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Liquid-Phase Hydration of Acrylonitrile on Skeletal Copper Catalysts Prepared from Cu–Ti and Cu–Zr Amorphous Alloys

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Synopsis. Liquid-phase hydration of acrylonitrile has been carried out on the skeletal copper catalysts which were prepared by treating pulverized amorphous Cu–Ti and Cu–Zr alloys with an HF solution. The catalysts from amorphous alloys were more effective to produce acrylamide selectively than those from crystalline alloys. This high activity was brought about by the highly homogeneous structure of the amorphous alloys.

Since Komiyama et al. have reported the primary work on the catalysis of amorphous alloys,$^{1)}$ various works have been performed to reveal the usefulness of amorphous alloys as catalysts or precursors for catalysts and the surface structures before and after various pretreatments and reactions.$^{2—5)}$ We have developed effective methods for enhancement of catalytic activity, e.g. pretreatments with hydrogen and oxygen,$^{6)}$ with hydrogen fluoride,$^{7)}$ with doping and leaching of a zinc atom,$^{8)}$ and pulverization of amorphous ribbons by a simple method.$^{9)}$ In these works, catalysis by amorphous alloys have extensively been studied by performing reactions in a gas-phase at fairly high temperatures. Since amorphous alloys are thermally unstable and liable to crystallize, it is worthy to study the reactivity at a low temperature. We report here an application of an amorphous alloy for a reaction in a liquid-phase under mild conditions.

Synthesis of acrylamide is an important reaction in industry. Hydration of acrylonitrile (AN) to acrylamide (AA) is catalyzed by a metallic copper,$^{10—12)}$ copper-nickel alloy,$^{11)}$ a Raney-type alloy,$^{10)}$ and metal oxides$^{13)}$ in a liquid-phase reaction. These catalysts occasionally produce ethylene cyanohydrin (EC) and bis(2-cyanoethyl) ether as by-products to some extent. It was reported that the reduced copper gave a 100% selectivity, but the catalytic activity was improved by the alloying.$^{11)}$ We found here that skeletal copper catalysts prepared by treating pulverized amorphous Cu–Ti and Cu–Zr alloys with an HF solution catalyze the liquid-phase hydration of AN more selectively and with the higher activity than those prepared from crystalline alloys.

Experimental

Amorphous $Cu_{67}Ti_{33}$ and $Cu_{62}Zr_{38}$ ribbon alloys were prepared from crystalline mother alloys by the rapid-quenching method,$^{7)}$ pulverized by a vibratory mill and sieved under 400 mesh. The powder alloys were treated with an aqueous HF solution (0.1—2 mol dm^{-3}) for 5 min to extract Zr and Ti from alloys. Some catalysts were treated with 13.3 kPa hydrogen at 473 K for 2 h. After the pretreatment, the catalyst (100 mg) was placed in a 30 cm^3 flask under N_2 atmosphere and the reaction of AN (32 mmol) and water (5 ml) was performed at 338 K with magnetically stirring. The products were analyzed by GLC. XPS and XRD analyses were carried out with Shimadzu ESCA-750 and Rigaku Geigerflex 2013, respectively.

Results and Discussion

Table 1 shows the effects of the pretreatment conditions on the catalytic activity, selectivity, and surface state of catalysts. Products were AA and EC in the present liquid-phase reaction on Cu–Ti and Cu–Zr catalysts. Without the HF treatment, catalysts exhibited very little activities. This result is ascribed to their small B.E.T. surface area and low concentration of the surface copper species. The catalysts treated with an HF solution exhibited a high activity to produce AA selectively. The pretreatment with HF also brought about an increase in the surface area and the surface copper concentration, indicating that Zr and Ti species of the alloys were extracted selectively into an HF solution to form the skeletal copper catalysts. The treatment with HF in a 1 mol dm^{-3} was more effective for the preparation of catalysts than that in the higher concentration.

The crystalline powder alloys prepared by the pulverization of mother Cu–Ti and Cu–Zr alloys and commercial copper metal powder were also investigated for comparison (Table 1). Crystalline alloys became active by the HF treatment, but the catalytic activity and AA selectivity were much higher with catalysts prepared from amorphous alloys than from crystalline catalysts. This result is parallel to the greater enhancement of surface area and surface copper concentration by the HF treatment of amorphous alloys than of crystalline alloys.

As shown in Fig. 1, the catalyst obtained from the amorphous alloy exhibited the broader peak in the XRD pattern (Fig. 1b) than that from the crystalline alloy (Fig. 1c). This indicates that fine copper particles are formed by the segregation of copper atoms after the HF treatment, and the size of the particles is smaller with the catalyst from the amorphous alloy than from the crystalline alloy. This result implies that the concentration of low coordination sites, e.g. kink and ledge

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Table 1. Surface State and Catalytic Activity of Catalysts Prepared from Amorphous and Crystalline Cu–Ti and Cu–Zr Alloys

Catalyst	HF concn[a)]	AN conv.[b)]	AA sel.	Surface area[c)]	I_{Cu}[d)]
	$mol\,dm^{-3}$	%	%	$m^2\,g^{-1}$	$I_{Cu}+I_{Ti,Zr}$
Amor. Cu–Ti	None[e)]	Tr	—	0.2	43
	0.2	1	100	2.3	74
	1	11	98	7.9	82
	2	6	98	4.2	86
Amor. Cu–Zr	None[e)]	Tr	—	2.9	27
	0.2	26	99	6.0	63
	1	35	100	8.2	97
	2	22	97	7.1	98
Crys. Cu–Ti	1	3	93	6.8	80
Crys. Cu–Zr	1	14	93	7.0	89
Powder Cu metal	None[e)]	2	91	0.7	100

a) Concentration of HF solution for pretreatment. b) AN conversion after reaction for 4 h. c) Kr physisorption at 77 K. d) Surface atomic ratio (%) calculated from XPS peak intensity in Cu ($2p_{3/2}$), Ti ($2p_{5/2}$ and $2p_{3/2}$), and Zr ($3d_{5/2}$ and $3d_{3/2}$). e) Samples were treated with H_2 at 473 K for 1 h.

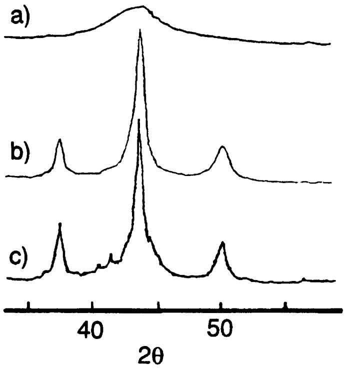

Fig. 1. XRD patterns of Cu–Ti catalysts. a) Amorphous alloy without treatment with HF; b) amorphous alloy after treatment with HF; c) crystalline alloy after treatment with HF.

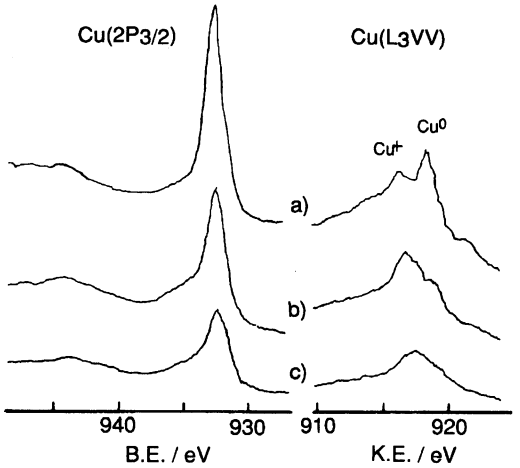

Fig. 2. XPS spectra of Cu–Ti catalysts. a) Amorphous alloy after treatment with HF (1 $mol\,dm^{-3}$, 5 min) and H_2 (473 K, for 1 h); b) amorphous alloy after treatment with HF; c) crystalline alloy after treatment with HF.

sites which may be the active sites, is higher at the surface of the catalyst prepared from the amorphous alloy than that from the crystalline alloy. The highly homogeneous structure of the raw amorphous alloy may be effective for the formation of small copper particles, that is also responsible for the high activity of catalyst from the amorphous alloys.

Figure 2 shows the XPS spectra of the catalysts after the HF treatment of the amorphous and crystalline alloys (Figs. 2b and 2c) and after the HF and H_2 treatments of the amorphous alloy (Fig. 2a). The small satellite peak in Cu($2p_{3/2}$) spectra of these three samples indicated that surface Cu species were mainly in the Cu^0 and/or Cu^I state. In Cu(L_3VV) spectra, the catalyst after the H_2 treatment exhibited the highest intensity of peak due to Cu^0 species. The H_2 treatment brought about a slight increase in the activity and a decrease in the formation of EC (100% AA selectivity), compared with the case only with the HF treatment. Since it is reported that the oxidation of copper catalyst promotes the production of EC in stead of AA,[14)] the above results support that the surface Cu^0 species is active to produce AA selectively.[12)]

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