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Liquid-Phase Hydration of Acrylonitrile to Acrylamide over the Copper-Nickel Alloy Catalysts

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The liquid-phase hydration of acrylonitrile to acrylamide has been examined over various metal catalysts at 75 °C. Five metal elements-Cu, Ag, Fe, Co, and Ni-showed the catalytic conversion of acrylonitrile. The Cu and Ag catalysts gave the acrylamide with a 100% selectivity, while the other metals, Fe, Co, and Ni, yielded three products: acrylamide, ethylene cyanohydrin, and bis(2-cyanoethyl) ether. The alloying of Cu and Ni led to an increase in the formation of acrylamide with keeping the high selectivity to acrylamide. Especially, Cu-Ni alloys, with a range of 20—70% Cu in their bulk composition, were much more active catalysts than Cu. The maximum yield of acrylamide was obtained on the Cu-Ni alloy catalysts was observed, although such a retardation occurred on the Cu catalyst surface. The maximum synergistic effect was observed over the alloy with the surface component ratio of Cu to Ni of 4; this effect was discussed.

In relation to the liquid-phase hydration of acrylonitrile(AN) over various metal oxides or metals, it has been found that acrylamide(AA), ethylene cyanohydrin(ECH), and bis(2-cyanoethyl) ether(BCE) are chiefly produced.[1)] Commercially available AA, which is used as paper-strengthening agents and flocculants etc., can be obtained by the selective hydration of the cyano group in an AN molecule. This hydration is effectively catalyzed by a metallic Cu such as the Cu prepared by reduction with H_2, Raney and Ullmann Cu.[2-4)]

It is known that the catalytic hydration processes using metallic Cu catalysts have a number of excellent characteristics, such as simplicity of outline, easy handling, and the absence of any by-product formation.[5)] A modification of the catalysts is rather effective if one aims to study the improvement of the hydration process. In the investigation of the basic design of highly active catalysts on AA production, as has been reported in a previous paper,[6)] we recently found out that Ni-enriched Cu-Ni alloys had more ability for the AA formation than did the Cu catalysts in the liquid-phase hydration of AN. In this paper, the synergistic effect of Cu and Ni on the AA formation will be reported.

Experimental

Catalyst Preparation: The Cu-Ni alloys employed in this work were prepared by the reduction of the oxides obtained by the thermal decomposition, in air, of the Cu-Ni carbonates coprecipitated from their nitrates in aqueous solutions; this was done in the manner described by a number of workers.[7-11)] In a typical preparation of the present investigation, a 5 wt% Na_2CO_3 aqueous solution was slowly added to a 0.5 M solution of mixed nitrates (Kanto Chemicals), keeping it at 32 °C, until the pH value of 9.5 was reached; and the suspension was then stirred for 1 h and left to stand overnight. After the resulting slurry has been filtered, the precipitate was washed with a large amount of ion-exchanged water until the pH value of the filtrate attained 8.0. The mixed carbonate was dried overnight at 120 °C and then calcined in air for 3 h at 300 °C. The resulting oxide powder was sieved from 20 to 60 mesh. The oxide was then reduced in a Pyrex tube with deoxygenated hydrogen-first at a flow rate of 10 ml min^{-1} for 1 h at 150 °C and then at 100 ml min^{-1} for 1.5 h at 300 °C. The reduced metal catalyst was kept in a deoxygenated nitrogen atmosphere.

Pure Cu, Ni, and other metals were prepared by similar procedures. Five wt% Rh, Pd, and Pt, supported on silica, were prepared by the manner described by Benesi et al.[12)]

Activity Measurements: The hydration of AN was carried out in a conventional batch reactor equipped with a reflux condenser. After the air in the reactor had been replaced with deoxygenated nitrogen, pure water (100 ml) and purified AN (8.5 ml) were introduced into the reactor, and the mixture was kept at 75 °C. A prereduced catalyst (2.5 g) was transferred from the tube to the reactor in a stream of nitrogen for further reduction. The reaction products were analyzed by the use of a FID gas chromatograph. The detailed procedure was described in a previous paper.[13)]

Adsorption Measurements: The chemisorption measurements were carried out in a pulse system with the apparatus described in detail elsewhere.[14)] The absorption measurements were done as follows: the samples in the adsorption-tube, connected with a vacuum line, were reduced in the same manner as in the catalyst reduction described above, and then evacuated to 1×10^{-5} Torr (1 Torr=133.322 Pa). The amount of hydrogen chemisorbed on the Ni surface of the catalyst was measured by the pulse chemisorption method. The total surface area of the catalysts was determined by the BET method using N_2 physisorption.

TPD and XRD Analysis: In order to examine the materials, such as AN and AA, adsorbed on the metal-catalyst surface, the TPD experiments were performed. Desorbed molecules were analyzed by means of a quadrupole gas analyzer(ANERVA: NAG-110). The temperature was increased from room temperature to 400 °C at a rate of 5 °C min^{-1}. The crystal structures of the metal catalysts used were identified by X-ray-diffraction measurements.

Results and Discussion

Activity and Selectivity of Metal Catalysts: As shown in Table 1, the selectivity of the catalysts differed entirely between the Group IB and Group VIII metals. AA was selectively formed on the metallic Cu and Ag catalysts, while AA, ECH, and BCE were produced on the Fe, Co, and Ni catalysts. The other metals, such as Rh, Pd, and Pt supported on silica were inactive.

In order to improve the catalytic activity of metallic Cu, various Cu-based binary metals, such as Cu-Ni, -Co, and -Fe, were prepared. As shown in Table 1, it has been found that the combination of Cu and Ni leads to an increase in the AA formation while keeping a high selectivity to AA. Even in the case of a comparison of the catalytic activity per specific surface area, the amount of AA obtained on the Cu-Ni binary metal was greater than that of the Cu catalyst. Binary metal catalysts combined with Cu and Fe or Co exhibited a low selectivity to AA. When the crystal structures of the binary metals were identified by means of the X-ray-diffraction method, it was observed that a single-phase alloy of Cu and Ni was formed, but in the case of Cu-Fe and -Co no such phase could be detected.

Catalytic Properties of Cu-Ni Alloys: Figure 1 shows the catalytic activity and AA selectivity as a function of the bulk composition of Cu in the Cu-Ni alloys. The catalytic activity of Cu-Ni alloys was greater than that of Cu over a wide range of Cu bulk compositions. Especially, Cu-Ni alloys, having 20—70% Cu in their bulk composition, were much more active catalysts than was neat Cu. The maximum conversion of AN was obtained on the Cu-Ni alloy catalyst containing 35% of Cu in the bulk phase.

Table 1. Catalytic Activity and Selectivity over Various Metals on Liquid-Phase Hydration of Acrylonitrile at 75 °C

Catalyst	Reduction temperature/°C	Conversion of AN/%	Selectivity to AA/%	Yield of AA/%
Cu	300	29.5	100	29.5
Ag	120	1.5	100	1.5
Fe	400	3.1	<20[c]	<0.6
Co	300	18.1	32.8	5.9
Ni	300	1.6	19.1	0.3
Rh[a]	300	0	—	—
Pd[a]	300	0	—	—
Pt[a]	300	0	—	—
Cu-Fe (1:1)[b]	300	18.3	71.3	13.0
Cu-Co (1:1)[b]	300	53.7	57.0	30.6
Cu-Ni (1:1)[b]	300	38.0	100	38.0

a) 5 wt% M/SiO_2. b) Atomic ratio of Cu/M. c) The coexistence of polymers of the unidentified structure was observed.

It is known that Cu is concentrated on the surface of the alloy; [15] this finding is in agreement with the results of this study, as shown in Table 2. By alloying Ni with a small amount of Cu (e.g., only 3% of Cu), the Cu was concentrated on the surface of the alloy to a value of more than 10 times. Especially, when the content of Cu increased over 20% in the bulk composition, the concentration of Cu on the surface attained 70 to 90%, which agreed with the results reported in the literature.[9–11,16] It seems reasonable that the Cu atom on the alloy surface is the active site for the hydration of AN to AA, because Ni shows a poor catalytic activity.

Figure 2 illustrates the change in turnover frequency (TOF) at the initial stage, i.e., the number of reacted molecules of AN per minute per number of surface Cu or Ni atoms of the alloys. The TOF based on the Cu atom of the alloys increased with an increase in the surface concentration of Cu and attained its maximum at 80% Cu. The TOF based on the Ni atoms was negligibly small in comparison with

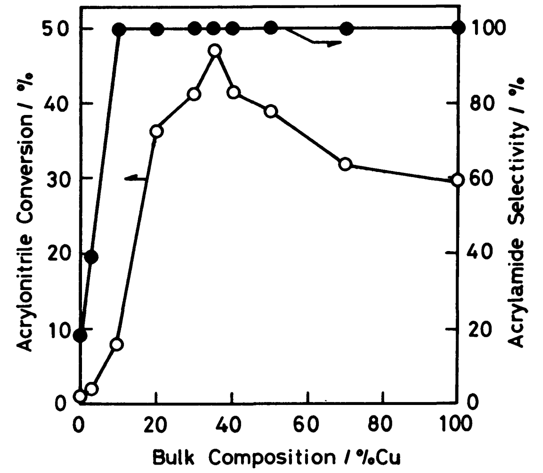

Fig. 1. Catalytic activity and selectivity on the liquid-phase hydration of acrylonitrile to acrylamide at 75 °C by Cu-Ni alloy catalysts.

Table 2. Charcateristics of Cu-Ni Alloy Catalysts

Cu bulk atomic fraction	BET surface area m^2 g^{-1}	H_2 chemisorption × 10^{19} atoms m^{-2}	Surface Cu atomic fraction
0	6.5	1.51	0
0.03	3.1	0.99	0.34
0.20	5.0	0.41	0.73
0.35	5.2	0.32	0.79
0.40	4.5	0.27	0.82
0.50	4.1	0.30	0.80
0.70	5.5	0.12	0.92
1.0	5.8	0.00	1.0

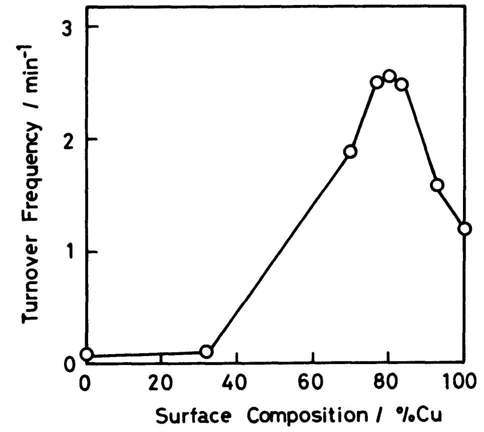

Fig. 2. Relation between turnover frequency and surface composition of Cu–Ni alloy catalysts.

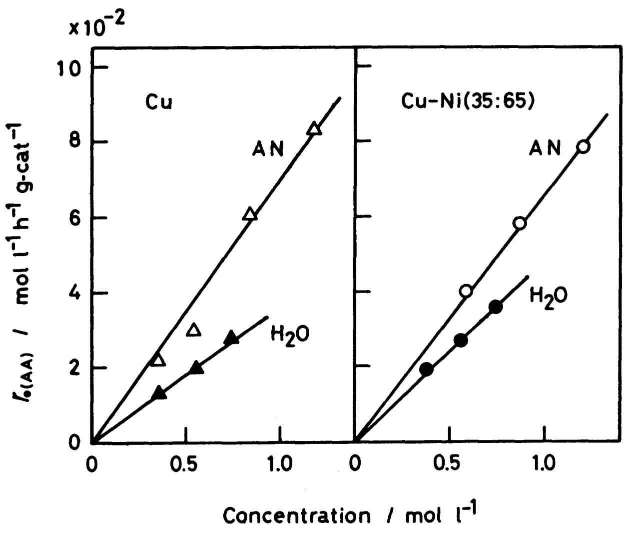

Fig. 3. Reaction order of Cu and Cu–Ni (35:65) catalysts.

that of Cu.

Kinetic Parameters at the Initial Stage of the Reaction: The initial rate of AA formation on Cu–Ni and Cu catalysts was examined in various concentrations of AN and water. On the Cu–Ni (35:65) and Cu catalysts, a first-order concentration dependency of both AN and water was obtained, as shown in Fig. 3. In addition, the values of the apparent activation energy of the Cu–Ni (35:65) and Cu catalysts were 10.9 and 12.1 kcal mol^{-1} (1 cal=4.184 J) respectively. These results indicate that the hydration on the Cu–Ni (35 : 65) and Cu catalysts proceeds according to the same mechanism at the initial state of the reaction.

Effect of Product Retardation: Differences in the catalytic activity between the Cu and Cu–Ni (35:65) catalysts were observed a few hours after the start of the reaction. Deviations from the first-order plots were observed on the Cu catalyst at a higher conversion of AN, while in the case of the Cu–Ni (35:65) alloy catalyst no deviation was observed.

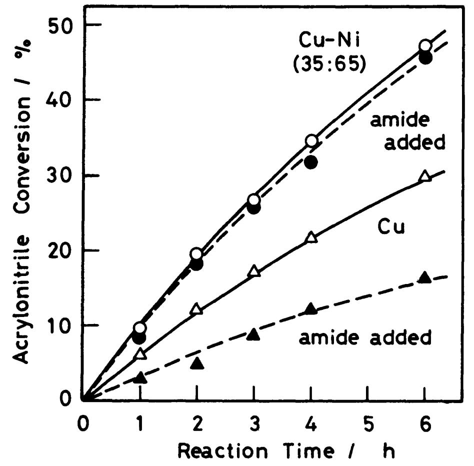

Fig. 4. Addition effect of acrylamide; amount of AA added is 1 g.

Hayashi et al.[17] have proved that the catalytic activity of Cu supported on MgO–SiO$_2$ is depressed by the accumulation of AA on the catalyst surface. It is predictable that the retardation on the support-free Cu catalyst in this study is also caused by AA. Therefore, the effect of the addition of AA on the reaction was investigated.

Figure 4 shows the plots of the time course of the hydration in the existence and in the absence of AA. In the case of the Cu catalyst, the activity dropped to 55% of its original value upon the addition of AA. On the other hand, the catalytic activity of the Cu–Ni (35:65) alloy was not affected at all by the AA addition. It can be thought that AA is not liable to adsorb on the Cu–Ni catalyst surface.

In order to further ascertain the effect of AA on the Cu and Cu–Ni catalysts, the solution in the reactor, after the reaction had finished, was removed by means of a syringe equipped with a long needle in a N$_2$ atmosphere, leaving the catalyst in the reactor. After the catalyst had then been washed with pure water a few times, the reaction was started again by charging AN and water into the reactor. The relations of AN conversion to the reaction time were shown by exactly the same dotted lines as those shown in Fig. 4. Thus, the retardation was observed on Cu, and not on Cu–Ni, catalysts. Therefore, it is necessary also to examine the absorption behavior of AA and AN on the Cu and Cu–Ni catalysts.

By assuming the pseudo-first-order kinetics from the reaction conditions being rich in water, the hydration rate of AN may be expressed as:

$$r_{AN} = k\theta_{AN} \tag{1}$$

where k represents the rate constant and where θ is the surface coverage of AN.

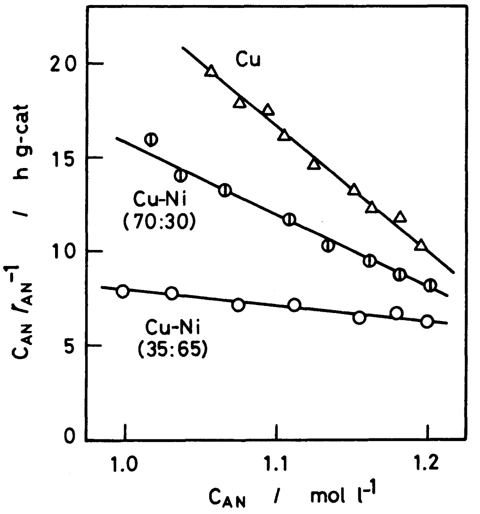

Fig. 5. Verification of Eq. 4.

Table 3. Adsorption Equilibrium Constants of Acrylonitrile and Acrylamide on Cu and Cu-Ni Alloy Surface

Catalyst	Cu atomic fraction		$\frac{K_{AN}}{\text{l mol}^{-1}}$	$\frac{K_{AA}}{\text{l mol}^{-1}}$
	Bulk	Surface		
Cu	1.0	1.0	1.6	20.5
Cu-Ni	0.70	0.92	0.7	11.4
Cu-Ni	0.35	0.79	0.3	2.1

In the case of the competitive adsorption of AN and AA, the surface coverage of AN can be expressed as:

$$\theta_{AN} = \frac{K_{AN}C_{AN}}{1+K_{AN}C_{AN}+K_{AA}C_{AA}} \tag{2}$$

where K_{AN} and K_{AA} represent the adsorption equilibrium constants of AN and AA respectively. In Eq. 2, the adsorption term of water is neglected, for scarcely water is absorbed on the Cu catalysts.[18–20]

As the hydration product is AA alone:

$$C_{AA} = C_{AN_0} - C_{AN} \tag{3}$$

By substituting Eqs. 2 and 3 into Eq. 1, we obtain:

$$\frac{C_{AN}}{r_{AN}} = \frac{1+K_{AA}C_{AN_0}}{kK_{AN}} + \left(\frac{K_{AN}-K_{AA}}{kK_{AN}}\right)C_{AN} \tag{4}$$

Figure 5 shows excellent fits of the data with Eq. 4. The negative slopes indicate that K_{AA} is greater than K_{AN}. The adsorption constants in Eq. 4 were calculated to be as shown in Table 3. These results indicate that AA is rather more strongly adsorbed on the Cu surface than is AN. The values of K_{AA} decreased with the increase in the concentration of Ni atoms on the Cu-Ni alloy surface. This suggests that the coexistence of Cu and Ni on the alloy surface leads to the smooth desorption of AA from that surface.

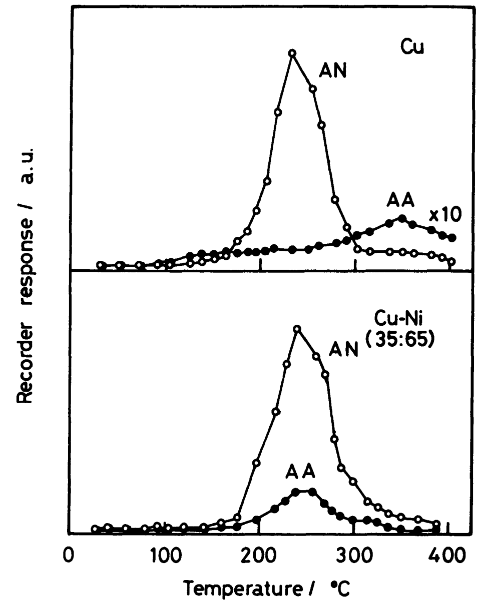

Fig. 6. TPD profiles of Cu and Cu-Ni (35:65) alloy.

TPD Profiles: The TPD profiles of Cu and Cu-Ni (35:65) catalysts after a 6-h reaction are shown in Fig. 6. On the Cu surface, a small amount of AA desorption at a higher temperature (ca. 350 °C) and a large amount of the desorption of AN at a lower temperature (ca. 250 °C) were observed. On the other hand, on the Cu-Ni alloy catalyst the desorption peak of AA shifted to a lower temperature. Thus, it seems clear that AA can easily desorb from the catalyst surface as a result of the functioning of Ni in Cu-Ni alloy. Consequently, it can be concluded that the deactivation of the Cu catalyst by product retardation can be prevented by alloying Cu and Ni, thus leading to the improvement of the hydration catalyst to a more active one.

Conclusion

The results of the liquid-phase hydration of AN to AA over the metal catalysts can be summarized as follows:

1) Cu and Ag in Group IB selectively produced AA, while Fe, Co, and Ni in Group VIII yielded AA, ECH, and BCE.

2) The Cu-Ni alloy with the surface concentration of 80% Cu was the best catalyst for the AA formation.

3) The Ni in the Cu-Ni alloy contributes to the smooth desorption of AA from the catalyst surface, preventing the retardation of AA; a high activity can thus be preserved.

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