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ISOTOPIC EXCHANGE REACTION OF ETHYLBENZENE WITH DEUTERIUM OXIDE

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It is shown by means of the isotopic exchange reaction that the reaction intermediate in the oxidative dehydrogenation of ethylbenzene is not desorbed from the catalyst surface.

As previously reported1), a bismuth molybdate catalyst is not useful for the synthesis of styrene by the oxidative dehydrogenation of ethylbenzene, although it is one of the most typical catalysts for the oxidation or oxidative dehydrogenation of lower olefins. On the contrary, on the Sn-P(10/1)2) and silica-alumina catalysts which are reported as the catalysts useful for the styrene synthesis by Murakami et al.3) and Echigoya et al.,4) respectively, isomerization of 1-butene prevails over the oxidative dehydrogenation (cf. Table 1). It is therefore recognized that these oxidative dehydrogenations occur selectively over the different catalysts. However, it has not been indicated at all what brings about such a difference. This study will be concerned with an isotopic exchange reaction of ethylbenzene with deuterium oxide from such a point of view.

An exchange reaction was carried out using D_2O from E. Merck Co., Ltd. (99.0%) in the conventional continuous-flow method. The percentages of undeuterated hydrocarbon, hydrocarbon-d_1, hydrocarbon-d_2, etc., which were isolated by gas-chromatography, were determined mass-spectrometrically. The low electron-accelerating voltage (∿10V) was used to prevent fragmentation of the molecules. In addition, assignment of deuterated compounds was made by the infrared spectroscopy.

The SnO_2 and Sn-P(10/1) catalysts used in the present study were prepared from tin hydroxide gel and ortho-phosphoric acid. Tin hydroxide gel was prepared by adding more ammonium hydroxide than equivalent to a tin chloride solution in order to precipitate it and then by washing with water till the pH equaled 7.

Table 2 shows the result of isotopic exchange reaction of ethylbenzene with deuterium oxide over the SnO_2 and Sn-P(10/1) catalysts, also including the results of 1-butene with D_2O as a reference. In the case of ethylbenzene with deuterium oxide, only a small amount of hydrogen was exchanged with deuterium irrespective of the catalyst. On the other hand, the exchange reaction proceeded fast only in the case of 1-butene with deuterium oxide on the Sn-P(10/1) catalyst having a high activity in the isomerization. Fig. 1 shows the infrared spectrum of the reaction product obtained in the ethylbenzene oxidation over the Sn-P(10/1)

TABLE 1. Activities of SnO_2 and Sn-P(10/1) Catalysts in Oxidative Dehydrogenations of Ethylbenzene and 1-Butene.[3, 5]

Catal.	Yield (%)				
	from Ethylbenzene[a)]		from 1-Butene[b)]		
	Styrene	$CO+CO_2/8$	Butadiene	2-Butene	$CO+CO_2/4$
SnO_2	6.8	2.6	13.7	1.3	6.0
Sn-P(10/1)	25.5	1.2	7.2	19.2	1.4

a) catalyst weight, 4.5g; reaction temperature, 450°C; total flow rate, 208 mmol/hr; $(EB;O_2;N_2;H_2O)=(0.20;0.10;0.39;0.31)$atm.

b) catalyst weight, 0.8g; reaction temperature, 386°C; total flow rate, 161 mmol/hr; $(1\text{-}B;O_2;N_2)=(0.13;0.11;0.76)$atm.

catalyst. In the C-D stretching vibration region, only a weak absorption band was appeared at 2250 cm^{-1} for the ethylbenzene oxidation. Accordingly, the infrared spectrum is consistent with the measurement about the degree of exchange by the mass spectrometer. The weak absorption at 2250 cm^{-1} in Fig. 1 is caused by the C-D stretching vibration in the benzene ring[6)]. Therefore, it is considered that hydrogens in the ethyl group of ethylbenzene are not exchanged with deuteriums at all. Moreover, it is also found that the deuteration was not observed in the side chain of product styrene.

It has been believed in the literature that oxidative dehydrogenation of olefins is initiated by the abstraction of allylic hydrogen with action of surface oxygen.[7,8)] After the analogy of this reaction mechanism, it is considered that oxidative dehydrogenation of ethylbenzene is also initiated by the abstraction of α-position hydrogen in the ethyl group. When deuterium oxide is present in the reaction system, a part of surface -OH (hydroxyl) is converted to surface -OD. If the dehydrogenated reaction intermediate is desorbed from the catalyst surface by the uptake of deuterium, it follows that hydrogens of the molecule should exchange with deuteriums.

Therefore, it is strongly suggested that the dehydrogenated reaction intermediate of ethylbenzene is not desorbed from the catalyst surface, because the hydrogens in the ethyl group of ethylbenzene are not exchanged with deuteriums at all irrespective of the catalyst.

TABLE 2. Isotopic Exchange Reaction of Ethylbenzene and 1-Butene with Deuterium Oxide at 400°C[a].

Reactant	Catal.	(%)						
		d_0	d_1	d_2	d_3	d_4	d_5	ϕ[b]
Ethyl-benzene	SnO_2	89	8	4				1.5
	Sn-P	86	8	6				2.0
Butenes	SnO_2	71	20	9				4.8
	Sn-P	15	36	27	14	6	2	21
2-Butenes	Sn-P	14	35	28	15	6	3	22

a) Partial Pressure of oxygen, deuterium oxide, and ethylbenzene (or 1-butene): 0.190, 0.167, and 0.036 (or 0.048) atm.

b) $\phi = (1/10) \sum_{i=1}^{10} i\, d_i$, or $(1/8) \sum_{i=1}^{8} i\, d_i$.

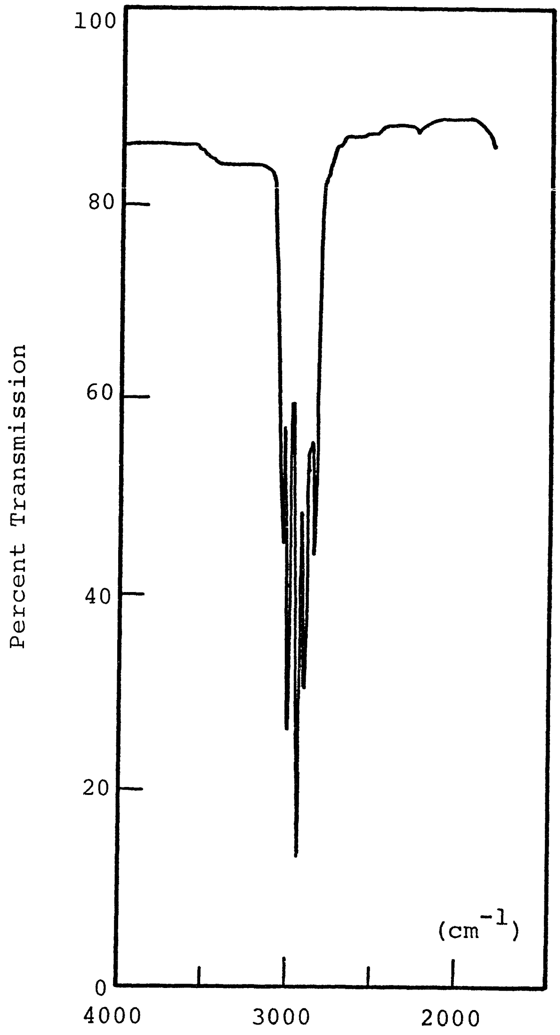

Fig. 1. Infrared spectrum of the product obtained in the exchange reaction of ethylbenzene with D_2O over the Sn-P(10/1) catalyst in the C-H and C-D stretching vibration regions.

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