT is a cation exchanger which can be used as sorbent of hazardous substances of both organic and inorganic nature. It was proposed to be used for the uptake of hazardous compounds and metal ions from contaminated waters and industrial liquid waste streams [17–19].

For the preparation of alumina pillared MMT the detailed information about morphology, surface area and porosity changes taking place in course of the intercalation and subsequent thermal treatment of the intermediate products is requested. The conditions for the heat treatment must be chosen so that ensure optimal sorption properties of the product. The ETA has been demonstrated as a suitable method to yield this information.

Thermal behaviour of hydroxyaluminium intercalated MMT

In Fig. 1 we present results of the radon release measurement the radon release rate E from the hydroxyaluminium intercalated MMT sample at 'in situ' conditions of heating from 20 550°C and subsequent isothermal heating at 550°C (curves 1 and 2, resp. Fig. 1). The surface area of the sample at the beginning of the heat treatment was S=51 $m^2 g^{-1}$, after the heating to 550°C, S=272 $m^2 g^{-1}$, the basal spacing d_{001}=1.86 nm. The effect (curve 1 in Fig. 1) at temperatures 30 100°C corresponds to the release of physically sorbed water. The enhanced release of radon on heating above 300°C reflects the formation of open porosity in the intercalated MMT. During heating from 300 to 490°C the surface area of the sample increased from 120 to 290 $m^2 g^{-1}$. At the temperature of 490°C the break down of the radon release rate is observed, corresponding to the onset of the surface area decrease, leading to the partial consolidation of the highly disordered structure of the sample. On heating to 550°C the surface area decreased to 272 $m^2 g^{-1}$, the basal spacing d_{001}, decreased to 1.81 nm. The slight decrease of

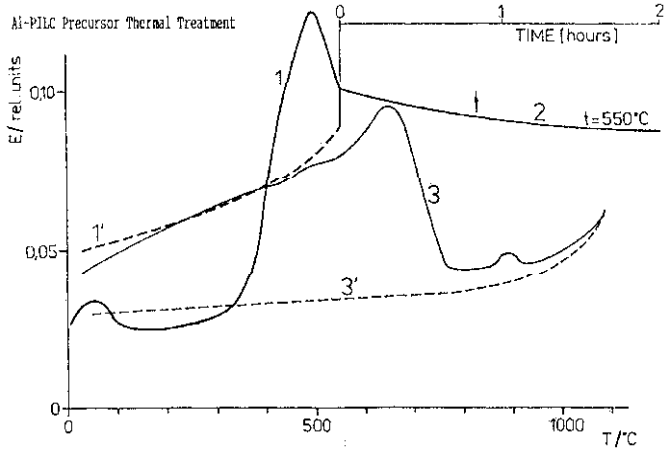

Fig. 1 ETA curves characterising morphology changes of intercalated montmorillonite: curve 1 – hydroxyaluminium montmorillonite heated from 20 to 550°C at the heating rate 2.5 K min^{-1}, curve 2 – subsequent isothermal heating of the same sample at 550°C, curve 1' – subsequent cooling of the same sample from 550 to 20°C, curve 3 – alumina pillared montmorillonite heated from 20 to 1100°C at the heating rate of 2.5 K min^{-1}, curve 3'– subsequent cooling of the same sample from 1100 to 20°C

the radon release rate observed during isothermal heating at 550°C (curve 2, Fig. 1) monitored the decrease of surface area attaining a constant value after 2 h heating.

During this heating the co-ordinated water and water from condensation of hydroxyl groups is released. We determined the water loss from both processes by means of thermogravimetry measurements on heating the samples. It was found, that the dehydrated pillars, rehydrated when exposed to water. After the thermal treatment to 500°C about 60% of the original hydroxyl groups were recovered by wetting [10].

Thermal behaviour of the alumina pillared MMT

Thermal behaviour of the alumina pillared MMT is characterised by the ETA results as curve 3 in Fig. 1. The sample was heated from 20 to 1100°C in air. In the interval from 30 to 400°C no changes in the morphology were observed. The increase of E perfectly coincides with the ETA curve measured during previous cooling of the sample. This demonstrated a good reproducibility of the ETA results. Curve 3, Fig. 1 showed that on heating above 400°C the alumina pillared MMT structure has a higher thermal stability than that of the intermediate product characterised by curve 1 in Fig. 1. The decrease of radon release rate E observed on the curve 3 in the temperature interval 615–750°C corresponds to the decrease of surface area and porosity. By the combination of the thermal analysis methods (DTA, TG) and ion exchange procedures we have shown that the alumina MMT pillars are converted to inert oxides after the heating to 750°C. At lower temperatures the alumina pillars can actively participate in catalytic processes.

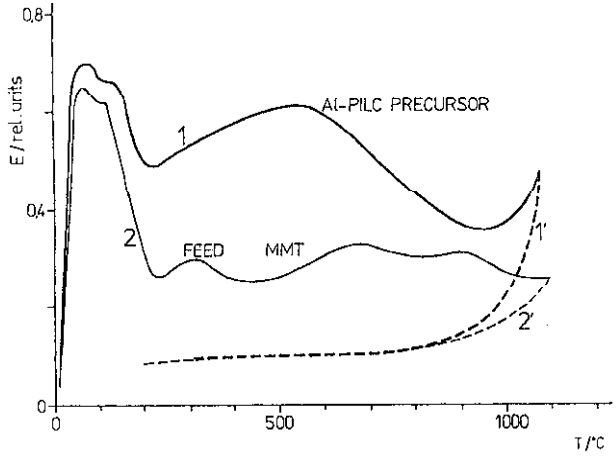

Fig. 2 ETA curves of the hydroxyaluminium intercalated MMT (curve 1) and feed montmorillonitic clay (curve 2) measured during heating from 20–1100°C and subsequent cooling in air

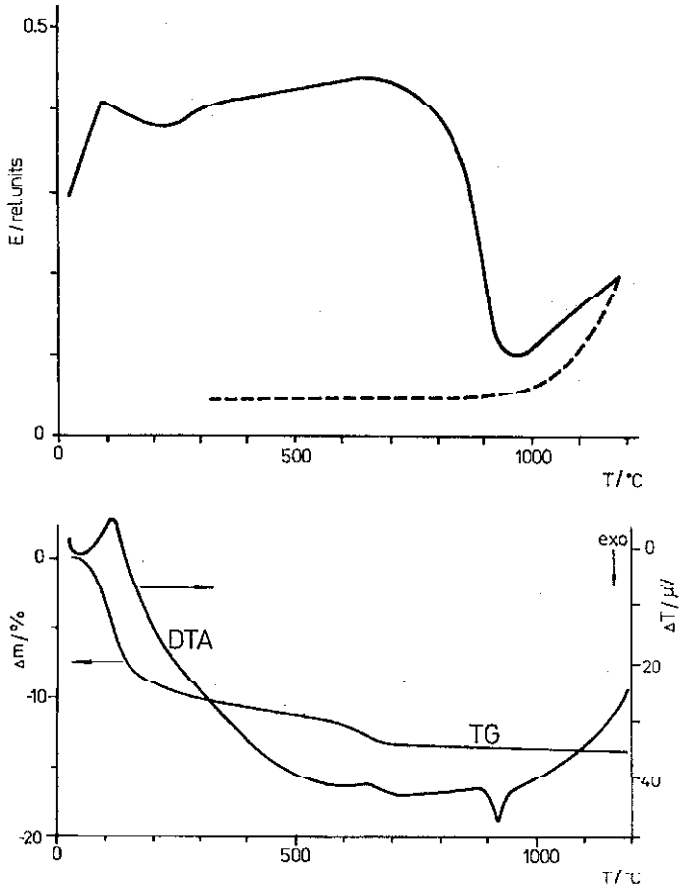

Fig. 3 Characterisation of thermal behaviour of alumina pillared montmorillonite prepared at Texas A and M University. The heat treatment was carried out in air at the heating/cooling rate of 5 K min^{-1}. a) ETA heating and cooling (dotted line) curves of the sample additionally labelled by adsorption of ^{228}Th and ^{228}Ra; b) DTA and TG curves

The ETA results in curve 3, Fig. 1 demonstrated that the porous system of the sample collapsed on the heating above 750°C. The surface area of the sample after the heat treatment to 1000°C was 1 2 m^2 g^{-1}. In the temperature range 870 915°C the effect on curve 3 revealed the high temperature recrystallization (structural transition) of the sample. This process is accompanied by an exothermal effect on the DTA curve which can be ascribed to the recrystallization of alumina present in the sample (Fig. 3b).

The radon release rate was measured also during sample cooling from 1100 to 20°C (Fig. 1, curve 3′). From this curve it follows that no structure nor phase transition take place during sample cooling.

In Fig. 2 we compare the ETA curves of hydroxyaluminium intercalated MMT (considered as the precursor of the alumina pillared MMT) and the feed montmorillonitic clay (Jelšovsky Potok, Slovak Republic). As it was already pointed out, the changes of the radon release rate E indicate morphology changes of the solid samples taking place on heating. In general, the increased values of E measured for the intercalated material correspond well with the hypothesis that the porosity and surface area of the intercalated MMT develop on heating, forming the pillared material. The enhanced release of radon, starting at 200°C, reveal the formation of the porous system of the sample during its heating. The break down of E observed after the temperature of 550°C indicated the thermal stability limit of the porous sample, which, when heated above this temperature looses its porosity and catalytic activity.

Different behaviour was observed with the feed montmorillonitic clay: in the temperature interval 20–400°C two effects on the ETA curves were observed indicating the presence of Ca–MMT (where the dehydration was reported in two steps [3]). The dehydroxylation process at the temperature 600–700°C is accompanied with the formation of pseudo-amorphous meta-montmorillonite, which recrystallizes on further heating.

In Fig. 3 we compare of the results of ETA, DTA and TG of alumina-pillared montmorillonite prepared at Texas A and M University [16]. The optimal conditions (heating to 500 °C for 3 h) were used for the preparation of this alumina pillared MMT. For the ETA measurements the sample was labelled by surface impregnation with ^{228}Th and ^{224}Ra, as described in paragraph Experimental. The ETA (Fig. 3a) and DTA and TG (curve 3b) reflected similar thermal behaviour of the sample with the sample prepared at the same experimental conditions in our laboratory.

Conclusions

It was demonstrated that the ETA is suitable for monitoring surface area and porosity changes during heat treatment of the intercalated MMT at 'in-situ' conditions. The information about the temperature to be used for the thermal treatment of the intermediate products of alumina pillared MMT was obtained from the ETA results. Giving the possibility to use optimal temperature for preparation of the alumina pillared MMT with required sorption properties the temperature of 500°C was recommended for isothermal treatment of the intermediate products during the preparation of alumina pillared MMT.

Moreover, the temperature at which the collapse of the porous system of the alumina pillared MMT takes place was determined from the ETA results. This information was used for the design of the technology of the heat treatment of used sorbent in order to encapsulate the hazardous sorbed elements and compounds in the matrix of the sorbent.

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