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Reaction Mechanism of Ethanol Dehydration on/in Heteropoly Compounds: Analysis of Transient Behavior Based on Pseudo-Liquid Catalysis Model

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The transient behavior of ethanol dehydration on/in heteropoly compounds was studied. Ethylene formation lasted for a long time after the ethanol feed had stopped, while ether formation decreased monotonously with time. A reaction model which includes the participation of sorbed alcohol was proposed: Ethylene formation occurs through a unimolecular decomposition of ethanol, while ether formation takes place through a coupling of chemically activated ethanol with the physically sorbed one. Both reactions occur in the bulk phase of the compounds. Transient curves as well as kinetic behavior under the stationary reaction conditions could be satisfactorily simulated by this model for both products. © 1987 Academic Press, Inc.

1. INTRODUCTION

Recently, considerable attention has been focused on catalysis of heteropoly compounds (*1–3*). We have reported acid catalysis of the compounds (*4–7*) as well as oxidative ones (*8–10*). We have also emphasized one of their unique properties, namely, polar reactants, such as nitrogen bases, alcohols, ethers, and ketones, are readilly absorbed and participate in the catalytic reactions (*7, 11*). Misono *et al.* have termed it "pseudo-liquid phase catalysis" (*12*). This property may become a useful tool in differentiating reactant and/or product molecules and resulting in a "polar–nonpolar selective catalysis," which might be analogous to molecular sieving catalysis of zeolites which are able to discriminate reactant or product molecules on the basis of their "size and shape."

In a previous paper (*7*) the dehydration of various alcohols on/in 12-tungstophosphates was reported. A abnormal kinetic behavior observed during the study was attributed to their absorptive properties, and could be qualitatively interpreted in view of a reaction mechanism involving the participation of the sorbed alcohol.

The main objective of the present work to confirm the reaction model which was given in the previous paper. This is done by simulating transient response curves based on the reaction model and comparing them with the experimentally observed ones.

2. EXPERIMENTAL

2.1. *Catalyst Preparation*

Barium salt of 12-tungstophosphoric acid was chosen as a catalyst because of its high catalytic activity for ethanol dehydration (*7*). It was prepared by the double decomposition of $BaCO_3$ and $H_3PW_{12}O_{40}$. Both reagents were commercially available from Wako Pure Chemical Co. Prior to use, the catalyst was pretreated *in situ* at 673 K for 30 min in a stream of He.

2.2. *Reaction*

Dehydration of ethanol was carried out in a conventional flow-type reactor under

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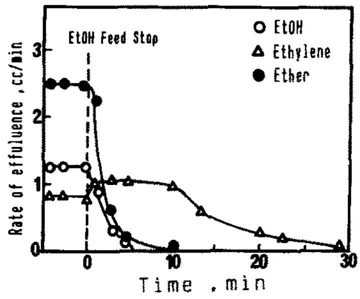

FIG. 1. Typical transient response curves for ethanol dehydration. Catalyst, $Ba_{1.5}PW_{12}O_{40}$ 1.5 g; W/F for stationary reaction, 14.6 g-cat h/mol; reaction temperature, 498 K; EtOH concentration, 22.6% to 0.

atmospheric pressure. Ethanol was fed with a syringe-type microfeeder, vaporized in a preheating zone, and introduced to the reactor in a stream of helium. The reactor was a Pyrex U-tube of 8-mm i.d., and the catalyst bed was 1.5 cm^3 in volume or 3 cm in length.

Transient response data were obtained in the following procedure. The reaction was performed under a total flow rate, F = 0.199 mol/h = 36 cm^3 NTP/min, W = 1.5 g, until the stationary catalytic activity was established. Then, the ethanol feed was stopped and instantaneously supplemental He flow was started so as to keep the total flow rate constant. These operations were done by operating a 4-way valve. Effluent gas was sampled periodically through a 6-port sampling valve, and analyzed by gas chromatography. The dead volume of the system, from the preheating zone to the sampling valve, was roughly estimated to be 30 cm^3, corresponding to a time delay less than 1 min which was taken into account in the illustration of figures.

3. RESULTS AND DISCUSSION

3.1. *Transient Behavior of Ethanol Dehydration*

Figure 1 shows the transient behavior of the reaction after the ethanol feed had been stopped (*7*). The transient response curves for the two products, ethylene and ether, differ significantly: Ether formation decreases with time on stream from the very beginning while that of ethylene keeps a value similar (or even a little higher) to the stationary one for about 10 min, and then starts to decrease. It is also worth noting that ethylene formation starts to decrease at the time when ether ceases to be produced. Transient response curves for isopropanol dehydration were also measured, and a similar behavior was observed except that little ether was observed.

Integration of these transient response curves (corresponding to reactant and products) gives the amount of sorbed substances under stationary condition. It amounted to 2.27 × 10^{-4} mol ethanol/g catalyst or 0.7 molecule ethanol/polyanion ($PW_{12}O_{40}^{3-}$: Keggin unit or K.U.). On taking the independently determined surface area value of 2–3 m^2/g into account, the sorbed amount is more than 10 times larger than the one calculated from monolayer adsorption, suggesting that the ethanol is absorbed into the solid lattice of the compounds.

Based on these findings, a reaction model was proposed (Fig. 2). The key feature of this mechanism is that the two kinds of sorbed ethanol molecules are present in the bulk, and the equilibrium between these two species is established. Physically absorbed or simply "physisorbed" ethanol, EtOH, denotes the one existing like a crystalline water, without any strong chemical

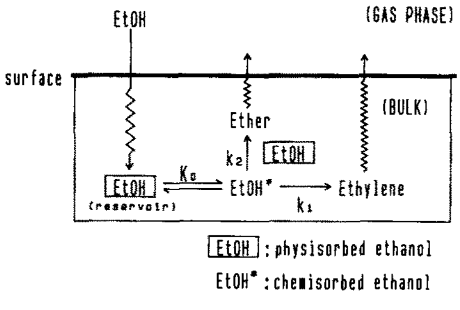

FIG. 2. Pseudo-liquid phase catalysis model for ethanol dehydration.

activation, while "chemisorbed" ethanol, EtOH*, represents the one chemically bonded to a acid center, e.g., $C_2H_5OH_2^+$. Assuming a Langmuir-type equilibrium, between these two species, we get

$$[\mathrm{EtOH}^*] = \frac{NK_0[\mathrm{EtOH}]}{1 + K_0[\mathrm{EtOH}]} \qquad (1)$$

Here, N is amount of active sites for ethanol dehydration and K_0 is an equilibrium constant between EtOH and EtOH*. On taking into consideration the strong acidic nature of heteropoly compounds and the relatively low reaction temperature, K_0 may be assumed large enough so that Eq. (1) will result in a constant concentration of EtOH* when physisorbed ethanol coexists. When chemisorbed ethanol converted to products, it is supplied from the physically sorbed ethanol which behaves like a "reservoir." When all the physisorbed ethanols are consumed either by reactions or by desorption, concentration of chemisorbed ethanol starts to decrease by yielding ethylene. This view explains the characteristics of the response curve qualitatively well.

Based on these considerations, analysis of the curves depicted in Fig. 1 was carried out. Ten minutes after the stoppage (hereafter termed t_0) ethylene formation starts to decrease, suggesting that the physisorbed ethanol was depleted by time t_0, and accordingly, all the remaining alcohol may be regarded as chemisorbed ethanol. At first, we are concerned about the behavior after t_0, when ethylene was produced exclusively and no desorption of ethanol was observed. The analysis procedure is similar to the one reported previously (*13*). The amount of chemisorbed ethanol remaining at time t ($t > t_0$) is proportional to the integrated amount of ethylene produced from time t to infinity:

$$[\mathrm{EtOH}^*] = C\int_t^\infty f(t)\,dt \qquad (2)$$

Here, $f(t)$ is a function which expresses the transient response curve of ethylene formation and C a proportionality constant. Assuming that the rate of ethylene formation is first order with respect to concentration of chemisorbed ethanol, we obtain

$$r_1 = -\frac{d[\mathrm{EtOH}^*]}{dt} = k_1[\mathrm{EtOH}^*] \qquad (3)$$

which on integration gives

$$\ln\frac{[\mathrm{EtOH}^*]_{t_0}}{[\mathrm{EtOH}^*]} = k_1(t - t_0) \qquad (4)$$

Combining Eqs. (2) and (4), we finally obtain

$$\ln\left(\int_{t_0}^\infty f(t)\,dt\Big/\int_t^\infty f(t)\,dt\right) = k_1(t - t_0) \qquad (5)$$

The left-hand side of Eq. (5) can be calculated from Fig. 3a for any values of t, and a verification of this equation (Fig. 3b) resulted in a fairly good straight line through the origin. The slope of the line in Fig. 3b gives a first-order rate constant with respect to chemisorbed ethanol, i.e.,

$$k_1 = 0.15\ \mathrm{min}^{-1} \qquad (6)$$

The rate of ethylene formation extrapolated to time t_0 is given by

$$r_1 = k_1[\mathrm{EtOH}^*]_{t_0} \qquad (7)$$

where $[\mathrm{EtOH}^*]_{t_0}$ is the amount of chemisorbed ethanol in the coexistence of physi-

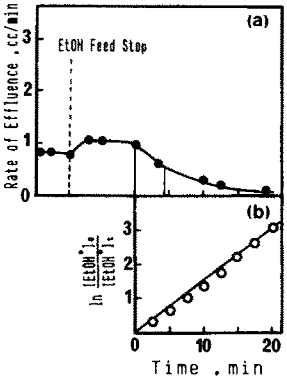

FIG. 3. Analysis of the transient response curve for the time t_0 to infinite.

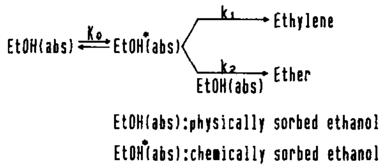

FIG. 4. Reaction scheme for ethylene and ether formation.

sorbed ethanol and is calculated by integrating the curve from t_0 to infinity, yielding

$$[\mathrm{EtOH}^*]_{t_0} = 7.73 \text{ cc NTP} \quad (8)$$

Combining Eqs. (6) and (8), we obtain the rate of ethylene formation for a complete occupation of acid sites (or at time t_0),

$$r_1 = 0.15 \times 7.73 = 1.20 \text{ cc NTP/min} \quad (9)$$

This value should be comparable to the ethylene formation rate at the plateau of the transient response curve ($0 < t < t_0$) or to the one under the stationary catalytic reaction condition. These values were estimated to be 1.1 and 0.8 (cc NTP/min), respectively, in good agreement with the calculated value. These findings indicate that the reaction mechanism depicted in Fig. 2 is valid for both the transient and stationary conditions, under which gas phase ethanol is present.

Although the reason for a small increase in the ethylene formation rate, observed after stoppage of ethanol feed (Fig. 1), is not all clear at present, many probable causes can be considered. For example, the diffusion rate of the products may be affected by the coexisting reactant, or the concentration of the water produced may have some effect on the intrinsic catalytic reaction rate.

3.2. Simulation of Transient Response Curve

Figure 4 illustrates the reaction scheme in the absence of gas-phase ethanol. Transient behavior of the formation rate of ethylene and ether, as well as the concentration of EtOH and EtOH* in sorbed phase, are described by the following set of differential equations:

$$\frac{d}{dt}([\mathrm{EtOH}] + [\mathrm{EtOH}^*])$$

$$= k_1[\mathrm{EtOH}^*] + k_2[\mathrm{EtOH}^*][\mathrm{EtOH}] \quad (10)$$

rate of ethylene formation

$$= k_1[\mathrm{EtOH}^*] \quad (11)$$

rate of ether formation

$$= k_2[\mathrm{EtOH}^*][\mathrm{EtOH}] \quad (12)$$

These equations were derived with the following assumptions.

1. Ethanol absorbed into the bulk is consumed by the formation of ethylene and ether. Desorption is negligible.
2. The rate of ethylene formation is first order with respect to chemisorbed ethanol, having a rate constant k_1.
3. The rate of ether formation has first-order dependency on chemisorbed and physisorbed ethanol, resulting in an overall second-order rate law. This is analogous to Rideal–Eley mechanism of ether formation proposed by Murakami for this reaction over Al_2O_3 (*14*).
4. Further conversion of formed diethyl ether can be ignored.

The last assumption must be a subject of criticism, since it is widely accepted that ether can also be dehydrated over solid acid

TABLE I

RELATIVE REACTIVITY OF ETHANOL AND DIETHYLETHER[a]

Reactant	*W/F* (g h/mol)	Conv. (%)	Pseudo-first-order rate const
Ethanol	21.7	82.4	1.0 (standard)
Diethylether	33.7	19.5[b]	0.08

[a] Catalyst, $Ba_{1.5}PW_{12}O_{40}$; reaction temperature, 210°C; concentration of the reactants, 22%.

[b] Products observed are solely water and ethylene.

catalysts. However, its reactivity is far smaller than that of ethanol, when contacted with heteropoly compounds. Table 1 compares the reactivities of ethanol and ether. In spite of the longer contact time for diethyl ether reaction, the conversion is only $\frac{1}{4}$ that for ethanol reaction. The pseudo-first-order rate constant for diethyl ether reaction is less than $\frac{1}{10}$ the latter. Furthermore, the effect of contact time on the product distribution was also investigated and signs of successive reaction of diethyl ether were not so apparent. Therefore, to a first approximation, such a reaction of diethyl ether may be reasonably ignored.

Equations (1) and (10) combined with simple material balance considerations yield

$$\frac{d[\mathrm{EtOH}]}{dt} = \frac{NK_0[\mathrm{EtOH}](1 + K_0[\mathrm{EtOH}])(k_1 + k_2[\mathrm{EtOH}])}{(1 + K_0[\mathrm{EtOH}])^2 + NK_0} \tag{13}$$

$$\frac{d[\mathrm{EtOH^*}]}{dt} = \frac{N^2K_0^2[\mathrm{EtOH}](k_1 + k_2[\mathrm{EtOH}])}{(1 + K_0[\mathrm{EtOH}])((1 + K_0[\mathrm{EtOH}])^2 + NK_0)} \tag{14}$$

At $t = 0$,

$$[\mathrm{EtOH}] + [\mathrm{EtOH^*}] = A_0 \tag{15}$$

$$[\mathrm{EtOH^*}] = C\int_{t_0}^{\infty} f(t)\,dt \tag{16}$$

If [EtOH] and [EtOH*] can be expressed as functions of time, the rates of formation of ethylene and ether can be calculated from Eqs. (11) and (12). Alternatively, [EtOH*] at any time $t < t_0$ can also be calculated from Eq. (1) instead of Eq. (14), if [EtOH] is known. Actually the latter alternative was adopted in this study for the simplicity of numerical calculations. Although Eqs. (13)–(15) contain five parameters, two of them, K_1 and N, were already determined. Furthermore, a rough value of A_0 can be obtained by integrating the transient response curves of ethylene and ether. Selecting appropriate values for the remaining two parameters and by using the Runge–Kutta method for numerical integration, the results illustrated in Fig. 5 were obtained. Expressing the concentration of any sorbed species in terms of cm^3 NTP/catalyst bed, the units of the pararmeters are: K_0 (cm^{-3} NTP), N and A_0 (cm^3 NTP), k_1 (min^{-1}), and k_2 (min^{-1} cm^{-3} NTP). The simulated curves satisfactorily express the principal characteristics of the experimentally observed ones, namely, ether formation decreases exponentially upon stoppage of ethanol feed while that of ethylene keeps the same value for a time and then starts to decrease.

For the sake of simplicity, we have so far ignored the desorption of ethanol, although it was observed experimentally. The rate of ethanol desorption may be considered of first order with respect to physically sorbed ethanol, indicating that the transient response curve for ethanol desorption should be analogous to that of ether formation. Because ether formation was assumed to have first-order dependence on both physically and chemically sorbed ethanol, while the latter value is constant for the time range 0–t_0 and the former value is 0 for time t_0 to infinity. The experimentally observed curve for ethanol desorption is quite similar to the simulated curve for ether formation.

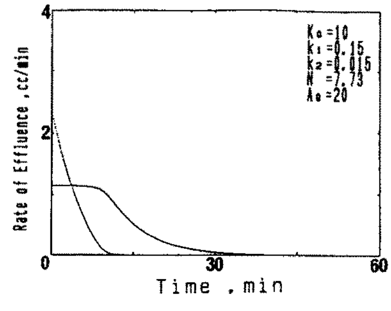

FIG. 5. Simulated curves of transient response experiment.

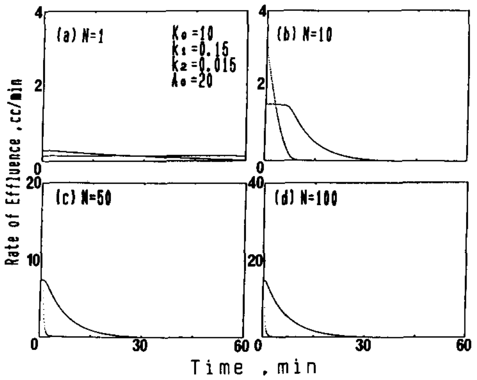

FIG. 6. Effect of N value on simulated curves.

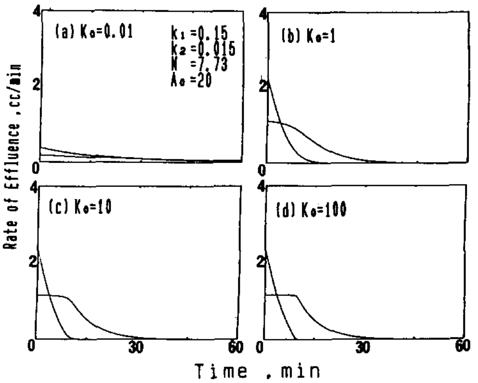

FIG. 7. Effect of K_0 on simulated curves.

Also ignored are reabsorption of the desorbed products or the reactant. If reabsorption takes place, the rate of reaction will be a function of position and in such a case, we have to integrate the contribution of the individual parts along the catalyst bed in order to simulate the response curves. Fortunately, such an effect may not important, since the rate of absorption was found to depend strongly on the pressure of sorbable molecules. As soon as the reactant feed stopped, the pressure of the reactant and products decreased rapidly, resulting in a sharper decrease of the rate of readsorption.

The effect of the number of active sites, available for the catalytic reaction (N) on the simulated curves, is shown in Fig. 6. N must be small enough compared to A_0 for a better fit of the observed curves. Changes of simulated curves with the change of N is quite acceptable in view of its physical meaning.

Figure 7 shows the effect of K_0. With the increase of K_0, the simulated curves reproduce the characteristics more clearly. However, the shape of these curves becomes insensitive for the larger values of K_0, suggesting that the determined value of K_0 may contain some uncertainty.

Based on the most adequate values for K_0, k_1, k_2, N, and several A_0 values, the formation rate of both ethylene and ether at the stationary state can be backcalculated, as illustrated in Fig. 8 by rate vs A_0 curves. The results may be comparable to the experimentally observed rate vs gaseous concentration data (*7*) given in Fig. 9, since A_0 will have a positive dependence on the gas-phase concentration. The agreement is satisfactory, in the sense that the rate of ether formation has a larger pressure dependence compared to that of ethylene formation. However, the horizontal axes of Figs. 8 and 9 have a different meaning, and for a strict comparison, the absorption isotherm which relates the gaseous concentration to A_0 is necessary. Unfortunately, no such data are available for ethanol at this temperature; however, we may expect that the sorbed amount

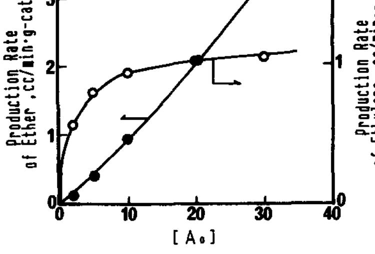

FIG. 8. Effect of A_0 on the stationary reaction rate, backcalculated from predetermined rate parameters.

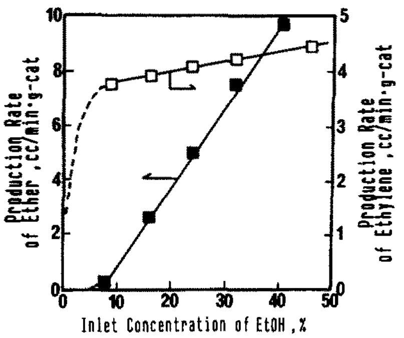

FIG. 9. Effects of gas-phase concentration of EtOH on stationary catalytic activity: Experimental findings. Catalyst, $Ba_{1.5}PW_{12}O_{40}$; reaction temperature, 518 K; W/F = 10.5 g-cat h/mol.

increases more sharply than expected from a simple proportionality relationship. Such a relation was found for methanol absorption under the condition for MTBE (methyl–tersiary–butyl ether) synthesis (5). It was also observed, in a separate experiment, that the sorption of a polar molecule enhances the sorption of the other molecules. Such an effect is empirically expressed by a second-order absorption isotherm, namely, sorbed amount (A_0) = const × (gas-phase pressure)^2. In other words, $A_0^{1/2}$ is proportional to gas-phase pressure. The calculated data, rate vs $A_0^{1/2}$, are given in Fig. 10, which shows quite a similar pattern to that given in Fig. 9.

It is necessary to make some comments on the values of N evaluated from this analysis. N is defined as the number of active sites and, in the present case, that of acid sites. Integration of $f(t)$ from t_0 to infinity yields a value 0.3/Keggin unit, indicating that more than a single cation participates in the creation of an acid site. This may not be unreasonable in view of the following scheme of acid site formation:

$$\begin{aligned}&-\mathrm{Ba}^{2+}-(\mathrm{PA})^{3-}-(\mathrm{Ba})_2^{4+}-(\mathrm{PA})^{3-}-\\ &+ \mathrm{H_2O} \rightarrow -[\mathrm{Ba, H}]^{3+}-(\mathrm{PA})^{3-}-[\mathrm{Ba(OH)},\\ &\qquad\qquad \mathrm{Ba}]^{3+}-(\mathrm{PA})^{3-}- \qquad (17)\end{aligned}$$

This scheme expresses a one-dimensional array of divalent cations Ba^{2+} and trivalent anions PA^{3-}. The key feature of this scheme is that strong electrostatic fields, due to lattice composition of divalent cations and trivalent anions, can be partially homogenized by hydrolysis (4). If this is true, the number of active sites is 1/3 of that of cations or 0.5/Keggin unit, in good agreement with the experimentally observed value.

3.3. Superiority of Heteropoly Compounds in Reactions of Alcohols

We have reported that heteropoly compounds have high activity and selectivity for MTBE (methyl tertiary–butyl ether) synthesis from MeOH and *t*-BuOH (5). The superiority of these compounds over typical solid acid catalysts can be explained in view of the reaction model illustrated in Fig. 2.

The key feature of this mechanism is that ether formation occurs via a bimolecular coupling between chemically activated and physically sorbed alcohol. In order to obtain a high selectivity to ether, the unimolecular decomposition of the alcohol (in the present case, *t*-BuOH) should be suppressed. It can be done by creating the condition under which the chemically activated alcohol or carbenium ion is surrounded by a large amount of the physically sorbed alcohol. The circumstances will be readily established by the high absorb-

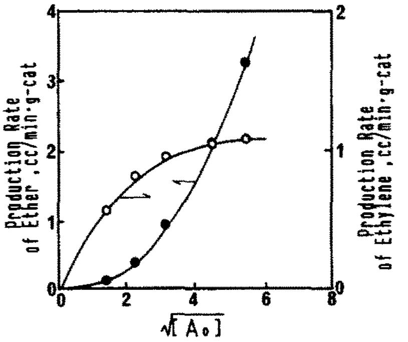

FIG. 10. Relationship between $A_0^{1/2}$ and stationary rate of reaction, backcalculated from predetermined rate parameters.

ability of MeOH into the compounds. The superior catalytic functions of the compounds are undoubtedly related to their absorptive properties, which established the most adequate ratio of [*t*-BuOH*]/[MeOH] in the vicinity of the active sites.

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