

New NiSO<sub>4</sub>/ZrO<sub>2</sub> Catalyst for Ethylene Dimerization

Jong Rack Sohn\* and Won Cheon Park

Department of Industrial Chemistry, Engineering College, Kyungpook National University, Taegu 702-701, Korea  
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Nickel oxide on silica or silica-alumina is an effective catalyst for ethylene dimerization and *n*-butene isomerization at room temperature.<sup>1-6</sup> It has been suggested that the active site for ethylene dimerization is formed by an interaction of a low valent nickel ion with an acid site.<sup>7</sup> In the previous papers from our laboratory, it has been shown that NiO-TiO<sub>2</sub> and NiO-ZrO<sub>2</sub> modified with sulfate or tungstate ion are very active for ethylene dimerization.<sup>8-11</sup> 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. As an extension of the study on the ethylene dimerization, we have prepared a new catalyst of NiSO<sub>4</sub>/ZrO<sub>2</sub> which is active for ethylene dimerization even at room temperature.

The catalysts were prepared as follows. The precipitate of Zr(OH)<sub>4</sub> was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride at room temperature with stirring until the pH of mother liquid reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected with AgNO<sub>3</sub> solution, and was dried at 100 °C. The precipitate powdered below 100 mesh was impregnated with aqueous solution of NiSO<sub>4</sub> · 6H<sub>2</sub>O followed by evaporating water, drying, and calcining in air at 500 °C for 1.5 h. It was used as catalyst after evacuation at different temperatures for 1 h. This series of catalysts are denoted by the weight percentage of NiSO<sub>4</sub>. For example, 15-NiSO<sub>4</sub>/ZrO<sub>2</sub> means the catalyst having 15 wt% of NiSO<sub>4</sub>.

The catalytic activity for ethylene dimerization was determined at 20 °C by 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 catalytic activities of NiSO<sub>4</sub>/ZrO<sub>2</sub> for the reaction of ethylene dimerization were examined and the results are shown as a function of NiSO<sub>4</sub> content in Figure 1, where the catalysts were evacuated at 500 °C for 1 h before reaction. It is confirmed that the catalytic activity gives a maximum at 15 wt% of NiSO<sub>4</sub>. This is due to the increase of specific surface area and the subsequent increase of active sites. Catalytic activity is closely correlated to the acidity of catalysts. Namely, the more the acidity, the higher was the catalytic activity. As listed in Table 1, the BET surface area and acidity attained a maximum when the NiSO<sub>4</sub> content in the catalyst is 15 wt%. The acidity of NiSO<sub>4</sub>/ZrO<sub>2</sub> was determined

by the amount of NH<sub>3</sub> irreversibly adsorbed at 230 °C.<sup>6,11</sup> It is known that acidity is required for the ethylene dimerization.<sup>5,6</sup> Although the ZrO<sub>2</sub> without NiSO<sub>4</sub> was inactive as catalyst for ethylene dimerization, the NiSO<sub>4</sub>/ZrO<sub>2</sub> exhibited high catalytic activity even at room temperature.

The effect of evacuation temperature on the catalytic activity of 15-NiSO<sub>4</sub>/ZrO<sub>2</sub> was also examined, where the catalysts were evacuated for 1 h. As shown in Figure 1, the maximum activity is obtained with the catalyst evacuated at 500 °C. To examine the effect of evacuation temperature on surface area, BET surface area of 15-NiSO<sub>4</sub>/ZrO<sub>2</sub> at various evacuation temperature (300-700 °C) was measured. However, no particular changes of surface area were observed, giving about 136-141 m<sup>2</sup>/g regardless of evacuation temperature. Therefore, it seems likely that the variation of catalytic activity is not due to the change of surface area but due to the easy formation of active site upon calcination temperature. All the NiSO<sub>4</sub>/ZrO<sub>2</sub> catalysts dimerized ethylene selectively to *n*-butenes. The composition of *n*-butenes analyzed by gas chromatography was such that 1-butene was found to be the dominant species at the initial reaction time as compared with *cis*-butene or *trans*-butene. However, it was shown that the amount of 1-butene decreases, while the amount of 2-

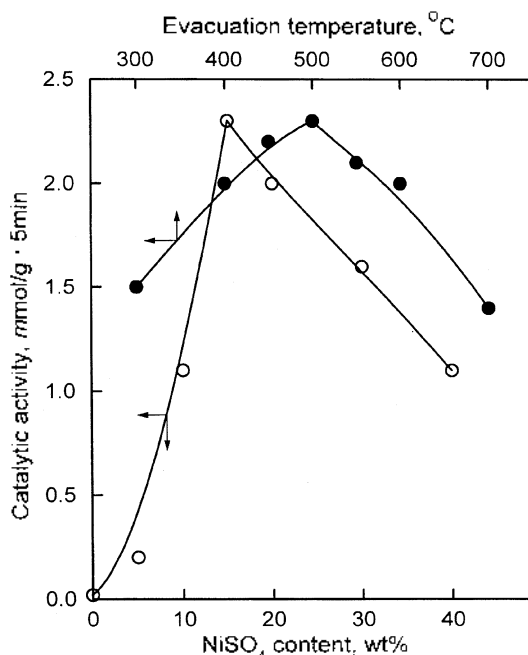


Figure 1. Variations of catalytic activity for ethylene dimerization with NiSO<sub>4</sub> content and evacuation temperature: (○) NiSO<sub>4</sub>/ZrO<sub>2</sub> having different NiSO<sub>4</sub> contents and evacuated at 500 °C; (●) 15-NiSO<sub>4</sub>/ZrO<sub>2</sub> evacuated at different temperatures.

**Table 1.** Specific Surface Area and Acidity of NiSO<sub>4</sub>/ZrO<sub>2</sub> Catalysts Calcined at 500 °C for 1.5 h

Weight percentage of NiSO <sub>4</sub>	Surface area (m <sup>2</sup> /g)	Acidity (μmole/g)
0	64	71
5	109	161
10	136	237
15	141	262
20	123	239
30	93	237
40	60	232
100	30	79

**Table 2.** Acid Strength of Samples

Hammett indicator	pKa value of indicator	ZrO <sub>2</sub>	5-NiSO <sub>4</sub> /ZrO <sub>2</sub>
Benzeneazodiphenylamine	+1.5	+	+
Dicinnamalacetone	-3.0	-	+
Benzalacetophenone	-5.6	-	+
Antraquinone	-8.2	-	+
Nitrobenzene	-12.4	-	+
2,4-Dinitrofluorobenzene	-14.5	-	+

butene increases with the reaction time. Therefore, it seems likely that the initially produced 1-butene is also isomerized to 2-butene during the reaction.

The acid strength of the samples was examined by a color change method, using Hammett indicator<sup>12</sup> in sulfuric 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 results are listed in Table 2. In this table, + means that the color of base form was changed to that of conjugate acid form. The acid strength of ZrO<sub>2</sub> was found to be  $H_0 \leq +1.5$ , while NiSO<sub>4</sub>/ZrO<sub>2</sub> was estimated to have a  $H_0 \leq -14.5$ , indicating the formation of new stronger acid site than that of ZrO<sub>2</sub>. An acid stronger than  $H_0 = -11.93$ , which corresponds to an acid strength of 100% H<sub>2</sub>SO<sub>4</sub>, is known as a superacid.<sup>13</sup> Consequently, NiSO<sub>4</sub>/ZrO<sub>2</sub> would be a solid superacid. Such superacid properties are attributed to the inductive effect of S=O of sulfate ion supported on ZrO<sub>2</sub>.<sup>14</sup>

ZrO<sub>2</sub> alone without NiSO<sub>4</sub>, whose acid strength was found to be  $H_0 < +1.5$ , was totally inactive for the dimerization reaction at room temperature. These results indicate that ethylene dimerization requires acid sites stronger than  $H_0 = +1.5$ . 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.<sup>7-10</sup> In fact, it is known that ZrO<sub>2</sub> modified with sulfate ion is an acid.<sup>14</sup> The term low-valent 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 prone to chemisorb carbon monoxide.<sup>7</sup> In this work, all catalysts added with NiSO<sub>4</sub> were poisoned by 1 μmol g<sup>-1</sup> 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 NiSO<sub>4</sub>/ZrO<sub>2</sub> catalyst. X-ray powder diffraction showed that for the calcination temperature of 500 °C NiSO<sub>4</sub>/ZrO<sub>2</sub> having 10-30 wt% of NiSO<sub>4</sub> was amorphous, but 5-NiSO<sub>4</sub>/ZrO<sub>2</sub> exhibited only tetragonal phase of ZrO<sub>2</sub>.

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