

Fullerene-Coated Beads as Reusable Catalysts

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New heterogeneous catalysts that use oxygen and light to generate singlet oxygen ($^1\text{O}_2$) have been prepared. The catalysts facilitate various types of singlet oxygenation reactions including the Ene reaction, the Diels–Alder reaction, and others. The catalysts are made by stirring a heterogeneous mixture of fullerene- C_{60} (dissolved in toluene) with aminomethylated poly(styrene-*co*-divinylbenzene) beads. Also, catalysts for aqueous photooxidations are made by reacting the initial catalysts with poly(allylamine) to create an outer layer that is more hydrophilic.

Introduction

Singlet oxygen ($^1\text{O}_2$) is a reagent used for a variety of organic reactions. These reactions include the Ene reaction,¹ the Diels–Alder reaction,² and others.³ Singlet oxygen may be made by the reaction of ozone with triphenyl phosphite,⁴ hypochlorite oxidation of hydrogen peroxide,⁵ or photosensitization of ground-state oxygen.⁶ The last method requires only a catalytic amount of the photosensitizer. Various sensitizers are available (fullerenes,^{7,8} Rose Bengal,⁹ methylene blue,⁹ and others⁹).

In 1973 Blossey et al. described the preparation of Rose Bengal coated beads and their use as heterogeneous catalysts for $^1\text{O}_2$ reactions.^{10–12} These catalysts were patented¹³ and commercially available for several years. The ability to simply filter them out of the solution after the reaction is complete is a major advantage to using them. The initial catalysts that were made are used primarily for reactions in organic solvents. Similar catalysts have also been developed for singlet oxygenations in aqueous solutions.^{14,15} More recently, other heterogeneous $^1\text{O}_2$ catalysts have been developed by using clay,¹⁶ silica,¹⁷ and zeolite^{18,19} solid supports.

The aim of this research is ultimately to build heterogeneous $^1\text{O}_2$ catalysts with chiral outer layers where stereoselective oxidation reactions could occur.²⁰ The first step in developing such catalysts is to coat beads with a $^1\text{O}_2$ sensitizer that may be easily covered with a material to which chiral outer layers may later be attached.²⁰ Buckminsterfullerene (C_{60}) is an ideal sensitizer to ac-

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compish this objective. It efficiently catalyzes the conversion of $^3\text{O}_2$ to $^1\text{O}_2$ (even after derivatization with various organic groups). It has multiple reactive units, which provide a scaffolding to cover the fullerenes once they have been added to beads. And it has good thermal and photochemical stability.

C_{60} placed on a film can be used to photochemically form $^1\text{O}_2$.²¹ Unfortunately, films lack sufficient surface area to be able to make enough $^1\text{O}_2$ for those materials to be as useful as bead-coated catalytic materials. In fact, prior to our bead studies, we prepared fullerene films and were unable to generate enough $^1\text{O}_2$ to catalyze a significant amount of even the most reactive $^1\text{O}_2$ reactions.

Fullerene-coated beads have been made before. A patent was filed in 1994 that describes the preparation of various fullerene-coated beads.²² However, the main derivatization reaction described in the patent is cumbersome. It utilizes a three-step process that involves reduction of the fullerene, addition of Br_2 to a double bond, and replacement of one of the fullerene bromines with 8-bromo-1-octanol. Once prepared, this derivative is added to an amine-coated bead, which the authors suggest is able to displace the tethered primary bromine. Other groups have connected fullerenes to beads coated with dienes via Diels–Alder reactions.^{23,24} However, these adducts undergo reverse Diels–Alder reactions at around 110 °C. A Prato reaction adduct has been made that requires derivatization of commercially available beads via a three-step process.²⁴ Fullerenes have also been linked to beads with Cryptand-22 (a macrocycle containing two amines).²⁵

Results and Discussion

For this project, commercially available amine-coated beads²⁶ were reacted with fullerenes directly in one step. Amines react quickly with fullerenes at or slightly above ambient temperature.²⁷ Thus, fullerene-coated beads were easily prepared by adding the beads to a solution of C_{60} in toluene and stirring the mixture overnight at 35 °C (see Scheme 1).²⁰ A hydrophilic fullerene-coated bead for aqueous photooxidations was also prepared by stirring Catalyst I in a methanolic solution of poly(allylamine) for about 2 h (see Scheme 2).²⁰

During the initial reaction between C_{60} and the beads, the solution visibly loses some of its purple fullerene color as the beads are coated. From the color change, the reaction is probably completed in just a few hours; however, stirring overnight may increase the loading.

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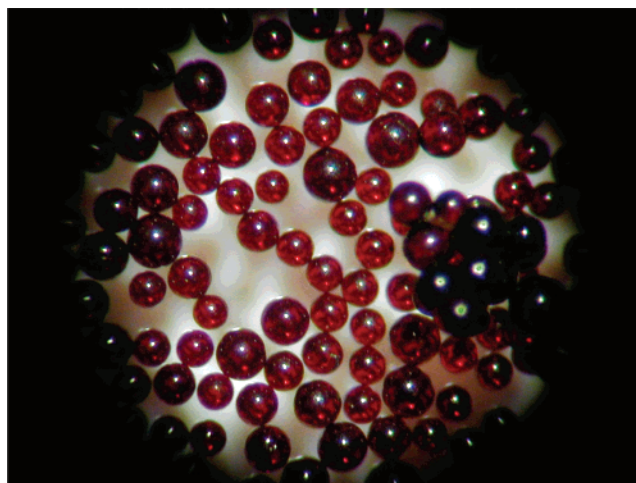
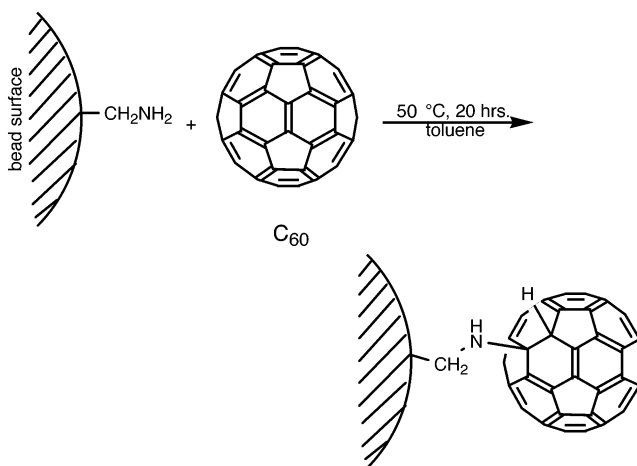
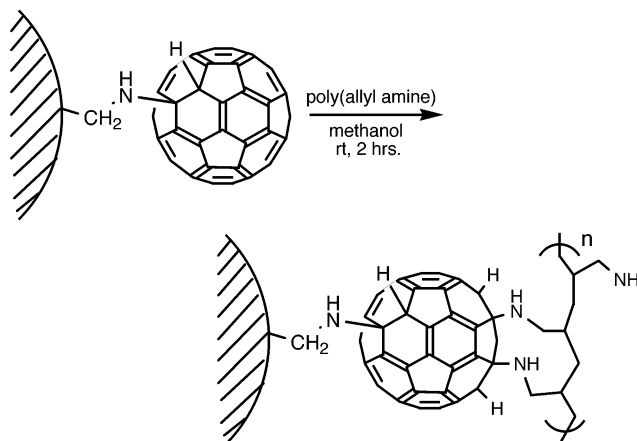


FIGURE 1. Digital photograph of Catalyst I.

SCHEME 1. Bead-Coating Reaction (Formation of Catalyst I)

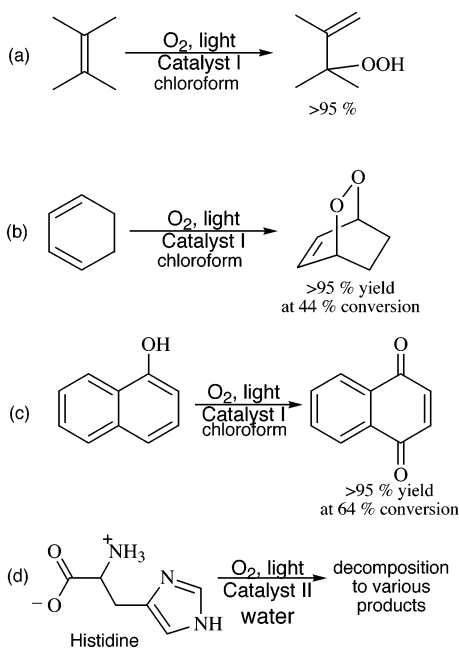


SCHEME 2. Formation of Aqueous Catalyst (Catalyst II)



After coating, the beads were briefly rinsed in toluene. Further rinsing, sonication, and Soxhlet extraction indicated that the initial washing had removed any fullerene molecules that were loosely associated with the bead surface. Before coating, the beads are clear. After coating they are reddish-purple (see Figure 1).

SCHEME 3. Catalysis with Catalyst I or Catalyst II



Four reactions were carried out to test the catalytic ability of the beads. The first three (a, b, and c in Scheme 3) are representative of classes of $^1\text{O}_2$ reactions (Ene reaction, Diels–Alder reaction, and oxidation of phenols). The last reaction (d in Scheme 3) was chosen to test Catalyst II because it is an aqueous reaction. All four reactions proved to be successfully catalyzed by either Catalysts I or II.

The first three reactions were all performed in CDCl_3 , so that the progress of the reactions could be followed by ^1H NMR. Tetramethylethylene (TME) is converted to 3-hydroperoxy-2,3-dimethyl-1-butene. Because the product of the TME oxidation does not absorb light > 280 nm, this reaction could be irradiated through Pyrex. Under these conditions, Catalyst I completely oxidizes TME to product cleanly in less than 1 h and 20 min, an order of magnitude faster than the previously reported irradiation time.¹⁰ Irradiation of 1,3-cyclohexadiene forms 5,6-dioxabicyclo[2.2.2]oct-2-ene as the only product by NMR after only 65 min. Rose Bengal catalysts give a 69% yield of bicyclic product after 9.5 h of irradiation of 1,3-cyclohexadiene.¹¹ Photooxidation of 1-naphthol gives 64% conversion to only 1,4-naphthoquinone (by NMR) after only 35 min. Previously, this reaction had been done with 90% yield after 10 h of irradiation with dissolved methylene blue sensitizer.²⁸

The L-histidine reaction is done in D_2O . The reaction of L-histidine with singlet oxygen forms multiple products.²⁹ The success of catalysis was therefore determined by ^1H NMR through comparison of the integration of histidine against an internal standard. Catalyst I was unable to oxidize histidine in D_2O ; however, Catalyst II did catalyze the reaction. When Catalyst II was used the histidine reaction was 24% complete after 1 h and 37%

complete after 2 h based on the ratios of starting material to the internal standard.

The bead loading for the beads with C_{60} was determined to be between 3 and 4.0% (of available amine sites) from direct bead counting of massed bead samples, as well as spectroscopic analysis of the original fullerene solutions used for coating. This is comparable to Rose Bengal-coated beads.¹¹ The low loading most likely occurs because many of the amine groups are within the core of the beads.

Bead reusability was checked by repeating the TME oxidation several times. The same beads were rinsed each time between uses with CHCl_3 to remove any product that may have adhered to the beads. The beads catalyzed the reactions each time to yield the same amount of product.

Conclusion

Heterogeneous catalysis of singlet oxygenations can be achieved with fullerene-coated polymer beads. The beads are easily prepared by stirring a heterogeneous mixture of C_{60} and the beads. Also, because only Catalyst II was able to decompose histidine in D_2O , it appears that poly-(allylamine) did successfully coat the fullerene layer of Catalyst I with hydrophilic amine groups. Thus, it should be possible to coat Catalyst I with layered polyelectrolyte structures or other architectures which may lead to stereoselective catalysts. Studies directed toward that end are in progress.²⁰

Experimental Section

Starting Materials and Reagents. Aminomethylpolystyrene resin (PL-AMS) beads (in the 50–100 mesh size) were obtained from a commercial source. C_{60} , ethyl acetate, DMF, toluene, ethanol, methanol, chloroform-*d*, methylene chloride, and deuterium oxide were high purity commercial samples. The tetramethylethylene, 1-naphthol, 1,3-cyclohexadiene, and L-histidine were also purchased from chemical suppliers and used without further purification.

General Procedure for Preparation of Catalyst I. C_{60} (100.0 mg) was dissolved in 50.0 mL of toluene by heating to 35 °C while stirring and using a water condenser to ensure no loss of toluene. (Sonication helps the C_{60} dissolve faster.) When the C_{60} was dissolved, the solution was dark purple. To this solution was added 500 mg of PL-AMS beads (50–100 mesh) with stirring for 20 h at 50 °C with a water condenser attached. The beads were filtered through a fritted vacuum funnel and washed with 2–100 mL aliquots of hot toluene (50 °C) until the color of the toluene passing through the filter was clear. The beads were allowed to completely dry on the vacuum funnel for 12 h. The vacuum funnel containing the dry beads was then placed on a new flask and the beads were rinsed with 200 mL of methylene chloride. (If the toluene is still wet on the beads, addition of CH_2Cl_2 causes them to break. When broken, the beads take on a brownish color, but still appear to catalyze the reactions.) The beads were then placed on a Petri dish and dried in a vacuum oven for 12 h at 45 °C.

Bead Loading. Bead loading was determined by two different methods: Spec. 20 and direct counting. The procedure for the Spec. 20 involved determining the concentration of the C_{60} remaining in the solvent after bead coating. This amount of C_{60} remaining was the amount that did not adhere to the bead surface. A calibration curve was plotted with absorbances at 600 nm. The absorbance of the washing was then measured and its concentration was calculated from the equation of the linear regression.

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The direct bead counting was carried out by counting a measured mass of uncoated (and then coated) beads under a 40 \times power dissecting microscope. The difference in mass per bead was determined, which is the value for the average amount of dye that was coated onto each bead. From this mass, the millimoles of C₆₀ per bead was determined. The millimoles of C₆₀ per bead was then divided by the number of millimoles of amine groups in the total mass of beads used. (The values for millimoles of amine sites are provided by the manufacturer of the beads.)

General Photochemical Reaction Procedure. Within a photochemical reaction chamber, the light source (450 W medium-pressure Hg arc lamp) was placed inside of a cylindrical Pyrex filter, which was then placed inside of a quartz water-cooled jacket. A square filter was clamped next to the jacket to block wavelengths below 330 nm (although it was found that the TME reaction can be run without this filter, vide supra). The reactants, solvent, and catalyst were placed into a Pyrex test tube for each reaction. The test tube was clamped against the square filter. Compressed air was bubbled through the reactions at a constant rate to maintain a constant supply of oxygen to the reaction and also to stir the beads, ensuring even exposure to the light source. The entire setup was submerged in an ice bath to keep each reaction at a relatively constant temperature.

Tetramethylethythlene Photochemical Reaction. Tetramethylethylene (TME, 2,3-dimethyl-2-butene; 0.14 mL) was placed in a Pyrex test tube containing 100.0 mg of Catalyst I and 5 mL of CDCl₃. The reaction was complete by ¹H NMR (formed only 3-hydroperoxy-2,3-dimethyl-1-butene as determined by NMR)¹⁰ after 1 h and 20 min (without the 330 cutoff filter). With the 330 cutoff filter, the conversion to product was 55% after 65 min (only 3-hydroperoxy-2,3-dimethyl-1-butene). This reaction was also conducted five additional times, rinsing the same beads with CHCl₃ each time to verify reusability of the beads. The reactivity each time was essentially the same.

1,3-Cyclohexadiene Photochemical Reaction. 1,3-Cyclohexadiene (0.11 mL) was added to a test tube containing 100 mg of C₆₀ Catalyst I and 5 mL of CDCl₃. The reaction was allowed to run for 65 min and was found to be 44% converted to only 5,6-dioxabicyclo[2.2.2]oct-2-ene as determined by ¹H NMR.¹¹

1-Naphthol Photochemical Reaction. 1-Naphthol (15 mg), 100 mg of C₆₀ catalyst (Catalyst I), and 10 mL of CDCl₃ were irradiated as described above. The reaction was 64% converted to only 1,4-naphthoquinone after 35 min as determined by ¹H NMR. When higher concentrations of 1-naphthol are used, the solution darkens to the point where ¹O₂ generation is inhibited.

General Procedure for Preparation of Catalyst II, Poly(allylamine)-Coated Catalyst. Catalyst I beads (75 mg) were stirred for 2 h in a solution of poly(allylamine) [1.9758 g of poly(allylamine)/89.0 mL of methanol]. The mixture was filtered through a fritted vacuum funnel and rinsed with 200 mL of H₂O. The beads were allowed to dry on the funnel for 2 h. The beads appeared to disperse in water much better than Catalyst I beads.

Histidine Photochemical Reaction. L-Histidine (35 mg) and D₂O (5 mL) were placed into a clean dry graduated cylinder and stirred until the histidine dissolved. A 1.0-mL portion was removed and spiked with 10 μ L of acetone (internal standard) for ¹H NMR comparison. The remaining 4 mL of D₂O and histidine mixture was transferred to a test tube. Catalyst II beads (70 mg) were added to the mixture and the reaction was allowed to run for 2 h. Samples (1 mL) were removed after 1 h and 2 h, 10 μ L of acetone was added to each sample, and ¹H NMR analysis was performed.

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