Fractal analysis of bentonite modified with heteropoly acid using nitrogen sorption and mercury intrusion porosimetry

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Abstract: Experimental adsorption isotherms were used to evaluate the specific surface area and the surface fractal dimensions of acid-activated bentonite samples modified with a heteropoly acid (HPW). The aim of the investigations was to search for correlations between the specific surface area and the geometric heterogeneity, as characterized by the surface fractal dimension and the content of added acid. In addition, mercury intrusion was employed to evaluate the porous microstructures of these materials. The results from the Frankel–Halsey–Hill method showed that, in the p/p_0 region from 0.75 to 0.96, surface fractal dimension increased with increasing content of heteropoly acid. The results from mercury intrusion porosimetry (MIP) data showed the generation of mesoporous structures with important topographical modifications, indicating an increase in the roughness (fractal geometry) of the surface of the solids as a consequence of the modification with the heteropoly acid. By comparison, MIP is preferable for the characterization because of its wide effective probing range.

Keywords: heteropoly acid; bentonite; fractal geometry; mercury intrusion porosimetry.

INTRODUCTION

Heteropoly acids supported on clay are complex mesoporous systems with an enormous potential for application in adsorption and catalysis processes.[1–4] It is widely known that the optimum performance of solids in several applications requires an exhaustive control of both the structural and textural characteristics. Hence, the control of porosity and surface area are crucial aspects that largely determine the use of these materials.[5,6] The fractal dimension is a parameter used to assess quantitatively the fractal geometry and it represents a measure of the ire-

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gularities on the surface of a solid. The value for this parameter may vary from 2 to 3, whereby the lowest value (2) corresponds to a perfectly smooth surface, while the upper limit (3) corresponds to a totally irregular or rough surface.[7] It is known that the irregularities and roughness of a surface are attributed to the existence of distributed pore sizes that contributes to the value of the fractal dimension (D).[8] The magnitude of the surface fractal dimension of mesoporous materials has a great influence on such important physico-chemical processes as adsorption, surface diffusion and catalysis. Nevertheless, it is still an ambiguous problem to measure the value of D, which may vary according to the method used. One of the simplest relationships employed to determine the fractal dimension of a solid, based on adsorption data, was proposed by Avnir and Jaroniec[9] from the Frankel–Halsey–Hill (F–H–H) Equation. F–H–H methods[10] are the easiest way to calculate the value of D using nitrogen adsorption data without having to calculate the pore surface area.

In addition, mercury intrusion is a popular method employed to evaluate the microstructures of porous materials. Conventional interpretations of the original mercury intrusion porosimetry data include porosity, density, and pores size distribution, *etc*. Besides these, other structural factors have also been determined based on a calculation model deduced from fractal theories and the Washburn Equation.[11]

A better description of pore size distribution across a wide range of pore size is not possible using one method. Therefore, the aim of this study was to quantify fractal geometry by employing two methods.

EXPERIMENTAL

Material

The results of previous investigations on the modelling and optimization of bentonite activation *via* the response surface methodology[12] were applied to a modified bentonite, which was also used as the support in the current study. Bentonite obtained under the optimal conditions (AAB) possessed the following chemical composition (mass %): SiO_2, 73.66; Al_2O_3, 12.28; Fe_2O_3, 4.73; CaO, 0.70; MgO, 1.99; Na_2O, 0.60; K_2O, 0.30; TiO_2, 0.57; loss on ignition, 5.17. Polycrystalline $H_3PW_{12}O_{40}\cdot6H_2O$ (HPW) was prepared from commercial phosphotungstic acid (microscopy grade $H_3[P(W_3O_{10})_4]_{aq.}$, Fluka) by heat treatment at 353 K for 1 h.

12-Tungstophosphoric acid/acid-activated bentonite was prepared according to the method described in the literature.[13] HPW was dissolved in methanol and the resulting solution was added slowly to 5, 10 or 20 mass % of acid-activated bentonite (HPW5, HPW10 and HPW20). To remove the residual methanol, the wet samples were dried in a water bath and further dried in an oven for 2 h at 100°C. The samples were stored in sealed bottles until use.

Characterisation

The nitrogen sorption experiments were performed at 77 K using a Sorptomatic 1990 Thermo Finningen apparatus. The samples were first degassed under vacuum at 453 K until no significant changes in the vacuum were observed (5nm $< t <$ 10 nm). The adsorbed amount of nitrogen was measured by volume at standard temperature and pressure. The specific sur-

face area of the catalysts was calculated by fitting the adsorption data to the linear range of the BET Equation[14] (relative to p/p_0 (0.05–0.35)).

Mercury porosimetry experiments were performed using Carlo Erba porosimeter 2000. First, physisorbed gases were removed under vacuum from the interior of the sample. The intrusion of mercury volumes were measured at stepwise increasing pressures allowing for equilibration at each pressure step.

Methods

The classical Frenkel–Hill–Halsey (F–H–H) Equation describes the continuous growth of an adsorbate film with thickness z on a flat surface when x→1, *i.e.*:[14]

$$\ln\left(\frac{1}{x}\right) = \frac{\alpha}{z^m} \tag{1}$$

where α and m depend on the solid–adsorbate interaction. The value of m is determined experimentally by plotting the experimental isotherm:

$$\frac{N}{N_m} \approx \left(\ln\left(\frac{1}{x}\right)\right)^{-\frac{1}{m}} \tag{2}$$

where N is the number of adsorbed moles of nitrogen at a given relative pressure, N_m is the number of adsorbed moles in a monolayer and, in general, $2 \leq m \leq 3$.

Fractal F–H–H type equations were proposed by Avnir *et al.*[9] and Pfeifer *et al.*[15]. In spite of the different adsorption mechanisms of multilayer formation considered by Avnir *et al.*,[9] they obtained the following isotherm:

$$\frac{N}{N_m} \approx \left(\ln\left(\frac{1}{x}\right)\right)^{-(3-D)} \tag{3}$$

for micropores and mesopores size distributions, where $2 < D < 3$ is the surface fractal dimension.

To calculate D from mercury intrusion porosimetry, the following expression was deduced from fractal theories and the Washburn Equation:[11]

$$\log\left(\frac{\mathrm{d}V}{\mathrm{d}R}\right) = \log k_1 + (2 - D)\log R \tag{4}$$

where V is the volume of mercury intruded at a given pressure, R is the pore radius, k_1 an isoportionality constant and D is the fractal dimension. Hence, D values can be derived from the slop of log (dV/dR) *vs*. log R plots.

RESULTS AND DISCUSSION

Adsorption–desorption isotherms of acid-activated bentonite and bentonite modified with different amounts of HPW are shown in Fig 1. According to the Brunauer, Deming and Teller (BDDT) classification,[16] all isotherms belong to type IV isotherms. A type IV isotherm shape is generally associated with mesoporous adsorbents. The mesopores capacity is the amount adsorbed at the plateau and the mesopore volume is then obtained by assuming the condensate density to be that of liquid nitrogen. Hysteresis loops, which appear in the multilayer range

of physisorption isotherms, are generally associated with the filling and emptying of mesopores. The desorption branch of an isotherm was favoured for mesopore size analysis, but this practice is now considered to be questionable since the desorption path may be dependent on network–percolation effects or variation of the pore diameter along single channels.[17] On the other hand, the persistence of a metastable multilayer is likely to delay the condensation process on the adsorption branch,[18] especially if the pores tend to be slit-shaped.[19]
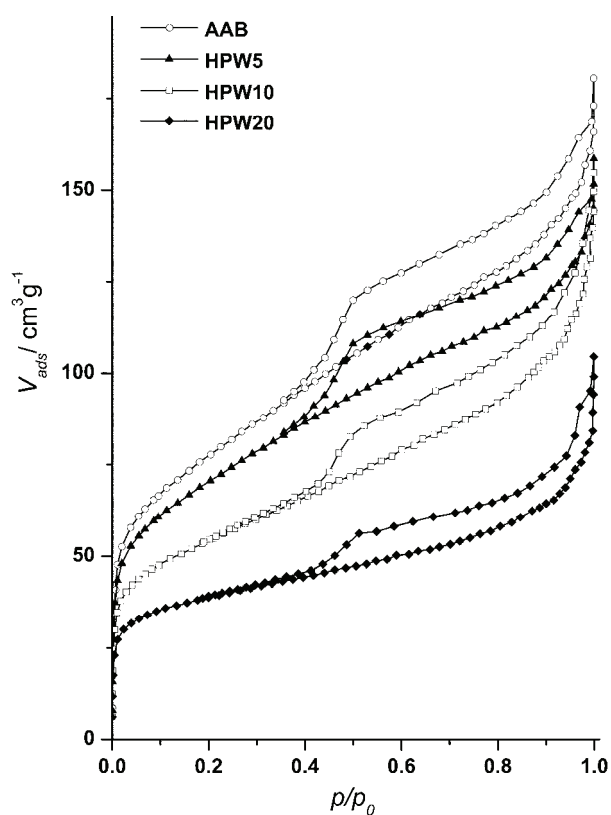

Fig. 1. Adsorption–desorption isotherm of the acid-activated bentonite (AAB) and bentonite modified with different amounts of HPW (HPW5, HPW10 and HPW20).

All isotherms exhibited a hysteresis loop of the H3 type, characteristic for slit-shaped pores. The general shape of the isotherms did not change after impregnation with HPW, showing only a slight decrease in the amount of nitrogen adsorbed.

The dependences of both the fractal dimension obtained from Eq. (1) and the specific surface area on the amount of HPW used to modify the acid-activated bentonite are presented in Table I.

In all cases, there was an excellent linear adjustment for the F–H–H Equation within the range of relative pressures between $0.75 < p/p_0 < 0.96$. The results

showed a slightly decrease in the value of the fractal dimension for the sample with the smallest amount of HPW with respect to the acid-activated bentonite, revealing a decrease in the roughness and the subsequent topographic modification of the surface of the materials as a consequence of the modification process. Addition of HPW to the bentonite reduced the geometric heterogeneity of the sample, probably by closing the existing pores. This was also reflected in a decrease of the specific surface area. These results improve the knowledge to be obtained of the surface characteristic of these solids and, consequently, a better understanding of their catalytic performance. Likewise, it is important to stress how the complexity of the assessed system (acid-activated bentonite modified with HPW) did not interfere with the application and validity of the employed model.

TABLE I. Fractal dimensions of the support and supported samples calculated from the F–H–H equation

Sample	Fractal dimension	R^2	S_{BET} / m^2 g^{-1}
AAB	2.907	0.9982	272
HPW5	2.911	0.9986	246
HPW10	2.859	0.9997	188
HPW20	2.858	0.9980	130

On the other hand, the mercury intrusion porosimetry curves of acid-activated bentonite and bentonite modified with HPW are shown in Fig. 2. The raw data from mercury porosimetry experiments on all samples analyzed using the conventional Washburn Equation:[11]

$$p = \frac{2\gamma_{Hg}\cos\theta}{R} \tag{5}$$

where p is the external pressure (Pa) applied in the vacuum chamber, γ_{Hg} is the surface tension of mercury, θ is the contact angle of mercury and R is the pore radius (nm).

The mercury entered the aggregates of the acid-activated bentonite at the highest pressure, which corresponds to a pore radius of 5 nm. Samples modified with HPW had small particle size that resulted in the smallest pores within aggregates. However, this could also be due to specific orientation of flat bentonite particles. In addition, the small porosity of the acid-activated bentonite (16 %) and samples with HPW loadings of 5, 10 or 20 % (23, 24 and 26 %, respectively) suggested a broad size distribution of the particles or their specific shape and orientation.

The results of the fractal dimension for the bentonite modified with HPW, calculated from mercury intrusion porosimetry, are shown in Fig. 3. In the cases of the HPW modified samples, there was a good linear adjustment for Eq. (4),

but the acid-activated bentonite had very high pore surface fractal dimensions, larger than 3, which is restricted theoretically.
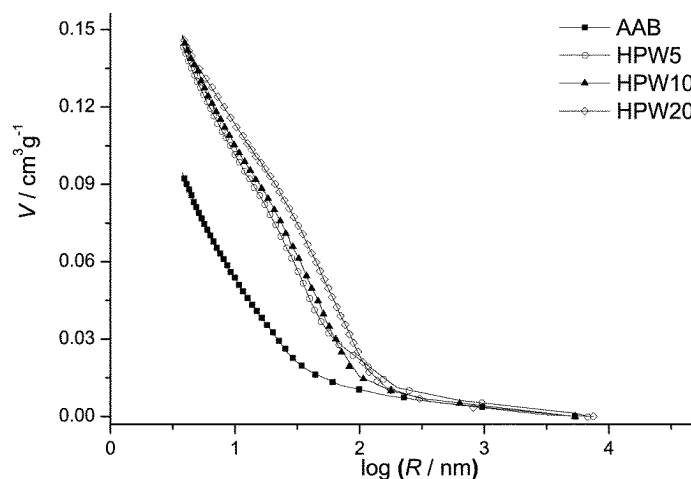

Fig. 2. Mercury intrusion curves for the acid-activated bentonite (AAB) and bentonite modified with different amounts of HPW (HPW5, HPW10 and HPW20).
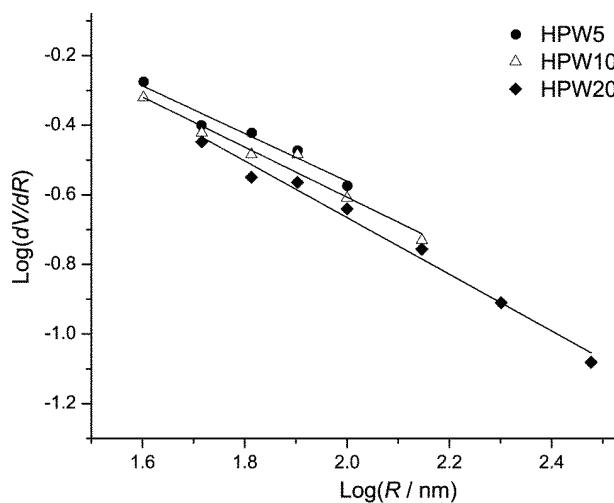

Fig. 3. The dependence of the surface fractal dimension of the modified acid-activated bentonites on the amount of HPW (5, 10 and 20 mass %).

Possibly, pores formed from voids connected by narrower necks started to dominate, due to the removal of the finest particles residing previously in the larger pores. Therefore, a greater pore volume (voids) was attributed to a given pore radius than was formally possible to calculate $D = 3$ in a cylindrical pore model. Thus, dV/dR was also higher, which led to higher D values.

In general, the fractal dimensions of the pore surfaces decreased, indicating a decrease in the complexity of the pore system. The analysis confirmed that fractal dimension calculated from F–H–H method presents the topological complexity of the configuration of the total pores. Similarly, for mercury intrusion porosimetry, the fractal dimension values were different in each pore size range.

CONCLUSIONS

The porous structures of acid-activated bentonite modified with different loadings of HPW were characterized quantitatively by both isothermal N_2 sorption and mercury intrusion porosimetry. The fractal analysis of the nitrogen adsorption isotherms showed a slightly decrease in the value of the fractal dimension for the sample with the smallest amount of HPW with respect to the acid-activated bentonite. Analysis of the mercury intrusion data showed that the small porosity of the acid-activated bentonite (16 %) and the samples with HPW loadings of 5, 10 or 20 % (23, 24 and 26 %, respectively) suggested broad size distributions of the particles or their specific shape and orientation. The results of the two approaches indicate significant differences in porosity, pore size, surface area and pore size distribution.

The analysis of adsorption–desorption and intrusion data always produces several different *D* values, which correlate to the various pores within different size ranges and reflect rough surface morphology and/or complex topology of the pores. By comparison, mercury intrusion porosimetry is preferable for the characterization due to its wide effective probing ranges.

ИЗВОД

ФРАКТАЛНА АНАЛИЗА БЕНТОНИТА МОДИФИКОВАНОГ ХЕТЕРОПОЛИ КИСЕЛИНОМ КОРИШЋЕЊЕМ ПОДАТАКА СОРПЦИОНЕ АНАЛИЗЕ И ЖИВИНЕ ПОРОЗИМЕТРИЈЕ

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Специфична површина и фрактална димензија површине узарака киселински активираног бентонита модификованог хетерополи киселином (HPW) израчунате су на основу података из адсорпционих изотерми азота. Циљ овог истраживања био је да се нађе корелација између специфичне површине и геометријске хетерогености, као и зависност фракталне димензије површине од садржаја додате хетерополи киселине. Такође, метода живине порозиметрије је коришћена за испитивање порозне микроструктуре синтетисаних узорака. Резултати Frankel–Halsey–Hill методе, примењене у области релативног притиска од 0,75 до 0,96, показују да фрактална димензија површине расте са порастом садржаја хетерополи киселине. Резултати живине порозиметрије су показали да је дошло до значајних топографских промена (пораст храпавости) и развоја мезопорозне структуре узорака, као по-

следица модификације хетерополи киселином. Поређење је показало да је метода живине порозиметрије применљива у ширем опсегу пречника пора.

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