CHEMISTRY LETTERS, pp. 1047-1050, 1983.

POLYMER-PROTECTED COPPER COLLOIDS AS CATALYSTS FOR SELECTIVE HYDRATION OF ACRYLONITRILE

Hidefumi HIRAI,* Hidehiko WAKABAYASHI, and Makoto KOMIYAMA
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Stable colloidal dispersion of copper in water is prepared by the reduction of copper sulfate with sodium tetrahydroborate in the presence of poly(vinylpyrrolidone), poly(vinyl alcohol), dextrin, or poly(methyl vinyl ether). The poly(vinylpyrrolidone)-protected copper colloids are effective for the selective catalysis in hydration of acrylonitrile to acrylamide at 80°C in water.

Colloidal dispersions of noble metals were prepared by the reduction of the metal salts with hydrogen,[1,2] hydrazine,[3] or alcohols[4-7] in the presence of various protective polymers. Previously, the colloids of rhodium[4-6] and palladium,[7] prepared by use of alcohols as reducing agents, exhibited large catalytic activity and selectivity in hydrogenation of olefins and dienes. However, little has been known on the preparations and properties of colloidal dispersions of non-noble metals in liquids.

Recently, it has been shown that heterogeneous catalysts such as a copper powder[8] and a copper supported on silica-magnesia[9] or γ-alumina[10] have catalytic activities in the hydration of acrylonitrile to acrylamide.

This paper describes the preparation of stable colloidal dispersions of copper in water using various polymers as protective colloids. Their catalytic activities in the homogeneous hydration of acrylonitrile to acrylamide will be shown as well.

Copper sulfate ($CuSO_4 \cdot 5H_2O$: guaranteed grade, Yoneyama Chemical Co.) was recrystallized from water twice. Poly(N-vinyl-2-pyrrolidone)s, poly(vinyl alcohol)s, and dextrin were purified by repeated reprecipitations (5, 2, and 2 times, respectively) from water solutions with acetone (1 / 10 v/v). Sodium tetrahydroborate ($NaBH_4$: extra pure grade, Koso Chemical Co.) was stored over silica gel and dissolved in water immediately before use. Acrylonitrile was distilled under nitrogen after being washed successively with 5 wt% aqueous sodium hydroxide solution and 5 wt% aqueous phosphoric acid solution, and was stored at -10°C. Doubly distilled water was degassed by boiling under a reduced pressure. Other reagents in commercially obtainable highest purities were used without further purifications. Nitrogen gas, which had the purity higher than 99.9995%, was obtained from Nippon Sanso Co.

Typical procedure for the preparation of colloidal copper dispersions was as follows. Copper sulfate (37.5 mg : 0.15 mmol) and polymers (6.0 mmol as monomeric residue) were dissolved in 27 cm^3 of water and stirred magnetically at 80°C under nitrogen for 1 h. The stirring was made at 25°C instead of 80°C only for the case of poly(methyl vinyl ether), since this polymer dissolved in water at 25°C but not at 80°C. Then, 11.3 mg (0.30 mmol) of sodium tetrahydroborate in 3 cm^3 of water was added at 25°C. Immediately, the colloidal dispersions in water were formed as homogeneous solutions.

Electron micrographs of the colloids were obtained by a Hitachi Model HU-12A electron microscope operated at 100 kV at a magnification of 100,000. Sample films were prepared from the colloidal dispersions by evaporating the solvent to dryness on collodion films coated with a carbon layer.

The hydration of acrylonitrile was carried out at 80°C under atmospheric pressure of nitrogen. Acrylonitrile (0.6 cm^3 : 9.1 mmol) was added to the resultant solutions of the colloidal copper dispersions. The initial concentrations of acrylonitrile and copper were 0.30 and 0.005 $mol \cdot dm^{-3}$, respectively. The products were analyzed by gas liquid partition chromatography with a 2 m × 3 mm glass column packed with Tenax GC at 170°C.

As shown in Table 1, the formation of colloidal copper dispersions in water depends remarkably on the polymers used.

When poly(N-vinyl-2-pyrrolidone)s were used, homogeneous copper colloids were successfully prepared in a wide range of the degree of polymerization. The resulting colloids were quite stable and no precipitates were observed after standing under nitrogen at room temperature for 9 days or more. Homogeneous colloidal dispersions of copper were also obtained by use of poly(vinyl alcohol), dextrin, and poly(methyl vinyl ether) in place of poly(vinylpyrrolidone).

In the electron micrographs of the colloids, highly dispersed copper particles

Table 1. PREPARATIONS OF COLLOIDAL COPPER DISPERSIONS USING VARIOUS POLYMERS AND THEIR CATALYTIC ACTIVITIES FOR THE HYDRATION OF ACRYLONITRILE

Polymer	Degree of polymerization	Colloid		Acrylamide
		Formation	Average particle diameter / Å	Yield / mol % [a)]
Poly(vinylpyrrolidone)	3240	yes[b)]	100	25.4
	90	yes[b)]	48	7.5
Poly(vinyl alcohol)	2000	yes[c)]	d)	8.6
	1500	yes[c)]	150	6.0
	360	yes[c)]	d)	6.9
Dextrin	d)	Yes[c)]	90	2.5
Poly(methyl vinyl ether)	570	Yes[c)]	d)	——
Poly(ethylene oxide)	110	No	——	——
β-Cyclodextrin	7	No	——	——
Poly(acrylic acid)	3840	No	——	0.0
None	——	No	e)	0.3[f)]

a) Reaction conditions : temperature, 80°C; reaction time, 2 h; solvent, water; $[Cu]_0 = 5\ mmol{\cdot}dm^{-3}$; $[acrylonitrile]_0 = 300\ mmol{\cdot}dm^{-3}$.

b) Reddish dark brown c) Black d) Not determined.

e) The value is not estimated since the particle diameters are widely distributed from 40 to 3300 Å.

f) Catalysis by the copper precipitate.

without any aggregations were observed. For the colloid with poly(vinylpyrrolidone) of the degree of polymerization 3240, for example, the particle size was distributed from 30 to 180 Å, and the average particle diameter was 100 Å.

These results were in contrast with the rapid formation of black precipitate in the absence of these polymers. The precipitation took place immediately after the addition of sodium tetrahydroborate to an aqueous solution of copper sulfate.

Colloidal dispersions were not obtained when the polymers other than poly(vinylpyrrolidone), poly(vinyl alcohol), dextrin, and poly(methyl vinyl ether) were used. The preparation in the presence of poly(ethylene oxide) or β-cyclodextrin resulted in rapid precipitation of copper particles. In the case of poly(acrylic acid), no reduction of copper(II) ions occurred even after the addition of sodium tetrahydroborate.

The fifth column in Table 1 shows the catalytic activities of the colloidal copper dispersions for the hydration of acrylonitrile to acrylamide. Here the initial molar ratio of copper to acrylonitrile is 0.017. The catalytic activities of all the colloidal dispersions are much larger than that of the copper precipitate prepared by the reduction of copper sulfate with sodium tetrahydroborate in the absence of polymer. Especially, the colloid prepared using poly(vinylpyrrolidone) of the degree of polymerization 3240 is effective as catalyst for the hydration. Even after standing under nitrogen for 9 days, this colloid exhibited an identical catalytic activity.

For all the catalytic hydrations by the present colloidal dispersions, the selectivity for the production of acrylamide was 100%. Ethylenecyanohydrin, usually formed as a byproduct in the hydration of acrylonitrile,[8-10] was not produced at all. The formation of the byproduct was not detected even at the 80% yield of acrylamide, which was attained after 42 h using the colloid with poly(vinylpyrrolidone) of the degree of polymerization 3240.

Throughout the catalytic hydration, the colloidal dispersions with poly(vinylpyrrolidone)s and dextrin were homogeneous, and no changes in colors were perceived. The reaction with the poly(vinylpyrrolidone) of the degree of polymerization 3240 satisfactorily followed a first order equation with respect to the concentration of acrylonitrile when the conversion of acrylonitrile was smaller than 47% in the reaction time of 10 h. This result indicates that the catalytic activity of the colloidal dispersion remains virtually constant during the reaction. In the case of the colloids with poly(vinyl alcohol)s, however, considerable amounts of black precipitate were observed after the reactions.

The authors would like to thank Mr. Koichi Adachi for valuable assistance in the electron microscope measurements.

References

1) C. Paar and C. Amberger, Chem. Ber., 37, 124 (1904).
2) A. Skita and W. A. Meyer, Chem. Ber., 45, 3579 (1912).
3) L. D. Rampino and F. F. Nord, J. Am. Chem. Soc., 63, 2745 (1941).
4) H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. Sci., Chem., A13, 633 (1979).
5) H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. Sci., Chem., A12, 1117 (1978).
6) H. Hirai, Y. Nakao, and N. Toshima, J. Macromol. Sci., Chem., A13, 727 (1979).
7) H. Hirai, H. Chawanya, and N. Toshima, Makromol. Chem., Rapid Commun., 2, 99 (1981).
8) T. Kurata, T. Okano, A. Tamaru, S. Nagashima, Y. Murata, and K. Ohuchi, Jpn. Kokai Tokkyo Koho 79 27326 (1979).
9) H. Hayashi, H. Nishi, Y. Watanabe, and T. Okazaki, J. Catal., 69, 44 (1981).
10) H. Miura, T. Hattori, K. Keitoku, K. Sugiyama, and T. Matsuda, Nippon Kagaku Kaishi, 1982, 692.

(Received April 25, 1983)