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Linear Free Energy Relationships in Heterogeneous Catalysis

IV. Regional Analysis for Solid Acid Catalysis*

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A new method, "regional analysis" for heterogeneous catalysis, is presented in order to find quantitative correlations between the reaction rate over catalysts and either acid strength distribution over solid acids for an acid catalysis or excess oxygen distribution over oxides for an oxidation-reduction catalysis. This analysis is based on the assumption that, in the case of acid catalysis, the reaction rate on an acid site is determined solely by the acid strength of the site, without depending upon the chemical composition of catalysts as far as similar catalysts are concerned. Methods of least squares are employed to find the regional rates or regional rate constants. Oligomerization of propylene and depolymerization of paraldehyde, both on nickel sulfate calcined at various temperatures, were analyzed as examples. In the latter reaction, it was suggested that the Brönsted catalysis law may hold even in heterogeneous catalysis.

INTRODUCTION

Activity of solid acid catalysts like silica-alumina and nickel sulfate for some acid-catalyzed reactions has been related with the measured amounts of acid sites over the catalyst. Since Benesi (*1*) developed a new method to measure the acid strength distribution, the distribution of acid content according to acid strength, by means of the amine titration with several Hammett indicators, it has widely been shown that the acid strength distribution of a catalyst has a rational correlation with its catalytic activity. In the amine titration method or the other methods such as the adsorption of ammonia, the extent of the acid content is usually divided into some regions for the convenience of experimental procedures. Acid sites in every region over a catalyst may have their own catalytic activity, therefore it is worthy of thorough study to find correlations between the acid strength of a region and its catalytic activity.

In homogeneous acid-catalyzed reactions, the Brönsted catalysis law and correlations of rates with the Hammett acidity function have already been well established. As for heterogeneous catalysis, Tanabe *et al.* qualitatively estimated the regional rate of oligomerization of propylene (*2*) and depolymerization of paraldehyde (*3*) over a set of nickel sulfate catalysts. Wilmot *et al.* (*4*) derived a regional rate equation for olefin isomerizations and presented valuable criteria for this kind of analysis; their concept, however, had restrictions, since its application was limited to one catalyst, and therefore the regional activity was estimated by simply subtracting the activity lost by successive poisoning. Ogino (*5*) estimated the most effective region for hydration of propylene over various metal sulfates, although it was done in a qualitative way.

In the present paper, a new method, "regional analysis," will be proposed; it consists in using the method of least

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* Part III I. Mochida and Y. Yoneda, *J. Catalysis* 8, 223 (1967).

squares to find regional rates over a set of catalysts with different acid strength distributions.

METHOD OF ANALYSIS

The following items will reasonably be assumed as the basis of this analysis.

(i) Reaction rate on an acid site is decided solely by its acid strength and the kind of reaction, without depending upon the chemical composition of the catalyst as far as a set of similar catalysts are concerned.

(ii) The difference between Brönsted and the Lewis acids is ignored in view of catalysis, until any precise method may be developed for measuring both their acid strengths and contents on a catalyst, distinguishing the types of acid sites.

(iii) Reaction kinetics remains unchanged and the degree of coverage of the reactant is kept low for all regions.

(iv) No reaction path exists that is indifferent to acid sites; for example, a purely thermal homogeneous reaction or a wall reaction.

Acid strength distribution is represented by both the acid content and its acid strength in every region, which may be determined by any experimental method, including the amine titration. The overall rate of a reaction r over the *i*th catalyst of unit weight [$v_i(\mathrm{r})$, moles/min g catalyst] will be given as the sum of products of the regional rate of the *i*th region [$v_{0j}(\mathrm{r})$, moles/min meq of acid content] and the regional acid content of the same region on the *i*th catalyst of unit weight (s_{ij}, meq/g catalyst),

$$v_i(\mathrm{r}) = \sum_j^P v_{0j}(\mathrm{r})s_{ij} \qquad (1)$$

where P is the number of regions.

When the reaction rate is expressed as a function f of the reactant partial pressure, $p(\mathrm{R})$, the overall rate, $v_i(\mathrm{r})$, will reasonably be given by the following equation:

$$v_i(\mathrm{r}) = \sum_j^P \{k_{0j}(\mathrm{r})s_{ij}f[p(\mathrm{R})]\} \qquad (2)$$

where $k_{0j}(\mathrm{r})$ is the regional rate constant of the reaction r per unit acid content in the *j*th region. The overall rate is expressed also by Eq (3),

$$v_i(\mathrm{r}) = k_i(\mathrm{r})f[p(\mathrm{R})] \qquad (3)$$

where $k_i(\mathrm{r})$ is the overall rate constant of the reaction r on the *i*th catalyst of unit weight. According to the assumption (iii), $f[p(\mathrm{R})]$ is the same for all regions; hence, Eq (4) is derived from Eqs. (2) and (3),

$$k_i(\mathrm{r}) = \sum_j^P k_{0j}(\mathrm{r})s_{ij} \qquad (4)$$

Because $v_i(\mathrm{r})$ or $k_i(\mathrm{r})$ and s_{ij} can be experimentally determined for a particular reaction r and for each catalyst, a set of probable values of $v_{0j}(\mathrm{r})$ or $k_{0j}(\mathrm{r})$ will easily be estimated by means of the method of least squares, when the number of catalysts employed, M, is greater than that of the regions, P.

The acid strength distribution is usually measured with fresh catalysts. In the working state of a catalyst, there generally exists some poisoning by reactants, products, or both. Strictly speaking, the above equations should hold only for the analysis of initial, unpoisoned rates. In the case of stationary states, modified regional rates or rate constants should be introduced, or otherwise the acid strength distribution *during* the reaction should be measured. The poisoning by substrates is, however, usually not so severe that it would be worthy of study to apply the above analysis to the reaction rates, even if they were measured in stationary states.

RESULTS AND DISCUSSION

Very few data have been published that are available for this analysis. The rates should be measured over a sufficient number of catalysts which presumably have the same kind of acid sites and possibly have different acid strength distributions from each other. Moreover, the maximum acid strength should be measured because the catalytic activity of the strongest region will probably not be ignored. The following two examples will verify the usefulness of this analysis.

Example 1. Oligomerization of Propylene on Nickel Sulfate Catalysts

The acid strength distribution measured by the amine titration and the overall rates of the oligomerization of propylene at 100°C and 400 mm Hg were measured by Tanabe *et al.* (*2*) and their data were summarized in Table 1. Reportedly no acid content was observed beyond the strongest region given in Table 1.

When a set of equations derived from Eq. (1) is solved by the method of least squares, the standard deviations of the parameters are mainly dependent upon the degree of freedom. In this example a set of nine equations is to be solved. When all of the five regions were adopted in the calculation, the estimated values of regional rates did not make sense because of their remarkable standard errors due to the small degree of freedom. In order to increase the degree of freedom, it is necessary to reduce the number of regions. Hence, two or more regions of smaller acid content or presumably of less activity were combined into one region. A set of regional rates thus calculated is shown in Fig. 1, where eventually three regions, that is, regions (1 + 2 + 3), 4, and 5 were adopted. Short arrows upon the abscissa show the representative acidity function $(H_0)_{0j}$ of each region. This value is defined as a modified logarithmic mean of H_0 values of its strongest limit, $(H_0)_{\max}$, and its weakest limit, $(H_0)_{\min}$,

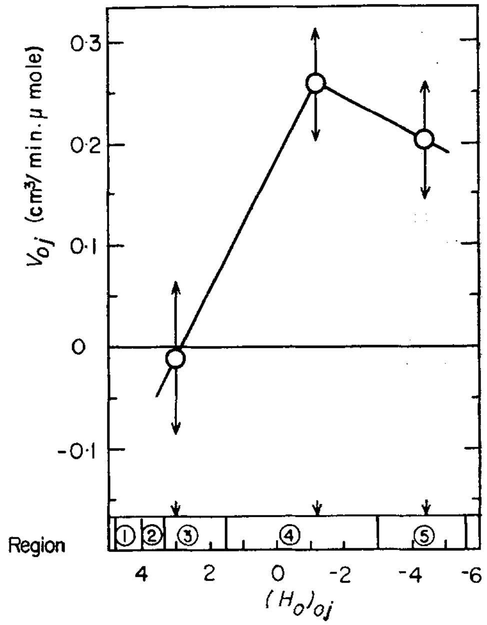

FIG. 1. Regional rates of propylene oligomerization on nickel sulfate vs. acid strength (*2*). Regions (1 + 2 + 3), 4, and 5 (No. 310).

$$k_{0j}{}^{\alpha'} = \frac{K_{\max}{}^{\alpha'} - K_{\min}{}^{\alpha'}}{\alpha' \ln(K_{\max}/K_{\min})} \quad (5)$$

where the K's are the hypothetical dissociation constants corresponding to H_0's,

TABLE 1

ACID STRENGTH DISTRIBUTION AND CATALYTIC ACTIVITY[a,b]

		Acid content, s_{ij} (μmole/g)					
Calcination temp (°C)	Region: $(H_0)_{0j}$:	1 4.8–4.0	2 4.0–3.3	3 3.3–1.5	4 1.5–−3.0	5 −3.0–−5.6	v_i (cm³/min g)
600°		10	22	0	0	0	0
150°		4	4	0	23	0	9.1
250°		0	7	3	15	11	9.3
350°		12	2	0	46	28	13
464°		2	24	1	42	0	13
367°		10	14	0	60	9	15
300°		11	8	6	33	34	16
400°		0	9	6	41	30	16
325°		0	18	2	55	63	28

[a] Tanabe *et al.*, ref. (*2*).

[b] Catalyst, nickel sulfate; reaction, oligomerization of propylene at 100° and its partial pressure of 400 mm Hg.

while α' is 0.3, whose meaning will be given later. The arrows around circles show the standard deviation. The original authors claimed that the acid sites having acid strength stronger than $H_0 = +1.5$ are catalytically active for this reaction. With the values of standard deviation taken into consideration, their intuitive interpretation was proved to be valid and, in addition, the regional rates of regions 4 and 5 are found nearly equal from the above analysis. The coincidence between the observed values of rates and the calculated ones is as shown in Fig. 2, where the plotted values lie along the diagonal line.

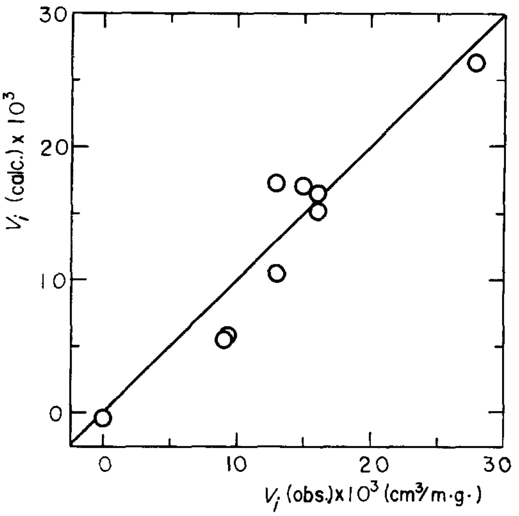

FIG. 2. Coincidence between observed and calculated rates of propylene oligomerization Regions (1 + 2 + 3), 4, and 5 (No. 310).

Example 2. Depolymerization of Paraldehyde on Nickel Sulfate

The reaction rate constants at 30°C in benzene and the acid strength distributions of the catalysts were also measured by Tanabe *et al.* (*3*), as summarized in Table 2, the numerical values of which were obtained by a private communication from the original authors. In this example, rate constants and regional acid content were given in the unit per square meter instead of per gram. By following the previously described procedures, the regional rate constants were calculated for three regions (1 + 2 + 3), 4, and 5. The results are given in Fig. 3, where the ordinate is the logarithm of the regional rate constant, k_{0j}. The value of k_{0j} for the region (1 + 2 + 3) was estimated as -3.5×10^{-7}/min μmole with standard deviation of 1.1×10^{-5}/min μmole. Accordingly k_{0j} of this region may reasonably be assumed to be negligible. The original authors claimed that alone the region 5, having acid strength stronger than $H_0 = -3.0$, had catalytic activity for this reaction. By the above analysis, however, region 4, having acid strength between 1.5 ~ −3.0, was found to have a regional rate constant of about one-third of that of the region 5.

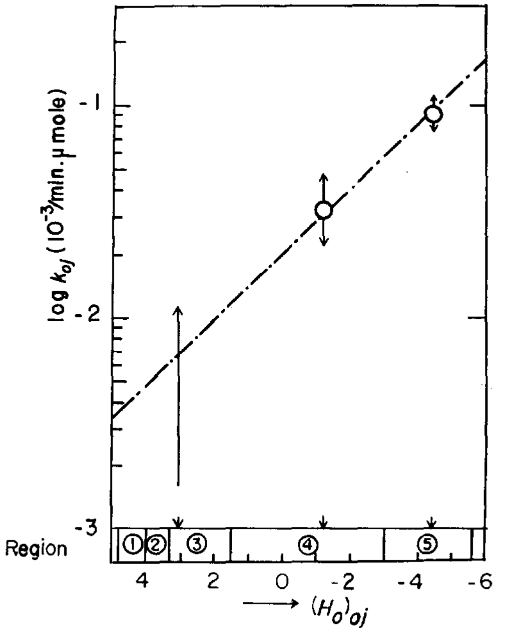

FIG. 3. Regional rate constants of depolymerization of paraldehyde on nickel sulfate vs. acid strength (*3*): ○, Regions (1 + 2 + 3), 4, and 5 (No. 28); Chain line, Brönsted (No. 2002).

Suppose that the Brönsted catalysis law holds even among regions on a heterogeneous catalyst. Then the following equation will be given for the rate constant of the jth region:

$$k_{0j} = k_{00}K_{0j}^{\alpha} \qquad (6)$$

where K_{0j} is the representative dissociation constant of acid sites in the jth region and

TABLE 2

Acid Strength Distribution and Catalytic Activity[a,b]

Calcination temp. (°C)		Acid content, s_{ij} (μmole/m^2)					
	Region: $(H_0)_{0j}$:	1 4.8–4.0	2 4.0–3.3	3 3.3–1.5	4 1.5–−3.0	5 −3.0–−5.6	$k_i \times 10^3$ (min^{-1}m^{-2})
150°		0.6	0.6	0	3.4	0	0.076
250°		0.2	0.6	0.3	2.7	1.6	0.20
325°		0	1.3	0.2	4.1	4.7	0.63
350°		0	1.2	0.3	4.2	4.6	0.54
375°		0	1.2	0.7	4.0	4.9	0.49_5
400°		0	0.9	0.6	4.0	2.9	0.44
464°		0.3	2.7	0.1	4.7	0	0.17_5
600°		1.6	3.3	0	0	0	0

[a] Tanabe *et al.* (*3*).

[b] Catalyst, nickel sulfate; reaction, depolymerization of paraldehyde.

$\log K_{0j} = -(H_0)_{0j}$, and both α and k_{00} are constants, dependent on neither catalysts nor regions. Substituting Eq. (6) into Eq. (2), k_i will be given as follows:

$$k_i = k_{00} \sum_j^P K_{0j}{}^{\alpha} s_{ij} \tag{7}$$

Because the values of k_i, s_{ij}, and K_{0j} are observable, two parameters, α and k_{00}, can be estimated from a set of Eq. (7) by means of a nonlinear method of least squares, the computer program for which was named BRONSTED. In this case, the degree of freedom is equal to $M-2$; therefore, all of the regions were employed for the analysis without any combination.

The values thus obtained were as follows:

$$k_{00} = 0.019 \pm 0.006$$

$$\alpha = 0.15 \pm 0.04$$

The regional rate constant calculated from Eq. (6) and the overall rate constant from Eq. (7) are shown in Figs. 3 and 4, respectively. It is worthwhile to mention that even the rate constants over these heterogeneous catalysts are well described by the Brönsted catalysis law.

The representative acidity function of the *j*th region was defined in Eq. (5). This quantity is a weighted mean with the catalytic activity of acid sites of increasing acid strength within a region, by assuming the Brönsted relationship given in Eq. (6) with α of 0.3. Although this value of $\alpha' = 0.3$ in Eq. (5) is tentatively chosen and different from the estimated value in this reaction, it will be worth little consideration in the present stage of discussions.

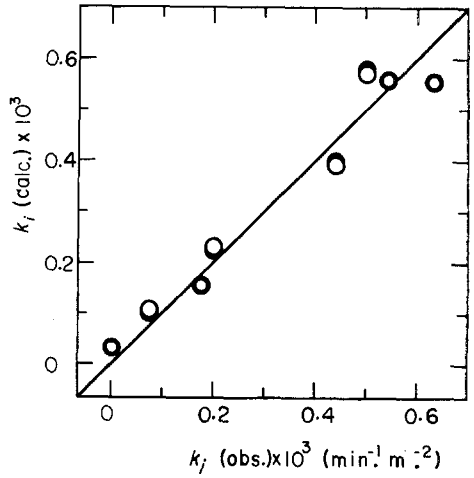

FIG. 4. Coincidence between observed and calculated rate constants of depolymerization of paraldehyde: ○, Regions (1 + 2 + 3), 4, and 5 (No. 28); ●, Brönsted (No. 2002).

PROPOSED VERSATILITY

Applicability of the regional analysis for solid acid catalysis was demonstrated with two reactions both on nickel sulfate. The analyses of rate data for propylene hydration by Ogino (*5*) and some isomerizations by Wilmot *et al.* (4), however, were tried in vain, because either the number of data was too small for the present purpose or the catalysts were so different in nature among them that they could not be assumed to be similar ones.

When more accurate values of acid strength distribution, especially beyond $H_0 = -8.3$, are supplied, together with their initial and stationary rate data, more extensive discussion will easily be made as an extention of the concept given in this paper. This regional analysis will be applied also to the oxidation-reductions by oxide catalysts, where the excess oxygen distribution on their surface will replace the acid strength distribution in solid acid catalysis.

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