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The Isomerization of Propylene Oxide on Metal Phosphate Catalysts

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The isomerization of propylene oxide was carried out on metal phosphate catalysts. The main products were allyl alcohol, propionaldehyde, acetone, and 1-propanol. It was found that allyl alcohol is produced by acid-base bifunctional catalysts, acetone, by basic-site catalysts only, and propionaldehyde, by acid-site catalysts. 1-Propanol may be produced by the hydrogen-transfer reaction of allyl alcohol. The conversion to propionaldehyde is proportional to the acidity of the catalyst, the strength of which is stronger than $H_0=+4.8$. The sum of the conversions to allyl alcohol, acetone, and 1-propanol correlate linearly with the observed basicity ($H_0 \geqq +7.2$) of the catalyst. The selectivity and activity are determined by the basic and acidic properties of the catalyst. The mechanisms of the propylene oxide isomerization are also discussed.

The activity and selectivity for a reaction on solid acids and bases are considered to be determined by the acidic and basic properties of the catalysts, and it is important to clarify the reaction between the acidic and basic properties of the catalysts and the selectivities and activities for the reactions. The relations between the activities and the observed acidities or basicities have already been reported by many workers.[1-4] However, as regards the relationship between the selectivity and the acidic and basic properties of the catalysts, little work has been done. Misono and his co-workers[5,6]

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[1] A. Tada, Y. Yamamoto, M. Ito, and A. Suzuki, Annual Meeting of the Chemical Society of Japan, 22nd, Tokyo, Preprints of Papers, No. 06421 (1969).

[2] K. Tarama, S. Teranishi, K. Hattori, and T. Ishibashi, *Shokubai* (Tokyo), **4**, 69 (1962).

[3] Y. Ogino, *ibid.*, **4**, 73 (1962).

[4] K. Saito and K. Tanabe, *ibid.*, **11**, 206 (1969).

[5] M. Misono, Y. Saito, and Y. Yoneda, *J. Catal.* **9**, 135 (1967).

[6] M. Misono, Y. Saito, and Y. Yoneda, *ibid.*, **10**, 88 (1968).

have reported that the selectivities for the *n*-butene isomerization reaction over metal sulfates are determined by the acid strength of the catalyst. According to Niiyama and E. Echigoya[7] the selectivity for the dehydration and dehydrogenation of alcohols over acid-base bifunctional catalysts is controlled by the acid and base properties of catalysts. In our preceding paper,[8] the selectivity for the propylene-oxide isomerization on zeolite catalysts was determined by the acid strength of the catalysts. In this paper, the selectivity and activity for the propylene-oxide isomerization over metal phosphates will be investigated with respect to the acidic and basic properties of the catalysts.

Propylene oxide is generally isomerized to acetone, propionaldehyde, and allyl alcohol, but only a trace of allyl alcohol wasproduced on zeolite catalysts.[8] Fowler and Fitzpatrick[9] have reported that basic lithium phosphate has a high selectivity to allyl alcohol. It has been reported by Mathieu and co-workers[10,11] that propylene oxide is isomerized to allyl alcohol by basic sites on lithium phosphates and to propionaldehyde by acid sites on the 3.9 $Cr_2O_3 \cdot 1.1\ WO_3 \cdot 1.8\ H_2O$ catalyst.

The isomerization of propylene oxide on metal phosphates will be studied here. The relations between the selectivities and activities and the acidic and basic characteristics of catalysts are discussed. Moreover, a possible reaction mechanism of the isomerization is also discussed.

Experimental

Materials. The catalysts used were as follows: $NaLi_2PO_4$ (basic lithium phosphate), KLi_2PO_4, Na_2LiPO_4, K_2LiPO_4, $AlPO_4$, $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$, and Li_3PO_4. Basic lithium phosphate was prepared according to the method by Fowler and Fritzpatrick.[9] KLi_2PO_4, Na_2LiPO_4, and K_2LiPO_4 were prepared from potassium phosphate monobasic, sodium phosphate dibasic, and potassium phosphate dibasic respectively by neutralizing them with equivalent amounts of lithium hydroxide at 40°C. The following procedures were the same as those for basic lithium phosphate. The other reagents were commercial grade.

Procedures. The reactions were carried out using a usual pulse reactor in helium gas as the carrier. The catalysts (about 20 mg) were heated at a reaction temperature for about 2 hr in streaming helium before the reaction, The amount of reactant injected was 2 *μl*. Deactivation of the catalysts used was observed, and the material balance was found to hold approximately in this reaction.

The acidic and basic strengths of catalysts which had been heated at 300°C for 2 hr in air were measured by the conventional indicator method using a Hammett indicator. The acid and base contents were determined by the simple titration method, using *n*-butylamine and benzoic acid as the titers respectively.

Results and Discussion

The acid and basic strengths, the acidity ($H_0 \leq +6.8$ and $+4.8$), the basicity ($H_0 \geq +7.2$), and the surface area measured by the BET method are listed in Table 1 for each catalyst. Lithium phosphate has only acidic character, but Li_2MPO_4- and LiM_2PO_4-type phosphates (M=Na or K) have both basic and acidic properties. The product distributions of propylene oxide isomerization are shown in Table 2. The "other products" in the last column of Table 2 contain acrolein, polymers, and condensed products. Only small amounts of gaseous products and acetaldehyde, which may be products decomposed of propylene oxide and other products, are formed. High selectivities for allyl alcohol were obtained with sodium- or potassium-type lithium phosphates. The activation energies for allyl alcohol, acetone, propionaldehyde, 1-propanol, acetaldehyde, and gaseous products were 13.2, 6.1, 12.9, 12.0, 12.3, and 6.6 kcal/mol respectively over a basic lithium phosphate catalyst.

Generally, it is known[12-14] that when the oxygen atom of propylene oxide is attacked by a proton, the epoxide ring opens at the oxygen-α carbon linkage, and that when the β carbon is attacked by an anion, propylene oxide gives a product in which the oxygen-β carbon bond breaks. On the basis of these facts, it can be estimated that propionaldehyde is produced on acid

TABLE 1. ACIDIC AND BASIC PROPERTIES OF THE CATALYSTS

Catalyst	Surface area (m^2/g)	Maximum acid strength (H_0)	Acidity (mmol/g)[a]	Acidity (mmol/g)[b]	Maximum basic strength (H_0)	Basicity (mmol/g)[c]
Li_3PO_4	1	+4.8	0.020	0.006	—	—
Li_2NaPO_4	39	+6.8	0.025	—	+9.3	0.126
Li_2KPO_4	22	+6.8	0.014	—	+9.3	0.046
$LiNa_2PO_4$	15	+6.8	0.050	—	+9.3	0.040
Li_2KPO_4	19	+6.8	0.066	—	+9.3	0.016
$Ca_3(PO_4)_2$	54	+4.8	0.075	0.066	+7.1	0.052
$Mg_3(PO_4)_2$	8	+4.8	0.032	0.036	—	—
$AlPO_4$	28	+1.5	1.14	0.166	—	—

a) Measured at $H_0 = +6.8$ b) Measured at $H_0 = +4.8$ c) Measured at $H_0 = +7.2$

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[7] H. Niiyama and E. Echigoya, This Bulletin, **44**, 1739 (1971).

[8] T. Imanaka, Y. Okamoto, and S. Teranishi, in press.

[9] G. W. Fowler and J. Fitzpatrick, US 2426264.

[10] M. Coudurier, M. N. Mathieu, M. Prettre, B. Imerik, and M. E. Degeorges, *Bull. Soc. Chim. Fr.*, **1968**, 1821.

[11] G. France and M. B. Mathieu, *ibid.*, 2891 (1970).

[12] F. C. Elderfield "Heterocyclic Compounds," Vol. 1 J. Wiley & Sons Inc., New York, London (1959).

[13] A. Weissberger "Heterocyclic Compounds," Vol. 19 Part 1, Part 2, Interscience (1964).

[14] M. Sander, *Chem. Rev.*, **66**, 297, 341 (1966).

Table 2. Product distributions on the propylene oxide isomerization

Catalyst	R. T. (°C)	Conv[a] (%)	G. P. (%)	A (%)	PA (%)	AC (%)	1-PrOH (%)	AA (%)	O. P. (%)
Li_3PO_4	280	1.97	2.52	2.80	65.1	12.4	—	17.2	—
Li_2NaPO_4	260	28.7	0.14	1.11	4.78	2.76	2.79	86.0	2.40
Li_2KPO_4	240	28.2	0.17	1.09	13.3	10.3	2.54	71.2	1.45
$LiNa_2PO_4$	260	15.6	0.09	0.74	14.7	11.4	3.00	68.8	1.30
LiK_2PO_4	260	12.9	0.45	0.78	35.9	17.3	2.00	43.6	5.00
$AlPO_4$	280	42.7	0.14	0.10	91.7	—	0.72	4.44	2.92
$Mg_3(PO_4)_2$	260	20.0	0.71	0.42	75.2	4.70	1.95	15.8	1.31
$Ca_3(PO_4)_2$	260	40.2	0.59	0.59	37.3	13.5	15.0	20.3	11.5

a) Conversion (%)/10 mg cat.

G. P.: Gaseous products, A: Acetaldehyde, PA: Propionaldehyde, AC: Acetone, 1-PrOH: 1-Propanol, AA: Allyl alcohol, O. P.: Other products.

sites and that acetone is formed on basic sites. The poisoning effects of pyridine and dichloroacetic acid on the propylene oxide isomerization reaction were investigated in order to confirm these estimations. Figures 1a and 1b show the effects of pyridine injected with reactants over basic lithium phosphate. The conversions to propionaldehyde, allyl alcohol, and *n*-propanol decrease gradually with an increase in the amount of pyridine added, but those to acetone, acetaldehyde, and gaseous products increase with added pyridine. Without catalysts, only smallamounts of gaseous products and acetaldehyde were produced, and no effects of pyridine were observed. Hence, pyridine shows no catalytic effects in the gas phase. Consequently, it is considered that pyridine is adsorbed on acid sites and makes a basic site strong by means of an inductive effect.

Figures 2a and 2b show the effects of dichloroacetic acid on the reaction. The conversions to acetone, allyl alcohol, 1-propanol, and acetaldehyde decrease gradually with the addition of dichloroacetic acid, but those to propionaldehyde and gaseous products are un-

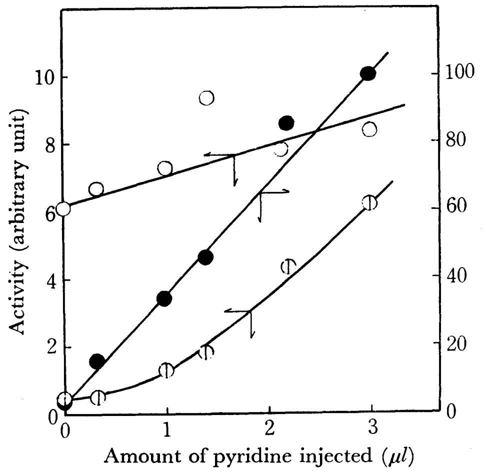

Fig. 1a. Effects of pyridine on the reaction
○: acetone, ●: acetaldehyde, ⦶: gaseous products

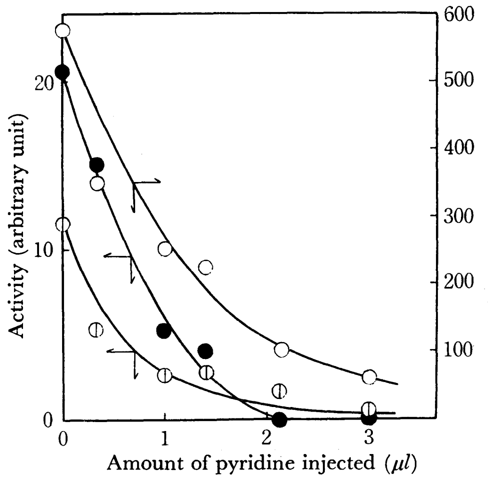

Fig. 1b. Effects of pyridine on the reaction
○: allyl alcohol, ●: propionaldehyde, ⦶: *n*-propanol

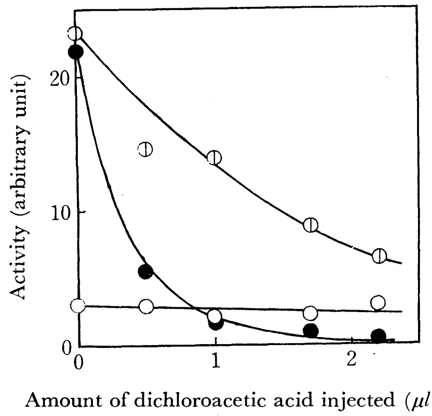

Fig. 2a. Effects of dichloroacetic acid on the reaction
○: gaseous products, ●: acetaldehyde, ⦶: acetone

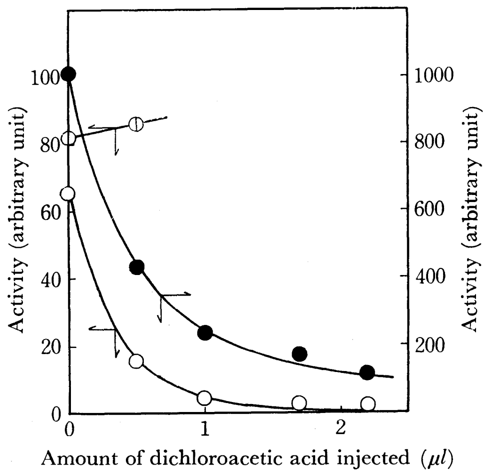

Fig. 2b. Effects of dichloroacetic acid on the reaction
○: 1-propanol, ●: allyl alcohol, ⦶: propionaldehyde

changed. Therefore, it may be concluded that propionaldehyde is produced on acid sites; acetone, acetaldehyde, and gaseous products, on basic sites, and allyl alcohol and 1-propanol, on acid-base bifunctional sites.

According to Table 2, a calcium phosphate catalyst produces larger amount of 1-propanol than do the other catalysts investigated. 1-Propanol is hydrogenated compound of propylene oxide, allyl alcohol, and propionaldehyde. The addition of water to the reaction system has no effect on the formation of 1-propanol. Moreover, in the case of the isomerization of propylene oxide, the amount of acrolein formed over calcium phosphate is 7.1% in the product distribution, but in the case of other catalysts, it is smaller than 1%. Hence, it is considered that the hydrogen atoms in 1-propanol come from the reactant and/or products by hydrogen-transfer reaction. The difference between the amount of 1-propanol and that of acrolein is deduced to be due to the fact that acrolein makes polymers easily. According to Figs. 1 and 2, the amount of 1-propanol gradually decreases as that of allyl alcohol does upon pyridine and dichloroacetic acid poisoning. Since the hydrogen-transfer reaction is considered to be catalyzed by basic sites, according to Schachter and Pines,[15] allyl alcohol must be at least concerned in the 1-propanol formation. Therefore, it may be deduced that 1-propanol and acrolein are produced by the hydrogen-transfer reactions between allyl alcohol and propylene oxide, propionaldehyde, and allyl alcohol.

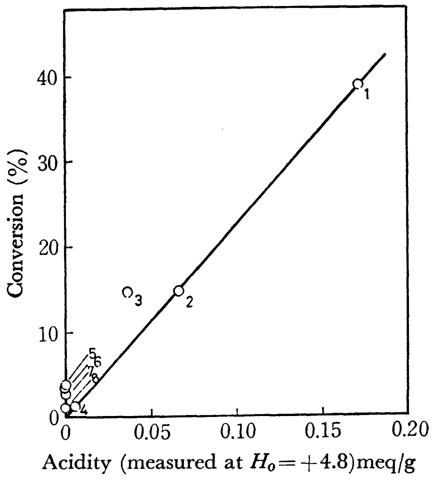

Fig. 3. Correlation between the conversion of propionaldehyde and the acidity measured at $H_0=+4.8$
1: $AlPO_4$, 2: $Ca_3(PO_4)_2$, 3: $Mg_3(PO_4)_2$, 4: Li_3PO_4, 6: KLi_2PO_4, 7: Na_2LiPO_4, 8: Li_2NaPO_4

The relationship between the conversion to propionaldehyde and the amount of the acid site, the strength of which is stronger than $H_0=4.8$, is shown in Fig. 3. However, there was no correlation when the acid content measured at $H_0=+6.8$ was taken into consideration. Therefore, it may be concluded that propionaldehyde is formed on stronger acid sites than $H_0=+4.8$. This conclusion is consistent with the results estimated from the propylene-oxide isomerization over a series of zeolite catalysts.[8] Figure 4 shows the relation between the observed basicity ($H_0=+7.2$) and the sum of the conversions to acetone, allyl alcohol, and 1-propanol. Acetaldehyde and gaseous products were disregarded in view of the small amounts of them formed. However, there were no good correlation between the basicity and the respective conversion to them. Consequently, acetone, allyl alcohol, and 1-propanol are considered to be formed competitively over basic sites.

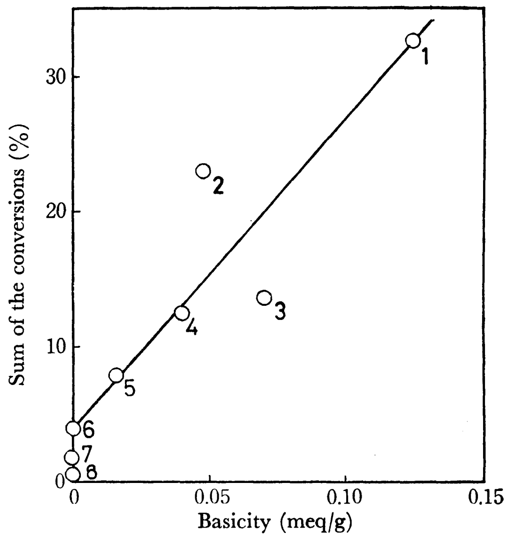

Fig. 4. Correlation between the sum of the conversions to allyl alcohol, acetone, and *n*-propanol and the basicity of the catalyst
1: Li_2NaPO_4, 2: KLi_2PO_4, 3: $Ca_3(PO_4)_2$, 4: Na_2LiPO_4, 5: K_2LiPO_4, 6: $Mg_3(PO_4)_2$, 7: $AlPO_4$, 8: Li_3PO_4.

The formation of allyl alcohol needs both acid and basic sites. However, the Li_2NaPO_4 catalyst, which is most active in allyl alcohol formation, has only weak acid ($H_0=+6.8$). Therefore, it may be concluded that the acid sites which are active for allyl alcohol production are weak ones. According to Fig. 1, the amount of propionaldehyde decreases more rapidly than that of allyl alcohol does. This fact supports our conclusion. As regards the selectivities of acetone and allyl alcohol, the strong base is considered to be favorable for allyl alcohol formation from the following facts. According to Table 1 and Table 2, the Li_2NaPO_4, Li_2KPO_4, $LiNa_2PO_4$, and LiK_2PO_4 catalysts have stronger basic sites and higher selectivities of acetone and propionaldehyde than do the other catalysts. Therefore, it can be concluded that the selectivity and the activity for the propylene oxide isomerization are controlled by the acidic and basic properties of the catalyst.

On the basis of these facts, the reaction mechanisms may be considered to be as follows. In the case of allyl alcohol formation, propylene oxide is adsorbed on the basic site, thus forming carbanion, the carbanion attacks acid sites and the epoxide ring is opened to produce allyl alcohol consequently. The rate-determining step of allyl alcohol formation is considered to be the proton-abstraction process on basic sites on the basis of the facts that the formation of allyl alcohol is controlled by the basicity of the catalyst. As regards acetone, the β carbon of propylene oxide attacks the basic site and the

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[15] Y. Schachter and H. Pines, *J. Catal.*, **11**, 147 (1968).

oxygen-β carbon bond is broken. In the case of propionaldehyde, propylene oxide adsorbs with the oxygen atom on the acid site and the oxygen-α carbon linkage opens. The stronger the acid strength, the more easily the bond is broken, as was shown in the preceding paper.[8)]