

## High Catalytic Activity of NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> for Ethylene Dimerization

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A series of catalysts, NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>, for ethylene dimerization were prepared by coprecipitation followed by treatment with H<sub>2</sub>SO<sub>4</sub>. It was found that NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> containing equimolar composition of NiO and TiO<sub>2</sub> and evacuated at 400°C for 1.5 hr showed maximum catalytic activity at room temperature. However, NiO-TiO<sub>2</sub> which was not treated with H<sub>2</sub>SO<sub>4</sub> was inactive as catalyst for ethylene dimerization. Infrared spectra of the H<sub>2</sub>SO<sub>4</sub>-treated catalyst showed bidentate sulfate ion coordinated to Ti<sup>4+</sup> or Ni<sup>2+</sup>. The high catalytic activity of NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> was correlated with the increase of acid strength by the inductive effect of sulfate ion. The decrease of catalytic activity above 400°C of evacuation temperature was due to the structural change from amorphous phase to crystalline followed by the decrease of surface area. © 1986 Academic Press, Inc.

### INTRODUCTION

Nickel oxide-silica 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<sub>2</sub>H<sub>4</sub>-C<sub>2</sub>D<sub>4</sub> equilibration acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid (7).

In a previous paper (8), it was reported that the active sites on the NiO-SiO<sub>2</sub> catalyst for ethylene dimerization are classified into two types: montmorillonite and antigorite, the optimum temperature for them being around 100 and 600°C, respectively. It was also previously reported that the acid site responsible for the catalytic activities is Brønsted acid on montmorillonite, while Lewis acid on antigorite (9), as evidenced by the effect of water content or of sodium ion contamination and the infrared spectra of adsorbed pyridine. As an extension of

study on the ethylene dimerization, these authors tried to prepare other catalyst systems by combining nickel hydroxide to give low valent nickel after decomposition with TiO<sub>2</sub> treated with H<sub>2</sub>SO<sub>4</sub> which is known to be acidic (10, 11). A new catalyst system of NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> was found to be very active for the dimerization of ethylene.

### EXPERIMENTAL

**Catalysts.** The coprecipitate of Ni(OH)<sub>2</sub>-Ti(OH)<sub>4</sub> was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of nickel chloride, titanium tetrachloride, and hydrochloric acid at room temperature with 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 the treatment with sulfate ion was performed by pouring 30 ml H<sub>2</sub>SO<sub>4</sub> into 2 g of the powdered sample on a filter paper and drying the sample in air. The dry solid powder was used as catalyst after decomposing at different evacuation temperatures for 1.5 hr. This series of catalysts are denoted by

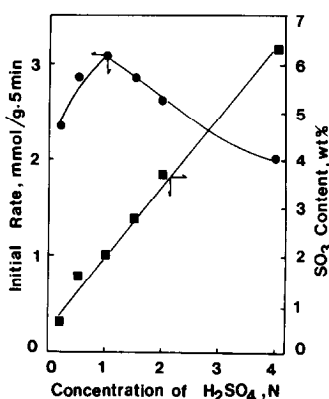


FIG. 1. Relationship between initial rate for ethylene dimerization and SO<sub>3</sub> content of 50-catalyst treated with different concentrations of H<sub>2</sub>SO<sub>4</sub>.

following a mole percentage of nickel oxide. For example, 50-catalyst means the catalyst having the nickel oxide of 50 mol%.

**Procedure.** The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 280 Torr. Fresh catalyst sample, 0.2 g, was used for every run after evacuation to 10<sup>-4</sup> Torr at different temperatures for 1.5 hr and the catalytic activity was calculated as the amount of ethylene consumed in the initial 5 min. Reaction products were analyzed by gas chromatography 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 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.

The infrared spectra were recorded in a heatable gas cell at room temperature on a JASCO IR-2 spectrometer. X-Ray diffractograms of catalyst were taken by a Jeol

Model JDX-88 X-ray diffractometer using copper target and nickel filter at 30 kV and 800 cps. The sulfur content remaining on the catalyst after the evacuation at 400°C was determined by a Rigaku X-ray fluorescent spectrometer.

#### RESULTS AND DISCUSSION

The catalytic activity for 50-catalysts treated with H<sub>2</sub>SO<sub>4</sub> of different concentrations was examined, and the results are given in Fig. 1, where the catalysts were evacuated at 400°C for 1.5 hr. The maximum activity was observed at about 2% of SO<sub>3</sub> content or 1 N concentration of H<sub>2</sub>SO<sub>4</sub>. Therefore, in this paper emphasis has been placed on the catalysts treated with only 1 N H<sub>2</sub>SO<sub>4</sub>. It is probably considered that the decrease of activity above 2% of SO<sub>3</sub> content is attributed to the decrease in the number of active sites due to the adsorption of large amounts of sulfate ion.

Ethylene was selectively dimerized to *n*-butenes. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decreases with the reaction time, while the amount of 2-butene increases. Therefore, it seems that the initial product of ethylene dimerization is 1-butene and the produced 1-butene is also isomerized to 2-butene during the reaction time.

The infrared spectra of the 50-catalyst treated with 1 N H<sub>2</sub>SO<sub>4</sub> are given in Fig. 2. The catalyst showed infrared absorption bands at 1220, 1140–1135, 1060–1045, and 980 cm<sup>-1</sup> which are assigned to the bidentate sulfate ion coordinated to Ti<sup>4+</sup> or Ni<sup>2+</sup> (12). The  $\nu$ SO spectra from the adsorbed sulfate in the  $\nu_1$  and  $\nu_3$  frequency region (900–1400 cm<sup>-1</sup>) support a species of reduced C<sub>2v</sub> symmetry with four bands arising from  $\nu_1$  and splitting of the triply degenerate  $\nu_3$  vibration (13). Other catalysts treated with sulfate ion of different concentrations also showed similar IR absorption bands.

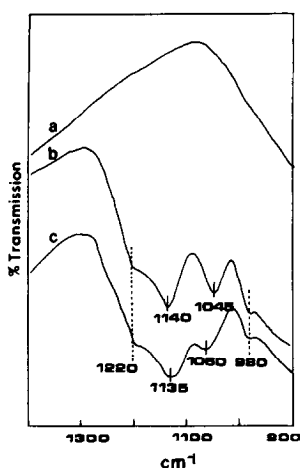


FIG. 2. Infrared spectra of 50-catalyst treated with  $H_2SO_4$ : (a)  $Ni(OH)_2-Ti(OH)_4$ , (b)  $Ni(OH)_2-Ti(OH)_4$  treated with 1 N  $H_2SO_4$ , (c)  $Ni(OH)_2-Ti(OH)_4$  treated with 1 N  $H_2SO_4$  followed by evacuating at  $400^\circ C$  for 1.5 hr.

Even after evacuation at  $400^\circ C$  for 1.5 hr, strong absorption bands of sulfate ion are left to indicate a very strong interaction between sulfate ion and the cations.

The effect of composition on the initial rate was examined where the catalysts were evacuated at  $400^\circ C$  for 1.5 hr. As shown in Fig. 3, the maximum activity is obtained at equimolar composition. This seems to be due to the increase of surface area and the subsequent increase of active

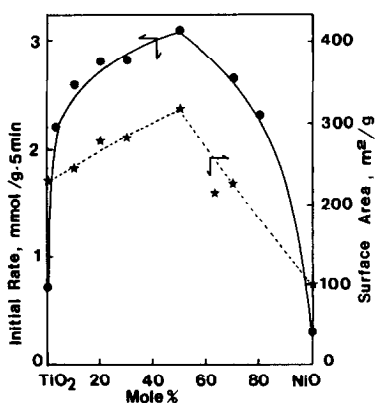


FIG. 3. Variations of initial rate for ethylene disappearance and specific surface area with the catalyst composition of the  $NiO-TiO_2/SiO_4^{2-}$  system.

site. In fact, Fig. 3 also shows that the specific surface area attained a maximum by the equimolar mixture of nickel oxide and titanium oxide.

The initial rates are plotted against the evacuation temperature using 50-catalyst as shown in Fig. 4. It can be seen that the activity appears above  $200^\circ C$  reaching a maximum at  $400^\circ C$ . The decomposition of nickel hydroxide is known to begin at  $230^\circ C$  (14). Therefore, it is very likely that the activation of catalyst above  $200^\circ C$  is related to the decomposition of the catalyst. Figure 4 also shows the decrease of activity after the evacuation temperature above  $400^\circ C$ . As shown in Fig. 3, the catalytic activity was correlated to the surface area of catalyst. The surface areas of 50-catalyst at various evacuation temperatures are also illustrated in Fig. 4. It is clear that the decrease of activity above  $400^\circ C$  is due to the decrease of surface area. To explain the reason for the decrease of surface area, the structure of catalyst at different evacuation temperatures was checked by X-ray diffraction. As shown in Fig. 5, the structure of catalyst varied depending on the evacuation temperature. The catalyst was amorphous to X rays up to  $400^\circ C$ , rutile and nickel titanium oxide ( $NiTiO_3$ ) at  $450^\circ C$ , rutile, anatase, and nickel titanium oxide at  $500^\circ C$ , and only anatase above  $550^\circ C$ . It is very clear that the dual decrease of surface area which appears above  $400^\circ C$  is due to the structural change from amorphous phase to crystal-

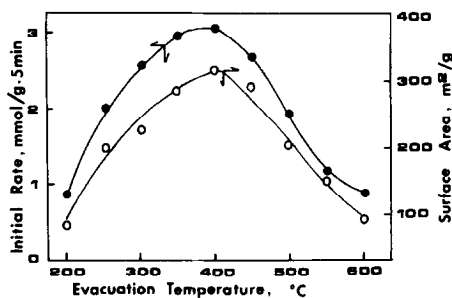


FIG. 4. Variations of initial rate for ethylene dimerization and specific surface area of 50-catalyst with evacuation temperatures.

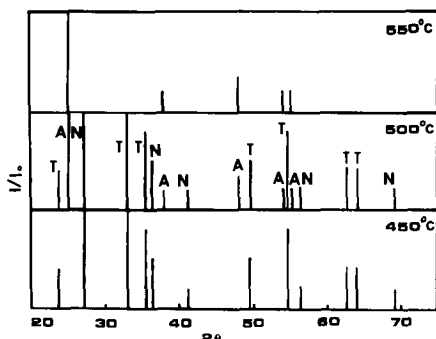


FIG. 5. X-Ray diffraction patterns of 50-catalyst at various evacuation temperature: A, anatase; R, rutile; N, nickel titanium oxide.

line. The effect of calcination temperature on the acidic properties of pure alumina was reported (15).  $\eta$ -Al<sub>2</sub>O<sub>3</sub> calcined at 500°C had low crystallinity and maximum acidity, while that calcined at 600°C exhibited high crystallinity and minimum acidity.

It is remarkable that the coprecipitated samples which were not treated with H<sub>2</sub>SO<sub>4</sub> were inactive as catalyst for ethylene dimerization, but the samples treated with H<sub>2</sub>SO<sub>4</sub> exhibited high catalytic activity. The active site responsible for dimerization is suggested to consist of a low valent nickel ion and an acid as observed in the NiO-SiO<sub>2</sub> catalyst (6, 9). The term "low valent

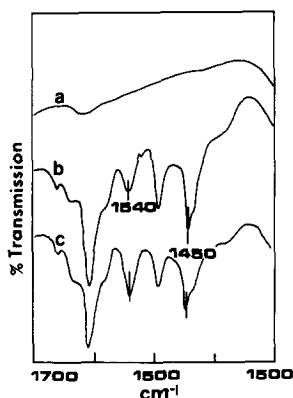


FIG. 6. Infrared spectra of pyridine adsorbed on 50-catalyst: (a) background of 50-catalyst after evacuation at 300°C for 1.5 hr; (b) pyridine adsorbed on (a), where gas phase was evacuated at 200°C for 1 hr after adsorption; (c) after adding water vapor and then evacuated at room temperature.

nickel" originated from the fact that the NiO-SiO<sub>2</sub> catalyst was drastically poisoned by carbon monoxide, since a low valent nickel is favorable to chemisorb carbon monoxide (6). In the system of NiO-TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>, the catalyst was poisoned by 1  $\mu$ mol/g of carbon monoxide for dimerization reaction. The nickel oxide treated with H<sub>2</sub>SO<sub>4</sub> exhibited low activity for dimerization as shown in Fig. 3, but nickel oxide alone without sulfate ion was inactive. These results support more certainly the fact that the active site for dimerization is formed by an interaction of a low valent nickel ion with an acid. In fact, TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> alone without nickel ion was inactive for dimerization, but exhibited low activity for polymerization. It is well known that acid catalyst SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> is effective for the polymerization of ethylene and propylene (15).

It is interesting to examine the acid properties of the sample treated with H<sub>2</sub>SO<sub>4</sub>. It has been established that Brønsted and Lewis acid sites are distinguishable by infrared spectra of adsorbed pyridine (16). Figure 6 shows the IR spectra of pyridine adsorbed on 50-catalyst. Both the pyridinium ion band at 1540 cm<sup>-1</sup> and the coordinated pyridine band at 1450 cm<sup>-1</sup> are found with the catalyst evacuated at 300°C. Spectrum c shows the changes which occur upon the addition of water vapor to the catalyst. The increase in the 1540-cm<sup>-1</sup> band indicates that a considerable amount of Brønsted acid has been formed, and the decrease in the 1450-cm<sup>-1</sup> band shows a concomitant decrease in Lewis acidity.

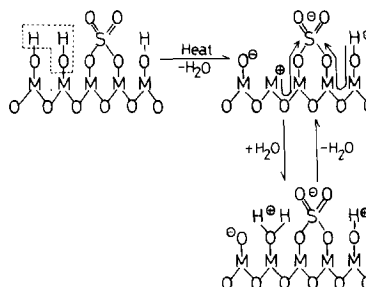


FIG. 7. A model of acid sites generated by the interaction with sulfate ion.

TABLE I  
Measurement of the Acid Strength of 4-Catalyst

| Hammett indicator        | $pK_a$ value of indicator | Evacuation temperature |       |
|--------------------------|---------------------------|------------------------|-------|
|                          |                           | 350°C                  | 400°C |
| Dicinnamalacetone        | -3.0                      | +                      | +     |
| Benzalacetophenone       | -5.6                      | +                      | +     |
| Antraquinone             | -8.2                      | +                      | +     |
| Nitrobenzene             | -12.4                     | +                      | +     |
| 2,4-Dinitrofluorobenzene | -14.5                     | +                      | +     |

This indicates that the Lewis site is converted to the Brønsted site by water molecules as shown in Fig. 7.

As mentioned above, the samples without sulfate ion were not effective for ethylene dimerization. This means that the samples do not have enough acid strength to catalyze the dimerization reaction. Titanium oxide prepared from titanium chloride and ammonium hydroxide, heat treated at 400–500°C, has acid strength of  $H_0 \cong 1.5$  (15). The acid strength of the present samples treated with  $H_2SO_4$  was examined by a color change method using Hammett indicators, when a powdered sample was added to an indicator dissolved in dried benzene. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high nickel oxide content, the low percentage of nickel oxide (4-catalyst) was used in this experiment. The results are listed in Table 1. In this table, + means that the color of basic form was changed to that of the conjugate acid form. Since the color of all used indicators was changed, the acid strength of the present catalyst is at least  $H_0 \cong -14.52$ . The acid stronger than  $H_0 = -11.93$ , which corresponds to the acid strength of 100%  $H_2SO_4$ , is known as superacid (17). Consequently, the present catalyst would be a solid superacid. Superacidic properties are attributed to the double bond nature of S=O of the complex formed by the interaction of NiO–TiO<sub>2</sub> with sulfate

ion. Both Lewis and Brønsted acid strength becomes stronger by the inductive effect of S=O in the complex as illustrated in Fig. 7. Enhancement of electron deficiency on M<sup>+</sup> and OH bonds by the introduction of sulfate ion is the origin of superacidic properties.

#### CONCLUSION

A new catalyst system of NiO–TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> for ethylene dimerization is prepared and the following fact is demonstrated in the present work.

(1) It was found that NiO–TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> is very active for ethylene dimerization, but NiO–TiO<sub>2</sub> without sulfate ion does not exhibit catalytic activity completely.

(2) The high catalytic activity of NiO–TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> correlates with the increase of acid strength by the inductive effect of sulfate ion coordinated to Ti<sup>4+</sup> or Ni<sup>2+</sup>.

(3) TiO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> alone without nickel is inactive for ethylene dimerization, but exhibits low activity for polymerization.

(4) The catalytic activity and surface area decrease gradually above 400°C of evacuation temperature due to the structural change from the amorphous phase to crystalline.

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