

NOTES

Linear Free Energy Relationships in Heterogeneous Catalysis

II. Dealkylation and Isomerization Reactions on Various Solid Acid Catalysts

INTRODUCTION

In the previous paper (1), the reactivity of a series of alkylbenzenes in the dealkylation reaction on two kinds of solid acid catalysts was correlated with $\Delta H_{C^*}(R_1)$, the enthalpy change of hydride abstraction from the corresponding paraffin.

In the present work, this correlation was found to hold generally over various kinds of solid catalysts. Furthermore, a linear

relationship of the reaction rates was observed among the dealkylation and some other acid-catalyzed reactions over the various kinds of solid catalysts. The latter relationship would suggest that the catalytic activity of a catalyst for one of these reactions, for instance, the dealkylation of isopropylbenzene, can be employed as a variable which characterizes the catalyst itself.

TABLE 1
CATALYSTS

No.	Symbol	Catalyst Name	γ_i'	$\log k_i(0)$	Surface area ^a (m ² /g)	Composition	Remarks
1	SA-1	Silica-alumina	0.124	12.8	540	13% Al ₂ O ₃	<i>b</i>
2	[SA-1-Na-1	Silica-alumina-NaOH	0.130	13.0	450	0.048 meq Na/g	<i>c</i>
3	SA-1-Na-2	Silica-alumina-NaOH	0.143	13.8	480	0.087 meq Na/g	<i>c</i>
4	SA-1-Na-3	Silica-alumina-NaOH	0.148	13.2	480	0.168 meq Na/g	<i>c</i>
5	SA-Na-HCl	Silica-alumina-NaOH-HCl	0.126	12.9	—	0.119 meq Na/g	<i>d</i>
6	SA-Na-HAcO	Silica-alumina-NaOH-HAcO	0.139	13.0	—	0.200 meq Na/g	<i>d</i>
7	A-B-1	Alumina-boria	0.127	12.9	290	10% B ₂ O ₃	<i>e</i>
8	SM-1	Silica-magnesia	0.160	13.4	560	16% MgO	<i>f</i>
9	Al-S	Aluminum sulfate on SiO ₂	0.120	12.7	—	0.4 mmole Al ₂ (SO ₄) ₃ /g	<i>g</i>
10	A-3	Alumina	0.167	12.2	170		<i>h</i>
11	A-3-F	Alumina-NH ₄ F	0.150	14.0	80		<i>i</i>

^a Measured by the BET method with N₂.

^b "Nippon Cat," a cracking catalyst of the Shokubai Kasei Co.

^c By impregnation of SA-1 with the respective amount of NaOH aq. soln.

^d By treatment of SA-Na (another lot of silica-alumina impregnated with NaOH) with the respective acid.

^e By coprecipitation of Al(NO₃)₃ and H₂BO₃ with NH₄OH.

^f TY-13, a cracking catalyst of the Nikki Kagaku Co.

^g By impregnation of silica gel with Al₂(SO₄)₃ aq. soln.

^h F-110, an active alumina of Alcoa.

ⁱ By treatment of A-3 with NH₄F aq. soln.

TABLE 2
REAGENTS

No.	Abbreviation	Reagent	Reaction	$\lambda(r)^a$	$\kappa(r)^a$
1	Et	Ethylbenzene	Dealk.	1.06	-1.20
2	<i>n</i> -Pr	<i>n</i> -Propylbenzene	Dealk.	1.02	-0.90
3	iso-Pr	Isopropylbenzene	Dealk.	1.00 ^b	0.00 ^b
4	<i>n</i> -Bu	<i>n</i> -Butylbenzene	Dealk.	1.02	-0.84
5	<i>sec</i> -Bu	<i>sec</i> -Butylbenzene	Dealk.	0.97	0.40
6	<i>tert</i> -Bu	<i>tert</i> -Butylbenzene	Dealk.	0.86	1.25
7	CHE	Cyclohexene	Isom.	1.00 ^c	1.43 ^c
8	<i>o</i> -X	<i>o</i> -Xylene	Isom.	1.02 ^d	-0.58 ^d

^a See text.^b By definition.^c At 300°C.^d At 450°C.

EXPERIMENTAL

The rate constants were measured by means of the microcatalytic gas chromatographic technique (1, 2). The catalysts used in this work are listed in Table 1, together with some of their properties. All of them were calcined at 550°C for 8 hr in the atmosphere. The reagents used in this work are listed in Table 2. The details of the experimental procedures are described in the previous paper (1).

RESULTS AND DISCUSSION

The following equation was proposed for the dealkylation reaction of monoalkylbenzenes on SA-1 and SM-1 in the previous paper (1):

$$\log k_i(R_1) = \log k_i(0) - \gamma_i' \Delta H_{C^+}(R_1) / 2.303RT \quad (1)$$

where $k_i(0)$ is a characteristic value dependent only on the catalysts and the kind of reactions, but not upon the reactants. This equation was found to hold good in the dealkylation reaction of monoalkylbenzenes on all catalysts used in the present work, as is shown in Fig. 1, where some examples are plotted. Thus, the rate of dealkylation at 400°C on solid acids can be generally estimated by Eq. (1) by using the well-known values of $\Delta H_{C^+}(R_1)$ and two measured values of $k_i(0)$ and γ_i' , which are given in Table 1. The value of γ_i' is rather small for the catalyst of high catalytic activity, but it varies only a

little among catalysts: 0.12 for Al-S is the minimum and 0.167 for A-3 the maximum.

Comparison of the catalytic activity among dealkylation and isomerization reactions is made over the catalysts given in

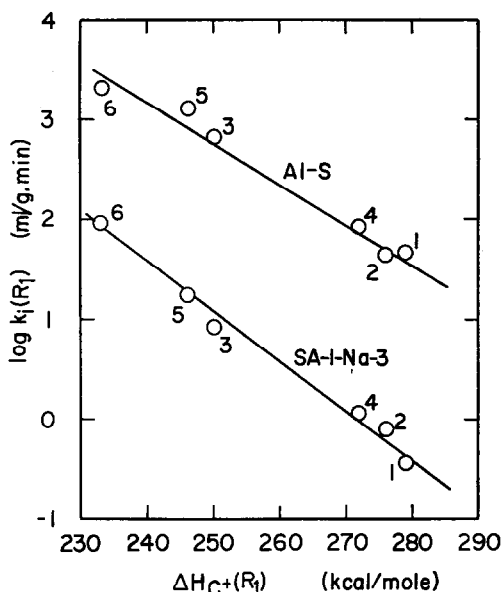


Fig. 1. Rate constants of dealkylation vs. the enthalpy change for hydride abstraction, $\Delta H_{C^+}(R_1)$. Numbers represent the reactants given in Table 2.

Table 1. Deisopropylation of isopropylbenzene was tentatively selected as the standard reaction of the heterogeneous acid catalysis. Correlation among them is partly shown in Fig. 2. The abscissa gives the

logarithm of the rate constant of this standard reaction. The ordinate gives the logarithm of the rate constants of four kinds of representative reactions. Rate constants of the isomerization reactions were measured in the same way as in the dealkylation (3). The reaction temperature of isomerization of cyclohexene to methylcyclopentene and that of *o*-xylene to *m*-xylene were 300° and 450°C, respectively. There are fine linear relationships among these constants of acid-catalyzed reactions with a spread of about three orders of magnitude, including some deviation of Al-S in the cyclohexene isomerization. These relationships can be formulated by the following equation:

$$\log k_i(r) = \lambda(r) \log k_i(\text{iso-Pr}) + \kappa(r) \quad (2)$$

where $k_i(r)$ and $k_i(\text{iso-Pr})$ are the rate constant of the reaction r and that of deisopropylation over the i th catalyst, re-

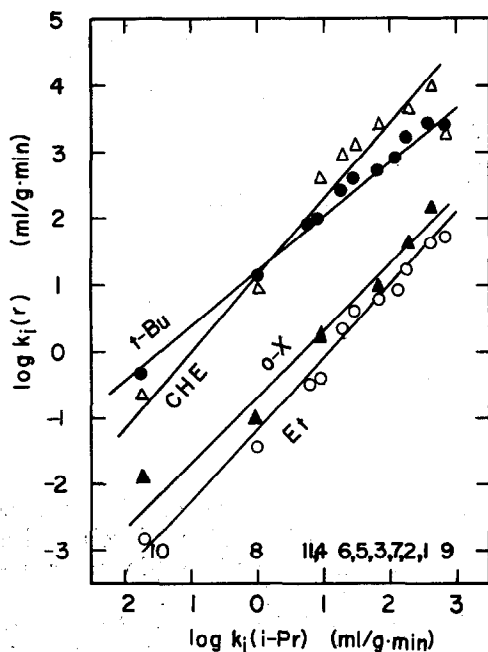


FIG. 2. Correlations among rate constants of dealkylation and isomerization reactions on the solid acid catalysts: Δ , isomerization of cyclohexene (CHE); \bullet , dealkylation of *tert*-butylbenzene (*t*-Bu); \blacktriangle , isomerization of *o*-xylene (*o*-X); \circ , dealkylation of ethylbenzene (Et). Numbers are for the catalysts given in Table 1.

spectively, and both $\lambda(r)$ and $\kappa(r)$ are constants dependent only upon the reaction r . Hence activity on a certain catalyst can be estimated by Eq. (2) with the knowledge of $\lambda(r)$ and $\kappa(r)$. The values of $\lambda(r)$ and $\kappa(r)$ are given in Table 2; $\lambda(r)$ is almost unity for all reactions. In the case of the dealkylation, Eq. (2) will be derived from Eq. (1), as far as γ_i' is approximately linear to the rate constant of a certain reactant, e.g., isopropylbenzene; details will be given in a future paper.

Fine correlations obtained among these reactions to be described by Eq. (2) would

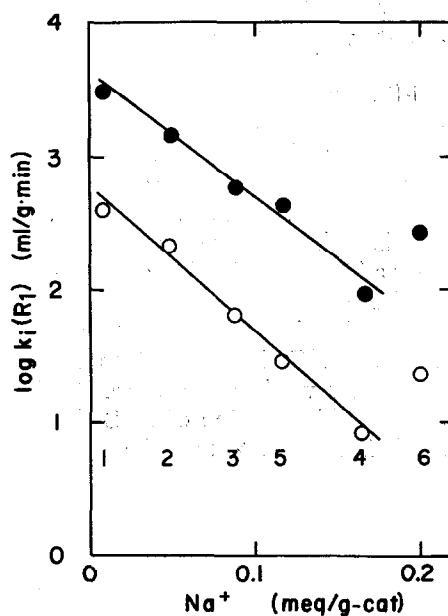


FIG. 3. Rate constants of dealkylation vs. the sodium content of the SA-1 and SA-1-Na catalysts. Open circles are for iso-propylbenzene and solid ones for *tert*-butylbenzene.

suggest that the mechanism of these reactions, including dealkylations and isomerizations, on these catalysts are similar to each other and that some common nature, presumably the acidity, of the catalysts would play an essential role in their catalytic activity.

In Fig. 3, the amount of Na^+ ion in the set of the SA-1-Na catalysts is compared with their catalytic activity. The logarithm of the rate constants is linearly correlated with the amount of Na^+ ion except for SA-

1-Na-HAcO. This fact may be understood if the reaction rate is not determined simply by the amount of acid sites, but is correlated substantially with the acid strength of the catalysts. The correlation of the acid strength with the catalytic activity in some acid-catalyzed reactions was reported by Dzisko (4).

Among the various catalysts employed, alumina sulfate on silica gel, Al-S, has some particular features. Al-S is as high as or even higher than SA-1 in catalytic activity for dealkylation and xylene isomerization, while the former is lower than the latter for the cyclohexene isomerization. The γ_i' value of Al-S is a little smaller than that of SA-1, which suggests that Al-S may have stronger acid sites than SA-1, according to the tendency of γ_i' values among the SA-1-Na series where the stronger acid sites were successively poisoned with sodium ions. Moreover, Al-S, in fact, is liable to lose its catalytic activity by additional injection of the reactant pulse. If the cyclohexene isomerization reaction, which takes place at a temperature as low as 300°C, is assumed to be catalyzed even by weaker acid sites, the lower activity for this reaction of Al-S than that expected from Fig. 2 may be reasonably

explained by its strong acidic nature, while its content is presumably small. Actually strong acid sites were detected on this catalyst by the preliminary measurement with the Hammett indicators.

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Dependence of the Catalytic Activity on Thickness of the Oxide Layer on Metal

One of the experimentally verifiable conclusions resulting from Volkenstein's electronic theory of catalysis is the effect of thickness of the oxide layer deposited on a metal on its catalytic activity and selectivity (1, 2). The theory postulates that the catalytic activity should change on passing from oxide layers of thickness smaller than the so-called "screening length" (10^{-5} – 10^{-6} cm) to layers of greater thickness.

The character of this change is determined by a number of parameters involving

both the catalyst (sign of the surface charge, position of the Fermi level) and a reaction which takes place (donor or acceptor rate-determining step).

The theoretical dependence of the reaction yield on the parameters given above is rather complex, the reaction yield decreasing or increasing monotonically with the thickness of oxide layer in some cases, or passing through an extremum for some systems of parameters. The aim of the present work has been to test experiment-