Characterization of nickel sulfate supported on SiO$_2$ for ethylene dimerization and promoting effect of Al$_2$O$_3$ on catalytic activity

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Abstract

A series of catalysts, NiSO$_4$/SiO$_2$, for ethylene dimerization was prepared by the impregnation method using an aqueous solution of nickel sulfate. No diffraction line of nickel sulfate was observed up to 20 wt%, indicating good dispersion of nickel sulfate on the surface of SiO$_2$ and SiO$_2$–Al$_2$O$_3$. The addition of Al$_2$O$_3$ to NiSO$_4$/SiO$_2$ improved the thermal stability of catalyst and increased the number of acid sites on the surface of catalyst. Consequently, the Al$_2$O$_3$-promoted catalyst exhibited remarkably higher catalytic activity than non-promoted NiSO$_4$/SiO$_2$. The catalytic activities of supported NiSO$_4$ catalysts were correlated with the acidity of catalysts measured by the ammonia chemisorption method, regardless of the kind of support (SiO$_2$ or SiO$_2$–Al$_2$O$_3$).
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Keywords: NiSO$_4$/SiO$_2$ catalyst; Promoting effect of Al$_2$O$_3$; Ethylene dimerization; Acidity

1. Introduction

Heterogeneous catalysts for the dimerization and oligomerization of olefins, consisting mainly of nickel compounds supported on oxides, have been known for many years. The dimerization of olefins is an important method for the production of higher olefins which are extensively used as industrial intermediates. A considerable number of papers have dealt with the nickel-containing catalysts for ethylene dimerization [1–12]. One of the remarkable features of this catalyst system is its activity in relation to a series of n-olefins. In contrast to usual acidic catalysts, nickel oxide on silica or silica–alumina shows a higher activity for lower olefin dimerization, particularly for ethylene dimerization [1–6,11]. 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$_2$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].

The previous papers from this laboratory have 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. However, catalytic functions have been improved by loading additional components. Sulfated zirconia incorporating Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature [20,21]. The promotion of activity of the catalyst has been confirmed by several other research group [22–24]. Coelho et al. have discovered that the addition of Ni to sulfated zirconia causes an activity enhancement comparable to that caused the addition of Fe and Mn [25]. It has been reported by several workers that the addition of platinum to zirconia modified by sulfate ions enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen [26–28]. Recently, it has been found that a main group element Al can also promote the catalytic activity and stability of sulfated zirconia in *n*-butane isomerization [29,30].

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Many metal sulfates generate fairly large amounts of acid sites of moderate or strong strength on their surfaces when they are calcined at 400–700 °C [31,32]. The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization. However, 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 [9,10,33].

Pure silica gel shows neither acidic nor basic properties. However, in some cases silica gel exhibits weak acidity and this may be caused by impurities. Binary metal oxides are expected to exhibit better catalytic activity for some reactions due to their solid acid or base properties [34]. Among various binary oxide, the SiO_2–Al_2O_3 is a representative binary oxide which has been extensively studied [35–39]. As an extension of the study on the ethylene dimerization, in this paper we report a nickel sulfate supported on SiO_2 and the promoting effect of Al_2O_3 on the catalytic activity of $NiSO_4$ supported on SiO_2.

2. Experimental

2.1. Catalysts

Silica gel was obtained from Davison Speciality Chemical Co., Baltimore, MD. Silica–alumina having 66 and 82 wt% silica contents were obtained from Nikki Chemical Co., Japan. Silica gel or silica–alumina was impregnated with an aqueous solution of $NiSO_4 \cdot 6H_2O$ 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. This series of catalysts is denoted by the weight percentage of $NiSO_4$. For example, 15-$NiSO_4$/SiO_2 and 15-$NiSO_4$/66-SiO_2–Al_2O_3 (or 15-$NiSO_4$/82-SiO_2–Al_2O_3) means the catalyst having 15 wt% of $NiSO_4$ using silica and silica–alumina of 66 (or 82) wt% silica.

2.2. Procedure

The catalytic activity for ethylene dimerization was determined at 20 °C using a conventional static system by following the pressure change with an initial pressure set at 290 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 during the initial 5 min. Reaction products were analyzed by gas chromatograph with a VZ-7 column at room temperature.

Chemisorption of ammonia was employed as a measure of the number of acid sites of each catalyst. The amount of chemisorption was obtained as the irreversible adsorption of ammonia [4,6,9,40]. 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.

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.
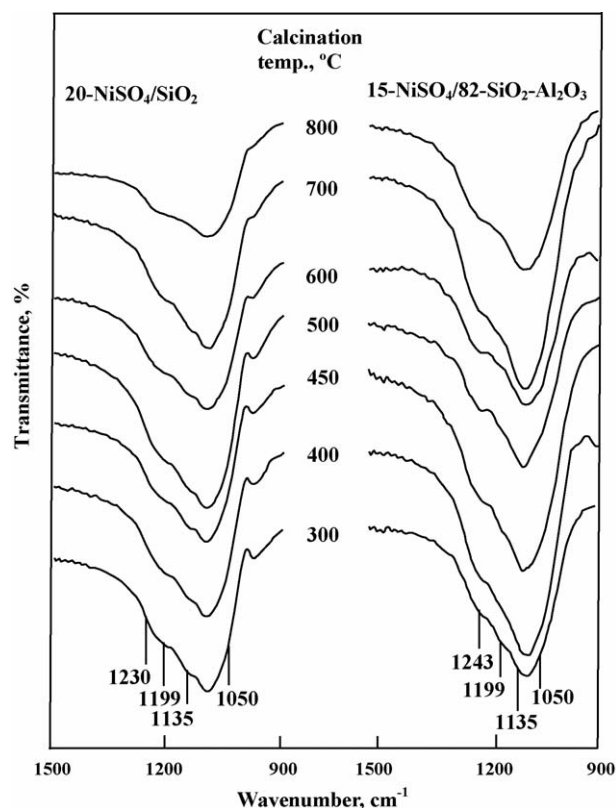

Fig. 1. Infrared spectra of 20-$NiSO_4$/SiO_2 and 15-$NiSO_4$/82-SiO_2–Al_2O_3 calcined at different temperatures.

Fourier transform infrared (FTIR) spectra were obtained in a heatable gas cell at room temperature using a Mattson Model GL6030E spectrometer. Self-supporting catalyst wafers weighed about 9 mg/cm^2. Prior to obtaining the spectra, the samples were heated under vacuum at 100–600 °C for 1 h.

3. Results and discussion

3.1. Infrared spectra of $NiSO_4$/SiO_2 and $NiSO_4$/SiO_2–Al_2O_3

The infrared spectra of 20-$NiSO_4$/SiO_2 and 15-$NiSO_4$/66-SiO_2–Al_2O_3 (KBr disc) calcined at different temperatures (300–800 °C) are given in Fig. 1, respectively. Both samples calcined up to 700 °C showed IR absorption bands at 1230, 1199, 1135, and 1050 cm^{-1} for 20-$NiSO_4$/SiO_2 and at 1243, 1199, 1135, and 1050 cm^{-1} for 15-$NiSO_4$/66-SiO_2–Al_2O_3, which are assigned to bidentate sulfate ion coordinated to the metal such as Si^{4+} and Al^{3+} [9]. However, these bands are overlapped with the characteristic bands of SiO_2 and SiO_2–Al_2O_3 in the region of 1300–900 cm^{-1}. Upon calcination at 800 °C, IR bands by the sulfate ion disappeared because of the decomposition of sulfate ion, as shown in Fig. 1.

For the metal oxides modified with the sulfate ion followed by evacuating above 400 °C, a strong band assigned to S=O stretching frequency is commonly found in the range of 1360–1410 cm^{-1} [9,41,42]. Infrared spectra of 15-$NiSO_4$/66-SiO_2–Al_2O_3 after evacuation at 25–600 °C for 1 h are shown in
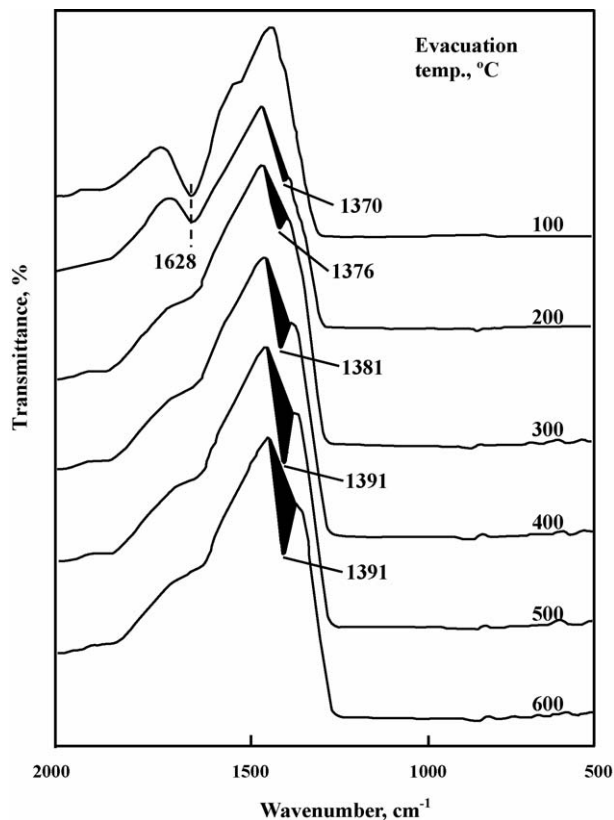
Fig. 2. Infrared spectra of 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ evacuated at different temperatures.

Fig. 2. In this work, the corresponding band was not observed because water molecules in the air were adsorbed on the surface of catalysts. These results are very similar to those reported by other authors [41,43,44]. The band at 1628 cm^{-1} after evacuation at 100 °C is due to water molecules adsorbed on the surfaces of catalysts. However, from 200 °C the band appeared at 1370 cm^{-1} as a shoulder, and the band intensity increased with increasing evacuation temperature and the position of the band shifted to a higher wavenumber up to 500 °C. That is, the higher the evacuation temperature, the larger the shift of the asymmetric stretching frequency of the S=O bonds. However, at 600 °C the band intensity decreased without further band shift because of desorption of sulfate ions. It is likely that the surface sulfur complexes formed by the interaction of oxides with the sulfate ions in these highly active catalysts have a strong tendency to reduce their bond order by the adsorption of basic molecules, such as H$_2$O [9,41,42]. Consequently, as shown in Fig. 2, 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. This is probably due to the fact that the adsorbed water reduces the bond order of S=O from a highly covalent double-bond character to a lesser double-bond character. The strong ability of the sulfur complex to accommodate electron from a basic molecule such as H$_2$O is a driving force in generating superacidic properties [9,42,45]. However, in the case of NiSO$_4$ supported on SiO$_2$ we failed to obtain IR spectra of NiSO$_4$/SiO$_2$ followed by evacua-
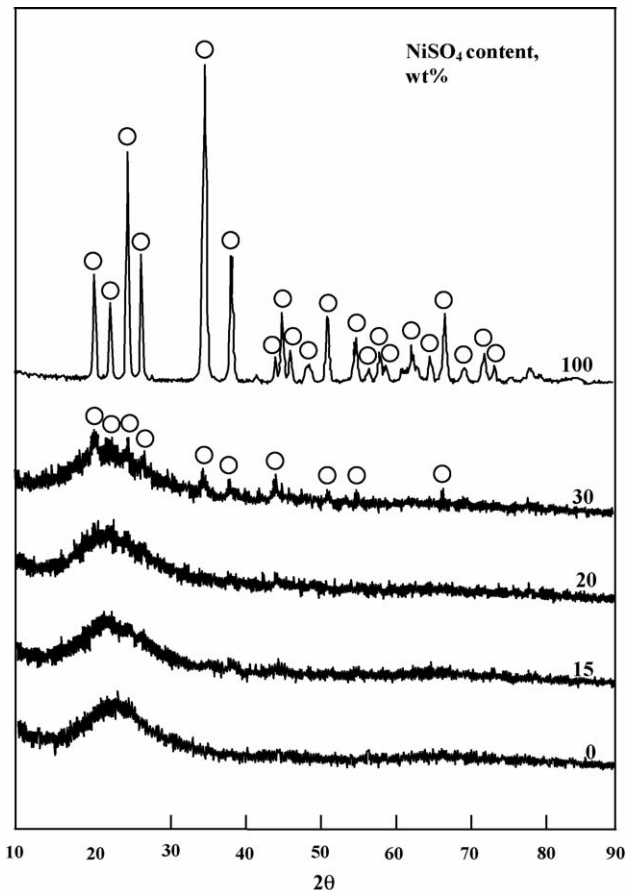

Fig. 3. X-ray diffraction patterns of NiSO$_4$/SiO$_2$ containing different NiSO$_4$ contents (wt%).

tion above 400 °C. This is probably because of the instability of sulfate species bonded to the surface of SiO$_2$ under the condition of evacuation at high temperature. Therefore, it is very important to add the Al$_2$O$_3$ component to NiSO$_4$/SiO$_2$ in order to improve the thermal stability and catalytic property of catalyst.

3.2. Structure of catalysts

XRD patterns of NiSO$_4$/SiO$_2$ containing different nickel sulfate contents and calcined at 400 °C for 1.5 h are shown in Fig. 3. The support, SiO$_2$ and SiO$_2$–Al$_2$O$_3$ were amorphous to X-ray diffraction. For 15-NiSO$_4$/SiO$_2$ and 20-NiSO$_4$/SiO$_2$, no crystalline phase of nickel sulfate was observed, indicating that most of nickel sulfate is present as amorphous matter on the surface of SiO$_2$ due to the interaction between them [33]. However, as shown in Fig. 3, for 30-NiSO$_4$/SiO$_2$ samples, an orthorhombic phase of NiSO$_4$ was observed. Therefore, it is assumed from the XRD results that the content of NiSO$_4$ forming a complete monolayer on the surface of SiO$_2$ is about 20 wt%. XRD patterns of NiSO$_4$/SiO$_2$–Al$_2$O$_3$ were similar to those of NiSO$_4$/SiO$_2$.

3.3. Surface properties

It is necessary to examine the effect of nickel sulfate on the surface properties of catalysts, that is, specific surface area and

Table 1
Specific surface area, acidity, and catalytic activity of $NiSO_4/SiO_2$ calcined at 400 °C for 1.5 h

$NiSO_4$ (wt%)	Surface Area (m^2/g)	Acidity ($\mu mol/g$)	Catalytic activity (mmol/g 5 min)
0	350	30	–
5	343	113	0.21
10	298	117	0.23
15	278	120	0.26
20	270	137	0.42
30	130	115	0.16
40	75	96	0.10

acidity. The specific surface areas of $NiSO_4/SiO_2$, $NiSO_4/66$-$SiO_2–Al_2O_3$, and $NiSO_4/82$-$SiO_2–Al_2O_3$ samples are listed in Tables 1 and 2, where $NiSO_4/SiO_2$ and $NiSO_4/SiO_2–Al_2O_3$ were calcined at 400 and 500 °C, respectively. The presence of nickel sulfate strongly influences the surface area in comparison with the supports SiO_2 and $SiO_2–Al_2O_3$. Specific surface areas of $NiSO_4/SiO_2$ and $NiSO_4/SiO_2–Al_2O_3$ samples decrease gradually with increasing nickel sulfate content because of the blocking of SiO_2 and $SiO_2–Al_2O_3$ pores by the increased $NiSO_4$ loading.

The acidity of catalysts, as determined by the amount of NH_3 irreversibly adsorbed at 230 °C [4,6,9,46], is listed in Tables 1 and 2. The acidity increases abruptly upon the addition of nickel sulfate [5 wt% of $NiSO_4$] to SiO_2 and $SiO_2–Al_2O_3$, and then the acidity increases very gently with increasing nickel sulfate content up to 20 wt% for $NiSO_4/SiO_2$ and up to 15 wt% for $NiSO_4/SiO_2–Al_2O_3$. The acidity of 20-$NiSO_4/SiO_2$ increased with increasing calcination temperature, reaching a maximum at 400 °C, while maximum acidity of 15-$NiSO_4/SiO_2–Al_2O_3$ was obtained at 500 °C. When Tables 1 and 2 are compared, the surface areas of three supports, SiO_2, 66-$SiO_2–Al_2O_3$, and 82-$SiO_2–Al_2O_3$ are similar. However, the addition of Al_2O_3 to SiO_2 enhanced the acidity remarkably, showing that the acidity of binary oxide $SiO_2–Al_2O_3$ is about three times higher than that of SiO_2. It has been reported that the high surface acidity of the binary oxide is attributed to the charge imbalance on the generation of Al–O–Si bonding [47]. The structure of acid sites on binary oxides have been proposed by several researchers [31]. If an aluminum ion, which is trivalent, is substituted isomorphouly for a silicon ion, which is quadravalent, in a silica lattice compris-
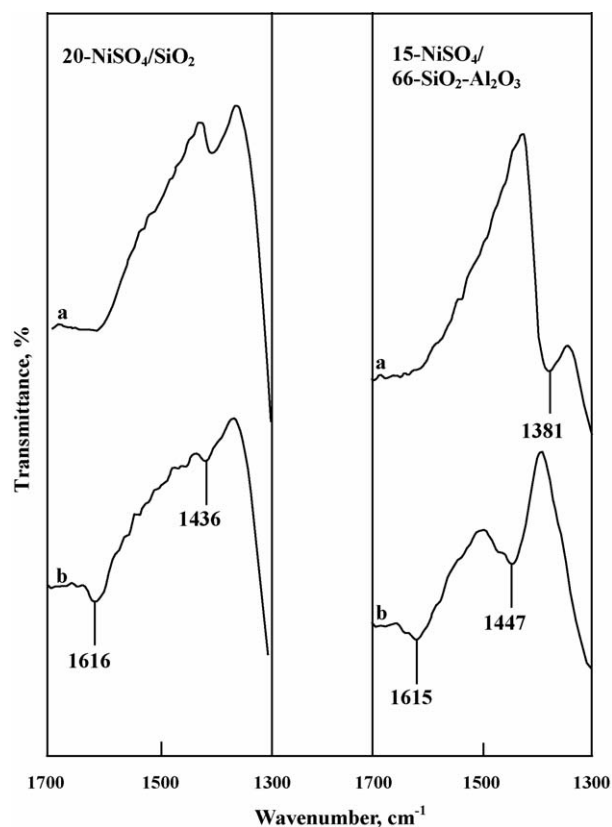

Fig. 4. Infrared spectra of NH_3 adsorbed on 20-$NiSO_4/SiO_2$ and 15-$NiSO_4/66$-$SiO_2–Al_2O_3$: (a) background of catalysts after evacuation at 400 °C for 1 h, (b) NH_3 adsorbed on (a), where gas was evacuated at 230 °C for 1 h.

ing silica tetrahedra, the net negative charge must be stabilized by a nearby positive ion such as a proton. A new hypothesis regarding the acidity generation of binary oxides has been also proposed by Tanabe et al. [31]. According to the hypothesis, acidity generation is caused by an excess of a negative or positive charge in the model structure of a binary oxide.

Fig. 4 shows the infrared spectra of ammonia adsorbed on 20-$NiSO_4/SiO_2$ and 15-$NiSO_4/66$-$SiO_2–Al_2O_3$ samples evacuated at 500 °C for 1 h. The bands at 1436 cm^{-1} on 20-$NiSO_4/SiO_2$ and at 1447 cm^{-1} on 15-$NiSO_4/66$-$SiO_2–Al_2O_3$ are the characteristic peaks of an ammonium ion, which are formed on the Brönsted acid sites; the absorption peaks at 1616 and 1615 cm^{-1}

Table 2
Specific surface area, acidity, and catalytic activity of 15-$NiSO_4/66$-$SiO_2–Al_2O_3$ and 15-$NiSO_4/82$-$SiO_2–Al_2O_3$ calcined at 500 °C for 1.5 h

$NiSO_4$ (wt%)	Surface area (m^2/g)		Acidity ($\mu mol/g$)		Catalytic activity (mmol/g 5 min)	
	15NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$	15NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$	15NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$	15NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$	15NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$	15NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$
0	360	407	105	89	–	–
5	352	350	305	250	2.10	2.00
10	342	287	338	332	2.21	2.40
15	292	272	374	353	2.40	2.61
20	236	213	352	291	2.30	2.30
30	290	164	344	220	1.92	1.41
40	180	136	235	160	0.82	0.73
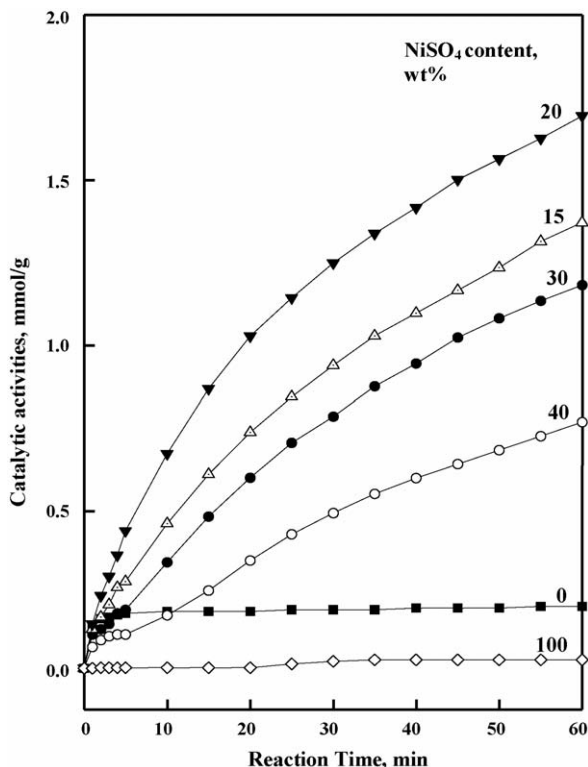
Fig. 5. Catalytic activities of $NiSO_4/SiO_2$ for ethylene dimerization as a function of the $NiSO_4$ content (wt%).

Fig. 6. Catalytic activities of $NiSO_4/SiO_2$ for ethylene dimerization as a function of calcination temperature.: (■) 300 °C; (●) 400 °C; (▲) 500 °C; (▽) 600 °C; (◯) 700 °C; (♦) 800 °C.

are contributed by ammonia coordinately bonded to Lewis acid sites [36,48], indicating the presence of both Brönsted and Lewis acid sites on the surface of the 20-$NiSO_4/SiO_2$ and 15-$NiSO_4/66$-SiO_2–Al_2O_3 samples. The intense band at $1381\,cm^{-1}$ on 15-$NiSO_4/66$-SiO_2–Al_2O_3 after evacuation at 500 °C is assigned to the asymmetric stretching vibration of S=O bonds having a high double-bond character [41,42,49]. However, the drastic shift of the infrared band from $1381\,cm^{-1}$ to a lower wavenumber (not shown due to the overlaps of skeletal vibration bands of SiO_2–Al_2O_3) after ammonia adsorption indicates a strong interaction between an adsorbed ammonia molecule and the surface complex. Namely, 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 [41,42].

3.4. Ethylene dimerization over $NiSO_4/SiO_2$

$NiSO_4/SiO_2$ catalysts were tested for their effectiveness in ethylene dimerization. It was found that for $NiSO_4/SiO_2$, ethylene was continuously consumed. This is shown in Fig. 5, for catalysts that were evacuated at 450 °C for 1.5 h. Over $NiSO_4/SiO_2$, ethylene was selectively dimerized to *n*-butenes. However, a small amount of hexenes from the phase adsorbed on the catalyst surface was detected. Therefore, the deactivation of catalyst occurred slowly due to the adsorption of oligomers. In the com-
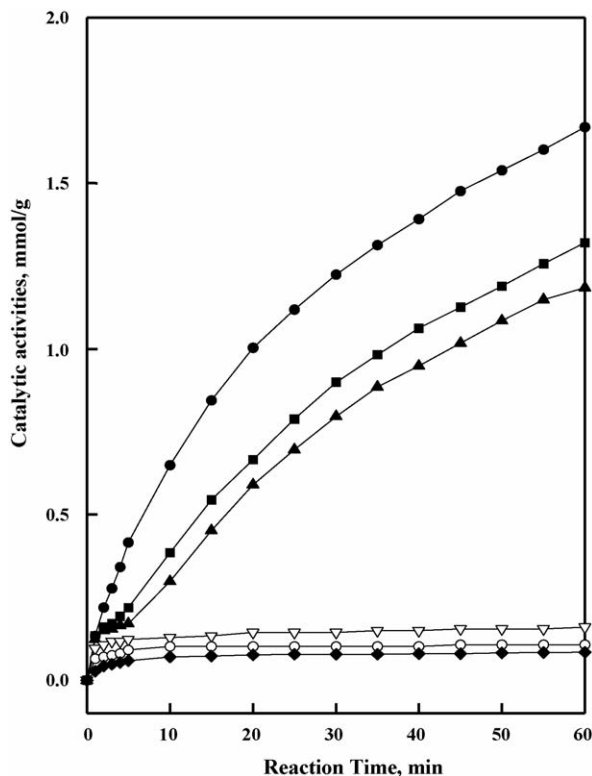
position of *n*-butenes analyzed by gas chromatography, 1-butene was found exclusively at the initial reaction time, as compared with *cis*- and *trans*-2-butenes. However, the amount of 1-butene decreases with the reaction time, while the amount of 2-butenes increases. Therefore, it seems likely that the initially produced 1-butene is also isomerized to 2-butene during the reaction [4,9]. $NiSO_4/SiO_2$ was effective for ethylene dimerization, but SiO_2 without $NiSO_4$ and pure $NiSO_4$ without SiO_2 exhibited absolutely no catalytic activity.

The catalytic activities of $NiSO_4/SiO_2$ were tested as a function of the $NiSO_4$ content; the results are shown in Fig. 5. The activities increased with increasing $NiSO_4$ content, reaching a maximum at 20 wt% $NiSO_4$, and then the activities decreased. The decrease in catalytic activity above 20 wt% $NiSO_4$ seems to be due to the decrease in acidity. In fact, as seen in Table 1, the acidity of 20-$NiSO_4/SiO_2$ among catalysts was found to have a maximum value, 137 μmol/g.

The catalytic activities of 20-$NiSO_4/SiO_2$ were tested as a function of calcination temperature; the results are shown in Fig. 6. The activities increased with increasing calcination temperature, reaching a maximum at 400 °C, and then the activities decreased. The decrease in catalytic activity after calcination above 400 °C seems to be due to the thermal instability of sulfate species bonded to SiO_2. As discussed below, the addition of Al_2O_3 to $NiSO_4/SiO_2$ not only improves the thermal stability of sulfate species, but increases the acidity of catalysts. As seen in Fig. 6, 20-$NiSO_4/SiO_2$ calcined above 600 °C is inactive for ethylene dimerization.
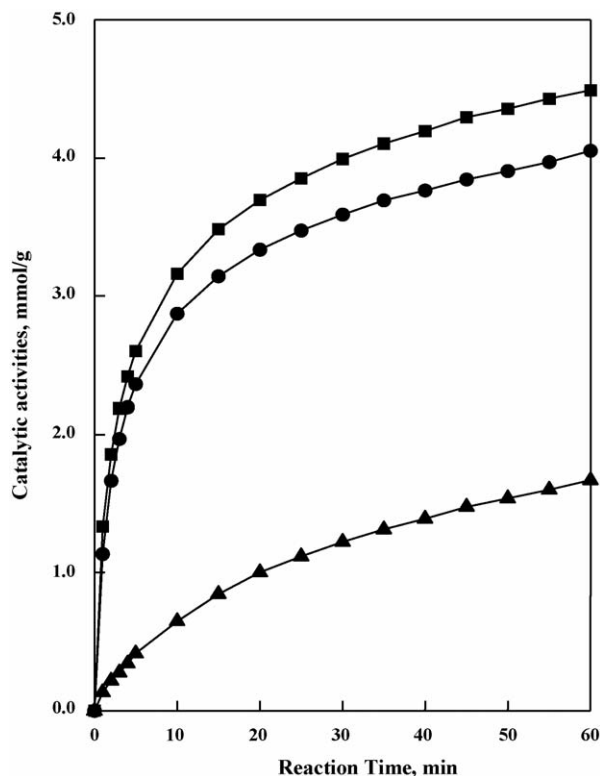
Fig. 7. Catalytic activities of 20-NiSO$_4$/SiO$_2$, 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ and 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$ against reaction time: (■) 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$; (●) 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$; (▲) 20-NiSO$_4$/SiO$_2$.

Fig. 8. Catalytic activities of 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ as a function of calcination temperature: (■) 300 °C; (△) 400 °C; (●) 500 °C; (○) 600 °C; (□) 700 °C; (▲) 800 °C.

3.5. Promoting effect of Al$_2$O$_3$ on catalytic activity

As mentioned above, the addition of Al$_2$O$_3$ to SiO$_2$ enhanced its acidity remarkably, showing that the acidity of 82-SiO$_2$–Al$_2$O$_3$ and 66-SiO$_2$–Al$_2$O$_3$ is about three times as high as that of SiO$_2$. As listed in Table 2, the addition of NiSO$_4$ to SiO$_2$–Al$_2$O$_3$ also caused the acidity of NiSO$_4$/SiO$_2$–Al$_2$O$_3$ to increase remarkably compared to SiO$_2$–Al$_2$O$_3$, because the addition of NiSO$_4$ to SiO$_2$–Al$_2$O$_3$ generates new acid sites by the inductive effect of sulfate species bonded to SiO$_2$–Al$_2$O$_3$ [31,49,50]. Namely, the number of acid sites for 20-NiSO$_4$/SiO$_2$ is 137 μmol/g, while that of acid sites for 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ and 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$ is 374 and 353 μmol/g, respectively.

We examined the promoting effect of Al$_2$O$_3$ on the catalytic activity for ethylene dimerization. The catalytic activities for 20-NiSO$_4$/SiO$_2$ and two catalysts promoted with Al$_2$O$_3$, 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ and 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$ against reaction time are plotted in Fig. 7. It is clear that the catalytic activities of two Al$_2$O$_3$-promoted catalysts (2.4–2.6 mmol/g 5 min) are about six times as high as that of 20-NiSO$_4$/SiO$_2$ (0.4 mmol/g 5 min). This can be rationalized in terms of that the number of acid sites of Al$_2$O$_3$-promoted catalysts, which is remarkably larger than that of non-promoted catalyst, 20-NiSO$_4$/SiO$_2$, as seen in Table 2. It has been reported that the catalytic activity for ethylene dimerization is closely correlated with the acidity of the catalyst [4,10,50]. Therefore, it is concluded that the promoting effect of Al$_2$O$_3$ is related to an increase
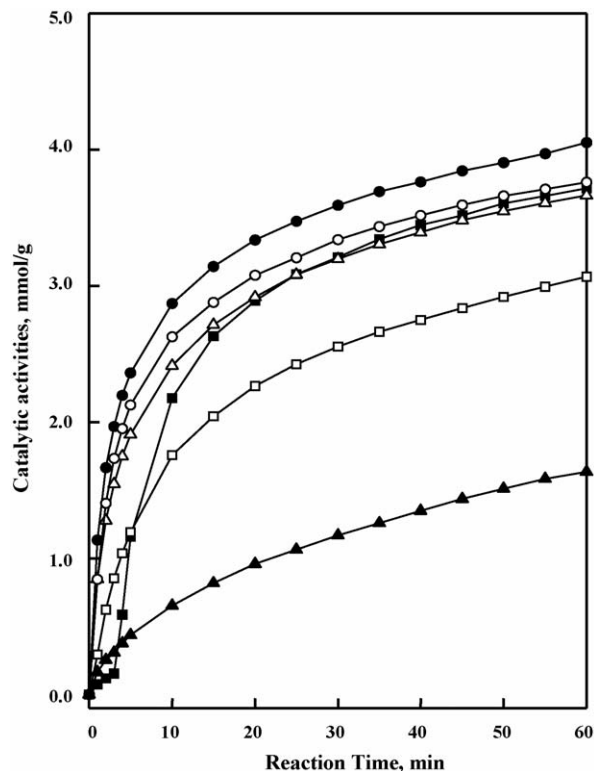
in the number of surface acidic sites and to the improved thermal stability of Al$_2$O$_3$-promoted catalyst. Cai also reported the catalytic activities of NiSO$_4$/SiO$_2$ and NiSO$_4$/SiO$_2$–Al$_2$O$_3$ for ethylene dimerization without the interpretation concerning the thermal stability effect of Al$_2$O$_3$ addition to NiSO$_4$/SiO$_2$ [51].

3.6. Effect of calcination temperature on catalytic activity

As shown in Fig. 7, for the Al$_2$O$_3$-promoted catalysts, 15-NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$ and 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$ containing 15 wt% NiSO$_4$ exhibited maximum catalytic activities after evacuation at 500 °C. We examined the effect of calcination temperatures on the catalytic activity; the results are shown in Figs. 8 and 9. In the case of 20-NiSO$_4$/SiO$_2$, as shown in Fig. 6, the catalyst calcined at 400 °C exhibited maximum catalytic activity, and the catalysts calcined above 600 °C were inactive for ethylene dimerization due to the thermal instability of catalyst at high calcination temperature. However, in the case of Al$_2$O$_3$-promoted catalysts, the catalysts calcined at 500 °C exhibited maximum catalytic activities, and then activities decreased gradually, as shown in Figs. 8 and 9, indicating that the thermal stability of Al$_2$O$_3$-promoted catalysts was improved by the addition of Al$_2$O$_3$ compared to the non-promoted catalyst, NiSO$_4$/SiO$_2$. Moreover, as shown in Figs. 8 and 9, the catalysts calcined even at 800 °C exhibited catalytic activity. Therefore, it is concluded that the high catalytic activity of Al$_2$O$_3$-promoted catalyst can be explained by two factors. The first one is that the addition of Al$_2$O$_3$ to SiO$_2$ generates new acid sites due
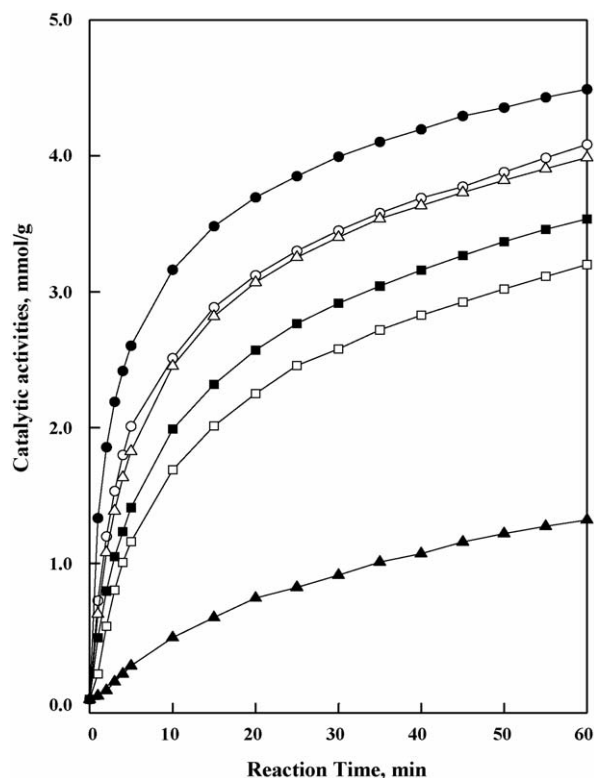
Fig. 9. Catalytic activities of 15-NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$ as a function of calcination temperature: (■) 300 °C; (△) 400 °C; (●) 500 °C; (○) 600 °C; (□) 700 °C; (▲) 800 °C.

Fig. 10. Correlationship between catalytic activity for ethylene dimerization and acidity: (■) NiSO$_4$/SiO$_2$; (●) NiSO$_4$/66-SiO$_2$–Al$_2$O$_3$; (○) NiSO$_4$/82-SiO$_2$–Al$_2$O$_3$.

to the bonding between SiO$_2$ and Al$_2$O$_3$. The second one is that the addition of Al$_2$O$_3$ improves the thermal stability of the catalyst, because sulfate species bonded to Al$_2$O$_3$ is more stable under high calcination temperature conditions than sulfate species bonded to SiO$_2$ [52].

3.7. Correlation between catalytic activity and acidity

As mentioned above, the active site responsible for dimerization is suggested to consist of a low valent nickel ion and an acid, as observed in the nickel-containing catalyst [4,17,18]. 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 [49,53]. Previously, from the results of IR of CO adsorbed on NiSO$_4$/γ-Al$_2$O$_3$ and XPS to indentify low valent nickel species, we reported that the active sites responsible for ethylene dimerization consist of a low-valent nickel, Ni$^+$ and an acid [49]. Kazansky et al. concluded that Ni$^+$ ions in NiCa-Y zeolite are responsible for the catalytic activity, using EPR spectroscopy to identify low valent nickel species [15]. Therefore, the nickel species should be active site for ethylene dimerization. In fact, SiO$_2$ or SiO$_2$–Al$_2$O$_3$ without NiSO$_4$ is inactive for ethylene dimerization.

It is known that for ethylene dimerization the variations in catalytic activities are closely correlated to the acidity values of catalyst [50,54]. The acidity values of NiSO$_4$/SiO$_2$ and NiSO$_4$/SiO$_2$–Al$_2$O$_3$ catalysts after evacuation at 400 °C are

listed in Tables 1 and 2 together with their surface areas. In view of Tables 1 and 2, the catalytic activities substantially run parallel to the acidity values. The catalytic activities of NiSO$_4$/SiO$_2$ and NiSO$_4$/SiO$_2$–Al$_2$O$_3$ containing different NiSO$_4$ contents were examined; the results are shown as a function of acidity in Fig. 10, where catalysts were evacuated at 400 °C for 1 h before reaction. It is confirmed that the catalytic activity gives a maximum at 15 wt% NiSO$_4$. This seems to be correlated to the specific surface area and to the acidity of the catalysts. The acidity of NiSO$_4$/SiO$_2$ calcined at 400 °C was determined by the amount of NH$_3$ irreversibly adsorbed at 230 °C [3,4,6,9,46]. In the case of NiSO$_4$/SiO$_2$–Al$_2$O$_3$, samples calcined at 500 °C were used for the measurement of their acidity. As shown in Fig. 10, the higher the acidity, the higher the catalytic activity. In this way it is demonstrated that the catalytic activity of NiSO$_4$/SiO$_2$ and NiSO$_4$/SiO$_2$–Al$_2$O$_3$ essentially runs parallel to the acidity. Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids. It has been reported that the catalytic activity of nickel-containing catalysts in ethylene dimerization as well as in butene isomerization are closely correlated with the acidity of the catalysts [3,4,6,50]. Up to now, a correlation between catalytic activity for ethylene dimerization and acidity has been studied using supported NiSO$_4$ [9,49,50,54], where only one kind of support material such as Al$_2$O$_3$, TiO$_2$–ZrO$_2$, and Al$_2$O$_3$–ZrO$_2$ was used. However, in this work we used different supports, SiO$_2$ and two kinds of SiO$_2$–Al$_2$O$_3$. In this case of NiSO$_4$ supported on different materials, there was also a correlation between catalytic activ-

ity for ethylene dimerization and acidity, regardless of the kind of support (SiO_2 or SiO_2–Al_2O_3), although due to the thermal instability of sulfate species the catalytic activity of $NiSO_4/SiO_2$ was remarkably lower than that of $NiSO_4/SiO_2$–Al_2O_3.

4. Conclusions

A series of catalysts, $NiSO_4/SiO_2$, for ethylene dimerization was prepared by the impregnation method using an aqueous solution of nickel sulfate. We examined the promoting effect of Al_2O_3 on the catalytic activity for ethylene dimerizaiton. The following conclusions were drawn. The addition of Al_2O_3 to $NiSO_4/SiO_2$ improved the thermal stability of the catalyst and increased the number of acid sites on the surface of the catalyst. Consequently, Al_2O_3-promoted catalyst exhibited remarkably higher catalytic activity than non-promoted $NiSO_4/SiO_2$. $NiSO_4/SiO_2$ calcined above 600 °C exhibited no catalytic activity, while Al_2O_3-promoted catalysts, $NiSO_4/SiO_2$–Al_2O_3 exhibited catalytic activity even after calcination at 800 °C due to their high thermal stability.

Acknowledgements

References

[1] K. Urabe, M. Koga, Y. Izumi, J. Chem. Soc., Chem. Commun. (1989) 807.
[2] F. Bernardi, A. Bottoni, I. Rossi, J. Am. Chem. Soc. 120 (1998) 7770.
[3] J.R. Sohn, J.S. Lim, Catal. Today 111 (2006) 403.
[4] J.R. Sohn, A. Ozaki, J. Catal. 61 (1980) 29.
[5] G. Wendt, E. Fritsch, R. Schöllner, H.Z. Siegel, Anorg. Allg. Chem. 467 (1980) 51.
[6] J.R. Sohn, D.C. Shin, J. Catal. 160 (1996) 314.
[7] G.F. Berndt, S.J. Thomson, G.J. Webb, J. Chem. Soc. Faraday Trans. 1 79 (1983) 195.
[8] T.V. Herwijnen, H.V. Doesburg, D.V. Jong, J. Catal. 28 (1973) 391.
[9] J.R. Sohn, W.C. Park, H.W. Kim, J. Catal. 209 (2002) 69.
[10] J.R. Sohn, W.C. Park, Bull. Korean Chem. Soc. 21 (2000) 1063.
[11] G. Wendt, D. Hentschel, J. Finster, R. Schöllner, J. Chem. Soc. Faraday Trans. 1 79 (1983) 2013.
[12] K. Kimura, A. Ozaki, J. Catal. 3 (1964) 395.
[13] K. Maruya, A. Ozaki, Bull. Chem. Soc. Jpn. 46 (1973) 351.
[14] M. Hartmann, A. Pöppl, L. Kevan, J. Phys. Chem. 100 (1996) 9906.
[15] I.V. Elev, B.N. Shelimov, V.B. Kazansky, J. Catal. 89 (1984) 470.
[16] H. Choo, L. Kevan, J. Phys. Chem. B 105 (2001) 6353.
[17] J.R. Sohn, H.J. Kim, J. Catal. 101 (1986) 428.
[18] J.R. Sohn, S.Y. Lee, Appl. Catal. A: Gen. 164 (1997) 127.
[19] J.R. Sohn, J.S. Han, Appl. Catal. A: Gen. 298 (2006) 168.
[20] C.Y. Hsu, C.R. Heimbuch, C.T. Armes, B.C. Gates, J. Chem. Soc., Chem. Commun. (1992) 1645.
[21] T.K. Cheung, B.C. Gates, J. Catal. 168 (1997) 522.
[22] V. Adeeva, H.W. de Haan, J. Janchen, G.D. Lei, V. Schunemann, L.J.M. van de Ven, W.M.H. Sachtler, R.A. van Santen, J. Catal. 151 (1995) 364.
[23] K.T. Wan, C.B. Khouw, M.E. Davis, J. Catal. 158 (1996) 311.
[24] X. Song, K.R. Reddy, A. Sayari, J. Catal. 161 (1996) 206.
[25] M.A. Coelho, D.E. Resasco, E.C. Sikabwe, R.L. White, Catal. Lett. 32 (1995) 253.
[26] T. Hosoi, T. Shimadzu, S. Ito, S. Baba, H. Takaoka, T. Imai, N. Yokoyama, Prepr. Symp. Div. Petr. Chem., American Chemical Society, Los Angeles, CA, 1988, p. 562.
[27] K. Ebitani, J. Konishi, H. Hattori, J. Catal. 130 (1991) 257.
[28] M. Signoretto, F. Pinna, G. Strukul, P. Chies, G. Cerrato, S.D. Ciero, C. Morterra, J. Catal. 167 (1997) 522.
[29] W. Hua, Y. Xia, Y. Yue, Z. Gao, J. Catal. 196 (2000) 104.
[30] J.A. Moreno, G. Poncelet, J. Catal. 203 (2001) 153.
[31] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New Solid Acids and Bases, Kodansha\Elsevier, Tokyo, 1989, p. 185.
[32] K. Arata, M. Hino, N. Yamagata, Bull. Chem. Soc. Jpn. 63 (1990) 244.
[33] J.R. Sohn, J. Ind. Eng. Chem. 10 (2004) 1.
[34] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, J. Kitagawa, Bull. Chem. Soc. Jpn. 47 (1974) 1064.
[35] E.P. Parry, J. Catal. 2 (1963) 371.
[36] M.R. Basila, T.R. Kantner, J. Phys. Chem. 70 (1967) 467.
[37] J. Ward, R.C. Hansford, J. Catal. 13 (1969) 354.
[38] J.W. Hightower, W.K. Hall, J. Am. Chem. Soc. 89 (1967) 7778.
[39] J.W. Hightower, W.K. Hall, J. Phys. Chem. 71 (1967) 1015.
[40] J.R. Sohn, J.G. Kim, T.D. Kwon, E.H. Park, Langmuir 18 (2002) 1666.
[41] T. Yamaguchi, Appl. Catal. 61 (1990) 1.
[42] T. Jin, T. Yamaguchi, K. Tananbe, J. Phys. Chem. 90 (1986) 4794.
[43] O. Saur, M. Bensitel, A.B.M. Saad, J.C. Lavalley, C.P. Tripp, B.A. Morrow, J. Catal. 99 (1986) 104.
[44] B.A. Morrow, R.A. McFarlane, M. Lion, J.C. Lavalley, J. Catal. 107 (1987) 232.
[45] J. Miciukiewicz, T. Mang, H. Knőzinger, Appl. Catal. A 122 (1995) 151.
[46] J.R. Sohn, J.S. Han, J. Ind. Eng. Chem. 11 (2005) 439.
[47] J.C. Wu, C.S. Chung, C.L. Ay, I. Wang, J. Catal. 87 (1984) 98.
[48] A. Satsuma, A. Hattori, K. Mizutani, A. Furuta, A. Miyamoto, T. Hattori, Y. Murakami, J. Phys. Chem. 92 (1988) 6052.
[49] J.R. Sohn, W.C. Park, Appl. Catal. A: Gen. 239 (2003) 269.
[50] J.R. Sohn, E.S. Cho, Appl. Catal. A: Gen. 282 (2005) 147.
[51] T. Cai, Catal. Today 51 (1999) 153.
[52] R.V. Siriwardane, J.A. Poston Jr., E.P. Fisher, M.S. Shen, A.L. Miltz, Appl. Surf. Sci. 152 (1999) 217.
[53] K. Kimura, H.A.-I.A. Ozaki, J. Catal. 18 (1970) 271.
[54] J.R. Sohn, S.H. Lee, Appl. Catal. A: Gen. 266 (2004) 89.