COMPARISON OF CATALYTIC PROPERTIES OF Ni/CeO₂ AND Ni/La₂O₃ PREPARED BY LOW-TEMPERATURE OXIDATION

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An attempt was made with rare earth intermetallic compounds to prepare highly active catalysts by low-temperature oxidation. CeNi₅ was chosen as the starting material, because works on LaNi₅ have shown that surface area increase and Ni crystallite growth are closely related to oxidation rate, and because the Ce oxidation rate is much higher than that of La.

It was found that low-temperature oxidation of CeNi₅ was accompanied by an increase in surface area without the growth of Ni crystallites. The reaction rate of CO hydrogenation per Ni weight was about 500-fold higher for Ni/CeO₂ than for Ni/La₂O₃ at 535 K. This was connected with increased Ni surface area (180-fold) and high turnover frequency (2.8-fold). Moreover, C₂ and C₃ products increased with increasing conversion of Ce oxidation.

Introduction

Recently, a new method that utilizes the decomposition of rare earth intermetallic compounds by gas-solid reactions has been proposed for preparing metal catalysts supported on lanthanide oxides, and the decomposed products have been found to be active catalysts for CO hydrogenation.^{1,2,6,10)} The principle of this method is based on the difference in oxidation rate between Ni and rare earth metals.^{11,12)} Work on LaNi₅¹⁰⁾ has shown that preparation can be divided into three regions—La oxidation (region I), Ni oxidation (region II) and NiO reduction (region III).

Well-dispersed Ni catalysts can be obtained from LaNi₅ by either of two procedures: low-temperature oxidation or high-temperature oxidation.^{11,13)} The former resulted in the selective oxidation of La (region I) and Ni crystallite of small size, while the specific surface area of the catalyst was low. High-temperature oxidation resulted in both La and Ni oxidation (regions I and II).

The objective of Ni oxidation in region II and NiO reduction in region III was an increase in surface area due to structural changes from Ni into NiO and the reverse transformation.⁹⁾ However, the growth of Ni crystallites was considerable in the high-temperature range, and the increase in surface area did not fully overbalance the adverse effect of Ni crystallite growth.

The present work is an attempt to prepare highly active catalysts by low-temperature oxidation of rare earth intermetallic compounds. CeNi₅ was chosen as the starting material, because both surface area increase and Ni crystallite growth are closely related to oxidation rate, and the oxidation rate of Ce is much higher than that of La.¹²⁾ In addition, the most stable oxide of cerium is CeO₂, while for most rare earths the most stable are Ln₂O₃ as sesquioxides, suggesting the possibility of different solid-state properties.^{4,16)} Moreover, considerable attention has been paid to the high catalytic activity of platinum supported on CeO₂ in methanation, water-gas shift reactions and ethylene oxidation,^{7,8)} and a strong interaction between metal and CeO₂ has been expected.

The influence of low-temperature oxidation of CeNi₅ on surface area change and catalytic activity was examined in comparison with that of LaNi₅ and it was found that Ce oxidation was accompanied by an increase in surface area without the growth of Ni crystallites. This is not consistent with the case of La oxidation, where both surface area and Ni crystallite size were unchanged. Moreover, the turnover frequency of CO hydrogenation was higher for Ni/CeO₂ than for Ni/La₂O₃ prepared at low temperature.

1. Experimental

1.1 Materials

Ce (99.7 wt% purity, 0.3 wt% other rare earths) and Ni (99.97 wt% purity, 0.03 wt% Cu, Co or Fe) were mixed at a given atomic ratio (Ni/Ce=5) and CeNi₅ was prepared by induction-melting in a water-cooled

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copper boat under a purified argon atmosphere. Similarly, La and Ni were mixed at the same ratio and LaNi_5 was obtained. Both CeNi_5 and LaNi_5 were screened to 100/170 mesh.

1.2 Preparing catalysts by oxidation^{9,11)}

Weight change of each intermetallic compound during oxidation and reduction was measured by a thermogravimeter (Shimadzu TG-30, 31), and gas samples were analyzed by TCD and FID gas chromatography. Oxidation temperatures T_I in region I and T_{II} in region II were kept constant at 623 K and 723 K, respectively. To keep the sample isothermal, oxygen partial pressure P_{O_2} was kept below 14.5 kPa. Reduction temperature T_{III} was kept constant at 623 K and hydrogen pressure P_{H_2} was 101 kPa. To confirm the selective oxidation of Ce, hydrogen was conducted to the oxidized CeNi_5 . Total gas flow rate F_T was $136 \mu\text{mol} \cdot \text{s}^{-1}$ to reduce the influence of gas-film resistance sufficiently.

1.3 Measurement of physical properties

Physical properties of catalysts were measured in the same way as described in the previous papers.^{9,11)}

1) Ni crystallite size by XRD method X-ray diffraction of powdered samples of catalyst was performed and Ni crystallite size was calculated according to Scherrer's equation.

2) Observation of vertical section of samples in region I after buffing Vertical sections of the oxidized CeNi_5 in region I after buffing were observed by optical micrography. Buffing was conducted as follows: Rough polishings of samples were carried out with four emery papers (#600–2000), followed by a series of five final polishings using an aqueous solution of fine powdered alumina (0.05–15 μm).

3) Specific surface area by BET method Powdering and cracks were examined by measuring the surface area, which was determined by nitrogen adsorption at liquid nitrogen temperature.

1.4 Measurement of CO chemisorption by pulse technique

CO pulse technique³⁾ was employed to examine the relation between specific surface area and active sites of exposed Ni metals during oxidation treatment of oxidized intermetallic compounds, and Ni dispersion δ_{CO} (moles of chemisorbed CO per moles of Ni) and turnover frequency TF_{CO} were calculated. Experimental apparatus for the CO pulse technique is shown in Fig. 1. A deoxidizing agent (8) and a sample of catalyst packed in the reactor (16) (3 mm internal diameter) were reduced by pure hydrogen at a flow rate of $40.8 \mu\text{mol} \cdot \text{s}^{-1}$ for two hours at 623 K. The hydrogen in the reactor was then purged by helium using a 4-way valve (3) and a 6-way valve (9), with the flow rate of helium kept at $27.2 \mu\text{mol} \cdot \text{s}^{-1}$ by needle valves (4)–(6). A CO pulse was then introduced to the sample using a 6-way valve (10) at 298 K. The weight of

Fig. 1. Experimental apparatus for CO pulse technique

packed catalyst was varied at each measurement in order that exposed Ni metal would become saturated in about 4 CO pulse counts.

1.5 Measurement of reaction activity for CO hydrogenation

The synthesis gas reaction was employed in a thermogravimeter using samples described in 1.2, and 10–100 mg of sample was reduced at 623 K by hydrogen. After reduction hydrogen was purged by helium and synthesis gas ($\text{H}_2/\text{CO}=4$) was passed at a total flow rate of $136 \mu\text{mol} \cdot \text{s}^{-1}$. At 493–651 K, differential reaction conditions ($X_{\text{CO}} \leq 0.1$) were employed under atmospheric pressure.

2. Results and Discussion

2.1 Comparison of catalytic activity per Ni weight prepared by selective oxidation of Ce and La

To examine the catalytic activity of Ni/CeO_2 and $\text{Ni}/\text{La}_2\text{O}_3$ obtained by selective oxidation of rare earth metals, CeNi_5 or LaNi_5 was placed on a sample cell in a thermogravimeter and Ni/CeO_2 or $\text{Ni}/\text{La}_2\text{O}_3$ catalyst was prepared by oxidation of La or Ce at 623 K ($X_{\text{La}} = X_{\text{Ce}} = 0.9$). Figure 2 shows a comparison of reaction rate of CO per Ni weight at steady state with Ni/CeO_2 and $\text{Ni}/\text{La}_2\text{O}_3$. It is evident that the activity of Ni/CeO_2 is about 500-fold greater than that of $\text{Ni}/\text{La}_2\text{O}_3$ at 535 K, although the Ni content in Ni/CeO_2 (63.0 wt%) is nearly equal to that in $\text{Ni}/\text{La}_2\text{O}_3$ (61.1 wt%). To examine the difference in catalytic activity, detailed experiments with changes in physical properties during Ce oxidation were carried out.

2.2 Findings on Ce oxidation at low temperature

Figure 3 shows the time course of weight increase ω ($= \Delta W/W_0$) caused by low-temperature oxidation of CeNi_5 at 623 K. The oxidation is fast at the initial stage, and gradually slows down, indicating that

Fig. 2. Comparison of reaction rate of CO with Ni/CeO₂ ($X_{Ce}=0.9$) and that with Ni/La₂O₃ ($X_{La}=0.9$)

Fig. 3. Time course of weight increase during Ce oxidation at 623K; A, B and C are points of 1.5, 3.0 and 4.5 wt% increase, respectively

different types of mechanisms are involved in Ce oxidation. To examine the change of physical properties, oxidation was stopped at points A–C and hydrogen was conducted to the oxidized CeNi₅, where A, B and C are points of 1.5, 3.0 and 4.5 wt% increase, respectively. The vertical section of each sample was subjected to X-ray diffraction analysis observation by using optical micrographs.

Figures 4-a)–c) show optical micrographs at points A–C. Cracks were observed at point A (Fig. 4-a)), grains were formed at point B (Fig. 4-b)), while a clear interface between the ash layer (CeO₂, Ni) and the unreacted core (CeNi₅) was observed in each grain at point C (Fig. 4-c)). It was also confirmed that the weight increase and oxidation time necessary to reach the termination of the initial stage differed greatly with varying oxidation temperature and oxygen partial pressure.

2.3 Comparison of surface area increase for oxidized CeNi₅ and LaNi₅

To examine surface area change during Ce ox-

Fig. 4. Optical micrographs of vertical section of samples at points A, B and C in Fig. 3

Fig. 5. Relations between specific surface area per initial weight and conversion of rare earth metals in region I

idation, low-temperature oxidation of CeNi₅ was stopped at Ce conversion X_{Ce} of 0.30, 0.60 and 0.90, and specific surface area per initial weight in region I S_I [m²·kg⁻¹] was measured by the BET method. Similarly the change in S_I during La oxidation was examined. Figure 5 shows that the S_I value of oxidized CeNi₅ increased greatly from 90 m²·kg⁻¹ to 6500 m²·kg⁻¹ with increasing X_{Ce} , whereas the S_I value of oxidized LaNi₅ remained approximately the

same ($33\text{--}45\text{ m}^2\cdot\text{kg}^{-1}$) during La oxidation.

The Pilling-Bedworth ratio PB [—] is often used as a measure of adherence between the ash layer and the unreacted core.¹⁴⁾ Considering that the value of PB is 1.12 when Ce is oxidized to CeO_2 , and is nearly 1.11 for oxidation of La to La_2O_3 , it was assumed that the surface area increase accompanying Ce oxidation was inexplicable on the basis of volume expansion. Lories,⁵⁾ however, reported in the case of low-temperature oxidation of Ce that Ce_2O_3 was initially formed under dry air and then converted into CeO_2 rapidly. The increase in surface area is thus ascribed in part to the effects of electronic structure on oxida-

tion mechanisms; i.e., Ce exists in the unstable forms Ce^{3+} or Ce^{4+} , while La exists in the stable form La^{3+} .

2.4 Relation between surface area increase and δ_{CO} in Ce oxidation region

Figure 6 shows that dispersion δ_{CO} calculated from CO chemisorption in the Ce oxidation region increased in proportion to X_{Ce} . On the other hand, the relation between δ_{CO} and X_{La} cannot be clarified because the quantity of CO chemisorbed on oxidized LaNi_5 is too small in the La oxidation region.

From X-ray diffraction patterns, peaks of CeNi_5 , CeO_2 and Ni were observed in the Ce oxidation region, and S_1 may be expressed as

$$S_1 = \frac{W_0(1 - X_{\text{Ce}})S_1 + W_0X_{\text{Ce}}(M_2/M_1)S_2 + W_0X_{\text{Ce}}(5M_3/M_1)S_3}{W_0(1 + 0.074X_{\text{Ce}})} \quad (1)$$

where M_i [—] and S_i [$\text{m}^2\cdot\text{kg}^{-1}$] are molecular weight and specific surface area of each species i (1, 2 and 3 are CeNi_5 , CeO_2 and Ni), and W_0 [kg] is initial weight of CeNi_5 . Because the specific surface area of CeNi_5 is negligible and $0.074X_{\text{Ce}}$ is far smaller than 1.0, specific surface area per Ni weight S_{NiI} [$\text{m}^2\cdot\text{kg}^{-1}$] is approximately expressed as

$$S_{\text{NiI}} = S_1/(5M_3/M_1)X_{\text{Ce}} = 0.59S_2 + S_3 \quad (2)$$

As shown in Fig. 6, good linearity was confirmed between S_{NiI} and X_{Ce} , which implies that $(0.59S_2 + S_3)$ should be proportional to X_{Ce} .

In preliminary pulse-technique experiments, it was clear that the quantity of chemisorbed CO on CeNi_5 and CeO_2 was negligible in comparison with that on Ni, which indicates that δ_{CO} is proportional to S_3 .

Consequently, the correlation between X_{Ce} and S_3 showed good linearity, it was assumed that the S_3/S_2 ratios are maintained constant, and/or that S_3 is far larger than S_2 , and the value of S_{NiI} varies in proportion to the amount of exposed Ni metal.

Figure 7 shows that Ni crystallite size R_{cNi} [nm] is constant during Ce oxidation,⁹⁾ which indicates that the increase in δ_{CO} may be independent of Ni crystallite size.

2.5 Comparison of TF_{CO} for Ni/ CeO_2 and Ni/ La_2O_3

To compare δ_{CO} for Ni/ CeO_2 and Ni/ La_2O_3 , the CO pulse technique was employed for three catalysts, namely S-1, Ni/ CeO_2 ($X_{\text{Ce}}=0.60$) prepared by Ce oxidation at 623 K; S-2, Ni/ CeO_2 ($X_{\text{Ce}}=1.0$ and $X_{\text{Ni}}=0.51$) prepared by Ce and Ni oxidation at 723 K and NiO reduction at 623 K; and S-3, Ni/ La_2O_3 ($X_{\text{La}}=1.0$ and $X_{\text{Ni}}=0.52$) prepared by La and Ni oxidation at 723 K and NiO reduction at 623 K.

Figure 8 shows the time course of catalytic activity on Ni/ CeO_2 ($X_{\text{Ce}}=0.60$, S-1). The reaction rate of CO was gradually decreased and steady state was reached after one hour. On the other hand, that on Ni/ La_2O_3 catalyst ($X_{\text{Ni}}=0.52$, S-3) was gradually increased and

then reached steady state.

Specific surface area, δ_{CO} , R_{cNi} and TF_{CO} for three catalysts are shown in Table 1. Comparison between S-1 and S-3 showed that δ_{CO} of Ni/ CeO_2 was 6-fold that of Ni/ La_2O_3 when the specific surface areas of the catalysts were very similar. A comparison between S-2 and S-3 showed that δ_{CO} of Ni/ CeO_2 was 28-fold that of Ni/ La_2O_3 at the same conversion of Ni oxidation. As described in the following sections, the values of TF_{CO} changed during Ce oxidation.

Fig. 6. Relations between δ_{CO} , S_{NiI} and X_{Ce}

Fig. 7. Effect of X_{Ce} on R_{cNi}

Fig. 8. Time course of catalytic activity for CO hydrogenation on Ni/CeO₂ ($X_{\text{Ce}}=0.60$, S-1) and Ni/La₂O₃ ($X_{\text{Ni}}=0.52$, S-3) at 523 K

Table 1. Physical properties and activity of catalysts

No.	Catalyst	$S \times 10^{-3}$ [m ² ·kg ⁻¹]	$\delta_{\text{CO}} \times 10^4$ [—]	TF_{CO}^* [s ⁻¹]	Rc_{Ni} [nm]
S-1	Ni/CeO ₂ ($X_{\text{Ce}}=0.60$)	2.71	21.2	5.3	7.2
S-2	Ni/CeO ₂ ($X_{\text{Ni}}=0.51$)	32.8	101.0	12.0	17.0
S-3	Ni/La ₂ O ₃ ($X_{\text{Ni}}=0.52$)	3.30	3.67	4.3	10.5

* 535 K

Therefore, it is assumed by comparison between S-2 and S-3 at the same X_{Ni} that TF_{CO} of Ni/CeO₂ was 2.8-fold that of Ni/La₂O₃.

Consequently, the high catalytic activity of Ni/CeO₂ in comparison with Ni/La₂O₃ in Fig. 2 (about 500-fold at 535 K) might be attributed to increased surface area in the Ce oxidation region (180-fold) and high TF_{CO} of Ni/CeO₂ (2.8-fold).

2.6 Activity for CO hydrogenation of oxidized CeNi₅ catalyst

Using the catalysts under conditions described in 2.3, CO hydrogenation was conducted at 493–546 K.

The tendency toward a decrease of activity as shown in Fig. 8 was observed on all Ni/CeO₂ catalysts ($X_{\text{Ce}}=0.30$ and 0.90). No change of weight was observed in the catalyst during reaction at 535 K, confirming that the effect of the dissociative oxygen of CO on a structural change of Ni/CeO₂ is negligible.

Figure 9 shows Arrhenius plots of values of TF_{CO} , which were determined using values of δ_{CO} calculated from the amount of CO adsorbed. The apparent activation energy ΔE of each catalyst was calculated to be 94.8 kJ·mol⁻¹, and was not influenced by Ce conversion. In addition, the value of ΔE for Ni/CeO₂ agreed with the case of Al₂O₃ supported Ni catalyst

Fig. 9. Arrhenius plots of TF_{CO} calculated by δ_{CO} on Ni/CeO₂ catalysts

Fig. 10. Effect of X_{Ce} on selectivity

prepared by impregnation.¹⁵⁾

2.7 Selectivity for CO hydrogenation of oxidized CeNi₅ catalyst

As Fig. 9 shows, TF_{CO} decreases as X_{Ce} increases, indicating the possibility of changes in product as a result of an increase of CeO₂. Accordingly, the relation between X_{Ce} and selectivity for CO hydrogenation at steady state was examined and the results are shown in Fig. 10. It was confirmed by varying contact time at 535 K that selectivity was little influenced by CO conversion.

As shown in Fig. 10, it is clear that methane as C_1 compound decreased while C_2 and C_3 compounds increased with increasing CeO_2 .

Conclusion

1) Surface area increase was observed during low-temperature oxidation of $CeNi_5$. This is inconsistent with the case of $LaNi_5$.

2) Ni dispersion δ_{CO} calculated by CO chemisorption was higher in Ni/CeO_2 than in Ni/La_2O_3 , and δ_{CO} in Ni/CeO_2 increased in proportion to Ce conversion X_{Ce} .

3) Specific surface area per Ni weight during Ce oxidation S_{Ni} increased in proportion to X_{Ce} .

4) Catalytic activity per Ni weight was about 500-fold higher in Ni/CeO_2 than in Ni/La_2O_3 at 535 K. This was connected with increase in surface area (180-fold) and high turnover frequency TF_{CO} (2.8-fold).

5) TF_{CO} of Ni/CeO_2 decreased with increasing X_{Ce} .

6) With increasing X_{Ce} , C_2 and C_3 products increased.

Nomenclature

ΔE	= activation energy	[kJ·mol ⁻¹]
F_T	= total gas flow rate	[mol·s ⁻¹]
M	= molecular weight	[—]
Rc_{Ni}	= nickel crystallite size	[nm]
P	= pressure	[kPa]
$r_{W_{Ni}}$	= reaction rate of CO per nickel weight	[mol·kg ⁻¹ _{Ni} ·h ⁻¹]
S	= specific surface area per unit of catalyst weight	[m ² ·kg ⁻¹]
S_{Ni}	= specific surface area per nickel weight	[m ² ·kg ⁻¹]
T	= temperature	[K]
T_r	= reaction temperature in CO hydrogenation	[K]
t	= time	[h], [min]
TF_{CO}	= turnover frequency calculated by δ_{CO}	[s ⁻¹]
X_{Ce}	= conversion of cerium in region I	[—]
X_{CO}	= conversion of CO	[—]
X_{La}	= conversion of lanthanum in region I	[—]
X_{Ni}	= conversion of nickel in region II	[—]
W	= catalyst weight	[kg]

δ_{CO}	= dispersion of Ni calculated from amount of CO adsorbed	[—]
ω	= dimensionless weight (= $\Delta W/W_0$)	[—]

<Subscript>

0	= initial
1	= $CeNi_5$
2	= CeO_2
3	= Ni
I	= cerium or lanthanum oxidation region
II	= nickel oxidation region
III	= nickel reduction region
H ₂	= hydrogen
O ₂	= oxygen

Literature Cited

- 1) Daly, F. P.: *J. Catal.*, **89**, 131 (1984).
- 2) Dang, T. A., L. Petrakis, C. Killy and D. M. Hercules: *J. Catal.*, **88**, 26 (1984).
- 3) Freil, J.: *J. Catal.*, **25**, 139 (1972).
- 4) Krill, G., J. P. Kappler, A. Meyer and M. F. Ravet: *J. Phys. F: Metal Phys.*, **11**, 1713 (1981).
- 5) Lories, L.: *Compt. Rend.*, **231**, 522 (1951).
- 6) Luengo, C. A., A. L. Cabrera, H. B. MacKay and M. B. Maple: *J. Catal.*, **47**, 1 (1977).
- 7) Mendelovici, L. and M. Steinberg: *J. Catal.*, **93**, 353 (1985).
- 8) Mendelovici, L. and M. Steinberg: *J. Catal.*, **96**, 285 (1985).
- 9) Onoe, K., K. Inoue and T. Shiotsuka: *Kagaku Kogaku Ronbunshu*, **13**, 831 (1987).
- 10) Onoe, K. and T. Shiotsuka: Kagaku Kogaku Symposium Series **13**, "Shokubai Gijutsu no atarashii Tenkai," p. 23, Kagaku Kogaku Kyokai (1987).
- 11) Shiotsuka, T., K. Onoe and A. Yokoyama: *J. Chem. Eng. Japan*, **19**, 91 (1986).
- 12) Shiotsuka, T., K. Onoe and A. Yokoyama: *J. Chem. Eng. Japan*, **19**, 347 (1986).
- 13) Shiotsuka, T., K. Onoe and A. Yokoyama: *J. Chem. Eng. Japan*, **19**, 519 (1986).
- 14) Stringer, J.: *Corros. Sci.*, **10**, 513 (1970).
- 15) Vannice, M. A.: *J. Catal.*, **37**, 462 (1975).
- 16) Yamaguchi, T., N. Ikeda, H. Hattori, and K. Tanabe: *J. Catal.*, **67**, 324 (1981).

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