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APPLICATIONS OF FRACTAL GEOMETRY FOR CHARACTERIZING HYDROTREATING CATALYSTS

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The characterization of heterogeneous catalysts or porous solids involves a description of a reacting interface. The physical and chemical properties of catalysts – surface area, active site density and reactivity – have recently been quantified by fractal geometry. The use of fractal dimension rather than N_2 BET surface area provides for the determination of effective surface area for any adsorbate. The concept may be useful in predicting the reactivity of individual components in hydroprocessing. Similarly, the effects of particle size on surface area and reactivity, or the distribution of active sites on a catalyst, may be quantified by fractal geometry. Applications are discussed with specific examples.

1. Introduction

The geometry of a reacting interface is extremely important in most industrial reaction systems. In heterogeneous catalysis, the performance of a catalytic system is dictated by the geometry of the interface as well as by the chemical reactions which occur at that interface. The application of fractal geometry for characterizing boundaries or porous materials is currently receiving considerable attention. This paper discusses potential application of fractal geometry in heterogeneous catalysis, particularly hydroprocessing.

The concept of spatial dimension has normally been represented by integers. In classical Euclidean geometry, a line, rectangle or cube are described as one, two, or three-dimensional. The physical world, however, involves nontrivial geometries. Mandelbrot [1] introduced the term fractal as a dimensionless number which quantifies the degree of irregularity or ruggedness of a boundary. A fractal therefore is an object that has a fractional dimension. A rough surface, for example, may have an intermediate dimension between a 2-dimensional smooth surface and a 3-dimensional volume. The fractal dimension of a surface, D, is therefore a quantitative measure of the space-filling ability of that surface.

In the field of heterogeneous catalysis, the coupling of geometry and chemistry introduces the phenomenon of structure sensitivity. The complex geometry of the interface may be described quantitatively by a fractal dimension if the interface is symmetric to transformations of scale, i.e., self-similar. This simply means that for a fractal, the same type of features are observed at different magnifications. In heterogeneous catalysis this change of scale can involve reactants of different molecular sizes (as in the sorption of a series of adsorbates), or catalyst particles of different sizes with the same reactants, or supported catalysts with varying amounts of active sites. Avnir and colleagues [2,3] have introduced two simple equations to quantify the scaling phenomena of surfaces. If a catalyst surface is a fractal, the accessible surface area, A, is related to catalyst particle radius, R, by:

$$A = k_1 R^{D-3} \tag{1}$$

where D is the surface fractal dimension. In addition, accessible surface area is related to the effective cross-sectional area of the adsorbate, a_m, by:

$$A = k_2 a_m^{(2-D)/2} \tag{2}$$

The surface fractal dimension is a very useful quantitative parameter for characterizing typical hydroprocessing catalysts.

Nitrogen BET specific surface area is most often used as a quantitative measure of surface area. The porous materials used as supports for hydrotreating catalysts – amorphous alumina and silica-alumina – have a surface fractal dimension between 2 and 3. The larger the fractal dimension, approaching 3, the more rugged the catalyst surface. In the limit, the surface will fill a volume of space. The concept of the space-filling ability of a catalyst leads to a slightly different approach in describing catalytic reactions. In effect, a catalytic reaction may not so much occur on a surface as in a surface. The active sites are normally viewed as elements of disorder – kinks, vacancies – when perhaps an alternate picture for hydroprocessing catalysts is an element of order in a disordered surface.

2. Discussion

The equations above are useful not only in measuring D but also in calculating accessible surface area, effective cross-sectional area of adsorbates or even particle size. For reactions of large molecules, the use of accessible surface area for each reactant/product is preferable to the use of N_2 BET surface area. Table 1 was calculated from eq. (2) for three hypothetical hydrotreating catalysts of surface fractal dimension $D = 2.10$, 2.50 or 2.90. The proportionality constant was determined by assuming a value of 200 m^2g^{-1} for the N_2 BET area, and then the accessible areas for benzene, naphthalene, and anthracene were calculated.

Similarly, by assuming an anthracene surface area of 100 m^2g^{-1} the N_2 BET specific surface area can be calculated as in table 2.

The area occupied by an adsorbate molecule in a monolayer, a_m, was calculated from liquid density values [4]. The tables indicate that N_2 BET surface area

Table 1
Accessible surface area

absorbate	a_m (nm^2)	Calculated accessible surface area (m^2g^{-1})		
		$D = 2.10$	$D = 2.50$	$D = 2.90$
nitrogen	0.162	200	200	200
benzene	0.305	194	171	150
naphthalene	0.383	192	176	136
anthracene	0.410	191	159	132

is a poor parameter for characterizing the three catalyst surfaces. Considering a complex mixture of reactants (such as hydrogen, benzene, napthalene and anthracene) it is possible to choose a catalyst that has relatively more surface accessible to anthracene, for example, by choosing the catalyst with the lowest surface fractal dimension. The underlying assumption, of course, is that the active sites are evenly distributed throughout the catalyst surface.

For catalytic hydrocracking then, the catalyst with the lowest surface fractal dimension (assuming equivalent N_2 BET areas) should present the highest accessible area for asphaltenes. Hydroprocessing catalysts are often described as sponges or as porous solids with very high "internal" surface as opposed to "external" surface. High "internal" surface is ascribed to a pore structure where the classical mathematical model of a pore is a cylinder with smooth walls. This model may be described by a Menger sponge model [1,5]. The alternate picture of these materials is as a very rugged surface which is space-filling to a degree described quantitatively by a surface fractal dimension. The relationship between surface fractal dimension, D, and average cylinder-equivalent pore diameter has been explored [6]. The surface fractal dimension, D, is clearly a useful quantitative parameter for surface characterization.

An interesting catalyst has been described for the ASVAHL hydrodemetallization (HDM) process [7]. This is a burr-shaped catalyst with no "internal" surface as opposed to a sponge. The branching of this burr appears to be self-similar over a range of scale. The outside of the burr would appear smooth to a large asphaltene molecule. The initial reactions of HDM and cracking occur at the outside of the catalyst particle and it is here that metals are deposited. Smaller

Table 2

adsorbate	Calculated N_2 BET surface area (m^2g^{-1})		
	$D = 2.10$	$D = 2.50$	$D = 2.90$
anthracene	100	100	100
nitrogen	105	126	152

molecules penetrate the burr where further reactions may occur. The entire catalyst then would appear to open up to expose new surface to geometrically smaller molecules. In describing this catalyst as a porous material, one would model it as a solid with pore sizes ranging from very large at the outside edges to small in the center of the burr.

Equation (1) quantifies the effect of particle size on apparent surface area. For a high D particle, the apparent surface area is independent of R. For particles of intermediate surface fractal dimension (such as most transition metal oxides), this equation gains importance as it does in fine particle science [8]. Nitrogen BET data for microporous materials should be treated with caution. Applications of fractal geometry in adsorption studies on microporous petroleum coke have been examined [8b].

3. Reaction dimension

The numerous parameters which dictate the chemical reactivity of a fractal boundary may be described by an empirical scaling exponent, D_R the reactive surface fractal dimension. This can be interpreted as the effective fractal dimension of an interface towards reaction. It has been demonstrated [9] that the initial rate of reaction, v, with the surface of a particle i.e., thermal decomposition or gasification is related to particle size by:

$$v = k_3 R^{D_R - 3}. \tag{3}$$

The reactive surface fractal dimension is a measure of the activity of the reactive surface which is a sub-set of the total particle surface. Farin and Avnir have reviewed several examples of eq. (3) and discussed the relationship between D_R and D [9]. Equation (3) should also find application in heterogeneous catalytic reactions.

The catalytic activity of metal catalysts dispersed on high surface area supports has been shown [10] to exhibit similar scaling behaviour:

$$a = k_4 R_P^{D_R} (\text{mol s}^{-1} \text{ per particle}) \tag{4}$$

$$a = k_5 R_P^{D_R - 2} (\text{mol s}^{-1} \text{ per exposed surface site}) \tag{5}$$

$$a_g = k_6 R_P^{D_R - 3} (\text{mol s}^{-1} \text{ g}^{-1}). \tag{6}$$

In eqs. (4) to (6), R_P represents the radius of the metal particles on the support and D_R is the reaction dimension. The reaction dimension provides a quantitative measure of structure sensitivity. Farin and Avnir [10] have noted a range of values from $D_R = 0.4$ to $D_R = 6$. The reaction dimension is affected not only by specific molecule/metal interactions but also by the support morphology.

When catalytic activity per exposed surface atom is independent of metal crystallite size, the reaction is structure insensitive. This occurs when $D_R = 2$, eq.

(5). In terms of activity per particle, eq. (4), the activity scales with R^2. Therefore, all surface atoms contribute equally to catalytic activity regardless of crystal plane. The reaction dimension is easily determined from log-log plots of eqs. (4), (5) or (6). The real value of D_R, however, occurs when specific active site populations can be assigned to D_R values. The easiest specific sites to visualize may be corners, edges, and planes. Where D_R is less than 2 and the surface of the metal crystallite has dimension 2, a subset of active sites, n_a, exists which grows slower than the total number of surface sites, n_s. The opposite case, D_R greater than 2, means that the subset of active sites grows faster than the total number of surface sites. The performance of this particle size scaling analysis indicates that if the particle is magnified by a factor of N, then a total of N^D features appear.

4. Applications of reaction dimension

A great deal of published literature can be examined to demonstrate a scaling analysis of typical Mo/Al_2O_3 catalysts. The rate of hydrodesulphurization (HDS), for example, may be related to the effects of molybdenum loading. Where eq. (6) relates catalytic activity to metal crystallite size in supported catalysts, it is perhaps easier to relate HDS activity to molybdenum loading for hydrotreating catalysts. The data of Okamoto et al. [11] are plotted in fig. 1 for thiophene HDS. This is a log-log plot of thiophene conversion (400 °C, atmospheric pressure) against molybdenum loading. The loading has been expressed as the number of molybdenum atoms per square nanometer of N_2 BET surface area. This unit of loading was chosen as a better approximation of surface site density to facilitate comparisons of different alumina supported catalysts. Figure 1 exhibits regions of structure sensititivity for thiophene HDS above and below a molybdenum loading of 2.7 Mo nm^{-2}. The reaction dimensions for the two linear regions calculated from the slope of the log-log plot using eq. (6) are 5.2 and 3.7 for the low and high loadings.

Similarly, the data of Thomas et al. [12] for thiophene HDS (400 °C, atmospheric) are presented in fig. 2. These data were generated to observe the effects of impregnation methods (i.e., wet and dry) on catalyst activity. Clearly, when plotted in terms of m^3 thiophene converted per gram-catalyst second, the various preparation techniques produce final catalysts with the same structure sensitivity. The reaction dimension, D_R, determined from these data is 4.5 below a loading of 2.7 Mo nm^{-2} and 3.4 above. Bachelier et al. [13] have examined the effect of molybdenum loading on thiophene HDS (420 °C, atmospheric) and on oxygen sorption at 60 °C. Catalysts were prepared by a normal aqueous impregnation of gamma alumina using ammonium heptamolybdate. The data are shown in fig. 3 as a log-log plot of reaction rate (mol $g^{-1}h^{-1}$) or oxygen adsorption (μmol g^{-1}) against loading. Two linear regions were again observed. For thiophene HDS, a reaction dimension of 5.2 is calculated for loadings below 2 Mo nm^{-2} and 3.7 at

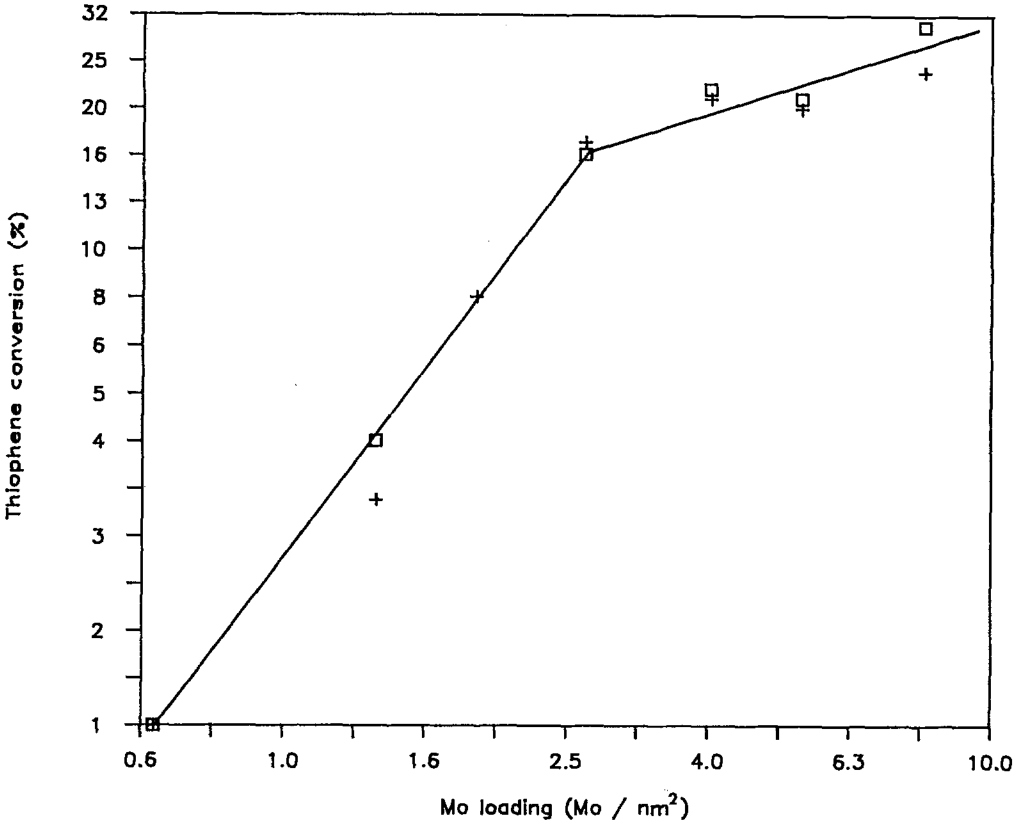

Fig. 1. The conversion of thiophene over a series of Mo/Al_2O_3 catalysts □, ref. [11a]; +, ref. [11b].

higher loadings. The oxygen adsorption data followed similar trends with calculated reaction dimensions of 5.0 and 3.2 for the low and high loadings, respectively.

The three examples demonstrate that the structure sensitivity of thiophene HDS can be quantified by a reaction dimension, D_R. In all cases, there is a change in structure sensitivity at molybdenum loading between 2 and 3 Mo nm^{-2}. It is anticipated that this point coincides with the beginning of molybdenum aggregation with increased loading.

It is apparent [14–16] that MoO_3 can be detected by laser Raman Spectroscopy (LRS) only at loadings above 3 Mo nm^{-2} after calcination at 500 °C. Extended X-ray adsorption fine structure (EXAFS) indicated no evidence of MoO_3 in a catalyst of 2.4 Mo nm^{-2} loading [17,18]. The EXAFS study suggest a large degree of disorder with very small amounts of crystalline material, i.e., less than 1 nm diameter. At loadings below which MoO_3 or $Al_2(MoO_4)_3$ are detectable by LRS or EXAFS, an interaction species has been described [14,19]. A tetrahedral coordination for molybdenum predominates at low loadings, tetrahedral and octahedral coordinations at 2.8 Mo nm^{-2}. An increase in both octahedral and

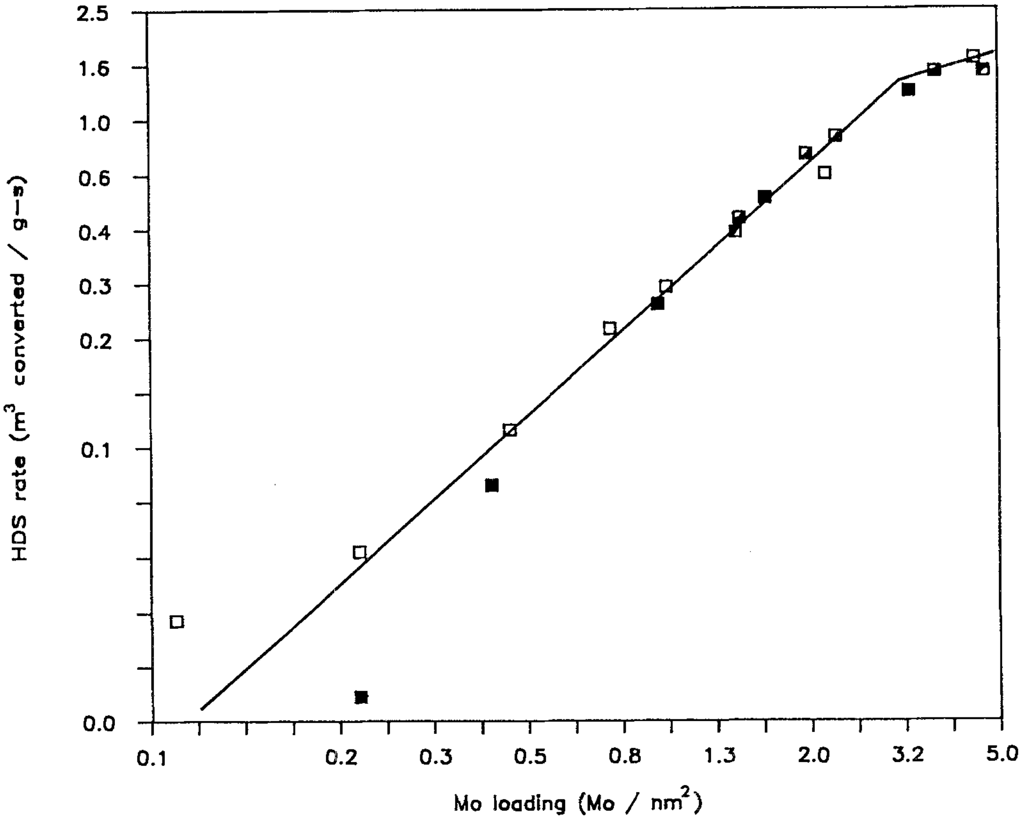

Fig. 2. The rate of thiophene HDS for a series of Mo/Al_2O_3 catalysts; □ dry impregnation; ■, wet impregnation; ◩, effect of pH, ◪; boehmite; ref. [12].

tetrahedral molybdenum with increased loading was observed [14]. A maximum in tetrahedral coordination occurred at 1.7 Mo nm^{-2} and in octahedral at 4.5 Mo nm^{-2} loadings. Tetrahedral molybdenum was thought to occur in isolation, i.e., well-dispersed whereas octahedral molybdenum was thought to exist in association with other Mo groups.

The data presented in the figures clearly describe an empirical scaling phenomenon. The application of a fractal descriptor, D_R, results in a quantitative description of catalyst structure sensitivity. This is useful in comparing catalysts prepared by different methods using various alumina supports. In addition, there is evidence to suggest that the molybdenum loading may be related to molybdenum dispersion, aggregation, or the size of ordered regions on the catalyst surface. There may be examples in the literature where rates of reaction for a series of reactants are presented. In some cases it has been stated that large molecules react at a lower rate than small molecules due to steric hinderance. The reaction rates are most often presented as moles per gram or moles per m^2 N_2 BET surface area. As indicated in tables 1 and 2 however, large molecules simply do

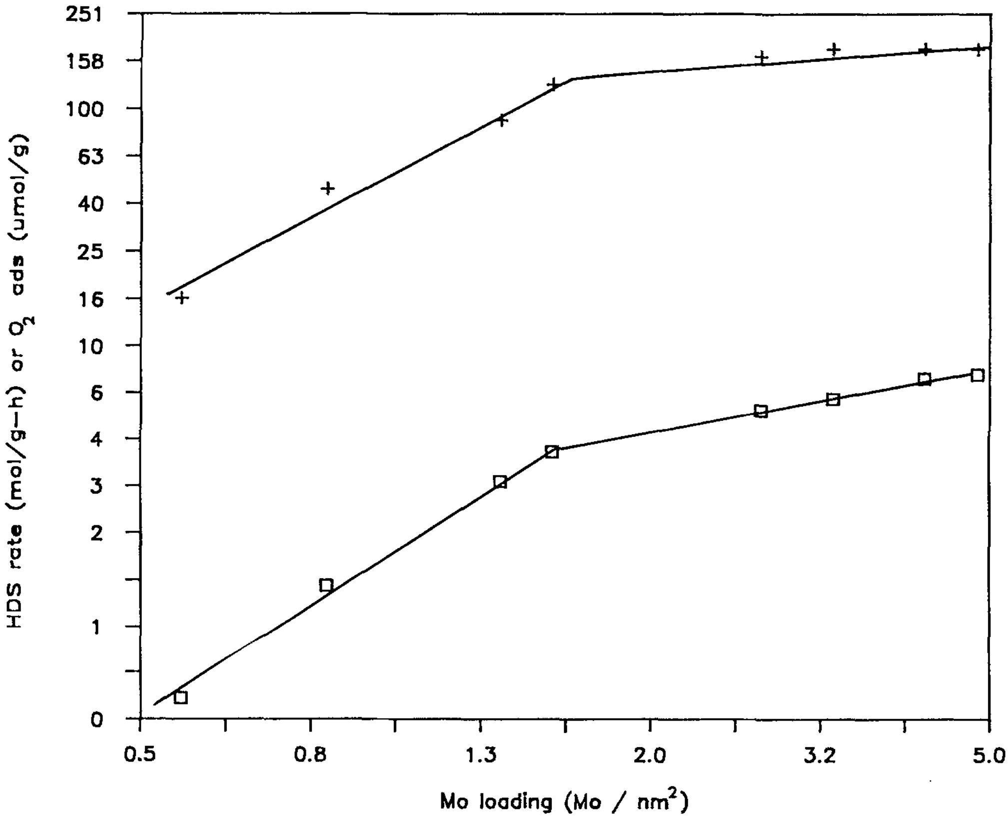

Fig. 3. Thiophene HDS activity, □, and oxygen chemisorption capacity, +, for a series of Mo/Al_2O_3 catalysts; ref. [13].

not "see" the same quantity of surface as small molecules. Where rate is controlled by molecular/surface geometry, the initial rate of reaction is controlled by the effective reactant cross-sectional area, a_m:

$$V = k_7 a_m^{-D_R/2}. \tag{7}$$

In this example, a log-log plot of rate of reaction against reactant cross-sectional area would give a straight line of slope $-D_R/2$.

Wilson et al. [20] present data for the hydrogenation of a synthetic crude middle distillate over a commercial $Mo\text{-}Ni/Al_2O_3$ hydrotreating catalyst. The feed and products were accurately characterized in terms of alkylbenzene, benzocycloparaffin and benzodicycloparaffin fractions. The rate of hydrogenation obviously decreased with increased reactant size. When plotted according to eq. (7), the data indicate a reasonable relationship, as shown in fig. 4. The effective cross-sectional areas of fractions were approximated as before [4] using benzene, tetralin, and octanthrene as model reactants. In spite of the approximations in the rate measurements and estimates for a_m, the trend is apparent. In this discussion, the scaling parameter is the size of the reactant molecule. The measured reaction

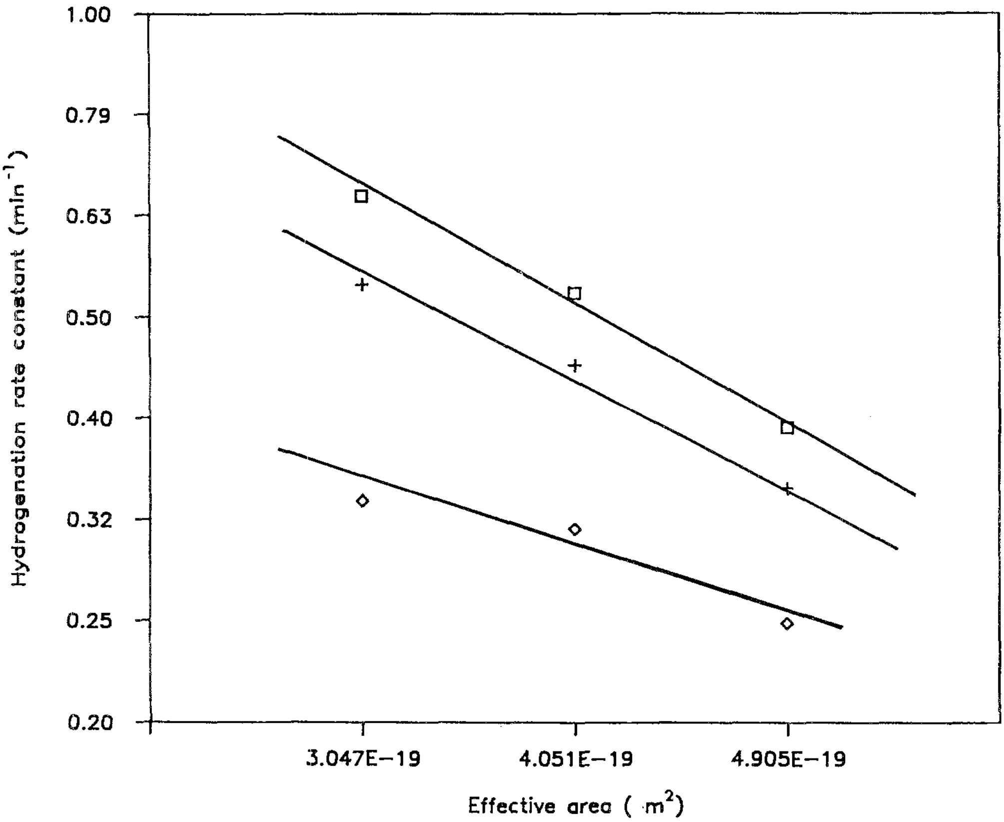

Fig. 4. The rate of hydrogenation as a function of reactant size for hydroprocessing a synthetic crude distillate over Mo-Ni/Al_2O_3; □, 380 °C; +, 360 °C; ◇, 340 °C; ref. [20].

dimension, $D_R = 2$, suggests that the reaction is not structure-sensitive with respect to reactant size. The catalyst, therefore, is equally accessible to all three molecules for hydrogenation. Since the accessible surface area varies with adsorbate size for a porous catalyst, eq. (2), the conclusion is that catalyst reactivity towards hydrogenetion occurs only on the external parts of the catalyst. Similar scaling analyses for other reactions such as hydrodesulphurization, hydrodenitrogenation, hydrodemetallization or asphaltene conversion would provide useful information on the structural sensitivity of these important reactions.

5. Conclusions

The properties of typical hydroprocessing catalysts have been discussed from the standpoint of fractal geometry. The potential of the fractal approach for characterizing catalysts and catalytic reactions has been demonstrated. The principal conclusion is that hydroprocessing catalysts are more accurately quantified by surface fractal dimension, D, rather than by N_2 BET. Equations relating the apparent surface area to particle size and adsorbate cross-sectional area are also appropriate for characterizing hydrotreating catalysts. The concept of a reaction dimension appears to be a promising parameter for characterizing the reactivity of heterogeneous catalytic systems.

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