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Selective Conversion of Nitriles to Amides over Suspended Copper Catalysts[1]

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Hydrolysis of various nitriles to amides was carried out in aqueous phase over suspended copper catalysts. Cross-linked poly(4-vinylpyridine), magnesia, and silica-magnesia were used as supports. Copper-on-polymer was highly active in comparison with copper powder. In spite of the larger crystallite size, copper-on-magnesia (68 Å) was much more active than copper-on-polymer (amorphous) for selective hydrolysis of nicotinonitrile to amide. A cooperative effect of copper and the basic support was suggested. However, weakly acidic silica-magnesia was favorable as support than basic magnesia for hydrolysis of aliphatic nitriles to amides. Selectivity to acrylamide over copper-on-magnesia was as high as 75%, which would be difficult to attain by the alkaline hydrolysis, but the side reaction to cyanohydrin (8%) was not negligible. Copper-on-silica-magnesia resulted in the predominant formation of acrylamide. An 88% conversion of acrylonitrile was obtained in 8 hr at 80°C with selectivities of 97% to amide and 0.8% to cyanohydrin. Results for propionitrile and benzonitrile are also described. The present catalysts were shown to degenerate on exposure to air. Hydrogen reduction was effective for complete regeneration of the deactivated copper-on-silica-magnesia, while it was unsuccessful for copper-on-polymer. The rate of hydrolysis revealed to deviate from first order kinetics at higher conversions. The kinetic behavior was explained by the product retardation.

INTRODUCTION

Hydrolysis of acrylonitrile to amide is usually carried out in the presence of a strong acid such as 84.5% sulfuric acid (*1*). Neutralization of the acid requires an alkali, which yields a large quantity of by-product salt, resulting in handling difficulties and economic disadvantages. To avoid these drawbacks, catalytic routes which by-pass sulfate are proposed in patent literatures (*2, 3*), where metallic copper or alloys such as Raney copper, Ullmann copper, or Adkins catalyst are disclosed.

Attempts were made in the present work for selective conversion of nitriles to amides to prepare copper catalysts highly dispersed over various supports such as cross-linked poly(4-vinylpyridine), magnesia, and silica-magnesia. An 88% conversion of acrylonitrile with 97% selectivity to acrylamide was obtained in 8 hr at 80°C over copper-on-silica-magnesia suspended in aqueous phase under nitrogen. Results for nicotinonitrile, benzonitrile, and propionitrile are also described. Deviations from first order kinetics were observed at higher conversions. The kinetic behavior was explained by the retarding effect of the product amide.

EXPERIMENTAL

Supports. Preparation, properties, and texture observed by scanning electron microscopy of cross-linked poly(4-vinylpyridine) were described in the previous paper (*4*). Abbreviations such as W-20, T-20, M-5 etc., given in the text, represent polymerization media (W, water; T, toluene; M, methanol) and degree of cross-linking (wt% of divinylbenzene) for skeletal polymers.

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These polymer supports cover various textures with simple gel, expanded gel, and macroreticular structure (*4*). Magnesia and silica-magnesia containing 25% MgO, calcined at 500°C in air for 5 hr, were used as inorganic supports. The preparations and acid–base properties were described in the previous paper (*5*).

Catalysts. Catalysts were prepared by impregnating the supports with cupric formate in solution. The solvents used were a mixture of methanol and formic acid (2 : 1 v/v) for the polymer supports, and water for the inorganic supports. Blue powder thus obtained were dried overnight *in vacuo*, and the formate was decomposed under hydrogen at 150°C for the polymer supports and at 300°C for the inorganic supports. A color change to black or brownish-black with some copper-brightness was observed at 110–150°C. Thermogravimetric analysis by electromicrobalance (Type RMB-50V of Shimazu, Kyoto) showed decomposition of anhydrous cupric formate to metallic copper at 135°C. After decomposition under hydrogen, the catalyst was handled carefully under nitrogen.

Hydrolysis of nitriles. Catalyst powder was added to 50 ml of an aqueous solution of a nitrile, and stirred magnetically at 80–100°C. To avoid contact with air, a nitrogen balloon was attached to the top of the reflux cooler. Water was deoxygenated in advance by boiling under bubbling of nitrogen. Sampling was conducted intermittently through a Teflon capillary for analysis by gas chromatography. Column packings used were as follows: 20% PEG 6000/Chromosorb W for nicotinonitrile and benzonitrile (150°C), 15% Triton X-305/Chromosorb WAW DMCS for nicotinamide and benzamide (220°C), 20% PEG 4000/Celite 545 for acrylonitrile and propionitrile (70°C), and for propionamide (150°C), and Porapack QS for acrylamide and ethylene cyanohydrin (160°C).

Powder X-ray diffraction. The crystallite size of copper was estimated by line-broadening of powder X-ray diffraction. An apparatus of Rigaku Denki, Tokyo, was used at 35 kV and 15 mA with Cu$K\alpha$ radiation. Powdered samples were suspended in a benzene solution containing 1% polystyrene (*6*) after hydrogen reduction, filtered, and dried overnight under vacuum.

RESULTS AND DISCUSSION

Copper-on-Polymer

Polymer supports used in the present work have N-sites of pyridine structure. When a white powder of the polymer was added to a solution of cupric formate in a ratio of Cu/N = 1, the copper found in the blue powder was usually Cu/N = 0.8–0.9 (atom/site), where N represents exchange capacity for hydrochloric acid (*4*). Thus, copper might be dispersed on an atomic scale in the stage of impregnation with formate. Succeeding decomposition of the formate under hydrogen may possibly result in some aggregate metallic copper, but it seems more likely that a highly dispersed copper catalyst will be obtained.

Figure 1 shows copper-on-polymer to be highly active, in comparison with copper powder, for selective hydrolysis of nicotinonitrile to amide. The conversion curves for catalysts utilizing polymer supports of differing textures were almost superposed, indicating the insignificance of

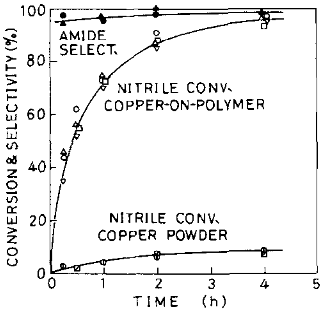


FIG. 1. Activity of copper-on-polymer and copper powder for hydrolysis of nicotinonitrile. Temperature, 100°C; nitrile, 0.20 *M* (50 ml); copper on catalyst, 0.05 g. ⦶, Copper from oxide; ▨, copper from formate; ○, W-20, Cu/N = 0.88_4; △, T-20, Cu/N = 0.87_2; □, M-5, Cu/N = 0.15_1; ▽, M-30, Cu/N = 0.24_7.

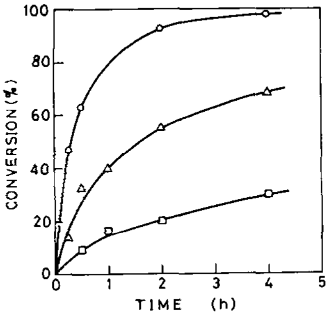


FIG. 2. Degeneration of activity of copper-on-polymer on exposure to air. Temperature, 100°C; catalyst, W-20, Cu/N = 0.24_8, 0.05 g Cu; Nitrile, 0.20 *M* (50 ml). ○, Handling under nitrogen; △, exposed to air for weighing, reaction under nitrogen; □, reaction under air.

polymer texture. Equal amounts of copper (0.05 g Cu/50 ml) were used with varying total amounts of catalyst. Figure 2 shows degeneration of a copper-on-polymer on exposure to air. A drastic decrease in activity was observed, even when exposed to air for only a minute for weighing. Attempts were made to regenerate the copper-on-polymer for recycling. Catalyst used was recovered by filtration, reduced under hydrogen at 150°C for 2 hr, and used again under the same conditions. The results were unsuccessful, as shown in Fig. 3.

Copper powder obtained by formate decomposition was shown by scanning electron microscopy to be an aggregate of distorted spherical particles of 5000 Å (Table 1a). Freshly prepared copper-on-polymer was amorphous (Table 1b). After the four recycle runs detailed in Fig. 3, a broad pattern appeared in X-ray diffraction and the copper size was estimated to be 63 Å (Table 1c).

The active component seems to be *reduced* copper with extremely small crystallite size. Copper was assumed to be highly dispersed on polymer, but some aggregations occurred on exposure to air. Although hydrogen treatment was effective for the reduction of copper oxides, the crystallite size of copper might be larger than those of the original catalyst.

Copper-on-Magnesia and Copper-on-Silica-Magnesia

The triangles and circles in Fig. 4 show the results for selective hydrolysis of nicotinonitrile to amide over magnesia and copper-on-magnesia, respectively. Comparing Fig. 4 with Fig. 1, copper-on-magnesia is much more active than copper-on-polymer. It would, however, be inadequate to attribute the high activity to the crystallite size effect. The crystallite size of copper-on-magnesia was 68 Å (Table 1d), which was of the same order as the degenerated copper-on-polymer (Table 1c). Hydrolysis of benzonitrile over copper-on-magnesia and nicotinonitrile over copper-on-silica-magnesia was rather slow, as shown in Fig. 5. Thus, an interesting con-

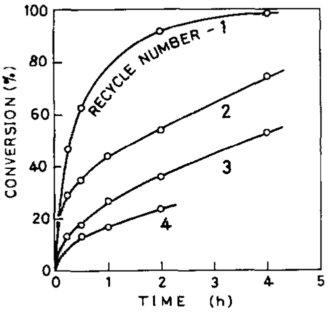


FIG. 3. Unsuccessful regeneration of copper-on-polymer by hydrogen reduction. Reaction conditions, same as Fig. 1; reduction, 150°C under hydrogen for 2 hr.

TABLE 1

Crystallite Sizes of Copper in Catalysts Estimated by Powder X-Ray Line-Broadening

Sample	$\bar{d}$ (Å), Cu(111)
a. Copper powder from formate	5000[a]
b. Copper-on-polymer (W-20, Cu/N = 0.24_8)	Amorphous
c. Copper-on-polymer, four times recycled[b]	63
d. Copper-on-magnesia	68
e. Copper-on-silica-magnesia	142

[a] Scanning electron microscopy.
[b] See Fig. 3.

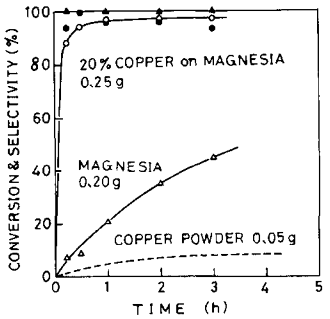
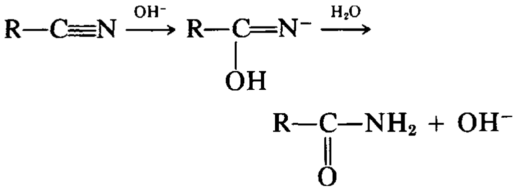


FIG. 4. Hydrolysis of nicotinonitrile over magnesia and copper-on-magnesia. Temperature, 100°C; nitrile, 0.20 *M* (50 ml). White symbols, conversion of nitrile; black symbols, selectivity to amide.

clusion suggested by Fig. 4 is that copper and the basic support have a cooperative effect. Nicotinonitrile has an N-site of pyridine structure, which is affinitive to copper. The neighboring basic site on magnesia is assumed to contribute to supply hydroxide ion, as in alkaline hydrolysis (*7*).


$$R{-}C{\equiv}N \xrightarrow{OH^-} R{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}N^- \xrightarrow{H_2O} R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2 + OH^-$$

The results given in Fig. 5 seem to be explained in an extension of the same discussion. Benzonitrile lacks coordinative N-site in structure. Unlike its component oxides, silica-magnesia was weakly acidic (*5*).

It is known to be difficult to obtain aliphatic amides by the alkaline hydrolysis of the corresponding nitriles (*8*). Aliphatic amides generally suffer consecutive hydrolysis to carboxylic acids, while aromatic amides are rather resistant.

$$RC{\equiv}N \xrightarrow{H_2O} RCONH_2 \xrightarrow{H_2O} RCOONH_4$$

However, attempted hydrolysis of propionitrile over supported copper catalysts was successful, as shown in Fig. 6. Propionamide was obtained in 50–60% selectivity over copper-on-magnesia (circles). If the support material without copper was used, conversion of propionitrile was 7% in 8 hr with the amide selectivity of less than 0.5%, suggesting the predominant activity of copper. Weakly acidic silica-magnesia was favorable as support than basic magnesia. Although the activity of copper-on-silica-magnesia (triangles) was similar to that of copper-on-magnesia (circles), the former yielded on amide selectivity of over 80%, as shown in Fig. 6.

Resulting from the activation of olefinic double bond by the cyano group, acrylonitrile undergoes various reactions in addition to amide formation. The most important of these side reactions is the base-catalyzed cyanoethylation (*9*) of water, which yields ethylene cyanohydrin. Further cyanoethylation might also be possible.

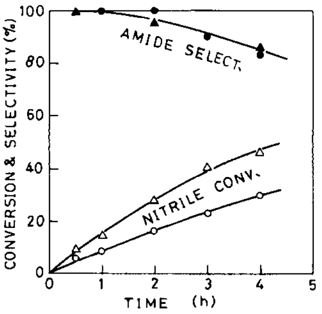


FIG. 5. Hydrolysis of benzonitrile and nicotinonitrile. Temperature, 100°C; nitrile, 0.20 *M* (50 ml); catalyst, 0.25 g. Circles, benzonitrile/copper-on-magnesia; triangles, nicotinonitrile/copper-on-silica-magnesia.

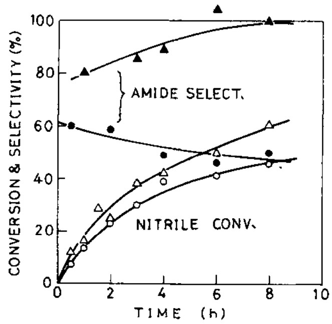
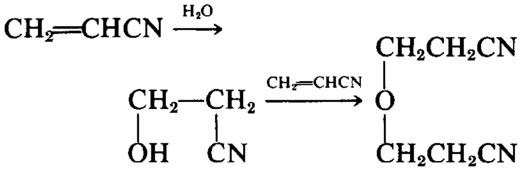


FIG. 6. Hydrolysis of propionitrile. Temperature, 80°C; nitrile, 0.19_2 *M* (50 ml); catalyst, 1.5 g. Circles, copper-on-magnesia; triangles, copper-on-silica-magnesia.



$$CH_2{=}CHCN \xrightarrow{H_2O} \underset{OH}{CH_2}-\underset{CN}{CH_2} \xrightarrow{CH_2{=}CHCN} O(CH_2CH_2CN)_2$$

Hydrolysis of acrylonitrile over magnesia (1.2 g/50 ml) at 80°C for 4 hr resulted in 22% conversion of nitrile with 63% selectivity to cyanohydrin and 14% to amide. Silica-magnesia gave 15% conversion of nitrile with 33% selectivity to cyanohydrin and 7.5% to amide at the same condition.

It is of interest that copper-on-magnesia and copper-on-silica-magnesia resulted in the predominant formation of amide. Figure 7 shows hydrolysis of acrylonitrile over copper-on-magnesia. Selectivity to acrylamide was as high as 75%, but the side reaction to cyanohydrin (8%) was not negligible. Figure 8 reveals an even more significant decrease in cyanohydrin selectivity over copper-on-silica-magnesia. The white symbols in Fig. 8 represent the first run with fresh catalyst. The average selectivity to acrylamide was 97%, while that to cyanohydrin was only 0.8%.

Like copper-on-polymer, copper-on-silica-magnesia was sensitive to air. Catalyst recovered by filtration and stored for 1 week under air was found to be largely deactivated, the conversion of nitrile being 13% with 45% selectivity to amide. Different from copper-on-polymer (Fig. 3), the deactivated copper-on-silica-magnesia was successfully regenerated by hydrogen reduction at 300°C (Fig. 8). The black symbols show the third run with the regenerated catalyst. Accounting for the loss of catalyst, the result seems to show complete regeneration. Favorably, no cyanohydrin was detected.

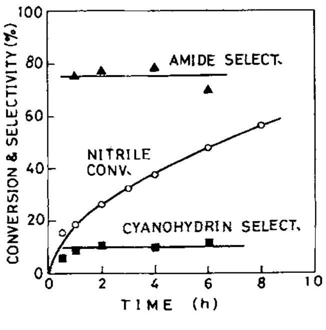


FIG. 7. Hydrolysis of acrylonitrile over copper-on-magnesia. Temperature, 80°C; nitrile, $0.18_4 M$ (50 ml); catalyst, 1.5 g.

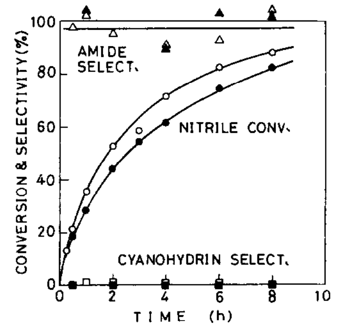


FIG. 8. Hydrolysis of acrylonitrile over copper-on-silica-magnesia and successful regeneration by hydrogen reduction. Temperature, 80°C; nitrile, $0.18_4 M$ (50 ml). White symbols: fresh catalyst, 1.5 g; black symbols: regenerated catalyst, 1.4 g.

The crystallite size of copper-on-silica-magnesia was estimated as 142 Å (Table 1e). Using powder X-ray line-broadening technique, Scholten and Konvalinka (*10*) estimated the crystallite sizes of copper-on-magnesia (38.6 and 39.6% Cu) and copper-on-magnesium silicate (30.9% Cu) to be 130–145 Å and 70 Å, respectively. These values are on the same order of magnitude

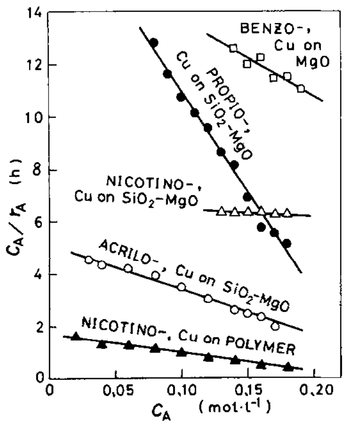


FIG. 9. Verification of Eq. (5).

as the present catalysts. It seems likely that catalysts with extremely high dispersion, while being active initially, lack sufficient properties for regeneration. Probably, copper-on-polymer is such a catalyst. Copper-on-silica-magnesia, an active catalyst for selective hydrolysis of various nitriles to amides, revealed the capability of the reproducible regeneration. The present results suggest an appropriate range of copper sizes.

Kinetic Behavior

Catalytic hydrolysis of nitriles attempted in the present work over supported copper catalysts resulted in favor of amides. Examining various nitriles such as propionitrile (saturated aliphatic), acrylonitrile (unsaturated aliphatic), benzonitrile (aromatic), and nicotinonitrile (pyridine derivates), the corresponding amides were obtained in high selectivities. The reactions were carried out in the presence of large amounts of water and were expected to result in a pseudo-first order kinetics. However, deviations from the first order plots were observed at higher conversions. Since the present catalysts were quite sensitive to air, the authors suspected that the catalyst was degenerated due to traces of dissolved oxygen. Although the solvent water was degassed prior to use, it is difficult to distinguish the effect of catalyst degeneration from those of product retardation by a suspended catalyst run. Fortunately, the possibility of the catalyst degeneration was excluded by the results of fixed-bed flow operations, which would be published elsewhere (*22*). Copper-on-silica-magnesia was shown to be stable during over 70 hr on-stream. The deviation from first order kinetics was observed reproducibly among steady-state conversion vs reciprocal space velocity data.

The second possibility, that the deviations from the first order kinetics were due to product retardation, proved to be a successful explanation. The rate of reaction of type A → B is expressed as

$$r_A = k\theta_A, \tag{1}$$

where k represents the apparent rate constant involving catalyst concentration, and θ_A the surface coverage of nitrile.

Assuming competing adsorption of nitrile (A) and amide (B), the surface coverage of A and B can be expressed as

$$\theta_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B}, \tag{2}$$

and

$$\theta_B = \frac{K_B C_B}{1 + K_A C_A + K_B C_B}, \tag{3}$$

where K_A and K_B are absorption constants.

For a high selective conversion of A to B,

$$C_B = C_{A0} - C_A. \tag{4}$$

Thus, we obtain

$$\frac{C_A}{r_A} = \frac{1 + K_B C_{A0}}{kK_A} + \left(\frac{K_A - K_B}{kK_A}\right) C_A. \tag{5}$$

Figure 9 shows excellent fit of data with Eq. (5). The negative slopes indicate that

TABLE 2

Kinetic Parameters for Eq. (5) Obtained from the Results Given in Fig. 9

Catalyst	Copper/total[a]	Nitrile	Temp.	k	K_A	K_B
	(g)		(°C)	(mol l^{-1} hr^{-1})	(l mol^{-1})	
Copper-on-polymer	0.05/—	Nicotino-	100	3.64	0.93_5	22.3_8
Copper-on-magnesia	0.05/0.25	Benzo-	100	0.33	0.29_5	3.1_4
	0.05/0.25	Nicotino-	100	0.44	0.39_5	0.8_6
Copper-on-silica-magnesia	0.30/1.50	Propio-	80	0.67	0.37_4	18.7_5
	0.30/1.50	Acrylo-	80	0.92	0.63_1	10.8_7

[a] For 50 ml of solution.

$K_A < K_B$. Kinetic parameters calculated by the standard nonlinear least-squares regression method are summarized in Table 2. The relative values of adsorption constants lie in a range of $K_B/K_A = 10-50$, showing strong retardation by the product amide. Using the parameter values, the surface coverage of nitrile and amide can be estimated from Eqs. (3) and (4). For the hydrolysis of acrylonitrile over copper-on-silica-magnesia plotted in Fig. 8 (white symbols), the value of $\theta_{A0} = 0.10_4$, and that of $\theta_{B0} = 0$. At 80% conversion of nitrile, $\theta_A = 0.008$ and $\theta_B = 0.61_5$. These estimations show that about 10% of the catalyst surface was covered initially by nitrile, while the remaining surface was bare. At 80% conversion, 61.5% of the surface was covered by amide.

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