

New Syntheses of Active Solid Catalysts for Ethylene Dimerization

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The dimerization of alkenes is an important method for the production of higher olefins which find extensive application as industrial intermediates. A considerable number of papers have dealt with the problems of nickel-containing catalysts for ethylene dimerization.¹⁻⁸ In the previous papers from our laboratory, it has been shown that NiO-TiO₂ and NiO-ZrO₂ modified with sulfate or tungstate ion are very active for ethylene dimerization.⁹⁻¹² High catalytic activities in the reaction were attributed to the enhanced acidic properties of the modified catalysts, which originated from the inductive effect of S=O or W=O bonds of the complex formed by the interaction of oxides with sulfate or tungstate ion. Metal sulfates fairly large amounts of acid sites of moderate strength on their surface when they are calcined at about 400 °C.¹³ However, nickel sulfate catalysts supported on titania have not been supported, especially as a catalyst for ethylene dimerization. As an extension of the study on the ethylene dimerization, we have synthesized new catalysts of NiSO₄/TiO₂ which is active for ethylene dimerization even at room temperature.

The catalysts were prepared as follows. The precipitate of Ti(OH)₄ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride (TiCl₄) and hydrochloric acid at room temperature with stirring until the pH of aqueous solution reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected by AgNO₃ solution, and was dried at 100 °C for 12 h. Silica gel was obtained from Davison Speciality Chemical Co., Baltimore, Maryland. The dried Ti(OH)₄ precipitate powdered below 100 mesh or silica gel was impregnated with aqueous solution of NiSO₄ · 6H₂O followed by evaporating water, drying, and calcining in air at 300-800 °C for 1.5 h. It was used as catalyst after evacuation at different temperatures for 1 h. These series of catalysts are denoted by the weight percentage of NiSO₄. For example, 15-NiSO₄/TiO₂ or 15-NiSO₄/SiO₂ means the catalyst having 15 wt% of NiSO₄.

The catalytic activity for ethylene dimerization was determined at 20 °C with a conventional static system by monitoring pressure decrease from an initial pressure of 300 Torr. Fresh catalyst sample of 0.2 g was used for every run and the catalytic activity was calculated as the amount of ethylene consumed in the initial 5 min. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature.

The infrared spectra of several NiSO₄/TiO₂ catalysts (KBr disc) calcined at 500 °C are given in Figure 1. The catalysts showed infrared absorption bands 1212, 1138, 1050, and 998 cm⁻¹ which are assigned to bidentate sulfate⁹ coordinated to the metal such as Ti⁴⁺ or Ni²⁺, indicating a bonding of nickel sulfate on the surface of TiO₂. In general, for the metal oxides modified sulfate ion followed by evacuating above 400 °C, a

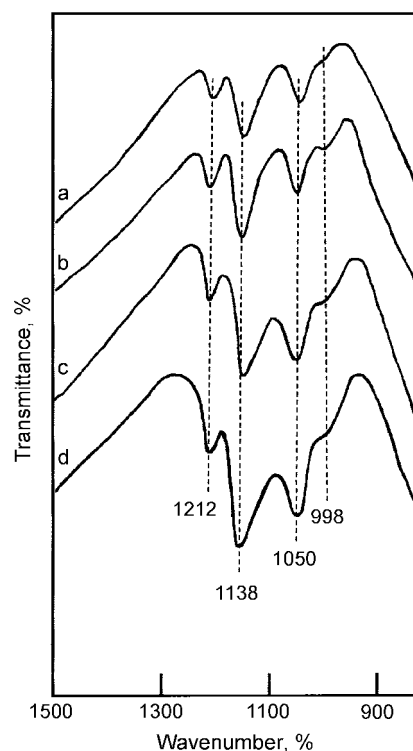


Figure 1. Infrared spectra of NiSO₄/TiO₂ having different NiSO₄ contents and calcined at 500 for 1.5 h: (a) 5-NiSO₄/TiO₂, (b) 10-NiSO₄/TiO₂, (c) 15-NiSO₄/TiO₂, and 20-NiSO₄/TiO₂.

strong band assigned to S=O stretching frequency¹⁴ is observed at 1380-1370 cm⁻¹. In this work, the corresponding band for samples exposed to air was not found because water molecules in air were adsorbed on the surfaces of catalysts.

The catalytic activities of NiSO₄/TiO₂ and NiSO₄/SiO₂ for the reaction of ethylene dimerization were examined and those as a function of NiSO₄ content are shown in Figure 2, where the catalysts were evacuated at 500 °C for 1 h before reaction. The catalytic activities of NiSO₄/TiO₂ are very high compared with those of NiSO₄/SiO₂ in spite of high surface areas for NiSO₄/SiO₂ (270-350 m²). Hereafter, emphasis is placed to only the NiSO₄/TiO₂. It is confirmed that the catalytic activity gives a maximum at 15 wt% of NiSO₄. This is due to the increase of specific surface area and the subsequent increase of active sites. It seems likely that the interaction between nickel sulfate and TiO₂ protects catalysts from sintering. Catalytic activity is closely correlated to the acidity of catalysts. Namely, the higher the acidity, the higher was the catalytic activity. As listed in Table 1, the BET surface area and acidity attained a maximum when the NiSO₄ content in the catalyst is 15 wt%. The maximum surface area and acidity at 15 wt% of nickel sulfate can be explained in terms of

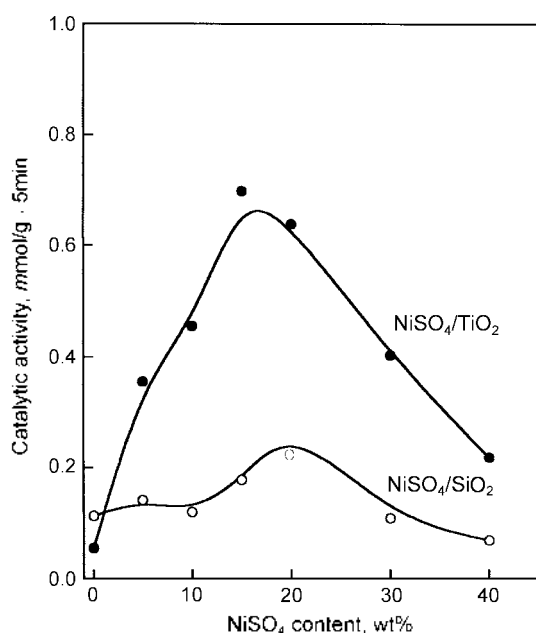


Figure 2. Variations of catalytic activity for ethylene dimerization with NiSO₄ content.

Table 1. Specific surface area and acidity of NiSO₄/TiO₂ catalysts calcined at 500 °C for 1.5 h

Weight percentage of NiSO ₄	Surface area (m ² /g)	Acidity (μmole/g)
0	52	80
5	87	108
10	113	138
15	116	172
20	74	160
30	63	116
40	48	101
100	24	79

the fact that the content of nickel sulfate forming a complete monolayer on the surface of TiO₂ is 15% in views of previous report.¹⁵ The acidity of NiSO₄/TiO₂ was determined by the amount of NH₃ irreversibly adsorbed at 230.^{7,12} It is known that acidity is required for the ethylene dimerization.^{6,7} Although the TiO₂ without NiSO₄ was inactive as catalyst for ethylene dimerization, the NiSO₄/TiO₂ exhibited high catalytic activity even at room temperature.

The effect of calcination temperature on the catalytic activities of 15-NiSO₄/TiO₂ and 15-NiSO₄/SiO₂ was also examined, where the catalysts were calcined for 1 h. The maximum activity is obtained with the catalyst calcined at 500 °C. With 15-NiSO₄/SiO₂ the catalytic activity is also very low at all calcination temperatures. All the NiSO₄/TiO₂ catalysts dimerized ethylene selectively to *n*-butenes.

The acid strength of the samples was examined by a color change method, using Hammett indicator¹⁶ in sulfuryl chloride. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high nickel sulfate content, the low percentage of nickel sulfate (5 wt%) was used in this experiment. The acid strength of TiO₂ was found to be $H_0 \leq -3.0$, while NiSO₄/TiO₂ was estimated to have a $H_0 \leq -14.5$,

indicating the formation of new stronger acid site than that of TiO₂. An acid stronger than $H_0 = -11.93$, which corresponds to an acid strength of 100% H₂SO₄, is known as a superacid.¹⁷ Consequently, NiSO₄/TiO₂ would be a solid superacid. Such superacid properties are attributed to the inductive effect of S=O of sulfate ion supported on TiO₂.¹⁸

TiO₂ alone without NiSO₄, whose acid strength was found to be $H_0 \leq -3.0$, was totally inactive for the dimerization reaction at room temperature. These results indicate that ethylene dimerization requires acid sites stronger than $H_0 = -3.0$. The catalyst calcined at 900 °C, which has no sulfate ion due to the complete decomposition, was also inactive for dimerization. Therefore, it is believed that the active site responsible for dimerization consists of a low-valent nickel and an acid, as observed in the NiO-containing catalysts.^{8-11,19} In fact, it is known that TiO₂ modified with sulfate ion is an acid.¹⁸ The term "low-valent nickel" originated from the fact that the NiO-SiO₂ catalyst was drastically poisoned by carbon monoxide, since a low-valent nickel is prone to chemisorb carbon monoxide.⁸ In this work, all catalysts added with NiSO₄ were poisoned by 1 μmol · g⁻¹ of carbon monoxide for dimerization. It seems that the formation of low-valent nickel is caused by evacuation at high temperature.

The existence of both Bronsted and Lewis acid sites was shown by the IR spectra of ammonia adsorbed on NiSO₄/TiO₂ catalyst. X-ray powder diffraction showed that for the calcination temperature of 500 °C NiSO₄/TiO₂ exhibited both anatase and rutile phases of TiO₂.

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