CHEMISTRY LETTERS, pp. 141-144, 1989.

Liquid Phase Methanol Synthesis on Cu-Zn Ultrafine Particles Prepared by Chemical Deposition in Liquid Phase

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Liquid phase methanol synthesis was investigated over ultrafine particle (UFP) catalysts prepared by chemical deposition in liquid phase. The UFP prepared by reduction of Cu and Zn acetylacetonates by $LiAlH_4$ in THF solution showed a very high methanol productivity which is greater than twice that of a Cu-Zn-Al coprecipitated oxide catalyst.

The synthesis of methanol from CO and H_2 is a very exothermic reaction, and low temperatures favor the synthesis thermodynamically. One of the most important features of this process is the method to remove the heat of reaction. In the ordinary gas phase synthesis, conversion per pass is controlled to very low, and recycle of cooled unreacted syngas is employed to regulate the reaction temperature.

Liquid phase methanol synthesis using a slurry bed reactor has been invented in 1975 by Chem Systems,1) and the research has been taken over by Air Products and Chemicals. The reaction is performed with a solid catalyst suspended in the liquid medium which efficiently removes the heat of reaction. Consequently, the control of the reaction temperature in this type of reactor is reported to be much better than in ordinary gas phase reactors, allowing a higher conversion per pass. Liquid phase methanol processes have so far been investigated at Akron University,2) Norwegian Institute of Technology,3) Brookhaven National Laboratory,4) and so on.

It has been reported in our previous paper5) that ultrafine particles (UFP) of Fe prepared by the gas evaporation method show excellent catalytic properties for the liquid phase Fischer-Tropsch synthesis. The UFP catalyst exhibits a greater activity than an ordinary precipitated Fe catalyst, in spite of almost equal BET surface area. This has been interpreted as being due to an effect of catalyst structure. These results awaken an interest in the application of UFP to a catalyst for liquid phase methanol synthesis.

The purpose of the present work is to determine the catalytic activity of Cu-Zn UFP for liquid phase methanol synthesis.

Liquid phase methanol synthesis from CO and H_2 was studied in a high pressure flow system. The liquid phase (slurry) reactor was a stainless steel autoclave equipped with a stirrer and had an internal volume of 100 cm^3. Syngas was fed to the reactor from the bottom through a nozzle having a 3 mm inside diameter, and was allowed to react on the catalyst suspended in 50 ml of a liquid medium commercially designated as Carnation (a mixture of hydrocarbons having 16-35 carbon atoms, supplied by Witco Chemicals). The stirring rate was 2000 rpm, which was sufficient to stir the reaction system so that higher stirring rate did not increase the reaction rate. The product gas stream passed through a pressure regulator to an ice-cooled scrubbing bottle containing water, and the flow rate was measured using a soap-film meter. The composition of products and the level of CO conversion were determined by means of gas chromatography. It was shown that no detectable amount of methanol was accumulated in the liquid medium.

Ultrafine particles of Cu-Zn, a Cu-Zn-Al co-precipitated oxide, and a commercial methanol synthesis catalyst were used as catalysts in the present work. The UFP catalysts were prepared by the chemical deposition in liquid phase (CDL) method: a solution of the reducing agent ($NaBH_4$, KBH_4, or $LiAlH_4$) was added to a solution of Cu and Zn salts with a Cu:Zn molar ratio of 7:3.

An aqueous solution of $NaBH_4$ or KBH_4 was added dropwise to an aqueous solution of Cu and Zn nitrates, sulfates, or chlorides. The solution was mixed by stirring, and the precipitate was washed with water and then with acetone. After drying *in vacuo*, the catalyst was crushed to fine powder in N_2 atmosphere. On the other hand, $LiAlH_4$ dissolved in tetrahydrofuran (THF) was added to a THF solution of Cu and Zn acetylacetonates or chlorides. The obtained black "solution" was dried *in vacuo* and crushed in N_2 atmosphere. An ultrasonic generator was used to prepare a suspension of the UFP catalyst prior to reaction.6)

A co-precipitated Cu-Zn-Al catalyst was prepared according to the method described by Herman et al.7) The catalyst was activated in a stream of H_2(2%)/N_2(98%) at 350 °C for 3 h.

The activity of crushed commercial catalysts for liquid phase methanol synthesis was investigated at 250 °C, 30 atm with a feed of $2H_2$+1CO syngas. Table 1 summarizes the activities of the crushed catalysts, expressed by the average reaction rate in the initial 5 h of run (r), with determined BET surface areas (SA) of the catalysts. The catalytic activity increased with decreasing particle size (d), irrespective of almost equal BET surface area. This is interpreted as being caused by diffusion resistance. The reactant diffuses into the pores and reacts on the catalyst surface. If the reaction is faster than diffusion, the

Table 1. Effect of Particle Size on Catalytic Activity of Commercial Catalyst

d/mm	SA/m^2 g^{-1}	$r^{a)}$x10^4/CO-mol g-catal^{-1} min^{-1}
≥ 0.105	43.4	1.01
0.075 - 0.105	43.8	1.12
0.063 - 0.075	46.3	1.26
0.046 - 0.063	43.5	1.41
≤ 0.046	46.1	1.58

a) Reaction conditions: temperature, 250 °C; pressure, 30 atm; H_2/CO, 2; W/F, 810 g-catal min CO-mol^{-1}.

Table 2. Catalytic Activities of Various Catalysts Reduced by $NaBH_4$, KBH_4, or $LiAlH_4$

Catalyst	Cu precursor	Zn precursor	Reducing agent	$r^{a)}\times10^5$/CO-mol g-catal^{-1} min^{-1}
1	$Cu(NO_3)_2$	$Zn(NO_3)_2$	$NaBH_4$	4.8
2	$Cu(NO_3)_2$	$Zn(NO_3)_2$	KBH_4	4.0
3	$CuSO_4$	$ZnSO_4$	$NaBH_4$	2.2
4	$CuSO_4$	$ZnSO_4$	KBH_4	2.2
5	$CuCl_2$	$ZnCl_2$	$NaBH_4$	5.3
6	$CuCl_2$	$ZnCl_2$	KBH_4	5.6
7	$Cu(OCOCH_3)_2$	$Zn(NO_3)_2$	$NaBH_4$	6.2
8	$Cu(OCOCH_3)_2$	$Zn(OCOCH_3)_2$	KBH_4	5.9
9	$Cu(acac)_2$	$Zn(acac)_2$	$LiAlH_4$	25.9
10	$CuCl_2$	$ZnCl_2$	$LiAlH_4$	9.0

a) Reaction conditions: temperature, 250 °C; pressure, 30 atm; H_2/CO, 2; W/F, 810 g-catal min CO-mol^{-1}.

concentration of reactant falls along the distance from the pore mouth. Thus, if the catalyst is composed of large particles with rather deep pores compared with small particles, more limited portions of the catalyst surface can be used for reaction. This consideration suggests that the use of a catalyst of smaller particles, for instance UFP, is effective for the liquid phase methanol synthesis.

Table 2 lists the average rates of reaction in the initial 5 h of run on various Cu-Zn UFP prepared by the CDL method. The difference in activity between $NaBH_4$-reduced and KBH_4-reduced catalysts was not serious, whereas the $LiAlH_4$-reduced catalysts, especially prepared from acetylacetonates (catalyst 9), were more active for the liquid phase methanol synthesis. Methanol was a sole product on these UFP catalysts, though a slight amount of CO_2 was formed over the co-precipitated catalyst.

A further investigation was carried out using catalysts 7 and 9, which were prepared using KBH_4 and $LiAlH_4$ as reducing agents, respectively. The transmission electron micrographs (TEM) of catalysts 7 and 9 were shown in Fig. 1. The average particle size of catalyst 7 was ca. 45 nm, as shown in Fig. 1(a). The X-ray

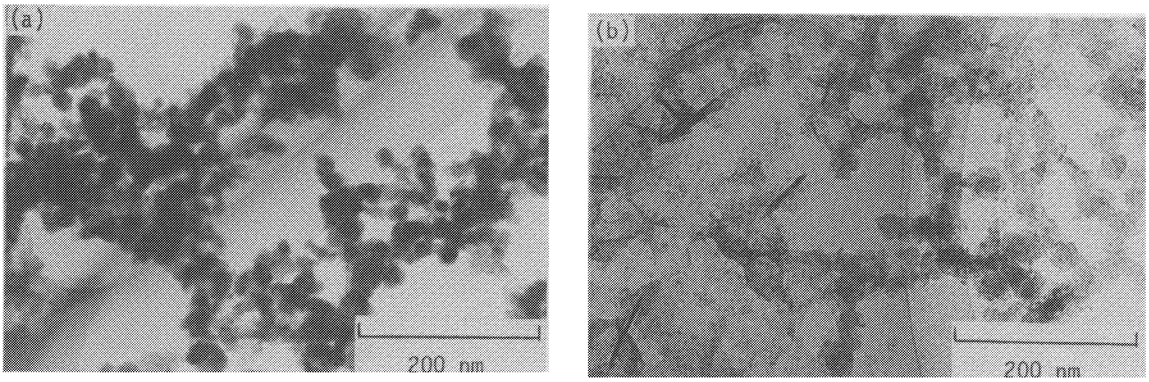

Fig. 1. Transmission electron micrographs of catalysts 7(a) and 9(b).

diffraction study on this catalyst revealed that the reflection lines due only to Cu was present, and no crystalline compound containing Zn was detectable. These results indicate that Zn is present in very small crystallites or in the amorphous phase. As shown in Fig. 1(b), two types of particles, i.e. spherical and fibrous, were observed in catalyst 9 by means of a TEM. The average size of the spherical particles was ca. 20 nm. The X-ray diffraction pattern of this catalyst showed only a broad line, indicating low crystallinity. The BET surface areas of catalysts 7 and 9 were 43.2 and 68.1 m^2 g^{-1}, respectively.

Figure 2 shows the variations in the activity of catalysts 7 and 9 represented by CO conversion (X), in a comparison with the co-precipitated catalyst. The activity of catalyst 7 deteriorated with time on stream (t), although that of the co-precipitated catalyst scarcely changed at least for 5 h. On the other hand, the activity of catalyst 9 slightly increased at the initial stage of run. This catalyst showed a very high methanol productivity, and the rate of methanol formation at the steady state was 15.6 mol kg-catal^{-1} h^{-1}, which is more than twice that of the co-precipitated catalyst.

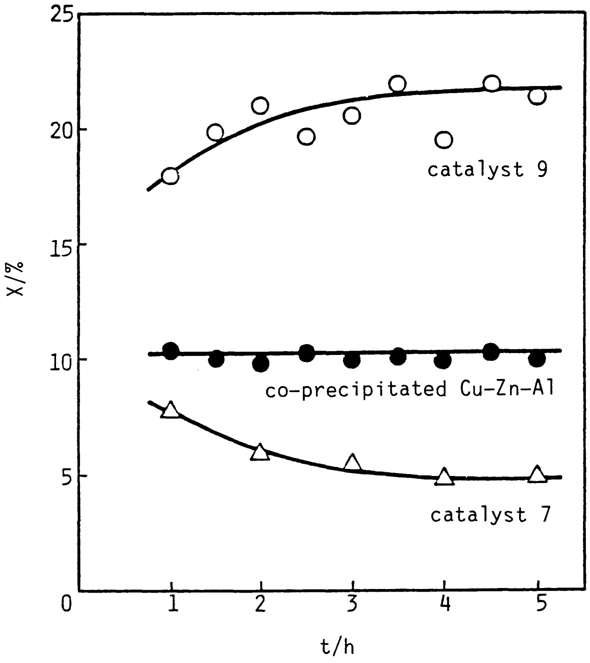

Fig. 2. Catalytic activities of various catalysts as a function of time on stream. Reaction conditions: temperature, 250 °C; pressure, 30 atm; H_2/CO, 2; W/F, 810 g-catal min CO-mol^{-1}.

It is known that the powder prepared by the CDL method using $LiAlH_4$ contains Al,[8] which is one of the important components of ordinary catalysts for methanol synthesis. Therefore, the excellent activity of the $LiAlH_4$-reduced Cu-Zn UFP may be due to Al in particles.

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(Received October 15, 1988)