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Vapor-Phase Esterification Catalyzed by Decationized Y Zeolites

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The kinetics of acetic acid esterification with ethyl alcohol, in vapor phase, have been studied in the presence of decationized Y zeolite catalysts. Two kinetic models have been considered: a Rideal model and a bimolecular surface reaction model. Both of these models satisfactorily fit the experimental data. The choice of the better model has been made on the basis of the physical significance of the parameters obtained by nonlinear regression analysis of the data. Suggestions are given on the mechanism of the reaction, which appears to be similar to that occurring under homogeneous liquid-phase conditions.

INTRODUCTION

The esterification of ethyl alcohol by acetic acid is a well-known reversible reaction, catalyzed by an acid environment and usually performed in liquid phase (*1*, *2*). Equilibrium for the stoichiometric mixture is reached at about 66% of conversion to ethyl acetate (*2*). In order to obtain higher yields, the reaction must be forced to completion by removing the water produced and by operating with an excess of one of the reagents (*2*). The low conversions obtainable in liquid phase are due to the low values of equilibrium constants (*1*, *3*).

It is known (*1*, *4*), and can easily be calculated (*5*), that the same reaction is thermodynamically favored when performed in vapor phase. For this reason the catalytic esterification, performed in vapor phase, has in the past received considerable attention (*1*). Several materials such as silica gel, zirconia, vanadium pentoxide, cobalt oxide, etc., have been proven to be catalysts.

Some publications have sought to determine the equilibrium constants for the reaction performed in vapor phase. More reliable data have recently been collected and reinterpreted by Hawes and Kabel (*4*).

The kinetics of the esterification reaction of both ethanol and propanol by acetic acid, catalyzed by silica gel, have been described (*6–9*). Until recently, however, little attention had been given to the possibility of employing zeolites for promoting this reaction.

The use of large-pore zeolites such as X and Y for catalyzing the esterification has recently been suggested by Bergk (*10*) and no relationship between the activity and its surface acidity was observed.

A recently published patent (*11*) reported that decationized Y zeolites are very active and selective catalysts for esterification reactions, and that catalytic activity is strongly related to the surface acidity. According to this patent, energy can be saved by producing ethyl acetate, in vapor phase, in the presence of decationized Y zeolite catalysts.

In the present paper, we will study the kinetic behavior of the esterification reaction between ethyl alcohol and acetic acid, in the presence of decationized Y zeolite. We will also study the influence of surface acidity on the reaction rate. Finally we will evaluate the number of active sites, by poisoning the catalyst.

Thermodynamic Aspects of the Reaction

Several authors have experimentally measured the equilibrium constants of the esterification of acetic acid by ethanol, in vapor phase, but the data reported are rather scattered (*1*). In some cases the data

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are wrong or unreliable, probably because they were collected during the transient period of the reaction. In other cases, the authors overlooked the influence of the formation of small amounts of by-products and that of the equilibrium of dimerization of the acid.

By reinterpreting the data of many other authors, Hawes and Kabel (*4*) obtained the following relationships for the equilibrium constants of the reaction:

$$\log K_e = \frac{649}{T} + 0.042, \quad (1)$$

$$\log K_e = \frac{724}{T} + 0.127. \quad (2)$$

The first relation should be employed together with that suggested by Potter *et al.* (*12*) for the dimerization constants,

$$\ln K_d = \left(\frac{3000}{T}\right) - 10.149 \ (\text{mm Hg}^{-1}), \quad (3)$$

while the second should be used together with the relation suggested by Taylor (*13*),

$$\ln K_d = \frac{3347}{T} - 10.931 \ (\text{mm Hg}^{-1}). \quad (4)$$

In the present paper Eq. (1) has been adopted together with Eq. (3), to calculate the composition of the reaction mixtures.

EXPERIMENTAL

Apparatus and Methods

The kinetic runs were performed in a stainless-steel tube reactor with a 1-cm internal diameter and 1.25-cm external diameter and 36-cm length. The reactor was placed inside a thermostated chamber. A sampling valve was connected to the outlet of the reactor and to the gas chromatograph employed for the analysis. This valve was particularly useful for following the transient period of the reaction.

The reaction products, together with the unreacted reagents, were condensed at the outlet of the reactor in a frozen trap. The mixtures obtained were then analyzed for further control when steady-state conditions were reached.

The analyses were performed by a Perkin–Elmer Sigma 3 gas chromatograph using a column filled with Chromosorb 102 containing 15% by weight of Carbowax 20 (100–120 mesh) and a hot-wire detector. Helium was employed as the carrier gas. Reagents were fed by a micrometric pump in a heated worm and evaporated before entering the reactor. Small stainless-steel balls with a 0.3-cm diameter were placed in front of the catalytic bed in order to obtain plug flow conditions. No catalytic activity was revealed by these nonporous balls.

A schematic diagram of the apparatus is shown in Fig. 1. Decationized Y zeolite, in cylindrical pellets of about 0.13 cm of equivalent diameter, was used as a catalyst. The decationized form of zeolite was obtained by ion exchange of the Na–Y zeolite of Union Carbide, commercial-type LZY-52, with ammonium chloride four times at 100°C, for 2 h. The exchanged zeolite was filtered, dried at 120°C, and heated at 500°C for 4 h.

Kinetic runs on decationized Y zeolite were performed at atmospheric pressure and at three temperature levels in the range of 150–200°C, while the feed ratio between acetic acid and ethanol was widely changed. Runs performed at several feed rates, and using pellets of different sizes, showed that external and internal mass transfer effects were negligible under these experimental conditions. It is also possible to exclude the influence of intracrystalline diffusion effects by applying the criterion suggested by Dogu and Dogu (*14*) with the value of the intracrystalline diffusion coefficient reported by Ruthven and Keng Lee (*15*).

Then, in order to verify the influence of surface acidity on the reaction rate, Y zeolite was exchanged with various ions and the surface acidity was determined by titration with *n*-butylamine dissolved in anhy-

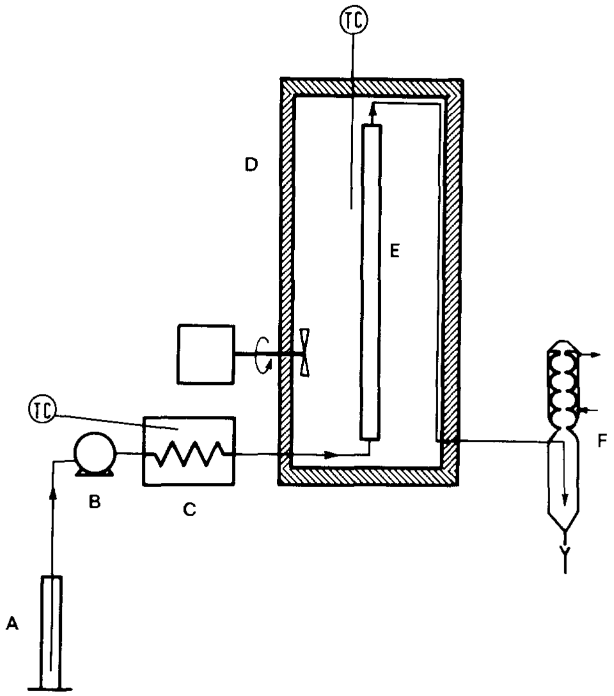


FIG. 1. Schematic diagram of the apparatus employed for the kinetic runs. A = Mixture of reagents; B = micropump; C = preheater; D = thermostated chamber; E = reactor; F = frozen trap.

drous benzene, in the presence of indicators as described in the literature (*16–18*).

Table 1 shows the employed indicators together with the p*K* values for their color change. The number of active sites, on Y decationized zeolite, was determined by poisoning the catalyst with pyridine dissolved in the reagents.

TABLE 1

Indicators Employed in the Measurements of Surface Acidity of Zeolites

Type of indicator	p*K*
Anthraquinone	−8.2
Benzolacetophenone	−5.6
Thymol blue	1.5
Methyl yellow	3.3
Methyl red	4.8
Neutral red	6.8
Bromothymol blue	7.1
2,4-Dinitroaniline	9.0
Phenolphthalein	9.3

RESULTS AND DISCUSSION

The esterification reaction occurs on Y decationized zeolite with a long transient period. Separation of the components by the zeolite also occurs during this time, as shown in Fig. 2, in which the molar fractions of the compounds, analyzed at the outlet of the reactor, are reported as a function of time. The run to which this figure is related, was performed on 20 g of decationized Y zeolite, at atmospheric pressure and 150°C, by feeding acetic acid and ethanol with a molar ratio of 2 at a feed rate of 0.28 cm^3/min.

As can be seen, acetic acid is the most strongly adsorbed component, because, though it is present in excess, its breakthrough curve is the last to appear. On the contrary, ethyl acetate appears as the first component at concentrations that are much higher than those expected for the complete conversion of the reagents. This behavior, similar to that which can be seen in dis-

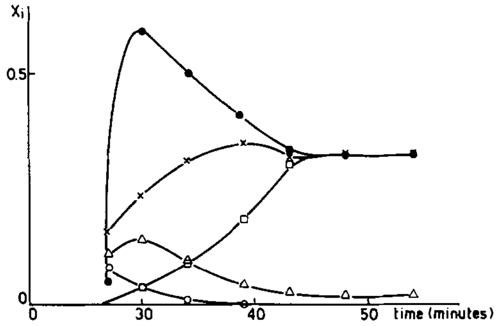


FIG. 2. Transient effects in the esterification reaction catalyzed by Y decationized zeolite. (●) = Ethyl acetate; (×) = water; (□) = acetic acid; (△) ethyl alcohol; (○) ethyl ether.

placement chromatography, had been already observed and explained with regard to xylene separation by adsorption on Y zeolite (*19*).

Small amounts of ethyl ether are produced in the initial part of the transient period. This is probably due to the fact that ethanol molecules remain in contact with acid sites for a long time when the separating action of the zeolite takes place.

Table 2 shows the operating conditions and the results for kinetic runs performed under steady-state conditions.

In order to elaborate the kinetic data of Table 2, it is necessary to express the molar fractions of the components of the reaction mixture as a function of the conversion, and to take into account the dimerization equilibrium.

If we assume the stoichiometric number of moles of acetic acid in the liquid mixture of reagents to be

TABLE 2

Conversions Obtained for the Esterification Reaction by Changing Temperature, Residence Time, and Initial Molar Ratio of the Reagents[a]

Run no.	T (°C)	n_{ac}/n_{al}	W (g)	F_{tot} (cm³/min)	F/W $\left(\frac{\text{mole of alcohol}}{\text{h} \cdot \text{kg}}\right)$	Experimental conversion (%)	Calculated conversion (%)
1	150	2:1	5.04	0.71	47.94	15.18	16.42
2	150	2:1	5.08	0.41	27.68	22.75	26.20
3	150	2:1	5.08	1.50	101.28	8.50	8.28
4	151	2:1	14.00	1.00	24.52	28.10	29.92
5	151	2:1	14.00	2.00	4.90	79.50	77.45
6	151	3:1	14.00	1.00	18.39	32.00	32.74
7	151	1:1	14.00	1.00	36.78	24.83	24.20
8	152	2:1	5.04	0.67	44.22	17.33	19.06
9	152	10:1	5.04	0.67	12.43	22.80	23.99
10	152	29:1	5.04	0.67	4.56	31.43	25.39
11	152	1:3	5.04	0.71	108.70	9.87	8.58
12	152	1:5	5.04	0.71	120.77	6.54	6.25
13	153	1:10	5.04	0.67	124.33	6.51	4.04
14	153	1:5	5.04	0.67	128.21	4.09	2.88
15	153	1:29	5.04	0.67	132.20	2.49	1.60
16	182	10:1	5.04	0.67	12.43	58.95	59.14
17	182	1:3	5.04	0.71	108.70	22.46	20.13
18	182	1:5	5.04	0.67	113.97	14.94	13.92
19	184	2:1	5.08	0.41	27.68	63.59	65.34
20	201	10:1	5.04	0.67	12.43	82.69	81.75
21	201	1:5	5.04	0.67	113.97	17.37	17.90
22	201	1:3	5.04	0.67	102.57	26.72	27.60

[a] The calculated conversions are those obtained from the Rideal model.

$$W_1{}^0 = n_1{}^0 + 2n_2{}^0 = \frac{V_1 d_1}{M_1} \tag{5}$$

and consider the following relationship for the dimerization equilibrium:

$$K_d = \frac{n_2{}^0(n_1{}^0 + n_2{}^0 + n_3{}^0)}{(n_1{}^0)^2}, \tag{6}$$

the initial composition of the reagents, in vapor phase, will thus be

$$n_1{}^0 = \frac{-n_3{}^0 + \sqrt{(n_3{}^0)^2 + (4K_d + 1)(2n_3{}^0 + W_1{}^0)W_1{}^0}}{(4K_d + 1)}, \tag{7}$$

$$n_2{}^0 = \frac{W_1{}^0 - n_1{}^0}{2}, \tag{8}$$

$$n_3{}^0 = \frac{V_3 d_3}{M_3}. \tag{9}$$

The composition obviously changes due to the effect of the reaction; accordingly the equilibrium relation becomes

$$K_d = \frac{n_2(n_1 + n_2 + n_3 + n_4 + n_5)}{(n_1)^2}, \tag{10}$$

where

$$n_1 = \frac{-n_3{}^0(1 + \lambda) + \sqrt{[n_3{}^0(1 + \lambda)]^2 + W_1[W_1 + 2n_3{}^0(1 + \lambda)](4K_d + 1)}}{(4K_d + 1)}, \tag{11}$$

$$n_2 = \frac{W_1 - n_1}{2} = \frac{W_1{}^0 - n_3{}^0\lambda - n_1}{2}, \tag{12}$$

$$n_3 = n_3{}^0(1 - \lambda), \tag{13}$$

$$n_4 = n_5 = n_3{}^0\lambda, \tag{14}$$

λ being the degree of advancement of the reaction.

For each value of λ, therefore, the composition of the reaction mixture is known. It is reasonable to assume that acetic acid can react only in the monomeric form.

Let us now consider the runs performed at about 150°C, reported in Table 2, and initially apply to these a kinetic law of a pseudo second order, that is,

$$r = k_2 \left[X_1 X_3 - \frac{X_4 X_5}{K_e}\right] P^2. \tag{15}$$

The values of the kinetic constant k_2 calculated for the mentioned runs are reported in Fig. 3 as a function of the initial molar feed ratio between the reagents. Calculations were made by numerical integration of Eq. (15). By observing the trend of Fig. 3, we find that a pseudo-second-order kinetic model can be adopted satisfactorily only at high values of the ratio n_{ac}/n_{al}. According to Fig. 3 acetic acid shows a considerable depressing effect on reaction rates.

On the contrary, the depressing effect of alcohol is negligible. The effect of the reaction products has also been neglected. Therefore, experimental data have been interpreted by adopting a bimolecular surface (B.S.) model of the type

$$r = \frac{k_{app} b_1}{(1 + p_1 b_1)^2}\left(p_1 p_3 - \frac{p_4 p_5}{K_e}\right), \tag{16}$$

and a Rideal (R) model of the type

$$r = \frac{k b_1}{(1 + p_1 b_1)}\left(p_1 p_3 - \frac{p_4 p_5}{K_e}\right). \tag{17}$$

Both of these models have been subjected to statistical analysis using the method described in (*20*). The objective function was

$$\Phi(\boldsymbol{\beta}) = \sum_{1}^{N} (\lambda_{exp} - \lambda_{cal})^2, \tag{18}$$

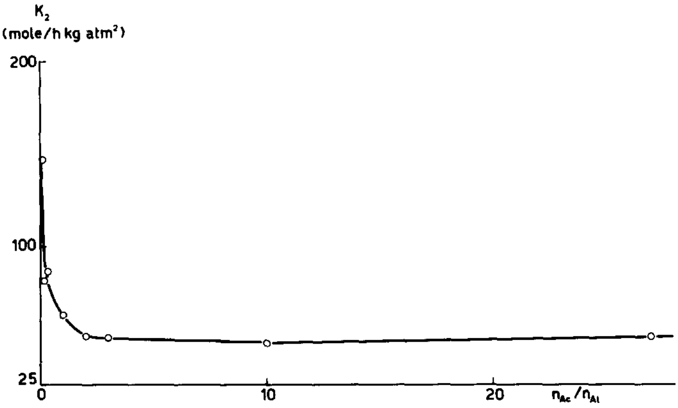


FIG. 3. The kinetic constants obtained by interpreting data with second-order kinetics with an equilibrium, as a function of the initial volume ratio of the reagents.

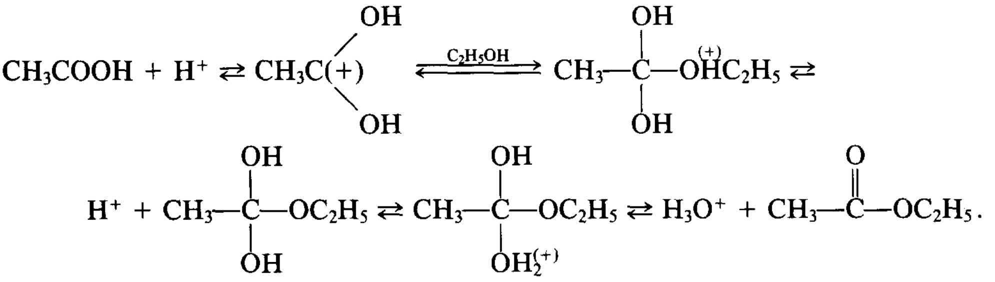
where β signifies the set of parameters of the model considered.

The kinetic parameters obtained for the two models are reported in Table 3 together with the results of the statistical analysis. According to these results, both models satisfactorily describe the experimental data. The choice of the better model should be made on the physical reliability of the kinetic parameters obtained.

Let us consider, first, the adsorption constant:

$$b_0 = e^{\Delta S_{ads}/R}. \qquad (19)$$

The values obtained for this parameter for the two models are similar. They lead to the following values of the entropy change of acetic acid: −12.85 e.u. for the (R) model and −12.8 e.u. for the (B.S.) model. The translational entropy of acetic acid molecules in vapor phase is about 40.0 e.u. According to these data, the acetic acid molecules, involved in the reaction, would have high residual mobility. These results, as it will be seen, are not contrasting with the observation that acetic acid is the most strongly adsorbed component. Moreover, the enthalpy changes for acetic acid adsorption reveal moderately exothermic effects. All these facts can be justified on the basis of a reaction mechanism similar to the one suggested for the liquid-phase reaction (*3*):



$$\mathrm{CH_3COOH + H^+ \rightleftarrows CH_3C(+)}\genfrac{}{}{0pt}{}{\diagup\mathrm{OH}}{\diagdown\mathrm{OH}} \xrightleftharpoons{\mathrm{C_2H_5OH}} \mathrm{CH_3{-}\overset{OH}{\underset{OH}{C}}{-}\overset{(+)}{O}HC_2H_5} \rightleftarrows$$

$$\mathrm{H^+ + CH_3{-}\overset{OH}{\underset{OH}{C}}{-}OC_2H_5 \rightleftarrows CH_3{-}\overset{OH}{\underset{OH_2^{(+)}}{C}}{-}OC_2H_5 \rightleftarrows H_3O^+ + CH_3{-}\overset{O}{\overset{\|}{C}}{-}OC_2H_5}. \qquad (20)$$

The protonation of the acetic acid molecules, which is usually considered to be the rate-determining step, is reported as an endothermic process (*3*). This would explain both the apparent mobility of the acetic acid molecules involved in the reaction, and the low enthalpy changes in their adsorption. In fact, the acetic acid molecules, strongly

TABLE 3

Statistical Comparison of the Two Models[a]

	I B.S.	II R
k_0 (mole/h kg atm^2)	3.08×10^{11}	2.314×10^{11}
ΔE (cal/mole)	17,990	18,540
b_0 (atm^{-1})	1.588×10^{-3}	1.557×10^{-3}
ΔH (cal/mole)	−4,817	−5,686
Correlation index	0.9968	0.9969
Standard deviation	0.0221	0.0216
Mean of error (% on the conversion)	10.86	10.15

[a] Model I is the bimolecular surface model (B.S.), while Model II is the Rideal model (R).

adsorbed on zeolite are not necessarily involved in the reaction. Only the molecules adsorbed on the acidic sites, with a less favored thermodynamic process, can react.

Finally let us consider the preexponential factors. As we can see, the values obtained are high, if compared with other heterogeneous catalyzed reactions.

This fact suggests that reagents and products can be considered as being in a condensed phase within the zeolite cavities. The only difference with respect to the reaction performed in liquid phase, seems to be the immobility of the acidic sites. But these suggestions are reliable only for the (R) model in which the kinetic constant is not apparent. In fact, in the case of the (B.S.) model, the calculated kinetic constant is the product of the true kinetic constant times the adsorption constant of alcohol. This is consistent with a very high value for the rate constant, which is difficult to justify on a physical basis.

This fact, together with the high residual mobility and the low enthalpy changes observed for the acetic acid molecules involved in the reaction, suggests that the Rideal model is more reliable. On the other hand, given that acetic acid is the more strongly adsorbed component, and that its protonation is the first step of the reaction, it is reasonable to assume that ethanol reacts without adsorption.

TABLE 4

Catalytic Activities for Y Zeolites Exchanged in Various Ways

Zeolite	Acidity at pK = 4.8 (mmole/g)	$k_0 \times 10^{10}$ (mole/h kg atm^2)
KY	0.00	0.70
NaY	0.06	2.74
LiY	0.73	3.46
CaY	0.89	5.82
HY	1.76	23.14

The absence of ethyl ether in the reaction products under steady-state conditions confirms these suggestions. In Table 2, the conversions calculated for the Rideal model, with the parameters reported in Table 3, are reported and compared with the experimental data.

The influence of surface acidity on catalytic activity has been examined. To this end Y zeolite was exchanged with different cations and the surface acidity was measured by titration with *n*-butylamine in the presence of the indicators summarized in Table 1. Catalytic activities were measured by using 5 g of the exchanged zeolite, at

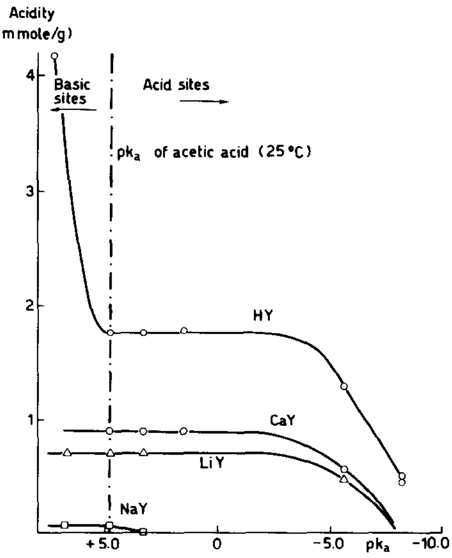


FIG. 4. Distribution of the acid sites for variously exchanged Y zeolites.

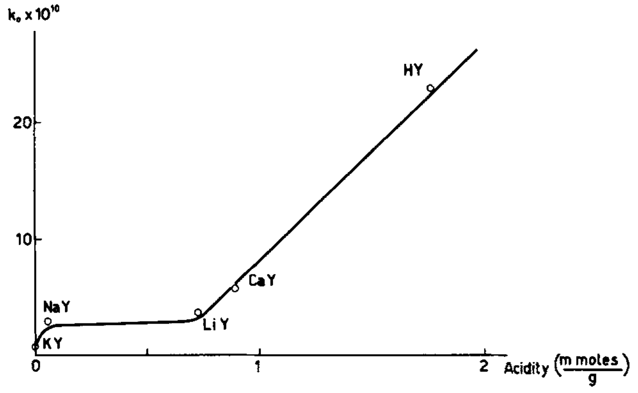


FIG. 5. The behavior of the catalytic activity as a function of surface acidity.

150°C and atmospheric pressure, a feed rate of 1 cm^3/min, and a volumetric initial ratio of acid/alcohol = 2.

Table 4 presents the activities obtained for the variously exchanged zeolites, together with the corresponding surface acidities. Figure 4 shows the distribution of the acidic sites for the catalysts employed. For decationized Y zeolite, also the basic sites, as shown in Fig. 4, have been determined by titration with benzoic acid dissolved in anhydrous benzene and in the presence of indicators having pK > 7 (*21*). Data obtained are in agreement with the findings of Morita *et al.* (*22*). The basic sites are responsible for the strong adsorption of acetic acid observed in the transient period of the reaction.

By plotting the kinetic constants of the reaction as a function of acidity, we obtain the curve shown in Fig. 5. The trend of the curve suggests that the rate law should contain two contributions: one depends on the surface acidity while the other does not.

This finding is confirmed by poisoning the catalyst with pyridine. In fact, the catalyst cannot be completely poisoned and a residual activity remains, as can be seen in Fig. 6.

This residual activity is less than 10% of the overall activity which is within an order of magnitude of experimental error. There-

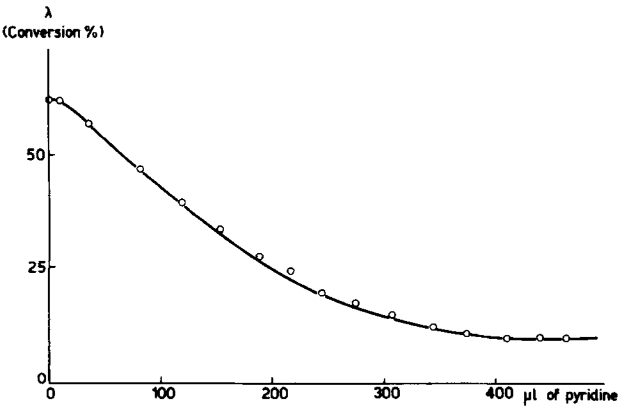


FIG. 6. The effect of pyridine poisoning on decationized Y zeolites. This run was performed at 202°C, on 5.67 g of catalyst, with a feed rate of 0.67 cm^3/min, and an initial volumetric ratio between acetic acid and ethanol of 2.

fore, the presence of a different mechanism, not dependent upon acidity, does not seriously affect the evaluated kinetic parameter and, in agreement with the trend of Fig. 5, the preexponential factor can be roughly arranged as follows:

$$k_0 = k_0' + k_0''a \simeq 2.314 \times 10^{10} + 1.183 \times 10^{11}a, \quad (21)$$

where a is the acidity of the surface as expressed in Table 4.

From the amount of pyridine adsorbed for poisoning the catalyst, it is possible to evaluate the number of active sites on the decationized zeolite employed, that is, 5.3×10^{20} sites/g.

This value is about one-third less than that reported by Turkevic (*23*) for the cracking of cumene at much higher temperatures. It is also about two-thirds of the acid sites determined by titration. It can be concluded that, in our case, only two-thirds of the acid sites present on decationized zeolite are able to protonate acetic acid molecules.

APPENDIX: LIST OF SYMBOLS

Italic Symbols

b_{0i} = Preexponential factor for adsorption of i component
b_i = Adsorption constant of i component
d_i = Density of the reagent i in liquid phase
ΔE = Activation energy
F = Molar flow rate of alcohol
ΔH = Enthalpy change
k_0 = Preexponential factor in kinetic law
k_2 = Pseudo-second-order kinetic constant
k_{app} = Kinetic constant in B.S. model
K_{d} = Dimerization equilibrium constant
M_i = Molecular weight of i component
n_i^0 = Initial number of moles for i component
n_i = Number of moles of i component
p_i = Partial pressure of i
P = Total pressure
r = Reaction rate
ΔS_{ads} = Entropy change in adsorption
T = Absolute temperature
v_i = Volume of i in liquid phase
W_i^0 = Stoichiometric number of moles of i in liquid phase
W = Weight of catalyst
X_i = Molar fraction of i component

Greek Symbols

λ = Conversion expressed as moles of alcohol reacted per mole of alcohol fed

Subscripts

i = Component
1 = Acetic acid monomer
2 = Acetic acid dimer
3 = Alcohol
4 = Water
5 = Ethyl acetate

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