

Ethylene Dimerization Catalyst of Nickel Sulfate Supported on Silica-Alumina

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Abstract—Catalysts containing various nickel sulfate content were prepared by dry impregnation of silica-alumina or silicagel with aqueous solution of nickel sulfate. $\text{SiO}_2\text{-Al}_2\text{O}_3$ alone without NiSO_4 was totally inactive for the ethylene dimerization reaction at room temperature. However, $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ was found to be very active even at room temperature compared with $\text{NiSO}_4/\text{SiO}_2$.

Key words: Ethylene Dimerization, Nickel Sulfate/Silica-Alumina, Impregnation

INTRODUCTION

The dimerization of alkenes is an important method for the production of higher olefins which find extensive application as industrial intermediates. A considerable number of papers have dealt with the problem of nickel-containing catalysts for ethylene dimerization [Sohn and Ozaki, 1980; Wendt et al., 1983; Urabe et al., 1989; Bonneviot et al., 1983]. In contrast to usual acid-type catalysts, the nickel oxide on silica or silica-alumina shows a higher activity for a lower alkene dimerization, particularly for ethylene [Sohn and Ozaki, 1980; Wendt et al., 1983]. The catalyst is also active for the isomerization of n-butenes, the mechanism of which has been proved to be of a proton donor-acceptor type [Ozaki and Kimura, 1964]. It was reported that the dimerization activities of such catalysts are related to the acidic properties of the surface and low valent nickel ions [Kimura and Ozaki, 1970; Sohn and Shin, 1996]. Nickel catalysts supported on alumina are also used for hydrodenitrogenation and hydrodesulfurization [Kwak and Moon, 1999; Park and Rhee, 1998]. Previous papers from our laboratory have shown that NiO-TiO_2 and NiO-ZrO_2 modified with sulfate or tungstate ion are very active for ethylene dimerization [Sohn and Kim, 1986; Sohn et al., 1987, 1990; Sohn and Lee, 1997; Sohn and Shin, 1996]. 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 synthesized new catalysts of $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ which is active for ethylene dimerization even at room temperature.

EXPERIMENTAL

The catalysts were prepared by the impregnation method using aqueous solution of nickel sulfate [Kim et al., 1997; Coh et al., 1997]. Silica-alumina having 82 wt% silica contents was obtained from Nikki Chemical Co., Japan. Silica gel was obtained from Davison Speciality Chemical Co., Baltimore, Maryland. Silica-alu-

mina or silica gel was impregnated with aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ followed by evaporating water, drying, and calcining in air at 300–800 °C for 1.5 h. It was used as catalyst after evacuation at different temperatures for 1 h. These series of catalysts are denoted by the weight percentage of NiSO_4 . For example, 15- $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ or 15- $\text{NiSO}_4/\text{SiO}_2$ means the catalyst has 15 wt% of NiSO_4 used silica-alumina of 82 wt% silica or silica.

Chemisorption of ammonia was employed as a measure of acidity of catalysts. The amount of chemisorption was obtained as the irreversible adsorption of ammonia [Sohn and Ozaki, 1980; Sohn and Shin, 1996; Sohn and Bae, 2000]. Thus, the first adsorption of ammonia at 20 °C and 300 torr was followed by evacuation at 230 °C for 1 h and readsorption at 20 °C, the difference between two adsorptions at 20 °C giving the amount of chemisorption. 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.

RESULTS AND DISCUSSION

The catalytic activities of $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\text{NiSO}_4/\text{SiO}_2$ for the reaction of ethylene dimerization were examined and the results are shown as a function of NiSO_4 content in Fig. 1, where the catalysts were evacuated at 500 °C for 1 h before reaction and the acidity of catalyst is also given. The catalytic activities of $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ are very high compared with those of $\text{NiSO}_4/\text{SiO}_2$. Hereafter, emphasis is placed only on the $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$. It is confirmed that the catalytic activity for $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ gives a maximum at 15 wt% of NiSO_4 . This is due to the increase of acidity by adding NiSO_4 to $\text{SiO}_2\text{-Al}_2\text{O}_3$. Comparing Fig. 1 and Table 1, catalytic activity is closely correlated to the acidity of catalysts. Namely, the higher the acidity, the higher was the catalytic activity. Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids. For example the rates of both the catalytic decomposition of cumene and the polymerization of propylene over $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts were found to increase

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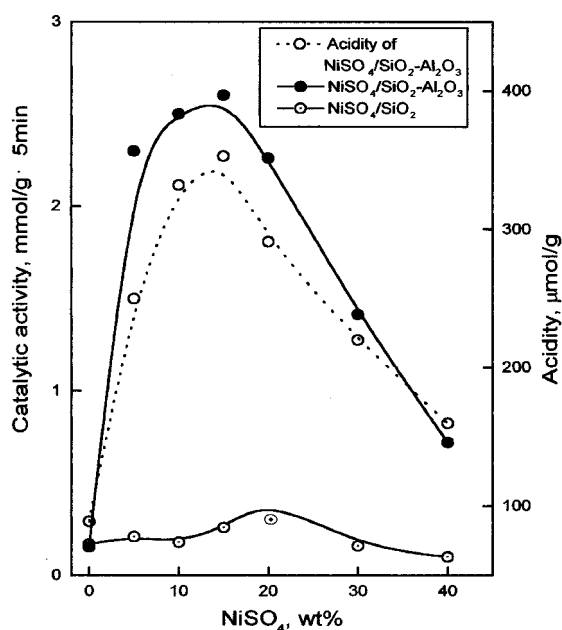


Fig. 1. Variations of catalytic activity for ethylene dimerization with NiSO₄ content.

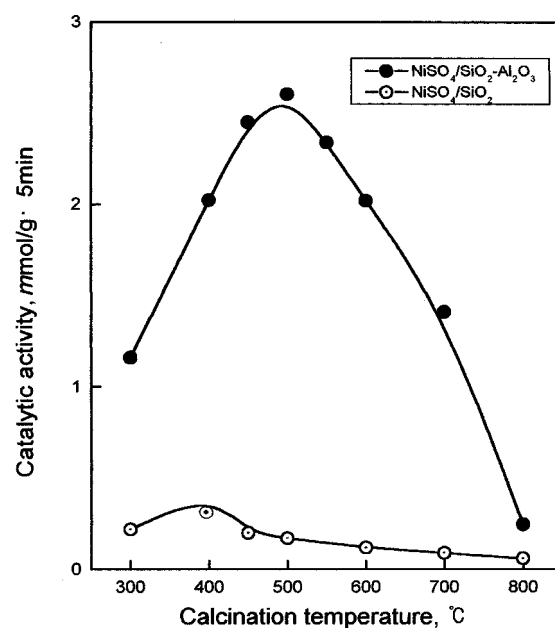


Fig. 2. Variations of catalytic activity for ethylene dimerization with calcination temperature.

with increasing acid amounts at strength $H_0 \leq +3.3$ [Tanabe, 1970]. It was also reported that the catalytic activity of nickel silicates in the ethylene dimerization as well as in the butene isomerization was closely correlated with the acidity of the catalyst [Sohn and Ozaki, 1980]. As listed in Table 1, the acidity attained a maximum when the NiSO₄ content in the catalyst is 15 wt%. However, the BET surface area decreases with an increasing nickel sulfate content, because nickel sulfate blocks the pores of SiO₂-Al₂O₃. It is known that acidity is required for the ethylene dimerization [Sohn and Ozaki, 1980] and SiO₂-Al₂O₃ is a typical solid acid [Tanabe, 1970]. However, the SiO₂-Al₂O₃ without NiSO₄ was inactive as catalyst for ethylene dimerization, but the NiSO₄/SiO₂-Al₂O₃ exhibited high catalytic activity even at room temperature.

The effect of calcination temperature on the catalytic activities of 15-NiSO₄/SiO₂-Al₂O₃ and 15-NiSO₄/SiO₂ was also examined, where the catalysts were calcined for 1 h. As shown in Fig. 2, the maximum activity is obtained with the catalyst calcined at 500 °C. The maximum activity at a calcination temperature of 500 °C can be explained in terms of the maximum acidity at 500 °C. The ac-

idity of 15-NiSO₄/SiO₂-Al₂O₃ calcined at various temperatures is listed in Table 1. Comparing Table 1 and Fig. 2, catalytic activity as a function of calcination temperature is also correlated to the acidity of catalysts. With 15-NiSO₄/SiO₂ the catalytic activity is also very low at all calcination temperatures. All the NiSO₄/SiO₂-Al₂O₃ 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-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 [Sohn and Shin, 1996] in sulfoluric acid. Since it was very difficult to observe the color of indicators adsorbed on the catalyst of high nickel sulfate content, a low percentage of nickel sulfate (5 wt%) was used in this experiment. The acid strength of SiO₂-Al₂O₃ was found to be $H_0 \leq -8.2$,

Table 1. Specific surface area and acidity of NiSO₄/SiO₂-Al₂O₃ calcined at 500 °C for 1.5 h and 15-NiSO₄/SiO₂-Al₂O₃ calcined at various temperatures

Weight % of NiSO ₄	Acidity (μmol/g)	Surface area (m ² /g)	Calcination temperature (°C) of 15-NiSO ₄ /SiO ₂ -Al ₂ O ₃	Acidity (μmol/g)	Surface area (m ² /g)
0	89(0.22)	407	300	308(1.10)	279
5	250(0.71)	350	400	342(1.24)	275
10	332(1.12)	287	450	347(1.27)	273
15	353(1.30)	272	500	353(1.30)	272
20	291(1.37)	213	550	349(1.29)	270
30	220(1.34)	164	600	330(1.22)	271
40	160(1.18)	136	700	241(0.90)	269
100	79(2.63)	30	800	83(0.32)	260

Acidity of μmol/m² unit given in parenthesis.

while $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ was estimated to have a $H_0 \leq -14.5$, indicating the formation of new stronger acid site than that of $\text{SiO}_2\text{-Al}_2\text{O}_3$. An acid stronger than $H_0 = -11.93$, which corresponds to an acid strength of 100% H_2SO_4 , is known as a superacid [Tanabe et al., 1989]. Consequently, $\text{NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ would be a solid superacid. Such superacid properties are attributed to the inductive effect of S=O of sulfate ion supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$.

$\text{SiO}_2\text{-Al}_2\text{O}_3$ alone without NiSO_4 , whose acid strength was found to be $H_0 \leq -8.2$, was totally inactive for the dimerization reaction at room temperature. 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 [Kimura and Ozaki, 1970; Sohn and Kim, 1986; Sohn et al., 1995; Sohn and Shin, 1996]. The term "low-valent nickel" originated from the fact that the NiO- SiO_2 catalyst was drastically poisoned by carbon monoxide, since a low-valent nickel is prone to chemisorb carbon monoxide [Kimura and Ozaki, 1970]. In this work, all catalysts added with NiSO_4 were poisoned by $1 \mu\text{mol g}^{-1}$ of carbon monoxide for dimerization. It seems that the formation of low-valent nickel is caused by evacuation at high temperature.

Fig. 3 shows the infrared spectra of the ammonia adsorbed on the $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ evacuated at 400°C for 1 h. The band at $1,447 \text{ cm}^{-1}$ is the characteristic peak of ammonium ion, formed at a Brönsted acid site, whereas the absorption peak at $1,625 \text{ cm}^{-1}$ can be attributed to ammonia coordinately bonded to a Lewis acid site [Satsuma et al., 1988], thereby indicating the presence of both Brönsted and Lewis acid sites on the surface of $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$. As shown in Fig. 3a, the intense band at $1,381 \text{ cm}^{-1}$ after evacuation at 400°C can be attributed to the asymmetric stretching vibration of S=O bonds that have a high double-bond nature [Yam-

aguchi, 1990]. However, the drastic shift of the infrared band from $1,381 \text{ cm}^{-1}$ to lower wavenumber (not shown due to the overlaps of skeletal vibration bands of $\text{SiO}_2\text{-Al}_2\text{O}_3$) after ammonia adsorption (Fig. 3b) indicates a strong interaction between the adsorbed ammonia molecules and surface sulfur complex. X-ray powder diffraction showed that for the calcination temperature of 500°C $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ exhibited only orthorhombic phase of NiSO_4 .

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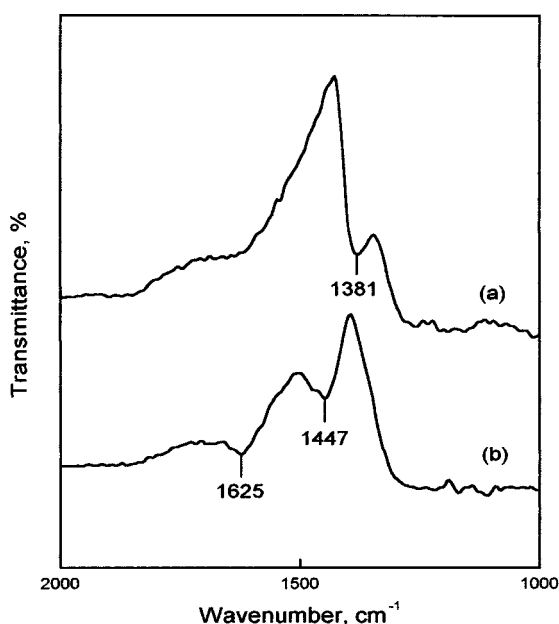


Fig. 3. Infrared spectra of NH_3 adsorbed on $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$; (a) background of $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$ and (b) ammonia adsorbed on $15\text{-NiSO}_4/\text{SiO}_2\text{-Al}_2\text{O}_3$. Gas phase NH_3 was evacuated at 200°C for 1 h after adsorption in (b).

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