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Methanol Synthesis Reaction over Copper–Group IV Metal Amorphous Alloys as Catalyst Precursor

Amorphous alloys made by rapid quenching techniques have drawn increasing interest due to their superior mechanical, chemical, and magnetic properties. Several studies have been reported on the catalysis over amorphous alloys applied to, for instance, *trans*-isomerization of *cis*-cyclododecene (*1*), hydrogenation of olefins (*2*), hydrogenation of CO (*3*), and so on. Yokoyama *et al.* (*4*) have reported that a highly active methanation catalyst was prepared from an amosphous $Pd_{35}Zr_{65}$ alloy.

This paper describes methanol synthesis reaction over copper–group IV metal amorphous alloys as catalyst precursor and the activation process of the amorphous alloys.

Pure copper (99.9%) and a group IV metal (99.9% Ti, 99.6% Zr, 96% Hf) were arc-melted together in argon atmosphere. From these alloys, amorphous alloy ribbons of 0.01–0.03 mm thick by 0.5–1.5 mm wide were fabricated by a single-roll-type melt quenching method in argon atmosphere. Crystallized samples (CuZr(crys.)) were obtained from an amorphous $Cu_{70}Zr_{30}$ alloy (CuZr(am.)) by heating at 873 K for 30 min *in vacuo*.

One-half gram of the alloy sample was put into a tubular reactor. The temperature of the catalyst was measured by a thermocouple which was inserted in the center of the catalyst bed layer. The reaction was carried out under a gas pressure of 6.0 MPa using a flow reactor. The gas mixture of CO, H_2, and Ar ($CO/H_2/Ar = 31/64/5$, $O_2 <$ 1 ppm) in the cylinder was used without further purification.

The crystalline phase in the catalyst was identified by X-ray diffraction. The average size of copper particles formed in the crystallized samples was estimated from the half-value width of X-ray diffraction peaks. DTA measurement under various gas atmospheres of 1.0 MPa was carried out using a high-pressure DTA–TG apparatus (Shinku Riko Co. Ltd.).

Figure 1 shows how the catalytic activity of CuZr(am.) changes with time on stream at 500 K. In the initial stage, mainly methane was produced at a very low CO conversion. In the later stage after about 10 h, the CO conversion started to increase, and methanol and dimethyl ether were produced. After 30 h of the induction period, the reaction reached a steady state.

The pretreatment of CuZr(am.) with H_2 or O_2 decreased the time of the initial stage and the induction period. The induction period was 15 h in pure H_2 and 3 h in O_2 diluted with N_2 (O_2; 2 vol%) at 500 K for 5 h. However, the selectivity to methanol slightly decreased at the steady state after such pretreatments.

Table 1 summarizes the results of the reaction over various Cu–group IV metal alloys at the steady state. CuZr(am.) had high selectivity (98%; based on CO) to methanol (+dimethyl ether). CuZr(crys.) was less active in CO conversion than CuZr(am.) at the same temperature. CuZr(crys.) was more selective in the formation of methane and CO_2 than CuZr(am.) at the same total conversion level. The performance of the amorphous $Cu_{63.5}Hf_{36.5}$ alloy (CuHf(am.)) was similar to CuZr(crys.). The amorphous $Cu_{60}Ti_{40}$ alloy (CuTi(am.)) was inactive even at 600 K.

Both amorphous and crystalline CuZr alloys changed to Cu and ZrO_2 phase after reaction. CuHf(am.) changed to Cu and

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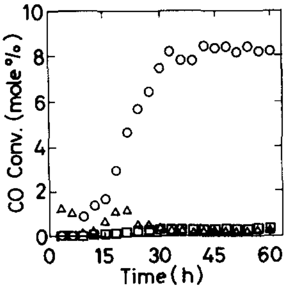

FIG. 1. Activity change in CuZr(am.) as catalyst precursor under a total pressure of 6.0 MPa ($CO/H_2/Ar$ = 31/64/5) at 500 K. CH_3OH, ○; CH_3OCH_3, □; CH_4, △.

HfO_2. On the contrary, CuTi(am.) changed to Cu, Cu–Ti metallic compounds, and $TiH_{1.924}$.

The BET surface area of all the alloys was less than 1 m^2/g in as-quenched state, and increased to a value between 31 and 67 m^2/g except for CuTi(am.) after the reaction. By means of a scanning electron microscope, many cracks were observed on the surface of used samples which gave the increase in the surface area.

Average size of copper particles in alloy catalysts formed during the reaction was in a range between 13 and 30 nm. After the reaction, CuZr(crys.) and CuHf(am.), which were more active at higher temperature but poorer in selectivity to methanol, had smaller BET surface area and larger average size of copper particles than CuZr(am.).

Figure 2 shows DTA curves of CuZr(am.) in various atmospheres. CuZr(am.) was simply crystallized in Ar or CO at about 780 K, while in H_2 it changed to Cu and ZrH_2 at a temperature between 500 and 600 K and in CO/H_2 appeared Cu and ZrO_2 at a temperature between 600 and 800 K. The same crystalline phases as appeared after the methanol synthesis reaction was observed only when heated in H_2 and CO. X-Ray diffraction analysis was made with DTA samples heated to the tail end (A, B, C in Fig. 2) of these peaks on DTA curves taken in CO/H_2. At the point A, weak diffraction peaks from ZrO_2 and broadening of peaks from amorphous phase, which suggests the absorption of hydrogen, were observed. Increased intensity in the peaks from ZrO_2 and weak peaks from Cu were obtained at the point B. Strong peaks from ZrO_2 and Cu were obtained at the point C.

TABLE 1

Results of Methanol Synthesis Reaction over Cu–Group IV Metal Alloys as Catalyst Precursor under a Total Pressure of 6.0 MPa ($CO/H_2/Ar$ = 31/64/5)

Catalysts	Reaction temp. (K)	CO conversion (mole%)				
		CH_3OH	CH_3OCH_3	CH_4	CO_2	Total
CuZr(am.)	500	8.4	0.3	0.2	0.0	8.9
CuZr(crys.)	505	4.4	0.1	0.1	0.0	4.6
	553	6.1	0.8	0.7	0.6	8.2
CuHf(am.)	541	7.9	1.2	0.7	0.7	10.5
CuTi(am.)	600	0.0	0.0	0.1	0.1	0.2

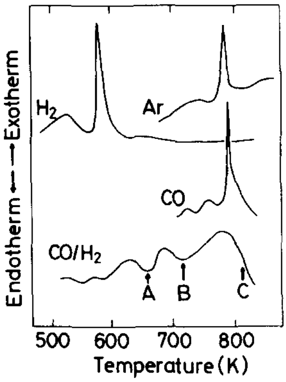

FIG. 2. DTA curves of CuZr(am.) in various atmospheres: heating rate; 0.17 K/s.

It has been reported that the surface of amorphous alloys containing zirconium are covered with thin ZrO_2 layer (5). At the initial stage of the reaction, the amorphous Cu–Zr phase swells due to the absorption of hydrogen, and then cracks are formed in the surface ZrO_2 layer. CO and H_2 penetrate into these cracks, and the methanation reaction take place on the amorphous Cu–Zr phase. Then zirconium is oxidized by water or oxygen produced during the methanation or by trace amounts of impurity oxygen in the mixed gas. Due to the oxidation of zirconium, zirconium content in the amorphous phase decreases. This makes the amorphous phase unstable and the alloy changed to crystalline Cu and ZrO_2. At the same time, new cracks may form in the newly formed ZrO_2 layer beneath the original ZrO_2 layer. This process makes the catalyst have a large surface area which contains fine Cu particles dispersed in ZrO_2.

Klier *et al.* (*6*) point out that the Cu^+ dissolved in the ZnO phase is an active site in the methanol synthesis reaction. An active site of the catalyst derived from an amorphous Cu–Zr alloy might be Cu^+ similar to the Cu/ZnO catalyst. Further studies are under way to establish the character of these catalysts.

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