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Tetrahydropyranylation of Alcohols and Phenols Using Polystyrene Supported Lewis Acids as Catalysts

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Polystyrene supported $TiCl_4$ (Ps-$TiCl_4$) and polystyrene supported $FeCl_3$ (Ps-$FeCl_3$) were prepared by coordinating Lewis acids with polystyrene. The catalysts were characterized by TGA, BET, SEM, IR and pyridine-adsorbed IR. The loading of Ps-$TiCl_4$ and Ps-$FeCl_3$ were 0.35 and 0.3 mmol•g^{-1} respectively. Both catalysts were found to be efficient for the tetrahydropyranylation and detetrahydropyranylation of various alcohols and phenols in different solvents. Two catalysts can be recovered and reused for five times with good activity.

Keywords tetrahydropyranylation/detetrahydropyranylation, Ps-$TiCl_4$, Ps-$FeCl_3$, polystyrene supported, Lewis acids

Introduction

In the context of green chemistry, polymer supported Lewis acids are a class of important atom-economic and environmentally benign catalytic systems that have been developed and applied successfully in a variety of chemical reactions.[1] Generally, polymer-supported Lewis acids are prepared by immobilization of Lewis acids on solid supports such as polymeric microspheres or inorganic materials via covalent bonds or coordination. Heterogeneous supported Lewis acids active as its homogeneous counterpart have several distinguishing advantages like easy workup and separation from the reaction system, recyclability, nontoxicity, enhanced stability, *etc*.[2]

$TiCl_4$ and $FeCl_3$ are important Lewis acids that show powerful catalytic activity in a series of organic reactions.[3] Both of them are water-sensitive, $TiCl_4$ will even lose its activity in moist environments because it reacts with water easily. Thus, strict anhydrous conditions and stoichiometric amounts or more are needed in order to achieve good yields. Furthermore, tedious workup procedure after reaction to hydrolyze excess catalyst produces large amounts of acidic waste water. Hydrophobic polystyrene which protects water-sensitive Lewis acids from hydrolysis is used extensively as support in the field of heterogeneous immobilized Lewis acids. For example, Neckers *et al.*[4] first reported polystyrene supported $AlCl_3$ as a catalyst in Friedel-Crafts reaction,[5] and its applications in synthesis of pyrroles,[6] and preparation of dihydropyrimidinones.[7] Till now, the immobilization of $AlCl_3$ has been extensively studied, while the research on supporting of $TiCl_4$ and $FeCl_3$ is relative rare. In view of the wide applications and tunable reactivities of them in organic reactions, we began the study of the preparation of Ps-$TiCl_4$ and Ps-$FeCl_3$ and their physical and chemical properties.

Protection and deprotection of the hydroxy group in multistep organic synthesis in the manufacture of pharmaceuticals and other natural products are inevitable. Amongst many protocols used for the protection of alcohols and phenols, tetrahydropyranylation is one of the most frequently used method due to its easy introduction and removal, low cost, and stability of tetrahydropyranyl ethers (THP ethers) towards acylating and alkylating reagents, metal hydrides, redox reagents, Grignard reagents and catalytic hydrogenation. A large number of reagents have been developed as catalysts for tetrahydropyranylation, such as $Al(OTf)_3$,[8] PPTS,[9] sulfonic acid functionalized carbon catalyst,[10] modified zeolites,[11] $PdCl_2(CH_3CN)_2$,[12] benzene sulfonamide (BNBBS),[13] $CuSO_4•5H_2O$,[14] $Bi(OTf)_3•4H_2O$,[15] $LiPF_6$,[16] polyaniline salt,[17] dialkylimidazolium tetrachloroaluminates,[18] $AlCl_3·6H_2O$,[19] ceric ammonium nitrate,[20] vanadyl (IV) acetate,[21] lithium perchlorate,[22] $TaCl_5$-Silica gel,[23] and polystyrene supported Lewis acids,[24] *etc*.

However, some of these methods have several disadvantages including long reaction time, harsh reaction conditions, involving moisture sensitive reagents and tedious experimental procedures. Thus, it is still necessary to develop a simple and efficient method for tetrahydropyranylation/detetrahydropyranylation. In the

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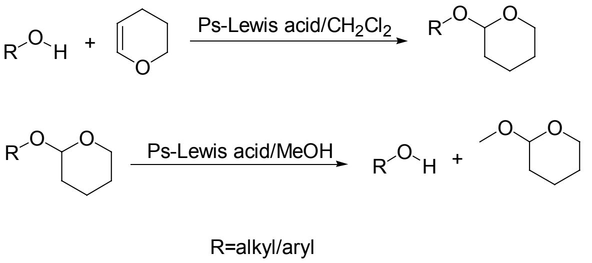
present work, we report the preparation and characterization of Ps-$TiCl_4$ and Ps-$FeCl_3$ as well as their use as catalysts for tetrahydropyranylation of alcohols and phenols with 3,4-dihydro-2*H*-pyran and the subsequent detetrahydropyranylation of the obtained THP ethers with methanol (Scheme 1).

Scheme 1 Tetrahydropyranylation of alcohols and phenols and depyranylation catalyzed by Ps-Lewis acid



Experimental

General

Polystyrene (8% divinylbenzene) was purchased from Nanjing Microspheres Hi-Efficiency Isolation Carrier Co., Ltd. It was washed with chloroform, acetone, water and methanol, and then dried to constant weight under vacuum before use. Chemicals used were analytical reagent and purchased from Sinopharm Chemical Reagent Co. Ltd. ^{1}H NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a Bruker spectrophotometer at 500 MHz.

Characterization

Thermal analysis tests were made in SDT Q600 TA equipment. The samples were heated from 20 ℃ up to 800 ℃ at a rate of 10 ℃•min^{-1} in air atmosphere with flow rate of 120 mL•min^{-1} without a reference material. The amount used for this experiment was 10 mg for each sample. The surface properties such as BET specific surface area, total pore volume, and mean pore diameter were determined from N_2 adsorption isotherms at 77 K with a Micrometrics Tristar3020. Specific surface areas and pore size distribution were calculated with the BET equation and the BJH method respectively. The total pore volume was taken from the desorption branch of the isotherm at $p/p_0=0.95$, assuming complete pore saturation. SEM images were recorded on a scanning electron microscope (SEM, S-4800) at an operating voltage of 3.0 kV.

The polystyrene, Ps-$TiCl_4$ and Ps-$FeCl_3$ were dehydrated in an Infrared (IR) cell at 100 ℃ for 2 h under vacuum before pyridine adsorption. Pyridine was led into the IR cell at 100 ℃. Pyridine adsorption IR spectra of polystyrene, Ps-$TiCl_4$ and Ps-$FeCl_3$ were measured at room temperature after desorption at 100 ℃ for 2 h using a Bruker Tensor 27.

Typical procedure for preparation of Ps-$TiCl_4$[25]

Excessive anhydrous $TiCl_4$ was added to polystyrene (8% divinylbenzene, 3.5 g) in carbon disulfide (25 mL). The mixture was stirred under reflux for 2.5—3 h, cooled to room temperature and then poured into ice water (50 mL) to destroy excess $TiCl_4$. The mixture was stirred until the brown-red color disappeared and the catalyst became light yellow. It was then filtered, and the polymer beads were collected, washed with water (350 mL), then with ether, acetone and ether, and dried to constant weight under vacuum at 40 ℃.

Typical procedure for preparation of Ps-$FeCl_3$[26]

Anhydrous $FeCl_3$ (4.5 g) was added to polystyrene (8% divinylbenzene, 3.0 g) in chloroform (30 mL). The mixture was stirred under reflux for 2 h and cooled to room temperature. The polymer beads were then filtered and washed with chloroform (100 mL) and ethyl ether (100 mL) and dried in vacuum overnight at 40 ℃.

Typical procedure for tetrahydropyranylation

To a solution of 1-butanol (10 mmol) and 3,4-dihydro-2*H*-pyran (DHP 12 mmol) in methylene chloride (10 mL), Ps-$TiCl_4$ or Ps-$FeCl_3$ (1.5 mmol) was added, and the reaction mixture was stirred at room temperature, after the completion of the reaction as monitored by TLC, the mixture was filtered. Ps-$TiCl_4$ or Ps-$FeCl_3$ was washed with methylene chloride to remove any physisorbed reagents, dried and used in next run under the same reaction conditions. The filtrate was concentrated under reduced pressure, and then it was purified through a short basic alumina column to give the almost pure product. All the obtained tetrahydropyranyl ethers were characterized by ^{1}H NMR spectroscopy.

2-(Allyloxy)tetrahydro-2*H*-pyran Colorless liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.95—5.91 (m, 1H), 5.30 (dd, $^2J=1.5$, $^3J=17$ Hz, 1H), 5.17 (dd, $^2J=1.5$, $^3J=10.5$ Hz, 1H), 4.65 (t, $J=3.5$, 1H), 4.24 (dd, $^2J=5$, $^3J=13$ Hz, 1H), 3.98 (dd, $^2J=6$, $^3J=13$ Hz, 1H), 3.87 (q, $J=5.5$ Hz, 1H), 3.51 (t, $J=5$ Hz, 1H), 1.86—1.84 (m, 1H), 1.736—1.730 (m, 1H), 1.64—1.51 (m, 4H).

Typical procedure for deprotection of tetrahydropyranyl ethers

To a solution of THP ether (10 mmol) in methanol (15 mL), Ps-$TiCl_4$ or Ps-$FeCl_3$ (1.5 mmol) was added, and the reaction mixture was stirred at room temperature or under reflux, after the completion of the reaction as monitored by TLC, the mixture was filtered, and the filtrate was concentrated under reduced pressure to give the corresponding alcohol.

Results and Discussion

Two supported Lewis acids (Ps-$TiCl_4$, Ps-$FeCl_3$) were prepared through immobilizing anhydrous Lewis acids on polystyrene (8% divinylbenzene) in carbon disulfide or chloroform under reflux. Although free

$TiCl_4$ and $FeCl_3$ were moisture sensitive and corrosive, polystyrene supported $TiCl_4$ and $FeCl_3$ were stable, water-resistant and could be stored in air for a few months without appreciable loss of activity. The supported catalysts were characterized by TGA, BET, IR, pyridine-adsorbed IR and SEM.

The thermal stability of Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$ was measured by TGA analysis (Figure 1). Little weight loss (less than 1.1% of total weight) was observed over the range from 20 to 350 ℃ for Ps which indicated that Ps was chemically stable. 2.17% and 7.74% of initial weight loss which was due to the removal of adsorbed water were observed for Ps-$TiCl_4$ and Ps-$FeCl_3$ respectively, then the biggest weight loss of Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$ were observed from 400 to 500 ℃ which was attributed to the decomposition of samples. As was shown in the DTA curves, the endothermic peaks of Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$ were observed at 421, 431 and 430 ℃, respectively. It is clear that the thermal stability of Ps was increased after the immobilization.

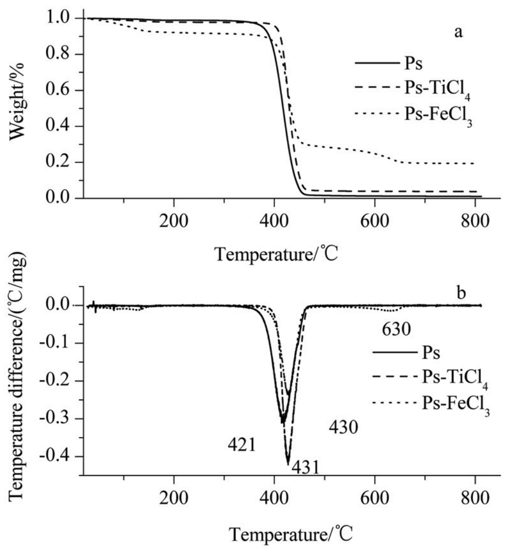


Figure 1 TGA thermograms for Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$.

BET surface area, pore volume and pore diameter of polystyrene and Ps-Lewis acids were measured after drying in vacuum at 90 ℃ for 3 h in order to verify the introduction of Lewis acids onto polystyrene. In the case of polystyrene (Table 1), the surface area was found to be 13.35 $m^2•g^{-1}$, the pore volume was 0.13 $mL•g^{-1}$ and pore diameter was 38.9 nm, therefore, it was classified as a mesoporous material. For Ps-$TiCl_4$, the surface area was 2.65 $m^2•g^{-1}$, the pore volume was 0.01 $mL•g^{-1}$ and pore diameter was 17.6 nm, indicating that immobilization of $TiCl_4$ on polystyrene resulted in a reduction of surface area, pore volume, and pore diameter. This was because that the difference in specific density between $TiCl_4$ and polystyrene had an effect on the specific surface area, and the immobilization blocked pores of polystyrene. Interestingly, immobilization of $FeCl_3$ on polystyrene resulted in an increase of the surface area and pore volume, but the reduction of pore diameter, and these results were explained by SEM.

Table 1 Physical and chemical properties of support and catalyst

Sample	Surface area/ ($m^2•g^{-1}$)	Pore volume/ ($mL•g^{-1}$)	Pore diameter/ nm	Catalyst loading [a]/ ($mmol•g^{-1}$)
Polystyrene	13.35	0.13	38.9	0
Ps-$TiCl_4$	2.65	0.01	17.6	0.35
Ps-$FeCl_3$	28.40	0.16	26.0	0.30

[a] The capacity of the supported catalysts based on its chloride content.[27]

SEM images of Ps, Ps-$TiCl_4$, and Ps-$FeCl_3$ were shown in Figure 2. From the image of Ps, the morphology of Ps was smooth ball with many pores on the surface, and it was shown that the surface of Ps-$TiCl_4$ was dispersed with small amount of TiO_2 particles, which was due to the hydrolysis of $TiCl_4$ in the preparation process. In the image of Ps-$FeCl_3$, lots of small irregular $FeCl_3$ molecules were adsorbed on the surface of the ball which led to the increase in surface area and pore volume of Ps-$FeCl_3$ compared with Ps.

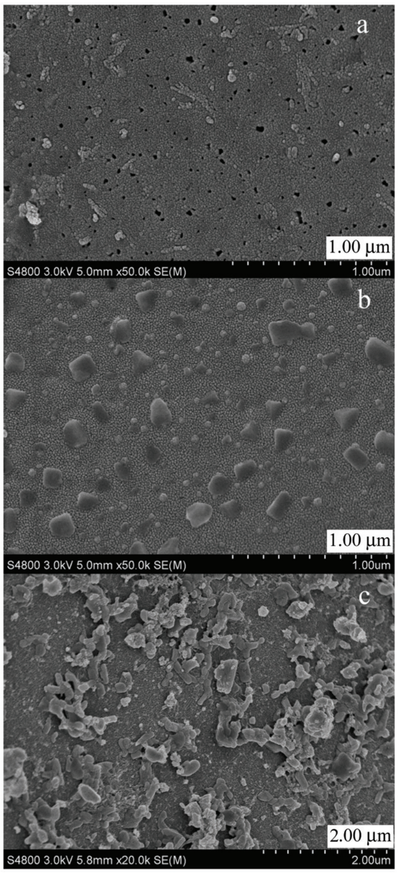


Figure 2 SEM images of Ps (a), Ps-$TiCl_4$ (b), Ps-$FeCl_3$ (c).

The infrared spectra of polystyrene, Ps-$TiCl_4$ and

Ps-$FeCl_3$ were shown in Figure 3. The peak at 3026 cm^{-1} was related to C—H stretching vibration of benzene ring, and the peak at 2920 and 2850 cm^{-1} belonged to C—H stretching vibration of CH_2. Comparing the IR spectra of supported catalysts and polystyrene, it is shown that the main difference lies in 1450—1500 and 2900—3100 cm^{-1}. Those regions of IR spectra corresponded to C=C and C—H stretching vibration of aromatic ring. These data proved that the complex was formed between the Lewis acids and polystyrene.[25]

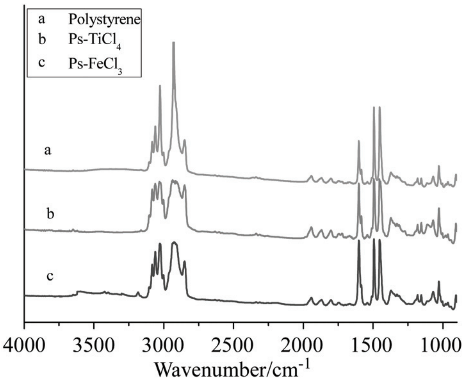


Figure 3 FTIR spectra of Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$.

The nature of the surface acidic sites in solid was defined by Bronsted acidic site and Lewis acidic site. FT-IR spectroscopy of adsorbed pyridine is a useful technique widely used for distinguishing of Lewis and Bronsted acid sites. The adsorbed pyridine tends to couple with protonic (Bronsted) or aprotic (Lewis) acidic centers through the nitrogen lone-pair electrons and thus could be detected by monitoring their ring vibrations. The FT-IR spectra of pyridine adsorbed on two Ps-Lewis acids samples in Figure 4 showed characteristic bands at 1450 cm^{-1} which was attributed to L-sites,[28] however, no band was monitored on Ps sample. It was proved again that the Lewis acids were successfully immobilized on polystyrene.

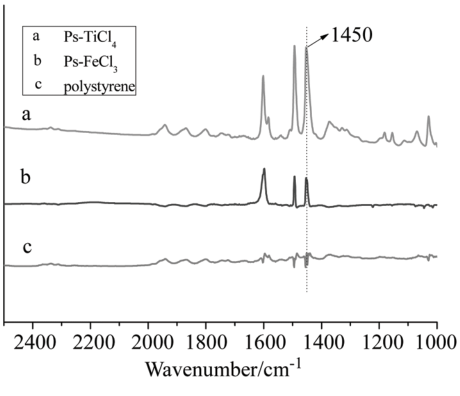


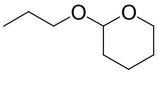
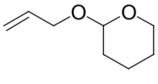
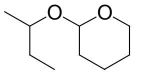
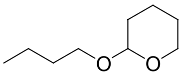
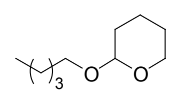
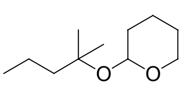
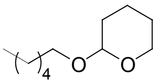
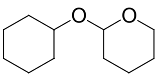
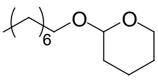
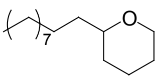
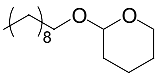
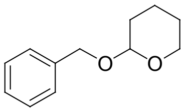
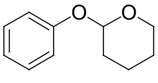
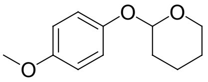
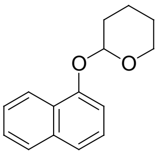
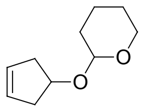
Figure 4 Pyridine-adsorbed FTIR of Ps, Ps-$TiCl_4$ and Ps-$FeCl_3$.

In our initial research, a model reaction of 1-butanol (10 mmol) and 3,4-dihydro-2*H*-pyran (DHP 12 mmol) was selected to determine the optimal reaction conditions. Various solvents such as toluene, cyclohexane, *n*-hexane, acetonitrile, water, methylene chloride were tried for the reaction, and methylene chloride was proved to be the best one. It was because the polystyrene swelled in methylene chloride, so the substrates could smoothly access to the catalytic centers wrapped in the pores of polystyrene. 80—180 min of reaction time was needed for good yields, while only 50 min was needed for the tetrahydropyranylation catalyzed by anhydrous $TiCl_4$ because the acidity of the supported $TiCl_4$ was weaker than that of anhydrous $TiCl_4$. Moreover, mesoporous pores and channels of polystyrene were unfavorable for the molecular mass transfer process. The amount of Ps-Lewis acid had influence on the yield, 15 mol% of catalyst was sufficient to give 1-butanol tetrahydropyranyl ether in 94% yield, however, increasing the amount of catalyst did not improve the yields, and the reaction did not occurred without catalysts or only with polystyrene. To find out whether the reaction took place in the solid matrix of Ps-$TiCl_4$ and Ps-$FeCl_3$ or catalyzed by free $TiCl_4$ and $FeCl_3$ released from the support, Ps-$TiCl_4$ and Ps-$FeCl_3$ were stirred in methylene chloride for 120 min, and filtered off, then reactants were added to the filtrates and stirred for 120 min, and no products appeared. Encouraged by the results, we investigated different kinds of alcohols (primary, secondary, tertiary, allylic and benzylic) and phenols using Ps-$TiCl_4$ and Ps-$FeCl_3$ as catalysts to give the corresponding THP ethers at room temperature or under reflux (for Ps-$FeCl_3$) in good to excellent yields (Table 2). As shown in Table 2, the order of catalytic activity of the two catalysts was Ps-$TiCl_4$>Ps-$FeCl_3$. This was because the acidity of $TiCl_4$ was stronger than that of $FeCl_3$.

As to the reaction process, it could be rationalized based on the theoretical and experimental approaches reported in the literature. The mechanism pathway may proceed via the coordination of Ps-$TiCl_4$ to the oxygen atom of alcohol generating intermediate complex A. This intermediate may be in equilibrium with chelate B (in which the Ps-$TiCl_4$ is coordinated with both the oxygen atom of the alcohol as well as the C=C double bond of DHP) and complex C (in which only the C=C double bond is coordinated with the Ps-$TiCl_4$) (Figure 5).[29] Finally, these transition states lead to the formation of THP ethers.

Interestingly, we found that Ps-$TiCl_4$ and Ps-$FeCl_3$ could be used for depyranylation of THP ether further. For example, the Benzyl alcohol tetrahydropyranyl ether was depyranylated in methanol within 95 min in 94% yield with 15 mol% of Ps-$TiCl_4$. Similarly various THP ethers were converted to corresponding alcohols and phenols within 95—150 min in 81%—94% yields with Ps-$TiCl_4$ or Ps-$FeCl_3$, respectively, which was shown in Table 3. The recycling property which was a key factor in application was studied further, and it was found that Ps-$FeCl_3$ and Ps-$TiCl_4$ could be reused for five runs

Table 2 Tetrahydropyranylation of alcohols and phenols using Ps-$TiCl_4$ and Ps-$FeCl_3$ [a]

Entry	Product	Catalyst	Time/min	Yield/%
1		A	115	93
		B	120	78
2		A	110	93
		B	120	78
3		A	140	91
		B	160	79
4		A	120	94
		B	125	80
5		A	120	93
		B	125	79
6		A	125	91
		B	145	79
7		A	120	93
		B	135	80
8		A	135	92
		B	145	79
9		A	125	93
		B	135	80
10		A	125	93
		B	135	80
11		A	140	90
		B	150	79
12		A	80	95
		B	100	81
13		A	100	87
		B	115	76
14		A	95	89
		B	110	78
15		A	150	85
		B	180	72
16		A	135	91
		B	145	79

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[a] All reactions catalyzed by Ps-$TiCl_4$ were carried out in CH_2Cl_2 at room temperature except for the phenols (Entries 13—15), which were carried out under reflux condition; all reactions catalyzed by Ps-$FeCl_3$ were carried out in CH_2Cl_2 under reflux condition; A＝Ps-$TiCl_4$, B＝Ps-$FeCl_3$.

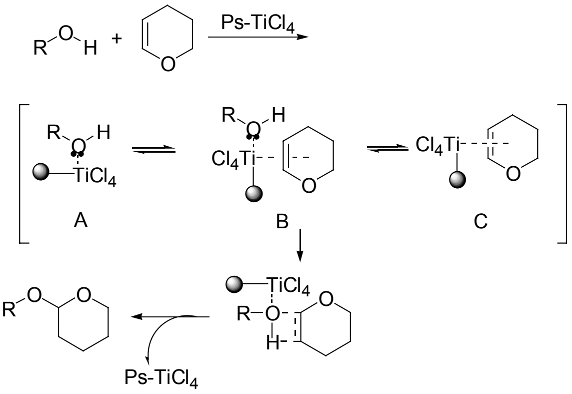
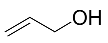
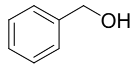
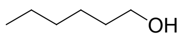
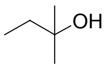
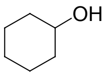
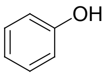


Figure 5 Proposed mechanism for tetrahydropyranylation of alcohol catalyzed by Ps-$TiCl_4$.

Table 3 Detetrahydropyranylation of THP ethers using Ps-$TiCl_4$ and Ps-$FeCl_3$ [a]

Entry	Product	Catalyst	Time/min	Yield/%
1		A	110	94
		B	120	87
2		A	95	94
		B	115	87
3		A	110	94
		B	120	85
4		A	125	93
		B	135	84
5		A	120	93
		B	125	85
6		A	135	90
		B	150	81

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[a] All reactions catalyzed by Ps-$TiCl_4$ were carried out in methanol at room temperature, all reactions catalyzed by Ps-$FeCl_3$ were carried out in methanol under reflux condition; A＝Ps-$TiCl_4$, B＝Ps-$FeCl_3$.

with good catalytic activity. The yield of each run was 94%, 94%, 92%, 87%, 85% for Ps-$TiCl_4$; for Ps-$FeCl_3$, it was 81%, 81%, 80%, 76%, 75%. Further comparison of Ps-$TiCl_4$ and Ps-$FeCl_3$ with various reported catalysts in tetrahydropyranylation was made, as shown in Table 4, better yields, easy separation and low cost were the obvious advantages when using them as catalysts.

Conclusions

In the present methodology, Ps-$TiCl_4$ and Ps-$FeCl_3$ as effective catalysts for tetrahydropyranylation and depyranylation of alcohols and phenols was studied. TGA analysis showed that polystyrene was chemically stable and its stability was increased after immobilization with $TiCl_4$ or $FeCl_3$. Pore analysis, SEM images as well as FT-IR spectroscopy indicated that $TiCl_4$ and $FeCl_3$ were successfully supported on polystyrene.

Table 4 Comparisons of Ps-$TiCl_4$ and Ps-$FeCl_3$ with various catalysts in tetrahydropyranylation[a]

Entry	Catalyst	Mol/%	Time/min	Yield/%
1	Ps-$TiCl_4$	15	80	95
2	Ps-$FeCl_3$	15	100	81
3	Ps-$AlCl_3$	15	42	97[24a]
4	Ps-tin porphyrin	1	4	97[24c]
5	Carbon catalyst	10[b]	120	96[10]
6	$CuSO_4 \cdot 5H_2O$	20	40	91[14]
7	$PdCl_2(CH_3CN)_2$	10	60	72[12]
8	polyaniline salt	17	480	59[17]

[a] Substrate: benzyl alcohol and DHP. [b] Mass percentage.

Experimental results suggested that tetrahydropyranylation occurred in the solid matrix of Ps-$TiCl_4$ and Ps-$FeCl_3$ rather than catalyzed by free $TiCl_4$ and $FeCl_3$ released from the support. Mild reaction conditions, good to excellent yields, easy preparation and low cost were the obvious advantages of the present approach, and these two supported catalysts can be recovered and reused for five times with good activity.

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