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An Application of $H_{0,\mathrm{max}}$ for Estimating the Catalytic Action of Solid Acids and Bases in the Isopropylation of *m*-Cresol

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A method of estimating the acid-base property of the active sites in terms of the correlation between the catalytic activities of various solids and their $H_{0,\mathrm{max}}$ values is presented. The $H_{0,\mathrm{max}}$ denotes an H_0 value of the strongest acidic sites and/or conjugate acids of the strongest basic sites. The types of catalytic actions over oxides, hydroxides, a sulfide, sulfates, phosphates, tungstates, and multi-component solid acids in the liquid-phase isopropylation of *m*-cresol without a solvent were classified into three groups: *via* a carbonium ion, *via* a carbanion, and concerted actions. The selectivity for the ortho-isopropylation over every catalyst increased with the increase of $H_{0,\mathrm{max}}$, and this effect of $H_{0,\mathrm{max}}$ was explained by the orientation of the adsorbed *m*-cresol on the catalyst surface.

It has been well known that a catalytic action changes continuously with the variation in the acid-base property of catalysts.[1,2] A quantitative description of the property with a universal parameter is required for reaction analysis, catalyst design, and developemtnt.[1] In liquid-phase reactions, the p*H* and acidity functions (*e.g.*, H_0 and H_- defined by Hammett *et al.*) have often been used as the parameters of homogeneous catalysts.[2] The electronegativities of metal ions[1] and effective negative charges on combined oxygens[1] have sometimes been used as the parameters of solid catalysts, but they are insensitive to the surface structure.[3]

As a measure of the acidic property of solid acid catalysts, "the highest acid strength" on the H_0 scale has been used in correlations with the catalytic activity and the selectivity for estimating catalytic actions.[4] Recently, the present authors reported a new titration method[5] of the acid-base strength distribution on the common H_0 scale, where the H_0 of the basic sites denotes the ability of proton donation of the conjugate acids. On the acid-base strength distributions of various solids, an H_0 value (termed $H_{0,\mathrm{max}}$) which indicates the H_0 value of the strongest acidic sites and/or the strongest basic sites was found. The $H_{0,\mathrm{max}}$ of acidic sites has essentially the same value as the highest H_0 value. The acidic sites of $H_0 \geq H_{0,\mathrm{max}}$ and the basic sites of $H_0 \leq H_{0,\mathrm{max}}$ coexisted on the same solid surface where both sites were measured. Therefore, the role of $H_{0,\mathrm{max}}$ as a parameter indicating a basic property as well as an acidic property on a common H_0 scale is noticeable.

On the other hand, the author and others[6] have been studying the development of solid catalysts in the liquid-phase isopropylation of *m*-cresol (I) with propylene, in order to prepare thymol (II), an important starting material for menthol. The isopropylation involved the multiple formation of the nuclear-substituted products and their ethers. It could not be estimated, on the basis of the literature,[7] whether and how the catalytic activity and the selectivity for the *ortho*-isopropylation of the OH group in I varied with the surface properties of the catalysts. In the vapor phase,[8] a few kinds of solids were investigated, but the results did not provide a guide for the catalyst development.

In this paper, $H_{0,\mathrm{max}}$ will be presented as a useful parameter for estimating the acid-base property of the active sites and the catalytic actions over a solid acid, base, and acid-base bifunctional catalysts.

An Approach to Estimate Catalytic Actions

The catalytic activities of solid acid-base catalysts were schematically correlated with their $H_{0,\mathrm{max}}$ values as is illustrated in Fig. 1 in the following semiquantitative approach. In the $R+R'H \rightarrow R''$ reaction, where the order of the acid strength of the reactants is $R'H>R$ and where the order of base strength is $R>R'H$, the catalytic action is expected to involve the formation of one or two activated species, *i.e.*, a carbonium ion (RH^+), a carbanion (R'^-), or coordination complexes (R_p and $R'H_p$) which are formed by acidic (A) and/or basic site (B).[9] R_p and $R'H_p$ represent

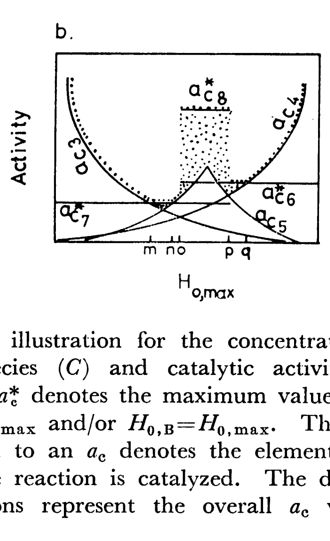


Fig. 1. An illustration for the concentration of activated species (C) and catalytic activities (a_c) *vs.* $H_{0,\mathrm{max}}$. a^*_c denotes the maximum value of a_c when $H_{0,A}=H_{0,\mathrm{max}}$ and/or $H_{0,B}=H_{0,\mathrm{max}}$. The numerical subscribed to an a_c denotes the elementary step *via* which the reaction is catalyzed. The dotted curves and regions represent the overall a_c value to be observed.

a kind of activated complex, $\{B^{+\delta}\rightarrow R^{-\delta}\cdots H^{+}\cdots A'^{-}\}$ and $\{B\cdots H^{+}\cdots R'^{+\delta-1}\rightarrow A^{-\delta}\}$. H'A denotes an acidic site (A) of the Brønsted type.

When the reaction proceeds *via* RH^{+} and/or R'^{-}, the strongest sites on the catalyst surface will be most effective in activating each reactant. At a low coverage of acidic and/or basic sites, the H_0 value of the strongest acidic or basic sites, $H_{0,\max}$, will affect the catalytic action more strongly than the site amounts of various strengths.

Then ratios of an activated ionic specie to reactant in an equilibrium may be expressed as:[2c]

$$\log(C_{\mathrm{RH}^+}/C_{\mathrm{R}}) = \alpha - H_{0,\max};\quad \alpha = \mathrm{p}K_{\mathrm{RH}^+} - \log(f_{\mathrm{Z}}f_{\mathrm{RH}^+}/f_{\mathrm{ZH}^+}f_{\mathrm{R}}) \tag{1}$$

$$\log(C_{\mathrm{R}'^-}/C_{\mathrm{R'H}}) = H_{0,\max} - \beta;\quad \beta = \mathrm{p}K_{\mathrm{R'H}} - \log(f_{\mathrm{Z}}f_{\mathrm{R'H}}/f_{\mathrm{ZH}^+}f_{\mathrm{R}'^-}) \tag{2}$$

where C, f, and K denote a concentration, an activity coefficient, and an ion dissociation constant defined by the suffix, and where $H_{0,\max}$ corresponds to the strongest ability of the proton donation of acidic sites or that of the conjugate acids of basic sites to Z.[5,10] Z represents the indicator base for the titration. C_{R} and $C_{\mathrm{R'H}}$ are regarded as the concentrations of R and R'H in a phase in contact with the surface of physically adsorbed on the surface. The correlation between C_{RH^+} or $C_{\mathrm{R}'^-}$ and $H_{0,\max}$ in a given reaction medium is illustrated in Fig. 1-a.

In a concerted action, proton or electron transfer between a reactant and active sites will be partial or imperfect. The strength of the individual action of active sites will go in parallel with their acid or base strengths.[3] Therefore, the strongest acidic or basic sites and the basic or acidic sites adjacent to them will be most effective in activating each reactant. It can be postulated as the first approximation that the functions of the strengths of active sites against $(C_{\mathrm{R_p}}/C_{\mathrm{R}})$ or $(C_{\mathrm{R'H_p}}/C_{\mathrm{R'H}})$ are expressed by $\{(\alpha'-H_{0,\max})+(H_{0,\mathrm{B}}-\beta')\}$, $\{(\alpha'-H_{0,\mathrm{A}})+(H_{0,\max}-\beta')\}$, $\{(\alpha''-H_{0,\max})+(H_{0,\mathrm{B}}-\beta'')\}$, and $\{(\alpha''-H_{0,\mathrm{A}})+(H_{0,\max}-\beta'')\}$, analogously to Eqs. 1 and 2. Here, $H_{0,\mathrm{A}}$ and $H_{0,\mathrm{B}}$ denote the H_0 value of the acidic or basic sites which are adjacent to the strongest basic or acidic sites respectively. That is, the arrangement of sites with various H_0 values plays an important role, as does the $H_{0,\max}$ value.[9] Provided that α', β', α'', and β'' are independent of $H_{0,\max}$, $C_{\mathrm{R_p}}$ and $C_{\mathrm{R'H_p}}$ are functions of $(H_{0,\mathrm{B}}-H_{0,\max})$ or $(H_{0,\max}-H_{0,\mathrm{A}})$. Because of $H_{0,\mathrm{B}}\leq H_{0,\max}$ and $H_{0,\mathrm{A}}\geq H_{0,\max}$, $C_{\mathrm{R_p}}$ and $C_{\mathrm{R'H_p}}$ have their maximum values, independent of $H_{0,\max}$, when $H_{0,\mathrm{B}}=H_{0,\max}$ and $H_{0,\mathrm{A}}=H_{0,\max}$. This corresponds to the case when the extreme surface where the acidic sites and the basic sites having $H_0=H_{0,\max}$ are adjacent to each other. In Fig. 1-a, $C_{\mathrm{R_p}}$ and $C_{\mathrm{R'H_p}}$ are illustrated as horizontal curves, which vary with the arrangement of sites. Here, the formation of R_p or $R'H_p$ can be expected only when $C_{\mathrm{R_p}}$ or $C_{\mathrm{R'H_p}}$ is greater than C_{RH^+} or $C_{\mathrm{R}'^-}$ respectively.

The activated species over active sites will participate in the following elementary steps:

$$RH^{+} + R'H \ (3);\quad R + R'^{-} \ (4);\quad RH^{+} + R'^{-} \ (5);$$

$$R_p + R'H \ (6);\quad R + R'H_p \ (7);\quad R_p + R'H_p \ (8)$$

In the steps involving a single activated specie (Eqs. 3, 4, 6, and 7), the rates are proportional to the concentration of the corresponding specie. In the steps involving two activated species (Eqs. 5 and 8), the rates are not always proportional to their concentrations, but depend predominantly on the second power of the minor activated specie. The catalytic activities (a_c's) of solids *via* each elementary step involving the formation of activated species in Fig. 1-a are illustrated in Fig. 1-b. Among Steps (3) to (8), the catalytic action of a solid with an $H_{0,\max}$ value involves the step which contributes to the highest a_c value. Then, the overall a_c throughout the $H_{0,\max}$ values illustrated by the dotted curve and the dotted regions in Fig. 1-b. The overall a_c means the a_c value observed experimentally.

The shape of the overall a_c curve and region depends on the acid-base properties and structures of the reactants concerned; especially, $C_{\mathrm{R_p}}$ or $C_{\mathrm{R'H_p}}$ will increase if the reactant possesses a functional group which accepts the push-pull action of the active sites.[9] It may be remarked that the bump and fall of the overall a_c curve reflects well the change in the predominant catalytic action at $H_{0,\max}=m$, n, or o, and at p or q on the abscissa. Therefore, the acid-base properties of the active sites and their catalytic actions can be estimated in terms of the correlation between a_c and $H_{0,\max}$ over various catalysts ranging widely in $H_{0,\max}$ values.

The correlations in Fig. 1 are similar to those in a homogeneous catalyst system,[2a] but somewhat different because of the effects of the "surface heterogeneity"[11] and the reduced freedom of an adsorbent, so that it reacts only with another species in its vicinity.

Results and Discussion

The formulae of the products and *m*-cresol (I) are shown in Fig. 2. The H_0 values of the strongest acidic sites ($\{H_{0,\max}\}_{\mathrm{A}}$) and the conjugate acids of the strongest basic sites ($\{H_{0,\max}\}_{\mathrm{B}}$) of catalysts and the compositions of the reaction mixtures are summarized in Table 1. Here, the catalysts are identified by the numerals used in the Experimental section. The values of $\{H_{0,\max}\}_{\mathrm{A}}$ and $\{H_{0,\max}\}_{\mathrm{B}}$ were the same when both of them were obtained. The $\{H_{0,\max}\}_{\mathrm{B}}$ values of CaO, $Ca(OH)_2$, and MgO were all greater than 6.8, although they could not be determined exactly because of the formation of a precipitate during basicity measurements.[5] Both $\{H_{0,\max}\}_{\mathrm{A}}$ and $\{H_{0,\max}\}_{\mathrm{B}}$ will be used below as the $H_{0,\max}$ value of a catalyst. γ-Al_2O_3 is sometimes regarded as acidic,[8] but no acidity of $H_0\leq 6.8$ was observed on γ-Al_2O_3 in this study. Some of the reaction mixture contained resin, but the resin content was not more than 5 mol% at the conversion of $I=90$ mol% and so was ignored in this study. CaO gave *ortho*-isopropylated products exclusively.[6]

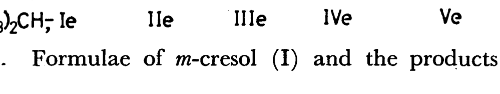


Fig. 2. Formulae of *m*-cresol (I) and the products.

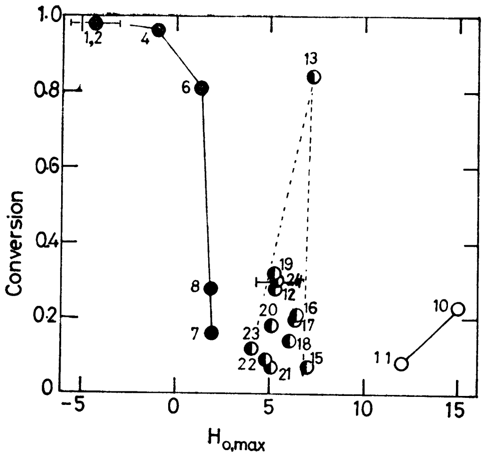


Fig. 3. Correlation between conversion and $H_{0,\max}$ in the isopropylation at 300 °C for 4 h.
●: $H_{0,\max}\leq 2$, ◐: $4\leq H_{0,\max}<8$, ○: $H_{0,\max}>10$.

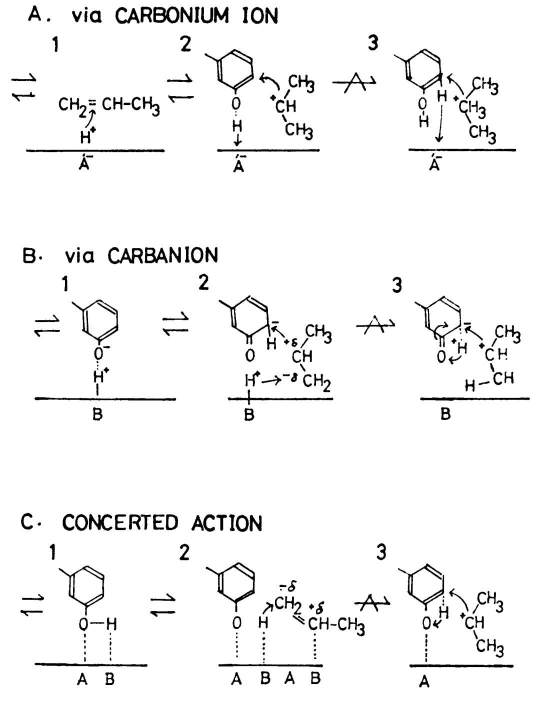
Apparent a_c vs. $H_{0,\max}$ Plots and Catalytic Actions. An apparent a_c was obtained as a total conversion of I (mole fraction) at a constant time and temperature. In Fig. 3, the conversions are plotted against the $H_{0,\max}$ values in the —5.6—+15 range. *m*-Cresol is a stronger acid ($\mathrm{p}K_a \fallingdotseq 10$) than propylene ($\mathrm{p}K_a \fallingdotseq 35$[12]). Therefore, catalytic actions *via* the isopropyl cation, the *m*-toluenide anion, or coordinated species of I and/or propylene were expected. The curves through the apparent a_c's in Fig. 3 indicate a bump-and-fall profile similar to the overall a_c curve in Fig. 1. The catalysts may be classified into three groups in terms of the $H_{0,\max}$ value: ≤ 2 (Group 1), 4—8 (Group 2), and ≥ 10 (Group 3).

In Fig. 3, the a_c in Group 1 increases monotonously with the decrease in $H_{0,\max}$ values. The catalytic action corresponds to Eq. 3, and can be explained by Scheme A.[8,13] The isopropyl cation must be formed by the acidic sites of $H_0\leq 2$. A'^- is more strongly basic than the original basic sites on the surface; the H_0 of the original basic sites is less than $H_{0,\max}$. Provided that the reaction occurs on a solid surface, the adsorption of I on A'^- is probable.

The a_c in Group 3 is regarded as increasing monotonously with $H_{0,\max}$. This corresponds to Eq. 4. Therefore, the catalytic action must proceed *via* the carbanion, as is shown in Scheme B. Over the basic sites of $H_0\geq 10$, the abstraction of a proton from the OH group of I occurs easily in Step 1. Hence, *m*-toluenide anions are formed.

In Fig. 3, the plots of Group 2 are raised to various heights above the extension from the conversion-$H_{0,\max}$ curves of Groups 1 and 3. The a_c's of Group 2 correspond to a_{c5}, a_{c6}, a_{c7}, or a_{c8}, and the catalytic action of Eq. 5, 6, 7, or 8 is estimated. Provided that *m*-cresol and/or propylene can accept a concerted action, the variations among the a_c's of Group 2 can be explained in terms of their dependence on the arrangement of sites on the surface. This arrangement will be most suitable for concerted actions over γ-Al_2O_3 (No. 13), while it will be most inadequate over the catalysts plotted at the bottom in Group 2 (21, 22, and 15). The most effective catalytic action on the overall a_c of catalysts corresponds to Eq. 8.

On the solid surfaces in Group 2, acidic and basic sites of moderate strength coexist. Compared with Group 1 or 3, the acidic sites in Group 2 are too weak to protonate propylene or to abstract a proton from the OH group of I. Therefore, concerted actions may be postulated as Scheme C. On the surface of a metal oxide, I will be adsorbed by leaving a proton on an oxygen anion (B) and by forming a *m*-tolyloxide with the adjacent metal ion (A). This corresponds to the adsorption model of phenol on MgO[14] and may be comparable to the phenoxide formation on γ-Al_2O_3.[15] It should be noted that the smaller the H_0 of conjugate acidic sites (BH^+), the more easily isopropyl cations are formed. In Scheme C, it is assumed that isopropyl cations are formed by the proton from the OH group of I. As supporting evidence, isopropyl *m*-tolyl ether (I_e) was not isopropylated over CaO under the same conditions as in the isopropylation of I.



Effects of $H_{0,\max}$ on the Selectivity. In order to compare it with the *para*-isopropylation, the selectivity for the *ortho*-isopropylation (ϕ) was defined as follows:

$$\phi=\frac{\text{total } ortho\text{-isopropylated products}}{\text{total isopropylated products except } I_e}$$

where one-half of the *ortho*-*para*-isopropylated products (V and V_e) were considered the ortho-isopropylated products.

In Fig. 4, the ϕ's are plotted against the $H_{0,\max}$ values by using the data at the conversion of $I\geq 0.2$. At a conversion of less than 0.2, the trace of the para-isopropylated products could not be detected with sufficient accuracy. ϕ increases roughly with the $H_{0,\max}$ values. An increase in $H_{0,\max}$ means an increase in the strength of the basic sites and a decrease in the strength of the acidic sites. Therefore, it can be interpreted in terms of the orientation of I adsorbed on the surface. The electrostatic repulsion between

Table 1. $\{H_{0,\max}\}_A$, $\{H_{0,\max}\}_B$, and composition of reaction mixtures

Catalyst			Composition						
No.	$\{H_{0,\max}\}_A$	$\{H_{0,\max}\}_B$	I	II	III	IV	V	I_e	II_e
1	−5.6∼−3	—	2.3	16.7	15.0	5.7	23.2	—	21.8
2	−5.6∼−3	—	2.5	18.0	10.8	2.8	34.1	—	18.3
4	−1.0	—	4.5	25.6	4.2	10.5	50.7	—	4.5
6	1.3	—	19.2	43.5	—	6.7	16.6	1.6	1.8
7	2.0	2.0	84.5	12.6	—	—	—	2.9	—
8	2.0	2.0	71.8	14.9	4.8	1.5	—	7.0	—
10	—	15	76.8	21.1	—	—	—	2.1	—
11	—	12	91.7	8.3	—	—	—	—	—
12	5.3	5.3	71.9	18.5	—	2.3	—	7.3	—
13	—	7.2	16.3	62.6	3.8	9.4	—	1.2	3.2
15	—	7	92.7	7.3	—	—	—	—	—
16	6.4	6.4	78.6	13.3	—	1.4	—	6.7	—
17	6.3	6.3	80.6	13.8	—	—	—	3.4	—
18	6.0	6.0	86.5	9.6	—	—	—	3.9	—
19	5.2	5.2	67.8	20.7	2.7	3.8	—	2.7	2.4
20	5.2	5.2	82.4	11.8	—	—	—	5.8	—
21	5.0	5.0	93.1	6.9	—	—	—	—	—
22	4.8	4.8	90.6	9.4	—	—	—	—	—
23	4.0	4.0	86.6	13.4	—	—	—	—	—
24	4∼6.8	4∼6.8	70.2	16.5	—	2.4	—	5.2	4.4
25	—	>6.8	29.0	55.5	—	15.5	—	—	—
26	—	>6.8	92.9	7.1	—	—	—	—	—
27	—	>6.8	91.5	8.5	—	—	—	—	—

a) The compositions of the ethers other than I_e and II_e were as follows: Catalyst No. 1; IV_e, 9.9, V_e, 5.4, No. 2; IV_e, 6.6, V_e, 6.9, No. 6; III_e, 10.4, No. 13; IV_e, 3.5, No. 17; III_e, 2.2, No. 24; III_e, 1.5; the others were not detected.

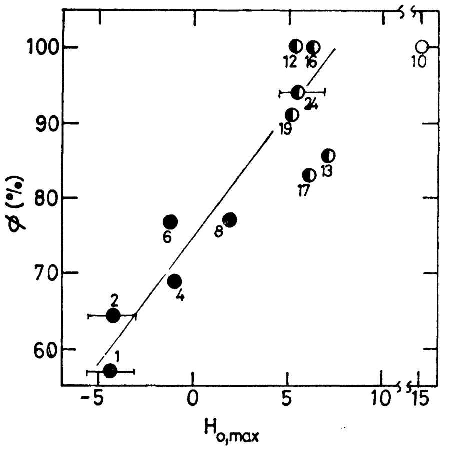


Fig. 4. Correlation between ϕ and $H_{0,\max}$ at the same reaction condition to Fig. 3. Catalysts are characterized by the same marks as used in Fig. 3.

π-electrons of the benzene ring of I and the surface will increase with an increase in the base strength (the ability of electron donation) of the surface, that is, with an increase in the $H_{0,\max}$ value. The distance of the *para*-position is further from the surface than the *ortho*-position. Consequently, ϕ increases with $H_{0,\max}$. The same interpretation has been presented in the methylation of phenol with methanol, for the *ortho*-selectivities over solid acids are lower than those over solid bases,[14,16] even though the interpretation in the literature is merely qualitative.

The $H_{0,\max}$ may, therefore, be considered a parameter to represent the surface acid-base property quantitatively. Apart from catalytic actions, $H_{0,\max}$ as a surface property of solid will be discussed elsewhere.[17]

Experimental

Catalysts. The following commercial available solids were ground and sieved to prepare a powder of 100—200 mesh. Oxides: WO_3 (6), Sb_2O_3 (7), BaO (10), γ-Al_2O_3 (13, Nikki Chemicals Co., Ltd.), ZnO (16), Bi_2O_3 (17), B_2O_3 (20), TiO_2 (22), ThO_2 (24), CaO (25), and MgO (27). Hydroxides: $Ba(OH)_2$ (15) and $Ca(OH)_2$ (26). A sulfide: ZnS (12). Sulfates: $Al_2(SO_4)_3$ (4) and $NiSO_4\cdot 7H_2O$ (8). Phosphates: $AlPO_4$ (18) and $Zn_3(PO_4)_2\cdot 4H_2O$ (19). Tungstates: $Na_2WO_4\cdot 2H_2O$ (11), $CaWO_4$ (21) and $MgWO_4$ (23). Others: Silica-Alumina-L (1, Nikki Chemicals Co., Ltd.) and Japanese acid clay (2, Wako Pure Chemicals Ind., Ltd.). The numerals in parentheses indicate the corresponding solids. The solids without proviso were of a guaranteed reagent grade. Prior to grinding, $NiSO_4\cdot 7H_2O$ and CaO were calcined at 300 °C for 4 h in a dry N_2 stream. The solids were stored in glass bottles in the same way as were the commercial reagent used in this study. No particular caution was taken to exclude the adsorption of a trace of moisture in the atmosphere.

Acid-Base Strength Distribution and $H_{0,\max}$. A new titration method[5] was used for the determination of acid-base strength distributions of the solids, which expressed in the distribution curves. The values of $\{H_{0,\max}\}_A$ and

$\{H_{0,\max}\}_B$ were obtained as the H_0 value at the intersection of the acid or base strength distribution curve and the abscissa indicating acidity=0 or basicity=0 respectively.[17] The $\{H_{0,\max}\}_A$ value was obtained when it was less than 6.8. The $\{H_{0,\max}\}_B$ value was obtained when it was greater than 1.5.

Isopropylation and Analysis of Reaction Products. Desired amounts of I (of a guaranteed reagent grade) and of a catalyst were weighed into an autoclave of a 100-ml capacity equipped with a magnetic stirrer and with gas inlet-outlet pipes. Displacing the air with dry N_2 gas, the apparatus was cooled to −60 °C. The liquid propylene was measured volumetrically as it passed into the autoclave through one of the pipes. The initial mole ratio of propylene to I was 3.0. The amount of the catalyst was 15 wt% against I. The apparatus was heated at 300 °C for 4 h and then cooled to room temperature. After the unreacted propylene had been released, the reaction mixture was dissolved with ether. The ether solution was washed with water, dried over Na_2SO_4, and concentrated. Then the reaction mixture was analyzed by means of a gas chromatograph, using a Kotaki Model GU-21A apparatus on a $2\,\text{m} \times 5\,\text{mm}\,\phi$ column packed with 20 wt% of silicone oil (D.C. 200) on Celite-545 (60—80 mesh). The column temperature was 165 °C, and He gas was used as the carrier at 1.2 kg/cm^2. Isopropyl benzoate was used as the internal standard. Some of the reaction mixture was fractionated into components by means of a modified fractional gas chromatograph, and each of them was identified by means of its infrared absorption spectrum in a Nujol mull.

The measurement of the acid-base strength distribution and that of the isopropylation were done at the same time.

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