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Short Communication

Nanocrystalline TiO₂–HClO₄ as a new, efficient and recyclable catalyst for the chemoselective trimethylsilylation of alcohols, phenols and deprotection of silyl ethers

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ABSTRACT

 TiO_2 -HClO₄, as a new solid acid, was found to be an efficient catalyst for the chemoselective trimethylsilylation of alcohols and phenols. Deprotection of the resulting trimethylsilylethers was achieved using the same catalyst in methanol solvent. The synthesized catalyst was characterized by FT-IR, SEM, TEM, BET and XRD analyses. Our novel synthetic method has the advantages of high yields, short reaction times, low cost and recyclability of the catalyst, simplicity and easy work-up compared to the conventional methods reported in the literature.

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1. Introduction

Protection and deprotection of organic functional groups play an essential role in the multi-step organic synthesis [1,2]. The conversion of hydroxyl groups to their corresponding trimethylsilyl ethers is one of the popular methods used for this purpose. Among the different reagents which are available for the silvlation of alcohols [3,4] hexamethyldisilazane (HMDS), as a cheap and commercially available reagent [5,6], is selected as one of the best candidates, because the handling of this reagent does not need special precautions and workup of the reaction mixture is not time consuming and giving NH₃ as the only by-product. The low silvlating power of HMDS is the main drawback for its application [7]. To overcome this restriction, a variety of catalysts have been reported for the activation of HMDS; of them, sulfonic acid-functionalized silica [8], SiO₂-HClO₄ [9], sulfonic acids [10], tungstophosphoric acid (H₃PW₁₂O₄₀) [11], I₂ [12], montmorillonite K10 [13], ZrCl₄ [14], Al(HSO₄)₃ [15], Fe(HSO₄)₃ [16], V(HSO₄)₃ [17], saccharin sulfonic acid [18] and nanocrystalline TiO₂ [19] are examples. Although these methods provide an improvement, in most cases long reaction times, low selectivity, forceful conditions or tedious work-up is needed. In addition, some of the reagents are expensive and toxic or have to be prepared in a time consuming procedure, and most of them are not able to catalyze the reverse reaction.

Deprotection of trimethylsilyl ethers to their parent hydroxyl compounds under mild conditions is a useful achievement in organic synthesis, and a wide variety of catalysts have been already reported for these transformations [20–22]. However, some of the reported methods suffer from one or more disadvantages, such as formation of large amounts of by-products, long reaction times, low yields of the products, high cost or toxicity of the reagent and non-recyclability of the catalyst. Therefore, an introduction of a milder, more selective and heterogeneous reagent for such functional group transformations is of practical importance and still in demand.

In recent years, there has been considerable growth of interest in the catalysis of organic reactions by solid acid catalysts. Solid acid catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments. These features can lead to improved processing steps, better process economics, and environmentally friendly industrial manufacturing.

Recently, nanocrystalline TiO₂ has been used as a solid acid catalyst in organic transformations; such as chemoselective trimethylsilylation of alcohols and phenols [19], Friedel–Crafts alkylation of indoles with epoxides [23], synthesis of bis(indolyl) methanes [24], Mannich synthesis of β –aminocarbonyls [25] and esterification of free fatty acids [26]. However traditional heterogeneous catalysts have many limitations in the nature of their active sites. For example nano particles of TiO₂ only can catalyze the reactions with their low Lewis acidic properties therefore modification of these nano particles very attended by chemists [27–30].

Recently, preparation and introduction of new catalysts for the functional group transformation became an important part of our research

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$$\Gamma iO_2$$
-HClO₄ (5 mg), MeOH, r. t

Scheme 1. Trimethylsilylation of alcohols and phenols and deprotection of silyl ethers.

program [14–19]. In continuation of these studies, herein, we wish to report the preparation of titania supported perchloric acid (TiO₂– HClO₄) and its application, as a new, efficient and recyclable catalyst, in trimethylsilylation of hydroxyl groups and cleavage of trimethylsilyl ethers at room temperature under mild conditions (Scheme 1). TiO₂– HClO₄ can be easily prepared by preparing a suspension of HClO₄ and TiO₂ in Et₂O and concentrating and heating the mixture at 100 °C for 2 h under vacuum. It is important to note that, this reaction is easy and clean without any extra work-up procedure. This white heterogeneous, nonhygroscopic solid acid is very stable under reaction conditions.

2. Experimental

2.1. Materials

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

2.2. Instrumentation

The FT-IR (KBr) spectra were recorded on a Shimadzu FT-IR-8900 spectrophotometer. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Philips PW 1820 diffractometer using Ni-filtered Co-K α radiation (λ = 0.15418 nm). N₂ physisorption at liquid nitrogen temperature using a SHIBATA APP. SA-1100 surface area analyzer and standard multipoint BET analysis methods was carried out. Samples were degassed in flowing N₂ for 2 h at 250 °C before N₂ physisorption measurements were obtained. Transmission electron microscopy (TEM) analysis was performed on a Philips model CM 10 instrument. Sample was prepared by sonicating a small amount of powder in methanol, then placing a drop of the mixture on



Fig. 1. FT-IR spectra of TiO₂ and TiO₂-HClO₄.

a 3 mm TEM Cu grid having a lacey carbon support film. Scanning election microphotographs (SEM) were obtained on a LEO 1430VP instrument.

2.3. Preparation of titania supported perchloric acid (TiO₂-HClO₄)

ROSiMe₃

 $HClO_4$ (0.14 g, 1 mmol, as a 70% aq solution) was added to a suspension of TiO_2 (2 g, It is a mixture of 80% anatase and 20% rutile and it has a particle size of 30 nm and BET specific area $34 \text{ m}^2 \text{ g}^{-1}$) in Et₂O (30 mL). The mixture was concentrated and the residue was heated at 100 °C for 2 h under vacuum to furnish TiO_2 – $HClO_4$ (0.013 mmol g⁻¹) as a white powder.

2.4. General procedure for trimethylsilylation of alcohols and phenols

To a stirring mixture of the substrate (1 mmol), and TiO_2 -HClO₄ (5 mg) in CH₃CN (3 mL), HMDS (120 mg, 0.75 mmol) was added at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and the filtrate was washed with acetonitrile (5 mL). Evaporation of the solvent gave almost pure product(s). Further purification proceeded by bulb to bulb distillation under reduced pressure or recrystallization to afford pure silyl ether (Table 2).

2.5. General procedure for deprotection of trimethylsilyl ethers

A mixture of the substrate (1 mmol) and TiO_2 -HClO₄ (5 mg) in methanol (1 mL) was stirred at room temperature. After completion of the reaction (indicated by TLC), the catalyst was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford pure alcohols and phenols (Table 2).



Fig. 2. XRD patterns of TiO₂ and TiO₂-HClO₄.



Fig. 3. SEM images of (A) neat TiO₂ and (B) the TiO₂-HClO₄ nanoparticles.



Fig. 4. TEM images of TiO₂-HClO₄.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. IR analysis

The infrared spectra of TiO_2 and TiO_2 – $HClO_4$ are presented in Fig. 1. In the case of TiO_2 , the peaks at ca. 3425 and 1649 cm⁻¹ corresponded to the –OH stretching vibration of the adsorbed water to TiO_2 . The spectrum of titania supported perchloric acid displays almost the same peaks at



Fig. 5. Absorption spectra of 4-nitroaniline (indicator) (A) and $\rm TiO_2-HClO_4$ (catalyst) (B) in CCl_4.

3404 and 1626 cm⁻¹ for adsorbed water. Also bands in 1086, 1111 and 1146 cm⁻¹ attributed to the ClO₂ asymmetric stretching vibration [31] this result shows modification of TiO₂ using perchloric acid.

3.1.2. Powder X-ray diffraction

The powder XRD patterns of TiO_2 and TiO_2 -HClO₄ are shown in Fig. 2. It seems the peak intensities of TiO_2 and TiO_2 -HClO₄ are almost the same and the peaks remained intact under the conditions used for modification. These results indicate an ordered mesoporosity of the supports even after the incorporation with perchloric acid.

3.1.3. Surface area and pore distribution measurements

 N_2 adsorption measurements, which have been a powerful tool for nano- or mesoporous material characterization, were performed to obtain more insights into the modified porous nano-silica materials. The textural properties of TiO₂ were substantially maintained over perchloric acid functionalization. A slight decrease in surface area was observed for TiO₂ and TiO₂–HClO₄ from 34 to 27 m²/g, respectively. This suggests that perchloric acid may be well confined in the pores of the nanocrystaline TiO₂, and indicate an ordered mesoporosity of the support even after modification [32].

Table 1

Calculation of Hammett acidity function (H_0) of TiO₂-HClO₄.

Entry	Catalyst	A _{max}	[I] _s %	$[IH^+]_s$ %	H ₀
1	–	1.4853	100	0	-
2	TiO ₂ –HClO ₄	0.5389	36.28	63.71	0.74

Condition for UV-visible spectrum measurement: solvent: CCl₄, indicator: 4-nitroaniline (pK(I)_{aq} = 0.99), 1.44×10^{-4} mol/L; Catalyst: TiO₂-HClO₄, 20 mg, 25 °C.

Table 2

Protection and deprotection of alcohols and phenols by formation and cleavage of trimethylsilyl ethers catalyzed by TiO2-HClO4.

Entry	Substrate	Protection	Protection		Deprotection	
		Time (min)	Yield (%) ^a	Time (min)	Yield (%) ^a	
1	C ₆ H₄CH₂OH	1	97	3	90	
2	4-ClC ₆ H ₄ CH ₂ OH	1	95	3	83	
3	$4-BrC_6H_4CH_2OH$	1	89	5	90	
4	$4-NO_2C_6H_4CH_2OH$	1	93	3	85	
5	4-0mec ₆ n ₄ cn ₂ 0n	1	94	2	69	
	CH ₂ OH					
6		2	89	5	85	
	CH ₂ OH					
7		2	80	5	87	
7		J	05	5	07	
	PhCH(OH)CH ₃					
8	PhCH(OH)CH ₃	1	91	4	95	
	OH					
9		2	94	5	88	
10	PhCH ₂ CH ₂ CH ₂ OH PhCH ₂ CH ₂ CH ₂ OH	1	95	3	90	
		•		5	50	
11		35	94	55	86	
12	∭ он	55	90	55	89	
13		5	89	8	93	
15	U OH	5	05	0	55	
14	\square	45	92	50	85	
17	Д ОН	-5	52	50	05	
15		<u>_</u>	22	10		
15	-OH	6	89	10	84	
	/					
16	Он	4	93	7	87	
	OH					
17		15	83	20	85	
	ОН					
18		15	91	18	84	
	~~~ 					
10	UH UH	10	05	25	00	
19		10	85	25	86	
	OH					
aab	Сн "					
205	Í Ì	18	88	20	87	
	НОСОН					
21	SH SH	01-	NDC			
21		011	IN.K.	-	-	
22		8h	N R ^c	_	_	
22		011	14.14			
23	∕SH	8h	N.R. ^c	-	-	
24	$\searrow$ NH ₂	8h	N.R. ^c	-	-	
25	$\langle \rangle_{\rm NH_2}$	8h	N.R. ^c	-	-	
26	NH ₂	8h	N.R. ^c	-	-	
	<u>`</u>					

^a Isolated yield. Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy and for deprotection products were characterized by their physical constants and comparison with their company's data. ^b 2.25 mmol of HMDS used for silylation.

^c 100% of starting materials were recovered.

# 3.1.4. pH analysis

To an aqueous solution of NaCl (1 M, 25 mL) with a primary pH 7.3, TiO₂-HClO₄ (500 mg) was added and the resulting mixture was stirred for 2 h after which the pH of solution decreased to 3.6. This is equal to a loading of 0.013 mmol HClO₄ $g^{-1}$ .

# 3.1.5. Microscopic analysis

The representative SEM and TEM photographs of TiO₂ and TiO₂– HClO₄ are shown in Figs. 3 and 4. From the SEM images, we find that the TiO₂–HClO₄ shows aggregation after modification with HClO₄ that corresponded with TEM images. The SEM micrographs of TiO₂ and catalyst showed that with modification the primary structure of TiO₂ changed. Also TEM image showed that the particle size of TiO₂ increased to 150 nm (from XRD patterns the particle size of TiO₂ was 30–40 nm). This observation shows that after the modification of TiO₂ with HClO₄ the TiO₂ nanoparticles greatly grow to an average particle size of 150 nm. Also the aggregation of TiO₂ nanoparticles is clearly observed in the TEM image.

#### 3.1.6. Hammett acidity

The Hammett acidity function can effectively express the acidity strength of an acid in organic solvents [33–35]. It can be calculated by the equation below:

$$H_{0} = pK(I)_{aq} + log([I]_{s}/[IH^{+}]_{s})$$

Here, "I" represents the indicator base (mainly substituted dinitroanilines),  $[IH^+]_s$  and  $[I]_s$  are respectively the molar concentrations of the protonated and unprotonated forms of the indicator. The pK(I)_{aq} values are already known (for example the pK(I)_{aq} value of 4-nitroaniline is 0.99) and can be obtained from many references. According to Lambert–Beer's Law, the value of  $[I]_s/[IH^+]_s$  can be determined and calculated through UV–visible spectrum.

In our experiment, 4-nitroaniline was chosen as the basic indicator and CCl₄ as the solvent because it is aprotic. The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 329 nm in CCl₄. As Fig. 5 shows, the absorbance of the unprotonated form of the indicator in  $TiO_2$ -HClO₄ was weak compared to the sample of the indicator in CCl₄, which indicated that the indicator was partially in the form of [IH⁺]. The results obtained are listed in Table 1, which shows the acidity strength of  $TiO_2$ -HClO₄.

#### 3.2. Catalytic activity

First, we tried to convert 4-chlorobenzyl alcohol (1 mmol) to its corresponding silylether with  $TiO_2$ -HClO₄ (15 mg, equal to  $1.95 \times 10^{-4}$  mmol of H⁺) and HMDS (0.75 mmol) in CH₃CN with stirring at ambient temperature, which is completed after 1 min. Reduction of the amount of TiO₂-HClO₄ to 5 mg/mmol of alcohol did not affect the result of the reaction (protection of 4-chlorobenzyl alcohol in the same reaction conditions completed after 20 min in the presence of 15 mg nano TiO₂) [19]. These results show that the modification of TiO₂ with HClO₄ efficiently increased its ability in the promotion of this reaction.

After optimization of the reaction condition various types of alcohols were subjected to trimethylsilylation using this method at room temperature in CH₃CN under completely heterogeneous reaction conditions (Table 2, entries 1–14). Trimethylsilylation of benzylic alcohols including acid sensitive, electron-donating or electron-withdrawing groups proceeded efficiently with relatively high isolated yields (Table 2, entries 1–9). Primary, secondary and tertiary aliphatic alcohols were also successfully converted to their corresponding trimethylsilyl ethers in almost quantitative yields under the same reaction conditions (Table 2, entries 10–14). Phenols also undergo silylation easily using this method, and their corresponding silyl ethers can be isolated in good to high yields (Table 2, entries 15–20).

Our studies revealed that  $TiO_2-HCIO_4$  can also be an efficient reagent for the conversion of trimethylsilyl ethers to the parent alcohols and phenols in MeOH at room temperature (note:  $TiO_2$  lonely could not carry out the reverse reaction [19]). All reactions were performed under mild and completely heterogeneous reaction conditions and resulted in good to excellent yields (Table 2, entries 1–20).

As shown in Table 2, thiols and amines are resistant to this reagent and do not react under the selected conditions (Table 2, entries 21–26). Thus, this methodology shows selectivity and is suitable for the selective trimethylsilylation of benzylic, primary, secondary and tertiary aliphatic alcohols and phenols in the presence of amines and thiols. The selectivity and versatility of the reaction were confirmed by the application of the general procedure for various examples (Table 3).

We have found that  $TiO_2$ -HClO₄ can be easily recovered by filtration, washing with CH₃CN, H₂O and acetone and drying at room temperature. The reusability of this reagent is exemplified

Entry	Substrate	Product	Time ( min)	Conversion
1	4-Br ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CH ₂ OSiMe ₃	1	100
	+	+		
	Фон	OSiMe ₃		0
2	PhCH ₂ CH ₂ CH ₂ OH	PhCH ₂ CH ₂ CH ₂ OSiMe ₃	1	100
	+	+		
	Юон	OSiMe ₃		0
3	——————————————————————————————————————	OSiMe ₃	5	100
	+	+		
	Юон	OSiMe ₃		0
4	4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CH ₂ OSiMe ₃	1	100
	+	+		
	SH SH	SSiMe ₃		0
5	PhCH ₂ CH ₂ CH ₂ OH	PhCH ₂ CH ₂ CH ₂ OSiMe ₃	1	100
	+	+		
	NH ₂	NHSiMe ₃		0



Fig. 6. Reusability of the catalyst.

by trimethylsilylation of 4-chlorobenzyl alcohol in the presence of the recycled reagent, which gave the requested product in 95, 91, 88, 86, 82 and 80% yields after six runs. The average time for 6 consecutive runs was 3.2 min and 100% conversion for all, which clearly demonstrates the practical recyclability of this catalyst (Fig. 6). The IR of the recovered catalyst after the fourth run showed the same spectra of unused catalyst, which shows the catalyst remained unchanged after four uses.

In all reactions, we have studied, fast evolution of ammonia gas was observed. With these observations we have proposed a mechanism in which the generation of  $NH_3$  and the catalytic role of  $TiO_2$ –HClO₄ are clarified (Scheme 2).

To illustrate the efficiency of the present method, Table 4 compares our results with the same results reported by the relevant reagents in the literature.

#### 4. Conclusion

In summary, the use of TiO₂-HClO₄ as a catalyst for this transformation avoids the problem in the recovery of Lewis acid catalysts. This procedure has several advantages: (1) The preparation of TiO₂– HClO₄ was very simple from easily available reagents; (2) TiO₂–HClO₄ could be directly reused after simple extraction; (3) TiO₂–HClO₄ shows efficient catalytic activity. Because of these significant features



Scheme 2. Proposed mechanism of the reaction.

#### Table 4

Compared performance of various catalysts in the trimethylsilylation of benzyl alcohol.

Catalyst / condition	Catalyst loading (mg)	Time (min)	Yield (%)	Ref.
TiO ₂ -HClO ₄ / CH ₃ CN, r.t.	5	1	97	Present method
Sulfonic acid-functionalized ordered nanoporous silica / CH ₂ Cl ₂ , r.t.	19	80	100	8
SiO ₂ -HClO ₄ /CH ₃ CN, r. t.	50	2	98	9
H ₃ PW ₁₂ O ₄₀ /neat, 55–60 °C	28	23	90	11
Montmorillonite K 10/neat, r.t.	100	21	92	13
Fe(HSO ₄ ) ₃ / CH ₃ CN, reflux	87.5	102	70	16
Fe(HSO ₄ ) ₃ / Neat, 90–100 °C	87.5	13	90	16
Nanocrystalline TiO ₂ /CH ₃ CN, r.t.	15	10	95	19

we believe it would be a useful addition to the available organic methodologies.

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