

Characterization of Nickel Sulfate Supported on γ -Al₂O₃ and its Relationship to Acidic Properties

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Abstract—A series of NiSO₄/ γ -Al₂O₃ catalysts were prepared by the impregnation method using an aqueous solution of nickel sulfate. The high catalytic activity of NiSO₄/ γ -Al₂O₃ for both 2-propanol dehydration and cumene dealkylation was related to the increase of acidity and acid strength due to the addition of NiSO₄. 20(wt%)-NiSO₄/ γ -Al₂O₃ calcined at 600 °C exhibited maximum catalytic activities for 2-propanol dehydration and cumene dealkylation. The catalytic activities for both reactions were correlated with the acidity of catalysts measured by the ammonia chemisorption method.

Key words: NiSO₄/ γ -Al₂O₃ Catalyst, Characterization, Acid Catalysis, 2-Propanol Dehydration, Cumene Dealkylation

INTRODUCTION

Solid acid catalysts play an important role in hydrocarbon conversion reactions in the chemical and petroleum industries [Cheung et al., 1995; Tanabe et al., 1989; Lee and Rhee, 1997; Sohn et al., 2002]. Many kinds of solid acids have been found; their acidic properties on catalyst surfaces, their catalytic action, and the structure of acid sites have been elucidated for a long time, and those results have been reviewed by Arata [Arata, 1990]. The strong acidity of zirconia-supported sulfate attracted much attention because of its ability to catalyze many reactions such as cracking, alkylation, and isomerization. The potential for a heterogeneous catalyst has yielded many papers on the catalytic activity of sulfated zirconia materials [Arata, 1990; Keogh et al., 1995; Figueras et al., 1997]. Sulfated zirconia incorporating Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature [Hsu et al., 1992; Adeeva et al., 1995].

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 [Ebitani et al., 1991; Vaudagna et al., 1997]. The high catalytic activity and small deactivation can be explained by both the elimination of the coke by hydrogenation and hydrogenolysis and the formation of Brønsted acid sites from H₂ on the catalysts [Ebitani et al., 1991]. Recently, Hino and Arata reported zirconia-supported tungsten oxide as an alternative material in reactions requiring strong acid sites [Arata, 1990; Hino and Arata, 1987]. Several advantages of tungstate, over sulfate, as dopant include that it does not suffer from dopant loss during thermal treatment and it undergoes significantly less deactivation during catalytic reaction.

On the other hand, 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 [Tanabe et al., 1989; Arata et al., 1990]. The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization [Tanabe et al., 1989; Sohn and Park, 2000; Arata et al., 1990]. 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 [Sohn and Park, 1998; Sohn et al., 2002].

This paper describes the characterization of nickel sulfate supported on γ -Al₂O₃ and its relationship to acidic properties. The characterization of the samples was performed by means of Fourier transform infrared (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Differential scanning calorimetry (DSC), and by the measurement of surface area. For the acid catalysis, 2-propanol dehydration and cumene dealkylation were used as test reactions.

EXPERIMENTAL

Catalysts containing various nickel sulfate contents were prepared by impregnation of γ -Al₂O₃ powder (JRC-ALO-2, surface area=240 m²/g) with an aqueous solution of NiSO₄·6H₂O 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-NiSO₄/ γ -Al₂O₃ indicates the catalyst containing 20 wt% of NiSO₄.

FTIR spectra were obtained in a heatable gas cell at room temperature using Mattson Model GL6030E spectrophotometer. The wafers contained about 9 mg/cm² self-supporting catalyst. Prior to obtaining the spectra the samples were heated under vacuum at 400-500 °C for 1.5 h. Catalysts were checked in order to determine the structure of the support as well as that of nickel sulfate by means of a Philips X'pert-APD X-ray diffractometer, employing Ni-filtered Cu K_α radiation. DSC measurements were performed by a

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[‡]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

PL-STA model 1500H apparatus in air, and the heating rate was 5 °C per minute. For each experiment 10-15 mg of sample was used.

The acid strength of catalyst was measured qualitatively by using a series of the Hammett indicators [Sohn et al., 1996; Sohn and Park, 1998]. The catalyst in a glass tube was pretreated at 500 °C for 1 h and filled with dry nitrogen. For the determination of acid strength of the catalyst the color changes of indicators were observed by spot test. 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 Ryu, 1993]. Thus the first adsorption of ammonia at 20 °C and 300 torr was followed by evacuation at 230 °C for 1 h and re-adsorption 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.

2-propanol dehydration was carried at 160 and 180 °C in a pulse micro-reactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 inch stainless steel was pretreated at 400 °C for 1 h in the nitrogen atmosphere. Diethyleneglycol succinate on Simalite was used as packing material of gas chromatograph and the column temperature was 180 °C for analyzing the product. Catalytic activity for 2-propanol dehydration was represented as mole of propylene converted from 2-propanol per gram of catalyst. Cumene dealkylation was carried out at 400-450 °C in the same reactor as above. Packing material for the gas chromatograph was Benton 34 on chromosorb W and column temperature was 130 °C. Catalytic activity for cumene dealkylation was represented as mole of benzene converted from cumene per gram of catalyst. Conversions for both reactions were taken as the average of the first to sixth pulse values.

RESULTS AND DISCUSSION

1. Infrared Spectra of NiSO₄/ γ -Al₂O₃

In general, for the metal oxides modified with the sulfate ion followed by evacuating above 400 °C, a strong bond assigned to S=O stretching frequency is observed in the range of 1,360-1,410 cm⁻¹ [Saur et al., 1986; Yamaguchi, 1990]. Infrared spectra of 20-NiSO₄/ γ -Al₂O₃ after evacuation at 100-600 °C for 1 h are shown in Fig. 1. There are sharp bands at 1,362-1,398 cm⁻¹ accompanied by four broad but split bands at 1,250, 1,157, 1,038, and 1,941 cm⁻¹, indicating the presence of two kinds of sulfated species. The bands at 1,362-1,398 cm⁻¹ correspond to the 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 [Jin et al., 1986; Yamaguchi, 1990]. These results are very similar to those of other workers [Jin et al., 1986; Saur et al., 1986]. However, the frequency shift of this band is different 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-NiSO₄/ γ -Al₂O₃ [Jin et al., 1986; Yamaguchi, 1990]. However, from 200 °C the band began to appear at 1,362 cm⁻¹ as a shoulder, and the band intensity increased with the evacuation temperature and the position of band shifted to a higher wavenumber. That is, the higher the evacuation temperature, the larger were the shifts of

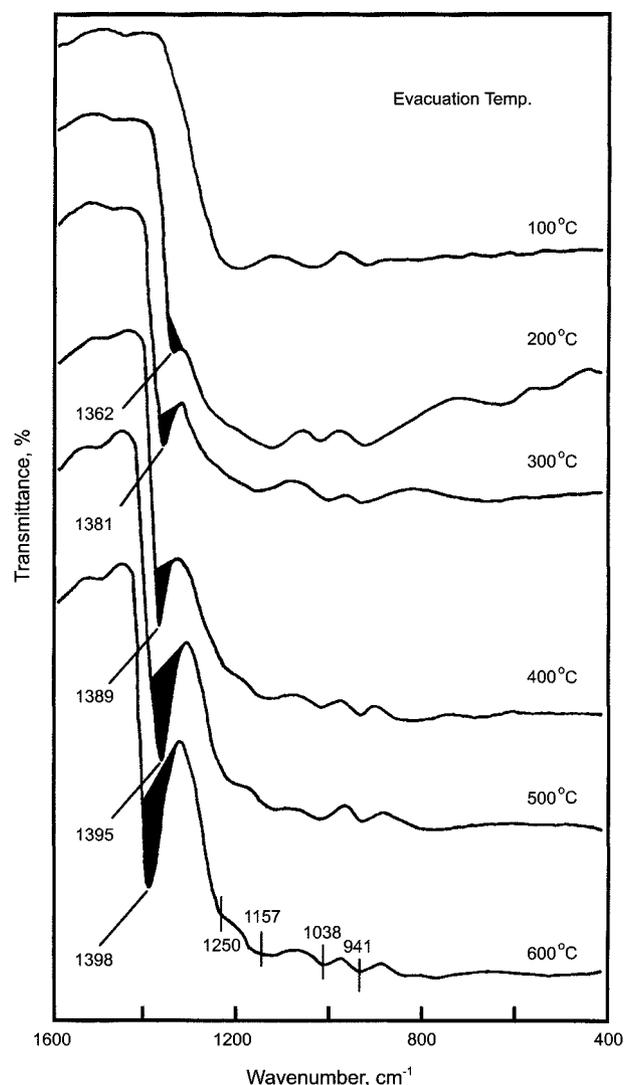


Fig. 1. Infrared spectra of NiSO₄/ γ -Al₂O₃ evacuated at different temperatures.

the asymmetric stretching frequency of the S=O bonds. 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 H₂O [Jin et al., 1986; Yamaguchi, 1990]. 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 one. Therefore, it is obvious that the asymmetric stretching frequency of the S=O bonds is related to the acidic properties and catalytic activity to be discussed later.

However, for the sample calcined at 800 °C no infrared absorption bands were observed in a separate experiment because of the complete decomposition of the sulfate group bonded to the surface of γ -Al₂O₃. These results are in good agreement with those of the thermal analysis described later.

2. Crystalline Structure of NiSO₄/ γ -Al₂O₃

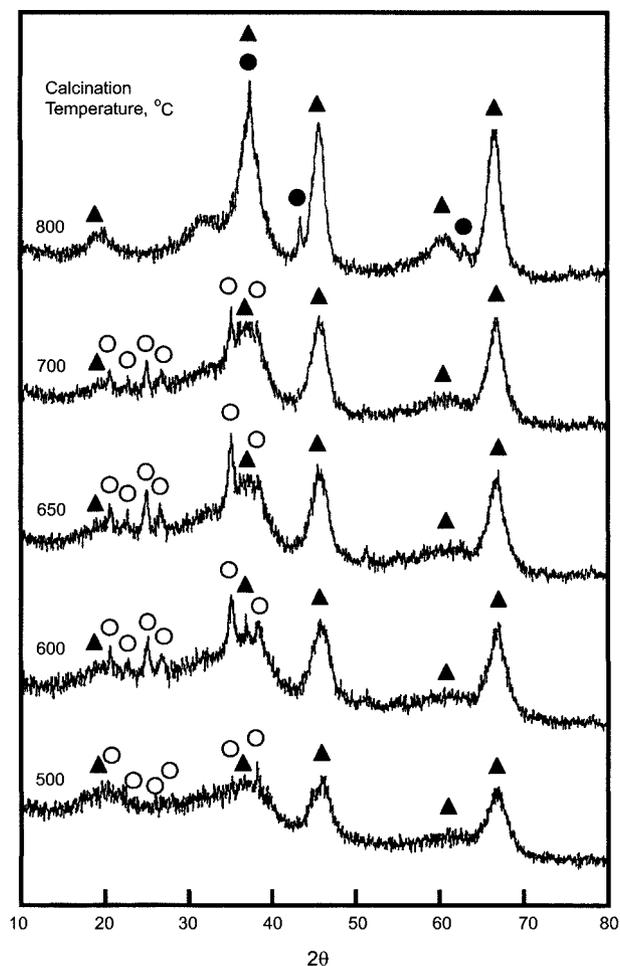


Fig. 2. X-ray diffraction patterns of 20-NiSO₄/γ-Al₂O₃ calcined at different temperatures: orthorhombic phase of NiSO₄; ○, cubic phase of NiO; ▲, γ-Al₂O₃ phase.

The crystalline structure of 20-NiSO₄/γ-Al₂O₃ calcined in air at different temperatures for 1.5 h was examined by X-ray diffraction. For the 20-NiSO₄/γ-Al₂O₃, as shown in Fig. 2, X-ray diffraction data indicated an orthorhombic phase of NiSO₄ and γ-Al₂O₃ phase at 400–700 °C. However, at 800 °C a cubic phase of nickel oxide was observed due to the decomposition of nickel sulfate, showing good agreement with the results of infrared spectra analysis mentioned above.

The XRD patterns of NiSO₄/γ-Al₂O₃ containing different nickel sulfate contents and calcined at 600 °C for 1.5 h are shown in Fig. 3. No diffraction line of nickel sulfate is observed at low NiSO₄ loading up to 10 wt%, indicating good dispersion of NiSO₄ on the surface of γ-Al₂O₃ due to the interaction between them. However, for the NiSO₄/γ-Al₂O₃ sample at nickel sulfate loading above or equal to 20 wt%, an orthorhombic phase of NiSO₄ was observed.

3. Thermal Analysis

To examine the thermal properties of precursors of NiSO₄/γ-Al₂O₃ samples more closely, thermal analysis has been carried out and the results are illustrated in Fig. 4. For pure NiSO₄·6H₂O, the DSC curve shows three endothermic peaks below 400 °C due to water elimination, indicating that the dehydration of NiSO₄·6H₂O occurs in three steps. The endothermic peak around 837 °C is due

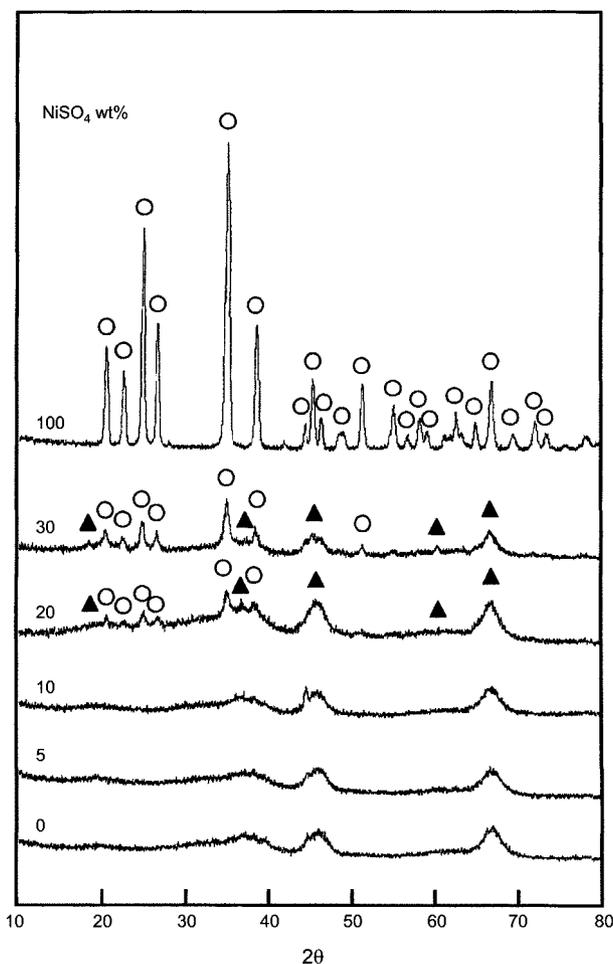


Fig. 3. X-ray diffraction patterns of NiSO₄/γ-Al₂O₃ having different NiSO₄ contents and calcined at 600 °C: ○, orthorhombic phase of NiSO₄; ▲, γ-Al₂O₃ phase.

to the evolution of SO₃ decomposed from nickel sulfate [Hua et al., 2000]. Decomposition of nickel sulfate is known to begin at 700 °C [Siriwardane et al., 1999].

However, for NiSO₄/γ-Al₂O₃ samples, the DSC patterns are somewhat different from that of NiSO₄·6H₂O. For 10-NiSO₄/γ-Al₂O₃, the endothermic peak around 790 °C is due to the evolution of SO₃ decomposed from the sulfate ion bonded to the surface of γ-Al₂O₃ [Hua et al., 2000]. However, for NiSO₄/γ-Al₂O₃ samples above or equal to 20 wt% of nickel sulfate, two endothermic peaks are observed around 785 and 829 °C due to the evolution of SO₃, showing that sulfated species with different thermal stability are present in the samples. It seems likely that the first peak around 785 °C is due to the decomposition of sulfate ion forming a monolayer and bonded to the surface of γ-Al₂O₃, while the second peak around 820 °C is ascribed to the decomposition of nickel sulfate existing on top of a monolayer on the surface of γ-Al₂O₃ because the intensity of the second peak increases with increasing nickel sulfate content compared with that of the first peak, as shown in Fig. 4.

4. Surface Properties of Catalysts

It is necessary to examine the effect of nickel sulfate on the surface properties of the catalysts, that is, specific surface area, acid strength, and nature of acid centers (Brønsted or Lewis type). The

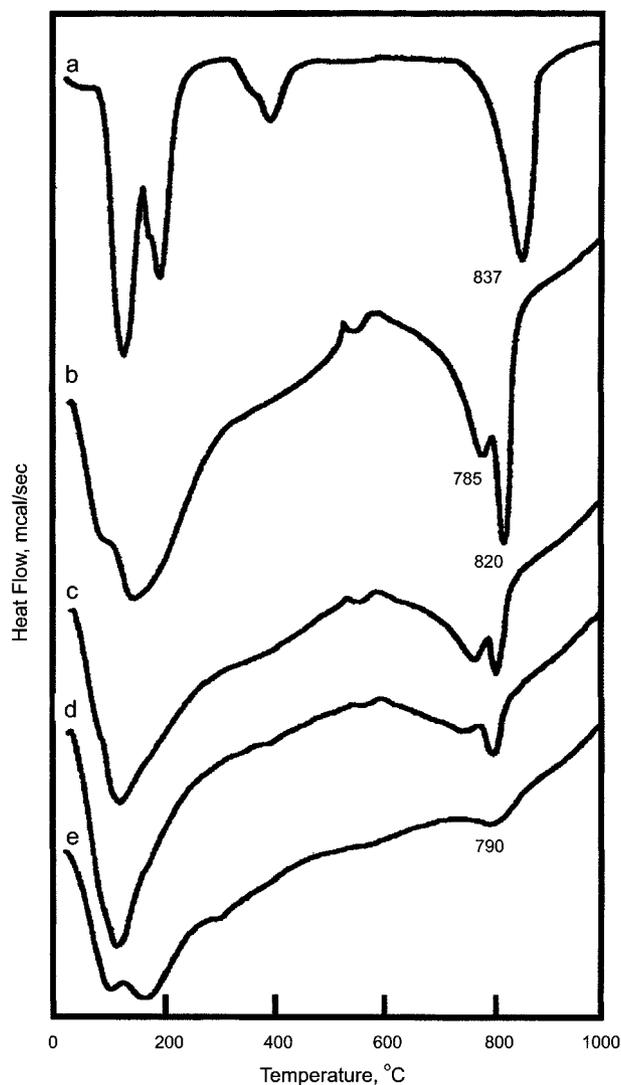


Fig. 4. DSC curves of NiSO₄/ γ -Al₂O₃ precursors having different NiSO₄ contents: (a) NiSO₄·6H₂O, (b) 30-NiSO₄/ γ -Al₂O₃, (c) 25-NiSO₄/ γ -Al₂O₃, (d) 20-NiSO₄/ γ -Al₂O₃, and (e) 10-NiSO₄/ γ -Al₂O₃.

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		

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 NiSO₄ content was 5 wt% and then showed a gradual decrease with increasing NiSO₄ content.

Infrared spectroscopic studies of ammonia adsorbed on solid sur-

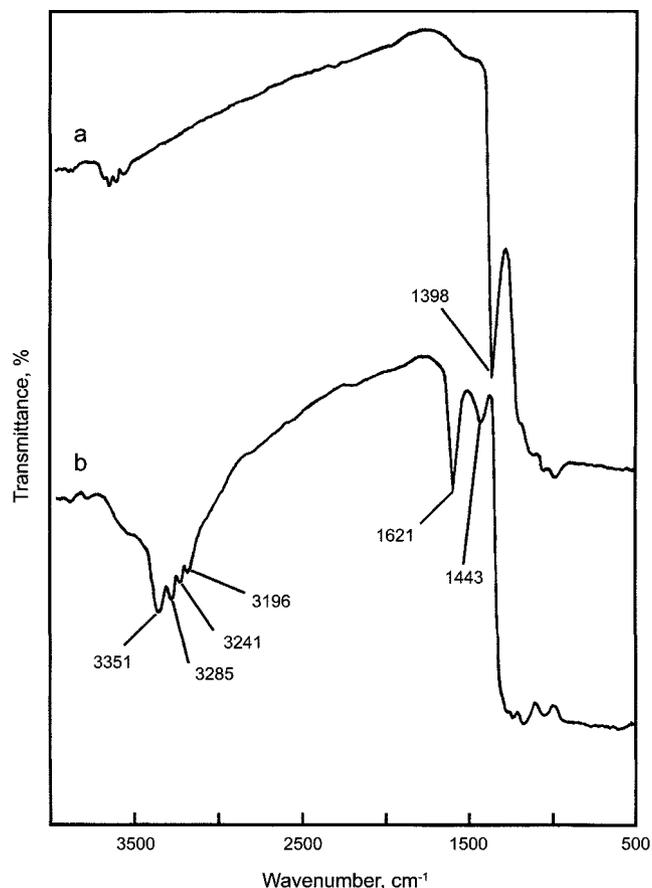


Fig. 5. Infrared spectra of NH₃ adsorbed on 20-NiSO₄/ γ -Al₂O₃: (a) background of 20-NiSO₄/ γ -Al₂O₃ after evacuation at 600 °C for 1 h, (b) NH₃ adsorbed on (a), where gas was evacuated at 230 °C for 1 h.

faces have made it possible to distinguish between Brönsted and Lewis acid sites [Sohn and Bae, 2000; Satsuma et al., 1988]. Fig. 5 shows the IR spectra of ammonia adsorbed on 20-NiSO₄/ γ -Al₂O₃ samples evacuated at 600 °C for 1 h. The absorption bands at 3,351 and 3,285 cm⁻¹ are assigned, respectively, to the asymmetric and symmetric vibration modes of the ammonia adsorbed on Lewis acid sites, while the bands at 3,241 and 3,196 cm⁻¹ are due to the asymmetric and symmetric vibration modes of ammonium ion adsorbed on Brönsted acid sites [Sohn and Bae, 2000; Satsuma et al., 1988]. The band at 1,443 cm⁻¹ is the characteristic peak of an ammonium ion, which is formed on the Brönsted acid sites; the absorption peak at 1,621 cm⁻¹ is contributed by ammonia coordinately bonded to Lewis acid sites [Sohn and Bae, 2000; Satsuma et al., 1988], indicating the presence of both Brönsted and Lewis acid sites on the surface of the 20-NiSO₄/ γ -Al₂O₃ sample. Other samples having different nickel sulfate content also showed the presence of both Lewis and Brönsted acids. As Fig. 5(a) shows, the intense band at 1,398 cm⁻¹ after evacuation at 600 °C is assigned to the asymmetric stretching vibration of S=O bonds having a high double bond nature [Yamaguchi, 1990; Sohn et al., 1990]. However, the drastic shift of the IR band from 1,398 cm⁻¹ to a lower wave number (not shown due to the overlaps of skeletal vibration bands of γ -Al₂O₃) after ammonia adsorption [Fig. 5(b)] 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 [Yamaguchi, 1990]. Acids stronger than $H_0 \leq -11.93$, which corresponds to the acid strength of 100% H_2SO_4 , are super acids [Tanabe et al., 1989; Yamaguchi, 1990; Olah et al., 1979; Arata, 1990]. The strong ability of the sulfur complex to accommodate electrons from a basic molecule such as ammonia is a driving force to generate superacidic properties [Tanabe et al., 1989; Yamaguchi, 1990; Sohn et al., 1990]. Consequently, $NiSO_4/\gamma-Al_2O_3$ catalysts would be solid superacids, in analogy with the case of metal oxides modified with a sulfate group [Sohn and Park, 2000; Sohn et al., 1995; Jin et al., 1986; Yamaguchi, 1990]. 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 $\gamma-Al_2O_3$ [Tanabe et al., 1989; Jin et al., 1986; Yamaguchi, 1990]. $NiSO_4/\gamma-Al_2O_3$ samples after evacuation at 500 °C for 1 h were also examined by color change method, using Hammett indicator in sulfuryl chloride [Sohn et al., 1996; Sohn and Ryu, 1993]. The samples were estimated to have $H_0 \leq -14.5$ indicating the formation of superacidic sites. In other words, the acid strength of $NiSO_4/\gamma-Al_2O_3$ becomes stronger by the inductive effect of S=O in the complex.

5. Catalytic Activities for Acid Catalysis

It is interesting to examine how the catalytic activity of acid catalyst depends on the acid property. The catalytic activities for the 2-propanol dehydration are measured and the results are illustrated as a function of $NiSO_4$ content in Fig. 6, where reaction temperatures are 160–180 °C. In view of Table 2 and Fig. 6, the variations in catalytic activity for 2-propanol dehydration are well correlated with

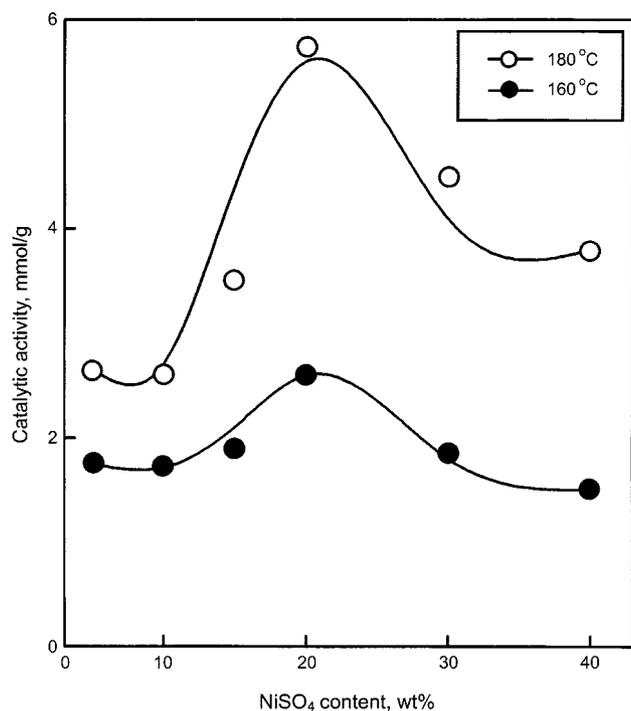


Fig. 6. Catalytic activities of $NiSO_4/\gamma-Al_2O_3$ for 2-propanol dehydration as a function of $NiSO_4$ content.

Table 2. Acidity and catalytic activity of $NiSO_4/\gamma-Al_2O_3$ for the 2-propanol dehydration and cumene dealkylation

Catalyst	Acidity, $\mu\text{mol/g}$	Catalytic activities	
		2-Propanol dehydration, ($\times 10^3$ mol/g) (180 °C)	Cumene dealkylation, ($\times 10^3$ mol/g) (450 °C)
5- $NiSO_4/\gamma-Al_2O_3$	262	2.10	0.71
10- $NiSO_4/\gamma-Al_2O_3$	383	2.83	1.08
15- $NiSO_4/\gamma-Al_2O_3$	450	3.48	2.49
20- $NiSO_4/\gamma-Al_2O_3$	526	5.68	4.68
25- $NiSO_4/\gamma-Al_2O_3$	478	5.05	3.70
30- $NiSO_4/\gamma-Al_2O_3$	433	4.51	2.77
40- $NiSO_4/\gamma-Al_2O_3$	337	3.76	2.18

the changes of their acidity, showing the highest activity and acidity for 20- $NiSO_4/\gamma-Al_2O_3$. It has been known that 2-propanol dehydration takes place very readily on weak acid sites [Sohn et al., 2002; Decanio et al., 1986]. 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 $SiO_2-Al_2O_3$ catalysts were found to increase 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].

Cumene dealkylation takes place on relatively strong acid sites of the catalysts [Sohn et al., 2002; Decanio et al., 1986]. Catalytic activities for cumene dealkylation against $NiSO_4$ content are pre-

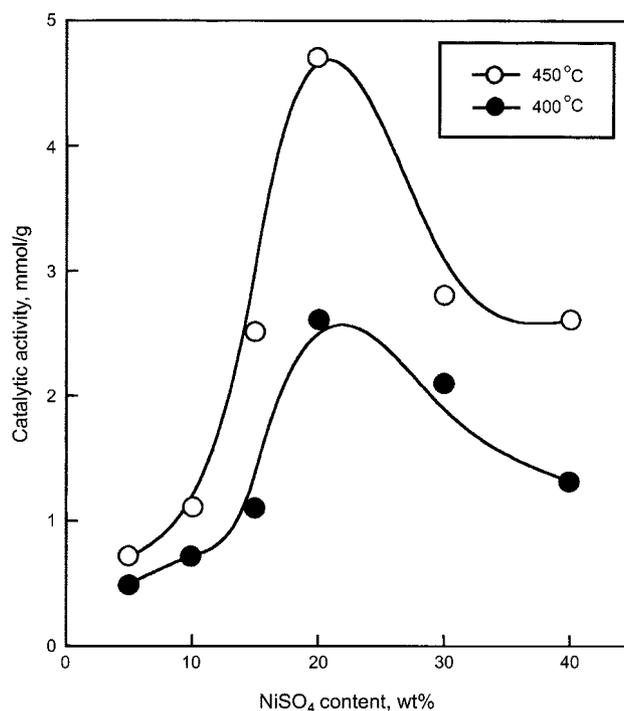


Fig. 7. Catalytic activities of $NiSO_4/\gamma-Al_2O_3$ for cumene dealkylation as a function of $NiSO_4$ content.

sented in Fig. 7, where reaction temperature is 400-450 °C. Comparing Table 2 and Fig. 7, the catalytic activities are also correlated with the acidity. The correlation between catalytic activity and acidity holds for both reactions, cumene dealkylation and 2-propanol dehydration, although the acid strength required to catalyze acid

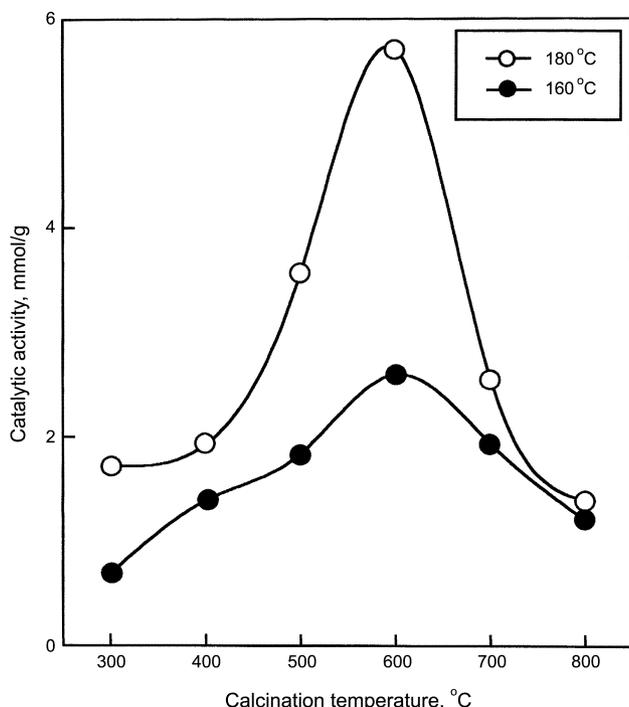


Fig. 8. Catalytic activities of 20-NiSO₄/γ-Al₂O₃ for 2-propanol dehydration as a function of calcination temperature.

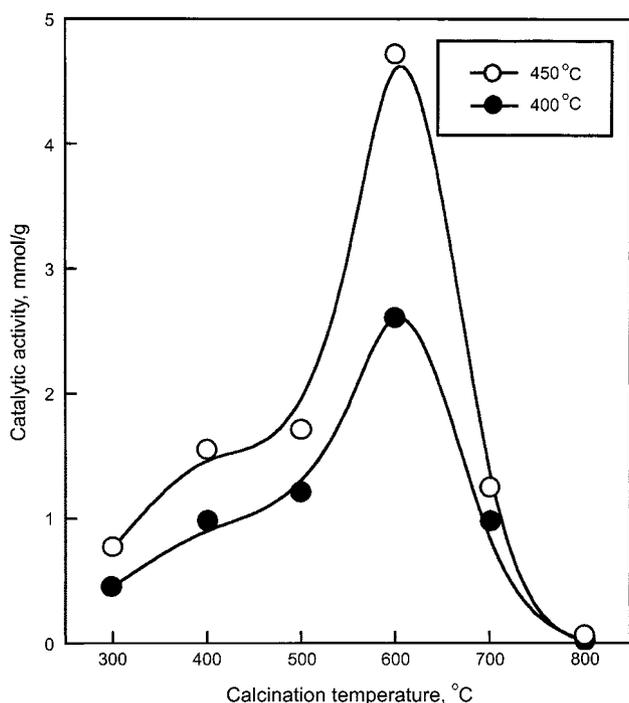


Fig. 9. Catalytic activities of 20-NiSO₄/γ-Al₂O₃ for cumene dealkylation as a function of calcination temperature.

reaction is different depending on the type of reactions. As seen in Figs. 6 and 7, the catalytic activity for cumene dealkylation, in spite of higher reaction temperature, is lower than that for 2-propanol dehydration.

Catalytic activities of 20-NiSO₄/γ-Al₂O₃ are plotted as a function of calcination temperature for 2-propanol dehydration in Fig. 8. The activities increased with the calcination temperature, giving a maximum at 600 °C and then the activities decreased. Catalytic activities of 20-NiSO₄/γ-Al₂O₃ for cumene dealkylation are also plotted as a function of calcination temperature in Fig. 9. The activities also exhibited a maximum at 600 °C. The decrease of activity for both reactions above 600 °C can be probably attributed to the fact that the surface area and acidity above 600 °C decrease with the calcination temperature.

CONCLUSION

This paper has shown that a combination of FTIR, DSC, and XRD can be used to perform the characterization of NiSO₄/γ-Al₂O₃ prepared by impregnation of powdered γ-Al₂O₃ with nickel sulfate aqueous solution followed by calcining in air. 20-NiSO₄/γ-Al₂O₃ calcined at 600 °C exhibited the highest catalytic activity. The high catalytic activity of NiSO₄/γ-Al₂O₃ was related to the increase of acidity and acid strength owing to the addition of NiSO₄. The correlation between catalytic activity and acidity holds for both reactions, cumene dealkylation and 2-propanol dehydration, although the acid strength required to catalyze acid reaction is different depending on the type of reactions.

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