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Catalytic Hydration of Unsaturated Nitriles to Unsaturated Amides Using Colloidal Copper Dispersions

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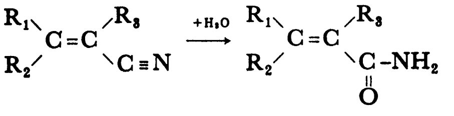
Homogeneous hydrations of unsaturated nitriles such as acrylonitrile, methacrylonitrile, and crotononitrile to the corresponding unsaturated amides have been carried out in water at 80°C by use of colloidal copper dispersions as catalysts. The dispersions are prepared by reduction of copper(II) sulfate, copper(II) chloride, and copper(II) acetate with sodium tetrahydroborate in the presence of various polymers. The dispersions with poly(*N*-vinyl-2-pyrrolidone), poly(vinyl alcohol), methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)-cellulose exhibit much larger catalytic activities than the copper precipitates prepared by reduction of the copper salts with sodium tetrahydroborate in the absence of the polymers. For all the catalytic reactions with the colloidal dispersions, selectivity for the unsaturated amides is 100% and formation of any by-products is not detected at all. Electron microscopy shows that no significant structural change occurs in the dispersions during the catalytic hydration. The catalytic activity monotonously increases with increasing amount of poly(*N*-vinyl-2-pyrrolidone) up to the charged ratio 20 of the monomeric residue to copper(II) ion, showing saturation at the ratio larger than 20. When the degree of the polymerization of poly(*N*-vinyl-2-pyrrolidone) is varied at a fixed residual molar ratio 40, the activity shows a maximum at the degree of polymerization 1440. The results are interpreted both by the change in the size of the colloidal copper particles and by the difference in the magnitude of the interactions between the polymers and the copper particles.

Hydration of unsaturated nitriles such as acrylonitrile and methacrylonitrile to the unsaturated amides such as acrylamide and methacrylamide (Eq. 1) is important in industry.[1,2] Many heterogeneous catalysts, most of which contain transition metals or their salts, have been reported.[1-6] Copper metal supported on silica,[3] magnesia,[3] or γ-alumina[4] showed high activity and high selectivity in the hydration of acrylonitrile to acrylamide. However, there have been few reports on homogeneous catalysts for selective hydrations of unsaturated nitriles to unsaturated amides.


(1)

Previously,[7] the authors showed that stable colloidal dispersions of copper metal could be prepared by the reduction of copper(II) sulfate with sodium tetrahydroborate in the presence of various polymers. The resulting colloidal dispersions were highly active and selective homogeneous catalysts for the hydration of acrylonitrile to acrylamide, as reported in a preliminary communication.[8]

This paper reports the catalytic activities of the colloidal copper dispersions, prepared by the reduction of copper salts in the presence of various polymers, for the hydration of acrylonitrile, methacrylonitrile, and crotononitrile to the corresponding unsaturated amides. Effects of the amounts of the protective polymers and their degrees of polymerization on the catalytic activities of the dispersions are described. Furthermore, dependence of the catalytic activity on the size of the colloidal copper particles is shown.

Experimental

Materials. Poly(*N*-vinyl-2-pyrrolidone)s, amylopectin, methylcellulose (degree of methylation 2.0), (2-hydroxyethyl)cellulose (degree of hydroxyethylation 1.6) (from Tokyo Kasei Kogyo Co.), poly(vinyl alcohol)s (from Junsei Pure Chemicals Co.), ethylcellulose (degree of ethylation 1.0) (from Nakarai Chemicals), and dextrin (from Kanto Chemicals) were repeatedly (2—5 times) reprecipitated from aqueous solutions with acetone. Methylamylopectin was prepared according to the literature,[9] and had a degree of methylation 1.1, as determined by ^{1}H-NMR spectroscopy.

Copper(II) sulfate from Yoneyama Chemical Co. was recrystallized from water twice. Copper(II) chloride, copper(II) acetate, copper(II) nitrate, and sodium tetrahydroborate were obtained from Koso Chemical Co.

Acrylonitrile was distilled after being washed successively with aqueous sodium hydroxide solution, aqueous phosphoric acid solution, and pure water. Methacrylonitrile and crotononitrile were purified by distillation.

Water was doubly distilled and then was degassed by boiling under a reduced pressure.

Nitrogen gas, which had a purity higher than 99.9995%, was purchased from Nippon Sanso Co.

Preparation of Colloidal Copper Dispersions.[7] Typical procedure for the preparation of colloidal copper dispersions is as follows. Copper(II) sulfate or the other copper salts (0.15 mmol) and various amounts of protective polymers were stirred in 22 cm^3 of water at 80 °C under nitrogen for 1 h. Then sodium tetrahydroborate (0.30 mmol) in 3 cm^3 of water was added at 25 °C. The color of the solution changed immediately, and colloidal copper dispersions were obtained as black or reddish dark brown homogeneous solutions.

Catalytic Hydration of Unsaturated Nitriles Using Colloidal Copper Dispersions. The hydrations of acrylonitrile, methacrylonitrile, and crotononitrile were carried out at 80 °C under nitrogen by adding the corresponding nitrile (9.1 mmol) to the colloidal copper dispersions. Product analyses were made with gas chromatography (Tenax GC

Table 1. Catalytic Activities of Colloidal Copper Dispersions Protected by Various Polymers in the Hydration of Acrylonitrile[a]

Polymer	Degree of polymerization	Average diameter of copper particles/A	Acrylamide formation	
			Yield[b] mol%	Selectivity %
Poly(*N*-vinyl-2-pyrrolidone)	6300	c)	20.8	100
	3240	100	25.4	100
	1440	60	27.3	100
	360	c)	24.3	100
	90	50	7.5	100
Poly(vinyl alcohol)	2000	c)	8.6	100
	1500	150	6.0	100
	360	c)	6.9	100
Poly(potassium vinyl sulfate)	c)	c)	3.5	92[d]
Dextrin	c)	90	0.5	100
Amylopectin	c)	100	0.2	100
Methylamylopectin	c)	c)	8.1	100
Methylcellulose	140	100	21.2	100
Ethylcellulose	c)	c)	20.2	100
(2-Hydroxyethyl)cellulose	c)	c)	21.7	100
None[e]	—	g)	0.3	97[f]

a) Reaction conditions: 80 °C, 2 h; $[\mathrm{Cu}]_0=5.0\times10^{-3}$, $[\text{acrylonitrile}]_0=3.0\times10^{-1}$, and $[\text{monomeric residue of polymer}]_0=2.0\times10^{-1}\,\mathrm{mol\,dm^{-3}}$. b) The value with respect to the charged acrylonitrile. c) Not determined. d) By-products were ethylene cyanohydrin and another unidentified product. e) Catalysis by the copper precipitates. f) By-product was ethylene cyanohydrin. g) The value was not estimated, since the particle diameters were widely distributed from 40 to 3500 A.

column, 2 m×3 mm glass column, 170 °C).

Electron Microscopy. Electron micrographs of the colloids were obtained by a Hitachi Model HU-12A electron microscopy operated at 100 kV. Sample films were prepared from the colloidal dispersions on collodion films coated with a carbon layer by evaporating the solvent to dryness.

Results

Catalytic Hydrations of Unsaturated Nitriles Using Colloidal Copper Dispersions. Table 1 shows the catalytic activities of the colloidal copper dispersions, prepared by the reduction of copper(II) sulfate with sodium tetrahydroborate in the presence of various polymers, for the hydration of acrylonitrile in water at 80 °C. The dispersions with poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinyl alcohol), poly(potassium vinyl sulfate), methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose exhibit much larger catalytic activities than the copper precipitates obtained by the reduction of copper(II) sulfate with sodium tetrahydroborate in the absence of the polymers. For example, the yield (27.3 mol%) of acrylamide for the colloidal copper dispersion with PVP of viscosity-averaged degree of polymerization (DP) 1440 is about 90 fold larger than that (0.3 mol%) for the copper precipitates.

The catalytic activity of the dispersion with methylamylopectin is 40 times as large as that with amylopectin. The dispersions with methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose show 40 fold larger catalytic activities than the dispersion with dextrin. Measurement of the catalytic activity of the dispersion with cellulose has not been successful yet due to poor solubility of cellulose in water.

In the catalytic hydration of acrylonitrile using all the colloidal copper dispersions, except for the one with poly(potassium vinyl sulfate), the product was acrylamide alone. Either the formation of ethylene cyanohydrin due to hydration of the C–C double bond in place of the C–N triple bond, or the formation of acrylic acid, due to hydrolysis of acrylonitirle or acrylamide, was not detected at all. In contrast, the reaction using the copper precipitates, prepared by the reduction of copper(II) sulfate in the absence of the polymers, yielded considerable amount of ethylene cyanohydrin, resulting in the selectivity 97% for acrylamide.

When the colloidal copper dispersion with poly(potassium vinyl sulfate) was used as catalyst, ethylene cyanohydrin was produced as by-product together with an unidentified by-product.

The open circles in Fig. 1 show the time-conversion curve for the catalytic hydration of acrylonitrile using the colloidal copper dispersion with PVP (DP=1440). The yield of acrylamide monotonously increases with reaction time, attaining 68 mol% at 15 h. Up to this yield, the reaction satisfactorily follows first-order equation, and the selectivity for acrylamide is 100%.

The catalytic rate for the colloidal copper dispersion is more than 50 fold larger than that for the copper precipitates-PVP suspension system (the closed circles in Fig. 1). In the suspension system, the copper precipitates were first prepared by reducing copper(II) sulfate with sodium tetrahydroborate in the absence

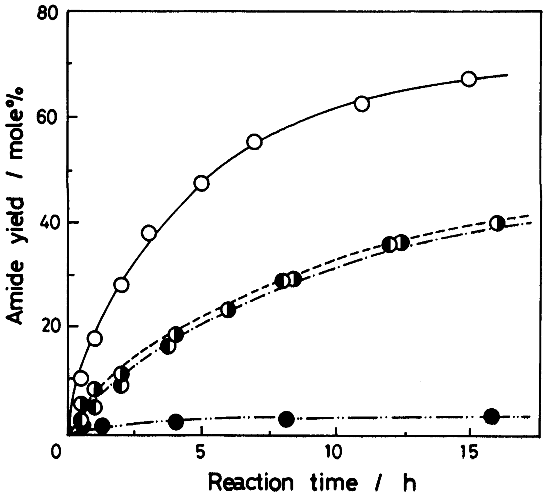


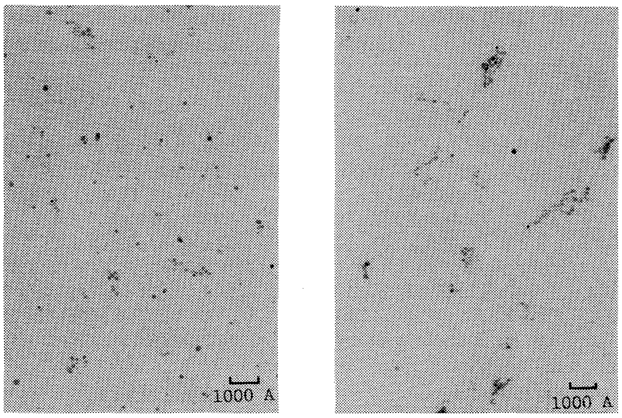
Fig. 1. Time course for the selective hydration of acrylonitrile (○), methacrylonitrile (◑), and crotononitrile (◐) catalyzed by the colloidal copper dispersion with PVP (DP=1440): 80 °C; $[\mathrm{Cu}]_0=5.0\times10^{-3}$, $[\text{unsaturated nitrile}]_0=3.0\times10^{-1}$, and $[\text{monomeric residue of PVP}]_0=2.0\times10^{-1}\ \mathrm{mol\,dm^{-3}}$; the closed circles refer to the catalysis by the suspension composed of copper precipitates and PVP (details are described in the text.).

of PVP, and then they were charged to the reaction mixture together with PVP. The amount of PVP added was exactly identical with that used for the preparation of the colloidal dispersion. With the catalysis by the copper precipitates-PVP suspension system, considerable amount of ethylene cyanohydrin was formed as by-product, and the selectivity for acrylamide was 97%. This is significantly in contrast with 100% selectivity achieved by the colloidal copper dispersions.

The colloidal copper dispersions also catalyzed the hydrations of methacrylonitrile and crotononitrile to the corresponding unsaturated amides (◑ and ◐ in Fig. 1). The selectivities are 100% for both of the reactions. The rates for these methyl-substituted acrylonitriles are about 1/2 of the value for acrylonitrile itself.

Stability of Colloidal Copper Dispersion in the Catalytic Hydration. Catalytic hydration of acrylonitrile using the colloidal copper dispersion, prepared with the use of PVP, proceeded homogeneously throughout the reaction time. Neither precipitation nor change in color of the dispersion was perceived. Figure 2 shows the electron micrographs of the dispersion with PVP (DP=1440), before and after the hydration. In both of the electron micrographs, dispersion of colloidal copper particles is fine. In addition, the average diameter (100 A) of the particles after the hydration is exactly identical with that (100 A) before it. Thus, no significant structural change in the colloidal dispersion occurs during the catalytic reaction.

The colloidal copper dispersions with poly(potassium vinyl sulfate), dextrin, amylopectin, methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose were also stable during the catalytic hydration. In the reaction using the dispersion with poly(vinyl alcohol), however, considerable amounts of black precipitates were formed during the reaction.



(a) (b)

Fig. 2. Electron micrographs of the colloidal copper dispersions prepared by use of PVP (DP=1440) at the charged ratio 20 of the monomeric residue with respect to copper(II) sulfate; (a) before the catalytic hydration; (b) after the catalytic hydration of acrylonitrile at 80 °C for 2 h.

Effect of Copper Species on the Catalytic Activity of Colloidal Copper Dispersion. Table 2 lists the catalytic activities of the colloidal copper dispersions prepared by the reduction of various copper salts with sodium tetrahydroborate in the presence of PVP (DP=1440). The dispersions prepared from copper(II) sulfate and copper(II) chloride show high catalytic activities and 100% selectivity for acrylamide. No precipitation and color change are found during the catalytic reactions here.

The dispersion from copper(II) acetate exhibits also 100% selectivity, although the catalytic activity is slightly smaller. This dispersion is less stable than the ones from copper(II) sulfate and copper(II) chloride, and black precipitates are formed in the course of the catalytic reaction.

In the case of the colloidal copper dispersion prepared from copper(II) nitrate, the color of the dispersion gradually changed from dark brown to yellowish green. Ethylene cyanohydrin is formed as by-product, and both the yield and the selectivity for acrylamide are low.

Dependence of the Catalytic Activity of the Colloidal Copper Dispersion on the Amount and the Degree of Polymerization of Protective Polymer. Figure 3 shows the plot of the catalytic activity of the colloidal copper dispersions for the hydration of acrylonitrile vs. the amount of PVP (DP=1440) used for the preparation of the dispersion. The activity gradually increases with increase in the charged ratio of the monomeric residue of PVP to copper(II) sulfate, up to the ratio 20. At the ratio larger than 20, however, the activity is almost independent of the amount of PVP.

Table 2. Catalytic Activities of Colloidal Copper Dispersions Prepared by the Reduction of Various Copper Salts in the Presence of PVP (DP=1440)[a)]

Copper salt	Color of colloidal dispersion	Acrylamide formation	
		Yield/mole%[b)]	Selectivity/%
$CuSO_4 \cdot 5H_2O$	Reddish dark brown	28.1	100
$CuCl_2 \cdot 2H_2O$	Reddish dark brown	26.8	100
$Cu(OCOCH_3)_2$	Dark brown	17.2	100
$Cu(NO_3)_2$	Dark brown[c)]	0.4	81[d)]

a) Reaction conditions: 80 °C, 2 h; $[Cu]_0 = 5.0 \times 10^{-3}$, $[\text{acrylonitrile}]_0 = 3.0 \times 10^{-1}$, and $[\text{monomeric residue of PVP}]_0 = 1.0 \times 10^{-1}\ \text{mol dm}^{-3}$. b) Value with respect to the charged acrylonitrile. c) The color gradually changed to yellowish green during the catalytic reaction. d) By-product was ethylene cyanohydrin.

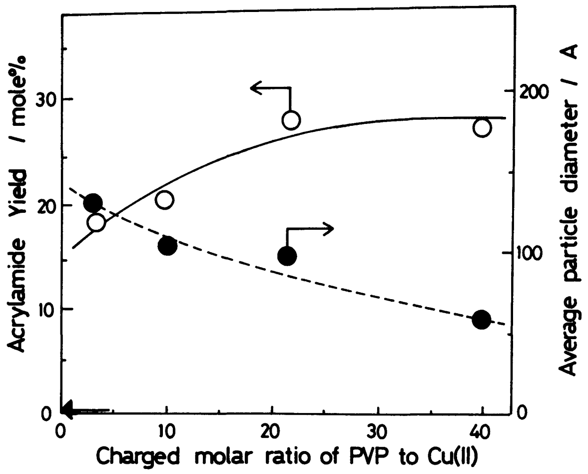


Fig. 3. Plots of the catalytic activity (○) of the colloidal copper dispersion in the hydration of acrylonitrile and the average diameter (●) of the colloidal copper particles as functions of the amount of PVP (DP=1440) used for the preparation of the dispersion: reaction conditions, 80 °C, 2 h; $[Cu]_0 = 5.0 \times 10^{-3}$ and $[\text{acrylonitrile}]_0 = 3.0 \times 10^{-1}\ \text{mol dm}^{-3}$, the arrow refers to the result for the catalysis by the copper precipitates prepared in the absence of PVP.

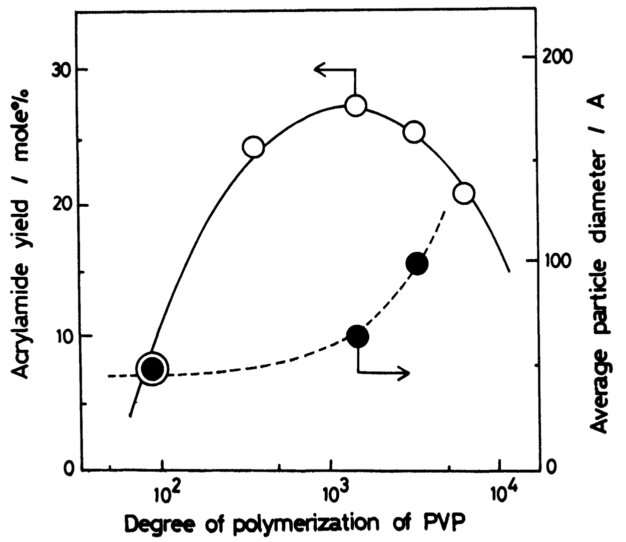


Fig. 4. Plots of the catalytic activity (○) of the colloidal copper dispersion in the hydration of acrylonitrile and the average diameter (●) of the colloidal copper particles as functions of the degree of polymerization of PVP: the charged ratio of the monomeric residue of PVP to copper(II) sulfate was kept constant at 40; reaction conditions, 80 °C, 2 h; $[Cu]_0 = 5.0 \times 10^{-3}$ and $[\text{acrylonitrile}]_0 = 3.0 \times 10^{-1}\ \text{mol dm}^{-3}$.

Even at the ratio 3 of monomeric residue of PVP to copper(II) sulfate, the dispersion is stable throughout the reaction time. The activity of this dispersion is about 50 times as large as that, shown by the arrow in Fig. 3, of the copper precipitates prepared without PVP.

In Fig. 4, the catalytic activity of the colloidal copper dispersion is plotted against the degree of polymerization (DP) of PVP. Here, the ratio of monomeric residue of PVP to copper(II) sulfate is kept constant at 40. The activity increases with increasing degree of polymerization below DP 1440. Above DP 1440, however, the activity decreases with increasing degree of polymerization.

The closed circles in Figs. 3 and 4 show the average diameters of colloidal copper particles, determined by electron microscopy, for the corresponding dispersions. The average particle diameter decreases with increasing amount of PVP (Fig. 3) and with decreasing degree of polymerization of PVP (Fig. 4). Relationship between the catalytic activity and the average particle diameter will be discussed in the Discussion Section.

Discussion

Catalytic Activities of the Colloidal Copper Dispersions for the Hydration of Unsaturated Nitriles to Unsaturated Amides. The higher catalytic activities of the colloidal copper dispersions than the copper precipitates (Table 1) is mainly attributable to the fact that the effective surface area of copper metal is larger due to smaller particle diameter. The diameter of all the particles in the colloidal copper dispersion with PVP (DP=1440), exhibiting the largest catalytic activity, for example, are between 20 to 190 Å, as described previously.[7)] However, the particle diameter in the copper precipitates, prepared in the absence of polymer, ranges from 40 to 3500 Å. Here, dominant part of the charged copper atoms is used for the

Table 3. Comparison of the Catalytic Activity for Colloidal Copper Dispersion Using PVP (DP=3240) with the Value for Copper on Silica-Magnesia in the Hydration of Acrylonitrile[a]

	Amount of the charged copper in the catalyst	Acrylamide formation		Rate of formation of acrylamide per the charged copper g·atom
		Yield	Selectivity	
	10^{-4} g·atom	mol%	%	mol dm^{-3} min
Colloidal copper dispersion[b]	1.4	7.2	100	0.31
Copper on silica-magnesia[c]	47.2	21	97	0.027

a) Reaction conditions: 80 °C, 30 min; [acrylonitrile]$_0$=1.8×10^{-1} mol dm^{-3}. b) [monomeric residue of PVP]$_0$/[Cu]$_0$=20. c) Date from Ref. 3.

formation of large particles, resulting in small value of the total surface area. The catalytic activity of the precipitates is small even in the suspension system formed by the addition of PVP (● in Fig.1).

In addition, the colloidal copper catalysts are more active than the copper precipitates, since the reactions proceed homogeneously and thus the contacts between the copper metal particles and the unsaturated nitriles are much more efficient. The catalytic activity of the dispersion prepared from copper(II) acetate, which shows precipitation of copper particles during the reaction, is about 2/3 of the values of the dispersions from copper(II) sulfate and copper(II) chloride, which are homogeneous throughout the reactions (Table 2).

Table 3 shows the comparison of the catalytic activity of the homogeneous colloidal copper catalyst with the value of a heterogeneous catalyst, copper supported on silica-magnesia.[3] Reaction conditions are identical with each other except for the fact that the amount of copper used in the colloidal copper catalyst is about 34 fold smaller than that used in the heterogeneous catalyst. The rate of formation of acrylamide per the charged copper atom for the colloidal copper catalyst is 11 fold larger than the value for the heterogeneous catalyst. The selectivity for acrylamide is 100% for the colloidal catalyst, whereas the selectivity is 97% for the heterogeneous catalyst. Thus, the colloidal copper catalyst is superior to the heterogeneous catalyst, at least with respect to the catalytic activity and selectivity.

Selective catalyses by the colloidal copper dispersion are probably associated with absence or minimal amount of lattice defects, suppressing undesired side reactions. As shown by the previous electron diffraction experiments,[7] the copper atoms in the colloidal copper particles are arranged in an ordered way, which is almost identical with that in the crystal of bulk copper metal. Selective catalyses by the colloidal dispersions of noble metals such as rhodium and palladium in the hydrogenation of olefins and dienes have been known.[10,11]

Factors Governing the Catalytic Activity of Colloidal Copper Dispersion. The increase of the catalytic activity of the colloidal copper dispersion with increasing amount of PVP at the charged ratio 20 or smaller of monomeric residue of PVP to copper(II) sulfate (Fig. 3) is ascribed to increase in the surface area of copper particles due to decrease in the particle size. The increase of the activity with decreasing degree of polymerization of PVP at the DP 1440 or larger (Fig. 4) is also attributed to increasing surface area. The protective polymers protect fine colloidal copper particles from mutual coaggregation both in the preparation of the colloidal dispersion and in the catalytic hydration, providing effective contacts between the copper particles and the substrates unsaturated nitriles.

The catalytic activities of the colloidal copper dispersions are also dependent on the magnitude of the interactions between the polymers and the colloidal copper particles.[12] The stronger interactions reduce the catalytic activities by competitive suppression of the interactions of the substrates unsaturated nitriles with the copper particles. The 4 fold decrease in the catalytic activity with decreasing degree of polymerization from 1140 to 90, in spite of decreasing average particle diameter from 60 to 50 A (Fig. 4), is attributable to this effect. The magnitude of the interactions of PVP with colloidal metal particles increases with decreasing degree of polymerization.[13] Increase of the residual molar ratio of PVP with respect to copper(II) sulfate from 20 to 40 shows virtually no increase in the catalytic activity (Fig. 3), since enhancement of the competitive suppression by PVP on the interactions of the nitriles with the copper particles compensates the acceleration due to decrease in the average particle diameter from 100 to 60 A.

Large catalytic activities of the dispersions with methylamylopectin, methylcellulose, ethylcellulose, and (2-hydroxyethyl)cellulose than the values for the dispersions with dextrin and amylopectin (Table 1) are also consistent with the arguments. Alkylation of the hydroxyl groups prevents hydrogen bondings between the monomeric residues in the polysaccharides, resulting in more flexible and stretching conformations of the polymers. Thus, the surface of the copper metal particles in the dispersions protected by these alkylated polysaccharides is more favorable for the unsaturated nitriles to make interactions than the surface in the dispersions protected by the polymers with rigid and compact conformations.

With the use of the polymers such as poly(ethylene oxide) and β-cyclodextrin, which interact with the colloidal copper particles too weakly, no colloidal copper dispersions are obtained. Only copper precipitates are formed on the reduction of copper(II) sulfate with sodium tetrahydroborate in the presence of these polymers.⁷⁾

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