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Short communication

Oxidation of styrene using TiO_2-graphene oxide composite as solid heterogeneous catalyst with hydroperoxide as oxidant

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ABSTRACT

The catalytic activity of TiO_2 nanoparticles supported on graphene oxide (GO) namely TiO_2/GO is reported in the oxidation of styrene (**1**) using *t*-butylhydroperoxide (TBHP) as an oxidant in acetonitrile at 70 °C. The oxidation of **1** results mainly in benzaldehyde (**2**) and styrene oxide (**3**) using TiO_2/GO as catalyst using TBHP as an oxidant. Furthermore, the product selectivity of **3** increases with increasing the wt% of TiO_2 on GO under the present reaction conditions. Also, the 5%TiO_2/GO catalyst was recycled for four cycles without any drop in conversion of **1** under the present experimental conditions.

1. Introduction

In a pioneering work, Shell has coproduced propylene oxide through the catalytic epoxidation of propylene with ethylbenzene hydroperoxide using a silica-supported titanium as heterogeneous catalyst [1]. Later, Sumitomo chemical company has developed a process for the epoxidation of propene to propene oxide which is fundamentally similar to the organic peroxide methods, but the major feature of the former is using a high performance epoxidation catalyst that uses cumene as the reaction medium [2]. However, design and synthesis of an efficient titanium based heterogeneous catalysts [3] for the epoxidation of olefins is an intensive research area due to the commercial importance of epoxides [4]. On the other hand, styrene oxide is synthesised through the epoxidation of **1** catalyzed by peracids [5], but although peracids show rather high catalytic activity, this process suffers in terms of formation of by-products like benzoic acid which would bring severe environmental pollution. Recently, considerable attentions have been paid on the epoxidation of **1** using safer and more environmentally friendly oxidizing agents, such as H_2O_2 [6], and TBHP [7]. This reaction has also been reported with solid heterogeneous catalysts like metal organic frameworks [8] and metal-coordination polymers [9]. In recent years, selective oxidation of **1** to benzaldehyde has been reported using CuO [10], WO_3 [11], molybdenum(VI)-oxodiperoxo complex anchored on the surface of magnetic nanoparticles [12], nickel mono substituted polymolybdophosphate [13] and Au nanoparticles supported on titania [14] as heterogeneous solid catalysts in the presence of TBHP as oxidant.

GO is a new class of two-dimensional carbon nanomaterials made up of conjugated sp^2 carbons arranged in a three dimensional honeycomb structure prepared by 'Hummers' method [15]. A vigorous oxidation of graphite into GO leads to the formation of oxygen-containing functional groups like –OH, –SO_3H, –COOH, epoxide, etc. These abundant deficient sites allow GO to behave as solid catalysts for the aerobic oxidation of tetralin [16] as well as acetalization of benzaldehyde [17] and ring opening of styrene oxide by methanol [18]. Recently, it has been reported that the existence of diverse defects, chemical functionalities on the graphene layers including oxygenated functional groups, carbon vacancies and holes, edge effects, and the presence of dopant elements can act as active sites in promoting a series of reactions like oxidations, acid catalyzed reactions and reduction reactions [19]. Furthermore, GO can also be used as a support for the immobilization of active species due to its high surface area and the resulting composite materials have been employed as catalysts for a variety of reactions [20,21].

TiO_2 based nanomaterials have been reported successfully for many electrochemical applications like oxygen reduction [22] and methanol oxidation [23]. TiO_2 based nanocomposites widely used in photochemical applications such as dye sensitised solar cells [24], hydrogen evolution reaction [25] and water treatment technologies [26].

Recently, GO/TiO_2 nanocomposite was reported as heterogeneous catalyst for the esterification of benzoic acid with dimethyl carbonate to give methylbenzoate [27]. It was also observed that the activity of GO/

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TiO_2 is superior to either with GO or TiO_2 or with the physical mixture of GO and TiO_2. Recently, macro-*meso* porous TiO_2-GO composite was reported for the epoxidation of olefins using TBHP as an oxidant [28]. Nano-sized TiO_2 was used as a catalyst for Aldol condensation reaction between acetone and furfural [29]. Continuing with this line of research, we wish to report here the catalytic performance of GO/TiO_2 nanocomposite in the oxidation of **1** using TBHP under mild reaction conditions. In addition, the effect of TiO_2 loading on GO in altering the product selectivity is also studied. Furthermore, the catalytic activity of TiO_2/GO is compared with GO, TiO_2 or with the physical mixture of GO and TiO_2 under identical reaction conditions.

2. Experimental section

2.1. Materials

Styrene, TBHP and hydrogen peroxide were purchased from Sigma-Aldrich and used as received without further purification. Also, acetonitrile and acetone were purchased from Alfa Aesar and used as received without any purification. Graphite powder was purchased from Sigma Aldrich and potassium permanganate (99%), sulfuric acid (98%), hydrogen peroxide (H_2O_2, 30% purified), hydrochloric acid (37%), TiO_2 were procured from Alfa Aesar. All the raw materials were of analytical grade and used as received.

2.2. Instrumentation methods

The as-synthesised catalysts were characterized by atomic force microscopy (AFM) (non-contact mode, A100 SGS, APE Research), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) (TECNAI, model - CM 200), powder x-ray diffraction (XRD) (Brucker D8 Advance X-ray Diffractometer) and FT-IR (Bruker optik). Conversion and selectivity were determined using Agilent 7820 gas chromatography with flame ionization detector using nitrogen as carrier gas. The oxidation products were confirmed by injecting the reaction mixture in gas chromatography coupled with mass spectrometry measurements with Perkin Elmer Clarius 500 spectrometer.

2.3. Synthesis of GO nanosheets

GO was obtained from Hummers and Offeman's technique [15] with a slight modification followed by exfoliation. In a typical synthesis, 120 ml of H_2SO_4 was taken in an ice bath and the temperature was maintained below 5 °C. To this solution, 5 g of graphite powder and 15 g of $KMnO_4$ was added slowly and allowed to stir for 24 h by maintaining the temperature not exceeding 35 °C. Then, 250 ml of deionized water was then slowly added to dilute the solution, which was further stirred for 2 h. Furthermore, 700 ml of deionized water and 20 ml of 30% H_2O_2 were added and stirred for 12 h. Then, the solution was washed with HCl to remove impurities. Then, the slurry was washed with deionized (1 L) water to remove the residual acid. This solution was then centrifuged at 5000 rpm and the precipitate was collected and dried to obtain graphite oxide. Then, 30 mg of graphite oxide was suspended in 20 ml of deionized water, and this mixture was stirred for about 10 min, followed by ultrasonication for 2 h to exfoliate GO nanosheets. This solution was then centrifuged at 5000 rpm and the precipitate was collected and dried to obtain GO nanosheets.

2.4. Synthesis of 5 wt% TiO_2/GO nanocomposite

An appropriate amount of GO suspension was concurrently added with 5 wt% of TiO_2 NPs suspended in 200 ml of deionized water and ultrasonication was performed for 10 min. Further, this suspension was magnetically stirred for 24 h to obtain TiO_2/GO nanocomposite. The above mixture was then washed with deionized water through centrifugation at 5000 rpm and the precipitate was collected and dried to obtain TiO_2/GO nanocomposite.

2.5. Experimental procedure for oxidation of 1

In a typical reaction, 20 mg of a given catalyst was added to a solution of 1 mmol of styrene dissolved in 2 ml of acetonitrile in a 30 ml glass reaction tube. This reaction mixture was placed on the pre-heated oil bath maintained at 70 °C. Then, TBHP was added to this reaction mixture as an oxidant and stirred continuously for the required time. Samples were taken periodically to determine the reaction kinetics and product selectivity in GC using nitrobenzene as internal standard. The oxidation products were confirmed by GC–MS analytical technique. Reusability experiments were performed by following the same procedure as described above except that the catalyst is removed from the reaction mixture by centrifugation and washing with acetonitrile.

3. Results and discussion

The as-synthesised TiO_2/GO nanocomposite was prepared by adopting an earlier reported procedure [27]. This composite has already been well characterized by UV–visible spectroscopy, FT-IR spectroscopy, powder X-ray diffraction, scanning electron microscope, transmission electron microscopy and atomic force microscope techniques (See supporting information) [27]. Three different weight loadings of TiO_2 were supported on GO namely 1, 3 and 5 wt% and they are referred as 1%TiO_2/GO, 3%TiO_2/GO and 5%TiO_2/GO, respectively. The catalytic activity of these nanocomposites was studied in the oxidation of **1** using TBHP as an oxidant in acetonitrile at 70 °C. Table 1 shows the oxidation of **1** with TiO_2/GO as catalyst using TBHP as oxidant and the various oxidation products formed under the present experimental conditions. This reaction afforded benzaldehyde (**2**), styrene oxide (**3**), acetophenone (**4**) and benzoic acid (**5**) as the oxidation products under the present reaction conditions. Although the formation of products like **2**, **3** and **5** is quite common in the oxidation of **1**, the detection of product **4** in the oxidation of **1** is also reported with oxovanadium(IV) complexes covalently anchored on SBA-15 [30], Pd in ionic liquids [31], ultra-thin gold nanowire [32], Au-Pd/Al_2O_3 [33] and a metal–organic framework assembled from palladium porphyrin building blocks and cadmium(II) connecting nodes as catalyst [34]. In general, the conversion was mainly dependent on the concentration of oxidant and the catalyst loading.

The use of 5%TiO_2/GO afforded 72% conversion of **1** with 54% of **2** and 31% of **3** (entry 1, Table 1) whereas reducing the TBHP concentration under identical catalyst loading reduced the conversion to 64% without much variation in the product distribution between **2** and **3** (entry 2, Table 1). Under identical conditions, a blank control experiment in the absence of catalyst gave 16% conversion of **1** with 1 mmol of oxidant (entry 2, Table 1). On the other hand, a significant decrease in the conversion of **1** was noticed either in decreasing the catalyst loading of 5%TiO_2/GO or TBHP concentration (entries 3–4, Table 1) but, however, the product selectivity towards **2** enhanced to 75% while the product selectivity to **3** decreased to 15%. Similarly, the use of 3%TiO_2/GO gave 45% conversion of **1** with 80% selectivity to **2** and 10% to **3** (entry 5, Table 1). Furthermore, decreasing the loading of catalyst showed a negligible influence on conversion of **1** and selectivity of **2** and **3** (entry 6, Table 1), while decreasing TBHP from 2 to 1 mmol under identical catalyst loading showed a significant decrease in the conversion of **1** (entry 7, Table 1) but did not alter the product selectivity. On the other hand, the conversion of **1** was 34% with identical catalyst loading (20 mg) using 1%TiO_2/GO as catalyst with the selectivity to 90% for **2** (entry 8, Table 1). It is interesting to note that the product selectivity to **3** decreases considerably with 1%TiO_2/GO compared to 3% and 5%TiO_2/GO catalysts under identical conditions (entries 2, 5 and 8, Table 1). On the other hand, the catalytic activity of 5%TiO_2/GO composite was compared with the physical