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Hydrogenation properties of lanthanide-dosed Ag bimetallic catalysts

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Abstract

Ln-dosed Ag/SiO_2 (Ln = Eu and Yb) bimetallic catalysts were prepared by the reaction of SiO_2-supported Ag (Ag/SiO_2) with a solution of lanthanide metals dissolved in liquid ammonia. The catalytic properties were extensively studied by the hydrogenation of ethene and buta-1,3-diene. The hydrogenation behaviors varied markedly with the loading amounts of silver in the catalyst precursors (7, 20, 30 and 50 wt.% Ag/SiO_2) and the lanthanide content in the bimetallic Ln–Ag catalysts. The activity increased with the loading of silver in the precursor and the lanthanide content. The catalytic nature of the bimetallic Ln–Ag surface drastically changed between the low and high lanthanide content. Ln–Ag/SiO_2 exhibited changes in reactivity for ethene and buta-1,3-diene; thus in the region of low lanthanide content in Ln–Ag the order of decreasing activity for the hydrogenation was obtained as buta-1,3-diene and ethene, and reversely for higher contents. For the hydrogenation of buta-1,3-diene, but-1-ene and *cis*-but-2-ene were primarily produced in the region of low lanthanide content ($0 < Yb/Ag < 0.15$), while *trans*-but-2-ene was major for higher contents ($0.15 < Yb/Ag$).

Keywords: Lanthanide-dosed Ag bimetallic catalysts; Hydrogenation properties

1. Introduction

Since lanthanide (Ln) elements have specific electron configurations based on 4f-orbitals, they are expected to catalyze various reactions that cannot be achieved with d-block transition metals. Recently, there has been a growing interest in the specific properties of lanthanides and related compounds as a heterogeneous catalyst [1].

It is known that among the lanthanide metals especially Eu and Yb readily dissolve in liquid ammonia to yield a homogeneous solution containing the solvated electrons [2]. By using the solvating ability of liquid ammonia for the lanthanide metals, we have recently developed methods for the preparation of a new catalytic material containing lanthanides and have demonstrated that they exhibit specific catalytic properties [3–8].

We now report catalytic behavior of novel Ln-dosed Ag/SiO_2 bimetallic catalysts (Eu-Ag/SiO_2 and Yb–Ag/SiO_2) obtained when the dissolved lanthanide metals in liquid ammonia react with Ag/SiO_2. There have been few studies published of catalyst materials containing lanthanide–silver systems. Lambert et al. [9] have recently reported the use of binary Ce–Ag alloys for methanol synthesis. It has been found that the dissolved lanthanide metals in liquid

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ammonia react with silver metal powder to form unsupported lanthanide–Ag bimetallic catalysts [10]. It is of great interest to investigate the effects of lanthanide metal overlayer on adsorption characteristics and their catalytic consequences in connection with the synergism of the bimetallic lanthanide–silver system.

2. Experimental

2.1. Catalyst preparation

Silver catalyst precursor was prepared using the precipitation method by adding NaOH solutions dropwise to an aqueous solution of $AgNO_3$ (99.8%; Wako) containing silica gel (Degussa Aerosil) suspended in water. The precipitate was thoroughly washed by repeated decantation and filtration, followed by drying at 573 K, air calcination at 573 K and finally reduction at 423 K in hydrogen for 6 h. To obtain the silver loadings of 7, 20, 30 and 50 wt.% shown in Table 1, the silver nitrate solutions with different concentrations were used.

The method of the lanthanide addition to Ag/SiO_2 was similar to that previously described for the $Ln–Ni/SiO_2$ catalyst [7]. Ag/SiO_2 that had been reduced was placed in a Schlenk tube containing a solution of liquid ammonia (15–20 cm^3; Iwatani) at 198 K. Turnings or granules of Eu or Yb (99.9%; Shin-Etsu) were added to the Ag catalyst suspended in liquid ammonia with vigorous stirring. Upon dissolution of the lanthanide metal in liquid ammonia solvent, a blue homogeneous solution was immediately formed, which was characteristic of the solvated electrons [2]. The blue color gradually disappeared as a result of the reaction of the dissolved lanthanide metal with Ag/SiO_2. On disappearance of the blue color, the reaction tube was allowed to warm up to room temperature and the excess of ammonia was pumped off leaving bimetallic $Ln–Ag/SiO_2$ catalysts. All sample preparation steps were carried out in an atmosphere of dry nitrogen, otherwise the catalysts became unreactive.

Table 1
Surface areas and silver crystal sizes of Ag/SiO_2 precursors

Ag precursor	Surface area ($m^2 g^{-1}$)	Crystallite size (nm)
7 wt.% Ag/SiO_2		15
20 wt.% Ag/SiO_2	120	20
30 wt.% Ag/SiO_2		22
50 wt.% Ag/SiO_2	76	24

2.2. Reaction procedures

The catalytic reactions were performed on a recirculation reactor constructed of Pyrex glass. Ethene and buta-1,3-diene were of research purity and further purified by triple distillation. Prior to the reaction the catalyst was subjected to evacuation treatment at elevated temperatures (294–673 K) for 2 h, set at 294–358 K of the reaction temperature and then the hydrogenation was initiated by admitting reactant gases. The reacting gas in the system was periodically collected by a gas sampler and analyzed by a Shimazu TCD gas chromatography to determine the gas composition.

3. Results and discussion

3.1. Behavior of ethene hydrogenation

Using the bimetallic $Ln–Ag/SiO_2$ catalysts obtained from Ag/SiO_2 with different loadings (7, 20, 30 and 50 wt.%) of silver, the hydrogenation of ethene was mainly studied at partial pressures of ethene (20 Torr) and hydrogen (40 Torr) and at temperatures in the range 294–358 K. The catalytic activity for the hydrogenation as a function of Eu or Yb content in $Ln–Ag/SiO_2$ is depicted in Fig. 1. Irrespective of loading amounts of silver on silica, Ag/SiO_2 alone exhibited negligible activity. Interesting features of the catalyst are that the hydrogenation activity abruptly appeared upon addition of lanthanide of more than certain Ln/Ag atomic

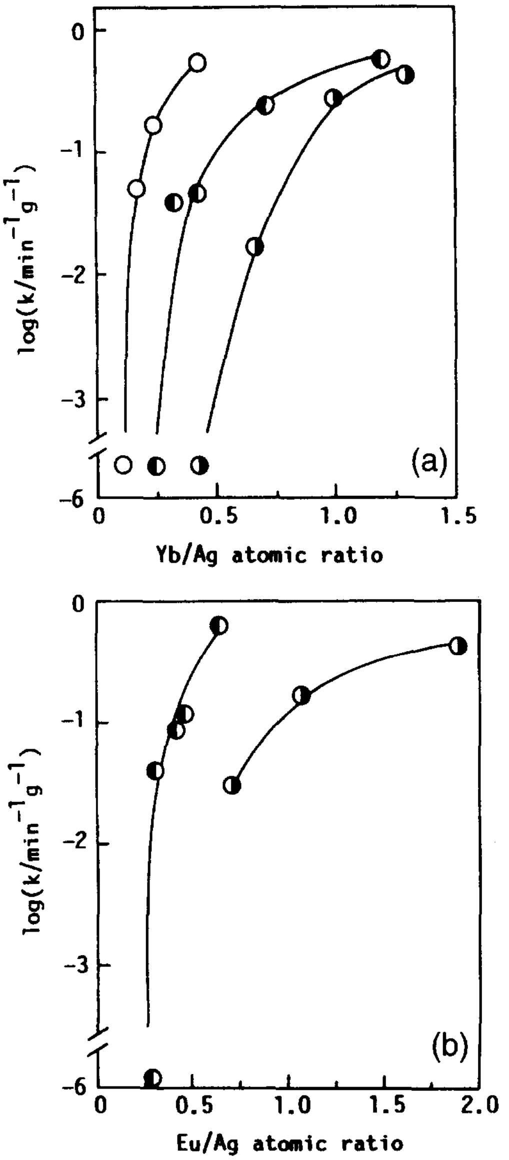

Fig. 1. Activity of ethene hydrogenation vs. lanthanide content in (a) Yb–Ag/SiO_2 and (b) Eu–Ag/SiO_2. The Ln–Ag/SiO_2 catalysts were prepared with 20 wt.% Ag/SiO_2 (shaded right), 30 wt.%Ag/SiO_2 (shaded left) and 50 wt.% Ag/SiO_2 (open circle). The catalysts were evacuated at 673 K for 2 h before the reaction. $P(C_2H_4) = 20$ Torr, $P(H_2) = 40$ Torr, 294 K.

ratios and that the rates of hydrogenation showed a tendency to increase markedly in very limited addition ranges (Fig. 1). The catalytic behavior was further dependent upon the characteristics of Ag/SiO_2 as a precursor, in particular the loading amounts of Ag metal of Ag/SiO_2. The Ln/Ag ratios at which the activity appeared increased with a decrease in loading of silver on silica in the silver precursors. On the whole, the catalytic activity of Ln-dosed Ag catalysts increased with an increase in loading of silver (7, 20, 30 and 50 wt.%) on silica of Ag/SiO_2. Even upon introduction of lanthanide onto Ag/SiO_2 with low loading of silver of as little as 7 wt.%, there was only an indication of very low activity up to 423 K. When 50 wt.% Ag/SiO_2 was used as a precursor, the catalytic activity of Yb–Ag/SiO_2 (Yb/Ag = 0.25) was higher by over three orders of magnitude than that seen for Yb–Ag/SiO_2 (Yb/Ag = 0.11) (Fig. 1a). Irrespective of the changes in catalyst composition investigated, the rate of hydrogenation was represented by a first-order equation with respect to pressures of hydrogen. Hence, the activity in Fig. 1 was expressed using a first-order rate constant (k).

It has been shown that the lanthanide metal catalysts prepared by the metal vapor technique are active for ethene hydrogenation under the similar conditions to reach a value of 1.6×10^{-3} min^{-1} g^{-1} (a first-order rate constant) for the Yb catalyst at 323 K [11], but this specific activity of lanthanide alone was two or three orders of magnitude lower than that of Ln–Ag/SiO_2 catalysts. Thus, the dependence of activity on the lanthanide content obviously indicates that some synergetic interactions between the lanthanide and silver metals rather than individual components constitute active sites, as previously observed in the lanthanide-containing Ni [4,5], Co [6] or Cu [10] bimetallic systems.

As shown in Fig. 1, the Ln/Ag ratios at which the hydrogenation activity appeared varied markedly with alteration in Ag loading of the silver precursors. Yb–Ag/SiO_2 with Ag loading of 20, 30 or 50 wt.% showed the appearance of activity at the Yb/Ag ratios of ca. 0.11, 0.25 or 0.43, respectively (Fig. 1a). Table 1 shows the silver crystallite sizes evaluated from XRD (using the Scherrer equation) for all Ag/SiO_2 precursors prepared at different silver loading, as described in the experimental section. It has been found that differences in particle sizes of the metal used as a counterpart in this type of lanthanide-containing bimetallic systems affect the catalytic properties [12]. In Ln–Ni and Ln–Co catalysts, such a phenomenon is interpreted by variations in coverage of Ni or Co with the lanthanide metal, due to the difference in particle sizes of the parent Ni or Co metal even at the same lanthanide content. It has been concluded that the pronounced synergism of these bimetallic systems appears above a certain surface coverage of lanthanide [4–6]. For controlled deposition of Yb onto Ni(100), at higher coverages with lanthanide a considerable reaction with the Ni substrate occurs and forms a specific surface intermetallic compound [13]. This is probably the case for the present Ln–Ag system. Thus, for the Ln–Ag bimetallic catalysts prepared from the catalyst precursors of 20, 30 and 50 wt.% Ag/SiO_2 with different Ag particle sizes (ca. 20, 22 and 24 nm), respectively, the levels of lanthanide coverage even at the same Ln/Ag ratios increased with an increase in average particle sizes of silver, probably leading to enhanced activity in this order (Fig. 1). This presumption is consistent with CO chemisorption measurements (Table 2) as described later.

$Eu–Ag/SiO_2$ and $Yb–Ag/SiO_2$ exhibited similar behavior in the composition range investigated, but comparing both systems on the basis of the same atomic ratio of Ln:Ag, the activity of Eu-containing systems was, in most cases, higher than that of Yb-containing ones. For support-free Ln–Ag bimetallic catalysts prepared with Ag metal powders, it has been shown that the Ag metal is similarly used more efficiently when dosed with the lanthanide metal [10]. The pressure dependence of hydrogenation was the same as that of the supported Ln–Ag catalysts. Moreover, the catalytic consequence as a function of lanthanide content and the ordering of lanthanide metals according to increasing promotion effect (Yb < Eu) were mostly similar to those for the supported catalysts. However, relatively large quantities of lanthanides were required for the supported Ln–Ag catalyst system, due to extra lanthanide deposited on the SiO_2 support.

Table 2
CO chemisorption of $Ln–Ag/SiO_2$ [a]

Ln/Ag ratio in $Ln–Ag/SiO_2$	CO uptake (μmol g^{-1})
Eu/Ag = 0	0.05
Eu/Ag = 0.11	6.9
Eu/Ag = 0.15	16.8
Eu/Ag = 0.19	26.5
Yb/Ag = 0.09	2.0
Yb/Ag = 0.13	13.7
Yb/Ag = 0.17	29.3
Yb/Ag = 0.17 [b]	4.5
Yb/Ag = 0.17 [c]	1.0

[a] The catalyst was prepared with 50 wt.% Ag/SiO_2 and was evacuated at 673 K for 2 h prior to the measurement.
[b] The silver catalyst precursor was 30 wt.% Ag/SiO_2.
[c] The silver catalyst precursor was 20 wt.% Ag/SiO_2.

3.2. *Behavior of buta-1,3-diene hydrogenation*

The hydrogenation of buta-1,3-diene was also studied over $Ln–Ag/SiO_2$ catalysts in the same manner as the hydrogenation of ethene. The catalytic properties varied markedly with changes in loading of Ag on silica and the amounts of Eu and Yb dosed. Fig. 2 reveals the mode of the variation in reaction behavior of $Yb–Ag/SiO_2$ as a function of lanthanide content, which was essentially the same as that obtained for the hydrogenation of ethene (Fig. 1). The activity of $Ln–Ag/SiO_2$-catalyzed buta-1,3-diene hydrogenation at 294 K was gradually increased with an increase in lanthanide content. For all catalysts within the levels of Ln/Ag atomic ratios examined, only butenes were yielded as a main product, and the type of butene composition obtained also varied when altering the dose of the lanthanide metals. Since the composition of butene isomers produced remained unchanged throughout the reaction, probably no isomerization of butenes occurs; therefore, relative yields of butene isomers formed over the catalysts depend on the conformational characteristics of adsorbed precursors.

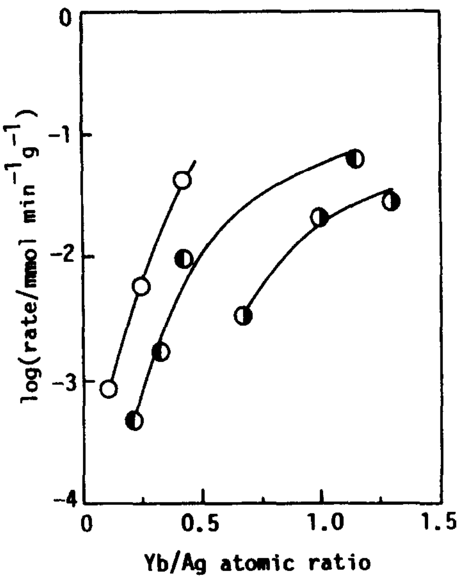

Fig. 2. Hydrogenation rates of buta-1,3-diene vs. lanthanide content in Yb–Ag/SiO_2. The Yb–Ag/SiO_2 catalysts were prepared with 20 wt.% Ag/SiO_2 (shaded right), 30 wt.% Ag/SiO_2 (shaded left) and 50 wt.% Ag/SiO_2 (open circle). The catalysts were evacuated at 673 K for 2 h before the reaction. $P(C_4H_6) = 20$ Torr, $P(H_2) = 40$ Torr, 294 K.

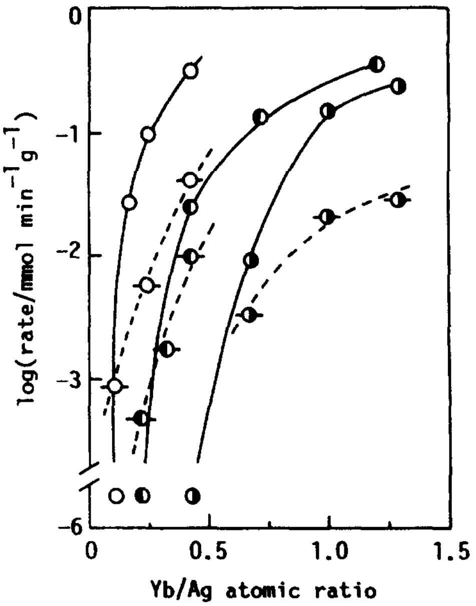

Fig. 3. Rate of hydrogenation of ethene (solid line) and buta-1,3-diene (dashed line) at 294 K over Yb–Ag/SiO_2. The Yb–Ag/SiO_2 catalysts were prepared with 20 wt.% Ag/SiO_2 (shaded right), 30 wt.% Ag/SiO_2 (shaded left) and 50 wt.% Ag/SiO_2 (open circles).

As shown in Fig. 3, the hydrogenation activity of the catalysts for ethene and buta-1,3-diene was reversed at certain Yb/Ag ratios in Yb–Ag/SiO_2 with different loadings of silver (20, 30 and 50 wt.%). Ln–Ag/SiO_2 with Ag loading of 50 wt.% exhibited changes in reactivity toward reactants at about 0.15–0.17 of the Ln:Ag ratio; thus, in the region of low lanthanide contents in Ln–Ag the order of decreasing activity for the hydrogenation was obtained as buta-1,3-diene and ethene and reversely for higher contents (Fig. 4). It has been generally accepted that for d-block transition metals ethene is more reactive than buta-1,3-diene [14]. The selectivity of butene isomers formed simultaneously changed around the similar Yb/Ag ratios (Fig. 5). But-1-ene (*1*-C_4) and *cis*-but-2-ene (*c*-C_4) were primarily produced in the region of low lanthanide contents ($0 < \text{Yb/Ag} < 0.15$), while *trans*-but-2-ene (*t*-C_4) became major for higher contents ($0.15 < \text{Yb/Ag}$). These experimental facts strongly suggest that such Ln/Ag component ratios in the catalysts essentially

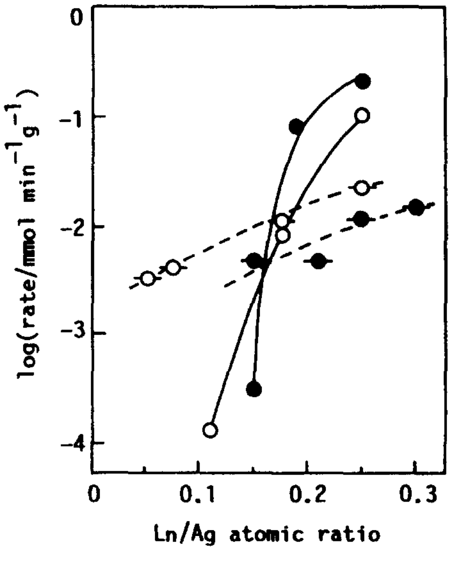

Fig. 4. Comparison of the hydrogenation of ethene (solid line) and buta-1,3-diene (dashed line) at 358 K over Eu–Ag/SiO_2 (●, -●-) and Yb–Ag/SiO_2 (○, -○-). The catalysts were prepared with 50 wt.% Ag/SiO_2. Hydrogenation of ethene: $P(C_2H_4) = 20$ Torr, $P(H_2) = 40$ Torr. Hydrogenation of buta-1,3-diene: $P(C_4H_6) = 20$ Torr, $P(H_2) = 40$ Torr.

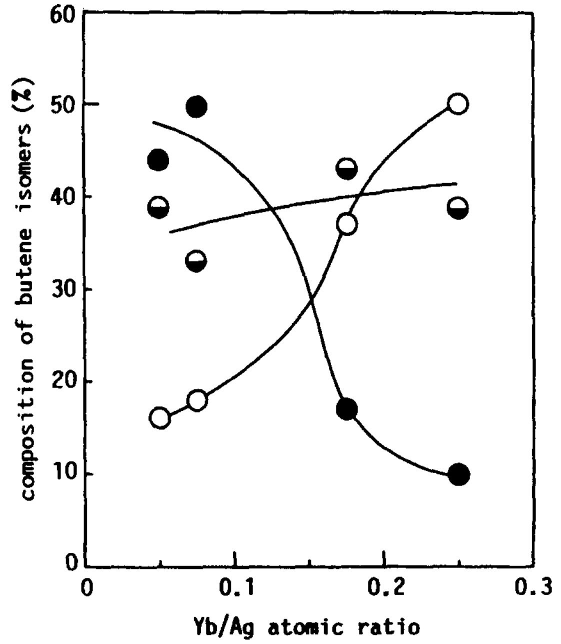

Fig. 5. Selectivity of butene isomers vs. lanthanide content in Yb–Ag/SiO_2. But-1-ene (filled circle), *cis*-but-2-ene (shaded bottom), *trans*-but-2-ene (open circle). The catalysts were prepared with 50 wt.% Ag/SiO_2.

separate the nature of the Ln–Ag bimetallic surface. The preferential formation of *trans*-but-2-ene which was observed for the catalysts with higher contents of lanthanide similarly occurs over the silver-free lanthanide metal catalysts [11]. This is consistent with an increase in the surface concentration of lanthanide determined by XPS of Eu–Ag [10].

For the bimetallic catalysts ranging in Ln/Ag ratios from ca. 0.05 to ca. 0.2, as shown in Fig. 4, the resulting synergetic effects generate new active sites, while at higher ratios the coverage with lanthanides occurs, in which the property of the lanthanide elements rather than the newly produced sites gradually become dominant. In the selectivity for the hydrogenation of buta-1,3-diene (Fig. 5), the surface of the bimetallic catalysts with higher lanthanide contents exhibited catalytic behavior close to that of the lanthanide catalyst itself with the selectivity of *1*-C_4: 20%, *t*-C_4: 52% and *c*-C_4: 28% for Yb catalysts [11]. The catalysts with higher contents of lanthanide are those in which the surface is coated with the lanthanide. The Ln/Ag ratios at which the drastic changes in the reactivity with ethene and buta-1,3-diene and the selectivity toward butene isomers occurred also exhibited a tendency to decrease with increasing Ag loading of the silver precursors.

The hydrogenation kinetics were also dependent upon the composition ratios of Ln–Ag. The hydrogenation of buta-1,3-diene obeyed first-order kinetics with respect to the pressure of hydrogen over Yb–Ag/SiO_2 with higher lanthanide contents (Yb/Ag = 0.25; silver precursor: 50 wt.% Ag/SiO_2). This was the same as that observed for the hydrogenation of ethene. In marked contrast to Yb–Ag/SiO_2 (Yb/Ag = 0.25), Yb–Ag/SiO_2 (Yb/Ag = 0.11) showed different kinetic behavior with lower contents; thus the orders in buta-1,3-diene were slightly positive and the hydrogen orders lay between 0.5 and 1.0.

3.3. Properties of Ln–Ag bimetallic catalysts

To evaluate the number of active sites on the catalyst surface, CO chemisorption of Eu–Ag/SiO_2 and Yb–Ag/SiO_2 which was prepared with a silver precursor of 50 wt.% Ag/SiO_2 is summarized in Table 2. The CO uptake increased as the lanthanide metals were introduced onto the silver catalysts. This is qualitatively consistent with the results of the hydrogenation. Moreover, compared with the uptake at the same Ln/Ag ratios (0.17) in Ln–Ag/SiO_2 with different loadings (20, 30 and 50 wt.%) of silver, the quantity of adsorbed CO increased markedly with an increase in Ag loading of the silver precursors.

The thermal treatment of Eu–Ag/SiO_2 strongly affected the catalytic activity. The hydrogenation activity (*k*: rate constant) increased notably with increasing the evacuation temperature to 673 K (Table 3). Investigated were the powder diffraction patterns and the crystalline phases detected for all Ln–Ag/SiO_2 catalysts, prepared at different silver loadings on silica and lanthanide contents. XRD spectra showed

Table 3
Effects of the thermal treatment on the hydrogenation activity of ethene [a]

Evacuation temperature (K)	Activity k (min^{-1} g^{-1})
294	3.2×10^{-5}
358	3.7×10^{-4}
473	3.5×10^{-2}
573	6.1×10^{-2}
673	1.5×10^{-1}

[a] Eu–Ag/SiO_2 (Eu/Ag = 0.22, silver precursor: 50 wt.% Ag/SiO_2) was evacuated for 2 h before the reaction. $P(C_2H_4)$ = 20 Torr, $P(H_2)$ = 40 Torr, 294 K.

no diffraction peaks assigned to the lanthanides and only the existence of metallic silver in the cubic structure. Unlike XRD of the unsupported Ln–Ag catalysts [10], the spectra of Ln–Ag/SiO_2 showed nondistinguishable changes in lattice parameter of the silver metal upon the introduction of lanthanide. Unsupported Eu(14.8 at.%)–Ag catalysts obtained when europium is introduced onto the Ag powder showed some shifts of Ag diffraction peaks to lower degrees of 2θ, due to the formation of solid solutions. Subsequently, upon heating the unsupported Eu–Ag at elevated temperatures of more than 473 K, the XRD spectra showed the original peak position of the cubic structure of Ag metal, indicating the thermal degradation of the solid solutions [10]. Such a thermal treatment of the bimetallic Ln–Ag catalysts induces some rearrangement of the catalyst surface, accompanying decomposition of the solid solutions under certain conditions. Thus, the supported Ln–Ag catalysts seem to undergo the similar surface rearrangement or reconstruction by the thermal treatment, leading to their enhanced activity. Activation of other lanthanide-containing Ni [4,5], Co [6] and Cu [10] bimetallic catalysts has been found to be also a consequence of surface reconstruction resulting from such thermal treatments.

Acknowledgements

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