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Mechanism of Ether Formation from Alcohols over Alumina Catalyst

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The kinetics of vapor-phase dehydration of methanol and ethanol over alumina catalyst has been explained by proposing a reaction mechanism wherein the surface reaction between an adsorbed ROH molecule on an acidic site and an adsorbed alkoxide anion on a basic site is assumed to be the rate-controlling step.

INTRODUCTION

The mechanism of vapor-phase dehydration of ethanol over alumina catalyst to yield ethylene as proposed by many has been discussed by Emmett (*1*), whereas the mechanism of ether formation from alcohols has been reported by only a few (*1*). Balaceanu and Jungers (*2*) studied the kinetics of dehydration of methanol over alumina. They concluded that a second-order reaction mechanism between two adsorbed methanol molecules explained their experimental data with the least discrepancy, but did not present a suitable correlating equation. Knoezinger and coworkers (*3*, *4*) fitted kinetic data on methanol and ethanol dehydration to corresponding ethers over alumina catalyst with an "empirical" equation of the following form:

$$r_e = (r_o\sqrt{P_a})/(\sqrt{P_a} + bP_w). \qquad (1)$$

They explained that the dependence of the rate of ether formation upon the square root of partial pressure of alcohol was due to possible dual-site adsorption of alcohols on the alumina surface. The present authors (*5*) found that Balaceanu and Jungers' (*2*) kinetic data can best be explained by Eq. (1).

Jain and Pillai (*6*) proposed a reaction mechanism for the dehydration of methanol and ethanol to ethers over alumina catalyst by studying the effect of different diluents on the rate of ether formation. Their proposed mechanism calls for dual-site adsorption of alcohols as anticipated by Knoezinger and co-workers (*3*, *4*) while proposing Eq. (1). The present authors have extended this mechanism in this article and have derived a kinetic-rate expression for the dehydration of methanol over alumina catalyst.

MECHANISM OF DEHYDRATION REACTION

Jain and Pillai (*6*) concluded that ether is formed by a nucleophilic-displacement reaction caused by an adsorbed ROH molecule on another ROH molecule adsorbed on a different kind of active site shown on page 89, where A and B represent an acidic and a basic site, respectively. Chemisorption of alcohol on a basic site represented as a hydrogen bonding to the surface, increases the nucleophilicity of the oxygen of that molecule resulting in an incipient alkoxide anion. Jain and Pillai (*6*) have pointed out that the type of hydrogen bonding explained above finds parallel in the proposed nature of chemisorption of water on alumina by de Boer *et al.* (*7*) and the spectroscopic evidence for the adsorption of formic acid to form

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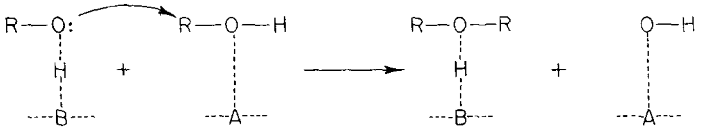

formate ions (*8*) and the adsorption of acetylene through the acidic hydrogen (*9*).

The reaction mechanism proposed in this article for ether formation is shown by Eqs. (2)–(7) below.

$$CH_3OH + s_A \rightleftharpoons CH_3OH \cdot s_A \quad (2)$$

$$CH_3OH + s_B \rightleftharpoons CH_3OH \cdot s_B \quad (3a)$$

$$CH_3OH \cdot s_B + s_B \rightleftharpoons CH_3O^- \cdot s_B + H^+ \cdot s_B \quad (3b)$$

$$CH_3OH + 2s_B \rightleftharpoons CH_3O^- \cdot s_B + H^+ \cdot s_B \quad (3c)$$

$$CH_3OH \cdot s_A + CH_3O^- \cdot s_B \rightleftharpoons CH_3OCH_3 \cdot s_B + OH^- \cdot s_A \quad (4)$$

$$H^+ \cdot s_B + OH^- \cdot s_A \rightleftharpoons H_2O \cdot s_B + s_A \quad (5)$$

$$CH_3OCH_3 \cdot s_B \rightleftharpoons CH_3OCH_3 + s_B \quad (6)$$

$$H_2O \cdot s_B \rightleftharpoons H_2O + s_B \quad (7)$$

Equation (3c), which is obtained by summing the Eqs. (3a) and (3b), represents B-type adsorption of methanol molecule accompanied by dissociation into alkoxide anion and a proton. Summation of Eqs. (2)–(7) [not including (3a) and (3b)] gives the overall reaction in the heterogeneous phase [Eq. (8)].

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad (8)$$

Derivation of Kinetic-Rate Equation

The following assumptions will be made in the derivation of a kinetic-rate equation for the dehydration of methanol and ethanol over silica–alumina catalyst:

1. There are two types of active sites upon which methanol can be adsorbed and they are as follows:
   a. an acidic site, referred to as s_A, saturated with methanol.
   b. a basic site, referred to as s_B, not saturated with methanol.
2. The methanol adsorbed on basic site is weakly dissociated, the proton being transferred to another basic site as shown in Eq. (3b).
3. The adsorbed water molecule on s_B is more weakly dissociated than the adsorbed methanol molecule on s_B, so that the source of proton is only provided by Eq. (3b).
4. A nucleophilic-displacement reaction caused by an adsorbed alkoxide anion [Eq. (4)] occurs on the positively polarized carbon atom of the methanol adsorbed on the acidic site. This reaction of an adsorbed alkoxide anion (basic site) with an adsorbed methanol molecule (acidic site) is assumed to be the rate-controlling step. Hence adsorption of methanol, desorption of products, and the formation of water from H^+ and OH^- ions [Eq. (5)] are at equilibrium, and external and internal diffusional resistances are negligible.
5. The alumina surface is saturated with A-type adsorption, so that the dehydration reaction does not appreciably change the surface concentration of methanol adsorbed on A sites.
6. The concentration of vacant basic sites on the catalyst surface is negligible compared to the total concentration of adsorbed molecules.

The net adsorption rate of methanol molecule on a basic site with subsequent dissociation of the methanol molecule can be expressed as follows.

$$(r_{ad})_a = (k_{ad})_a P_a C_v{}^2{}_{,B} - [(k_{ad})_a/K_a] C_{alk,B} C_{p,B}, \quad (9)$$

where the subscript B on C_{alk} and C_p terms indicates that alkoxide anions and protons are adsorbed on B-type sites. Since Eq. (3c) is at equilibrium $(r_{ad})_a = 0$, and noting that $C_{p,B} = C_{alk,B}$ as per assumption number 3, the above equation gives

$$C_{p,B} = C_{alk,B} = \sqrt{K_a P_a} C_{v,B}. \quad (10)$$

The rate-controlling step, Eq. (4) gives

$$r_s = (k_4 C_{a,A} C_{alk,B}/C_t), \quad (11)$$

where $C_{a,A}$ = concentration of adsorbed alcohol on A site. According to assumption number 5, $C_{a,\mathrm{A}}$ is approximately constant (similar to pseudo first-order reaction).

$$r_s = k'_4 C_{\mathrm{alk},\mathrm{B}}, \tag{12}$$

where $k'_4 = (k_4 C_{a,\mathrm{A}}/C_t)$.

Combining Eqs. (10) and (12) we get,

$$r_s = k'_4 \sqrt{K_a P_a}\, C_{v,\mathrm{B}}. \tag{13}$$

Equation (6) at equilibrium gives

$$C_{e,\mathrm{B}} = K_e P_e C_{v,\mathrm{B}}. \tag{14}$$

Equation (7) at equilibrium gives

$$C_{w,\mathrm{B}} = K_w P_w C_{v,\mathrm{B}}. \tag{15}$$

Now,

$$C_t = C_{v,\mathrm{A}} + C_{v,\mathrm{B}} + C_{a,\mathrm{A}} + C_{\mathrm{alk},\mathrm{B}} + C_{p,\mathrm{B}} + C_{e,\mathrm{B}} + C_{w,\mathrm{B}}. \tag{16}$$

Since $C_{a,\mathrm{A}}$ is approximately constant (assumption number 5), $C_{v,\mathrm{B}}$ is negligible (assumption number 6) and $C_{v,\mathrm{A}} = 0$ (assumption number 1a), Eq. (16) reduces to Eq. (17) below.

$$C_t - C_{a,\mathrm{A}} = C_{\mathrm{alk},\mathrm{B}} + C_{p,\mathrm{B}} + C_{e,\mathrm{B}} + C_{w,\mathrm{B}} = \text{constant}. \tag{17}$$

Combining Eq. (17), (10), (14), and (15), and noting that $P_e = P_w$,

$$C_{v,\mathrm{B}} = \frac{C_t - C_{a,\mathrm{A}}}{2\sqrt{K_a P_a} + (K_e + K_w) P_w}. \tag{18}$$

Equations (13) and (18) can be combined to get

$$r_s = \frac{k'_4 (C_t - C_{a,\mathrm{A}}) \sqrt{K_a P_a}}{2\sqrt{K_a P_a} + (K_e + K_w) P_w}. \tag{19}$$

Rearranging Eq. (19) to group the constants, we get

$$r_s = \frac{1}{2} \left(\frac{k'_4 (C_t - C_{a,\mathrm{A}}) \sqrt{P_a}}{\sqrt{P_a} + [(K_e + K_w)/(2\sqrt{K_a})] P_w} \right). \tag{20}$$

CONCLUSIONS

Noting that $r_e = r_s/2$, Eq. (20) can be reduced to Eq. (1), the kinetic-rate equation, which fits the data of Knoezinger and co-workers (*3*, *4*), the data of Balaceanu and Jungers (*2*), and the data of Padmanabhan (*5*):

$$r_e = r_o \sqrt{P_a} / (\sqrt{P_a} + b P_w), \tag{1}$$

where r_o and b can be obtained from Eq. (20) as follows:

$$r_o = k'_4 (C_t - C_{a,\mathrm{A}})/4 = \text{constant}$$

and

$$b = (K_e + K_w)/(2\sqrt{K_a}).$$

It is interesting to note here that Knoezinger and co-workers (*3*, *4*) suggested that the constant b involved the ratio of K_W and $\sqrt{K_a}$.

NOMENCLATURE

A,B	Subscripts denoting acidic and basic sites, respectively.
alk,p,a,e,w	Subscripts denoting alkoxide anion, proton, alcohol, ether, and water molecules, respectively.
b	Constant, $(\mathrm{atm})^{-1/2}$.
$C_{j,i}$	Molal concentration of adsorbed component j, moles per unit mass of catalyst. Subscript i indicates the type of site on which the component j is adsorbed.
C_t	Molal concentration of total active sites per unit mass of catalyst.
$C_{v,i}$	Molal concentration of vacant adsorption sites per unit mass of catalyst. Subscript i indicates the type of active sites.
K_j	Adsorption equilibrium constant for component j, atm^{-1}.
k_4	Forward reaction-rate constant for the nucleophilic-displacement surface reaction 4.
k_{ad}	Adsorption velocity constant, time^{-1} atm^{-1}.
P_j	Partial pressure of component j, atm.
r_{ad}	Net adsorption rate, moles per unit time per unit mass of catalyst.
r_e	Rate of ether formation, moles per unit time per unit mass of catalyst.
r_o	Initial reaction-rate constant, moles per unit time per unit mass of catalyst.
r_s	Net surface reaction rate, moles per unit time per unit mass of catalyst.
s_A,s_B	Acidic and basic active sites.

REFERENCES

1. EMMETT, P. H., *Catalysis* **7,** 112 (1960).
2. BALACEANU, J. C., AND JUNGERS, J. C., *Bull. Soc. Chim. Belg.* **60,** 476 (1951).
3. KNOEZINGER, H., AND KALLO, D., *Chem. Ing. Tech.* **39,** 676 (1967).
4. KNOEZINGER, H., AND RESS, E., *Z. Phys. Chem. (Frankfurt am Main)* **154,** 136 (1967).
5. PADMANABHAN, V. R., "Characterization of Flow in a Fluidized Bed," Ph.D. thesis, 1970, University of Louisville, Louisville, KY.
6. JAIN, J. R., AND PILLAI, C. N., *J. Catal.* **9,** 322 (1967).
7. DE BOER, J. H., FORTUIN, J. M. H., LIPPENS, B. C., AND MEIJS, W. M., *J. Catal.* **2,** 1 (1963).
8. HIROTA, K., KUWATA, K., OKAI, T., AND ANN, S., *Actes Congr. Int. Catal. 2nd 1960* **1,** 809 (1961).
9. YATES, D. J. C., AND LUCCHESI, P. J., *J. Chem. Phys.* **35,** 243 (1961).