# CATALYTIC ACTIVITIES AND ACID STRENGTHS OF NiO-ZrO₂ CATALYSTS MODIFIED WITH ACIDS

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**Abstract**—A series of NiO-ZrO₂ catalysts were prepared by coprecipitation from the mixed aqueous solution of nickel chloride-zirconium oxychloride, and were modified with acids, $H_2SO_4$, $H_3PO_4$ and $H_3BO_3$. It was found that the NiO-ZrO₂ catalyst containing 25 mole percent of nickel oxide and evacuated at 400°C for 1.5 hr showed maximum catalytic activities for 1-butene isomerization and ethylene dimerization. The catalytic activities for both isomerization and dimerization were correlated with the acid strengths of the catalysts. The isomerization activity of 1-butene ran parallel with the dimerization activity of ethylene, although the isomerization took place on relatively weak acid sites as compared with the dimerization.

## INTRODUCTION

Nickel oxide on silica or silica-alumina is known to be effective for the dimerization of ethylene at room temperature [1-4]. The catalyst is also active for the isomerization of n-butene, the mechanism of which has been proved to be of a proton donor-acceptor type [5]. 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 [6]. In fact nickel oxide which is active for $C_2H_4$-$C_2D_4$ equilibration acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid [7]. In the previous papers from this laboratory, it has been shown that the NiO-TiO₂ and NiO-ZrO₂ modified with sulfate ion are very active for ethylene dimerization even at room temperature [8-10]. High catalytic activities in the above 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.

However, the dependency of the catalytic activity on the acid strength was reported by numerous investigators [11-13]. 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 [14]. The acid strength is expressed by the Hammett acidity function Ho [15]

$$Ho = pKa + \log [B]/[BH^+] \qquad (1)$$

$$or \quad Ho = pKa + \log [B]/[AB] \qquad (2)$$

where Ka is the equilibrium constant of dissociation of the acid, [B] and [BH⁺] are respectively the concentrations of the neutral base and its conjugate acid, and [AB] is the concentration of the addition product formed by adsorption of B onto a Lewis site. On the other hand, the amount of acid on a solid is usually expressed as the number or mmole of acid sites per unit weight or per unit surface area of the solid, and is sometimes called "acidity". Dehydration of tert-butanol takes place very readily even on the weaker acid sites, while dealkylation of tert-butylbenzene and skeletal isomerization of isobutylene require exceedingly strong acid sites [16]. In this work, we report the correlation between catalytic activity and acid strength of NiO-ZrO₂ modified with various acids, $H_2SO_4$, $H_3PO_4$, and $H_3BO_3$. For this purpose, the isomerization of 1-butene and the dimerization of ethylene which are known to be catalyzed by acid catalysts are chosen as test reactions.

## EXPERIMENTAL

### 1. Catalysts and Materials

The coprecipitate of Ni(OH)₂-Zr(OH)₄ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride and zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The ratio of nickel chloride to zirconium oxychloride was varied.

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The coprecipitate 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 modified with acids by pouring each 30 m$l$ of 1 N $H_2SO_4$, $H_3PO_4$, and $H_3BO_3$, respectively, onto each 2g 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 temperatures for 1.5 hr. The catalysts modified with $H_2SO_4$, $H_3PO_4$ and $H_3BO_3$ were referred to as NiO-$ZrO_2/SO_4^{-2}$, NiO-$ZrO_2/PO_4^{-3}$, and NiO-$ZrO_2/BO_3^{-3}$, respectively. And 25-NiO-$ZrO_2/SO_4^{-2}$ meant the catalyst having 25 mole percent of the nickel oxide. Ethylene and 1-butene were obtained from Korea Petrochemical Industrial Co. and were purified by the freeze-thaw technique using liquid nitrogen and dry ice-acetone baths.

## 2. Procedure

The isomerization of 1-butene was carried out at 20°C reacting 50 torr of 1-butene on 0.2g catalyst in a closed circulating system of 146 m$l$ capacity. The catalytic activity for ethylene dimerization was determined at 20°C by pressure change from an initial pressure of 280 torr in a coventional static system. Fresh catalyst sample, 0.2g, was used for every run after evacuation to $10^{-4}$ torr at different temperatures for 1.5 hr and the catalytic activity was calculated with the amount of ethylene consumed during the first 5 minutes. Reaction products were analyzed by a gas chromatograph equipped with a VZ-7 column at room temperature. The specific surface area was determined by applying the BET method to the adsorption of nitrogen at $-196$°C. The infrared spectra were recorded in a heatable gas cell at room temperature on a JASCO IR-2 spectrometer.

The acid strength of the catalysts was measured qualitatively after the pretreatments using a series of the Hammett indicators. The catalysts were pretreated in glass tubes by the same procedure as for the reactions. They were cooled to room temperature and filled with dry nitrogen. The color changes of a series of indicators were observed for each catalyst by the spot test under dry nitrogen.

## RESULTS AND DISCUSSION

### 1. Infrared spectra of 25-NiO-ZrO$_2$ modified with acids

The infrared spectra of 25-NiO-$ZrO_2$ modified with acids are given in Fig. 1. 25-NiO-$ZrO_2/SO_4^{-2}$ showed infrared absorption bands at 1230, 1140, 1060 and 990 cm$^{-1}$ which are assigned to the bidentate sulfate ion
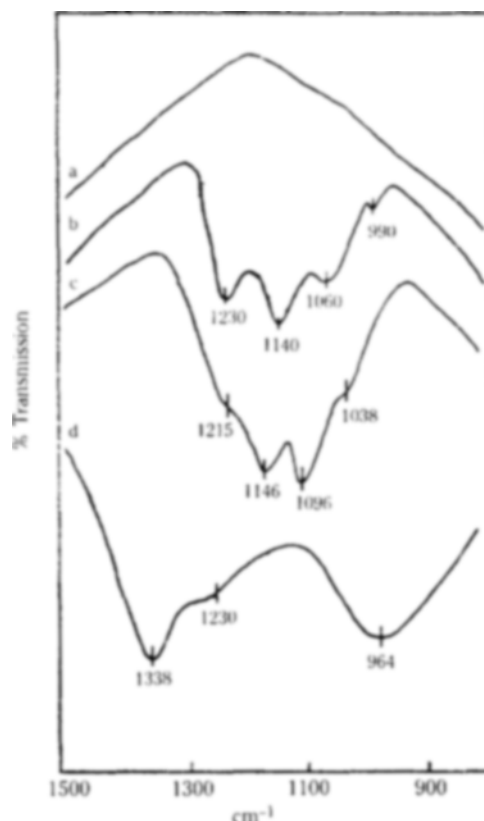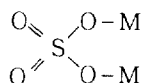


**Fig. 1. Infrared spectra of 25-NiO-ZrO$_2$ modified with acids.**

(a) background of 25-NiO-$ZrO_2$, (b) 25-NiO-$ZrO_2/SO_4^{-2}$, (c) 25-NiO-$ZrO_2/PO_4^{-3}$, and (d) 25-NiO-$ZrO_2/BO_3^{-3}$, where each sample was evacuated at 400°C for 1.5 hr.

coordinated to the metal as follows [17]:

$$\begin{array}{c} O\diagdown \quad \diagup O-M \\ \quad\quad S \\ O\diagup \quad \diagdown O-M \end{array}$$

The $\nu_{SO}$ spectra from the adsorbed sulfate in the $\nu_1$ and $\nu_3$ frequency region (900-1400 cm$^{-1}$) support a species of reduced $C_{2v}$ symmetry with four bands arising from $\nu_1$ and splitting of triply degenerate $\nu_3$ vibration [18]. Even after evacuation at 400°C for 1.5 hr, strong absorption bands of sulfate ion still remain suggesting a very strong interaction between the sulfate ion and the metal.

On the other hand, 25-NiO-$ZrO_2/PO_4^{-3}$ showed infrared absorption bands at 1215, 1146, 1096, and 1038 cm$^{-1}$. A band at 1215 cm$^{-1}$ is assigned to the P-O-H in-plane deformation vibration, while that at 1146 cm$^{-1}$ is assigned to the P = O stretching vibration [19]. Since the bands at 1096 and 1038 cm$^{-1}$ can be assigned to
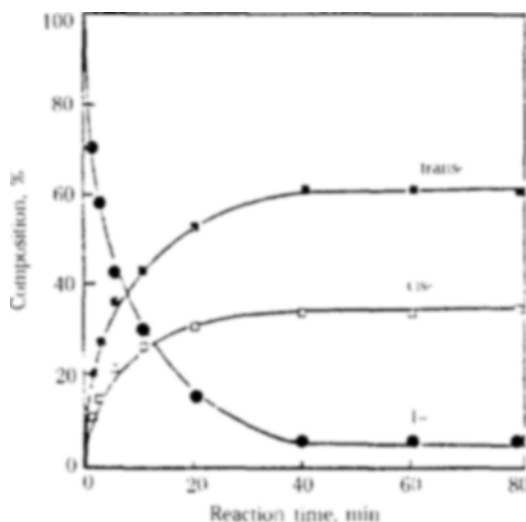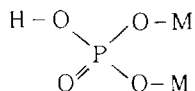
Fig. 2. Composition change of n-butene with reaction time in 1-butene isomerization.



Fig. 3. First order plot for disappearance of 1-butene over 25-NiO-ZrO$_2$/SO$_4^{-2}$ at 20°C.

the P-O degenerate stretching vibration [20], it is suggested that phosphoric acid is coordinated to the surface of the catalyst as follows:

$$H - O \diagdown \quad \diagup O - M$$
$$P$$
$$O \diagup \quad \diagdown O - M$$

For 25-NiO-ZrO$_2$/BO$_3^{-3}$, the broad bands at 1338, 1230, and 964 cm$^{-1}$ are observed. It is widely accepted that the broad band structure in the region 1150-1500 cm$^{-1}$ is attributed to the B-O bond stretching of BO$_3$ units, while that in the region 850-1100 cm$^{-1}$ is attributed to the B-O stretching of BO$_4$ units [21]. On the basis of the above assignments it is obvious that, upon calcinating the sample, some BO$_3$ units are converted into BO$_4$ units.

## 2. Isomerization of 1-butene

The double bond migration isomerization of 1-butene was carried out at 20°C on NiO-ZrO$_2$/SO$_4^{-2}$ in a circulating system. No product other than cis- and trans-2-butene was detected in the reaction mixture. Fig. 2 shows the composition change of n-butene with reaction time in 1-butene isomerization, where 25-NiO-ZrO$_2$/SO$_4^{-2}$ catalyst was evacuated at 400°C for 1.5 hr. In the initial stage the amount of 1-butene decreases rapidly with reaction time, while the amounts of 2-butenes increase with time. It is noted that a very rapid isomerization from 1-butene to 2-butenes takes place in the beginning. However, after about 40 min the conversion reaches steady state.

Several investigators who have studied n-butene isomerization over oxide catalysts have suggested that the reactions follow first order kinetics [22-24]. High-
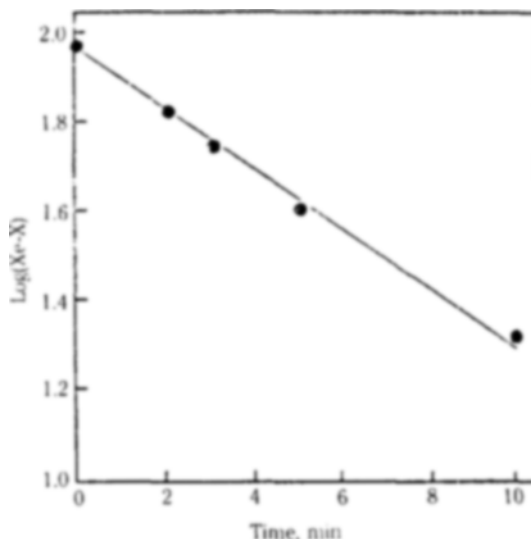
tower et al. have clearly demonstrated that 1-butene isomerization is first order over alumina and silica-alumina at temperatures below 100°C [25]. In order to correlate the isomerizing activities with the acidic properties of the catalysts, a kinetic study of 1-butene isomerization has been undertaken. Fig. 3 shows the first order plot of 1-butene isomerization. The data were plotted according to

$$-\ln (X_e - X) = kt - \ln X_e \qquad (3)$$

where X and Xe refer to conversion at time t and at equilibrium, respectively. The initial rate is obtained from the slope of first order plot as in Fig. 3. Thus the isomerization activity is represented by the first order rate constant. The results for 25-NiO-ZrO$_2$ catalysts modified with acids are listed in Table 2.

## 3. Effect of catalyst composition

The effect of catalyst composition on the initial rate was examined using NiO-ZrO$_2$/SO$_4^{-2}$ catalysts which were evacuated at 400°C for 1.5 hr. As shown in Fig. 4, the maximum activities for both 1-butene isomerization and ethylene dimerization reactions are obtained at 25 mole percent of nickel oxide. This is to be due to the increase of specific surface area of the catalyst and the subsequent increase of active site. In fact, a previous work showed that the specific surface are became maximized when the content of nickel oxide in catalyst was 25 mole percent [9]. The specific surface areas of some samples are listed in Table 1. The above result suggests that the isomerization activity runs parallel with the dimerization activity, because
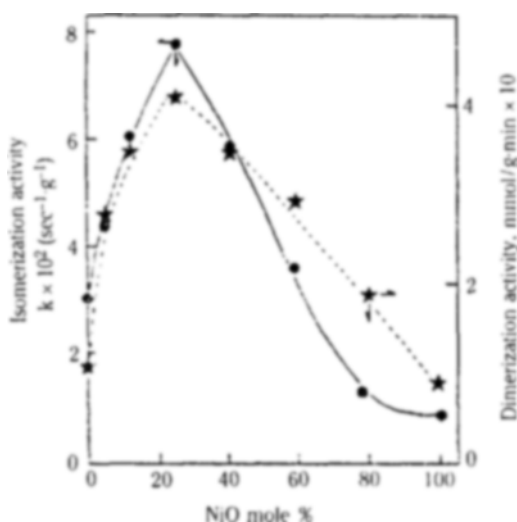
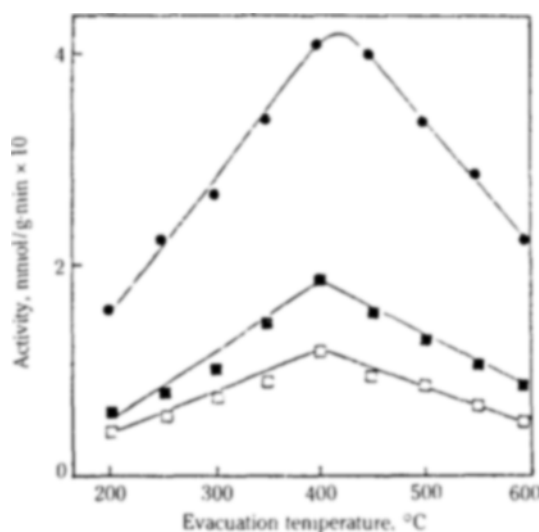**Fig. 4. Variations of isomerization and dimerization activities on NiO-ZrO$_2$/SO$_4$$^{-2}$ with mole % of NiO.**

**Table 1. Specific surface area of catalysts (m$^2$/g)**

| Catalyst | Surface area |
|---|---|
| 25-NiO-ZrO$_2$ | 186.4 |
| 25-NiO-ZrO$_2$/SO$_4$$^{-2}$ | 230.1 |
| 25-NiO-ZrO$_2$/PO$_4$$^{-3}$ | 231.3 |
| 25-NiO-ZrO$_2$/BO$_3$$^{-3}$ | 228.3 |

both of the reactions require acids as active sites. Hereinafter, emphasis has been placed to the only 25-NiO-ZrO$_2$ modified with acids.

## 4. Dimerization of ethylene

The catalytic activities for the dimerization of ethylene are examined and the results are shown as a function of evacuation temperature in Fig. 5, where the nickel oxide mole percent of the catalyst is 25. It is shown that the activity appears above 200°C reaching a maximum at 400°C. The decomposition of nickel hydroxide is known to begin at 230°C [26]. Therefore, it is very likely that the activation of catalyst above 200°C is related to the decomposition of the catalyst. The activity decrease above 400°C is reasonably explained by the solid phase rearrangement or sintering of the catalyst as demonstrated by the decrease of surface area in the previous work [9]. Although the samples which were not modified with acids were inactive as catalysts for ethylene dimerization, those modified with acids exhibited high catalytic activity. In particular, 25-NiO-ZrO$_2$/SO$_4$$^{-2}$ showed the most effective catalysis. On all the 25-NiO-ZrO$_2$ catalysts modified



**Fig. 5. Variations of dimerization activity with evacuation temperature.**
● 25-NiO-ZrO$_2$/SO$_4$$^{-2}$;  ■ 25-NiO-ZrO$_2$/PO$_4$$^{-3}$;  □ 25-NiO-ZrO$_2$/BO$_3$$^{-3}$.

with acids, the products obtained from the gas phase were exclusively n-butenes, in anology with nickel-containing catalysts [1-3, 6-10]. However, a small amount of hexenes from the phase adsorbed on the catalyst surface was detected.

## 5. Correlation between catalytic activity and acid strength

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 Hammett indicators. Since it was very difficult to observe the color of indicators adsorbed on catalysts of high nickel oxide content, a low percent of nickel oxide (5 mole %) was used in this experiment. The results are listed in Table 2, 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 Ho $\leq$ -3.0. However, the acid strengths of NiO-ZrO$_2$/SO$_4$$^{-2}$, NiO-ZrO$_2$/PO$_4$$^{-3}$, and NiO-ZrO$_2$/BO$_3$$^{-3}$ were estimated to be Ho $\leq$ -14.5, Ho $\leq$ -8.2, and Ho $\leq$ -5.6, respectively.

NiO-ZrO$_2$ alone without acid modification, whose acid strength was found to be Ho $\leq$ -3.0, was totally inactive for the dimerization reaction at room temperature, although it exhibited a low activity for the isomerization of 1-butene. These results indicate that ethylene dimerization requires acid sites stronger than Ho = -3.0 and that 1-butene isomerization takes place on relatively weak acid sites in comparison with ethyl-

**Table 2. The catalytic activities and acid strengths of NiO-ZrO$_2$ modified with acids**

| Hammett indicator | pka value of indicator | NiO-ZrO$_2$·SO$_4^{-2}$ | NiO-ZrO$_2$/PO$_4^{-3}$ | NiO-ZrO$_2$/BO$_3^{-3}$ | NiO-ZrO$_2$ |
|---|---|---|---|---|---|
| Dicinnamalacetone | −3.0 | · | · | · | · |
| Benzalacetophenone | −5.6 | · | · | · | |
| Anthraquinone | −8.2 | · | · | | |
| Nitrobenzene | −12.4 | · | | | |
| 2,4-Dinitrofluorobenzene | −14.5 | · | − | | |
| Catalytic activity for isomerization (k × 10$^2$ sec$^{-1}$·g$^{-1}$) | | 7.85 | 2.62 | 1.92 | 0.82 |
| Catalytic activity for dimerization* (× 10 mmol g$^{-1}$·min$^{-1}$) | | 4.02 | 1.84 | 1.16 | 0 |

Obtained at 400°C of evacuation temperature from Fig. 5.

ene dimerization. Clear dependence of catalytic activity upon acid strength is shown in Table 2. The order of catalytic activity for both dimerization and isomerization reactions was found to be NiO-ZrO$_2$/SO$_4^{-2}$ ≫ NiO-ZrO$_2$/PO$_4^{-3}$ > NiO-ZrO$_2$/BO$_3^{-3}$ > NiO-ZrO$_2$. Namely, catalysts modified with acids exhibited high catalytic activities as compared with that without modification. Especially NiO-ZrO$_2$/SO$_4^{2-}$ showed the most effective catalysis. 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 catalyst modification [8,9].

## CONCLUSION

A series of NiO-ZrO$_2$ catalysts modified with acids were found to be active for 1-butene isomerization and ethylene dimerization and the following results were obtained in this work.

1. NiO-ZrO$_2$ modified with acids enhanced the catalytic activities for both 1-butene isomerization and ethylene dimerization in comparison with NiO-ZrO$_2$ without modification.

2. The catalytic activities for the above two reactions were correlated with the acid strengths of the catalysts. The order of catalytic activity was found to be NiO-ZrO$_2$/SO$_4^{-2}$ ≫ NiO-ZrO$_2$/PO$_4^{-3}$ > NiO-ZrO$_2$/BO$_3^{-3}$ > NiO-ZrO$_2$.

3. The 1-butene isomerization activity ran parallel with the ethylene dimerization activity, but the isomerization took place on relatively weak acid sites in comparison with the dimerization.

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