Catalytic Activity for Methanol Synthesis over a Copper-Lanthanide Oxide Complex System Prepared from a Copper-Lanthanide Complex Oxide of $Cu_6O_8Yb(NO_3)$

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(Received August 12, 1998; CL-980619)

High catalytic performance for methanol production from CO and H_2 was confirmed over copper-lanthanide oxide binary catalyst which was prepared from a characteristic copper-lanthanide complex oxide of $Cu_6O_8Ln(NO_3)$. The catalyst exhibited high activity from lower temperatures compared with copper-zinc catalyst systems under the same condition.

Copper based catalysts have been widely applied to various hydrogenations.[1,2] Since the catalytic ability of copper metal itself is not enough, various modifications, such as the addition of suitable promoters and the combination of effective components, have been carried out. It is reported that copper-lanthanide binary systems show characteristic properties, not only the improvement of the activity but also the selectivity of products, for hydrogenation reactions[3-7]. Particularly, when copper-lanthanide alloy catalyst was applied to CO hydrogenation, methanol is produced selectively with high activity at relatively low temperatures, compared with copper-zinc methanol synthesis catalysts. In the system, lanthanide metal in the alloy oxidized in the initial stage of the reaction to form homogeneous mixture of copper and the lanthanide oxide. Although various precursors to prepare copper lanthanide oxide binary catalyst can be expected, few investigations have been performed to prepare the binary catalysts except for the alloy precursors. We have recently reported that copper-lanthanide oxide catalyst can be easily and effectively prepared from copper-lanthanide complex oxide of $Cu_6O_8Ln(NO_3)$ and also confirmed that the prepared catalyst exhibited high catalytic performance to various hydrogenations.[7]

In this work, we are investigating the catalytic property of copper-lanthanide oxide catalyst system prepared from the oxide precursors to the hydrogenation of CO. Here we report on the catalytic property of copper ytterbium oxide catalyst prepared from the complex oxide of $Cu_6O_8Yb(NO_3)$ to the reaction.

The preparation of the complex oxide of $Cu_6O_8Yb(NO_3)$ was shown in previous paper.[8] The prepared complex oxide (0.1 g as $Cu\text{-}Yb_2O_3$) was mounted on quartz wool in a reactor tube, connected with a closed circulation system, and reduced under H_2 atmosphere at prescribed temperature for 10 h as a pretreatment. The reaction was performed under the mixed gas of H_2 and CO ($H_2/CO=3$) in 400 Torr in the same system. The reactor effluent containing products was passed through a liquid nitrogen cooled sampling tube for gaschromatograph in the system to condense the products in it. The products were analyzed by gaschromatograph which was equipped with both of thermal conductivity and flame ionization detector.(Shimadzu GC-14B)

Time course of the reaction at 523 K over the catalyst pretreated at 523 K is shown in Figure 1. The product of hydrogenation was mainly methanol and the selectivity was more than 98%. Lower hydrocarbons, such as methane and ethane, were observed as the by-products of hydrogenation. Beside the products of hydrogenation, CO_2 was mainly confirmed. As shown in Figure 1, CO_2 produced selectively in the initial stage of the reaction, the activity decreased with passing time, and that became constant after 3 h. On the other hand, methanol is produced constantly after the induction period for 2 h. Here, the activity of methanol production shows the amount of produced methanol for the initial 8 h per gram catalyst. The reaction was carried out for more longer time and we also confirmed that the activity and the selectivity maintained constantly for more than 5 days. In the previous paper,[4-6] copper-lanthanide oxide system prepared from alloy precursor irreversibly decreased the activity by CO_2. The copper lanthanide oxide system in this study was

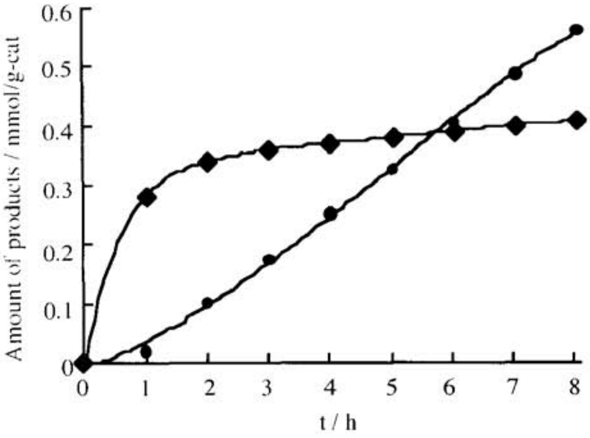

Figure 1. Time courses of the hydrogenation of CO at 573 K over $Cu\text{-}Yb_2O_3$ catalyst obtained from reduction of $Cu_6O_8Yb(NO_3)$ at 523 K;●: methanol, ◆: CO_2.

Table 1. Catalytic activity for methanol production from CO and H_2 over various Cu based catalysts

Catalysts	Pretreat.Temp /K	React.Temp /K	Activity[a] /μ-mol/g-cat.
$Cu\text{-}Yb_2O_3$	473	473	315
	523	473	560
	573	453	97
	573	473	428
	573	523	306
	573	573	76
$Cu/ZnO/Cr_2O_3$	573	473	18
	573	523	121
	573	573	40
$Cu/ZnO/Al_2O_3$	523	473	60
	623	523	134

[a] amount of produced methanol for 8 h.

not observe the decrease of the activity for a long period nevertheless CO_2 was co-produced. This is one of the noticeable point of this catalyst system. These results indicate that the homogeneous mixture of copper-ytterbium oxide prepared from the complex oxide of $Cu_6O_8Yb(NO_3)$ shows the characteristic performance for methanol production from the hydrogenation of CO.

The results of the catalytic activity of methanol production from CO and H_2 over various copper based catalysts were listed in Table 1. In Table 1, the activities of Cu-Yb_2O_3 prepared from the complex oxide and general copper based methanol synthesis catalysts of Cu/ZnO/Cr_2O_3 (Cu:Zn:Cr=6:3:1) and Cu/ZnO/Al_2O_3 (Cu:Zn:Al=4:5:1) at various pretreatment conditions are shown. From Table 1, among the various pretreatment and reaction conditions of Cu-Yb_2O_3, the catalyst which was pretreated at 523 K show the maximum activity at 473 K. On the other hand, from the results of the catalytic activity of Cu-ZnO systems, the maximum activity can be observed at 523 K. If the values of the activities are compared with both of the catalyst systems, it is notice that Cu-Yb_2O_3 system show noticeable high activity at low reaction temperature. Particularly, Cu-Yb_2O_3 catalyst prepared in this work showed the activity at 453 K. The maximum activity of Cu-Yb_2O_3 catalyst was observed at 473 K when the catalyst was pretreated at 573 K and the value was 428 μmol/g-cat, while the value of Cu/ZnO/Cr_2O_3 was 18 μmol/g-cat under the same reaction condition. From these results, it is clear that the Cu-Yb_2O_3 catalyst which was prepared from the complex oxide exhibits excellent catalytic performance to methanol production from CO and H_2 compared with copper-zinc catalyst systems. As one can also notice in Table 1, the catalytic activity of prepared Cu-Yb_2O_3 catalysts changed by changing the pretreatment condition of the complex oxide. We also investigated the effects of the pretreatment condition to the catalytic activity to elucidate the contribution of surface conditions to the reaction.

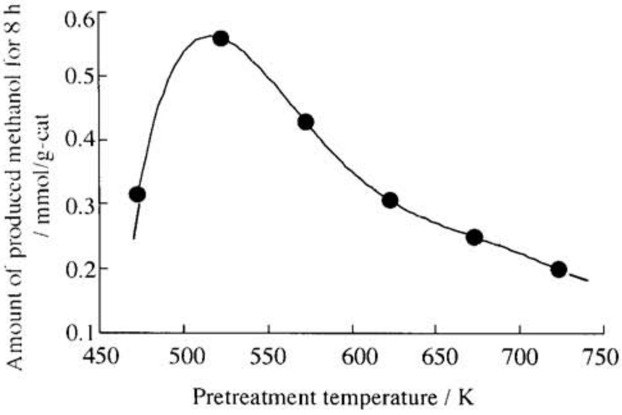

Figure 2. Dependence of the activity of methanol production from the hydrogenation of CO over the Cu-Yb_2O_3 catalyst upon pretreatment temperature. The reaction was carried out at 473 K.

The dependence of the catalytic activity of methanol production at 473 K upon the pretreatment temperatures are shown in Figure 2. From Figure 2, the catalytic activity improved by increasing the pretreatment temperature and the optimum activity showed when the catalyst was pretreated at 523 K. When the pretreatment temperature was increased over 523 K, the activity decreased monotonously with the increase of the pretreatment temperature. This result is suggesting that the catalytic activity strongly depends on the state of the catalyst originated from the pretreatment condition. Our previous paper clarify the morphology of the catalyst at various pretreatment conditions and shows the relation between the states of the catalysts and the hydrogenation activities of ethene and acetone.[7] In the case of the hydrogenation of acetone, the surface where cluster like ytterbium oxide highly dispersed in copper, is desirable. From the present result, the dependency of the activity for CO hydrogenation upon the pretreatment conditions are similar with the dependency of that for acetone hydrogenation. It indicates that the desirable surface condition of the catalyst for methanol production from CO and H_2 is similar with that for the hydrogenation of acetone according to our previous paper.[7]

From the previous papers,[4-6] the copper-lanthanide oxide systems are mainly studied to the catalyst prepared from copper-lanthanide alloy. Present investigations indicate that this system easily prepared from the oxide precursor and the catalytic performance can be controlled by changing the preparation condition.

This work was partially supported by Grant-in Aid for Scientific Research from Japanese ministry of Science, Sports and Culture. We are grateful to Dr. K. Ohdan and Dr. R. Sugise of UBE Co. Ltd. for valuable discussion.

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