

Immobilization of Phosphomolybdate Anions on the Surface of Magnetite Nanoparticles Modified with Quaternary Phosphonium Cations

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Abstract

A new hybrid nanomaterial was developed by immobilization of phosphomolybdate anions on the surface of modified magnetite nanoparticles with quaternary phosphonium cations. Silica coated magnetic nanoparticles supported phosphonium cations, Ph_3P^+ -SCMNPs, were prepared by covalent attachment of chloropropylsilyl groups on the surface of silica coated magnetite nanoparticles and next reaction with triphenylphosphine. Then, reaction of the prepared Ph_3P^+ -SCMNPs nanomaterial with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ resulted in the preparation of $\text{PMo-Ph}_3\text{P}^+$ -SCMNPs hybrid nanomaterial. The $\text{PMo-Ph}_3\text{P}^+$ -SCMNPs hybrid nanomaterial was characterized with different physicochemical methods such as FT-IR and ICP-AES spectroscopies, XRD, VSM, SEM, and TEM analyses. VSM analysis showed superparamagnetic properties of the prepared nanomaterial. TEM and SEM analyses indicated the aggregated nanoparticles with about 15 nm average size.

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1. Introduction

In recent years, heteropolyacids (HPAs) due to their unique physicochemical properties are widely used as homogeneous and heterogeneous acid and oxidation catalysts. These compounds show strong Bronsted acidity values, approaching the superacid region. They are also of great interest as model systems for studying

fundamental problems of catalysis [1]. Pure heteropolyacids have high solubility in polar reaction systems which prevent their applications as heterogeneous catalysts and so results in separation problems during the isolation of the product after reaction completion. Thus, supported heteropolyacids have attracted great interests and

some methods have been developed for the preparation of this type of materials [1-3].

On the other hand, magnetic nanoparticles have recently emerged as attractive materials as support for immobilization of homogeneous catalysts [4-6]. The main advantage of a catalytic system based on magnetic nanoparticles is that the nanoparticles can be efficiently isolated from the reaction mixture through a simple magnetic separation process after completing the reaction. Among various magnetic nanoparticles, magnetite (Fe_3O_4) has gained extensive attention due to its interesting superparamagnetic properties. Thus, much attention has been focused on the surface modification of magnetic nanoparticles with different silylating reagents to anchor the catalytically active compounds [7-16].

To the best of our knowledge, there are few reports devoted to the immobilization of polyoxometalates on magnetite nanoparticles [17-19]. Our current interest in the preparation of new hybrid nanomaterials based on magnetite nanoparticles [17,18,20-22] led us to investigate the preparation and characterization of a new hybrid nanomaterial based on immobilization of phosphomolybdate anion on the surface of silica coated magnetite nanoparticles modified with quaternary phosphonium cations. The preparation of this hybrid nanomaterial is based on the functionalization of the surface of magnetite nanoparticles with quaternary phosphonium cations in the first step. Next reaction of the prepared nanomaterial with phosphomolybdic acid resulted in the immobilization of phosphomolybdate anions on the surface of magnetite nanoparticles. Due to the presence of magnetite core, the prepared hybrid nanomaterial has superparamagnetic properties which made its

easy recovery and reuse in potential catalytic applications.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck chemical company and used without further purification. $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was prepared according to the literature method [23].

Fourier transform infrared (FT-IR) spectra were recorded on Rayleigh WQF-510 spectrophotometer using pellets of the materials diluted with KBr. Chemical analyses of the samples for determination of phosphorous content were carried out with VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer. The crystalline phase of the nanoparticles were identified by means of X-ray diffraction measurements using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of $2\text{-}80^\circ$. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of -8000 Oe to 8000 Oe at room temperature. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Philips EM 208S instrument with an accelerating voltage of 100 kV . Samples were prepared for TEM by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera.

2.2. Preparation of $\text{PPh}_3\text{-SCMNPs}$ and $\text{PMo-PPh}_3\text{-SCMNPs}$ nanomaterials

Magnetite nanoparticles (MNPs) were prepared according to the reported method [14]. For preparation of SCMNPs, the magnetite

nanoparticles (1 g) were dispersed in deionized water in a 250 ml round-bottom flask with sonication and then an aqueous solution of TEOS (10% (v/v), 80 ml) was added, followed by addition of glycerol (50 ml). The pH of the suspension was adjusted to 4.5 using glacial acetic acid, and the mixture was then stirred and heated at 90°C for 2 h under a nitrogen atmosphere. After cooling to room temperature, the silica coated magnetite nanoparticles was separated from the reaction mixture using a permanent magnet and washed several times with distilled water and methanol. The obtained SCMNPs (2 g) were suspended in ethanol (100 ml) and then chloropropyltrimethoxysilane (2 ml) was added under dry nitrogen atmosphere. The mixture was refluxed for 12 h and the resulted solid was magnetically separated, washed with methanol to remove the unreacted residue of silylating reagent and then vacuum dried at 80 °C.

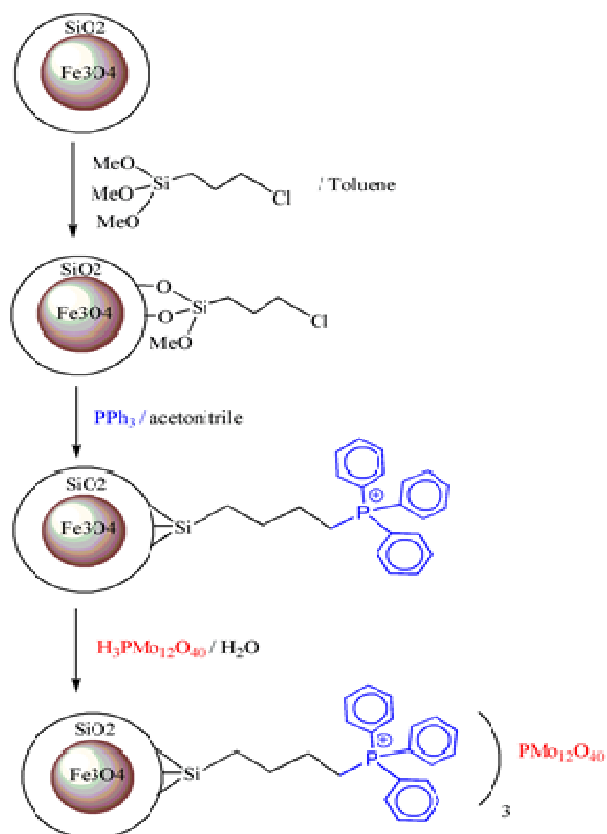
For immobilization of phosphonium cations, ClpSCMNPs (2 g) was suspended in 100 ml of acetonitrile with sonication. To this mixture was added excess of triphenylphosphine (4 mmol) and the resulted mixture was refluxed for 24 hours. The produced solid was separated magnetically and then washed with ethanol several times to remove the unreacted residue of the triphenylphosphine and dried under vacuum at 80°C.

In the final step, the Ph₃P-SCMNPs (1 g) were dispersed in 50 ml deionized water with sonication. Then, a solution of H₃PMo₁₂O₄₀ (2 mmol) in 20 ml deionized water was added to the above mixture and stirred for 12 hours to yield PMo-PPh₃-SCMNPs. The product was magnetically separated and washed several times with deionized water and then dried under vacuum at 80°C.

3. Results and discussion

The sequence of reactions for the preparation of PMo-Ph₃P-SCMNPs is depicted in Scheme 1. The first step involves the preparation of magnetite nanoparticles by using co-precipitation method in alkaline solution. Then, the external surface of magnetite nanoparticles was coated with a silica layer to obtain SCMNPs. In the next step, reaction of silanol groups of SCMNPs with chloropropyltrimethoxysilane resulted in the preparation of chloropropylated magnetite nanoparticles (ClpSCMNPs). Then, addition of triphenylphosphine to the resulted nanomaterial gives the quaternary phosphonium cation supported on magnetite nanoparticles, Ph₃P-SCMNPs. Finally, by adding phosphomolybdic acid, the PMo-Ph₃P@SCMNPs hybrid nanomaterial was formed.

The FT-IR spectra of Ph₃P-SMNPs and PMo-Ph₃P-SMNPs are shown in Fig. 1. The spectra of the prepared nanoparticles showed two strong absorption bands at around 422 and 587 cm⁻¹ which were assigned to the Fe–O vibration frequencies of magnetite core. The observed bands around 1000-1100 cm⁻¹ can be assigned to Si–O–Si and Si–O–H asymmetric stretching vibrations and confirmed the presence of silica shell in the prepared nanomaterials. The bands at about 2900-3000 cm⁻¹ were attributed to the stretching vibrations of C-H bonds and confirmed the presence of anchored propyl groups. In the FT-IR spectrum of Ph₃P-SCMNPs the weak bands at around 1300-1600 cm⁻¹ can be assigned to the stretching vibrations of phenyl groups in quaternary phosphonium cation. It has been shown that Keggin type heteropolyanions give four characteristic peaks in wavenumber region of 800-1100 cm⁻¹ [24].



Scheme 1. The sequence of events involved in the preparation of PMo-Ph₃P-SCMNPs nanomaterial.

As can be seen in the FT-IR spectrum of the prepared PMo-Ph₃P-SCMNPs nanomaterial, the corresponding peaks for Mo=O and Mo-O-Mo stretching vibrations are observed at 960 (stretching vibration of Mo=O), 883 and 808 cm⁻¹ (corner and edge sharing Mo-O-Mo stretching vibrations). As a consequence of overlap with strong asymmetric Si-O-Si stretching vibration, the P-O stretching vibration at around 1060 cm⁻¹ can not be seen here. These observations indicate the existence of Keggin type heteropolyanions in the prepared nanomaterial. The Mo-O-Mo stretching vibration frequencies of the prepared nanomaterial increased in comparison with the neat phosphomolybdic acid. Compared with bulk phosphomolybdic acid, the $\nu_{\text{as,corner sharing Mo-O-Mo}}$ and $\nu_{\text{as,edge sharing Mo-O-Mo}}$ peaks in PMo-Ph₃P-

SCMNPs nanomaterial shifted from 868 to 883 cm⁻¹ and 791 to 808 cm⁻¹, respectively. The higher wavenumbers for Mo-O-Mo stretching vibrations are consistent with strong interactions existing between phosphomolybdate anions and phosphonium cations in the hybrid nanomaterial [25].

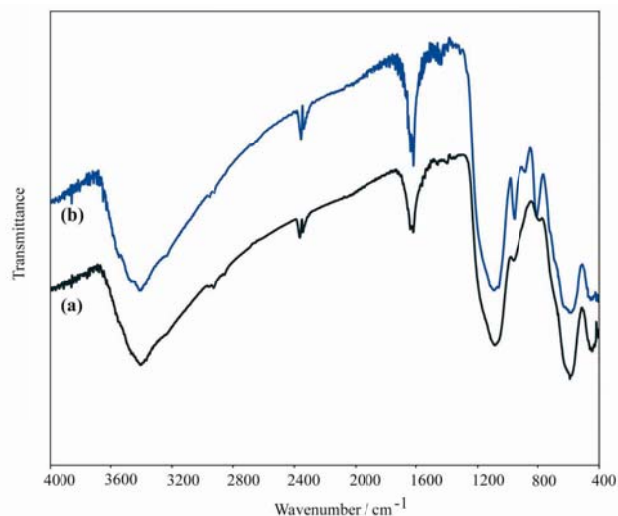


Fig. 1. FT-IR spectra of (a) Ph₃P-SCMNPs and (b) PMo-Ph₃P-SCMNPs nanomaterials.

Stoichiometry and chemical composition of the prepared nanomaterials were examined by ICP-AES analysis. On the basis of ICP-AES chemical analysis the phosphorous content of the prepared Ph₃P-SCMNPs nanomaterial was found to be 0.5 mmol.g⁻¹. After reaction with phosphomolybdic acid the ratio of phosphonium cation to phosphomolybdate anion (measured by P:Mo ratio after subtracting the phosphorous content of phosphomolybdate anions) was estimated to be 1: 0.29 which indicates that main portion of the supported phosphonium cations was involved in the interaction with phosphomolybdate anions.

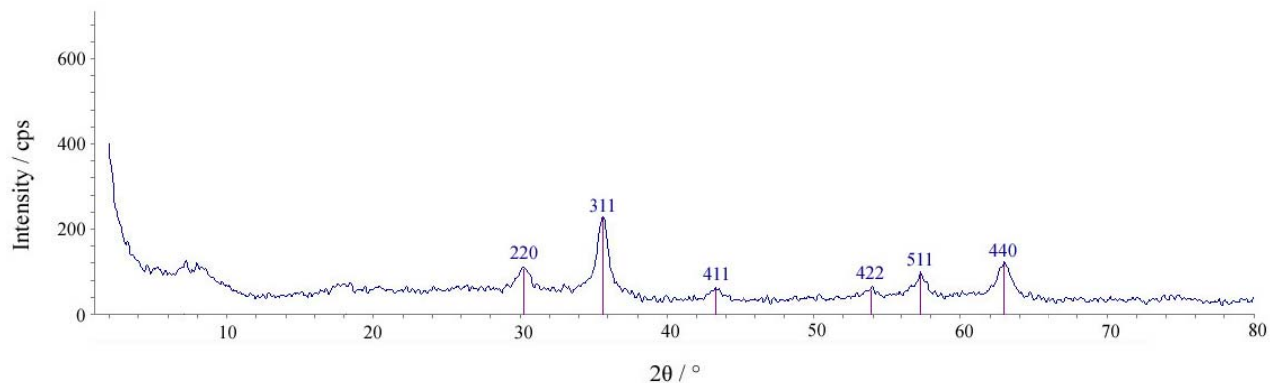


Fig. 2. XRD pattern of prepared PMo-Ph₃P-SCMNPs nanomaterial.

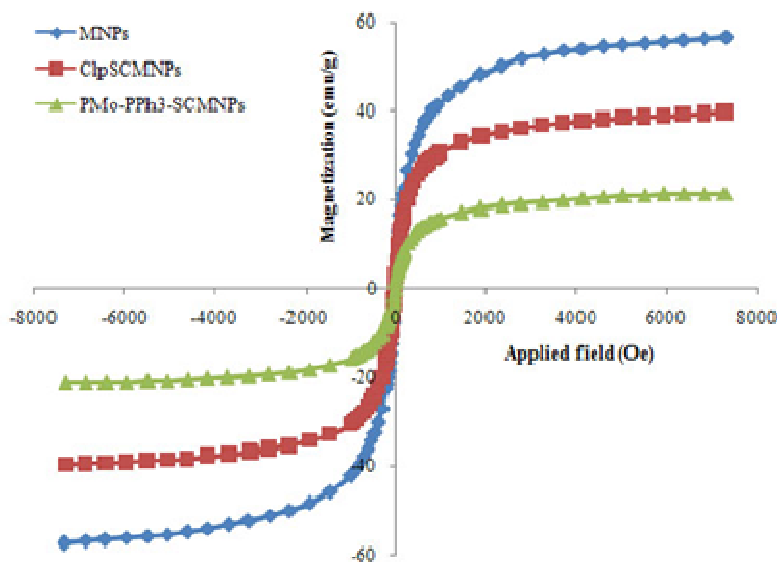


Fig. 3. Magnetization curves of (a) MNPs, (b) ClpSCMNPs, (c) PMo-Ph₃P-SCMNPs nanomaterial.

The phase composition and structure of the prepared PMo-Ph₃P-SCMNPs were analyzed by X-ray diffraction analysis (Fig. 2). The characteristic peaks were marked by their corresponding miller indices which match well with the standard XRD data card of Fe₃O₄ crystal (JCPDS No. 19-0629). Moreover, there are no characteristic peaks of phosphomolybdic acid in the XRD spectrum of PMo-Ph₃P@SCMNPs. This indicates that phosphomolybdate anions are well-

dispersed on the surface of the functionalized MNPs and there is no any crystalline phase of phosphomolybdate anions to be detected by XRD analysis.

VSM analysis was used to evaluate magnetization of the prepared nanomaterials as a function of applied external magnetic. Based on the obtained VSM curves (Fig. 3) at room temperature, magnetization curve of MNPs exhibited no remanence effect and the hysteresis

loop feature indicates that the MNPs have superparamagnetic property with saturation magnetization of about 60 emu/g. Also, as a consequence of the external surface functionalization of MNPs, the curves of the prepared ClpSCMNPs and PMo-Ph₃P-SCMNPs nanomaterials showed that saturation magnetizations were decreased to about 38 and 19 emu/g, respectively, but still exhibited superparamagnetic properties.

Figure 4a shows the SEM image of the prepared PMo-Ph₃P-SCMNPs nanomaterial. The SEM image indicates that the obtained product is composed of nearly spherical nanoparticles. Aggregation gives rise to increasing the size of observed nanoparticles as seen in the SEM image.

Transmission electron micrograph of the PMo-Ph₃P-SCMNPs nanomaterial was shown in Fig. 4b. As can be seen, the prepared nanoparticles are aggregated and in the edges of the aggregated nanoparticles, the nanoparticle size is about 15 nm.

4. Conclusion

In summary, we have successfully developed a novel type of immobilized polyoxometalate using surface-modified Fe₃O₄ magnetic nanoparticles as a support. First, the external surface of silica coated magnetite nanoparticles were modified with chloropropyltrimethoxysilane. Afterwards, reaction with triphenylphosphine resulted in immobilization of quaternary phosphonium cations on the surface of modified magnetite nanoparticles. Subsequent reaction of the supported triphenylphosphonium cations with phosphomolybdic acid afforded a new hybrid polyoxometalate-magnetite nanomaterial.

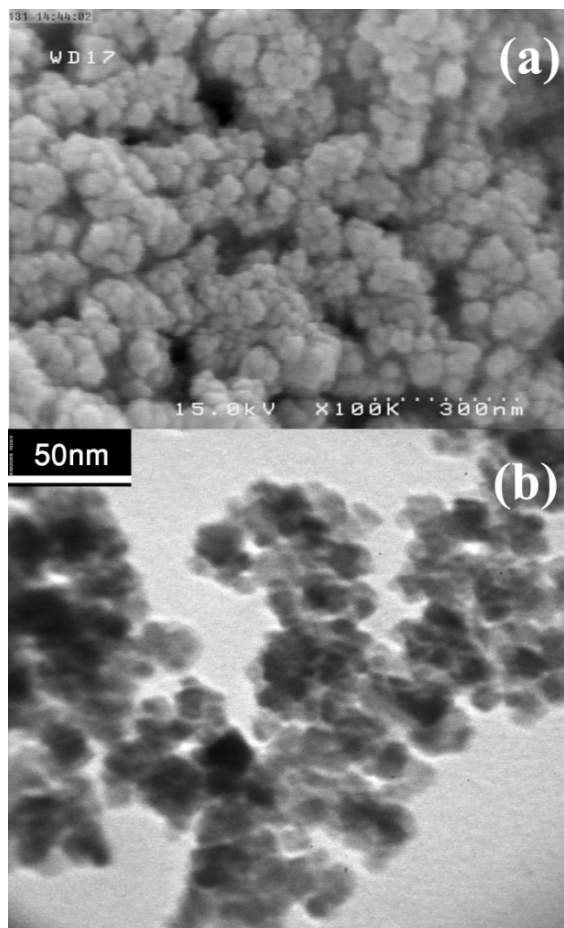


Fig. 4. (a) SEM and (b) TEM images of prepared PMo-Ph₃P-SCMNPs nanomaterial.

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