

# Preparation and catalytic property of a copper–lanthanide oxide binary system for hydrogenation reaction

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## Abstract

The characteristic copper–lanthanide complex oxide of  $\text{Cu}_6\text{O}_8\text{Ln}(\text{NO}_3)$  was found to be easily decomposed and reduced under hydrogen atmosphere to form the homogeneous mixture of copper metal and the lanthanide oxide with relatively high surface area. The catalytic property of the mixture obtained from Cu–Yb complex oxide,  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)$ , for different types of hydrogenations was investigated. It was confirmed that this mixture exhibited high catalytic activity for ethene and acetone hydrogenation and the catalytic property can be controlled by changing the temperature of hydrogen pretreatment. It is clear that the highly dispersed lanthanide oxide–copper metal binary catalyst can be easily and effectively prepared by the decomposition of complex oxide precursor under  $\text{H}_2$  atmosphere. The affection of the surface state of the catalyst to the hydrogenations are also discussed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:*  $\text{Cu}_6\text{O}_8\text{Ln}(\text{NO}_3)$ ; Copper–lanthanide oxide catalyst; Preparation condition; Hydrogenation; Ethene; Acetone

## 1. Introduction

Lanthanide metals, ions and oxides have been widely applied to various catalyst systems. Particularly, these are often used as supports, promoters and additives of catalysts [1–15]. If metal catalysts are modified or promoted by lanthanides, the catalytic performances are improved noticeably in most cases, and generation of interesting properties can be sometimes identified. Among the lanthanide compounds, oxides are often applied as suitable promoters or additives in the catalyst systems.

When a copper catalyst was promoted by lanthanide oxides, the generation of high catalytic performances for hydrogenation reaction, in particular, for the hydrogenation of CO to methanol have been reported [3,4,10]. In the catalyst system, copper–lanthanide alloy was used as the precursor of the catalyst for the reaction. The lanthanide metal in the alloy was oxidized in the induction period of the reaction, and the catalyst under the steady state reaction was homogeneous mixture of metallic copper and the lanthanide oxide. The homogeneous mixture exhibited high catalytic performance for methanol production from CO hydrogenation at relatively low temperatures compared with the conventional copper based methanol synthesis

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catalysts [3,4,10]. Beside using the copper–lanthanide alloy as a precursor for this catalyst system, various materials and methods can be expected for the preparation of the catalysts. However, applications of the other starting materials and methods are found in few cases.

$\text{Cu}_6\text{O}_8\text{Ln}(\text{NO}_3)$  ( $\text{Ln}=\text{Tb-Lu}$ ) is one of the recently synthesized copper–lanthanide complex oxide, which can be synthesized by the thermal decomposition of the homogeneous mixture of copper and lanthanide nitrate in blowing oxygen or inert gas at 673 K [16,17]. Copper, ytterbium and nitrate ions are regularly arranged in the cubic structure of the oxide and the oxide shows characteristic properties, such as the magnetic property and high electron conductivity [16,17]. We have investigated the catalytic property of this complex oxide [18]. However, further investigations about the catalytic property of the complex oxide and its derivatives have not been performed yet.

In this work, we have studied the catalytic properties of copper metal–lanthanide oxide binary system which was prepared from the complex oxide for hydrogenations. Here we report the catalytic properties of the system obtained from the decomposition of a copper–ytterbium complex oxide of  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)$  under hydrogen atmosphere. We have carried out ethene and acetone hydrogenation, as the examples of  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  bond hydrogenation, and characterized the catalyst prepared under various pretreatment temperatures in order to clarify the contribution of the surface of the catalyst to the hydrogenation of the different groups as well as examine the effective preparation condition of the catalyst.

## 2. Experimental

### 2.1. Preparation of catalyst

The complex oxide was prepared from calcination of the homogeneous mixture of  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Yb}(\text{NO}_3)_3$  ( $\text{Cu}:\text{Yb} = 6:1$  in molar ratio)

under oxygen blowing at 700 K for 5 h referred to in the previous paper [16–18]. The structure of crystal of the prepared complex oxide was confirmed by XRD. The catalyst was obtained from the decomposition and the reduction of the prepared complex oxide under hydrogen atmosphere at prescribed temperature as pretreatment before the reaction.

### 2.2. Catalytic reaction

All reactants, gases and reagents used in the present work are at research grade. The pretreatment and catalytic reaction were carried out in a closed-gas circulation system for ethene hydrogenation and a fixed bed flow system under atmospheric pressure for acetone hydrogenation. The 200 mg of complex oxide was mounted on quartz wool in a reactor tube and set to the systems. The oxides was pretreated under hydrogen atmosphere and then the reaction was started.

Ethene hydrogenation was performed with ethene-hydrogen mixed gas (total pressure 60 Torr ( $\text{H}_2:\text{C}_2\text{H}_4 = 2:1$ )). We have confirmed that the rate of the reaction depended on the first order of  $\text{H}_2$  pressure and the zero order of ethene pressure over the catalyst, so that the activity is show in this text as the rate constant  $k$ . On the other hand, the hydrogenation of acetone was performed in the flow of  $\text{H}_2$  mixed with acetone vapor under atmospheric pressure. The partial pressure of acetone was kept at 5.8 Torr in the mixed gas and the total flow rate was kept at 25 ml per min. The reaction was carried out at 353 K and the catalytic activity shows the value calculated from the formula of  $\ln(1 - \alpha)^{-1}$  where  $\alpha$  is a conversion of acetone under the steady state. All products were collected to 1 ml of a sample loop attached to the reaction system and analyzed by on-line gaschromatograph (Shimadzu GC-14B).

### 2.3. Characterization of catalysts

The surface areas of the catalysts before and after pretreatments were evaluated by  $\text{N}_2$  ad-

sorption at 77 K by B.E.T. method. The structure of crystal was measured by a X-ray diffractometer with using the irradiation of Cu K $\alpha$  (XRD, Shimadzu XD D1). The detail morphology of the catalyst was observed by a transmission electron microscope (TEM) equipped with UTW type Si detector for energy dispersed X-ray spectroscopic analysis (EDX) (JEOL JEM-2010).

### 3. Results and discussion

Our previous paper [18] reported that the complex oxide,  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ , is stable to 723 K in vacuo, decomposed to CuO and  $\text{Yb}_2\text{O}_3$  over 773 K, and the catalytic activity for ethene hydrogenation appeared when it was pretreated over 573 K in vacuo. In this study, first, we have confirmed that the complex oxide was decomposed and reduced under  $\text{H}_2$  atmosphere at 423 K to form copper metal particles observed by XRD. The decomposition temperature under  $\text{H}_2$  atmosphere was very low compared with that in vacuo. This suggests that characteristic lanthanide ion contained copper metal can form by the decomposition of the complex oxide under  $\text{H}_2$  atmosphere. We investigated the catalytic property of the oxide decomposed under  $\text{H}_2$  atmosphere for the hydrogenations.

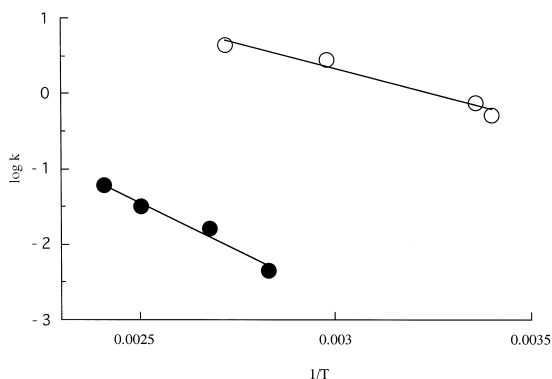


Fig. 1. Arrhenius plots for ethene hydrogenation over E- and R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ .

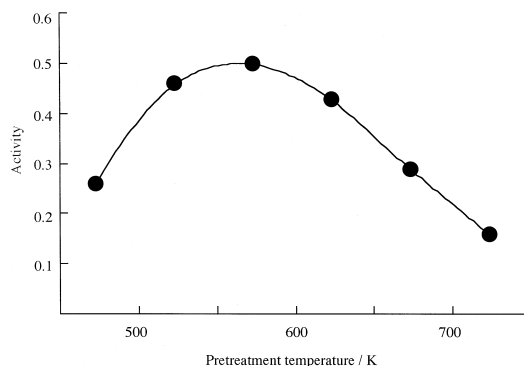


Fig. 2. Dependence of the activity of ethene hydrogenation upon pretreatment temperatures.

The hydrogenation of ethene was carried out over pretreated  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ , where the complex oxide was pretreated in vacuo at 673 K (E- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ ), and pretreated under  $\text{H}_2$  atmosphere at 573 K (R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ ). Arrhenius plots for the hydrogenation of ethene over E- and R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$  are shown in Fig. 1. The activity was further improved by pretreating under  $\text{H}_2$  atmosphere at 573 K instead of in vacuo at 673 K. When the ethene hydrogenation was performed over Cu metal prepared from the reduction of copper oxide with  $\text{H}_2$  at 473 K, the activity at 298 K was zero within detection limit, which was reported our previous paper [5] and also confirmed in this work. The activation energy for the reaction can be evaluated from the slope of the Arrhenius plots and the values are 27 kJ/mol and 12 kJ/mol over E- and R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ , respectively. These suggest that the hydrogenation activity of the R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$  catalyst is very high compared with the E- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$  catalyst and different types of active centers are operating for the hydrogenation over E- and R- $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ , the latter showed higher activity.

Dependence of the activity of the ethene hydrogenation upon  $\text{H}_2$  pretreatment temperature is shown in Fig. 2. From Fig. 2, it is noticed that the pretreatment temperature at 573 K was the optimized condition for preparing the highly active catalyst for ethene hydrogenation.

Therefore, it is suggested that the state of the catalyst is strongly influenced by the pretreatment temperature.

The hydrogenation of acetone was carried out as an example of C=O bond hydrogenation over the catalyst pretreated under the various conditions, and the results are shown in Fig. 3. The product of acetone hydrogenation in the present work was 2-propanol in 100% selectivity. The catalytic activity was improved by increasing the pretreatment temperatures and reached the maximum at 523 K pretreatment. This suggests that the activity for acetone hydrogenation also depends on the pretreatment temperature of the catalyst similarly to ethene hydrogenation. However, the optimized pretreatment temperature for acetone hydrogenation was lower than that of ethene hydrogenation and the strong dependency was observed. This difference is probably reflected by the contributions of the different surface states to the hydrogenation of ethene and acetone.

In order to make clear the change of the surface states and the contributions of the catalyst surface to each hydrogenation, the states of the catalysts at various pretreatment conditions were examined.

XRD patterns of the catalysts pretreated at various conditions are shown in Fig. 4. The values of surface area and the crystal size of components are listed in Table 1. The crystal sizes in Table 1 was evaluated from the XRD

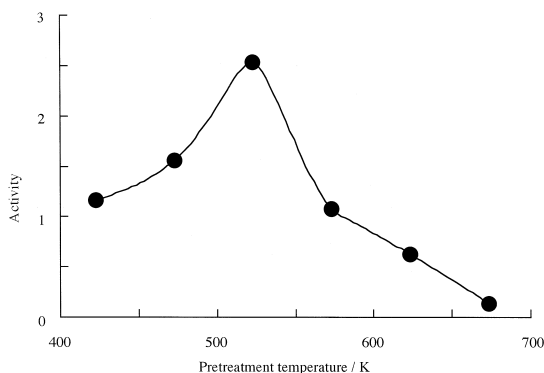


Fig. 3. Dependence of the activity of acetone hydrogenation upon  $H_2$  pretreatment temperatures.

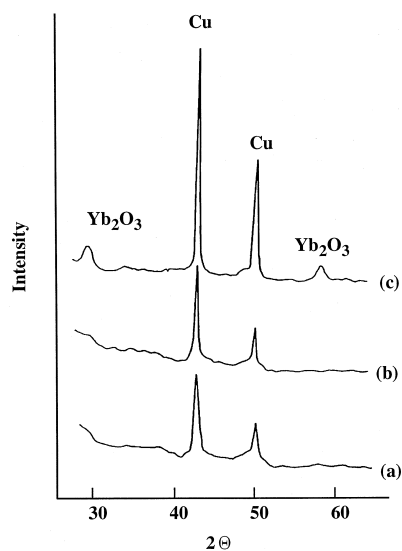


Fig. 4. XRD pattern of pretreated complex oxide at (a) 523 K, (b) 623 K and (c) 723 K.

patterns of the catalysts pretreated at various conditions by Scherrer formula. Only the diffract pattern due to copper metal was observed when the catalysts were pretreated at lower than 623 K, while both diffract patterns of copper metal and ytterbium oxide were clearly observed when the catalysts were pretreated at higher than 673 K. From the results in Fig. 4, it is noticed that only the diffract pattern due to copper metal was observed to the catalysts pretreated at the optimized temperatures for both of the hydrogenation. From the results in Table 1, when the mixed oxide decomposed in  $H_2$  atmosphere, the

Table 1

Surface area and the particle size of components of the catalyst at various pretreatments

Pretreatments (K)	Surface area ( $m^2 g^{-1}$ )	Particle size <sup>a</sup> (nm)	
		Cu	$Yb_2O_3$
700E <sup>b</sup>	10	–	–
473R	64	16.8	–
523R	72	13.6	–
573R	41	16.5	–
623R	40	17.5	–
673R	37	19.5	8.2
723R	23	19.9	9.1

<sup>a</sup>The values were evaluated from XRD peak by the Scherrer formula.

<sup>b</sup>E; Evacuation, R; Hydrogen pretreatment.

surface area increased remarkably compared with the evacuated complex oxide. The value increased with increasing the pretreatment temperature and reached the maximum at 523 K pretreatment, while that was decreasing with increasing the pretreatment temperature over 523 K. The change of crystal size of copper metal was corresponding to changing the surface area of catalyst, where the value was becoming smaller with increasing the pretreatment temperature and the value reach minimum at 523 K pretreatment, while that was increased with increasing pretreatment temperature over 523 K. The diffract pattern of ytterbium oxide was also confirmed when the complex oxide was pretreated at higher than 673 K. These suggest that the decomposition of the structure probably proceeded to the pretreatment temperature at 523 K and the growth of the crystals proceeded over 523 K pretreatment.

From these results, it is elucidated that when the complex oxide was treated in  $H_2$  atmosphere, the oxide decomposed and reduced to the mixture of copper metal and ytterbium oxide and the crystallization of the components were proceeding individually by increasing pretreatment temperature. These suggest that the morphology of the catalyst may be systematically changing by changing the pretreatment temperature. This probably affected the catalytic hydrogenation activity. The activity increased with increasing the pretreatment temperature. The surface area was simultaneously increased. This suggests that the active surface was appearing during the process of reduction and decomposition of the complex oxide by increasing the pretreatment temperature. In the preferable pretreatments for ethene and acetone hydrogenation, the surface area of the catalyst was expressed very high; the value was  $72 \text{ m}^2/\text{g}$  when the catalyst was pretreated at 523 K and  $41 \text{ m}^2/\text{g}$  when the catalyst was pretreated at 573 K. Under these conditions, the XRD pattern of ytterbium oxide was not observed as shown in Fig. 4, so that the state of ytterbium is regarded as amorphous or fine particles dispersed in the

catalyst. On the other hand, the decrease of the catalytic activity by increasing the pretreatment temperature over the optimized value is probably originated from the changes of the catalyst states.

In order to examine the states of the catalyst in detail, the states of the catalysts were examined by TEM–EDX system.

TEM photographs of the catalysts pretreated at 523 K and 623 K are shown in Fig. 5. Fig. 5a shows the picture of the catalyst pretreated at 523 K. In this photograph, the particles of crystals of ca. 10 to 15 nm in diameter are observed. From the result in Table 1, this particle can be attributed to the crystal of copper metal. Other small crystals, which can be attributed to ytterbium oxide, are difficult to observe in this photograph. EDX analysis was performed under the same condition. Cu and Yb atom can be detected in the stoichiometric ratio of the original complex oxide at every particle in the photograph. These results strongly suggest that, when the complex oxide was pretreated under optimum condition for hydrogenation reaction, ytterbium oxide dispersed homogeneously in the crystal of copper metal and ytterbium oxide exist as very fine particles, such as nano-oxide cluster. The TEM–EDX analysis was also performed to the catalyst pretreated at 573 K and nearly the same morphology was observed. Therefore, it is very difficult to know the difference of the catalyst morphology at the optimum pretreatments for both of hydrogenations directly from the TEM–EDX examination. To know the difference, it is necessary to examine how to change the morphology by increasing the pretreatment temperature.

Fig. 5b shows the photograph of the catalyst pretreated at 623 K. In this photograph, particles 15 to 20 nm and a few nanometers in diameter can be observed. EDX analysis was also performed to the same catalyst and the results clearly suggested that the large particles mainly consist of copper metal and the small one mainly consist of ytterbium oxide. From these results, the crystal of ytterbium oxide can be confirmed

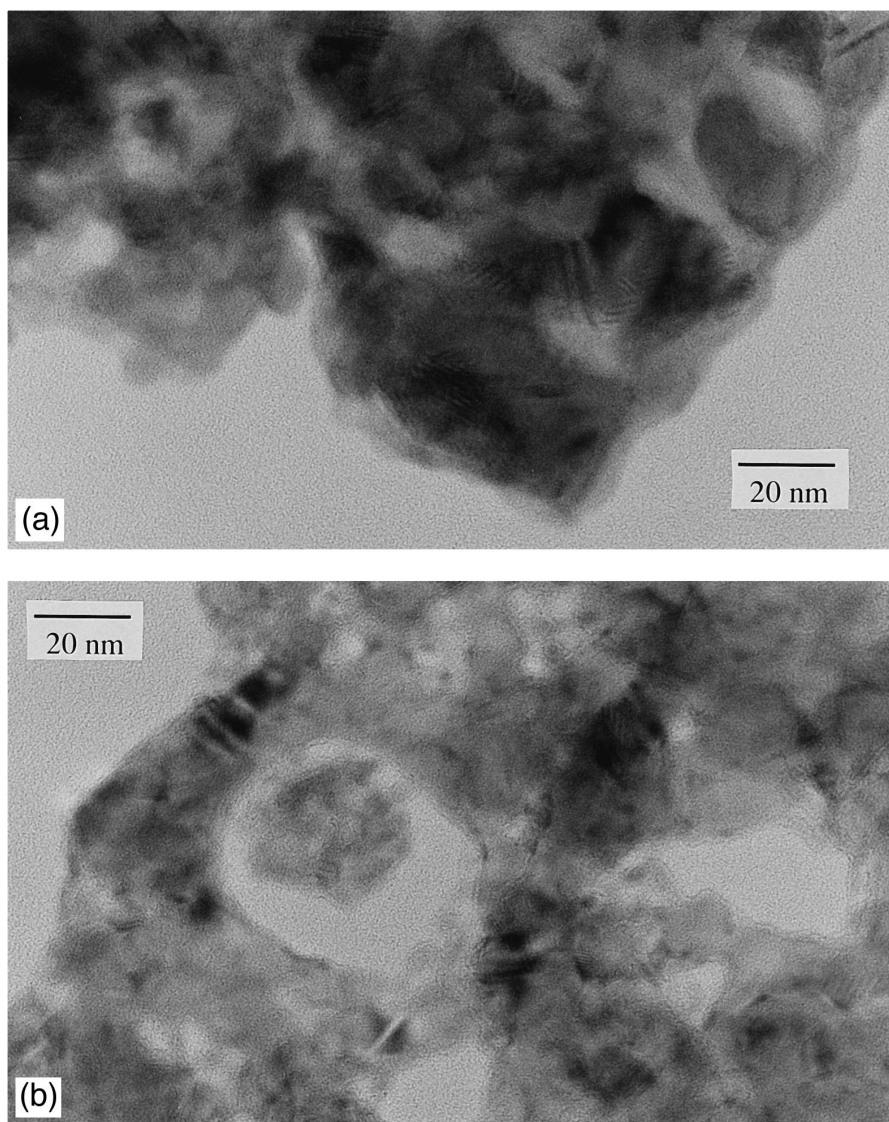


Fig. 5. TEM pictures of the catalysts pretreated at (a) 523 K and (b) 623 K.

as particles with a few nanometers in diameter in the catalyst, although, in the results of XRD as show in Fig. 4 and Table 1, the diffract pattern of ytterbium oxide cannot be observed clearly to the catalyst pretreated under the same condition. The results in Fig. 5b clearly expresses the procedure of crystallization ytterbium oxide in the catalyst by increasing the pretreatment temperature.

From the results of characterization, the affection of the pretreatment temperature to the

catalyst morphology and the optimum condition of the catalyst for the hydrogenations can be discussed. The morphology of the catalyst at the optimum conditions for the hydrogenations is a homogeneous mixture of copper metal and ytterbium oxide, where cluster-like ytterbium oxide in nano-scale is homogeneously dispersed in the crystal of the copper metal. It is clearly confirmed that the crystals of copper metal and ytterbium oxide grow individually with increasing the pretreatment temperature over its opti-

imum values. These suggest that the dispersion of ytterbium oxide decreases with increasing the pretreatment temperature, so that an interaction (it is probably electrostatic interaction [19]) between the copper metal and ytterbium oxides decrease. The catalytic hydrogenation activity of copper metal itself is very low as we mentioned at the beginning of this section. Therefore, an effective interaction between the copper metal and ytterbium oxide is necessary and important for improving the hydrogenation activity as well as ability for hydrogen activation over the surface. It can be explained that the decrease of the interaction is one of the cause of decreasing the catalytic activity for hydrogenations by increasing the pretreatment temperature.

The differences of the preferable pretreatment temperature and the dependency of the activity upon the temperatures between ethene and acetone hydrogenation also suggest the different contribution of the surface to the reactions. The optimum activity for ethene hydrogenation was obtained by the catalyst pretreated at 573 K though the surface area of the catalyst was not the maximum value, which was obtained by the catalyst pretreated at 523 K.

Although the difference of the detail morphology between the catalyst pretreated at both of the optimum pretreatment temperatures, which are 523 K and 573 K for acetone and ethene hydrogenation, respectively, are not clear from the results of TEM–EDX, the difference can be estimated from the tendency of changing the morphology by increasing the pretreatment temperature. From the tendency, the dispersion of ytterbium oxide in copper metal in the catalyst is decreasing with increasing the pretreatment temperature. Therefore, when the catalyst was pretreated at 523 K, the dispersion of the ytterbium oxide in copper metal is higher than that in the catalyst pretreated at 573 K. It can also be observed in Table 1 that the average particle size of copper metal is smaller and the surface area is becoming larger. Moreover, the dependency of the activity on the pretreatment

temperature for acetone hydrogenation is sharper than that of ethene hydrogenation. These suggest that the surface where cluster-like ytterbium oxide highly disperses in copper metal is desirable for acetone hydrogenation, while the increase of metallic surface is desirable for ethene hydrogenation. Of course, both of the surfaces must have the ability for high hydrogen activation.

These differences are probably originated from the different contributions of the catalyst surface to the hydrogenation of different groups, such as C=C and C=O, in the molecules. Since the appearance of the metallic copper over the surface is desirable for ethene hydrogenation, the metallic surface which show the ability for the high activation of hydrogen contributes the C=C bond hydrogenation. On the other hand, since the surface where the cluster-like ytterbium oxide highly dispersed over copper metal is desirable for acetone hydrogenation, the boundary between the copper metal and the ytterbium oxide probably contributes the activation of C=O bond to hydrogenate beside the ability of hydrogen activation. The sharp dependency of the activity on the pretreatment temperature for acetone hydrogenation also supports to lead the same discussion. These information are noticeable and important for considering the selectivity of hydrogenation reaction over the binary functional surface.

It was reported that the copper–lanthanide binary alloy catalysts exhibit a characteristic activity for the hydrogenation of CO to selective formation of methanol [4,10]. In the system, lanthanide metals were oxidized to oxide under the induction period of the reaction to form a homogeneous mixture of copper metal and lanthanide oxide. This catalyst showed high activity at relative low temperatures to the reaction. However, the fundamental catalytic property for hydrogenations were not shown in detail. In this work, we have prepared the system from the precursor of complex oxide,  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)_3$ , and clarified the catalytic property for hydrogenations. It is interesting to note that decompo-

sition and reduction of the complex oxide is one of the effective ways to prepare the copper metal and lanthanide oxide binary catalyst system and the catalytic performance of the system for hydrogenation can be easily controlled by changing the preparation condition.

#### 4. Conclusion

In this paper, We have investigated the catalytic property of the copper–ytterbium oxide binary catalyst as an example of copper–lanthanide oxide system, which is prepared from characteristic copper–ytterbium complex oxide of  $\text{Cu}_6\text{O}_8\text{Yb}(\text{NO}_3)$ , for hydrogenation reactions and following conclusions are obtained.

(1) The copper–ytterbium oxide system which is prepared from characteristic copper lanthanide complex oxide under hydrogen atmosphere exhibit high activity for ethene hydrogenation. The activity remarkably improved compared to the activity of the base complex oxide.

(2) The catalytic activity depends on the condition of hydrogen pretreatment. Different catalytic behaviors were observed by changing the reactant from ethene to acetone. The optimum activity express the catalyst pretreated at 573 K for ethene hydrogenation, while at 523 K for acetone hydrogenation.

(3) The catalyst morphology changes by the change of the pretreatment temperature. When the catalyst was pretreated at optimum temperature for hydrogenation, cluster-like ytterbium oxide homogeneously dispersed in copper metal, while the crystal grew individually with the increase of the pretreatment temperature. This morphology strongly affects the catalytic performance of hydrogenation.

(4) The different catalytic behaviors between ethene hydrogenation and acetone hydrogenation are originated from the different contributions of the activation of the reactants. Exposing the metal surface is desirable for ethene hydro-

genation, while the surface where a number of boundaries between the metal and the oxide exist is desirable for acetone hydrogenation.

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