Aliphatic alcohols oxidation with Hydrogen Peroxide in water catalyzed by supported Phosphotungstic acid (PTA) on Silica coated MgAl$_2$O$_4$ nanoparticles as a recoverable catalyst

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INTRODUCTION

The selective oxidation reaction of alcohols to aldehydes and ketones is a basic reaction in organic synthesis [1-2]. Most common inorganic compounds in order to oxidize alcohols are well known, such as KMnO$_4$, MnO$_2$ and K$_2$Cr$_2$O$_7$ [3], but these oxidants are toxic. Due to beneficial properties of hydrogen peroxide, significant progresses have been achieved for oxidation of aliphatic alcohols with hydrogen peroxide, catalyzed by nanocomposite. Hydrogen peroxide is an environmentally safe and interesting oxidant for different organic oxidation reactions [4-5].

Polyoxometalates (POM) are categorized as one of the most important catalysts in inorganic metal oxide cluster group. Metropolyacid (HPAs) compounds of keggin have attracted many attentions, because of their applications, such as significant catalytic properties and high activity [6-8]. The problem of HPAs is the low available surface area. Supporting compounds on nanoparticles is the best solution for improving their effective surface area and solubility in polar solvents. Mesoporous materials such as zeolites, silica, and titania have been used as supports for PTA [9-13]. Due to its chemical and physical stability, hydrophilic nature and being mesoporous, Silica (SiO$_2$) has attracted growing attentions in diverse applications [14-15]. Using Polyoxometalates dissolved in polar solvents composed of homogeneous catalysts provides convenience in use due to the ease of their recovery. A utilized method is immobilizing POM species on the surface of nanoparticles which can be isolated and recovered from the reaction system by a simple filtration. Similar research has been done in recent years [16-17].

Magnesium aluminate has attracted many
attentions as catalyst support because of its structure stability and high melting point. Magnesium aluminate has a good resistance against chemical changes. Also it has high resistance at very high temperatures, has a very high melting point (2135) and low density (3.58 g/cm³) [18]. Different methods for production of magnesium aluminate nanoparticles include sol-gel [19-20] co-precipitation [21] and self-combustion. These methods are mainly expensive in large scale production. In general, smaller particle size along with higher surface area is suitable for various catalytic applications [22].

In this research, a new composite was prepared by a simple method for oxidation of aliphatic alcohols to aldehydes and ketones with hydrogen peroxide as oxidant and water as solvent. This nanocomposite was proved to be useful for immobilization of PTA on silica coated magnesium aluminate nanoparticles. Primary alcohols were converted to aldehydes with high selectivity and conversion ratios. Cyclohexanol was converted to cyclohexanone with a high selectivity [23-27]. At the end of the reaction, the products were isolated from the aqueous phase by a simple filtration (see Fig. 1).

**EXPERIMENTAL**

*Materials and methods*

All chemicals were purchased from Sigma-Aldrich or Merck with analytical grade and used as received. H₃PW₁₂O₄₀ (PTA) was purchased from Sigma-Aldrich. Fourier transform infrared (FT-IR) spectra were obtained using FT BOMEM MB102 IR spectrophotometer. X-ray diffraction (XRD) patterns of the synthesized samples were determined with a Philips X-ray diffractometer (model PW1730). The SEM images were obtained by Hitachi Japan S4160. The Scanning Electron Microscopy analysis was performed along with an Energy Dispersive Spectroscopy (EDX).

**Synthesis of MgAl₂O₄@SiO₂–PTA nanocomposite**

MgAl₂O₄ was prepared using the method reported by Mostafa Y. Nassar [28]. Coating of MgAl₂O₄ nanoparticles with a layer of silica was performed by the following method. In this method, ethanol (1/5 ml) and H₂O (10 ml) were mixed and put in ultrasonic bath for 1 hour. After that, NH₃ (1/5 ml) was added to this mixture. Then, 2g of MgAl₂O₄ particles were dispersed in it and the mixture was vigorously stirred at 40°C for 10 minutes. Then, TEOS (0/53ml) was added and mixing was continued for 1 hour and the mixture was stirred overnight. The coated particles were separated by filtration and washed with ethanol several times and dried at 80°C in the oven. In this process, for synthesis of the nanocomposite, ethanol/water (80 : 20 ratio) solution was prepared and then 1.0 g of PTA was added and the solution was stirred at room temperature for 1 hour. After that, 1.0 g of MgAl₂O₄ @SiO₂ was dispersed in it and the mixture was stirred for another 3 hours. The resulting precipitation was separated by filtration. At last, this nanocomposite was washed with ethanol and dried in an oven at 100 °C for 2 hours. The typical preparation of composite (MgAl₂O₄@SiO₂–PTA) is shown in Fig. 2.

**Catalytic studies**

A mixture of an alcohol (1mmol), catalyst (0.015 mmol), water (3 ml), and H₂O₂ (30% aq.) were stirred at 90 for the specified time. The reaction was characterized by TLC. CH₃Cl was added to dilute the reaction mixture and the organic layer was isolated by filtration. At the end of the reaction, the isolated solution was purified on a silica-gel plate to obtain pure product. After separation of

![Fig. 1. Synthesis of aliphatic alcohols in presents of MgAl₂O₄@SiO₂–PTA using H₂O₂/water at 90°C](image-url)
product, recycled catalyst was reused for the next oxidation cycle with alcohols (1 mmol), H$_2$O$_2$ (30% aq) and water.

RESULTS AND DISCUSSION

Characterization of MgAl$_2$O$_4$@SiO$_2$–PTA composite

FT-IR spectra

MgAl$_2$O$_4$@SiO$_2$–PTA was synthesized by a simple method. MgAl$_2$O$_4$ was prepared via sol-gel combustion method as a support for nanocomposite. Then, it was coated by thin layer of silica. The FT-IR spectra of MgAl$_2$O$_4$ and MgAl$_2$O$_4$@SiO$_2$–PTA, is presented in Fig. 3. In the IR spectra, the MgAl$_2$O$_4$ sample display two characteristic at 555 cm$^{-1}$ and 700 cm$^{-1}$ consecration to the [AlO$_6$] groups, the lattice vibration of Mg–O stretching, and displaying the formation of MgAl$_2$O$_4$ spinel [29-30]. Two
vibration bands at 3358 cm\(^{-1}\) and 1607 cm\(^{-1}\) appeared in the IR spectra of the products could be attributed to the stretching and bending vibrations of the molecular surface adsorbed water interacting with MgAl\(_2\)O\(_4\) [31-34]. Two bands at 1080 cm\(^{-1}\) and 794 cm\(^{-1}\) were observed which are ascribed to the symmetrical and asymmetrical vibrations of the Si–O–Si bonds. Two other bands at 894 cm\(^{-1}\) and 981 cm\(^{-1}\) were attributed to the immobilized PTA [35].

**X-ray diffraction**

The XRD patterns of MgAl\(_2\)O\(_4\) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA, are displayed in Fig. 4. The peaks are compatible with pure MgAl\(_2\)O\(_4\) phase (JCPDS card no. 98-007-5897), indicating the retention of spherical spinel structure of MgAl\(_2\)O\(_4\) during the functionalization and coating process. The crystallite size of MgAl\(_2\)O\(_4\) nanoparticles was determined about 40 nm using Debye-Scherrer formula (Fig. 4A). The XRD patterns of MgAl\(_2\)O\(_4\), after coating with silica and functionalization with PTA (Fig. 4B), are more or less the same as previous MgAl\(_2\)O\(_4\) with the same spinel structure.

Comparison to XRD patterns of MgAl\(_2\)O\(_4\) (A) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA (B). (see Table 1).

**Scanning Electron Microscopy (SEM)**

The morphology of MgAl\(_2\)O\(_4\) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA were investigated by SEM and are shown in Fig. 5. SEM images display that MgAl\(_2\)O\(_4\) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA particles are well dissolved and most of the fabricated nanoparticles have spherical structures (Fig. 5 A and B). As it is shown in the Fig. 3, the maximum of particles size is 31 nanometer.

**EDX Microscopy and Brunauer-Emmett-Teller (BET) surface area analysis**

The EDX spectrum is shown in Fig. 6. The spectrum clearly reveals the presence of all the expected main elements (O, Si, P, Al, Mg, and W) including the three component composite. The surface area of MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA was also estimated by using the N\(_2\) gas adsorption (BET) method and a value of 36.73 m\(^2\) g\(^{-1}\) was found for this composite.

![XRD patterns of MgAl\(_2\)O\(_4\) (A) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA (B).](image-url)

Table 1. Comparison to XRD patterns of MgAl\(_2\)O\(_4\) (A) and MgAl\(_2\)O\(_4\)@SiO\(_2\)–PTA (B).

<table>
<thead>
<tr>
<th>2Theta peak</th>
<th>(1 1 1)</th>
<th>(0 2 2)</th>
<th>(1 1 3)</th>
<th>(0 0 4)</th>
<th>(2 2 4)</th>
<th>(1 1 5)</th>
<th>(0 0 4)</th>
<th>(3 3 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl(_2)O(_4) (A)</td>
<td>19</td>
<td>32</td>
<td>36</td>
<td>45</td>
<td>56</td>
<td>60</td>
<td>66</td>
<td>87</td>
</tr>
<tr>
<td>MgAl(_2)O(_4)@SiO(_2)–PTA (B)</td>
<td>21</td>
<td>33</td>
<td>37</td>
<td>46</td>
<td>57</td>
<td>61</td>
<td>67</td>
<td>87</td>
</tr>
</tbody>
</table>
**Aliphatic alcohols oxidation**

As indicated in Table 2. The primary alcohols (amyl alcohol and ethanol) were converted to aldehydes after oxidation. The linear aliphatic alcohols (amyl alcohol, ethanol and 2-propanol) were more difficult to oxidize than cyclohexanol. Consequently, 5/1 molar ratio H$_2$O$_2$/alcohol and 6 hours reaction time was needed for oxidation of these alcohols (entries 2-4).

**Table 2. Synthesis of diversified alcohols in the presence of MgAl$_2$O$_4$@SiO$_2$-PTA.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>product</th>
<th>H$_2$O$_2$/substrate molar ratio</th>
<th>Time (h)</th>
<th>yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>2/1</td>
<td>1/5</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>HO</td>
<td>OH</td>
<td>5/1</td>
<td>6</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>5/1</td>
<td>6</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>5/1</td>
<td>6</td>
<td>88</td>
</tr>
<tr>
<td>5$^a$</td>
<td></td>
<td></td>
<td>2/1</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Alcohols (1mmol) water (3 ml), and H$_2$O$_2$ (30% aq) was stirred at 90°C without catalyst.

All reaction condition: alcohol (1mmol) catalyst (0.015 mmol), water (3 ml) and H$_2$O$_2$ (30% aq.) was stirred at 90°C.

$^b$ Isolated yields.
About cyclohexanol (entry 1) the 2/1 molar ratio received of H$_2$O$_2$/cyclohexanol was appropriate for this reaction (see Table 2).

The reaction of cyclohexanol, hydrogen peroxide and MgAl$_2$O$_4$@SiO$_2$-PTA was chosen as a model for aliphatic alcohols oxidation reaction. In order to obtain the best results, different solvents such as water, acetonitrile, toluene, chloroform and solvent free condition were employed. The results are displayed in Table 3. The best results were obtained as soon as this reaction was terminated by H$_2$O (see Table 3).

Although cyclohexanol is very active in this system, the control experiment displayed that no product was detected in cyclohexanol oxidation without the catalyst. MgAl$_2$O$_4$, MgAl$_2$O$_4$@SiO$_2$, MgAl$_2$O$_4$@SiO$_2$-PTA and H$_3$PW$_{12}$O$_{40}$ were used to evaluate the effectiveness of catalyst on this reaction. As shown in Table 4. MgAl$_2$O$_4$@SiO$_2$-PTA displayed the best catalytic activity for oxidation of cyclohexanol (see Table 4).

The oxidation of cyclohexanol to cyclohexanone by MgAl$_2$O$_4$@SiO$_2$-PTA with various molar ratio of H$_2$O$_2$/ cyclohexanol was studied in details and

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**Table 3. Effect of various solvents on the cyclohexanol oxidation.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water</td>
<td>1.5</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>Acetonitrile</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>Chloroform</td>
<td>3</td>
<td>61</td>
</tr>
<tr>
<td>4</td>
<td>Solvent free</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>5</td>
<td>62</td>
</tr>
</tbody>
</table>

All reaction conditions cyclohexanol (1mmol) catalyst (0.015 mmol), solvent (3 ml) and H$_2$O$_2$ (2 mmol) was stirred at 90°C.
The recovery process of MgAl$_2$O$_4$@SiO$_2$–PTA in this system has the same process as the optimized conditions. The catalyst was isolated from final product by a simple filtration. After that, it washed twice with water and ethanol. After drying the isolated catalyst at 100 °C for 2 hours, it was reused in a new reaction. The results are listed in Table 6. The recovered catalyst could be reused for four times with no changes in activity (see Table 6).

CONCLUSIONS

In this study a novel nanocomposite as a recyclable catalyst was introduced for oxidation of aliphatic alcohols in water with hydrogen peroxide. The synthesized catalyst was analyzed by X-ray diffraction (XRD), FT-IR, SEM, EDX and Brunauer-Emmett-Teller (BET) surface area analysis techniques. Cyclohexanol was converted to cyclohexanone with a high yield by controlling the ratio of H$_2$O$_2$ to cyclohexanol. The reaction of this nanocomposite is environmentally friendly. Also, the catalyst is recyclable in aliphatic alcohols oxidation process. This catalyst could be recovered by simple filtration and reused for four times without any loss of activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this review article.

REFERENCES


