BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1739—1742 (1971)

Dehydration and Dehydrogenation of Alcohols over Acid-Base Bifunctional Catalysts

Hiroo NIIYAMA and Etsuro ECHIGOYA

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received November 12, 1970)

Alkaline earth silicates having both acidic and basic sites can be considered as acid-base bifunctional catalysts. Dehydration and dehydrogenation of alcohols over these catalysts were carried out. Correlation between the selectivity and acid-base properties of alcohols and the catalysts was studied. It was found that acid-base properties of both the catalysts and the alcohols were cooperative in determining the selectivity of reaction.

The dehydration and dehydrogenation of alcohols over oxide catalysts have been studied by many investigators. Some oxides particularly tend to promote dehydration, whereas others have mainly dehydrogenating effects. Several hypotheses[1] were proposed concerning the cause of selectivity; *i.e.*, (1) a geometric factor of the surface structure,[2] (2) type of semiconductor,[3] (3) acidic and basic characters,[4] and (4) some other special parameters, *e.g.*, $\eta\equiv$(cation radius)^3/(mol volume per cation) (charge of cation) proposed by Eucken[5] and Wicke.[6] These attempts were partially successful. However, the relation between the surface properties and reaction mechanism or the nature of the active sites is still obscure. It was the object of this study to clarify the cause of selectivity using acid-base bifunctional catalysts.

Experimental

Preparation of Catalysts. Colloidal silica (Nissan Chem. Co., Snowtex O) was kneaded with equal moles of an alkaline earth hydroxide ($Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$) for 3 hr and calcined at 100°C for 24 hr. It was then heated at 290°C for 24 hr in an autoclave with aqueous ammonia under 80—90 kg/cm^2 pressure. Products were washed several times with ion-exchanged water and then calcined at 600°C for 3 hr.

Measurements of Acidity and Basicity. A titration method in an aprotic medium was employed. Before the measurement, samples were heated at 550°C for 1 hr under air and then degassed at 300°C under 10^{-5}mmHg pressure. *n*-Butylamine (0.02N) and benzoic acid (0.02N) in benzene were used for titration in acidity and basicity measurements, respectively. The following indicators were used; neutral red ($pK_a+6.8$), methyl red ($pK_a+4.8$), dimethyl yellow ($pK_a+3.3$), benzeneazodiphenylamine ($pK_a+1.5$), benzalacetophenon ($pK_a-5.6$), and phenolphtalein ($pK_a+9.3$).

Preparation of Deutrated n*-Propanol* (C_3H_7OD).[7] 200 m*l* of *n*-propanol was subjected to reaction with 5 g of metallic sodium. Unreacted *n*-propanol was removed by vacuum distillation and then 3 g of D_2O were introduced. Produced *n*-C_3H_7OD was trapped with liquid nitrogen. Deutrium concentration was estimated by IR spectroscopy from OD and OH absorption bands and the amount of *n*-C_3H_7OH was confirmed to be negligible.

Reaction Apparatus. The usual fixed bed flow type reactor was employed. A reactant was kept in an evaporator maintained at a constant temperature and introduced into the catalyst bed with hydrogen as the carrier gas. In front of the reactor, a sample inlet made of rubber was attached in order to inject poisonous materials.

All the system was heated to prevent the condensation of reactant or products. Vaporous products were taken out by a sampling cock and analyzed by gas chromatography.

Results and Discussion

Acid-base properties of the catalysts. The properties of the catalysts are given in Table 1. All the catalysts

---

[1] P. Mars, "The Mechanism of Heterogeneous Catalysis," Elsevier Pub. Co., Amsterdam, (1960), p. 49.

[2] A. A. Ballandin, "Advances in Catalysis," Vol. 10, Academic Press, New York (1958).

[3] Z. G. Szabo and F. Solimosi, *Z. Anorg. Allg. Chem.*, **301**, 225, (1959).

[4] K. Tanaka and K. Tamaru, This Bulletin, **37**, 1862 (1964).

[5] A. Eucken, *Naturwissenschaften*, **36**, 48 (1949).

[6] E. Wicke, *Z. Elektrochem.*, **53**, 279 (1949).

[7] A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Vol. 2, Interscience Pub. Inc., New York (1958), p. 1340.

Table 1. Structure and surface properties of the catalyst

Catalyst	Structure	Surface area (m^2/g)	Maximum acid strength(H_0)	Acidity [a] (10^{-7} eq/m^2)	Basicity [b] (10^{-7}eq/m^2)
$MgO \cdot SiO_2$	Speolite	194	−5.6	22.4	[c]
$CaO \cdot SiO_2$	Xonotlite	46	+3.3	7.5	13.7
$SrO \cdot SiO_2$	Strontium metasilicate	9.0	+3.3	3.3	18.9
$BaO \cdot SiO_2$	Barium metasilicate	2.0	+4.8	0	30.3

a) Measured at $H_0=3.3$ b) Measured at $H_0=9.3$ c) Abnormal color was observed.

except for $MgO \cdot SiO_2$ showed fine patterns in X-ray diffraction. The order of acidic nature (acidity and acid strength) was as follows. $MgO \cdot SiO_2 > CaO \cdot SiO_2 > SrO \cdot SiO_2 > BaO \cdot SiO_2$.

The acidic nature of $MgO \cdot SiO_2$ was attributed to the unsaturation of the bond which was produced by the replacement of four coordinated silicon with magnesium.[8] The degree of unsaturation decreases with the increase of ionic radius of the replaced cation and also with the decrease of electronegativity of metal. Thus the sequence of acidic nature can be explained.

On the other hand, the order of basicity was as follows. $BaO \cdot SiO_2 > SrO \cdot SiO_2 > CaO \cdot SiO_2 > MgO \cdot SiO_2$. This was the complete reverse of the order of acidic nature but the same as that of basic nature of the corresponding alkaline earth oxides (BaO>SrO>CaO>MgO).[9] Thus the basicity could be attributed to the small electronegativity of the alkaline earth metals. The amount of uncombined alkaline earth oxides unavoidably present before the progress of chemical reaction in the solid phase, was very small and confirmed to be negligible.[10] It is concluded that these silicates have basic sites as well as acidic sites.

Dehydration and dehydrogenation of alcohols. $CaO \cdot SiO_2$, which showed both acidic and basic natures in comparable degree was chosen as the catalyst in the selectivity studies of this reaction. It showed both dehydration and dehydrogenation activities.

Addition of acidic and basic materials. Figures 1 and 2 show the effects of pyridine and phenol addition on the decomposition of *n*-butanol. These poisons gave no reaction products. 10 *μl* of the substances were introduced into the system as a pulse. Addition of pyridine brought a decrease in the dehydration activity with considerable increase in dehydrogenation activity. On the other hand, phenol inhibited the dehydrogenation reaction and gave no effect on dehydration. The effects were reversible. Thus it was concluded that dehydration took place on acidic sites and dehydrogenation on basic sites.

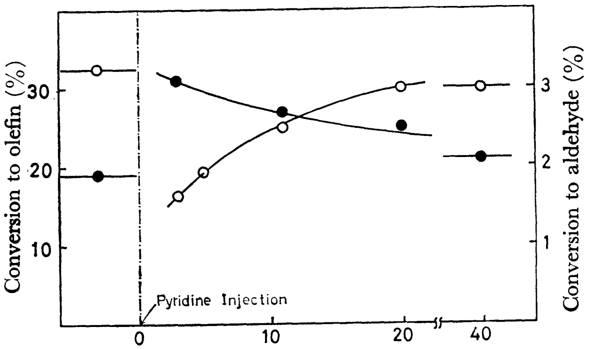


Fig. 1. The effect of pyridine injection on the decomposition of *n*-Butanol over CaO–SiO_2.
—○— butene
—●— butylaldehyde
Reaction temperature; 340°C W/F; 1.49 g-hr/mol Pressure of alcohol; 0.0116 atm.

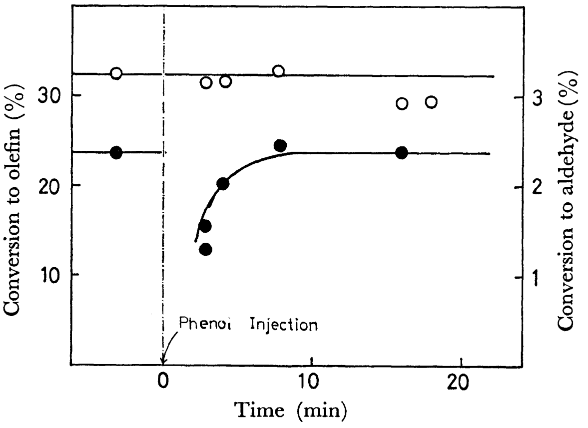


Fig. 2. The effect of phenol injection on the decomposition of *n*-butanol over $CaO \cdot SiO_2$.
—○— butene
—●— butylaldehyde
Reaction temperature; 340°C W/F; 1.49 g-hr/mol Pressure of alcohol; 0.0116 atm

The promoter action of pyridine can be attributed to the inductive effect of adsorbed pyridine. Because of high electron donating ability of pyridine, adjacent sites become rich in electron density and these sites act as basic sites. This hypothesis was confirmed.

Isotope effects on both reaction rates. Either *n*-C_3H_7OH or *n*-C_3H_7OD was introduced into the reactor alternatively. Reaction rates were estimated in the steady state. Experiments were repeated several times and the mean values are given in Table 2. No isotope

Table 2. Isotope effects on both reaction rates over $CaO \cdot SiO_2$

	Conversion(%)		Isotope effects k_D/k_H
	n-PrOH	*n*-PrOD	
Dehydration	1.58	1.51	0.96
Dehydrogenation	1.11	0.59	0.53

Reaction temperature 340°C
Partial pressure of alcohol: 0.1atm
Feed rate of carrier gas: 0.134mol/hr
Weight of catalyst: 1.0g

---

[8] C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949).

[9] J. Take, S. Kikuchi, and Y. Yoneda, *Syokubai*, **10**, 127 (1968).

[10] E. E. Pressler, B. Brunauer, and D. L. Kantro, *Anal. Chem.*, **28**, 896 (1956).

Table 3. Dehydration and dehydrogenation of five alcohols over CaO·SiO$_2$

Reactant	Reaction temperature	Reaction product	Rate of reaction (mol/g hr)		Activation energy (kcal/mol)	
			Dehydration	Dehydrogenation	Dehydration	Dehydrogenation
Ethanol	320—360°C	Ethylene, Ether Acetaldehyde	7.0×10^{-5} b)	1.8×10^{-4}	35b)	14
n-Propanol	290—320°C	Propylene Propionaldehyde	8.6×10^{-5}	6.2×10^{-5}	29	19
n-Butanol	310—350°C	*n*-Butene Butylaldehyde	1.7×10^{-4}	1.5×10^{-5}	26	23
Isopropanol	290—240°C	Propylene Acetone	1.5×10^{-3}	3.5×10^{-6}	23	17
t-Butanol	150—190°C	Isobutene	1.3		33	

a) Sum of the ethylene and ether formation.

b) Activation energy of ethylene formation. Activation energy of (ethylene+ether) formation was 30 kcal/mol.

effect was found in the dehydration reaction while the value 0.53 was obtained for k_D/k_H in the dehydrogenation. This value was close to 0.34 which was obtained by calculation[11] on the assumption that an isotope effect comes from the difference of the zero point energy of reactants. It was concluded that OH rupture was the rate determining step in the dehydrogenation reaction.

Decomposition of five Alcohols. Dehydration and dehydrogenation of five alcohols were carried out. Experimental conditions and the results are given in Table 3. In the dehydration of ethanol, ethylene, and ether were found in the products. Ethylene formation and ether formation took place competitively in the low conversion region. The activation energy shown in Table 3 and Fig. 4 was calculated from the rate of ethylene formation because the reaction paths differed from each other. The reaction rate at 310°C under 55 mmHg of alcoholic pressure was taken as an index of the reactivity of alcohol.

Correlation between the reactivity and Taft's σ^*[12] which represents the electron donating ability of the aliphatic group attached to OH group is shown in Fig. 3. Negative correlation for dehydration and a positive one for dehydrogenation were obtained.

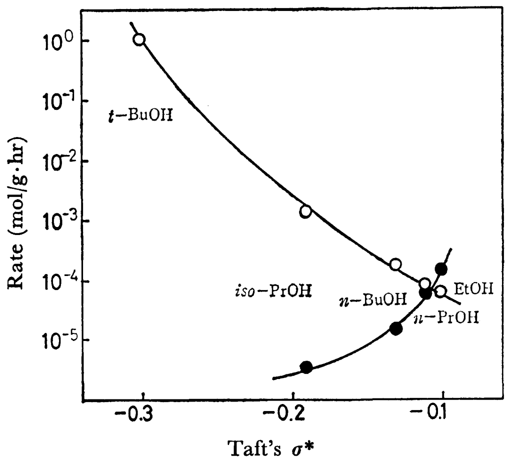


Fig. 3. Correlation between Taft's σ^* and reactivity of alcohols.
—○— dehydration rate
—●— dehydragenation rate

The heat of carbonium ion formation ($\Delta Hc+$) could also be an index of electron donating ability.[13] The larger the $\Delta Hc+$, the more unstable the carbonium ion and thus, the smaller the electron donating ability. Figure 4 shows the correlation between $\Delta Hc+$ and reactivity. Almost the same correlation were obtained.

The activation energies for primary alcohols are also plotted in Fig. 4. Good correlation between ΔHc_+ and the activation energy of primary series indicates that this reactivity sequence can be referred to an energetic factor.

Both horizontal axes in the figures can also be considered to express electron density of OH group, or acid-base properties of alcohol. Therefore, it is concluded that dehydration tend to take place as the basicity of alcohol increases and dehydrogenation becomes predominant as the acidity of the alcohol increases.

The reactivity sequence of alcohols over this catalyst is quite different from that observed over metal catalysts. Over the copper catalyst which is commonly used in the dehydrogenation of alcohols, ethyl, *n*-propyl, and *n*-butyl alcohol have almost the same reactivity,

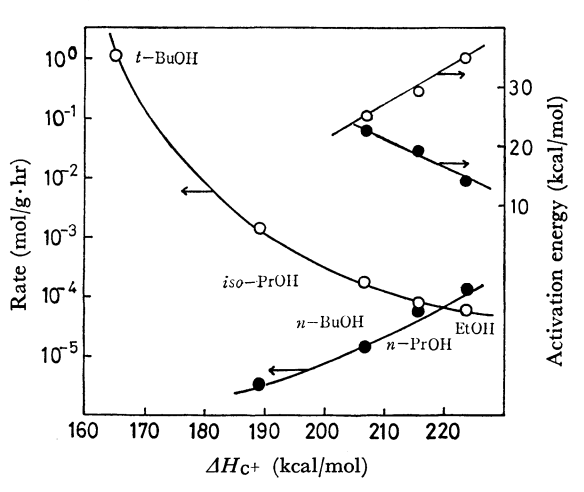


Fig. 4. Correlation between ΔHc+ and reactivity of alcohols.
—○— dehydration
—●— dehydrogenation

---

11) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, (1960), p. 17

12) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons Inc., New York (1956).

13) I. Mochida and Y. Yoneda, This Bulletin, **40**, 2711 (1967).

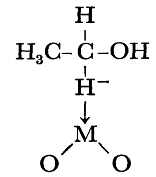
TABLE 4. CATALYTIC ACTIVITY OF VARIOUS ALKALINE EARTH SILICATES

Silicates	Dehydration rate		Dehydrogenation rate		Selectivity[c)]
	mol/g·hr	mol/meq·hr[a)]	mol/g·hr	mol/meq·hr[b)]	
$MgO \cdot SiO_2$	65×10^{-3}	147×10^{-3}	——	——	0
$CaO \cdot SiO_2$	2.8×10^{-3}	82×10^{-3}	0.18×10^{-3}	2.9×10^{-3}	0.06
$SrO \cdot SiO_2$	0.018×10^{-3}	12×10^{-3}[d)]	0.015×10^{-3}	0.88×10^{-3}	0.45
$BaO \cdot SiO_2$	0.0097×10^{-3}	——	0.0065×10^{-3}	1.1×10^{-3}	0.40

a) Rate per unit acidity (H_0 +3.3)
b) Rate per unit basicity
c) Selectivity is defined as dehydrogenation rate/total rate.
d) Acidity measured was below 0.003, and the value 0.0015 was assumed for the acidity.

and isopropanol reactivity five times higher than that of primary alcohols.[14] This suggests that the hydrogen release from carbinol carbon is the rate determining step over metal catalysts.

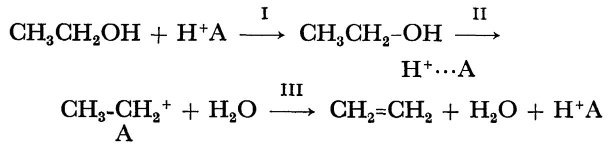
Eucken showed that the dehydrogenation selectivity increased over various oxides in the decomposition of ethanol could be correlated well with η[5]. Selectivity increased as η became greater. They considered that the matal atom was exposed on the surface of the oxide as the ionic radius, as well as η, increased. They proposed the following mechanism. If the dehydrogenation activity of this catalyst is attributed to the hydride ion affinity of metal, the reactivity sequence would differ from the one obtained.



Tanaka *et al.*[4] pointed out that the physical meaning of η is acid-base properties of the surface. This coincides with our results.

Reaction mechanisms. Reaction mechanisms for both reactions (for example, ethanol decomposition) can be expressed as follows.

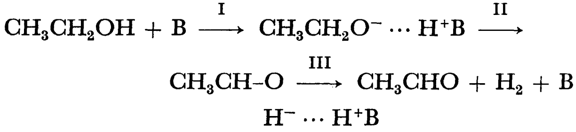
Dehydration



$$CH_3CH_2OH + H^+A \xrightarrow{I} \underset{H^+\cdots A}{CH_3CH_2\text{-}OH} \xrightarrow{II} \underset{A}{CH_3\text{-}CH_2^+} + H_2O \xrightarrow{III} CH_2{=}CH_2 + H_2O + H^+A$$

The reactivity sequence suggests that either process I or II is rate determining.

Dehydrogenation



$$CH_3CH_2OH + B \xrightarrow{I} CH_3CH_2O^- \cdots H^+B \xrightarrow{II} \underset{H^- \cdots H^+B}{CH_3CH\text{-}O} \xrightarrow{III} CH_3CHO + H_2 + B$$

H^+A; acidic site B; basic site

The reactivity sequence and existence of an isotope effect suggest that process I is the rate determinig step.

Activity and Selectivity of the Various Alkaline Earth Silicates. Decomposition of *n*-butanol over alkaline earth silicates with various acidity and basicity was studied. No dehydrogenation reaction was found over $MgO \cdot SiO_2$, while both reactions were observed over $CaO \cdot SiO_2$, $SrO \cdot SiO_2$, $BaO \cdot SiO_2$. Reaction rates at 350°C are given in Table 4. Selectivity was defined as dehydrogenation rate/total consumption rate.

Selectivity increased with the increase of the basic nature of the catalyst. Dehydration rate per unit acidity showed no specific value. It increased with the increase of acid strength. Besides acidity, acid strength also plays a role in the dehydration of alcohols. On the other hand, dehydrogenation rate per unit basicity remained constant.

---

[14] W. G. Palmer and F. H. Constable, *Proc. Roy. Soc.*, **107A**, 255 (1925).