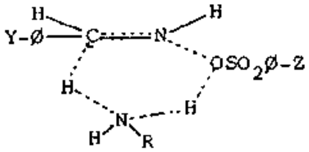
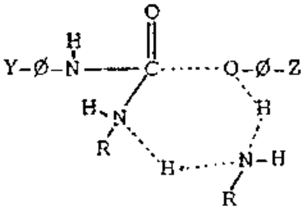
ruled out, since the ρ_{YZ} value of zero was



(II)

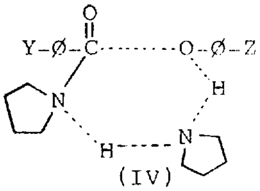
obtained for this reaction as shown in Table 1.

However such mechanism in which the $|\rho_{YZ}|$ values are abnormally large can be found in the base-catalyzed addition-elimination type of the nucleophilic substitution reaction in which elimination is rate limiting.[4] Two examples are: (i)[5] $YC_6H_4NH\ COOC_6H_4Z + RNH_2 \rightarrow YC_6H_4NHCONHR + HOC_6H_4Z$ (2) The $|\rho_{YZ}|$ values for the two reaction paths, i.e., uncatalyzed (k_2) and base catalyzed (k_3), of this reaction were determined to be 1.02 and 4.00, respectively. For the latter, the TS of the type (III) can therefore be predicted.



(III)

(ii)[6] pyrrolidine $+ YC_6H_4COOC_6H_4Z \rightarrow YC_6H_4CONC_4H_8 + HOC_6H_4Z$ (3) The two $|\rho_{YZ}|$ values obtained for k_2 and k_3 paths of this reaction were 1.76 and 9.33 respectively. The latter base-catalyzed path is predicted to have the base-bridged TS of the type (IV).



(IV)

We therefore conclude that the cross interaction constants are useful in characterizing an elimination with a base-bridged TS as well as in distinguishing the specific type of TS in the E2 mechanism.

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Correlation between Catalytic Activity and Acid Strength

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It has been known that the catalytic activity of a catalyst is deeply affected by the method of catalyst preparation and the condition of pretreatment[1-2]. In the previous papers from this laboratory, it has been shown that the NiO-TiO_2 and NiO-ZrO_2 modified with sulfate ion is very active for ethylene dimerization even at room temperature[3-6]. High catalytic activities in the reactions were attributed to the enhanced acidic properties of the modified catalysts, which originated from the inductive effect of S=O bonds of the complex formed by the interaction of oxides with sulfate ion.

In this communication, we report the correlation between catalytic activity and acid strength of TiO_2 modified with various acids, H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4. For this purpose, the isomerization of 1-butene which is known to be catalyzed by acid catalysts[7-9] was chosen as test reaction.

The catalysts were prepared as follows. The precipitate of $Ti(OH)_2$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and hydrochloric acid at room temperature with stirring until the pH of mother liquor reached about 7. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature. The dried precipitate was powdered below 100 mesh, and then the modification with acids was performed by pouring each 30 m*l* of 1N H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4 into 2 g of the powdered sample on a filter paper, respectively, followed by drying in air. The dry solid powder was used as catalyst after decomposing at different evacuation temperature for 1.5 hr. The catalysts modified with H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4 are referred as TiO_2/SO_4^{2-}, TiO_2/PO_4^{3-}, TiO_2/BO_3^{3-}, and TiO_2/SeO_4^{2-}, respectively.

The isomerization of 1-butene was carried out at 20°C by

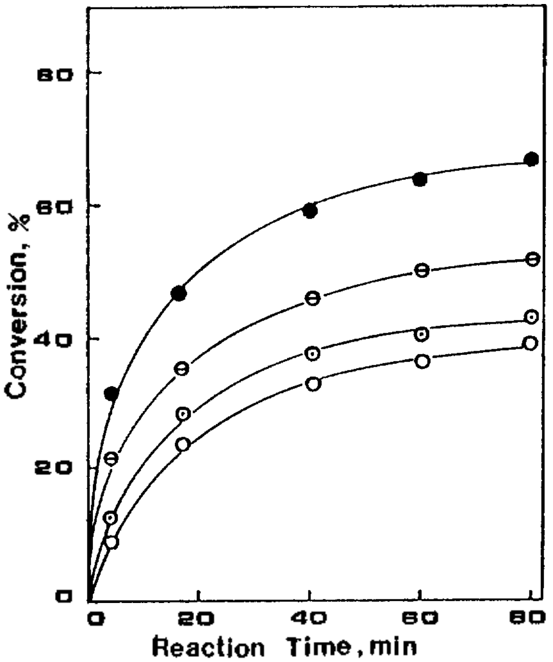

Figure 1. Conversion of 1-butene against reaction time, ● ; TiO_2/SO_4^{2-}, ⊖ ; TiO_2/PO_4^{3-}, ⊙; TiO_2/BO_3^{3-}, ○ ; TiO_2/SeO_4^{2-}.

use of 0.2g of catalyst in a closed circulating system of 146m*l* capacity. 50 torr of 1-butene was used. The products were analyzed by gas chromatography using a VZ-7 column at room temperature. The catalytic activities for 1-butene isomerization were examined and the results are shown as a function of reaction time in the figure 1, where the catalysts were pretreated at 400°C in evacuation for 1.5 hr. Although the pure TiO_2 which was not modified with any acids was inactive as catalyst for the isomerization, those modified with acids exhibited high catalytic activity. Especially TiO_2/SO_4^{2-} showed the most effective catalysis. The time course of isomerization was in agreement with the first order rate law.

The acid strength of the samples modified with acids was examined by a color change method using Hammett indicators[4,10], when a powdered sample was added to an indicator dissolved in dried benzene. The results are listed in Table 1. In this table, + means that the color of base form was changed to that of conjugate acid form. The acid strength of the pure TiO_2 without acid treatment was found to be $Ho \leqq 1.5$. However, the acid strengths of TiO_2/SO_4^{2-}, TiO_2/PO_4^{3-}, TiO_2/BO_3^{3-}, and TiO_2/SeO_4^{2-} were estimated to be $Ho \leqq -14.5$, $Ho \leqq -8.2$, $Ho \leqq -5.6$ and $Ho \leqq -5.6$, respectively.

It is of considerable interest that the catalytic activities are correlated with the acid strengths of catalysts. Clear dependence of catalytic activity upon acid strength is shown in Table 1, where the isomerization activity is represented by the first order rate constant. The order of catalytic activity

Table 1. The acid strengths and catalytic activities of TiO_2 modified with acids

Hammett indicatior	pKa value of indicator	TiO_2/SO_4^{2-}	TiO_2/PO_4^{3-}	TiO_2/BO_3^{3-}	TiO_2/SeO_4^{2-}	TiO_2
Benzeneazo-diphenylamine	1.5	+	+	+	+	+
Dicinnamal-acetone	-3.0	+	+	+	+	-
Benzalaceto-phenone	-5.6	+	+	+	+	-
Anthraqui-none	-8.2	+	+	-	-	-
Nitrobenzene	-12.4	+	-	-	-	-
2,4-Dinitro-fluorobenzene	-14.5	+	-	-	-	-
Catalytic activity ($k \times 10^2 sec^{-1} g^{-1}$)		2.84	1.95	1.32	1.00	0

was found to be $TiO_2/SO_4^{2-} > TiO_2/PO_4^{3-} > TiO_2/BO_3^{3-} > TiO_2/SeO_4^{2-}$. However, the discrepancy between the catalytic activies of TiO_2/BO_3^{3-} and TiO_2/SeO_4^{2-} having the same acid strength is probably due to the fact that no indicators with pKa between -5.6 and -8.2 were used. The above results indicate that the double-bond shift reaction of 1-butene requires at least acid sites stronger than Ho = 1.5.

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