

Sulfonic acid-functionalized ordered nanoporous Na⁺-montmorillonite (SANM) as an efficient and recyclable catalyst for the tetrahydropyranlation and detetrahydropyranlation of alcohols and phenols

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Abstract Sulfonic acid-functionalized ordered nanoporous Na⁺-montmorillonite, as a newly reported solid acid nanocatalyst, was efficiently used for the tetrahydropyranlation and detetrahydropyranlation of alcohols and phenols. All reactions were performed at room temperature in high to excellent yields. Ease of preparation and handling of the catalyst, heterogeneous reaction conditions, easy work-up of the products, high reaction rates and reusability of the catalyst are the main advantages of this method.

Keywords Na⁺-montmorillonite ·
Tetrahydropyranlation · Alcohols · Phenols ·
Reusability of the catalyst

Background

Because of the presence of the hydroxyl group in a large number of biological and synthetic compounds, protection of this group during multi-step synthesis as an important

process has attracted the considerable attention of organic chemists [1].

Between the several methods available for the protection of this group, tetrahydropyranlation has attracted the attention because tetrahydropyranyl ethers are very stable in various conditions.

The formation of tetrahydropyranyl ethers is carried out by the reaction of alcohols or phenols with excess amounts of dihydropyran (DHP) in the presence of a catalyst.

A wide variety of catalysts such as Sn^{IV}(TPP)(OTf)₂ [2], polystyrene-supported GaCl₃ [3], silica sulfuric acid [4], solid silica based sulfuric acid [5], melamine trisulfonic acid [6], CuSO₄·5H₂O [7], acetic acid assisted copper *o*-toluenesulfonate [8], Fe(ClO₄)₃ [9], Al(OTf)₃ [10], Sn^{IV}(TNH₂PP)(OTf)₂@CMP [11], Al/AT-silica [12], {[K.18-crown-6]Br₃}_n [13], NbCl₅ [14], La(NO₃)₃·6H₂O [15], Fe(CH₃SO₃)₂·4H₂O [16], preyssler heteropolyacid [17], AlCl₃/SiO₂ [18], [V(TPP)(OTf)₂] [19] and pyridinium chloride [20] have been applied for tetrahydropyranlation of alcohols and phenols. However, many of these methods suffer from disadvantages such as long reaction times [9, 10], unsatisfactory yields, harsh reaction conditions [8], expensive reagents [11, 13, 19], hazardous and toxic solvents or catalysts [17, 18], tedious work-up, formation of polymeric by-products of the dihydropyran (DHP) and isomerization. Therefore, introduction of efficient and economical catalysts that solves these drawbacks is desirable.

In recent years, clays as nanostructured materials have been widely used in organic transformations as solid acid catalysts [21–23]. These compounds have some advantages such as accessibility, cheapness, easy modification, non-toxicity and recyclability. The montmorillonite minerals are one of the most widely used clays which have very small micron-sized particles and are extremely fine-grained and thin-layered [24].

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Methods

General

Chemicals were purchased from Southern Clay Products, Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. All the products were characterized by their physical constants and comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silicagel polygram SILG/UV 254 plates or gas chromatography (GC). Thermogravimetric analyses (TGA) were conducted using a TGA PYRIS 1 thermoanalyzer instrument. Samples were heated at 25–600 °C at ramp 10 °C/min under N₂ atmosphere. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Simence D-500 X-ray diffractometer (Germany), using Ni-filtered Co-K α radiation ($\lambda = 0.15418$ nm).

Table 1 Reaction of 4-chlorobenzyl alcohol with DHP in different conditions

Entry	Catalyst (mg)	DHP (mmol)	Solvent	Time (min)	Isolated yield (%)
1	4	1.4	CH ₂ Cl ₂	7	50
2	8	1.4	CH ₂ Cl ₂	3	98
3	12	1.4	CH ₂ Cl ₂	3	98
4	8	1.2	CH ₂ Cl ₂	3	80
5	8	1	CH ₂ Cl ₂	3	50
6	8	1.4	CH ₃ CN	5	90
7	8	1.4	<i>n</i> -Hexane	15	0
8	8	1.4	CCl ₄	10	0
9	8	1.4	CHCl ₃	10	0
10	8	1.4	Solvent-free	5	70

General procedure

Tetrahydropyranylation of alcohols and phenols

A mixture of the substrate (1 mmol), 3,4-dihydro-2*H*-pyran (1.4 mmol, 0.12 g) and SANM (3.06 mol %, 8 mg) in CH₂Cl₂ (3 mL) was stirred at room temperature. The progress of the reaction was monitored by TLC (*n*-hexane: EtOAc = 10:1) and/or GC. After completion of the reaction, the mixture was filtered to separate the solid catalyst. Then, the solution was filtered through a silica gel pad and washed with CH₂Cl₂ (2 × 5 mL). Evaporation of the solvent gave the desired products in high purity.

Deprotection of tetrahydropyranyl ethers

A mixture of the substrate (1 mmol) and SANM (3.06 mol %, 8 mg) in MeOH (3 mL) was stirred at room temperature. The progress of the reaction was monitored by TLC (*n*-hexane: EtOAc = 10:1) and/or GC. After completion of the reaction, the mixture was filtered to separate the solid catalyst. The combined filtrates were concentrated on a rotary evaporator to remove MeOH, the crude residue was purified through a short silica gel column and the desired products were obtained in high yields.

Results and discussion

In recent years, introduction of new catalysts for the promotion of organic transformations became an important part of our ongoing research program [25–29].

Herein, and in continuation of these studies, we wish to report the applicability of sulfonic acid-functionalized ordered nanoporous sodium montmorillonite (SANM) [30–32], as a newly reported solid acid nanocatalyst in the promotion of

Scheme 1 Tetrahydropyranylation/detetrahydropyranylation of alcohols and phenols catalyzed by SANM

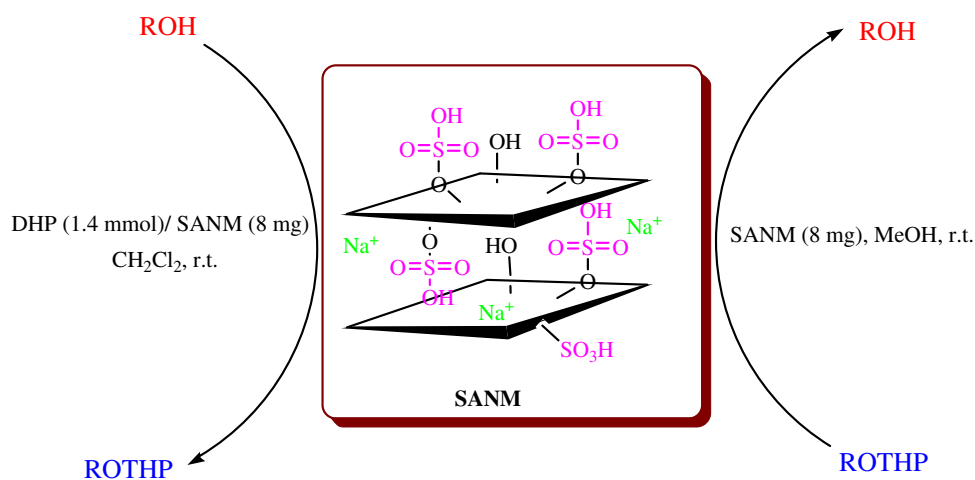
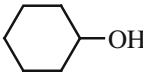
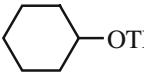
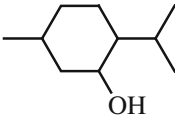
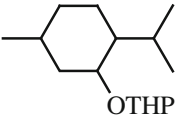
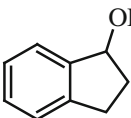
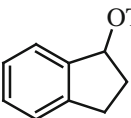
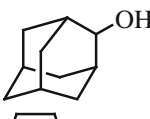
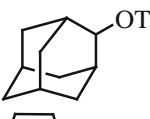

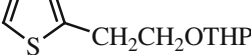
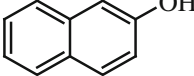
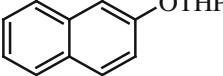


Table 2 Tetrahydropyranylation and detetrahydropyranylation of alcohols and phenols catalyzed by SANM

Entry	Substrate	Product	Protection		Deprotection	
			Time (min)	Yield (%)	Time (min)	Yield (%)
1	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ OTHP	5	98	5	98
2	2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CH ₂ OTHP	3	95	5	98
3	4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CH ₂ OTHP	3	98	5	98
4	2-BrC ₆ H ₄ CH ₂ OH	2-BrC ₆ H ₄ CH ₂ OTHP	4	98	6	98
5	4-BrC ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CH ₂ OTHP	4	98	6	98
6	3,4-Cl ₂ C ₆ H ₃ CH ₂ OH	3,4-Cl ₂ C ₆ H ₃ CH ₂ OTHP	5	98	6	98
7	2-MeC ₆ H ₄ CH ₂ OH	2-MeC ₆ H ₄ CH ₂ OTHP	4	98	6	98
8	3-MeOC ₆ H ₄ CH ₂ OH	3-MeOC ₆ H ₄ CH ₂ OTHP	5	98	12	98
9	4-MeOC ₆ H ₄ CH ₂ OH	4-MeOC ₆ H ₄ CH ₂ OTHP	5	98	10	98
10	3-NO ₂ C ₆ H ₄ CH ₂ OH	3-NO ₂ C ₆ H ₄ CH ₂ OTHP	8	90	12	98
11	4-NO ₂ C ₆ H ₄ CH ₂ OH	4-NO ₂ C ₆ H ₄ CH ₂ OTHP	7	98	10	98
12	4-Me ₃ CC ₆ H ₄ CH ₂ OH	4-Me ₃ CC ₆ H ₄ CH ₂ OTHP	4	98	25	98
13	4-Me ₂ CHC ₆ H ₄ CH ₂ OH	4-Me ₂ CHC ₆ H ₄ CH ₂ OTHP	5	98	25	98
14	Ph ₂ CHOH	Ph ₂ CHOTHP	5	98	18	98
15	PhCH(OH)Me	PhCH(OTHP)Me	5	98	15	98
16	C ₆ H ₅ CH=CHCH ₂ OH	C ₆ H ₅ CH=CHCH ₂ OTHP	30	90	15	90 ^b
17	C ₆ H ₅ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CH ₂ OTHP	4	98	45	90
18			5	90	25	98
19			25	90	60	98
20			4	98	50	97
21			8	98	15	96
22			5	98	10	90 ^b
23	C ₆ H ₅ OH	C ₆ H ₅ OTHP	6	98	45	90
24	2-MeC ₆ H ₄ OH	2-MeC ₆ H ₄ OTHP	12	95	35	95
25	3-MeC ₆ H ₄ OH	3-MeC ₆ H ₄ OTHP	5	98	35	98
26	4-EtC ₆ H ₄ OH	4-EtC ₆ H ₄ OTHP	3	98	45	80
27	4-Me ₂ CHC ₆ H ₄ OH	4-Me ₂ CHC ₆ H ₄ OTHP	8	95	40	90
28			6	98	10	90 ^a

Isolated yield (%)

^a 70 °C

the acceleration of the tetrahydropyranylation and detetrahydropyranylation of alcohols and phenols under mild conditions.

To optimize the reaction conditions, the reaction of 4-chlorobenzyl alcohol with DHP was studied in the presence of SANM as a model reaction. The reaction was



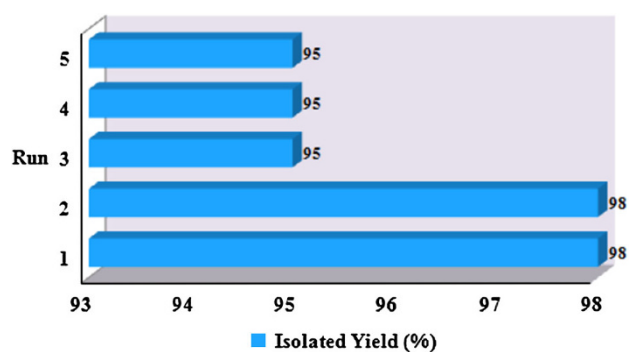


Fig. 1 Reusability of SANM in the synthesis of 4-chlorobenzyl tetrahydropyranyl ether

performed in different solvents and also under solvent-free conditions, using different amounts of the catalyst and DHP at room temperature. The results are shown in Table 1.

The obtained results showed that the reaction using 8 mg of the catalyst and 1.4 mmol of DHP in CH_2Cl_2 at room temperature proceeded in highest yield during very short time (Table 1, entry 2).

The selected condition is shown in Scheme 1.

After optimization of the reaction conditions and to show the general applicability of this method, different types of alcohols were subjected to the same reaction under the determined conditions. The results are summarized in Table 2.

Different types of benzylic alcohols (including electron-donating or electron-withdrawing groups) were tetrahydropyranylated with DHP in the presence of catalytic amounts of SANM in high to excellent yields (Table 2, entries 1–16).

Primary and secondary aliphatic alcohols were also efficiently converted to their corresponding products under the same reaction conditions (Table 2, entries 17–20). This method was found to be useful for the protection of hindered secondary and tertiary alcohols, and isomerization and dehydration of these compounds were not observed (Table 2, entries 19–21).

Under the selected conditions, 2-(thiophen-2-yl) ethanol was also transformed smoothly to the corresponding ether in high yields (Table 2, entry 22).

The reaction conditions are mild enough not to induce any damage to moieties like methoxy benzyl alcohol or cinnamyl alcohol (Table 2, entries 8, 9, 16).

Our investigations also showed that under the same reaction conditions SANM is able to catalyze the tetrahydropyranylation of phenols in high to excellent yields (Table 2, entries 23–28).

We have also found that the conversion of tetrahydropyranyl ethers to their corresponding alcohols or phenols can be easily catalyzed in the presence of SANM in

methanol. All reactions were performed at room temperature in good to high yields (Scheme 1; Table 2).

In continuation, we decided to study the catalytic activity of the recycled catalyst for the synthesis of tetrahydropyranyl ethers. We have found that SANM is a very stable catalyst and can be recycled by filtration, washing with acetone and drying at 100 °C. For the reaction of 4-chlorobenzyl alcohol with DHP, even after five cycles, the catalyst still has excellent yields (Fig. 1). It implied that SANM can be reused without appreciable loss of its activity.

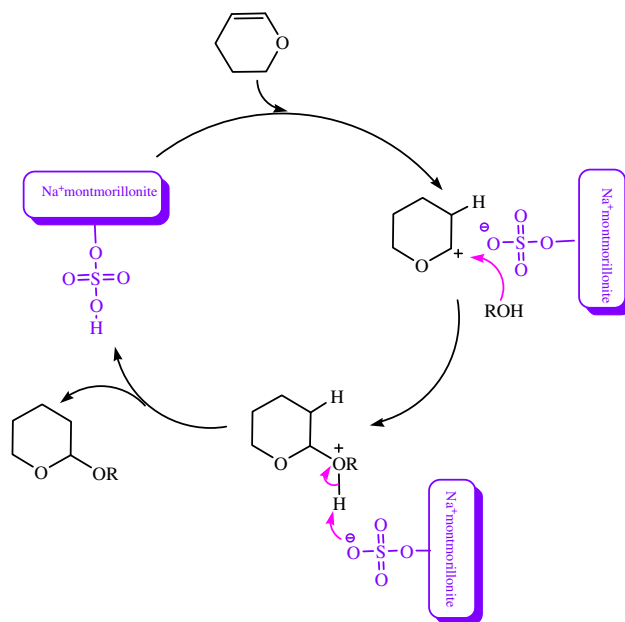
A plausible mechanism for this reaction is shown in Scheme 2.

To show the efficiency of the present method, we have compared our results obtained from the tetrahydropyranylation of alcohol catalyzed by SANM with other results reported in the literature (Table 3).

The results indicated that SANM is a very efficient catalyst for this reaction in terms of yield and reaction rate.

It is interesting to note that, to compare the applicability and efficiency of SANM with the other catalysts, we have tabulated the TOF (turnover frequency) of these catalysts in this reaction. As it is clear, SANM is superior in terms of TOF to the compared catalysts.

In addition, although some of these catalysts have high TOF (e.g., solid silica based sulfuric acid [5] or $\text{Sn}^{\text{IV}}(\text{TNH}_2\text{PP})(\text{OTf})_2@\text{CMP}$ [11]), its preparation is difficult when compared with SANM.



Scheme 2 Proposed mechanism of SANM-catalyzed synthesis of tetrahydropyranyl ethers

Table 3 Comparison of the results of the tetrahydropyranylation of PhCH₂OH catalyzed by SANM with those obtained by reported catalysts at room temperature

Entry	Catalyst [Ref.]	Catalyst load (mol %)	Solvent	Time (h)	Yield (%)	TOF (h ⁻¹)
1	Polystyrene-supported GaCl ₃ [3]	10	CH ₂ Cl ₂	0.42	98	23.3
2	Silica sulfuric acid [4]	3.9	CH ₂ Cl ₂	0.5	91	46.7
3	Solid silica based sulfuric acid [5]	0.5	CHCl ₃	0.25	92	736
4	Melamine trisulfonic acid [6]	3	CH ₂ Cl ₂	0.58	95	54.6
5	CuSO ₄ ·5H ₂ O [7]	20	CH ₃ CN	0.67	91	6.8
6	Fe(ClO ₄) ₃ [9]	3.08	Et ₂ O	1.5	98	21.2
7	Al(OTf) ₃ [10]	0.1	CH ₂ Cl ₂	8	87	109
8	Sn ^{IV} (TNH ₂ PP)(OTf) ₂ @CMP [11]	1	THF	0.07	97	1,386
9	Al/AT-silica [12]	9.8	CH ₂ Cl ₂ ^a	0.75	95	13
10	{[K.18-crown-6]Br ₃] _n [13]	0.1	CH ₃ CN	0.33	93	2,818
11	NbCl ₅ [14]	10	CH ₂ Cl ₂	2.5	90	3.6
12	La(NO ₃) ₃ ·6H ₂ O [15]	10	Solvent-free	2.5	93	3.7
13	Fe(CH ₃ SO ₃) ₂ ·4H ₂ O [16]	2	Solvent-free	1	97	48.5
14	SANM [this work]	3.06	CH ₂ Cl ₂	0.083	98	386

^a 40 °C

Conclusion

In conclusion, we have introduced sulfonic acid-functionalized ordered nanoporous Na⁺-montmorillonite (SANM) as a novel heterogeneous catalyst for the promotion of the tetrahydropyranylation/detrahydropyranylation of alcohols and phenols under mild conditions. Ease of the preparation and handling of the catalyst, simple procedure and easy work-up, high reaction rates, excellent yields of the products and reusability of the catalyst are among the other advantages of this method, which make this procedure a useful and attractive addition to the available methods.

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