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# Doping Effect of Polyaniline Derivatives on Synthetic Metal Catalytic System for Dehydrogenative Oxidation of Benzylamine

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The catalytic activity of polyaniline derivatives in the dehydrogenative oxidation of benzylamine to *N*-benzylidenebenzylamine is effected by protonic acid doping.

Conducting polymers such as polyanilines constitute a redox system based on their conjugate structure.1) Our previous paper2) has demonstrated that one-electron redox capability of polyaniline is allowed to construct a catalytic system for oxidation reactions, where a reversible redox cycle is achieved under oxygen.3) Doping and electronic structure are revealed to be key factors to control the properties of conducting polymers, which prompted us to investigate electronic effects of polyaniline derivatives on dehydrogenative oxidation of benzylamine.

Benzylamine (**1**) was oxidized to *N*-benzylidenebenzylamine (**2**) with a catalytic amount of polyaniline under oxygen (Eq. 1).4) Chemical properties of polyanilines are known to depend on oxidation methods to polymerize anilines, but the oxidation yield was almost independent on the chemical oxidants, $Cu(BF_4)_2$5) and $(NH_4)_2S_2O_8$,6) in polymerization as listed in Table 1.

$$\underset{\mathbf{1}}{PhCH_2NH_2} \xrightarrow[O_2,\ 80\ ^\circ C]{\text{cat. polyaniline derivative}} \underset{\mathbf{2}}{PhCH{=}NCH_2Ph} \qquad (1)$$

The relationship between protonic acid doping and oxidation capability was addressed since protonation of emeraldine base with aqueous HCl has been reported to increase conductivity.7) The higher catalytic activity of polyaniline was attained with increase of protonic acid doping. On the contrary, the imine **2** was produced only in 12% yield with the deprotonated polyaniline. Acidity of polyaniline is considered to play an important role in the oxidation efficiency.

Another aspect to be studied is the substituent effect of polyaniline derivatives, which were prepared by chemical polymerization of the corresponding anilines with $(NH_4)_2S_2O_8$. Substitution with an electron-releasing methyl or methoxyl group on the phenyl ring and the nitrogen atom did not effect the oxidation reaction so much under the conditions employed here.

Dehydrogenation proceeds in acetonitrile or even in ethanol although polyaniline (polymerized with $Cu(BF_4)_2$, pH 4.3) is sparingly soluble or insoluble in these solvents, respectively.2) The blue supernatant of the heterogeneous mixture supported the involvement of its oxidized form in acetonitrile. Use of polyaniline with higher solubility 8) instead resulted in the efficient catalysis in *N*-methylpyrrolidone (NMP) with the higher conversion to **2** ( reaction time 10 h). Dedoping ( pH 9.6) of the polyaniline with higher solubility decreased the

Table 1. Oxidation of Benzylamine Catalyzed by Polyaniline Derivatives

| Polyaniline Derivative | | | Solvent | Time/h | **2** Yield/% b) |
|---|---|---|---|---|---|
| | Oxidant for Polymerization | pH a) | | | |
| — | — | — | MeCN | 50 | trace |
| Polyaniline (Ref. 5) | $Cu(BF_4)_2$ | 2.8 c) | MeCN | 50 | 75 |
| Polyaniline (Ref. 5) | $Cu(BF_4)_2$ | 4.3 | MeCN | 50 | 61 |
| Polyaniline (Ref. 5) | $Cu(BF_4)_2$ | 8.1 c) | MeCN | 50 | 12 |
| Polyaniline (Ref. 6) | $(NH_4)_2S_2O_8$ | 2.1 c) | MeCN | 50 | 79 |
| Polyaniline (Ref. 6) | $(NH_4)_2S_2O_8$ | 3.1 c) | NMP | 10 | 52 (41) |
| Polyaniline (Ref. 8) | $(NH_4)_2S_2O_8$ | 3.2 c) | NMP | 10 | 77 (18) |
| Polyaniline (Ref. 8) | $(NH_4)_2S_2O_8$ | 9.6 c) | NMP | 10 | 4 (89) |
| Poly(*o*-anisidine) (Ref. 6) | $(NH_4)_2S_2O_8$ | 3.5 | MeCN | 50 | 73 |
| Poly(*o*-toluidine) (Ref. 6) | $(NH_4)_2S_2O_8$ | 3.1 | MeCN | 50 | 87 |
| Poly(*N*-methylaniline) (Ref. 6) | $(NH_4)_2S_2O_8$ | 2.9 | MeCN | 50 | 88 |

a) pH of aqueous suspension (50 ml) of polyaniline derivative (20 mg). b) Glc yield. The numbers in parentheses represent the yields of recovered benzylamine. c) Adjustment of pH was carried out by treatment with aqueous HCl or NaOH.

activity as described above.

The present results indicate that the catalysis of polyanilines in the dehydrogenative oxidation depends on their electronic state. Electronic interaction with a copper or iron salt has also been disclosed to enhance the oxidation capability via coordination.2) Further investigation on the development of a more efficient synthetic metal catalytic system is now in progress.

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3) D.-K. Moon, M. Ezuka, T. Maruyama, K. Osakada, and T. Yamamoto, *Macromolecules*, **26**, 364 (1993).
4) A mixture of **1** (1.0 mmol) and polyaniline (10 mg) in acetonitrile (1.0 ml) was stirred at 80 °C under oxygen at atmospheric pressure. Ether was added to the reaction mixture, which was filtered and concentrated. Glc analysis showed the formation of **2**.
5) Polyaniline was prepared by chemical oxidation of aniline with copper(II) salt and $HBF_4$ and contains less than 2 ppm of copper species after washing. We thank Mitsubishi Kasei Co. for the gift of polyaniline.
6) A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and N. L. D. Somasiri, "Conducting Polymers," ed by L. Alcacer, Reidel Publ. (1987), p. 105. Chemical polymerization of anilines was performed with 1/4 molar equivalent of $(NH_4)_2S_2O_8$.
7) A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Metals*, **18**, 285 (1987).
8) Polyaniline with higher solubility due to the structural difference was obtained by chemical oxidation with one molar equivalent of $(NH_4)_2S_2O_8$. Ref. M. Abe, A. Ohtani, H. Higuchi, M. Ezoe, S. Akizuki, K. Nakamoto, and K. Mochizuki, JP 91-28229.

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