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Linear Free Energy Relationships in Heterogeneous Catalysis. XIII. The Dehydration of Aliphatic Alcohols over Silica-Alumina

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In order to survey the applicability of linear free-energy relationships to the catalytic dehydration of aliphatic alcohols, isopropyl alcohol and *n*-, *s*-, and *t*-butyl alcohols were dehydrated over silica–alumina at 54—166 °C. The dehydration was zero order in alcohol over the pressure range of 0.01 to 0.1 atm. The true activation energies were 32.0, 35.3, 31.7, and 29.9 kcal/mol for isopropyl alcohol and *n*-, *s*-, and *t*-butyl alcohols, respectively. The zero-order rate constants were exclusively affected by the activation energy. A linear relationship was found between the true activation energy, as well as the logarithm of the zero-order rate constant, and the heterolytic bond dissociation energy for the C–O bond in alcohols, $D(R^+OH^-)$. The activation energy increased and the rate constant decreased with an increase in the $D(R^+OH^-)$. These correlations were explained in terms of the heterolytic fission of the C–O bond in the rate-determining step.

The catalytic dehydration of alcohols on oxides has been extensively studied and reviews have appeared by Winfield,[1] Pines and Manassen,[2] Knözinger,[3] and Notari.[4] However, there have been few studies of linear free-energy relationships (LFER) and, furthermore, such studies as have been made have been restricted mainly to alumina. In previous LFER studies of the dealkylation[5] and isomerization[6] of alkylbenzenes over silica–alumina, we found that the apparent activation energies, as well as the logarithms of the first-order rate constants, have linear correlations with $\Delta H_{C^+}(R)$, the enthalpy change for hydride abstraction from the corresponding paraffin.

The present study was devoted to a survey of the applicability of the LFER to the catalytic dehydration of aliphatic alcohols over silica–alumina.

Experimental

Materials. The silica–alumina (SA-1, 13% Al_2O_3) in powder form was taken from the same batch as that used earlier.[6] The catalyst was calcined at 550 °C for 8 h in the atmosphere. The alcohols used were GR-grade reagents: the isopropyl alcohol and *n*- and *s*-butyl alcohols were dried over CaO and distilled; the *t*-butyl alcohol was shaken with $CaCl_2$ for 20 min and then distilled. The alcohols were finally stored over a molecular sieve 4A.

Apparatus. A continuous-flow mode was used for the reaction, as is shown in Fig. 1. Hydrogen as a carrier gas was deoxygenated with a Deoxo column (B), divided into three streams, and then dried by means of dry ice–ethanol traps (D_1—D_3). Each alcohol was introduced into the first hydrogen stream with a flow rate of about 40 STP ml/min from a microfeeder (F), vaporized, and then diluted with the second hydrogen stream, whose flow rate was usually above 600 STP ml/min. A vessel (H, with an effective volume of about 90 ml) filled with glass beads reduced a small but unnegligible cyclic fluctuation (*ca.* ±15%) in the feed rate of the reactant to a satisfactory extent (below ±5%). A conventional TCD cell (G) in the vaporizer (I) monitored the reactant pressure. The stream through a glass reactor (J) was led to a gas-sampling valve (K) of a GLC apparatus (M). A wet gas meter (N) determined the total flow rate of the carrier gas after the removal of the condensable materials with a dry ice–ethanol or an ice-NaCl trap (D_4). A column of PEG 400 (2m) or of PEG 6000 (0.7 m) was used for analysis. In some experiments, a DMS column (6 m) was also used for the analysis of olefins.

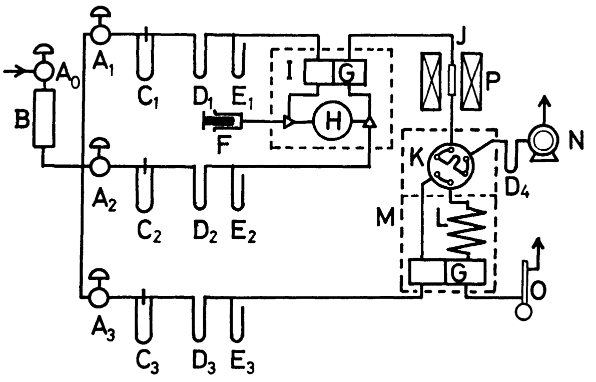

Fig. 1. Schematic diagram of the apparatus.
(A) Pressure regulator, (B) Deoxo column, (C) orifice meter, (D) cold trap, (E) mercury manometer, (F) microfeeder, (G) TCD cell, (H) vessel (*ca.* 90 ml), (I) vaporizer, (J) reactor, (K) six-way gas-sampling valve, (L) analytical column, (M) GLC apparatus, (N) wet gas meter, (O) soap-film meter, (P) furnace.

Procedures. The catalyst was held in the reactor with quartz wool plugs and activated at 450 °C for 1—2 h in a hydrogen stream with a flow rate of about 50 ml/min. The alcohol pressure was modified over the range of 0.01 to 0.1 atm by changing the feed rate of the alcohol. The alcohol were dehydrated at 120—166 °C for a primary alcohol, at 100—145 °C for a secondary one, and at 54—80 °C for a tertiary one. A proper amount of the catalyst (0.01—5.4 g) was used depending upon the reaction temperature and the reactivity of the alcohols. In all the runs, the fractional conversion was less than 0.1 (in most runs, less than 0.05), so that the reactor was regarded as differential. Under the above reaction conditions, only a dehydration reaction occurred to yield olefin, which resulted from β-elimination, and water. No other products were dected by GLC. The activity of the catalyst was almost constant during the course of the reaction.

Results

External Diffusion Effects. These experiments were performed with the most reactive *t*-butyl alcohol and moderately reactive *s*-butyl alcohol by changing the total flow rate of the carrier gas. The results are shown

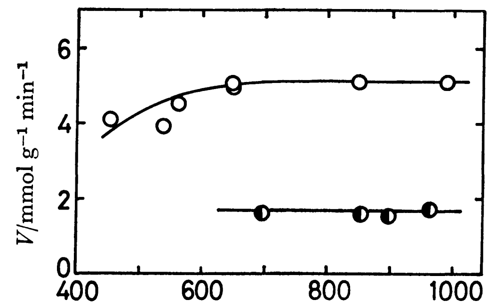

Fig. 2. Influence of flow rate of carrier on dehydration rate.
○: *t*-Butyl alcohol at 80 °C and 0.025 atm;
◐: *s*-butyl alcohol at 135 °C and 0.01 atm.

in Fig. 2. The dehydration rates of *t*-butyl alcohol at 80 °C, the highest in the present study, show no change in magnitude when the flow rate of the carrier is kept higher than about 650 STP ml/min, indicating that no external diffusion affects the reaction rate under such conditions. The carrier was, therefore, passed through at a flow rate higher than 650 STP ml/min in all subsequent runs.

Effects of Alcohol Pressure. The effect of the alcohol pressure on the dehydration rate was investigated at the high-temperature extreme for each alcohol. As is shown in Fig. 3, the dehydration rates are zero order in alcohol over the entire pressure range employed, implying that the rate-determining step is one which involves the reactions of adsorbed species. The zero-order kinetics should hold over the entire temperature range applied to each alcohol since the heat of adsorption is generally exothermic. With *t*- and *s*-butyl alcohols this was ascertained to be the case. The dehydration rates, therefore, give the rate constants of the dehydration of the adsorbed species.

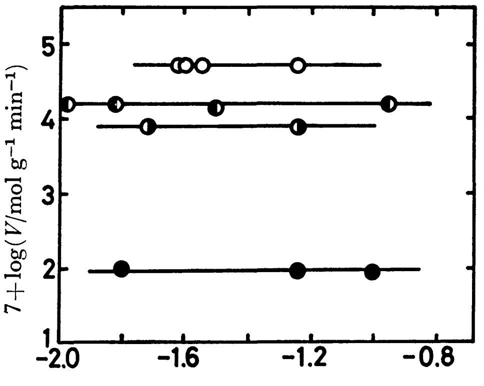

Fig. 3. Influence of alcohol pressure on dehydration rate.
○: *t*-Butyl alcohol (80 °C); ◐: *s*-butyl alcohol (136 °C); ●: butyl alcohol (149 °C); ◑: isopropyl alcohol (145 °C).

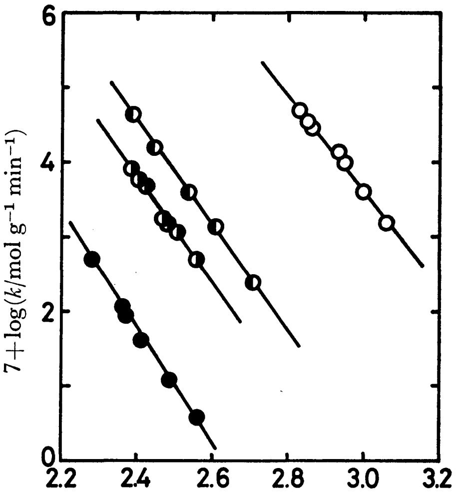

Fig. 4. Influence of temperature on dehydration rate constant.
○: *t*-Butyl alcohol; ◐: *s*-butyl alcohol; ●: butyl alcohol; ◑: isopropyl alcohol.

Effects of Reaction Temperature. The experiments were carried out at a constant alcohol pressure of about 0.02 atm. The zero-order rate constants are plotted in Arrhenius diagrams (Fig. 4). The Arrhenius parameters were determined by means of a least-squares method. The results are given in Table 1. This table also shows, as $\log(k/k_0)$, the rate constants relative to those for butyl alcohol at the low- and high-temperature extremes used. The rate constants for temperatures not covered by the experimental data were determined by extrapolation.

Internal Diffusion Effects. The effects were examined using the formula given by Weisz:[7]

$$\Phi = \frac{dN}{dt}\frac{1}{C_0}\frac{R^2}{D_{\mathrm{eff}}},$$

where dN/dt is the reaction rate in mol s⁻¹ cm⁻³; C_0,

Table 1. RATE CONSTANTS AND ARRHENIUS PARAMETERS FOR THE DEHYDRATION OF ALCOHOLS OVER SILICA–ALUMINA

Alcohol	$\log(k/k_0)$[a] at t/°C=166	$\log(k/k_0)$[a] at t/°C=54	E_A[b] / kcal mol⁻¹	$\log\left(\frac{A^{b)}}{\text{mol g}^{-1}\text{ min}^{-1}}\right)$
Butyl	0	0	35.3±0.6	13.5±0.3
Isopropyl	1.85	2.41	32.0±1.3	13.7±0.7
s-Butyl	2.49	3.11	31.7±0.7	14.2±0.4
t-Butyl	5.39	6.32	29.9±0.2	16.2±0.2

a) The rate constant, k_0, is for butyl alcohol dehydration; k_0/mol g⁻¹ min⁻¹=7.8×10⁻⁵ and 7.3×10⁻¹¹ at t/°C=166 and 54, respectively. b) E_A is the zero-order activation energy; A, the preexponential factor.

the reactant concentration in mol cm^{-3}; R, the catalyst particle radius in cm, and D_{eff}, the effective diffusion constant in cm^2 s^{-1}. In the present study, the extreme values for these coefficients are as follows: $\mathrm{d}N/\mathrm{d}t=10^{-4}$ mol s^{-1} cm^{-3}; $C_0=10^{-6}$ mol cm^{-3}; $R=10^{-3}$ cm. According to Weisz, the approximate value of D_{eff} is 10^{-3} for the system of a gel such as silica–alumina with a high surface area and a reactant whose molecular weight is about 150. From these data we obtain $\Phi=10^{-1}$. Weisz has shown that the diffusion effect can be excluded when $\Phi \leqslant 6$ for zero-order reactions.

Discussion

Table 1 shows that α-methylation (isopropyl to *t*-butyl) has a marked effect on the rate of dehydration, whereas the effect of β-methylation (isopropyl to *s*-butyl) is small. Thus, the reactivity of alcohols falls in the following order: butyl$\ll$isopropyl$<$*s*-butyl$\ll$*t*-butyl for dehydration. This trend is quite similar to that of the increasing stability of alkyl cations (see $\Delta H^\circ_f(\mathrm{R}^+)$ in Table 2). Analogous rate relationships are found in the literature concerning a variety of heterogeneously or homogeneously catalyzed elimination reactions in the gas phase: the dealkylation of monoalkylbenzenes over silica–alumina;[5a] the dehydration of aliphatic alcohols over alumina[8] and hydroxyapatite,[9] or with gaseous hydrogen halide molecules;[10] the dehydrohalogenation of monohaloalkanes over salt catalysts,[11] and the dehydrosulfurization of alkyl mercaptans over silica–alumina.[12] The rate-constant data in Fig. 4 and Table 1 are for zero-order kinetics; therefore, the activation energies should not include heats of adsorprion. The major factor affecting the dehydration rates is clearly the activation energy, since the preexponential factor, *A*, does not vary except in the case of *t*-butyl alcohol. The activation energy decreases in the following order:

butyl > isopropyl > *s*-butyl > *t*-butyl

A similar sequence is also found in the literature.

Mochida and Yoneda[5b] obtained a linear relationship between the apparent activation energy, or the logarithm of the first-order rate constants, for the dealkylation of monoalkylbenzenes over silica–alumina and $\Delta H_{\mathrm{C}^+}(\mathrm{R})$, the enthalpy change for the hydride abstraction from the corresponding paraffins. They explained this relationship in terms of the heterolytic fission of the $\mathrm{C}_{\mathrm{alkyl}}$–$\mathrm{C}_{\mathrm{phenyl}}$ bond in the rate-determining step. For the gas-phase dehydrohalogenation of monohaloalkanes, Maccoll and his co-workers[10] found a linear relationship between the activation energy and the heterolytic bond dissociation energy of the C–X bond, $D(\mathrm{R}^+\ \mathrm{X}^-)$ (in this case, X=Cl, Br, and I). This correlation led them to the conclusion that the rate of elimination was determined by the heterolysis of the C–X bond.

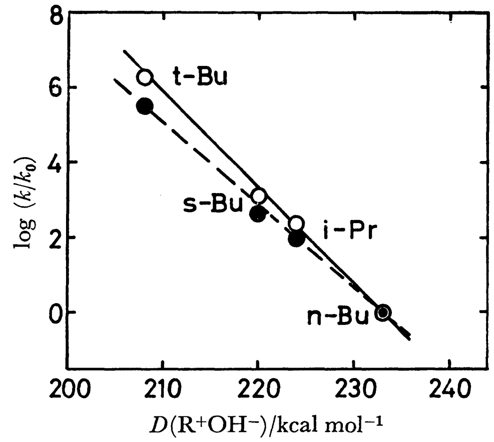

Fig. 5. Correlations of dehydration rate constant on silica–alumina with heterolytic bond dissociation energy, $D(\mathrm{R}^+\mathrm{OH}^-)$, of the C–O bond.
○: At t/°C=54; ●: at t/°C=166.

TABLE 2. HETEROLYTIC BOND DISSOCIATION ENERGY AND RELATED THERMODYNAMICAL QUANTITIES[a,b,c]

R and X	ΔH°_f(R or X)[d] kcal mol^{-1}	IP(R)[e] or EA(X) kcal mol^{-1}	$\Delta H^\circ_f(\mathrm{R}^+$ or $\mathrm{X}^-)$ kcal mol^{-1}	ΔH°_f(ROH)[f] kcal mol^{-1}	ΔH°_f(RH)[f] kcal mol^{-1}	$D(\mathrm{R}^+\mathrm{OH}^-)$ kcal mol^{-1}	$D(\mathrm{R}^+\mathrm{H}^-)$ kcal mol^{-1}
R=							
Et	25.7	193.3	219.0	−56.12	−20.24	242	273
n-Pr	21.0	186.8	207.8	−61.55	−24.82	236	267
i-Pr	17.6	174.1	191.7	−65.15	−24.82	224	251
n-Bu	16.0	184.7	200.7	−65.15	−30.15	233	265
i-Bu	14.0	184.7	198.7	−67.9[g]	−32.15	234	265
s-Bu	12.4	170.9	183.3	−69.86	−30.15	220	248
t-Bu	6.8	159.8	166.6	−74.7[h]	−32.15	208	233
X=							
OH	9.3	42.2[i]	−32.9				
H	52.1	17.9[j]	34.2				

a) ΔH°_f is the standard heat of formation; *IP*, the ionization potential; *EA*, the electron affinity; $D(\mathrm{R}^+\mathrm{X}^-)$, the heterolytic bond dissociation energy for the R–X bond. b) $\Delta H^\circ_f(\mathrm{R}^+)=\Delta H^\circ_f(\mathrm{R})+IP(\mathrm{R})$, $\Delta H^\circ_f(\mathrm{X}^-)=\Delta H^\circ_f(\mathrm{X})-EA(\mathrm{X})$, $D(\mathrm{R}^+\mathrm{X}^-)=\Delta H^\circ_f(\mathrm{R}^+)+\Delta H^\circ_f(\mathrm{X}^-)-\Delta H^\circ_f(\mathrm{RX})$. c) Et=ethyl, Pr=propyl, Bu=butyl. d) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). e) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970). f) D. S. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, New York (1969). g) H. A. Skinner and A. Snelson, *Trans. Faraday Soc.*, **56**, 758 (1960). h) E. T. Beynon and J. J. McKetta, *J. Phys. Chem.*, **67**, 2761 (1963). i) L. M. Branscom, *Phys. Rev.*, **148**, 11 (1966). j) D. Feldmann, *Z. Naturforsch.*, **25a**, 621 (1970).

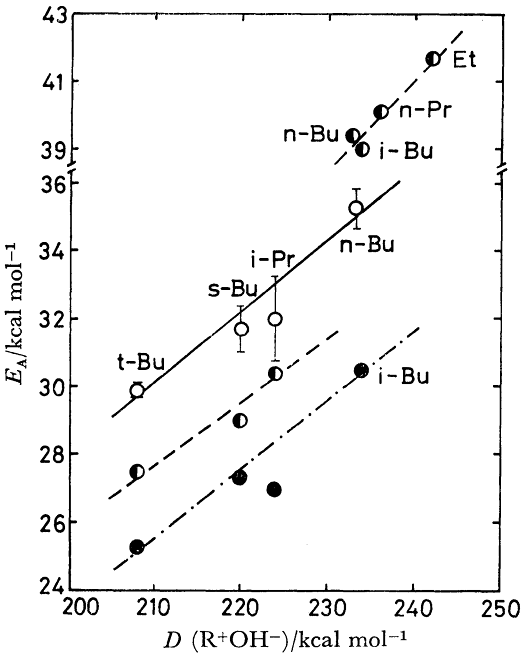

Fig. 6. Correlations of zero-order activation energy for alcohol dehydration on various catalysts with heterolytic bond dissociation energy, D(R$^+$OH$^-$), of the C–O bond.
○: The present study (on silica–alumina); ●: Knözinger and Scheglila[8] (on γ-alumina); ◐: Kibby and Hall[9] (on Ca-deficient hydroxyapatite).

Figure 5 shows the correlation between the relative rate constant of dehydration and the heterolytic bond dissociation energy, D(R$^+$OH$^-$), for alcohols. The relationship of the activation energy with D(R$^+$OH$^-$) is also shown in Fig. 6. From the definition, D(R$^+$X$^-$) is the enthalpy change of the $RX \rightarrow R^+ + X^-$ process, where R is the alkyl group, and X, the substituent, such as OH, halogen or H, so that the previous parameter, $\Delta H_{C^+}(R)$, is D(R$^+$H$^-$). The bond energy, D(R$^+$X$^-$), was calculated for X=OH and H from recent thermodynamical data, as is shown in Table 2. Although D(R$^+$X$^-$) has a linear correlation with $\Delta H_{C^+}(R)$ for each X$^-$, the former seems more attractive than the latter in that it may function as a simple parameter describing the effects of both R and X on the reactivity.

The logarithms of the rate constants relative to that for butyl alcohol have a linear relationship with D(R$^+$OH$^-$) over the range of about six orders of magnitude in the rate constants (Fig. 5), indicating that the lower the heterolytic bond dissociation energy, the higher the rate constant. The activation energies also show a linear relationship with D(R$^+$OH$^-$) (Fig. 6); that is, the activation energy increases with an increase in D(R$^+$OH$^-$). Both linear correlations can readily be explained in terms of the heterolytic rupture of the C–O bond in the rate-determining step. Yamaguchi and Tanabe[13] found no primary isotope effect of C$_\beta$–D in the zero-order dehydration of 2-propanol-d_8 on silica–alumina at 160 °C; they proposed an E1-like mechanism. Thus, the presently obtained LFER, in cooperation with the isotope-effect data, strongly supports the E1-like character of the alcohol dehydration over silica–alumina.

Knözinger and Scheglila[8] found high primary isotope effects in the zero-order dehydration of C$_\beta$-deuterated butyl alcohols, $(CH_3)_2CDCH_2OH$, $C_2D_5CH(OH)CH_3$, and $(CD_3)_3COH$, on alumina at 120—200 °C. They deduced an E2-like mechanism which contains a certain degree of ionic contributions. Their activation-energy data on undeuterated alcohols[8,14] are also plotted in Fig. 6. These activation energies also fall on a straight line, which is separate from, but nearly the same in slope as the line for silica–alumina. Comparisons of the two linear correlations provide information concerning the rate-determining participation of the heterolytic C–O bond fission during the E2-like dehydration couse. The equality in the slope indicates that the heterolytic bond strength of the C–O bond plays as important a role in determining the activation energy for the E2-like dehydration as it does for the E1-like dehydration. The heterolytic loosening of the C–O bond in the transition state may not differ much in the two modes of dehydration.

Furthermore, the activation energy on silica–alumina is approximately 5 kcal/mol higher than that on alumina for each alcohol, as is shown in Fig. 6. Knözinger and Scheglila[8] also found that the deuterium effect on the preexponential factor, A_H/A_D, was approximately 0.01 for each alcohol. More recently, this abnormally low A_H/A_D ratio was taken as evidence by the same group of researchers[14] to demonstrate a certain tunnel contribution to the β-proton abstraction. The tunnel effect is also supported, though they did not claim so, by their own experimental results that the deuterium effect on the activation energy, $E_D - E_H$, was about 5 kcal/mol for each alcohol.[8] This effect greatly exceeds in magnitude the zero-point energy difference between the C$_\beta$–H and C$_\beta$–D stretching vibrations in the initial state, ΔE_0, which is about 1.1 kcal/mol for the substrates in question. The $E_D - E_H < \Delta E_0$ relation also provides strong evidence for proton tunneling.[15] The difference of about 5 kcal/mol for $E_D - E_H$ is comparable to the activation-energy difference between silica–alumina and alumina for the undeuterated alcohol dehydration. The activation energies for deuterated alcohol dehydration on alumina and those for undeuterated alcohol dehydration on silica–alumina will, therefore, fall on a single straight line if they are plotted in Fig. 6. Since tunneling should be much less in the β-deuteron abstraction than in the β-proton abstraction, the observed tunneling contribution to the β-proton abstraction presumably explains most of the slight lowering of the activation energy in the dehydration of undeuterated alcohols over alumina. In addition, the stabilization of the transition state through the interaction of β-deuterium, probably, with a basic site does not seem very large. Therefore, it is highly probable that the activation energy for the E2-like dehydration is determined primarily by the heterolytic bond strength of the C–O bond, much as with that for the E1-like dehydration.

Figure 6 also shows a plot of the activation-energy data reported by Kibby and Hall,[9] who obtained them from the zero-order reaction rates on calcium-deficient hydroxyapatite at 150—400 °C; they presumed an E1-like mechanism for tertiary alcohol and an E2-like one with an ionic character for primary and secondary alcohols. The sequence of increasing activation energy is the same as that of increasing $D(\mathrm{R}^+\mathrm{OH}^-)$. Isopropyl alcohol and *s*- and *t*-butyl alcohols fall on a single straight line, which is quite similar in both slope and the magnitude of activation energy to those for silica–alumina and alumina, although primary alcohols appear to follow a separate straight line. It is clear that, on this catalyst, the activation energy is also determined by the heterolytic bond strength of the C–O bond.

In spite of the fact that these three catalysts are quite different materials, the alcohol dehydrations catalyzed by them are very similar in the magnitude of the activation energy and its dependence upon $D(\mathrm{R}^+\mathrm{OH}^-)$. This may be a reflection of a similarity in the nature of the active centers which first attack the oxygen atom of the C–O bond. As such active centers, Knözinger and his co-workers,[3] and Kibby and Hall[9] proposed acidic surface hydroxyls on their catalysts. With silica–alumina, Brønsted acid sites are most likely to be active centers in view of the experimental finding[16] that the response of the ethanol dehydration rates to the Na^+-poisoning of silica–alumina is very similar to that of the cumene dealkylation rates, which have been believed to be determined by the Brønsted acidity. For alumina[17,18] and even silica–alumina,[19] on the other hand, another active-center model has been proposed in which incompletely coordinated aluminium ions in the surface are responsible for attacking the oxygen atom of the C–O bond. This problem, then, requires further investigations to be solved.

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