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The Catalytic Isomerization of Butenes over a Samarium Oxide

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Synopsis. The ratio, *cis*-2-/*trans*-2-butene, formed from 1-butene isomerization, was 22.2. The reaction profile of butenes isomerization obtained from the relative rate constants was of the *cis*-convex type. The basic sites on the oxide surface have been revealed by the benzoic acid titration method.

The catalytic isomerization of butenes over metal oxides has been extensively investigated in view of the acid-base catalysis.[1] The acid-base natures and the catalytic activity of rare-earth oxides has recently been reviewed in a book by Tanabe et al.[2] Hattori et al.[3] investigated the isomerization of 1-butene over 13 kinds of rare-earth oxides. A few studies on the isomerization of 2-butenes over rare-earth oxides, on the other hand, has been reported; the activity of lanthanum oxide, yttrium oxide and cerium oxide have been reported so far.[4] Although the rare-earth oxides have been classified as the base catalysts on the basis of the O_{1s} binding energy study of the oxides,[5] and of the reaction characteristics (e.g. the reaction activity of aldol addition of acetone[3]) the basicity of their surface has not been measured by the titration method with benzoic acid. In the present work we investigated the isomerization of butenes over a samarium oxide, Sm_2O_3, and measured the basicity of its surface in order to obtain more information concerning the acid-base nature of rare-earth oxides.

Experimental

A closed circulating system connected to a conventional vacuum line and a gas chromatograph was used to follow the isomerization. The reaction mixtures were occasionally analyzed by means of gas chromatography.

Aqueous ammonium (0.1 mol dm^{-3}) was added to 0.06 mol dm^{-3} samarium nitrate solution in order to precipitate samarium hydroxide. The samarium nitrate was supplied from Wako Pure Chemical Industries, Ltd. The solution with the precipitate was kept for 2 h at pH 10. The precipitate was then filtrated and was washed by distilled water until the pH of the solution became 7. The washed precipitate was dried at 383 K for 24 h and was calcined at 723 K for 3 h in the presence of air. The samarium oxide, Sm_2O_3, thus obtained, was employed for isomerization as the catalyst. The catalyst was then evacuated at 973 K under ca. 10^{-3} Pa for 3 h.

The 1-butene, and *cis*- and *trans*-2-butenes used as the reactants were obtained from the Tokyo Kasei Kogyo Co. Ltd., and were purified by repeated distillation to be more than 99%.

The amount and strength of the basic sites on the surface were measured by the benzoic acid titration method .[6,7] The indicators employed were Bromothymol Blue ($H_-=7.2$), 2, 4-dinitroaniline ($H_-=15.0$), 4-chloro-2-nitroaniline ($H_-=17.2$), and 4-nitroaniline ($H_-=18.4$). The oxide samples (*ca.* 0.05 g), which had been evacuated beforehand, were weight in separate glass tubes (18 cm long, 1.0 cm in outside-diameter), and solutions of appropriate indicators in benzene (0.2 ml) were introduced with a microsyringe (1 ml) to each sample tube. Then, benzoic acid in benzene (0.01 mol dm^{-3}) was added for titration. From the resultant color changes of the indicators adsorbed on the catalyst samples, where the color of their basic state just disappeared, the end point of titration was visually determined. All of the operations for the measurement were conducted under a dry argon atmosphere.

Results and Discussion

Figure 1 shows a typical result of the isomerization of 1-butene over a samarium oxide, where the composition of butenes changed with time at 233 K. *cis*-2-Butene was predominantly formed. The double-bond migration of 1-butene and the cis-trans isomerization of 2-butenes took place over the samarium oxide catalysts employed. No skeletal isomerization could be observed, and no gaseous hydrocarbon other than butenes could be detected in the reaction mixtures under the present experimental conditions.

The isomerization rates of butenes, based on product formation, were almost proportional to the pressure of the reactants. During the initial stage of the reactions, the rate constants were determined. The rate constants at 233 K and the activation energies of the reactions are shown in Table 1. The BET surface area of the Sm_2O_3 was estimated to be 34 m^2 g^{-1} by the nitrogen-adsorption method. The ratio, k_{1c}/k_{1t}, was 22.2, which was very high.

Figure 2 shows the amount of basic sites per weight of the catalyst plotted against the basic strength for the samarium oxide. The superbasic site ($H_-\geqslant 26$) defined

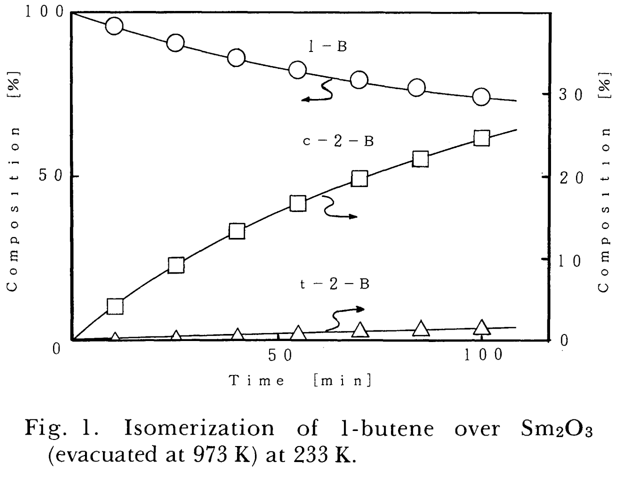

Fig. 1. Isomerization of 1-butene over Sm_2O_3 (evacuated at 973 K) at 233 K.

Table 1. The Rate Constants at 233 K and the Activation Energies of Isomerization of Butenes over Sm_2O_3 (Evacuated at 973 K)

Reactant	Product	Rate constant[a)	Activation energy
		k_{ij}/min^{-1} g^{-1}	E_a/kJ mol^{-1}
1-Butene	*trans*-2-Butene	3.13×10^{-3}	33.8
	cis-2-Butene	6.95×10^{-2}	26.3
cis-2-Butene	1-Butene	4.28×10^{-3}	30.9
	trans-2-Butene	3.82×10^{-4}	39.5
trans-2-Butene	*cis*-2-Butene	5.70×10^{-5}	46.1
	1-Butene	2.85×10^{-5}	45.1

a) e. g. $k_{ij}=k_{1t}$, where the reactant is 1-butene and the product is *trans*-2-butene.

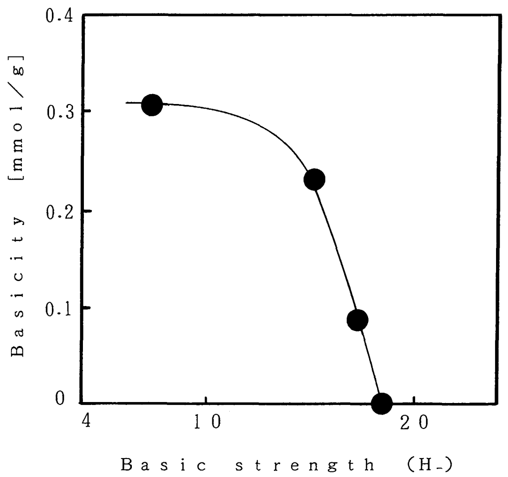

Fig. 2. Basicity vs. basic strength (H–) of Sm_2O_3.

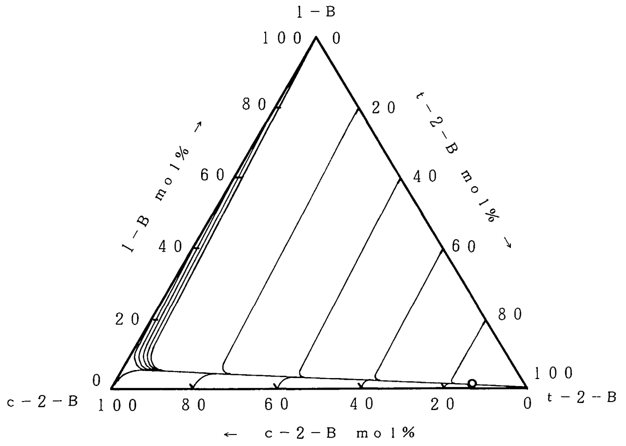

Fig. 3. Reaction profile of isomerization of butenes over Sm_2O_3 (evacuated at 973 K) at 233 K.

by Tanabe[6] was not found on the samarium oxide surface.

Figure 3 shows the reaction profile of the isomerization of butenes over the samarium oxide, Sm_2O_3, at 233 K. The profile was obtained in a manner similar to that described previously.[8] The mol% of 1-butene, *cis*-, and *trans*-2-butenes corresponing to the reaction time are shown in a triangular graph, when the isomerization of butenes proceeds. The line, which starts from the top of the triangle, represents the change of the composition with time, when 1-butene is the reactant of isomerization. Since the curves, which originate from the left side of the triangle, bend in a convex manner to the left, this profile can be classified as being the *cis*-convex type.

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