12-Molybdophosphoric acid anchored on aminopropylsilanized magnetic graphene oxide nanosheets (Fe₃O₄/GrOSi(CH₂)₃–NH₂/H₃PMo₁₂O₴₀): a novel magnetically recoverable solid catalyst for H₂O₂-mediated oxidation of benzylic alcohols under solvent-free conditions

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In this work, 12-molybdophosphoric acid (H₃PMo₁₂O₴₀, HPMo) was chemically anchored onto the surface of aminosilanized magnetic graphene oxide (Fe₃O₄/GrOSi(CH₂)₃–NH₂) and was characterized using different physicochemical techniques, such as powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), BET specific surface area analysis and magnetic measurements. The results demonstrated the successful loading of HPMo (~31.5 wt%) on the surface of magnetic aminosilanized graphene oxide. XRD patterns, N₂ adsorption–desorption isotherms and SEM images confirm the mesostructure of the sample. FT-IR and EDX spectra indicate the presence of the PMo₁₂O₴₀⁻⁻ polyanions in the nanocomposite. The as-prepared Fe₃O₄/GrOSi(CH₂)₃–NH₂/HPMo nanocomposite has a specific surface area of 76.36 m² g⁻¹ that is much higher than that of pure HPMo. The selective oxidation of benzyl alcohol to benzaldehyde was initially studied as a benchmark reaction to evaluate the catalytic performance of the Fe₃O₄/GrOSi(CH₂)₃–NH₂/HPMo catalyst. Then, the oxidation of a variety of substituted primary and secondary activated benzylic alcohols was evaluated with H₂O₂ under solvent-free conditions. Under the optimized conditions, all alcohols were converted into the corresponding aldehydes and ketones with very high selectivity (≥99%) in moderate to excellent yields (60–96%). The high catalytic performance of the nanocomposite was ascribed to its higher specific surface area and more efficient electron transfer, probably due to the presence of GrO nanosheets. The nanocomposite catalyst is readily recovered from the reaction mixture by a usual magnet and reused at least four times without any observable change in structure and catalytic activity.

1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds, i.e., benzyl alcohol to benzaldehyde, is one of the most important and vital transformations in synthetic organic chemistry. Typically, the chemoselective oxidation of alcohols to aldehydes or ketones without traceable over-oxidation products (i.e., carboxylic acids) is attractive for the preparation of fine chemicals owing to the nature of aldehydes or ketones as an intermediate for producing carbonyl products, which are of great importance and versatility for the chemical industry and pharmaceutical synthesis. Numerous efforts on developing efficient catalysts towards these oxidations have been progressed and reported. Solvent-free approach is an attractive green process for selective oxidation of benzyl alcohol and oxidants like molecular oxygen, hydrogen peroxide (H₂O₂) and TBHP are in the order as green options. Molecular oxygen as oxidant is not very active, while H₂O₂ is an active oxygen donor in catalytic oxygen-transfer reactions. However, most of the catalyst systems using H₂O₂ are based on noble metals such as Pt, Pd, and Ru which are expensive and difficult to synthesize. From the practical and environmental points of view, there is a strong demand for the screening out efficient catalytic systems using inexpensive and environmentally benign metal catalysts and non-toxic H₂O₂ or O₂ as the sole terminal oxidant. In this context, polyoxometalates (POMs) are definitely an attractive alternative in terms of economic viability and easy-to-manufacture alternative with a heterogeneous nature.

Polyoxometalates (POMs) are a large family of bulky clusters of transition metal oxide anions with structural diversity. Among various POMs, Keggin-type heteropoly acids (e.g. H₃PMo₁₂O₴₀ and H₃PW₁₂O₴₀) have received much attention and
numerous organic transformations can be catalyzed by them, not only due to their controllable and reversible multielectron redox and acidic properties, but also due to their environmentally benign behavior.\textsuperscript{4–10} Moreover, these compounds have moderately high thermal stability in solid state, relatively simple synthesis procedure, and ability to form pseudo-liquid phases.\textsuperscript{11} In spite of the above advantages, there exist two major drawbacks in the catalytic systems involving pristine POMs: (i) low surface area in nonpolar solvents (<10 m\textsuperscript{2} g\textsuperscript{-1}) hindering accessibility of reactants to active sites and (ii) high solubility in polar solvents producing recovery and reuse problems. To overcome these obstacles, many researchers have tried to design heterogeneous catalysts by incorporating HPAs into the structure of solid supports such as SiO\textsubscript{2},\textsuperscript{12,13} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{14} activated carbon,\textsuperscript{15} TiO\textsubscript{2},\textsuperscript{16} zeolites,\textsuperscript{37} organic materials,\textsuperscript{18,19} clays,\textsuperscript{20} ZrO\textsubscript{2}–CeO\textsubscript{2} (ref. 21) and metal–organic frameworks (MOFs).\textsuperscript{22,23} However, most of these supports have some limitations, such as low loading of POM, high leaching of POM especially in polar medium and/or active sites that are unevenly dispersed. Therefore, finding suitable solid supports to overcome the drawbacks is important. Supports modified with functional groups such as carboxylic groups, lactam, amide, imide or amino-groups can allow solving this problem.\textsuperscript{24,25} Especially, the amino-modified metal oxides supports are commonly used for immobilizing POMs not only because of the exceptionally high stability and surface area but also because the amount and the basicity of anchored functional amino groups can be expected to be important in determining the guest–host interactions of the materials.\textsuperscript{26–29} This approach allows obtaining high dispersion of the POMs with minimal leaching. Despite facile recovery, such heterogeneous POM catalysts often suffer from the poor accessibility of the H\textsubscript{2}O\textsubscript{2} during the oxidation of alcohols with aqueous H\textsubscript{2}O\textsubscript{2} due to the hydrophobicity of support. Hence, enhancing the accessibility of the oxidant is crucial to the heterogeneous catalyst in the alcohols oxidation with H\textsubscript{2}O\textsubscript{2}.

Among various carbon-based nanomaterials, graphene oxide (GrO) has been proven as an effective support for the immobilization of inorganic and organic materials owing to its large theoretical specific surface area (~2630 m\textsuperscript{2} g\textsuperscript{-1}) and the presence of numerous oxygen containing functional groups on its surface.\textsuperscript{31–39} Due to these rich functional groups, GrO can be easily reacted with organic molecules to generate stable chemically functionalized GrO.\textsuperscript{39} In addition, in comparison with other carbonaceous nanomaterials, GrO may be more environmental friendly and have better biocompatibility.\textsuperscript{40} However, it is difficult to separate GrO from aqueous solutions using traditional filtration and centrifugation methods during and after the process due to its hydrophilic nature and small particle size which increases the cost of industrial application.\textsuperscript{41} The magnetic separation method is considered as a rapid and effective technique for separating nanomaterials from aqueous solution.\textsuperscript{42–45} Hence, magnetic graphene-based composites with large specific surface area and magnetic separation have begun to be used in the field of organic transformations.\textsuperscript{46–50}

On the basis of the above discussions, in this work, aminoorganosilane functionalized magnetic graphene oxide (Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2}) was synthesized by a facile method and used as a novel magnetic GrO-based support. Due to relatively high surface area and porosity, insolubility in water and easy magnetically separation, the Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2} is an appropriate solid support to anchor Keggin-type PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3–}polyanion. The ternary magnetic nanocomposite material (abbreviated as Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2}/HPMo) was prepared by a simple acid–base electrostatic interaction between H\textsubscript{3}PMo\textsubscript{12}O\textsubscript{40} and amino groups of the Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2} support. The coupling of PMo\textsubscript{12}O\textsubscript{40}\textsuperscript{3–} anion with Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2} could improve the surface area and avoid the dissolution of HPMo. This novel magnetically recyclable heterogeneous catalyst was used for selective oxidation of alcohols with H\textsubscript{2}O\textsubscript{2} as a green oxidant under solvent free conditions. Our catalysts showed high catalytic performance in H\textsubscript{2}O\textsubscript{2}-mediated alcohol oxidations under solvent-free conditions. The resulting Fe\textsubscript{3}O\textsubscript{4}/GrOSi(CH\textsubscript{2})\textsubscript{3}NH\textsubscript{2}/HPMo composite could be used as a magnetically separable and efficient catalyst for alcohol oxidation under solvent free conditions.

2. Experimental

2.1 Materials

12-Molybdophosphoric acid (H\textsubscript{3}PMo\textsubscript{12}O\textsubscript{40}, 98%), graphite powder (C, 99.95%) and 3-aminopropyltriethoxysilane (APTES, 99%) were purchased from Merck Chemical Co. All alcohols and other chemicals were commercially purchased and used without further purification.

2.2 Preparation of aminosilanized magnetic graphene oxide

Graphene oxide (GrO) was prepared by the modified Hummers method through the oxidation of graphite powder.\textsuperscript{51–53} Briefly, graphite powder (2.0 g) and NaNO\textsubscript{3} (1.0 g) were mixed with 40 mL of concentrated H\textsubscript{2}SO\textsubscript{4} in a 500 mL flask and stirrer for 1 hour in an ice bath. Then KMnO\textsubscript{4} (6.0 g) was added into the vigorously stirred suspension slowly below 15 °C. The ice bath was then removed, and the mixture was stirred at room temperature until it slowly became a brownish slurry, and then it was diluted with 100 mL of water. The reaction temperature was rapidly increased to 98 °C with effervescence, and the color changed to brown. After that, 200 mL of water and 20 mL of H\textsubscript{2}O\textsubscript{2} (30 wt%) were added. For purification, the mixture was centrifuged and washed with 10% HCl and then deionized water several times to remove the residual metal ions and acid. After centrifuging and drying at room temperature, GrO was obtained as a powder. To prepare Fe\textsubscript{3}O\textsubscript{4}/GrO, 0.25 g of GrO was dispersed in 90 mL water by sonication for 1 hour. Then, 0.84 g of (NH\textsubscript{4})\textsubscript{2}Fe(SO\textsubscript{4})\textsubscript{2} and 2.08 g of (NH\textsubscript{4})Fe(SO\textsubscript{4})\textsubscript{2} were added to the GrO dispersion and its pH was adjusted at 12 by adding 1 mol L\textsuperscript{-1} NaOH. The mixture was stirred at 50 °C for 2 h, filtered and washed with water and ethanol three times. The resulting solid was Fe\textsubscript{3}O\textsubscript{4}/GrO. To prepare amino functionalized magnetic graphene oxide, 0.40 g of the as-synthesized Fe\textsubscript{3}O\textsubscript{4}/GrO dispersed in 50 mL of water, 150 mL ethanol and 5 mL of 3-aminopropyltriethoxysilane (APTES) were added to a round bottom flask. The mixture was stirred for 30 min in room