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Mn(III)-porphyrin/graphene oxide nanocomposite as an efficient catalyst for the aerobic oxidation of hydrocarbons

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ABSTRACT

In this study, manganese porphyrin was grafted on the surface of graphene oxide nanosheets via covalent bonding to produce a heterogeneous catalyst. The prepared nanocomposite was characterized using X-ray diffraction, UV–vis spectroscopy, scanning electron microscopy, Fourier transform infrared, and thermogravimetric analysis. Atomic absorption spectroscopy was also used to determine the amount of the loaded catalyst. The catalytic efficiency of the immobilized Mn-porphyrin was investigated for the aerobic oxidation of alkenes and saturated alkanes in acetone under mild reaction conditions. The prepared heterogenized catalyst displays superior catalytic performance as compared to the homogeneous catalyst. Moreover, the excellent turnover number (more than 31,767) achieved for the oxidation of styrene indicates the high longevity of the supported catalyst. The catalyst structure is preserved well after the oxidation reaction and is simply reused at least five times, without any significant loss of the catalytic efficiency.

1. Introduction

Catalytic oxidation of hydrocarbons in the liquid phase is a significant research area in synthetic organic chemistry due to the importance of the products being produced. These products are considered as valuable intermediates for the synthesis of various important substances, such as plasticizers, perfumes, and epoxy resins [1,2]. Since many years ago, metalloporphyrins as a useful model of cytochrome P-450 enzymes have held an important position in the catalytic oxidation reactions [3–6]. Recently, because of many benefits of heterogeneous catalysts like the ease of separation and reusability, metalloporphyrins are immobilized on the surface of various organic/inorganic substances for designing biomimetic heterogeneous catalysts [7–10]. According to the literature, different methods depending on the nature of solid supports and metalloporphyrins could be applied for the preparation of heterogenized metalloporphyrins. These methods mainly include encapsulation, adsorption, ionic interaction, axial coordination, and covalent bonding [11–14]. Graphene oxide (GO) with a large number of functional groups and a high surface area could be an excellent candidate as a solid support for the covalent immobilization of a variety of catalysts [15–17]. The use of green oxidants in the catalytic oxidation reactions remains an important challenge from the point of view of green chemistry [18,19]. Hydrogen peroxide as an inexpensive and environmentally friendly oxidant has been greatly used since long for catalytic oxidations of various organic substrates [20–22]. However, the instability of hydrogen peroxide in the catalytic reactions decreases its efficiency. This is considered as a major drawback in applying H_2O_2 as a green oxidant in the catalytic reactions. Molecular oxygen as a perfect oxidant with economically and environmentally friendly characters offers attractive prospects, especially in the industrial fields [23–25]. However, because of a poor product selectivity resulted for the catalytic oxidation reactions in which O_2 is used as an oxidant, many efforts have been focused on the

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mechanistic study of these reactions. In addition, a great deal of attention has been paid to developing the selectivity and efficiency of the aforementioned reactions. As a continuation of our work on the oxidation of various organic substrates with green oxidants catalyzed by supported metalloporphyrins [8,14,26], herein, we report a reusable, highly efficient catalyst for aerobic oxidation of hydrocarbons under mild conditions.

2. Experimental section

2.1. Materials and characterization

Analytical grade chemicals were purchased from Merck and Fluka and used without further purification. Fourier transform infrared (FT-IR) spectra were obtained using potassium bromide pellets in the range 400–4000 cm^{-1} on an ABB Bomem FTLA 200-100 spectrophotometer. A Varian AA240 atomic absorption spectrometer was used for manganese determination. The UV–vis spectra were recorded using a Cam-Spec-M330 model. Scanning electron micrograph was taken using an EDf Oxford Mat 50 (Tescan vega3, lab6 model, magnification: 100,000). Gas chromatography experiments were performed by an Agilent 7890B instrument using an SAB-5 capillary column (phenyl methyl siloxane 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector. The thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) was carried out using Mettler Toledo (TGA-DSC), and X-ray diffraction (XRD) was recorded by Philips PW3710 at the angle range of 5–150° using Cu Kα radiation.

2.2. Preparation of Mn(THPP)OAc

5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrin (H_2THPP) was successfully prepared by the addition of 4-hydroxybenzaldehyde (1.1 g, 14.5 mmol) and pyrrole (0.62 mL, 14.46 mmol) to refluxing propionic acid as described by Adler et al. [27]. Mn(THPP)OAc was also prepared according to the procedure reported elsewhere [28].

2.3. Preparation of GO

GO was synthesized from natural graphite powder according to the modified Hummers' method [15,29]. Briefly, H_2SO_4 (360 mL) and H_3PO_4 (40 mL) were stirred and the graphite powder (3 g) was added to the acidic solution and sonicated for 30 min. Then, $KMnO_4$ (18 g) was gradually added to the mixture with stirring in an ice bath. After that, the mixture was stirred for 24 h at 50 °C to achieve GO. Subsequently, the mixture was diluted with deionized ice water (400 mL), and the oxidized product was treated with H_2O_2 (6 mL) to remove the residual permanganate ions. The GO product was collected by centrifuge and dried at 60 °C before further use.

2.4. Preparation of [Mn(THPP)OAc@GO]

Mn-porphyrin was covalently grafted to the GO nanosheets by the ester bond forming between the porphyrin hydroxyl groups and carboxylic acid groups of the GO. In this process, TBTU ((2-1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate) as a highly effective uronium salt is used as an activation agent for carboxylic acids to prepare esters in the presence of DIPEA (*N*,*N*-diisopropylethylamine) by the following procedure [30,31]: GO (1.5 g), TBTU (0.4 g), and DIPEA (0.3 g) were added to a solution of Mn(THPP)OAc (0.63 g) in DMF (70 mL), and the reaction mixture was vigorously stirred at room temperature for 48 h. The black solids were then collected by filtration, washed thoroughly with ethanol, and dried at 50 °C for about 24 h. Mn-porphyrin was immobilized onto the GO surface via the ester bond as reported in our previous study. Preparation of the catalyst has been schematically described in Scheme 1.

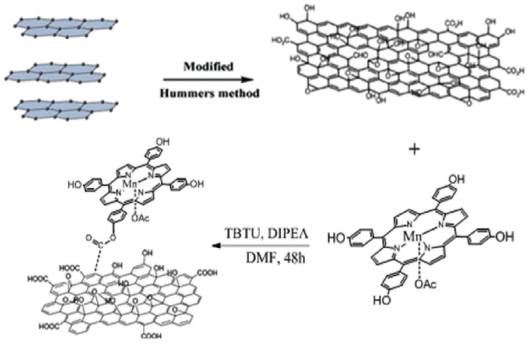
2.5. General procedure for aerobic oxidation of hydrocarbons

Oxidation of hydrocarbons (0.192 mmol) was initiated in a 5 mL test tube consisting of 1 mL acetone, 90 μL isobutyraldehyde (IBA) (0.960 mmol), 0.002 g catalyst, and 0.026 mmol imidazole (ImH) under the oxygen atmosphere, where the reaction mixture was stirred for 120 min at room temperature. The heterogenized catalyst was separated from the reaction media by a simple filtration. Gas chromatography was used to monitor the reaction progress, and the oxidation products were identified by comparison with the genuine samples.

3. Results and discussion

3.1. Characterization of the [Mn(THPP)OAc@GO] catalyst

Mn(THPP)OAc is anchored to the GO through covalent bonding between the hydroxyl group of the Mn-porphyrin and the carboxylic acid group of GO. The FT-IR spectra confirmed the covalent anchoring of Mn(THPP)OAc to the surface of GO (Fig. 1). An absorption band was observed at 856 cm^{-1} in the spectra of GO, which is related to the asymmetric epoxy on the GO surface [32]. Furthermore, the two peaks appeared at 1155 and 1596 cm^{-1} are respectively, related to the C–O and C=O stretching bands existing on the GO surface, and the broad peak observed at 3406 cm^{-1} corresponds to the –OH stretching band of GO. All these observations demonstrate that graphene was successfully converted to GO. In addition, the sharp peak



Scheme 1. Preparation of [Mn(THPP)OAc@GO].

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