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SHORT COMMUNICATION

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FRACTAL ANALYSIS OF PHYSICAL ADSORPTION ON SURFACES OF ACID ACTIVATED BENTONITES FROM SERBIA

Solid surfaces are neither ideally regular, that is, morphological and energetically homogeneous, nor are they fully irregular or fractal. Instead, real solid surfaces exhibit a limited degree of organization quantified by the fractal dimension, D. Fractal analysis was applied to investigate the effect of concentrations of HCl solutions on the structural and textural properties of chemically activated bentonite from southern Serbia. Acid treatment of bentonites is applied in order to remove impurities and various exchangeable cations from bentonite clay. Important physical changes in acid-activated smectite are the increase of the specific surface area and of the average pore volume, depending on acid strength, time and temperature of a treatment. On the basis of the sorption-structure analysis, the fractal dimension of the bentonite surfaces was determined by Mahnke and Mögel method. The fractal dimension evaluated by this method was 2.11 for the AB_3 and 1.94 for the $AB_{4.5}$ sample. The estimation of the values of the fractal dimension of activated bentonites was performed in the region of small pores, 0.5 nm < r_p < 2 nm.

Key words: fractal analysis; adsorption isotherm; BET method; bentonite.

Physical, chemical and adsorption properties of natural adsorbents depend on the crystal structure of their constituent clay minerals [1]. The adsorption properties of adsorbents based on bentonite are a function of the content of montmorillonite and the nature and the number of interlayer cations. In order to remove impurities and various exchangeable cations from smectite and produce a homogeneous and well-defined material for use as an adsorbent and a catalyst, different treatments have been used, most frequently with inorganic acids [2,3].

Activation proceeds with partial dissolution of smectite, described by pseudo first order kinetics [4,5] and is characterized by the initial replacement of the interlayer cations by H^+ [6], followed by dissolution of the tetrahedral and octahedral sheets and a subsequent release of the structural cations [6-9]. Octahedral cations, such as Al^{3+}, Fe^{2+}, Fe^{3+} and Mg^{2+} can be depleted by treating the clay minerals with acids at elevated temperatures with the rates of depletion ge-

nerally following the order Mg^{2+} > Fe^{2+} > Fe^{3+} > Al^{3+} [10,11,17]. Important physical changes in acid-activated smectite are the increase of the specific surface area and of the average pore volume, depending on the acid strength, time and temperature of the treatment [12-18].

Gas adsorption is a method frequently used to determine the surface fractal dimension of porous media. Several different theories have been developed to analyze gas adsorption data and obtain the surface fractal dimension [19-21].

Fripiat *et al.* [22] extended the BET formalism, which originally was designed for perfectly flat surfaces. Besides being non-applicable for the case of irregular surfaces, their formula exhibits the inconsistent behavior in the limiting case of the surface fractal dimension, *D* = 3. Mahnke and Mögel [23] developed a generalized BET formula, which solves the inconsistency problem. An approximate version of this formula offers an easy method for calculating the fractal dimension from adsorption data.

This version is applied to determine the fractal dimension of surfaces of chemicaly activated bentonite samples.

EXPERIMENTAL

Material

Bentonite with a particle size below 0.74 μm was used for the acid treatment. The chemical composition of the bentonite samples was: SiO_2 - 69.12 %, Al_2O_3 - 14.01 %, Fe_2O_3 - 5.43 %, MgO - 2.57 %, CaO - - 1.62 %, Na_2O - 1.33 %, K_2O - 0.66 %, H_2O - 4.69 %.

Acid activation

The chemical activation was carried out at 90 °C, during 2 h with solid-liquid ratio 1:4, with concentrations of 3 M (sample AB_3) and 4.5 M (sample $AB_{4.5}$) HCl, under the atmospheric pressure in a jacketed glass reactor equipped with a reflux condenser, a thermometer and a stirrer. A typical run was carried out as follows: specified amounts of hydrochloric acid of known concentration and smectite clay were loaded into the glass reactor. The stirring speed was held constant by means of a digitally controlled stirrer. At the end of the experiment, the content of the reactor was immediately filtered. The activated clay was washed free of chlorides with hot water to pH 4.5 and dried at 110 °C to a constant weight.

Adsorption measurements

Nitrogen adsorption-desorption isotherms were determined in a high vacuum volumetric apparatus at -196 °C. Prior to the adsorption measurement, the samples were outgassed at 200 °C at the pressure of 1 mPa, for 3 h. The monolayer capacity and the specific surface area of the adsorbents were evaluated by the BET method.

RESULTS AND DISCUSSION

The complete N_2 adsorption-desorption isotherms of the sample AB_3 and $AB_{4.5}$ are shown in Figure 1, where V is the volume of the adsorbed gas at equilibrium pressure (p) and p_0 is the saturation pressure.

The isotherms are reversible under a lower relative equilibrium pressure, but under a higher relative pressure they exhibit a hysteresis loop of the H3 type [24]. Such hysteresis loops exist in the slit-shaped pores or in the ink-bottle pores (pores with narrow necks and wide bodies). The specific surface areas, S_{BET}, the monolayer volume, V_m, and C_{BET} were calculated from nitrogen adsorption isotherms of activated bentonite samples using relative pressure (p) data up to 0.3.

For the purpose of fractal analysis, only the adsorption part of the isotherm was used. The plot (Figure 2) adapted from logarithmical functionality (1):

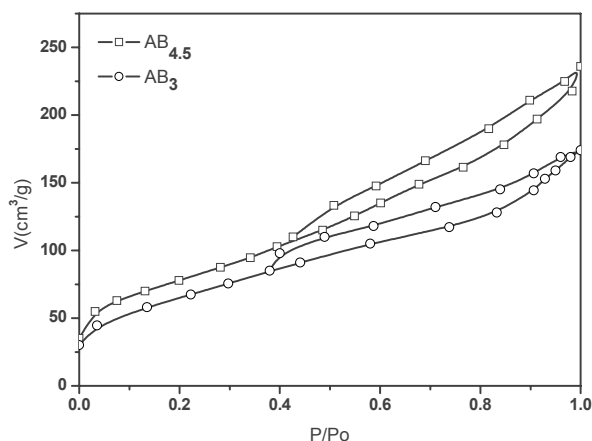$$\log(\frac{V(1-p+C_p)}{V_m C_p}) \ vs. \ -\log(1-p) \qquad (1)$$

is nearly linear.

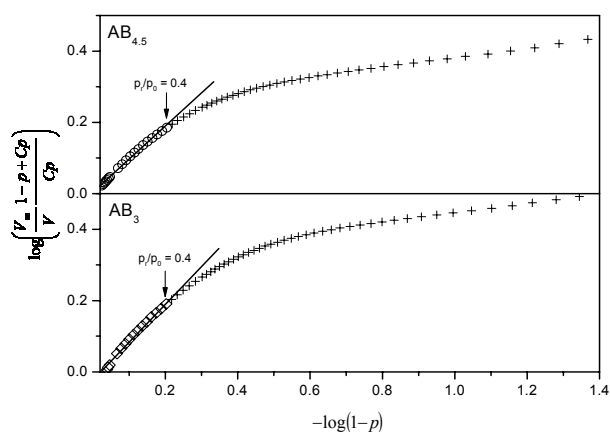*Figure 1. Nitrogen adsorption-desorption isotherms of the acid-activated samples.*

Figure 2. Estimation of fractal dimension, D, according to logarithmical functionality (1).

The straight line fitted for $0.05 < p < 0.42$ using values of C and V_m measured directly from the BET approximation, has a slope, α, of 0.89 for AB_3 and 1.06 for $AB_{4.5}$, which points to a surface fractal dimension, D, of 2.11 and 1.94, respectivaly.

The isotherms calculated from Equation (2):

$$V = \frac{V_m C_p}{(1-p+C_p)(1-p)^{\alpha}} \qquad (2)$$

with these parameters are shown in Figure 3.

As it can be seen from Figure 3, the line fits the dependence equally well for the values of p up to 0.55 (for AB_3) and up to 0.45 (for $AB_{4.5}$). In the low pressure region the estimated fractal dimension is near 2 which indicates that irregularities of the surface are

larger than the size of the adsorbate. In this region of the pressure only one or at most two layers are participating in the adsorption. For high pressure newly build layers lie outside the fractal regime of the surface and the omitted lateral interactions tend to smooth the interface surface. We, therefore, estimate fractal dimension, D, for the samples in the relative pressure region up to hysteresis.
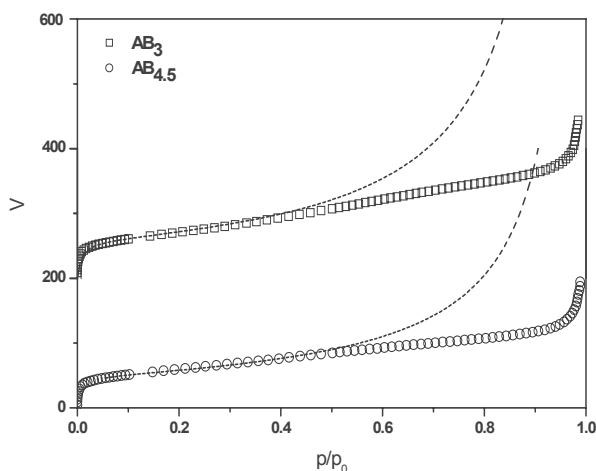

Figure 3. Estimated N_2 isotherms according to the Equation (2).

The knowledge of the fractal dimension of the surface and of the specific surface areas of the activated bentonites samples offers the possibility of estimating, by use of fractal geometry, the effective surface for the adsorption of molecules with cross-sectional surface areas greater than that of the nitrogen molecule, which is of great importance for the application of these materials in adsorption and catalytic processes [25].

CONCLUSION

The approximate version of Mahnke-Mögel isotherm was used to estimate the fractal dimension of the surface of porous bentonite clay. The fractal dimension evaluated by this method was 2.11 for AB_3 and 1.94 for $AB_{4.5}$ sample. The estimation of the values of the fractal dimension of activated bentonites was performed in the region of small pores, 0.5 nm < < r_p < 2 nm.

The isotherm has been successfully fitted to N_2 adsorption data of activated bentonite samples, in the region of the relative pressures 0.05-0.55 for AB_3 sample and 0.05-0.45 for $AB_{4.5}$ sample.

The fractal dimension evaluated by Mahnke-Mögel method can be used for calculation of the effective surface for the adsorption of molecules with cross-sectional surface areas greater than that of nitrogen mo-

lecule. The knowledge of the effective surface of the acid activated bentonites is very important for the various industrial applications of these materials as adsorbents and catalysts.

Acknowledgments

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