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Catalytic transfer hydrogenation of butene on hydrogen-absorbing alloys ($LaNi_5$, $CaNi_5$ and $LaNi_4Al$)

Hayao Imamura*, Yutaka Noda, Yoshihisa Sakata, Susumu Tsuchiya

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan

Abstract

The transfer hydrogenation of 2-butene with cyclohexene or 2-propanol on hydrogen-absorbing alloys ($LaNi_5$, $CaNi_5$ and $LaNi_4Al$) which have different equilibrium pressures has been examined as a model study for hydrogen transfer catalysis. $CaNi_5$ showed the most interesting characteristics as an active catalyst for the transfer hydrogenation of butene. Cyclohexene was effectively dehydrogenated to yield benzene at 423 K, in which 63% of the dissociated hydrogen was absorbed by the $CaNi_5$ alloy to form the hydride and the rest was released as gaseous hydrogen. When the alloy was hydrided to some extent, butene was efficiently hydrogenated by the absorbed hydrogen rather than the gaseous hydrogen to yield butane. The overall reaction on $CaNi_5$ was expressed as catalytic transfer hydrogenation of 2-butene from cyclohexene through the formation of metal hydride intermediates, rather than the direct reaction between 2-butene and cyclohexene on the alloy. $LaNi_5$ and $LaNi_4Al$ did not work like $CaNi_5$, and hence showed lower activities for the transfer hydrogenation. The reaction behavior of the alloys was strongly dependent on their surface properties for hydrogen transfer catalysis rather than their thermodynamic properties. The effectiveness of cyclohexene and 2-propanol as hydrogen donors is discussed.

Keywords: Catalytic transfer hydrogenation; $LaNi_5$; $LaNi_4Al$; $CaNi_5$; Hydrogen-absorbing alloy; Catalyst

1. Introduction

It has been shown that certain intermetallic compounds such as $LaNi_5$, $LaCo_5$ and $CaNi_5$ absorb large amounts of hydrogen rapidly and reversibly. Since hydrogen is absorbed dissociatively, the gas must exist at least fleetingly as monatomic hydrogen on the surface. This suggests that the surfaces of these intermetallics are quite active, a feature that has attracted interest in them as active catalysts [1–5]. In particular, for the reactions in which hydrogen participates, the appearance of high activity and specificity can be expected. By the adroit use of hydrogen-absorbing ability, the hydrogenation and dehydrogenation can be combined as follows

$$\text{Saturated compound} + \text{M} \underset{\text{hydrogenation}}{\overset{\text{dehydrogenation}}{\rightleftarrows}} \text{unsaturated compound} + \text{MH}_x$$

The hydrogen produced by the dehydrogenation on hydrogen-absorbing alloys (M) can be absorbed to form the metal hydrides, and vice versa, the resulting metal hydrides (MH_x) contain reactive hydrogen atoms able to hydrogenate efficiently the unsaturated compounds. The direction of the reactions is determined thermodynamically by the reaction conditions used. We have proposed a novel reaction system using $CaNi_5$ acting as a useful hydrogenation and dehydrogenation medium at the same time, in which catalytic transfer hydrogenation between 2-butene as a hydrogen acceptor and 2-propanol as a hydrogen donor has been studied at 393–473 K [6]. By considering the hydriding–dehydriding characteristics under the conditions applied to the reaction, $CaNi_5$ seems to be suitable for this purpose [7–9]. 2-Propanol was effectively dehydrogenated at 423 K to yield acetone in which the dissociated hydrogen was completely absorbed by $CaNi_5$ to form the metal hydride. When the alloy was hydrided to some extent, butene was hydrogenated by the absorbed hydrogen to yield butane. Thus, $CaNi_5$ effectively repeated hydriding–dehydriding cycles during the present reaction; hydriding of $CaNi_5$ by 2-propanol dehydrogenation with subsequent dehydriding for the hydrogenation of 2-butene.

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*Corresponding author.

E-mail address: hi-khm@po.cc.yamaguchi-u.ac.jp (H. Imamura).

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The overall reaction is expressed as catalytic transfer hydrogenation through the formation of metal hydride intermediates ($CaNi_5H_n$). This is a model study for hydrogen transfer catalysis

$$\text{2-butene} + \text{2-propanol} \xrightarrow[CaNi_5H_n]{\text{transfer hydrogenation}} \text{butane} + \text{acetone}$$

In this study, cyclohexene is examined as a hydrogen donor. Further attention has been focused on the catalytic transfer hydrogenation of 2-butene with cyclohexene using $LaNi_5$, $CaNi_5$ and $LaNi_4Al$ which have different equilibrium pressures, by making use of hydrogen-absorbing characteristics.

2. Experimental

2.1. Materials

$CaNi_5$ (Japan Steel Works) and $LaNi_5$ and $LaNi_4Al$ (Santoku Metal) were commercially available. The alloys were pulverized with a mortar and a pestle. Cyclohexene, 2-propanol and 2-butene (Tokyo Chemical) were reagent grade and further purified by triple distillation.

2.2. Reaction procedures

Before each catalytic run the alloy powders were heated in the reactor to 673 K under vacuum for about 10 h, exposed to hydrogen of 600 Torr and then cooled to 203 K for 12 h. These procedures were repeated to obtain steady absorption and desorption of hydrogen by the alloy.

The catalytic reactions were performed on a recirculation reactor (~210 cm^3) equipped with a high vacuum system. After the activation the alloy was evacuated at 673 K for about 4 h, set at 393–423 K of the reaction temperatures, and then the transfer hydrogenation was initiated by admitting cyclohexene and/or 2-butene. The reacting gases in the system were periodically collected by a gas sampler and analyzed using a Shimadzu gas chromatograph.

3. Results and discussion

To determine how the transfer hydrogenation of 2-butene from cyclohexene or 2-propanol as a hydrogen donor occurs on $LaNi_5$, $CaNi_5$ and $LaNi_4Al$, and how the absorbed hydrogen affects the reaction, we carried out two types of reaction differing in the modes of addition of the reactants (2-butene and cyclohexene or 2-propanol).

3.1. Catalytic transfer hydrogenation on $CaNi_5$

After conventional activation procedures consisting of repeated hydriding–dehydriding cycles, $CaNi_5$ (1.0 g) showed catalytic activity for the dehydrogenation to benzene when brought into contact with cyclohexene (21 Torr) at 423 K. The time courses of the reaction are shown in Fig. 1. Cyclohexene was readily dehydrogenated to benzene and simultaneously converted to cyclohexane and benzene by disproportionation. Unlike the reaction with 2-propanol, hydrogen was detected in the gas phase during the reaction; a part of hydrogen dissociated from cyclohexene was immediately coupled with subsequent liberating as hydrogen gas before absorption by $CaNi_5$ to form the hydride. The dehydrogenation of cyclohexene was much faster than that of 2-propanol under the same reaction conditions; this is believed to be due to the fact that the rates of hydrogen absorption by $CaNi_5$ do not overtake the rates of cyclohexene dehydrogenation. After reaction for 19 h, the formation of benzene (11 Torr), cyclohexane (6 Torr) and hydrogen (6 Torr) was observed in the gas phase. Assuming that the disproportionation of cyclohexene to benzene and cyclohexane stoichiometrically occurs in the ratio of 1:2, 8 Torr out of 11 Torr of benzene formed would be attributed to the dehydrogenation of cyclohexene. Therefore, hydrogen of 16 Torr should be formed by the dehydrogenation, in which the amount of hydrogen corresponding to 10 Torr is considered to be absorbed by $CaNi_5$. This corresponded to the hydrogen concentration of $CaNi_5H_{0.11}$. This type of dehydrogenation is thermodynamically more favorable than regular dehydrogenation [10–12].

Normal dehydrogenation of cyclohexene to benzene ($C_6H_{10} \rightarrow C_6H_6 + 2H_2$) is accompanied by an increase in the standard Gibbs free energy ($\Delta G°$ at 25°C) by $\sim +22$ $kJ\,mol^{-1}$ of benzene formed. However, $\Delta G°$ for the dehydrogenation of cyclohexene on $CaNi_5$ to form benzene and the metal hydride ($C_6H_{10} + CaNi_5 \rightarrow C_6H_6 + CaNi_5H_4$) is advantageous for the energy of hydride formation [8]. Thus the hydride formation provides the driving force for the dehydrogenation of cyclohexene.

When the conversion of cyclohexene was reached at about 80% (as shown by an arrow in Fig. 1) 2-butene of 30

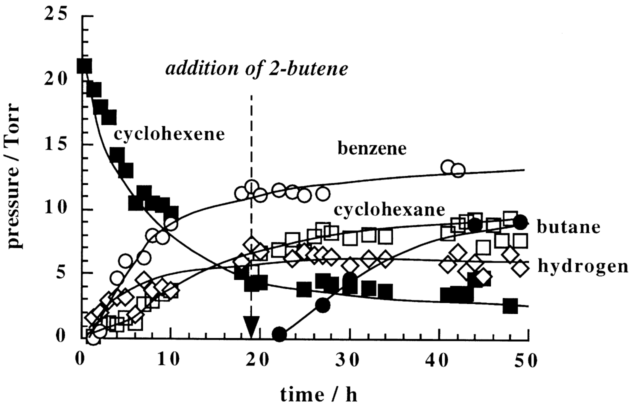

Fig. 1. Time courses of the reaction at 423 K on $CaNi_5$ upon addition of cyclohexene and, subsequently, 2-butene.

Torr was added to the circulating gases. Butane was formed immediately, followed by steady formation. From the results using a mixture of cyclohexene and 2-butene as described later, it seems that no direct transfer hydrogenation between both occurs under the reaction conditions; thus butane observed here is largely formed by the hydrogenation with the aid of absorbed hydrogen. This is supported by the fact that the amounts of the gaseous hydrogen were hardly changed during the formation of butane. It has been shown that the absorbed hydrogen is effectively consumed for the reaction with olefin without evolution as hydrogen gas [13–16]. In addition, the proportions of benzene and butane formed remained almost constant in the latter half of the reaction, indicating that the steady hydrogenation of butene occurs by consuming the absorbed hydrogen, and simultaneous cyclohexene dehydrogenation efficiently makes up for the consumption of absorbed hydrogen. Thus, the reaction of cyclohexene and butene on $\mathrm{CaNi_5}$ follows the stoichiometric relationship as catalytic transfer hydrogenation through intermediate formation of metal hydrides

$$\begin{array}{lclclcl}
\mathrm{C_6H_{10}} & + & \mathrm{nCaNi_5} & \longrightarrow & \mathrm{C_6H_6} & + & \mathrm{nCaNi_5H_{4/n}} \\
\mathrm{nCaNi_5H_{4/n}} & + & \mathrm{C_4H_8} & \longrightarrow & \mathrm{nCaNi_5} & + & \mathrm{C_4H_{10}} \\
\hline
\mathrm{C_6H_{10}} & + & \mathrm{C_4H_8} & \longrightarrow & \mathrm{C_6H_6} & + & \mathrm{C_4H_{10}}
\end{array}$$

At a lower reaction temperature of 393 K (Fig. 2), the dehydrogenation activity of $\mathrm{CaNi_5}$ decreased, while the disproportionation occurred to a significant extent. When butene was added to the reaction system after reaction for 10 h, butane was rapidly formed in the beginning and subsequently, not markedly. First such reaction behavior strongly suggests that no direct transfer hydrogenation between cyclohexene and 2-butene on $\mathrm{CaNi_5}$ occurs. Because of the drop in dehydrogenation activity, the amounts of hydrogen absorbed by $\mathrm{CaNi_5}$ decreased and besides, the change in reaction temperature from 423 to 393 K led to a lowering of the dissociation pressures of hydrogen for $\mathrm{CaNi_5H}_x$. Therefore, the participation of the absorbed hydrogen in the hydrogenation should be depressed to a significant extent, resulting in lower activity.

The reaction was examined by admitting a mixture of cyclohexene (23 Torr) and 2-butene (30 Torr) at 393 K. Fig. 3 shows that the rates of cyclohexene dehydrogenation and butane formation decreased, compared to admitting the reactant gases separately (Fig. 2). This is probably due to the competitive adsorption of cyclohexene and butene on $\mathrm{CaNi_5}$, leading to low activity for the dehydrogenation of cyclohexene. Consequently, there was a further decline in the concentration of hydrogen absorbed in $\mathrm{CaNi_5}$; the activity for the hydrogenation of butene also dropped. To initiate the hydrogenation of butene using the hydrogen in the hydride, absorbed hydrogen of more than a certain concentration in $\mathrm{CaNi_5H}_x$ is required [14].

3.2. Catalytic transfer hydrogenation on $\mathrm{LaNi_4Al}$

Using $\mathrm{LaNi_4Al}$ which had lower equilibrium pressures than $\mathrm{CaNi_5}$ [17], the same reaction was examined. When only cyclohexene (23 Torr) was brought into contact with $\mathrm{LaNi_4Al}$ (1.0 g) at 423 K (Fig. 4), the dehydrogenation activity was low compared to the results on $\mathrm{CaNi_5}$. Contrary to our expectation, almost all the hydrogen dissociated from cyclohexene was released in the gas phase without absorption by $\mathrm{LaNi_4Al}$. When 2-butene was additionally introduced into the reaction system, only a very little butane product was observed. It seems that the low surface activity of $\mathrm{LaNi_4Al}$ is reflected in such behavior.

$\mathrm{LaNi_4Al}$ showed very low activity for the dehydrogenation and hydrogenation upon contact with a mixture of cyclohexene and butene. The hydrogen formed during the reaction was scarcely absorbed. These conditions are unfavorable for the catalytic transfer hydrogenation through the formation of metal hydride intermediates.

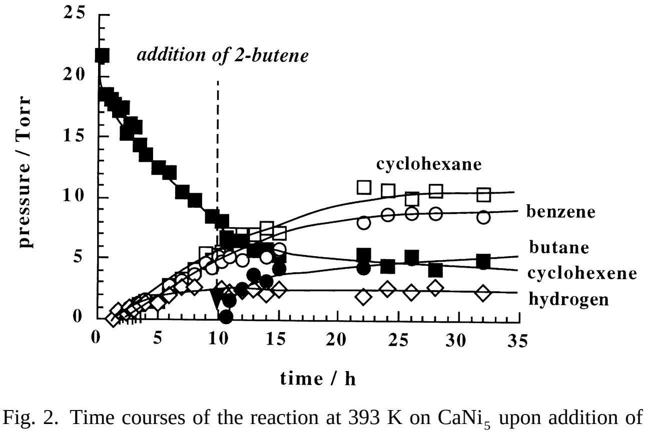

Fig. 2. Time courses of the reaction at 393 K on $\mathrm{CaNi_5}$ upon addition of cyclohexene and, subsequently, 2-butene.

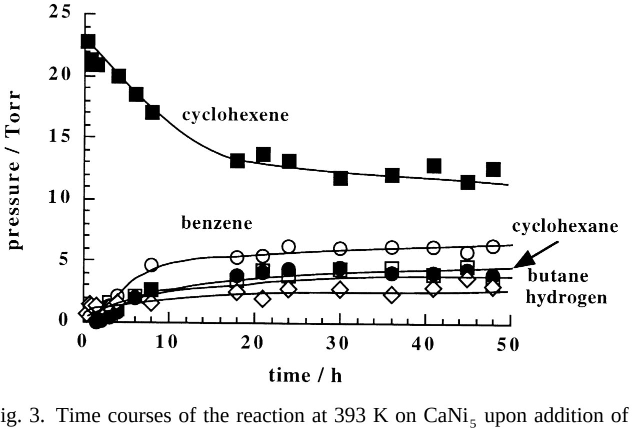

Fig. 3. Time courses of the reaction at 393 K on $\mathrm{CaNi_5}$ upon addition of a mixture of cyclohexene and 2-butene.

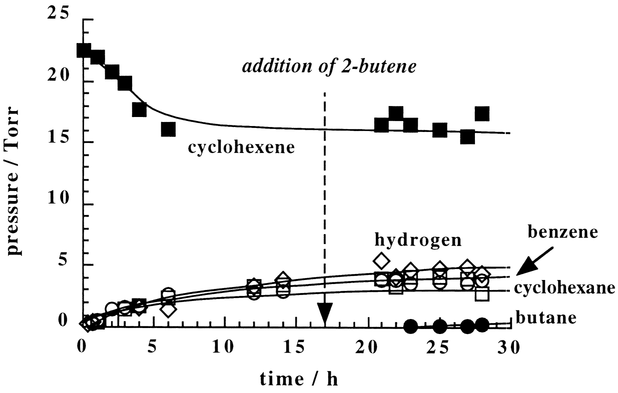

Fig. 4. Time courses of the reaction at 423 K on $LaNi_4Al$ upon addition of cyclohexene and, subsequently, 2-butene.

3.3. Catalytic transfer hydrogenation on $LaNi_5$

$LaNi_5$ with the highest equilibrium pressures was used. The dehydrogenation activity was not so high at 423 K (Fig. 5). Most of the hydrogen formed by the dehydrogenation could not thermodynamically exist in $LaNi_5$, but the activity for butane formation was higher than that of $LaNi_4Al$. This seems to be due to a difference in surface activity or in the ease of hydriding–dehydriding of the alloys. Upon contact of a mixture of cyclohexene and 2-butene, only a very little butane was formed in the beginning, and subsequently, the reaction was not so different from that observed in Fig. 5. 2-Propanol was further examined as a hydrogen donor instead of cyclohexene. Slight dehydrogenation of 2-propanol occurred with simultaneous liberation of hydrogen in the gas phase and butane was formed, similarly to when using cyclohexene.

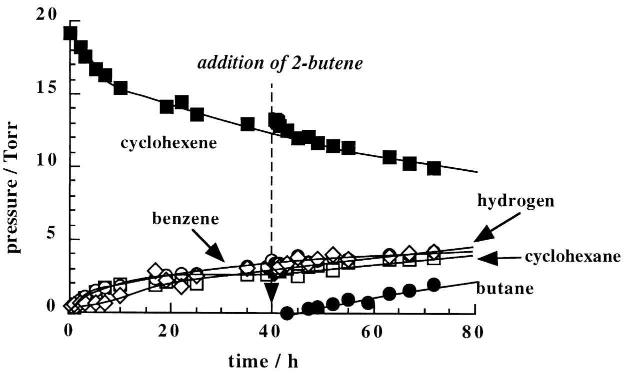

Fig. 5. Time courses of the reaction at 423 K on $LaNi_5$ upon addition of cyclohexene and subsequent 2-butene.

4. Conclusion

The reaction of 2-butene and cyclohexene was carried out on hydrogen-absorbing alloys ($LaNi_5$, $CaNi_5$ and $LaNi_4Al$) which had different equilibrium pressures. The reaction behavior was strongly dependent on surface activity rather than on thermodynamic properties; $CaNi_5$ was the most suitable, acting as an active catalyst for the transfer hydrogenation of 2-butene from cyclohexene through the formation of metal hydride intermediates. $LaNi_4Al$ and $LaNi_5$ did not work like $CaNi_5$, having low activities for the transfer hydrogenation. The absorbed hydrogen in $LaNi_4Al$ was stable and the surface activity of $LaNi_4Al$ was low.

References

[1] H. Imamura, S. Tsuchiya, Hyomen 26 (1988) 857.
[2] F.P. Netzer, E. Bertner, in: K.A. GschneidnerJr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 5, North-Holland, Amsterdam, 1983, Chapter 3.
[3] S.T. Oyama, G.L. Haller, in: Catalysis, Specialist Periodical Report, Vol. 5, The Chemical Society, London, 1982, p. 353.
[4] W.E. Wallace, Chemtech, 1982, 752.
[5] W.E. Wallace, A. Elattar, H. Imamura, R.S. Craig, A.G. Moldovan, in: W.E. Wallace, E.C. Subbarao (Eds.), The Science and Technology of Rare Earth Materials, Academic Press, New York, 1980, p. 329.
[6] H. Imamura, T. Tanaka, Y. Sakata, S. Tsuchiya, Catal. Lett. 56 (1998) 65.
[7] K. Yagisawa, A. Yoshikawa, T. Matsumoto, J. Less-Common Met. 99 (1984) 205.
[8] G.D. Sandrock, J.J. Murray, M.L. Post, J.B. Taylor, Mat. Res. Bull. 17 (1982) 887.
[9] Y.K. Cho, R. Yamamoto, M. Doyama, S. Ono, K. Imanari, T. Tabata, J. Less-Common Met. 88 (1982) 125.
[10] H. Imamura, T. Takada, S. Kasahara, S. Tsuchiya, Appl. Catal. 58 (1990) 165.
[11] H. Imamura, S. Kasahara, T. Takada, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 1, 84 (1988) 765.
[12] H. Imamura, K. Nukui, K. Yamada, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 743.
[13] K. Soga, K. Otsuka, M. Sato, T. Sano, S. Ikeda, J. Less-Common Met. 71 (1980) 259.
[14] K. Soga, H. Imamura, S. Ikeda, J. Catal. 56 (1979) 119.
[15] K. Soga, H. Imamura, S. Ikeda, J. Phys. Chem. 81 (1977) 1762.
[16] K. Soga, H. Imamura, S. Ikeda, Nippon Kagaku Kaishi, 1977, 1299.
[17] M.H. Mendelsohn, D.M. Gruen, A.E. Dwight, Nature 269 (1977) 45.