

Al₂O₃-Promoted Highly Active Catalyst, NiSO₄/Al₂O₃-TiO₂ for Ethylene Dimerization

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A considerable number of papers have dealt with the problem of nickel-containing catalysts for ethylene dimerization.¹⁻³ 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.^{1,4} Previously, it has been shown that nickel sulfate supported on TiO₂ is active for ethylene dimerization.⁵ However, a major disadvantage associated with TiO₂ 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 Al₂O₃, by taking advantage of the high thermal stability and high surface area of Al₂O₃. In this paper we report a new catalyst for ethylene dimerization, NiSO₄/Al₂O₃-TiO₂ prepared by promoting TiO₂ with Al₂O₃ and supporting NiSO₄ to improve catalytic activity and thermal stability.

The coprecipitate of Al(OH)₃-Ti(OH)₄ 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.^{1,6} Catalysts containing different nickel sulfate contents were prepared by the impregnation of Al(OH)₃-Ti(OH)₄ powder with an aqueous solution of NiSO₄, followed by calcining at different temperatures for 1.5 h in air. 15-NiSO₄/5Al₂O₃-TiO₂ indicates the catalyst containing 5 mol % Al₂O₃ and 15 wt % NiSO₄. The catalytic activity was calculated as initial rate calculated from the initial activity slope.

The infrared spectra of self-supported 15-NiSO₄/5Al₂O₃-TiO₂ after evacuation at different temperatures for 1 h are shown in Figure 1. There are the sharp bands at 1362-1383 cm⁻¹ accompanied by four broad and intense bands below 1230 cm⁻¹ due to the overlapping of the Al₂O₃-TiO₂ skeletal vibration, thereby, indicating the presence of different adsorbed species depending on the treatment conditions of the sulfated sample.^{1,7} The strong intense band at 1383 cm⁻¹ after evacuation at 500 °C is related to the superacidic property,^{1,7} which is attributable to the double bond nature of the S=O in the complex formed by the interaction between Al₂O₃-TiO₂ and sulfate.

To examine the promoting effect of Al₂O₃ on catalytic activity, the catalytic activities of Al₂O₃-promoted and non-promoted catalysts were tested; the results are shown in Figure 2, where the catalysts were evacuated at 500 °C for

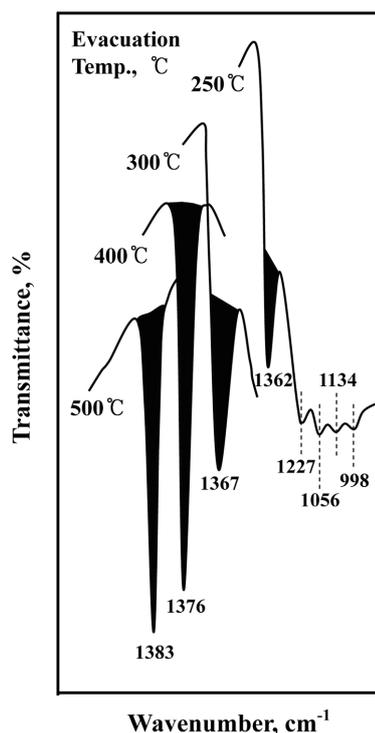


Figure 1. An asymmetric S=O stretching frequency of 15-NiSO₄/5Al₂O₃-TiO₂ evacuated at different temperatures for 1 h.

1 h before reaction. It was found that over 15-NiSO₄/5Al₂O₃-TiO₂ and 15-NiSO₄/TiO₂ ethylene was continuously consumed and was selectively dimerized to n-butenes. However, Al₂O₃-promoted 15-NiSO₄/5Al₂O₃-TiO₂ exhibited extremely higher catalytic activity than non-promoted 15-NiSO₄/TiO₂, showing the clear promoting effect of Al₂O₃. 15-NiSO₄/5Al₂O₃-TiO₂ exhibited two times high catalytic activity as compared with 15-NiSO₄/TiO₂ without Al₂O₃ (see Table 1).

Since the promoting effect of Al₂O₃ 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 Al₂O₃-TiO₂ is probably responsible for the observed enhancement in the amount of acid sites for the Al₂O₃-promoted catalysts.⁸ As listed in Table 1, the specific surface area and acidity of Al₂O₃-promoted samples increased with increasing Al₂O₃ content up to 5 mol %. According to the principle of electronegativity equalization

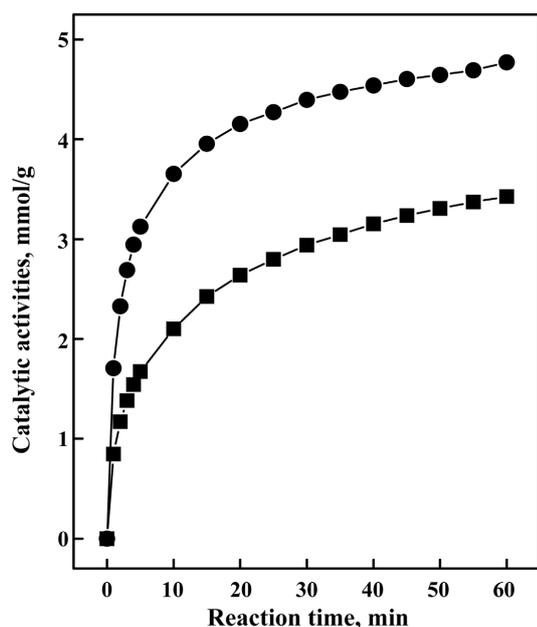


Figure 2. Catalytic activities for ethylene dimerization over catalysts evacuated at 400 °C for 1 h: (●) 15-NiSO₄/5Al₂O₃-TiO₂, (■) 15-NiSO₄/TiO₂.

proposed by Sanderson,⁹ since the electronegativity of Al³⁺ is larger than that of Ti⁴⁺, 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.⁸ 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 Al₂O₃-promoted catalyst is increased. In fact, the endothermic peak due to the evolution of SO₃ decomposed from sulfate species bonded to the surface of pure TiO₂ appeared at 734 °C, while that from sulfate species bonded to the surface of Al₂O₃-promoted TiO₂(5Al₂O₃-TiO₂) 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 H₂O and NH₃, and is related to the driving force which generates highly acidic properties, acid strength and the number of strong acidity.^{1,6} 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 ² g ⁻¹	Acidity /μmolg ⁻¹	Catalytic activity /mmolg ⁻¹ min ⁻¹
TiO ₂	93	180	
1Al ₂ O ₃ -TiO ₂	124	204	
3Al ₂ O ₃ -TiO ₂	171	248	
5Al ₂ O ₃ -TiO ₂	253	251	
15-NiSO ₄ /TiO ₂	158	211	0.84
15-NiSO ₄ /1Al ₂ O ₃ -TiO ₂	214	265	1.11
15-NiSO ₄ /3Al ₂ O ₃ -TiO ₂	278	292	1.62
15-NiSO ₄ /5Al ₂ O ₃ -TiO ₂	290	301	1.71

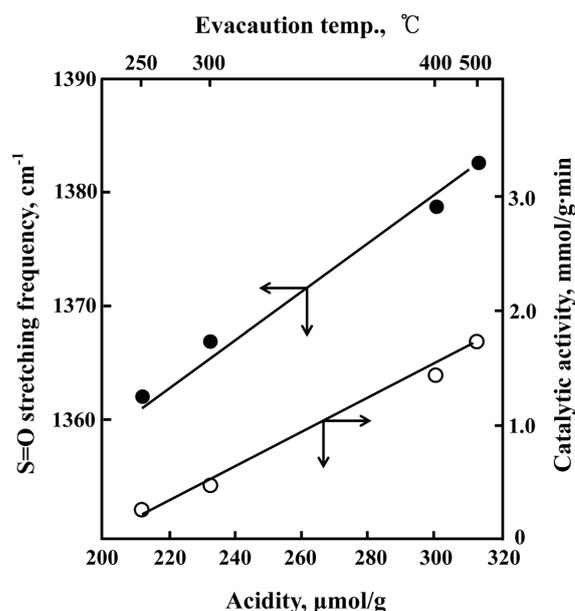


Figure 3. Correlations among asymmetric stretching frequency of the S=O bond, catalytic activity, and acidity for 15-NiSO₄/5Al₂O₃-TiO₂ evacuated at different temperatures.

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-NiSO₄/5Al₂O₃-TiO₂ 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-NiSO₄/5Al₂O₃-TiO₂, catalytic activity for ethylene dimerization, and acidity.

In summary, the role of Al₂O₃ is to form a thermally stable NiSO₄/Al₂O₃-TiO₂ catalyst having high surface area and consequently to give high acidity and catalytic activity of the sample.

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