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The Isomerization of Propylene Oxide on Zeolite Catalysts

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The selectivity and activity of propylene oxide isomerization have been investigated over zeolite catalysts at 100°C. It has been found that the acid strength of a catalyst is a dominant factor in the selectivity and activity. The stronger the acid strength, the larger the ratio of acetone to propionaldehyde. The reaction intermediates are deduced to be a propylene oxide protonated or that adsorbed on a Lewis-acid site. It has also been found that, in the cases of HY, Silnex (SiO_2), and HY treated with pyridine, the selectivity and activity correlate with the strength of the interaction between the propylene oxide and the surface hydroxyl group. Moreover, it has been clarified that the H_0 value of the surface hydroxyl group observed at 3660 cm^{-1} on HY is -8.2—-5.6, while that found at 3540 cm^{-1} is $+4.0$—$+4.8$.

The activities and selectivities for reactions catalyzed by solid acid are determined by means of the acid properties of catalysts. The relations between activities for reactions catalyzed by acid and the observed acidities of catalysts have already been reported by many investigators,1—7) but there have been few studies of the relations between the selectivity and the acid properties. Misono and his coworkers8,9) have shown that the selectivities for the isomerization of *n*-butenes over metal sulfates are controlled by the acid strength of the catalysts or by the electronegativities of the metal ions. The acid strength determines the electron distributions of the reaction intermediates and consequently controls their stabilities and reactivities. Therefore, it is considered that the acid strength elucidates the selectivity of an acid-catalyzed reaction. In this investigation, the isomerization of propylene oxide on zeolite catalysts was studied in order to clarify the reactions between the selectivity and the acid strength.

Venuto and Landis10) have reported that propylene oxide is isomerized to propionaldehyde, acetone, and allyl alcohol on NaX and REX catalysts at 100—200°C. Matsumoto and his coworkers11) have studied the selectivity for propylene oxide isomerization over metals supported on silica, metal oxides, and metal sulfates. Mathieu *et al.*12,13) have reported that propylene oxide is isomerized to allyl alcohol on the basic sites of lithium phosphates and to propionaldehyde on acid sites of the 3.9 $Cr_2O_3 \cdot 1.1\ WO_3 \cdot 1.8\ H_2O$ catalyst.

In this report, the isomerization of propylene oxide will be studied and the relation between the selectivity (acetone/propionaldehyde) and the acid strength will be discussed. Moreover, the relation between the selectivity for isomerization and the strength of the interaction of the surface hydroxyl group with the reactant will be studied.

Experimental

Materials. The NaY and 10X zeolites were commercial grade. The HY was prepared by conventional ion-exchange procedures using analytical-grade NH_4Cl. The exchange degree of the sodium ion in NaY was found to be 75% according to flame-photometric analysis. The PtY, PdY, and PdHY were prepared from NaY and NH_4Y by the ion-exchange method using chloroplatinic acid and palladiumtetramine dichloride respectively. The degrees of ion exchange were 3.8% for PtY and PdY, and 6.9% for PdHY. PyHY represents the catalyst which was exposed to pyridine vapor of 5 mmHg at 150°C for 30 min and then evacuated at the same temperature for 1 hr under a vacuum of 10^{-4} mmHg. The Silnex (P-526N); SiO_2 was supplied by the Mizusawa Chemical Company.

Procedures. The isomerization of propylene oxide was carried out in a batch reactor at 100°C for 1 hr after treating the catalysts at 400°C for 4 hr under a vacuum of 10^{-4} mmHg. The total pressure was maintained at 10 cmHg by adding propylene oxide to the system in order to compensate for the pressure drop due to adsorption on the catalyst. The weight of the catalyst used was 0.5 g in all cases. The mixture was trapped in a glass ampoule at the temperature of liquid nitrogen, and the liquid components were analyzed by means of gas chromatography.

The infrared spectra of pyridine and propylene oxide adsorbed on catalysts were observed in a IR cell by means of a Hitachi infrared spectrometer. The disks of zeolites and Silnex were prepared by pressing them between polished stainless steel plates to a pressure of about 10 ton/cm^2. After the disks had been treated at 400°C for 4 hr in the IR cell under a vacuum, adsorption experiments were carried out at room temperature.

The acid strength of the catalysts, which had been evacuated at 400°C for 4 hr, were measured by a conventional indicator method using Hammett indicators.

Results and Discussion

The main products arising from the isomerization of propylene oxide on zeolite catalysts were propional-

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13) G. France and M. V. Mathieu, *ibid.*, **1971**, 2891.

Table 1. Conversion and selectivity of the propylene oxide isomerization and acid strength of the catalysts

Catalyst	Conversion (%)		Acetone/ Propion- aldehyde	Acid strength H_0
	Acetone	Propion- aldehyde		
HY	7.2	12.8	0.63	−8.2——5.6
PdHY	4.7	9.3	0.51	−5.6—0.8
PdY	2.9	10.1	0.29	0.8—2.0
PtY	5.1	9.9	0.51	0.8—2.0
10X	7.0	13.0	0.54	0.8—2.0
NaY	0.0_{02}	0.0_{1}	0.20	4.0—4.8
PyHY	0.07	0.23	0.37	4.0—4.8
Silnex	0.27	6.2	0.043	4.0—4.8

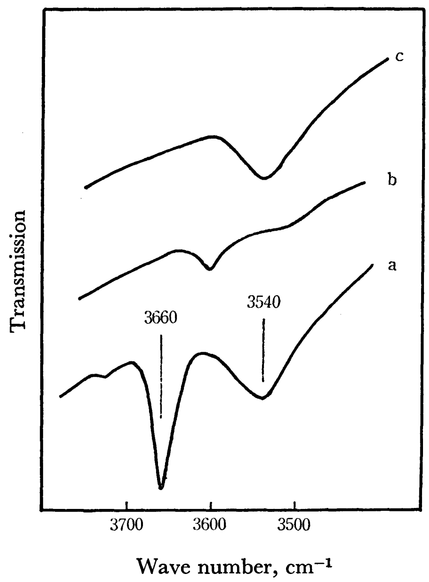

Fig. 1. IR spectra of HY and PyHY catalysts. a: HY, b: HY treated with pyridine vapor of 5 mmHg at 150°C for 30 min c: PyHY ---- after treatment with pyridine vapor, evacuation was carried out at 150°C for 1 hr.

dehyde and acetone. Traces of allyl alcohol, acrolein, water, and condensed products were observed. Table 1 shows the conversions of propylene oxide to propionaldehyde and acetone and the selectivities (acetone/propionaldehyde) for each catalyst. The observed acid strength of each catalyst is presented in the last column of Table 1. The acid strength of PyHY (H_0=+4.0—+4.8) is as weak as those of NaY and Silnex. The IR spectra of PyHY and HY are shown in Fig. 1. HY zeolite has two species of surface hydroxyl groups, which are observed at 3660 cm^{-1} and 3540 cm^{-1}. However, the PyHY catalyst has only one kind of surface hydroxyl group, observed at 3540 cm^{-1}. Therefore, it is considered that the H_0 value of the surface hydroxyl group observed at 3660 cm^{-1} is −8.2——5.6, while the one found at 3540 cm^{-1} is +4.0—+4.8. The acid strength of each surface hydroxyl group has been measured by Hair and Hertl[14] by comparing the frequency shifts observed during the adsorption of basic compounds on surface hydroxyl groups of several oxides with those of alcohols. However, no measurements have been reported using the indicator method.

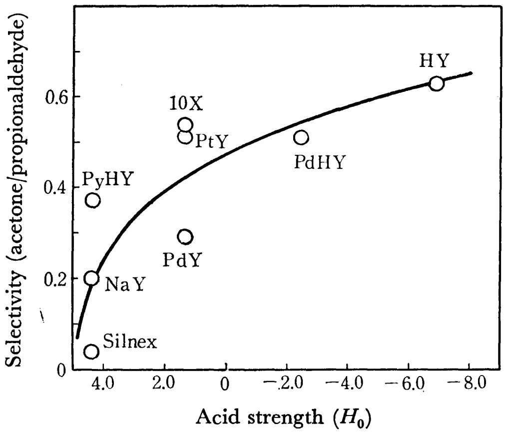

Fig. 2. Correlation between the selectivity (at 100°C) and the acid strength of the zeolite catalyst.

Figure 2 shows the relation between the selectivities for propylene oxide isomerization and the acid strengths of the catalysts used. It is surprising that the stronger the acid strength, the larger the ratio of acetone to propionaldehyde. The only product may be propionaldehyde when the acid strength of the catalyst becomes weaker.

The IR spectra of the HY and Silnex catalysts exposed to propylene oxide are shown in Fig. 2. In the case of Silnex catalyst, the surface hydroxyl group observed at 3740 cm^{-1} interacts with propylene oxide and produces a new broad absorption band at 3370 cm^{-1}, but the surface hydroxyl group found at 3650 cm^{-1} has no interaction with the reactant. The difference between these two hydroxyl groups has been reported by Basila[15] for several compounds adsorbed on silica gel. The adsorption band due to CH_2 in the epoxide ring of propylene oxide exists at 3040 cm^{-1}, and there is no absorption band due to a carbonyl group. These

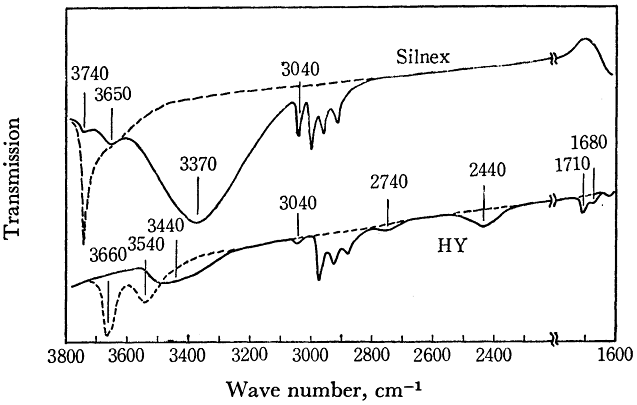

Fig. 3. IR spectra of HY and Silnex after exposure to propylene oxide. Dotted line: before exposure, Solid line: after exposure. Introduction of propylene oxide (pressure; HY: 8 mmHg, Silnex: 18 mmHg), subsequent evacuation for 1 hr, and measurements of IR spectra were carried out at room temperature.

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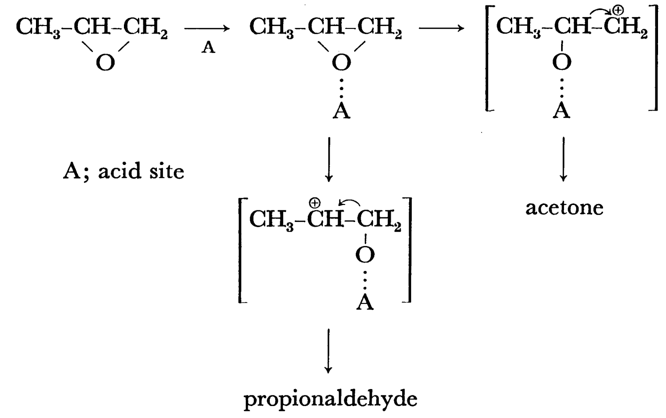
[14] M. L. Hair and W. Hertl, *J. Phys. Chem.*, **74**, 91 (1970).

[15] M. R. Basila, *J. Chem. Phys.*, **35**, 1151 (1961).

facts show that the epoxide ring is not open, and that propylene oxide adsorbs on Silnex to form a protonated propylene oxide. In the case of the HY catalyst, however, a weak absorption band of CH_2 is observed and new bands appear immediately after exposure to propylene oxide at room temperature; these bands are 1710 cm^{-1} (due to carbonyl groups of physisorbed acetone and propionaldehyde), 1680 cm^{-1} (carbonyl groups of chemisorbed acetone and propionaldehyde), 1380 cm^{-1} (CH bending of acetone), and 2740 cm^{-1} (CHO of propionaldehyde). These facts show that acetone and propionaldehyde are produced. Both of the surface hydroxyl groups on HY catalysts observed at 3660 cm^{-1} and 3540 cm^{-1} are considered to interact with propylene oxide to form broad new bands at 3440 cm^{-1} and 2440 cm^{-1}. The reason for this is that when a small amount of acetone or propionaldehyde is adsorbed on the HY catalyst, strong absorption bands due to carbonyl group are observed, but the strength of the band due to surface hydroxyl group is not particularly reduced. The weak absorption bands due to carbonyl groups are observed only in the case of propylene oxide adsorption. Therefore, it is considered that the shifts of the hydroxyl groups can be ascribed to the interaction with propylene oxide. The surface hydroxyl group observed at 3540 cm^{-1} on the PyHY catalyst interacts with propylene oxide to produce a new band at 3440 cm^{-1}, but no bands at about 1700 cm^{-1} and 2440 cm^{-1}. Consequently, the surface hydroxyl group observed at 3660 cm^{-1} interacts with the oxygen atom of the propylene oxide to form a new band at 2440 cm^{-1} and produces two isomerized products, acetone and propionaldehyde, immediately after exposure, while that observed at 3540 cm^{-1} gives a new band at 3440 cm^{-1} because of the interaction with propylene oxide. In the cases of the other catalysts, the propylene oxide interacting with a proton of adsorbed water and the propylene oxide adsorbed on a Lewis-acid site may be reaction intermediates.

The strength of interaction between the surface hydroxyl group and the propylene oxide is measured in terms of $\Delta\nu_{OH}$ that is, the difference between the wave number of the perturbed hydroxyl group and that of the unperturbed hydroxyl group. The values of $\Delta\nu_{OH}$ are 1220 cm^{-1}, 370 cm^{-1}, and 100 cm^{-1} for 3660 cm^{-1} on HY; 3740 cm^{-1} on Silnex, and 3540 cm^{-1} on the HY and PyHY catalysts. The total conversions of propylene oxide to acetone and propionaldehyde are 20.0, 6.47, and 0.30% for the HY, Silnex, and PyHY catalysts, as is shown in Table 1. Fig. 4 shows the relation between the strength of the interaction and the conversion. The relation between the selectivity and $\Delta\nu_{OH}$ is also shown in Fig. 4. It has been reported[16,17] that the acidities of the HY catalyst are about 1 mmol/g in the regions of $-8.2 \leqq H_0 \leqq -5.6$ and $-5.6 \leqq H_0 \leqq +4.8$, and that the acid content of silica gel is also about 1 mmol/g. Therefore, it can be deduced that Fig. 4 shows the approximate effect of the acid strength. The selectivity of isomerization to acetone on the PyHY catalyst in Table 1 is higher than the value estimated from Fig. 4. It is considered, from the IR studies, that the pyridine interacting with the 3660 cm^{-1} hydroxyl group is desorbed partially by the adsorption of propylene oxide during the reaction, and that consequently the isomerized products on PyHY contain some products arising from the HY catalyst. These facts support the idea that the protonated propylene oxide is a reaction intermediate on the HY, PyHY, and Silnex catalysts, and that the acid strength of catalyst controls the selectivity. Therefore, the reaction path may be as follows:



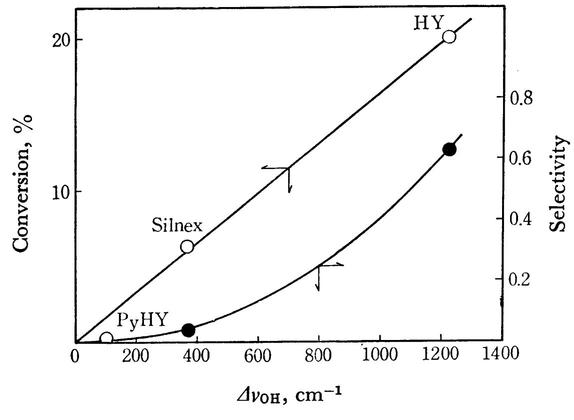


Fig. 4. Correlation between $\Delta\nu_{OH}$ and the reactivity of propylene oxide isomerization.

The selectivity for this reaction is determined by the acid strength of the catalyst, as is shown in Fig. 2 and 4. This fact can be explained as follows. It is generally considered that the stronger the acid strength of the catalyst, the more strongly is the electron drawn from carbon-oxygen bonds in the epoxide ring by the acid site. In the case of strong acid, the bond strengths of O–CH(α-bond) and O–CH_2(β-bond) are consequently weakened, but the methyl group releases electrons and strengthens the α-bond. Therefore, the ratio of the probability of β-bond opening to that of α–that is, the selectivity of acetone to propionaldehyde–is large. However, in the case of weak acid, since the acid site draws the electron mildly, the electron released by the methyl group enters the antibonding

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[16] S. Otoma, Y. Arai, and H. Ukihashi, Preprints for the 20th Annual Meeting of the Chemical Society of Japan (April 1967), No. 11209.

[17] W. K. Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *J. Catal.*, **2**, 506 (1963).

level[18] of the α-bond and the strength of the α-bond is weakened. Hence, the α-bond opening becomes more easily than the β-bond opening; that is, the selectivity of acetone to propionaldehyde becomes lower.

In this reaction, the deactivation for HY and PdHY is caused by the formation of coke and polymerized products which have an absorption band at 1570 cm^{-1}. Propylene oxide is dehydrated by sulfuric acid and forms cokes, but no coke is formed by hydrochloric acid, which has no dehydration ability. Therefore, the deactivation may be due to the large dehydration ability of the surface hydroxyl groups on HY and PdHY, mainly the 3660 cm^{-1} hydroxyl groups.

The selectivity of isomerization at 200°C becomes lower than that at 100°C except for PtY; (selectivity at 200°C; 0.53) and PdY (0.99). Matsumoto and his co-workers[11] have reported that the selectivity of acetone to propionaldehyde is high on platinum (0.42 at 350°C) and palladium metals (1.89 at 256°C). It is considered that the activity of metal ions becomes comparable at 200°C with that of acid sites. The metal ions on zeolites are deduced to be active as metals supported on silica, metal sulfates, and metal oxides.

Conclusions

The activity and selectivity of the propylene oxide isomerization of a zeolite catalyst are found to be controlled by the acid strength of the catalyst. It is considered that the reaction intermediates are the protonated propylene oxide and propylene oxide adsorbed on the Lewis-acid site. The electron distributions of intermediates may be determined by the acid strength of the catalyst, and, consequently, the selectivity and activity may be controlled by the acid strength.

Interestingly, it is found that, in the cases of the HY, PyHY, and Silnex catalysts, the activity and selectivity are related to the strength of the interaction, which is represented by $\Delta\nu_{\text{OH}}$.

Moreover, it is clarified that the H_0 value of the surface hydroxyl group observed at 3660 cm^{-1} on HY zeolite is -8.2—-5.6 while that found at 3540 cm^{-1} is $+4.0$—$+4.8$.

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