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The Site Densities of Solid Catalysts

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The number of catalytically-active sites per unit area, the site density, is often several orders of magnitude less than usually supposed. From the results obtained for representative systems, it is estimated that in 20–40% of modern catalytic systems the site densities are 10^{11} cm^{-2} (i.e., 0.01% coverage) or less, with many site densities 10^{9} cm^{-2} or less. Several unrelated methods of obtaining site densities lead to the same general conclusion. The catalysts of the representative systems are amorphous and crystalline acidic oxides, transition metal and rare earth oxides, transition metals, and salts. The reactions discussed are hydrocarbon isomerization, cracking, and polymerization; decomposition of NH_3, HCOOH, and alcohols; oxidation, hydrogenation, and dehydrogenation; O transfer, *p–o* H_2 conversion, and H_2–D_2 equilibration. It is shown that in spite of the frequency of occurrence of low site densities, that high site densities are often uncritically assumed. Therefore, attempts to correlate surface properties with catalytic activity are open to question.

I. INTRODUCTION

Often as a solid catalyst is treated or used its activity drops from a high value to zero. For example, the surface may become poisoned. If the entire surface of the untreated catalyst is active, the fraction which is active passes through all values from unity to zero during the treatment. There is usually some uncertainty concerning which method of catalyst preparation will produce the best catalyst. Since catalyst preparation and catalyst treatment can be the same operation, it is possible that many potentially active sites will become poisoned (or destroyed in some other way) during catalyst preparation. It has also been suggested that the introduction of the reactant may modify the catalyst, and that such modification might be the cause of a decrease in the fraction of the surface which is active. For a given catalyst it should be assumed, in the absence of reliable information concerning the fraction of the surface which is active, that the active fraction may be *any* value between zero and unity. Chemists do, however, tend to center their attention on the most active catalysts, and therefore the active fraction for most catalysts is expected to be high.

We might expect to find some low site densities (i.e., low active fractions) merely by considering the nature of catalysis by solids. Catalysis involves chemisorption, and the surface is often heterogeneous for chemisorption. The values of whatever surface property is important for catalysis (e.g., the chemisorption energy) are also likely to vary over the surface. The observed rate may depend much more upon sites possessing a certain value of this property than upon sites possessing other values, and consequently it is possible that in some catalytic systems only a small number of sites is responsible for catalytic action.

The existence of the compensation effect might also indicate that the site densities of some catalysts are low. When the rate constant, v, is given by

$$v = A \exp(-E/RT) \qquad (1)$$

compensation in a series of catalysts exists if E, the activation energy, and A increase simultaneously. The catalysts of the series might be identical except, for example, for the temperature of activation. In many reactions the site density is proportional to A; therefore, changing the temperature of activation could alter both the number of sites and the activation energy. If A is proportional to site density in a given reaction, and if a wide range of A-values is found, it is almost certain that the low values of A in the series correspond to low site densities. But compensation can be observed only when a set of related catalysts is available. When a catalyst of interest is not one of a set, its A-value or site density can still be the same as that of *any* catalyst of a compensation series, including one of low A-value or low site density.

In this study we attempted to show (i) that the site densities of modern representative catalysts vary over an extremely wide range, and (ii) that high site densities are, nevertheless, usually assumed. In the present discussion an emphasis has been put on recent data. Catalytic systems have not been excluded because of the results of a site density determination, and therefore a bias for either high or low site densities has been minimized. However, we have excluded for the most part systems involving a catalyst for which irradiation is a necessary part of catalyst preparation and systems in which the rate-determining step is not a surface unimolecular step.

II. DETERMINING SITE DENSITIES

Several methods of determining site densities exist. Some procedures which have often been assumed to provide site densities actually provide only an upper or a lower limit to the possible values of the site density. For example, determining the amount of catalyst poison chemisorbed when catalytic activity just vanishes provides only an upper limit to the site density; some poison chemisorption sites might not be catalytically active sites.

A. Transition State Method

Using transition state theory, Glasstone *et al.* (*1*) show for the reaction

$$\text{reactant} + \text{surface} \rightarrow \text{products},$$

assuming the rate-determining step to be the unimolecular change of absorbed reactant, that

$$v = A \exp(-E/RT) = c_a(kT/h) \exp(\Delta S/R) \exp(-E/RT) \quad (2)$$

where c_a is the concentration of catalytically-active sites, or, when the proper units are used, the site density; k and h are the Boltzmann and Planck constants, respectively, and ΔS is the entropy of activation. [The transmission coefficient is not included because it is usually considered to be the order of unity (*2*). In isolated cases the transmission coefficient has been shown to be very small, as, for example, in the chemisorption of NO by Al_2O_3 (*3*)]. Usually, the partition functions of the adsorbed molecule and the activated complex are assumed to cancel each other, and they are therefore not included in Eq. (2). If ΔS is known, or if it is assumed to be approximately zero because both reactant and activated complex are adsorbed species, then the site density can be determined when experimental values of v and E are known. [An error is introduced when E is determined from an Arrhenius plot, since this method neglects the occurrence of T in the pre-exponential factor (*4*); the error is small, and if taken into account would yield a slightly smaller value for the site density.] For this determination the rates measured must be those obtained when the surface is fully covered; i.e., the rate must be zero order in reactant pressure or concentration. If the observed rate is not zero order, the zero-order rate can often be deduced (*2*).

Various applications of Eq. (2) to the site density question are now discussed. In the first group of examples, the validity of the transition state method is demonstrated by agreement of the site densities obtained using Eq. (2) with those obtained by other, quite reliable means. The second group of examples demonstrates that the method is used with confidence in systems quite different from each other. These two groups of examples are typical of the use of the transition state method in analyses of surface reactions. For a full explanation of the method, and for justification of the simplifying assumptions given above in connection with Eq. (2), the references describing these examples should be consulted. The success of the method with the second group of examples is offered in the present work as additional evidence that the method is reliable.

The third group of examples illustrates that the method can be used for still other systems where the data are available; with these systems the calculation has either not been made or, if it has been made, the results have not been compared with the site densities of other systems. With some of the systems of this group some very low site densities have been found. The fourth group of examples shows that there *may* be low site densities in still other systems.

1. Verification of the transition state method. Phenylpicrylhydrazine adsorbed on TiO_2 (10^{13} molecules cm^{-2}) dehydrates because of the presence of F-center electrons, whose concentration was 10^{11} cm^{-2} in the sample studied; using the observed activation energy, an entropy change of zero, and a site density of 10^{11} cm^{-2}, the calculated and observed rates were shown to agree within a factor of 20 (*5*). The amount of chemisorbed H_2 on a saturated Ni surface, 1.5×10^{15} molecules cm^{-2}, was properly taken to be the site density in H_2 desorption; the calculated (assuming dual adsorption sites) and observed rates agreed within an order of magnitude (*6*). For the dehydration of 2-butanol over hydroxyapatites, discussed in Sect. II-C, the calculated and experimentally-determined rates agreed.

The range of the site densities reported in this work is an additional indication of the validity of the transition state method. Because of the dimensions of even the smallest surface species, a sharp upper limit to an actual site density is $\sim 10^{15}$ cm^{-2}; the range of site densities obtained using this method approaches this upper limit, but never exceeds it.

2. Normal applications of the transition state method to catalysis. The transition state method has often been applied with confidence even though an *a priori* value of the site density was not always available. [In some instances the equation used is a modification of Eq. (2)]. Assuming a site density of $\sim 10^{14}$ cm^{-2} in benzene hydrogenation over supported Pt, Pd, and Ni (estimated using the number of metal atoms covered by a benzene molecule lying flat on the surface), the observed and calculated values of the activation energy agree (*7*). For oxygen transfer from CO_2 to CO over pure and doped TiO_2, Cha and Parravano (*8*) fitted their rate data into the appropriate transition state equation [including Eq. (2)] for each of three possible mechanisms for five catalysts. Estimating site densities of $\sim 10^{14}$ cm^{-2}, they were able to choose the one mechanism for each catalyst for which the calculated and observed rates agreed.

Taking the surface to be virtually saturated with active sites (i.e., $\sim 10^{15}$ cm^{-2}) in the liquid phase isomerization of *n*-hexane over $AlCl_3$ supported on Al_2O_3, Oelderik and Plateeuw (*9*) used the observed rate and were able to calculate the correct value of the activation energy. In a study of NH_3 decomposition over Rh at low pressure and 600°K, the N_2 coverage was calculated, from the rate of N_2 desorption, to be 5×10^{15} atoms cm^{-2} (*10*). (A possible justification for the calculation is the large value of the coverage which was determined; the site density could hardly be a larger number.)

3. Further application of the transition state method. If the previous examples indicate that the transition state method can be applied with confidence, then it seems reasonable to apply the method wherever the needed experimental data are available, even if the results obtained are surprising.

For cumene (isopropylbenzene) cracking over SiO_2–Al_2O_3 (prepared either by a cogelling procedure or by impregnation of SiO_2 gel with $Al(NO_3)_3$), we calculated, using observed rates and activation energies, site densities of 10^7–10^9 cm^{-2} (*2*, *11*). Thus, 10^{-4}–10^{-6}% of the surface is active. Richardson (*12*) suggested that the technique of Prater and Lago (*13*) should be used to check our results. We did show, however, that the later work of Lago was in agreement with ours (*11*). The site densities we reported agreed with those we calculated (*2*) using the data of Pansing and Malloy (*14*). A cracking site may consist of two different, nearby species (*11, 15*). If the surface were sparsely covered with respect to each species, the two species would rarely be near each other, and a low site density would be accounted for.

Richardson calculated (assuming $\Delta S = 0$) site densities of 10^{12}–10^{16} g^{-1}, or $\sim 10^{6}$–10^{10} cm^{-2}, for cumene cracking over faujasites containing various cations (*16*). Turkevich *et al.* (*17*) in a study of other crystalline SiO_2–Al_2O_3 catalysts, partially decationated zeolites, concluded that many sites are involved in a single cracking event (proposing an "ensemble" mechanism), suggesting a large negative value of ΔS. Their mechanism requires the active sites to be Lewis sites, not the less numerous Bronsted sites. But Ward (*18–23*), Hildebrandt and Skala (*24*), and others have shown that the Lewis site hypothesis for zeolites is not sufficient, rendering the ensemble mechanism, which requires many sites, difficult to maintain. Turkevich *et al.* (*17*) assumed that valid site densities of $\sim 10^{20}$ g^{-1} ($\sim 10^{14}$ cm^{-2}) could be obtained using a poisoning technique and assuming the crystalline nature of the catalyst; but the poisoning technique provides only an upper limit and the crystallinity concept is not too useful when the possibility of crystal defects exists. If the kinetic data of Turkevich *et al.* are treated without assuming site densities, and if the usual entropy assumption is made, viz, $\Delta S = 0$, then the site densities of their zeolites are found to be 10^{6}–10^{10} cm^{-2}, similar to the values of site densities calculated by Richardson (*16*).

For cyclohexene dehydrogenation over transition metal oxides, Dixon *et al.* (*25*) deduced that the rate-determining step is the breaking of two C–H bonds in a metal-molecule surface complex. Both reactant and product are adsorbed, and therefore ΔS must be near zero. The site densities calculated for the catalysts in the systems in which the reaction was found to be zero order in cyclohexene, V_2O_3 and MnO, are $\sim 10^{9}$ and $\sim 10^{8}$ cm^{-2}, respectively.

Figueras-Roca *et al.* (*26*) showed that the dehydration of ethanol over SiO_2–Al_2O_3 is zero order with respect to both alcohol and ether production above 50 Torr ethanol pressure. Application of Eq. (2) to their data indicates the site density to be $\sim 10^{11}$ cm^{-2}.

4. Possible applications of the transition state method to the question of site density. Application of the transition state method indicates that a low site density is a possibility in still other systems; the results are less certain with these systems than with those discussed in the previous sections.

By assuming 10^{20} sites g^{-1} ($\sim 10^{14}$ sites cm^{-2}) for the isomerization of 1-butene over Al_2O_3, Brouwer calculated $\Delta S = -40$ eu. Brouwer (*27*) suggested that the true entropy change might be much nearer zero, corresponding to fewer sites. If ΔS were ~ -20 eu, a more likely situation, the site density is found to be $\sim 10^{10}$ cm^{-2}.

In the liquid phase isomerization of *n*-hexane over $AlCl_3$ supported on Al_2O_3 a site density of $\sim 10^{15}$ cm^{-2} was consistent with the observed rate and activation energy (*9*) [see Sect. II-A(2)]. However, for this reaction over $AlCl_3$ supported on SiO_2–Al_2O_3, described in the same work, the calculated value of the apparent activation energy is 18.8 kcal $mole^{-1}$, vs. an observed value of 10.4 kcal $mole^{-1}$. The authors suggested that the calculated and observed values agreed in the one case but not in the other because of a diffusion limitation in the pores of SiO_2–Al_2O_3, a limitation not found with Al_2O_3. However, the pore diameters, 47 and 70 Å for the unimpregnated bases, respectively, do not seem to differ enough to warrant this explanation. The calculated apparent activation energy, determined by using a per-site reaction rate, agrees with the observed apparent activation energy for the silica–alumina case if a site density of 10^{9}–10^{10} cm^{-2} is assumed.

The catalytic decomposition of formic acid (both dehydrogenation and dehydration) has been studied extensively.

Among MgO and Al_2O_3 catalysts, A of Eq. (1) varied from 10^{20} to 10^{28} molecules cm^{-2} sec^{-1}, with compensation (*28*). The reaction is almost zero order; assuming zero order and $\Delta S = 0$, calculation reveals that site densities vary from $\sim 10^7$ to $\sim 10^{15}$ cm^{-2}. Bond mentioned that over metals A varies from 10^{20} to 10^{28} (*29*). In a series of Cu_3Au catalysts differing only in the prior heat treatment, the reaction was zero order and compensation was found (*30*). The authors calculated, using a method other than the transition state method and using the assumptions that the rate-determining step is the migration of defects and that the site density is $\sim 10^{15}$ cm^{-2}, a rate $\sim 10^6$ times greater than the observed rate. It was suggested that the conformation of the decomposing molecule is important, i.e., there is an entropy effect. A recalculation of the data, using Eq. (2), indicates either that $|\Delta S|$ is large, or that the site density varies (at 600°K) from 10^5 to 10^{10} cm^{-2} in the series. Kubokawa and Miyata (*31*) noted for a Ag catalyst that E was temperature-sensitive, a very low site density in one temperature range being postulated. For Ag, Lawson (*32*) suggested a bimolecular reaction between chemisorbed and physically adsorbed molecules. An entropy change of as much as 26 eu was found, assuming that all chemisorption sites, $\sim 10^{13}$ cm^{-2}, are active sites. The evidence for the mechanism is good, but the large entropy change calculated suggests that the actual entropy change may be smaller, corresponding to a low site density.

B. Other Theoretical Methods

Ashmead *et al.* (*33*) calculated the high temperature (588°K) rate of para–ortho hydrogen conversion and H_2–D_2 equilibration over Nd_2O_3, assuming dissociative adsorption to be the rate-determining step. In their calculation they used the collision number, the sticking coefficient, the fraction of the surface which is active, and the observed activation energy. Calculated and observed rates agreed if the active fraction was taken to be $\sim 10^{-3}$, corresponding to a site density of $\sim 10^{12}$ cm^{-2}, and the authors therefore accepted the mechanism. Similarly, Jones and Loebl (*34*) deduced for the reaction over sodium–tungsten bronze catalysts (between 273 and 473°K) that the fractional coverage must have been $\sim 3 \times 10^{-3}$, corresponding to a site density of at least 10^{12} cm^{-2}, even though the amount of hydrogen chemisorption thus called for was less than they could detect. With a similar calculation Harris and Rossington (*35*) showed that the observed and calculated rates for TiO_2 catalyst above 473°K agreed only if the active fraction was $\sim 10^{-8}$, corresponding to a site density of $\sim 10^7$ cm^{-2}. Adsorption was rejected as the rate-determining step because values of the active fraction lower than 10^{-3} are, they said, "not very probable." They suggested that isolated double sites are the active sites; a double-site density of $\sim 10^7$ cm^{-2} (not counting single, and therefore inactive, sites) is possible if low site densities are not ruled out *a priori*.

At low temperatures, different mechanisms have been postulated for these two reactions. For a TiO_2 catalyst at 93°K, the calculated and observed conversion rates agreed, assuming that the rate-determining step involved the vibration of H_2 on a paramagnetic site and that the H_2 coverage was 10^{12} molecules cm^{-2}, corresponding to a site density of at least 10^{12} cm^{-2} (*35*). For Al_2O_3 containing paramagnetic sites, assuming a vibration mechanism and the number of paramagnetic sites, 3.3×10^{12} cm^{-2}, to be the site density, at 77°K the calculated conversion rate was much smaller than the observed rate (*36*); thus there was no evidence for a low site density. However, for the equilibration reaction above 170°K over Cu, the Arrhenius plot exhibited a break around 293°K. There was a lower activation energy and, by a factor of 10^6, a lower pre-exponential factor in the low temperature range (*37*). It was suggested that the low temperature sites are defects. with a site density of 10^8–10^{10} cm^{-2}, and that the high temperature sites are lattice points, with a site density of $\sim 10^{15}$ cm^{-2}. Such a simultaneous change in the pre-exponential factor and the activation energy, i.e., compensation, has been observed for many reactions and many ways of altering the catalyst.

In some studies the idea of a high site density has been consistent with certain theoretical considerations. For the kinetics of isopropyl alcohol dehydrogenation over ZnO, Kolboe (*38*) showed, by comparing calculated and observed rates, that a site density of $\sim 10^{14}$ cm^{-2} is consistent with the known vibrational frequency of the hydrogen atom in molecules and the concept that there are five sets of sites. Schlosser and Herzog (*39*) showed for CO and H_2 oxidation over NiO catalysts that the observed pre-exponential factors are consistent with their kinetic scheme and a site density of 10^{15} cm^{-2}, determined by the amount of surface nickel ion. Boudart *et al.* (*40*) described *facile* reactions, reactions which are insensitive to the mode of catalyst preparation, to catalyst reaction with the support, and to the size of the catalyst crystallites. Such reactions depend only upon the nature of the individual atoms of the catalyst, and a site density of $\sim 10^{15}$ cm^{-2} is expected. Some facile reactions over Pt are cyclohexane dehydrogenation, H_2 oxidation, and H_2–D_2 exchange. Rye and Hansen (*41*) in a theoretical analysis of the bimolecular reaction between adsorbed hydrogen and adsorbed ethylene on clean W, assumed a site density of 10^{15} cm^{-2}. A high site density is reasonable, since in a bimolecular reaction active sites must have active neighbors. In examples of this type, the rate is proportional to the square of the site density.

C. Experimental Methods

Sometimes it is possible to make an estimate of the site density with only a minimum use of theory.

Isobutane reactions over SiO_2–Al_2O_3 must involve isobutane chemisorption. Yet MacIver *et al.* (*42*) found the site density for chemisorption to be only 3×10^{10} cm^{-2} at 25 and 150°C, providing a rather low upper limit to the site density for catalyzed isobutane reactions. At 200°C, the infrared spectrum of Al_2O_3 previously saturated with C_2H_4 did not change as H_2 was added to the system, and the spectrum remained the same during the 48-hr period in which observations were made (*43*). On the other hand, the catalyzed H_2–C_2H_4 reaction, leading to C_2H_4 removal, proceeded rapidly when C_2H_4 was continuously available. The most likely explanation of the anomaly is a site density several orders of magnitude less than the $\sim 10^{14}$ C_2H_4 molecules adsorbed per square centimeter.

The polymerization of C_2H_4 over supported chromium oxide proceeds by the insertion of C_2H_4 monomer between the propagating molecule and the active site (*44*). $^{14}CH_3O$ was incorporated into the chain as the reaction was quenched with $^{14}CH_3OH$, and the catalyst–polymer-^{14}C content was determined. In this way site densities of 10^{10}–10^{11} cm^{-2} were obtained for three oxide supports, and $\sim 10^{12}$ cm^{-2} for a fourth. For ethylene oxide polymerization over metal oxides, hydroxides, and carbonates, Krylov *et al.* (*45*) found essentially no chain termination, enabling them to determine site densities of 10^{13}–10^{14} cm^{-2} by obtaining the weight and average molecular weight of the adsorbed polymer.

Bett and Hall (*46*) determined site densities of 10^{13}–10^{14} cm^{-2}, in agreement with the values calculated using the transition state method, for 2-butanol dehydration over a series of hydroxyapatite catalysts. In their method they determined the amount of product desorbed in a microcatalytic reactor at infinite flow rate, under conditions such that the reactant occupied, and then desorbed as product from, all the active sites.

III. UNCRITICAL ASSUMPTIONS CONCERNING SITE DENSITIES

Probably a low site density cannot be said to be a certainty in any one catalytic system described in Sect. II. But all the examples taken together, representing a wide variety of catalysts which were not selected according to the site density obtained, suggest that there are low site densities in 20–40% of the modern catalytic systems in which there is only a single surface reactant. "Low site densities" are those of the order of 10^{11} cm^{-2} or less, corresponding to a coverage of ~0.01% or less. The site densities of many of the catalytic systems in this low range are apparently orders of magnitude less than 10^{11} cm^{-2}.

We now show that site densities of at least 10^{12} cm^{-2}, and more likely 10^{13}–10^{15} cm^{-2}, are almost always uncritically assumed. We cite recent literature almost exclusively; and because very many examples are available, only representative ones are given.

A. Catalyst Poisons

The assumption that a site density is high is usually equivalent to the assumption that the bulk, or collective, properties of the catalyst are related to its catalytic properties. [It has only rarely been acknowledged that surface heterogeneity introduces complexities in correlating collective and catalytic properties (*47*, *48*)]. Thus, the amount of poison just needed to reduce the catalyst activity to zero has often been taken to be just the amount needed to block all the active sites. Zeolite site densities of 10^{12}–10^{14} cm^{-2} in acid-catalyzed reactions have been reported using quinoline as poison (*17*, *49*). Attempts to bypass the heterogeneity problem with non-equilibrium adsorption of poison (*17*, *50*) do not seem to meet the objection that any poison method merely establishes an upper limit to a site density. The distribution of NH_3 adsorption sites has been determined for several oxides (e.g., SiO_2–Al_2O_3, Al_2O_3, and zeolites) and it has been assumed that a *macroscopic* fraction of each distribution constitutes the set of active sites in acid-catalyzed reactions (*24*, *51*, *52*). (The entire group of active sites has often been identified with a macroscopic fraction of the distribution of surface acidity, or with all of a certain kind of acidity, such as Bronsted acidity. Acidity distributions have sometimes been determined by titration, using a series of indicators.)

Aqueous metal ions have been assumed to poison SiO_2–Al_2O_3 by removal of active protons, and the amount of such removal has been taken to indicate a high site density (*53*, *54*). Actually, the metal ion removes Al (*2*, *55*), but site densities determined by the amount of Al removed [3.7×10^{13} cm^{-2} in Ref. (*55*)] are much larger than those given in Sect. II.

B. Reactant or Product Chemisorption

Although Taylor *et al.* (*56*) and others have warned that the possibility of surface heterogeneity renders questionable an identification of the entire amount of either reactant or product chemisorption with active sites, such an identification has frequently been made. Thus, a site density of ~10^{12} cm^{-2} was claimed when the number of active sites in ethane dehydrogenation over potassium-promoted chromia–alumina was taken to be the same as the number of chemisorbed ethane molecules (*57*). The amount of aromatic hydrocarbon adsorbed on Co and Rh supported on MgO was equated to the amount of precursor or active site complex in hydrogenation (*58*). Gas chromatographic flash desorption peaks of the products of C_2H_4 polymerization over Al_2O_3 were assumed to represent molecules which left catalytically-active sites, and a site density of ~10^{12} cm^{-2} was claimed (*59*).

C. Infrared Spectra of Surface Species

Attempts to correlate the infrared spectra of surface species with catalyst activity can lead to error, since the concentration of the active-site species might be too small to produce a measurable spectrum, and the spectrum actually observed would then not be of interest. However, Ward has measured the infrared spectra of the zeolite surface and of the surface as modified by chemisorbed poison in catalytic studies (*18*, *20–23*, *60*). In one instance the change in the surface spectrum was followed as the catalytic reaction proceeded (*60*). Infrared spectra have been used in attempts to characterize the catalytic acid sites of SiO_2–Al_2O_3 and other catalysts (*61*, *62*). It has been assumed that infrared spectra could be used to determine the nature of both reactant and product adsorbed on chromia–silica active sites in the oxidation of Co (*63*), and the nature of the molybdate active sites in oxidation reactions (*64*). Spectra of adsorbed species have been used to aid in the formulation of reaction mechanisms. Ethanol (*65*) and formic acid (*66*) decomposition over Al_2O_3 are examples. Infrared studies have played an important part in Gardner's comprehensive intermedion theory of catalysis (*67*).

D. Other Surface Properties

Other surface properties, which by their very nature would not be observable if they were associated only with the active sites of catalysts of low site density, have been correlated with catalytic activity. It was suggested that comparing the esr spectrum of a $ZnO–Cr_2O_3$ catalyst before use with that obtained after use can aid in indicating what occurred at the active sites (*68*). For the conjugated polymers active in N_2O decomposition, it was assumed that the surface free spins determined by esr are active sites, although exceptions were allowed for (*69*). A similar correlation for chromia–alumina in dehydrogenation activity was attempted (*70*).

Other correlations have been attempted. These include the work function of nickel supported on Cr_2O_3 with its effectiveness in catalyzing isotope exchange between H_2 and H_2O (*71*), the distribution of oxidation power over the surface of a series of NiO catalysts with the distribution of catalytic sites in H_2O_2 decomposition (*72*), the thermodynamic properties of a surface with its catalytic properties (*73*), and magnetic susceptibility with catalytic properties (*74*). Also, it was assumed, since O_2 changes observable properties of chromia supported on $SiO_2–Al_2O_3$, that the surface Cr(IV) is the active site in C_2H_4 polymerization (*75*).

A relationship between crystallinity and catalysis has often been postulated. It was assumed that the catalytically-active site in $Ni–MgO–Fe_2O_3$ could be observed in a crystallographic study (*76*), that a relationship exists between the degree of crystallinity of $MoO_3–Bi_2O_3$ catalysts and their effectiveness in butene dehydrogenation (*77*), and that the regularity of the zeolite crystal permits a calculation of the site density, with a definite number of sites per unit cell (*78*). An argument which was presented in favor of the dynamic field theory of zeolite activity was the correlation of catalytic activity with a gross change in the crystal—i.e., either replacing Ca^{2+} with Na^+ or decationization (*79*).

IV. CONCLUSIONS

The assumption of a high site density (unless the assumption is proven) can be responsible for questionable conclusions concerning mechanisms. In several studies cited in Sect. III the conclusions which were made concerning site density (using the methods of poisoning, infrared, etc.) were made in order that a mechanism could be worked out. Similarly, Rabo *et al.* (*80*) implied that the site density is high in acid-catalyzed reactions over rare earth Y zeolites when they concluded that either O-deficient and –OH sites possess equal activity, or neither kind of site is active and the source of activity is unknown. If the site densities of these zeolites had been assumed to be low, such a conclusion could not have been made.

Since reliable methods of determining site densities are available, and since there is a reasonable probability that a site density cannot be safely estimated, it appears that a site density should be determined before its value is assumed. Finally, it should be evident that a low site density may indicate that the nature of the site is different from that supposed when a high site density is assumed. If site densities are routinely determined, we might conclude for certain systems that catalytic activity is caused by factors not heretofore known.

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