

Correlation between the Infrared Band Frequency of Asymmetric S=O Stretching Vibration in NiSO₄/ γ -Al₂O₃ Catalyst and Activity for Ethylene Dimerization

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Ethylene dimerization is an important reaction and worthy of study. A considerable number of papers have dealt with the problems of nickel-containing catalysts for ethylene dimerization.¹⁻⁹ In the previous papers from our laboratory, it has been shown that supported nickel sulfate catalysts are very active for ethylene dimerization.⁸⁻¹⁰ High catalytic activities in the reaction were attributed to the enhanced acidic properties of the supported nickel sulfate catalysts, which originated from a strongly electrophilic nature of S=O bonds of the complex formed by the interaction of oxides with sulfate ion. However, it is expected that the acidic properties and catalytic activities of the sulfated catalysts are different depending on the frequency of asymmetric S=O stretching vibration and pretreatment conditions. Therefore, in this paper we report the correlation between the band frequency of the asymmetric S=O stretching vibration in NiSO₄/ γ -Al₂O₃ catalysts and ethylene dimerization activity.

The catalysts containing 20 wt% nickel sulfate were prepared by impregnation of γ -Al₂O₃ powder (JRC-ALO-2, surface area = 240 m²/g) with aqueous solution of NiSO₄·6H₂O followed by calcining at 600 °C for 1.5 h in air. The catalytic activity for ethylene dimerization was determined at 20 °C by a conventional static system following pressure change from an initial pressure of 290 Torr.⁸⁻¹⁰ 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 FTIR (Fourier transform infrared) spectra were obtained in a heatable gas cell at room temperature using Mattson Model GL6030E spectrometer. The self-supporting catalyst wafers contained about 9 mg/cm².

The absorption of asymmetric stretching frequency of S=O bonds is commonly found in the range of 1360-1410 cm⁻¹. Infrared spectra of NiSO₄/ γ -Al₂O₃ after evacuation at 100-600 °C for 1 h are shown in Figure 1. There are the sharp bands at 1362-1398 cm⁻¹ accompanied by four broad but split bands at 1250, 1157, 1038, and 941 cm⁻¹, indicating the presence of two kinds of sulfated species. The bands at 1362-1398 cm⁻¹ corresponds to asymmetric S=O stretching frequency of sulfate ion bonded to γ -Al₂O₃ under the dehydrated condition, while the latter four bands are assigned to bidentate sulfate ion coordinated to γ -Al₂O₃.^{11,12} These results are very similar to those of other worker.¹¹⁻¹³ However, the frequency shift of this band is different depending on the evacuation temperature as shown in Figure 1. At 100 °C an

asymmetric stretching band of S=O bonds was not observed because the water molecule are adsorbed on the surface of NiSO₄/ γ -Al₂O₃.^{11,12} However, from 200 °C the band began to appear at 1362 cm⁻¹ as a shoulder, and the band intensity increased with the evacuation temperature and the position of band was shifted to higher wavenumber. It is likely that the surface sulfur complexes formed by the interaction of oxides with sulfate ion in highly active catalysts have a strong tendency to reduce its bond order by the adsorption of basic molecules such as H₂O.^{11,12} Consequently, as shown in Figure 1, an asymmetric stretching band of S=O bonds for the sample evacuated at lower temperature appears at lower frequency compared with that for the sample evacuated at higher temperature because the adsorbed water reduces the bond order of S=O from a highly covalent double-bond character to a lesser double-bond character. Therefore, it is obvious that the asymmetric stretching frequency of the S=O bonds can be related to the acidic properties and catalytic

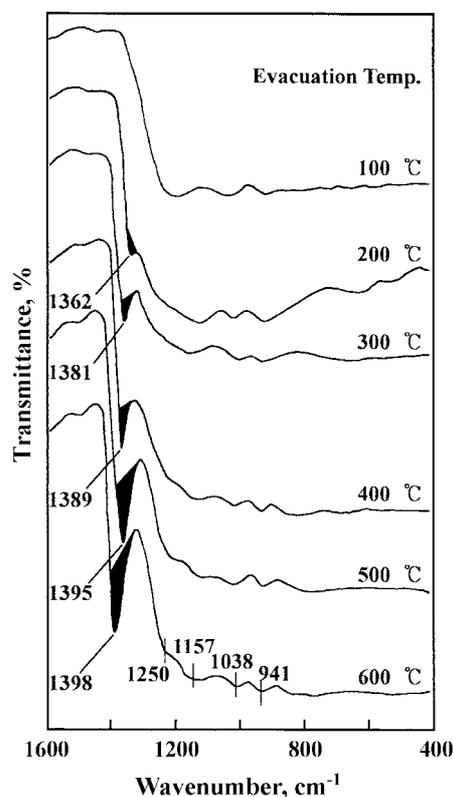


Figure 1. Infrared spectra of NiSO₄/ γ -Al₂O₃ evacuated at different temperatures.

activity discussed later.

The catalytic activities of $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ for the reaction of ethylene dimerization were examined and the results are shown as a function of evacuation temperature in the Figure 2, where the catalysts were evacuated for 1.5 h before reaction. The catalytic activity increased with increasing the evacuation temperature, reaching a maximum at 600 °C. To examine the effect of evacuation temperature on surface area, BET surface area of $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ at various evacuation temperatures (300-700 °C) was measured. However, the particular change of surface area was not observed, giving about 190-193 m^2/g regardless of evacuation temperature. Therefore, it seems likely that the variation of catalytic activity is not related to the change of surface area but to the easy formation of active site depending on the evacuation temperature. On all the catalysts of $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$, ethylene was selectively dimerized to *n*-butenes.

Comparing Figures 1 and 2, catalytic activity is closely correlated to the asymmetric stretching frequency of the S=O bonds. Namely, the higher the frequency of the S=O bonds, the higher the catalytic activity for ethylene dimerization. It was reported that the catalytic activity of nickel-containing catalysts in the ethylene dimerization as well as in the butene isomerization was closely correlated with the acidity of the catalyst.^{4,8,9} The acidity of $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ after evacuation at different temperatures was determined by the amount of NH_3 irreversibly adsorbed at 230 °C.^{4,6} The results are listed in Table 1 together with the asymmetric frequency of the S=O bonds and catalytic activity for ethylene dimerization. The higher the frequency, the larger the acidity and catalytic activity of catalyst, showing maxima for frequency, acidity and catalytic activity at the evacuation temperature of 600 °C. The decrease of catalytic activity after the evacuation at

Table 1. Asymmetric stretching frequency of the S=O bonds, acidity and catalytic activity for $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst evacuated at different temperatures

Evacuation Temperature, °C	Frequency, cm^{-1}	Acidity, $\mu\text{mol/g}$	Catalytic activity, $\text{mmol/g} \cdot 5 \text{ min}$
100	—	48	0
200	1362	75	1.4
300	1381	154	2.3
400	1389	216	3.1
500	1395	283	3.7
600	1398	520	4.3
700	1378	375	1.8

700 °C can be explained in terms of that the high evacuation temperature resulted in the decrease of sulfate group bonded to the surface of $\gamma\text{-Al}_2\text{O}_3$ as well as the decrease of acidity, and the change of oxidation state of nickel ion. It is known that the active sites responsible for ethylene dimerization consist of a low valent nickel, Ni^+ and an acid.¹⁰ An asymmetric frequency of the S=O bonds is a measure of ability (acid strength) of a sulfur complex to pull basic molecules such as H_2O and NH_3 , and is a driving force to generate highly acidic properties, acid strength and acidity.^{11,12} In view of Figures 1 and 2, and Table 1, there is a good correlation between the infrared band frequency of the asymmetric S=O stretching vibration in $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ and catalytic activity for ethylene dimerization. Therefore, it is concluded that we can use the asymmetric stretching frequency of the S=O bonds in $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ catalyst as a measure of catalytic activity for ethylene dimerization.

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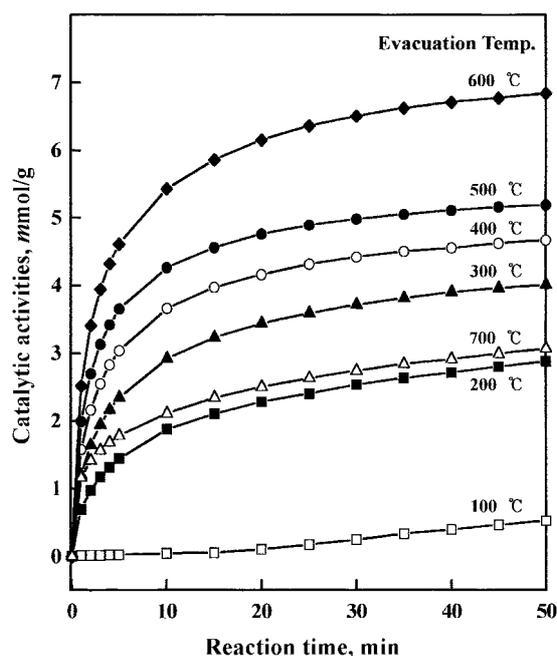


Figure 2. Catalytic activities of $\text{NiSO}_4/\gamma\text{-Al}_2\text{O}_3$ for ethylene dimerization as a function of evacuation temperature.

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