

## Al<sub>2</sub>O<sub>3</sub>-Promoted Highly Active Catalyst, NiSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> for Ethylene Dimerization

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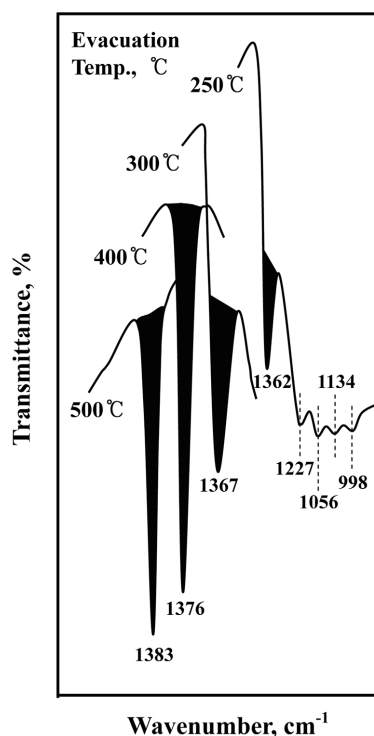
**Key Words :** Ethylene dimerization, Al<sub>2</sub>O<sub>3</sub>-promoted NiSO<sub>4</sub> catalyst, Acidic properties

A considerable number of papers have dealt with the problem of nickel-containing catalysts for ethylene dimerization.<sup>1-3</sup> It has been reported that the dimerization activities of such catalysts are related to the acidic properties of the surface and low-valent nickel ions.<sup>1,4</sup> Previously, it has been shown that nickel sulfate supported on TiO<sub>2</sub> is active for ethylene dimerization.<sup>5</sup> However, a major disadvantage associated with TiO<sub>2</sub> support is its low specific surface area and low thermal stability of the anatase structure at high temperatures. To overcome these deficiencies, titania was combined with Al<sub>2</sub>O<sub>3</sub>, by taking advantage of the high thermal stability and high surface area of Al<sub>2</sub>O<sub>3</sub>. In this paper we report a new catalyst for ethylene dimerization, NiSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> prepared by promoting TiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> and supporting NiSO<sub>4</sub> to improve catalytic activity and thermal stability.

The coprecipitate of Al(OH)<sub>3</sub>-Ti(OH)<sub>4</sub> was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of aluminum nitrate and titanium tetrachloride (Junsei Chemical Co.) at room temperature with stirring until the pH of the mother liquor reached about 8. Chemisorption of ammonia was employed as a measure of the acidity of catalysts.<sup>1,6</sup> Catalysts containing different nickel sulfate contents were prepared by the impregnation of Al(OH)<sub>3</sub>-Ti(OH)<sub>4</sub> powder with an aqueous solution of NiSO<sub>4</sub>, followed by calcining at different temperatures for 1.5 h in air. 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> indicates the catalyst containing 5 mol % Al<sub>2</sub>O<sub>3</sub> and 15 wt % NiSO<sub>4</sub>. The catalytic activity was calculated as initial rate calculated from the initial activity slope.

The infrared spectra of self-supported 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> after evacuation at different temperatures for 1 h are shown in Figure 1. There are the sharp bands at 1362-1383 cm<sup>-1</sup> accompanied by four broad and intense bands below 1230 cm<sup>-1</sup> due to the overlapping of the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> skeletal vibration, thereby, indicating the presence of different adsorbed species depending on the treatment conditions of the sulfated sample.<sup>1,7</sup> The strong intense band at 1383 cm<sup>-1</sup> after evacuation at 500 °C is related to the superacidic property,<sup>1,7</sup> which is attributable to the double bond nature of the S=O in the complex formed by the interaction between Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> and sulfate.

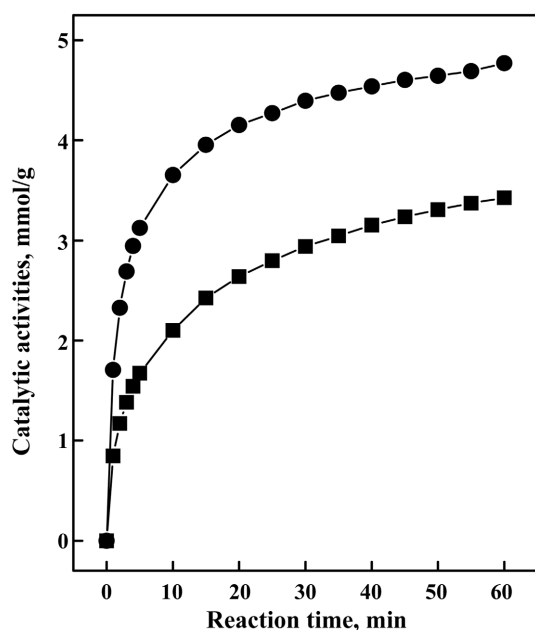
To examine the promoting effect of Al<sub>2</sub>O<sub>3</sub> on catalytic activity, the catalytic activities of Al<sub>2</sub>O<sub>3</sub>-promoted and non-promoted catalysts were tested; the results are shown in Figure 2, where the catalysts were evacuated at 500 °C for



**Figure 1.** An asymmetric S=O stretching frequency of 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> evacuated at different temperatures for 1 h.

1 h before reaction. It was found that over 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> and 15-NiSO<sub>4</sub>/TiO<sub>2</sub> ethylene was continuously consumed and was selectively dimerized to n-butenes. However, Al<sub>2</sub>O<sub>3</sub>-promoted 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> exhibited extremely higher catalytic activity than non-promoted 15-NiSO<sub>4</sub>/TiO<sub>2</sub>, showing the clear promoting effect of Al<sub>2</sub>O<sub>3</sub>. 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> exhibited two times high catalytic activity as compared with 15-NiSO<sub>4</sub>/TiO<sub>2</sub> without Al<sub>2</sub>O<sub>3</sub> (see Table 1).

Since the promoting effect of Al<sub>2</sub>O<sub>3</sub> is related to an increase in number of surface acidic sites, it would be of interest to examine various factors influencing the enhancement of these surface acidic sites. The formation of Al-O-Ti bond in the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> is probably responsible for the observed enhancement in the amount of acid sites for the Al<sub>2</sub>O<sub>3</sub>-promoted catalysts.<sup>8</sup> As listed in Table 1, the specific surface area and acidity of Al<sub>2</sub>O<sub>3</sub>-promoted samples increased with increasing Al<sub>2</sub>O<sub>3</sub> content up to 5 mol %. According to the principle of electronegativity equalization



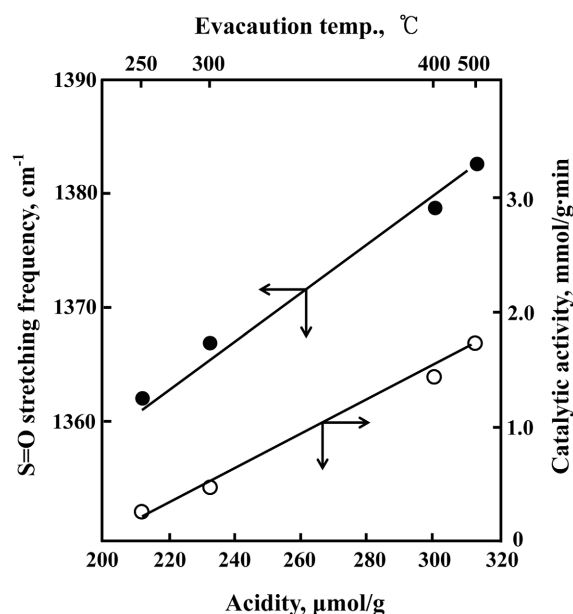
**Figure 2.** Catalytic activities for ethylene dimerization over catalysts evacuated at 400 °C for 1 h: (●) 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, (■) 15-NiSO<sub>4</sub>/TiO<sub>2</sub>.

proposed by Sanderson,<sup>9</sup> since the electronegativity of Al<sup>3+</sup> is larger than that of Ti<sup>4+</sup>, the positive charge on Ti atom is increased as a result of the formation of Al-O-Ti bond, which generates stronger acidity on these sites.<sup>8</sup> At the same time, the stronger Al-O-Ti bond formed by the charge transfer from Ti atom to neighboring Al atom results in an increase in the thermal stability of the surface sulfate species and consequently the acidity of Al<sub>2</sub>O<sub>3</sub>-promoted catalyst is increased. In fact, the endothermic peak due to the evolution of SO<sub>3</sub> decomposed from sulfate species bonded to the surface of pure TiO<sub>2</sub> appeared at 734 °C, while that from sulfate species bonded to the surface of Al<sub>2</sub>O<sub>3</sub>-promoted TiO<sub>2</sub>(5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>) appeared at 768 °C.

An asymmetric frequency in the S=O bonds is a measure of the acid strength of a sulfur complex ability to bond to basic molecules such as H<sub>2</sub>O and NH<sub>3</sub>, and is related to the driving force which generates highly acidic properties, acid strength and the number of strong acidity.<sup>1,6</sup> Both the acid strength and the number of acid sites increase with an

**Table 1.** Specific surface area, acidity, and catalytic activity of some catalysts calcined at 400 °C for 1.5 h

Catalyst	Surface area /m <sup>2</sup> g <sup>-1</sup>	Acidity /μmolg <sup>-1</sup>	Catalytic activity /mmolg <sup>-1</sup> min <sup>-1</sup>
TiO <sub>2</sub>	93	180	
1Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	124	204	
3Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	171	248	
5Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	253	251	
15-NiSO <sub>4</sub> /TiO <sub>2</sub>	158	211	0.84
15-NiSO <sub>4</sub> /1Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	214	265	1.11
15-NiSO <sub>4</sub> /3Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	278	292	1.62
15-NiSO <sub>4</sub> /5Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	290	301	1.71



**Figure 3.** Correlations among asymmetric stretching frequency of the S=O bond, catalytic activity, and acidity for 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> evacuated at different temperatures.

increase in the evacuation temperature up to 500 °C, because water adsorbed on the catalyst surface is desorbed at high temperature, resulting in the formation of new acid sites and an increase in the bond order of S=O. The frequency of the asymmetric S=O stretching vibration and catalytic activity of 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> after evacuation at different temperatures were plotted against the acidity in Figure 3. There are good correlations among the infrared band frequency of the asymmetric S=O stretching vibration in 15-NiSO<sub>4</sub>/5Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, catalytic activity for ethylene dimerization, and acidity.

In summary, the role of Al<sub>2</sub>O<sub>3</sub> is to form a thermally stable NiSO<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst having high surface area and consequently to give high acidity and catalytic activity of the sample.

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## References

- Sohn, J. R.; Park, W. C.; Kim, H. W. *J. Catal.* **2002**, *209*, 69.
- Choo, H.; Kevan, L. *J. Phys. Chem. B* **2001**, *105*, 6353.
- Urabe, K.; Koga, M.; Izumi, Y. *J. Chem. Soc. Chem. Commun.* **1989**, 807.
- Sohn, J. R.; Ozaki, A. *J. Catal.* **1980**, *61*, 29.
- Sohn, J. R.; Park, W. C. *Bull. Korean Chem. Soc.* **2000**, *21*, 1063.
- Pae, Y. I.; Bae, M. H.; Park, W. C.; Sohn, J. R. *Bull. Korean Chem. Soc.* **2004**, *25*, 1881.
- Jin, T.; Yamaguchi, T.; Tanabe, K. *J. Phys. Chem.* **1986**, *90*, 4794.
- Hua, W.; Xia, Y.; Yue, Y.; Zao, Z. *J. Catal.* **2000**, *196*, 104.
- Sanderson, R. T. *Chemical Bonds and Bond Energy*; Academic Press: New York, 1976; p 75.