Journal of Catalysis 259 (2008) 1–4

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Priority Communication

Facile synthesis of polyaniline using gold catalyst

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ARTICLE INFO

Article history:
Received 7 July 2008
Revised 14 July 2008
Accepted 15 July 2008
Available online 12 August 2008

Keywords:
Catalysis
Conductive polymer
Gold
Polyaniline

ABSTRACT

The oxidative polymerization of aniline was investigated using H_2O_2 as an oxidant and metallic gold as a catalyst. In the form of colloidal nanoparticles, gold produces the conductive polyaniline only in a low yield, whereas when supported on carbon and titania, it improves the polymerisation reaction. For an Au/TiO_2 catalyst, a synergistic effect between the metal and the support has been demonstrated that allows the production of polyaniline at high yield (70%). Morphological aspects, derived by TEM and SEM techniques, allow identification of the polymeric material in form of nanospheres 45–600 nm in diameter.

1. Introduction

Polyaniline (PANI), one of the most important conducting polymers, has been intensively studied in recent years because of its tunable conductivity, which is useful in a wide variety of applications, notably in light-emitting display devices, photovoltaic cells, batteries, and capacitors [1,2]. In fact, PANI is unique among conductive materials in that the degree of acid-doping and oxidation strongly influences its conductivity. Optimum conductivity is maintained when the polymer contains equal numbers of oxidized and reduced units (emeraldine form) with 1 proton doping every 2 units.

In recent years, the morphology of PANI nanostructure, as nanofibers and nanotubes, has attracted much research interest. In general, PANI nanostructures are synthesized through a "template synthesis" route. Different templates, including zeolite channels, track-etched polycarbonate, and nanodized alumina membrane, have been used to direct the growth of PANI nanostructures [3]. In most applications, the template must be removed, requiring additional workup and causing disorder or modification of the micro/nanostructures. Moreover, it has been demonstrated that the morphology and chemical properties of PANI are closely associated with the preparation method, and many synthetic procedures have been explored [4]. Generally, the polymerization of aniline is carried out through oxidative coupling of aniline or its dimer, *N*-(4-aminophenyl)aniline, using oxidants such as ammonium persulfate (APS), $K_2Cr_2O_7$, KIO_3, and others.

APS is the most common oxidant used for the preparation of conducting polymers; however, its inorganic byproduct (ammonium sulfate) represents a drawback in subsequent applications [5]. Similar problems are encountered when using other metals in as high an oxidation state as the oxidant [3–7]. Recently, it has been found that chloroauric acid ($HAuCl_4$) can be applied as an oxidant for the polymerization of aniline to produce nanofibers, nanotubes [8], and nanoballs [1]. Chattopadhyay et al. reported a new method for synthesizing Au–PANI composites based on the use of H_2O_2 as the bifunctional reagent for the reduction of $HAuCl_4$ and the oxidation of aniline, leading to the formation of interesting PANI–gold composite [6]. The introduction of metal particles in the polymeric framework also can be done in two separate steps [9]. Mallick et al. [10] have described preparation methods and applications of gold–polyaniline composites. Preformed metallic gold nanoparticles have not been used as a catalyst in the oxidative polymerization of aniline, even though the use of more environmentally friendly reagents, such as O_2 and H_2O_2, in combination with a catalyst appears to be a challenging alternative to stoichiometric oxidants. Using this advantageous procedure, Bicak and Karagoz investigated the synthesis of emeraldine base from aniline and gaseous oxygen with Cu(II) as the catalyst [11]. Despite the promising yield, however, the need for organic solvents and a soluble catalyst makes this experiment difficult and far to represent a green process.

H_2O_2 is an important oxidant with wide-ranging industrial uses. Its reduction product, H_2O, eliminates the need for post-

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0021-9517/$ – see front matter
doi:10.1016/j.jcat.2008.07.006

treatment and simplifies recycling of the reagent. Thus, the use of H_2O_2 for aniline polymerisation appears to be attractive mainly for large-scale applications. Up to now, the reaction rate has been considered too slow, and efforts have been devoted to the development of catalytic systems for improving the kinetics [5]. In this context, Sivakumar and Gedanken reported a new method for producing conductive polyaniline by ultrasonic irradiation [12]. Au–polyaniline composites have been obtained in the presence of chloroauric acid [6,12].

Owing to the importance of catalytic methods for conductive polymer preparation, in previous work we described the efficient catalysis by gold nanoparticles in the oxidative polymerization of pyrrole [13]. In this communication, we report a simple and clean catalytic method for oxidising aniline to conductive polyaniline using hydrogen peroxide as the oxidant in the presence of gold-based catalysts under mild conditions. Another investigation of the oxidation of *N*-(4-aminophenyl)aniline (aniline dimer) to polyaniline will be discussed in a forthcoming paper.

2. Experimental

2.1. Reagents and instruments

Aniline (Aldrich, 99%), H_2O_2 (Fluka, 30%), HCl (Carlo Erba, 37%), gaseous oxygen (SIAD, 99.99%), gold sponge (Fluka, 99.999%), D-(+)-glucose monohydrate (Fluka, $\geqslant$99%), sodium tetrahydrogenborate powder (Aldrich, 98%), carbon X40S ($S = 1300\ m^2/g$, $VP = 0.37\ cm^3/g$, Camel chemicals S.p.A), titania P_{25} (30% rutile and 70% anatase, $VP = 0.3\ cm^3/g$, Degussa), KBr (Aldrich $\geqslant$99.0%), and 1-methyl-2-pyrrolidone $\geqslant$98% (Fluka) were used as the starting materials. Morphological characterisation of the products was performed by transmission electron microscopy (TEM; LEO 912AB microscope) and scanning electron microscopy (SEM; LEO 1430 microscope). TEM determination was done by depositing a drop of the solid ultrasonically dispersed in water onto a carbon-coated copper grid (FCF 200 mesh) and allowing it to dry in oven at 60 °C for several hours. The SEM specimens were prepared by dropcasting the polymeric suspension onto aluminium foil. XRD analysis was performed using a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu$K\alpha$ radiation, and the size of the metal crystallites was calculated according to Scherrer's equation. FT-IR spectra were recorded with a JASCO FT/IR-410 spectrometer as KBr dispersed samples in the 380–4000 cm^{-1} range. The UV–vis spectra were recorded on a Hawlett-Packard 8453 instrument using 1-methyl-2-pyrrolidone as the solvent. The specific electrical conductivity σ (S/cm^{-1}) was obtained by measuring the bulk pellet resistance, R (Ω), by electrochemical impedance spectroscopy (EIS). AC-impedance measurements were performed on pressed pellet of polymers using an AUTOLAB PGSTAT 30 Metrohm in the frequency range of 10 mHz to 1 MHz with applied excitation ac voltage of 10 mV rms. Platinum plates were used to ensure contact between the two sides of the pellets. This instrument used a four-point system suitable for measuring the resistance or conductivity of samples excluding the contact resistance. Pellets for the conductivity measurements were prepared by uniaxially pressing the powder into a 16-mm-diameter die at 200 MPa for 0.5 h.

2.2. Preparation of the gold catalysts

2.2.1. Colloidal gold dispersion

A colloidal dispersion of gold was prepared by treating a 50 mg/L (2.5×10^{-4} M) of aqueous solution of gold (as $HAuCl_4$) with $NaBH_4$ ($NaBH_4$:Au molar ratio = 5) under N_2 atmosphere, in the presence of a large excess of glucose as a stabilizer (0.35 M) [14]. The resultant brown sol contained metal particles, stable for several hours, with a mean diameter of 3.6 nm, as determined by TEM and XRD analysis. A less stable dispersion, prepared in the absence of glucose, was used in a few experiments to exclude any interference from glucose.

2.2.2. Preparation of the 0.5% Au/C catalyst

The 0.5% Au/C catalyst was prepared by deposition of the preformed gold solution on carbon. The gold solution was prepared following the procedure described in Section 2.2.1. The metal particles were immobilized by adding carbon to the metal dispersion under stirring for several hours until the supernatant solution became clear. The amount of support was calculated to produce a metal loading of 0.5%. After filtration, the solid was washed many times with distilled water and dried at 373 K overnight. ICP analysis of the solution confirmed the total loading of gold onto the support.

2.2.3. Preparation of the 1% Au/TiO_2 catalyst

The 1% Au/TiO_2 catalyst was prepared similarly to the 0.5% Au/C catalyst, with deposition of the preformed gold solution on P25 titania (from Degussa) under stirring until the supernatant solution became clear. The amount of support was calculated to produce a metal loading of 1%, confirming this result by ICP analysis. After filtration, the solid was washed many times with distilled water and dried at 373 K overnight.

2.3. Oxidative polymerization procedure of aniline

2.3.1. Polymerization of aniline with hydrogen peroxide

The experiments were performed in a glass reactor by dissolving 0.5 g of aniline in 3 mL of HCl 1 M. After the prespecified amount of H_2O_2 was added, the solution was diluted to 100 mL under nitrogen atmosphere and stirred at room temperature (ca. 293 K). After 1 day, no precipitate was observed.

2.3.2. Catalyzed oxidative polymerization of aniline with hydrogen peroxide and gold nanoparticles

These experiments were performed as described in Section 2.3.1, but in the presence of different amounts of the gold sol. The insoluble green polymer was collected by filtration after 1 day. The catalyst was not removed from the products. The yields were evaluated by weighting the solid after washing the product with acetone and drying at 383 K overnight.

2.3.3. Catalyzed oxidative polymerization of aniline with hydrogen peroxide and 0.5% Au/C

The experiments were performed in a glass reactor by dissolving 0.5 g of aniline in 3 mL of HCl 1 M. After the prespecified amount of H_2O_2 was added, the solution was diluted to 100 mL. The proper amount of catalyst (An/Au = 1000 mmol/mmol) was added under nitrogen atmosphere and stirred at room temperature (ca. 293 K) for 1 day. The solid reaction products were collected by filtration, washed with acetone to remove the oligomers, and extracted with 1-methyl-2-pirrolidone to dissolve the polymeric material. Emeraldine salt (ES) was collected by removing the solvent (1-methyl-2-pirrolidone) through evaporation at 373 K under vacuum (1 kPa).

2.3.4. Catalyzed oxidative polymerization of aniline with hydrogen peroxide and 1% Au/TiO_2

These experiments were performed as described in Section 2.3.3, but using 108 mg of 1% Au/TiO_2 as the catalyst.

2.3.5. Blank tests of the oxidative polymerization of aniline with hydrogen peroxide and unloaded supports

These experiments were performed as described in Section 2.3.1, but using 108 mg of TiO_2 and then 216 mg of C as the reference material. In both cases, no solid ES was collected after the workup of the reaction.

2.3.6. *Polymerization of aniline with molecular oxygen*

The reactions reported in Sections 2.3.1–2.3.5 were repeated using molecular oxygen as the oxidant. The experiments were performed in a glass reactor dissolving 0.5 g of aniline in 3 mL of HCl 1 M. The solution was diluted to 100 mL, and the proper catalyst was added under O_2 (3 KPa) and stirred at room temperature (ca. 293 K). After 3 days, no precipitate was observed.

3. Results and discussion

According to previously reported electrochemical data [15], the aniline/emeraldine emichloridrate redox potential is quite high (ca. 1.46 V), suggesting a thermodynamic barrier to the aerobic oxidation of aniline (E° $O_2/H_2O = 1.23$ V). In contrast, the stronger oxidant H_2O_2 ($E^\circ = 1.78$ V) would be expected to be effective in affording the conductive polymer. Consequently, no aerobic oxidative polymerisation of aniline was observed using different catalytic systems with O_2 at 3 bar and room temperature, whereas a modest catalytic effect (typically 4–5% yield) was detected when a small amount of colloidal gold (aniline:Au = 1000) was used as a catalyst in combination with the H_2O_2 reagent. No product was isolated in the absence of catalyst, and no benefit was observed from using an excess of H_2O_2 (supplementary material, Table 1). However, the PANI yield could be increased by increasing the gold amount in the range Au:An = 0.001–0.004 (molar ratio) reaching the asymptotic value of 27% in 24-h tests (supplementary material, Fig. 1).

The short catalytic life of unsupported gold particles in oxidation reactions could be responsible for the limited conversion of aniline to PANI. For this reason, the oxidative polymerisation of aniline was tested also in the presence of supported gold catalyst (0.5% Au/C, 1% Au/TiO_2), which had proven to be more stable in previous catalytic applications [14]. The results, summarized in Table 1, show better performance in the presence of supported gold. In particular, the high activity of Au/TiO_2 can be ascribed to a strong contribution of the TiO_2 support.

In fact, whereas unloaded carbon resulted inert in aniline polymerisation by H_2O_2, P25 titania catalyzed the partial oxidation of aniline to soluble dark oligomers. No solid material was formed, however.

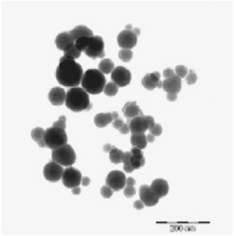
The products obtained in all of the preparations were identified as ES according to the FT-IR [9]. UV–vis [2], and XRD spectra [3,12] reported in supplementary material, Figs. 2–4. The morphology of the products, investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM), revealed emeraldine in form of nanospheres of 44–160 nm (Fig. 1A) alternating with micrometric rods (Figs. 1B and 2).

Although the presence of gold particles cannot be ascertained from our TEM images, XRD patterns (supplementary material, Fig. 4b) of the products show the broad reflections of metallic particles with a mean diameter of 42 nm in the crude reaction product (supplementary material Table 1, exp. 1–4), along with the polymeric material. No particular templating effect of gold is recognizable.

Concerning the morphological properties, keep in mind that solvent extraction of the polymeric material tends to homogenize the resulting aspect. Therefore, similar nanospheres with an average diameter of 45–600 nm were obtained for the Au/C and TiO_2 catalysts. In the case of Au/TiO_2, however, the nanospheres were assembled in a cluster-like organization, which was absent in the product derived using the carbon-supported catalyst (supplementary material, Figs. 5–8).

Table 1
Polymerization of aniline by supported gold catalysts

Experiment	Aniline/H_2O_2	Catalyst	Yield
1	1	0.5% Au/C	11.4%
2	1	1% Au/TiO_2	70.1%


(A)

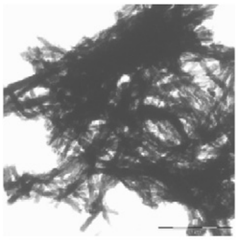

(B)

Fig. 1. TEM images of PANI synthesized with (A) (Bar = 200 nm), H_2O_2 and (B) (Bar = 1 µm), “naked” gold nanoparticles.

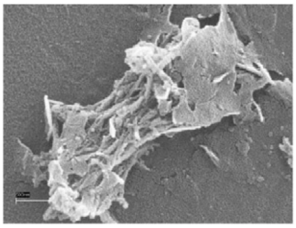


Fig. 2. SEM images of PANI synthesized with H_2O_2 and “naked” gold nanoparticles (Bar = 500 nm).

The conductivity of the polymer obtained in the high-yield conversion of aniline with Au/TiO_2 catalyst (Table 1, entry 2) was 1.5×10^{-1} S/cm (supplementary material, Fig. 9). 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 with 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 obtained at 0, 0.5, and 1 V at room temperature and in static air.

All spectra exhibit a well-defined semicircle denoting typical RC behaviour for the polymer. All tests demonstrate an exact intercept at high frequency, with the low frequency intercepts not easily fixed. This has been attributed to the use of a fitting curve. The pellet shows a decreasing polarization resistance from about 7400 $\Omega\,cm^2$ to about 6500 $\Omega\,cm^2$ as the voltage was increased from 0 to 1 V. The ohmic resistance (R_s) remained constant at 63 $\Omega\,cm^2$. This result was obtained under all conditions studied. This R_s value indicates a bulk conductivity independent of this voltage range (0–1 V).

4. Conclusion

We have shown for the first time that conductive PANI, mainly in form of nanospheres, can be easily fabricated from aniline by

H_2O_2 oxidation in the presence of gold nanoparticles as a catalyst. A particular synergistic effect, allowing 70% yield, has been demonstrated in the case of gold supported on P25 titania. The conductivity values, correlated with the bulk resistance of this polymer, are similar to those obtained through other polymerisation methods [12,16].

Supplementary material

Supplementary material for this article may be found on ScienceDirect, in the online version.

Please visit DOI: 10.1016/j.jcis.2008.07.006.

References

[1] K. Mallick, M.J. Witcomb, A. Dinsmore, M.S. Scurrell, Macromol. Rapid Commun. 26 (2005) 232.
[2] K. Mallick, M.J. Witcomb, A. Dinsmore, M.S. Scurrell, J. Polym. Res. 13 (2006) 397.
[3] K. Mallick, M.J. Witcomb, A. Dinsmore, M.S. Scurrell, Langmuir 21 (2005) 7964.
[4] Y. Wang, Z. Liu, B. Han, Z. Sun, Y. Huang, G. Yang, Langmuir 21 (2005) 833.
[5] Z. Sun, Y. Geng, J. Li, X. Wang, X. Jing, F. Wang, J. Appl. Polym. Sci. 72 (1999) 1077.
[6] T.K. Sarma, D. Chowdhury, A. Paul, A. Chattopadhyay, Chem. Commun. (2002) 1048.
[7] D.K. Moon, K. Osokada, T. Maruyama, T. Yamamoto, Makromol. Chem. 193 (1992) 1723.
[8] X. Feng, G. Yang, Q. Xu, W. Hou, J.-J. Zhu, Macromol. Rapid Commun. 27 (2006) 31.
[9] X. Feng, C. Mao, G. Yang, W. Hou, J.-J. Zhu, Langmuir 22 (2006) 4384.
[10] K. Mallick, M.J. Witcomb, M.S. Scurrell, Gold Bull. 39/4 (2006).
[11] N. Bicak, B. Karagoz, J. Polym. Sci. A 44 (2006) 6025.
[12] M. Sivakumar, A. Gedanken, Synth. Met. 148 (2005) 301.
[13] C. Della Pina, E. Falletta, M. Lo Faro, M. Pasta, M. Rossi, Gold Bull. (2008), in press.
[14] M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, Angew. Chem. Int. Ed. 43 (2004) 5812.
[15] S.K. Manohar, A.G. MacDiarmid, Synth. Met. 41–43 (1991) 711.
[16] W. Li, H.-L. Wang, J. Am. Chem. Soc. 126 (2004) 2278.