Articles

Highly Active Catalyst of Nickel Sulfate Supported on Titania for Ethylene Dimerization

Jong Rack Sohn[*] **and Won Cheon Park**

Department of Industrial Chemistry, Engineering College, Kyungpook National University, Taegu 702-701, Korea
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A series of catalysts, NiSO$_4$/TiO$_2$, for ethylene dimerization was prepared by the impregnation method using aqueous solution of nickel sulfate. On the basis of the results obtained from X-ray diffraction, the addition of NiSO$_4$ shifted the transition of TiO$_2$ from the anatase to the rutile phase toward higher temperatures due to the interaction between NiSO$_4$ and TiO$_2$. Nickel sulfate supported on titania was found to be very active even at room temperature. The high catalytic activity of NiSO$_4$/TiO$_2$ closely correlated with the increase of acidity and acid strength due to the addition of NiSO$_4$. It is suggested that the active sites responsible for ethylene dimerization consist of low valent nickel, Ni$^+$, with an acid.

Keywords : Ethylene dimerization, Nickel sulfate, Titania, Acidity, Acid strength.

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.[1-10] One of the remarkable features of this catalyst system is its activity in relation to a series of n-olefins. In contrast to usual acid-type catalysts, nickel oxide on silica or silica-alumina shows a higher activity for a lower olefin dimerization, particularly for ethylene.[1-6,11] The catalyst is also active for the isomerization of *n*-butenes, the mechanism of which has been proven to be of a proton donor-acceptor type.[12] It was reported that the dimerization activities of such catalysts are related to the acid property of surface and low valent nickel ions. In fact, nickel oxide, which is active in C$_2$H$_4$-C$_2$D$_4$ equilibration, acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid.[13] A transition metal can also be supported on zeolite in the state of a cation or a finely dispersed metal. Several papers have treated ethylene dimerization on transition-metal cation exchanged zeolites.[14-16]

In the previous papers from this laboratory, it has been shown that NiO-TiO$_2$ and NiO-ZrO$_2$ modified with sulfate or tungstate ions are very active for ethylene dimerization.[6,17-19] 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 or tungstate ions. Many metal sulfates generate fairly large amounts of moderate strength on their surfaces when they are calcined at about 400 °C. However, nickel sulfate catalysts supported on titania have been not reported, especially as catalysts for ethylene dimerization except for our communication report.[10] As an extension of our study on ethylene dimerization, these authors tried to prepare other catalyst systems by supporting nickel sulfate on titania. In this paper, characterization of NiSO$_4$/TiO$_2$ and catalytic activity for ethylene dimerization are reported.

Experimental Section

Catalysts. The catalysts were prepared as follows. The precipitate of Ti(OH)$_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and hydrochloride acid at room temperature with stirring until the pH of the mother liquid reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ions were not detected in AgNO$_3$ solution. Then, it was dried at 100 °C for 12 h. The precipitate powdered below 100 mesh was impregnated with aqueous solution of NiSO$_4$·6H$_2$O followed by evaporating water, drying and calcining in air at different temperatures for 1.5 h. It was used as a catalyst after evacuation at different temperatures for 1 h. This series of catalysts is denoted by the weight percentage of NiSO$_4$. For example, 15-NiSO$_4$/TiO$_2$ means the catalyst has 15 wt% of NiSO$_4$.

Procedure. The catalytic activity for ethylene dimerization was determined at 20 °C using a conventional static system following pressure change from an initial pressure of 300 Torr. A 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 minutes. Reaction products were analyzed by gas chromatograph with a VZ-7 column at room temperature.

Chemisorption of ammonia was employed as a measure of acidity of catalysts. The amount of chemisorption was

obtained as the irreversible adsorption of ammonia.[4,6] 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 specific surface area was determined by applying the BET method to the adsorption of nitrogen at −196 °C.

The infrared spectra were recorded using a Mattson model GL6030 FTIR spectrometer. For IR studies of pyridine adsorbed on a catalyst, self-supported discs of about 10 mg·cm^{-2} were used. X-ray diffractograms of catalysts were taken by a Jeol Model JDX-88 X-ray diffractometer using a copper target and a nickel filter at 30 kV and 800 cps.

Results and Discussion

Crystalline structure of catalyst. The crystalline structure of catalysts calcined in air at different temperatures for 1.5 h were checked by X-ray diffraction. In the case of a single TiO_2, most TiO_2 calcined at 300 °C was present in amorphous form to X-ray diffraction together with a tiny amount of anatase. However, as shown in Figure 1, the amount of anatase TiO_2 increased remarkably at the calcination temperature of 350 °C, indicating that amorphous TiO_2 was transformed into an anatase form. In addition, TiO_2 was present in anatase form up to 500 °C. There was a two-phase mixture of the anatase and rutile forms at 550-600 °C but
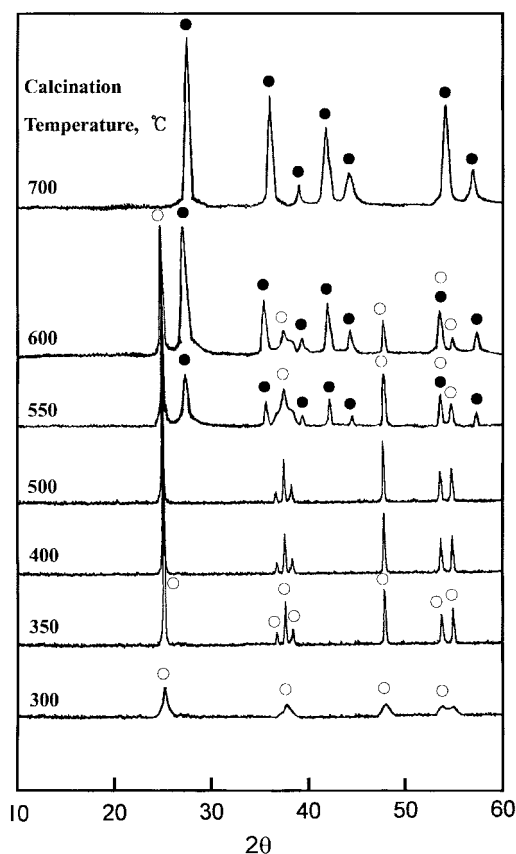
only the rutile form at 700 °C. Three crystal structures of TiO_2 (the anatase, rutile and brokite phases) have been reported.[21,22]

In the case of the $NiSO_4/TiO_2$ catalysts, the crystalline structures of samples were different from that of pure TiO_2. For the 15-$NiSO_4/TiO_2$, as shown in Figure 2, X-ray diffraction data indicates an anatase phase of TiO_2 at 400-700 °C without the observation of any rutile phase of TiO_2. As shown in Figure 1, however, for pure TiO_2 without $NiSO_4$, an anatase phase began to transform into a rutile form at the calcination temperature of 550 °C and became only a rutile form at 700 °C. It is assumed that the strong interaction between nickel sulfate and TiO_2 hinders the transition of TiO_2 from the anatase to rutile phase.[23-25] Most $NiSO_4$ was present in amorphous form, showing only very small amounts of the crystalline phase of nickel sulfate and indicating a good dispersion of nickel sulfate on the surface of the TiO_2 support due to the interaction between them. The presence of nickel sulfate strongly influences the development of textural properties with temperature in comparison to pure TiO_2. At 800 °C, the cubic phase of nickel oxide was observed due to the decomposition of nickel sulfate. In addition, a very tiny amount of rutile was formed due to the phase transition from the anatase to rutile phase.

The XRD patterns of $NiSO_4/TiO_2$ containing different nickel sulfate contents and calcined at 500 °C for 1.5 h are shown in Figure 3. From pure TiO_2 to 30-$NiSO_4/TiO_2$, TiO_2 was present in anatase form without the observation of any rutile phase of TiO_2. For $NiSO_4/TiO_2$ samples equal to or above 15 %, an orthorhombic phase of $NiSO_4$ was observed.

Figure 1. X-ray diffraction patterns of TiO_2 calcined at different temperatures for 1.5 h: (○) anatase phase; (●) rutile phase.
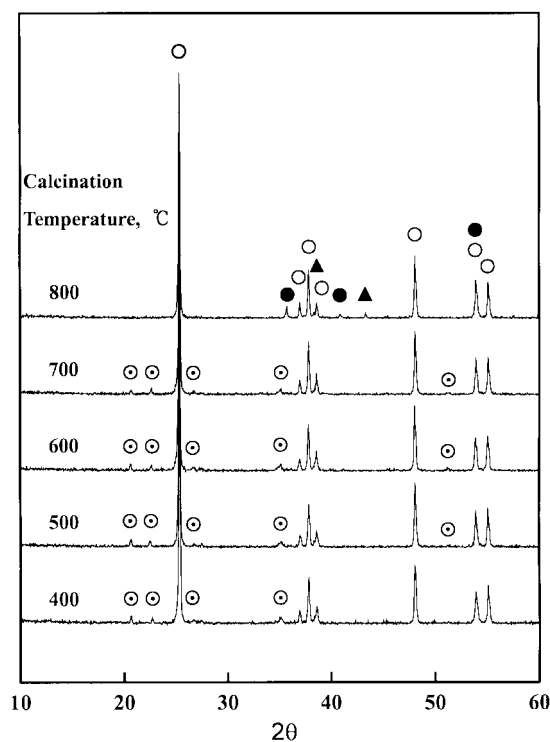

Figure 2. X-ray diffraction patterns of 15-$NiSO_4/TiO_2$ calcined at different temperatures.: (○) anatase phase; (⊙) orthorhombic phase of $NiSO_4$; (△) cubic phase of NiO.
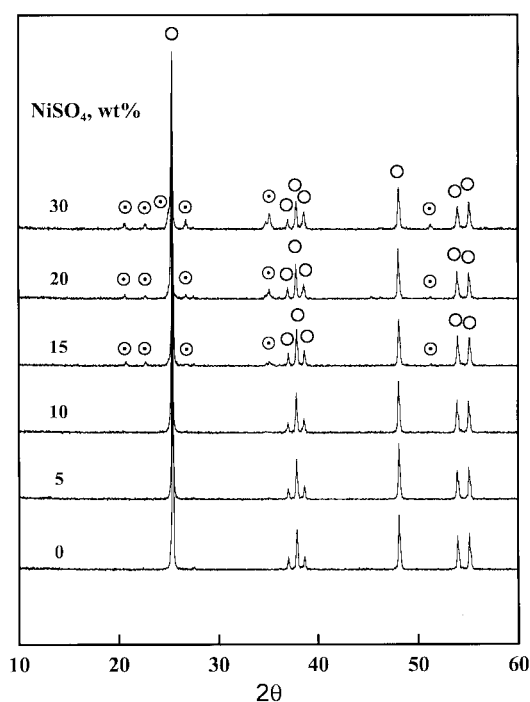
Figure 3. X-ray diffraction patterns of 15-NiSO$_4$/TiO$_2$ with different NiSO$_4$ contents calcined at 500 ^{o}C: ($\bigcirc$) anatase phase; ($\odot$) orthorhombic phase of NiSO$_4$.

Infrared spectra. The infrared spectra of several NiSO$_4$/TiO$_2$ catalylsts (KBr disc) calcined at 500 ^{o}C are given in Figure 4. The catalysts showed infrared absorption bands at 1212, 1138, 1050 and 998 cm^{-1}, which can be attributed to the bidentate sulfate ion coordinating with metals such as Ti^{4+} or Ni^{2+},[19] indicating a bonding of nickel sulfate on the surface of TiO$_2$.

In general, metal oxides modified with sulfate ions followed by evacuating above 400 ^{o}C exhibit a strong band assigned to an S=O stretching frequency at 1380-1370 cm^{-1}.[26,27] In this work, no corresponding band for the samples exposed to air was found because the water molecules in the air were adsorbed on the surfaces of the catalysts. These results are very similar to those reported by other authors.[26,27] However, in a separate experiment, the infrared spectrum of self-supported 5-NiSO$_4$/TiO$_2$ after evacuation at 400 ^{o}C for 2 h was examined. In this case there was an intense band at 1371 cm^{-1}, accompanied by broad and intense bands below 1250 cm^{-1} due to the overlapping of the TiO$_2$ skeletal vibration [Figure 5e]. This indicates the presence of different adsorbed species depending on the treatment conditions of the sulfated sample.[27]

Surface properties of catalysts. It is necessary to examine the effect of nickel sulfate on the surface properties of catalysts, that is, specific surface area, acid strength, and nature of acid centers (Brönsted or Lewis type). The specific surface areas of some samples calcined at 500 ^{o}C for 1.5 h are listed in Table 1. The surface area increases gradually upon addition of NiSO$_4$ to TiO$_2$, reaching a maximum at 15-NiSO$_4$/TiO$_2$. As shown in Table 1, however, the surface area of the NiSO$_4$/TiO$_2$ samples increased compared with that of
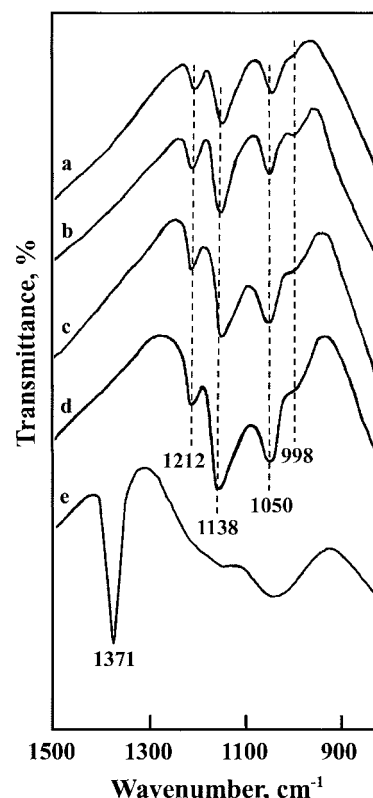

Figure 4. Infrared spectra of 5-NiSO$_4$/TiO$_2$ having different NiSO$_4$ contents and calcined at 500 ^{o}C: (a) 5-NiSO$_4$/TiO$_2$, (b) 10-NiSO$_4$/TiO$_2$, (c) 15-NiSO$_4$/TiO$_2$, (d) 20-NiSO$_4$/TiO$_2$, and (e) after evacuation at 400 ^{o}C for 2 h.

Table 1. Specific surface area and acidity of NiSO$_4$/TiO$_2$ catalysts calcined at 500 ^{o}C for 1.5 h

Weight percentage of NiSO$_4$	Surface area (m^2/g)	Acidity (mole/g)
0	52	80
5	87	108
10	113	138
15	116	172
20	74	160
30	63	116
40	48	101
100	24	79

Table 2. Acid strength of samples

Hammett indicator	pKa value of indicator	TiO$_2$	5-NiSO$_4$/TiO$_2$
Benzeneazodiphenylamine	+1.5	+	+
Dicinnamalacetone	−3.0	+	+
Benzalacetophenone	−5.6	−	+
Antraquinone	−8.2	−	+
Nitrobenzene	−12.4	−	+
2,4-Dinitrofluorobenzene	−14.5	−	+

pure TiO$_2$. It seems likely that the interaction between nickel sulfate and TiO$_2$ protects catalysts from sintering.[23,25]
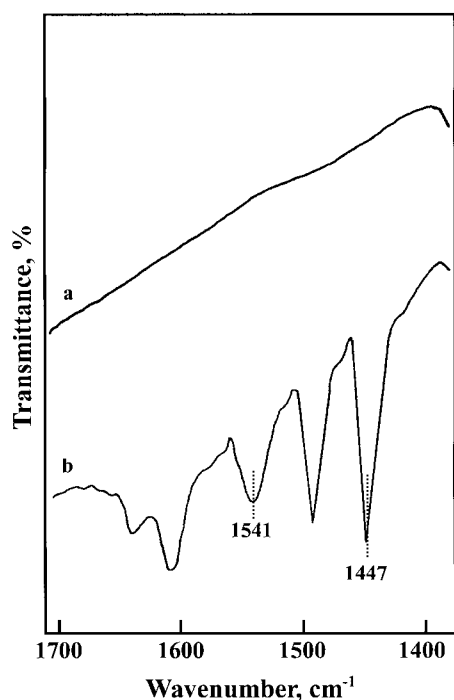
Figure 5. Infrared spectra of pyridine adsorbed on 15-NiSO$_4$/TiO$_2$: (a) background of 15-NiSO$_4$/TiO$_2$ (b) pyridine adsorbed on 15-NiSO$_4$/TiO$_2$, gas phase was evacuated at 250 °C for 1 h after adsorption in (a).

The acid strength of the catalysts was examined by a color change method, using a Hammett indicator[22-25] in sulphuryl chloride. Since it was very difficult to observe the color of indicators adsorbed on catalysts of high nickel sulfate content, a low percentage of nickel sulfate content (5 wt%) was used in this experiment. The results are listed in Table 2. In this table, (+) indicates that the color of the base form was changed to that of the conjugated acid form. TiO$_2$ evacuated at 500 °C for 1.5 h has an acid strength $H_o \leq -3.0$, while 5-NiSO$_4$/TiO$_2$ was estimated to have a strength $H_o \leq -14.5$, indicating the formation of new acid sites stronger than that of TiO$_2$. Acids stronger than $H_o \leq -11.93$, which corresponds to the acid strength of 100% H$_2$SO$_4$, are superacids.[28] Consequently, NiSO$_4$/TiO$_2$ catalysts would be solid superacids. This superacidic property is attributed to the double bond nature of the S=O in the complex formed by the interaction between NiSO$_4$ and TiO$_2$.[27,29] In other words, the acid strength of nickel sulfate supported on titania becomes stronger by the inductive effect of S=O in the complex.

Infrared spectroscopic studies of pyridine adsorbed on solid surfaces make it possible to distinguish between Brönsted and Lewis acid sites.[18,19] Figure 5 shows the infrared spectra of pyridine adsorbed on the 15-NiSO$_4$/TiO$_2$ samples evacuated at 400 for 1 h. For 15-NiSO$_4$/TiO$_2$, the band at 1541 cm^{-1} is a characteristic peak of pyridinium ions, which is formed on Brönsted acid sites. Other absorption peak at 1445 cm^{-1} is contributed by pyridine coordinately bonded to Lewis acid sites,[18,19] thus indicating the presence of both Brönsted and Lewis acid sites. Other samples having different nickel sulfate contents also showed the presence of
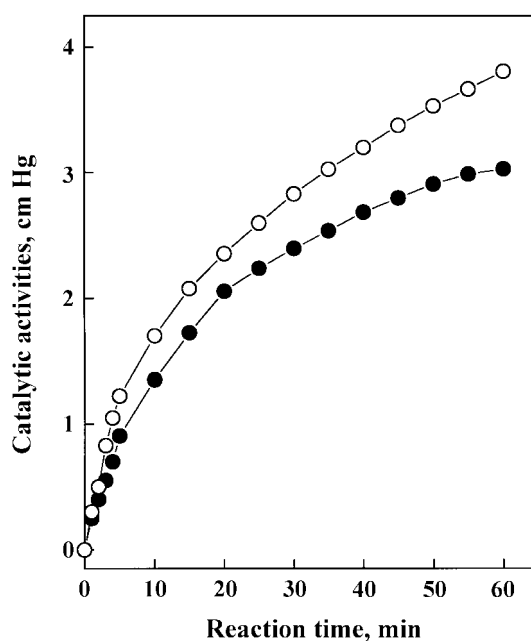

Figure 6. Time-course of ethylene dimerization over catalysts: (○) 15-NiSO$_4$/TiO$_2$; (●) 10-NiSO$_4$/TiO$_2$.

both Lewis and Brönsted acids.

Ethylene dimerization over NiSO$_4$/TiO$_2$. NiSO$_4$/TiO$_2$ catalysts were tested for their effectiveness in ethylene dimerization. It was found that over 10-NiSO$_4$/TiO$_2$ and 15-NiSO$_4$/TiO$_2$, ethylene was continuously consumed, as shown by the results presented in Figure 6, where catalysts were evacuated at 500 °C for 1.5 h. Over NiSO$_4$/TiO$_2$, 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 to *cis*-butene and trans-butene. However, 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 time.[17-19]

The catalytic activities of 15-NiSO$_4$/TiO$_2$ for ethylene dimerization are plotted as a function of the calcination temperature in Figure 7. The activities increased with the calcination temperature to a maximum at 500 °C but thereafter decreased. The decrease in activity above 500 °C can probably be attributed to a decrease in the surface area and acidity above 500 °C.

The catalytic activities of NiSO$_4$/TiO$_2$ for the reaction of ethylene dimerization were examined. The results are shown as a function of NiSO$_4$ content in Figure 8, where the catalysts were evacuated at 500 °C for 1.5 h before reaction. It is confirmed that the catalytic activity gives a maximum at 15 wt% of NiSO$_4$. It is known that in the case of the nickel containing catalysts for ethylene dimerization the variations in catalytic activities are closely correlated to the acidity of the catalysts.[4] Another series of experiments was carried out to study the correlation between acidity and catalytic
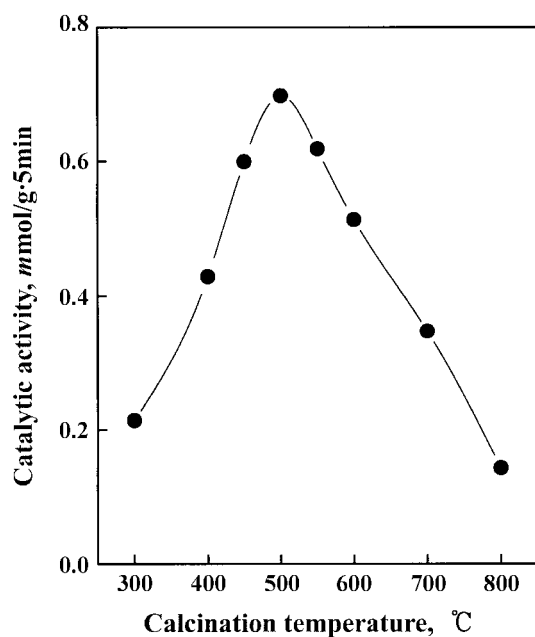
Figure 7. Variation of catalytic activity for ethylene dimerization of 15-NiSO$_4$/TiO$_2$ with calcination temperature.
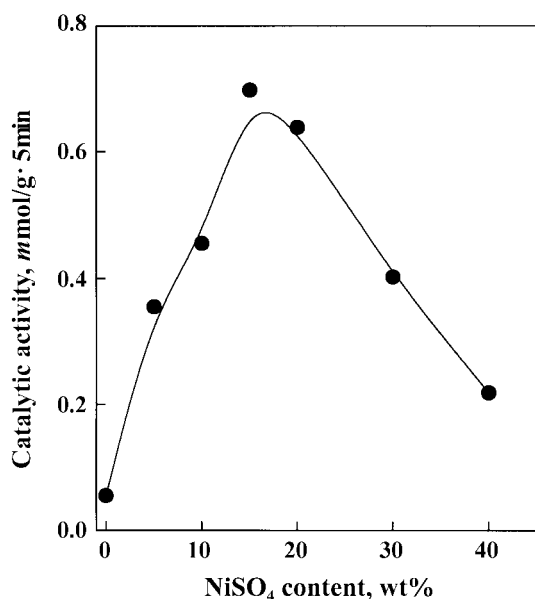

Figure 8. Variation of catalytic activity for ethylene dimerization with NiSO$_4$ content.

Figure 9. The infrared spectra of CO adsorbed on 15-NiSO$_4$/TiO$_2$: (a) background of 15-NiSO$_4$/TiO$_2$ evacuated at room temperature, (b) after the introduction of 40 Torr CO to sample (a), (c) after the introduction 90 Torr CO to the sample evacuated at 500 °C for 1 h, and (d) after the introduction of 140 Torr to the sample (c).

activities. The acidity was measured by the ammomia chemisorption method.[4,6] The acidity of some samples after evacuation at 500 °C is listed in Table 1. In views of Table 1 and Figure 8, the catalytic activities substantially run parallel to the acidity. Therefore, it is very likely that the surface areas and acidity affect the catalytic activities for ethylene dimerization. As listed in Table 1, the BET surface area attained a maximum when its NiSO$_4$ content in the catalyst is 15 wt%.

It is remarkable that the TiO$_2$ without NiSO$_4$ was inactive as a catalyst for ethylene dimerization, but the NiSO$_4$
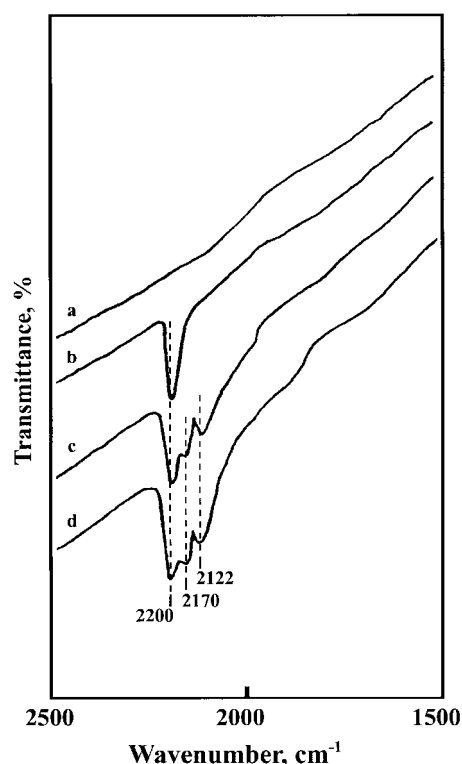
supported on TiO$_2$ exhibited high catalytic activity. The active site responsible for dimerization is suggested to consist of a low valent nickel ion and an acid, as observed in the NiO-SiO$_2$ catalyst.[4,19,30] The term "low valent nickel" originated from the fact that the NiO-SiO$_2$ catalyst was drastically poisoned by carbon monoxide since a low valent nickel is favorable to chemisorb carbon monoxide.[30] Kazansky concluded that Ni$^+$ ions in NiCaY zeolite are responsible for the catalytic activity, using EPR spectroscopy to identify low-valent nickel species.[15] To obtain further information on the oxidation state of low-valent nickel species, infrared spectroscopy using CO as a probe was used. When the sample (15-NiSO$_4$/TiO$_2$) was exposed to CO (40 Torr) at room temperature, the adsorbed CO band appeared at 2200 cm^{-1}, as shown in Figure 9. The band might be assigned to the stretching vibration for CO adsorbed on Ni^{2+}.[31,32] However, when the sample evacuated at 500 °C for 1 h was exposed to CO (90 Torr), two bands at 2170 and 2122 cm^{-1}, in addition to the band at 2200 cm^{-1}, were observed. The intensities of the two bands increased concomitantly with increasing CO concentration (140 Torr). Therefore, it seems likely that the two bands originated from one species, Ni$^+$(CO)$_2$. The bands at 2170 and 2122 cm^{-1} are assigned to symmetrical and asymmetrical stretching vibrations of Ni$^+$(CO)$_2$, respectively.[31,32] In view of the EPR results by Kazansky,[15] these results suggest that Ni$^+$ ions are responsible for the low valent nickel species. Therefore, it is suggested

that the active sites responsible for ethylene dimerization consist of a low valent nickel, Ni^+, with an acid.

Conclusions

A series of catalysts, $NiSO_4/TiO_2$, for ethylene dimerization was prepared by the impregnation method using aqueous solution of nickel sulfate. The interaction between nickel sulfate and titania influences the physicochemical properties of prepared catalysts with calcination temperature. The presence of $NiSO_4$ delays the phase transition of TiO_2 from anatase to rutile and the specific surface area of catalysts increases as compared with pure TiO_2. $NiSO_4/TiO_2$ is very effective for ethylene dimerization, but TiO_2 without $NiSO_4$ does not absolutely exhibit catalytic activity. The high catalytic activity of $NiSO_4/TiO_2$ closely correlates with the increase of acidity and acid strength through the addition of $NiSO_4$. It is suggested that the active site for dimerization is formed by an interaction of a low valent nickel, Ni^+, with an acid.

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