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Characterization of Nickel Sulfate Supported on γ-Al_2O_3 for Ethylene Dimerization and Its Relationship to Acidic Properties

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Nickel sulfate supported on γ-Al_2O_3 was found to be very active even at room temperature, giving a maximum in both activity and acidity when catalyst containing 20% $NiSO_4$ was calcined and evacuated at 600°C. The high catalytic activity of $NiSO_4/\gamma$-Al_2O_3 was related to the increase of acidity and acid strength due to the addition of $NiSO_4$. The asymmetric stretching frequency of the S=O bonds for $NiSO_4/\gamma$-Al_2O_3 samples was related to the acidic properties and catalytic activity. The active sites responsible for ethylene dimerization consist of a low-valent nickel, Ni^+, and an acid, as evidenced by the IR spectra of CO adsorbed on $NiSO_4/\gamma$-Al_2O_3 and Ni 2P XPS. © 2002 Elsevier Science (USA)

Key Words: **ethylene dimerization; nickel sulfate on γ-Al_2O_3; acidic properties; active sites; asymmetric S=O stretching frequency.**

INTRODUCTION

Heterogeneous catalysts for the dimerization and oligomerization of olefins, consisting mainly of nickel compounds supported on oxides, have been known for many years (1–9). One of the remarkable features of this catalyst system is its activity in relation to a series of *n*-olefins. In contrast to the usual acid-type catalysts, nickel oxide on silica or silica-alumina shows a higher activity for a lower olefin dimerization, particularly for ethylene (4, 5, 7, 8, 10). It has been suggested that the active site for dimerization is formed by the interaction of a low-valent nickel ion with an acid site (11). It has been reported that the dimerization activities of such catalysts are related to the acidic property of surface and low-valent nickel ions. In fact, nickel oxide, which is active for C_2H_4–C_2D_4 equilibration, acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid (12).

In 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 (5, 13–15). 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. The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization (16, 17). However, the structural and physicochemical properties of supported metal sulfates are considered to be in different states compared with bulk metal sulfates because of their interaction with supports (18). As an extension of our study on ethylene dimerization, these authors tried to prepare other catalyst systems by supporting nickel sulfate on γ-Al_2O_3. In this paper, characterization of $NiSO_4/\gamma$-Al_2O_3 for ethylene dimerization and its relationship to acidic properties are reported.

EXPERIMENTAL

Catalysts containing various nickel sulfate contents were prepared by dry impregnation of γ-Al_2O_3 powder (JRC-ALO-2, surface area = 240 m^2/g) with an aqueous solution of $NiSO_4 \cdot 6H_2O$ followed by calcining at different temperatures for 1.5 h in air. 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 nickel sulfate. For example, 20-$NiSO_4/\gamma$-Al_2O_3 indicates the catalyst containing 20 wt% $NiSO_4$. The catalytic activity for ethylene dimerization was determined at 20°C using a conventional static system following pressure change from an initial pressure of 290 Torr. A fresh catalyst sample of 0.2 g was used for every run and the catalytic activity was exhibited as the initial rate calculated from the initial slope of the time-course curve for ethylene dimerization. The isomerization of 1-butene was carried out at 20°C in a closed circulating system. 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 specific surface area was determined by applying the BET method to the adsorption of nitrogen at −196°C.

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X-ray diffractograms of catalysts were taken by a Philips X'pert-APD X-ray diffractometer using a copper target and a nickel filter at 30 kV and 800 cps. FTIR (Fourier transform infrared) spectra were obtained in a heatable gas cell at room temperature using a Mattson Model GL6030E spectrometer. X-ray photoelectron spectra were obtained with a VG Scientific Model ESCALAB MK-11 spectrometer. Al $K\alpha$ and Mg $K\alpha$ 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.

RESULTS AND DISCUSSION

Infrared Spectra of $NiSO_4/\gamma$-Al_2O_3

The absorption of the asymmetric stretching frequency of S=O bonds is commonly found in the range of 1360–1410 cm^{-1}. Infrared spectra of 20-$NiSO_4/\gamma$-Al_2O_3 after evacuation at 100–600°C for 1 h are shown in Fig. 1. There are 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 the asymmetric S=O stretching frequency of sulfate ion bonded to γ-Al_2O_3 under the dehydrated condition, while the latter four bands are assigned to bidentate sulfate ion coordinated to γ-Al_2O_3 (19, 20). These results are very similar to those of other workers (19, 20). However, the frequency shift of this band differs depending on the evacuation temperature, as shown in Fig. 1. At 100°C an asymmetric stretching band of S=O bonds was not observed because the water molecules are adsorbed on the surface of 20-$NiSO_4/\gamma$-Al_2O_3 (21, 22). 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 shifted to a higher wavenumber. It is likely that the surface sulfur complexes formed by the interaction of oxides with sulfate ions in highly active catalysts have a strong tendency to reduce their bond order by the adsorption of basic molecules such as H_2O (19, 20). Consequently, as shown in Fig. 1, an asymmetric stretching band of S=O bonds for the sample evacuated at lower temperature appears at a 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 are related to the acidic properties.

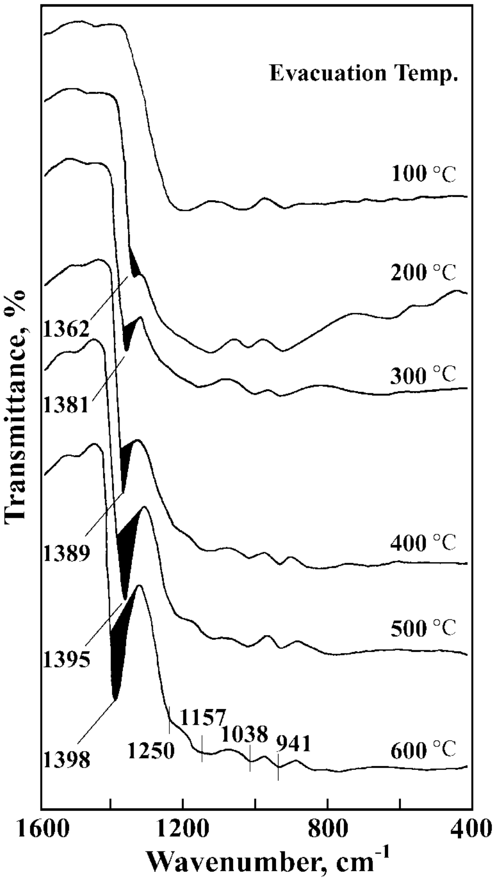

FIG. 1. Infrared spectra of $NiSO_4/\gamma$-Al_2O_3 evacuated at different temperatures.

TABLE 1

Specific Surface Area of $NiSO_4/\gamma$-Al_2O_3 Catalysts Calcined at 600°C

Catalyst	Surface area (m^2/g)
γ-Al_2O_3	240
2-$NiSO_4/\gamma$-Al_2O_3	287
5-$NiSO_4/\gamma$-Al_2O_3	290
7-$NiSO_4/\gamma$-Al_2O_3	225
10-$NiSO_4/\gamma$-Al_2O_3	217
15-$NiSO_4/\gamma$-Al_2O_3	210
20-$NiSO_4/\gamma$-Al_2O_3	193
25-$NiSO_4/\gamma$-Al_2O_3	159
30-$NiSO_4/\gamma$-Al_2O_3	139
40-$NiSO_4/\gamma$-Al_2O_3	130
100-$NiSO_4/\gamma$-Al_2O_3	25

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 (Brønsted or Lewis type). The specific surface areas of samples calcined at 600°C for 1.5 h are listed in Table 1. The surface area attained a maximum when the $NiSO_4$ content was 5 wt% and then showed a gradual decrease with increasing $NiSO_4$ content. The IR spectra of ammonia adsorbed on 20-$NiSO_4/\gamma$-Al_2O_3 samples evacuated at 600°C for 1 h were examined (not shown here). The absorption bands at 3351 and 3285 cm^{-1} are assigned, respectively, to the asymmetric and symmetric vibration modes of the ammonia adsorbed on Lewis acid sites, while the bands at 3241 and 3196 cm^{-1} are due to the asymmetric and symmetric vibration modes of ammonium ion adsorbed on Brønsted acid sites (24, 25). The band at 1443 cm^{-1} is the characteristic peak of an ammonium ion, which is formed on the Brønsted acid sites; the absorption peak at 1621 cm^{-1} is contributed by ammonia coordinately bonded to Lewis acid sites (24, 25), indicating the presence of both Brønsted and Lewis acid sites on the surface of the 20-$NiSO_4/\gamma$-Al_2O_3 sample. The surface sulfur compound in the highly acidic catalysts has a strong tendency to reduce the bond order of S=O from a highly covalent double-bond character to a lesser double-bond character when a basic ammonia molecule is adsorbed on the catalysts (20). The strong ability of the sulfur complex to accommodate electrons from a basic molecule such as ammonia is a driving force in generating superacidic properties (16, 18, 20). This superacidic property is attributable to the double-bond nature of the S=O in the complex formed by the interaction between $NiSO_4$ and γ-Al_2O_3 (16, 19, 20).

Correlation between Catalytic Activity and Acid Amount

$NiSO_4/\gamma$-Al_2O_3 catalysts were tested for their effectiveness in ethylene dimerization. It was found that over 20-$NiSO_4/\gamma$-Al_2O_3 and 40-$NiSO_4/\gamma$-Al_2O_3, ethylene was continuously consumed, as shown by the results presented in Fig. 2, where catalysts were evacuated at 400°C for 1.5 h. Over $NiSO_4/\gamma$-Al_2O_3, ethylene was selectively dimerized to *n*-butenes. However, a small amount of hexenes from the phase adsorbed on the catalyst surface was detected. $NiSO_4/\gamma$-Al_2O_3 was very effective for ethylene dimerization, but γ-Al_2O_3 alone without $NiSO_4$ was completely inactive. The catalytic activities for 1-butene isomerization at 20°C were also measured to examine the sulfation effect using 20-$NiSO_4/\gamma$-Al_2O_3 and γ-Al_2O_3. 20-$NiSO_4/\gamma$-Al_2O_3 exhibited catalytic activity 15 times higher than that of pure γ-Al_2O_3 without $NiSO_4$, showing the high effect of sulfation on 1-butene isomerization activity.

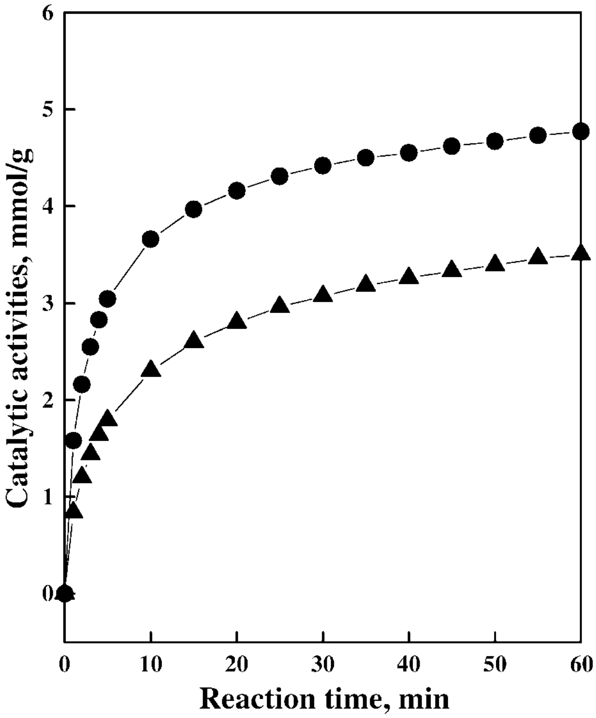

FIG. 2. Time-course of ethylene dimerization over catalysts evacuated at 400°C for 1.5 h: ●, 20-$NiSO_4/\gamma$-Al_2O_3; ▲, 40-$NiSO_4/\gamma$-Al_2O_3.

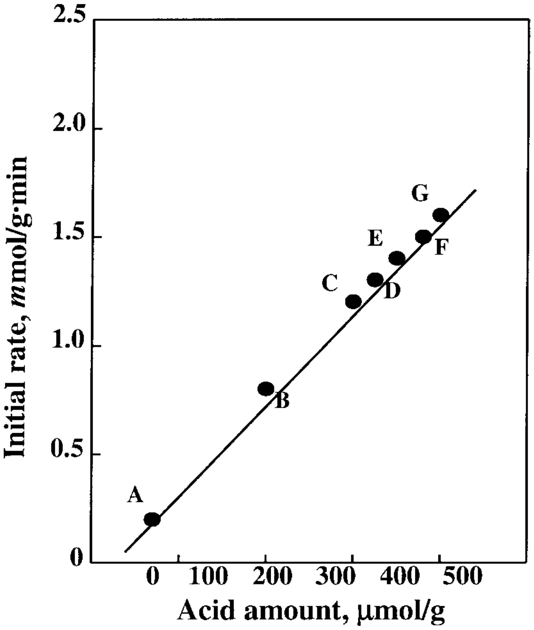

FIG. 3. Correlationship between acidity and catalytic activity of $NiSO_4/\gamma$-Al_2O_3 for ethylene dimerization. A, 5-$NiSO_4/\gamma$-Al_2O_3; B, 40-$NiSO_4/\gamma$-Al_2O_3; C, 10-$NiSO_4/\gamma$-Al_2O_3; D, 30-$NiSO_4/\gamma$-Al_2O_3; E, 15-$NiSO_4/\gamma$-Al_2O_3; F, 25-$NiSO_4/\gamma$-Al_2O_3; G, 20-$NiSO_4/\gamma$-Al_2O_3.

The catalytic activities of $NiSO_4/\gamma$-Al_2O_3 containing different $NiSO_4$ contents were examined; results are shown as a function of acid amount in Fig. 3, where catalysts were evacuated at 400°C for 1.5 h before reaction. Figure 3 shows good correlation between the catalytic activity and the acid amount. It is confirmed that the catalytic activity gives a maximum at 20 wt% $NiSO_4$. This seems to be correlated not to the specific surface area but to the acid amount of catalysts. The acid amount of $NiSO_4/\gamma$-Al_2O_3 calcined at 600°C was determined by the amount of NH_3 irreversibly adsorbed at 230°C (4, 5). As listed in Table 1, the BET surface area attained a maximum extent when the $NiSO_4$ content in the catalyst was 5 wt% and then showed a gradual decrease with increasing $NiSO_4$ content. However, as shown in Fig. 3, the higher the acid amount, the higher the catalytic activity. In this way it is demonstrated that the catalytic activity of $NiSO_4/\gamma$-Al_2O_3 essentially runs parallel to the acid amount. It has been reported that the catalytic activity of nickel-containing catalysts in ethylene dimerization

TABLE 2

Asymmetric Stretching Frequency of the S=O Bonds, Acidity, and Catalytic Activity for $NiSO_4/\gamma$-Al_2O_3 Catalyst Evacuated at Different Temperatures

Evacuation temperature (°C)	Frequency (cm^{-1})	Acid amount (μmol/g)	Initial rate (mmol/g · min)
100	—	48	0
200	1362	75	0.69
300	1381	154	1.19
400	1389	216	1.58
500	1395	283	1.99
600	1398	520	2.52
700	1378	375	1.16

as well as in butene isomerization is closely correlated with the acid amount of the catalyst (4, 8).

The catalytic activities of 20-$NiSO_4/\gamma$-Al_2O_3 after evacuation at various temperatures for the reaction of ethylene dimerization were examined and the results are listed in Table 2. The catalytic activity increased with an increase in evacuation temperature, reaching a maximum at 600°C. To examine the effect of evacuation temperature on surface area, BET surface area of 20-$NiSO_4/\gamma$-Al_2O_3 at various evacuation temperatures (300–700°) was measured. However, a 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 in catalytic activity relates not to the change in surface area but to the easy formation of an active site depending on the evacuation temperature.

Comparing Fig. 1 and Table 2, catalytic activity closely correlates to the asymmetric stretching frequency of the S=O bonds. That is, the higher the frequency of the S=O bonds, the higher the catalytic activity for ethylene dimerization. The decrease in catalytic activity after evacuation at 700°C can be explained by the high evacuation temperature, resulting in the decrease in the sulfate group bonded to the surface of γ-Al_2O_3 accompanied by the decrease in acid amount as well as by the change in the oxidation state of the nickel ion. An asymmetric frequency in the S=O bonds is a measure of the ability (acid strength) of a sulfur complex to pull basic molecules such as H_2O and NH_3 and is a driving force in generating highly acidic properties, acid strength, and acid amount (21, 22). Both acid strength and acid amount increase with an increase in the evacuation temperature up to 600°C, because water adsorbed on the catalyst surface is desorbed at high temperature, resulting in the formation of new acid sites and the increased bond order of S=O. Espinoza *et al.* also reported that the oligomerization activity of ethylene increased with an increase in acid strength of the support (1). In view of Fig. 1 and Table 2, there is a good correlation between the infrared band frequency of the asymmetric S=O stretching vibration in $NiSO_4/\gamma$-Al_2O_3 and the catalytic activity for ethylene dimerization. Therefore, it is concluded that we can use the asymmetric stretching frequency of the S=O bonds in the $NiSO_4/\gamma$-Al_2O_3 catalyst as a measure of catalytic activity for ethylene dimerization.

Active Sites for Ethylene Dimerization

The active site responsible for dimerization has been suggested to consist of a low-valent nickel and an acid, as observed in the NiO-containing catalysts (12, 13, 15, 26). In fact, it is known that sulfated alumina is an acid (19, 21). 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 (26). The IR spectra of CO adsorbed on 20-$NiSO_4/\gamma$-Al_2O_3 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. 4b. The band might be assigned to the stretching vibration for CO adsorbed on Ni^{2+} (27, 28). However, when the sample evacuated at 600°C for 1 h was exposed to CO (100 Torr), two bands were observed, at 2170 and 2122 cm^{-1}, in addition to the band at 2200 cm^{-1} (Fig. 4c). The intensities of the two bands increased in accordance with an increase in CO

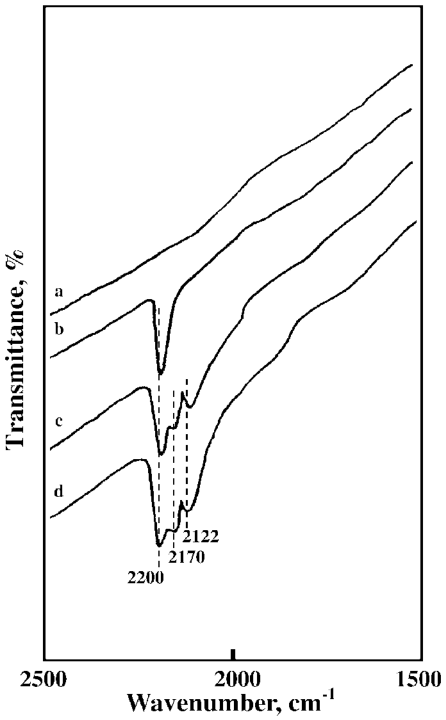

FIG. 4. The IR spectra of CO adsorbed on 20-$NiSO_4/\gamma$-Al_2O_3. (a) Background of 20-$NiSO_4/\gamma$-Al_2O_3 evacuated at room temperature; (b) after the introduction of 50 Torr CO into sample (a); (c) after the introduction of 100 Torr CO into the sample evacuated at 600°C for 1 h; (d) after the introduction of 150 Torr CO into sample (c).

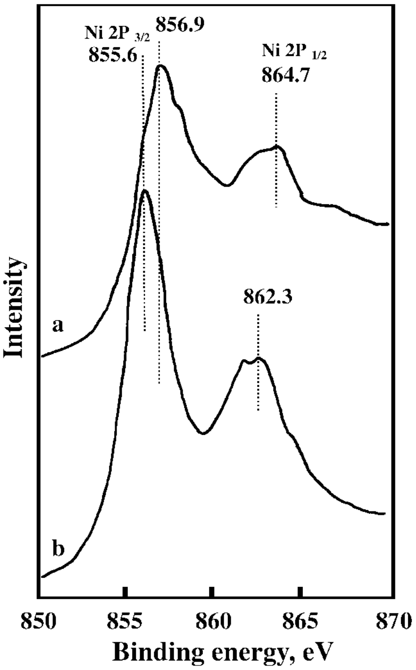

FIG. 5. The Ni 2P XPS of 20-$NiSO_4/\gamma$-Al_2O_3 calcined at 600°C: (a) after evacuation at room temperature; (b) after evacuation at 600°C for 1 h.

concentration, as shown in Fig. 4d. 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 (27, 28).

To obtain further information on the oxidation state of low-valent nickel species, Ni 2P XPS of 20-$NiSO_4/\gamma$-Al_2O_3 was measured; the results are shown in Fig. 5. In agreement with previous reports 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. 5a indicate the positions of the peaks relative to Ni^{2+} (29, 30). However, for the sample evacuated at 600°C, the positions of the vertical lines in Fig. 5b were shifted to the lower binding energies, indicating the formation of low-valent nickel species by evacuation at 600°C. In views of IR results and a previous report (30), 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 relative to low-valent nickel species, Ni^+. In view of the IR and XPS results, it is concluded that the active sites responsible for ethylene dimerization consist of a low-valent nickel, Ni^+, and an acid.

Roles of Active Sites

In the foregoing section, it was concluded that the active sites for ethylene dimerization consist of a low-valent nickel, Ni^+, and an acid. So then, it is necessary to examine the roles of active sites, that is, a low-valent nickel, Ni^+, and acid sites in the ethylene dimerization. It is known that a low-valent nickel is favorable for chemisorption of carbon monoxide (26), as shown in Fig. 4. Figure 6 shows how the dimerization activity activated at 600°C is poisoned by carbon monoxide. It is obvious that ethylene over 20-$NiSO_4/\gamma$-Al_2O_3 is rapidly consumed with no induction period. However, over 20-$NiSO_4/\gamma$-Al_2O_3 preadsorbed with 1 μmol/g of CO, the pressure change with reaction time stops, indicating that the preadsorbed CO prevents the subsequent adsorption of ethylene. Therefore, it is concluded that the adsorption site of CO, that is, a low-valent nickel, is also responsible for the adsorption site of ethylene.

What is the role of an acid site? Generally carbon monoxide is not adsorbed by acid catalysts such as silica–alumina and the acid site is characterized by butene isomerization (12). Therefore, the nature of active site for 1-butene isomerization was examined by the effect of preadsorbed carbon monoxide. It was found that 1 μmol of carbon monoxide per g of catalyst had no effect on the extent of isomerization, although carbon monoxide completely inhibits ethylene dimerization, as mentioned above. Therefore, it is clear that the active site for isomerization is an acid alone. However, as shown in Fig. 4, there is a good correlation between dimerization activity and acidity. Therefore, it seems likely that the acid sites are responsible for the formation of a reaction intermediate such as ethyl cation. Finally, it is concluded that a low-valent nickel, Ni^+, plays the role of adsorption site for ethylene, while acidic sites are responsible for the formation of reaction intermediates such as ethyl cations.

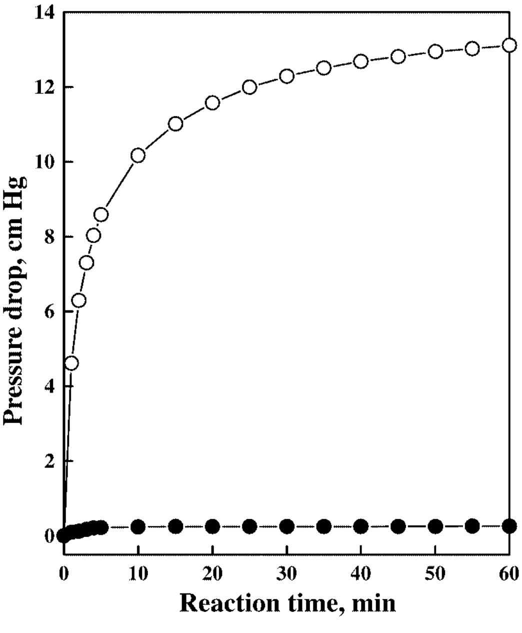

FIG. 6. Time-course of ethylene dimerization over 20-$NiSO_4/\gamma$-Al_2O_3 evacuated at 600°C for 1.5 h. Solid circles show the run with preadsorbed CO of 1 μmol/g.

CONCLUSIONS

$NiSO_4/\gamma$-Al_2O_3 was very effective for ethylene dimerization, but γ-Al_2O_3 alone without $NiSO_4$ was completely inactive. The high catalytic activity of $NiSO_4/\gamma$-Al_2O_3 was related to the increase of acidity and acid strength owing to the addition of $NiSO_4$. The asymmetric stretching frequency of the S=O bonds for $NiSO_4/\gamma$-Al_2O_3 samples was related to the acidic properties and catalytic activity; that is, the higher the frequency, the larger both the acid amount and catalytic activity. The active sites responsible for ethylene dimerization consist of a low-valent nickel, Ni^+, and an acid, as evidenced by the IR spectra of CO adsorbed on $NiSO_4/\gamma$-Al_2O_3 and Ni 2P XPS. It is concluded that a low-valent nickel, Ni^+, plays the role of adsorption site for ethylene, while acidic sites are responsible for the formation of reaction intermediates such as ethyl cations.

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