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## The Reaction Dimension in Catalysis on Dispersed Metals

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**Abstract:** We report that the relation between catalytic activity,  $a$  (mol·time<sup>-1</sup>·particle<sup>-1</sup>), and particle size,  $2R$ , of dispersed catalysts obeys in very many cases the following scaling law:  $a \propto R^{D_R}$ , where  $D_R$ , the reaction dimension, is a characteristic parameter of the catalytic reaction which provides quantitative means of comparative evaluation of the degree of structure sensitivity. The observation crosses all catalysis. Examples include hydrogenations, hydrogenolyses, oxidations, isomerizations, and photochemical and electrochemical reactions. Catalysts include Pt, Pd, Ir, Ag, Rh, Fe, Ni, and bimetallic catalysts dispersed on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, and charcoals. A wide range of  $D_R$  values was found: from  $D_R = 0.2$  for ethylene oxidation on Ag/SiO<sub>2</sub>, indicating weak dependence of the activity on particle size and a very low proportion of reactive surface sites, through  $D_R \sim 2$  cases indicating structure insensitivity, and up to  $D_R = 5.8$  for ammonia synthesis on Fe/MgO, indicating extreme structure sensitivity. It is suggested that the activity power law reflects a parallel scaling relation in the population of reaction-specific active sites, i.e., that particle size change by a factor of  $N$  changes the number of sites by a factor of  $N^{D_R}$ . For  $D_R < 2$  cases it is furthermore suggested that the pattern of distribution of active sites is invariant to the scale changes, i.e., that  $D_R$  is the fractal dimension of the reactive subset of surface atoms. Of the many cases presented, two are discussed in some detail, showing the following agreement between experimental  $D_R$  values and model-calculated  $D_R$  values (reaction: experimental  $D_R$ , model  $D_R$ )—ethylene oxidation on Ag/SiO<sub>2</sub> to CO<sub>2</sub>:  $0.71 \pm 0.16$ ,  $0.70 \pm 0.04$ ; and to ethylene oxide:  $1.16 \pm 0.11$ ,  $1.18 \pm 0.03$ ; methanation on Pd/SiO<sub>2</sub>,  $2.90 \pm 0.15$ ,  $2.77 \pm 0.09$ .

## I. Introduction

It is well established today that the performance of heterogeneous catalysts is dictated inseparably by both the geometrical details and the chemical nature of the reacting system.<sup>1,2</sup> The phenomenon is generally termed "structure sensitivity", in which the broad term "structure" refers to crystal planes,<sup>3</sup> porosity,<sup>4</sup> but mainly to particle size.<sup>5</sup> Much progress has been achieved in the understanding of the interplay between geometry and chemistry in the case of the reactivity of the well-defined surfaces of single metal crystals.<sup>3</sup> Less understood are the commonly encountered structure sensitivity relations observed in the case of dispersed metal catalysts on high surface area supports, for which, in many cases, a dependency is found between activity and particle size.<sup>1,2,5</sup> The origin of this effect has been the issue of continuous debate,<sup>2</sup> in which a leading idea has been the notion that the relative distribution of the active sites and nonactive sites changes with particle size. Yet the picture is so complex that the phenomenon, perhaps typical of the state of its understanding, is often reported "only" in the form of a figure or a table depicting the actual observed relation. The lack of a general characteristic parameter that can be used as a quantitative measure, capable of answering questions such as "by how much is a given catalytic reaction more structure sensitive than another one?" renders a situation in which comparative analyses of the voluminous literature in this field becomes very cumbersome.

Here we wish to report our finding of such a general parameter which seems to provide a solution to this need and which is capable of quantifying structure sensitivity in dispersed catalysts.

The law we found is phenomenological. Such laws serve routinely in science, especially at the early stages of attempts to decipher complex phenomena; their use is justified if they fulfil four criteria: (1) that they are sufficiently general; (2) that they help in condensing experimental observations into few (one, in

our case) parameters; (3) that they allow comparative analyses; and (4) that they provide additional insight of the studied phenomenon, for instance by providing a preliminary rationale for the very existence of the phenomenological law. Below we try to show that the parameter we suggest, the reaction dimension,  $D_R$ , fulfils, at least partially, all four criteria.

## II. The Scaling Law

We found that in very many cases the relation between catalytic activity,  $a$  (mol·time<sup>-1</sup>·particle<sup>-1</sup>) and the particle size,  $2R$ , of the metal catalyst obeys the simple scaling law

$$a \propto R^{D_R} \quad (1)$$

in which  $D_R$  is defined (for reasons described below) as the reaction dimension.  $D_R$  is a measure for the sensitivity of the catalytic performance to changes in catalyst size (the scale). It reflects (Section IV) the relative distribution of the active and nonactive sites on the surface of the metal crystallite. Equation 1 is obeyed virtually across the whole field of catalysis (Section III), including reductions, oxidations, isomerizations, and photo- and electrocatalytic reactions. Typical values of  $D_R$  are from close to 0 up to 6.

We were led to the hypothesis of eq 1 by our general observation,<sup>6,7</sup> verified also in other laboratories,<sup>8</sup> that molecule/surface

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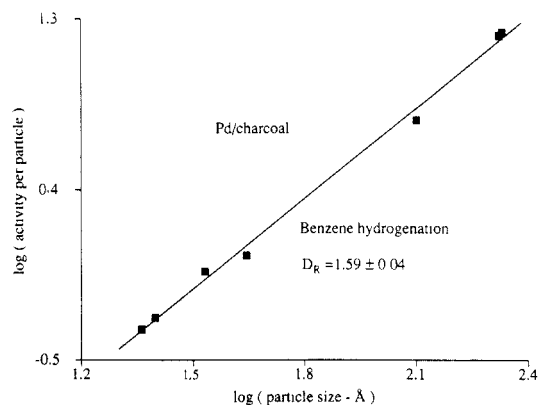
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**Figure 1.** Catalytic activity ( $\text{mol} \times 10^3 \cdot \text{s}^{-1} \cdot \text{surface atom}^{-1} \cdot R^2$ , related to  $\text{mol} \cdot \text{h}^{-1} \cdot \text{particle}^{-1}$  through a constant) as a function of Pd particle size for benzene hydrogenation.

interactions are describable in terms of power laws of similar nature. Of these power laws, the two that led directly to eq 1 are

$$n_m \propto R^{D-3} \quad (2)^{9,10}$$

$$v \propto R^{D_R-3} \quad (3)^{6a,11}$$

in which  $n_m$  is the monolayer value of physisorbed molecules ( $\text{mol/g}$ ),  $v$  is the initial reaction rate ( $\text{mol} \cdot \text{time}^{-1} \cdot \text{g}^{-1}$ ) with a surface (reactive dissolutions, thermal decompositions, etc.), and  $D$ , the fractal dimension of the surface, is a measure for the degree of surface roughness (e.g.,  $D = 2$  is the classical flat two-dimensional surface and higher values indicate an increase in the degree of irregularity).  $D_R$  in eq 3 measures the irregularity of the reactive surface. Since not all surface sites which are available for physisorption participate in a reaction,  $D$  and  $D_R$  need not have the same values.<sup>6a,11</sup> We return to the physical, fractal, and nonfractal interpretation of  $D_R$  in eq 1, in Section IV.

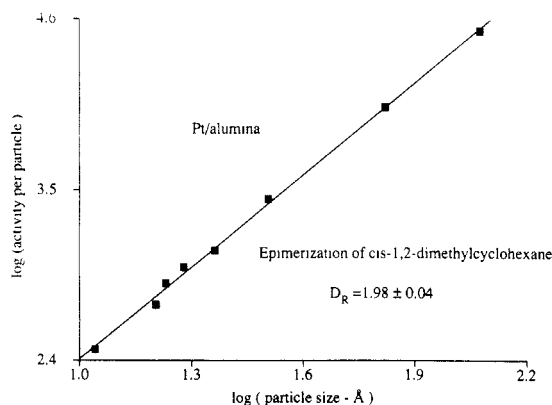
In the data analyses presented in Sections III and IV, we follow a common assumption in catalysis,<sup>2</sup> i.e., that in the metallic nanometer scale crystallites, the number of all surface atoms and the number of all bulk atoms in the particle scale with  $\sim R^2$  and  $\sim R^3$ , respectively. By our terminology, this means that the small crystallites are not fractals. Although this picture is an approximation, for a large volume of catalytic reactions it is not a bad one, as shown by various experimental techniques. For instance, it is quite often found<sup>12</sup> that  $R$  values from microscopy or from adsorption or from X-ray scattering are not very different from each other. This would not have been the case for mass or surface fractals. Recently, Romeu et al.<sup>13</sup> determined the surface fractal dimension of small particles of Au, Pd, and Pt and indeed found  $D \sim 2.1$ . (The case of metallic particles which deviate strongly from  $D = 2$  (surface) and  $D = 3$  (mass) is not treated in this report.)

In turnover units of  $\text{mol} \cdot \text{time}^{-1} \cdot (\text{surface atom})^{-1}$ , eq 1 becomes

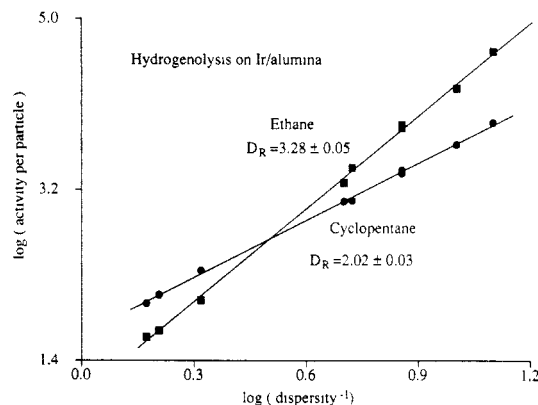
$$a_t \propto R^{D_R-2} \quad (4)$$

It can now be seen that according to the current convention, as proposed by Boudart,<sup>14</sup> structure insensitivity would mean  $D_R = 2$ . In units of activity/g, eq 1 becomes

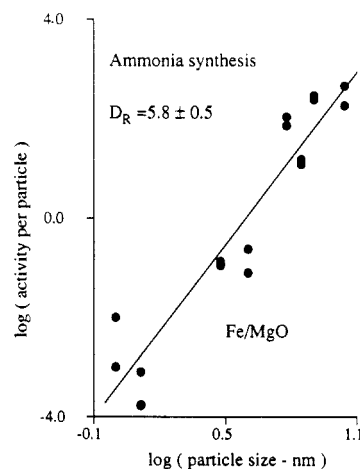
$$a_g \propto R^{D_R-3} \quad (5)$$



**Figure 2.** Catalytic activity ( $\text{mol} \cdot \text{h}^{-1} \cdot \text{surface atom}^{-1} \cdot R^2$ , related to  $\text{mol} \cdot \text{h}^{-1} \cdot \text{particle}^{-1}$  through a constant) as a function of Pt particle size for the epimerization of *cis*-1,2-dimethylcyclohexane.



**Figure 3.** Catalytic activity ( $\text{mol} \times 10^3 \cdot \text{h}^{-1} \cdot \text{dispersity}^{-1}$ , related to  $\text{mol} \cdot \text{h}^{-1} \cdot \text{particle}^{-1}$  through a constant) as a function of Ir particle size (dispersity<sup>-1</sup>) for ethane and cyclopentane hydrogenolyses.



**Figure 4.** Catalytic activity ( $\text{mol} \times 10^3 \cdot \text{s}^{-1} \cdot \text{surface atom}^{-1} \cdot R^2$ , related to  $\text{mol} \cdot \text{s}^{-1} \cdot \text{particle}^{-1}$  through a constant) as a function of Fe particle size for ammonia synthesis.

Under the above mentioned condition, dispersion can be used instead of  $R$ :

$$\text{dispersion} \propto R^{-1} \quad (6)$$

Finally, like all physical power laws, eq 1 is bound by inner and outer cutoffs. In this study, however, we have limited ourselves to cases where either all experimental points obey eq 1 (most cases) or where only one or two of the end points could not be included, as indicated in Table I.

### III. Results: The Generality of the Phenomenon

In Tables I and II we have summarized the results of the re-analysis of various structure-sensitivity studies according to eq 1 and 5, and in Figures 1–4 we show some of the entries in Table

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Table I. Reaction Dimensions of Various Catalytic Processes

No.	reaction	catalyst	reaction dimension $D_R$	particle size (Å) or dispersity range <sup>a</sup> (no. of data points)	data source
1	ethane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.8 ± 0.2	10–118 (8)	Table 1 & Figure 1 in ref 28
2	ethane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.9 ± 0.2	32–147 (5)	Table 2 in ref 28
3	ethane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	3.1 ± 0.3	23–150 (9)	Table 3 in ref 28
4	ethane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	3.1 ± 0.1	0.07–0.81 <sup>b</sup> (12)	Figure 1 in ref 29
5	ethane hydrogenolysis	Ir/Al <sub>2</sub> O <sub>3</sub>	3.28 ± 0.05	0.08–0.67 (9)	Table 1 & Figure 1 in ref 29
6	cyclopropane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.29 ± 0.07	13–175 (7)	Table 1 in ref 30
7	cyclopentane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.2 ± 0.1	0.08–0.42 <sup>b</sup> (5)	Figure 2 in ref 29
8	cyclopentane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.1 ± 0.1	19–175 <sup>b</sup> (6)	Figure 1 in ref 31
9	cyclopentane hydrogenolysis	Pt/Al <sub>2</sub> O <sub>3</sub>	2.02 ± 0.05	66–150 (5)	Table 1 in ref 31
10	cyclopentane hydrogenolysis	Ir/Al <sub>2</sub> O <sub>3</sub>	2.02 ± 0.03	0.08–0.67 (9)	Table 1 & Figure 2 in ref 29
11	cyclopentane hydrogenolysis	Rh/Al <sub>2</sub> O <sub>3</sub>	3.1 ± 0.2	0.21–1.00 (6)	Figure 2 in ref 32
12	propene hydrogenation	Ni/Al <sub>2</sub> O <sub>3</sub>	1.65 ± 0.05	8–224 (4)	Figure 4 in ref 33
13	benzene hydrogenation	Rh/Al <sub>2</sub> O <sub>3</sub>	2.25 ± 0.06	0.20–0.87 <sup>b</sup> (7)	Table 4 in ref 34
14	benzene hydrogenation	Pd/charcoal	1.59 ± 0.04	23–213 (7)	Table 1 & Figure 1 in ref 12
15	benzene hydrogenation	Pt/SiO <sub>2</sub>	1.1 ± 0.1	66–379 (5)	Table 1 & Figure 1 in ref 35
16	ethylene oxidation to ethylene oxide	Ag/Cab-O-Sil	1.2 ± 0.1	61–290 (5)	Table 3 in ref 15
17	ethylene oxidation to ethylene oxide	Ab/Cab-O-Sil	0.7 ± 0.2	200–450 <sup>b</sup> (7)	Tables 1 & 5 in ref 20
18	ethylene oxidation to ethylene oxide	Ag/silica Z	1.6 ± 0.1	66–392 <sup>b</sup> (5)	Table 3 in ref 15
19	ethylene oxidation to CO <sub>2</sub>	Ag/Cab-O-Sil	0.4 ± 0.2	61–290 (5)	Table 3 in ref 15
20	ethylene oxidation to CO <sub>2</sub>	Ag/Cab-O-Sil	0.2 ± 0.2	200–450 <sup>b</sup> (7)	Tables 1 & 5 in ref 20
21	ethylene oxidation to CO <sub>2</sub>	Ag/silica Z	0.7 ± 0.2	66–392 <sup>b</sup> (5)	Table 3 in ref 15
22	electrooxidation of hydrogen	Pt-Pd/C	1.97–2.51 (see Table II)	0.01–0.55 (4–5)	Table 1 in ref 26
23	electroreduction of oxygen	Pt-Pd/C	2.20–2.44 <sup>c</sup>	0.01–0.55 (4–5)	Table 1 in ref 27
24	ammonia synthesis	Fe/MgO	5.8 ± 0.5	10–110 (17)	Figure 5 in ref 24
25	CO methanation	Ni/Al <sub>2</sub> O <sub>3</sub>	2.8 ± 0.2	21–144 (5)	Table 1 & Figure 4 in ref 36
26	epimerization of <i>cis</i> -1,2-dimethylcyclohexane	Pt/Al <sub>2</sub> O <sub>3</sub>	1.98 ± 0.04	11–118 (8)	Table 1 in ref 37
27	photocatalytic decomposition of MeOH	Pt/TiO <sub>2</sub>	1.4 <sup>d</sup>	50–350 (15)	Figure 3 in ref 38
28	coke deposition	Pt/Al <sub>2</sub> O <sub>3</sub>	2.33 ± 0.07	0.04–1.00 <sup>e</sup> (5)	Figure 2 in ref 25
29	CO methanation	Pd/SiO <sub>2</sub>	2.90 ± 0.15	0.20–0.85 (7)	Figures 3 & 4 in ref 21

<sup>a</sup> Determined by one or more of the following techniques: X-ray line broadening, microscopy, chemisorption. <sup>b</sup> Smallest one or two particles not included. <sup>c</sup> Lower correlation coefficients (0.960–0.996) than for electrooxidations (no. 22). <sup>d</sup> Slope calculated in ref 38. <sup>e</sup> Smallest dispersion not included.

Table II. Reaction Dimensions for Hydrogen Electrooxidation in a Fuel Cell with Bimetallic Catalysts

catalyst	dispersity range (no. of points)	reaction dimension $D_R$
Pt-Pd <sub>0</sub> /C	0.1–0.54 (5)	1.97 ± 0.01
Pt-Pd <sub>25</sub> /C	0.1–0.44 (4)	2.10 ± 0.04
Pt-Pd <sub>50</sub> /C	0.1–0.50 (5)	2.14 ± 0.08
Pt-Pd <sub>75</sub> /C	0.1–0.55 (4)	2.24 ± 0.04
Pt-Pd <sub>100</sub> /C	0.1–0.53 (5)	2.51 ± 0.09

I, in an order of increasing  $D_R$ . It is seen that the simple scaling law of eq 1 is quite common in catalysis, i.e., that the reactivity of a variety of many catalytic processes is describable in terms of the reaction dimension,  $D_R$ . As mentioned above, the sensitivity of the activity changes to particle radius can be as weak as  $D_R = 0.2$  for oxidation of ethylene on Ag/SiO<sub>2</sub> (no. 19 in Table I) or as exceptionally strong as  $D_R = 5.8$  for the catalytic synthesis of ammonia (Figure 4; no. 24 in Table I). It is also seen that  $D_R$  is an applicable concept for all types of energies involved in the catalytic reactions: heat, light (no. 27 in Table I), or electricity (no. 22 and 23 in Table I).

We believe that this widely encountered phenomenon is of general interest in itself for the reasons described above, i.e.,  $D_R$  provides a general quantitative structure sensitivity scale. We notice that quite often catalytic reactions of dispersed metals have been described in "black and white" terms (structure sensitive or structure insensitive) and that quantification of this property has been often limited to the use of adjectives (weak or strong structure sensitivity).

In the next Section, we suggest preliminary interpretations for the existence of the power law and for the specific  $D_R$  values observed. We do so by highlighting some of the examples in Table I and in particular by demonstrating a fit between suggested underlying models and experimental observations.

#### IV. Discussion: Case Analyses and Suggested Interpretations

##### 1. Catalytic Reactions with $D_R \leq 2$ : Fractal Distributions of Reactive Sites. The starting reference cases for our discussion

will be the structure insensitive reactions.<sup>14</sup> As mentioned above, the situation  $D_R = 2$  indicates that the activity per exposed surface atom is independent of particle size: The exponent in eq 4 becomes zero. In units of activity per particle (eq 1),  $D_R = 2$  carries the simple geometric interpretation that the surface area of a spherical crystallite particle scales like  $R^2$ , or that surface atoms contribute equally to the activity regardless of the types of crystal planes involved. Two representative examples are the hydrogenolysis of cyclopentane on Ir/Al<sub>2</sub>O<sub>3</sub> (Figure 3, no. 10 in Table I) and the epimerization of *cis*-1,2-dimethylcyclohexane to the trans form on Pt/Al<sub>2</sub>O<sub>3</sub> (Figure 2, no. 26 in Table I).

As indicated in Table I,  $D_R$  can be smaller than 2 down to very close to 0. For discussion of this case we shall concentrate on the study of Wu and Harriott.<sup>15</sup> These authors studied the O<sub>2</sub> oxidation of ethylene to CO<sub>2</sub> and to ethylene oxide on Ag dispersed on two nonporous silicas: silica Z and Cab-O-Sil. Ample experimental data are provided in their study to corroborate the simple  $\sim R^2$  relation between radius and total number of surface atoms: crystallites appear spherical in electron microscopy, and  $R$  values calculated by this technique agree within 10% with values calculated from analysis of X-ray data and from O<sub>2</sub> adsorption. Analysis of their adsorption data (Table 3 in ref. 15) was also performed by our approach (from eqs. (2),(6)) according to

$$A \propto R^D \quad (7)$$

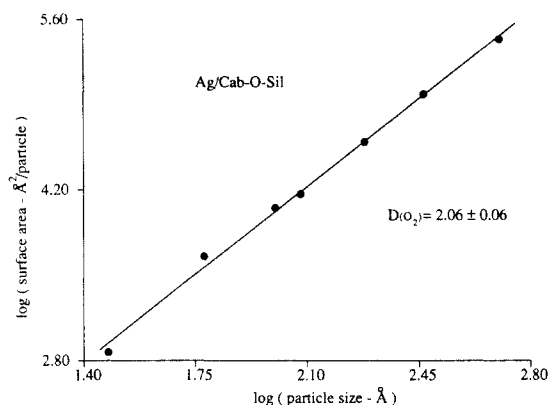
where  $A$  is the surface area per particle measured by O<sub>2</sub> adsorption, ( $A = 4/3\pi R(O_2)^2$ ),  $R(O_2)$  is the particle radius measured by O<sub>2</sub> adsorption,  $R$  is the particle radius from TEM, and  $D$  is the surface fractal dimension of the Ag surface. The result,  $D = 2.06 \pm 0.06$ , is shown in Figure 5.

The following  $D_R$  values were obtained from the analysis of Wu and Harriott's study (Figures 7 and 8 in ref 15; no. 16, 18, 19, and 21 in Table I): 1.16 ± 0.11 and 1.58 ± 0.11 for the oxidations to ethylene oxide on Cab-O-Sil and silica Z, respectively, and 0.43 ± 0.18 and 0.71 ± 0.16 for the oxidations to CO<sub>2</sub> on these two

**Table III.** Edge Atom Statistics of Ag Cubooctahedron Max-B<sub>5</sub> for the Oxidation of Ethylene to Ethylene Oxide

$2R$ (Å) <sup>a</sup>	$n_T$ <sup>b</sup>	$m$ <sup>c</sup>	$n(C_7^5)$ <sup>d</sup>	$n(C_7^9)$ <sup>e</sup>	$n(C_{10})$ <sup>f</sup>	$n(C_{11})$ <sup>g</sup>	total no. of edge atoms	total no. of edge atoms/g ( $\times 10^{-20}$ )
61.3	7245	7.985	335	167	263	120	885	68406
100.3	31736	12.785	680	340	494	235	1749	30862
184.2	196568	23.225	1432	716	995	485	3628	10336
289.4	762325	36.375	2379	1190	1626	801	5996	4405
511.8	4216430	64.205	4383	2181	2191	1469	11005	1462

<sup>a</sup>The experimental values. <sup>b</sup> $n_T = (2R/1.1/d_{at})$ ;  $d_{at}(Ag) = 2.88$  Å. <sup>c</sup>From:  $16m^3 - 3m^2 - 108m + 144 - n_T = 0$ . <sup>d</sup> $n(C_7^5) = 24(3m - 10)$ . <sup>e</sup> $n(C_7^9) = 12(3m - 10)$ . <sup>f</sup> $n(C_{10}) = 24(2m - 5)$ . <sup>g</sup> $n(C_{11}) = 24(m - 3)$ .

**Figure 5.** Surface area (from O<sub>2</sub> chemisorption) per particle as a function of Ag particle size (from microscopy).

silicas, respectively. Two questions will be treated with regard to these observations: First, what is the physical meaning of  $D_R < 2$ , and in particular, what is the physical meaning of *non-integer* values of  $D_R$ ? In answering these questions we are using the basic hypothesis which is applied in this field and which was mentioned above, i.e., that the changes in activity with particle size originate mainly from changes in the relative number,  $n$ , of surface active sites:

$$a \propto n \propto R^{D_R} \quad (8)$$

In the case of structure-insensitive reactions, all surface atoms,  $n_s$ , participate, and hence the observed  $D_R = 2$ :

$$a(\text{structure insensitive}) \propto n_s \propto R^2 \quad (9)$$

A  $D_R < 2$  value indicates therefore a situation in which the growth in the number of reaction sites,  $n$ , as  $R$  grows, lags behind the parallel growth of the total number of surface atoms,  $n_s$ . The recognition of this fact dates back to the dawn of heterogeneous catalysis. For instance, Schwab and Rudolph suggested already in 1931<sup>16,17</sup> that if the reaction occurs selectively only on the *edges* then

$$a \propto n \propto R^1 \quad (10a)$$

i.e., by our terminology,  $D_R = 1$ ; and similarly, since the number of corners of a crystal do not change with its size, an experimental  $D_R = 0$  value will suggest that it is only corner atoms that are active:

$$a \propto n = \text{constant} \quad (D_R = 0) \quad (10b)$$

It is seen therefore that simple geometric considerations can explain  $D_R = 2, 1, 0$ , reflecting two-dimensional (area), one-dimensional (line) and zero-dimensional (point) zones of activity. One of the main contributions of fractal geometry has been the clarification of the physical meaning of *non-integer* dimensions and the creation of continuous scale of dimensions. Here we very briefly summarize the physical interpretation of the non-integer, fractal dimension,  $D$ . A more detailed discussion can be found in ref 17 and, re-

garding molecule/surface interactions, in some of our earlier publications.<sup>6</sup> The existence of a scaling relation between a property (in our case the number of active sites) and a scale (in our case the particle diameter) in the form of the above power law indicates that the effective shape related to that property is symmetric to transformations of scale, i.e., that over a given range of sizes, magnification of an object by a factor of  $N$  will increase the total number of features by a factor of  $N^D$ . This definition brings the  $D = 2, 1, 0$  and the non-integer dimensions into a unified picture. The subscript R in  $D_R$  was added to emphasize a number of points: first, that it is derived from the analysis of a reaction performance; second, that we are considering an *effective* surface geometry which is of relevance to the reaction but need not coincide with the "true" geometry of the object; and third, we define  $D_R$  as the reaction dimension and not as the fractal reaction dimension because of those  $D_R$  values (Section IV.2) for which strict fractal interpretations do not apply.

Returning now to Wu and Harriott's study, we notice that the authors reach a qualitative conclusion that "the changing proportions of edge or step sites relative to sites on low index planes might be the reason for the observed" structure sensitivity and that "edge, corner or step sites [produce] mainly CO<sub>2</sub> [while sites] on low index faces would produce mainly ethylene oxide". This conclusion is in keeping with the *quantitative* evaluation of the degree of structure sensitivity in the various oxidations as given by the reaction dimension  $D_R$ : the  $D_R < 1$  values for CO<sub>2</sub> production indicate according to our approach a reactive surface that is composed of corners and edges; the  $D_R = 1.16$  value for ethylene oxide production on Cab-O-Sil indicates mainly edge participation; and the  $D_R = 1.58$  for ethylene oxide production on silica Z indicates the existence of a subset of reactive sites which probably includes also the crystallite planes.

We now show that it is possible to attach specific active-site populations to an observed  $D_R$  value. We first show that the value  $D_R = 1.16$  for oxidation to ethylene oxide agrees nicely with a model suggesting that only the edges of the Ag crystallite participate in the reaction. We do so by counting the relevant surface atoms according to van Harveld and Hartog's (VH) surface-atom statistics calculations.<sup>18</sup>

A cubooctahedron model is suggested by Wu and Harriott for the Ag crystallites. Since they also assumed imperfections such as an excess layer over part of the crystal plane, we took what was termed by VH a max-B<sub>5</sub> crystal, i.e., a situation in which each of the crystal planes is covered by an extra layer of atoms forming step-sites, the construction of which requires 5 atoms/step site (for illustrations of max-B<sub>5</sub> cubooctahedrons, COM5, see Figure 10 in ref 18b and Figure 12 in ref 18a). For comparison of experimental results to model, the following procedure was employed (Table III): From the experimental size values,  $2R$ , the total number of the atoms in the crystallite,  $n_T$ , was calculated from<sup>18b</sup>

$$n_T = (2R/1.1/d_{at})^3$$

where  $d_{at}$  is the atom size in the crystal, 2.88 Å for Ag.<sup>19</sup> From

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(16) Interestingly, these authors looked for a general power law relation, but for the specific case they analyzed they could not find a constant exponent.

Table IV. Edge and Corner Atom Statistics of Ag Cubooctahedron Max-B<sub>3</sub> for the Oxidation of Ethylene to CO<sub>2</sub>

$2R$ (Å) <sup>a</sup>	$n_T$ <sup>b</sup>	$m$ <sup>c</sup>	$n(C_7^5)^d$	$n(C_7^6)^e$	$n(C_{10})^f$	$n(C_{11})^g$	6% $n_{\text{edges}}$	6% $n_{\text{edges}} + n_{\text{corners}}^h$	6% $n_{\text{edges}} + n_{\text{corners}}^h / g (\times 10^{-20})$
66.4	9083	8.575	377	189	292	134	60	180	11068
96	27827	12.255	642	321	468	222	99	219	4412
140	86304	17.715	1035	518	730	353	158	278	1805
166.7	145697	21.045	1275	638	890	433	194	314	1208
392	1894530	49.215	3303	1652	2242	1109	498	618	183

<sup>a-c</sup> See Table III. <sup>h</sup> Corner atoms:  $nC_6^6 (=96) + nC_3^4 (=24)$ .

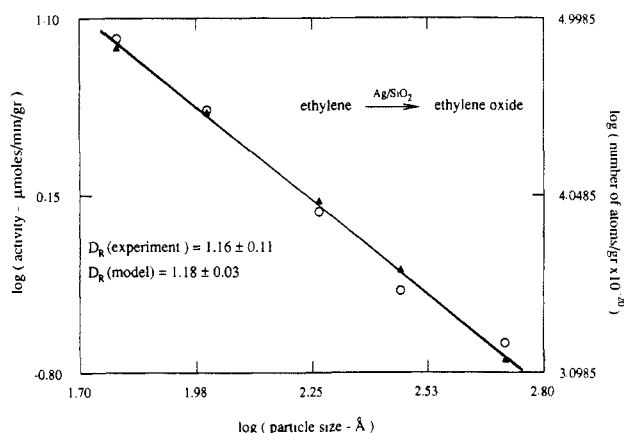


Figure 6. Catalytic activity (O) and number of edge atoms (Δ) in a cubooctahedron max-B<sub>3</sub>, as a function of Ag particle size for the oxidation of ethylene to ethylene oxide.

this,  $m$ , the "equivalent crystallite size" in the polynomial which describes  $n_T$ , can be calculated. For COM5 it is<sup>18b</sup>

$$n_T = 16m^3 - 3m^2 - 108m + 144 \quad (11)$$

There are four types of edge atoms in COM5 and their total number is calculated, knowing  $m$ , as detailed in Table III. Having  $n(\text{edges})/g$  and  $R$ ,  $D_R$  is then obtained from eq 5. The  $D_R$  value thus calculated is  $1.18 \pm 0.03$  (correlation coefficient 0.999), virtually identical with the experimental  $1.16 \pm 0.11$  value (Figure 6). (Inclusion of the corner atoms or using the perfect cubooctahedron crystal gives lower  $D_R$  values, all around 1.1.)

The other experimental  $D_R$  values from Wu and Harriott's work indicate a combination of corners, edges, and plane atoms. For instance, the experimental  $D_R = 0.71 \pm 0.16$  may reflect the very simple (non-fractal) combination of all corner atoms and of 6% of the length of edges (Table IV) as suggested by the perfect fit with the  $D_R = 0.70 \pm 0.04$  value (Figure 7), or a fractal Cantor set distribution (see below) of gaps of activity on the edges.<sup>7d</sup> We can also conclude that if 6% of edge fractions are necessary for a  $D_R = 0.70$  value, then the lower experimental  $D_R = 0.43$  probably requires even smaller edge fraction. How the actual (fractal) distribution looks for a  $D_R = 0.70$  Ag crystallite cannot be answered at this stage; electron-tunnelling microscopy will hopefully provide direct answers. We are forced, therefore, to content ourselves in such cases with the identification of the general type of active sites. In other cases, like the previous one and the next case analysis, more specific assignment of surface atoms is possible.

To conclude the analysis of Wu and Harriott's paper, we notice also the following two points: first the  $D_R$  pairs 0.43, 0.71 for CO<sub>2</sub> production and 1.18, 1.58 for ethylene oxide production reflect a support effect on the degree of structure sensitivity—the higher  $D_R$  values in each pair belong to the silica Z; and secondly, one of the tests for the applicability of a new approach is whether independent studies of the same problem provide similar results. Indeed, Jarjoui et al. have independently studied the oxidation of ethylene on Ag/Cab-O-Sil,<sup>20</sup> analysis of their results reveals

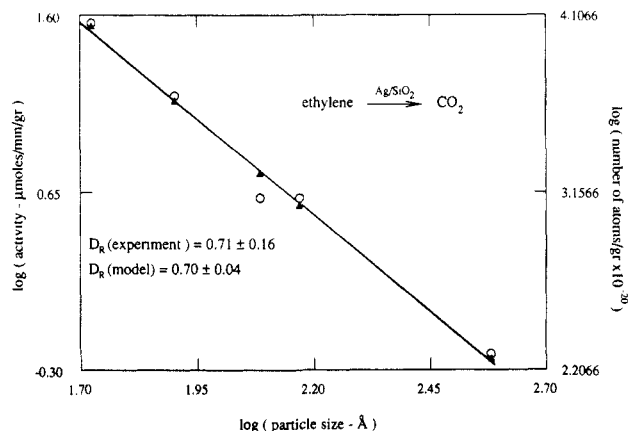


Figure 7. Catalytic activity (O) and number of (6% edge + corner) atoms (Δ) as a function of Ag particle size, for the oxidation of ethylene to CO<sub>2</sub>.

virtually the same values:  $D_R(\text{CO})_2 = 0.2$ ;  $D_R(\text{C}_2\text{H}_4\text{O}) = 0.7$  (no. 17 and 20 in Table I).

**2. Catalytic Reactions with  $D_R > 2$ .** As indicated in Table I, many catalytic reactions are characterized by  $D_R > 2$  values. These cases defer on the one hand from the  $D_R < 2$  reactions but on the other hand originate from the same type of arguments. We explain this statement: If the dimension of the surface of the crystallite is  $\sim 2$  then a subset of the surface points can have a fractal dimension which is only smaller than 2. Hence the suggested fractal interpretation to the  $D_R < 2$  site distributions in the previous Section. In those  $D_R < 2$  cases, large particles are similar to a small one in the sense that the former is a magnified version of the latter. This is still correct for rough and irregular surfaces, for which the surface fractal dimension is  $2 \leq D < 3$ . But since the  $D_R > 2$  values we observe come from  $D \sim 2$  crystallites, the similarity argument cannot hold any longer. However,  $D_R < 2$  reactions and  $D_R > 2$  reactions belong to the same family by virtue of the procedure that reveals the existence of the power law, i.e., the performance of a particle size scaling analysis. For both cases it still holds that if the particle is magnified by a factor of  $N$ , then a total of  $N^{D_R}$  surface features appear. The situation  $D_R > 2$  with  $D \sim 2$  means that there is a subset of active sites which, although always smaller than the total number of surface sites,  $n_s$ , grows faster (and not slower, as in  $D_R < 2$ ) with  $R$  than  $n_s$ . Particle similarity (fractality) does not exist in this case since the splitting procedure of one surface feature into  $N^{D_R}$  ones can only be such that the area of location of the new features overlap each other; the arrangement of the active sites on the crystal surface will then not be similar on particles with different radii. (For the interested reader: consider the procedure by which a Cantor set is formed from repeated trisections of a bar (p 80 in ref 17a); one can in principle use another construction algorithm in which the initial bar is split not to two bars of size  $1/3$  but to, say, ten bars of size  $1/20$ ; each iteration in the latter procedure will form an object that is not similar to the previous iterations.)

What is then the origin of the observed power laws with  $D_R > 2$ ? In order to suggest an interpretation we shall now con-

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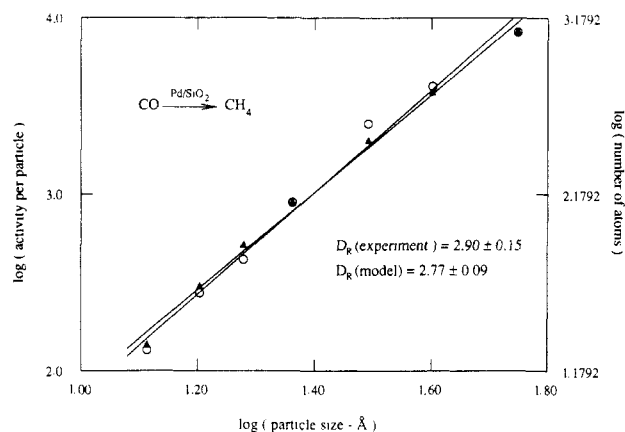
**Table V.**  $C_8$  and  $C_9$  Surface Atoms Statistics of Cubooctahedron, for CO Methanation

$2R$ (Å) <sup>a</sup>	$n_T$ <sup>b</sup>	$m$ <sup>c</sup>	$n(C_9^3)$ <sup>d</sup>	$n(C_8^{4,5})$ <sup>e</sup>	total $C_9^3$ and $C_8^{4,5}$ atoms per particle
13	80	2.381	20	1	21
16	150	2.783	41	4	45
19	250	3.176	69	8	77
23	444	3.706	118	17	135
31	1088	4.762	257	46	303
40	2337	5.949	477	94	571
56	6414	8.057	1034	220	1254

<sup>a</sup>  $R$  was calculated from the dispersion according to Table I in ref 2a. (An average value between spherical and cubic particle was taken.) <sup>b</sup>  $n_T = (2R/1.1/d_{at})$ ,  $d_{at}(\text{Pd}) = 2.74$  Å. <sup>c</sup> From:  $16m^3 - 33m^2 + 24m - (n_T + 6) = 0$ . <sup>d</sup>  $n(C_9^3) = 8(3m^2 - 9m + 7)$ . <sup>e</sup>  $n(C_8^{4,5}) = 6(m - 2)^2$ .

centrate on one of the  $D_R > 2$  cases, i.e., the methanation study of Rieck and Bell,<sup>21</sup> performed on Pd/SiO<sub>2</sub> (Cab-O-Sil). We first notice that the experimental data in ref 21 indicate a  $D \sim 2$  surface for the Pd crystallites: the dispersion of the catalyst as determined from H<sub>2</sub>/O<sub>2</sub> titrations gave equivalent values for both H<sub>2</sub> and O<sub>2</sub> titers which were then further corroborated by XRD line broadening analysis. On the basis of turnover data and on temperature desorption data, the authors suggest the following picture, which, as shown below, is in complete agreement with the  $D_R$  value we obtained: the observation has been that as  $R$  increases, the temperature for the onset of CO dissociation decreases. This was attributed to an increase in the relative population of bridge-bonded sites, which, in turn, was linked to a parallel increase in the ratio Pd(111)/Pd(100) sites. This structure-sensitivity assignment is based on a number of studies<sup>22</sup> which indicated that linearly adsorption of CO occurs on Pd(100) sites, while the bridged conformation is found on the Pd(111) plane. Since activation energies for methanation were found to be comparable on Pd(100) and Pd(111),<sup>21</sup> the change in reaction rates originates primarily from the change in the frequency factor in the Arrhenius equation, i.e., the dependence of the activity on  $R$  can be analyzed in terms of changes in the number of active sites, which is indeed suggested by Rieck and Bell: they observed that the trend of the observed structure sensitivity is in keeping with the atoms-type population calculation of VH for a Pd cubooctahedron. The relative number of  $C_9$  atoms, which according to VH terminology are the Pd(111) atoms, increases with  $R$  faster than  $C_8$  atoms, which are the Pd(100) plane atoms. What we show here is that the experimental  $D_R$  as obtained from analysis of the data in ref 21 and the  $D_R$  as calculated from the VH surface-atoms statistics of  $C_8$  and  $C_9$  are in very good agreement: 2.9 and 2.8, respectively. Details of the calculations are collected in Table V and the comparison shown in Figure 8 (no. 29 in Table I). This observation adds to our tentative suggestion that the observed  $D_R$  values originate mainly from surface-atom and surface-site statistics, in which the relative proportion of non-active sites is determined as in VH calculations if such correlations are found as shown above, or by poisoning and blocking of sites. Furthermore, by drawing parallels from the recent intensive investigations of random processes and randomly generated objects,<sup>17,23</sup> it seems to us that it should be even easier to obtain power-law behavior from imperfect crystallites than from the models used above.

**3. Some Additional Highlights from Table I.** Before summarizing our conclusions we highlight briefly a few more of the entries in Table I. The aim of this Section is merely a phenomenological one, i.e., to re-emphasize the applicability of  $D_R$  to many catalytic reactions and to underline some of the aspects of catalysis which



**Figure 8.** Catalytic activity ( $\text{mol} \times 10^4 \cdot \text{s}^{-1} \cdot \text{surface atom}^{-1} \cdot R^2$ , related to  $\text{mol} \cdot \text{s}^{-1} \cdot \text{particle}^{-1}$  through a constant) (O) and the number of  $C_8^{4,5}$  and  $C_9^3$  (▲) atoms in a cubooctahedron, as a function of Pd particle size for CO methanation.

are due for further investigation according to the approach presented here.

**(a) Ammonia Synthesis: The Highest  $D_R$ .** One of the examples with  $D_R > 2$  concerns a corner stone in catalysis studies—ammonia synthesis by reduction of nitrogen. Re-analysis of the work of Topsoe et al., with Fe/MgO<sup>24</sup> (Figure 4; no. 24 in Table I), reveals the highest structure sensitivity we could find so far, with  $D_R = 5.8 \pm 0.5$ . A six-order magnitude of change in activity is observed by changing  $R$  by a factor of 10. It is interesting to notice that despite the extreme sensitivity, the authors favor an explanation that is based only on a sharp increase in the number of active sites with increase in  $R$ , over other possibilities discussed there; i.e., in their view, surface statistics is a sufficient cause for the apparent  $D_R \gg 2$ .

**(b) Catalyst Poisoning.** Structure sensitivity for this notorious problem is expected and indeed found. Analysis in terms of  $D_R$  is applicable for these processes as well. An example is the study of Barbier et al. of the poisoning of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts by deposited coke in the case of hydrogenolysis of cyclopentane.<sup>25</sup> The authors explain the observed structure sensitivity in that poisoning takes place preferentially on the active sites for the hydrogenolysis. Re-analysis of the relation between coke-deposition rate and particle size (no. 28 in Table I) reveals  $D_R = 2.33 \pm 0.07$ . We indeed notice that similar low structure sensitivity  $D_R$  values were observed for other cycloalkane Pt/Al<sub>2</sub>O<sub>3</sub> hydrogenolyses (no. 6–9 in Table I).

**(c) Bimetallic Catalysts.** There is a growing interest in bimetallic catalysts in which changes in activity can be fine-tuned by careful control of the composition of the alloy. We found that the parameter  $D_R$  is sensitive to gradual changes in composition as revealed by a parallel gradual change in  $D_R$ . In another study of Barbier et al.<sup>26</sup> a series of five Pt–Pd/C catalysts was used for the electrooxidation of hydrogen in a fuel cell. Analysis of their data reveals the results collected in Table II: Pt–Pd<sub>0</sub> is structure insensitive with  $D_R = 2$ , Pt–Pd<sub>100</sub> is the most structure sensitive, with the highest  $D_R$  value; and  $D_R$  for the bimetallic catalysts increase gradually with increase in Pd contents. Electroreduction of oxygen by the same bi-metallic catalysts<sup>27</sup> reveals a similar trend (no. 23 in Table I).

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## V. Conclusions and Summary

1. We have shown that structure sensitivity in dispersed metal catalysts is describable in terms of a simple scaling power law.

2. A single parameter, the reaction dimension  $D_R$ , allows quantitative evaluation of the degree of structure sensitivity and comparative evaluation of (unrelated) reactions and catalysts.

3. This tool is general and applicable to virtually all types of catalytic reactions as indicated in Table I.

4. A wide range of  $D_R$  values has been revealed: from close to 0 up to 6.

5. It is suggested that the observed  $D_R$  values originate from specific dependencies of the relative proportion of active surface atoms or sites on particle size. This hypothesis was tested by fitting three of the experimental  $D_R$  values to surface-atom statistics of suggested crystallite models. For experimental  $D_R = 0.71, 1.16,$

2.77 the calculated  $D_R = 0.79, 1.18, 2.90$  were obtained (Figures 6-8).

6. For crystallites with surface fractal dimension  $\sim 2$ ,  $D_R \leq 2$  has been interpreted in terms of invariance of the pattern of distribution of active sites to scale transformation, i.e., that  $D_R$  reflects the fractal dimension of the subset of active sites out of all surface atoms. Pattern invariance does not hold for  $D_R > 2$  (or more generally for  $D_R > D$ ) values, but common to all  $D_R$  values is the scaling behavior: magnifying by a factor of  $N$  increases the number of relevant surface features to  $N^{D_R}$ .

The main purpose of this paper has been to report the phenomenon, its generality, and its potential applications and to suggest preliminary interpretations. In following publications we concentrate on specific families of heterogeneous catalytic reactions and on chemisorptions. For preliminary reports see ref 6a,d and 7d.

**Acknowledgment.** An earlier version of this manuscript has been subjected to critical reviewing by colleagues and experts. This revised version is the outcome of very useful comments, questions, and advice we received, especially from P. Pfeifer, M. Asscher, G. C. Bond, J. R. Anderson, J. Klafter, and two anonymous referees. This study was supported by the Israel Academy of Sciences and by the Aronberg Foundation.

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# SINDO1 Study of the Photochemical Reaction Mechanism of Di- $\pi$ -methane

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**Abstract:** SINDO1 calculations on the configuration interaction (CI) level were performed in an investigation of the photochemical di- $\pi$ -methane rearrangement. Several diradical intermediates and one transition structure were located on the lowest triplet potential surface. Correlation diagrams are presented for two alternative pathways to vinylcyclopropane. The diagrams confirm the general idea of the mechanistic pathway suggested by Zimmerman. The singlet mechanism is efficient if no barriers on the first excited singlets occur during the reaction. This is the case for central dimethyl substitution of the reactant. Here cyclopropyldicarbonyl is not an intermediate. The triplet mechanism can be efficient only if the cyclopropyldicarbonyl triplet intermediate is circumvented during the reaction so that back reaction to the reactant ground state is avoided.

## I. Introduction

The di- $\pi$ -methane rearrangement is a photochemical reaction that was discovered and the mechanism proposed by Zimmerman so that it is sometimes called the Zimmerman rearrangement. The experimental data and mechanistic scheme are lucidly described in a recent review.<sup>1</sup> According to the mechanism the unsubstituted di- $\pi$ -methane undergoes a rearrangement to vinylcyclopropane after irradiation with light. In the mechanistic scheme (Figure 1) it is assumed that two diradicals are involved in the reaction which serve to establish a bridge bond between the two  $\pi$  bonds and subsequently break one of the two single CC bonds of the initially central carbon atom. Finally the two new diradical centers rearrange and form the three-membered ring. Zimmerman is cautious in pointing out that the two diradicals need not be energy minima on the potential surface. The symmetry of the simple scheme of Figure 1 is modified if substituents render the two  $\pi$  bonds unequivalent. According to Zimmerman acyclic di- $\pi$ -methane reactants react effectively from their singlet excited states. This claim was supported by experimental evidence on

*cis*- and *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene,<sup>2</sup> where direct irradiation led to a normal di- $\pi$ -methane rearrangement whereas sensitized irradiation, in which the reactant was in the triplet state, led to no di- $\pi$ -methane rearrangement. It was shown that triplet excitation was diverted into a rotation about one of the acyclic  $\pi$  bonds. In the singlet rearrangement it should also be operative, but the rates of rotational relaxation are too slow compared with the rates of rearrangement.

To our knowledge no experimental data are available on the rearrangement of the parent di- $\pi$ -methane compound in solution, but a few symmetrically substituted molecules were investigated. For 1,1,5,5-tetraphenyl-1,4-pentadiene a hydrogen migration mechanism was found to be operative with low product yield.<sup>3</sup> In other cases the central carbon atom had two methyl groups attached to itself. Here the mechanism of Figure 1 is characteristic. More extensive studies were done with asymmetric substitution at the vinyl groups. In these cases regioselectivity favors one of the two possible products. This observation was

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