

APPLICATION OF A UNIDIRECTIONALLY SOLIDIFIED LaNi_5 -Ni EUTECTIC
 ALLOY TO HYDROGEN DIFFUSIVE PLATE TYPE CATALYST FOR
 HYDROGENATION OF ETHYLENE

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Summary

The hydrogenation of ethylene has been conducted over the plate type catalyst of unidirectionally solidified LaNi_5 -Ni eutectic alloy possessing the material function of a unidirectionally diffusive hydrogen supply. The hydrogenation to ethane has been confirmed in all the plate type specimens having different microstructures. It is found that the reaction activity strongly depends on the magnitude of LaNi_5 -Ni interface area and is higher in the state of α solid solution phase than that in β hydride phase.

1. Introduction

Our recent studies[1] have accomplished a modification of the mechanical strength of brittle LaNi_5 with ductile Ni resulting in unidirectionally solidified LaNi_5 -Ni eutectic alloy. Characteristics for the hydriding and dehydriding equilibrium have been investigated on the plate type specimens [2,3]. The improved eutectic alloy is proved to have excellent resistance to disintegration.

Hydrogen in hydriding intermetallic compounds of transition metals has been known so far to be atomic and active to several chemical reactions in the form of powder specimens[4,5,6].

On the contrary, the hydrogenation study using bulky metal hydride alloys is little[8]. In this work we aimed to elucidate catalytic behavior of hydrogen atoms in the phases of α solid solution and β hydride, and role of interfaces of this unidirectionally solidified eutectic alloy with disintegration resistance.

2. Experimental

Two kinds of unidirectionally solidified LaNi_5 -Ni eutectic alloy specimens were prepared by zone melting process[1,2,3]. The coarse structure specimen grown under low moving rate (5.0 $\mu\text{m/s}$) is denoted as #1; the fine structure specimen grown under high moving rate (7.8 $\mu\text{m/s}$) as #2. The specimen shape was disk with 10 mm diameter and 5 mm thick, having buffing surface.

These specimens possess the hydrogen absorption-dissociation characteristics shown in Fig.1. After the specimen was set in the flow reactor shown in Fig.2, activation treatment was done by five cycles composing of evacuation at 80°C for 30 min and hydriding at 40°C for 1 hour by 0.5 MPa hydrogen gas. Then hydrogen gas was applied to the A-surface as shown in Fig.2. The mixture of ethylene and carrier hydrogen gas was introduced with the rate of 0.75 ml/s hydrogen and 0.083 ml/s ethylene in order to retard coke formation on the B-surface. The area of the B-surface exposing to the reaction gas is 30.7 mm^2 . The products were analysed by FID gas chromatograph through on-line gas sampler. The reaction was carried out at the temperature of 30 to 50°C, and under the pressure of 0.15 to 1.5 MPa.

3. Results and discussion

The hydrogenation to ethane has been confirmed in all specimens and under all experimental conditions. Fig.3 shows the plots of first order rate constant k_s against square root of hydrogen pressure $p_{\text{H}_2}^A$ applied to the A-surface for the specimen #1. The value of k_s is proportional to $\sqrt{p_{\text{H}_2}^A}$ in the α solid solution region below about 0.36 MPa (: 0.6 $\text{MPa}^{0.5}$).

Above 0.36 MPa in hydrogen pressure, the value of k_s decreased steeply and is almost independent of $\sqrt{p_{H_2}^A}$. The phenomenon of dropping in k_s with increasing hydrogen pressure $p_{H_2}^A$ appears similarly for the specimen #2, as shown in Fig.4. These observed dropping phenomena in k_s are considered to correspond to the transition of α solid solution state to β metal hydride, as can be seen from the CPI curves in Fig.1. It shows that the value of k_s is obeyed to the Sieverts rule[7] in the range of α phase. Fig.5 shows Arrhenius plots at three different hydrogen pressures corresponding to α phase(0.15 MPa), $\alpha+\beta$ phase(0.5 MPa) and β phase(1.5 MPa). This gives the same value of 41.9 kJ/mol- C_2H_4 of the apparent activation energy for three different pressure regions. It suggests that the surface chemical reaction is the rate determining step for every pressure, while the frequency factors are in the order of α , $\alpha+\beta$ and β phases depending on the density of hydrogen atoms on the B-surface. The k_s value for the specimen #2 is six times larger than that for the specimen #1, and the specimen #2 has a micro structure giving higher activity for hydrogenation.

To elucidate the difference between the two specimens, the micro structure of the transverse cross section was examined through the composition image of EPMA. Fig.6 reveals clear distinction between the two specimens. Namely, the specimen #2 with fine structure has large interface between $LaNi_5-Ni$ and Ni phases. It is concluded that the layers of the $LaNi_5-Ni$ eutectic interface having high diffusivity is main route carrying hydrogen atoms from the A-surface to the B-surface on the basis of the micro structure observation.

4. Conclusion

A new unidirectionally solidified $LaNi_5-Ni$ eutectic alloy was successfully used as a disk plate type catalyst. The hydrogenation to ethane was confirmed in all the plate type specimens having different micro structures according to the material function of a unidirectionally diffusive hydrogen supply. It was found that the reaction activity strongly depends on the magnitude of $LaNi_5-Ni$ interface area and is

higher in the state of α solid solution phase than in β hydride phase.

5. Literature cited

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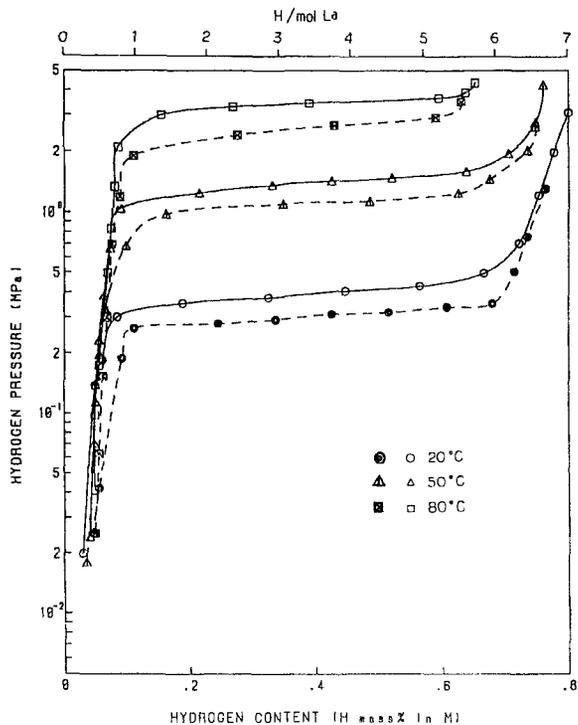


Fig.1 Hydrogen Content-Pressure Isotherm(CPI) curves for $\text{LaNi}_5\text{-Ni}$ alloy. Hydrogen absorption ($\circ\Delta\Box$) and Dissociation ($\ominus\blacktriangle\blacksquare$) at different temperatures.

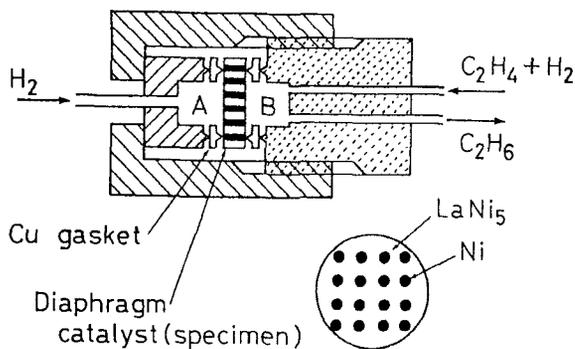


Fig.2 Plate(Diaphragm) type catalyst reactor.

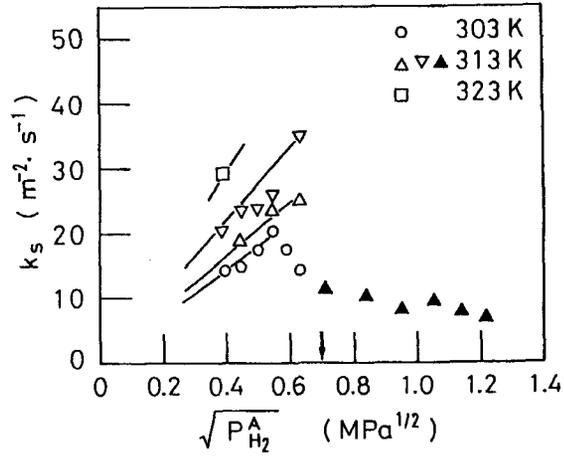


Fig.3 Specific reaction rate of C_2H_4 hydrogenation against $p_{H_2}^A$ to A-surface for specimen #1.

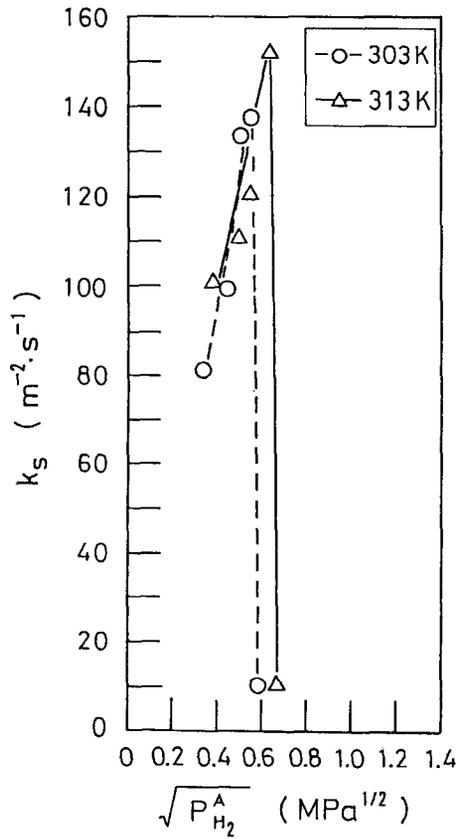


Fig.4 Specific reaction rate of C_2H_4 hydrogenation against $p_{H_2}^A$ to A-surface for specimen #2.

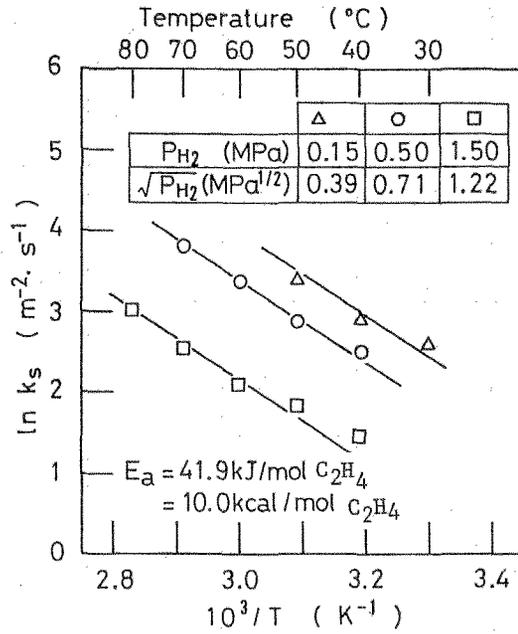


Fig.5 Arrhenius plots at three different H_2 pressure at A-surface giving the same apparent activation energy.

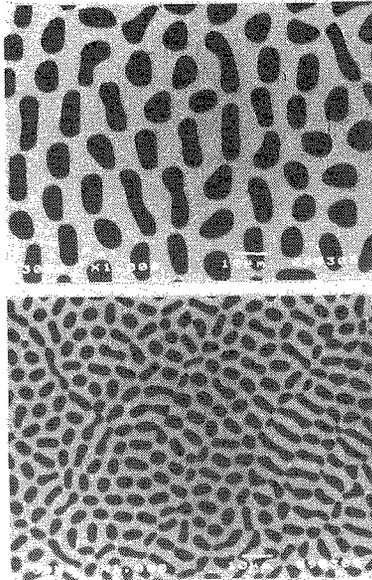


Fig.6 EPMA composition images of $LaNi_5$ (white part)-Ni(black) eutectic structure for the specimen #1(upper) and #2(bottom).The same magnification.