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Polystyrene-supported $GaCl_3$: A new, highly efficient and recyclable heterogeneous Lewis acid catalyst for tetrahydropyranylation of alcohols and phenols

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ABSTRACT

A new, simple and highly chemoselective method for tetrahydropyranylation of alcohols and phenols with 3,4-dihydro-2*H*-pyran (DHP) in the presence of polystyrene-supported gallium trichloride (PS/$GaCl_3$) as a highly active and reusable heterogeneous Lewis acid catalyst at room temperature is presented. In this catalytic system, primary, secondary and tertiary alcohols, as well as phenols, were converted to the corresponding tetrahydropyranyl (THP) ethers with short reaction times and high yields. The heterogenized catalyst is of high reusability and stability in the pyranylation reactions and was recovered several times with negligible loss in its activity and with negligible catalyst leaching, and also there is no need for regeneration. The method also shows good chemoselectivity for mono-tetrahydropyranylation of symmetrical diols.

1. Introduction

Replacement of conventional, toxic and polluting Bronsted and Lewis acid catalysts with eco-friendly reusable heterogeneous catalysts is an area of current interest. Nowadays, studies focused on the development of highly efficient, selective and safe Lewis acid-based promoting systems are a topic for numerous researchers. In this context, immobilized Lewis acid catalysts are receiving a great deal of attention due to environmental, practical and economical concerns [1]. Of particular relevance are the polymer-supported metal catalysts that, due to the fine tuning of their physico-chemical properties, are emerging as alternative promoting agents for several challenging organic transformations [2]. Immobilization of a catalyst on a solid support improves the stability, hygroscopic properties, handling and reusability of the catalyst, all factors which are important in industry [3]. A large number of polymer supported Lewis acid catalysts have been prepared by immobilization of the catalysts on polymers via coordination or covalent bonds [4]. Such polymeric 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, recyclable, easier to handle, non-toxic and having enhanced stability and improved selectivity in various organic reactions. 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 [5]. It is well known that gallium trichloride is a strong Lewis acid and an important catalyst in organic transformations. However, it easily hydrolyzes in air, so that its use, storage and separation from reaction mixtures are inconvenient and difficult. Polystyrene-supported gallium chloride, PS/$GaCl_3$, which is a tightly bound and stable complex between anhydrous $GaCl_3$ and polystyrene–divinylbenzene copolymer beads, was described for the first time by Ruicheng et al. [6]. The use of the PS/$GaCl_3$ complex catalyst has several advantages over a conventional Lewis acid catalyst, such as its ease of handling (as a bench top catalyst), recyclability and tunable Lewis acidity.

The protection of alcohols and phenols are fundamental and useful transformations in organic synthesis. Among the many protecting groups for hydroxyls, tetrahydropyranyl ether (THP) is a very attractive choice for the protection of the alcohol and phenol hydroxyl group, and is used with high frequency due to its low cost, easy installation as well as its stability and compatibility [7]. This behavior is possible under different reaction conditions and with several reagents, such as metal hydrides and Grignard reagents. A variety of catalysts, including protonic and Lewis acid catalysts such as *p*-toluenesulfonic acid (*p*-TSA) [8], acidic montmorillonite K-10 clay [9], bis[trimethylsilyl] sulfate [10], $Ru(CH_3)_3(triphos)(OTf)_2$ [11], $(CH_3)_3SiI$ [12], $CuCl_2$ [13], DDQ [14], heteropolyacids [15], alumina impregnated with $ZnCl_2$ [16], silica chloride [17], silica-based sulfonic acid [18], $ZrCl_4$ [19], I_2 [20], ionic liquids [21], polyaniline

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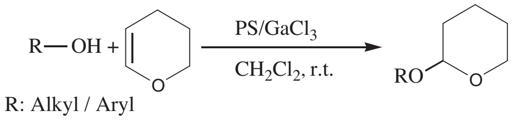

Scheme 1. Tetrahydropyranylation of alcohols and phenols with DHP catalyzed by PS/GaCl$_3$.

sulfate salt [22], LiOTf [23], La(NO$_3$)$_3$·6H$_2$O [24], Amberlyst [25], Nafion-H [12], zeolites [26], tetrabutyl ammonium tribromide (Bu$_4$N$^+$Br$_3^-$) [27], In(OTf)$_3$ [28], [Sn(TPP)(OTf)$_2$] [29], PdCl$_2$(CH$_3$CN)$_2$ [30], CuSO$_4$·5H$_2$O [31], SiO$_2$/AlCl$_3$ [32], VO(OAc)$_2$ [33], Bi(NO$_3$)$_3$·5H$_2$O [34], BF$_3$·Et$_2$O [35] and [V(TPP)(OTf)$_2$] [36], have been developed for the tetrahydropyranylation of hydroxy functions in alcohols and phenols. Although a large number of procedures for this conversion are available, many suffer from limitations, like long reaction times, harsh reaction conditions, poor selectivity, the occurrence of side reactions (for example the formation of polymeric by-products of dihydropyran (DHP) and isomerization), toxic reagents, intolerance of other functional groups and a high catalyst to substrate ratio. In addition, some of these catalysts are not recyclable and require work-up of the reaction mixture. Thus, there is still demand for the introduction of mild, selective and environmentally benign methods, especially using recyclable heterogeneous catalysts for this transformation.

In continuation of our recent works on the use of polymeric Lewis acid catalysts in organic transformations [37,38], herein the preparation and investigation of the catalytic activity of polystyrene-supported gallium chloride as a stable, highly active and reusable heterogeneous catalyst in the tetrahydropyranylation of alcohols and phenols with 3,4-dihydro-2*H*-pyran at room temperature is reported (Scheme 1).

2. Experimental

All chemical reagents were obtained from Fluka or Merck chemical companies and were used without further purification. Cross-linked polystyrene (8% divinylbenzene, grain size range: 0.25–0.68 mm) was prepared via suspension polymerization, as reported in the literature [37]. PS/AlCl$_3$ was prepared as reported previously [37]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 Avance spectrometer at 250.13 MHz. FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} on a Unicam Matteson 1000 spectrophotometer. UV spectra were taken using a Pharmacia Biotech Ultraspec 3000 model 80-2106-20 spectrometer. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or carbowax 20 M. The capacity of the catalyst was determined by the gravimetric method (Mohr titration method) and the 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.

2.1. Preparation of polystyrene-supported gallium trichloride (PS/GaCl$_3$)

Anhydrous GaCl$_3$ (4 g) was added to polystyrene (8% divinylbenzene, grain size range: 0.25–0.68 mm, 8 g) in carbon disulfide (30 mL) as the reaction medium. The mixture was stirred using a magnetic stirrer under reflux conditions for 1 h, cooled, and then water (50 mL) was cautiously added to hydrolyze the excess GaCl$_3$. The mixture was stirred until the bright red color disappeared and the polymer became yellow. The polymer beads were collected by filtration and washed with water (300 mL), and then with 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/GaCl$_3$ was 4.17%, as analyzed by the Mohr titration method [39], and the loading capacity of GaCl$_3$ on the polymeric catalyst or the amount of GaCl$_3$ complexed with polystyrene was calculated to be 0.391 mmol/g.[1]

2.2. General experimental procedure for tetrahydropyranylation of alcohols and phenols with DHP catalyzed by the PS/GaCl$_3$ complex

To a solution of alcohol or phenol (1 mmol) and DHP (1.1–1.3 mmol) in methylene chloride (5 mL) was added PS/GaCl$_3$ (0.1 mmol), and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the catalyst was filtered off and washed with methylene chloride (2 × 10 mL) and the filtrate was concentrated on a rotary evaporator under reduced pressure to afford the crude product. Further purification was achieved by column chromatography on silica gel (Merck, 100–200 mesh, hexane–EtOAC, 8:2). The spent polymeric catalyst from different experiments was combined, washed with ether and dried overnight in a vacuum oven and reused. All of the THP-ether products are known and gave satisfactory physical and spectral data compared with those of authentic samples.

2.3. Catalyst recovery and reuse

The reusability of the catalyst was checked in the multiple tetrahydropyranylation of benzyl alcohol with DHP. At the end of each reaction, the solvent was evaporated, ether (Et$_2$O, 10 mL) was added and the catalyst was filtered. The recovered catalyst was used with fresh benzyl alcohol, DHP and CH$_2$Cl$_2$.

3. Results and discussion

3.1. Preparation of the PS/GaCl$_3$ complex

First, the cross-linked polystyrene (8% divinylbenzene, grain size range: 0.25–0.68 mm) was prepared via suspension polymerization, as reported in the literature [37]. Then, PS/GaCl$_3$ was prepared by addition of anhydrous gallium chloride to polystyrene (8% divinylbenzene) in carbon disulfide under reflux conditions. The loading capacity of the polymeric catalyst, obtained by the gravimetric method and checked by the atomic absorption technique, was 0.391 mmol GaCl$_3$/g of complex beads catalyst [39]. The data obtained by these two techniques showed, within experimental error, that the catalyzing species are in the form of GaCl$_3$ supported on the polymeric support. The UV spectrum of a solution of the PS–GaCl$_3$ complex in CS$_2$ showed a new strong band at 470 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 gallium trichloride. The FT IR spectrum of PS/GaCl$_3$ showed new absorption peaks due to the C–C stretching vibration and the C–H bending vibration of the benzene ring at 1500–1560 and 400–800 cm^{-1}, by which complex formation was demonstrated. The structure of the PS–GaCl$_3$ complex is similar to that of the PS–AlCl$_3$ complex, as suggested by Neckers et al. [40], because the Lewis acid GaCl$_3$ is complexed with the benzene rings of the polystyrene and GaCl$_3$ is stabilized due to the decreased mobility of the benzene rings, hindered by the long polystyrene chain. The PS–GaCl$_3$ complex catalyst is a non-hygroscopic, water tolerant and especially stable

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[1] 1.0 g of solid catalyst (PS/GaCl$_3$) was decomposed by burning with Na metal, extracted with 10 mL of water and filtered. The chlorine content of the filtrate was determined by the Mohr titration method [39].

Table 1
Reaction condition optimization in the tetrahydropyranylation of benzyl alcohol with DHP catalyzed by PS/$GaCl_3$ at room temperature.[a]

Entry	Solvent	Catalyst (mol%)	Time (min)	Yield[b] (%)
1	*n*-Hexane	10	25	17
2	THF	10	25	25
3	CH_3Cl	10	25	39
4	CH_3CN	10	25	56
5	H_2O	10	25	NR[d]
6[c]	CH_2Cl_2	–	60	NR
7	CH_2Cl_2	0.1	50	21
8	CH_2Cl_2	1	50	41
9	CH_2Cl_2	5	25	64
10	CH_2Cl_2	5	50	72
11	CH_2Cl_2	10	25	98
12	CH_2Cl_2	20	25	97
13[e]	CH_2Cl_2	–	25	NR
14[f]	CH_2Cl_2	–	25	36
15[g]	CH_2Cl_2	10	10	40[h]
16[i]	CH_2Cl_2	10	25	72

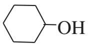
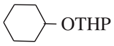
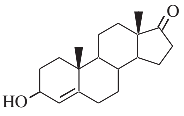
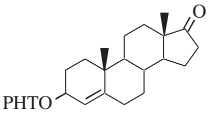
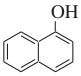
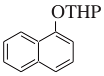
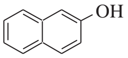
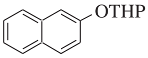
[a] Reaction conditions: benzyl alcohol (1 mmol), DHP (1.1 mmol), solvent (5 mL).
[b] Isolated yield.
[c] No catalyst.
[d] NR: no reaction.
[e] PS was used as the catalyst.
[f] The toluene–$GaCl_3$ complex was used as the catalyst.
[g] The catalyst was filtered after 10 min.
[h] GC yield.
[i] PS/$AlCl_3$ was used as the catalyst.

species. In addition, this polymeric catalyst is easy to prepare, stable in air for a long time (over 2 years) without any change, easily recycled and reusable without any appreciable loss of its activity.

3.2. Tetrahydropyranylation of alcohols and phenols with DHP catalyzed by PS/$GaCl_3$

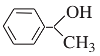
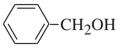
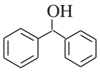
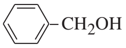
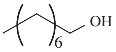
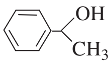
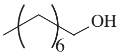
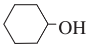
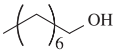
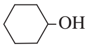
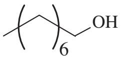
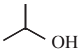
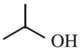
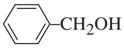
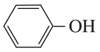
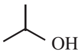
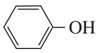
In our initial evaluations, we used as the model reaction, the reaction of benzyl alcohol (1 equiv) with DHP (1.1 equiv). The choice of the solvent appeared crucial in order to maximize the yield. Among the various solvents surveyed, the highest yield was obtained in CH_2Cl_2 (Table 1, entry 11). The 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. No reaction occurred when H_2O was used as the solvent (Table 1, entry 5), because of the aggregation of the catalyst caused by its hydrophobic nature, leading to inadequate access of substrates to the active sites of the catalyst [41]. In addition, we further studied the influence of the amount of PS/$GaCl_3$ on the reaction yields. In the presence of 10, 5, 1 and 0.1 mol% PS/$GaCl_3$, the corresponding yields were 98%, 72%, 41% and 21%, respectively (Table 1, entries 7, 8, 10 and 11). The optimum molar ratio of the polymeric catalyst to hydroxyl compound was found to be 0.1:1. The key role played by the Lewis acidity of the heterogeneous catalyst PS/$GaCl_3$ was proved by employing

Table 2
Tetrahydropyranylation of alcohols and phenols catalyzed by PS/$GaCl_3$.[a]

Entry	ROH	Subst./DHP	Product (THP-ether)	Time (min)	Yield[b] (%)
1	$C_6H_5CH_2OH$	1:1.1	$C_6H_5CH_2OTHP$	25	98
2	*p*-(Cl)$C_6H_4CH_2OH$	1:1.1	*p*-(Cl)$C_6H_4CH_2OTHP$	30	95
3	*p*-(NO_2)$C_6H_4CH_2OH$	1:1.2	*p*-(NO_2)$C_6H_4CH_2OTHP$	60	92
4	*o*-(NO_2)$C_6H_4CH_2OH$	1:1.2	*o*-(NO_2)$C_6H_4CH_2OTHP$	80	91
5	*p*-(CH_3)$C_6H_4CH_2OH$	1:1.1	*p*-(CH_3)$C_6H_4CH_2OTHP$	25	96
6	*p*-(OCH_3)$C_6H_4CH_2OH$	1:1.1	*p*-(OCH_3)$C_6H_4CH_2OTHP$	20	97
7	$C_6H_5CH_2CH_2CH_2OH$	1:1.1	$C_6H_5CH_2CH_2CH_2OTHP$	25	97
7	*n*-$CH_3(CH_2)_6CH_2OH$	1:1.1	*n*-$CH_3(CH_2)_6CH_2OTHP$	40	95
9	*n*-$CH_3(CH_2)_5CH_2OH$	1:1.1	*n*-$CH_3(CH_2)_5CH_2OTHP$	40	95
10	$CH_3(CH_2)_3CH(OH)CH_3$	1:1.1	$CH_3(CH_2)_3CH(OTHP)CH_3$	40	94
11	$(CH_3)_2CHOH$	1:1.2	$(CH_3)_2CHOTHP$	45	93
12	$C_6H_5CH(CH_3)CH_2OH$	1:1.1	$C_6H_5CH(CH_3)CH_2OTHP$	50	93
13	$C_6H_5CH(CH_3)OH$	1:1.2	$C_6H_5CH(CH_3)$ OTHP	50	95
14	$C_6H_5C(CH_3)_2OH$	1:1.3	$C_6H_5C(CH_3)_2OTHP$	60	95
15		1:1.2		55	93
16	$CH_2{=}CHCH_2OH$	1:1.2	$CH_2{=}CHCH_2OTHP$	60	92
17		1:1.3		90	92
18	C_6H_5OH	1:1.3	C_6H_5OTHP	45	94
19	*p*-(OCH_3)C_6H_4OH	1:1.2	*p*-(OCH_3)C_6H_4OTHP	35	93
20	*p*-(CH_3)C_6H_4OH	1:1.2	*p*-(CH_3)C_6H_4OTHP	40	93
21	*p*-(Cl)C_6H_4OH	1:1.2	*p*-(Cl)C_6H_4OTHP	40	91
22		1:1.3		60	91
23		1:1.3		60	92
24	$HOCH_2(CH_2)_3CH_2OAc$	1:1.1	$PHTOCH_2(CH_2)_3CH_2OAc$	40	92
25	$HOCH_2(CH_2)_6CH_2OBn$	1:1.1	$PHTOCH_2(CH_2)_6CH_2OBn$	35	92
26	$HOCH_2(CH_2)_6CH_2OBz$	1:1.1	$PHTOCH_2(CH_2)_6CH_2OBz$	35	92
27	$HOCH_2(CH_2)_3CH_2OTr$	1:1.1	$PHTOCH_2(CH_2)_3CH_2OTr$	45	91
28	$HOCH_2(CH_2)_3CH_2OTs$	1:1.1	$PHTOCH_2(CH_2)_3CH_2OTs$	45	91

[a] All reactions were carried out in CH_2Cl_2 (5 mL) in the presence of PS/$GaCl_3$ (0.1 mmol) at room temperature.
[b] Isolated yield.

Table 3
Selective tetrahydropyranylation of alcohols and phenols catalyzed by PS/$GaCl_3$.[a]

Entry	Subst. 1	Subst. 2	Subst. 1/subst. 2/DHP	Time (min)	Yield (%)[b]	
					THP-ether 1	THP-ether 2
1			1:1:1.1	45	3	93
2			1:1:1.1	50	2	93
3			1:1:1.1	45	4	94
4			1:1:1.1	45	3	94
5			1:1:1.1	60	5	93
6			1:1:1.1	50	4	92
7			1:1:1.1	45	3	94
8			1:1:1.1	75	3	92
9			1:1:1.1	50	5	92
10			1:1:1.2	70	3	94
11			1:1:1.2	50	3	95
12	$HOCH_2CH_2CH_2OH$		1:1.1	70	8[c]	91[c]
13	$HOCH_2(CH_2)_3CH_2OH$		1:1.1	75	7[c]	91[d]
14	$HOCH_2(CH_2)_4CH_2OH$		1:1.1	72	3[c]	95[d]
15	$HOCH_2(CH_2)_6CH_2OH$		1:1.1	75	3[c]	96[d]

[a] All reactions were carried out in CH_2Cl_2 in the presence of PS/$GaCl_3$ (0.1 mmol) at room temperature.
[b] Yields based on GC and NMR.
[c] Di THP-ether.
[d] Mono THP-ether.

polystyrene beads (Table 1, entry 13) and the $GaCl_3$–toluene complex (Table 1, entry 14) as catalysts. In fact, while in the former case no reaction occurred, which indicated that polystyrene itself did not promote the reaction, in the later, the desired product was isolated in a low yield of 36% (Table 1, entry 14). Also, PS/$GaCl_3$ was found to be a more effective catalyst than PS/$AlCl_3$ for tetrahydropyranylation of benzyl alcohol under identical conditions (Table 1, entry 16).

The lifetime and leaching of active sites into the reaction mixture are important issues to consider when heterogeneous and metal-supported catalysts are used, particularly for practical applications of the reaction. Our preliminary investigations demonstrated that the PS/$GaCl_3$ catalyst (a stable π complex) is very stable to air and moisture. To rule out the presence of concurrent homogeneous catalysis, the model reaction was carried out in the presence of the catalyst PS/$GaCl_3$ until the conversion was 40% (10 min), and at that point the catalyst was removed by filtration. Further treatment of the filtrate under similar reaction conditions did not proceed significantly (Table 1, entry 15). On the other hand, after each run the filtrates were used for determination of catalyst leaching (gallium content), which showed a negligible release of $GaCl_3$ by atomic absorption or ICP measurements. The capacity of the catalyst after six uses was 0.38 mmol of $GaCl_3$ per gram. Also, the catalytic behavior of the separated liquid was tested by addition of fresh benzyl alcohol and Ac_2O to the filtrates after each run. Execution of the acetylation reaction under the same reaction conditions, as with the catalyst, showed that the obtained results were as same as the blank experiments. These findings suggest that PS/$GaCl_3$ is stable, no significant leaching of Lewis acid moieties is operating under our reaction conditions and that the observed catalysis is truly heterogeneous in nature.

Further, we carried out reactions between DHP and various alcohols to explore the reaction scope of the PS/$GaCl_3$-catalyzed tetrahydropyranylation, and the results are summarized in Table 2. As can be seen, all reactions proceeded very cleanly (checked by GC) in good to excellent yields. A broad selection of alcohols, including primary (benzylic and linear ones), secondary (including aliphatic and aromatic alcohols), tertiary and allylic alcohols, were converted to their corresponding THP-ethers successfully at room temperature (Table 2). It is noteworthy that in the case of both tertiary and allylic alcohols, which are acid-sensitive alcohols, no elimination product or isomerization of C=C bonds was observed and they were also converted to their corresponding THP-ethers in high yields (Table 2, entries 14 and 16). Unlike strong acidic catalysts that produce polymeric by-products from the dihydropyran [7,42], no polymerization of the dihydropyran was detected when PS/$GaCl_3$ was used, probably due to its mild catalytic activity. We were then interested in whether the same catalyst could be employed for the tetrahydropyranylation of phenolic compounds. By following identical reaction procedures as described for the alcohols, various phenols (Table 2, entries 18–23) were smoothly converted into the corresponding THP-ethers in good yields. As can be seen, a phenol whose benzene ring is substituted with a strong electron-donating group reacted quickly with an excellent yield (Table 2, entries 19 and 20). We then turned our attention to whether the same catalyst could be useful for tetrahydropyranyla-

Table 4
Comparison of the results obtained for the tetrahydropyranylation of benzyl alcohol catalyzed by $PS/GaCl_3$ with those obtained by some reported catalysts.

Entry	Catalyst (mol%)	Conditions	Time (min)	Yield (%)	Refs.
1	$Bi(NO_3)_3 \cdot 5H_2O$ (5)	CH_2Cl_2/RT	20	92	[34]
2	$H_{14}[NaP_5W_{30}O_{110}]$ (0.1)	CH_2Cl_2/reflux	120	90	[43]
3	$CuCl_2$ (15)	CH_2Cl_2/RT	20	83	[13]
4	$Fe(CH_3SO_3)_2 \cdot 4H_2O$ (2)	Solvent-free/RT	60	97	[44]
5	$H_6P_2W_{18}O_{62}$ (1)	Toluene/RT	120	98	[45]
6	$AlCl_3$@PS (15)	CH_2Cl_2/RT	0.7 h	97	[46]
7	$NbCl_5$ (10 mol%)	CH_2Cl_2/RT	150	90	[47]
8	n-$Bu_4N^+Br_3^-$ (25 mol%)	CH_2Cl_2/RT	60	85	[27]
9	Polyaniline sulfate salt (17 mol%)	$CHCl_3$/RT	480	59	[22]
10	LiOTf (60 mol%)	CH_2ClCH_2Cl/reflux	150	96	[23]
11	Vanadyl (IV) acetate (27 mol%)	$CHCl_3$/RT	60	95	[33]
12	$PdCl_2(CH_3CN)_2$ (10 mol%)	THF/RT	60	72	[30]
13	$ZrCl_4$ (5 mol%)	CH_2Cl_2/reflux	180	92	[19]
14	$Fe(ClO_4)_3$ (3)	Et_2O/RT	90	98	[48]
15	Ionic liquid/$pph_3 \cdot HBr$ (10)	Solvent-free/RT	240	96	[21]
16	$CuSO_4 \cdot 5H_2O$ (20)	CH_3CN/RT	40	91	[31]
17	$La(NO_3)_3 \cdot 6H_2O$ (10)	Solvent-free/RT	150	93	[24]
18	$Ru(acac)_3$ (2)	Solvent-free/RT	16 h	80	[49]
19	Silicasulfuric acid (3.9)	CH_2Cl_2/RT	30	91	[50]
20	$PS/GaCl_3$ (10)	CH_2Cl_2/RT	25	98	This work

Table 5
Reusability of [a]$PS/GaCl_3$ in the pyranylation of benzylalcohol with DHP.[b]

Run	THP-ether[c] (%)	Time (min)
1	98	25
2	98	25
3	97	25
4	96	25
5	95	25
6	94	25

[a] The capacity of the catalyst after six uses was 0.38 mmol $GaCl_3$ per gram.
[b] Reaction conditions: benzyl alcohol (1 mmol), DHP (1.1 mmol), $PS/GaCl_3$ (0.1 mmol), CH_2Cl_2 (5 mL).
[c] Isolated yield.

tion of substrates containing other protecting groups. We observed that various protected alcohols (Table 2, entries 24–28) containing protecting groups such as acetyl, benzyl, benzoyl, trityl and tosyl were smoothly converted into the corresponding THP-ethers without affecting the other protecting groups.

Since this catalyst was highly active in the tetrahydropyranylation of alcohols and phenols, we decided to examine the chemoselectivity of the present method. A set of competitive reactions was allowed between primary alcohols and secondary or tertiary alcohols, or phenol with DHP in the presence of $PS/GaCl_3$ (Table 3). The results indicated that $PS/GaCl_3$ was able to discriminate between different types of alcohols and or phenols from each other, a transformation that is difficult to accomplish via conventional methods (Table 3, entries 1–11). Also, we found that symmetrical diols in the presence of a limited amount of DHP were protected as their mono THP-ethers, selectively (Table 3, entries 12–15). It is worth mentioning that diols with a higher number of carbon atoms showed more selectivity towards mono THP-ether formation (Table 3, entries 14 and 15). Although the reason for the observed chemoselectivity is definitely unclear, it is possibly due to factors such as the mild catalytic activity of $PS/GaCl_3$, its pore size and its hydrophobic nature or the more lipophilic microenvironment of the metal particles in the polymer-supported catalyst, which affected the extent of penetration (that is the access to the active sites) of different hydroxyl compounds in the swollen beads [5]. The present chemoselectivities could be suitable for the protection of alcohols and phenols in the syntheses of complex molecules by multistep processes.

In order to show the efficiency and applicability of the present method, the catalytic activity of $PS/GaCl_3$ was compared to 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, mol% of the catalyst used and yields. As demonstrated in Table 4, $PS/GaCl_3$ is an equally or more efficient catalyst for the tetrahydropyranylation reaction in terms of yield and reaction rate.

3.3. Catalyst reusability

Finally, the reusability of this catalyst was also tested in the multiple tetrahydropyranylation of benzyl alcohol with DHP under the same reaction conditions described in the general procedure. At the end of each of the repeated reactions, the catalyst was filtered, washed exhaustively with methylene chloride and then diethyl ether, and dried before using with fresh benzyl alcohol and DHP. The catalyst was consecutively reused six times with negligible loss in its activity and there is no need for regeneration (Table 5).

4. Conclusion

In conclusion, in this paper a simple, mild, efficient and highly chemoselective method for tetrahrdropyranylation of alcohols and phenols using the stable and heterogeneous polystyrene-supported gallium trichloride is reported. The short reaction times, high to excellent yields, low cost, easy preparation and handling of the polymeric Lewis acid catalyst are the advantages of the present method. In addition, the use of water-tolerant $PS/GaCl_3$ has resulted in a reduction in unwanted and hazardous waste, and a minimum amount of product contamination with metal that is produced during conventional homogeneous processes. Most importantly, the work-up is reduced to a mere filtration and evaporation of the solvent. Finally, this catalytic system showed good catalytic activity in these reactions and this polymeric catalyst can be recovered unchanged and used again at least six times with negligible loss in its activity. Other applications of the $PS/GaCl_3$ complex are currently under investigation and will be reported in due course.

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