

EFFECTS OF OXIDATION OF LaNi_5 ON Ni DISPERSION

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It is known that the catalytic activity of LaNi_5 increases during CO hydrogenation due to a structure change into $\text{Ni/La}_2\text{O}_3$ by oxygen. Oxidation treatment is therefore thought to be useful in controlling nickel dispersion on the surface area. However, few studies of the relation between oxidation of LaNi_5 and nickel dispersion have been made. Consequently, in this study the effects of oxidation on nickel dispersion under various oxidation temperatures and uptakes of oxygen per total weight were examined.

Introduction

Industrially, most catalysts are used in the form of supported metals. This allows more economical use of expensive transition metals dispersed over supports such as active alumina or kieselgur, which are highly.

Recently, however, considerable attention has been paid to techniques for producing hyperfine metal particles and a great deal of work has also been done on producing catalysts, emphasizing improved dispersion.

However, a great deal of experimental work will be necessary on techniques for dispersing metals on supports. Moreover, the influence of different supports and calcining and reducing temperatures on dispersion is not fully understood. In addition, techniques for producing hyperfine metals are far from the stage of practical application. In this study, the relations between dispersion and various influencing factors were examined by varying oxidation temperature and oxygen uptake, using LaNi_5 as the starting material. Attention was focused on oxidation treatment, because rare earth intermetallic compounds (LaNi_5 , CeNi_5 , SmNi_5 , etc.) had been found to exhibit the feature that catalytic activity increases during CO hydrogenation, this being attributed to the transformation of LaNi_5 into Ni well-dispersed on La_2O_3 by oxidation.^{4,8)} The present study showed that nickel dispersion of oxidized LaNi_5 was as high as for conventional supported catalysts, although nickel weight content was about ten times as great as in the case of conventionally supported catalysts.

1. Experimental

1.1 Materials

La (99.8 wt% purity, 0.2 wt% other rare earths) and Ni (99.97 wt% purity, 0.03 wt% Cu, Co or Fe) were mixed at a given atomic ratio ($\text{Ni/La}=5$) and the mixture was induction-melted in a water-cooled copper boat in an argon atmosphere. The formation of LaNi_5 was elucidated by X-ray diffraction. LaNi_5 was then screened to 100/170 mesh.

1.2 Experimental apparatus with thermogravimeter

As shown in Fig. 1, weight measurement was performed by a thermogravimeter (Shimadzu TG-30), and gas samples were analyzed with a 6-way valve by TCD (14) and FID (15), using active carbon and VZ-10 columns, respectively. A platinum sample cell (8 mm diameter) was used as the reactor, which was hung on the balance by a quartz string and covered with a quartz tube (25 mm diameter). The catalyst was well-dispersed on the sample cell. Temperature was measured by a thermocouple, which was placed 2 mm above the reactor, and the heating rate was kept at $20 \text{ K} \cdot \text{min}^{-1}$ by means of an electric furnace.

1.3 Experimental procedure for oxidation treatment

1.3.1 Parameters with oxidation treatment
Oxidation temperature T [K] and moles of oxygen passing over the catalyst Q [O_2 mol/initial weight of LaNi_5] were employed as parameters of oxidation. A variety of analytical methods (described in the following sections) were employed to characterize the catalysts after oxidation treatment under different conditions.

1.3.2 Procedures under different oxidation conditions

(1) Weight measurement

100 mg of screened LaNi_5 (100/170 mesh) was set

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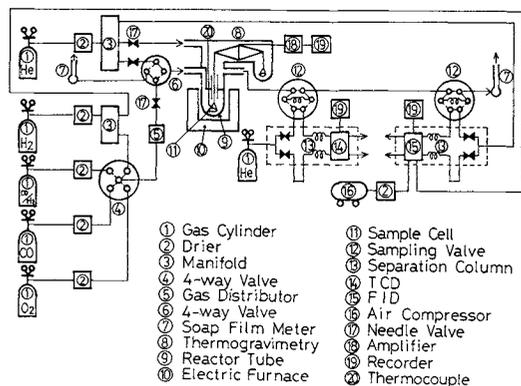


Fig. 1. Experimental apparatus.

on the sample cell and initial weight was measured by a thermogravimeter. The air in a quartz tube was purged by helium and the absence of impurities was confirmed by TCD and FID. The reactor (9) was then heated using an electric furnace (10). After the desired temperature was obtained and the weight change had become negligible, various amounts of oxygen controlled by a needle valve (17) were passed through the reactor, using a 4-way valve. At this point, partial pressure of oxygen was controlled by a gas distributor (5). Weight change was then measured by a thermogravimeter and recorded continuously.

(2) X-Ray diffraction

Transformation of LaNi_5 into La_2O_3 , Ni and NiO was determined by X-ray diffraction. Ni crystallite size was determined by X-ray line-broadening measurement of the Ni peak at $2\theta = 44.5^\circ$ (Cu-K_α), using Scherrer's equation.⁹⁾ Ni dispersion was calculated directly from the value of Ni crystallite size on the assumption that the Ni crystallite is cubic.

(3) BET surface area

Powdering and cracks were examined by measuring surface area, which was determined at liquid nitrogen temperature by means of nitrogen adsorption.

(4) Observation of vertical section of samples after emery grinding³⁾

To verify the validity of the core model,⁶⁾ the vertical section of oxidized LaNi_5 was observed after it had been ground with emery. Powdered samples were first embedded in methyl methacrylate (Kulzer Ltd. Technovit 4004) and ground with emery (#2000). Then, optical micrographs were taken.

(5) Measurement of particle size by optical microscope

To evaluate particle size distribution of samples before and after oxidation, approximately 2000 particles were photographed, using an optical microscope.

1.4 Measurement of initial activity for CO hydrogenation

100 mg of oxidized LaNi_5 was placed on a sample

cell in a thermogravimeter and the air in a quartz tube was purged with helium as described in 1.3.2. Samples were then reduced with hydrogen ($61 \mu\text{mol}\cdot\text{s}^{-1}$) at 723 K. After reduction, synthesis gas ($\text{CO}/\text{H}_2 = 3/7$) was passed over samples at a total flow rate of $61 \mu\text{mol}\cdot\text{s}^{-1}$ at 673 K, and initial activity was measured by an ordinary flow technique.

2. Results and Discussion

2.1 Transformation by oxidation

Figure 2 shows the time course of weight increase ω ($= \Delta W/W_0$) caused by oxidation. When both La and Ni are completely oxidized into La_2O_3 and NiO (thermodynamically, La_2O_3 and NiO are possible forms of oxides), the weight increase can be calculated to be 24.0%, whereas the value is 5.5% when only La is completely oxidized.

Accordingly, at point C of the weight increase curve of Fig. 2, both La and Ni were considered to have been entirely oxidized, while at point D, where reduction treatment with hydrogen was conducted at 723 K, only La_2O_3 was considered to exist as an oxide. To confirm these phenomena, X-ray diffraction patterns were taken of fresh LaNi_5 and oxidized LaNi_5 at each point (A, B, C and D). As shown in Fig. 3, peaks of only NiO and La_2O_3 were observed at point C, and it was found from points A and B that La oxidation was completed at point A because the NiO peaks increased from point A to B, whereas the La_2O_3 peaks showed no increase in this range.

The selective oxidation of La can be reconfirmed by thermodynamical data: the standard free energy of La_2O_3 formation is more than ten times that of NiO. It was also confirmed experimentally that La_2O_3 cannot be reduced under these conditions.

The selective oxidation of La was much more obvious at 623 K, and the weight increase was no more than 5.5%. It was evident from X-ray diffraction information that only La was oxidized at 623 K.

Considering these facts, if dispersion is determined by the stage of oxidation, it seemed possible to oxidize La selectively and to control Ni dispersion by maintaining an appropriate oxidation temperature.

2.2 Oxidation in low and high temperature regions

As shown in Fig. 2, the final weight increase and oxygen uptake necessary to reach the final weight increase differed greatly for low and high temperature oxidation. In fact, Ni oxidation seems to have an oxidation point between 623 K and 673 K.

I) Low-temperature oxidation (623 K)

Only LaNi_5 is oxidized. No powdering is observed because the effect of volume expansion with La oxidation is very slight, with the value of volume change ratio when La changes into La_2O_3 being only 1.18.

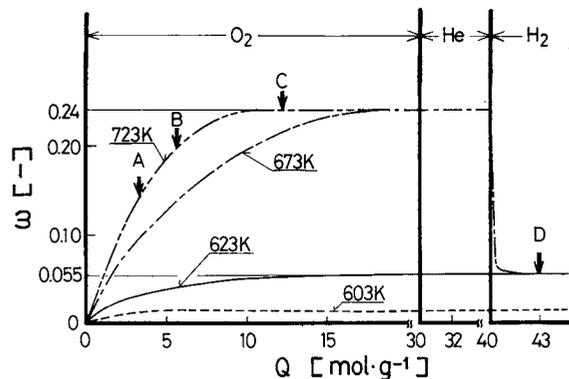


Fig. 2. Time course of weight change under O_2 , He and H_2 atmosphere at various temperatures.

O, $LaNi_5$ (100/170 mesh) before oxidation; A, point of 14.0 wt% increase at 723 K; B, point of 20.0 wt% increase at 723 K; C, point of 24.0 wt% increase at 723 K where both La and Ni were completely oxidized; D, point of 5.5 wt% increase from initial weight by reduction with hydrogen at 723 K after oxidation.

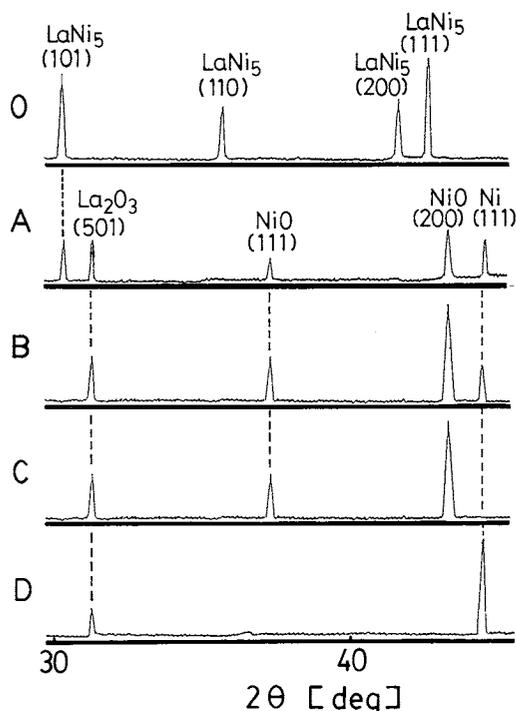


Fig. 3. Powder X-ray diffraction patterns of each point in Fig. 2.

II) High-temperature oxidation (673, 723 K)

Both La and Ni are oxidized. Powdering occurs to some extent because the volume change ratio for Ni oxidation is 1.65, indicating that the effect of volume expansion is considerable. Below 623 K, e.g. at 603 K in Fig. 2, La oxidation was not completed, and dispersion changed during synthesis gas reaction after oxidation treatment. Therefore, samples were subjected to oxidation treatment at temperatures higher than 623 K.

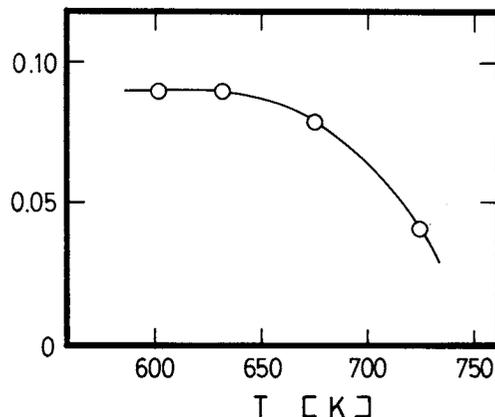


Fig. 4. Effects of oxidation temperatures on dispersion.

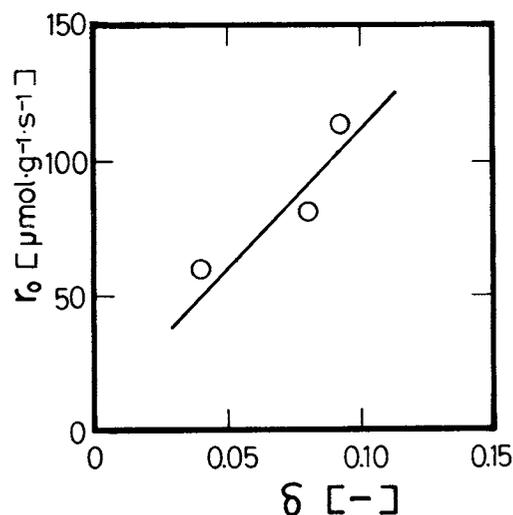


Fig. 5. Effects of dispersion on initial activity.

2.3 Effects of oxidation temperature on dispersion

To study the effect of dispersion on oxidation temperature, dispersion of each sample was measured, as shown in Fig. 4. 100 mg of $LaNi_5$ was oxidized until no further weight increase was observed at 603 K, 623 K, 673 K or 723 K, and then reduced by hydrogen ($61 \mu\text{mol}\cdot\text{s}^{-1}$) at 723 K. Figure 4 clearly shows that dispersion was in inverse proportion to oxidation temperatures. The results agree with the case of metal-supported catalysts.^{1,7)} At temperatures higher than 723 K, sintering of Ni particles appears to occur easily, and nickel oxide diffuses on the surface rapidly.

2.4 Relation between initial activity and dispersion

To examine the relation between initial activity and dispersion, samples which were completely oxidized at various temperatures and reduced at 723 K, as in 2.2, were subjected to synthesis gas reaction, and initial CO conversion was measured. It should be borne in mind that reduction treatment was found experimentally to have no effect on dispersion. The results are shown in Fig. 5. Over 99% of gases produced was methane. It should be mentioned that

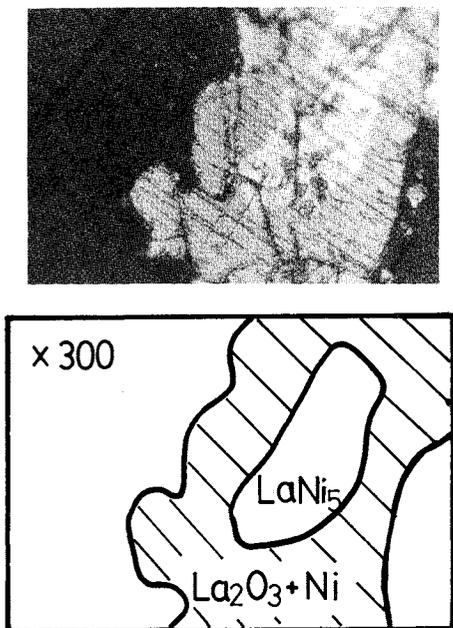


Fig. 6. Optical micrograph of vertical section of oxidized LaNi_5 (mainly La oxidation).

the dispersion values correspond to the number of Ni atoms on the surface because all samples were reduced to 5.5%, which indicates that all NiO was reduced to Ni. As shown in Fig. 5, initial activity was approximately proportional to dispersion, which implies that turnover frequency TF (defined as molecules of CO consumed per second per Ni atom on the surface) did not decrease with an increase of dispersion up to 9% at the stage of complete oxidation of La.

According to Carter *et al.*,²⁾ TF of Ni/SiO₂, Al₂O₃ increases to 20-fold as dispersion doubles from 0.1–0.2. In considering an explanation for the effect of dispersion on TF , they noted that the concentration of defects in the metal crystallites, which are responsible for catalytic activity, increases more rapidly than the surface area, thus causing an increase in TF . Consequently, it is clear that the catalyst obtained from LaNi_5 has different properties from supported metals with regard to the relation between dispersion and TF .

2.5 Findings relating to dispersion at low temperature oxidation

2.5.1 Observation of a vertical section of emery-ground sample To observe the vertical section of a La-oxidized sample, 100 mg of LaNi_5 was oxidized at 623 K to the point of 5% weight increase. Figure 6 shows the vertical section of sample after it had been ground with emery (#2000). La_2O_3 clearly developed into the center of the LaNi_5 particle, adhering closely to the LaNi_5 layer. There was a clear interface of La_2O_3 (black part in Fig. 6) and LaNi_5 (white part in Fig. 6). The facts show that the core model was valid

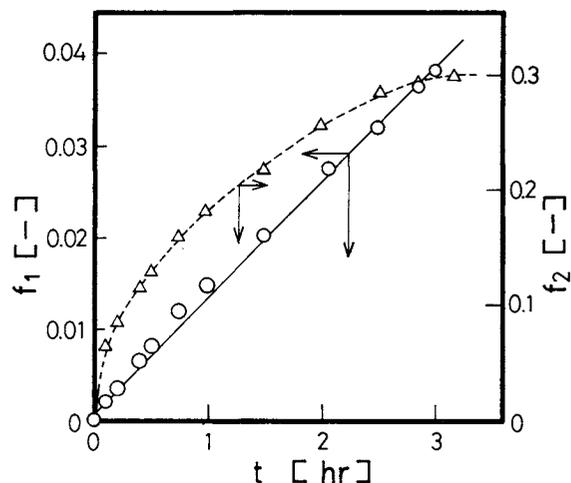


Fig. 7. Determination of rate-controlling step.

for La oxidation.

2.5.2 Model of selective oxidation of La in LaNi_5 At 623 K, La was selectively oxidized, and no change of particle size owing to powdering was observed. Consequently, the core model could be used. At an oxygen flow rate of $61 \mu\text{mol} \cdot \text{s}^{-1}$, in which gas film diffusion resistance was negligible, the correlation between f_1 or f_2 (expressed in Eqs. (1) and (2)) and the oxidation time t (which expressed the time after oxygen (0.10 MPa) had been passed through 100 mg of LaNi_5 (100/170 mesh)), was examined by plotting to determine a rate-controlling step (Fig. 7).

$$f_1 = 1/2 - (1 - X/\mu)^{2/3} / 2 - X/3\mu \quad (1)$$

(Ash Diffusion Control)

$$f_2 = 1 - (1 - X/\mu)^{1/3} \quad (2)$$

(Chemical Reaction Control)

As f_1 was proportional to t , ash diffusion was found to be a rate-controlling step.

Diffusion coefficient D of oxygen was evaluated from the gradient of the line,

$$D = 2.18 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}.$$

Hence, the relation between Q and dimensionless weight ω ($= X/\mu$) can be expressed as in Eqs. (3) and (4).

$$Q = A \{ 1/2 - (1 - \omega)^{2/3} / 2 - \omega/3 \} \quad (3)$$

$$A = \rho R^2 / \nu C_g D \quad (4)$$

The theoretical values of ω , calculated using Eq. (3), were in fairly good agreement with experimental results. Incidentally, Eq. (3) can be simplified to Eq. (5) by estimating the values of the second term of Eq. (3) using Taylor's expansion.

$$\omega = A' \cdot Q^{1/2}, \quad A' = A^{-1/2} \quad (5)$$

It is evident from Eq. (5) that ω is proportional to

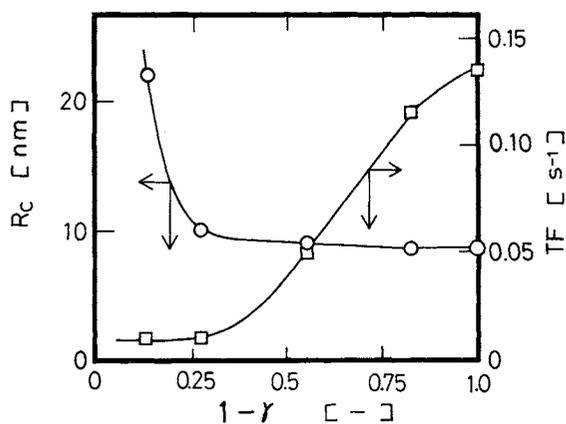


Fig. 8. Dependence of crystallite size and TF on radial position.

$Q^{1/2}$.

2.5.3 Change of Ni crystallite size and turnover frequency in the radial direction during oxidation at 623 K Figure 8 shows the change of Ni crystallite size and the turnover frequency during oxidation of La at 623 K. Here, oxygen uptake Q was converted to the radial position of interface, which is expressed as dimensionless radial distance γ in order to clarify the change of Ni crystallite size in the direction of the radius. The radial position was calculated using diffusion coefficient D of the core model. The number of Ni atoms on the surface was determined by using the value of dispersion and the number of total Ni atoms calculated from weight increase during oxidation. As shown in Fig. 8, Ni crystallite size contracted from 20 nm to 9 nm, and turnover frequency increased greatly as oxidation progressed, i.e. the interface of Ni/La₂O₃ and LaNi₅ proceeded inward to the center of the particle, in accordance with the core model. It should be noted that Ni crystallite size, calculated by use of Scherrer's equation, was the mean value, and the value of mean size was found experimentally not to be influenced by the total number of Ni atoms. The decrease in crystallite is thus ascribed in part to the migration of Ni crystallite on La₂O₃. The contraction of Ni crystallite size also suggests that there is a gradient of Ni dispersion in the radial direction.

The decrease in crystallite size appears to have stopped near the end of oxidation, possibly because the effects of sintering are considerable with small Ni crystallites.

The cause of the increase in turnover frequency is still under investigation. However, as Inui *et al.*⁵⁾ have reported, it might be attributed to the mechanism of hydrogen spillover on La₂O₃, the amount of which increased gradually during oxidation.

In spite of the fact that Ni weight content of oxidized LaNi₅ catalyst was as great as 54%, Ni dispersion was high (0.04–0.09), which indicates that oxidation treatment of LaNi₅ is an effective way of

producing highly-dispersed catalysts.

Conclusions

1) Oxidation treatment was found to be an effective way of producing highly-dispersed Ni catalysts.

2) Dispersion can be controlled by oxidizing La in LaNi₅ selectively at an appropriate temperature (623 K in this study). No powdering was observed during La oxidation, indicating that the effect of volume expansion was negligible and that La oxidation can be represented using the core model.

3) By assuming La oxidation using the core model, the relation between dispersion and weight change was clarified. The phenomenon of decrease in Ni crystallite size indicates that there is a gradient of dispersion in the direction of the radius.

Nomenclature

C_g	= oxygen concentration in bulk phase	[mol·cm ⁻³]
D	= diffusion coefficient	[cm ² ·s ⁻¹]
Q	= gas uptake per initial weight of catalyst	
R	= radius of solid particle	[cm]
R_c	= Ni crystallite size	[nm]
r	= reaction rate of CO	[mol·g ⁻¹ ·s ⁻¹]
T	= temperature	[K]
TF	= turnover frequency	[s ⁻¹]
t	= time	[s]
W	= weight of solid particle	[g]
X	= conversion of solid particle	[—]
γ	= dimensionless radius	[—]
δ	= dispersion	[—]
θ	= glancing angle	[deg]
μ	= theoretical coefficient of oxidation	[—]
ρ	= mole density of solid particle	[mol·cm ⁻³ ·solid]
ν	= stoichiometric coefficient	[—]
ω	= dimensionless weight (= $\Delta W/W_0$)	[—]
ω	= dimensionless weight (= ω/μ)	[—]

<Subscript>

0 = initial

Literature Cited

- 1) Arai, H.: *Hyoumen*, **17**, 675 (1979).
- 2) Carter, J. L., J. A. Cusumano and J. H. Sinfelt: *J. Phys. Chem.*, **70**, 2257 (1966).
- 3) Gokyu, I.: "Metallurgy Experimental," p. 59, Maruzen (1972).
- 4) Imamura, H. and W. E. Wallace: *J. Phys. Chem.*, **83**, 2009 (1979).
- 5) Inui, T., M. Funabiki, M. Suehiro and T. Sezume: *J. Chem. Soc., Faraday Trans. I*, **75**, 787 (1979).
- 6) Mckewan, W. M.: *Trans. Met. Soc. AIME*, **212**, 791 (1958).
- 7) Nakayama, T., M. Arai and Y. Nishiyama: *J. Catal.*, **87**, 108 (1984).
- 8) Shiotsuka, T., K. Onoe, A. Yokoyama and K. Inoue: Preprints of the 50th Annual Meeting of The Soc. of Chem. Engrs., Japan, p. 364 (1985).
- 9) Whyte, T. E. Jr.: *Cat. Rev.*, **8**, 117 (1974).