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Elimination Reactions on Solid Acid Catalysts

II. Esterification of Ethanol with Acetic Acid

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Esterification of ethanol with acetic acid on silica-alumina, alumina-boria, sodium-poisoned silica-alumina, and alumina has been investigated by the pulse technique and compared with ethanol dehydration. The catalysts could be classified into two groups according to their catalytic behavior; silica-alumina, alumina-boria, and sodium-poisoned silica-alumina belong to one group and alumina to another. Concerning the silica-alumina group, it was recognized from a LFER approach and from poisoning with organic bases that the esterification proceeded on even weaker acid sites than other acid-catalyzed reactions such as dealkylation and dehydration. From simple kinetics based on a Langmuir-Hinshelwood mechanism, distinct differences were found between the two groups in that acetic acid adsorbed more tightly than ethanol on alumina and the reverse on the silica-alumina group, and that the activity ratios of esterification to dehydration were much larger on the silica-alumina group than on alumina. These characteristic behaviors of ethanol and acetic acid on silica-alumina and alumina were satisfactorily interpreted by the assumption that the active sites for esterification were protonic acid sites on the silica-alumina group, but Lewis acid sites on alumina. On the basis of these findings, an esterification mechanism was proposed.

INTRODUCTION

In a previous paper (*1*), dehydration of ethanol on solid acid catalysts was studied in the context of poisoning by acidic and basic substances. An interesting contrast was found in the behavior of acetic acid on silica-alumina and alumina; on silica-alumina dehydration was little poisoned by acetic acid and ester was formed, whereas on alumina, dehydration was severely poisoned, but little ester was formed. This fact may be a reflection of the differences in the nature of adsorbed acetic acid, and invited an expectation of elucidating the reaction mechanisms of these reactions as well as the nature of the solid acidity by an investigation on the esterification of ethanol with acetic acid.

The homogeneous acid-catalyzed esterification has been investigated for many years (*2, 3*). The reaction mechanism proposed was an electrophilic attack of protonated acetic acid on ethanol (*4*). Heterogeneous reactions have also been reported using such catalysts as ion-exchange resin (*5*) and silica-alumina (*6*), and a correlation between acidities and activities of catalysts has been discussed (*6*). Jain and Pillai (*7*) studied the dehydration of alcohol in the presence of acetic acid on alumina catalyst. Despite the many works, there seems lacking an understanding both of the contrast between silica-alumina and alumina, two typical solid acids of markedly different behavior, and of the relation between esterification and dehydration.

In the present work, esterification of ethanol with acetic acid has been investigated on acid catalysts by a linear free energy relationship (LFER) approach (*8*) and simple kinetics with the pulse technique.

EXPERIMENTAL

Reagents

Ethanol of G.R. grade (Hayashi Junyaku Co.) and acetic acid, n-butylamine and pyridine of E.P. grade (Wako Junyaku Co.) were used without further purification. Isopropylbenzene of G.R. grade (Wako Junyaku Co.) was used after removal of peroxide by an adsorption column of silica and alumina gels (*9*).

Catalysts

The catalysts are listed in Table 1, together with some of their properties. They were all calcined at 550°C for 8 hr in the atmosphere.

Apparatus and Procedures

An ordinary pulse technique with a hydrogen carrier gas was adopted (*1, 10*). For esterification, Tween 80 + 20% H_3PO_4 (Gas Chro Kogyo Co.) was used in the analytical column (2 m, 50°C). Two to approximately 5 mg of catalyst was used, and the flow rate of the carrier gas was 90 ml/min, so the residence time in the catalyst zone was of the order of 10^{-3} sec. To evaluate poisoning, activity was measured 1 min after injection of 1 μl organic base. Approximately 2 μl of the mixture of ethanol and acetic acid in various mole ratios was injected for kinetic analysis. The total number of the moles injected was fixed, taking into account the specific gravities and molecular weights of the reactants. The injection procedures were carried out so carefully that both reactants evaporated immediately to give the homogeneous mixture, and the pulse shapes were similar in each run. The fulfillment of these situations was ascertained from the gas chromatogram without the analytical column. The conversion was below 20%, except for the cases of the lowest concentration of either reactants. These precautions permit a simple kinetic study with the pulse technique, although the accuracy may be sacrificed to a certain degree. The reaction rate was expressed as μl of reacted ethanol (liquid state) at ml/min g-catalyst. One μl of ethanol corresponds to 1.7×10^{-5} mole. The rate of deisopropylation was expressed as a conversion at ml/min g-catalyst. Details of the experiments were described previously (*1*).

RESULTS

Comparison of the Catalytic Activities in Dehydration, Esterification, and Dealkylation

δ_C effects, the effects due to the catalysts (*8*) of SA, SA–Na, AB, and A for dehydration of ethanol, esterification of ethanol

TABLE 1
CATALYSTS

Abbreviation	Name	Surface area (m^2/g)	Composition	Remarks
A	Alumina	190		(a)
AB	Alumina-boria	390	10 % B_2O_3	(b)
AB–Na	Alumina-boria-NaOH	290	0.33 meq Na/g	(c)
SA	Silica-alumina	550	13 % Al_2O_3	(d)
SA–Na	Silica-alumina-NaOH	500	0.42 meq Na/g	(e)

(a) By precipitation of $Al(NO_3)_3$ with NH_4OH.
(b) By coprecipitation of $Al(NO_3)_3$ and H_3BO_3 with NH_4OH.
(c) By impregnation of AB with aq NaOH.
(d) Nippon cat., a cracking catalyst of the Shokubai Kasei Co.
(e) By impregnation of SA with aq NaOH.

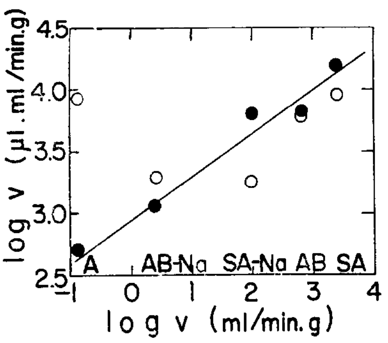


FIG. 1. Correlations of deisopropylation with dehydration and esterification. The abscissa corresponds to deisopropylation, the ordinate to dehydration and esterification, with ○ for dehydration of ethanol, and ● for esterification of ethanol with acetic acid. The units of the rates are given in the text.

with acetic acid, and deisopropylation of isopropylbenzene, are shown in Fig. 1, where a linear correlation between esterification and deisopropylation on these catalysts can be seen. Hermann Tezanos (*11*) reported a similar relation. This relation showed a similar δ_C effect as found among dealkylations of alkylbenzenes and isomerization reactions of o-xylene and cyclohexene (*8*), so that it may be concluded that the active sites of each catalyst are common to these reactions. (The authors imagine these to be protonic sites for SA, SA–Na and AB, and Lewis acid sites for A.) The slope for esterification in Fig. 1 was notably smaller than those of other reactions (*8*).

In contrast to esterification, the dehydration activity of A was peculiarly high and out of the correlation line (Fig. 1). This fact may correspond to the special behavior that distinguished A from other solid acids in dehydration (*1*).

The Effect of n-Butylamine and Pyridine Poisoning Before the Reaction

The decreases of the rate of the ethanol–acetic acid reaction on SA by n-butylamine and pyridine additions are shown in Table 2, where ethylene formation is seen to be much more retarded than ester formation. Taking into account the poisoning against ether formation in the absence of acetic acid (*1*), esterification was concluded to proceed on even weaker acid sites. This conclusion may correspond to the small slope of esterification in Fig. 1, and the high selectivity for ester formation on SA–Na which was poisoned by sodium ions. Homogeneous esterification is well known to proceed under milder conditions than dehydration (*12*).

TABLE 2
RELATIVE RATE AFTER POISONING ON SA WITH ORGANIC BASE

Base	Ethylene	Ethyl-ether	Ethylacetate
n-Butylamine	8[a]	decrease[b]	25[a]
Pyridine	20[a]	decrease[b]	60[a]

[a] Relative rate against one on virgin SA (%).
[b] Too small to be measured.

Reaction Orders of Esterification

Reaction rates on SA–Na and A at 350° are plotted against various ethanol-acetic acid mole ratios in Figs. 2 and 3. On SA–Na, the amount of reacted ethanol increased to four times larger than that in the dehydration of ethanol alone, whereas it decreased to one-ninth on A.

Simple kinetic analyses were made with regard to the esterification rate data shown in Figs. 2 and 3. Although a more precise analysis with regard to reactions of order other than first order, taking into account

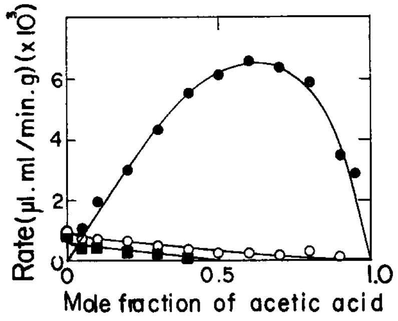


FIG. 2. Rates of dehydration and esterification with acetic acid on SA–Na at 350°C under various mole fractions of acetic acid with ● for ethylacetate, ○ for ethylene, and ■ for ethylether.

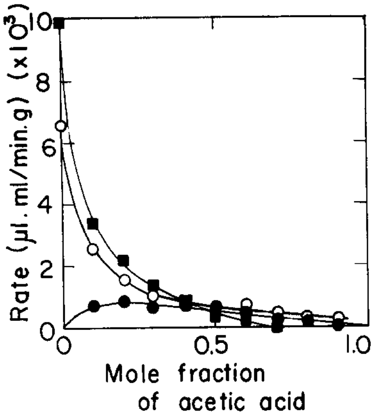


FIG. 3. Rates of dehydration and esterification with acetic acid on A at 350°C for various mole fractions of acetic acid with ● for ethylacetate, ○ for ethylene, and ■ for ethylether.

the accurate pulse form, has been reported (*13*), the present reaction orders were calculated by the following equations, assuming that the form of the pulse was rectangular.

$$v = kP^{n+m}x^n(1-x)^m, \qquad (1)$$

where k, P, and x are the rate constants, the sum of the partial pressures of both reactants, and mole fraction of acetic acid, respectively, and n and m are reaction orders for acetic acid and ethanol, respectively. The $x_{\max}$, which gives the maximum rate in Figs. 2 and 3, must satisfy the equation of $dv/dx = 0$, so the following equation is derived, and α is defined:

$$n/m = x_{\max}/1 - x_{\max} = \alpha. \qquad (2)$$

By substituting Eq. (2) in Eq. (1), Eq. (3) or (4) is obtained,

$$v = k'\{x^\alpha(1-x)\}^m, \qquad (3)$$

or

$$\log v = \log k' + m \log x^\alpha(1-x), \qquad (4)$$

where $k' = kP^{n+m}$, because the number of moles injected was constant. The values of α were calculated as 3/2 and 1/4 from Figs. 2 and 3, respectively. Using these values for α, the observed data can be well correlated with Eq. (4) as shown in Figs. 4 and 5. The value of m is given by the slope of the lines, and then n was calculated from m and α using Eq. (2). The results are shown in Table 3. A is different from the other three catalysts, SA, SA–Na, and AB. AB showed similar behavior to A in the dehydration (*1*), but distinctly belongs to the SA group in the esterification.

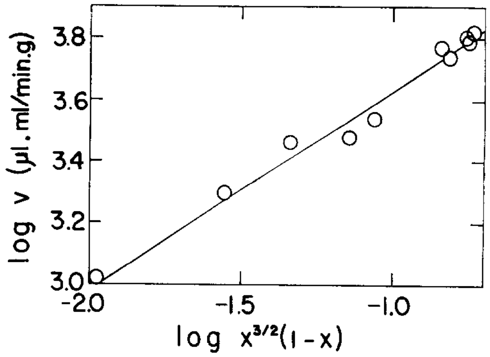


FIG. 4. Log–log plots of esterification rate on SA–Na at 350°C.

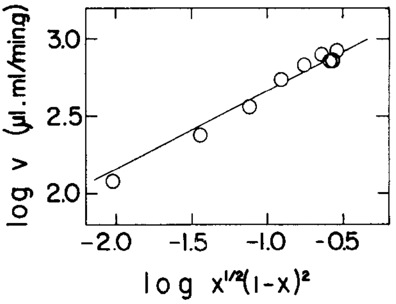


FIG. 5. Log–log plots of esterification rate on A at 350°C. The value of $x^\alpha(1-x)$ is squared in the abscissa for convenience, so that the value of m is twice the slope.

Analysis for Langmuir–Hinshelwood and Rideal Mechanisms

If the reaction proceeds via a Langmuir–Hinshelwood mechanism, then the rate equation of esterification can be described as follows:

$$v = \frac{kK_1K_2P^2x(1-x)}{\{1 + K_1Px + K_2P(1-x)\}^2}, \qquad (5)$$

or

$$\sqrt{\frac{x(1-x)}{v}} = \sqrt{\frac{1}{kK_1K_2}}\left\{\frac{1}{P} + K_2 + (K_1 - K_2)x\right\}, \qquad (6)$$

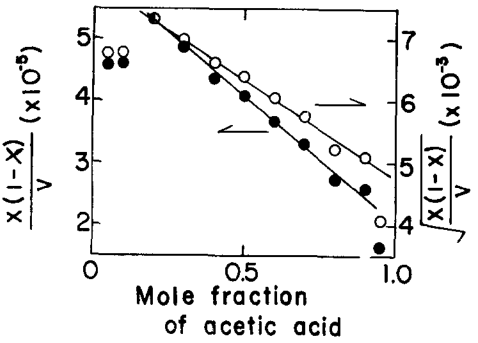


FIG. 6. Kinetic plots of esterification on SA–Na at 350°C, using ○ as the Langmuir–Hinshelwood mechanism, and ● as the Rideal mechanism.

where K_1 and K_2 are adsorption equilibrium constants for acetic acid and ethanol, respectively. Two hypotheses are assumed in Eq. (5), viz., that acetic acid and ethanol adsorb on the same active sites, and that the adsorption of the reaction products can be neglected because of the low conversion. The value of $x(1-x)/v$ is plotted against x in Figs. 6 and 7 for SA–Na and A, respectively. Linearity was obtained except for a few points with regard to SA–Na, which correspond to values at low concentration of either reactant. The signs of $K_1 - K_2$ on SA, SA–Na, AB, and A are shown in Table 3. Acetic acid adsorbed more weakly than ethanol on the first three catalysts, whereas on A acetic acid adsorbed more strongly.

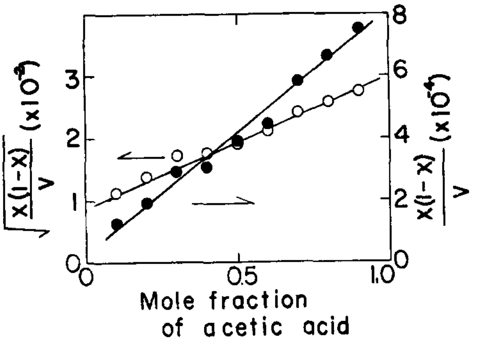


FIG. 7. Kinetic plots of esterification on A at 350°C, using ○ as the Langmuir–Hinshelwood mechanism, and ● as the Rideal mechanism.

A Rideal mechanism may also be considered because we had first order with regard to one of the reactants on each catalyst (SA–Na and A). In this case, the rate equation is expressed as follows:

$$v = \frac{kK_2P^2x(1-x)}{1 + K_2P(1-x)} \tag{7}$$

for SA–Na, and

$$v = \frac{kK_1P^2x(1-x)}{1 + K_1Px} \tag{8}$$

for A. These equations can be transformed into the following:

$$\frac{x(1-x)}{v} = \frac{1}{kK_2}\left\{\frac{1}{P^2} + \frac{K_2}{P} - \frac{K_2x}{P}\right\} \tag{9}$$

for SA–Na, and an analogous equation for A. The applications are shown in Figs. 6 and 7 for SA–Na and A, respectively. The linearities of the plots for both mechanisms are of the same degree, so that discrimination between the two mechanisms is difficult. The Langmuir–Hinshelwood mechanism, however, seems rather more probable, because the formation of ester, when acetic acid was injected on to SA in advance of the ethanol pulse, revealed the adsorption of acetic acid. Further evidence was that the reaction orders of both reactants became less than unity at 250°C on SA.

DISCUSSION

The active sites of the two catalyst groups for esterification seem different from one to another. On the silica-alumina

TABLE 3

KINETIC PARAMETERS FOR ESTERIFICATION

Catalyst	SA–Na	AB	SA	SA	A
Reaction temp	350°C	350°C	300°C	250°C	350°C
n^a	1.0	1.0	1.0	0.7	0.3
m^a	0.7	0.7	0.7	0.2	1.0
$K_1 - K_2{}^a$	−ve	−ve	−ve	−ve	+ve

[a] See text.

group catalysts, more basic ethanol adsorbed more strongly than acetic acid. Kinetics on the ion-exchange resin (*5*) were similar to those on the silica-alumina group. Alumina-boria which consisted of 90% alumina behaved like silica-alumina in esterification, in spite of behavior similar to alumina in dehydration (*1*). These facts suggest that the active sites on the silica-alumina group may be protonic sites. On the other hand, the acetic acid adsorbed more strongly than ethanol on alumina. The active sites on alumina may be Lewis acid sites, because the carbonyl group of xanthone interacted more intimately with Lewis acid (*14*).

Two types of esterification routes are possible on the silica-alumina group, based on the Langmuir–Hinshelwood mechanism:

(i) Via carbonium ion from ethanol,

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2^+,$$

$$CH_3C(O)OH + H^+ \leftrightarrows CH_3C(OH)_2^{+*},$$

$$CH_3CH_2OH_2^+ \rightarrow CH_3CH_2^+ + H_2O,$$

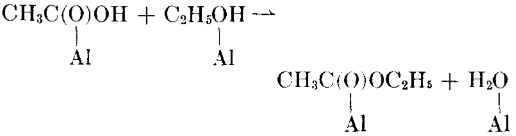
$$CH_3CH_2^+ + CH_3C(OH)_2^+ \rightarrow CH_3C(O)OC_2H_5 + 2H^+;$$

(ii) Via oxonium ion from acetic acid,

$$CH_3C(OH)_2^+ + CH_3CH_2OH_2^+ \rightarrow CH_3(O)OC_2H_5 + H_3O^+ + H^+.$$

The alkyl carbonium ion formation process seems likely to be rate-determining if the reaction proceeds via route (i). This process is rate-determining commonly for dehydration. If so, the rate of ethanol disappearance should be equal in both reactions. However, this was not true, as shown above. Thus route (ii), which is proposed for the homogeneous esterification (*2–4*), may also be probable for the heterogeneous one. Protonated acetic acid may be essential for esterification, although the adsorption equilibrium constant of ethanol was larger than that of acetic acid. In these routes, the disadvantage caused by the repulsion of two positively charged species may be overcome by the advantage of adsorption on the catalyst.

As for alumina, a similar mechanism may be applied, by substitution of an aluminum ion for a proton.



$$\underset{Al}{CH_3C(O)OH} + \underset{Al}{C_2H_5OH} \rightarrow \underset{Al}{CH_3C(O)OC_2H_5} + \underset{Al}{H_2O}$$

It may be noted that the rate of ethanol disappearance was considerably decreased by the presence of acetic acid on alumina, in contrast to the case on the silica-alumina group. The fact that acetic acid adsorbed on basic sites of alumina and retarded dehydration was reported previously (*1*). Similar phenomena may take place during the esterification and furthermore the adsorbed species of $CH_3C(OAl)$-OH is not so reactive for ester formation as the corresponding adsorbed one on protonic sites, whereas adsorption of acetic acid was stronger.

The Lewis sites on alumina are very strong but not so catalytically active (*8, 16*) except for some reactions such as dehydrohalogenation from chloroethanes (*17*), reaction with methylene chloride (*18*), and homolytic H_2–D_2 exchange (*19, 20*). For dehydration, alumina may become active through a concerted mechanism supported by the cooperation of the basic sites (*1*). These situations may be reflected in Fig. 1. An explanation must be abandoned that the high activity of alumina for dehydration is due to a number of weak protonic acid sites (*16b*), because esterification proceeds on weaker protonic acid sites than dehydration.

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* Regarding the structure of protonated acetic acid, two alternatives have been proposed; $CH_3C(O)OH_2^+$ (*2–4*), $CH_3C(OH)_2^+$ (*15*). Which alternative is more probable for the intermediate of esterification is in question, but the latter structure has been adopted here because its existence was confirmed by ir (*15*).

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