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Polystyrene-supported $TiCl_4$ as a novel, efficient and reusable polymeric Lewis acid catalyst for the chemoselective synthesis and deprotection of 1,1-diacetates under eco-friendly conditions

Ali Rahmatpour [*], Sara Mohammadian

Polymer Science and Technology Division, Research Institute of Petroleum Industry (RIPI), 14665-1137 Tehran, Iran

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ABSTRACT

Copolymer beads of styrene and divinylbenzene (5–7%) were synthesized and combined with titanium tetrachloride in CS_2 to form a stable complex. The PS/$TiCl_4$ complex was used as a mild and efficient polymer-supported Lewis acid catalyst for the preparation of 1,1-diacetates from various types of aldehydes under heterogeneous conditions at room temperature. Deprotection of the resulting 1,1-diacetates has also been achieved using the same catalyst in methanol. This new protocol has the advantages of easy availability, stability, reusability of the eco-friendly catalyst, high to excellent yields, chemoselectivity, simple experimental and work-up procedure. Moreover, this polymeric catalyst could be recovered easily and reused several times without significant loss in activity.

1. Introduction

The selective protection and deprotection of carbonyl groups are essential steps in synthetic organic chemistry [1]. The protection of aldehydes, such as acetals, acylals, oxathioacetals or dithioacetals, is common practice for manipulation of other functional groups during multi-steps synthesis. 1,1-Diacetates (acylals) are appropriate candidates to this aim due to their stability under both neutral and basic media and under acidic conditions and also their easy conversion into parent aldehydes [2]. Moreover, the acylal functionality can be converted into other useful functional groups by reaction with appropriate nucleophiles [3,4] and they are used as cross-linking agents for cellulose in cotton [5]. Over the years, several types of the catalysts have been used for the preparation of 1,1-diacetates from aldehydes and acetic anhydride, such as sulfuric acid [6], triflic acid [7], CH_3SO_3H [7], LiOTf [8], $InCl_3$ [9], $LiBF_4$ [10], PCl_3 [11], NBS [12], I_2 [13], TMSCl–NaI [14], $FeCl_3$ [15], $Cu(OTf)_2$ [16], $Bi(OTf)_3$ [17], $Bi(NO_3)_3 \cdot 5H_2O$ [18], $Al(HSO_4)_3$ [19], tetrabutylammonium tribromide (TBATB) [20], Wells–Dawson acid ($H_6P_2W_{18}O_{62} \cdot 24H_2O$) [21], zeolite-Y(β) [22], P_2O_5/Al_2O_3 [23], SSA [24], montmorillonite clay [25], PS/$Al(OTf)_3$ [26], expansive graphite [27], sulfated zirconia [28] and Brønsted acidic ionic liquids under ultrasonic irradiation [29]. Although these methods are suitable for many synthetic conditions, many of these are associated with several drawbacks, which include prolonged reaction time and low yields, harsh reaction conditions, use of moisture sensitive and costly catalysts, use of excess acetic anhydride, poor selectivity and use of unrecyclable catalysts, which eventually result in the generation of a large amount of environmentally hazardous waste materials. In addition, a few of the above-mentioned catalysts are claimed to give protection as well as deprotection. Therefore, there is a scope to develop an alternative method for the protection of aldehydes as 1,1-diacetates and their deprotection using catalysts that could be superior or equivalent to the existing ones with regard to

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[*] Corresponding author.
E-mail address: rahmatpoura@ripi.ir (A. Rahmatpour).

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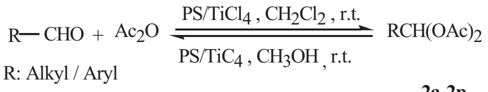
selectivity, handling, reusability, toxicity, and environmental compatibility.

The utility of polymer-supported catalysts is now well-recognized because of their ease of work-up and of separation of products and catalysts, from the economical point of view, and in application to industrial processes, etc. [30,31]. In general, catalysts are immobilized on polymers via coordinate or covalent bonds. A large number of polymer-supported Lewis acid catalysts have been prepared by immobilization of the catalysts on polymer via coordination or covalent bonds [32,33]. Such heterogeneous supported Lewis acids or polymeric Lewis acid catalysts are usually as active and selective as their homogeneous or solution-phase counterparts while having the distinguishing characteristics of being easily separable from the reaction mixture, recyclability, easier handling, non-toxicity, enhanced stability, and improved selectivity in various organic reactions. Cross-linked polymers with specific properties are widely used as catalyst supports as they are inert, nontoxic, and nonvolatile and offer the advantageous features of heterogeneous catalysis, such as thermal stability, selectivity, and recyclability [34,35].

Titanium tetrachloride ($TiCl_4$), as a powerful Lewis acid, has found many applications in organic synthesis and industry [36,37]. However, this compound is a liquid and highly aggressive material that creates clouds of HCl when it is exposed to air and moisture. Therefore, its handling needs serious precautions and strict anhydrous conditions and stoichiometric amounts or more are needed in order to achieve good yields. Furthermore, tedious work-up procedure after reaction to hydrolyze excess catalyst produces large amounts of acidic waste water.

Polystyrene is one of the most widely studied heterogeneous and polymeric supports due to its environmental stability and hydrophobic nature which protects water-sensitive Lewis acids from hydrolysis by atmospheric moisture until it is suspended in an appropriate solvent where it can be used in a chemical reaction [38]. Neckers et al., first, reported polystyrene-supported $AlCl_3$ as a catalyst in Friedel–Crafts reaction and then was used for some organic transformations [39]. Although the use of immobilized catalysts is of continuing interest, few examples are known for polymer-supported Lewis acids [40]. In continuation of our recent works on the preparation and use of polymeric Lewis acid catalysts in organic transformations [41–45], herein, we use the reported strategy to support $TiCl_4$ on cross-linked polystyrene, and the polymer catalyst obtained ($PS/TiCl_4$) is used as an effective as well as highly chemoselective heterogeneous catalyst for the synthesis of 1,1-diacetates from structurally diverse aldehydes and the subsequent deprotection of the obtained 1,1-diacetates with methanol (Scheme 1).



1 **2a-2p**

Scheme 1.

2. Experimental

2.1. Materials and instruments

All chemical reagents were purchased from Fluka and Merck chemical companies and were used without further purification. Cross-linked polystyrene (5–7% divinylbenzene, mesh size: 16–60) was prepared via suspension polymerization as reported in the literature [41]. $PS/AlCl_3$ was prepared as reported previously [41]. The products were characterized by comparing the physical data with those of known samples or by their spectral data. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 Advance spectrometer at 250.13 MHz. FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} using a Unicam Matteson 1000 spectrophotometer. UV spectra were taken using a Pharmacia Biotech Ultraspec 3000 model 80-2106-20 spectrometer. The capacity of the catalyst was determined by the Mohr titration method and atomic absorption technique using a Philips atomic absorption instrument. Reaction monitoring and purity determination of the products were accomplished by TLC on silica gel polygram SILG/UV_{254} plates. All yields refer to isolated products.

2.2. Preparation of $PS/TiCl_4$

Anhydrous $TiCl_4$ (4 g) was added to polystyrene (5–7% divinylbenzene, mesh size: 16–60, 10 g) in carbon disulfide (30 mL) as the reaction medium. The mixture was stirred using a magnetic stirrer under reflux condition for 2 h, cooled, and then water (50 mL) was cautiously added to hydrolyze the excess $TiCl_4$. The mixture was stirred until the brown red color disappeared, and the polymer became light yellow. The polymer beads were collected by filtration and washed with water (300 mL) and then with

Table 1
Reaction conditions optimization[a] in the acetylation of 4-methylbenzaldehyde with Ac_2O catalyzed by PS/TiCl4 at room temperature.

Entry	Solvent	Catalyst (mol %)	Time (min)	Yield[b] (%)
1	*n*-Hexane	10	30	28
2	EtOAc	10	30	51
3	C_2H_5OH	10	30	14
4	CH_3CN	10	30	62
5[c]	CH_2Cl_2	–	90	NR
6	CH_2Cl_2	1	60	48
7	CH_2Cl_2	5	45	76
8	CH_2Cl_2	10	40	93
9	CH_2Cl_2	15	40	93
10[d]	CH_2Cl_2	–	30	NR
11[e]	CH_2Cl_2	–	40	52
12[f]	CH_2Cl_2	10	15	NR
13[g]	CH_2Cl_2	10	40	51

NR: no reaction.
[a] Reaction conditions: 4-methylbenzaldehyde (1 mmol), Ac_2O (1.2 mmol), solvent (3 mL).
[b] Isolated yield.
[c] No catalyst.
[d] PS was used as catalyst.
[e] The toluene–$TiCl_4$ complex was used as a catalyst.
[f] Catalyst was filtered after 15 min.
[g] $S/AlCl_3$ (0.15 mmol, 0.47 mmol $AlCl_3$/g) was used as a catalyst.

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Table 2
$PS/TiCl_4$ catalyzed protection[a] of aldehydes as 1,1-diacetates and their deprotection.

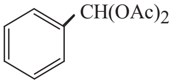
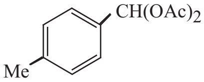
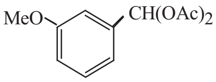
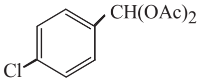
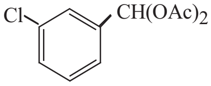
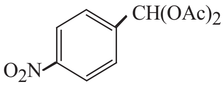
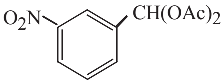
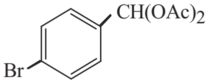
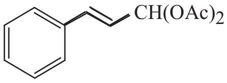
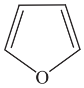
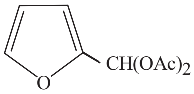
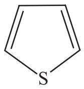
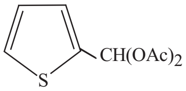
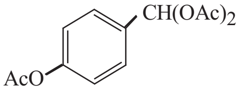
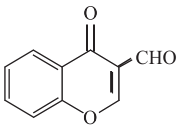
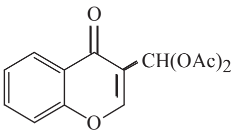
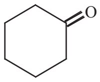
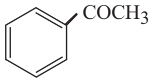
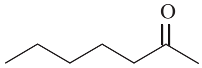
Entry	R (1)	Product (2)	Protection		Deprotection	
			Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	C_6H_5	 **2a**	40	93	55	88
2	4-Me–C_6H_4	 **2b**	40	93	50	90
3	3-MeO–C_6H_4	 **2c**	40	94	70	87
4	4-Cl–C_6H_4	 **2d**	40	94	50	86
5	3-Cl–C_6H_4	 **2e**	45	94	50	85
6[c]	4-O_2N–C_6H_4	 **2f**	75	84	80	85
7[c]	3-O_2N–C_6H_4	 **2g**	60	85	75	83
8	4-Br–C_6H_4	 **2h**	40	88	50	85
9	$C_6H_5CH{=}CH–$	 **2i**	40	89	50	86
10		 **2j**	40	87	50	85
11		 **2k**	40	86	45	84
12	C_6H_{13}	$CH_3(CH_2)_4CH_2CH(OAc)_2$ **2l**	40	87	50	86
13	C_3H_7	$CH_3(CH_2)_2CH(OAc)_2$ **2m**	40	88	50	85
14	$C_6H_5CH_2$	 **2n**	40	90	75	84
15[d]	4-HO–C_6H_4	 **2o**	50	88	80	85
16		 **2p**	60	91	90	87
17		NR	90	0	–	

Table 2 (*Continued*)

Entry	R (1)	Product (2)	Protection		Deprotection	
			Time (min)	Yield[b] (%)	Time (min)	Yield[b] (%)
18		NR	90	0	–	
19		NR	90	0	–	

NR: no reaction.

[a] Reaction conditions: aldehyde (1 mmol), Ac_2O (1.2 mmol), PS/$TiCl_4$ (0.1 mmol) at room temperature.

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

[c] 1.5 equiv of acetic anhydride was used.

[d] 3 equiv of acetic anhydride was used.

ether (30 mL) and chloroform (30 mL). The catalyst was dried in a vacuum oven overnight at 50 °C before use. The chlorine content of PS/$TiCl_4$ was 10.32% analyzed by the Mohr titration method [46] and the loading capacity of $TiCl_4$ on the polymeric catalyst or the amount of $TiCl_4$ complexed with polystyrene, was calculated to be 0.726 mmol/g [47].

2.3. General experimental procedure for the synthesis of 1,1-diacetates (2)

A mixture of aldehyde (**1**, 1 mmol), freshly distilled acetic anhydride (1.2–1.5 mmol), and PS/$TiCl_4$ (0.1 mmol) in methylene chloride (3 mL) was stirred at ambient temperature for an appropriate time (Table 2). The progress of the reaction was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After completion of the reaction, the mixture was diluted with methylene chloride (10 mL) and filtered to separate the catalyst, and washed with methylene chloride. The filtrate was washed with water (10 mL) and the organic phase was dried over anhydrous Na_2SO_4, and concentrated on a rotary evaporator under reduced pressure to afford the pure 1,1-diacetate or chromatographed on silica gel [Merck, 100–200 mesh, petroleum ether (60–80 °C)-ethyl acetate] where necessary. After each reaction, the spent polymeric catalyst from different experiments was combined, washed with ether and dried overnight in a vacuum oven and reused.

2.4. General experimental procedure for the deprotection of 1,1-diacetates (2)

A mixture of 1,1-diacetate (**2**, 1 mmol) and PS/$TiCl_4$ (0.1 mmol) in methanol (3 mL) was stirred vigorously at ambient temperature for an appropriate time (Table 2). The course of the reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was diluted with Et_2O (10 mL) and filtered to separate the catalyst. The filtrate was washed with water to remove excess acetic anhydride and dried over anhydrous Na_2SO_4. The solvent was evaporated on a rotary evaporator under reduced pressure. The resultant product was passed through a short column of silica gel to afford the pure product. The spent polymeric catalyst from different experiments was combined, washed with ether and dried overnight in a vacuum oven and reused.

2.5. Catalyst recovery and reuse

The reusability of the catalyst was checked in the multiple acylation reaction of 4-methylbenzaldehyde with acetic anhydride. At the end of each reaction, the catalyst was recovered from the reaction mixture by addition of methylene chloride, simple filtration and drying in a vacuum oven, and then reused. The recycled catalyst was used for further runs with fresh 4-methylbenzaldehyde, Ac_2O and CH_2Cl_2.

2.6. The spectral data for selected compounds

(Table 2, entry 2, **2b**): IR (KBr) υ: 3033, 2360, 1771, 1367, 1241, 1206, 1068, 1006, 959, 816 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.62$ (s, 1H, C$\underline{H}$(OAc)$_2$), 7.42 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.22 (d, $J = 8.4$ Hz, 2H, Ar-H), 2.4 (s, 3H, CH_3), 2.15 (s, 6H, 2 × $COCH_3$) ppm.

(Table 2, entry 2, **2d**): IR (KBr) υ: 3090, 2990, 2920 1760, 1738, 1592, 1490, 1376, 1242, 1200, 1084, 1060, 1010, 993, 970, 938, 910, 840, 820, 608, 540 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.60$ (s, 1H, C$\underline{H}$(OAc)$_2$), 7.40 (d, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.2$ Hz, 2H), 2.11 (s, 6H, 2 × $COCH_3$) ppm.

(Table 2, entry, **2l**): IR (Neat) υ: 2930, 2863, 1762 (CO), 1465, 1378, 1250, 1214, 1112, 1015, 968 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.98$ (t, 3H, $J = 6.8$ Hz, CH_3), 1.22–1.40 (m, 8H, CH_2), 1.66–1.80 (m, 2H, CH_2), 2.07 (s, 6H, 2 × $COCH_3$), 6.77 (t, 1H, C$\underline{H}$(OAc)$_2$) ppm.

(Table 2, entry 16, **2p**): m.p. 131-132 °C; IR(KBr) υ: 3085, 2987, 2940, 1761, 1645, 1625, 1612, 1470, 1417, 1192, 1073, 933 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) $\delta = 8.27$ (d, $J = 9$ Hz, 1H), 8.24 (m, 1H, Ar-H), 7.61 (s, 1H), 7.47-7.52 (m, 2H, Ar-H), 2.16 (s, 6H, 2 × $COCH_3$).

3. Results and discussion

3.1. Preparation of PS/$TiCl_4$ complex

First, cross-linked polystyrene (5–7% divinylbenzene, mesh size: 16–60) was prepared via suspension polymerization as previously reported in the literature [41]. Then, PS/$TiCl_4$ was prepared by addition of anhydrous $TiCl_4$ to polystyrene (5–7% divinylbenzene) in carbon disulfide under reflux conditions. The loading capacity of the polymeric catalyst, obtained by gravimetric method and checked by atomic absorption technique, was 0.726 mmol

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$TiCl_4$/g of complex beads catalyst [46]. The data obtained by these two techniques showed, within experimental error, that the catalyzing species are in the form of $TiCl_4$ supported on the polymeric support. The UV spectrum of the solution of PS/$TiCl_4$ complex in CS_2 showed a new strong band at 390–491 nm, which is due to the formation of a stable $\pi \rightarrow p$ type coordination complex between the benzene rings in the polystyrene carrier with $TiCl_4$. The FT-IR spectrum of PS/$TiCl_4$ showed new absorption peaks due to the C–C and C–H stretching vibrations, and the C–H bending vibration of the benzene ring at 1450–1500, 2950–3100 and 400–800 cm^{-1}, whose complex formation between Lewis acid $TiCl_4$ and polystyrene was demonstrated. The structure of the PS/$TiCl_4$ complex is similar to that of the PS/$AlCl_3$ and PS/$GaCl_3$ complex, as suggested by Neckers et al. [39] and our prior works [41–44], because the Lewis acid $TiCl_4$ is complexed with the benzene rings of the polystyrene and the $TiCl_4$ is stabilized due to the decreased mobility of the benzene rings hindered by the long polystyrene chain. The PS/$TiCl_4$ complex catalyst is a non-hygroscopic, water tolerant, and especially stable species. In addition, this polymeric catalyst is easy to prepare, stable in air for a long time (over 1 year) without any change, easily recycled and reused without appreciable loss of its activity.

3.2. Synthesis and deprotection of 1,1-diacetates

In order to find the most appropriate reaction conditions and evaluate the catalytic efficiency of PS/$TiCl_4$ catalyst on the protection of aldehydes as the corresponding 1,1-diacetates, initially the reaction of 4-methylbenzaldehyde with acetic anhydride was chosen as a model reaction. The swelling property of cross-linked resin (PS) in organic solvents is an important factor for effective solid-phase reactions [48]. To select the best solvent, this transformation was studied in various organic solvents, such as *n*-hexane, ethyl acetate, ethanol, acetonitrile, methylene chloride. Among them, the highest yield was obtained in CH_2Cl_2 (Table 1, entry 8) and the reaction in CH_2Cl_2 proceeds faster than in other organic solvents in the same volume of solvent. The highest yield obtained by using CH_2Cl_2 as the solvent can be ascribed to the fruitful swelling of the polymer network of the catalyst in this media, allowing the metal particles located inside the polymer matrix to effect the catalysis. In protic solvents, such as ethanol, this protection reaction proceeded in longer reaction time and with very poor yield, which may be related to the instability of acetic anhydride in protic solvents (Table 1, entry 3). In addition, we further studied the influence of the amount of PS/$TiCl_4$ on the reaction yields. In the presence of 15, 10, 5, and 1 mol% PS/$TiCl_4$, the corresponding yields were 93, 93, 76, and 48%, respectively (Table 1, entries 6–9). The optimum molar ratios of the polymeric catalyst to aldehyde and 4-methylbenzaldehyde to acetic anhydride were found to be 0.1:1 and 1:1.2, respectively. Blank experiment in the absence of catalyst showed that the reaction did not take place, even after 12 h. The results show clearly that PS/$TiCl_4$ is an effective catalyst for this transformation, although a lower catalyst loading (13.8 mg, 1 mol% of PS/$TiCl_4$) could be used to accomplish this protection, which indicated that the $TiCl_4$ was the real active site in the supported catalyst, 138 mg (10 mol%) of PS/$TiCl_4$ per 1 mmol of aldehyde were optimum in terms of reaction time and isolated yield. The key role played by the Lewis acidity of the heterogeneous catalyst PS/$TiCl_4$ was proved by employing the polystyrene beads (Table 1, entry 10) and the $TiCl_4$–toluene complex (Table 1, entry 11) as catalysts. In fact, while in the former case no reaction occurred, which indicated that polystyrene itself did not promote the reaction, in the latter, the desired product was isolated in low yield 52% (Table 1, entry 11). Also, PS/$TiCl_4$ was found to be a more effective catalyst than PS/$AlCl_3$ for protection of 4-methylbenzaldehyde under identical conditions (Table 1, entry 13).

When using a supported catalyst, one of the most important issues is the possibility of leaching of the reactive center into the reaction mixture. To rule out the contribution of homogeneous catalysis (free $TiCl_4$ released from the support) in the results shown in Table 1, the catalyst was stirred in methylene chloride for 15 min under operated temperature and filtered off (Table 1, entry 12). We observed that when the reactants were added to the filtrates and stirred for 1 h, no reaction took place. This result indicates that any $TiCl_4$ species that leached into the reaction mixture is not an active homogeneous catalyst (the release of catalyst is negligible) and that the observed catalysis is truly heterogeneous in nature.

To establish the generality, a variety of aromatic and aliphatic aldehydes were subjected to 1,1-diacetate formation **2a-2p** in high yields under the catalytic influence of PS/$TiCl_4$ at ambient temperature (Table 2). Various functional groups were tolerated under the present conditions, for example Me, Cl, Br, OMe, NO_2. Deactivated aromatic aldehydes, bearing electron-withdrawing substituents, such as nitrobenzaldehyde (Table 2, entries 6,7) also produced good yields under the selected conditions but need a longer time. It is noteworthy to mention that the acid-sensitive substrates like cinnamaldehyde (Table 2, entry 9), furan-2-carbaldehyde (Table 2, entry 10), and thiophene-2-carbaldehyde (Table 2, entry 11) gave the expected acylals in high yields without any by-product formation. Moreover, the protocol could also equally work with aliphatic aldehydes (Table 2, entries 12-14). We also investigated the reaction of 4-hydroxybenzaldehyde (Table 2, entry 15) under the above-mentioned conditions and observed that both the carbonyl and phenolic group were acylated. Furthermore, when aldehyde and ketone groups are present in the same molecule, only the aldehyde diacetate was obtained, the ketone moiety remained intact. When this reaction was extended to 3-formyl benzopyran-(4*H*)-4-one, its formyl diacetate was obtained in excellent yield (Table 2, entry 16). Several aliphatic and aromatic ketones (Table 2, entries 17–19), including cyclohexanone, acetophenone and 2-heptanone were not reactive under the described experimental conditions, even after 1.5 h under reflux conditions.

The difference in reactivity of aldehydes and ketones for 1,1-diacetate formation encouraged us to test and extend the present protocol for chemoselective synthesis of 1,1-diacetate of an aldehyde in the presence of ketone. We

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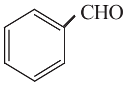
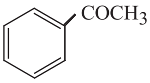
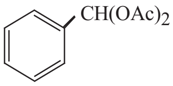
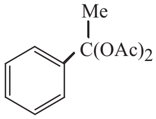
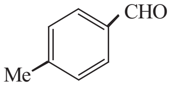
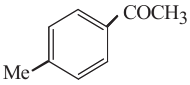
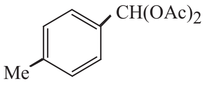
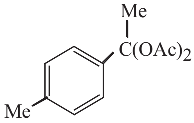
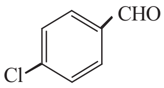
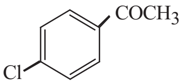
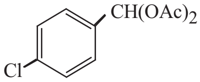
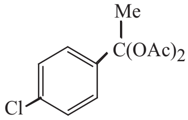
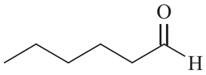
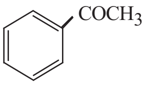
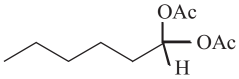
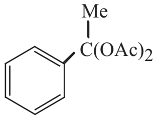
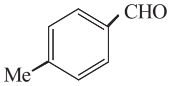
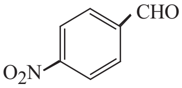
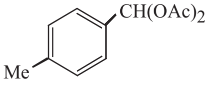
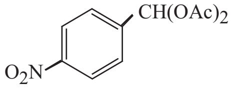
Table 3
Competitive acylal formation of aldehydes using Ac_2O in the presence of PS/$TiCl_4$ at room temperature.

Entry	Substrates			Product (selectivity %)[a]	
1	 (1 mmol)	 (1 mmol)	$\xrightarrow[CH_2Cl_2, 40min]{Ac_2O(1.2mmol), PS/TiCl_4(0.1mmol)}$	 (100%)	 (0%)
2	 (1 mmol)	 (1 mmol)	$\xrightarrow[CH_2Cl_2, 40min]{Ac_2O(1.2mmol), PS/TiCl_4(0.1mmol)}$	 (100%)	 (0%)
3	 (1 mmol)	 (1 mmol)	$\xrightarrow[CH_2Cl_2, 40min]{Ac_2O(1.2mmol), PS/TiCl_4(0.1mmol)}$	 (100%)	 (0%)
4	 (1 mmol)	 (1 mmol)	$\xrightarrow[CH_2Cl_2, 40min]{Ac_2O(1.2mmol), PS/TiCl_4(0.1mmol)}$	 (100%)	 (0%)
5	 (1 mmol)	 (1 mmol)	$\xrightarrow[CH_2Cl_2, 40min]{Ac_2O(1.2mmol), PS/TiCl_4(0.1mmol)}$	 (96 %)	 (0 %)

[a] Conversion (GC).

studied the competitive acylation reactions of aromatic aldehydes in the presence of ketones using PS/$TiCl_4$. Under these conditions, exclusive acylation of the aldehyde functions was observed. The chemoselective acylations of benzaldehyde, 4-methylbenzaldehyde, 4-chlorobenzaldehyde and hexanal in the presence of acetophenone, 4-methylacetophenone, 4-chloroacetophenone and acetophenone are shown in Table 3 (entries 1–4). In addition, the acylation of 4-methylbenzaldehyde versus 4-nitrobenzaldehyde in the presence of 1.2 mmol of acetic anhydride has been investigated (entry 5). This reaction also proceeded with high selectivity using this catalytic system and showed the importance of the electronic effect upon this reaction.

In order to show the efficiency and applicability of the present method, the catalytic activity of PS/$TiCl_4$ was compared with that of some reported catalysts in the literature, the results are summarized in Table 4. The results have been compared with respect to the reaction times, catalyst loading, and yields. The results show that

Table 4
Comparison of the efficiency of PS/$TiCl_4$ with some other catalysts for the acylation of 4-methylbenzaldehyde.

Entry	Catalyst (mol %)	Conditions	Time	Yield (%)	Reference
1	$InCl_3$	CH_2Cl_2, r.t	1 h	96	[9]
2	NBS (10 mol %)	Solvent free, r.t	9 h	93	[12]
3	$LiBF_4$ (10)	Solvent free, 40 °C	24 h	92	[10]
4	$Bi(NO_3)_3{\cdot}5H_2O$ (10 mol %)	CH_3CN, r.t	5 h	79	[18]
5	$H_3PW_{12}O_{40}$/MCM-41 (20 wt %)	Solvent free, 60 °C	2 h	84	[21b]
6	P_2O_5/Al_2O_3 (15, 0.1 g)	Solvent free, r.t	45 min	87	[23]
7	ß-zeolite (50 wt %)	Solvent free, 60 °C	2 h	93	[22]
8	$H_6P_2W_{18}O_{62}{\cdot}24H_2O$ (45 mg)	Solvent free, r.t	30 min	92	[21a]
9	PS/$Al(OTf)_3$ (10)	CH_2Cl_2, r.t	1 h	94	[26]
10	$Bi(OTf)_3{\cdot}xH_2O$ (31 mg)	CH_3CN, r.t	3.5 h	87	[17]
11	$Cu(OTf)_2$ (2.5)	CH_2Cl_2, r.t	2 h	98	[16]
12	LiOTf (20 mol %)	Solvent free, r.t	12 h	95	[8]
13	Sulfated zirconia (ZrO_2/SO_4^{2-}, 25 mg)	CH_3CN, 0 °C	5 h	94	[28]
14	TBATB (10)	Solvent free, r.t	2.5 h	94	[20]
15	PS/$TiCl_4$ (10)	CH_2Cl_2, r.t	40 min	93	This work

r.t: room temperature.

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Table 5
Reusability of [a]PS/$TiCl_4$ in the acylation of 4-methylbenzaldehyde with Ac_2O[b].

Run	Product (%)[c]	Time (min)
1	93	40
2	92	40
3	89	40
4	88	45
5	85	45

[a] The capacity of the catalyst after five uses was 0.633 mmol, PS/$TiCl_4$ per gram.

[b] Reaction conditions: 4-methylbenzaldehyde (1 mmol), Ac_2O (1.2 mmol), PS/$TiCl_4$ (0.1 mmol), CH_2Cl_2 (3 mL), r.t.

[c] Isolated yield.

PS/$TiCl_4$ is an equally or competitive and more efficient catalyst for this acylation reaction in terms of yield, reaction conditions, reaction time, and amount of catalyst. Moreover, this protocol offers advantages over many of the methodologies in terms of safety, efficiency, mild conditions and reusability of the catalyst, which, thus, makes them environmentally more acceptable.

We have also found that the deprotection of 1,1-diacetates to their corresponding aldehydes can be easily catalyzed by treatment of acylals in methanol at room temperature. By this procedure, several aliphatic, aromatic and α,β-unsaturated 1,1-diacetates have been transformed into the corresponding aldehydes in high yields (Scheme 1, Table 2, entries 1–16).

3.3. *Catalyst reusability*

Finally, the possibility of recycling the catalyst was examined using the reaction of 4-methylbenzaldehyde and acetic anhydride under the same reaction conditions described in the general procedure. At the end of each of the repeated acylation reactions, the catalyst was recovered by filtration, washed with methylene chloride, dried in an vacuum oven and the catalyst was reused in the next reaction using fresh 4-methylbenzaldehyde and acetic anhydride, taking into account the partial loss of catalyst during the recovery. The recycled catalyst was consecutively reused five times with negligible loss in its activity and there was no need for regeneration (Table 5). To improve the catalytic activity of catalyst after the fifth cycles, it is favored to separate the support by filtration, washed carefully with methylene chloride and dried, then treated with $TiCl_4$ again to prepare a fresh PS immobilized $TiCl_4$ catalyst. The polymer support can be used several times for the immobilization of $TiCl_4$. So, the recyclability of the polymer support makes the method environmentally safe and friendly.

4. Conclusion

In conclusion, we have developed a simple, efficient and chemoselective protocol for the acylation of various aldehydes and deprotection of the obtained 1,1-diacetates using polystyrene-supported $TiCl_4$ as a novel heterogeneous polymeric Lewis acid catalyst. The mild reaction conditions and simplicity of the procedure, excellent yields, ease of preparation and handling of the catalyst, cost efficiency and stability and effective reusability of the catalyst are noteworthy advantages of this method. Studies on the use of the catalyst for other functional group transformations are ongoing in our laboratory.

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