Catalysis Letters 56 (1998) 65–67

Catalytic transfer hydrogenation on a hydrogen-absorbing alloy ($CaNi_5$) using hydriding–dehydriding properties

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Received 23 July 1998; accepted 2 October 1998

By using the characteristics of a hydrogen-absorbing alloy, the hydrogen produced by catalytic dehydrogenation of saturated compounds can be absorbed to form metal hydrides, and, vice versa, the resulting metal hydrides are able to hydrogenate efficiently unsaturated compounds upon dehydriding. Gas-phase reactions between 2-butene and 2-propanol on a hydrogen-absorbing alloy $CaNi_5$ have been studied in the temperature range of 393–473 K. $CaNi_5$ showed interesting characteristics as an active catalyst for the catalytic transfer hydrogenation of butene from propanol as a hydrogen donor. 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 in the metal hydride to produce butane. The overall reaction on $CaNi_5$ was expressed as catalytic transfer hydrogenation of 2-butene from 2-propanol through intermediate formation of metal hydrides, rather than the direct reaction between butene and propanol on the alloy. Thus, $CaNi_5$ effectively repeated hydriding–dehydriding cycles: hydriding of $CaNi_5$ by 2-propanol dehydrogenation with subsequent dehydriding for the hydrogenation of 2-butene. The use of hydrogen-absorbing $CaNi_5$ provides a novel reaction system for the catalytic transfer hydrogenation.

Keywords: catalytic transfer hydrogenation, hydrogen-absorbing alloy, $CaNi_5$, catalyst, hydriding–dehydriding

1. Introduction

It has been shown that certain intermetallic compounds such as $LaNi_5$, Mg_2Ni, Zr_2Ni and TiFe 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 heterogeneous 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:

$$\text{unsaturated compound} + MH_x \underset{\text{dehydrogenation}}{\overset{\text{hydrogenation}}{\rightleftharpoons}} \text{saturated compound} + M$$

Metal hydrides (MH_x) contain reactive hydrogen atoms able to hydrogenate efficiently the unsaturated compounds, and, vice versa, the hydrogen produced by the dehydrogenation on hydrogen-absorbing alloy (M) catalysts can be absorbed to form the metal hydrides. The direction of these reactions is determined thermodynamically by the reaction conditions applied.

In this study, we have studied the catalytic transfer hydrogenation of 2-butene with 2-propanol over $CaNi_5$. We propose a novel reaction system using hydride-forming alloys acting as a useful hydrogenation and dehydrogenation method at the same time, in which catalytic transfer hydrogenation between olefin and alcohol consequently occurs. By considering the hydriding–dehydriding properties under the conditions applied to the present reaction, $CaNi_5$ seems to be suitable for this purpose [6–8]. Much attention has been also focused on the catalysis of $CaNi_5$ by making use of hydrogen-absorbing characteristics.

2. Experimental

2.1. Materials

$CaNi_5$ (Japan Steel Works, Ltd.) was commercially available and pulverized with a mortar and a pestle. 2-propanol and 2-butene (Tokyo Chemical Ind. Co., Ltd.) were reagent grade and further purified by triple distillation.

2.2. Reaction procedures

Before each catalytic run $CaNi_5$ was 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 $CaNi_5$.

The catalytic reactions were performed on a recirculation reactor (ca. 255 cm^3) equipped with a high-vacuum system. After the activation, the alloy catalyst was evacuated at 673 K for about 4 h, set at 393–473 K of the reaction temperatures and then the transfer hydrogenation was initiated by admitting 2-propanol and/or 2-butene. The

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reacting gas in the system was periodically collected by a gas sampler and analyzed using a Shimazu gas chromatograph.

3. Results and discussion

To determine how the transfer hydrogenation of 2-butene from 2-propanol occurs on the $CaNi_5$ catalyst and how the absorbed hydrogen affects the reaction, we carried out two types of reaction differing in addition modes of propanol and butene.

3.1. Exposing $CaNi_5$ to 2-propanol, followed by addition of 2-butene

First we studied the reaction observed when only 2-propanol (30 Torr) was brought into contact with $CaNi_5$ (1.0 g) at 423 K. $CaNi_5$ showed the catalytic activity for the dehydrogenation of 2-propanol after conventional activation procedures consisting of repeated hydriding–dehydriding cycles. Time courses of the dehydrogenation are shown in figure 1. 2-propanol was readily converted to acetone with a selectivity of nearly 100%. However, hydrogen was scarcely detected in the gas phase during the dehydrogenation; all hydrogen dissociated from 2-propanol was immediately absorbed in $CaNi_5$ to form the hydride before coupling with subsequent liberation of hydrogen gas. This type of dehydrogenation was thermodynamically more favorable than regular dehydrogenation [9–11].

Normal dehydrogenation of 2-propanol to acetone ($CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + H_2$) is accompanied by an increase in the standard Gibbs free energy (ΔG° at 25 °C) by ca. $+25\ \mathrm{kJ\,mol^{-1}}$ of acetone formed. However, ΔG° for the dehydrogenation of 2-propanol on $CaNi_5$ to form acetone and the metal hydride ($CH_3CH(OH)CH_3 + CaNi_5 \rightarrow CH_3COCH_3 + CaNi_5H_2$) is advantageous for the energy of hydride formation [7]. Thus the hydride formation provides the driving force for the dehydrogenation of 2-propanol.

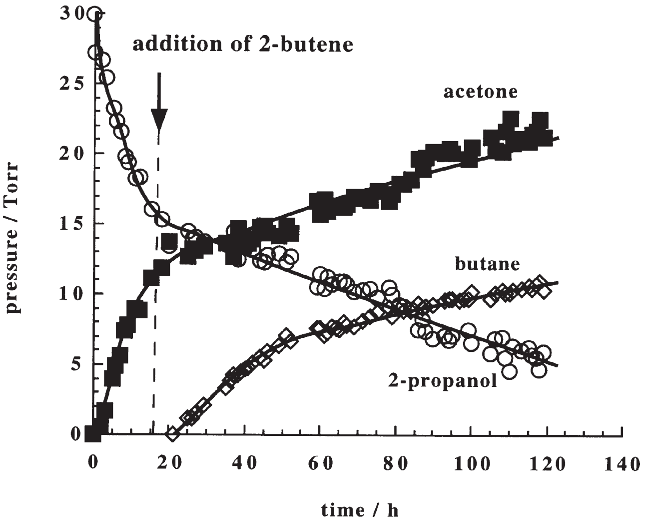

Figure 1. Time courses of the reaction at 423 K upon addition of 2-propanol and subsequent 2-butene.

When the conversion of 2-propanol was reached at about 50% (as shown by an arrow in figure 1), 2-butene of 30 Torr was added into the circulating propanol. The butane product was formed immediately after addition, followed by steady formation. Since no direct transfer hydrogenation between 2-propanol and 2-butene occurs from the beginning as described in section 3.2, butane observed here is largely formed by the hydrogenation with the aid of absorbed hydrogen. It has been shown that the absorbed hydrogen is effectively consumed for the reaction with olefin without evolution as hydrogen gas [12–15]. Furthermore, the proportions of acetone and butane formed were nearly the same during the reaction. This indicates that the steady hydrogenation of butene occurs by consuming the absorbed hydrogen, and simultaneous occurrence of propanol dehydrogenation efficiently makes up for the consumption of absorbed hydrogen. Thus, the reaction of propanol and butene on $CaNi_5$ follows the stoichiometric relationship as catalytic transfer hydrogenation through intermediate formation of metal hydrides:

$$
\begin{array}{l}
CH_3CH(OH)CH_3 + nCaNi_5 \rightarrow \\
\quad CH_3COCH_3 + nCaNi_5H_{2/n} \\
nCaNi_5H_{2/n} + C_4H_8 \rightarrow nCaNi_5 + C_4H_{10} \\
\hline
CH_3CH(OH)CH_3 + C_4H_8 \rightarrow CH_3COCH_3 + C_4H_{10}
\end{array}
$$

At a lower reaction temperature of 393 K (figure 2), the dehydrogenation activity of $CaNi_5$ was decreased despite thermodynamic advantages. Then, butene was similarly added to the reaction system, but the hydrogenation rates of butene were very low compared to the reaction at 423 K. Since the amounts of hydrogen absorbed by $CaNi_5$ are decreased for the drop in dehydrogenation activity and,

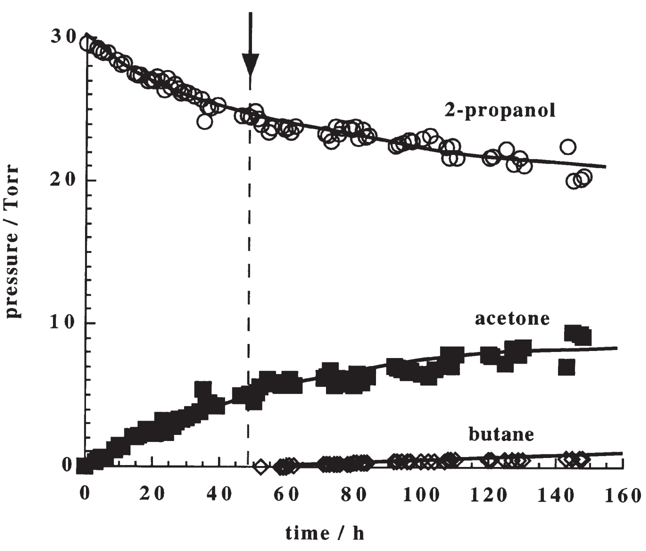

Figure 2. Time courses of the reaction at 403 K upon addition of 2-propanol and subsequent 2-butene.

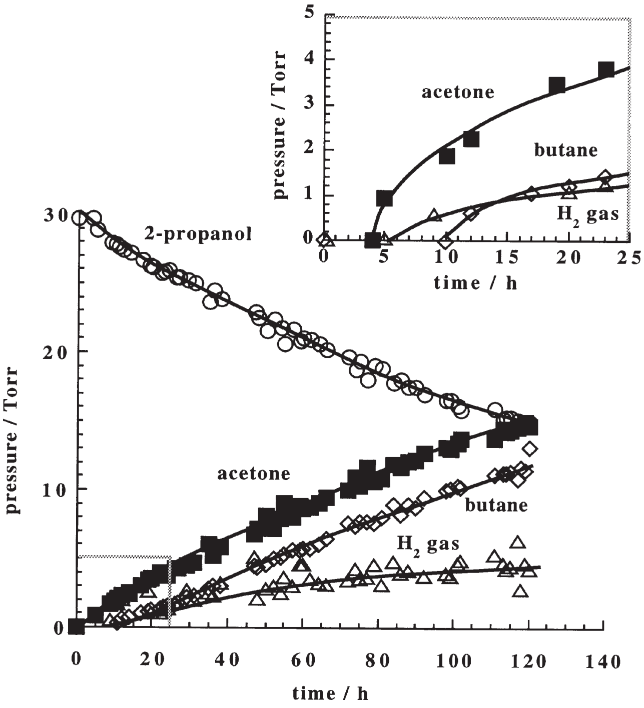

Figure 3. Time courses of the reaction at 423 K upon addition of a mixture of 2-propanol and 2-butene.

besides, the dissociation pressures of hydrogen fall for the decrease from 423 to 393 K, the participation of the absorbed hydrogen in the hydrogenation would be depressed to a significant extent. In addition, it is strongly suggested from figure 2 that direct transfer hydrogenation between 2-propanol and 2-butene on $CaNi_5$ hardly occurs either.

When the reaction temperature was raised to 473 K, the dehydrogenation of propanol more effectively occurred. However, in this dehydrogenation, hydrogen of about 3 Torr was detected in the gas phase during the dehydrogenation, probably due to a rise in dissociation pressures of hydrogen. The pressure of hydrogen observed remained unchanged during the reaction. Upon addition of butene, the transfer hydrogenation similarly proceeded. That the hydrogen in the gas phase other than the absorbed hydrogen can simultaneously participate in the hydrogenation of butene is considered. However, in the hydrogenation of olefin on hydrogen-absorbing alloys, the reactivity of hydrogen gas is usually lower than that of absorbed hydrogen [13,14]; therefore, most of the butane product can be attributable to the absorbed hydrogen.

3.2. Exposing $CaNi_5$ to a gaseous mixture of 2-propanol and 2-butene

The reaction was initiated by admitting a mixture of 2-propanol (30 Torr) and 2-butene (30 Torr) at 423 K (figure 3). There was an obvious induction period for the dehydrogenation and hydrogenation. The dehydrogenation of propanol began after about 4 h and afterwards, after a while, the slow formation of butane was observed. From these facts, it now seems quite certain that no direct transfer hydrogenation of butene from propanol as hydrogen donor occurs on $CaNi_5$.

In contrast to the case of the previous run (addition of propanol alone; figure 1), the dehydrogenation slowly proceeded with liberation of some hydrogen in the gas phase and the formation rates of butane were also low. In this case, the concentration of hydrogen absorbed in $CaNi_5$ was naturally low; to initiate the addition reaction to butene on the hydride, absorbed hydrogen of more than a certain concentration in $CaNi_5$ is presumably required [13]. This causes lower hydrogenation activities for butene with a long induction period. The presence of competitively adsorbed butene on $CaNi_5$ hinders the adsorption of propanol with subsequent dissociation and absorption processes. This is probably a reason why there was the induction period and why hydrogen was not necessarily absorbed with liberation in the gas phase during the reaction. This observation of gaseous hydrogen is rather surprising in view of the results obtained from the previous runs (section 3.1). Some questions still remain as to why the hydrogen dissociated from propanol was effectively absorbed and not necessarily, upon differing mode of addition of propanol and butene.

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