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Effect of Acid Strength on the Catalytic Activity of NiO–TiO_2 Modified with Acids

Nickel oxide–silica is known to be effective for the dimerization of ethylene at room temperature (1–5). The catalyst is also active for the isomerization of *n*-butane, the mechanism of which has been proved to be of a proton donor–acceptor type (*6*). It has been suggested that the active site for dimerization is formed by an interaction of a low valent nickel ion with an acid site (*7*). 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 (*8, 9*). 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. The dependency of the catalytic activity on the acid strength was reported by numerous investigators (*10–12*). The acid strength of a solid is the ability of the surface to convert an adsorbed neutral base into its conjugate acid as described by Walling (*13*). The present paper is concerned with the preparation of NiO–TiO_2 modified with various acids, H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4, and the dependence of catalytic activity on acid strength. For this purpose, 1-butene isomerization and ethylene dimerization, which is known to be catalyzed by acid catalysts (*8, 14*), were chosen as test reactions.

The catalysts were prepared as follows. The coprecipitate of $Ni(OH)_2$–$Ti(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride, titanium tetrachloride, and hydrochloric acid at room temperature while stirring until the pH of the mother liquid 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 for 12 hr. The dried precipitate was powdered below 100 mesh, and then modification with acids was performed by pouring each 30 mℓ of 1 *N* H_2SO_4, H_3PO_4, H_3BO_3, and H_2SeO_4 into 2 g of the powdered sample on a filter paper, followed by drying in air. The resultant solids were used as catalysts 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 to as NiO–TiO_2/SO_4^{2-}, NiO–TiO_2/PO_4^{3-}, NiO–TiO_2/BO_3^{3-}, and NiO–TiO_2/SeO_4^{2-}, respectively.

The isomerization of 1-butene was carried out 20°C by use of 0.2 g of catalyst in a closed circulating system of 146 mℓ capacity. Fifty Torr of 1-butene was used. The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following the pressure change from an initial pressure of 280 Torr. Fresh catalyst sample of 0.2g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed in the initial 5 min. Reaction products for two reactions were analyzed by gas chromatography with 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 Fig.

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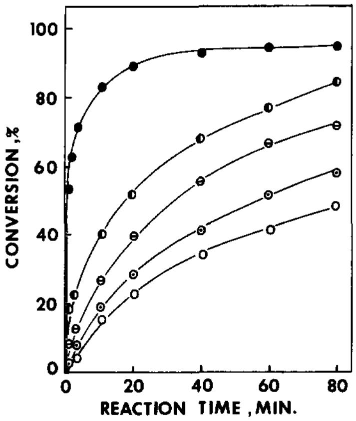

FIG. 1. Conversion of 1-butene against reaction time: ● $NiO–TiO_2/SO_4^{2-}$, ◐ $NiO–TiO_2/PO_4^{3-}$, ⊖ $NiO–TiO_2/BO_3^{3-}$, ⊙ $NiO–TiO_2/SeO_4^{2-}$, ○ $NiO–TiO_2$.

1. No product other than *cis*- and *trans*-2-butene was detected in the reaction mixture. When the NiO mol% of catalyst is 25 and the catalysts are evacuated at 400°C for 1.5 hr, the catalyst exhibited the highest activity. Therefore, in this paper emphasis is placed to the only catalyst having 25 mol% of NiO content and evacuated at 400°C. After evacuation at 400°C for 1.5 hr, strong IR absorption bands of anions of acids were left to indicate a very strong interaction between anions and oxides, and any decomposition or evaporation of anions were not observed. The content of anion in the catalysts after calcining at 400°C was estimated to be about ~3–4 wt%. As shown in Fig. 1, the catalysts modified with acids exhibited higher catalytic activity than the unmodified catalyst. $NiO–TiO_2/SO_4^{2-}$ showed the most effective catalysis. Time course of isomerization was in agreement with the first rate law and the first-order rate constants are listed in Table 1. The order of catalytic activity was found to be $NiO–TiO_2/SO_4^{2-} \gg NiO–TiO_2/PO_4^{3-} > NiO–TiO_2/BO_3^{3-} > NiO–TiO_2/SeO_4^{2-} > NiO–TiO_2$.

The catalytic activities for ethylene dimerization were also examined and the results are listed in Table 1, where the catalyst of 25 mol% of NiO was evacuated at 400°C. $NiO–TiO_2$ alone without acid modification was totally inactive for the ethylene dimerization at room temperature unlike 1-butene isomerization. However, all the modified catalysts exhibited catalytic activity, showing the highest activity of $NiO–TiO_2/SO_4^{2-}$ like the case of 1-butene isomerization. On all the $NiO–TiO_2$ modified with acids, the product obtained from the gas phase was exclusively *n*-butene, in analogy with nickel containing catalysts (*3–9, 15, 16*). However, a small amount of hexenes from the phase adsorbed on the catalyst surface was detected. The order of catalytic activity was the same as that for isomerization. These results indicate that the modification with acids enhances the catalytic activities for both 1-butene isomerization and ethylene dimerization, and the 1-butene isomerization activity runs parallel with the ethylene dimerization activity.

It is interesting to examine how the activity of solid acid catalysts depends upon the acid strength. The acid strengths of the present samples modified with acids were examined by a color change method using a series of Hammett indicators (*17*) as described in the previous paper (*8, 9*). The catalysts were pretreated in glass tubes by the same procedure as for the reactions. Since it was very difficult to observe the color of indicators adsorbed on catalysts of high nickel oxide content, a low percentage of nickel oxide (4 mol%) was used in this experiment. The results are listed in Table 1, where + indicates that the color of the base form changed to that of the conjugate acid form. The acid strength of the sample without acid modification was found to be $H_0 \leqq -3.0$. However, the acid strength of $NiO–TiO_2/SO_4^{2-}$, $NiO–TiO_2/PO_4^{3-}$, $NiO–TiO_2/BO_3^{3-}$, and $NiO–TiO_2/SeO_4^{2-}$ were estimated to be $H_0 \leqq -14.5$, $H_0 \leqq -8.2$, $H_0 \leqq -5.6$, and $H_0 \leqq -5.6$, respectively. As described above, $NiO–TiO_2$ alone without acid modification, whose acid strength was found to be $H_0 \leqq -3.0$, was totally inactive for the dimerization of ethylene at room temperature, although it exhibited a low activity for the isomerization of 1-butene. These results in-

TABLE 1

Acid Strength and Catalytic Activity of NiO–TiO$_2$ Modified with Acids

Hammett indicator	p*K*a value of indicator	NiO–TiO$_2$/SO$_4^{2-}$	NiO–TiO$_2$/PO$_4^{3-}$	NiO–TiO$_2$/BO$_3^{3-}$	NiO–TiO$_2$/SeO$_4^{2-}$	NiO–TiO$_2$
Dicinnamalacetone	−3.0	+	+	+	+	+
Benzalacetophenone	−5.6	+	+	+	+	−
Antraquinone	−8.2	+	+	−	−	−
Nitrobenzene	−12.4	+	−	−	−	−
2,4-dinitrofluorobenzene	−14.5	+	−	−	−	−
Catalytic activity for isomerization (k × 10^2 sec − 1 g − 1		11.66	3.32	2.22	1.47	0.81
Catalytic activity for dimerization (m mol g − 1 5 min − 1)		2.71	1.32	0.98	0.56	0
Surface area (m^2/g)		234.1	235.2	229.8	227.4	189.6

dicate that ethylene dimerization requires acid sites stronger than $H_0 \leqq -3.0$ and that 1-butene isomerization takes place on relatively weak acid sites in comparison with ethylene dimerization. Clear dependence of catalytic activity upon acid strength is shown in Table 1. However, the discrepancy between the catalytic activities of NiO–TiO$_2$/BO$_3^{3-}$ and NiO–TiO$_2$/SeO$_4^{2-}$ having the same acid strength is probably due to the fact that no indicators with p*K*a between −5.6 and −8.2 were used. The high catalytic activities of modified catalysts were correlated with the increase of acid strength by the inductive effects which were different depending on the anions of acids treated for the modification.

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