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#### Supported Platinum Nanoparticles onto the Polymeric Ionic Liquid Functionalized Magnetic Silica: As an Effective and Reusable Heterogeneous Catalyst for Selective Oxidation of Alcohols in Water

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#### Abstract

In this research, the synthesis of core-shell nanostructure of magnetic silica, functionalization by polymeric ionic liquid and immobilization of platinum nanoparticles, are described. Firstly, the magnetic silica nanoparticles was synthesized and modified by amine-containing organosilane through the single-step process. The nanostructures were functionalized by synthesis and polymerization of pyridinium ionic liquid and methyl methacrylate monomer onto their surfaces, respectively. The platinum nanoparticles were immobilized on the functionalized nanoparticles. The obtained functionalized nanostructures have been used in selective aerobic oxidation of primary and encumbered secondary aliphatic alcohols in the aqueous medium with high activity at mild temperature.

**Keywords:** Magnetic silica, Pyridinium ionic liquid, Platinum nanoparticle, Aerobic oxidation, Alcohol

#### Introduction

The selective oxidation of hydrocarbons and of other organic compounds has become of considerable importance as a means for the direct synthesis of valuable oxygen-containing compounds such as aldehydes, ketones and carboxylic acids.<sup>1-4</sup> The selective oxidation of alcohols is one of the most effective approaches to produce this compound that was abundantly used in the recent decades.<sup>5-7</sup> The conventional methods for oxidation of alcohols are consisted of using stoichiometric amount of hazardous reagent such as nitric acid, potassium dichromate,

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potassium permanganate, sodium hypochlorite and organic peroxides.<sup>8-10</sup> These methods have any environmental issue include producing abundant wastes using mentioned oxidant.<sup>11, 12</sup> Aerobic oxidation of alcohols in presences of transition metals or organic free-radical initiator is attractive choice that was reported more than other methods in recent years.<sup>13-15</sup>

Heterogeneous catalyst systems, as a significant goal of green chemistry to maximize the efficiency of the reactants and minimize the production of wastes, are highly regarded in organic process, especially in the oxidation of alcohols.<sup>13, 16</sup> Heterogeneous catalyst systems have many advantage in compare to homogeneous systems such as more recyclability, simple workup process, low toxicity and more selectivity to produce the controllable approaches in the reactions.<sup>17</sup> Recently, numerous methods have been developed for design and preparation of heterogeneous catalysts based on synthetic and natural nanomaterials such as nanoparticles, polymeric nanostructures and carbon allotropes.<sup>18-21</sup> Among them, silica nanoparticles (NPs) due to theirs high specific surface area, extraordinary thermal and mechanical properties, and high stability to different conditions has been thought to be an ideal support in heterogeneous catalysis.<sup>22, 23</sup> The silica NPs have potential to produce the advance catalysts because these particles can be easily functionalized by wide range of organic and inorganic active species via physical and chemical interactions.<sup>24</sup> The organic functionalization of the silica NPs was carried out by initial modification of particles surface using organosilane agents that were provided the ability to make covalent bonds with any organic or polymeric groups.<sup>25</sup> The metal cations (or nanoparticles) can be effectively loaded onto the more suitable sites of organic functionalized silica NPs via electrostatic interactions and coordination with negative potential of porous silica structure and surface active species, respectively.<sup>26</sup> Recently, abundant papers were reported the synthesis of multi-functional silica NPs by various methods using large scope of organic and inorganic reagent that was used in the organic reactions as a heterogeneous catalyst.<sup>27-31</sup>

Herein, we have focused on the design and preparation of a novel magnetic silica NPs with highly disperse properties and good affinity for immobilization of platinum NPs as an efficient heterogeneous catalyst for oxidation of alcohols in aqueous medium. For this reason, the magnetic silica nanoparticles was prepared and modified using amine-containing organosilane (APTES). The resultant particles were functionalized by sequential reaction with 4-(Bromomethyl)pyridine, 2-bromoethanol and 2-bromo-2-methylpropanoyl bromide to produce pyridinium ionic liquid onto their surfaces as an initiator in the copper-mediated atom transfer

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radical polymerization (ATRP) of methyl methacrylate (MMA) to afford well-defined polymer with pyridinium ionic functionality situated between the chain and particle surfaces. Due to the existence of the ionic center, ability of ester functions of polymeric chain to interaction with water and hydrophilic nature of silica, these NPs have good dispersity in aqueous mediums. Next the platinum NPs successfully immobilized on these NPs, and the final catalyst (Pt@MS-IL-PMMA) was characterized by FTIR, TGA, ICP-OES, EDX, SEM, TEM and XRD techniques (Scheme 1).



Scheme 1. Preparation of Platinum NPs supported on ionic liquid based poly(methyl methacrylate)functionalized magnetic silica NPs (Pt@MS-IL-PMMA).

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#### **Experimental**

#### General

Tetraethoxysilane (TEOS, 99%), aminopropyltriethoxysilane (APTES, 99%) and all material and solvent were purchased from Merck and Aldrich companies and used without further purification.

#### **Characterization techniques**

FTIR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Transmission electron microscopy (TEM) analysis was performed using a ZEISS EM-900 at an acceleration voltage of 80 kV. Scanning electron microscopy (SEM) and EDX were performed on a Philips XL-300 instrument. The sample was sputtered by gold to avoid undesirable electron charging. Catalysis products were analyzed using a Varian 3900 GC by the undecane internal standard. Ultrasonication was performed in a EUROSONIC 4D ultrasound cleaner with a frequency of 50 kHz and an output power of 350 W. Thermogravimetric analysis (TGA) was carried out using an STA 1500 instrument at a heating rate of 10 °C min<sup>-1</sup> in air. X-ray powder diffraction (XRD) data were collected on an XD-3A diffractometer using Cu Karadiation. The concentration of Platinum was estimated using inductively coupled plasma optical emission spectrometer (ICP-OES) Varian Vista PRO Radial. <sup>1</sup>H NMR spectra were acquired using 300 MHz NMR and 400 MHz Bruker spectrometers.

#### General procedure for preparation of the amine-modified magnetic silica

The Fe<sub>3</sub>O<sub>4</sub> NPs were synthesized using previously report by co-precipitation method. In the first, FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O with molar ratio of 1: 2 (2 mmol: 4 mmol) were dissolved in the deionized water (250 mL) and temperature of the solution was increased to 60 °C under stirring. After 30 min ammonia solution (20 mL, 25 %) was added to the reaction (pH raised to 11), and the reaction mixture was cooled to ambient temperature. The magnetic NPs was collected using external magnet and after washing three times by water and ethanol, dried at 80 °C for 6 h. Next, the Fe<sub>3</sub>O<sub>4</sub> NPs (0.05 g) and TEOS (0.20 g, 1 mmol) were added to 2-propanol (30 mL) with ultrasonic irradiation. After 10 minute, ammonia solution (10 mL, 2 %) was added to the solution and stirred the reaction mixture for 12 h. the obtained NPs were separated *via* external magnet, washed by water and dried at 100 °C for 3 h. the modification of magnetic silica NPs (0.1 g) was performed in the toluene (15 mL) as solvent by mixing NPs (0.1 g) and APTES (0.22 g, 1 mmol) and the reaction temperature raised 110 °C under

vigorously stirring. After completion of the reaction modified NPs was collected and washed two times with ethanol and dried at 100 °C for 3 h.

General procedure for synthesis of pyridinium based ionic liquid onto the surface of SiO<sub>2</sub>@  $Fe_3O_4$ -NH<sub>2</sub>

The SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub> NPs (0.10 g), 4-(bromomethyl)pyridine (0.25 g, 1 mmol) and Sodium hexafluorophosphate (0.17 g, 1 mmol) were poured in deionized water (30 mL) and sunicated for 1 h. Then, the 2-bromoethanol (0.13 g, 1 mmol) was added to reaction mixture and refluxed for 6 h. At the end of this time, the 2-bromo-2-methylpropanoyl bromide (0.23 g, 1 mmol) solution in acetonitrile (10 mL) was injected to the reaction mixture and stirred for more 4 h at 80 °C. After completion of the reaction, the NPs were sparated using external magnet, washed two times by ethanol and water and dried under reduced pressure at 80 °C to obtain MS-IL NPs.

#### General procedure for synthesis of Pt@MS-IL-PMMA NPs

The PMMA functionalization of MS-IL NPs was carried out by ATRP method.<sup>32</sup> The MS-IL NPs, CuBr (0.0067 g, 0.05 mmol) and bpy (0.0147 g, 0.1 mmol) were added to a Schlenk flask containing DMF (10 mL) and the flask capped and sealed. The reaction flask air was removed under nitrogen blowing, then MMA (1 mL) injected to the mixture and temperature was raised to 45 °C. Finally, the Pt@MS-IL-PMMA NPs were separated by external magnet, washed by CHCl<sub>3</sub> and water, and dried at 80 °C.

#### General procedure for selective oxidation of primary alcohols to aldehydes

The catalyst (0.03 g, 4.8 mmol %) was added to the mixture of alcohol (1 mmol) in deionized water and stirred at 80 °C. The completion of reaction was monitored by tin layer chromatography (TLC). At the end of reaction, the catalyst was separated by external magnet, the reaction solution was extracted by CHCl<sub>3</sub> analyzed by GC method.

## General procedure for selective oxidation of primary alcohols to carboxylic acid and secondary alcohols to ketones

The catalyst (0.03 g, 4.8 mmol %) was added to the mixture of alcohol (1 mmol) and  $K_2CO_3$  (0.014g) in deionized water and stirred at 80 °C. The completion of reaction was monitored by tin layer

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chromatography (TLC). At the end of reaction, the catalyst was separated by external magnet and the reaction solution was extracted by CHCl<sub>3</sub> analyzed by GC method.

#### **Results and discussion**

The FTIR spectra of the each step of preparation of the Pt@MS-IL-PMMA are provided and shown in Fig. 1I. The Fe<sub>3</sub>O<sub>4</sub> peaks are appeared at 647, 593 and 448 cm<sup>-1</sup> correspond to the stretching vibrations of Fe–O bonds, while the absorption peak at 3248 cm<sup>-1</sup> is the OH stretching vibration characteristic peak, indicating the existence of some amount of ferric hydroxide in Fe<sub>3</sub>O<sub>4</sub>.<sup>33</sup> These peaks are appeared in the all of spectra. In the spectrum of the magnetic silica NPs and next steps, the peaks at 463, 1088 cm<sup>-1</sup> and 585 cm<sup>-1</sup> are respectively resulted by stretching and bending vibrations of Si–O–Si and stretching vibrations Fe–O–Si, and the absorption peaks of silanol groups (Si–OH) are observed at 3460, 1100 and 960 cm<sup>-1</sup>.<sup>34</sup> After modification of the NPs, the peaks of aliphatic C-H are at 2847 and 2926 cm<sup>-1</sup>, and the C-N peaks are covered by the broad peaks of Si-OH and Si–O–Si bonds. In the case of the MS-IL, the broad peak at 1486-1760 cm<sup>-1</sup> can be explained by presence of C=O, C=N and C=C, and the P-F with C-Br peaks vibrations are appeared in 580-600 cm<sup>-1</sup> respectively.<sup>35, 36</sup> Due to the formation of polymeric chain in the Pt@MS-IL-PMMA, the broad peak at 1440-1780 cm<sup>-1</sup> was observed corresponding to the C=O vibrations of ester groups.<sup>37</sup>

The XRD patterns of the magnetic silica and Pt@MS-IL-PMMA are shown in the Fig. 1II, that are confirmed the retention of  $Fe_3O_4$  NPs in the structure of the both cases and existence of the Pt NPs onto the surface of the Pt@MS-IL-PMMA catalyst. The characteristic diffractions of  $Fe_3O_4$  and Pt NPs are noted in their patterns that are in good agreement with previously reports.<sup>38, 39</sup>

The TGA analysis of the magnetic silica, MS-IL-PMMA and Pt@MS-IL-PMMA NPs are used to specify the presence of desired function and measurement the amounts of the organic content and Pt NPs. As seen in the Fig. 1III, the initial weight losses before 120 °C are occurred due to the elimination of moisture and Volatiles. In the case of MS-IL-PMMA and Pt@MS-IL-PMMA, the new step of the weight losing at 380 °C are occurred due to the decomposing their organic contents. Using comparison the remaining weights of the all of cases at 700 °C, the percentage of the organic contents and Pt NPs was measured 3.4 % and 1.2 %, respectively.



Figure 1. (I) FTIR spectra of Fe<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>-NH<sub>2</sub>, MS-IL, Pt@MS-IL-PMMA (a, b, c, d and e, respectively), (II) XRD pattern of SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub> (a) and Pt@MS-IL-PMMA (b), and (III) TGA analysis of SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub>(a), MS-IL-PMMA (b) and Pt@MS-IL-PMMA (c).

The SEM images of modified magnetic silica NPs and final catalyst are presented in the Fig 2, which are shown the Semi-spherical of magnetic silica with average diameters of 78-95 nm. After modification and functionalization process, due to the presence of MMA polymeric chain onto this surface, the particles have the sponge-like the morphology aggregated particles by average diameters less than 100 nm. In addition the TEM images of the final catalyst are confirmed the core-shell structure of the NPs with two types of the dispersed small particles in their structures. The average sizes of this small particles are measured 15-20 and low than 5 nm corresponding to Fe<sub>3</sub>O<sub>4</sub> and Pt NPs, respectively. Also, the EDX analysis from the Pt@MS-IL-PMMA are shown the all of desired elements (Fig 2).



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**Figure 2.** SEM images of SiO<sub>2</sub>@ Fe<sub>3</sub>O<sub>4</sub> (I, II), Pt@MS-IL-PMMA (III, IV), TEM images of Pt@MS-IL-PMMA (V, VI), and EDX analysis of Pt@MS-IL-PMMA (VII).

The characterized catalyst have a good dispersity in the water and protic solvents such as ethanol and methanol in compare to modified magnetic silica NPs, which are shown in the Fig. 3. All images were captured after 2 h of dispersion of particles in the solvents.



**Figure 3.** Dispersity properties of modified magnetic silica NPs in water (I), Pt@MS-IL-PMMA NPs in water (II), ethanol (III) and in methanol (IV) after 2 h.

To evaluate the catalytic properties of this catalyst, aerobic oxidation of the primary and encumbered secondary alcohols in the aqueous mediums is chosen. In order to optimize the reaction conditions, oxidation of benzyl alcohol was performed as a model reaction, and the reaction was carried out in the presence of various amounts of catalyst at different temperatures in deionized water under air blowing (Table 1). As seen in the below, when the reaction was examined in the deionized was water without any additives at room temperature, the low yield of benzaldehyde as the product was obtained. The yield of reaction was increased using the higher temperature in presence of same amounts of the catalyst (entries 1-3). Next, the reaction was examined in presence of different amounts of the catalyst (entries 3-5). In addition this reaction was examined in the some organic solvents such as EtOH, EtOAc and CH<sub>3</sub>CN, and the reaction was accomplished in the EtOAc and CH<sub>3</sub>CN with low and moderate yield, respectively (entries 6-8). At the end of this step of the optimization experiments, the 4.8 mmol % of the Pt@MS-IL-PMMA at 80 °C was selected as optimal amount of the catalyst and the best temperature to obtain the highest yield of the benzaldehyde in water. It is prominent to note that the reaction was produced the low yield of product in the presence of Pt NPs under optimized conditions (entry 9). Similarly, the reaction was repeated using same amount of MS-IL-PMMA that was failed (entry 10). The results confirmed the synergic effect of the composite structure of the support through the catalytic activity of Pt NPs. The main benefit of the ionic liquid polymeric shell seems to come from increased the interaction of nanocomposites with substrates by the hydrogen bands and dipole-dipole interactions also provided the dispersed Pt NPs. Additionaly, interactions

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between metal *d* orbital and  $\pi$ -level of dendrimer chains can effect on the delocalization of the electron density over both metal and ligand. These interactions may change the electrochemical properties of metal.<sup>40, 41</sup> In the second step, the reaction was carried out in the same conditions as previous step in presence of various base additive. The reaction was completed, but the obtained product is benzoic acid. K<sub>2</sub>CO<sub>3</sub> was selected as a mild additive in this reaction to produce the high yield of the benzoic acid (entry 13).

Entry	Gram of cat. (mmol %)	Solvent	Additive (mmol %)	T (°C)	Time (min	Yield <sup>b</sup> (%)
1	0.05 (8.0)	H <sub>2</sub> O	-	r.t.	120	10 <sup>c</sup>
2	0.05 (8.0)	$H_2O$	-	50	120	18 <sup>c</sup>
3	0.05 (8.0)	$H_2O$	-	80	30	90 <sup>c</sup>
4	0.03 (4.8)	$H_2O$	-	80	30	90 <sup>c</sup>
5	0.02 (3.2)	$H_2O$	-	80	30	53°
6	0.03 (4.8)	EtOH	-	70	120	Trace <sup>c</sup>
7	0.03 (4.8)	EtOAc	-	70	120	30 <sup>c</sup>
8	0.03 (4.8)	CH <sub>3</sub> CN	-	80	120	73°
9	$0.01 (4.8)^{e}$	$H_2O$	-	80	240	14 <sup>c</sup>
10	0.03 <sup>f</sup>	$H_2O$	-	80	240	0
11	0.03 (4.8)	$H_2O$	NaOH (10)	80	15	$78^{d}$
12	0.03 (4.8)	$H_2O$	KOH (10)	80	15	>99 <sup>d</sup>
13	0.03 (4.8)	$H_2O$	K <sub>2</sub> CO <sub>3</sub> (10)	80	60	96 <sup>d</sup>
14	0.03 (4.8)	H <sub>2</sub> O	Et <sub>3</sub> N (10)	80	120	$24^{d}$

**Table 1.** Optimization of reaction conditions<sup>a</sup>

<sup>a</sup>benzylalcohol (1 mmol) in solvent (5 mL) in presence of Pt@MS-IL-PMMA under stirring and air blowing, <sup>b</sup>CG measured yield, <sup>c</sup>yield of benzaldehyde, <sup>d</sup>yield of benzoicacid. <sup>e</sup>Pt nanoparticles and <sup>f</sup>MS-IL-PMMAwas used as catalyst.

In order to investigate the scope and limitations of this catalyst in the selective aerobic oxidation of alcohols, a variety of primary alcohols were used in the two optimized reaction conditions to obtain the corresponding aldehydes and carboxylic acids. All products were obtained in high yields. The structure of the products are presented in the Table 2. In view of the success of the above mentioned reactions, we decided to extend the study to secondary alcohols. In the case of secondary alcohols, the

### **Table 2**. Aerobic oxidation of primary alcohols<sup>a</sup>



<sup>a</sup> alcohol (1 mmol), catalyst (0.03 g, 4.8 mmol %), K<sub>2</sub>CO<sub>3</sub> (0.014g, 10 mmol%, in the cases of carboxylic acid preparation) water (5 mL) under air blowing at 80 °C, <sup>b</sup>CG measured yield.

best results was obtained in the presence of  $K_2CO_3$  as additive. As shown in Table 3, the reaction led to the formation of products in relatively good yields. Some of selected compounds were isolated and characterized by <sup>1</sup>H NMR analysis.



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<sup>a</sup> alcohol (1 mmol), catalyst (0.03 g, 4.8 mmol %), K<sub>2</sub>CO<sub>3</sub> (0.014g, 10 mmol%) water (5 mL) under air blowing at 80 °C, <sup>b</sup>CG measured yield.

The kinetics of benzyl alcohol oxidation was described by a first-order rate equation for the all cases of oxidation reactions; Equation (1).

$$r_{oxidation} = \frac{dC}{dt} = -k_{obs}.C$$
(1)

where  $r_{oxidation}$  is the rate of oxidation reaction, the time of reaction and  $k_{obs}$  is the rate constant.

The experiments were repeated under optimized conditions and pseudo first-order rate constants,  $k_{obs}$  were computed from the gradient of the graph of ln ( $C/C_o$ ), corresponding to ln ( $A/A_o$ ) vs. reaction time; Equation (2-4).  $C_o$  was the initial concentration of benzyl alcohol, and C was the concentration at time "t". The activation energy for the reaction were determined from the slope of the graph of the ln  $k_{obs}$  vs. inverse temperature (Fig. 4).

$$C = C_0 \cdot e^{-k_{obs} \cdot t} \tag{2}$$

$$-\ln\frac{c}{c_0} = k_{obs}.t\tag{3}$$

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$$A = \varepsilon b \mathcal{C} \tag{4}$$

where A is benzyl alcohol UV-Vis absorbance,  $\varepsilon$  is molar attenuation coefficient of sample and b path length of the beam of light through the material sample.



**Figure 4**. Plots of  $\ln (A/A_0)$  vs. time (i) and Plots of  $\ln k$  vs. invers temperature (ii) at optimized conditions for oxidation of benzyl alcohol to benzaldehyde and benzoic acid, and and 1-phenylethanol to acethophenone.

 Table 4. Activation energy for oxidation of benzyl alcohol to benzaldehyde and benzoic acid, and and 1-phenylethanol to acethophenone

Entry	Product	E <sub>a</sub> (kJ.mol <sup>-1</sup> )
1	Benzaldehyde	48.542
2	Benzoic acid	74.611
3	Acetophenone	65.542

The catalyst was collect using external magnet after the completion the reaction, washed three time by ethanol and water and dried at 80  $^{\circ}$ C. Next, reusability of the catalyst was evaluated in the aerobic oxidation of the primary alcohols in presence of K<sub>2</sub>CO<sub>3</sub> for 5 times. The results show that the activity of the catalyst was maintained after 5 time using and shown the slight decrease in yield of reaction (Fig. 5).



Figure 5. Recyclability of the catalyst in the synthesis of benzoic acid

The proposed mechanism for oxidation of alcohols in the presence of Pt NPs was depicted below with respect to other reports about oxidation of alcohols by transition metals.<sup>42,43</sup>



Figure 6. Proposed mechanism

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#### Conclusion

In conclusion, we demonstrated that the functionalized magnetic silica nanoparticles with poly(methylmethacrylate) using pyridinium based ionic liquid initiator by ATRP methods and immobilization of Pt nanoparticles on this surface is an efficient and recyclable catalyst system for the selective, aerobic oxidation of various primary and secondary alcohols. It is believed that the pyridinium groups with ester functions of polymeric chain onto the surface of the magnetic silica are provided the paths for the generation, stabilization, and homogeneous distribution of Pt nanoparticles and also they can afford a means of facilitating mass transfer of the starting materials to the active sites, which would enhance the performance of the catalyst.

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