

Letter

Nickel sulfate supported on γ -Al₂O₃ for ethylene dimerization

Jong Rack Sohn^{*}, Won Cheon Park

Department of Industrial Chemistry, Engineering College, Kyungpook National University, Taegu 702-701, South Korea

Received 24 July 1997; accepted 26 March 1998

Keywords: Ethylene dimerization; Nickel sulfate; γ -Al₂O₃

Ethylene dimerization is an important reaction and worthy of study. Nickel oxide on silica or silica–alumina is an effective catalyst for ethylene dimerization and *n*-butene isomerization at room temperature [1–8]. It has been suggested that the active site for dimerization is formed by an interaction of a low-valent nickel ion with an acid site [9]. In the previous papers from this laboratory, it has been shown that the NiO–TiO₂ and NiO–ZrO₂ modified with sulfate ion or tungstate ion is very active for ethylene dimerization [10–13]. High catalytic activities in the reactions 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 ion or tungstate ion. As an extension of the study on the ethylene dimerization, we have prepared a new catalyst of nickel sulfate supported on γ -Al₂O₃ which is active for ethylene dimerization even at room temperature.

The catalysts containing various nickel sulfate content were prepared by dry 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. This series of catalysts are denoted by their weight percentage of nickel sulfate. For example, 20-NiSO₄/ γ -Al₂O₃ indicates the catalyst containing 20 wt.% NiSO₄.

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. 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. Prior to obtaining the spectra, the samples were heated under vacuum at 400–600°C for 1 h. X-ray photoelectron spectra were obtained with a VG Scientific Model ESCALAB MK-11 spectrometer. Al K_α and Mg K_α were used as the excitation source, usually at 12 kV, 20 mA. The analysis chamber was 10⁻⁹ Torr or better and spectra of samples, as pressed wafer, were analyzed.

^{*} Corresponding author. Tel.: +82-53-950-5585; Fax: +82-53-950-6594; E-mail: jrsohn@bh.kyungpook.ac.kr

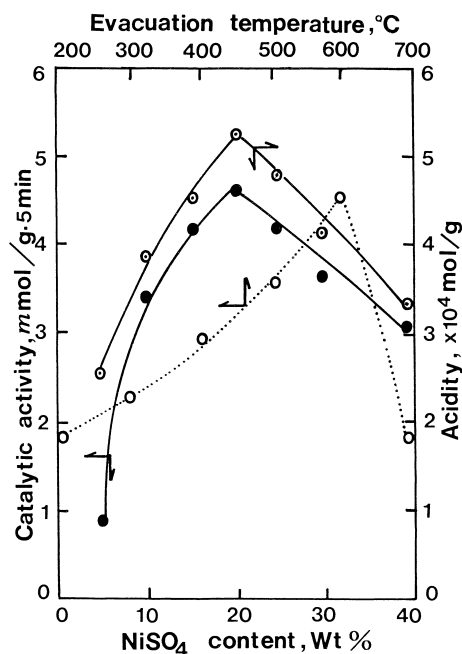


Fig. 1. Relationship between acidity and catalytic activity of NiSO₄/γ-Al₂O₃ for ethylene dimerization: (●) catalytic activity of NiSO₄/γ-Al₂O₃ having different NiSO₄ content and evacuated at 600°C; (○) catalytic activity of 20-NiSO₄/γ-Al₂O₃ evacuated at different temperature; (⊙) acidity of NiSO₄/γ-Al₂O₃ having different NiSO₄ content and evacuated at 600°C.

Infrared spectrum of 20-NiSO₄/γ-Al₂O₃ after evacuation at 400°C for 1 h was examined. There is an intense sharp band at 1398 cm⁻¹ accompanied by four broad but split bands at 1252, 1179, 1103, and 1017 cm⁻¹, indicating the presence of two kinds of sulfated species. A strong band at 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.

[14]. These results are very similar to those of other worker [14,15].

The catalytic activities of NiSO₄/γ-Al₂O₃ for the reaction of ethylene dimerization were examined and the results are shown as a function of NiSO₄ content in the Fig. 1, where the catalysts were evacuated at 600°C for 1.5 h before reaction. It is confirmed that the catalytic activity gives a maximum at 20 wt.% of NiSO₄. This seems not to be correlated to the specific surface area, but closely correlated to the acidity of catalysts. The acidity of NiSO₄/γ-Al₂O₃ calcined at 600°C was determined by the amount of NH₃ irreversibly adsorbed at 230°C [7]. Here, the acidity is the sum of Lewis and Brönsted acidity. As listed in Table 1, the BET (Brunauer–Emmet–Teller) surface area attained a maximum when the NiSO₄ content in the catalyst is 5 wt.% and then showed gradual decrease with increasing NiSO₄ content. However, as shown in Fig. 1, the more the acidity, the higher the catalytic activity. In this way, it is demonstrated that the catalytic activity of NiSO₄/γ-Al₂O₃ substantially runs parallel to the total acidity, regardless of the nature of acid site. In fact, it is known that either Lewis or Brönsted acidity is required for the ethylene dimerization [6,7].

The effect of evacuation temperature on the catalytic activity of 20-NiSO₄/γ-Al₂O₃ was also examined, where the catalysts were evacuated for 1.5 h. As shown in Fig. 1, the maximum activity is obtained with the catalyst evacuated at 600°C. To examine the effect of evacuation temperature on surface area, BET surface area of 20-NiSO₄/γ-Al₂O₃ at various evacua-

Table 1
Specific surface area of NiSO₄/γ-Al₂O₃ catalysts calcined at 600°C

Catalyst	Surface area (m ² /g)	Catalyst	Surface area (m ² /g)
γ-Al ₂ O ₃	240	20-NiSO ₄ /γ-Al ₂ O ₃	193
2-NiSO ₄ /γ-Al ₂ O ₃	287	25-NiSO ₄ /γ-Al ₂ O ₃	159
5-NiSO ₄ /γ-Al ₂ O ₃	290	30-NiSO ₄ /γ-Al ₂ O ₃	139
7-NiSO ₄ /γ-Al ₂ O ₃	225	40-NiSO ₄ /γ-Al ₂ O ₃	130
10-NiSO ₄ /γ-Al ₂ O ₃	217	100-NiSO ₄ /γ-Al ₂ O ₃	25
15-NiSO ₄ /γ-Al ₂ O ₃	210		

tion temperature (300–700°C) was measured. However, the particular change of surface area was not observed, giving about 190–193 m² g⁻¹ 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 NiSO₄/γ-Al₂O₃, ethylene was selectively dimerized to *n*-butenes. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decreases with the reaction time, while the amount of 2-butene increases. Therefore, it seems likely that the initially produced 1-butene is also isomerized to 2-butene during the reaction.

In a previous paper, it was demonstrated that the catalytic activities correlate with the acid strengths of the catalysts [11]. The acid strength of the present samples was examined by a color change method, using Hammett indicator [16] in sulfuryl chloride. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high nickel oxide content, the low percentage of nickel sulfate (5 wt.%) was used in this experiment. The acid strength of γ-Al₂O₃ was found to be $H_0 \leq -8.2$, while NiSO₄/γ-Al₂O₃ was estimated to have a $H_0 \leq -14.5$, indicating the formation of new acid site stronger than γ-Al₂O₃. 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/γ-Al₂O₃ would be a solid superacid. Superacid properties are attributed to the inductive effect of S=O of sulfate ion coordinated to γ-Al₂O₃ [10–12].

γ-Al₂O₃ alone without NiSO₄, whose acid strength was found to be $H_0 \leq -8.2$, was totally inactive for the dimerization reaction at room temperature. These results indicate that ethylene dimerization requires acid sites stronger than $H_0 = -8.2$. The catalyst calcined at 900°C,

which has no sulfate ion due to the complete decomposition, was inactive for dimerization. Therefore, the active site responsible for dimerization is suggested to consist of a low-valent nickel and an acid, as observed in the NiO-containing catalysts [9–12,18]. In fact, it is known that the sulfated alumina is an acid [14,15]. 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 [9]. 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.

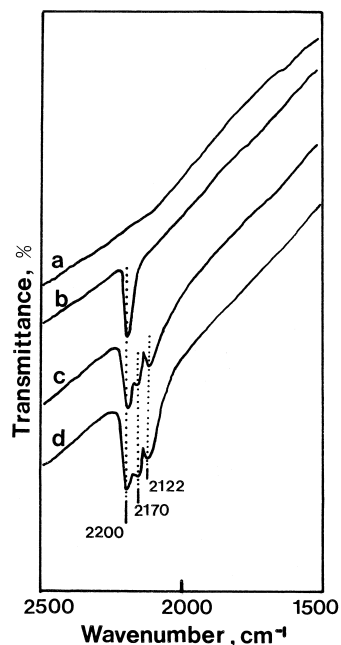


Fig. 2. The IR spectra of CO adsorbed on 20-NiSO₄/γ-Al₂O₃. (a) Background of 20-NiSO₄/γ-Al₂O₃ evacuated at room temperature. (b) After the introduction of 50 Torr CO to sample (a). (c) After the introduction of 100 Torr CO to the sample evacuated at 600°C for 1 h. (d) After the introduction of 150 Torr CO to the sample (c).

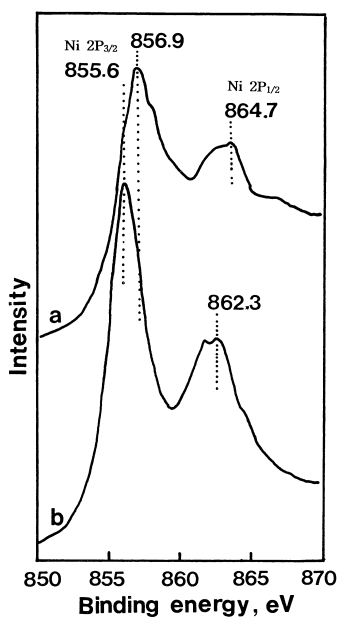


Fig. 3. The Ni 2P XPS of 20-NiSO₄/γ-Al₂O₃ calcined at 600°C. (a) After evacuation room temperature. (b) After evacuation at 600°C for 1 h.

The IR spectra of CO adsorbed on 20-NiSO₄/γ-Al₂O₃ were examined to clarify the formation of low-valent nickel. When the sample was exposed to CO (50 Torr) at room temperature, the adsorbed CO band appeared at 2200 cm⁻¹, as shown in Fig. 2b. The band might be assigned to the stretching vibration for CO adsorbed on Ni²⁺ [19,20]. However, when the sample evacuated at 600°C for 1 h was exposed to CO (100 Torr), the two bands at 2170 and 2122 cm⁻¹, in addition to the band at 2200 cm⁻¹, were observed (Fig. 2c). The intensities of two bands increased concomitantly with increasing CO concentration, as shown in Fig. 2d. Therefore, it seems likely that the two bands originate from one species, Ni⁺(CO)₂. The bands at 2170 and 2122 cm⁻¹ are assigned to a symmetrical and asymmetrical stretching vibrations of Ni⁺(CO)₂, respectively [19,20].

To obtain further information on the oxidation state of low-valent nickel species, Ni 2P XPS of 20-NiSO₄/γ-Al₂O₃ was measured and the results are shown in Fig. 3. For the sample evacuated at room temperature, the vertical lines

at 856.9 eV (Ni 2P_{3/2}) and 864.7 eV (Ni 2P_{1/2}) in Fig. 3a indicate the positions of the peaks related to Ni²⁺, in agreement with previous reports [21,22]. However, for the sample evacuated at 600°C, the positions of the vertical lines were shifted to the lower binding energies, indicating the formation of low-valent nickel species by evacuation at 600°C. In view of IR results and previous report [22], the vertical lines at 855.6 eV (Ni 2P_{3/2}) and 862.3 eV (Ni 2P_{1/2}) indicate the positions of the peaks related to low-valent nickel species, Ni⁺. In view of IR and XPS results, it is concluded that the active sites responsible for ethylene dimerization consist of a valent nickel, Ni⁺ and an acid.

The existence of both Brønsted and Lewis acid sites was shown by the IR spectra of ammonia adsorbed on NiSO₄/γ-Al₂O₃ catalyst. X-ray powder diffraction showed that 20-NiSO₄/γ-Al₂O₃ calcined at 600°C exhibited orthorhombic phase of NiSO₄ and γ-Al₂O₃ phase.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation through the Research Center for Catalytic Technology at Pohang University of Science and Technology.

References

- [1] J.P. Hogan, R.L. Banks, W.C. Lanning, A. Clark, *Ind. Eng. Chem.* 47 (1955) 752.
- [2] T. Shiba, A. Ozaki, *Nippon Kagaku Zasshi* 74 (1953) 295.
- [3] H. Uchida, H. Imai, *Bull. Chem. Soc. Jpn.* 35 (1962) 989, 995.
- [4] H. Uchida, H. Imai, *Bull. Chem. Soc. Jpn.* 38 (1965) 925.
- [5] G. Wendt, D. Hentschel, J. Finster, R. Schöllner, *J. Chem. Soc. Faraday Trans.* 179 (1983) 2103.
- [6] J.R. Sohn, A. Ozaki, *J. Catal.* 59 (1979) 303.
- [7] J.R. Sohn, A. Ozaki, *J. Catal.* 61 (1980) 29.
- [8] G. Wendt, E. Fritsch, R. Schöllner, H. Siegel, *Z. Anorg. Allg. Chem.* 467 (1980) 51.
- [9] K. Kimura, A. Ozaki, *J. Catal.* 18 (1970) 271.
- [10] J.R. Sohn, H.J. Kim, *J. Catal.* 101 (1986) 428.

- [11] J.R. Sohn, H.W. Kim, J.T. Kim, *J. Mol. Catal.* 41 (1989) 375.
- [12] J.R. Sohn, H.W. Kim, Y.M. Park, E.H. Park, J.T. Kim, S.E. Park, *Appl. Catal. A: Gen.* 128 (1995) 127.
- [13] J.R. Sohn, D.C. Shin, *J. Catal.* 160 (1996) 314.
- [14] T. Jin, T. Yamaguchi, K. Tanabe, *J. Phys. Chem.* 90 (1986) 4794.
- [15] O. Saur, M. Bensitel, A.B. Mohammed Saad, J.C. Lavalley, C.P. Tripp, B.A. Morrow, *J. Catal.* 99 (1986) 104.
- [16] L.P. Hammett, A.J. Deyrup, *J. Am. Chem. Soc.* 54 (1932) 2721.
- [17] F.G.A. Olah, G.K.S. Prakash, J. Sommer, *Science* 13 (1979) 206.
- [18] K. Maruja, A. Ozaki, *Bull. Chem. Soc. Jpn.* 46 (1973) 351.
- [19] M. Kermarec, D. Oliver, M. Richard, M. Che, F. Bozon-Verduraz, *J. Phys. Chem.* 86 (1982) 2818.
- [20] P.H. Kasai, R.J. Bishop Jr., D. Meleod Jr., *J. Phys. Chem.* 82 (1978) 279.
- [21] F. van Looij, J.W. Geus, *J. Catal.* 168 (1997) 154.
- [22] J.C. de Jesus, P. Pereira, J. Carrazza, F. Zaera, *Surf. Sci.* 369 (1996) 217.