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Sulfonic acid-functionalized LUS-1: an efficient catalyst for tetrahydropyranylation/depyranylation of alcohols

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Abstract Efficient acidic functionalization of mesoporous silica LUS-1 (Laval University Silica) and its application as a recyclable heterogeneous catalyst for DHP (3,4-dihydro-2*H*-pyran) protection of alcohols and the subsequent removal of the corresponding protecting group have been reported. This green method offers a number of advantages such as short reaction time, good yields of protection and deprotection, simple work-up procedure, recyclable catalyst, and environmentally friendly conditions.

Keywords Sulfonic acid functionalized LUS-1 · Tetrahydropyranylation · DHP · Protection · Deprotection · Nanoporous acid catalyst

Introduction

Mesoporous silica materials have received significant attention because of their potential applications as supports. Grafting organo-acidic groups (e.g., propyl sulfonic acid) to the pore walls of the mesoporous silica materials create heterogeneous acid catalysts [1–6]. Ordered mesoporous silica LUS-1 has a high surface area (800 cm^2/g), long range ordered pores, and hydrothermal stability [7], which can be used as a support for heterogeneous catalysts. In comparison to other ordered mesoporous silica, LUS-1 has more available silanol groups on the silica surface, which can react with more surface modifying groups [8].

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Tetrahydropyranylation is one of the most useful methods for the protection of hydroxyl groups, because the resulting tetrahydropyranyl ether is stable under a variety of reaction conditions such as basic media, acylating agents, and metal hydrides [9]. There are several methods reported in the literature for tetrahydropyranylation of alcohols in the presence of different catalysts such as ionic liquids [10], Brønsted acidic ionic liquid [morH]HSO_4 [11], silica chloride [12], modified zeolites [13], silica sulfonic acid [14], LiOTf [15], $Al(OTf)_3$ [16], and $Sn^{IV}(TPP)(OTf)_2$ [17]. As mentioned, alcohols are frequently protected as tetrahydropyranyl ethers, and a number of techniques for deprotection of tetrahydropyranyl ethers to the parent alcohols are reported in the literature by different catalysts such as $Bi(OTf)_3{\cdot}4H_2O$ [18], sulfonic acid- bearing polymer brushes [19], dialkylimidazolium tetrachloroaluminates [20], and LiBr [21]. In some cases both transformations (tetrahydropyranylation and depyranylation) can be catalyze by one catalyst such as *p*-toluenesulfonic acid (PTSA) [22], pyridinium *p*-toluenesulfonate (PPTS) [23], NH_4Cl [24], $ZrCl_4$ [25], and LiBr [21]. However, many of the reported methods have some disadvantages, such as long reaction times, low yields, harsh reaction conditions, using organic solvents, and large amounts of toxic, expensive or unrecyclable catalysts. In continuation of our previous works on the application of heterogeneous solid catalysts in organic synthesis [26, 27], herein, we would like to report LUS-Pr-SO_3H as a highly efficient catalyst for tetrahydropyranylation of alcohols and depyranylation of corresponding ethers in solvent-free conditions.

Experimental section

Melting points were measured using the capillary tube method with an electro thermal 9200 apparatus. IR spectra were recorded from a KBr disk using a FT-IR Bruker Tensor 27 instrument. The ^1H NMR was run on a Bruker, 250 MHz. The ^{13}C NMR was run on a Bruker, 62.9 MHz. Mass spectrometry (MS) analysis was performed on a model 5973 mass-selective detector (Agilent). The N_2 adsorption/desorption measurements were conducted at liquid nitrogen temperature (77 K) using BELSORP-mini II. Scanning electron microscopy (SEM) carried out on a LEO 1445 V microscope.

Synthesis and functionalization of LUS-1

The mesoporous compound LUS-1 was synthesized and functionalized according to our previous report [28]. Colloidal silica Ludox (15.5 g, 0.26 mol) was added to sodium hydroxide (2 g, 5×10^{-2} mol) in distilled water (50 mL), and the mixture was stirred at 70 °C until a clear solution was obtained. A second solution of Cetyltrimethylammonium *p*-toluene sulfonate (2.5 g, 5.5×10^{-3} mol) in distilled water (90 mL) was stirred at 40 °C for 1 h. The first solution was added drop wise to the second one, and then the mixture was stirred at 40 °C for 2 h. The resulting sol–gel was heated in an autoclave at 130 °C for 20 h. The surfactant was removed by treatment with HCl 0.1 M in ethanol for 2 h. After filtration and washing with

distilled water, the synthesized solid (LUS-1) was dried under vacuum at 100 °C. To a mixture of LUS-1 (10 g) in dry toluene, (3-Mercaptopropyl)trimethoxysilane (12 mL) was added and the mixture was refluxed for 24 h. The obtained LUS-Pr-SH was filtered, washed with acetone, and dried. Then, LUS-Pr-SH (10 g) was oxidized with H_2O_2 (50 mL) and one drop of H_2SO_4 in methanol (10 mL) for 24 h at room temperature, then the mixture was filtered, and washed with H_2O and then acetone to obtain pure LUS-Pr-SO_3H as catalyst.

General procedure for tetrahydropyranylation

The sulfonic acid functionalized LUS-1 (0.02 g) was activated in vacuum at 100 °C, and then, after cooling to room temperature, alcohol **1** (1 mmol) and 3,4-dihydro-2*H*-pyran (DHP) **2** (1.2 mmol) were added to it. The mixture was stirred in solvent free conditions for an appropriate time as shown in Table 2, and the completion of the reaction was monitored by TLC and/or GC. The mixture was dissolved in dichloromethane and filtered to remove heterogeneous catalyst. The solvent was dried in vacuum, and the residue was subjected to column chromatography on silica to provide the pure product. The catalyst was washed with diluted acid solution, water, and then acetone, dried under vacuum, and reused for several times without loss of significant activity.

General procedure for depyranylation

To a solution of THP-protected alcohols (1 mmol) in MeOH (1.0 mL), activated LUS-Pr-SO_3H (0.02 g) was added, and the mixture was stirred at room temperature for an appropriate time as shown in Table 3. After the completion of the reaction, the mixture was dissolved in methanol and filtered to remove heterogeneous catalyst. The solvent was dried in vacuum, and the residue was subjected to column chromatography on silica to provide the pure product.

The spectral data (^{1}H NMR, ^{13}C NMR, MS, and IR) for selected compounds are given below.

2-(4-methoxybenzyloxy)tetrahydro-2*H*-pyran ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.55–1.84 (*m*, 6H, $3CH_2$), 3.52–3.56 (*m*, 1H, $1OCH_2$), 3.78 (*s*, 3H, $1OCH_3$), 3.88–3.95 (*m*, 1H, $1OCH_2$), 4.43 (*d*, ^2J = 11.5 Hz, 1H, OCH_2), 4.72 (*d*, ^2J = 11.5 Hz, 2H, OCHO and OCH_2), 6.87 (*d*, *J* = 7.7 Hz, 2H, 2CH arom.), 7.30 (*d*, *J* = 7.7 Hz, 2H, 2CH arom.); ^{13}C-NMR (62.9 MHz, $CDCl_3$): δ = 19.41, 25.51, 30.59, 55.19, 62.09, 68.46, 97.42, 113.73, 129.49, 130.29, 159.12; EIMS *m/z* (rel. Int.) 222 (10) (M^+), 137 (5), 121 (100), 91 (5), 85 (8); IR (KBr): υ_{max} = 3031, 3026, 2943, 2871, 1613, 1586, 1514, 1461, 1387, 1351, 1300, 1248, 1205, 1177, 1121, 1072, 1031, 974, 904, 870, 817, 758, 524 cm^{-1}.

2-(2-chlorobenzyloxy)tetrahydro-2*H*-pyran ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.56–1.90 (*m*, 6H, $3CH_2$), 3.53–3.58 (*m*, 1H, $1OCH_2$), 3.87–3.95 (*m*, 1H,

1OCH$_2$), 4.60 (*d*, ^2J = 13.2 Hz, 1H, OCH$_2$), 4.77–4.96 (*m*, 2H, OCHO and OCH$_2$), 7.16–7.28 (*m*, 2H, 2CH arom.), 7.33 (*d*, *J* = 7.2 Hz, 1H, 1CH arom.), 7.52 (*d*, *J* = 7.0 Hz, 1H, 1CH arom.); ^{13}C-NMR (62.9 MHz, CDCl$_3$): δ = 19.31, 25.46, 30.51, 62.03, 66.22. 98.31, 126.69, 128.46, 128.91, 129.25, 132.86, 136.22; EIMS *m/z* (rel. Int.) 226 (2) (M$^+$), 180 (5), 145 (20), 138 (10), 125 (100), 101 (12), 85 (15); IR (KBr): υ_{max} = 3066, 2941, 2870, 1573, 1445, 1390, 1349, 1267, 1201, 1128, 1070, 1032, 973, 905, 871, 814, 752 cm^{-1}.

2-(9*H*-fluoren-9-yloxy)tetrahydro-2*H*-pyran ^{1}H-NMR (250 MHz, CDCl$_3$): δ = 1.68–1.91 (*m*, 6H, 3CH$_2$), 3.63–3.67 (*m*, 1H, 1CH), 4.10–4.19 (*m*, 1H, 1CH), 5.19 (*t*, *J* = 3.1 Hz, 1H, 1CH), 5.71 (*s*, 1H, 1CH), 7.26–7.71 (*m*, 8H, 8CH arom.); ^{13}C-NMR (62.9 MHz, CDCl$_3$): δ = 19.53, 25.52, 31.13, 62.79, 79.03. 98.87, 119.76, 119.95, 125.52, 126.13, 127.37, 127.64, 128.83, 128.88, 140.54, 140.65, 143.92, 144.08; EIMS *m/z* (rel. Int.) 266 (12) (M$^+$), 220 (8), 182 (25), 165 (100), 152 (8), 85 (20); IR (KBr): υ_{max} = 3039, 2943, 2869, 2846, 2640, 1580, 1468, 1449, 1390, 1352, 1323, 1304, 1274, 1210, 1179, 1151, 1125, 1076, 1037, 1013, 974, 951, 934, 906, 888, 840, 812, 766, 742, 664, 620, 596 cm^{-1}.

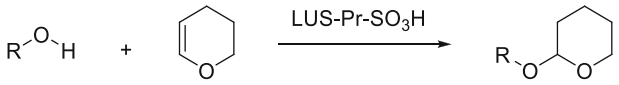
Results and discussion

In our first attempts at direct tetrahydropyranylation, we treated benzyl alcohol with 3,4-dihydro-2*H*-pyran (DHP) in the presence of LUS-Pr-SO$_3$H (0.02 g) as a heterogeneous acid catalyst in dichloromethane. As shown in Table 1, entry 1, the reaction was completed in 5 min at 95 % yield. We also studied the reaction of benzhydrol (Table 1, entry 2) in the same condition, but the reaction was not carried out successfully, it seems the steric effect of the second phenyl group decreased the yield and increased the reaction time. So we tried solvent free conditions for both reactions. As shown in Table 1, entries 3 and 4, the reactions were completed in 3 and 15 min for benzyl alcohol and benzhydrol with 98 and 85 % yields, respectively. Therefore, among the tested conditions, the best result was obtained in solvent-free and room temperature conditions (Scheme 1).

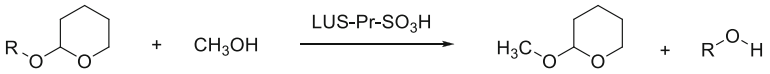
After optimizing the reaction conditions for tetrahydropyranylation, we next developed the best condition for depyranylation of THP-protected alcohols (Scheme 2). We first treated 2-(benzyloxy)tetrahydro-2*H*-pyran (1 mmol) with methanol (3 mL) in the presence of LUS-Pr-SO$_3$H (0.02 g) as a heterogeneous acid catalyst in reflux condition. As shown in Table 2, the reaction was completed in 10 min at 98 % yield. We also tried the room temperature condition for this

Table 1 The optimization of reaction conditions for protection of alcohols using LUS-Pr-SO$_3$H

Entry	Alcohol	Solvent	Time (min)	Yield (%)
1	Benzyl alcohol	CH_2Cl_2	5	95
2	Benzhydrol	CH_2Cl_2	40	30
3	Benzyl alcohol	–	3	98
4	Benzhydrol	–	15	85

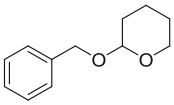
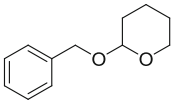


Scheme 1 Tetrahydropyranylation of alcohols in the presence of LUS-Pr-SO_3H



Scheme 2 Depyranylation of THP-protected alcohols in the presence of LUS-Pr-SO_3H

Table 2 The optimization of reaction conditions for depyranylation of 2-(benzyloxy)tetrahydro-2*H*-pyran using LUS-Pr-SO_3H

Entry	Ether	Condition	Time (min)	Yield (%)
1		Reflux	10	98
2		r.t.	15	98

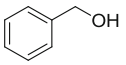
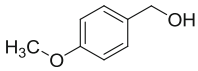
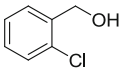
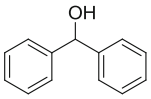
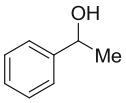
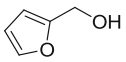
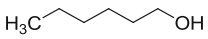
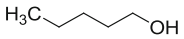
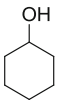
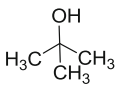
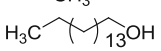
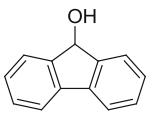
transformation by methanol (1 mL). As indicated in Table 2, entry 2, the reaction was completed in 15 min at 98 % yield. Because of the same yield of reactions, the room temperature condition was preferred to the reflux one.

After optimizing the reaction conditions, we next developed the selected conditions for protection and deprotection of other alcohols. Results are summarized in Table 3. By these conditions, the reactions were carried out easily for both aromatic and aliphatic alcohols in good yields. As shown in Table 3, protection of secondary and tertiary alcohols was carried out in a longer reaction time because of their steric effects. Also for alcohols that are solids and not soluble in DHP, even by increasing the amount of DHP up to 2 mmol, the reaction yield did not reach 90 %. This protocol has advantages such as its simple procedure and work-up, use of the green and reusable catalyst, and short reaction times. The products were characterized by melting points, ^{1}HNMR, ^{13}CNMR, Mass and IR spectroscopic analyses.

In these processes, LUS-Pr-SO_3H plays an important role in the accelerating of the reaction. A suggested mechanism for tetrahydropyranylation is proposed in Scheme 3. LUS-Pr-SO_3H initiates the tetrahydropyranylation of alcohol by protonation of 3,4-dihydropyran, the hydroxyl group attacks the protonated 3,4-dihydropyran, and finally LUS-Pr-SO_3H regenerates. The deprotection process involves protonation of THP ether oxygen by LUS-Pr-SO_3H, to form an oxonium ion followed by nucleophilic attack of methanol (Scheme 4). The high yields of the reactions are attributed to the nano pore effect of solid acid catalyst, which could act as a nano-reactor (Fig. 1).

The reusability of catalyst was investigated under optimized conditions for the protection of benzyl alcohol. As shown in Table 4, the recycling process was

Table 3 LUS-Pr-SO_3H catalyzed protection and deprotection of alcohols

Entry	Alcohol	Tetrahydropyranylation time (min)	yield[a] (%)	Depyranylation time (min)	yield[a] (%)	Refs.
1		97	3	98	15	[11]
2		93	3	95	15	[11]
3		89	5	95	15	[11]
4		85	15	92	15	[11]
5		90	15	93	15	[29]
6		96	3	90	15	[30]
7		94	3	98	15	[30]
8		91	3	93	15	[31]
9		91	15	89	15	[31]
10		96	10	93	15	[31]
11		89[b]	10	92	15	[32]
12		83[b]	15	89	15	New

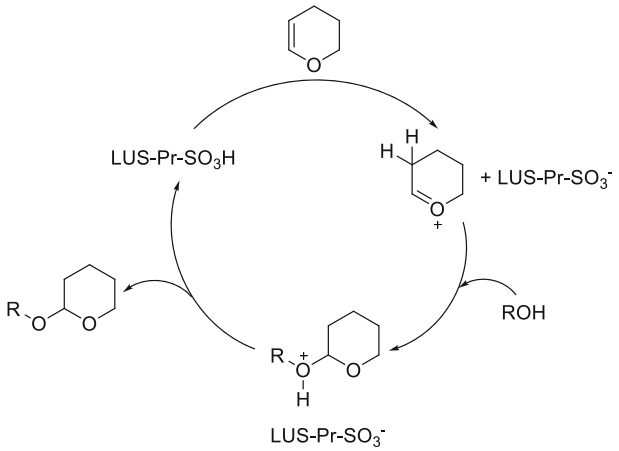
[a] GC yields

[b] For substrates that are solids and not soluble in DHP, the reactions were carried out with 2 mmol DHP

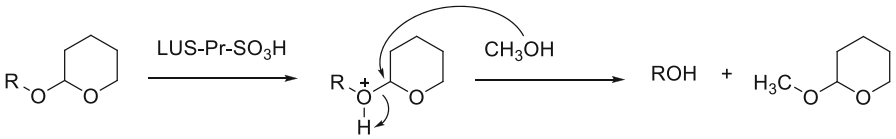
completed four times with no significant decrease of the catalyst activity. The yields for the four runs were found to be 97, 95, 91, and 89 %, respectively.

Synthesis and functionalization of LUS-1

The mesoporous compound LUS-1 was prepared and functionalized according to a previously reported method [28]. The catalyst was analyzed by different methods such as TGA, BET, XRD, and SEM methods, which have confirmed that propyl sulfonic acid groups were immobilized into the pores [28].



Scheme 3 Proposed mechanism for tetrahydropyranylation of alcohols in the presence of LUS-Pr-SO_3H



Scheme 4 Proposed mechanism for deprotection of tetrahydropyranyl ethers in the presence of LUS-Pr-SO_3H

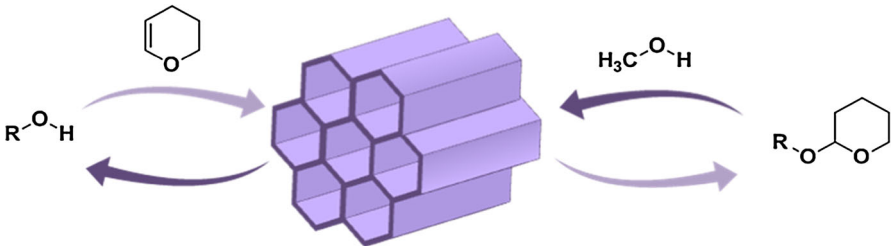


Fig. 1 LUS-Pr-SO_3H catalyst acts as nano-reactor

Table 4 Protection of benzyl alcohol with recycled LUS-Pr-SO_3H

	1st run	2nd run	3rd run	4th run
Time (min)	3	3	4	4
Yield (%)	97	95	91	89

The thermal gravimetric analysis (TGA) of LUS-Pr-SO_3H (Fig. 2) shows two major decomposition states: one below 100 °C (8 % weight loss), assigned to loss of water surface and one more mass loss between 200 and 600 °C (15 % weight loss), corresponding to the decomposition of organic groups grafted onto silica.

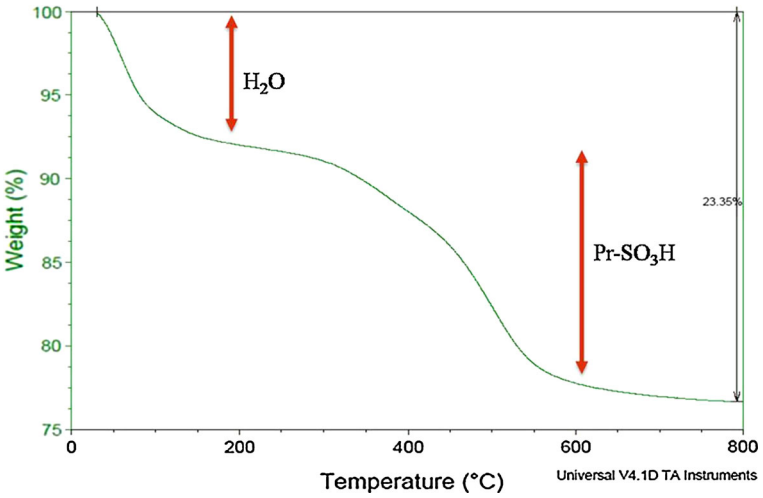


Fig. 2 TGA diagram of LUS-Pr-SO_3H

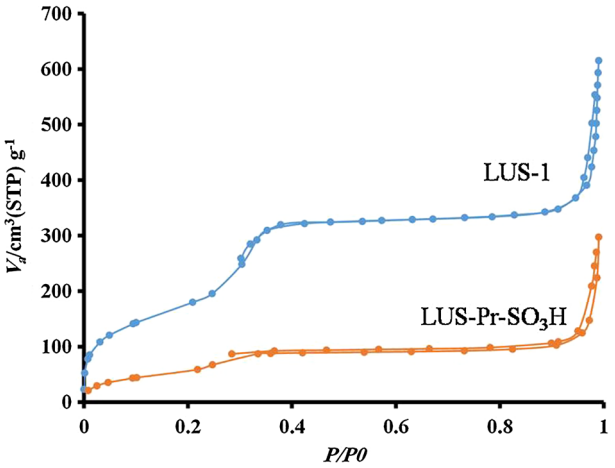


Fig. 3 Nitrogen adsorption–desorption of LUS-1 and LUS-Pr-SO_3H

Therefore, the concentration of immobilized acid (from the weight loss) can be estimated as 1.3 mmolg^{-1}.

Figure 3 illustrates N_2 adsorption–desorption isotherms of LUS-1 and LUS-Pr-SO_3H. Volumetric analyses shows "Type IV" N_2 adsorption–desorption isotherms with "H1-type" hysteresis for both materials, which are characteristic of periodic mesoporous materials.

The texture properties of LUS-1 and LUS-Pr-SO_3H calculated by the BET method are given in Table 5. The surface area, average pore diameter, and pore volume for LUS-Pr-SO_3H are 534 m^2g^{-1}, 2.4 nm and 0.545 cm^3g^{-1}, respectively, which are smaller than those of LUS-1 due to the immobilization of organic groups into the pores.

Table 5 Porosimetery values for LUS-1 and LUS-Pr-SO_3H

	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Pore diameter (nm)
LUS-1	870	0.841	2.9
LUS-Pr-SO_3H	534	0.545	2.4

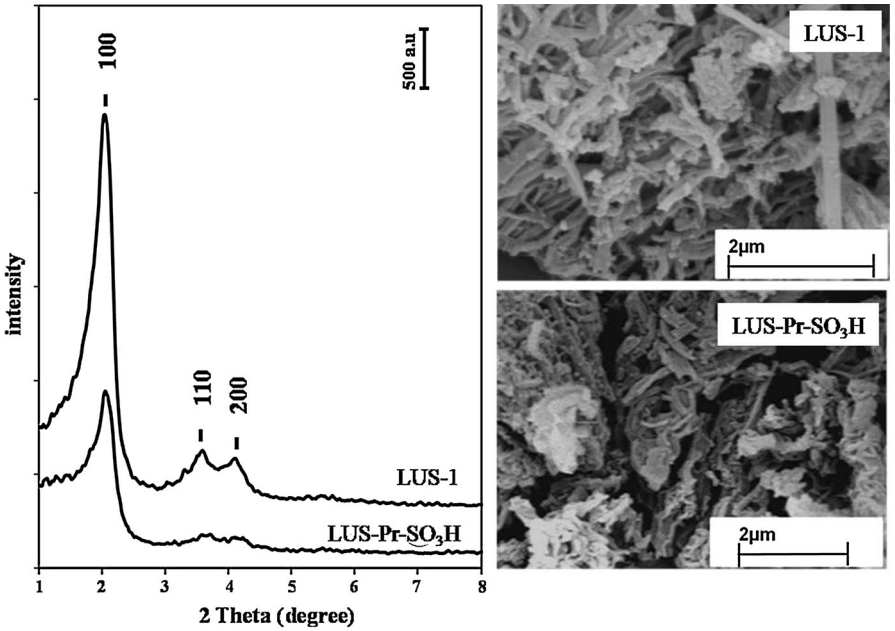


Fig. 4 X-ray diffraction pattern (*Left*) and SEM images (*Right*) of LUS-1 and LUS-Pr-SO_3H

Figure 4 illustrates a low-angle XRD pattern (Left) and the SEM images (Right) of LUS and LUS-Pr-SO_3H. The XRD pattern showed the same ordered mesoscopic structured silica with (100), (110), and (200) reflections for both materials, which exhibit a two-dimensional hexagonal symmetrical array of nano-channels. It means the structural nature of LUS-1 did not change during the surface modifications. On the other hand, the SEM image of both materials shows the same morphology. It means the grafting of the organic group did not affect the morphology of the solid.

Conclusion

In conclusion, we have established that LUS-Pr-SO_3H is an efficient and recyclable heterogeneous acid catalyst for protection of alcohols by DHP and deprotection of corresponding ethers. The short reaction times and simplicity of the procedure provide significant improvements in comparison to other existing methods.

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