# Lanthanide (Eu or Yb)-promoted Ni, Cu and Ag-catalyzed transfer hydrogenation with $NH_3$ as a hydrogen donor

Hayao Imamura [*], Yukihisa Miura, Koji Fujita, Yoshihisa Sakata, Susumu Tsuchiya

*Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755-8611, Japan*

## Abstract

Novel lanthanide (Ln)-promoted Ni, Cu and Ag catalysts prepared by the reaction of $Ni/SiO_2$, $Cu/SiO_2$ and $Ag/ZrO_2$ with the dissolved Eu or Yb metals in liquid ammonia have been studied for the catalytic transfer hydrogenation of ethene, buta-1,3-diene and propyne. The transfer hydrogenation with the aid of ammonia as a hydrogen donor was greatly enhanced by the Ln-promoted catalysts. The catalytic activity for the transfer hydrogenation increased with increasing lanthanide content in the bimetallic catalysts, which evidently reflected synergetic effects between the lanthanide and transition metals. The transfer hydrogenation of ethene with ammonia over $Eu–Ni/SiO_2$ proceeded to form ethane and nitrogen, maintaining the following stoichiometric relationships: $3C_2H_4 + 2NH_3 \rightarrow 3C_2H_6 + N_2$ The catalytic hydrogen transfer from ammonia to buta-1,3-diene or propyne similarly followed the stoichiometric relationships. The Ln-promoted catalysts showed substrate selectivity for the transfer hydrogenation using ammonia as the hydrogen source; $Ln–Ni/SiO_2$ was reactive for ethene and buta-1,3-diene, but not for propyne. $Ln–Cu/SiO_2$ was active for propyne and buta-1,3-diene. $Ln–Ag/SiO_2$ was relatively active for buta-1,3-diene. The major factors governing the catalytic transfer hydrogenation seem to be involved in the participation of the acceptor and donor molecules in the hydrogen transfer step rather than the ease of dehydrogenation of ammonia and the processes of hydrogen addition to the acceptor. The catalytic hydrogen transfer from ammonia to acceptor molecules occurs concertedly. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic transfer hydrogenation; Bimetallic catalyst; Lanthanide; Ammonia; Europium; Ytterbium

## 1. Introduction

Recently there has been a growing interest in the specific properties of lanthanides and related compounds as a catalyst [1–3]. It is known that Eu and Yb among the lanthanide metals (Ln) readily dissolve in liquid ammonia to yield a homogeneous solution containing the solvated electrons [4]. Upon addition of Fe, Co, Ni or Cu metal powders to this solution, it was first observed that the dissolved lanthanide metal in liquid ammonia reacted with the transition metal to form novel lanthanide metal overlayers [5]. By the use of dissolution of lanthanide metals in liquid ammonia, we

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[*] Corresponding author.

have developed methods for the preparation of novel lanthanide-containing catalytic materials and have demonstrated that they can effectively catalyze various reactions [6–14].

Catalytic transfer hydrogenation with hydrogen donors shows some interesting features which are of potential synthetic importance and use [15–21]. It has also been shown that an interesting alternative to conventional catalytic hydrogenation exists in the catalytic transfer hydrogenation in terms of higher selectivity, milder reaction conditions or more excellent yield than those of regular hydrogenation. We have previously reported that lanthanide-promoted catalysts prepared by reacting with Eu or Yb metal solutions in liquid ammonia are effective for the catalytic transfer hydrogenation, in which ammonia is a preferred hydrogen donor [22]. Such enhanced activity in the transfer hydrogenation evidently reflects synergetic actions between the lanthanide and transition metals.

There have been few studies reported on the transfer hydrogenation over lanthanide-containing bimetallic catalysts. Far less well known is the possibility of achieving reduction with the aid of ammonia as the hydrogen source in organic reactions. Therefore, in this work we elucidate the features of the reaction, the primary factors in determining the hydrogen transfer process from ammonia, and the mechanistic aspects for the transfer hydrogenation of ethene, buta-1,3-diene and propyne on $Ln-Ni/SiO_2$, $Ln-Cu/SiO_2$ or $Ln-Ag/ZrO_2$. Much attention is also devoted to the effect of lanthanides on the catalytic hydrogen transfer from ammonia to the acceptors over the Ln-promoted catalysts.

## 2. Experimental

### 2.1. Materials

Eu and Yb ingots (99.9%, Shin-Etsu Chemical) were used in the form of turnings or granules. $SiO_2$ (Degussa Aerosil 380) and $ZrO_2$ (Tosoh-Zirconia TZ-O) were commercially available. $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and $AgNO_3$ purchased from Wako were reagent-grade. $NH_3$ (Iwatani Ind.) was dried through a calcium oxide column and a sodium hydroxide column before use. $ND_3$ (99%; Isotec) was used without further purification. Ethene, but-1,3-diene and propyne were of research purity, and further purified by triple distillation.

### 2.2. Procedures of catalyst preparation and catalytic reactions

The following were prepared by impregnating $SiO_2$ or $ZrO_2$ with aqueous solutions of the metal salts: 20 mass% $Ni/SiO_2$, 30 mass% $Cu/SiO_2$ and 20 mass% $Ag/ZrO_2$. The impregnating slurry was vigorously stirred, dried, calcined at 623 K, and finally reduced with flowing hydrogen at a standard pressure (reduction temperature: 673 K for $Ni/SiO_2$, 573 K for $Cu/SiO_2$ and 423 K for $Ag/ZrO_2$).

The method of lanthanide addition to $Ni/SiO_2$, $Cu/SiO_2$ and $Ag/ZrO_2$ was similar to that previously described in earlier papers [8]. In a typical preparation of $Ln-Ni/SiO_2$, $Ni/SiO_2$ that had been reduced was placed in a Schlenk tube containing a solution of liquid ammonia (15–20 cm$^3$) at 198 K. Eu or Yb was added to this solution of $Ni/SiO_2$ suspended in liquid ammonia with vigorous stirring. Upon dissolution of the lanthanide metal in liquid ammonia, a blue homogeneous solution was immediately formed, which was characteristic of the solvated electrons [4]. The blue color gradually disappeared as a result of the reaction of the dissolved lanthanide metal with $Ni/SiO_2$. Upon complete disappearance of the blue color, the reaction tube was allowed to warm to room

temperature, and the excess ammonia was vaporized leaving $SiO_2$-supported Eu–Ni and Yb–Ni bimetallic catalysts. Extreme care for all operations was taken to prevent contamination by air. Ln–Cu/$SiO_2$ and Ln–Ag/$ZrO_2$ were similarly prepared.

The catalytic reactions were performed on a recirculation reactor equipped with a high vacuum system. Prior to each reaction the catalyst was briefly evacuated at room temperature, set at 403 or 453 K of the reaction temperature and then the transfer hydrogenation was initiated by admitting reactant and ammonia. The reacting gas in the system was periodically collected by a gas sampler and analyzed using a Shimazu gas chromatograph and a quadrupole mass spectrometer (MS).

## 2.3. Analyses

Temperature-programmed desorption (TPD) experiments were carried out at a constant heating rate of 10 K min$^{-1}$, evacuating the whole system by a diffusion pump. After brief evacuation of the catalyst as prepared at room temperature, the catalyst sample was heated in a programmed manner, and the desorbed gases were continuously monitored by MS.

# 3. Results and discussion

## 3.1. General features of transfer hydrogenation over various Ln-promoted catalysts

The catalytic transfer hydrogenation was carried out in the gas phase using a Pyrex gas-recirculation reactor. After the catalysts were briefly evacuated, a mixture of propyne (21 Torr) and ammonia (40 Torr) was introduced into the reactor to initiate the reaction at 453 K. The Ln-promoted Cu catalyst was active for propyne hydrogenation, while Ln–Ni/$SiO_2$ showed negligible activity. Time courses of reaction on Eu–Cu/$SiO_2$ (Eu/Cu = 0.33) are shown in Fig. 1, where the hydrogenation of propyne to propene occurred with ammonia as the source of hydrogen. Rapid conversion of propyne into the allene isomer initially occurred and simultaneously, the propene product and nitrogen as a dehydrogenated donor were steadily formed in a molar ratio of about 3:1, respectively. The Eu–Cu/$SiO_2$ catalyst was completely selective for propene formation, probably due to negligibly
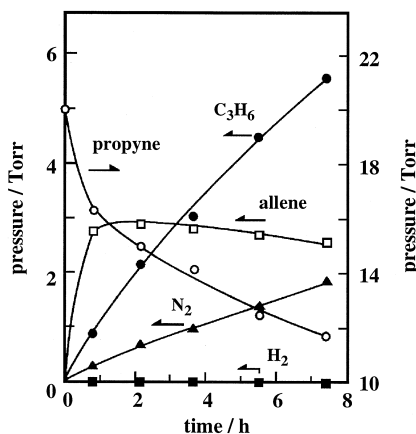


Fig. 1. Time courses of the catalytic transfer hydrogenation of propyne over Eu–Cu/$SiO_2$ at 453 K. Reaction conditions: Eu–Cu/$SiO_2$ (Eu/Cu = 0.33) = 0.1 g; propyne = 20 Torr; $NH_3$ = 40 Torr.

activity for the transfer hydrogenation of olefin from ammonia as described later. Considering that hydrogen was scarcely detected in the gas-phase, the catalytic hydrogen transfer from ammonia to propyne stoichiometrically proceeded to form propene and nitrogen, maintaining the stoichiometrical relationships shown below:

$$3C_3H_4 + 2NH_3 \rightarrow 3C_3H_6 + N_2$$
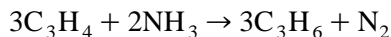
However, the catalytic transfer hydrogenation of propyne on Eu–Cu/SiO$_2$ might proceed in parallel with a reaction path through the allene intermediate as described in the later section.

When ethene was used as an acceptor, Eu–Ni/SiO$_2$ was active but Ln–Cu/SiO$_2$ was not so active. Ln–Ag/ZrO$_2$ was quite inactive. The transfer hydrogenation of ethene on Eu–Ni/SiO$_2$ (Eu/Ni = 0.72) are shown in Fig. 2. The catalytic hydrogen transfer from ammonia to ethene effectively occurred at 403 K to rapidly form ethane in the beginning of the reaction. As ammonia was consumed during the hydrogenation, nitrogen was stoichiometrically released and the formation of hydrogen was scarcely observed as well. Thus, the reaction followed the stoichiometric relationships:

$$3C_2H_4 + 2NH_3 \rightarrow 3C_2H_6 + N_2$$
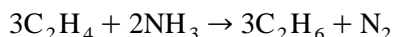
The catalytic transfer hydrogenation rates were negligibly dependent upon the ethene (4–98 Torr) and ammonia pressures (6–102 Torr).

The transfer hydrogenation of buta-1,3-diene similarly occurred over Ln–Ni/SiO$_2$, Ln–Cu/SiO$_2$ and Ln–Ag/ZrO$_2$ to stoichiometrically form butene and nitrogen. It was proved that for the catalytic transfer hydrogenation over such lanthanide-promoted catalysts, ammonia was effectively operative as hydrogen donor.

Furthermore, an interesting feature of the catalytic transfer hydrogenation by the use of ammonia is that substrate selectivity of such lanthanide-promoted catalysts is considerably high. The results using various catalysts are summarized in Table 1. In the transfer hydrogenation of ethene, Ln–Ni/SiO$_2$ was very reactive, but not for Ln–Cu/SiO$_2$ and Ln–Ag/ZrO$_2$. Ln–Ru/C was also active towards ethene hydrogenation [22]. Ln–Cu/SiO$_2$ showed much higher activity for the hydrogenation of propyne than other catalyst systems. Ln–Ag/ZrO$_2$ was inactive or less active for the transfer
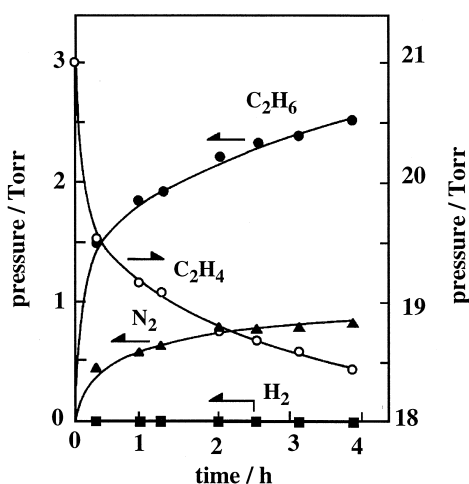


Fig. 2. Time courses of the catalytic transfer hydrogenation of ethene over Eu–Ni/SiO$_2$ at 403 K. Reaction conditions: Eu–Ni/SiO$_2$ (Eu/Ni = 0.72) = 0.4 g; C$_2$H$_4$ = 21 Torr; NH$_3$ = 40 Torr.

Table 1
Transfer hydrogenation from ammonia over Eu- and Yb-promoted catalysts[a]

| Reactant | Catalyst | Reaction temperature (K) | Activity (mmol $min^{-1}$ $g^{-1}$) |
|---|---|---|---|
| Ethene | 20 mass% $Ni/SiO_2$ | 403 | $2.0 \times 10^{-4}$ |
| | $Eu–Ni/SiO_2$ (Eu/Ni = 0.75) | 403 | $2.1 \times 10^{-3}$ |
| | $Yb–Ni/SiO_2$ (Yb/Ni = 0.47) | 403 | $2.4 \times 10^{-4}$ |
| | 30 mass% $Cu/SiO_2$ | 453 | $-^{b}$ |
| | $Eu–Cu/SiO_2$ (Eu/Cu = 0.33) | 453 | trace |
| | 20 mass% $Ag/ZrO_2$ | 453 | $-^{b}$ |
| | $Eu–Ag/ZrO_2$ (Eu/Ag = 0.67) | 453 | $-^{b}$ |
| | 5 mass% $Ru/C^{c}$ | 453 | $1.4 \times 10^{-4}$ |
| | $Eu–Ru/C$ (Eu/Ru = 4.0)$^{c}$ | 453 | $6.4 \times 10^{-4}$ |
| Buta-1,3-diene | 20 mass% $Ni/SiO_2$ | 403 | $7.1 \times 10^{-5}$ |
| | $Eu–Ni/SiO_2$ (Eu/Ni = 0.75) | 403 | $1.2 \times 10^{-3}$ |
| | 30 mass% $Cu/SiO_2$ | 453 | $-^{b}$ |
| | $Eu–Cu/SiO_2$ (Eu/Cu = 0.67) | 453 | $3.8 \times 10^{-3}$ |
| | 20 mass% $Ag/ZrO_2$ | 453 | $-^{b}$ |
| | $Eu–Ag/ZrO_2$ (Eu/Ag = 0.67) | 453 | $1.2 \times 10^{-4}$ |
| | $Yb–Ag/ZrO_2$ (Yb/Ag = 0.67) | 453 | $1.5 \times 10^{-5}$ |
| Propyne | 20 mass% $Ni/SiO_2$ | 453 | $-^{b}$ |
| | $Eu–Ni/SiO_2$ (Eu/Ni = 0.43) | 453 | trace |
| | 30 mass% $Cu/SiO_2$ | 453 | $2.6 \times 10^{-4}$ |
| | $Eu–Cu/SiO_2$ (Eu/Cu = 0.33) | 453 | $2.4 \times 10^{-3}$ |
| | 20 mass% $Ag/ZrO_2$ | 453 | $-^{b}$ |
| | $Eu–Ag/ZrO_2$ (Eu/Ag = 1.5) | 453 | $1.4 \times 10^{-6}$ |

[a] The reaction was conducted by admitting reactant (21 Torr) and $NH_3$ (40 Torr).
[b] The activity was zero within detection limits.
[c] See Ref. [22].

hydrogenation of ethene and propyne, but relatively active for buta-1,3-diene. $Ln–Cu/SiO_2$ and $Ln–Ni/SiO_2$ were also active for the transfer hydrogenation of buta-1,3-diene.

## 3.2. Effects of lanthanide addition

$Cu/SiO_2$ or $Ag/ZrO_2$ alone was virtually inactive for the transfer hydrogenation of any reactant substrates used or its activity was very low, if any. $Ni/SiO_2$ and $Ru/C$ showed some activity towards the ethene and buta-1,3-diene acceptors. On the other hand, Eu (or Yb)$/SiO_2$ exhibited only negligible activity. These transition metals studied were used more efficiently when dosed with the lanthanide metals. For the catalytic transfer hydrogenation of propyne by $Ln–Cu/SiO_2$, the activity markedly appeared upon introduction of lanthanides onto $Cu/SiO_2$ and increased with an increase in Ln/Cu ratios (0–0.33) (Fig. 3). In the hydrogenation of ethene on $Ln–Ni/SiO_2$, the similar dependence of activity upon lanthanide content was observed (Fig. 4). Particularly in higher Eu/Ni regions the activity increased over 10-fold relative to $Ni/SiO_2$. $Ln–Ru/C$ showed behavior similar to $Ln–Ni/SiO_2$ [22]. The catalytic activity of $Ln–Ag/ZrO_2$ was apparent upon addition of small amounts of lanthanides and increased abruptly by over two or three orders of magnitude with increase in lanthanide content. In the lanthanide-promoted Ni, Cu and Ag catalysts studied, the Eu-added
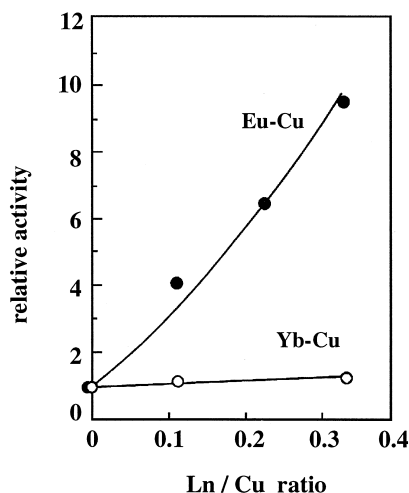
Fig. 3. Relative activities of the transfer hydrogenation of propyne (453 K) vs. Ln/Cu ratios of Ln–Cu/SiO$_2$. Reaction conditions: propyne = 21 Torr; NH$_3$ = 40 Torr.

systems were much more active than the Yb-added ones. The effects of Yb addition on the catalytic transfer hydrogenation was usually low, the reason for which is presently unknown. Such enhanced activities in the transfer hydrogenation evidently reflect synergetic action between the europium and transition metals (Ni, Cu and Ag). The synergy of the binary Ln–Co and Ln–Ni systems has been studied [23], in which it is ascertained to be more markedly appears with the formation of a specific surface intermetallic compound when the surface coverage with the lanthanide metals increases, as reported by Nix et al. [24]. It has been shown that Ln–Ni [14], Ln–Cu [13] and Ln–Ag [13,25] exhibit enhanced activities for normal hydrogenation with hydrogen. Furthermore, the catalytic activation of the H–H and C–H bonds is markedly promoted by introduction of lanthanides onto Co [11] or Ni [12,23] metal surfaces. Murata and Aika have reported that lanthanide (La, Ce or Sm)-added Ru/Al$_2$O$_3$ exhibits a higher activity for ammonia syntheses [26].
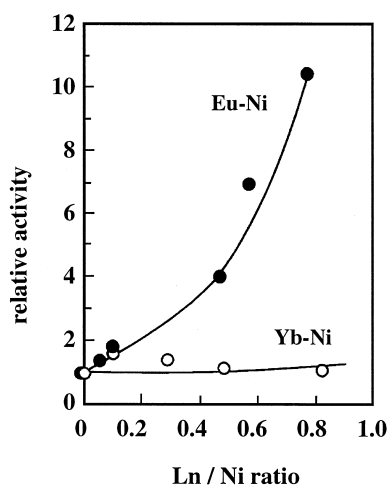


Fig. 4. Relative activities of the transfer hydrogenation of ethene (403 K) vs. Ln/Ni ratios of Ln–Ni/SiO$_2$. Reaction conditions: C$_2$H$_4$ = 21 Torr; NH$_3$ = 40 Torr.

The synergetic effect also reflected the selectivity of hydrogenated products. The Eu–Ni/SiO$_2$ (Eu/Ni = 0.61)-catalyzed buta-1,3-diene hydrogenation yielded preferential butene formation with high selectivity (ca. 100%). The yield of but-2-ene was relatively high compared with but-1-ene and the *trans*:*cis* ratio in the but-2-ene isomer was low. This was quite different from the results with Ni/SiO$_2$ or Ln/SiO$_2$ alone. Moreover, the product composition was obviously different from regular hydrogenation using hydrogen over Ln–Ni/SiO$_2$ [27]. Eu–Ag/ZrO$_2$ (Eu/Ag = 0.67) gave preferential but-2-ene formation with a low *trans*:*cis* ratio (0.42–0.45) compared with the results on normal catalytic hydrogenation over Ln–Ag catalyst [25].

## 3.3. Mechanistic considerations

As shown in the transfer hydrogenation from ammonia over Eu–Cu/SiO$_2$ (Fig. 1) and Eu–Ni/SiO$_2$ (Fig. 2), in any cases hydrogen was scarcely detected in the gas phase throughout the reaction; therefore, the preferential addition processes of hydrogen to the acceptor molecules seem to occur immediately before coupling with subsequent liberation of hydrogen gas. We exposed Eu–Ni/SiO$_2$ to 20 Torr of ammonia at 403 K for 2.5 h, followed by addition of the ethene acceptor (20 Torr). As shown in Fig. 5, there was no dehydrogenation of ammonia at 403 K or above when only ammonia was introduced to any Ln-promoted catalyst systems. Thus the reaction temperature available with ammonia is not sufficient to cause dehydrogenation at an adequate rate. Then, the addition of ethene resulted in rapid hydrogen transfer from ammonia to ethene (Fig. 5). Considering that Eu–Ni/SiO$_2$ is active for the catalytic transfer hydrogenation of ethene at 403 K, but not for propyne even at 453 K or above, the difference in reactivity does not reflect simply the relative ease of dehydrogenation of ammonia. Certainly, no isotopic exchange reaction occurred to form deuterioammonia NH$_{3-x}$D$_x$, even if a mixture of NH$_3$ + ND$_3$ was brought into contact with any Ln-promoted catalysts. It is strongly suggested that the present transfer hydrogenation occurs concertedly between the acceptor and donor units. This was the case for the transfer hydrogenation of propyne and buta-1,3-diene using Eu–Cu/SiO$_2$ at 453 K, in which ammonia was circulated over the catalyst and then propyne or buta-1,3-diene was added into the circulating ammonia. In the absence of any acceptors, ammonia remained unchanged on Eu–Cu/SiO$_2$ and then, upon introduction of acceptor molecules into the
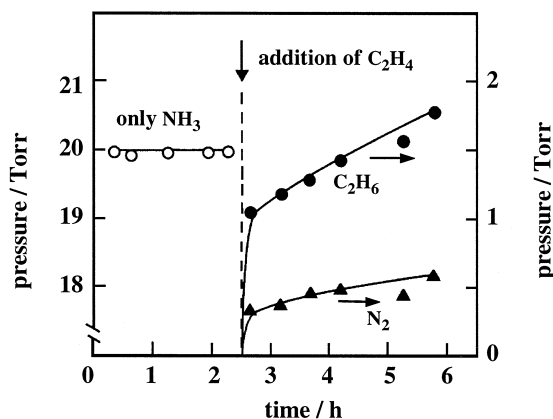


Fig. 5. The reaction of ammonia over Eu–Ni/SiO$_2$ at 403 K, followed by introduction of ethene (indicated by an arrow). $\bigcirc$: NH$_3$; $\bullet$: C$_2$H$_4$; $\blacktriangle$: N$_2$. Reaction conditions: Eu–Ni/SiO$_2$ (Eu/Ni = 0.54) = 0.4 g; NH$_3$ = 20 Torr; C$_2$H$_4$ = 20 Torr.

reaction system, the transfer hydrogenation from ammonia was initiated at reaction rates similar to the results observed when the mixed gases ($C_3H_4 + NH_3$ or $1,3\text{-}C_4H_6 + NH_3$) were used. The Ln–Ni [5,14] and Ln–Cu [13] catalysts are known to be quite active for normal hydrogenation even at much lower temperatures (206–273 K). Therefore, it is likely that the participation of the ammonia donor in the hydrogen transfer step over the Ln-promoted catalysts rather than the dehydrogenation of ammonia and the hydrogen addition to the acceptor is an important factor in determining the activity of the present transfer hydrogenation. In addition, this is closely associated with the appearance of substrate selectivity observed for the Ln–Ni, Ln–Cu and Ln–Ag catalysts.

Isotopic effects in Eu–Ni/$SiO_2$-catalyzed reaction kinetics obtained when the reactions of $C_2H_4 + ND_3$ or $C_2D_4 + NH_3$ were carried out at 403 K were $r_H/r_D = 1.5$ or 3.0, respectively, where $r_H/r_D$ is the ratio for the reaction rate ($r_H$) using $C_2H_4 + NH_3$. In the transfer hydrogenation of propyne on Eu–Cu/$SiO_2$, the isotopic effect of $C_3H_4 + NH_3$ to $C_3H_4 + ND_3$ was about 2.1. These results are consistent with the mechanistic discussion for the catalytic transfer hydrogenation, in which concerted hydrogen transfer proceeds between ammonia and acceptor molecules adsorbed on the catalysts.

The distributions of deuterium in the products of Eu–Ag/$ZrO_2$-catalyzed hydrogenation of $1,3\text{-}C_4H_6 + ND_3$ were examined. At conversion of ca. 6.8%, only $C_4H_6D_2$ (41%) was selectively produced as deuteriobutene products and the remainder was $C_4H_8$ (59%). At higher conversion, the relative proportion of the $d_2$-butene product to $d_0$-butene increased. This is due to that adsorbed ammonia derived from the catalyst preparation using liquid ammonia (see Section 2) remains on the catalyst surface and preferentially contributes to the initial hydrogenation. The butene products were certainly observed when only buta-1,3-diene was brought into contact with Eu–Ag/$ZrO_2$. The presence of adsorbed ammonia on Ln–Ni/$SiO_2$, Ln–Cu/$SiO_2$ and Ln–Ag/$ZrO_2$ as prepared was confirmed by TPD. Such adsorbed ammonia is considered highly reactive. The results obtained when only propyne was introduced to Eu–Cu/$SiO_2$ are shown in Fig. 6, comparing with the case using a mixture of propyne and ammonia. Even without the ammonia donor, the formation of propene was similarly observed initially, but afterward it was negligibly small. However, it should be noted that in this case, nitrogen as dehydrogenated donors, as well as propene, was formed in a nearly stoichiometric ratio of $N_2:C_3H_6 = 1:3$ (see the solid lines in Fig. 6). Furthermore, the effects of pre-adsorption of
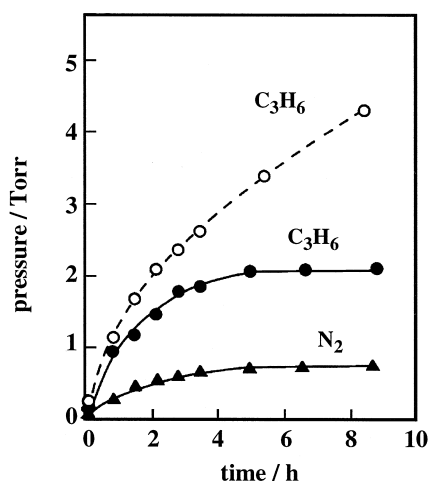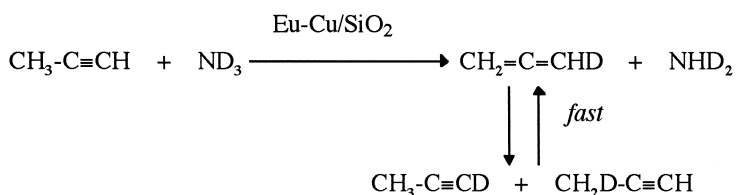


Fig. 6. Time courses of $C_3H_6$ formation upon introduction of only propyne (solid line) into the system of Eu–Cu/$SiO_2$ at 453 K, in comparison with the reaction of propyne and ammonia (dotted line). Reaction conditions: Eu–Cu/$SiO_2$ (Eu/Cu = 0.11) = 0.12 g; propyne = 21 Torr; $NH_3$ = 40 Torr.

ammonia or evacuation treatment of catalysts on the transfer hydrogenation was obviously observed; prior to the reaction, exposing the catalyst to ammonia beforehand resulted in enhanced activity and the activity was decreased upon evacuation of the catalyst at elevated temperatures.

The distributions of deuterium in the products obtained when the reaction of $C_3H_4 + ND_3$ was studied at 453 K using $Eu-Cu/SiO_2$ are depicted in Fig. 7. There were no products with mass number above $m/e$ 46. Time courses of the product of $m/e$ 41 is characteristic compared with other products, which approximately corresponds to the time course of the allene yield shown in Fig. 1. It has been previously described that no direct exchange reaction between $NH_3$ and $ND_3$ occurred on any Ln-promoted catalysts, but some deuterioammonia $NH_{3-x}D_x$ were formed in the reaction of $C_3H_4 + ND_3$. This is consistent with that the transfer hydrogenation on the Ln-promoted catalysts consists of concerted steps which permit reversible interconversion of propyne to allene. Thus the isomerization of propyne presumably contains dissociation–addition processes of hydrogen during the concerted reaction between $C_3H_4$ and $ND_3$; for instance, there is rearrangement of acetylenic hydrocarbons involving resonance-stabilized carbanions as intermediates [28]. Deuterioallene is operative as intermediates in further conversion to deuteriopropyne.

$$CH_3\text{-}C\equiv CH \quad + \quad ND_3 \xrightarrow{\quad Eu\text{-}Cu/SiO_2 \quad} CH_2=C=CHD \quad + \quad NHD_2$$

$$\downarrow\uparrow \quad fast$$

$$CH_3\text{-}C\equiv CD \quad + \quad CH_2D\text{-}C\equiv CH$$

The $C_3H_5D$ product is formed by hydrogen transfer from residual $NH_3$ adsorbed on the catalyst to propyne or allene $(C_3H_3D)$ thus produced. The butenes of $C_3H_4D_2$ and $C_3H_3D_3$ are produced by the reaction of $C_3H_4$ and $C_3H_3D$ with $ND_3$, respectively. The major factors governing the transfer hydrogenation on Ln-promoted catalysts seem to be involved in the participation of the acceptor and donor in the hydrogen transfer step rather than the ease of dehydrogenation of ammonia, and the hydrogen addition to the acceptor and its reverse reaction. Thus the catalytic hydrogen transfer from ammonia to acceptor molecules occurs concertedly.
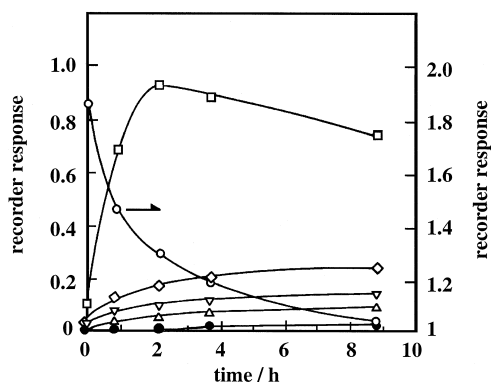


Fig. 7. Distributions of deuterium in the products by the reaction of $C_3H_4 + ND_3$ over Eu–Cu/SiO$_2$ at 453 K. ○: $m/e$ 40; □: $m/e$ 41; ◇: $m/e$ 42; ▽: $m/e$ 43; △: $m/e$ 44; ●: $m/e$ 45. Reaction conditions: Eu–Cu/SiO$_2$ (Eu/Cu = 0.33) = 0.1 g; propyne = 21 Torr; ND$_3$ = 40 Torr.

# References

[1] S.T. Oyama, G.L. Haller, Catalysis, Specialist Periodical Report, Vol. 5, The Chemical Society, London, 1982, p. 333.

[2] W.E. Wallace, CHEMTECH (1982) 752.

[3] F.P. Netzer, E. Berter, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 5, North-Holland, Amsterdam, 1983, Chap. 3.

[4] J.C. Thompson, Electrons in Liquid Ammonia, Clarendon Press, Oxford, 1976.

[5] H. Imamura, T. Mihara, M. Yoshinobu, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Chem. Commun. (1989) 1842.

[6] H. Imamura, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, North-Holland, Amsterdam, 1998, in press.

[7] H. Imamura, T. Konishi, E. Suda, Y. Sakata, S. Tsuchiya, Bull. Chem. Soc. Jpn. 69 (1996) 77.

[8] H. Imamura, K. Igawa, Y. Kasuga, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 90 (1994) 2119.

[9] H. Imamura, T. Konishi, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Chem. Commun. (1993) 1852.

[10] H. Imamura, T. Konishi, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 88 (1992) 2251.

[11] H. Imamura, S. Hiranaka, M. Takamoto, Y. Sakata, S. Tsuchiya, J. Mol. Catal. 77 (1992) 333.

[12] H. Imamura, S. Hiranaka, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 88 (1992) 1577.

[13] H. Imamura, M. Yoshinobu, T. Mihara, Y. Sakata, S. Tsuchiya, J. Mol. Catal. 69 (1991) 271.

[14] H. Imamura, K. Yoshimura, Y. Sakata, S. Tsuchiya, J. Chem. Soc., Faraday Trans. 87 (1991) 2805.

[15] Z. Dobrovolna, L. Cerveny, Chem. Listy 90 (1996) 93.

[16] G. Zassinovich, G. Mestroni, S. Gladiali, Chem. Rev. 92 (1992) 1051.

[17] R.A.W. Johnstone, A.H. Wilby, Chem. Rev. 85 (1985) 129.

[18] G. Brieger, T.J. Nestrick, Chem. Rev. 74 (1974) 567.

[19] A. Furst, R.C. Berlo, S. Hooton, Chem. Rev. 65 (1965) 51.

[20] P.E. Hattaway, M.E. Davis, J. Catal. 116 (1989) 263.

[21] H. Hartner, Kontakte 1 (1980) 3.

[22] H. Imamura, K. Fujita, Y. Miura, K. Mizuno, Y. Sakata, S. Tsuchiya, Chem. Commun. (1996) 1841.

[23] H. Imamura, Y. Kasuga, K. Abe, Y. Sakata, S. Tsuchiya, Catal. Lett. 32 (1995) 115.

[24] R.M. Nix, R.W. Judd, R.M. Lambert, Surf. Sci. 203 (1988) 307.

[25] H. Imamura, K. Fujita, Y. Sakata, S. Tsuchiya, Catal. Today 28 (1996) 231.

[26] S. Murata, K. Aika, J. Catal. 136 (1992) 118.

[27] H. Imamura, M. Yoshinobu, T. Mihara, in: S. Yoshida, N. Takezawa, T. Ono (Eds.), Catalytic Science and Technology, Vol. 1, Kodansha, Tokyo, 1990, p. 279.

[28] H. Pines, W.M. Stalick, Base-Catalyzed Reactions of Hydrocarbons and Related Compounds, Academic Press, New York, 1977.