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Mutarotation of α-D-Glucose over Several Al_2O_3 Catalysts

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The mutarotation of α-D-glucose to β-D-glucose has been studied at 25±0.1 °C using five kinds of alumina as catalysts. Two kinds of alumina with measurable surface basicities have exhibited high catalytic activities while the others with little surface basicities have exhibited low activities. Thus, the surface basic sites have been considered to be responsible for the catalytic activity observed. Any of crystal structures, surface areas, pore structures, and surface elemental compositions have no relation to the catalytic activity. It has also been revealed that the kinetics of the reaction is explained by a surface reaction mechanism

$$\alpha + 1 \underset{K_\alpha}{\rightleftarrows} \alpha_{ad} \overset{k_1}{\underset{k_2}{\rightleftarrows}} \beta_{ad} \underset{K_\beta}{\rightleftarrows} \beta + 1,$$

where 1, K_α, K_β, k_1, and k_2 denote the active site, the adsorption equilibrium constant for α, the adsorption equilibrium constant for β, the rate constant for the surface forward reaction, and the rate constant for the surface backward reaction, respectively, and the subscript ad denotes an adsorbed state. The result of kinetic analysis has revealed that $K_\beta > K_\alpha$, indicating that the adsorption of β-glucose is stronger than that of α-glucose. This also supports the view that the surface basic sites are responsible for the catalytic activity.

Although abundant information about the mutarotation of α-D-glucose (an optical rotation change brought about by the rearrangement of α-D-glucose to β-D-glucose) catalyzed by acids and bases in homogeneous solutions is available in literature,[1-3] we have only scanty information[4,5] about this reaction over heterogeneous catalysts. The mutarotation of α-D-glucose has been regarded as one of fundamental reactions related to enzymic biochemical reactions,[2] and heterogeneous catalyses in this field have been lately calling the attention of world scientists. It appears worthwhile, therefore, to accumulate basic knowledge about the heterogeneous catalysis of the glucose mutarotation reaction.

The present paper reports the results of a catalysis study on the mutarotation of α-D-glucose over several alumina catalysts at 25 °C. The kinetics of the reaction has been established and the activities of the alumina catalysts are compared with respect to their properties.

Experimental

Catalyst. Five kinds of alumina used as catalysts in the present study have been commercially obtained, and their main properties are shown in Table 1. Each of these catalysts was pulverized in a mortar for 30 min, and then dried in an oven at 120 °C for 24 h before use.

Catalyst Characterization. The following characterization experiments were carried out for each catalyst; crystal structure (powder X-ray diffraction; Rigaku Geigerflex 2320 instrument; Cu*Kα* radiation at 30 kV and 15 mA), surface elemental composition (XP spectra; Shimazu ESCA 750 instrument; Mg*Kα* radiation), surface area and pore structure (nitrogen adsorption at 77 K), surface basicity (benzoic acid titration method[6]).

Catalytic Activity. Anhydrous α-D-glucose (Nakarai Kagaku) was dried for 24 h in a desiccator containing P_2O_5 under a pressure of ca. 1 Pa and at a temperature of 60 °C. Dimethyl sulfoxide used as a solvent was dried for 24 h using calcium hydride and then followed by a vacuum distillation (ca. 10^3 Pa at 72 °C). The middle distillate, thus obtained, was kept in a bottle flashed with dry nitrogen.

The reaction was carried out in the following manner using a three-neck flask (300 cm^3). Firstly, 100 cm^3 of the dry solvent and 0.005 mol of α-D-glucose were taken into the flask flashed with dry nitrogen, and the flask was immersed in a water bath kept at a constant temperature of 25±0.1 °C. Then, the reactant solution was stirred with a magnetic stirrer and the catalyst powder was added to initiate the reaction. At appropriate time intervals, ca. 3 cm^3 of the reacting solution was withdrawn from the flask using a syringe equipped with a catalyst filter. The sample solution was analyzed using an automatic digital polarimeter (Union Giken PM-101 instrument). Such measurements as mentioned above were continued until no change in the optical

Table 1. Properties of Alumina Catalysts

Catalyst	Crystal from	Surface area	Pore volume	Pore size	Surface composition/atom %				
		$m^2\,g^{-1}$	$cm^3\,g^{-1}$	Å	Al	O	C	Si	Na
Al-1[a)]	γ	395	0.25	13	38.0	54.1	7.9	—	—
Al-2[b)]	χ	243	0.36	31	34.3	52.7	11.0	2.0	—
Al-3[c)]	χ	264	0.74	28	34.3	53.5	8.5	3.7	—
Al-4[d)]	χ	200	0.75	75	33.9	51.0	11.1	4.0	—
Al-5[e)]	χ	243	0.67	55	32.3	51.0	9.7	3.7	3.3

a) Activated alumina (Nakarai Kagaku), b) activated alumina (Nakarai Kagaku), c) Neobead-D (Mizusawa Kagaku), d) Neobread-DL (Mizusawa Kagaku), e) Neobead-P (Mizusawa Kagaku).

rotation (r) was observed (usually over 24 h).

Adsorption of Glucose. The amount of adsorption onto the catalyst was measured by a separate experiment. The experimental procedures were almost the same as those used in the activity measurement, except for the method of the glucose analysis. Namely, in this case, the sample solution taken out of the reaction system was analyzed to determine the total glucose using the anthrone colorimetric method;[7,8] an absorption intensity at 620 nm was measured using a Hitachi 330 spectrophotometer.

Results and Discussion

Mutarotation Activity. Part of the experimental results obtained in this work are shown in Fig. 1. The figure shows changes in the optical rotation (r) as a function of the reaction period (t). High activities of the catalysts Al-1 and Al-5 as well as low activities of the catalysts Al-2, Al-3, and Al-4 are evident in the figure. The dotted line in the figure represents the result of a repeated run over the Al-1 catalyst and demonstrates a good reproducibility of the measurement. The figure also contains part of the results of the adsorption measurements. It can be seen that the adsorption of glucose reaches equilibrium within 30 min while the mutarotation reaction is still continuing.

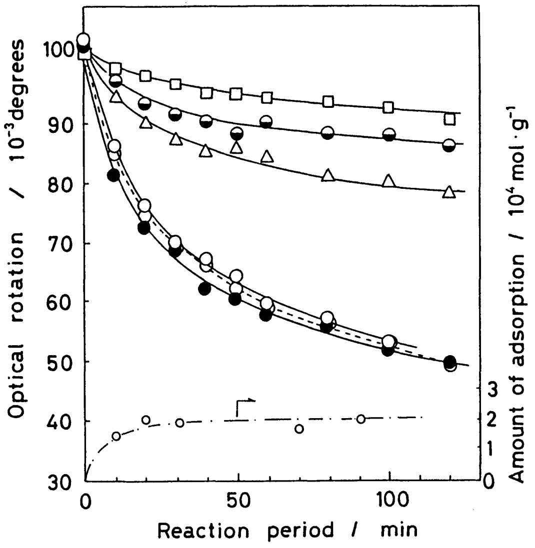

Fig. 1. Rates of mutarotation of α-D-glucose at 25 °C over alumina catalysts and the amount of glucose adsorption. ○: Al-1 (2.5 g), □: Al-2 (2.5 g), △: Al-3 (2.5 g), ◒: Al-4 (2.5 g), ●: Al-5 (2.5 g), ----: repeated run for Al-1 (2.5 g); initial concentration of glucose=0.05 mol·l⁻¹ (every cases mentioned above). -·-○-·-: amount of adsorption onto Al-5 (3 g; initial glucose concentration=0.056 mol·l⁻¹).

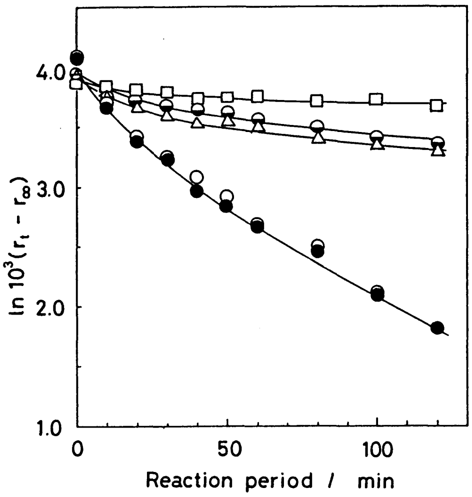

Fig. 2. The first order kinetic plots based on a homogeneous reaction model. ○: Al-1 (2.5 g), □: Al-2 (2.5 g), △: Al-3 (2.5 g), ◒: Al-4 (2.5 g), ●: Al-5 (2.5 g); initial concentration of glucose=0.05 mol·l⁻¹.

Kinetics. A homogeneous reaction model: As reported in literature,[1,2] the rearrangement of α-D-glucose to β-D-glucose accompanies a reduction of the optical rotation of the reacting solution until the reaction reaches equilibrium. In an homogeneous reaction, this change in the optical rotation obeys the first order reversible reaction kinetics.[1] Thus, the apparent rate constant defined by

$$\alpha \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \beta \tag{1}$$

can be obtained from

$$k_1 + k_2 = -(1/t)\ln[(r_t - r_\infty)/(r_o - r_\infty)], \tag{2}$$

where r_t, r_o, and r_∞ denote the optical rotation r at a reaction period t, r at $t=0$ ($r_o=r_\alpha$), and r at equilibrium ($t=\infty$), respectively.

Although the rate equation, Eq. 2, is very simple and has been employed by Pincock et al.[4] in analyzing their catalysis data over alumina catalysts, it appears to be an oversimplification to assume that fine catalyst powder suspended in a reaction solution can be regarded as a homogeneous molecular or an ionic catalyst similar to H_3O^+ or OH^-. Indeed, as can be seen in Fig. 2, plots of $\ln[(r_t-r_\infty)/(r_o-r_\infty)]$ against the reaction period t have been nonlinear. Pincock et al.[4] have attributed the deviation of the first order plot from the linearity to a catalyst poisoning and have infered that the poisoning is due to glucose.

The present authors consider that the oversimplification adopted in applying Eq. 2 has caused the disagreement between the theory and experiments. It is more likely that α-glucose and β-glucose are competing in adsorption onto active sites. It is reasonable to consider that the β-glucose produced by the reaction would occupy part of the active sites and retard the reaction.

Heterogeneous reaction models: On the basis of the above-mentioned discussion, the present authors have adopted the following heterogeneous reaction model:

$$\alpha + l \rightleftharpoons \alpha_{ad} \rightleftharpoons \beta_{ad} \rightleftharpoons \beta + l, \tag{3}$$

where l denotes an active site on the catalyst surface.

Although Pincock et al.[4)] have considered that the adsorption characteristics of α-glucose is identical with those of β-glucose, the present study assumes that the Langmuir type adsorption properties of α- and β-glucose are different from each other.

It must be pointed out that we have three different cases, even when the overall reaction is expressed by Eq. 3. Namely, there are three possible rate-determining steps, i.e. the surface reaction step, the adsorption step of α-glucose, and the desorption step of β-glucose. Each of these three cases yields its own rate equation, as can be seen below.

(1) When the surface reaction is the rate-determining step, the rate of decreasing of α-D-glucose concentration is expressed by

$$-\,\mathrm{d}[\alpha]/\mathrm{d}t = k_1[\alpha_{\mathrm{ad}}] - k_2[\beta_{\mathrm{ad}}], \tag{4}$$

where square bracket denotes the concentration, k_1 denotes the rate constant of the surface forward reaction, and k_2 denotes the rate constant of the surface backward reaction. If we define L_o, [G], K_α, and K_β as the total concentration of active sites, the total concentration of glucose $[\alpha]+[\beta]$, the adsorption equilibrium constants for α-glucose and β-glucose, respectively, Eq. 4 becomes

$$-\mathrm{d}X/\mathrm{d}t=[(1/(a+bX)][(\overrightarrow{k}_1+\overleftarrow{k}_2)/[\mathrm{G}]](X-k''), \tag{5}$$

where $X=[\alpha]/[\mathrm{G}]$, $a=(1/[\mathrm{G}])+K_\beta$, $b=K_\alpha-K_\beta$, $\overrightarrow{k}_1=k_1K_\alpha L_o$, $\overleftarrow{k}_2=k_2K_\beta L_o$, and $k''=\overleftarrow{k}_2/(\overrightarrow{k}_1+\overleftarrow{k}_2)$. An integration of Eq. 5 under the conditions that $X=1$ at $t=0$ and $X=X_\infty$ at $t=\infty$ gives

$$\begin{aligned}&[1/(1-X)]\ \ln[(X-X_\infty)/(1-X_\infty)]\\ &\quad=-At/(1-X)+B,\end{aligned} \tag{6}$$

where $A=(\overrightarrow{k}_1+\overleftarrow{k}_2)/(a+bX_\infty)$, and $B=b/(a+bX_\infty)$. It must be noted here that the relation $X_\infty=\overleftarrow{k}_2/(\overrightarrow{k}_1+\overleftarrow{k}_2)$ also results from the integration process. Now we can convert the variable X into the optical rotations r_t, r_o, and r_∞, i.e. $X=(r_t-r_\beta)/(r_\alpha-r_\beta)=(r_t-r_\beta)/(r_o-r_\beta)$ and obtain a final expression of the integral rate equation:

$$\begin{aligned}&[(r_o-r_\beta)/(r_o-r_t)]\ln[(r_t-r_\infty)/(r_o-r_\infty)]\\ &\quad=-At[(r_o-r_\beta)/(r_o-r_t)]+B.\end{aligned} \tag{7}$$

The rate equation, Eq. 7, can easily be compared with the experimental data. The value of the left hand side of Eq. 7 should have a linear relation with $(r_o-r_\beta)t/(r_o-r_t)$, and the straight line enables us to obtain the values of A and B. It must be pointed out that A should be positive because A has been defined by

$$A=(\overrightarrow{k}_1+\overleftarrow{k}_2)/[1+\{K_\alpha X_\infty+K_\beta(1-X_\infty)\}[\mathrm{G}]], \tag{8}$$

and $1-X_\infty>0$. On the other hand, B can be either positive or negative depending on the sign of $K_\alpha-K_\beta$, because B has been defined by

$$B=[\mathrm{G}](K_\alpha-K_\beta)/[1+\{K_\alpha X_\infty+K_\beta(1-X_\infty)\}[\mathrm{G}]]. \tag{9}$$

(2) When the adsorption of α-glucose is the rate-determining step, a rate equation with a form identical with that of Eq. 7 can easily be derived. In this case, however, the definition of A and B are different from those for the case (1), as we can see in Table 2.

(3) When the desorption of β-glucose is the rate-determining step, again a rate equation with the same form as Eq. 7 can be derived. The definition of A and B are, however, different from those for Eq. 7, as we can see in Table 2.

Comparison with experimental results: Plots of experimental values for $[(r_o-r_\beta)/(r_o-r_t)]\ \ln\ [(r_t-r_\infty)/(r_o-r_\infty)]$ against $(r_o-r_\beta)t/(r_o-r_t)$ values are exemplified in Figs. 3 and 4. Linear relations between the two quantities mentioned above are evident. This informs the validity of the heterogeneous reaction model discussed above. It must be pointed out that the linear plots shown in the figures reveal that $A>0$ and $B<0$. This implies that either the surface reaction mechanism (1) or the adsorption mechanism (2) is actually the case. The desorption mechanism (3) has to be excluded because this mechanism requires positive values of B (Table 2).

Although which of (1) and (2) is the true reaction mechanism can not be determined, from the kinetic treatments mentioned above, the adsorption data exemplified in Fig. 1 clearly indicate that the surface reaction mechanism is most probable. As already pointed out, the adsorption reaches equilibrium while the mutarotation reaction is still continuing (Fig. 1). If the adsorption of glucose controles the reaction rate,

Table 2. Properties of Kinetic Equations for Different Mechanisms

Rate-determining step	Definitions and properties of A and B	Notation
1. Surface reaction	$A=(\overrightarrow{k}_1+\overleftarrow{k}_2)/[1+\{K_\alpha X_\infty+K_\beta(1-X_\infty)\}[\mathrm{G}]]>0$ $B=[\mathrm{G}](K_\alpha-K_\beta)/[1+\{K_\alpha X_\infty+K_\beta(1-X_\infty)\}[\mathrm{G}]]>0$, or$<0$	$\overrightarrow{k}_1=L_oK_\alpha k_1$ and $\overleftarrow{k}_2=L_oK_\beta k_2$.
2. Adsorption of α-glucose[a)]	$A=(\overrightarrow{k}_1+\overleftarrow{k}_2)/[1+\tilde{K}(1-X_\infty)[\mathrm{G}]]>0$ $B=-\tilde{K}[\mathrm{G}]/[1+\tilde{K}(1-X_\infty)[\mathrm{G}]]<0$	$\overrightarrow{k}_1=L_o\tilde{k}_1$, $\overleftarrow{k}_2=L_o(K_\beta/K)\tilde{k}_2$, and $\tilde{K}=[(K_\beta/K)+K_\beta]$.
3. Desorption of β-glucose[a)]	$A=(\overrightarrow{k}_1+\overleftarrow{k}_2)/[1+\tilde{K}X_\infty[\mathrm{G}]]>0$ $B=[\mathrm{G}]\tilde{K}/[1+\tilde{K}X_\infty[\mathrm{G}]]>0$	$\overrightarrow{k}_1=L_oKK_\alpha\tilde{k}_1$, $\overleftarrow{k}_2=L_o\tilde{k}_2$, and $\tilde{K}=K_\alpha(1+K)$.

a) $\tilde{k}_1$ and $\tilde{k}_2$ denote the rate constants for the forward reaction and the backward reaction in the rate-determining step, respectively, and K denotes the equilibrium constant of the surface reaction $\alpha_{\mathrm{ad}} \rightleftarrows \beta_{\mathrm{ad}}$.

the reaction should reach equilibrium as soon as the adsorption reaches equilibrium. Thus, the mechanism (2) has to be discarded and we can conclude that the surface reaction mechanism (1) is most pertinent.

On the basis of the above-mentioned discussion, we can evaluate the kinetic parameters $\overrightarrow{k}_1$, $\overleftarrow{k}_2$, K_α, and K_β. For this purpose, linear relations between $(1/A)$ and [G] and between $([G]/B)$ and [G] together with the relation $\overleftarrow{k}_2/(\overrightarrow{k}_1+\overleftarrow{k}_2)=X_\infty$ are available.[9] Part of the linear relationships mentioned above are shown in Fig. 5 and kinetic parameters obtained are summarized in Table 3.

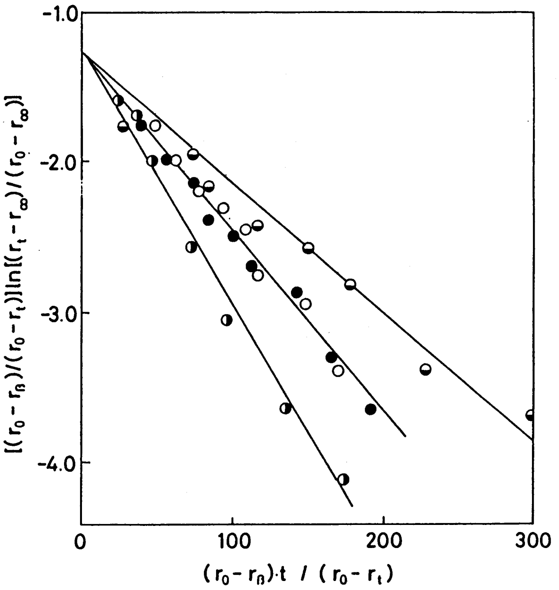

Fig. 3. Linear plots proving the applicability of the rate equation derived from a heterogeneous reaction model. ○: Al-1 (2.5 g), ◓: Al-5 (2.0 g), ●: Al-5 (2.5 g), ◑: Al-5 (4.0 g); initial concentration of glucose=0.05—0.056 mol·l^{-1}.

Activity and Property of Catalyst. As already pointed out, the Al-1 catalyst and the Al-5 catalyst exhibited approximately equal activities while crystal structures of these two catalysts were different from each other, i.e. γ-type for Al-1 and χ-type for Al-5 (Table 1). Furthermore, all of the less active Al-2, Al-3, and Al-4 catalysts were found to be the χ-type as the Al-5 catalyst while only the Al-5 catalyst exhibited a high catalytic activity. These facts inform that the crystal structures are not directly related to the catalytic activity. It has been reported by Pincock et al.[5] that α-alumina also exhibits a high catalytic activity for the glucose mutarotation.

Likewise, the surface areas, the pore sizes, and the surface elemental compositions shown in Table 1 did not influence the catalytic activities of the catalysts used in the present study. Insignificant relations between the catalytic activity and the pore structures shown in Table 1 and in Fig. 6 are particularly important, because this denies the pore diffusion controlling reaction mechanism. Pincock et al.[4] have also proven that the pore diffusion does not control the reaction rate by changing the size of the catalyst particle. An activation energy measurement would provide us with further support for the view mentioned above.

It appears most probable that the surface basic sites are responsible for the catalytic activity observed, though weak Brönsted acid sites have been postulated as the active sites over ordinary alumina catalysts.[4] As can be seen in Table 4, the Al-1 and Al-5 catalysts both exhibited high catalytic activities have been found to possess considerable amounts of surface basicity. On the other hand, the other catalysts (Al-2, Al-3, and Al-

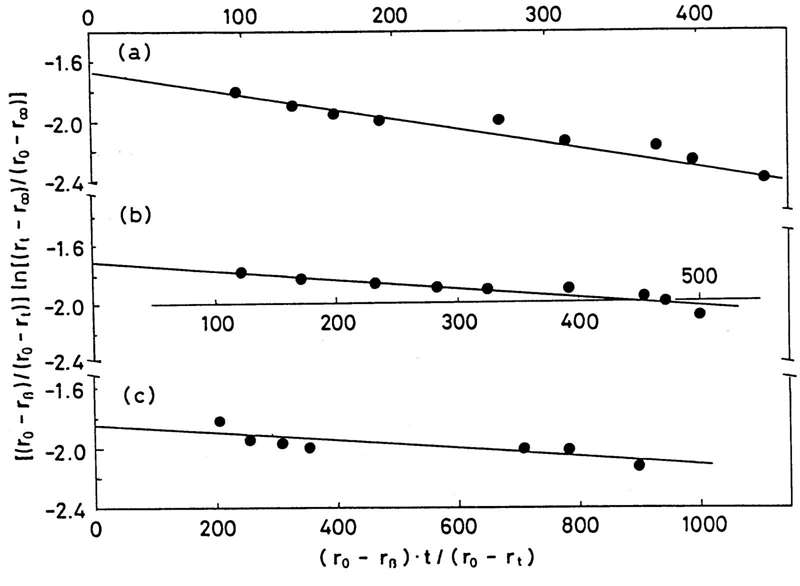

Fig. 4. Linear plots proving the applicability of the rate equation derived from a heterogeneous reaction model. (a) Al-3 (2.5 g), (b) Al-4 (2.5 g), (c) Al-2 (2.5 g); initial concentration of glucose=0.05 mol·l^{-1}.

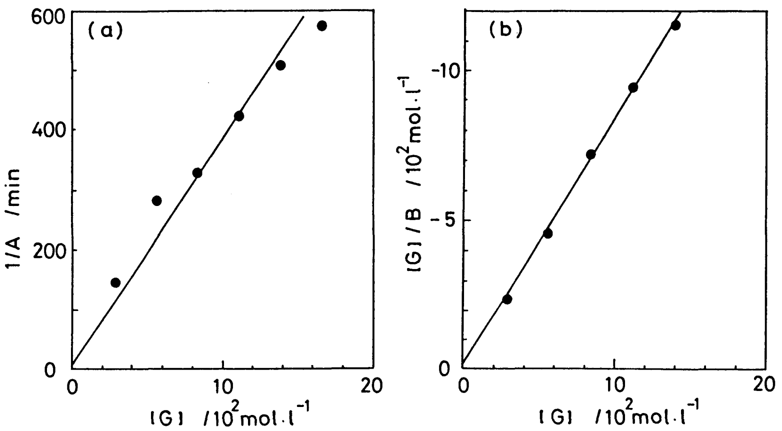

Fig. 5. Examples of linear plots between $1/A$ and [G] and between [G]/B and [G].

Table 3. Values for Kinetic Parameters[a)] Obtained with Al-5 Catalyst

$\overrightarrow{k}_1$ min^{-1}	$\overleftarrow{k}_2$ min^{-1}	K_α l·mol^{-1}	K_β l·mol^{-1}	L_o[b)] mol-site·l^{-1}	k_1 mol·min^{-1}·mol-site^{-1}	k_2 mol·min^{-1}·mol-site^{-1}
7.84×10^{-2}	2.62×10^{-1}	3.15×10^{2}	1.84×10^{3}	5.0×10^{-4}	4.98×10^{-1}	2.86×10^{-1}

a) For surface reaction controlling mechanism. b) Total concentration of basic sites in 100 cm^3 of the reactant solution containing 1 g of catalyst.

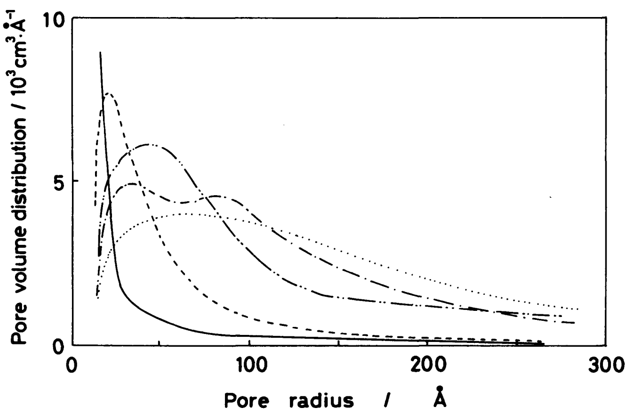

Fig. 6. Pore size distribution curves for the catalysts used. ——: Al-1, ----: Al-2, –·–·–: Al-3, ······: Al-4, –··–··–: Al-5.

4) which have exhibited low catalytic activities possess little surface basicities. Adsorbed water or surface hydroxyl groups might have been weak catalytic sites over these three catalysts.

More important information suggested by the basicity data shown in Table 4 is that the total basic sites ($H_- \geqq 7.3$) are considered to catalyze the reaction. As we can see in the table, the total basicity of the Al-1 catalyst is approximately equal to that of the Al-5 catalyst. This corresponds well with the experimental result, i.e. almost identical activities of these catalysts. On the other hand, the contents of stronger basic sites with H_- values larger that 9.3 is larger for the Al-5 catalyst than for the Al-1 catalyst. If we assume that the strong basic sites are responsible for the catalytic activity, the activity of the Al-5 catalyst must be much larger than that of the Al-1 catalyst. This does not agree with the experimental result.

Table 4. Surface Basicities of Catalysts

Catalyst	Surface basicity/m mol g^{-1}		
	$9.3 > H_- > 7.3$	$H_- > 9.3$	Total
Al-1	0.036	0.009	0.045
Al-2	0	0	0
Al-3	0	0	0
Al-4	0	0	0
Al-5	0.025	0.025	0.05

The surface reaction model coupled with the basic catalytic sites model is most probable in view of the different acidic properties of α- and β-glucose. Since the acid strength of β-glucose is about two times larger than that of α-glucose,[2)] a stronger adsorption of β-glucose onto the basic sites can be expected, and the relation $K_\beta > K_\alpha$ obtained by the kinetic analysis is quite reasonable. Thus, the rate constants, k_1 and k_2, have been evaluated by assuming that L_o represents the basic sites concentration in the reaction system. The results are also included in Table 3.

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