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Liquid Phase Methanol Synthesis on Copper and Zinc Ultrafine Particles Prepared by Gas Evaporation Method

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Liquid phase methanol synthesis was carried out over ultrafine particle (UFP) catalysts. A very high activity was obtained over Zn UFP modified using Cu acetylacetonate and $LiAlH_4$. The rate of methanol formation on this catalyst at the steady state was about 1.8 times as high as that of a co-precipitated catalyst.

Liquid phase methanol synthesis using a slurry bed reactor has been developed by Chem Systems, Inc. in 1975.[1] The reaction is accomplished using a solid catalyst suspended in the liquid medium. Since the liquid medium efficiently removes the heat of reaction, control of the reaction temperature in this type of reactor is much better than in ordinary gas phase reactors. Although the liquid phase methanol process has been investigated at Air Products and Chemicals, Inc.,[2] Akron University,[3] Norwegian Institute of Technology,[4] Brookhaven National Laboratory,[5] and so on, very few studies have been reported on the development of active catalysts for this process.

In our previous paper,[6] it has been reported that ultrafine particles (UFP) composed of Cu and Zn which are prepared by the chemical deposition in liquid phase (CDL) method show an excellent catalytic activity for the liquid phase methanol synthesis. The present work aims to determine the catalytic activity of Cu and Zn UFP prepared by the gas evaporation method and to find effective procedures for modification of the UFP.

Methanol synthesis was carried out in a slurry bed reactor, as previously described.[6] Syngas having a H_2/CO ratio of 2 was allowed to react on the catalyst suspended in a liquid medium commercially named as Carnation, which was a mixture of hydrocarbons having carbon number of 16 to 35 and supplied by Witco Co. The composition of products and the level of CO conversion were determined by means of gas chromatography. An ultrasonic generator was used to prepare the suspension of UFP prior to reaction. The detailed procedure for ultrasonic dispersion was described elsewhere.[7]

UFP composed of Cu or Zn were prepared by the gas evaporation method[8] and supplied by Vacuum Metallurgical Co., Ltd. (Chiba Prefecture). In some cases, the UFP catalyst of Cu or Zn were modified using the CDL method. The first series of modified UFP designated as Cu/Zn UFP were prepared as follows: An aqueous solution of $NaBH_4$ or N_2H_4 as a reducing agent was dropped into a suspension of the Zn UFP prepared by the gas evaporation method in an aqueous solution of

$Cu(NO_3)_2$. After sufficient stirring, the black product was separated from the solution by filtration, washed with water, and dried under reduced pressure. The catalysts thus prepared are denoted as Cu-$NaBH_4$/Zn UFP and Cu-N_2H_4/Zn UFP, respectively. In the case of the catalyst prepared using $LiAlH_4$ as a reducing agent, THF and $Cu(CH_2COCH_2COCH_3)_2$ were used instead of water and $Cu(NO_3)_2$, respectively. Since the product particle was too small for filtration, the solvent was evaporated to dryness under reduced pressure. This catalyst is denoted as Cu-$LiAlH_4$/Zn UFP. The second series of the modified UFP designated as Zn/Cu UFP was prepared in the same manner as above using a suspension of the Cu UFP prepared by the gas evaporation method in a solution of $ZnCl_2$ or $Zn(CH_2COCH_2COCH_3)_2$.

In a control experiment, a co-precipitated Cu-Zn-Al catalyst was used in the present work. The catalyst was prepared according to the method described by Herman et al.[9] and activated in a stream of H_2(2%)/N_2(98%) at 350 °C for 3 h.

Liquid phase methanol synthesis was carried out at 250 °C and 30 atm, using UFP composed of Cu or Zn as a catalyst. Figure 1 illustrates the variation of catalytic activities of Cu UFP, Zn UFP, and a physical mixture of them (denoted as Cu UFP + Zn UFP) represented by CO conversion (X), including the co-precipitated catalyst for comparison. Although the physical mixture of UFP, which was ultrasonicated in the liquid medium, was more active than the parent UFP catalysts, the activity of this catalyst was still lower than that of the conventional co-precipitated catalyst.

The activities of Cu/Zn UFP and Zn/Cu UFP catalysts were studied. All of the Zn/Cu UFP catalysts showed very low activities. Figure 2 compares the activities of various Cu/Zn UFP catalysts and Zn UFP.

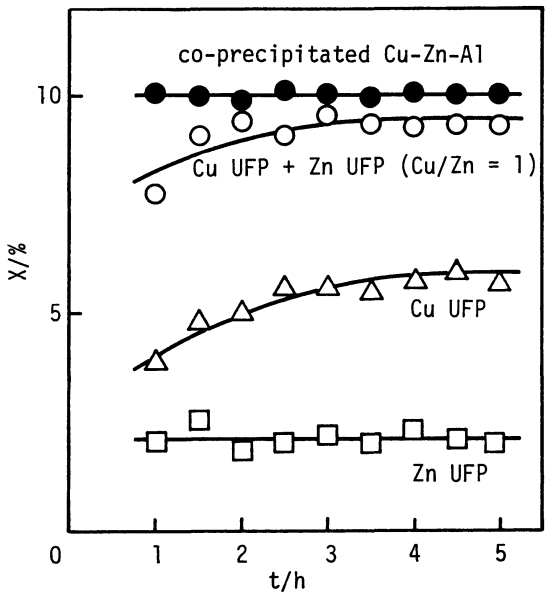

Fig. 1. Activities of UFP and co-precipitated catalysts as a function of time on stream. Reaction conditions: temperature, 250 °C; pressure, 30 atm; H_2/CO, 2; W/F, 810 g-catal min CO-mol^{-1}.

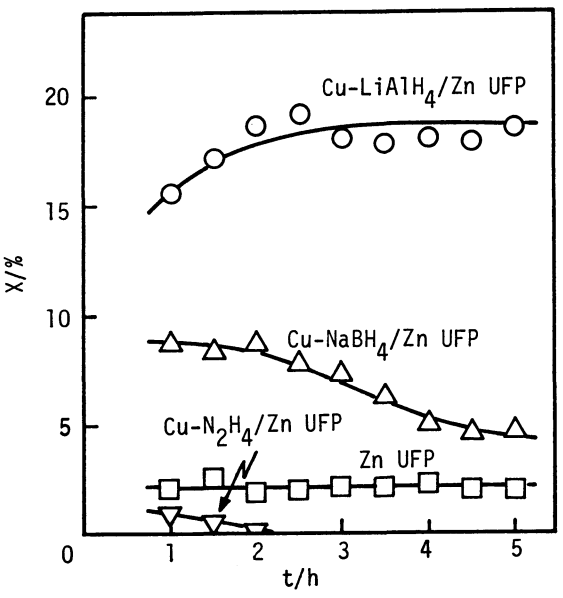

Fig. 2. Activities of various Cu/Zn UFP and Zn UFP catalysts as a function of time on stream. Reaction conditions: temperature, 250 °C; pressure, 30 atm; H_2/CO, 2; W/F, 810 g-catal min CO-mol^{-1}.

The catalytic activities of Cu-$NaBH_4$/Zn UFP and Cu-N_2H_4/Zn UFP were medium and low, respectively. On the other hand, a very high activity was obtained over Cu-$LiAlH_4$/Zn UFP catalyst. The rate of methanol formation on this catalyst at the steady state was 13.3 mol kg-catal^{-1} h^{-1}, which is about 1.8 times as high as that of the co-precipitated catalyst.

Table 1 summarizes the BET surface area (S) and the composition of these catalysts. It is apparent that the activities of these catalysts (shown in Fig. 2) increased with increasing BET surface area. However, the differences in the surface area were not sufficient to explain the remarkably high activity of Cu-$LiAlH_4$/Zn UFP catalyst.

Figure 3 shows the results of scanning electron microscopic (SEM) observation of these Cu/Zn UFP catalysts. Although two types of particles were present separately in Cu-N_2H_4/Zn UFP catalyst which showed a low activity, small particles stuck to the surface of the Zn UFP in Cu-$NaBH_4$/Zn UFP and Cu-$LiAlH_4$/Zn UFP. Moreover the stuck particles of Cu-$LiAlH_4$/Zn UFP, which was the most active catalyst, were smaller than those of Cu-$NaBH_4$/Zn UFP. The difference in the form of these catalysts may result in the difference in their activity.

Table 1. BET Surface Area and Composition of Various Cu/Zn UFP catalysts

Catalyst	S/m^2g^{-1}	Composition (wt%)				
		Cu	Zn	Al	B	Others
Cu-$LiAlH_4$/Zn UFP	23.3	7.9	81.8	6.7	---	3.6
Cu-$NaBH_4$/Zn UFP	14.5	8.3	86.6	---	3.1	2.0
Cu-N_2H_4/Zn UFP	13.1	8.6	88.7	---	---	2.7

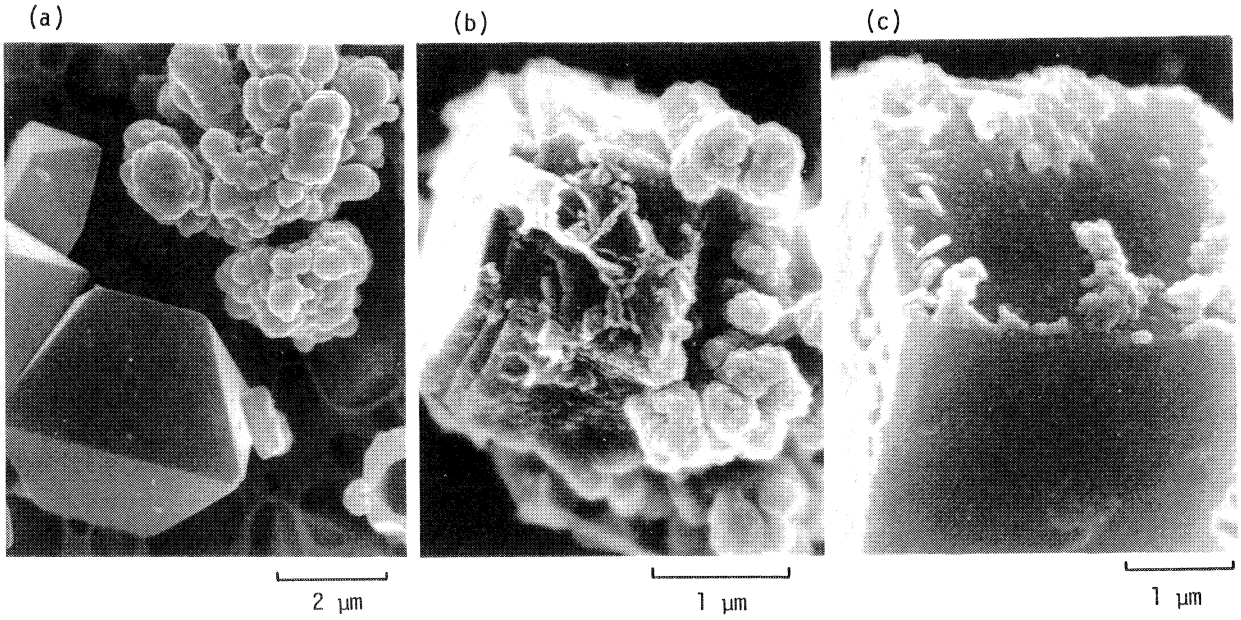

Fig. 3. Scanning electron micrographs of Cu-N_2H_4/Zn UFP (a), Cu-$NaBH_4$/Zn UFP (b), and Cu-$LiAlH_4$/Zn UFP (c).

As shown in Table 1, chemical analysis of the catalysts showed that Cu-$LiAlH_4$/Zn UFP contained Al derived from the reducing agent. Since it is known that Al is one of the important components of conventional catalysts for methanol synthesis,[10] the excellent activity of the Cu-$LiAlH_4$/Zn UFP may be also due to Al in the catalyst.

In the present work, we found an effective procedure for modification of the UFP. This procedure may be a countermeasure for difficulty in preparing UFP catalysts composed of several components.

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