Method to Evaluate the Fractal Dimensions of Solid Adsorbents

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A novel method to evaluate the fractal dimensions of solid adsorbents is developed in order to eliminate some of the drawbacks of the conventional methods. The Freundlich isotherm, which may be expressed as $n = A\,p^{1/b}$, is taken as a starting point for the calculations and the point-slopes of the ln n vs ln p plot representing the $1/b$ values are employed to trace the isotherms at any stage of adsorption. The determination of the most favorable $1/b$ values allows the estimation of the fractal dimensions to be made. This method enables the evaluation of the fractal dimensions of adsorbents by employing a single adsorption isotherm and data available for a reference adsorbent. The fractal dimensions of the zeolites 13X, 5A, and silicalite are first determined by employing the Pfeifer−Avnir method and the results obtained are compared with those obtained from the proposed point−slope method. An optimization is made to determine the most favorable $1/b$ values to be employed in the calculations that will result in the least amount of error when the adsorbates methane, ethane, and propane are utilized. As a result, it is observed that the point−slope method may provide a good estimation of the fractal dimensions of the zeolites investigated in this study, namely 13X, 5A, and silicalite, especially when the adsorbates methane and ethane are utilized.

Introduction

Although developed quite recently, the significance of fractal geometry has been rapidly understood. It has found widespread use in diverse areas of science to simulate irregular shapes and chaotic movements. Pfeifer and Avnir were the first to introduce the concept of fractal dimension into chemistry.[1,2] They demonstrated the possibility of measuring the fractal dimensions of adsorbents by making use of the adsorption isotherms obtained for various sizes of the adsorbates. Fractal geometry has also proven to be useful regarding the processes of diffusion and reaction occurring in porous catalysts.[3,4] Moreover, the fractal dimension is introduced as a helpful tool to depict and quantify the irregular nature of the phase transformations in zeolite A synthesis.[5]

On the other hand, the definition of fractality is still controversial and there exist some speculations in the literature[6] claiming that adsorbents may not be described as having fractal surfaces since the range of scale employed to evaluate the fractal dimension is limited by the sizes of real adsorbates, which do not vary for much more than 1 or 2 orders of magnitude. It is also mentioned that a Koch curve obtained by two iterations is not fractal because its fractal dimension value may change in case scales smaller than the size of the irregularities are used. If this is the case, however, no object may be proven to be fractal since there will always exist infinitely smaller scales to measure the infinitely smaller irregularities. It is possible to say that even if a fractal object may have a definite range of applicability for its characteristic fractal dimension value after which it tends to approach a whole number (2 for surfaces), depending on its nature, it actually never attains this value. We therefore, prefer to continue to use the term "fractal" for adsorbents that are experimentally shown to exhibit a fractal dimension value other than 2 on any scale of practical significance.

The fractal analysis by adsorption may be a convenient tool to provide the opportunity to make a comparison between various kinds of adsorbents regarding their structures, in case a proper method is used. A few distinct methods have been proposed for determining the fractal dimension of an adsorbent by employing the adsorption isotherms. The most commonly employed method is based on the fact that the accessible surface area of a solid increases with decreasing dimensions of the adsorbate molecules.[1,2] Thus, for this specific method, the monolayer adsorption capacities of the adsorbents for a series of adsorbates selected to be employed as well as the molar volumes or the cross-sectional area of the adsorbates should be known. However, this method has some drawbacks,[7,8] one of them being the uncertainty in the molecular size for most of the adsorbates which may change with the adsorption temperature and the adsorbent. Moreover, quite different values for the molecular sizes of the adsorbates may be obtained according to the manner of their deduction, being either experimental or theoretical.[9] Both the conventional theoretical[10] and experimental[11] methods used to evaluate the cross-sectional areas of adsorbates are not reliable; in many cases, the latter assumes the accessible surface area of an adsorbent to be the same for all adsorbates, that is, the fractal dimension is always equal to 2. Another drawback is the necessity that the adsorbate molecules employed be similar in shape such that they are the members of a homologous series. The necessity of defining specific monolayer adsorption capacities creates additional problems in some cases,[8,12] and this effect may get more pronounced when different sources of adsorption data are utilized. Another method (Frenkel−Halsey−Hill) that may be used for evaluating the fractal dimensions of adsorbents involves the employment of a single adsorption isotherm.[7,13] Despite the claims that the FHH method may be employed regardless of the adsorbate chosen, some contradicting results have also been obtained.[14] Anyhow, the FHH method cannot evaluate the fractal dimensions of microporous materials since it is valid only for multilayer adsorption. The adsorbent−adsorbate interactions

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which frequently play a significant role in the process of adsorption may also hinder an accurate estimation of the fractal dimension to be made, especially in cases where these interactions are relatively strong. For all of these reasons, it seems difficult and also cumbersome to determine the fractal dimensions of the microporous adsorbents.

In this study, a method is developed to evaluate the fractal dimensions of solid adsorbents, the zeolites in the first place. This method involves the employment of a single adsorption isotherm as long as data required to represent the characteristics of a reference adsorbent including data for the same adsorbate is already available. The reference adsorbent is utilized as a means of comparison in the evaluation of the fractal dimension of any other adsorbent. The fractal dimensions of the zeolites 13X, 5A, and silicalite are first calculated by the method developed by Pfeifer and Avnir[2] after which the novel method is employed for the same purpose. A theoretical background for the proposed method is provided, and the significance of the results is discussed by taking into account the results obtained from the Pfeifer−Avnir method and by estimation of the percentages of error in the calculations.

Theoretical Background

The fractal dimension takes into account how fast a curve, surface, or volume changes by measuring with smaller and smaller scales and may be expressed as

$$D = -\lim_{r \to 0}[\log N(r)/\log(r)] \qquad (1)$$

where r represents the measuring unit and N is the number of objects that may be measured by r. The same kind of reasoning may be used to determine the fractal dimensions of solid adsorbents and the way to accomplish such a task is elegantly described elsewhere.[1,2] When the size of the adsorbate is varied through a series of values, the fractal dimension of a zeolite may be determined as[2]

$$n_m(v) = fv^{-D+1} \qquad (2)$$

where n_m represents the number of moles adsorbed as a "so-called" monolayer (actually the formation of a true monolayer should not be expected in the case of adsorption on zeolites), f is a constant, and v denotes the molar volume of the adsorbate. According to this method developed by Pfeifer and Avnir, the value of the fractal dimension might be determined from the slope of a plot of log n vs log v. It is also necessary to mention at this point that the fractal dimension determined by employing adsorption data may represent an apparent value for adsorption, as seen by the processes involving adsorption, and may be somewhat different than the ones determined by other methods, such as small-angle X-ray scattering, electronic energy transfer, or scanning tunneling microscopy.

The presence of an effect of the fractal structure of the adsorbents on their adsorption properties is apparent considering the methods referred, which are employed to evaluate the fractal dimensions. In this study, a basic relationship between the adsorption isotherms of the adsorbents and their fractal dimensions is sought for. For this reason, the Freundlich isotherm, which depicts a direct relationship between the amount of moles of the adsorbate adsorbed and the partial pressure, is taken as a starting point for the calculations. The Freundlich isotherm may be expressed as

$$n = Ap^{(1/b)} \qquad (3)$$

The Freundlich isotherm may be assumed to be valid only for a limited part of most adsorption isotherms, that is at the stage of early adsorption where the relationship between n and p is more or less linear. As the bending of the isotherm starts, the Freundlich equation generally loses its validity. In this study, instead of determining a single $1/b$ value for each adsorption isotherm, the $1/b$ values corresponding to various stages of adsorption are evaluated. $1/b$ in eq 3 is representative of the shapes of the adsorption isotherms during the whole course of adsorption. Although its value generally changes between 0 and 1, it may exceed 1 slightly in some cases. During the early periods of adsorption, this term possesses a high value about 1, which denotes a linear relationship between n and p, after which it starts to decline. For the type 1 isotherms, $1/b$ approaches 0 near the end of the process of adsorption. These characteristics of $1/b$ make it an efficient tool to trace the adsorption properties of the adsorbents, when various adsorbates are used, during the whole course of adsorption. The task of searching for a relationship between the fractal dimension of an adsorbent and its adsorption properties might be accomplished by employing the variation of $1/b$ along the adsorption isotherms, from the beginning till the end of the adsorption process. The variation of $1/b$ may be assumed to reflect, at least partly, the fractal properties of various adsorbents.

Taking the natural logarithm of both sides in eq 3 gives

$$\ln n = \ln A + (1/b) \ln p \qquad (4)$$

and the point slopes at each $\ln p$ value in a plot of $\ln n$ vs $\ln p$ enable the determination of the $1/b$ values. To determine the $1/b$ values at each p, an appropriate method should be employed to calculate the point slopes.

For the determination of the most appropriate $1/b$ value to be employed in the evaluation of the fractal dimension, a reference adsorbent, a zeolite in this case, of which the fractal dimension is known can be employed. The relative magnitude of the most favorable $1/b$ value of a zeolite, in comparison with that of the reference zeolite, gives an indication about the fractal dimension of the zeolite investigated. The term defined as the most favorable $1/b$ value, signifies the existence of a specific part of the adsorption isotherm depending on the adsorbate used that will provide the most accurate value of the fractal dimension. To determine the most favorable $1/b$ value, a parameter (m) is defined which represents the derivative of $-1/b$ with respect to p and may be expressed as

$$-d(1/b)/dp = m \qquad (5)$$

In eq 5, p denotes the pressure and $1/b$ may be expressed as

$$1/b = d(\ln n)/d(\ln p) \qquad (6)$$

The point-slopes at each $1/b$ in a plot of $1/b$ vs p represent the m values (after changing sign) which may be determined by employing an appropriate method. The $1/b$ values corresponding to each m value might also be estimated. To determine the fractal dimensions of the zeolites, a suitable m value, the magnitude of which will depend on the adsorbate employed should be selected, such that, $m = m_1 = m_2$, where m_1 and m_2 denote the reference zeolite and any zeolite investigated, respectively. Thus, the $1/b$ values for each of the zeolites investigated, which are related to the magnitude of their fractal dimensions, might be obtained for the corresponding m value.

The values of $1/b$ may be expressed in terms of the fractal dimension by employing a suitable relationship. A general examination of the variation of the $1/b$ values obtained in this

study with respect to the fractal dimension values determined by employing the Pfeifer–Avnir method exhibits the fact that a relationship in the form of $1/b = k(D - 1)$ exists. k is a constant that varies with respect to the adsorbate employed, and D is the fractal dimension. To express the relationship given above in accordance with previously determined forms of D (related to other methods[2,13]), the following equation is proposed by assuming that $k = 1/c$:

$$1/b = (D - 1)/c \qquad (7)$$

The fractal dimension, D, is a characteristic of the adsorbent, while the magnitude of the most favorable $1/b$ value varies with respect to both the adsorbate and the adsorbent. As a consequence, it is possible to assume that the parameter c corresponds to the characteristics of the adsorbate employed, and this assumption is verified by the proximity of the c values determined by using the most favorable $1/b$ values corresponding to the same adsorbate but to different adsorbents and the D values estimated by the Pfeifer–Avnir method. Thus, c may be taken to be equal for the adsorbent investigated and the reference adsorbent. To evaluate the fractal dimension of a zeolite, the following expression might be employed:

$$D_2 = [(D_1 - 1)\,(1/b)_2/(1/b)_1] + 1 \qquad (8)$$

where the subscripts 1 and 2 denote the reference zeolite and the zeolite under investigation, respectively. In this manner, the fractal dimension of a zeolite may be evaluated by comparison with a reference zeolite of which the D and $1/b$ values are known. The most favorable $1/b$ values should be employed in the calculations and the fractal dimension of the reference zeolite might be determined by another method. The same adsorbate should be employed for both of the cases (reference and investigated) since the variation of the $1/b$ values exhibit a typical behavior dependent on the gas selected.

In this study, initially an optimization is made in order to be able to determine the most favorable m and thus the $1/b$ values corresponding to the employment of the adsorbates methane, ethane, and propane. To find an optimum m value for each adsorbate, the percentages of error resulting from the calculations performed are estimated and minimized by taking into consideration the deviation of the constants (c) from the c_{av} value, which represents the average of the constants ($c_{1,2...}$). Each constant c_i may be evaluated as:

$$c_i = (D_{\mathrm{PA}i} - 1)/(1/b)_i \qquad (9)$$

where $D_{\mathrm{PA}i}$ represents the fractal dimension obtained for any of the zeolites by employing the Pfeifer–Avnir method. The percentage of error in the calculations originating from the employment of any of the adsorbents might be expressed as

$$e_i = [|c_i - c_{av}|/c_{av}\,] \times 100 \qquad (10)$$

The average percentage of error resulting from the calculations performed to evaluate the fractal dimensions of the zeolites for any of the adsorbates employed might be expressed as

$$e = (e_1 + e_2 + ... e_w)/w \qquad (11)$$

In eq 11, w denotes the number of the zeolites utilized including the reference zeolite. This procedure is repeated for each adsorbate and the percentages of error corresponding to distinct cases, where various m values are employed, are

estimated. The m values providing the minimum amount of error in the calculations are thus determined.

Results and Discussion

The fractal dimensions of the zeolites 13X, 5A, and silicalite are evaluated by employing the Pfeifer–Avnir method in the first place, after which the results obtained are utilized as a basis for testing the accuracy of the novel method developed. In the literature, a few estimations concerning the fractal dimensions of the zeolites have been accomplished by employing the Pfeifer–Avnir method. The values obtained for zeolite 13X are 1.95[2] and 2.37[15] while those obtained for zeolite NaY and zeolite 5A are 2.03[16] and 2.57,[15] respectively. These results clearly show the difficulty of determining the exact values of the fractal dimensions of the zeolites by using the Pfeifer–Avnir method. However, the magnitudes of the fractal dimensions of the zeolites might be determined quite accurately, as long as similar conditions, such as the same adsorption temperature, the same source of adsorption data, and the same manner of determining the molar volume, might be employed for all the cases. In this study, the fractal dimensions of the zeolites 13X, 5A, and silicalite are evaluated by the Pfeifer–Avnir method by taking into account all these facts. From the literature, adsorption data of methane, ethane, and propane on the zeolites 13X[17,18] and 5A[17,19] as well as those of methane, ethane, propane, and butane on silicalite[20] are obtained. The adsorption isotherms obtained for each zeolite involve temperatures around 300 K. Except for the adsorption isotherms of zeolite 13X and 5A for ethane, the source of data is the same for all cases. To employ the Pfeifer–Avnir method, the monolayer capacities of the adsorbents for each of the adsorbates as well as the molar volumes of the adsorbates should be determined. In this study, the monolayer capacities of the zeolites 13X, 5A, and silicalite for methane, ethane, and propane as well as that of silicalite for butane are determined by using the Langmuir equation. To determine the molar volume of methane, ethane, propane, and n-butane at 300 K, a relationship between the number of carbon atoms and the molar volumes of n-hexane, n-heptane, and n-octane at the same temperature is approximated[21] and employed in the form

$$v = 16.135n_{\mathrm{c}} + 34.405 \qquad (12)$$

In eq 12, n_{c} represents the number of carbon atoms found in a normal paraffin whereas v denotes the molar volume in cm³/mol. The fact that the critical temperatures of methane and ethane are below or very close to the adsorption temperature has made the utilization of such an equation necessary, since otherwise inaccuracy in the calculations performed could be expected. The molar volumes of propane and n-butane are also determined by using eq 12 to avoid any inconsistency. Figure 1 depicts the relationship between the monolayer capacity and the molar volume of the adsorbate for the zeolites 13X, 5A, and silicalite. The slopes of these lines (after changing sign) plus 1 give the fractal dimensions of the zeolites, which are listed in Table 1. The fractal dimension of zeolite 13X is in fairly good agreement with the values previously obtained,[2,16] taking into account the fact that zeolites 13X and NaY have similar crystal structures. The fractal dimensions of zeolite 13X and 5A are quite close to each other, and both of them seem to have nearly planar adsorption surfaces. On the other hand, silicalite possesses a remarkably low value of fractal dimension which indicates that the adsorption sites in silicalite behave more like a curve than a surface. This observation increases the possibility that apparent fractal dimension values characteristic
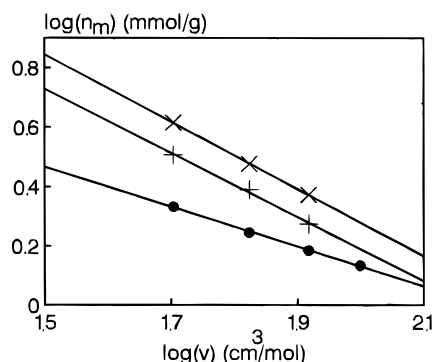
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Figure 1. The variations of the monolayer capacities of ($\times$) zeolite 13X, ($+$) zeolite 5A, and ($\bullet$) silicalite for methane, ethane, propane, and butane with respect to the molar volumes of these adsorbates represented in a log−log scale.
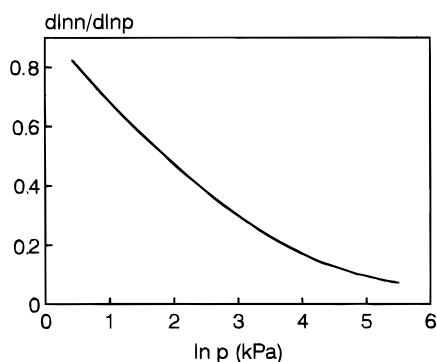

Figure 2. Smoothest d(ln n)/d(ln p) vs ln p curve drawn according to the equal-area graphical differentiation method for the adsorption of ethane in silicalite.

TABLE 1: Fractal Dimensions of Zeolites Characterized by Volume Adsorption (Pfeifer−Avnir Method) and the Corresponding Correlation Coefficients

	zeolite 13X	zeolite 5A	silicalite
D	2.13	2.08	1.68
r	0.9999	0.9978	0.9997

of the adsorption process exist and different values may be obtained in case methods other than adsorption (such as electronic energy transfer and scanning tunneling microscopy) are employed.

The same adsorption data are employed for the calculations made for the novel method developed. The first step required to determine the fractal dimensions of the zeolites 13X, 5A, and silicalite involves the determination of the $1/b$ values which represent the point slopes at each ln p in a plot of ln n vs ln p. To determine the $1/b$ values, any appropriate method may be employed; in this study, the equal-area graphical differentiation method[22] is preferred. The procedure of this method might be outlined as calculating $\Delta y_n/\Delta x_n$ as an estimate of the average slope in each interval x_{n-1} to x_n, plotting these values as a histogram versus approximately the midpoint values of x in the intervals, such that the smoothest curve that best approximates the area under the histogram is drawn, and reading the estimates of $(\mathrm{d}y/\mathrm{d}x)_i$ from this curve at the data points x_i. An advantage of this method is that it may compensate for inconsistent data originating from experimental errors. A plot of d(ln n)/d(ln p) vs ln p representing the smoothest curve obtained by employing the equal-area graphical differentiation method may be seen in Figure 2. This plot belongs to the case which involves the adsorption of ethane in silicalite. Similar plots are formed for
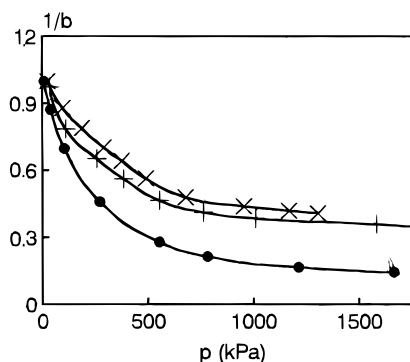

Figure 3. Relationship between the $1/b$ and pressure values when methane is used as the adsorbate for the adsorbents ($\times$) zeolite 13X, ($+$) zeolite 5A, and ($\bullet$) silicalite.
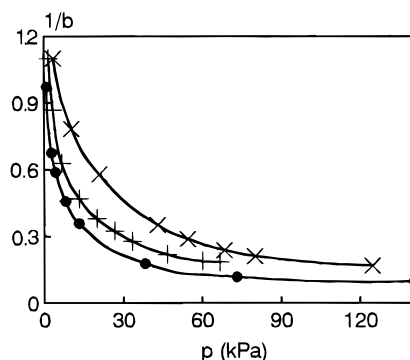

Figure 4. Relationship between the $1/b$ and pressure values when ethane is used as the adsorbate (legend as in Figure 3).
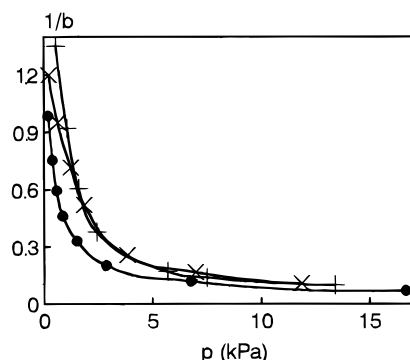

Figure 5. Relationship between the $1/b$ and pressure values when propane is used as the adsorbate (legend as in Figure 3).

the zeolites 13X, 5A, and silicalite concerning the adsorption of methane, ethane, and propane. The $1/b$ values corresponding to each pressure value employed might be determined by the help of these plots. Figures 3−5 depict the relationships between $1/b$ and pressure for the adsorbates methane, ethane, and propane, respectively. It may be observed that the $1/b$ values tend to stay nearly constant after a sharp fall when a specific stage of adsorption has been attained.

The next step involves the determination of the most favorable $1/b$ values to be employed in the evaluation of the fractal dimensions of the zeolites. For this aim, as mentioned above, a parameter (m) has been utilized which represents the derivative of $-1/b$ with respect to p. The m values are the point slopes (after changing sign) of a plot of $1/b$ vs p and may be determined by any appropriate method. In this study, the m values are evaluated again by employing the equal-area graphical differentiation method.[22] A plot of m vs $1/b$ representing the smoothest curve obtained may be seen in Figure 6. This plot

TABLE 2: Fractal Dimensions of Zeolites 5A and Silicalite Evaluated by the Novel Method Developed Employing Methane, Ethane, and Propane as the Adsorbates

	methane			ethane			propane		
	zeolite 13X (ref)	zeolite 5A	silicalite	zeolite 13X (ref)	zeolite 5A	silicalite	zeolite 13X (ref)	zeolite 5A	propane
D	2.13	2.06	1.68	2.13	2.11	1.73	2.13	2.06	1.81

TABLE 3: Values of the Parameters Obtained from the Novel Method Corresponding to the Optimum Conditions

	methane			ethane			propane		
	zeolite 13X	zeolite 5A	silicalite	zeolite 13X	zeolite 5A	silicalite	zeolite 13X	zeolite 5A	silicalite
$1/b$	0.539	0.506	0.324	0.193	0.189	0.125	0.277	0.260	0.201
c	2.10	2.13	2.10	5.87	5.70	5.43	4.09	4.15	3.38
e		0.65			2.70			8.40	
m_{opt} (kPa^{-1})		0.0005			0.001			0.05	
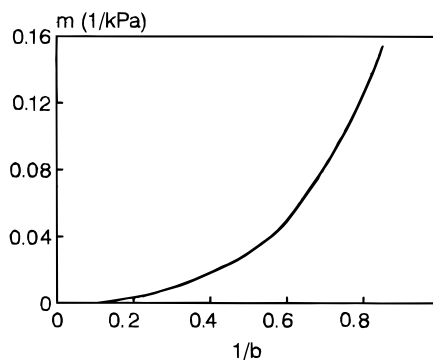
Figure 6. Smoothest m vs $1/b$ curve drawn according to the equal-area graphical differentiation method for the adsorption of ethane in silicalite.

belongs to the case involving the adsorption of ethane in silicalite, and similar plots are formed for all of the cases investigated. Arbitrary m values are selected for each of the adsorbates employed, and the corresponding $1/b$ values of the zeolites, namely zeolite 13X, 5A, and silicalite, are determined from the plots formed (such as Figure 6). The $1/b$ values obtained are utilized in determining the fractal dimensions of zeolites 13X, 5A, and silicalite corresponding to different m values. Zeolite 13X has been selected as the reference zeolite, and the fractal dimensions of 5A and silicalite are evaluated by taking into account the $1/b$ value of 13X as well as that of either 5A or silicalite for each calculation. The fractal dimension of zeolite 13X is assumed to be equal to the value obtained by employing the Pfeifer–Avnir method. The percentages of error in the calculations are estimated by using the fractal dimensions obtained from the Pfeifer–Avnir method. For this aim, the constants (c), which may be employed as indicators of the deviations of the fractal dimensions evaluated by the novel method from the ones determined by the Pfeifer–Avnir method, are estimated for each case. To determine the most favorable m and thus the $1/b$ values resulting in the least amount of error, an optimization is made. The optimum m values might be obtained for the cases where methane and propane are employed, whereas the percentage of error for the case involving the utilization of ethane seems able to be reduced further. This possibility cannot be verified because of the limitations originating from the adsorption data. The fractal dimensions obtained for zeolite 5A and silicalite, regarding the optimum m values, by taking zeolite 13X as the reference adsorbent, may be seen in Table 2 for the adsorbates methane, ethane, and propane. The results obtained for zeolite 5A and silicalite, while 13X is taken as the reference zeolite, are very close to the ones determined by employing the Pfeifer–Avnir method, and the best results correspond to the case where methane is used as

the adsorbate. The values of $1/b$, c, and e, which are determined for all the cases, are given in Table 3 together with the optimum m values. It might be easily concluded that when propane is employed as the adsorbate the amount of deviation in the values of the fractal dimensions will be fairly higher than the cases where methane and ethane are utilized. Actually, as the molecular size of the adsorbate gets larger, the amount of error in the calculations increases. The reason for this situation might be that a larger size of the adsorbate results in a loss of sensitivity in tracing the surfaces of the adsorbents. Another reason may be that a narrower range of pressure has been employed and thus the fewer adsorption data points available has resulted in less accurate results.

The results obtained in this study imply that the proposed method might be employed to determine the fractal dimensions of the zeolites 13X, 5A, and silicalite all of which exhibit type 1 isotherms. To find the fractal dimension of any adsorbent that exhibits type 1 isotherms, it is sufficient to obtain its adsorption isotherm for one of the adsorbates methane, ethane, or propane at a temperature around 300 K and take one of the zeolites investigated in this study as a reference adsorbent. However, it is necessary to indicate that in case special interactions between the adsorbents to be tested and the adsorbates investigated in this study exist, the estimated fractal dimension values may still be inaccurate. Zeolite 13X is recommended to be employed as the reference adsorbent when the adsorbates methane and propane are utilized, whereas zeolite 5A seems to give slightly better results for the case where ethane is employed. The validity of the proposed method for types of isotherms other than type 1 might also be tested, but in this case, the reference isotherm should better be of the same type as the one for which the fractal dimension will be evaluated. In this case, a new optimization should also be made and the most favorable m and $1/b$ values be determined.

The fractal dimensions of activated carbon and H-mordenite are also evaluated by employing zeolites 5A and 13X as the reference adsorbents, respectively. For the former case, ethane is utilized as the adsorbate, whereas propane is employed for the latter one, and the adsorption data required are obtained from the literature.[23,24] The optimum m values obtained for ethane and propane are employed for the evaluation of the fractal dimensions of activated carbon and H-mordenite, respectively. As a result, fractal dimensions of 2.14 ± 0.06 for activated carbon and 2.03 ± 0.17 for H-mordenite are obtained.

The results obtained clearly indicate that it is difficult to relate the optimum conditions determined in this study to a specific range of pressure or a degree of coverage (n/n_m). The degree of the coverages at the conditions providing the best results are observed to vary in significant amounts according to the adsorbate employed and for each type of zeolite. On the other

hand, for all the cases investigated, the optimum *m* values determined correspond to $1/b$ values (might be observed from Figures 3−5) that are found at a specific region of the curve signifying the end of rapid adsorption.

Conclusions

A method to evaluate the fractal dimensions of adsorbents is developed which involves the employment of a single adsorption isotherm, provided that data for a reference adsorbent pertaining to the same adsorbate is available. The point−slopes of the ln *n* vs ln *p* plot representing the $1/b$ values are employed to trace the isotherms at any stage of adsorption, and the determination of the most favorable $1/b$ values allows the estimation of the fractal dimensions. The most favorable $1/b$ values are evaluated by carrying out an error minimization which also gives an indication about the validity of the method for the adsorbent−adsorbate pairs employed. The results obtained by utilizing the proposed point−slope method are in good agreement with the ones obtained by using the Pfeifer−Avnir method especially when methane and ethane are employed as the adsorbates. The percentage of error in the calculations when propane is utilized is relatively higher, which may be due to loss of sensitivity originating from an increase in the molecular size. Actually, as the molecular size of the adsorbate gets larger, the amount of error increases which indicates that the employment of adsorbates, such as *n*-butane, *n*-pentane, etc., may result in even less accurate results.

The most favorable conditions that result in the least amount of error in the calculations performed to evaluate the fractal dimensions of the zeolites 13X, 5A, and silicalite are observed to correspond to the stage of adsorption where a fairly high amount of the adsorbate coverage has already been accomplished and the $1/b$ values tend to stay relatively constant. Adsorbates other than *n*-paraffins may also be tested for their suitability to be employed in the proposed method. The results and the optimum conditions obtained in this study are expected to be valid for most of the adsorbents using a small paraffin adsorbate as long as the isotherm obtained is of type 1. However, there may exist exceptional cases where special interactions between the adsorbate and the adsorbent take place resulting in

a difficulty in estimating the fractal dimension. In the case of utilizing adsorbents exhibiting isotherm types other than type 1, a different reference adsorbent should be selected and a new optimization be accomplished.

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