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# Heteropoly acid encapsulated into zeolite imidazolate framework (ZIF-67) cage as an efficient heterogeneous catalyst for Friedel–Crafts acylation



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#### 1. Introduction

The production of various pharmaceutical, pesticides, dyes and agrochemicals at industrial scale involves the synthesis and further transformation of aromatic ketones. The Friedel-Crafts acylation of aromatic compounds is an essential route for the synthesis of the aromatic ketones that are intermediates in the manufacturing of fine and special chemicals as well as pharmaceuticals [1]. Traditionally Lewis acid catalysts i.e. ZnCl<sub>2</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub> and Brönsted acid catalysts i.e. HCl, HF and H<sub>2</sub>SO<sub>4</sub> had been significantly used for the acylation of aromatic compounds [2]. Utilization of homogeneous acid catalyst for the acylation reactions caused a number of issues such as produced impurities along with desired products, production of large amounts of toxic waste, increase in expenditures, and utilization of catalyst more than stoichiometric quantity, and difficulty in recovery. For Friedel-Crafts reactions, incessant investigation for appropriate heterogeneous catalyst had led to growth of catalysts for example Re-Br(CO)<sub>5</sub>, LiClO<sub>4</sub>-acyl anhydride complex [3], acid-treated clays [4], HZSM-5 zeolite [5], cation exchange resins [6], Ln-(OTf)<sub>3</sub>-LiClO<sub>4</sub> [7], and heteropoly acids supported catalyst [8,9].

The literatures until now supply an array of catalysts and reage-

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#### ABSTRACT

A new strategy has been developed for the encapsulation of the phosphotungstic heteropoly acid  $(H_3PW_{12}O_{40}$  denoted as PTA) into zeolite imidazolate framework (ZIF-67) cage and the PTA@ZIF-67(ec) catalysts with different PTA content were prepared. The structure of the catalysts was characterized by XRD, BET, SEM, FT-IR, ICP-AES and TG. The catalytic activity and recovery properties of the catalysts for the Friedel-Crafts acylation of anisole with benzoyl chloride were evaluated. The results showed that 14.6–31.7 wt% PTA were encapsulated in the ZIF-67 cage. The PTA@ZIF-67(ec) catalysts had good catalytic activity for Friedel-Crafts acylation. The conversion of anisole can reach ~ 100% and the selectivity of the production can reach ~ 94% over 26.5 wt% PTA@ZIF-67(ec) catalyst under the reaction condition of 120 °C and 6 h. After reaction, the catalyst can be reused five times and the selectivity can be kept over 90%. © 2015 Elsevier Inc. All rights reserved.

nts employ for the Friedel-Crafts acylation of aromatic compounds. However, there is ambit to develop heterogeneous acid catalysts for the Friedel-Crafts acylation reaction. Solid catalysts are secure, reasonable and benign. Furthermore the methods using solid catalysts have advantages for instance better selectivity, moderate reaction conditions, minimize waste and cheap construction of material [9,10]. Acetic acid, acetic anhydride and acetyl chloride as acylating agents have been utilized for the acylation of activated aromatic compounds in presence of zeolites [10], acid-treated metal oxides [11] and heteropoly acids [12]. However, heteropoly acids (HPAs) have been used in excess of organic reactions [9,12]. Nevertheless heteropoly acids in unsupported form present poor stability, fast deactivation and low efficiency. A variety of supports, as mesoporous alumina silicate, mesoporous silica, carbon, alumina, zirconia and metal-organic frameworks (MOFs) have been employed to build up the stability and effectiveness of heteropoly acids [13]. Indeed, the catalytic activity and acidity of the supported heteropoly acids rely mainly on the loading and the nature of carrier, i.e. strong interaction with activated carbons cause low catalytic activity than that of the heteropoly acid itself, while dramatic leaching cause by low interactions of heteropoly acid with support. Direct synthesis of the Keggin structures inside the zeolite cavities (FAU) has been used to achieve the encapsulation of heteropoly acids. This method is revealed to solve the leaching problem, since the windows of the zeolitic cavities are smaller than the heteropoly acid clusters, but only very low loadings can be utilized (< 5 wt%) if diffusion limitations are to be avoided [14].

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Metal-organic frameworks (MOFs) consist of metallic nodes bonded by organic linker, are currently receiving significant attention because of their versatile properties [15-17]. They have been extensively utilized as gas storage [18], separation [19], ion exchange [20], sensor drug delivery [21] and catalysis [22,23]. MOFs as compared to traditional microporous and mesoporous inorganic materials reveal advantages such as tunable pore sizes, high surface area, structural diversity, flexibility and geometrical control by the functionalization and controlling the size of organic linkers [24,25]. However, MOFs used in catalysis are limited because of limited thermal and moisture stability including often completely blocked metal sites by the organic linker or solvent. leaving no free position available for substrate chemisorption's [26]. Zeolite imidazolate frameworks (ZIFs) classified as a novel subclass of MOFs, have fascinated important attention as they unite advantages from both zeolite and conventional MOFs [27,28]. In the past decade, research works have directed on synthesizing new ZIFs and utilizations in different fields. In the literature, there are a small number of applications of ZIFs as catalyst or catalyst supports for transformation of organic compounds as compare to conventional MOFs [29–31].

In this work, we wish to report a direct, synthetic encapsulation of active species such as phosphotungstic acid (PTA) into MOFs. We demonstrate that incorporation of highly dispersed PTA into zeolite imidazolate frameworks-67 (ZIF-67) cage is possible to achieve by following the one-pot synthesis approach. As far as we know, the Friedel–Crafts acylation reaction catalyzes by PTA encapsulated in ZIF-67 are not previously mentioned in the literature. The novel composite material PTA@ZIF-67(ec) has been utilized as an efficient heterogeneous catalyst for Friedel–Crafts acylation reaction of anisole with benzoyl chloride. High conversions have been achieved with PTA@ZIF-67(ec) catalyst without an inert atmosphere. PTA@ZIF-67(ec) catalyst was easily separated from the reaction mixture and reused without significant degradation in activity.

#### 2. Experimental

#### 2.1. Materials

Cobalt nitrate hexahydrate (99%), 2-methylimidazole (98%) and phosphotungstic acid were purchased from Aladdin Chemical Co., Ltd., China. Anisole ( $\geq$  98%) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Benzoyl Chloride (98%) was purchased from Tianjin Fuchen Chemical Reagents, China. Diethyl ether and methanol were purchased from Beijing Yili Fine Chemical Co. Ltd., China. Hydrogen gas and nitrogen gas were purchased from HaiPu Gas Industry Co. Ltd., China. All these reagents were used as received without further purification.

#### 2.2. Catalyst Preparation

#### 2.2.1. Zeolite imidazolate framework (ZIF-67) preparation

For the synthesis of ZIF-67, 0.722 g of Co  $(NO_3)_2 \cdot 6H_2O(2.48 \text{ mmol})$  was dissolved in 25 mL methanol and 1.629 g of 2-methylimidazole (19.84 mmol) was dissolved in 25 mL methanol separately, were stirred until dissolved. When both reagents were entirely dissolved in methanol, the solution consists of 2-methylimidazole was slowly added to the solution of Co  $(NO_3)_2 \cdot 6H_2O$ . The solution became purple immediately, and the resultant mixture was stirred for 2 h at room temperature. The solids were collected by centrifugation for 10 min and were washed with methanol for several times to remove excess 2-methylimidazole present on the surface and pores. Then solids were dried overnight in air oven, at room temperature. Finally, the sample was dried under vacuum at 130 °C for 2 h.

#### 2.2.2. PTA@ZIF-67(ec) Preparation

The encapsulation of the phosphotungstic acid in ZIF-67 has been done by the same procedure as follow in the synthesis of ZIF-67 with same synthesis mixture. But the phosphotungstic acid (PTA) was dissolved in 11 mL deionized water and added to Co  $(NO_3)_2 \cdot 6H_2O$  solution. Different loadings of phosphotungstic acid in ZIF-67 structure were achieved (14.6 wt% to 46.4 wt% according to ICP-AES), depending on the amount of phosphotungstic acid introduced into the synthesis mixture.

#### 2.3. Catalyst characterization

The power X-ray diffraction patterns of all samples were recorded at room temperature using a Cu Ka radiation source  $(\lambda = 1.54056 \text{ Å})$ , operating at 40 kV and 50 mA using a Rigaku D/ Max 2500 VB2+/PC diffractometer. The BET surface areas and pore size distributions were obtained from N<sub>2</sub> adsorption-desorption isotherms measured on the Micrometrics ASAP 2020 adsorption analyzer at 77 K. Structure and morphology of samples were characterized by scanning electron microscopy (SEM) on a Zeiss Supra55. Fourier transform infrared (FT-IR) spectra of the samples were collected on a Bruker Tensor 27, by dispersing the samples on KBr pellets in the range of 600–4000 cm<sup>-1</sup>. Thermogravimetric analysis (TGA) measurements were collected on a SETSYS Evolution from Setaram Instrumentation with a heating rate of 10 °C /min in air up to 800 °C. Elemental analysis was performed by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The samples were investigated with SPECTRO Analytical Instruments GmbH in order to calculate the amount of PTA encapsulated into the ZIF-67 structure. Gas chromatographic (GC) analyses were carried out using a Beijing Beifenruili SP-2100 with flame ionization detector (FID). GC-MS analyses were carried out using a Shimadzu GCMS-QP5000.

#### 2.4. Catalytic performance testing

The Friedel-Crafts acylation of anisole with benzoyl chloride using PTA@ZIF-67(ec) catalyst was carried out in the magnetically stirred round-bottom flask. In a typical reaction, a mixture of anisole and benzoyl chloride with molar ratio 1:2, n-Dodecane as an internal standard was charged into a 50 mL flask containing the PTA@ZIF-67(ec) catalyst. The reaction mixture was then heated to 120 °C with continuously stirring for 6 h. After 6 h, the reaction mixture was quenched with an aqueous NaOH solution (1%, 0.15 mL). The organic components were extracted using diethyl ether (2 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the product was analyzed by GC. The structure of the product was defined by GC-MS. For the investigating the reusability of the catalyst, the PTA@ZIF-67(ec) catalyst was separated by simple centrifugation from the reaction mixture, washed with abundant amounts of dichloromethane (DCM), dried under vacuum at room temperature for 6 h and reused in reaction.

#### 3. Results and discussion

#### 3.1. XRD and BET

Fig. 1 illustrates the XRD patterns of bare ZIF-67 and PTA@ZIF-67(ec) samples. The XRD patterns of synthesized samples in this work were in good agreement with simulated single crystal structure patterns in the Cambridge Structural Database (CCDC code=GITTOT). In the bare ZIF-67 sample, a very sharp peak was detected at 7.3° on the XRD pattern, demonstrating that the material was obtained, is highly crystalline material.

In fact, whenever MOF-based materials are synthesized, highly



**Fig. 1.** XRD patterns of simulated ZIF-67 obtained from Cambridge Structural Database(a), ZIF-67 synthesized in this work(b), 14.6 wt% PTA@ZIF-67(ec)(c), 26.5 wt% PTA@ZIF-67(ec)(d), 31.7 wt% PTA@ZIF-67(ec)(e) and 46.4 wt% PTA added in synthesis mixture caused to demolish the crystal structure(f).

crystalline material is always expected. However, the PTA@ZIF-67 (ec) sample patterns showed hardly any difference and good agreement with the peaks of bare ZIF-67 up to a certain amount of PTA added in the synthesis mixture (14.6–31.7 wt% PTA@ZIF-67 (ec)). While, the presence of higher amount of PTA (46.4 wt% PTA added in synthesis mixture) caused to lower the pH of the synthesis mixture. Low pH prevented ligand from coordination with metal due to protonation and resulted into demolishing the crystal structure. Apart from the fact that the crystal structure appeared to remain unchanged during the PTA encapsulation while the intensity of the peak at 7.3° decreased for the PTA encapsulated samples.

Fig. 2A shows the N<sub>2</sub> adsorption-desorption isotherms of bare ZIF-67 and PTA@ZIF-67(ec). The isotherms revealed type-I with sharply increased adsorption at low relative pressure, which is typical for microporous materials. No indication of pore blocking was observed in the isotherms. The pore size distribution curves of bare ZIF-67 and PTA@ZIF-67(ec) were transformed using the Horvath–Kawazoe (HK) method, which further supported the presence of two kinds of micropore in bare and encapsulated ZIF-

67 as shown in Fig. 2B. With the inclusion of PTA, the pore size and pore volume were substantially decreased. The result is evidence that the highly accessible structure of the ZIF-67 is maintained, even at high PTA loading.

Table 1 presents the results of BET surface area, pore size and total pore volume. The BET surface area of the ZIF-67 encapsulated phosphotungstic acid decreases from 1390.45 to  $600.27 \text{ m}^2/\text{g}$  with addition of PTA. The total pore volume of the ZIF-67 encapsulated phosphotungstic acid also decreases from 0.71 to 0.29 cm<sup>3</sup>/g.

#### 3.2. Structure and morphology

Fig. 3 shows the SEM micrographs of ZIF-67 and different PTA@ZIF-67(ec) samples, synthesized at room temperature. According to SEM micrographs, ZIF-67 revealed that well-shaped, hexagonal nano-crystals were obtained having an average particle size of about 200 nm (Fig. 3a) and as the amount of PTA encapsulated into the cage of ZIF-67 (14.6–31.7 wt%) keep up the crystal shape and structure (Fig. 3b and c). But the higher amount of PTA about 46.4 wt% could not encapsulate PTA in the cage and demolished the crystal structure as shown in Fig. 3d.

#### 3.3. FT-IR spectroscopy

FT-IR spectroscopic studies were carried out to confirm whether PTA and ZIF-67 structures were preserved in the novel composite materials PTA@ZIF-67(ec). FT-IR spectra of bare ZIF-67 and different PTA@ZIF-67(ec) samples are shown in Fig. 4.

The bands at 693 and 753 cm<sup>-1</sup> in the spectral region are associated with out-of-plane bending of the imidazole ring, while peaks in the region of between 900 and 1350 cm<sup>-1</sup> are assigned as in-plane bending. The peaks at 1576 and 1663 cm<sup>-1</sup> are attributed to the stretching and bending N–H vibration of the imidazole ring, respectively. The intense and convoluted bands at 1350–1500 cm<sup>-1</sup> are associated with the entire ring stretching, whereas two peaks at 2922 and 3131 cm<sup>-1</sup> are attributed to the aliphatic and the aromatic C–H stretch of the imidazole, respectively. As one can judge from the FT-IR spectra of bare ZIF-67 and PTA@ZIF-67(ec) presented in Fig. 4, the most intensive peaks belong to ZIF-67 and the matrix structure certainly retained upon PTA encapsulation in ZIF-67. The presence of strongly bonded water in the PTA@ZIF-67(ec) samples can easily be observed as shown in Fig. 4(A) (range between 800 and 4000 cm<sup>-1</sup>), from a broad absorption band between 3200 and



Fig. 2. N<sub>2</sub> adsorption-desorption isotherms(A) and pore size distribution curves(B) of ZIF-67 synthesized in this work(a), 14.6 wt% PTA@ZIF-67(ec)(b), 26.5 wt% PTA@ZIF-67 (ec)(c) and 31.7 wt% PTA@ZIF-67(ec)(d).

Table 1				
Structural	characteristics	of ZIF-67	and	PTA@ZIF-67(ec) samples.

Samples	BET Surface area (m <sup>2</sup> /g)	Pore size (nm)	Total pore volume (cm <sup>3</sup> /g)	PTA (wt%)	ZIF-67 (wt%)
ZIF-67	1390.45	2.04	0.71	-	100.00
14.6 wt%PTA@ZIF-67(ec)	994.85	2.21	0.55	14.60	85.40
26.5 wt%PTA@ZIF-67(ec)	647.42	1.98	0.32	26.50	73.50
31.7 wt%PTA@ZIF-67(ec)	600.27	1.95	0.29	31.70	68.30



Fig. 3. SEM micrographs of ZIF-67 synthesized(a), 14.6 wt% PTA@ZIF-67(ec)(b), 26.5 wt% PTA@ZIF-67(ec)(c) and 46.4 wt% PTA added in synthesis mixture caused to demolish the crystal structure(d).



Fig. 4. FTIR spectra of the phosphotungstic acid (PTA)(a), ZIF-67 synthesized(b), 14.6 wt% PTA@ZIF-67(ec)(c), 26.5 wt% PTA@ZIF-67(ec)(d) and 31.7 wt% PTA@ZIF-67(ec)(e).



Fig. 5. TGA analysis of the ZIF-67 synthesized(a), 14.6 wt% PTA@ZIF-67(ec)(b), 26.5 wt% PTA@ZIF-67(ec)(c) and phosphotungstic acid (PTA)(d).

 $3700 \text{ cm}^{-1}$  and the broad band centered at  $1305 \text{ cm}^{-1}$  [32]. The stretching band at  $1305 \text{ cm}^{-1}$  is also present in the bare ZIF-67 sample; however the width and intensity is increased in PTA encapsulated samples.

When focusing on the 800–1100 cm<sup>-1</sup> range (Fig. 4(B)), after subtraction the bare ZIF-67 FT-IR spectra from PTA@ZIF-67(ec) sample spectra. The FT-IR spectra of novel composite materials PTA@ZIF-67(ec) exhibit the principal stretching modes of the PTA Keggin units such as W–O–W, W=O and PO<sub>4</sub>. The PO<sub>4</sub> stretching appeared at 1060 cm<sup>-1</sup>. The bands at 956 and 888, 823 cm<sup>-1</sup>, clearly present in all PTA@ZIF-67(ec) samples, are related to the W=O and W–O–W stretching, respectively. This definitely indicated that the heteropolyanion structure was maintained after encapsulation.

#### 3.4. Thermal stability analysis

Thermal degradation of solid materials has significant importance for their application because most of them depend on their thermal stability. Fig. 5 shows the TGA curves of PTA, ZIF-67 and PTA@ZIF-67(ec) samples. It can be seen that PTA revealed a one-step degradation process; bare ZIF-67 and PTA@ZIF-67(ec) samples followed two-step degradation process. The TGA curve of PTA only illustrated a weight loss at about 160 °C, perhaps as a result of dehydration of water from crystalline structure, and no more considerable weight loss was observed until 800 °C.

The TGA curve of bare ZIF-67 revealed that only tiny weight loss up to 350 °C, concerning to the removal of guest molecules and un-reacted species, while the thermal stability of PTA@ZIF-67 (ec) samples were reduced in the range 200–350 °C owing it to the introduction of PTA. Therefore, when comparing the residual content of bare ZIF-67 and PTA@ZIF-67(ec) samples, it can be observed that TGA curves showed high residual content systematically with the increase of PTA content. From TGA, it can be seen that encapsulation of the PTA into ZIF-67 structure did not badly damage the thermal stability.



**Fig. 6.** Effect of catalyst content on the reaction conversion in the presence of catalyst: ZIF-67 synthesized(a), 14.6 wt% PTA@ZIF-67(ec)(b), 26.5 wt% PTA@ZIF-67 (ec)(c), 31.7 wt% PTA@ZIF-67(ec)(d), and 46.4 wt% PTA added in synthesis mixture caused to demolish the crystal structure(e).

#### 3.5. Catalytic performance testing

#### 3.5.1. Screening of catalysts

The performance of the PTA@ZIF-67(ec) as a heterogeneous catalyst in the Friedel–Crafts acylation of anisole with benzoyl chloride was assessed (Scheme 1). The benzoyl chloride was used as an acylating agent to form p-benzoylanisole as the major product and o-benzoylanisole as the minor product.

In this work, it was achieved that the Friedel–Crafts acylation of anisole with benzoyl chloride can take place in the presence of bare ZIF-67 and PTA@ZIF-67(ec) as a catalyst. The reaction was carried out at 120 °C for 6 h with anisole:benzoyl chloride molar ratio 1:2 and the results were graphically summarized in Fig. 6.

The bare ZIF-67 gave hardly 45% conversion with higher amount of catalyst. PTA@ZIF-67(ec) samples were found much more active catalysts as compared to bare ZIF-67 under the same condition. A conversion of 100% was achieved in the presence of 26.5 wt% PTA@ZIF-67(ec) catalyst under reaction condition without an inert atmosphere. As it can be observed from Fig. 6, the bare ZIF-67 did not reveal good catalytic activity, most probably caused by the lack of active sites on which the Friedel-Crafts acylation reaction could take place. On the other hand, the encapsulated PTA into the ZIF-67 cage gave dramatic increment of strongly active sites on PTA@ZIF-67(ec), which resulted in a boost in the reaction conversion.

Furthermore, it was also observed that the catalytic activities of 26.5 wt% PTA@ZIF-67(ec) and 14.6 wt% PTA@ZIF-67(ec) catalysts were better than the 31.7 wt% PTA@ZIF-67(ec) catalyst under the same conditions, that can be caused by active sites strongly bonded with carrier and could not take part in the reaction efficiently in 31.7 wt% PTA@ZIF-67(ec) catalyst. The demolish sample of ZIF-67 caused by the PTA, showed higher conversion than 31.7 wt% PTA@ZIF-67(ec) catalyst may be because of some trace amount of PTA present with demolishing structure after washing. But, further investigation would be required to examine the mechanism thoroughly.



Scheme 1. Friedel-Crafts acylation of anisole with benzoyl chloride using PTA@ZIF-67(ec) catalyst.

Table 2Effects of 26.5yielda.	wt% P	TA@ZIF-67(	ec)catalyst	content on	reaction	convers	sion ar	٦d
26 5 wt% DTA	@7IE	DTA Con	715 67	Conversi	on Colo	ativity	Viold	_

26.5 wt% PTA@ZIF- 67(ec) Content (wt%)	PTA Con- tent (wt%)	ZIF-67 Content (wt%)	Conversion (%)	Selectivity (%)	Yield (%)
2	0.53	1.47	44.31	92.53	40.99
4	1.06	2.94	82.14	93.51	76.81
6	1.59	4.41	95.75	93.03	89.08
8	2.12	5.88	99.21	93.88	93.14
10	2.65	7.35	99.99	94.47	94.46

 $^{\rm a}$  Reaction condition: anisole, 0.006 mol; benzoyl chloride, 0.012 mol; temperature, 120 °C; time, 6 h.

#### 3.5.2. Effect of catalyst content

Table 2 shows the effect of PTA@ZIF-67(ec) catalyst content on reaction conversion, selectivity and yield. In the literature, it was reported that the Friedel-Crafts acylation reaction can be needed an extra stoichiometric amount of the Lewis acid due to complex formation with the oxygen atom of aroyl products [33,34]. The catalyst concentration can be diminished dramatically with various solid catalysts for the Friedel–Crafts acylation reaction such as beta zeolite [35,36], metal triflate loaded SBA-15 [37], hybrid zeolite-mesostructured material [38] and mesoporous superacid catalyst [39,40]. In fact, the Friedel–Crafts acylation reaction can need less than 1 wt% to more than 10 wt% catalyst, depending on the nature of the catalyst as well as the substrate.

In this work, it was observed from the preliminary investigations that catalyst content is a significant factor that can considerably influence the reaction conversion as well as yield of product. The reaction rate was found directly proportional to the 26.5 wt% PTA@ZIF-67(ec) catalyst content. 44% to 100% conversions were achieved in the presence of 2 wt% to 10 wt% of 26.5 wt% PTA@ZIF-67(ec) catalyst. Moreover, the reaction conversion observed for the 26.5 wt% PTA@ZIF-67(ec) catalyst was higher than several previously reported Lewis acid catalysts, where higher catalyst loading and/or longer reaction time was needed for the same reaction [41]. The selectivity was found almost the same for all cases with  $\sim$  94% for *p*-benzoylanisole.

Previously, Firouzabadi and co-workers used aluminum dodecatungstophosphate for Friedel–Crafts acylation of anisole with benzoyl chloride, as heterogeneous catalyst and achieved 80% selectivity to the *p*-benzoylanisole [42].Chourdhary and co-workers used zeolite based catalyst for the same reaction and ameliorated the selectivity of *p*-isomer to 90% [43]. Kemnitz and co-workers utilized borate zirconia solid acid as a heterogeneous catalyst and enhanced the selectivity to 93-95%, but the reaction was carried out in the presence of nitrobenzene as solvent [44]. Therefore, the selectivity of 26.5 wt% PTA@ZIF-67(ec) catalyst in the Friedel-Crafts acylation of anisole with benzoyl chloride was comparable with those previously reported in the literature.

#### 3.5.3. Effect of reaction temperature

With such results in hand, we then decided to investigate the effect of reaction temperature on conversion. The Friedel–Crafts acylation reaction was performed using 4 wt% of 26.5 wt% PTA@-ZIF-67(ec) catalyst at 140, 130, 120, 110 and 100 °C, respectively. Aliquots from the reaction mixtures were withdrawn after 6 h and analyzed by GC to provide kinetic data for the course of the reaction. After 6 h, a conversion of 82% was achieved at 120 °C reaction temperature. A considerable drop in the reaction rate was observed by decreasing the reaction temperature, with 71% and 57% conversions being achieved after 6 h at 110 and 100 °C, respectively. In fact, increasing the reaction temperature was not



**Fig. 7.** Effect of temperature on the reaction conversion and *p*-isomer selectivity over 26.5 wt% PTA@ZIF-67(ec) catalyst. Reaction condition: anisole, 0.006 mol; benzoyl chloride, 0.012 mol; catalyst amount, 0.1 g; time, 6 h.

able to give a significant increase in reaction conversions at 130 and 140 °C (Fig. 7) because the reaction reached almost the equilibrium under 140 °C. The reaction selectivity was found almost unchanged at  $\sim$ 94% to *p*-benzoylanisole (Fig. 7).

Whenever a solid catalyst is used, a vital issue is the risk that some active sites can transfer to the liquid phase from the solid support and so on; these leached species can be a significant factor for the reaction conversion [45]. In order to find out either leaching of active sites occurred in Friedel-Crafts acvlation reaction using PTA@ZIF-67(ec) catalyst or not. An experiment was accomplished to assess the contribution of leached active species to the reaction conversion. A simple centrifugation was carried out during the conduct of the reaction to separate the solid catalyst from the reaction mixture. If the catalytic reaction still carried on after the separation of solid catalyst, this would indicate that the real active species was leached acid rather of the solid PTA@ZIF-67 (ec) catalyst. Within experimental error, after the solid catalyst was separated from the organic phase, no further reaction was found. Consequently, it can be concluded that there were no leached active species in the organic phase, and reaction could only be carried out in the presence of PTA@ZIF-67(ec) catalyst. Choudhary and co-workers previously investigated by using a zeolite-based catalyst and reported that the rate of the Friedel-Crafts acylation reaction was drastically enhanced in the presence of new Brönsted acid sites developed by the interaction of the Lewis acid sites of the catalyst with moisture [43]. Lewis acid sites combine with Brönsted acid sites could devote to the catalytic activity of solid catalyst in the Friedel-Crafts acylation reaction.

#### 3.5.4. Effect of electron donors and withdraws as substitution group

The study was then expanded to investigate the effect of different substrates on the Friedel–Crafts acylation reaction using PTA@ZIF-67(ec) catalyst. The reaction was accomplished by using 4 wt% of 26.5 wt% PTA@ZIF-67(ec) catalyst with substrate:benzoyl chloride molar ratio 1:2 for 6 h. Fernandes and co-workers reported that the most excellent yields of Friedel–Crafts acylation were observed in the presence of electron donor groups in the aromatic ring [33]. In this work, the results illustrated that the addition of an electron donor group on the aromatic ring increased the acylation reaction conversion as well as yield while the addition of an electron withdraw groups significantly decreased them. The acylation reaction of anisole with benzoyl chloride gave 82% conversion at 120 °C after 6 h, whereas 73% and 69% conversions

Table 3Effect of electron donating and withdraw substitution group on acylation reaction<sup>a</sup>.

Substrate , R	Conversion (%)	Selectivity (%)		Yield (%)
		p-isomer	o-isomer	
R=OCH <sub>3</sub>	82.14	93.51	6.49	76.81
R=CH <sub>3</sub>	73.04	88.54	11.46	64.67
$R = C_2 H_5$	69.11	87.63	12.37	60.56
R=Br	45.64	69.75	30.25	31.83
R=CHO	40.41	74.43	25.57	30.08

<sup>a</sup> Reaction condition: substrate, 0.006 mol; benzoyl chloride, 0.012 mol; catalyst amount, 0.1 g; temperature, 120  $^{\circ}$ C; time, 6 h.



**Fig. 8.** Effect of reusability of 26.5 wt% PTA@ZIF-67(ec) catalyst on reaction conversion and *p*-isomer selectivity. Reaction condition: anisole, 0.006 mol; benzoyl chloride, 0.012 mol; catalyst amount, 0.1 g; temperature, 120 °C; time, 6 h.

were observed in the acylation of toluene and ethyl benzene, respectively under similar reaction conditions. In this work, it was also observed that benzaldehyde and bromobenzene were carried out sluggish with benzoyl chloride in the acylation reaction and afforded only 40% and 46% conversion with low selectivity to *p*-benzoylanisole, respectively (Table 3).

#### 3.6. Reusability of catalyst

The ease of separation, deactivation and reusability of the solid catalyst is a crucial issue that must be taken on significance during the utilization of catalyst. Consequently, the PTA@ZIF-67(ec) catalyst was probed for the recoverability and reusability in the Friedel-Crafts acylation reaction over five consecutive runs. The reaction was carried out at 120 °C with anisole:benzoyl chloride molar ratio 1:2 using 4 wt% of 26.5 wt% PTA@ZIF-67(ec) catalyst for 6 h. By simple centrifugation, the catalyst was separated from the organic phase after the reaction, and then washed with abundant amounts of toluene and DCM to get rid of any physisorbed reagents, and dried under vacuum at room temperature for 6 h after each run. The recovered 26.5 wt%PTA@ZIF-67(ec) catalyst was reused under same reaction conditions to those of the first run, in further reaction with aliquots were withdrawn from the reaction mixture and analyzed by GC. It was observed that PTA@ZIF-67(ec) catalyst could be recovered easily and reused with a gradual decrease in activity (Fig. 8).

On the other hand, the catalyst could be reused with 82%, 76%, 67%, 62% and 59% conversions after 6 h for five consecutive runs, respectively. In all cases, the reaction selectivity was observed more or less unchanged with  $\sim$ 94% of *p*-benzoylanisole (Fig. 8).

#### 4. Conclusion

The Friedel-Crafts acylation of anisole with benzoyl chloride is investigated over novel PTA@ZIF-67(ec) catalyst. The PTA@ZIF-67 (ec) catalyst has been synthesized by direct addition of phosphotungstic acid to the synthesis mixture of ZIF-67 at room temperature. An excellent dispersion of phosphotungstic acid over the ZIF-67 sample is achieved. Different amount of phosphotungstic acid has been encapsulated in a ZIF-67 structure (14.6-31.7 wt%) depending on the amount of phosphotungstic acid introduced in the synthesis mixture. Among the various (14.6-31.7 wt%) PTA@-ZIF-67(ec) catalyst, 26.5 wt% PTA@ZIF-67(ec) catalyst reveals high activity, stability and reusability for acylation reaction. The effects of catalyst content, reaction temperature and electron donor and withdraw as substitution group on reaction conversion and yield have been discussed in detail. In conclusion, we have utilized ZIF structure as a support for heteropoly acid and develop a highly active, stable, reusable and environmentally friendly heterogeneous catalyst for the Friedel-Crafts acylation.

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