

Fe₃O₄@SiO₂-imid-PMAⁿ as a Novel, Efficient and Reusable Magnetic Nanocatalyst for the Chemoselective Preparation and Deprotection of 1,1-Diacetates

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Abstract Fe₃O₄@SiO₂-imid-PMAⁿ efficiently catalyzed the conversion of aromatic, heteroaromatic, and aliphatic aldehydes to 1,1-diacetates under solvent-free conditions at room temperature. Deprotection of the resulting 1,1-diacetates can also be achieved using the same catalyst in methanol. The acylation of aldehydes was highly chemoselective, and no ketone was acylated, which provided a method for the synthesis of acylals from aldehydes in the presence of ketones. Therefore, this method gives notable advantages such as excellent chemoselectivity, mild reaction condition, short reaction times and excellent yield. Also, nanocatalyst can be easily recovered by a magnetic field and is reusable without efficient loss of its catalytic activity.

Keywords Nanocatalyst · 1,1-Diacetates · Aldehydes · Chemoselective · Deprotection · Magnetic separation

1 Introduction

The selective protection and deprotection of carbonyl groups are often necessary during a multistep organic synthesis. Aldehydes are often present in organic

molecules so development of economical, efficient and mild procedures for the protection of them is very important for synthetic organic chemistry. The protection of aldehydes as acetals, acylals, oxathioacetals or dithioacetals is a common practice for manipulation of other functional groups during multi-step syntheses (Kochhar et al. 1983). Among various procedures for protection of aldehyde, acylals (1,1-diacetates) are appropriate candidates to this aim due to their stability in basic and neutral reaction media as well as in aqueous acids (Kochhar et al. 1983). 1,1-Diacetates are also important for the preparation of other compounds, for example, in reaction with appropriate nucleophiles they can be converted to other useful functional groups (Shirini et al. 2013).

Meanwhile, gem-diacetates derived from α,β -unsaturated aldehydes are useful as dienes for Diels–Alder cycloaddition reactions (Frick and Harper 1984). Moreover, acylals are used as crosslinking reagents for cellulose in cotton (Frick and Harper 1984). Numerous methods for the preparation of 1,1-diacetates from aldehydes and acetic anhydride have been reported (Borikar and Daniel 2011; Gao et al. 2009; Moosavifar et al. 2011; Romanelli et al. 2010; Shelke et al. 2009). Although some of these methods afford good to high yields of the corresponding diacetates, the majority suffer from one or more of the following disadvantages: reactions under oxidizing conditions, use of strong acids, high temperatures, long reaction times, poor selectivity, use of unreusable catalysts, moisture sensitivity as well as high cost and high toxicity of the reagents. In addition, a few of the above mentioned catalysts are claimed to give protection as well as deprotection. Thus, the development of simple, convenient, and environmentally benign methods for the protection of aldehydes as 1,1-diacetates and their deprotection is still required.

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In recent years, heteropoly acids (HPAs), especially Keggin type have attracted increasing interest due to their high acidity, low toxicity and tunable redox properties (Javidi et al. 2014). Although HPAs are versatile compounds in their acidic form, their main disadvantages are high solubility in polar solvents and low surface area (<10 m²/g). Therefore, in a homogeneous reaction the isolation of the products and the reuse of the catalyst after reaction become difficult. So, to overcome this problem, these materials disperse on supports (such as silica, acidic ion-exchange resins, active carbon, etc.) which possess large surface area (Zhang et al. 2011).

In the field of catalysis, superparamagnetic nanoparticles have been utilized as catalyst supports for organic transformations such as alcohol hydrogenation (Polshettiwar et al. 2009), olefin hydrogenation (Lu et al. 2004), olefin hydroformylation (Yoon et al. 2003), Sonogashira and Carbonylative Sonogashira reactions (Esmailpour et al. 2014a), Suzuki and Heck cross-coupling reactions (Esmailpour et al. 2014b), etc.

Development of catalysts working under mild reaction conditions is desirable. Recently, our group has reported the catalytic potentiality of Fe₃O₄@SiO₂@PMA as a nanocatalyst in the synthesis of 1-amidoalkyl-2-naphthols (Esmailpour et al. 2014c). In this article, we report a new and efficient method for protection and deprotection of aromatic and aliphatic aldehydes at room temperature in the presence of Fe₃O₄@SiO₂-imid-PMAⁿ as an effective as well as highly chemoselective heterogeneous catalyst (Scheme 1).

2 Experimental

2.1 General Methods

All chemicals were commercially available and used without further purification. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer in chloroform (CDCl₃) using tetramethylsilane (TMS) as an internal reference. Fourier transform infrared (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Melting points were obtained in open capillary tubes and were measured on an electrothermal 9200 apparatus. Mass spectra were obtained at 70 eV. All yields refer to the isolated products. The products were

characterized by comparison of their spectral and physical data with previously reported data or with the authentic samples.

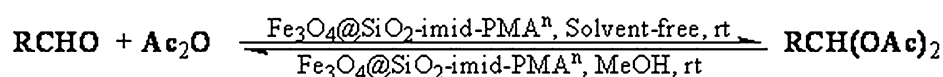
2.2 General Procedure

2.2.1 Preparation of Fe₃O₄@SiO₂ Core-Shell

The core-shell Fe₃O₄@SiO₂ nanospheres were prepared by a modified Stober method in our previous work (Mohsen Esmailpour et al. 2012). In a typical procedure, the mixture of FeCl₃·6H₂O (1.3 g, 4.8 mmol) in water (15 mL) was added to the solution of polyvinyl alcohol (PVA 15,000), as a surfactant, and FeCl₂·4H₂O (0.9 g, 4.5 mmol) in water (15 mL), which was prepared by completely dissolving PVA in water followed by addition of FeCl₂·4H₂O. The resultant solution was left to be stirred for 30 min at 80 °C. Then, hexamethylenetetramine (HMTA) (1.0 mol/l) was added drop by drop with vigorous stirring to produce a black solid product when the reaction media reaches pH 10. The resultant mixture was heated on water bath for 2 h at 60 °C and the black magnetite solid product was filtered and washed with ethanol three times and was then dried at 80 °C for 10 h. Then Fe₃O₄ nanoparticle (0.50 g, 2.1 mmol) was dispersed in the mixture of ethanol (50 mL), deionized water (5 mL) and tetraethoxysilane (TEOS) (0.20 mL), followed by the addition of 5.0 mL of NaOH (10wt %). This solution was stirred mechanically for 30 min at room temperature. Then the product, Fe₃O₄@SiO₂, was separated by an external magnet, and was washed with deionized water and ethanol three times and dried at 80 °C for 10 h.

2.2.2 Preparation of H₃PW₁₂O₄₀ Nanoparticles (PMAⁿ)

PMAⁿ nanoparticles were prepared in our previous work (Jaber and Mohsen 2013). In a typical procedure, 5 mmol of bulk H₃PW₁₂O₄₀ (PMA^b) was dispersed in 50 mL *n*-octane and the resulting dispersion was stirred vigorously for 30 min at room temperature to form a homogeneous dispersion. This dispersion was transferred into a Teflon-lined stainless autoclave filling 80 % of the total volume. The autoclave was sealed and maintained at 150 °C for 12 h. The autoclave was then cooled to room temperature. Finally, the resulted powder was filtered and washed several times by Octane, and dried in a vacuum at 80 °C for 12 h.



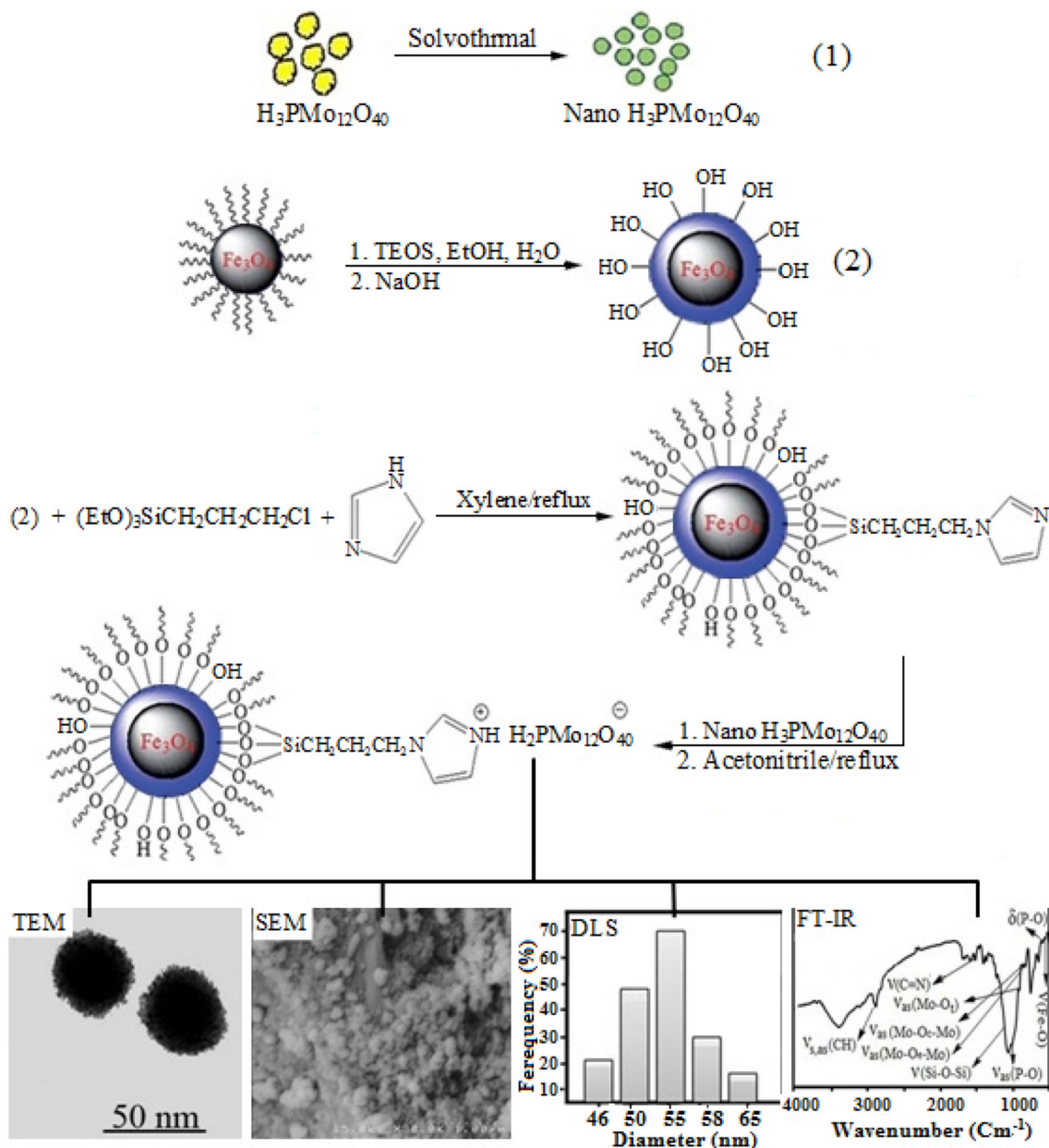
R= Aryl or Alkyl

Scheme 1 The protection and deprotection of aldehydes catalyzed by Fe₃O₄@SiO₂ imidazol-PMAⁿ

2.2.3 Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ (1 g) was added to the solution of 3-chlorotriethoxypropylsilane (1 mmol, 0.241 g) and imidazole (1 mmol, 0.0680 g) in *p*-xylene (20 mL) and the resultant mixture was under reflux for 24 h under nitrogen atmosphere. After refluxing for about 24 h, the mixture was cooled to room temperature, filtered by an external magnet and the product was washed with xylene to remove no reacted species and dried at 70 °C

for 6 h. $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid}$ (1.0 g) was added to an acetonitrile solution of PMA^n (1.0 mmol) in 20 mL that was taken in a round-bottom flask. The mixture was refluxed for 24 h under nitrogen atmosphere. After 24 h, the mixture was filtered by an external magnet, washed with acetonitrile and dichloromethane, and dried at 70 °C for 6 h. Also, the same method was used for the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^b$ ($\text{PMA}^n = \text{nano H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{PMA}^b = \text{H}_3\text{PMo}_{12}\text{O}_{40}$) (Esmailpour et al. 2014c).



Scheme 2 Process for preparation of immobilization of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ nanoparticles on imidazole functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticle (Jaber and Mohsen 2013)

2.2.4 General Procedure for the Preparation of 1,1-Diacetates

To a mixture of aldehyde (1 mmol) and acetic anhydride (2–3 mmol) 0.025 g $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ was added and the mixture was stirred at room temperature. The progress of the reaction was followed by thin-layer chromatography (TLC). After completion of the reaction, and separation of catalyst using magnetic field, the residue was extracted with CH_2Cl_2 (2 × 10 mL). The resulting solution was successively washed with 10 % NaHCO_3 (2 × 10 mL) solution and water (3 × 5 mL) and then dried over anhydrous Na_2SO_4 . After removal of the solvent in vacuum, the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:8).

2.2.5 General Procedure for Deprotection of 1,1-Diacetates

A mixture of the substrate (1 mmol) and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ (0.025 g) in methanol (2 mL) was stirred at room temperature for the specified time in Table 2. After completion of the reaction (monitored by TLC), the mixture was filtered using magnetic field to separate the catalyst. The combined filtrates were concentrated on a rotary evaporator to remove MeOH. Water (5 mL) was added and the product was extracted with Et_2O (5 mL). The organic phase was washed with 10 % aqueous solution of sodium bicarbonate (2 × 10 mL) to remove excess of Ac_2O and dried over Na_2SO_4 . The solvent was evaporated under

reduced pressure. The resultant product was passed through a short column of silica gel (*n*-hexane–EtOAc, 8:1) to afford the pure aldehyde.

3 Results and Discussion

First, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanosphere core–shell was synthesized. Then, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ nanoparticles were synthesized by the treatment of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ with *n*-octane as solvent by a solvothermal method and this nano heteropolyacid immobilized onto imidazole functionalized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles (Scheme 2) (Jaber and Mohsen 2013).

To find the most appropriate reaction conditions and evaluate the catalytic efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ catalyst on the protection of aldehydes as the corresponding 1,1-diacetates, initially the reaction of 4-chlorobenzaldehyde with acetic anhydride was chosen as a model reaction.

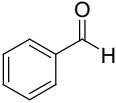
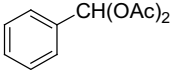
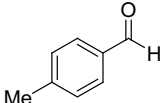
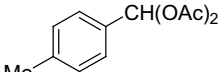
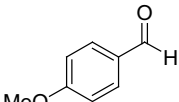
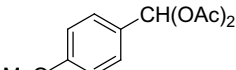
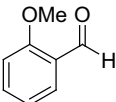
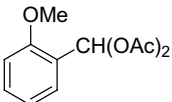
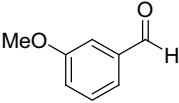
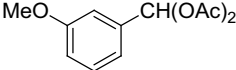
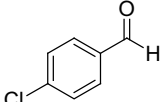
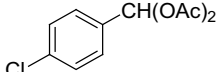
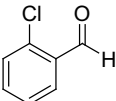
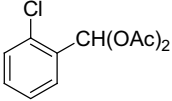
For optimization of the reaction media, 4-Chlorobenzaldehyde as model substrate and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PMA}$ as catalyst were conducted in different solvents. The results show that the efficiency and the yield of the reaction in solutions were much less than those observed under solvent-free conditions (Table 1, entries 1–9). According to the results, the proposed method (solvent-free conditions) is suitable for conversion of aldehydes to geminal diacetates (Table 1). Then the results showed that the best catalyst loading in solvent-free conditions was about 0.025 g. Lower amounts of catalyst resulted in lower

Table 1 Conversion of 4-Chlorobenzaldehyde to its corresponding diacetate in different solvents and amount of catalyst in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imidazol-PMA}^n$

Yield (%) ^a	Time (min)	Catalyst loading (g)	Solvents/ Ac_2O	Entry
68	60	0.025	$\text{CH}_3\text{CN}/(2 \text{ mmol})$	1
38	60	0.025	$\text{CH}_3\text{COCH}_3/(2 \text{ mmol})$	2
17	60	0.025	$\text{CH}_3\text{OH}/(2 \text{ mmol})$	3
71	60	0.025	$\text{CH}_2\text{Cl}_2/(2 \text{ mmol})$	4
12	60	0.025	$\text{EtOH}/(2 \text{ mmol})$	5
15	60	0.025	$\text{H}_2\text{O}/(2 \text{ mmol})$	6
63	60	0.025	<i>n</i> -Hexane/(2 mmol)	7
55	60	0.025	$\text{CH}_3\text{CO}_2\text{Et}/(2 \text{ mmol})$	8
96	15	0.025	Solvent-free/(2 mmol)	9
81	30	0.025	Solvent-free/(1.5 mmol)	10
48	60	0.025	Solvent-free/(1 mmol)	11
96	15	0.025	Solvent-free/(3 mmol)	12
–	240	–	Solvent-free/(2 mmol)	13
34	100	0.01	Solvent-free/(2 mmol)	14
66	45	0.015	Solvent-free/(2 mmol)	15
90	15	0.02	Solvent-free/(2 mmol)	16
95	15	0.03	Solvent-free/(2 mmol)	17
96	15	0.04	Solvent-free/(2 mmol)	18

^a The yields refer to isolated pure products

Table 2 Acylation of aldehydes and deprotection of acylals in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$

Entry	Substrate	Product	Protection ^a				Deprotection	
			Time (min)	Yield (%) ^b	M.p. (°C)		Time (min)	Yield (%) ^b
					Found	Reported		
1			10	94	43–45	44–45 (Jin et al., 2002)	20	93
2			15	92	80–81	81–82 (Jin et al., 2002)	20	88
3			20	90	65–66	64–65 (Jin et al., 2002)	35	86
4			25	87	68–70	70–71 (Negrón et al., 2005)	45	83
5			20	89	Oil	Oil (Hajipour et al., 2007)	40	86
6			10	96	81–82	82–83 (Jin et al., 2002)	25	94
7			20	90	57–59	58–60 (Niknam et al., 2009)	40	89

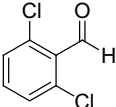
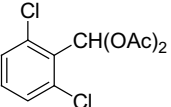
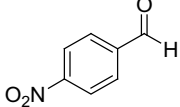
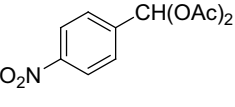
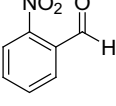
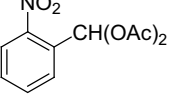
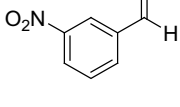
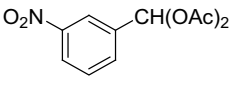
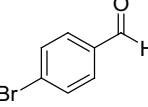
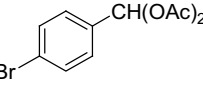
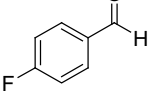
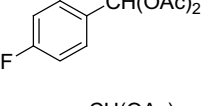
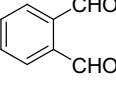
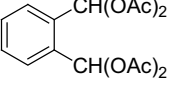
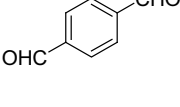
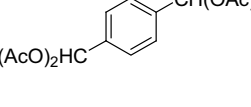
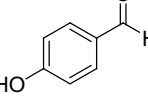
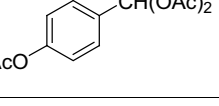
yields, while higher amounts did not affect the reaction times and yields (Table 1, entries 13–18). The amount of acetic anhydride was also optimized and the best result was obtained with a 2:1 molar ratio of acetic anhydride: aldehyde (Table 1, entries 9–12).

Under the optimized reaction conditions, a wide range of aldehydes were reacted with acetic anhydride in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imidazol-PMA}^n$ under solvent-

free conditions at room temperature and the corresponding 1,1-diacetates were obtained in good to excellent yields (Scheme 1) (Table 2).

As shown in Table 2, all aromatic aldehydes carrying either electron-donating (Tables 2 entries 2–5) or electron-withdrawing (Tables 2, entries 6–15) substituents reacted very well, giving good to excellent yields. We investigated the reaction of 4-hydroxybenzaldehyde under the above

Table 2 continued

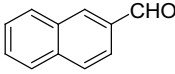
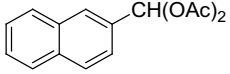
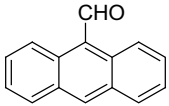
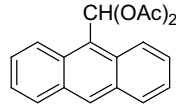
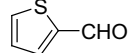
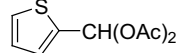
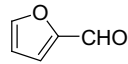
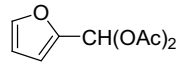
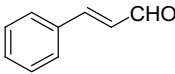
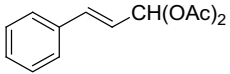
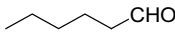
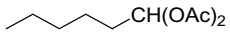
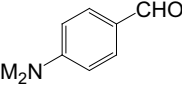
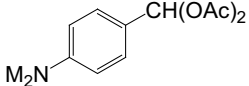
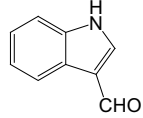
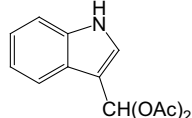
8			20	88	87-89	88-89 (Hajipour et al., 2007)	45	87
9			5	96	124-126	125-127 (Jin et al., 2002)	15	91
10			20	86	91	90-91 (Jin et al., 2002)	40	88
11			10	92	66-67	65-66 (Jin et al., 2002)	20	87
12			20	92	92-93	93-94 (Hajipour et al., 2007)	35	90
13			20	93	53-54	51-53 (Niknam et al., 2009)	35	90
14			10	94 ^c	136	137-139 (Zhang et al., 2011)	25	88
15			10	91 ^c	173-175	174-175 (Khan et al., 2006)	25	86
16			15	87 ^c	99-101	101-102 (Hajipour et al., 2007)	25	87

conditions and observed that both carbonyl and phenolic –OH groups were acylated (Table 2, entry 16).

Other aldehydes such as benzaldehyde, 2-naphthaldehyde and anthracene-10-carbaldehyde produced acylals in

good yields (Table 2, entries 1, 17–18). Heteroaromatic aldehydes such as thiophene-2-carbaldehyde and the acid sensitive substrate (furfural) are converted to 1,1-diacetate without the formation of any side products (Table 2, entries

Table 2 continued

17			10	93	100	101 (Khan et al., 2006)	20	88
18			20	94	197-198	197 (Negrón et al., 2005)	25	92
19			10	88	68-69	67-68 (Niknam et al., 2009)	25	87
20			10	85	52	52-53 (Jin et al., 2002)	25	85
21			10	92	84	85-86 (Jin et al., 2002)	20	90
22			35	81	Oil	Oil (Hajipour et al., 2007)	55	79
23			5h	-	-	-	5h	-
24			5h	-	-	-	5h	-

^a Reaction conditions: aldehyde (1 mmol), acetic anhydride (2 mmol), catalyst (0.025 g), room temperature, solvent-free

^b The products were characterized from their spectra (IR, ¹H NMR) and comparison with authentic samples

^c Ac₂O (3 mmol)

19–20). Aliphatics and α,β -unsaturated aldehydes produced acylals in good yields (Table 2, entries 21–22). Attempted acetylation of benzenedicarbaldehydes, gave the tetracylated products in good yields for phthalaldehyde and tere-phthalaldehyde. The tetracylated products were obtained in 94 and 91 % yields, respectively (Table 2, entries 14,15).

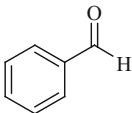
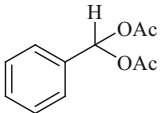
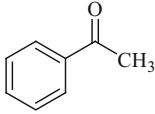
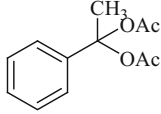
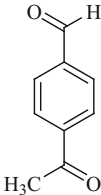
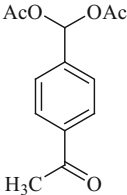
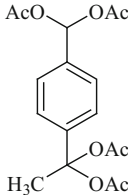
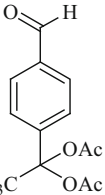
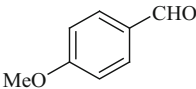
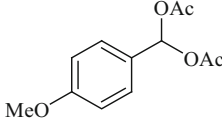
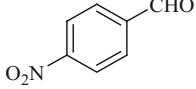
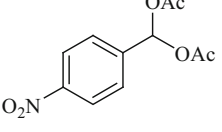
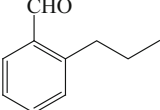
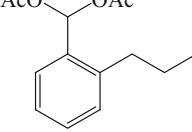
In accordance with the fact reported in the literature (Li et al. 1998), 4-dimethylamino benzaldehyde and indole-3-carbaldehyde (Table 2, entries 23 and 24) failed to give the corresponding 1,1-diacetates and the starting materials were quantitatively recovered after prolonged reaction times (Table 2, entries 23 and 24). This result may be due

to the strong electron donation of dimethylamino and NH groups. Also, a degree of tautomerization may occur with formation of a quinonoid structure, which decreases the reactivity of the aldehydic carbonyl group (Shirini and Jolodar 2012).

We have also found that the conversion of 1,1-diacetates to their corresponding aldehydes can be easily catalyzed in the presence of Fe₃O₄@SiO₂-imid-PMAⁿ in methanol. All reactions were performed at room temperature in good to high yields but need a longer time (Scheme 1 and Table 2).

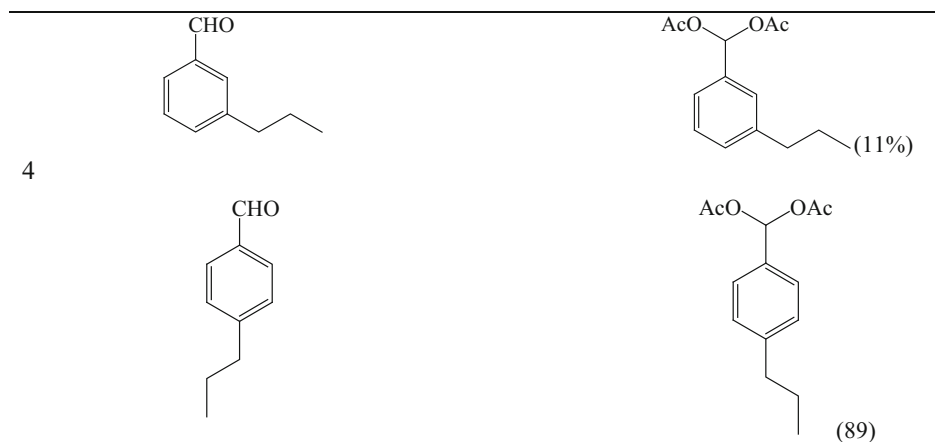
To evaluate the selectivity of this method, we studied the competitive reaction for the acylation of aldehydes in the presence of ketones using Fe₃O₄@SiO₂-imidazol-

Table 3 Competitive acylal formation of aldehydes using Ac₂O in the presence of Fe₃O₄@SiO₂-imidazol-PMAⁿ at room temperature

Entry	Substrate	Product (Selectivity %)
1		 (100%)
		 (0%)
2		 (100%)
		 (0%)
		 (0%)
3		 (7%)
		 (93%)
		 (0%)

PMAⁿ as the catalyst at room temperature (Table 3). With this catalytic system the highly selective conversion of aldehydes in the presence of ketones was observed (Table 3, entries 1–2). The acylation of 4-methoxybenzaldehyde versus 4-nitro-benzaldehyde also showed a high

selectivity in the presence of this catalyst, which indicated the importance of electronic effects upon these reactions (Table 3, entry 3). Also, to examine the steric effects, 2-propylbenzaldehyde, 3-propylbenzaldehyde and 4-propylbenzaldehyde were allowed to react with acetic

Table 3 continued

Reaction condition: each substrate 1 mmol, acetic anhydride 2 mmol, catalyst amount 0.025 g, room temperature, time 45 min

Table 4 Comparison of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{n}}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{b}}$ with the reported catalysts for the diacetylation of benzaldehyde

References	Yield (%) ^a	Time (min)	Temp (°C)	Solvent	Catalyst	Entry
Wang et al. (2007)	92	35	rt	Solvent-free	PEG—supported sulfonic acid (0.1 mmol)	1
Shirini et al. (2010)	90	48	rt	Solvent-free	Saccharin sulfonic acid (0.2 mmol)	2
Desai et al. (2006)	84	30	rt	Solvent-free	Silica sulfuric acid (200 mg, 0.52 mol %)	3
Nagy et al. (2002)	84	120	60 °C	Solvent-free	$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41}$ (20 wt%)	4
Satam and Jayaram (2008)	98	90	rt	Solvent-free	$(\text{NH}_4)_3\text{PW}_{12}\text{O}_{40}$ (0.5 mol %)	5
Wang and Cai (2009)	87	60	rt	Solvent-free	Chloroacetylated polystyrene-supported zinc complexes (5 mol %)	6
Kumar et al. (1995)	92	120	60 °C	Solvent-free	β -Zeolite (50 wt%)	7
Heravi et al. (2006)	99	35	rt	Solvent-free	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (2 mol %)	8
Romanelli et al. (2010)	96	30	20 °C	Solvent-free	$\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$ (1 mmol%)	9
Wang et al. (2006)	95	30	20 °C	Solvent-free	SiPW-8 (0.1 g)	10
Azarifar et al. (2005)	98	90	rt	Solvent-free	DBH (10 mol %)	11
Palacios-Grijalva et al. (2009)	97	360	0 °C	Solvent-free	Sulphated Zirconia (25 mg)	12
Aggen et al. (2004)	87	90	rt	CH_3CN	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (10 mol %)	13
This work	92	30	rt	Solvent-free	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{b}}$ (0.03 g)	14
This work	94	10	rt	Solvent-free	$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{n}}$ (0.025 g)	15

anhydride in the presence of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^{\text{n}}$ as a catalyst. As shown, the catalyst was able to discriminate between the aldehydes with different steric effects (Table 3, entry 4). As we can see from Table 3, 1,1-diacetate was produced only from 4-propyl benzaldehyde in good yields.

To test the worth of the present work in comparison with results in the literature, we compared results of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{n}}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{b}}$ with other applied Lewis and Bronsted acids in synthesis of 1,

1-diacetate. These data, which are shown in Table 4, revealed that $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{n}}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Imid-PMA}^{\text{b}}$ are better catalysts than most of the conventional catalysts mentioned with respect to reaction times and yields of the obtained products (Table 4, entries 14, 15).

After completion of the reaction, the catalyst was washed well with ethylacetate, and then dried at 80 °C prior to use and tested for its activity in subsequent run and fresh catalyst was not added. The recovered catalyst was found to be reusable for six cycles with a slight loss in their activities (Fig. 1).

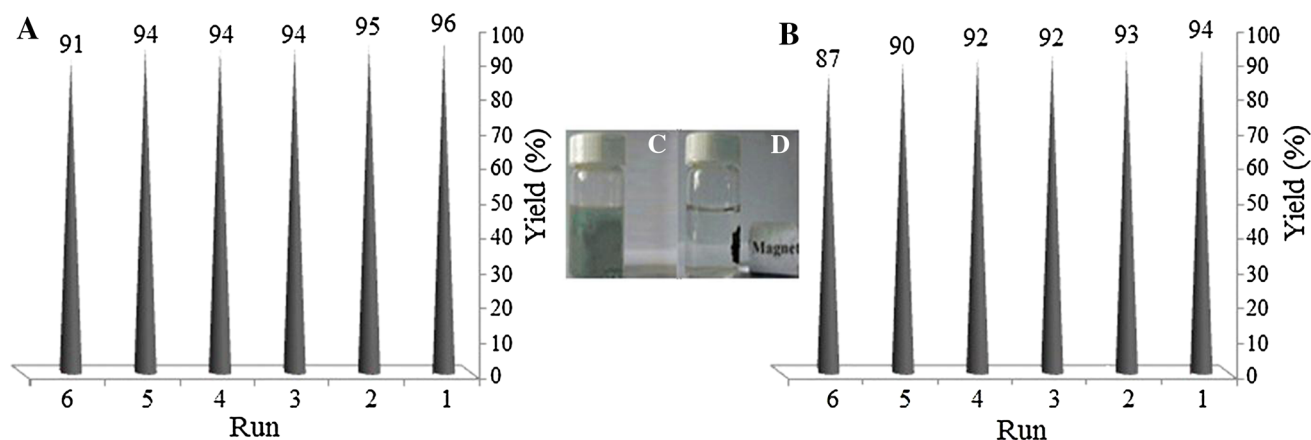


Fig. 1 Reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ in the conversion of 4-Chlorobenzaldehyde to its corresponding 1,1-diacetates (A) and deprotection of the obtained 1,1-diacetate (B). **a** Reaction conditions: 4-Chlorobenzaldehyde (1 mmol), acetic anhydride (2 mmol), catalyst

(0.025 g), room temperature, solvent-free. **b** Reaction conditions: 1,1-Diacetoxy-1-(4-chlorophenyl) methane (1 mmol), catalyst (0.025 g), room temperature, MeOH (2 mL)

4 Conclusion

In conclusion, a simple, efficient and chemoselective protocol has been developed for the acylation of various aldehydes and deprotection of the obtained 1,1-diacetates using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-imid-PMA}^n$ as a heterogeneous magnetic Brønsted acid catalyst. This method is highly selective for the synthesis of acylals from aldehydes in the presence of ketones. The use of an inexpensive and relatively nontoxic catalyst and also green reagent is another advantage of this method. In addition, the catalyst can be reused several times with magnetic field without use of toxic solvents for its reusability.

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