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OPTIMIZED PROCEDURE FOR CLAY PILLARING WITH ALUMINUM SPECIES USED IN DEPOLLUTION

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This study presents the improved method of smectite type clays pillaring, using aluminum salts. To achieve this goal, natural clay with a percentage of more than 95% montmorillonite was used. In order to analyze the pillaring process, a thermal procedure was used (thermal programmed desorption). The results of the pillaring process show that a controlled distance between the foliar band structures as long as $18\cdot10^{-10}$ m can be obtained. The clays modified by pillaring can be used as molecular sieves in microfiltration processes or as agents in residual water chemical depolluting processes. They also have zeolite properties which make them reusable.

Keywords: *clay pillaring, depollution, programmed thermodesorption*

Introduction

The clays' pillaring consists in insertion of 'pillars' containing polyhydroxy aluminum structure. With such a procedure we can create a distance between the foliar band structures of the montmorillonite that can reach $18\cdot10^{-10}$ m [1–3].

The ranking technique or that of the pillaring creates the micro porous materials having rigid structures and with properties similar to those of the zeolites. These rigid structures are realized after the intercalation process of Al_{13} using a thermal procedure. The intercalation process consists in impregnating the montmorillonite clay with an aluminum hydroxide solution, and precipitation with a sodium hydroxide solution (Scheme 1).

The reaction scheme is:

$$Al^{3+}+H_2O\rightarrow Al(OH)^{2+}+H^+$$

$$Al^{3+}+2H_2O\rightarrow Al(OH)_2^{+}+2H^+$$

$$2Al^{3+}+2H_2O\rightarrow Al_2(OH)_4^{2+}+2H^+$$

$$13Al^{3+}+28H_2O\rightarrow Al_{13}O_4(OH)_{24}^{7+}+32H^+$$

Scheme 1 Montmorillonite reactions

The intercalation process is followed by a thermal procedure [4], which gives the mechanical properties that make ready to use this structure. In order to be used, the new obtained material must have some properties: mechanical properties, ion exchange properties and fixed distance between lamellar layers. These properties have been studied by some specific methods, such as thermogravimetric analysis for acidity determination [5] and emanation thermal analysis [6]. The porosity of the materials obtained by pillaring can be controlled according to the nature and the characteristics of the cation; this cation has the pillar role in the pillaring process.

Experimental

Clay and microporous materials have an important contribution in actual depollution problems. In this context, some good results are obtained using microporous materials of chemical modified clays type or pillared clays, comparable with those obtained in the case of molecular sieves.

In this study, we present an improved method for pillaring the montmorillonite, a smectite class clay using aluminum solutions and a thermal procedure. Two different methods are envisaged, according to Fig. 1.

At 40°C is prepared a suspension containing 40 g L^{-1} clay in distilled water; in the same time, is prepared a solution that contains 30 mL NaOH 0.4 M and 25 mL of aluminum nitrate $[Al(NO_3)_3\cdot9H_2O]$ 0.4 M. These solutions are mixed up till the mixture becomes transparent, and then may rest for an hour, at 50°C. Colloidal particles are formed in suspension [7, 8].

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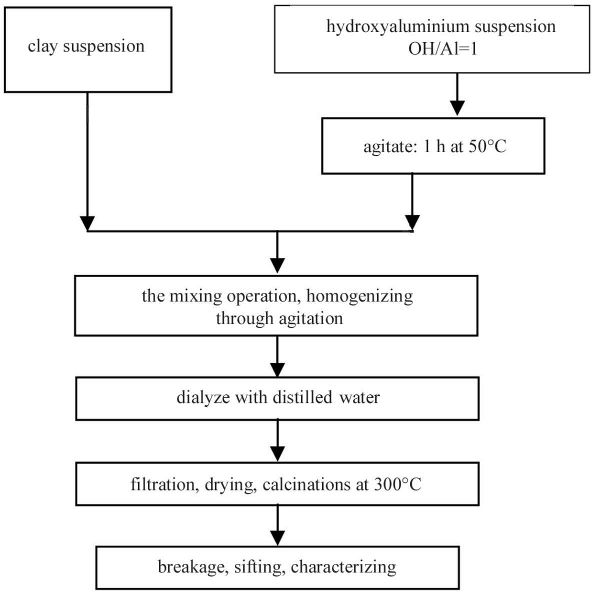

Fig. 1 Procedure for clay pillaring

The ‘pillars’ fixation is realized through an ionic shift and thermal treatment. At the beginning, the electrical charge from the surface of the clay sheet is the same with the one found in the clay diffusion. This happens because there is not a well determined centre for the introduction and the fixing of the Al_{13} ‘pillars’.

The controlled calcinations permit the further fixing of the ‘pillars’ through dehydration, resulting in a rigid structure, similar to those of the zeolites.

The device in which the pillaring process of the clay with aluminum was carried out is the one that it is described in literature [9]. The optimum utilization temperature is 40°C.

The aluminum polyhydroxide solution is introduced in the reaction flask, under agitation. The selected purified clay, with a 0.1–0.4 mm granulometry, is added in the flask.

The mixture is transferred into a porcelain recipient to dry it up at 50°C, followed by calcination.

The installation for acid-basic in situ determination for microporous materials is also described in the literature [9].

Thus, 0.200 g mixture is introduced in the microreactor of the programmed thermodesorption installation. Using this device, the acid-basic properties of the new material (the pillared clay with aluminum cations) are analyzed.

An ammonia flux passes over the pillared clay in order to determine the acidity. If the microporous material presents active centers of acid nature, these will fix the ammonia.

Then the device is cleaned with nitrogen. We can analyze the retained ammonia on clay using a soft procedure, commanded in the programmed thermodesorption installation.

Because the temperature is rising, ammonia is desorbed and taken out from the clay. The desorbed ammonia is sent to some test tubes that contain sulfuric acid solution in the same quantity and concentration.

The exceeding material is left out and the ammonia quantity which has been adsorbed at different temperatures is found out using subtraction [10].

Results and discussion

We can obtain microporous materials by mixing aluminum polyhydroxide solution with purified clay, through calcinations. The final material can also be investigated upon its acid-basic properties by using a thermodesorption device. Finally, the ammonia quantity that was adsorbed at different temperatures is determined.

The obtaining of the microporous materials (which are very important and useful in depollution) is a complex process.

Figure 2 presents the amount of ammonia desorbed at different temperatures. The ammonia desorption curve is shown in Fig. 2. For montmorillonite clay pillared with Al, the realized microporous material has acid proprieties and well defined centers in its structure. Also, it can be noticed that in this diagram the curve can get down exactly on the abscissa. The explanation is that we worked with a device in which we used rubber tubes that have the property of adsorbing gases, even if we tried to saturate them with nitrogen.

According to the diagram study, the basis molecules are connected to the acid centers. That means that an ammonia quantity, thermoadsorbed at a low temperature of 150–200°C, shows that the links between acid centers and ammonia are weak and they could be broken at low temperature.

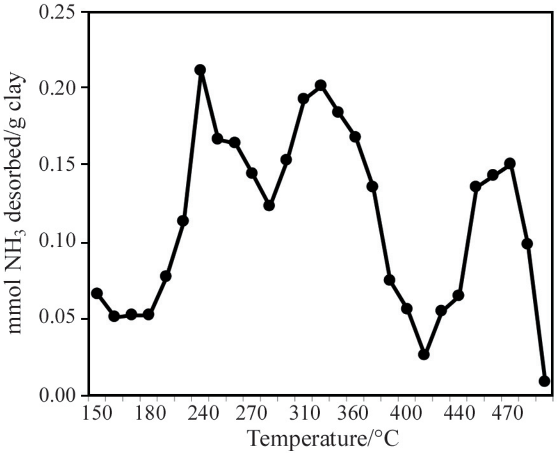

Fig. 2 NH_3 diagram of programmed thermodesorption for clay pillared with Al

Two points with medium links can be observed on the curve. It is also observed a point which shows a 'population' of acid centers that can not absorb at high temperatures. So, we can easily say that these links have a significant strength.

The sample that was submitted to the interspersion with the aluminum cations was observed with an electronic microscope. When the procedure is correctly carried out, it shows if the clay layers made apart by the pillars formed by aluminum polyhydroxyl cations it means were really created (Figs 3 and 4).

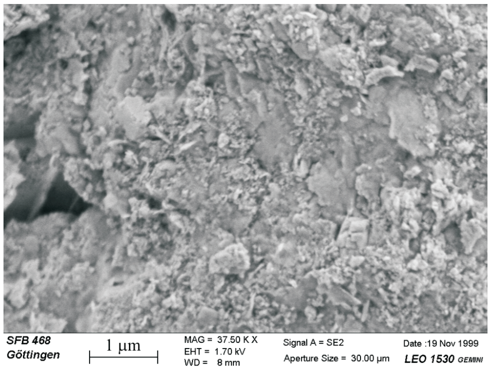

Fig. 3 Clays before pillaring

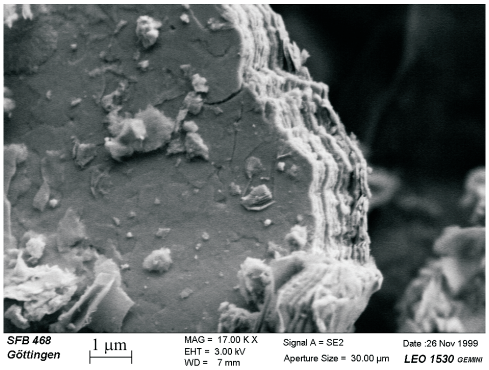

Fig. 4 Clays after pillaring with Al

Image of non pillared clay with a disordered structure is shown in Fig. 3. By difference, the clay got an ordered structure after pillaring. The parallel clay layers are shown in Fig. 4.

Total ion exchange of the clay pillared with the Cu^{2+} cation, at a constant temperature of 80°C

The clay pillared with Al was examined by an ion exchange kinetic study, with a solution that contains Cu^{2+} cation (Fig. 5). The study was carried out on an ultrathermostated bath, the ion exchange being studied at 80°C isotherm at different time ranges.

In order to evaluate the ion exchange possibilities of the clay, we calculated the ion exchange capacity for the Cu^{2+} cation at 80°C. Equations used in calculus are:

$$\mathrm{CSI}=\frac{e}{m} \tag{1}$$

$$e=\frac{m_\mathrm{f}-m_\mathrm{i}}{E_\mathrm{gM}^{2+}} \tag{2}$$

where e=number of exchanged ions in mmoles, m=mass of clay.

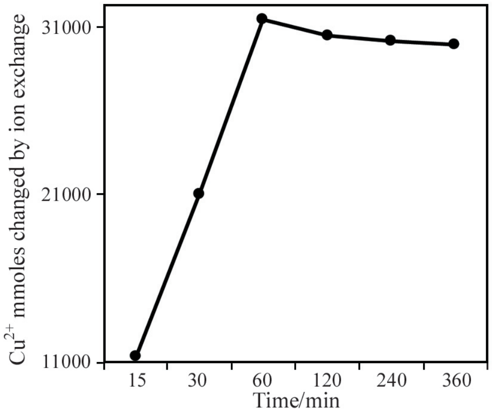

Fig. 5 Kinetic evolution for ion exchange with Cu^{2+} on the clays pillared with Al

The obtained ion exchange capacities are presented in Table 1.

Table 1 Ion exchange capacity of the pillared clay in Cu^{2+} solutions

Time/min	Ion exchange capacities/mmoles Cu^{2+}/g clay
15	1.1434
30	2.1007
60	3.1357
120	3.0415
240	3.0135
360	2.9896

These data show that by pillaring we can increase the diffusion velocity of the cations in the clay structure. This accelerates the ion exchange process, so it accelerates the fixing velocity of the polluted cations.

Conclusions

We think that studying the opportunities of using microporous materials already existing and of producing others that can put up with the modern requirements, represents a domain that did not say its last word.

- Thermal analyzes have proved to be a powerful tool for studying the processes occurring during the calcinations of intercalated clays, the last step of the synthesis of pillared clays. Textural analyzes have indicated that intercalated clays shows modifications of the structural characteristics after calcinations. Using the procedure presented in this study, a distance between the foliar band structures of the montmorillonite could be created. That distance can reach $18 \cdot 10^{-10}$ m.

- The study also shows that by pillaring with Al_{13} we can increase the diffusion velocity of some pollutant cations (e.g. Cu^{2+}) in the clay structure, thus increasing its fixing velocity.
- The pillaring procedure can realize a controlled porosity in clays, upon the materials that are used.

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