EFFECT OF Ni ATOMIC PERCENT ON Ni DISPERSION AND CATALYTIC ACTIVITY IN PREPARATION OF CATALYSTS FROM La-Ni INTERMETALLIC COMPOUNDS

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A previous study showed that oxidation of LaNi_5 could produce catalysts with a relatively high Ni dispersion.

This study focuses on the effect of Ni atomic percent α upon Ni dispersion δ and turnover frequency TF , using La-Ni compounds. It was found that the value of δ was higher in the order of $\text{LaNi}_5 > \text{La}_2\text{Ni}_7 > \text{LaNi}_3 > \text{LaNi}$ and that this order was related to oxidation rate. The value of TF , on the other hand, was higher in the reverse order, indicating that high oxidation rate causes severe defects on the surface of Ni crystallites.

Introduction

Recently, much attention has been paid to a new method of preparing catalysts by oxidation treatment of rare earth intermetallic compounds, because this method prevents the poisoning effect of residual ions or impurities upon catalytic activity and selectivity, which occurs with the conventional method using aqueous solutions.^{5,6)}

Additionally, in this intermetallic compound method, catalysts containing highly dispersed transition metals, such as Ni and Co, can be obtained by regulating several influencing factors, such as oxidation temperature, oxidation time and reduction temperature. For example, it was shown that in the case of LaNi_5 , only La can be oxidized selectively in the low-temperature region (approximately 623 K), and that well-dispersed Ni on La_2O_3 can be obtained.⁵⁾

This study concerns the effect of Ni atomic percent α [%] upon oxidation rate, Ni dispersion δ and turnover frequency TF of the synthesis gas reaction, using LaNi , LaNi_3 , La_2Ni_7 and LaNi_5 . It was found that only La could be oxidized in the low-temperature region, producing $\text{Ni/La}_2\text{O}_3$ catalysts with all four compounds.

1. Experimental

1.1 Materials

According to the phase diagram of La-Ni made by Buschow *et al.*,¹⁾ intermetallic compounds are formed when Ni/La atomic ratios are 1.0, 3.0, 3.5 and 5.0,

and they are stable up to about 1000 K at atmospheric pressure.

The crystal structures are known: LaNi is orthorhombic; LaNi_3 is rhombohedral; La_2Ni_7 and LaNi_5 are hexagonal.

To make these compounds, 99.7 wt% purity of La (impurities are 0.18 wt% Nd, 0.05 wt% Pr, 0.05 wt% Ce, 0.02 wt% Fe) and 99.97 wt% purity of Ni (impurities are 0.005 wt% Fe, 0.005 wt% Cu, 0.01 wt% Pb, the rest are Mn, C, S) were mixed in appropriate ratios in a copper boat. The mixture was repeatedly induction-melted in an argon atmosphere to obtain a homogeneous melt, and was then water-cooled to form sample crystals.

X-ray diffraction patterns of these samples showed that LaNi , LaNi_3 , La_2Ni_7 and LaNi_5 were formed.

1.2 Effects of impurities and grain boundaries on oxidation rates

It has been reported that oxidation rate is greatly influenced by impurities and grain boundaries in crystals.⁷⁾ The impurities and grain boundaries in these La-Ni compounds have the same effects upon both conductivity before oxidation and oxidation rate.

To study the effects of these factors upon oxidation rate, the conductivity σ of La-Ni compounds was measured, and the relation between σ and the number x of Ni atoms per unit of LaNi_x was examined as a tool for predicting the effect of impurities and grain boundaries upon the oxidation rate. Thus, if σ were found be correlated with x by Kirkpatrick's equation Eq. (1), the effect of impurities and grain boundaries upon the oxidation rate would be negligible or the

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same for all four La-Ni compounds.

$$\sigma = Ax^B \quad (1)$$

The apparatus for measuring conductivity is shown in Fig. 1. After the current was measured from the voltage drop across the standard resistance ① (1.000 Ω), samples (100/170 mesh) were placed in glass tube ② (5 mm diameter) and then pressed by weight ③ to pack them homogeneously. Conductivity was measured at 293 K with samples of the appropriate length at the appropriate pressure. It was determined that neither factor has any influence on conductivity.²⁾

1.3 Measurement of oxidation rate

Oxidation rate was measured using the thermogravimeter (Shimadzu TG-30).⁵⁾ A 100 mg sample (100/170 mesh) was placed on the cell, and the weight change was measured at 600–623 K in O₂/He gas at a flow rate sufficient to eliminate gas-film resistance.

1.4 Measurement of structural change and Ni crystallite size

The X-ray diffraction method was used to study changes in structure and to measure Ni crystallite size at the Ni(111) peak.

1.5 Measurement of catalytic activity

After samples were oxidized in the reactor of the thermogravimeter, the oxygen was replaced by helium, and samples were reduced at 723 K by hydrogen. Hydrogen was then purged by helium, and the initial activity was measured in H₂/CO gas (H₂/CO=3) at 673–723 K, using FID and TCD gas chromatography.

The oxidation, reduction and reaction were all conducted in the thermogravimeter.

2. Results and Discussion

2.1 Effects on oxidation rate of lattice spattering

According to Wagner's oxidation theory,⁴⁾ lattice spattering caused by impurities and grain boundaries changes the concentration of vacant sites and thus alters the diffusion rate in the oxide layers. As α changes,

1) lattices might be spattered differently by impurities such as other rare earth metals in the La, or Cu or Fe in the Ni; and

2) the properties of the grain boundaries might change, and lattices might be spattered differently.

Therefore, the conductivity of La-Ni intermetallic compounds was measured to study the effects of impurities and grain boundaries. The influence of x on conductivity σ [$\Omega^{-1} \cdot \text{m}^{-1}$] show good linearity on a log-log graph, Fig. 2, and the relation agrees with Kirkpatrick's equation Eq. (1), where:

$$A = 501 \Omega^{-1} \cdot \text{m}^{-1}$$

$$B = 2.5,$$

Fig. 1. Apparatus for measuring conductivity.

Fig. 2. Influence of number of Ni atoms per unit of LaNi_x on conductivity.

indicating that the diffusion rate in the oxide layers is not influenced by the impurities or grain boundaries in any of the La-Ni compounds studied.⁷⁾

2.2 Effect of α on La oxidation rate

The weight increase stopped at the weight change calculated for complete oxidation of La, as shown in Fig. 3. To confirm the nature of the substances formed during oxidation, powder X-ray diffraction studies were made. For the oxidized La-Ni compounds at the points corresponding to the weight increase for the complete conversion of La into La₂O₃, the diffraction patterns showed only the existence of La₂O₃ and metallic Ni.

This showed that for LaNi, LaNi₃ and La₂Ni₇, only La was oxidized at 623 K, and agrees with results

Fig. 3. Time course of weight change during oxidation of LaNi, LaNi₃, La₂Ni₇ and LaNi₅ at 623 K.

previously obtained for LaNi₅.⁵⁾ Additionally, no powdering during oxidation was observed with the optical microscope.

At oxidation temperatures lower than 603 K, La was not completely oxidized after 15 hours, and the catalytic activity changed owing to the transformation of unoxidized La in synthesis gas atmosphere. Therefore, all subsequent oxidation was conducted at 623 K.

Using emery-ground samples, the movement of a distinct interface between oxidized parts and inter-metallic compounds into the center of particles was observed, showing that La oxidation in the four La-Ni compounds follows the core model. It was found from the relation between oxidation time and conversion that diffusion in the oxide layer is the rate-determining step.

Based on the core model, the fraction of La oxidized X_s [-] is related to an oxidation parameter β [s⁻¹] in Eq. (2), where β is expressed by Eq. (3).

$$\beta = 1/t \{ 1/2 - (1 - X_s)^{2/3} / 2 - X_s/3 \} \quad (2)$$

$$\beta = vC_g D / (\rho \cdot R^2) \quad (3)$$

Figure 4 shows that the diffusion rate slows as α increases. In La oxidation, oxygen diffuses in the La₂O₃ crystal lattices;³⁾ therefore, it was assumed that the number of vacant sites decreases with increasing α because some of the La(III) cation points in the lattice are replaced by Ni(II) cations. The decrease of vacant sites seemed to slow the diffusion rate.

The high degree of linearity of the relationship in Fig. 4 indicates that the oxidation rate depends upon α but not on the crystal structure.

2.3 Effect of α on Ni dispersion

After the La of the four compounds was completely oxidized at 623 K, Ni dispersion was measured. Figure 5 shows that Ni dispersion is higher in the order of LaNi₅ > La₂Ni₇ > LaNi₃ > LaNi, i.e., Ni dispersion is higher with increases in α . Figures 4 and 5 show that δ decreases with increasing β .

As a result, it is concluded that the oxidation rate determines δ for different values of α . The same effect

Fig. 4. Relation between Ni atomic percent and oxidation rate parameter.

Fig. 5. Relation between Ni atomic percent and Ni dispersion.

was found in the case of different values of T .

It is to be noted that δ is controlled either by α , the structure factor, or/and by experimental factors such as the oxidation temperature or the oxygen partial pressure.

2.4 Effect of α on turnover frequency

The initial activity of catalysts prepared by the complete oxidation of La in the four compounds was measured, and Fig. 6 shows that the initial rate of CO conversion per gram of Ni, r_0 [mmol·kg⁻¹·s⁻¹], increased with decreasing α . Over 99% of the product was methane.

Next, turnover frequency TF [s⁻¹] was calculated. The number of active sites necessary for the calculation of TF was assumed to be the same as the number of Ni atoms on the surface, which was determined using the value of Ni dispersion and the total number of Ni atoms. Figure 7 shows that TF

Fig. 6. Relation between Ni atomic percent and initial activity for CO hydrogenation at 673 K.

Fig. 7. Relation between Ni atomic percent and turnover frequency at 673 K.

increases as α decreases. As noted in Section 2.5 below, the activation energy was the same for the four catalysts, so that the effective TF should be the same. The change in TF is believed to be due to the fact that the degree of defects varies with the oxidation rate which, in turn, varies with α . This supposition was supported by the fact that a steady rate of CO conversion was obtained earlier as α decreased.

2.5 Effect of α on activation energy

Arrhenius' plots of the four samples of catalysts

Fig. 8. Dependence of initial activity on temperature for CO hydrogenation over the four catalysts produced from La-Ni compounds.

Table 1. Activation energy for CO hydrogenation

	ΔE [kJ·mol ⁻¹]
LaNi	100
LaNi ₃	107
La ₂ Ni ₇	103
LaNi ₅	110

$T=673-723$ K, $H_2/CO=3$, $F_{CO}/W=152.5$ mmol·kg⁻¹·s⁻¹

prepared by complete oxidation of La are shown in Fig. 8. The reaction was conducted using synthesis gas at 673–723 K. To study the sintering of Ni crystallites, the four catalysts obtained after the complete oxidation of La were kept in helium at 723 K for 5 hours. The Ni crystallites were found to be of the same size, indicating that sintering did not occur. Figure 8 and Table 1 show that the apparent activation energy ΔE [kJ·mol⁻¹] does not depend upon α , and was approximately the same as for one of the conventional supported Ni catalysts⁸⁾ that have small Ni content (~ 1 wt%) and large pore volume.

Conclusion

1) For LaNi, LaNi₃, La₂Ni₇ and LaNi₅, only La was oxidized at temperatures lower than 623 K, and the oxidation mechanism followed the core model.

2) Ni dispersion in samples after complete oxidation of La at 623 K was greater in the order $\text{LaNi}_5 > \text{La}_2\text{Ni}_7 > \text{LaNi}_3 > \text{LaNi}$. This order was found to result from differences in the oxidation rates.

3) Turnover frequency calculated from the synthesis gas reaction was greater in the order $\text{LaNi} > \text{LaNi}_3 > \text{La}_2\text{Ni}_7 > \text{LaNi}_5$, and this can be attributed to the difference in the degree of defects, which varies with oxidation rate.

Nomenclature

C_g	= oxygen concentration in bulk phase	
D	= diffusion coefficient	$[\text{mol} \cdot \text{m}^{-3}]$
ΔE	= activation energy	$[\text{m}^2 \cdot \text{s}^{-1}]$
R	= radius of solid particle	$[\text{kJ} \cdot \text{mol}^{-1}]$
r_0	= initial rate of CO conversion per gram of Ni	$[\text{m}]$
		$[\text{mmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}]$
t	= time	$[\text{h}], [\text{s}]$
T	= temperature	$[\text{K}]$
TF	= turnover frequency	$[\text{s}^{-1}]$
x	= number of Ni atoms per unit of LaNi_x	$[-]$
X_s	= conversion of La to La_2O_3	$[-]$

α	= Ni atomic percent	$[\%]$
β	= oxidation rate parameter in Eq. (3)	$[\text{s}^{-1}]$
δ	= Ni dispersion	$[-]$
ν	= stoichiometric coefficient	$[-]$
ρ	= mole density of solid particle	$[\text{mol} \cdot \text{m}^{-3} \cdot \text{solid}]$
σ	= conductivity	$[\Omega^{-1} \cdot \text{m}^{-1}]$
ω	= dimensionless weight ($= \Delta W/W_0$)	$[-]$

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KINETICS AND MECHANISM OF ZINC EXTRACTION FROM SULFATE MEDIUM WITH DI(2-ETHYLHEXYL) PHOSPHORIC ACID

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Kinetic studies of the extraction of zinc from aqueous sulfate solution by di(2-ethylhexyl) phosphoric acid in kerosene were made, using a constant interfacial area cell. Measurements of the extraction and stripping rates led to the identification of rate expressions and a suggested mechanism of this reaction. Based on the nature of the extractant and the reaction mechanism for the formation of zinc complex in the aqueous phase, a simple extraction scheme is proposed in which the rate-controlling step is interfacial. The mass-action constant obtained in the present kinetic study is considered to agree with the extraction constant obtained in the previous equilibrium study. Effects of the total sulfate concentration in the aqueous phase on the extraction and stripping rates were also investigated.

Introduction

The kinetics of metal extraction by chelating agents is essential in solvent extraction and liquid membrane

operations. In most cases the extraction rate of metal ions is a function of both the kinetics of chemical reactions taking place in the system and the rates of diffusion of the species between the two phases. The simultaneous presence of both chemical reactions and diffusion processes in liquid-liquid mass transfer has

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