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Article

Chemistry

Nanocarbon-based TEMPO as stable heterogeneous catalysts for partial oxidation of alcohols

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Abstract Polymerized fullerene hollow spheres bonded with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) have been successfully synthesized via amination of C_{60} with 4-amino-TEMPO in the presence of H_2O_2, and then cross-linked by 1,6-hexanediamine. The hollow spheres were analyzed by fourier transform infrared spectrometer, electron spin resonance and X-ray photoelectron spectroscopy analysis, which indicated the presence of N–O free radicals in the products. When used as a typical heterogeneous catalyst for selective oxidation of alcohols to the corresponding aldehydes or ketones, it exhibited excellent activities, selectivity and recyclability. This synthesis route is convenient and effective, and may provide a new approach to developing immobilized fullerene based heterogeneous catalysts with high activity and recyclability.

Keywords Fullerene · Hollow sphere · TEMPO · Heterogeneous catalyst · Oxidation of alcohols

1 Introduction

Partial oxidation of alcohols to the corresponding aldehydes or ketones is a fundamental and pivotal transformation in organic chemistry [1–6]. Among all the catalysts, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a small organic molecular homogeneous catalyst has been attracting continuous attention over the past years [7–10]. However, it suffered from the difficulty in catalyst recycling from the products. To solve the above problem, methods to immobilize TEMPO via covalent bonding on the surface of supports such as silica [11, 12], polymers [13–15], and ionic liquids (ILs) [16–18] have been developed. However, most of the above catalysts were prepared in complicated methods, and they were prone to deactivation due to the instability of the supports. A better method is still desirable to prepare an active and stable heterogeneous catalyst bonded with TEMPO.

Very recently, Meng and co-workers [19] prepared a highly active porous polymerized 2,2,6,6-tetramethylpiperidine-1-oxyl (PPO-TEMPO) catalyst with high surface area, hierarchical porosity and superior chemical stability. Notably, compared to the silica, polymers, and ILs supports, carbon materials show significant tolerance to the chemical environments due to the inert stability [20, 21]. However, as far as we know, there is no report about TEMPO-bonding on the carbon support as heterogeneous catalyst for oxidation of alcohols. The difficulty may be in that carbon materials are not easy to be functionalized with TEMPO.

Fullerenes, as an important kind of carbon materials, are aromatic molecules with abundant double bonds, which can undergo a wide variety of reactions [22–24]. For example, Gruttadauria and co-workers [25] reported a novel fullerene functionalized with two TEMPO radicals and ten 1-propyl-3-methylimida-zolium bromide moieties

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($C_{60}IL_{10}TEMPO_2$ hybrid), and found that the functionalized fullerene could act as an excellent homogeneous catalyst for the selective oxidation of a wide series of alcohols. Our group reported C_{60} fullerenol (polyhydroxylated fullerene derivative) could be applied as an effective heterogeneous catalyst for Henry, Aldol, Michael addition and Friedel–Crafts reactions as well as cycloaddition CO_2 with various epoxides to produce cyclic carbonates [26, 27]. We also prepared amines functionalized C_{60} as a heterogeneous catalyst for Knoevenagel condensation and asymmetric intermolecular aldol reactions [28].

As part of our interests in fullerene catalysts, we herein show the polymerized fullerene bonded with TEMPO as an active and stable heterogeneous catalyst for partial oxidation of alcohols. The catalyst was rationally synthesized by the amination of C_{60} with 4-amino-TEMPO in the presence of H_2O_2, followed by cross-linked polymerization with 1,6-hexanediamine (HDA). Interestingly, hollow spheres were obtained for the final products. Fourier transform infrared spectrometer (FTIR), electron spin resonance (ESR) and X-ray photoelectron spectroscopy (XPS) analysis indicated the presence of N–O free radicals. Besides good activity and excellent selectivity, the catalyst showed outstanding recyclability for oxidation of alcohols.

2 Materials and methods

2.1 Preparation of C_{60}-TEMPO-HDA derivative

C_{60} 108 mg (0.15 mmol) was dissolved in 60 mL toluene, this purple solution was labeled as A. 4-Amino-TEMPO 257 mg (1.5 mmol, 10 equiv.) was dissolved in 4 mL water, then 0.51 mL H_2O_2 (30 wt%, 4.5 mmol, 30 equiv.) was added. This red solution was mixed with solution A, and 5 drops of tetrabutylammonium hydroxide (40 wt%) as a phase transfer catalyst was added. This mixture was stirred at 60 °C for 30 min, then HDA 174 mg (1.5 mmol, 10 equiv., in 2 mL water) was added and stirred for 30 min further. The upper liquid was removed, and 30 mL ethanol was added into the residual mixture. The solid was collected by filtration, and the filter cake was first washed with alcohol for 3 times, and then washed with water for 3 times. The product was dried at 60 °C for 12 h.

2.2 Preparation of MWCNT-TEMPO derivative, FWCNT-TEMPO derivative and RGO-TEMPO derivative

The multi-wall carbon nanotube (MWCNT)-TEMPO derivative was prepared by the following procedure. 50 mg MWCNT was dispersed in 5 mL ethanol with ultrasonic for 20 min, then 4-amino-TEMPO 119 mg (0.7 mmol), 0.3 mL H_2O_2 (30 wt%, 2.6 mmol) and 5 drops of tetrabutylammonium hydroxide (40 wt%) was added. After stirred for 24 h at 60 °C, the mixture was filtrated and washed with dichloromethane for 3 times. The product was dried at 60 °C for 12 h. The few-wall carbon nanotube (FWCNT)-TEMPO derivative and reduced graphene oxide (RGO)-TEMPO derivative were prepared in the same way except that FWCNT and RGO were used instead of MWCNT.

2.3 Characterizations

The morphology of the products was characterized by JEOL JEM-2100F transmission electron microscopy (TEM) (operating at an accelerating voltage of 200 kV) and JEOL-6701F scanning electron microscopy (SEM). The surface area was determined by N_2 adsorption/desorption isotherms using Quantachrome Autosorb AS-1 Instrument. Fourier transform infrared (FTIR) spectrum was performed on a TENSOR-27 type infrared spectrometer. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The ESR measurements were performed at room temperature on Bruker E500 instrument with continuous-wave X band. Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz for ^1H and ^{13}C using $(CD_3)_2SO$ as solvent. Elemental analysis was carried out on a Flash EA 1112 type elemental analyzer.

2.4 Typical procedure for oxidation of alcohols

A 1-octanol (1 mmol), chlorobenzene (0.5 mmol, as internal standard), dichloromethane (2 mL) and catalyst (10 mg) were added into a glass reactor, which was stirred in the ice bath. Then 3 mL NaClO solution (1.25 mmol, pH at around 9.1, in $NaHCO_3$ buffer solution) and KBr solution 0.2 mL (0.5 mol/L, 0.1 mmol) was added. After a stated time, the reaction solution was diluted with ethyl acetate, and the aqueous phase was removed. The products were analyzed by GC (SHIMADZU, GC-2010 Plus) and GC–MS (SHIMADZU, GCMS-QP2010s). To study the reusability of the catalyst, the catalyst was filtered and washed two times with dichloromethane before next cycle.

3 Results and discussion

Scheme 1 showed the synthetic route and proposed structure for polymerized fullerene bonded with TEMPO catalyst. It contained two steps under mild conditions: (1) C_{60}-TEMPO derivatives were first prepared through amination of C_{60} with 4-amino-TEMPO in the presence of H_2O_2; (2) C_{60}-TEMPO derivatives were then cross-linked by 1,6-