

## 여러가지 水酸化니켈의 特性和 酸化니켈의 觸媒活性

孫宗洛·李東鎮

慶北大學校 工科大学 工業化學科

(1983년 7월 9일 접수)

## Properties of Various Nickel Hydroxides and Catalytic Activity of their Nickel Oxides

Jong-Rack Sohn and Dong-Jin Ri

*Department of Industrial Chemistry, Engineering College,  
 Kyungpook National University, Taegu, 635, Korea*

(Received; July 9, 1983)

### 요 약

각각 다른 출발물질로부터 네 종류의 수산화니켈을 제조하여 이들의 성질을 X-선회절, 열분석, 적외선스펙트라를 이용하여 조사하였다. 그리고 수산화니켈을 진공분해시켜 산화니켈촉매를 얻었으며 이들의 콩기름 수소화에 대한 활성을 비교 검토하였다. 그 결과 요소의 가수 분해로 제조된 수산화니켈은 반결정성의 수화된 구조였으며, 암모니아수나, 수산화나트륨으로 침전시켜 제조된 것은 brucite 형의 육방정계의 구조를 하고 있었다. 그리고 수산화니켈의 제조 방법 및 출발물질의 상이에 따라 여러 종류의 흡착종 즉 질산기, 황산기, 이산화탄소, 요소, 암모니아에 의한 흡수도가 적외선스펙트라에 나타났으며, 이 중에서 황산기종과 질산기 종은 430°C의 높은 진공온도에서도 상당히 남아 있었다. 이들 흡착종은 촉매활성에 상당히 영향을 미쳤다. 또한 NiO(N-U) 촉매가 가장 높은 촉매활성을 나타내었으며, 400°C에서 1.5 시간동안 진공시켰을 때에 촉매활성이 최고로 나타났다.

### ABSTRACT

Four kinds of nickel hydroxide were prepared from different starting materials, and their properties were studied by means of X-ray diffraction, thermal analysis, and IR spectra. The nickel oxide catalysts were prepared by decomposing these nickel hydroxides in vacuo and their catalytic activity was tested for the hydrogenation of soybean oil. Consequently, it was

found that nickel hydroxide prepared by urea hydrolysis was semicrystalline of hydrated structure, while the others, three kinds of nickel hydroxide precipitated by ammonium hydroxide or sodium hydroxide were all the same hexagonal system of brucite type. The various adsorbed species including nitrate ion, sulfate ion, carbon dioxide, ammonia, and urea were observed in IR spectra. Among these species, nitrate and sulfate species were so stable that they remained considerably even after evacuation at 430°C. These adsorbed species affected the catalytic activity profoundly. Also, it was found that NiO (N-U) catalyst exhibited higher catalytic activity than any other catalysts and showed a maximum activity after evacuation at 400°C for 1.5 hrs.

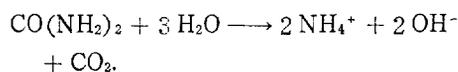
## 1. Introduction

Nickel catalyst for hydrogenation of organic compounds has been usually prepared by precipitation method.<sup>1-2</sup> However, it has been known that the catalytic activity of a catalyst is deeply affected by the method of catalyst preparation and the condition of pretreatment<sup>3-4</sup>. This seems to be responsible for the fact that the physical or chemical structure of a catalyst varies with the different method of preparation and the chemical species adsorbed on the surface affect profoundly the catalytic activities.

Arata and Hino<sup>5-9</sup> reported that remarkable increases in the surface acidity and in the catalytic activity of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub> were caused by treatment with sulfate ion, followed by calcination prior to crystallization. Recently, Tanabe et al.<sup>10</sup> found that Fe<sub>2</sub>O<sub>3</sub> obtained by hydrolysing iron-alum with urea showed high catalytic activity for the acid catalytic reaction which was explained in terms of the effectiveness of adsorbed sulfate ion.

In 1937, Willard and Tang<sup>11</sup> used the reaction of urea with water to precipitate Al<sup>3+</sup> ions from a homogeneous solution. At temperatures above 70°C urea reacts with water to

give the overall reaction,



The mechanism of this reaction was studied by Shaw and Bordeaux<sup>12</sup>. Since the urea molecules are distributed homogeneously in the solution, the OH ions are also generated homogeneously throughout the system and thus the occurrence of local OH<sup>-</sup> ion concentrations markedly higher than the average value is avoided. We also tried to prepare nickel hydroxide through a homogeneous precipitation method using urea as a precipitant.

In this paper, it is the object to study the properties of nickel hydroxides prepared by using various precipitants by means of infrared spectra, thermal analysis and X-ray diffraction, and to examine the catalytic activity of nickel oxides for the hydrogenation of soybean oil.

## 2. Experimental

Four kinds of nickel hydroxide were prepared from different starting materials as follows. An aqueous solution of nickel nitrate and urea was heated to about 90°C with stirring for 24 hours. The precipitation could be observed at about 1 hour of heating. The precipitate was filtered and washed with

distilled water at least 20 times, and dried in a drying oven at 100°C. The nickel hydroxide thus obtained was denoted by a symbol of Ni(OH)<sub>2</sub> (N-U) derived from starting materials. The second nickel hydroxide, Ni(OH)<sub>2</sub> (N-A) was precipitated from a solution of nickel nitrate with an aqueous solution of ammonia. The third nickel hydroxide, Ni(OH)<sub>2</sub> (N-S) was precipitated from a solution of nickel nitrate with a solution of sodium hydroxide. The fourth nickel hydroxide, Ni(OH)<sub>2</sub> (S-S) was precipitated from a solution of nickel sulfate with a solution of sodium hydroxide. These nickel hydroxides were filtered and washed with distilled water until nitrate ion and sulfate ion were not detected by diphenyl amine and barium salt solution, respectively. After drying at 100°C they were stored in a desiccator.

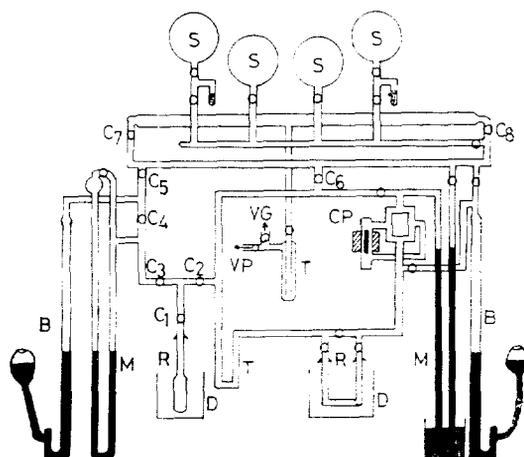
The nickel oxide catalyst was prepared from nickel hydroxide by decomposing it in vacuo in the reactor. The nickel oxide thus obtained was denoted by a symbol similar to that of nickel hydroxide. For example, NiO (N-U) means nickel oxide catalyst prepared by decomposing Ni(OH)<sub>2</sub>(N-U) in vacuo. Hydrogen from a commercial source was purified by passing through a liquid nitrogen trap. Soybean oil consisted of linoleic acid 51.2%, linolenic acid 8.5%, oleic acid 26.4% stearic acid 4.4%, and palmitic acid 9.2% was obtained from Jail Sugar Refining Co. and used after removing air in it.

To obtain IR spectra, nickel hydroxide powder was attached on the both sides of KBr disc by pressing at about 400 kg/cm<sup>2</sup> to prevent the collapse of pure Ni(OH)<sub>2</sub> disc due to the decomposition at the elevated temperature.

IR spectra of nickel hydroxide disc mounted in a heatable gas cell were recorded on a

JASCO IRA-2 spectrometer in the range of 4000~400 cm<sup>-1</sup> at room temperature. Then, the spectroscopic measurement and the degassing for at least 1 hour at several temperatures, 25°, 120°, 200°, 270°, 350°, and 430°C were repeated to examine the variation of Ni(OH)<sub>2</sub> spectra and to ascertain the adsorbed species during precipitation.

The catalytic activity for soybean oil hydrogenation was determined at 80~160°C by a conventional static system as shown in Fig. 1 following pressure change of hydrogen from an initial pressure of 440 torr. Fresh catalyst precursor of 0.05 gram was used for every run and decomposed at a different evacuation temperature for 2 hrs. And then, 5 ml of soybean oil was introduced into a



- VP : Vacuum pump
- VG : Vacuum gauge
- T : Trap
- S : Gas container
- CP : Circulation pump
- R : Reaction tube
- D : Dewar vessel
- M : Manometer
- B : Gas burette
- C : Cock

Fig. 1. Reaction apparatus for the soybean oil hydrogenation.

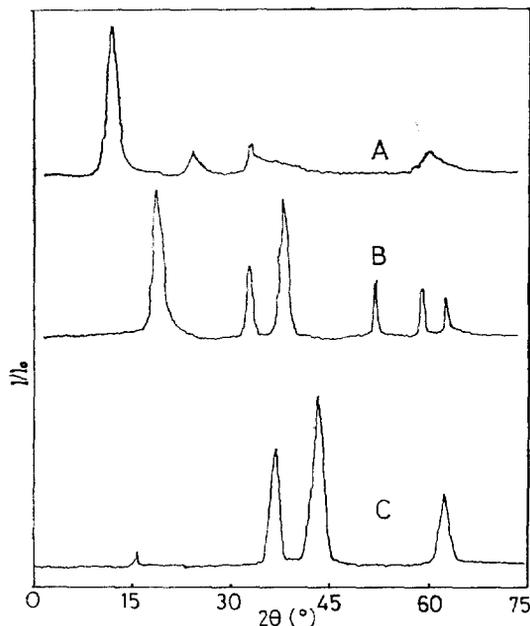
reactor and the catalyst was suspended in soybean oil by rotating a magnetic bar at a constant rate of 1000 rpm during reaction.

The specific surface area was determined by adsorption of nitrogen at  $-196^{\circ}\text{C}$ . X-ray diffractograms were taken by a Rigaku Denki Model D6C diffractometer using  $\text{Cu-K}\alpha$  radiation and nickel filter at 1000 cps. The thermal analysis was carried out with Rigaku Denki Thermoflex in air.

### 3. Results and Discussion

#### 3-1. X-ray diffraction pattern

Fig. 2. represents X-ray diffraction patterns of nickel hydroxides and nickel oxide prepared in this work. As shown in this figure, X-ray diffraction pattern of nickel hydroxide prepared by urea hydrolysis is very



A:  $\text{Ni}(\text{OH})_2$  precipitated by urea hydrolysis.  
 B:  $\text{Ni}(\text{OH})_2$  precipitated by ammonium hydroxide or sodium hydroxide.  
 C:  $\text{NiO}$  prepared by decomposing A or B sample in vacuo at  $400^{\circ}\text{C}$ .

Fig. 2. X-ray diffraction patterns.

different from that of nickel hydroxide prepared by using other precipitants, ammonium hydroxide or sodium hydroxide. This result indicates that different structures of nickel hydroxide are formed depending on the experimental condition and starting materials. Since three kinds of nickel hydroxide,  $\text{Ni}(\text{OH})_2(\text{N-A})$ ,  $\text{Ni}(\text{OH})_2(\text{N-S})$ , and  $\text{Ni}(\text{OH})_2(\text{S-S})$  exhibit the same X-ray diffraction pattern, these samples are believed to have all the same hexagonal layer structure of brucite type having a space group  $D_{3d}$ <sup>13</sup>. On the other hand, X-ray diffraction pattern of  $\text{Ni}(\text{OH})_2(\text{N-U})$  was very similar to that of hydrated magnesium hydroxide,  $\text{Mg}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  reported Shirasaki<sup>14</sup>, which was semi-crystalline and appeared like a petal under electron microscope. Therefore, it is probably considered that  $\text{Ni}(\text{OH})_2(\text{N-U})$  is hydrated nickel hydroxide, which is confirmed in DTA analysis as will be shown in the following section. With all the nickel oxide samples prepared by decomposing four kinds of nickel hydroxide in vacuo at  $400^{\circ}\text{C}$ , however, the same structure of cubic system was observed as shown in pattern C of Fig. 2.

#### 3-2. Thermal Analysis

In X-ray diffraction patterns, it was known that there are two different structures of nickel hydroxide. To examine the properties of nickel hydroxides more clearly, their thermal analysis was carried out and illustrated in Fig. 3. As for  $\text{Ni}(\text{OH})_2(\text{N-U})$ , two maxima of endothermic peak appeared at about  $100^{\circ}\text{C}$  and  $300^{\circ}\text{C}$ . It seems that the first peak in the range of  $80\sim 120^{\circ}\text{C}$  is attributed to the removal of hydrated water, while the second peak in the range of  $260\sim 340^{\circ}\text{C}$  is responsible for the decomposition of nickel hydroxide. The decomposition of nickel hydroxide is

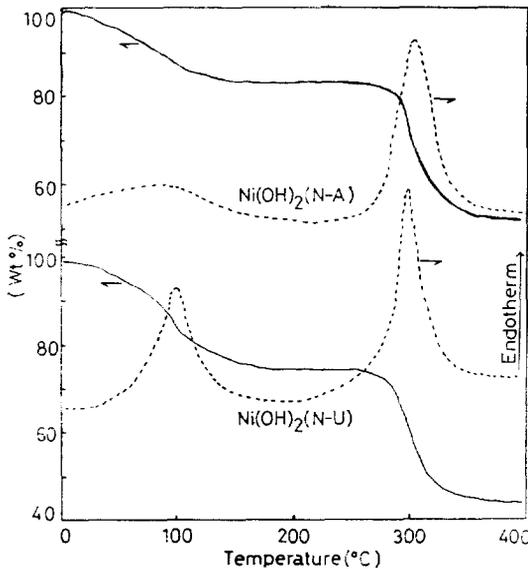


Fig. 3. DTA and TGA curves of nickel hydroxide.

known to begin at 230°C<sup>15</sup>. The above result makes sure that Ni(OH)<sub>2</sub>(N-U) is hydrated nickel hydroxide as indicated in X-ray diffraction pattern. As for Ni(OH)<sub>2</sub>(N-A), on the other hand, it is observed that there is only a peak due to the decomposition in the range of 250~340°C without observing the removal of hydrated water shown in the case of Ni(OH)<sub>2</sub>(N-U). It is considered that a very weak and broad peak in the range of 70~140°C is due to the removal of water adsorbed on the surface of the sample

### 3-4. IR spectra of Ni(OH)<sub>2</sub>(N-U)

Some IR spectra recorded during sequential heat treatments of the sample in vacuo are shown in Fig. 4. The spectrum after evacuation at 25°C for 1 hour showed a very broad absorption below 3660 cm<sup>-1</sup> attributed mainly to hydrated water, which was also confirmed in the deformation band of water at 1630 cm<sup>-1</sup>. Heat treatment in vacuo led to a considerable decrease of this band, indicating the removal of hydrated water. Degassing at high

her temperatures caused further removal of hydrated water and the sample became more transparent. The maximum of absorption band in these spectra is shown at 3660 cm<sup>-1</sup>. The high intensity and narrow width of this band is an evidence of the energetic homogeneity of the OH groups in nickel hydroxide. However, a considerable decrease of the intensity of this band is observed at the evacuation temperature of 270°C, indicating the occurrence of Ni(OH)<sub>2</sub>(N-U) decomposition. This result agrees with that of DTA. At the evacuation temperature of 350°C, the band of hydroxyl group is not observed, which means the complete decomposition of nickel hydroxide.

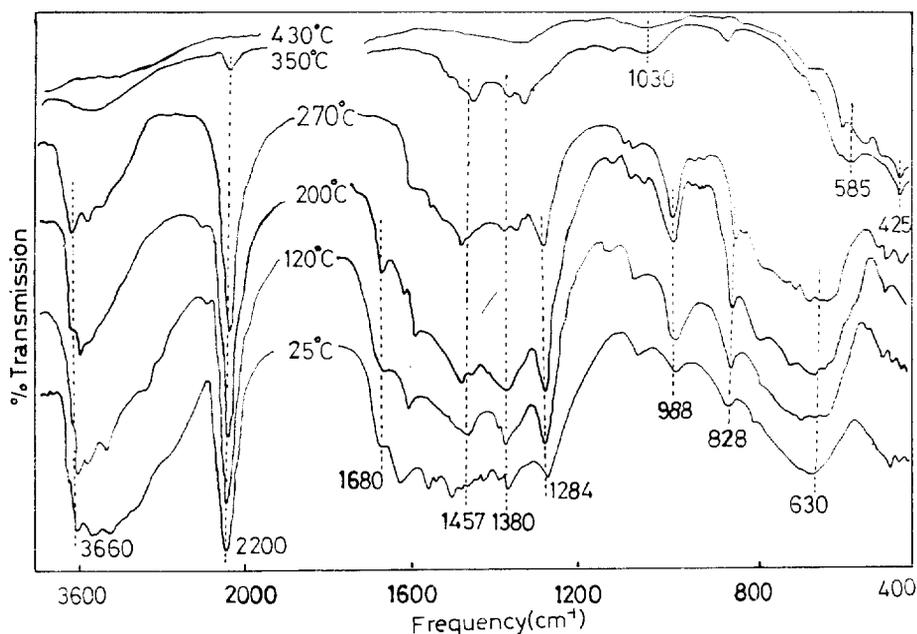
The intense peak at 2200 cm<sup>-1</sup> is assigned to the stretching vibration of linearly adsorbed carbon dioxide<sup>16</sup> which is formed during urea hydrolysis. This adsorbed species is very stable up to the evacuation temperature of 270°C, but disappears at above 350°C. Also, it is seen that there are various absorption bands in the region of 1680~800 cm<sup>-1</sup>. These bands are attributed to the absorption bands overlapped by nitrate ion, ammonia, and urea adsorbed on the surface of nickel hydroxide. In fact, the decomposition products formed from Ni(OH)<sub>2</sub>(N-U) were analyzed by a mass spectrometer during evacuation at temperatures between 250° and 550°C, and were found to be largely water and carbon dioxide including trace amounts of ammonia, nitrogen oxide, and nitrogen, indicating the presence of urea, nitrate ion, and ammonia. These results indicate that the species adsorbed during precipitation are scarcely removed owing to the strong interaction between adsorbed species and surfaces, although the precipitates are washed with distilled water many times. These bands are considerably stable even at

higher evacuation temperatures as shown in *Fig. 4*. However, at the evacuation temperature of 430°C, it is seen that most of the adsorbed species are desorbed, only leaving characteristic bands of nickel oxide<sup>17,18</sup> at 1030, 585, and 425 cm<sup>-1</sup>.

### 3-5. IR spectra of Ni(OH)<sub>2</sub>(N-A)

*Fig. 5* exhibits the IR spectra of Ni(OH)<sub>2</sub>(N-A) at various evacuation temperatures. The sharp band attributed to the OH stretching vibration of Ni(OH)<sub>2</sub> appears at 3675 cm<sup>-1</sup> which agrees very closely with 3676 cm<sup>-1</sup> reported by Erkelens<sup>19</sup>, together with the broad diffuse band below 3675 cm<sup>-1</sup> and that at 1630 cm<sup>-1</sup> due to adsorbed water. Compared with Ni(OH)<sub>2</sub>(N-U), degassing at higher temperatures caused further fast removal of adsorbed water as shown in *Fig. 5*. In consequence of this, the bands due to adsorbed water can not be seen after evacuation at 200°C for 1 hour.

It is probably considered that the triply splitted bands at 1500, 1387, and 1310 cm<sup>-1</sup> are attributed to the  $\nu_3$  asymmetric stretching mode of nitrate ion<sup>20</sup>. Then, these bands disappear simultaneously after evacuation at 350°C although a little amount of these bands remains even after evacuation at 430°C as shown in *Fig. 5*. The band at 993 cm<sup>-1</sup> is assigned to the  $\nu_1$  symmetric stretching mode of nitrate ion which is infrared inactive in the D<sub>3h</sub> anion, but the sharp feature results from activation of this mode through the adsorption of the anion on the surface. The assignment concerning nitrate  $\nu_1$  stretching mode can be more confirmed by the fact that the desorption behavior of bands at 1387 and 993 cm<sup>-1</sup> according to evacuation temperature is simultaneous as shown in *Fig. 5*. The above fact suggests that these bands result from the same chemical species. Pollard et al.<sup>21</sup> reported in IR study of group I nitrates that the sharp features at 1017 and 1030 cm<sup>-1</sup>



**Fig. 4.** IR spectra of Ni(OH)<sub>2</sub>(N-U) at various evacuation temperatures.

resulted from activation of nitrate  $\nu_1$  mode through the strong cation distortion of the anion. The adsorbed nitrate species is so stable that a little amount of this remains even after evacuation at  $430^\circ\text{C}$ , including the characteristic bands of nickel oxide at 1030, 584, and  $425\text{ cm}^{-1}$ .

The IR spectra of  $\text{Ni}(\text{OH})_2(\text{N-S})$  were similar to those of Fig. 5 in all the region except less intensity of nitrate ion so that they were not shown in this paper.

#### 6. IR spectra of $\text{Ni}(\text{OH})_2(\text{S-S})$

Fig. 6. represents the IR spectra of  $\text{Ni}(\text{OH})_2(\text{S-S})$  at various evacuation temperature. The pattern of these spectra is very different from those of Figs. 4 and 5. This seems to be responsible for the nickel hydroxide prepared by using nickel sulfate solution in place of nickel nitrate. The same results as in the other samples were gained in the region of OH stretching vibrations of nickel hy-

droxide and adsorbed water. However, new bands which were not observed in the other samples appeared below  $1200\text{ cm}^{-1}$  as shown in Fig. 6. The new bands at 1389, 1110, 1038, 925, and  $613\sim 710\text{ cm}^{-1}$  are attributed to the adsorbed sulfate ion because these bands are not observed in the other samples. Examining these spectra in detail, it seems like that there are at least two different adsorbed species. The first species which appears at  $1380\text{ cm}^{-1}$  is relatively stable up to the evacuation temperature of  $270^\circ\text{C}$ , but desorbs after evacuation at  $350^\circ\text{C}$ . This band is assigned to asymmetric  $S=0$  stretching mode of which frequency is rather closer to  $1440\sim 1350\text{ cm}^{-1}$  region<sup>22</sup> of covalent sulfates than to  $1160\sim 1030\text{ cm}^{-1}$  region of metal sulfates<sup>23</sup>.

The second species which appears doubly at 1100 and  $1038\text{ cm}^{-1}$  is very stable even after evacuation at  $430^\circ\text{C}$ . Hino and Arata<sup>6</sup> reported that the  $\text{ZrO}_2$  catalyst treated with sulfuric acid showed a superacid strength of

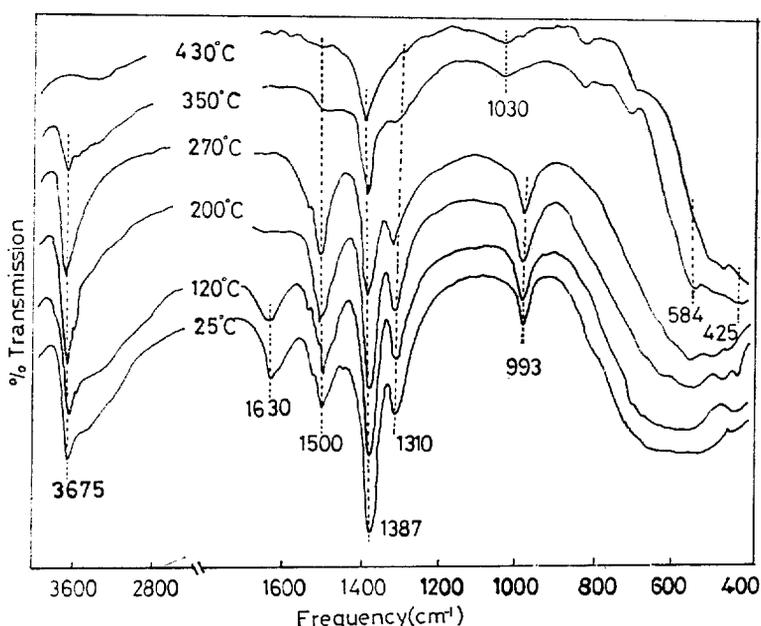


Fig. 5. IR spectra of  $\text{Ni}(\text{OH})_2(\text{N-A})$  at various evacuation temperature.

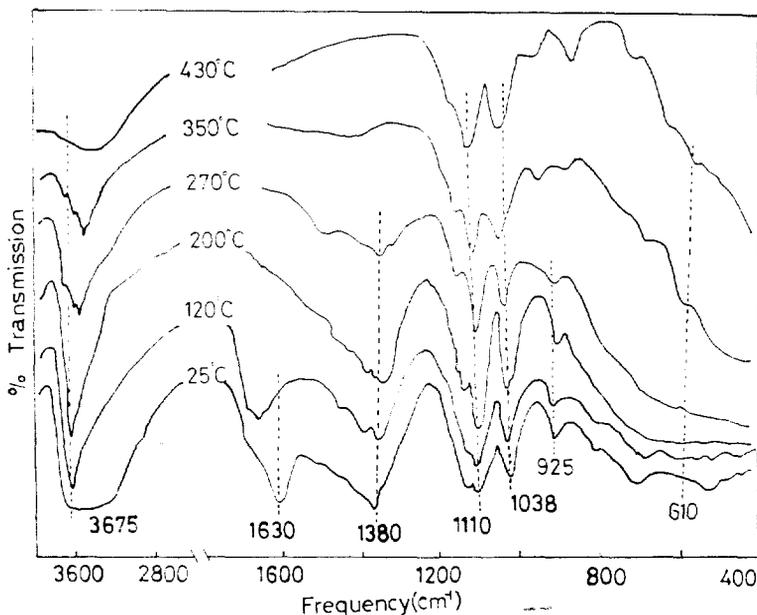


Fig. 6. IR spectra of  $\text{Ni}(\text{OH})_2(\text{S-S})$  at various evacuation temperatures.

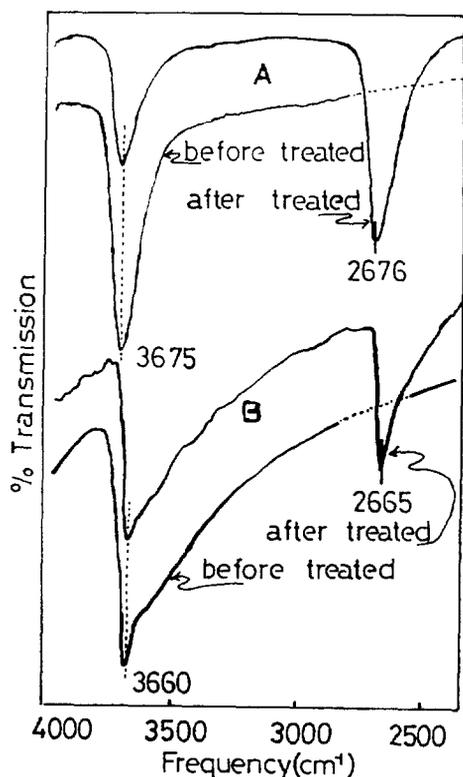
$H_0 \leq -13.75$ , with heat-treatment, even at  $800^\circ\text{C}$ , indicating that the adsorbed sulfate ion is very stable on the surface. These bands are assigned to asymmetric  $\text{SO}_4^{2-}$  stretching mode which is usually observed in inorganic sulfate ion<sup>23</sup>.

It is considered that the weak band near  $925\text{cm}^{-1}$  is attributable to the symmetric  $\text{SO}_4^{2-}$  stretching. The symmetric  $\text{SO}_4^{2-}$  stretching is normally forbidden by symmetry but may occasionally be seen as a weak band near  $1000\text{cm}^{-1}$  by the break of symmetry through adsorption<sup>20,24</sup>. The band near  $610\text{cm}^{-1}$  is assigned to  $\nu_4$  vibrational mode of adsorbed sulfate ion.

### 3-7. IR spectra of $\text{Ni}(\text{OH})_2$ treated with $\text{D}_2\text{O}$

The capacity for deuterium exchange was investigated with nickel hydroxide samples. The samples were first evacuated at  $200^\circ\text{C}$  to remove hydrated water or adsorbed water, and treated with  $\text{D}_2\text{O}$  at room temperature

for 12 hours followed by evacuation at  $200^\circ\text{C}$ . Deuteration of  $\text{Ni}(\text{OH})_2(\text{N-A})$  caused the sharp intense band observed at  $3675\text{cm}^{-1}$  to shift to  $2676\text{cm}^{-1}$ . For  $\text{Ni}(\text{OH})_2(\text{N-U})$ , the band at  $3660\text{cm}^{-1}$  was shifted to  $2665\text{cm}^{-1}$  as illustrated in Fig. 7. The bands at  $2676$  and  $2665\text{cm}^{-1}$  are assigned to the stretching vibrations of the structural OD groups formed as a result of the partial exchange of OH for OD. This is supported by the frequency ratio,  $\nu_{\text{OH}}/\nu_{\text{OD}} = 1.37$  in both samples. Similar spectral features were also observed for other two samples. With  $\text{Ni}(\text{OH})_2(\text{N-U})$  treated with  $\text{D}_2\text{O}$  followed by evacuation at  $200^\circ\text{C}$ , the broad diffuse bands are observed below  $3660$  and  $2665\text{cm}^{-1}$  respectively. These are attributed to the hydrated water,  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively. The broad diffuse nature of these bands suggests that they arise from lattice modes of the hydrogen bonded hydroxyl layers. Comparing spectra between two samples in Fig. 7, it is supposed that it is more difficult to remove water from nickel



A :  $\text{Ni}(\text{OH})_2(\text{N-A})$   
 B :  $\text{Ni}(\text{OH})_2(\text{N-U})$

Fig. 7. Shift in OH stretching band of nickel hydroxide through deuterium substitution. Evacuation temperature :  $200^\circ\text{C}$ .

hydroxide of hydrated structure than from nickel hydroxide of brucite type, for we can not observe the absorption bands due to water in IR spectra of  $\text{Ni}(\text{OH})_2(\text{N-A})$  after evacuation at  $200^\circ\text{C}$ .

### 3-8. Catalytic activity for the hydrogenation of soybean oil

Since the various adsorbed species remain considerably after evacuation at higher temperatures as mentioned, which depends on the kind of starting materials and preparation methods, it is expected that these adsorbed species will affect the catalytic activity. Four

catalysts were tested for their effectiveness of the soybean oil hydrogenation. It was found that on four kinds of nickel oxide, hydrogen was continuously consumed as shown for  $\text{NiO}(\text{N-U})$  in Fig. 8 although the catalytic activity was affected on the catalyst preparation method and decomposition temperature. Since the reaction rate was slow at the reaction temperature of  $80^\circ\text{C}$ , all the reactions hereafter were carried out at  $120^\circ\text{C}$ .

Catalytic activity has frequently been found to be dependent on the temperature at which the catalyst precursor has been pretreated<sup>25</sup>. In Fig. 9, the hydrogenation activities of catalysts are plotted against the evacuation temperature at which the catalyst was pretreated for 2 hrs. The catalytic activity was expressed as the amount of hydrogen consumed in the initial 8 minutes. For  $\text{NiO}(\text{N-U})$ , the catalytic activity appears above  $300^\circ\text{C}$  reaching a maximum at  $400^\circ\text{C}$ . Comparing the intensity of adsorbed  $\text{CO}_2$  in Fig. 4 with the catalytic activity of  $\text{NiO}(\text{N-U})$ , it can be seen that there is a correlation between them. Namely, the abrupt increase of activity from  $300^\circ\text{C}$  to  $350^\circ\text{C}$  is due to the desorption of  $\text{CO}_2$  adsorbed on the surface of  $\text{NiO}(\text{N-U})$ . As shown in Fig. 4, the intensity of adsorbed  $\text{CO}_2$  decreased remarkably after evacuation at  $350^\circ\text{C}$ . Also we can not see the peak of  $\text{CO}_2$  after the evacuation temperature of  $400^\circ\text{C}$  at which a maximum activity was obtained. From the above results, it is very likely that the active sites for hydrogenation are formed mainly by desorption of  $\text{CO}_2$  adsorbed on  $\text{NiO}(\text{N-U})$  catalyst. The remarkable decrease at the evacuation temperature of  $450^\circ\text{C}$  is probably explained in terms of the decrease of specific surface area of the catalyst due to sintering at higher temperature. The specific surface area of nickel oxides at

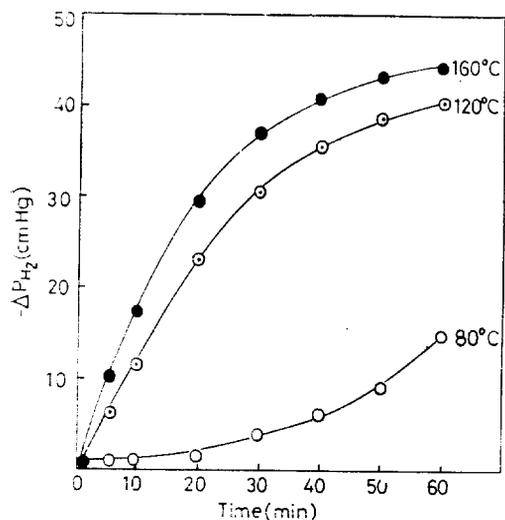


Fig. 8. Pressure change during the course of soybean oil hydrogenation over NiO(N-U) at various reaction times. NiO(N-U) was prepared by decomposing at 400°C.

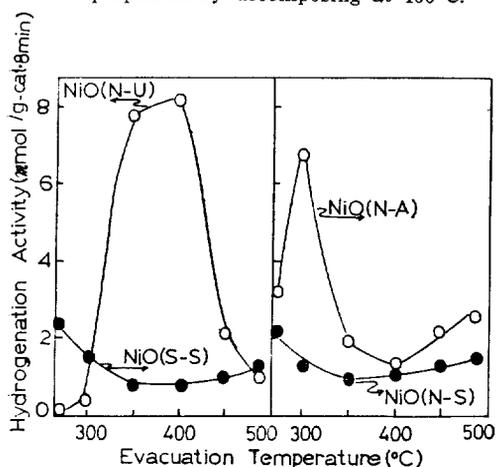


Fig. 9. Variation of the catalytic activity with evacuation temperature for the soybean oil hydrogenation. Evacuation period: 2 hrs.

various decomposition temperatures for 2 hrs is listed in Table 1.

The variation of catalytic activity with evacuation time at 400°C is illustrated in Fig. 10. The activity appeared most highly after evacuation for 1.5 hrs but dropped suddenly after 3 hrs due to the sintering of catalyst. Therefore, in this work, the decomposition of all nickel hydroxides was carried out for

Table 1. Specific surface area of nickel oxides at various decomposition temperatures. (m<sup>2</sup>/g)

Decomposition temperature(°C)	250	300	350	400	450	500
NiO(N-U)	124	136	130	114	67	61
NiO(N-A)	155	166	127	100	76	71
NiO(N-S)	76	69	51	39	30	25
NiO(S-S)	90	86	81	64	55	46

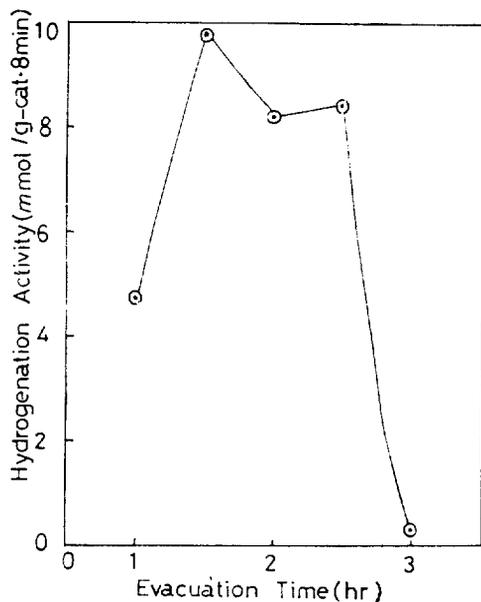


Fig. 10. Variation of the catalytic activity of NiO(N-U) with evacuation time at 400°C.

2 hrs constantly.

For NiO(N-A) catalyst, the pattern of catalytic activity against decomposition temperature is different from that of NiO(N-U), exhibiting a maximum activity at 300°C. At 350°C, however, the catalytic activity dropped suddenly unlike NiO(N-U) catalyst of which catalytic activity was very high at this temperature. This fact indicates that the formation mechanism of active site in two catalysts is different each other. Although the adsorbed nitrate species remained considerably after evacuation at 270~350°C as shown in Fig. 5.

a maximum catalytic activity at 300°C suggests that the active site is not formed from the desorption of nitrate species. It has been known that nickel metals are formed on the surface of nickel oxide when nickel hydroxide is decomposed in vacuo<sup>26,27</sup>. In case of NiO (N-A), it is likely that the active site is attributed to the nickel metal formed during decomposition in vacuo. The remarkable drop of activity after evacuation at 350°C is probably due to two factors. It is considered that main one is the decrease of surface area as shown in *Table. 1*, while minor one is the oxidation of active site which was brought out by the decomposition of adsorbed nitrate species. The detection of NO from NiO(N-A) by a mass spectrometer supports the above result.

As for NiO(N-S) and NiO(S-S) catalysts, the patterns of catalytic activity are very similar each other as shown in *Fig. 9*, not exhibiting a maximum point. Comparing with NiO(N-A), these catalysts exhibit not only low activity but also small surface area. As shown in *Fig. 6*, sulfate species adsorbed on NiO(S-S) remains considerably even after evacuation at 430°C. In case of NiO(N-S), nitrate species remains considerably in its IR spectra although the IR spectra are not shown in this paper. It is sure that these adsorbed species work as catalyst poison and deactivate the catalytic activity.

### Conclusion

The nickel hydroxide prepared by urea hydrolysis was semicrystalline of hydrated structure while the others, three kinds of nickel hydroxide precipitated by ammonium hydroxide or sodium hydroxide were all the same hexagonal system of brucite type. The

various adsorbed species including nitrate ion, sulfate ion, carbon dioxide, ammonia, and urea were observed in IR spectra differently depending on the preparation method and starting materials. These adsorbed species affected the catalytic activity for the soybean oil hydrogenation.

NiO(N-U) catalyst prepared by urea hydrolysis exhibited higher catalytic activity than any other catalysts and showed a maximum catalytic activity after evacuation at 400°C for 1.5 hrs.

### References

1. V.C.F. Holm and A. Clark, *J. Catal.*, 11 (1968), 305.
2. P.C. Gravelle and S.J. Teichner, *Advan. Catal.*, 20(1969), 167.
3. K. Morikawa, T. Shirasaki, and M. Okada, *Advan. Catal.*, 20(1969), 97.
4. K. Morikawa and F. Nozaki, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 64(1961), 898, 1562, 1568.
5. M. Hino and K. Arata, *J. Chem. Soc., Chem. Comm.*, (1979), 1148.
6. M. Hino and K. Arata, *ibid*, (1980), 851.
7. M. Hino and K. Arata, *J. Am. Chem. Soc.*, 101(1979), 6439.
8. M. Hino and K. Arata, *Chem. Lett.*, (1979), 477.
9. K. Arata and M. Hino, *ibid*, (1980), 1479.
10. T. Yamaguchi, Y. Kayo, and K. Tenabe, *Shokubai*, 24(1982), 82.
11. H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Anal. ed.*, 9 (1937), 357.
12. W.H.R. Shaw and J.J. Bordeaux, *J. Am. Chem. Soc.*, 77(1955), 4729.
13. F. Kober, *J. Electrochem. Soc.*, 112(1965), 1064.
14. T. Shirasaki, *Electro. Chem.*, 29(1961), 656, 708.
15. G.F. Hüttig and A. Pater, *Z. Anorg.*

- Chem., 189(1930), 183.
16. L.H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, 1960. pp. 66~67.
  17. V.N. Fillimonov, *Kinetika Kataliz*, 4 (1963), 367.
  18. M. Viltange, *Anal. Chem. Acta*, 53(1971) 169.
  19. J. Erkelens and S.H. Eggik-Du Burk, *Recueil*, 92(1973), 658.
  20. F.A. Miller and C.H. Wilkins, *Anal. Chem.*, 24(1952), 1253.
  21. G. Pollard, N. Smyrl, and J.P. Devlin, *J. Phys. Chem.*, 76(1972), 1826.
  22. L.J. Bellamy, "The Infrared Spectra of Complex Molecules," Mathuen, London, John Wiley, New York, 1964, pp. 357~364.
  23. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," third edition, John Wiley, New York, 1978, pp. 239~242.
  24. N.B. Colthup, L.H. Daly, and S.E. Wiberly, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, 1964. pp. 311.
  25. J.R. Sohn and A. Ozaki, *J. Catal.* 59 (1979), 303.
  26. S.J. Teichner and J.A. Morrison, *Trans. Faraday Soc.*, 51(1955), 961.
  27. R.B. Fahim and A.I. Abu-Shady, *J. Catal.* 17(1970), 10.