



# Nano-sized glass as an economically viable and eco-benign support to anchor heteropolyacids for green and sustainable chemoselective oxidation of sulfides to sulfoxides

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**Abstract.** In this work, glass wastes were employed as cost-effective supports for the immobilization of phosphomolybdic acid (5–25 wt.% PMA) through an impregnation method. The highly efficient and retrievable nanocatalyst named nano-glass waste-supported phosphomolybdic acid (n-GW/PMA) was fully characterized by several techniques such as: XRD, FE-SEM, EDX, FT-IR and TGA. The catalytic performance of the as-synthesized heterogeneous nanocatalyst was effectively investigated for the chemoselective oxidation of sulfides to sulfoxides in the presence of 30% H<sub>2</sub>O<sub>2</sub> as an oxidant at room temperature under solvent-free condition. Optimization of the reaction conditions was performed by means of central composite design (CCD), which is one of the powerful response surface methodologies. Based on the results obtained under the optimum condition, the sample of 16 wt.% of PMA loading offered high conversion rates and yields (97%). Besides, the beneficial points of the prepared catalyst were its recoverability and reusability for several reaction cycles, low-cost and toxicity, easy availability and facile production.

**Keywords.** Nano-glass; phosphomolybdic acid; impregnation method; nanocatalyst; sulfide oxidation; reusability.

## 1. Introduction

During the last decades, in the light of green chemistry approaches, implementation of more sustainable practices in industries has been undergoing considerable alteration. Green chemistry strives to protect the health and the environment in a cost-effective manner. In this context, significant improvement has been made for designing safer chemicals and eco-friendly solvents and catalysts. Catalysis is the central focus of green chemistry research in 21<sup>st</sup> century due to its applications in various systems with reduced toxicity, renewable and benign energy, and high reaction efficiency. Based on these facts, preparation of heterogeneous analogues of the most commonly used soluble and homogeneous catalysts can be approached through their immobilization on different insoluble supports. In the light of this situation, the simplification of catalyst removal and the

limitation in the amounts of wastes produced have been accomplished. However, in such heterogeneous systems, catalyst recovery through filtration or precipitation would be a major issue because of considerable time- and energy-consumption. Additionally, on account of the heterogeneous nature of the support materials in reaction media, steric and diffusion factors, the immobilized catalysts show a substantial decrease in the activity and selectivity.<sup>1,2</sup> Besides, in the systems where a great proportion of active species are deep inside the supporting matrix, the reactants encountered difficulties for accessing to the catalytic active sites.<sup>3</sup> Hence, for the economic viability preservation, the designed heterogeneous systems must exhibit the advantages with respect to minimization of waste formation, comparable or higher catalytic activities and selectivity over the existing homogenous routes. To address these challenges, nanoparticles (NPs), the alternative soluble matrixes,

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have been applied to support homogeneous catalysts or reagents. The advantages of the support materials lie with increasing the surface area on the basis of their nanometer sizes, higher catalyst loading capacity and dispersion comparable to the most common support matrixes.<sup>4-6</sup>

Polyoxometallates (POMs) stand for a diverse family of anionic metal oxide molecular species, which span a rich variety of sizes and shapes, with outstanding properties and functions as acid and redox catalysts both in the homogeneous and heterogeneous media.<sup>7</sup> Heteropolyacids (HPAs), an extremely large and varied class of polyoxometallates, as powerful oxidants, can display fast reversible multi-electron redox transformation under mild condition.<sup>8</sup> Thanks to their unique properties, heteropolyacids can open up the opportunity for catalyzing the reactions in both solution and solid state lowering the production of wastes or by-products. There is a plethora of large scale industrial transformations catalyzed by HPAs including alcohol dehydration, alkylation and esterification, etc.<sup>9,10</sup> However, the main drawbacks of HPA are pertained to their low surface areas and high solubility in polar solvents which render difficulties in respect of their recovery and catalytic useful life. Addressing these issues, such catalytically efficient HPAs are frequently immobilized onto the insoluble, easily separable solid matrixes with high surface areas<sup>7,11-13</sup> The attractive feature related to the supported HPAs is the fact that they are more active than typical solid acids. So far, numerous support materials such as silica,<sup>14</sup> zeolite,<sup>15</sup> alumina,<sup>16</sup> active carbon<sup>17</sup> and ion-exchange resin<sup>18</sup> have been employed for the immobilization of HPAs. However, the alternative routes show some problems including the formation of deposit (coke) on the catalyst surface which makes these types of supported catalysts to be susceptible against deactivation during organic reaction<sup>7</sup> In addition, HPAs supported on solid matrixes are prone to leaching in polar solvents which limit their reusability. Therefore, there is still much room for the improvement of such systems through the application and design of stable, inexpensive, active and available solid support for binding of HPAs. In this context, we postulated that the application of waste materials or products as solid supports for the immobilization of HPAs could provide a golden chance which one could achieve three goals, at the same time: (i) The waste materials or products can be recycled and in the subsequent step, the drastic impacts on the environment can be mitigated. (ii) An efficient solid heterogeneous catalyst can be prepared through the heterogenization of HPAs. (iii) An organic transformation can be rapidly catalyzed in a mild reaction condition.

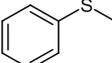
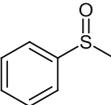
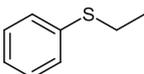
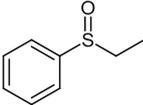
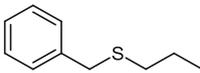
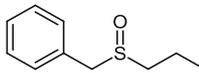
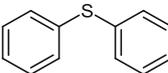
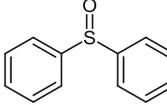
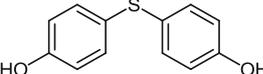
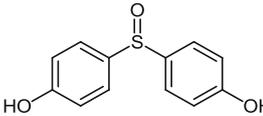
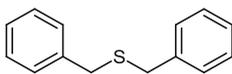
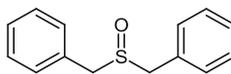
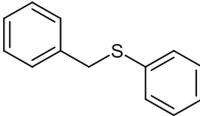
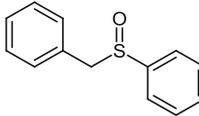
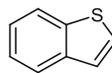
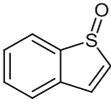
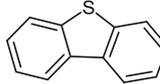
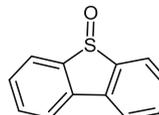
Glass in many forms such as packaging or container glass (bottles and jars), flat glass (windows and wind-screens), bulb glass (light globes) and cathode ray tube glass (TV screens, monitors, etc.), have a limited life. Therefore, it is essential to reuse or recycle them so as to prevent environmental problems related to their stockpiling or sending to the landfill.<sup>19</sup> As a result, we thought that the utilization of nano-glass waste for supporting heteropolyacids could go a long way towards the simultaneous reaching the above-mentioned targets. In this context, recently we reported nano-glass waste-supported sulfonic acid as an accessible, stable, recoverable, non-toxic and inexpensive solid acid nanocatalyst for multicomponent reactions.<sup>20</sup> However, to the best of our knowledge there are no literature reports on the exploitation of glass wastes for the immobilization of the highly applicable heteropolyacids. Among heteropolyacids, we chose phosphomolybdic acid (PMA) because it is one of the least expensive commercially available one. In continuation of our attempts for the preparation of different solid acid catalyst,<sup>21-28</sup> the present study consists of the synthesis of a novel solid acid nanocatalyst named nano-glass waste-supported phosphomolybdic acid (n-GW/PMA) and its application for the facile, fast, highly efficient, and chemoselective oxidation of sulfides to sulfoxides in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant under solvent-free conditions. Afterwards, the newly synthesized n-GW/PMA was fully characterized through FT-IR, EDX, FE-SEM and TGA techniques. The specific advantages of the catalyst are related to its high stability, facile recoverability, reusability, easy accessibility and low cost.

## 2. Experimental

### 2.1 Chemicals and apparatus

All the chemicals were purchased from Merck and Aldrich companies and used without any further purification. Glass wastes were provided from Sandis (Iran). Powder making of the glass waste was carried out through a two-cup planetary ball mill. The products purity was checked through thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using n-hexane/ethyl acetate mixture as mobile phase. All yields refer to the isolated products after purification. Products were characterized by melting points and spectroscopic data (FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra). Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. Fourier transform infrared spectroscopy (FT-IR) was recorded on a Shimadzu 8400 s spectrometer using KBr pressed powder discs. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a Bruker Avance 400 Ultrashield NMR spectrometer, in pure

**Table 1.** Oxidation of sulfides to sulfoxides in the presence of n-GW/PMA<sup>a</sup>.

Entry	Sulfide	Sulfoxide	T [min]	Yield[%] <sup>b</sup>	Selectivity (%)
1			25	91	100
2			15	96	100
3			10	95	100
4			10	95	100
5			65	83	100
6			10	97	100
7			20	95	100
8			25	88	100
9			50	91	100
10			60	92	100

<sup>a</sup>Reaction condition: sulfide (1 mmol), 30% H<sub>2</sub>O<sub>2</sub> (2.4 eq.) and n-GW/PMA 16. Wt. % (12 mg), solvent free, r.t.

<sup>b</sup>Yields refer to isolated products.

deuterated chloroform with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TGA) were performed on a DuPont 2000 thermal analysis apparatus at a heating rate of  $5^{\circ}\text{C min}^{-1}$  under air atmosphere. X-ray diffraction (XRD) was recorded by Philips using Cu-K $\alpha$  radiation of wavelength 1.54 Å. Field emission scanning electron microscope (FE-SEM) images were obtained through Tescan-vega II XMU Digital Scanning Microscope. The EDX spectra were acquired with the aid of a Mira 3-XMU scanning electron microscope equipped with an energy dispersive X-ray spectrometer operating. A central composite design (CCD) was performed to optimize the reaction condition for the oxidation method. 20 data analyses were carried out using Design-Expert trial version 7.0.0. (Stat-Ease Inc., Minneapolis).

## 2.2 Preparation of the neat glass waste powder

After washing glass wastes with 200 mL methanol and ethanol, they were turned into fine powder. Then, the prepared powder (20 g) was carefully washed with excess amount of distilled water three times. Afterwards, precipitated glass powder was filtered and rinsed with excess amount of water and then dried at  $120^{\circ}\text{C}$ .

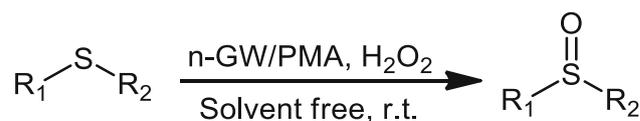
## 2.3 Synthesis of the glass waste-supported phosphomolybdic acid

The n-GW/PMA with the loadings of 5–25 wt.% were prepared by the aid of the wetness impregnation method. Typically, 2 g of n-GW was impregnated with an aqueous solution of PMA (0.06–0.375 g in 10–50 mL double distilled water). The mixture was vigorously stirred overnight at room temperature. Then, the water was completely evaporated using a rotary evaporator and the green sample was prepared after drying and calcination at  $150^{\circ}\text{C}$  for 2 h.

## 2.4 General procedure for the catalytic oxidation of sulfides

To a reactor equipped with a stirrer bar, a mixture of sulfide (1 mmol), 30%  $\text{H}_2\text{O}_2$  (2.4 eq.) and the n-GW/PMA 16Wt.% (12 mg) was added and allowed to be stirred at room temperature for appropriate time indicated in the Table 1. The progress of the reaction was monitored by TLC (n-hexane: EtOAc, 9:1). After the reaction was completed, the mixture was diluted with  $\text{Et}_2\text{O}$  (10 mL) and the catalyst was separated through centrifugation. Then, the combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and diethyl ether was evaporated under reduced pressure to afford the pure products in 83–97% yields.

2.4a 4, 4'-sulfinyldiphenol (Table 1, entry 6): IR (KBr)  $\nu/\text{cm}^{-1}$ : 3236, 2923, 1583, 1496, 1438, 1365, 1139, 1000, 721, 690;  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ , 400 MHz)  $\delta_{\text{H}}$ (ppm): 10.08 (s, 2H), 6.8–7.7 (dd, 8H);  $^{13}\text{C NMR}$  ( $\text{DMSO-d}_6$ , 400 MHz):  $\delta_{\text{C}}$  (ppm): 116.52, 127.04, 135.41, 160.07.



**Scheme 1.** Nano-GW/PMA catalyzed oxidation of sulfides to sulfoxides using  $\text{H}_2\text{O}_2$ .

2.4b dibenzo[b,d]thiophene 5-oxide (Table 1, entry 10): White solid, M.p.:  $215\text{--}217^{\circ}\text{C}$ . IR (KBr)  $\nu/\text{cm}^{-1}$ : 3083, 2982, 1591, 1452, 1288, 1164, 1047, 711, 698;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta_{\text{H}}$ (ppm): 7.5–7.8 (m, 8H).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta_{\text{C}}$  (ppm): 120.57, 121.132, 129.35, 130.57, 132.87, 136.65.

## 2.5 Investigation of the catalytic activity of n-GW/PMA for the oxidation of sulfides to sulfoxides

Owing to the fact that organic sulfoxides have been widely used in variable pharmaceutical and agrochemical sectors, the selective oxidation of sulfides to sulfoxides are considered as an important transformation in organic synthesis.<sup>29,30</sup> As a consequence, we were inspired by the investigation of the catalytic activities of our synthesized n-GW/PMA as a heterogeneous nanocatalyst for the chemoselective oxidation of structurally diverse sulfides to sulfoxides in the presence of 30%  $\text{H}_2\text{O}_2$  as an oxidant (Scheme 1).

Aiming at establishing the optimum reaction condition, we studied the model reaction of 4, 4'-thiodiphenol oxidation. At first, we tested the model reaction without any catalyst but the results were unsatisfactory (i.e., the yields were negligible (28%) in the prolonged reaction time (2 h)). Therefore, it was understood that the presence of the catalyst in the reaction was essential. Then, for acquiring the best condition for the oxidation reaction, central composite design (CCD) was chosen. When the number of effective parameters are lower than/or equal to four, central composite design (CCD), as one of the most applicable types of response surface model (RSM), could be helpful.

At the outset, preliminary experiments were performed for the evaluation of the suitable parameters and for the determination of the experimental domain. Considering these experiments, the effects of catalyst amount (A), PMA loading (B) and  $\text{H}_2\text{O}_2$  concentration (C), were studied on reaction yield as response in 10 min. Optimization is performed in condition at which the optimal parameters can be employed for all of the used derivatives. Since time was variable about each derivatives, it was not optimized. Therefore, in the optimization process, each run was tested in 10 min. A five-level CCD of three independent variables with their corresponding values was displayed in Table S1 in Supporting Information.

Based on the CCD method, total number of experiments was found to be twenty, which were comprised of eight full factorial points, six axial points and six central points. Conditions of 20 trials in addition to their respective yields are shown in Table S2 (See Supporting Information).

With the aid of performing analysis of variance (ANOVA) on the model, valuable information about significance of fitted model and its terms were achieved. According to the Table S3 (Supporting Information), the model *p*-value and lack of fit were lower and higher than 0.05, respectively indicating the fact that, fitted model was significant in confidence level of 95% and it was not needed to reduce to lower orders. Besides, the amounts of *R*-squared and adj *R*-squared were above 0.9 and close to each other which was a testimony for the high accuracy and reliability of the fitted model in prediction of the reaction yield. It was meant that there was a good agreement between experimental and the predicted responses which approved the suitability of the following fitted model regarding the significantly linear, quadratic and interaction terms based on their *p*-values.

$$Y = +1.90313 + 6.42339 A + 4.54018 B + 16.29883 C + 0.030000 AB - 0.16667 AC - 0.50000 BC - 0.27761 A^2 - 0.11497 B^2 - 1.07532 C^2$$

It can be found from the response equation that the three A, B and C parameters showed a linear effect on the product yield, therefore all factors (i.e., the amount of catalyst, PMA loading and H<sub>2</sub>O<sub>2</sub> concentration) were important in progressing of the reaction. In order to investigate the main interaction effects between two parameters on the yield of reaction, three and two dimensional profile of yield versus a pair of parameters were used (Figure S18 in Supporting Information).

Based on their *p*-values, it could be realized that the interaction of AB, AC and BC were significant; therefore, the simultaneous changing in the catalyst amount, PMA loading and H<sub>2</sub>O<sub>2</sub> concentration could alter the product yield. When catalyst amount (12 mg), PMA loading (16 wt.%) and H<sub>2</sub>O<sub>2</sub> (2.4 equiv.) were applied in the reaction, the product yields and the desirability were 96.92% and 0.99, respectively. The main target of this design was to optimize and maximize the yield of the reaction corresponded to the conditions of an experiment in which the response equation was maximized. In this work, determination of the optimal conditions was done with the help of desirability function by using Design-Expert 7.0.0. It was initially selected desired goals for each factor and for response to obtain the maximum product yield with high desirability function (close to one). Then, conditions possessing high desirability were tested three times. Negligible difference between the average yields and the prediction values of software, confirms the high accuracy and precision of optimum conditions. The results showed that 12 mg of the catalyst, 16 wt.% of PMA loading and 2.4 equivalent of

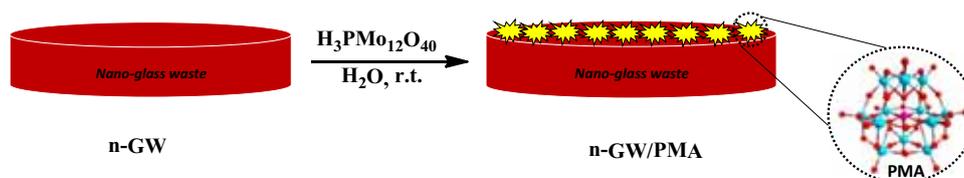
H<sub>2</sub>O<sub>2</sub> were the optimum conditions for the synthesis of 4, 4'-sulfinyldiphenol (Figure S19).

In order to study the effects of solvents on the reaction efficiency, the model reaction was carried out under optimum condition in the presence of EtOH, MeOH, CH<sub>3</sub>CN, H<sub>2</sub>O, and CH<sub>2</sub>Cl<sub>2</sub>. However, the best results in terms of reaction yields and time were related to the reactions operated under solvent free conditions.

The obtained results encouraged us to extent the application of this optimized catalytic protocol to the oxidation of various sulfides (Table 1). As could be observed from the table 1, a variety of sulfides like dialkyl sulfides, alkyl aryl sulfides and other sulfides with different functional groups could yield the corresponding sulfoxides with high conversion rate and outstanding selectivity. Additionally, under the designed reaction condition in the presence of the novel n-GW/PMA catalyst, the oxidation reactions were carried out smoothly without detecting any over oxidation products such as sulfones. Moreover, the steric effects of some sulfide derivatives were clear in this catalytic system. For example, the oxidation of diphenyl sulfide in comparison with isopropyl sulfide was performed in much longer reaction time which afforded a much lower reaction yields (Table 1, entries 4 and 5). The structures of some of the products were well characterized by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectral data.

### 3. Results and Discussion

The novel nano-glass waste supported phosphomolybdic acid (n-GW/PMA) was synthesized through impregnation method as briefly showed in Scheme 2. In order to synthesize the desired novel catalyst, firstly, nano-glass waste was prepared by crushing and powder making of the glass waste provided. Afterwards, an impregnation reaction occurred between the n-glass waste and PMA. At the subsequent step, the obtained catalyst was dried and calcinated at 150°C for 2 h and allowed to cool to room temperature. In order to explore the best amounts of PMA loaded on the n-GW support, a series of catalysts containing 5–25 wt.% PMA was synthesized. The results obtained showed that the catalyst with 16 wt.% loading exhibited better performance compared to the other catalysts. The newly prepared catalyst was characterized through FT-IR, FE-SEM, XRD, EDX and TGA techniques.



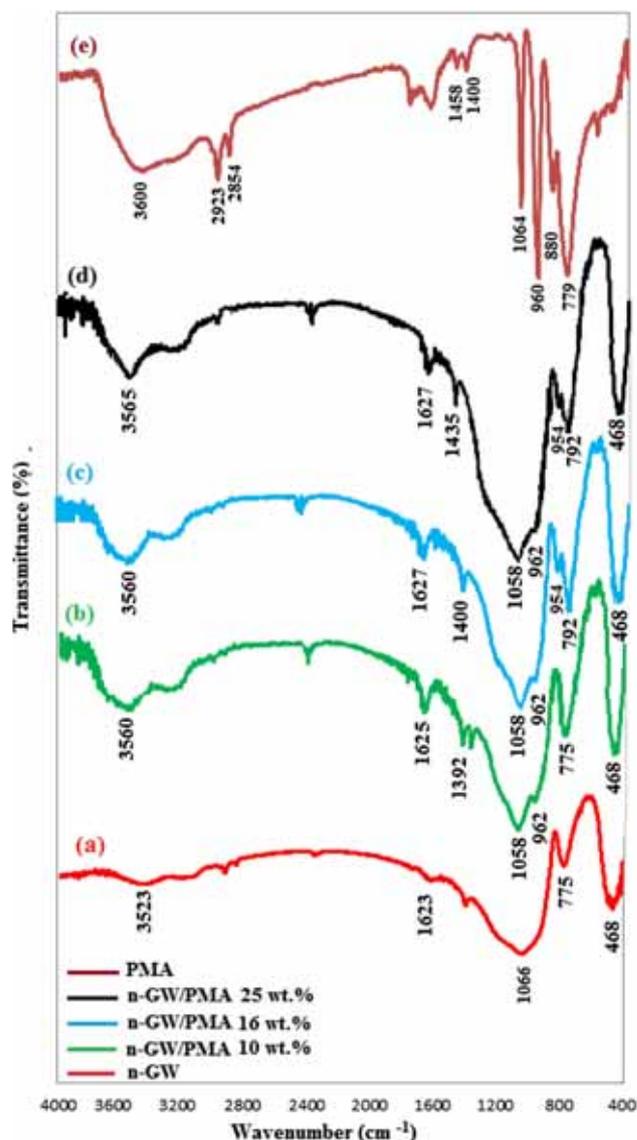
**Scheme 2.** Preparation of nano-glass waste-supported phosphomolybdic acid.

### 3.1 Characterization of n-GW/PMA

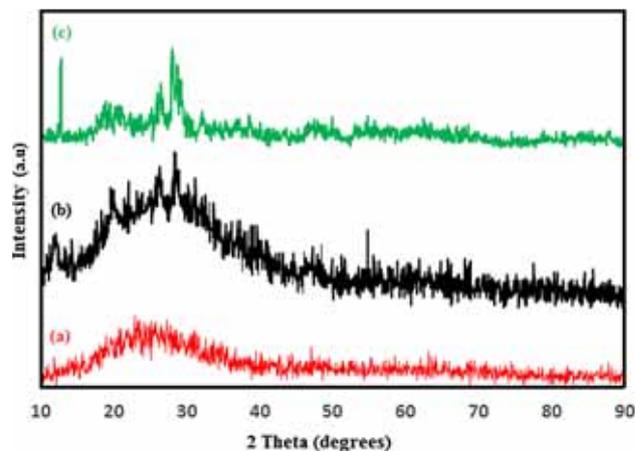
**3.1a FT-IR spectra of the samples:** FT-IR spectra were employed to establish the presence of PMA on the n-glass waste support. Figure 1 showed the FT-IR spectra of the n-GW, n-GW/PMA (10, 16 and 25 wt.%) and PMA. Curve (a) in Figure 1 shows the infrared spectrum of n-GW. About Figure 1a, the bands appeared at 3523 and 1623  $\text{cm}^{-1}$  are respectively assigned to the stretching and bending modes of the SiOH groups and the adsorbed water. The strong absorbance at 1066, 775 and 468  $\text{cm}^{-1}$  are related to the asymmetric stretching, symmetric stretching and bending modes of  $\text{SiO}_2$ , respectively.<sup>31</sup> The FT-IR spectrum of n-GW/PMA displayed the absorbance at 1058, 962, 882 and 792  $\text{cm}^{-1}$  which are attributed to the symmetric stretching of the central-atom-oxygen (P-O) bond of the  $\text{PO}_4$  tetrahedron, the asymmetric stretching of the peripheral-atom-terminal-oxygen (Mo-O) bond, and the Mo-O-Mo stretching of the inter- and intraoctahedral bridges of the trimetallic group, respectively (Figure 1c).<sup>32</sup> These observations confirmed the fact that the existence of PMA on support was in the Keggin structure. The vibrations due to molecular water present in the n-glass waste support and phosphomolybdic acid are identified at about 1627 and 3560  $\text{cm}^{-1}$ . The FT-IR spectrum of PMA (Figure 1e) reveals that the bands in n-GW/PMA are corresponded to those for the PMA (*i.e.*, the peaks at 1064, 960, 880 and 779  $\text{cm}^{-1}$ ). The FT-IR spectra of the different loading of PMA into n-GW indicated that most of characteristic bands of the parent Keggin structure could be found in PMA fingerprint region (1250–500  $\text{cm}^{-1}$ ). These findings clearly confirmed that the phosphomolybdic acid molecules are covalently bound to the n-GW support.

**3.1b X-ray diffraction analysis:** Figure 2 shows the XRD patterns of n-GW, pure PMA and 16 wt.% PMA supported on n-GW. According to Figure 2a, n-GW possessed the amorphous structure with the broad peak around  $2\theta$  equal to 27°. <sup>33</sup> As can be seen from Figure 2c, the crystalline peaks appeared between  $2\theta$  equal to 10–45° are attributed to the purely crystalline form of PMA. <sup>34</sup> The XRD pattern of n-GW/PMA 16% shows some reflections of Keggin structure PMA at 20–35° ( $2\theta$ ) (Figure 2b). From the XRD analysis, it can be concluded that the Keggin structure of the  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  was maintained after supporting on n-GW.

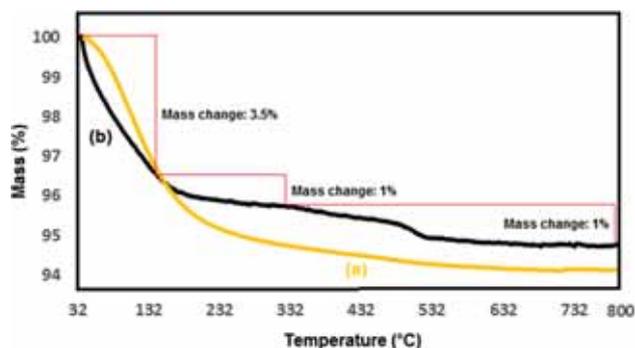
**3.1c Thermogravimetric (TGA) analysis:** Thermogravimetric analysis (TGA) was used for the evaluation of materials in terms of their thermal stability, chemisorption and bond formation. Figure 3 shows



**Figure 1.** FT-IR spectra of (a) n-GW, (b–d) n-GW/PMA 10–25 wt.% and (e) PMA.



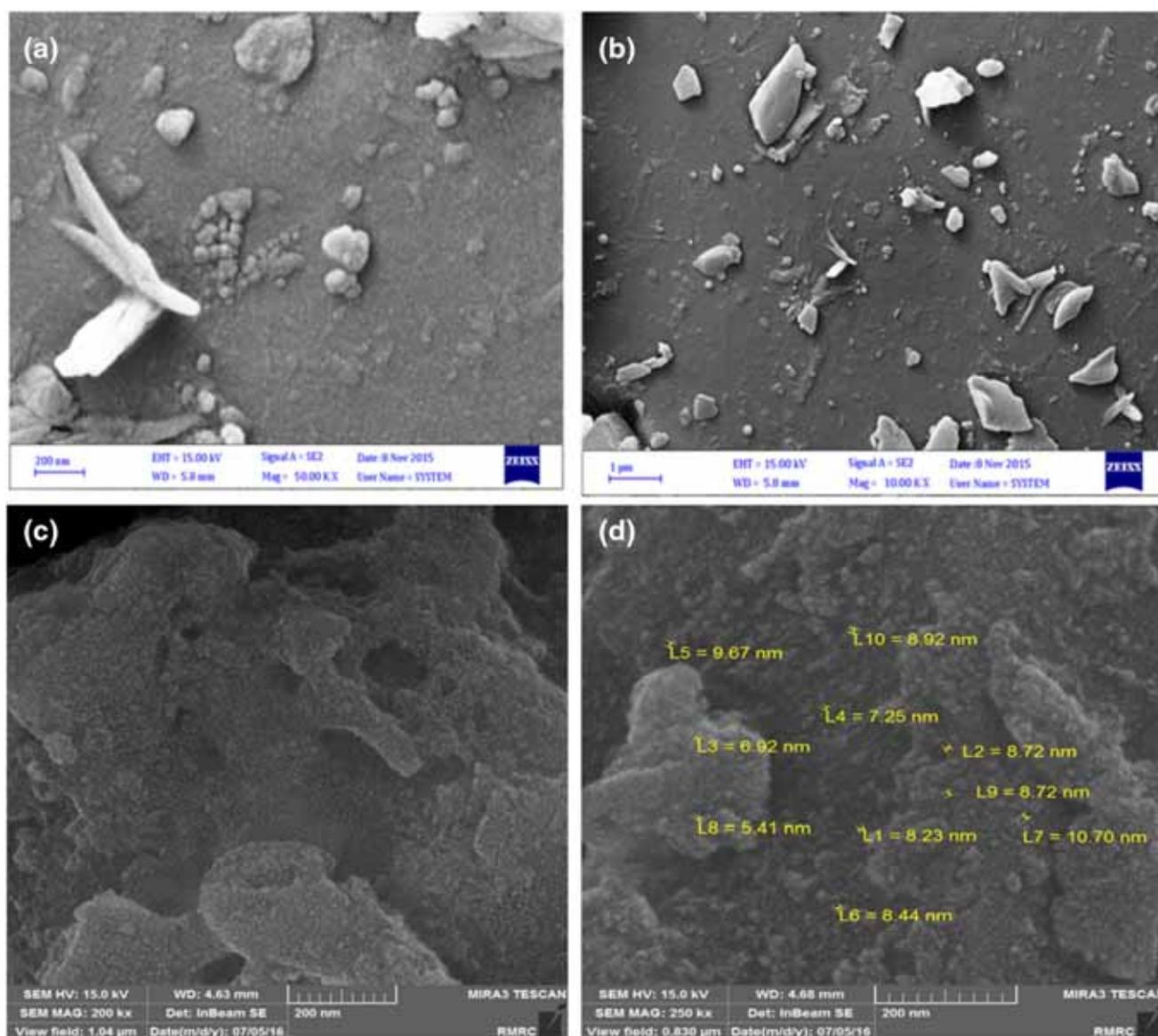
**Figure 2.** XRD spectra of (a) n-GW, (b) n-GW/PMA 16 wt.% and (c) bulk PMA.



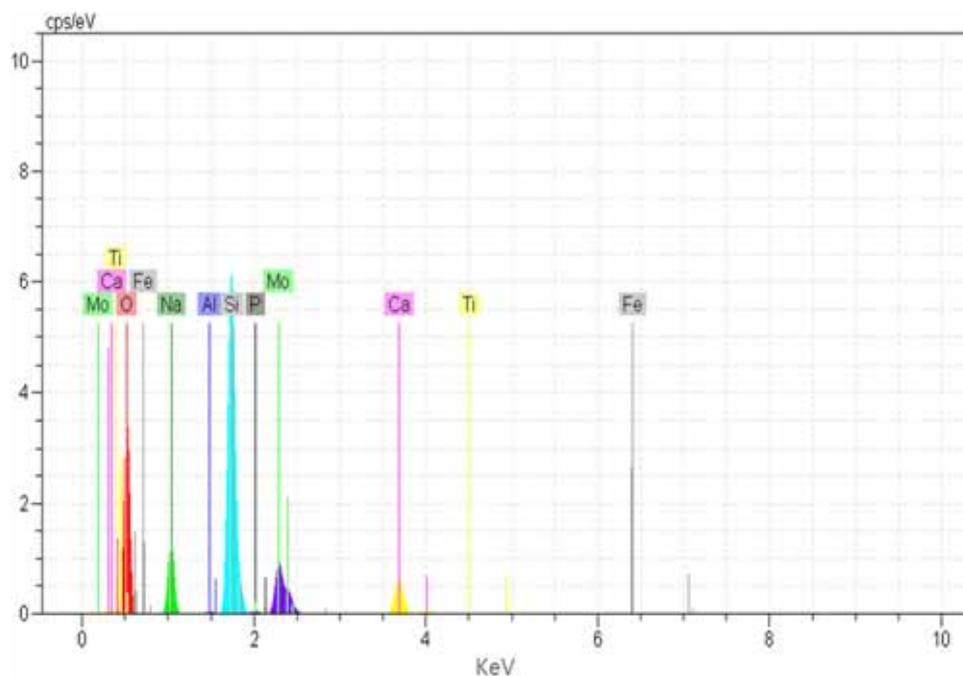
**Figure 3.** TGA curves of (a) n-GW and (b) n-GW/PMA 16 wt.%.

the TGA results for the n-GW and n-GW/PMA 16 wt.% in the temperature ranging from 30 to 800°C. As can be observed from Figure 3a, the naked n-GW

support shows a mass loss of about 4 wt.% in the temperature up to 100°C relating to the loss of physically adsorbed water. The steadily dehydroxylation of n-GW was occurred at the temperature lower than 600°C which caused 2 wt.% loss.<sup>35</sup> According to Figure 3b, n-GW/PMA exhibited the weight loss of 3.5 wt.% up to 100°C, attributed to removal of the physisorbed water. The second loss of weight (about 1 wt.%) between 130–300°C was ascribed to the dehydroxylation of chemisorbed water and the strongly adsorbed water on the n-GW support.<sup>36</sup> The continuous weight loss (1 wt.%) observed with further heating up to 800°C was due to the loss of water of the supported heteropolyacid and decomposition of the keggin units to give MoO<sub>3</sub>.<sup>37,38</sup> The results showed that the thermal stability of n-GW/PMA was more than 300°C which could be



**Figure 4.** FE-SEM images of n-GW (a, b), and n-GW/PMA (c, d).



**Figure 5.** The EDX spectrum of n-GW/PMA 16 wt.%.

**Table 2.** Comparison of n-GW/PMA for the oxidation of methyl phenyl sulfide with other reported procedures.

Entry	Reagent	T [min]	Yield [%]	Ref.
1	Thiourea dioxide/TBHP	210	93	39
2	NaBO <sub>3</sub> .4H <sub>2</sub> O/Silica Sulfuric acid/ KBr	840	55	40
3	Borax/H <sub>2</sub> O <sub>2</sub>	360	35	41
4	Clay-supported ceric ammonium nitrate (CAN)/O <sub>2</sub>	300	35	42
5	SiO <sub>2</sub> -W <sub>2</sub> -Py/H <sub>2</sub> O <sub>2</sub>	150	90	43
6	n-GW/PMA/H <sub>2</sub> O <sub>2</sub>	15	96	Present work

safely employed in organic reactions at temperatures up to 350°C.

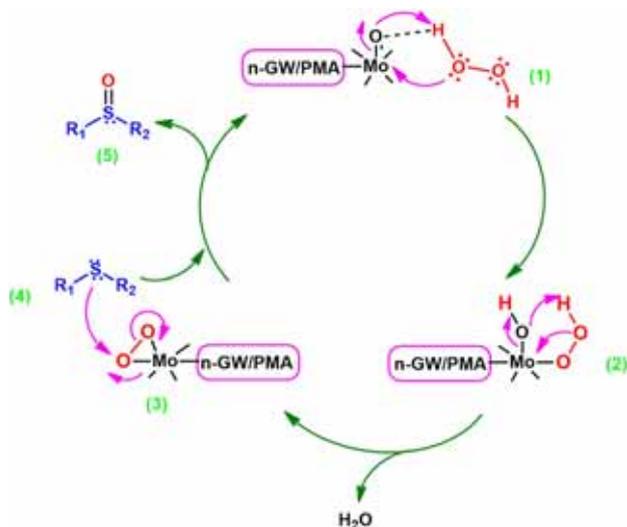
**3.1d Field emission scanning electron microscopy (FE-SEM):** FE-SEM images were employed in order to study the surface morphology, particle shape and size distribution of the as-synthesized materials (Figures 4a–e). Figures 6a and b show the SEM images of the n-GW which indicated that the material consisted of some particles on the surface. These non-homogeneous particles have the sizes in the range of 50 nm to 2 μm. On the other hand, as displayed in the Figures 4c and d, n-GW/PMA had completely different morphology and size ranges. As it was obvious in the micrographs, after the modification of n-GW with PMA, the obtained material had aggregated particles with quasi-spherical shape. Besides, the size distribution of the catalyst particles was nearly homogeneous and their diameter sizes were around 5–11 nm.

**3.1e Energy-dispersive X-ray spectroscopy (EDX):** The elemental composition of the n-GW/PMA from the EDX spectrum is depicted in the Figure 5. As it is obvious, the O, Si, Al, Ca, Fe, Ti, Na, P and Mo elements are present in the structure of the as-synthesized catalyst.

Table 2 displays the efficiency of our designed catalytic system in comparison with those reported in the literature. The result for the preparation of (methylsulfanyl benzene) in the presence of n-GW/PMA are compared with the data from the literature, which shows that the n-GW/PMA is superior to most of the others regarding the reaction times and product yields. Therefore, it could be concluded that n-GW/PMA is a very beneficial and efficient catalyst for the sulfide oxidation.

### 3.2 Plausible mechanism for the oxidation of sulfides to sulfoxides catalyzed by n-GW/PMA

Based on earlier reports,<sup>44,45</sup> we propose a mechanism for the oxidation of sulfides to sulfoxides in the presence



**Scheme 3.** Plausible mechanism for the oxidation of sulfides to sulfoxides in the presence of n-GW/PMA.

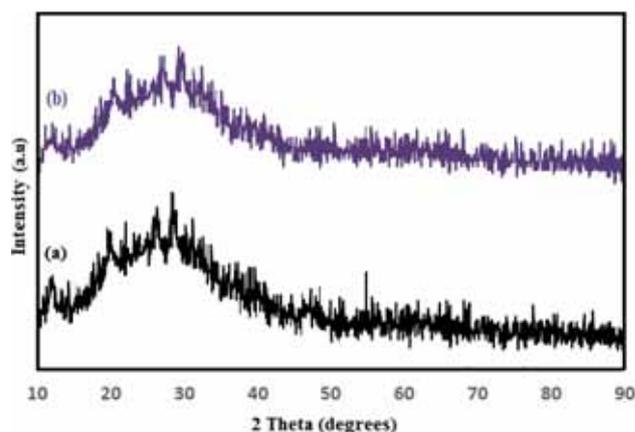
of n-GW/PMA (Scheme 3). The reaction is initiated with the nucleophilic attack of  $\text{H}_2\text{O}_2$  on the oxo ligands of Mo(VI) atom on the n-GW surface (i.e., species 1) to form the octahedral hydroperoxymolybdate (2). Then, monoperoxo species (3) is generated, followed by a loss of a water molecule. As a consequence, the peroxo group is electrophilically activated through the coordination to the high-valent molybdenum atom. Finally, the sulfoxide product (5) is formed when the sulfur atom in the organosulfur compounds (4) attacks on a peroxo group of intermediate (3) and regenerates polymolybdate or monoperoxo species.

### 3.3 Reusability of the designed catalyst

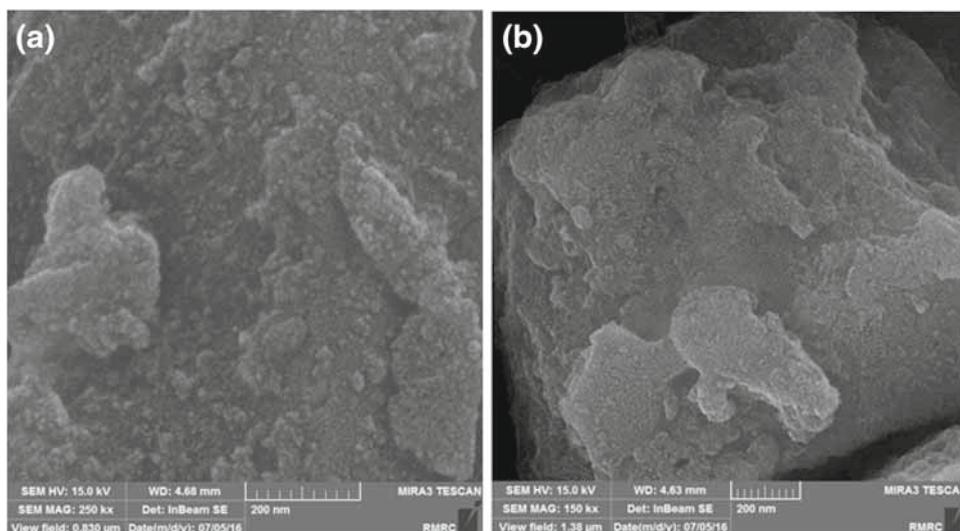
On account of the fact that the development of novel heterogeneous catalysts with the capability of good

recyclability has been one of the important criteria for organic transformations, we examine our new n-GW/PMA catalyst for its recyclability and reusability in the optimum reaction condition of selective sulfide oxidation. After each run, the catalyst was simply separated from the product by adding diethyl ether and, then by centrifugation. After that, the recovered catalyst was washed with extra amounts of ether and dried at  $100^\circ\text{C}$ . The dried recovered catalyst was capable to efficiently run the oxidation reaction for five runs without losing its activity. The yields in the first 5 runs were as follows: 97, 96, 94, 93 and 93%. These results indicated the fact of tight immobilization of the PMA function on the n-GW support.

The identity of the recovered catalyst was checked by FE-SEM which suggested that the nature of the catalyst remained intact and there was no change in the morphology during the reaction and recycling stages as compared to the fresh catalyst (Figure 6). Additionally,



**Figure 7.** XRD spectra of n-GW/PMA (a) before use and (b) after reuse for five times.



**Figure 6.** FE-SEM images of (a) fresh n-GW/PMA and (b) after 5<sup>th</sup> run.

the XRD patterns of the catalyst after five cycles were similar to the corresponding pattern before catalytic reaction which confirmed the existence of heteropoly-acid groups on the surface of catalyst (Figure 7).

#### 4. Conclusions

In conclusion, n-GW/PMA was synthesized as the eco-friendly, heterogeneous solid acid catalyst through the utilization of n-glass waste as an accessible and inexpensive solid support for the immobilization of phosphomolybdic acid. The strong binding of the PMA molecules on the surface of the n-GW/PMA caused the novel catalyst to show extraordinary activity and chemoselectivity for the synthesis of sulfoxides through the oxidation of sulfides. The designed reaction was green and economical since this transformation possessed several advantages, such as, short reaction times, high reaction yields, application of low amount of catalyst, solvent-free condition at room temperature, use of waste material as catalyst support, and utilization of H<sub>2</sub>O<sub>2</sub> as the green oxidant.

#### Supplementary Information (SI)

All additional information pertaining to characterization of some of the products (Table 1) using IR spectra (Figures S1, S3, S7, S10 and S15), <sup>1</sup>H NMR spectra (Figures S2, S4, S8, S11 and S16) and <sup>13</sup>C MNR spectra (Figures S13 and S17), and details for the optimization of the reaction conditions by CCD method (Figures S18 and S19 and Tables S1, S2 and S3) are given in the Supporting Information, which is available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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