Journal of Catalysis 267 (2009) 93–96

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

A green route to conducting polyaniline by copper catalysis

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ARTICLE INFO

Article history:
Received 25 June 2009
Revised 16 July 2009
Accepted 17 July 2009
Available online 16 September 2009

Keywords:
Catalysis
Copper
Hydrogen peroxide
Oxygen
Polyaniline

ABSTRACT

The oxidative polymerization of N-(4-aminophenyl)aniline (AD) to the conducting emeraldine salt (2.6×10^{-2} S cm^{-1}) has been investigated using dioxygen or hydrogen peroxide as the oxidant in aqueous solution under mild conditions. The spontaneous oxidation by O_2 takes place with a modest yield (13%) while H_2O_2 allows a better result (43% yield). On adding acetonitrile as a co-solvent, the polymerization is completely suppressed with both the reagents. A strong catalytic effect has been detected by using Cu, CuCl, and $CuCl_2$, being all these simple copper compounds similarly efficient using either O_2 or H_2O_2 reagents, thus allowing yields up to 86–93% of emeraldine. The poisoning effect of acetonitrile has been observed also in the case of the copper-catalyzed reactions but with a minor impact (5–14% decrement).

1. Introduction

New materials showing controllable electrical properties are of interest in the field of electronic and optic devices and polyaniline (PANI) is one of the most investigated compounds due to the high environmental stability [1]. The outstanding feature of PANI is related to a reversible acid/base, doping/dedoping chemistry which enables control over their characteristics and makes this material attractive for solar cells [2], antistatic materials [3], photovoltaic devices [4], and anticorrosion coatings [1].

The morphology of conducting polymers is an important factor that has a vital influence on characteristics and performance. Generally, templates were needed to fabricate the specific morphologies [5,6]. In order to obtain the required structures such as film and hollow materials, the template must be removed. However, the removal of the template is not only troublesome, but may also result in disorder or modification of the micro/nanostructures.

Generally, the synthesis of PANI is based on the oxidative polymerization of aniline, or its dimer N-(4-aminophenyl)aniline (AD), using strong oxidants, in particular ammonium peroxydisulfate, in the presence of acids with the aid of a template [5,7]. Biocatalytic polymerization using enzyme and electrochemical oxidation have been proposed as an alternative to chemical oxidation [8–10].

In this context, the use of more environmentally friendly reagents, as O_2 and H_2O_2, appears as a challenging opportunity. In such cases, however, the oxidative polymerization rate of aniline and other precursors is considered too slow for practical application: it can be improved by means of sonochemical energy [11,12] or by use of homogeneous catalysts [13–18].

Pyrrole [19] and aniline [20] polymerization by molecular oxygen or H_2O_2 has also been investigated by using gold catalysis.

Aniline conversion up to 70% has been observed using H_2O_2 as the oxidant [20].

By using the less expensive copper (II) salts as catalysts in the presence of molecular oxygen, Toshima et al. observed the oxidative polymerization of aniline. However, this route has allowed only low yields (5–48%) of bad quality polymer owing to the presence of branched structures [21]. Recently Dias et al. reported the oxidative polymerization of aniline dimer to polyaniline with H_2O_2 in the presence of a pyrazolylcopper (II) complex in a mixture 1:1 acetonitrile–water as solvent [14]. Under these conditions they obtained PANI in 50% yield and the catalytic effect of the copper complex was established by the lack of polymerization in its absence.

In this paper we have revisited the oxidative polymerization of aniline dimer and we have demonstrated that the eco-friendly route to produce the emeraldine conducting form can be performed using metal copper and simple copper compounds either with O_2 or H_2O_2 oxidants. With respect to previous reports, we have found that acetonitrile when used as a co-solvent inhibits the oxidative polymerization of AD.

2. Experimental

2.1. Reagents and instruments

Commercial high purity chemicals and deionized milliQ water were used in the experiments. The mean size of the copper powder was 0.04 mm.

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0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.07.007

The morphological characterization of the products was performed by transmission electron microscopy (TEM; LEO 912AB microscope) and scanning electron microscopy (SEM; LEO 1430 microscope). The TEM determination was done by depositing a drop of the solid ultrasonically dispersed in water onto a carbon-coated copper grid (FCF 200 mesh) and allowing them to dry in oven at 60 °C for several hours. The SEM specimens were prepared by drop-casting the polymeric suspension onto an aluminum foil. XRD analysis was performed using a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu Kα radiation. FT-IR spectra were recorded by a JASCO FT/IR-410 instrument as KBr-dispersed samples in the 400–4000 cm^{-1} range. The UV–vis spectra were recorded on a Hawlett Packard 8453 instrument using N,N-dimethylamide as solvent. The specific electrical conductivity σ ($S\ cm^{-1}$) was obtained by measuring the bulk pellet resistances R (Ω) through Electrochemical Impedance Spectroscopy (EIS). AC-Impedance measurements were performed on pressed pellet of polymers by using an AUTOLAB PGSTAT 30 Metrohm in the frequency range from 10 mHz to 1 MHz with an applied excitation ac-voltage of 10 mV rms. Platinum plates were used to assure the contact between the two sides of pellet. This instrument used a four-point system suitable for measuring the resistance or conductivity of samples excluding the contact resistance. Pellets for conductivity examination were prepared by uniaxial press of the powder into a 16-mm diameter die at 200 MPa for 0.5 h.

2.2. Polymerization of AD with molecular oxygen

Five hundred milligrams (2.72 mmol) of AD was dissolved in water or in a mixture $H_2O:CH_3CN = 1:1$ (total volume = 50 ml) in the presence of 2.72 mmol of HCl, under O_2 (3 bar) and stirred at room temperature (ca 293 K). After 3 days, acetone was added in order to separate the insoluble green material from soluble oligomers. The product was collected by filtration, washed with acetone, and dried at 383 K overnight. The reaction was repeated adding at the mixture the correct amount of catalyst (Cu, CuCl, or $CuCl_2$), maintaining a molar ratio AD/Cu = 20.

2.3. Polymerization of AD with hydrogen peroxide

Five hundred milligrams (2.72 mmol) of AD was dissolved in aqueous solution or in a mixture $H_2O:CH_3CN = 1:1$ (total volume = 50 ml) in the presence of 2.72 mmol of HCl. 0.37 g of H_2O_2 30% (4.1 mmol) was added to the green solution and, when reported, 0.136 mmol of Cu or CuCl, or $CuCl_2$ was added. The reactants were stirred under nitrogen atmosphere at room temperature (ca 293 K). The insoluble green material was collected and treated as above.

Table 1
AD = 2.7 moles, AD/HCl = 1 (molar ratio), AD/Cu = 20 (molar ratio), O_2 = 3 bar, reaction time = 3 days.

Experiment	Catalyst	Solvent	Temperature	PANI yield (%)
1	No	H_2O	25	13
2	No	H_2O/CH_3CN	25	0
3	Cu	H_2O	25	56
4	Cu	H_2O	80	93
5	$CuCl_2$	H_2O	25	72
6	$CuCl_2$	H_2O	80	89
7	CuCl	H_2O	25	76
8	CuCl	H_2O	80	87
9	Cu	H_2O/CH_3CN	80	77

3. Results and discussion

3.1. Oxidation by O_2–Blank test

N-(4-aminophenyl)aniline is sparingly soluble in water at room temperature but it becomes soluble upon treatment with HCl. By reacting an aqueous solution of AD in the presence of HCl (AD/HCl = 1) under O_2 pressure (3 bar) a slow, spontaneous polymerization occurs, producing a pale green insoluble material in 13% yield after three days (Table 1, exp. 1). Under similar conditions but using aniline as the reagent, no polymerization took place [20].

The product was identified as emeraldine salt (Fig. 1) by FT-IR (Fig. 2), UV–vis (Fig. 3) and XRD (Fig. 4) analyses. All the data are consistent with those reported in the literature [14,22,23].

The Fourier-transform IR spectrum (Fig. 2) shows a characteristic band at 1570 cm^{-1}, assigned to the C=C stretching of the quinoid rings (N=Q=N) and two peaks at 1498 cm^{-1} and 1484 cm^{-1}, assigned to the C=C stretching vibration mode for the benzenoid rings (N–B–N). The peaks at 1311 cm^{-1} and 1246 cm^{-1} are related to the C–N and C=N stretching modes and those at 1027 cm^{-1} and 889 cm^{-1} to the in-plane and out-of-plane bending of C–N. The peaks at 754 cm^{-1} and 692 cm^{-1} correspond to deformation vibration modes for the aromatic rings, while the peak at 573 cm^{-1} is characteristic for the 1,4 di-substituted benzene [6].

The UV–vis spectrum (Fig. 3) of the product shows three characteristic bands at 311, 432, and 603 nm. The absorption band at 311 nm is due to the π–π^* transition of the benzenoid rings. The band at 432 nm is assigned to the polaron/bipolaron transition. The band at 603 nm is due to the transition from a localized benzenoid highest occupied molecular orbital to a quinoid lowest unoccupied molecular orbital, that is a benzenoid to quinoid excitonic transition [24].

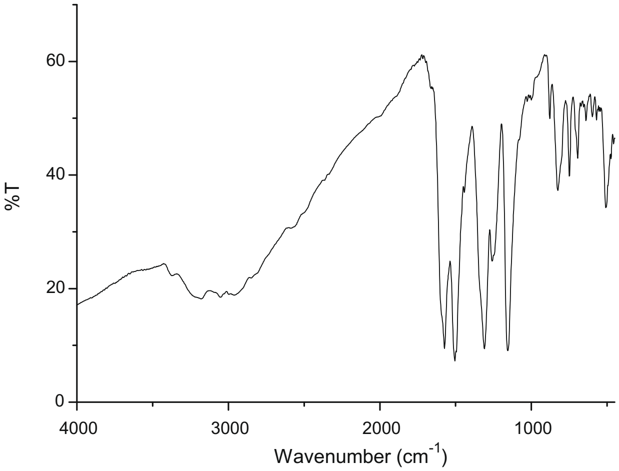

Fig. 2. FT-IR spectrum of emeraldine salt in KBr pellet.

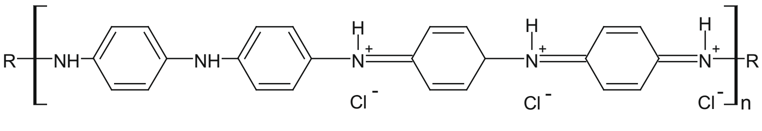

Fig. 1. Molecular structure of emeraldine salt.

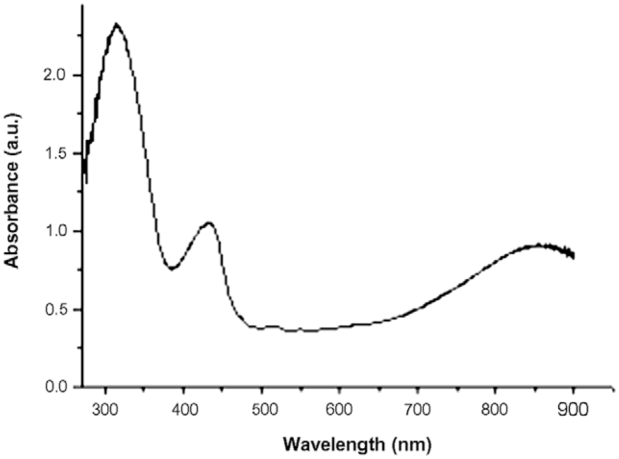

Fig. 3. UV–vis spectrum of PANI–emeraldine using N,N-dimethylamide as the solvent.

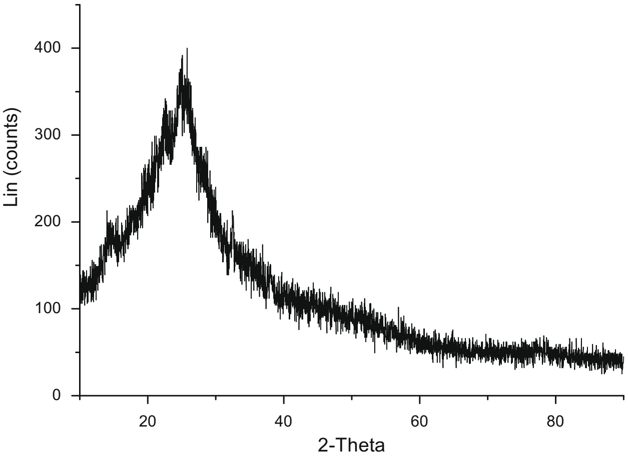

Fig. 4. X-ray diffraction pattern of PANI–emeraldine.

The XRD pattern (Fig. 4) shows the characteristic Bragg diffraction peak at $2\theta \approx 25.4°$ of the PANI [11].

Concerning the morphological properties, TEM and SEM techniques showed irregular shapes of the polymer consisting in 1–10 μm plates surmounted by worm-like wires (Figs. 5 and 6). These structures are similar to the nanotubes obtained from aniline with strong oxidant (ammonium peroxydisulfate) in the presence of acetic acid, as described by Konyushenko et al. [25].

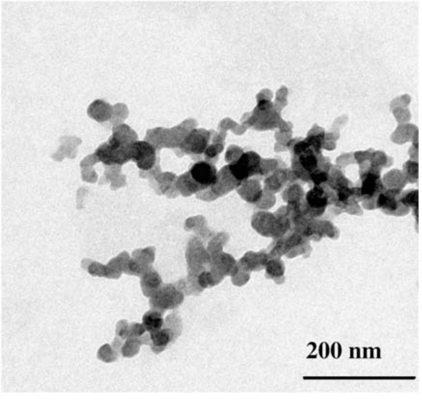

Fig. 5. TEM image (Bar = 200 nm) of PANI synthesized with O_2.

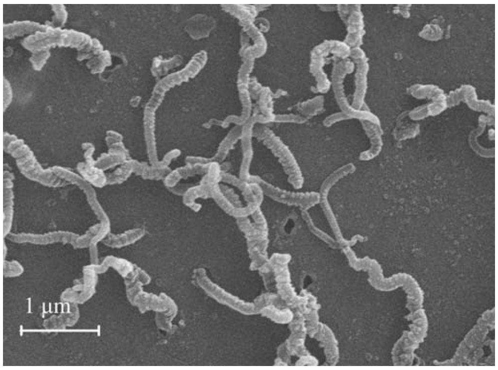

Fig. 6. SEM image (Bar = 1 μm) of PANI synthesized with O_2.

The conductivity of the synthesized polyaniline was determined with a standard conductivity cell as previously described [20].

The ohmic (series) resistance, correlated to the bulk resistance, was obtained from the high frequency intercept on the real axis of the spectrum. The polarization resistance (R_p), correlated to slow processes (e.g. diffusion processes), was derived from the difference between the low frequency and high frequency intercepts on the real axis. All impedance measurements were taken at 0 V, 0.5 V, and 1 V at room temperature and static air.

The pellet shows a polarization resistance decreasing from about 7400 $\Omega\,cm^2$ to about 6500 $\Omega\,cm^2$ as the voltage increases from 0 V to 1 V. The recorded ohmic resistance ($R_s = 63\ \Omega\,cm^2$) indicates a bulk conductivity independent of the voltage (from 0 V to 1 V).

The value of the conductivity for the product was worth about $2.6 \times 10^{-2}\ S\,cm^{-1}$, which is similar to those reported in the literature for chemically synthesized emeraldine [6,15,20].

On adding acetonitrile as a co-solvent (acetonitrile:water = 1, instead of pure water), the spontaneous aerobic oxidation of aniline dimer was completely suppressed (Table 1, exp. 2).

3.2. Oxidation by O_2–catalytic tests

Catalytic tests were performed at 25 and 80 °C in the presence of Cu(0), Cu(I), and Cu(II) catalysts using pure water as the solvent.

As shown in Table 1, all the Cu catalysts strongly improved the yields and copper powder at 80 °C produced the highest value (93% PANI).

In order to examine the effect of acetonitrile on the aerobic oxidation of AD, we have repeated test 4 of Table 1 with the most effective catalyst (powdered metal copper at 80 °C) by using the mixture of acetonitrile: water 1:1 as the solvent (exp. 9): the drop of yield from 93% to 77% confirms the relevant inhibiting effect of acetonitrile also in the presence of catalyst.

The above experiments on the aerobic oxidation of AD to polyaniline represents the basis for evaluating other oxidation reagents. Among them, H_2O_2 is of interest owing to its general use as a clean and cheap reagent for oxidation reactions.

3.3. Oxidation by H_2O_2–Blank tests

Hydrogen peroxide is a more effective reagent than molecular oxygen for AD polymerization in the absence of catalysts. In fact, by reacting aniline dimer with H_2O_2 in the presence of HCl ($AD:HCl:H_2O_2 = 1:1:1.5$) in aqueous solution, a faster reaction occurred producing emeraldine salt in 43% yield after 24 h (exp 10, Table 2).

By increasing the H_2O_2:AD molar ratio up to 3:1 we found no benefit on the yield.

Table 2
H_2O_2/AD = 1.5 (molar ratio), room temperature, AD/HCl = 1 (molar ratio), AD/Cu = 20.

Experiment	Catalyst	Solvent	PANI yield (%)
10	No	H_2O	43
11	No	H_2O/CH_3CN	3
12	Cu	H_2O	86
13	Cu	H_2O/CH_3CN	82
14	CuCl	H_2O	79
15	CuCl	H_2O/CH_3CN	70
16	$CuCl_2$	H_2O	83
17	$CuCl_2$	H_2O/CH_3CN	71

On adding acetonitrile as a co-solvent, the uncatalyzed oxidation became almost suppressed (Table 2, exp. 11).

3.4. Oxidation by H_2O_2–catalytic tests

In Table 2 the results of the catalytic tests carried out in pure H_2O and in CH_3CN/H_2O 1/1 (v/v) solution are compared.

From these data, we can note the excellent effect of copper species in promoting AD polymerization, along with a small depressing effect of acetonitrile on copper catalysis (ca 5–14% decrement).

All the products obtained in Tables 1 and 2 were shown to be spectroscopically and morphologically similar to the emeraldine salt obtained and characterized in experiment 1. In the XRD pattern of the products obtained in experiments 3–9, Table 1, and exp. 12–17 of Table 2, no diffraction signals due to copper species could be detected.

For all the products, the conductivity reached a value close to 2×10^{-2} S cm^{-1}.

According to Toshima et al. [21] and Genies et al. [26], the oxidative polymerization of aniline dimer can be interpreted by assuming the formation of an organic radical cation intermediate, promoted by a redox Cu(I)–Cu(II) couple, acting as electron transfer from the organic molecule to molecular oxygen or hydrogen peroxide. The reactivity of metal copper toward dioxygen and the resulting catalytic activity are also documented [27]. In this case the particle size of copper powder affected its dissolution time (ca 2 h for 0.04 mm particles and ca 6 h for 0.1 mm particles), but not the long time (three-day) polymerization test.

4. Conclusions

Owing to a lower redox potential [28], aniline dimer undergoes an easier polymerization to the emeraldine conducting salt with respect to aniline, using either O_2 or H_2O_2.

The slow polymerization can be implemented by using simple copper catalysts as Cu, CuCl, and $CuCl_2$, which are able to enhance the reaction yield from 13–43% up to 86–93%. It is surprising to observe that all the tested copper species behave similarly. However, these results are consistent with the behavior of the same copper compounds observed during 2-aminophenol oxidation [27], and suggest the *in situ* formation of copper radical species of similar catalytic efficiency. The use of acetonitrile as a co-solvent causes a strong inhibition effect on the uncatalyzed reactions, probably due to a radical trap behavior, whereas in the presence of catalyst only a minor effect has been detected.

Acknowledgment

We thank Dr. Massimiliano Lo Faro (CNR-ITAE Istituto di Tecnologie Avanzate per l'Energia ''Nicola Giordano'', Messina, Italy) for conductivity measurements.

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