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Determination of micropore volume and external surface of zeolites

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ABSTRACT

Original and thermally degraded FAU type zeolites were characterized by nitrogen adsorption at 77 K and compared with isotherms for amorphous silica from literature. The isotherms were evaluated by the method of Remy and Poncelet which is an additive composition of the Dubinin-Radushkevich and the BET equation. Nonlinear fits typically generate two optimal values. One is attributed to very low, the other to very high values of the *C*-constants of the BET part. The conversion of the DR-isotherm to a set of Langmuir isotherms with different affinities shows that the low value is correct. For comparison all data were compared with those obtained by the *t*-plot method. The *t*-plot generally yields a less good fit with the experimental data, lower micropore volumes and deviating external surfaces, especially in the case of thermally degraded zeolites with an enhanced degree of mesopores. The entire isotherms from $p/p_o = 0.5$ to 0.98 are covered by an additive combination of the Dubinin-Radushkevich equation and the general Aranovich equation. That equation, however, fails for the determination of the external surface.

1. Introduction

A lot of classical procedures exist to evaluate the data of N_2 adsorption isotherms at 77K. They range from methods claming to be universal [1] or with a sophisticated view to the adsorbent surface on the molecular level [2]. The aim of this contribution is the evaluation of a method of data analysis for materials with micropores and an external surface, especially for zeolites.

Although adsorption data analysis based on molecular simulation of adsorbate-adsorbent interaction, such as NLDFT [3], has found a growing scientific and commercial interest, the application of classical methods prevails. The calculation of micropore volumes and external surfaces of zeolites is mostly done by the *t*-plot method originally developed by de Boer [4]. Sing has evidenced the strong influence of the chemical composition of the surface on the evolution of the statistical thickness *t* [5]. It was recommended to choose a non-porous material of the same chemical composition [6] or characterized by the same *C*-value of the BET-plot [7]. But such a look to a reference material is effortful. Mostly the universal *t*-plot accounting for the average surface property of a lot of different materials is used [8].

In addition to the question which type of *t*-plot is appropriate, the extrapolation procedure generally depends on the arbitrarily used pressure range [9]. Furthermore, Galarneau et al. have also shown that this type of extrapolation has principally to be questioned [2], and in addition, the thickness *t* calculated according to de Boer is only correct in case of ideally flat surfaces. In reality, the surface curvature has an effect which cannot be neglected [2]. The incorporation of that effect into the *t*-plot method requires data which are not available in the most cases of routine characterizations of porous materials. Therefore a simple mathematical tool for the reliable determination of the micropore volume and the external surface is requested.

For the practical use the method should especially focus on the course of the isotherm describing the transition between micro and mesopores. Remy and Poncelet defined that region as an additive superposition of the Dubinin-Radushkevich (DR) equation for micropore adsorption [10] and a BET term [11] for the behaviour on the external surface (DR-BET method [12]). The authors have compared their results with the external surface obtained by the *t*-plot (2 types of reference systems) and by the usual BET method. Great discrepancies were found. The question remains if the method of Remy and Poncelet [12] is sound enough to replace commonly used methods. Based on the DR term in combination with BET one has to address the weakness of both equations alone. The clearness of the BET theory is based on ideal prerequisites which are the homogeneous solid surface, neglected “horizontal” interactions in the same adsorbed layer, and identical forces between each layers from the first up to infinite [13,14]. But in reality these conditions are only partly fulfilled. As a consequence it was

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emphasized that the *C*-parameter should not be considered as a constant [1], and in the practice the usual BET method is only applied for pressures not larger then $p/p_o = 0.3$ [13]. The DR equation is based on the arbitrary assumption that the fraction of filled micropore volume is proportional to a Gaussian energy distribution. Furthermore the isotherm does not obey the Henry law at the limit $p = 0$ [15]. It is therefore more of empirical than theoretical nature.

Up to now, the application of the DR-BET method is rare. Remy and Poncelet transferred their method to the characterization of further zeolites [16,17] and pillared clays [18]. Two publications deal with the comparison of different methods including the DR-BET-method for zeolites [19,20]. Quite other porous materials were also characterized [21]. For the characterization of super-microporous materials the DR-BET method was extended by a limited number of BET layers [22,23]. Another group extended the method by an additional Henry term [24].

At last, the description of the full isotherm by a modification with up to 3 additional parameters has to be mentioned [25]. It is obvious that the increase of adjustable parameters generates a higher statistical degree of freedom during the non-linear fitting process. In addition, the physical meaning of some parameters may be unclear or of less importance. Therefore, this contribution has the focus on the evaluation if the number of parameters can be reduced to the essential ones.

2. Material and methods

The industrial FAU type zeolites CBV500, CBV760, CBV 780 were obtained from Zeolyst, Y307, Y411, Y 756 and Y100 came from Albemarle, HSZ390 from Tosoh, DAY from the former Degussa company, and a 13X zeolite (Köstrolith 13XBF) in the form of binder-free pellets from CWK Bad Köstritz in Germany. The zeolites covered a Si/Al ratio between 1.3 and 400. Some zeolites were dealuminated by contact for 20 h in 1N HCl at room temperature. Others were treated for up to 20 days in pure boiling water, some of these treatment liquids additionally contained NaCl or HCl. All samples were analyzed by nitrogen adsorption at 77 K with the equipment of BELSORP max (BEL Japan Inc.). Prior to the measurement the samples were heated up to 400 °C with a heating rate of 3 K min^{-1} up and hold there for 16 h. The final pressure was $p < 5\ 10^{-2}$ Pa. The isotherms were analyzed by non-linear regression via SigmaPlot (Systat Software Inc.) based on the algorithm of Levenberg and Marquardt [26]. The analysis via the method of Remy and Poncelet [12] was performed with different boundary conditions. For comparison, all data were analyzed by the *t*-plot method using the universal curve [7]

$$t^2 = 13{,}99/(\log(1/x) + 0{,}034) \tag{1}$$

with $x = p/p_o$ and p_o being the atmospheric pressure. Most samples showed a linear curve for $0.4 < t < 1$ nm, and the micropore volume was obtained by extrapolation to $t = 0$ while the external surface was taken from the slope

$$S_{\mathrm{ext}} = \Delta V/\Delta t \tag{2}$$

Respective results for industrial zeolites and an amorphous silica are compiled in Table 1.

3. Theory

According to Dubinin and Radushkevich [10,27] the isotherm for the filling of micropores with adsorbed condensed nitrogen is assumed to obey a Gaussian distribution

$$\frac{V_1}{V_{micro}} = \exp\left\{-\left(\frac{E}{E_o}\right)^2\right\} \tag{3}$$

where V_1 is the micropore volume filled by nitrogen, V_{micro} the total micropore volume, E_o the characteristic energy[1] and E is given by the Polanyi equation [28].

$$E = RT\ \ln(p/p_o) \tag{4}$$

The adsorption on the external surface is described by the common BET equation [11].

$$V_2 = V_{ext}\ C\ \frac{x}{(1-x)\ (1+(C-1)\ x)} \tag{5}$$

with V_2 being the volume filled by multilayer adsorption on the external surface, V_{ext} is the volume of a monolayer, and *C* is the adsorption constant, while *x* is the partial pressure

$$x = p/p_o \tag{6}$$

With respect to the molecular mass of nitrogen M_{N2}, its density at 77 K ($\rho_{77K} = 0.808$ g cm^{-3}), and its cross-sectional area ($\sigma = 0.162$ nm^2) the external surface is given by

$$S_{ext} = V_{ext}\rho_{77K}N_A\sigma/M_{N2} = s_v V_{ext} \tag{7}$$

The total volume filled with nitrogen at a certain value of *x* is then defined by the sum of V_1 and V_2 and the equation of the isotherm is

$$V = V_{micro}\ \exp\left\{-k\ (\ln(1/x))^2\right\} + \frac{S_{ext}\ s_v\ C\ x}{(1-x)\ (1+(C-1)\ x)} \tag{8}$$

with

$$k = \left(\frac{RT}{E_o}\right)^2 \tag{9}$$

The latter equations are the basis for the concept of Remy and Poncelet called hereafter the DR-BET method [12]. 4 parameters have to be fitted with the experimental isotherm, namely V_{micro}, V_{ext}, *k*, and *C*. By this way only the lower part of the experimental isotherm is captured.

According to Marcilla et al. [25] in a lot of cases the full isotherm can be described by

$$V = V_{micro}\ \exp\left\{-k\ (\ln(1/x))^2\right\} + \frac{S_{ext}\ s_v\ C\ x}{(1-x)^m\ (1+(C-1)\ x)} \tag{10}$$

The additional parameter *m* is 1 for BET and 1/2 for the theoretical derived equation of Aranovich [29,30]. Characteristic values of *m* depending on the adsorbent were also proposed by Aranovich [31] and the physical meaning of *m* between 0 and 1 was interpreted in a density change of the adsorbed layer according to the Ono-Kondo lattice model. Equation (10) is called hereafter the DR-Aranovich isotherm.

An alternative version of the combined capture of micropores and external surface simply replaces the Dubinin-Radushkevich term by a constant and yields an equation with only 3 parameters [32].

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[1] more common in the literature is the substitution of E_o by $\beta\ E^*$ where β is a scaling factor.