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Nanoporous Na⁺-Montmorillonite Perchloric Acid as an Efficient and Recyclable Catalyst for the Chemoselective Protection of Hydroxyl Groups

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Nanoporous Na⁺-montmorillonite perchloric acid as a novel heterogeneous reusable solid acid catalyst was easily prepared by treatment of Na⁺-montmorillonite as a cheap and commercially available support with perchloric acid. The catalyst was characterized using a variety of techniques including X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDX), pH analysis and determination of the Hammett acidity function. The prepared reagent showed excellent catalytic activity for the chemoselective conversion of alcohols and phenols to their corresponding trimethylsilyl ethers with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) at room temperature. Deprotection of the resulting trimethylsilyl ethers can also be carried out using the same catalyst in ethanol. All reactions were performed under mild and completely heterogeneous reaction conditions in good to excellent yields. The notable advantages of this protocol are: short reaction times, high yields, availability and low cost of the reagent, easy work-up procedure and the reusability of the catalyst during a simple filtration.

Keywords: Na⁺-Montmorillonite, Silylation, Protection, Deprotection, Hexamethyldisilazane, Nanoclay.

1. INTRODUCTION

Protection and deprotection of functional groups are very important processes, which are widely used in the preparation of multifunctional target molecules.¹ Among different types of the protecting groups, silvlating ones have played increasingly important roles in the synthesis of complicated molecules, especially in the synthesis of biologically significant products.² Several methods are available for the silvlation of the hydroxyl groups, using a variety of silvlating agents. Some silvlating agents are not used so much due to their unavailability, lack of reactivity or the tedious processes for the purification of the products.^{3,4} 1,1,1,3,3,3-hexamethyldisilazane has emerged as the most versatile reagent in recent years for trimethylsilyl (TMS) protection of alcohols and phenols. HMDS is a stable, commercially available and inexpensive reagent. Its handling does not require special precautions, and the work-up is convenient, because the only by-product of the reaction is ammonia, which is simple to remove from the reaction

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is the main drawback to its application.⁶ To solve this problem, a variety of catalysts including LaCl₂,⁷ sulfonic acid-functionalized nanoporous silica,8 trichloroisocyanuric acid (TCCA),⁹ HClO₄-SiO₂,¹⁰ Fe(HSO₄)₃,¹¹ nanocrystalline TiO_2 ,¹² $Cu(NO_3)_2 \cdot 3H_2O$,¹³ saccharin sulfonic acid,¹⁴ tetrabutylammonium Bromide,¹⁵ TiO₂-HClO₄,¹⁶ ZnCl₄,¹⁷ H-β zeolite,¹⁸ SBA-15-Ph–Pr–SO₃H,²⁹ K-10 montmorillionite,²⁰ γ -Fe₂O₃@SiO₂-(CH₂)₃NH- $Sn(n-Bu)_{3}$,²¹ sulfamic acid,²² PhMe₃N⁺Br₃^{-,23} iodine,²⁴ ZrO(OTf)₂,²⁵ [Ti(salophen)(OTf)₂],²⁶ Bi(OTf)₃,²⁷ 1,3dichloro-5,5-dimethylhydantoin (DCH) and trichloromelamine (TCM)²⁸ and InBr₃²⁹ have been developed for the promotion of the trimethylsilylation of alcohols and phenols with HMDS. Even though the silvlating ability of HMDS was increased using these catalytic systems, most of them suffer from disadvantages such as long reaction times, low yields of the products, tedious work-up, vigorous reaction conditions, non-recyclability of the catalyst and use of toxic, expensive or moisture-sensitive reagents. In addition, some of the reagents are not able to catalyze the reverse reaction.

medium.⁵ However, the low silvlation power of HMDS

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Acids are widely used as catalysts in industry, producing more than 1×108 mt of products/year. The most commonly used acids are HF, H₂SO₄, HClO₄, and H₃PO₄.³⁰ Perchloric acid is a stronger acid than sulfuric and nitric acids. When it is hot, it can act as an oxidizing agent, while in aqueous solutions up to approximately 70% this reagent only show strong acidic features and no oxidizing properties. Perchloric acid is also used in the computer industry for etching liquid crystal displays in critical electronic applications as well as a solvent for many metals and alloys and the separation of certain materials.³¹

Heterogenization of homogeneous acid catalysts via their immobilization on various solid supports has been the subject of the extensive researchs during the past decade.32-35 This procedure leads to environmentally friendly industrial manufacturing and improvement of processing steps. Solid acids have many advantages such as simplicity in handling, eliminating toxicity, corrosion and environmental problems.³⁶ In recent years, clays as nanostructured materials have been widely used in organic transformations as solid acid catalysts.^{32, 34, 37} The main reasons for use of clays are accessibility, cheapness, noncorrosiveness, recyclability and easy modification. Montmorillonite (MMT) is one of the most widely used clays. Montmorillonite belongs to the family of 2:1 smectite minerals. It is basically composed of aluminosilicate layers, where one octahedral alumina sheet is sandwiched between two tetrahedral silica sheets (Fig.81).³⁸0.225 On:

Montmorillonite minerals have nano-sized particles, and they are extremely fine-grained and thin-layered.³⁹ Layers of MMT have a thickness of about 1 nm and a length of 100 nm or a little more. Broken bonds on the edge of MMT layers are common phenomena for layered silicates and lead to the free formation of hydroxyl groups,⁴⁰ which can be utilized for chemical modification.

Hence, in this study, considering the advantages of the above mentioned properties of montmorillonite and



solid acids and in continuation of our previous studies on the preparation and application of new catalysts in organic functional group transformations,^{11–17, 41, 42} we disclose the preparation of nanoporous Na⁺-montmorillonite supported perchloric acid (MMT-HClO₄) and its application, as a new, efficient and recyclable catalyst, in trimethylsilyl protection of hydroxyl groups and deprotection of trimethylsilyl ethers at room temperature under mild and heterogeneous conditions. In this reaction, the catalyst could be recycled several times without significant loss of its catalytic activity.

2. EXPERIMENTAL DETAILS

2.1. Material

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants, comparison with authentic samples. The purity determination of the substrate and reaction monitoring were accompanied by thin-layer chromatography (TLC) on silica-gel polygram SILG/UV 254 plates.

2.2. Instrumentation

The FT-IR spectra were recorded on a FT-IR Bruker Alpha spectrophotometer. The pristine clay and acidtreated derivative were dried at 100 °C in the oven before recording the spectrum. Thermogravimetric analyses were conducted by using a TGA PYRIS 1 thermoanalyzer instrument. Samples were heated 25 to 600 °C at ramp 10 °C/min under N₂ atm. X-ray diffraction measurements were performed at room temperature on a Philips PW 1840 diffractometer using Ni-filtered Cu-K α radiation ($\lambda = 0.15418$ nm). Scanning election microphotographs were obtained on a TESCAN MIRA3 FEG-SEM instrument equipped with EDX. The absorption spectra were recorded by a scanning UV-3100 spectrophotometer.

2.3. Catalyst Preparation

 $HClO_4$ (0.12 mL, 2 mmol, as a 70% aq solution) was added to a suspension of Na⁺-montmorillonite (Na⁺-MMT) (1 g) in Et₂O (50 mL). The mixture was refluxed for 4 h then the suspension was concentrated and the residue was consecutively washed with Et₂O (2 × 5 mL). After removal of ether using a rotary evaporator, the solid residue was dried at 100 °C for 10 h to afford MMT-HClO₄ (1.11 g) (Scheme 1).

2.4. General Procedure for Trimethylsilylation of Alcohols and Phenols

To a stirring mixture of the substrate (1 mmol) and MMT- $HClO_4$ (7 mg) in CH_3CN (3 mL), HMDS (0.75 mmol) was added at room temperature. After completion of the reaction, indicated by TLC, ethyl acetate: *n*-hexane (3:7), the mixture was filtered to separate the catalyst. The filtrate was washed with acetonitrile (5 mL). Removal of the

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Scheme 1. Preparation of the catalyst (MMT-HClO₄).

solvent under reduced pressure gave almost pure product in good to high yields. Further purification was carried out by column chromatography on silica gel (eluting with EtOAc:hexane = 1:4), if necessary.

2.5. General Procedure for Deprotection of Trimethylsilyl Ethers

A mixture of the substrate (1 mmol) and MMT-HClO₄ (10 mg) in ethanol (2 mL) was stirred at room temperature. The progress of the reaction was monitored by TLC, ethyl acetate: *n*-hexane (3:7). After completion of the reaction the catalyst was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc:hexane = 1:4) to gave the pure alcohol and/or phenol derivative in Tup good to high yields.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst

3.1.1. FT-IR Analysis

The infrared spectra of Na⁺-MMT and MMT-HClO₄ are presented in Figure 2. The FT-IR spectra of the pristine and acid-treated clay samples show the structural modification which occurs owing to acid activation. The spectrum of montmorillonite exhibits absorption bands at 3432 and 1639 cm⁻¹ which are assigned to the stretching and bending vibrations of the OH groups of the water molecules adsorbed on the clay surface, and a band at 3626 cm^{-1} representing the stretching vibration of the hydroxyl groups coordinated to the aluminum and/or magnesium in Na⁺-MMT.⁴³ In this spectrum the bands at 1035 and 919 $\rm cm^{-1}$ can be attributed to the Si–O stretching vibrations and bending modes of the hydroxyl groups of Al₂OH, respectively. The bands at 531 and 466 cm^{-1} are corresponded to Si-O-Al (octahedral) and Si-O bending vibrations respectively.44

The spectrum of Na⁺-MMT supported perchloric acid displays the broad band around 3418 cm⁻¹ that attributed to the OH group of perchloric acid and adsorbed water molecules, whereas deformational vibrations of adsorbed water molecules caused the absorption band to appear at 1636 cm⁻¹. MMT-HClO₄ also exhibited characteristic absorption bands at 1088, 1111, 1145 [ν_{asym} (ClO₄)], 630 [ν_{asym} (ClO₄)] and 467 [δ_{sym} (ClO₄)] cm⁻¹ which are assigned to the asymmetric and symmetric ClO₄ stretching and bending vibrations, respectively.⁴⁵ These results show modification of nanoporous Na⁺-MMT using perchloric acid.

3.1.2. Thermal Analysis

The thermal stability of Na⁺-MMT and MMT-HClO₄ was determined by thermogravimetric analysis (TGA). Figure 3 provides the TGA curves of pristine clay and catalyst. The TGA curve of Na⁺-MMT display a weight loss 11.5% below 100 °C which is attributed to dehydration of adsorption water. Another weight loss process occur at the temperature range 100–600 °C, possibly corresponding to the loss of the bonded H₂O within the gallery.

¹¹MMT-HClO₄ indicate four-stage decomposition. The first weight loss 22% below 150 °C which is corresponding to the loss of surface-physisorbed water. The second weight loss (at around 240–340 °C) can be attributed to



Figure 2. FT-IR spectra of Na⁺-MMT, HClO₄ and MMT-HClO₄.

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Figure 3. TGA curves of Na⁺-MMT and MMT-HClO₄.

the disintegration of the loaded perchloric acid.⁴⁵ Heating to a higher temperature (at around 340–450 °C) results in the collapse of the clay interlayer structure as the water is driven out. Further heating (above 450 °C) results eventually in complete dehydroxylation of the aluminosilicate lattice, producing a completely amorphous solid.⁴⁶ These results show that the catalyst is thermally-stable up to 240 °C.

3.1.3. Powder X-ray Diffraction

The XRD patterns of the pristine and acid-treated clay samples are given in Figure 4. The interlayer space of Na⁺-MMT was calculated using Bragg's equation. Na⁺-MMT exhibited a diffraction peak at $2\theta = 6.25^\circ$, with a corresponding basal spacing of 14.14 Å. As can be seen in the MMT-HClO₄ patterns, the increase in basal spacing from 14.14 Å in Na⁺-MMT to a 16.02 Å value in MMT-HClO₄ shows the changes in interlayer spaces as a result of the acid treatment. That is to say, the perchloric acid moiety has been intercalated into the montmorillonite layers. This increase in the basal spacing can lead to better interaction between the reactants in the acid catalysis reactions compared with sodium montmorillonite. These results also confirme that nanoporous Na⁺-montmorillonite has retained its layered structure and nanoporosity even after treatment with perchloric acid.



Figure 4. XRD patterns of Na⁺-MMT and MMT-HClO₄.



Figure 5. Absorption spectra of 4-nitroaniline (indicator) (a) and MMT- $HClO_4$ (catalyst) (b) in CCl_4 .

3.1.4. Hammett Acidity

The Hammett acidity function (H_0) can be used to effectively express the acidity strength of an acid in organic solvents.⁴⁷ The acidity of the solution is calculated by using the following Hammett equation:

$$H_0 = pK(I)_{aq} + log[I]_s / [HI^+]_s$$
 (1)

Where $[I]_s$ and $[HI^+]_s$ are the molar concentrations of the indicator and its conjugate acid in the solvent respectively and $pK(I)_{aq}$ is the pK_a value of aqueous solution of indicator. According to the Beer-Lambert law, the value of $[I]_{*}/[HI^{+}]_{*}$ can be determined and calculated using thegultraviolet-visible (UV-Vis) spectrum. For this purpose, 4-nitroaniline $(pK(I)_{aq} = 0.99)$ as the basic indicator and CCl₄ as the solvent were used. As Figure 5 shows, the maximum absorbance of the unprotonated form of 4-nitroaniline was observed at 330 nm in CCl₄. When MMT-HClO₄ as a solid acid catalyst was added to the indicator solution, the absorbance of the unprotonated form of the indicator decreased, which implied that the indicator was partially in the form of [HI⁺]. The results obtained are listed in Table I, which shows the acidity strength of MMT-HClO₄.

3.1.5. Energy Dispersive X-ray Spectroscopy

Figure 6 shows the EDX spectrum of MMT-HClO₄. As can be seen, the existence of O and Cl peaks indicates successful incorporation of HClO₄ within the montmorillonite interlayer spaces.

Table I. Calculation of Hammett acidity function (H_0) for MMT-HClO₄.

Entry	Catalyst	$A_{\rm max}$	$[I]_s \%$	$[\mathrm{HI^+}]_s~\%$	H_0
1	_	1.329	100	0	_
2	MMT-HClO ₄	0.334	25.132	74.868	0.516

Notes: Condition for UV-visible spectrum measurement: Solvent: CCl_4 , indicator: 4-nitroaniline (pK(I)_{aq} = 0.99), 1.44×10^{-4} mol/L; Catalyst: MMT-HClO₄, 20 mg, 25 °C.



Figure 6. EDX spectra of nanoporous MMT-HClO₄.

3.1.6. Morphological Analysis

Scanning electron microscopy analysis was used to show the particle size distribution and surface morphological changes created on the clay during the modification of sodium montmorillonite. In Figures 7(a)–(d) the SEM pictures of pristine and acid-treated clay are presented, respectively. SEM images corroborated the variation of Na⁺-MMT morphology after acid treatment. Figures 7(a)–(b) shows that montmorillonite have nanosized particles and there is a layer structure in pristine clay so that particles of montmorillonite are composed of irregular platelets that stack on top of each other. The SEM micrographs reveal that MMT-HClO₄ has a flaky form with plate-like particles that imply the layered structure of the prinstin clay has remained after acid treatment that confirm the results of X-ray diffraction analysis and successful modification.

3.1.7. pH Analysis of Catalyst

To 25 mL of an aqueous solution of NaCl (1 M) with a primary pH 5.7, MMT-HClO₄ (0.5 g) was added and the resulting mixture was stirred for 2 h at room temperature after which the pH of solution decreased to 1.66. This is equal to a loading of 1.09 mmol $H^+/g.^8$

3.2. Catalytic Activity

On the basis of the informations obtained from the above mentioned studies, we expected that nanoporous



Figure 7. SEM images of Na⁺-MMT (a, b) and MMT-HClO₄ (c, d). *J. Nanosci. Nanotechnol. 19, 2099–2107, 2019*

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	HMDS (0.75 mmol),MMT-HClO ₄ (7 mg), CH ₃ CN, r. t.	
ROH	`	ROSiMe ₂
	MMT HClO (7 mg) EtOH r t	5
	MM1-HClO ₄ ($/$ mg), EtOH, r. t.	

Scheme 2. Trimethylsilylation of alcohols and phenols and deprotection of silyl ethers.

MMT-HClO₄ can be used as an efficient solid acid catalyst for the promotion of the reactions which need the use of an acidic catalyst to accelerate. So we were interested in investigating the applicability of this catalyst in the promotion of the trimethylsilyl protection of hydroxyl groups with HMDS. In order to obtain the optimum reaction conditions, the preparation of trimethylsilyl ether derivative of 4-chlorobenzyl alcohol was studied in various conditions

Table II. Trimethylsilylation of alcohols with HMDS catalyzed by MMT-HClO₄ at room temperature.

Enter	Substrate	Product	Time (min)	Yield
	Substrate	Tioduct	(IIIII)	(70)
1	PhCH ₂ OH	PhCH ₂ OSiMe ₃	2	92
2	$2\text{-ClC}_6\text{H}_4\text{CH}_2\text{OH}$	$2\text{-ClC}_6\text{H}_4\text{CH}_2\text{OSiMe}_3$	4	92
3	$4-ClC_6H_4CH_2OH$	$4\text{-ClC}_6\text{H}_4\text{CH}_2\text{OSIMe}_3$	2	94
4	$3,4-\text{Cl}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	$3,4-\text{Cl}_2\text{C}_6\text{H}_4\text{CH}_2\text{OSIMe}_3$	2	92
5	$4-BIC_6H_4CH_2OH$	$4-BiC_6H_4CH_2OSIMe_3$	2	94
0	$2-BrC_6H_4CH_2OH$	$2 \operatorname{BrC}_6 \operatorname{H}_4 \operatorname{CH}_2 \operatorname{OSIMe}_3$	5	93
/	$2 - NO_2 C_6 H_4 C H_2 O H$	$2 - NO_2C_6H_4CH_2OSIMe_3$	/	90
0	$4 - NO_2 C_6 H_4 C H_2 O H$	$4 - NO_2C_6H_4CH_2OSIMe_3$	4	91
9	$4 \text{ M}_{2} \text{ CHC H CH OH}$	4 Ma CHC H CHOSiMab	1.2520 +- 2.m	04. I
10	$4 \operatorname{Me}_2\operatorname{CHC}_6\operatorname{H}_4\operatorname{CH}_2\operatorname{OH}$	$4 \text{ Me}_2 \text{CHC}_6 \text{H}_4 \text{CH}_2 \text{OSIMe}_3$	[2]	
12	$3 \text{ M}_{2} \text{ OC } \text{ U } \text{ CU } \text{ OU}$	$4 - Me_2 CHC_6 H_4 CH_2 OSIMe_3$	2	80
12	$4 \text{ M}_{2}\text{OC} + CH \text{ OH}$	4 MaOC H CH OSiMa	2	02
13	4 -MeOC ₆ Π_4 C Π_2 O Π	4 -MeOC ₆ H_4 C H_2 OSIMe ₃	2	92
14		\sim \downarrow \sim	5	90
15	Ŭ OH	OSiMe,	2	93
16	PhCH ₂ CH ₂ OH	PhCH ₂ CH ₂ OSiMe ₃	2	91
17	PhCH ₂ CH ₂ CH ₂ OH	PhCH ₂ CH ₂ CH ₂ OSiMe ₃	2	92
18	OH	OSiMe	3	92
	UT OH	USINIE ₃		
19	ОН	OSiMe	10	91
20	HO	Me,SiO 3	30	90
21			20	0.1
21		OSIMe ₃	20	91
22			25	00
22			23	90
	-OH	-OSIMe ₃	_	
23	OH OH	OSiMe ₃	7	94
24	4-EtC ₆ H ₄ OH	4-EtC ₆ H ₄ OSiMe ₃	7	89^{b}
25	3,5-Me ₂ C ₆ H ₃ OH	3,5-Me ₂ C ₆ H ₃ OSiMe ₃	4	93
26	2,4-Me ₂ C ₆ H ₃ OH	2,4-Me ₂ C ₆ H ₃ OSiMe ₃ 7	91	
27	2-MeC ₆ H ₄ OH	2-MeC ₆ H ₄ OSiMe ₃	10	92
28	3-MeC ₆ H ₄ OH	3-MeC ₆ H ₄ OSiMe ₃	5	93
29	4-MeC ₆ H ₄ OH	4-MeC ₆ H ₄ OSiMe ₃	5	92
30	M → M	N OSiMe3	2	90 ^c
	Н	Н		

Table II. Continued.						
Entry	Substrate	Product	Time (min)	Yield $(\%)^a$		
31	4-MeC ₆ H ₄ NH ₂	4-MeC ₆ H ₄ NHSiMe ₃	60	0^d		
32	4-ClC ₆ H ₄ NH ₂	4-ClC ₆ H ₄ NHSiMe ₃	60	0		
33	NH ₂	NHSiMe ₃	60	0		
34	PhCH ₂ NH ₂	PhCH ₂ NHSiMe ₃	60	0		
35	PhCH ₂ CH ₂ CH ₂ NH ₂	PhCH ₂ CH ₂ CH ₂ NHSiMe ₃	60	0		
36		NSiMe ₃	60	0		
37	M NH ₂	SiMe ₃ NHSiMe ₃	60	0^e		
38	4-BrC ₆ H ₄ SH	4-BrC ₆ H ₄ SSiMe ₃	60	0		
39	4-MeC ₆ H ₄ SH	4-MeC ₆ H ₄ SSiMe ₃	60	0		
40	PhCH ₂ SH	PhCH ₂ SSiMe ₃	60	0		
41	$4-ClC_6H_4CH_2OH$	4-ClC ₆ H ₄ CH ₂ OSiMe ₃	20	Trace ^f		

Notes: ^{*a*}Isolated yield. Products were identified spectroscopically and characterized by their physical constants, comparison with authentic samples. ^{*b*}1 mmol of HMDS used for silylation. ^{*c*}1.5 mmol of HMDS used for silylation. ^{*d*}Starting material was recovered unchanged. ^{*e*}1.5 mmol of HMDS used for silylation. ^{*f*}Reaction was performed in the presence of Na⁺-montmorillonite.

including different amounts of the catalyst, temperature and solvent. Finally, the best result was obtained using 10 mg of MMT-HClO₄ in acetonitrile at ambient temperature (Scheme 2). In order to investigate the applicability of this method we selected a wide variety of benzylic and aliphatic alcohols and phenols. As can be seen in Table II, using this method all of the selected compounds were successfully converted to the requested products in high yields and short times at room temperature in CH₃CN under completely heterogeneous reaction conditions.

As indicated in Table II, in the case of benzylic alcohols the nature of the substituents (acid sensitive, electronwithdrawing or electron-releasing groups) on the aromatic ring has no significant effect on the product yield (Table II, entries 1-15). Primary, secondary and tertiary aliphatic alcohols were also successfully converted to their corresponding trimethylsilyl ethers in high yields under the same reaction conditions (Table II, entries 16-22). Using this method unsaturated alcohols (Table II, 23) gave the corresponding TMS-ethers in high yields. Furthermore, trimethysilylation of different types of phenols with HMDS under the optimized conditions was performed cleanly in high yields (Table II, entries 24-29). In general, phenols underwent silvlation at longer reaction times compared to benzylic alcohols. It is worth mentioning that in the presence of Na⁺-MMT the reactions were so slow that a considerable amount of the starting material was recovered unchanged (Table II, entry 41). These results indicate that the modification of Na⁺-MMT with perchloric acid efficiently increased its ability in the promotion of trimethysilylation reaction and the catalyst is necessary to produce the desired products. Moreover, studies showed that this method was able to selectively protect the hydroxyl group against the amino group (Table II, 30).

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MMT-HClO.

Table IV. Deprotection of trimethylsilyl ethers

catalyzed by

Entry	Substrate	Product	Time (min)	Conver- sion
1	3,4-Cl ₂ C ₆ H ₃ CH ₂ OH	3,4-Cl ₂ C ₆ H ₃ CH ₂ OSiMe ₃	3	100
	+ 4-MeC ₆ H ₄ NH ₂	+ 4-MeC ₆ H ₄ NHSiMe ₃		0
2	4-BrC ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CH ₂ OSiMe ₃	3	100
	+ 4-ClC ₆ H ₄ NH ₂	+ 4-ClC ₆ H ₄ NHSiMe ₃		0
3	2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CH ₂ OSiMe ₃	5	100
	$+ 4 - MeC_6H_4SH$	+ 4-MeC ₆ H ₄ SSiMe ₃		0
4	PhCH ₂ CH ₂ OH	PhCH ₂ CH ₂ OSiMe ₃	3	100
	+4-BrC ₆ H ₄ SH	+ 4-BrC ₆ H ₄ SSiMe ₃		0

Thus, protection of amines and thiols was also investigated and it was found that amines and thiols were resistant to this reagent and the starting materials were recovered intact after 2 h (Table II, entries 31–40). Therefore, this methodology shows selectivity and is suitable for the selective trimethylsilylation of alcohols and phenols in the presence of amines and thiols. The obtained results are reported in Table III.

Moreover, the results obtained in this study clearly revealed that nanoporous Na^+ -montmorillonite perchloric acid (MMT-HClO₄) can also be an efficient reagent for the conversion of trimethylsilyl ethers to the parent alcohols and phenols in ethanol at room temperature. All reactions were performed under mild and completely heterogeneous reaction conditions with good to excellent yields (Scheme 2, Table IV).

3.3. Reusability of the Catalyst

To examine the reusability of the catalyst, it was recovered by filtration from the reaction mixture, washed with CH_3CN , H_2O and acetone and dried in oven. The recovered catalyst was reused under optimized reaction conditions for trimethylsilylation of 4-chlorobenzyl alcohol which gave the desired product in good yields after four runs. The obtained results were indicated that the reactions led to the requested products without significant changes in terms of reaction time and yield which clearly shows useful recyclability of MMT-HCIO₄ (Fig. 8). The IR of the recovered catalyst showed the same spectra of unused catalyst. This result indicates that the catalyst remained unchanged after recovery.

The evolution of ammonia gas (NH_3) was observed in all reactions. A conceivable mechanism that confirm the generation of NH_3 and the catalytic role of this catalyst has been proposed (Scheme 3).

In order to show the effectiveness of the presented method, we have compared the obtained results in the trimethylsilylation of alcohols with HMDS catalyzed by MMT-HClO₄ with some of those reported in the literature. As indicated in Table V, this method avoids disadvantages of other procedures such as excess reagents and long reaction times. Furthermore, the present method shows a preference to similar aluminosilicate structural systems,

	4			
			Time	Yield
Entry	Substrate	Product	(min)	$(\%)^{a}$
1	PhCH ₂ OSiMe ₃	PhCH ₂ OH	2	93
2	2-ClC ₆ H ₄ CH ₂ OSiMe ₃	2-ClC ₆ H ₄ CH ₂ OH	2	90
3	4-ClC ₆ H ₄ CH ₂ OSiMe ₃	4-ClC ₆ H ₄ CH ₂ OH	1	92
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OSiMe ₃	3,4-Cl ₂ C ₆ H ₃ CH ₂ OH	2	95
5	4-BrC ₆ H ₄ CH ₂ OSiMe ₃	4-BrC ₆ H ₄ CH ₂ OH	1	93
6	2-BrC ₆ H ₄ CH ₂ OSiMe ₃	2-BrC ₆ H ₄ CH ₂ OH	2	91
7	2-NO ₂ C ₆ H ₄ CH ₂ OSiMe ₃	2-NO ₂ C ₆ H ₄ CH ₂ OH	3	92
8	4-NO ₂ C ₆ H ₄ CH ₂ OSiMe ₃	4-NO ₂ C ₆ H ₄ CH ₂ OH	2	94
9	2-MeC ₆ H ₄ CH ₂ OSiMe ₃	2-MeC ₆ H ₄ CH ₂ OH	2	93
10	4-Me ₂ CHC ₆ H ₄ CH ₂ OSiMe ₃	4-Me ₂ CHC ₆ H ₄ CH ₂ OH	2	87
11	4-Me ₃ CC ₆ H ₄ CH ₂ OSiMe ₃	4-Me ₃ CC ₆ H ₄ CH ₂ OH	2	92
12	3-MeOC ₆ H ₄ CH ₂ OSiMe ₃	3-MeOC ₆ H ₄ CH ₂ OH	2	94
13	4-MeOC ₆ H ₄ CH ₂ OSiMe ₃	4-MeOC ₆ H ₄ CH ₂ OH	3	90
14	Ph ₂ CHOSiMe ₃	Ph ₂ CHOH	4	91
15	PhCH(OSiMe ₃)Me	PhCH(OH)Me	2	90
16	PhCH ₂ CH ₂ OSiMe ₃	PhCH ₂ CH ₂ OH	2	86
17	PhCH ₂ CH ₂ CH ₂ OSiMe ₃	PhCH ₂ CH ₂ CH ₂ OH	2	89
18	PhCH(Me)CH ₂ OSiMe ₃	PhCH(Me)CH ₂ OH	3	90
19			10	91
	OSiMe ₃	< >—он		
20			30	88
20	\rightarrow	\rightarrow	50	00
	/ <u>}_</u> /	/)/		
	Me ₃ SiO'	HO'		
21	OSiMe ₃	∕ ^{OH}	15	90
		$\Gamma \neg$		
1e, 25	Dec 2018 20:08:06	\sim	10	85
Scien	tific Publishers	$\left[\left(1 \right) \right]$	10	05
by Ing	enta OSiMe3	Л ОН		
23	4-EtC ₆ H ₄ OSiMe ₃	4-EtC ₆ H ₄ OH	5	90
24	3,5-Me ₂ C ₆ H ₃ OSiMe ₃	3,5-Me ₂ C ₆ H ₃ OH	3	93
25	2,4-Me ₂ C ₆ H ₃ OSiMe ₃	$2,4-Me_2C_6H_3OH$	5	92
26	2-MeC ₆ H ₄ OSiMe ₃	2-MeC ₆ H ₄ OH	5	90
27	3-MeC ₆ H ₄ OSiMe ₃	3-MeC ₆ H ₄ OH	3	91
28	4-MeC ₆ H ₄ OSiMe ₃	4-MeC ₆ H ₄ OH	3	90

Notes: ^{*a*}Isolated yield. Products were characterized by their physical constants and comparison with authentic samples.

such as H- β -zeolite and sulfonic acid-functionalized mesoporous silica (SBA) in terms of the catalyst amounts, the reaction times and conditions. According to Table I, MMT-HClO₄ shows better efficiency than other nanoparticles



Figure 8. Recyclability of the catalyst.

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Scheme 3. Proposed mechanism of the reaction.

such as nanoporous silica and nanocrystalline TiO_2 . As can be seen in Table V, among the reported catalysts the activity and amount of nano TiO_2 -HClO₄ is near to MMT-HClO₄. But it is noteworthy that clays have a natural origin and due to their enormous amounts in nature have cost much less than other nanomaterials and are more cost effective economically. This comparison also display

Table V. MMT-HClO₄ catalyzed TMS protection of alcohols in comparison with the other methods.

					<u>r America</u>
		Catalyst	Pagation	Time	Delivered
Entry	Catalyst	(mg)	conditions	(h)	Ref.
1	LaCl ₃	24	CH ₂ Cl ₂ , r.t.	2.5–5	7
2	Sulfonic acid- functionalized ordered nanoporous silica	19	CH ₂ Cl ₂ , r.t.	0.5–24	8
3	Trichloroiso- cyanuric acid (TCCA)	23	CH ₂ Cl ₂ , r.t.	2.5–12	9
4	SiO ₂ -HClO ₄	50	CH ₃ CN, r.t.	0.03–0.16	10
5	Fe(HSO ₄) ₃	87	CH ₃ CN, reflux	0.25–2.7	11
6	Nanocrystalline TiO ₂	15	CH ₃ CN, r.t.	0.16–5.16	12
7	Nanocrystalline TiO ₂ -HClO ₄	5	CH ₃ CN, r.t.	0.02–0.92	16
8	H- β zeolite	10% w/w	Toluene, r.t	7–30	19
9	SBA-15-Ph-Pr- SO ₂ H	19	CH ₂ Cl ₂ , 35 °C	0.33–24	20
10	Montmorillonite K 10	100	CH ₂ Cl ₂ , r.t.	0.2–8	21
11	SANM	20	CH ₃ CN, r.t.	0.08–1	33
12	MMT-HClO ₄	7	CH ₃ CN, r.t.	0.03–0.5	The present method

although sulfonic acid-functionalized ordered nanoporous Na⁺-montmorillonite (SANM) has similar reaction conditions to MMT-HClO₄ but SANM catalyzes this reaction using larger amounts of catalyst and longer reaction times than MMT-HClO₄. On the other hand, for the preparation of SANM, chlorosulfonic acid is used which is a colorless liquid, hygroscopic and a powerful lachrymator.⁴⁸ Furthermore, this method require a proper ventilation and a gas inlet tube for conducting the produced HCl gas over an adsorbing solution, but MMT-HClO₄ is produced easily through interaction of clay and perchloric acid without production of any harmful gas. As the pH analysis indicates the number of H⁺ sites of SANM arising from ClSO₂H was 0.88 mmol \cdot g⁻¹, but the number of H⁺ sites for MMT-HClO₄ arising from HClO₄ was 1.09 mmol H⁺/g. This comparison shows that perchloric acid is supported on clay more effectively than chlorosulfonic acid. It is necessary to report that the protection of alcohols in the presence of Montmorillonite K 10 completed during a long time (0.2-8 h) using large amounts of catalyst (100 mg). This comparison indicates that the modification of Na⁺-MMT with perchloric acid efficiently increases its activity.

4. CONCLUSIONS

In conclusion, in this study we have reported the preparation of MMT-HCIO₄₂ as a new, environmentally friendly and stable solid acid catalyst, and its application in the by chemoselective trimethylsilylation of alcohols and phenols, as well as in the deprotection of silyl ethers. The low cost and availability of the reagents, ease of preparation and handling of the catalyst, chemoselectivity, high yields of the products, easy procedure and work-up, short reaction times and the reusability of the catalyst are noteworthy advantages of this method and we believe it would be a useful addition to the available organic methodologies. Further work to explore this catalyst in other organic transformations is in progress.

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