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Estimation of the Zeolite Content of a Catalyst from Nitrogen Adsorption Isotherms

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The "zeolite area" of a catalyst is defined as the difference between the total area and the matrix area. The total area is the BET area, determined from whatever relative pressures are required to give a linear plot. The matrix area is calculated from the slope of the linear region of the *t* plot, with a small correction to put it on the same basis as the BET area. The zeolite area is approximately proportional to zeolite content and can be used to estimate the zeolite content, on an exchanged-cation-free basis. This technique is more sensitive than X-ray diffraction for measuring zeolite quantity in some cases, probably because loss of some short-range order has a greater effect on diffraction line intensity than on zeolite area determination. The second-order rate constant for catalytic cracking of a gas–oil in the MAT test can be expressed as the sum of two terms, one proportional to the matrix area, the other proportional to zeolite area. Zeolite is 15 times as active as amorphous catalyst on an area basis, but 30–150 times as active on a weight basis.

INTRODUCTION

Zeolites used as components of modern cracking catalysts are highly crystalline materials having microporosity as part of the crystalline structure. X-ray diffraction (XRD) techniques can identify these zeolites and provide an estimate of the quantity present. Sums of specific peak heights in XRD spectra run under standard instrument conditions can in principle be converted to percentage zeolite by comparison with the values for pure zeolite; however, there are various complicating factors.

The nitrogen adsorption isotherm for a pure zeolite is quite characteristic and distinguishable from the isotherms for amorphous materials. We have found in the past that a zeolite can be thermally treated in such a way as to decrease XRD intensity with much less effect on the nitrogen adsorption (expressed as BET surface area, for example). It therefore appears reasonable to use the nitrogen adsorption isotherm of a zeolitic catalyst to estimate the quantity of zeolite in that catalyst, if means can be found to separate the adsorption by the zeolite from that by the matrix.

Zeolite pores are micropores, with openings generally below 10–12 Å. They are essentially filled at $P/P_0 = 0.05$ on the nitrogen adsorption isotherm, at liquid nitrogen temperature. Most other catalyst pore systems are in the mesopore range, with pore radii at least 15–20 Å. For these materials, there will generally be a linear region, extending to the origin, in a *t* plot of the adsorption data, from the slope of which a surface area can be derived. There is generally good agreement between this surface area and the BET area calculated from the same adsorption data.

The *t* plot is a transformation of the

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adsorption isotherm in which relative pressure is replaced by t, the statistical thickness of the adsorbed layer on a nonporous material at the corresponding relative pressure. It was first proposed by Lippens and de Boer for determining various characteristics of pore systems, such as pore shapes (*1*)–(*3*). A concise review of the theory and development of the common t curve may be found in reference (*4*).

Sing (*5*) has suggested that the extrapolation of a linear t plot to $t = 0$ can yield the volume in micropores. Mieville (*6*) has demonstrated that micropore volumes of synthetic mesopore–micropore mixtures, determined in this way, are consistent with values calculated from the blend composition. A different approach has been taken in the present work, in that the measure of zeolite content, designated "Zeolite Area" is defined as the difference between the total (BET) area and the area determined from the slope of the t plot, adjusted to a common basis. The two approaches are essentially equivalent.

METHODS

Nitrogen adsorptions were measured using the same type of volumetric BET apparatus used in previous work from this laboratory (*7*). Catalysts were degassed overnight at about 350°C with a diffusion pump. For each point, P and P_0 were separately measured, and a minimum of 15 min was allowed for equilibrium. All adsorption data were corrected to a dry basis using loss on ignition at 1000°C.

Values of relative pressure (P/P_0) were converted to t values using the equation from de Boer *et al.* (*3*). This was derived by fitting the master isotherm of t vs P/P_0 to the Harkins and Jura adsorption equation (*8*):

$$t(\text{Å}) = \left(\frac{13.99}{\log\,(P_0/P) + 0.034}\right)^{\frac{1}{2}} \qquad (1)$$

This gives good results up to $t = 6$ Å, the upper limit of the linear region for most catalysts.

Y-zeolite obtained in 1963 from Linde Division of Union Carbide Corp., and designated SK-30 was exchanged 10 times at 82°C with ammonium nitrate solution, washed, and dried at 110°C. It contained 1.6% sodium. The dried material was used for the adsorption isotherm without further treatment, except for the degassing at 350°C.

The X-ray diffraction (XRD) measurements of relative zeolite content were made with filtered Cu$K\alpha$ radiation, using a Norelco diffractometer, by summing the six line intensities (in arbitrary units) at 15.6, 20.3, 23.3, 27.0, 31.4, and 34.1°. These represent reflections from the 331, 440 533, 642, 555, and 664 planes, respectively.

The Micro-Activity Test (MAT) for cracking activity has been described by Henderson and Ciapetta (*9*). The runs are made with 5.00 g of tabletted catalyst, feeding a specified gas–oil at 900°F, 2.2 WHSV, for 4.64 min. Conversion is defined as 100 − (percentage boiling over 204°C [400°F]).

Catalysts tested by the MAT test were samples removed from commercial cracking units. All had been manufactured by Davison Chemical Corp., and all contain type-Y zeolite. Five were identified as CBZ-1 (rare-earth-exchanged zeolite), eleven as XZ-25 (decationized zeolite), two as mixtures of these, plus seven miscellaneous types. The samples chosen for this study did not contain appreciable quantities of Ni or V contaminants.

RESULTS

Adsorption

Figure 1 shows portions of the adsorption isotherm for the fresh and the steamed amorphous silica–alumina, having BET areas of 451 and 207 m²/g, respectively. Also shown is the isotherm for the decationized Y-zeolite. Clearly, little adsorption occurs beyond $P/P_0 = 0.05$.

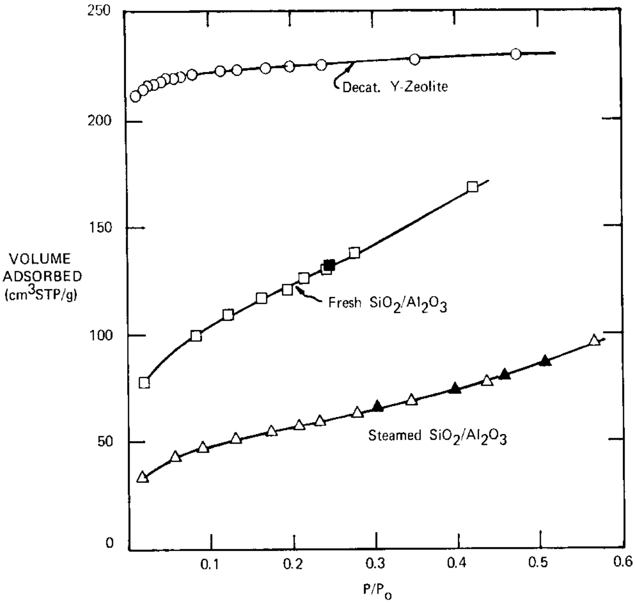

FIG. 1. N_2 adsorption isotherms at −195°C. Desorption points are shaded.

These data were converted to the *t* plots shown in Fig. 2. Since the quantity adsorbed can be converted from cubic centimeters (STP) of gas to milliliters of liquid, the slope will have the dimension of area. The surface areas derived from these plots

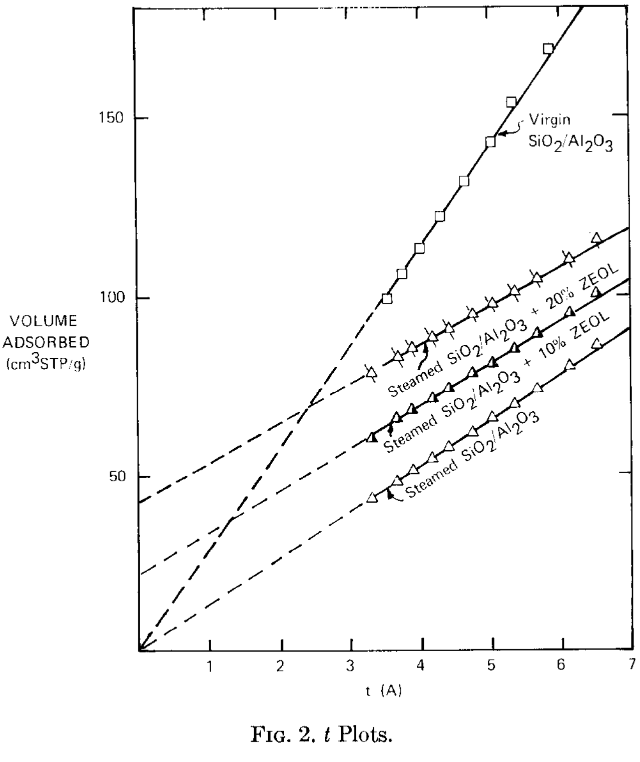

FIG. 2. *t* Plots.

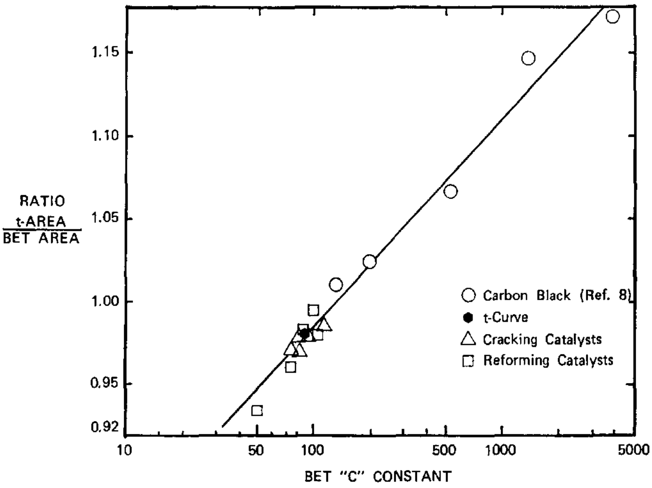

FIG. 3. *t* Area versus BET area.

(slope × 15.47) (*2*, *4*) were 438 and 202 m^2/g, respectively. No clearly linear *t* plot could be derived from the zeolite isotherm.

Also shown in Fig. 2 are the *t* plots for blends of 10 and 20% zeolite in the steamed silica-alumina. These were derived from isotherms calculated from those for the two components. Surface areas calculated from the slopes of these plots were 407 and 369 m^2/g. However, they extrapolate not to the origin, but to positive intercepts which may be taken as micropore volumes, after conversion of units.

In the absence of zeolite, that is to say when *t* plots can be extrapolated to the origin, there is fairly good agreement between *t* area and BET area. The agreement between *t* area and BET area depends somewhat on the nature of the adsorbing surface. For present purposes, the latter can be

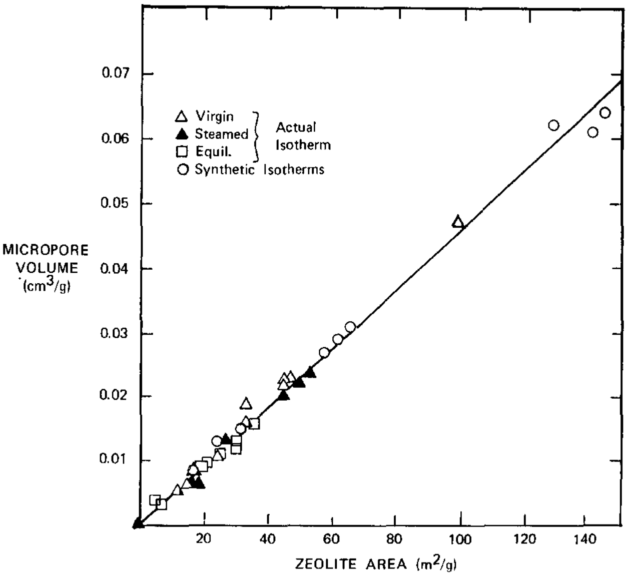

FIG. 4. Zeolite area versus micropore volume for cracking catalysts.

characterized by the BET *c* constant, which is derived from the same BET plots used to calculate area. The *c* constant is a function of the heat of adsorption in the first layer; a higher value means the attractive forces are higher. Brunauer and co-workers (*10*) published data for carbon blacks showing how the ratio of *t* area to BET area varied with *c*. These are plotted in Fig. 3. Included in this plot are data for cracking and alumina catalysts, and one point for the *t* curve calculated from Eq. (1). All of these data can be represented by the single line shown.

For the oxide-type catalysts with which we are most concerned, the *c* values range between about 50 and 110. An average value is 83, for which the ratio *t* area/BET area is 0.975. Therefore, the *t* areas can be corrected to the same basis as the BET areas by dividing by 0.975.

Corrected *t* area and BET areas generally agree within 2 m²/g. The *t* area corrected in this way will be referred to as "matrix area."

When zeolite is present, the linear portion of the BET plot extends to lower relative pressures than in the absence of zeolite. Above about 10% zeolite, the linear region does not extend beyond about $P/P_0 = 0.1$; the intercept is so low that the line approximately extrapolates to the origin.

The "zeolite area" (A_z) is a quantity defined as

$$A_z = A_t - A_m, \tag{2}$$

where A_t = BET area, A_m = matrix area = adjusted *t* area.

This quantity is proportional to the micropore volume determined by extrapolation of the *t* plot to $t = 0$, as in the work of Mieville (*5*). Figure 4 shows this relationship for a variety of catalysts. Included in the figure are data derived from adsorption isotherms on actual catalysts, as well as from isotherms calculated from those for the amorphous catalysts and the zeolite, as in Fig. 2. The plot of Fig. 4 is useful in verifying calculations; a wide deviation from the line indicates an error has been made. The slope of this plot is equivalent to an "average pore radius" of 9.2 Å. The only significance of this value is that it is reasonably close to known dimensions of Y-zeolite pores.

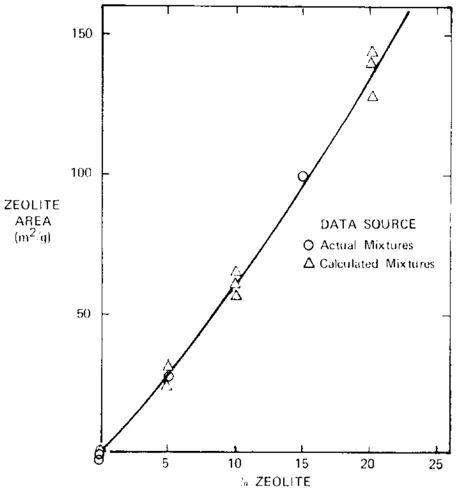

Fig. 5. Zeolite area versus percentage of zeolite.

Zeolite area data can be converted to percentage zeolite, as shown in Fig. 5. Here the weight basis is the ignited weight (at 1000°C) of the matrix and of the decationized Y-zeolite. The relationship holds for actual mixtures of the two components (zeolite and amorphous catalyst), as well as for adsorption isotherms obtained by calculation.

The relationship between XRD line intensities and zeolite area is illustrated in Fig. 6. The line is drawn between the origin and the point for 100% decationized Y-zeolite, for which the sum of XRD line intensities was 83. The points for the four virgin catalysts prepared to contain a known quantity of zeolite fit close to the calculated line. Many of the points for virgin and deactivated catalysts also fit close to the line. However, most fall to the right of the line, with no deviations to the left. Thus, the zeolite-area method detects micropore structure which can be ascribed

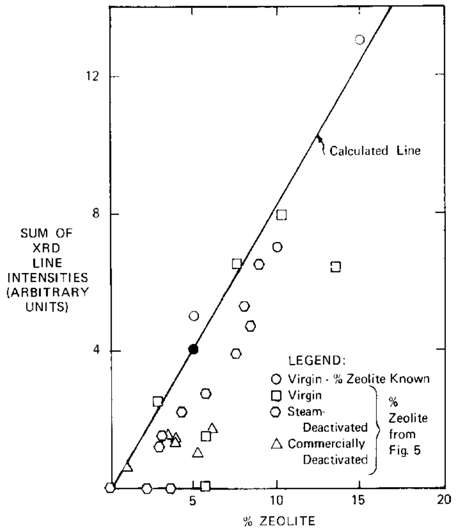

FIG. 6. Cracking catalysts.

to zeolite in zeolitic cracking catalysts, where XRD does not detect zeolite. Presumably, a loss of some short-range order can result in loss of XRD intensity while retaining the micropore structure detected by zeolite area.

Cracking Activity

The MAT values were analyzed in terms of second-order kinetics for gas–oil cracking:

$$\frac{X}{100 - X} = \frac{kc}{\mathrm{SV}}, \tag{3}$$

where X = percentage conversion, k = reaction rate constant, SV = space velocity, and c = initial gas–oil concentration.

It has long been recognized that the rate constant for catalytic cracking over an amorphous catalyst is proportional to the surface area of that catalyst. If the effects of matrix area and zeolite area are additive, Eq. (3) can be converted to:

$$\frac{X}{100 - X} = K_1A_\mathrm{Z} + K_2A_\mathrm{M}, \tag{4}$$

where K_1 and K_2 are proportionality constants.

Using published data from Davison (*9*) plus other MAT data (*11*) for amorphous (non-zeolitic) catalysts, the quantity $X/(100 - X)$ is found to be proportional to surface area, with a proportionality constant of 0.00938; therefore, $K_2 = 0.00938$.

For the zeolitic catalysts described in the Methods section, the quantity $X/(100 - X)$ was corrected by the contribution by the matrix area, then plotted against zeolite area in Fig. 7. There is some scatter of the data, but there is clearly a relationship. The slope of the best line drawn to the origin is 0.142, which therefore equals K_1.

The standard error in prediction of MAT values from the matrix area, zeolite area, and Eq. (4), by comparison with the observed values, is 1.9. Although this value is greater than the estimated standard error of the MAT test itself of 0.9, it is believed that the relationships given in Eq. (4) are essentially correct. One explanation for the greater scatter involves the assumption that K_1 is the same for all catalysts. Since some contain rare earth, while others are decationized, this assumption is probably only an approximation.

The ratio $K_1/K_2 = 15$, which is to say that the zeolite is 15 times as active as the matrix on an area basis. Depending upon the matrix area, the ratio of activities is therefore between about 30 and 150. A ratio of this magnitude is consistent with

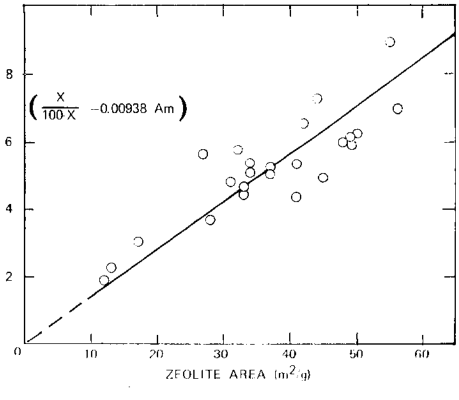

FIG. 7. Effect of zeolite area on MAT test.

what is generally known about the cracking activity of rare-earth or decationized zeolite, relative to amorphous silica–alumina, although there is wide variation among literature data. For example, Nace (*12*) finds an X-type zeolite to be 11 times as active as an amorphous silica–alumina for the cracking of hexadecane. Miale *et al.* (*13*), on the other hand, find ratios as high as 10,000.

These catalytic results are cited in order to demonstrate that the "zeolite area" is indeed a measure of the zeolite content of a catalyst. It is not necessary that this quantity be considered an actual representation of the surface area within the zeolite of a given catalyst. Rather, one should consider this to be an operationally defined quantity, representing the amount of zeolite present, on a cation-free basis.

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