

*N*¹-*N*⁴-Bis (3-(trimethoxysilyl)propyl)butane-1,4-diammonium trinitromethanide on titanium dioxide: An efficient nano-catalyst for the solvent-free acetyl protection of amines and alcohols

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Original Research

Abstract:

Received:
12 February 2024
Revised:
05 April 2024
Accepted:
02 May 2024
Published online:
11 May 2024

In this study, *N*¹-*N*⁴-bis (3-(trimethoxysilyl)propyl)butane-1,4-diammonium trinitromethanide on titanium dioxide TiO₂-Bis[TMS-NH₂⁺ C(NO₂)₃⁻]an, was prepared and characterized by the use of different techniques including energy dispersive X-ray analysis (EDX), Fourier transform infrared spectroscopy (FT-IR), thermo gravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), and X-ray diffraction (XRD). In continue, the use of the prepared reagent as an efficient nano-catalyst was examined in the acetylation of amines and alcohols under mild reaction conditions with good to excellent yields. In the studied reactions the catalyst can be recycled and reused for an acceptable period of runs.

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Keywords: Green synthesis; Acetylation; Immobilized ionic liquids; Heterogeneous catalyst

1. Introduction

Acylation is a common and versatile organic transformation that is widely used for the effective protection of thiols, phenols, alcohols, and amines in multi-step syntheses. These syntheses can be included cosmetics and foods, fragrances, emollients, flavorings, polymers, some drugs' natural compounds, biologically active compounds, and multi-functional molecules such as carbohydrates, nucleosides, flavanones, chalcones, naphthoquinones, pesticides, and steroids [1–4]. Considering the use of alcohols and amines in chemical reactions and their presence in many organic molecules, it is very important to protect this category of compounds. So far, acetylation of amines and alcohols has been done utilizing anhydrides and acetyl chlorides in the presence of various catalysts such as borated zirconia [5], tris(pentafluorophenyl)borane [6], copper (ii) sulfate pentahydrate (CuSO₄ · 5H₂O) [7], P(4-VPT) [8], ZnO₂ [9], Ce(OTf)₃ [10], NiCl₂ [11], P₂O₅/Al₂O₃

[12], silica-bonded sulfamic acid [13], La(NO₃)₃ · 6H₂O [14], polyvinylpyrrolidonium tribromide [15], acylimidazolium acetate [16], ZnAl₂O₄@SiO₂ [17], CoCl₂ [18], Ni/SiO₂ [19], anhydrous NiCl₂ [20], Cu(BF₄)₂ [21], and Fe/SBA-15 [22].

Although these methods have brought good progress, some of them are accompanied with disadvantages such as expensive reagents, the need to use non-recyclable catalytic systems, large amounts of the catalyst, and the use of reagents that are toxic to humans and the environment.

Therefore, the introduction of new methods and the use of useful and effective catalysts to perform the acetylation reactions with good efficiency is still under investigation.

Nano dimensions provide excellent conditions for using nanoparticles as the catalysts. Due to the small size of the particles and the high surface area, as well as the easy preparation, low cost, and availability, this capability is created in nano TiO₂ that it can be used as a nanocatalyst [23].

Surface functionalization is used to increase the catalytic activity of nano TiO_2 . In this regard finding the appropriate group to increase the level of activity is highly important. The selected group should have suitable characteristics, and be economical and environmentally friendly. One of the suitable selections for surface functionalization are ionic liquids. The molecular structure of ionic liquids consists of various cations and anions. Usually, the role of a cation is played by a bulky organic compound (with a positive charge), while anions (with a negative charge) are much smaller than cations in terms of volume, and their structure is inorganic or organic [24]. By the use of energetic species as anions or cations, ionic liquids can be changed to energetic materials [25].

Despite the advantages, such as high thermal stability, low vapor pressure, and ionic conductivity [26], there are also problems when working with ionic liquids. For example, the high viscosity of these compounds makes it necessary to use higher amounts of these compounds. Also, in most cases, the recycling of ionic liquids is time-consuming and causes some of them to be wasted. Stabilization of ionic liquids on suitable supports can solve the problems of working with them. With this method, the benefits of ionic liquids are preserved and, at the same time, their disadvantages such as catalyst reuse, recovery problems, high catalyst consumption, and high cost are eliminated [27]. Considering the properties and characteristics of titanium dioxide and ionic liquids, in this research we designed and synthesized a new nanocatalyst by the immobilization of an ionic liquid on titanium dioxide nano particles. After characterization the prepared reagent which is formulated as $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ was used in the efficient promotion of the acetyl protection of amines and alcohols in order to solve some of the problems which are associated with the use of other catalysts in the same reactions.

2. Experimental

2.1 General

Chemicals and solvents were purchased from Fluka, Merck, and Aldrich Chemical Companies. Titanium tetraisopropoxide (98%), 1,4-dichlorobutane (98%), and 3-aminopropyltrimethoxysilane (95%) were used during the catalyst preparation process. Amines and alcohols with

a purity of 92-98% have been used for the synthesis of the requested target molecules. All the reactions are monitored by thin-layer chromatography (TLC) with UV light as a detecting agent.

2.2 Instrumentation

The ^1H NMR and ^{13}C NMR were run on a 400MHz Bruker Avance in DMSO-d_6 using TMS as an internal standard. The FT-IR spectra were recorded with a VERTEX 70 (Bruker, Germany) instrument using KBr pellets for the samples in the range of $4000\text{-}400\text{ cm}^{-1}$. Energy dispersive spectrometer (EDS) and field emission scanning electron microscopy (FESEM) were performed on a TESCAN model MIRA ii and MIRA iii respectively (Czech Republic). Thermogravimetric analyses (TGA) were performed on Polymer Laboratories PL-TGA thermal analysis instrument. Samples were heated from 25 to 600°C at a ramp of $20^\circ\text{C}/\text{min}$ under N_2 atmosphere (America). X-ray diffraction (XRD) measurements were performed at room temperature on diffractometer Model XRD 6000, PHILIPS Xpert pro using $\text{Co-K}\alpha$ radiation ($K=1.54056\text{ \AA}$) with voltage 40 kV and current 30 mA in a 2 h range of $10\text{-}70^\circ$ with step size 0.01° and time step 1.0 s to assess the crystallinity of the catalyst (Netherlands).

2.3 Preparation of nanoporous TiO_2

The required amounts of titanium tetraisopropoxide (TTIP) was mixed with ethanol (TTIP: EtOH with a ratio of 1:4). Then, deionized water was slowly added to the resulting mixture (TTIP: water with a ratio of 1: 10), and the stirring was maintained for 2 h to hydrolyze TTIP completely. The prepared material was separated by filtration, washed with water, and dried at 80°C . Finally, the obtained solid was placed in a furnace at 500°C for 3 hours to obtain nanoporous TiO_2 (Fig. 1) [28].

2.4 Preparation of $\text{N}^1\text{-N}^4\text{-bis(3-(trimethoxysilyl)propyl)butane-1,4-diammonium trinitromethanide on titanium dioxide nano particles TiO}_2\text{- Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$

To prepare the catalyst, first, 1,4-dichlorobutane (2 mmol) was added to 3-aminopropyltrimethoxysilane (4 mmol) in acetonitrile (10 mL) and the reaction mixture was refluxed for 12 hours. The solid powder obtained was separated by

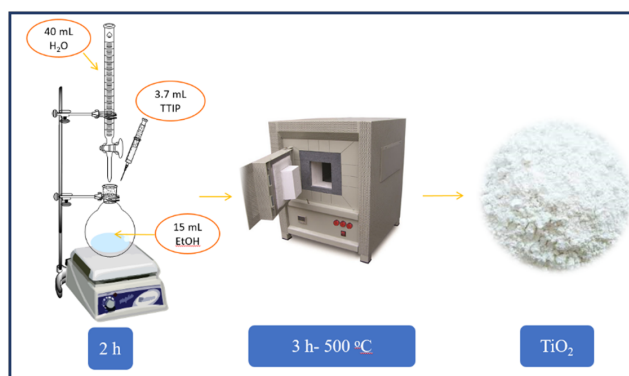


Figure 1. Preparation of nanoporous TiO_2 .

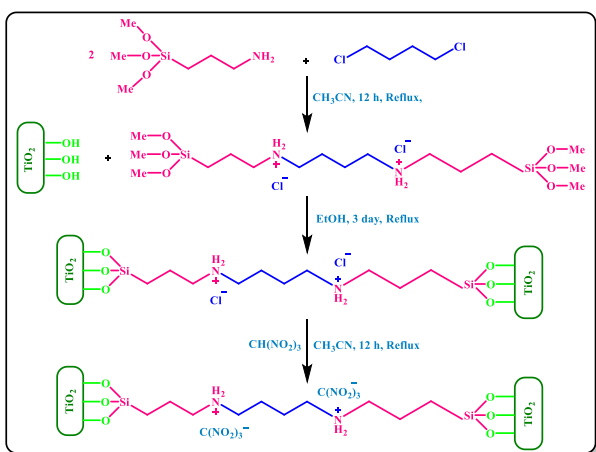
filtration, washed with diethyl ether (20 mL), and dried in an oven [29]. Then, the prepared ionic liquid (1 mmol) was added to nano titanium dioxide (1 g) in ethanol solvent (10 mL) and the reaction mixture was refluxed for 3 days. After the separation and drying of the reaction mixture, trinitromethane (2 mmol) in acetonitrile (10 mL) was added to the white powder obtained and after 24 hours of reflux, the reaction mixture was filtered and washed with diethyl ether (20 mL) and dried in an oven (Scheme 1).

2.5 General procedure for the acetylation of amines

To a mixture of 4-chloroaniline (1 mmol) and acetic anhydride (1.5 mmol), $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ (20 mg) was added and the resulting mixture was stirred at room temperature. The progress of the reaction was monitored by thin-layer chromatography (TLC) using a mixture of *n*-hexane: ethyl acetate (7:3) as the eluent. After the completion of the reaction, ethyl acetoacetate (10 mL) was added to the reaction mixture, and the catalyst was isolated by filtration. The organic phase was washed with water (2×20 mL) and the excess water was dried with Na_2SO_4 . After filtering and evaporating the solvent under vacuum, the desired products were obtained with high yields.

2.6 General procedure for the acetylation of alcohols

$\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ (20 mg) was added to a mixture of benzylalcohol (1 mmol), and acetylchloride (1.5 mmol) in a round bottom flask and the reaction mixture was stirred at 50°C . After completion of the reaction (monitored by TLC) using a mixture of *n*-hexane: ethyl acetate (7:3) as the eluent), ethyl acetate (10 mL) was added to the reaction mixture and the $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ catalyst was isolated by filtration. The organic phase was washed with water (2×20 mL) and the excess water was dried with Na_2SO_4 . After filtering and evaporating the solvent under vacuum, the desired products were obtained with good to high yields.



Scheme 1. Preparation of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$.

3. Results and Discussion

3.1 Characterization of the catalyst

3.1.1 FT-IR analysis

In Figure 2, the FT spectra of TiO_2 , $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+]$ and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ are compared with each other. In the FT-IR spectrum of TiO_2 , the peak related to the Ti-O-Ti stretching vibrations can be seen in the region of 659 cm^{-1} [30]. In this spectrum, the peaks located in the region of 1630 and 3431 cm^{-1} are related to the stretching vibrations of O-H of the absorbed surface water and the hydroxyl groups present on the surface [31]. In the spectrum related to $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+]$, the peak in the region of 1037 cm^{-1} and the peak in the region of 1127 cm^{-1} can be attributed to the stretching vibrations of Si-O and the bending vibrations of C-C-C, respectively. Also, in this spectrum, C-H and N-H stretching vibrations are appeared in the regions of 2960 and 3428 cm^{-1} , respectively [29]. In the spectrum related to the final catalyst, the peaks appearing in the 1384 and 1630 cm^{-1} regions are related to the symmetric and asymmetric stretching vibrations of the NO_2 group [32]. The set of information obtained from the spectra confirms the successful preparation of the catalyst to an acceptable extent.

3.1.2 Thermal analysis

The thermal stability of TiO_2 and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ was investigated using thermal analysis (Fig. 3). The TGA curve obtained for TiO_2 shows a slight weight loss below 100°C that occurs due to the removal of moisture. In the case of this compound, the curve is uniform up to the temperature of 600°C , which indicates the high thermal resistance of TiO_2 . The TGA curve of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ shows a different shape

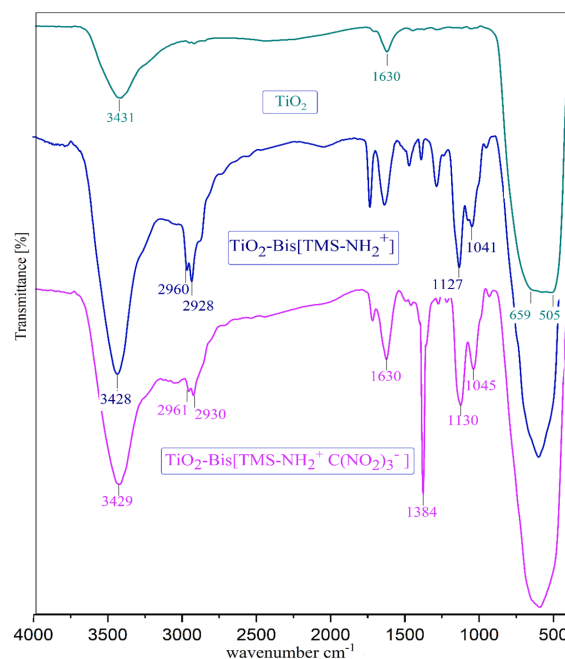


Figure 2. FT-IR spectra of TiO_2 , $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+]$ and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$.

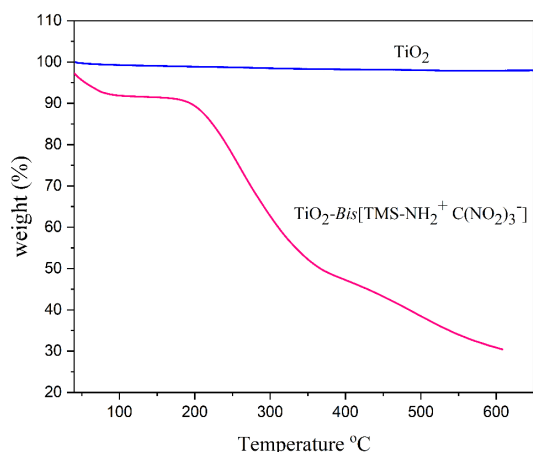


Figure 3. TGA curve of TiO_2 and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$.

compared to TiO_2 . Its low mass reduction at temperatures below 100°C can be related to the removal of the absorbed surface water. The second mass reduction that occurred at temperatures from 200 to 350°C can be due to the removal of the trinitromethane groups, and the thermal degradation of the catalyst that occurred after 350°C can be attributed to the decomposition of the organic part of the ionic liquid stabilized on the surface of TiO_2 .

3.1.3 Powder X-ray diffraction

The X-ray diffraction pattern (XRD) of TiO_2 and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ is shown in Figure 4. According to the evidence, it can be said that the intensity and position of the peaks in the substrate and the synthesized catalyst are the same, indicating that the phase of the TiO_2 substrate has not changed after its modification during the preparation of the catalyst.

3.1.4 Energy Dispersive Spectrometer (EDX)

In addition to the mentioned cases, the data obtained from the energy-dispersive X-ray analysis (EDS) of the new heterogeneous catalyst shows the presence of all the expected

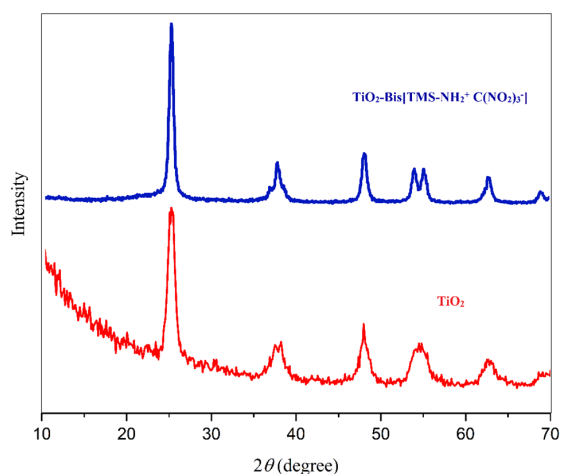


Figure 4. XRD patterns of TiO_2 and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$.

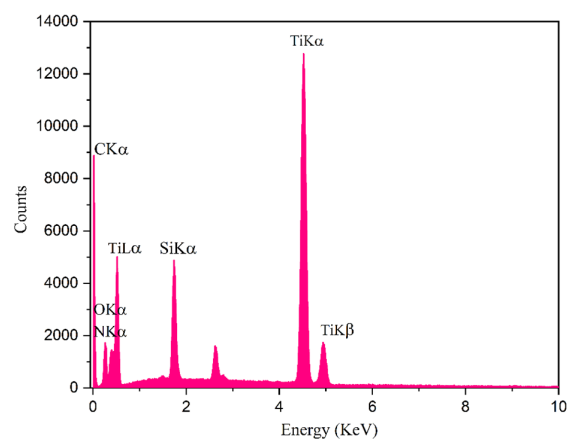


Figure 5. The EDX profiles of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$.

elements including carbon, nitrogen, oxygen, titanium, and silicon in the catalyst (Fig 5).

3.1.5 Field emission scanning electron microscopy (FE-SEM)

Samples of TiO_2 and the synthesized catalyst were also studied and analyzed with the help of field emission scanning electron microscope analysis. Figures 6 a, b, and 6 c, d show the FESEM images of TiO_2 and the synthesized catalyst, respectively. From the comparison of the obtained images, it can be concluded that although the initial morphology remains unchanged, the size of TiO_2 nanoparticles has changed and increased after the reaction with the ionic liquid. This increase in the particle size can be related to the incorporation of the ionic liquid linkages in the nano TiO_2 layers.

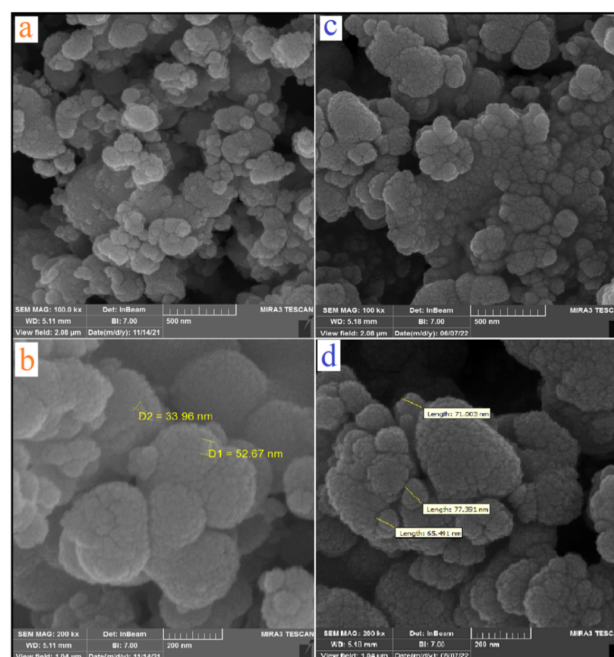


Figure 6. FESEM images of TiO_2 (a, b) and $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+ \text{C}(\text{NO}_2)_3^-]$ (c, d).

3.2 Catalytic activity

After performing various identification methods and making sure that the desired reagent was synthesized, and in order to check the activating ability of the prepared sample, it was used in the acetylation reactions of amines and alcohols.

Next, to find the optimal conditions, the reaction of 4-chloroaniline with acetic anhydride was selected as a model reaction, and the effect of various factors including temperature, solvent, amounts of the catalyst, and amounts of acetic anhydride was investigated. Finally, the obtained results showed that the best results can be achieved when the reaction has proceeded using 20 mg of catalyst $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$ and 1.5 mmol of acetic anhydride (for each NH group) at room temperature in the absence of solvent (Table 1, entry 5) (Scheme 2). Then, the obtained optimal conditions were applied for the acetylation of different types of aromatic amines. By utilizing this method, aromatic amines with electron-donating and electron-withdrawing groups in *ortho*, *meta*, and *para* positions, can be converted to their corresponding protected forms in very short times with high yields. The reasonable mechanism for the acetylation of amines is shown in Scheme 3. Based on this, the $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$ catalyst first activates the carbonyl group of acetic anhydride making it ready for the nucleophilic attack of the amine group to form the corresponding acetamide. After the good results obtained from the acetylation of amines in the presence of the used nano catalyst, we decided to study the acetylation of different alcohols. Our studies showed that the alcoholic hydroxyl groups cannot be effectively acetylated under the conditions used for the protection of amines using acetic anhydride. So, acetyl chloride was selected for this purpose.

Firstly, to optimize the reaction conditions, the effect of different amounts of the catalyst, temperature, amounts of acetyl chloride, and the presence and absence of solvent on the reaction of benzyl alcohol and acetyl chloride was studied (Table 3). The results clarified that the best conditions to perform the requested reaction are the conditions shown in Scheme 4. In the next step, several different benzyl alcohols were reacted under optimal conditions in the presence of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$ and the results are collected in Table 4. This table shows that in

this case, all types of alcohols containing electron-donating and electron-withdrawing groups are successfully converted to their corresponding products in good to excellent yields during short reaction times. The proposed mechanism for the acetylation of alcohols is given in Scheme 5. Based on this, at the first step, the catalyst activates the carbonyl group of acetyl chloride and makes it susceptible to the attack of the alcohol leading to the production of the final acetylated product. Table 5 compares the efficiency of some of the previously reported procedures and our new catalyst in the studied acetylation reactions. According to this table, $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$ is a suitable catalyst in terms of time, efficiency, and reaction conditions in comparison with the other catalysts. Also, the reusability of the catalyst was investigated in the model reaction of the amines under the related optimized reaction conditions. For this purpose and after the completion of the reaction, the catalyst was isolated according to the method explained in the experimental section and subsequently used in the same reaction. As shown in Figure 7, the catalyst can be reused at least 4 times without significant changes in the reaction efficiency.

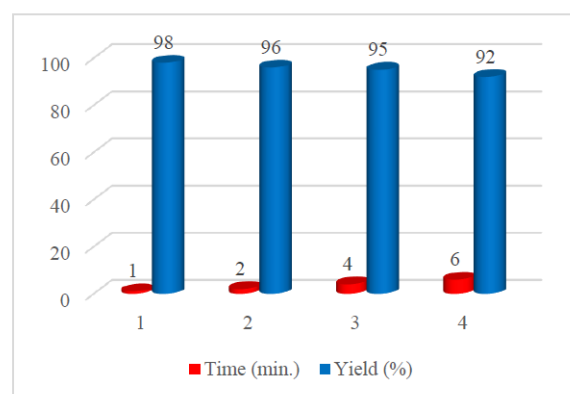




















Figure 7. Reusability of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$ in the acetylation of 4-chloroaniline with Ac_2O .

Table 1. Optimization experiments for the *N*-acetylation of 4-chloroaniline in the presence of $\text{TiO}_2\text{-Bis}[\text{TMS-NH}_2^+\text{C}(\text{NO}_2)_3^-]$.

Entry	Catalyst (g)	Ac_2O (mmol)	Solvent	Time (min.)	Yields (%)
1	-	1	-	15	30
2	0.012	1	-	15	50
3	0.020	1	-	15	50
4	0.020	1.2	-	5	90
5	0.020	1.5	-	1	98
6	0.020	1.5	H_2O	5	98
7	0.020	1.5	EtOH	3	98

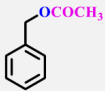
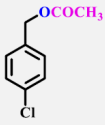
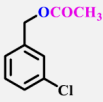
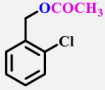
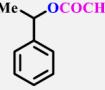
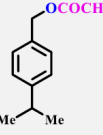

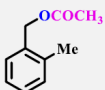
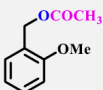
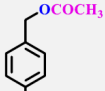
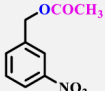
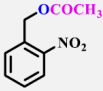
Table 2. *N*-Acetylation of various aniline derivatives with Ac₂O in the presence of TiO₂-Bis [TMS-NH₂⁺C(NO₂)₃⁻]^{[a][b]}.

 Immediately, 98% Ref: [33]	 Immediately, 98% Ref: [33]	 Immediately, 96% Ref: [34]
 Immediately, 98% Ref: [35]	 Immediately, 94% Ref: [37]	 Immediately, 95% Ref: [33]
 Immediately, 94% Ref: [33]	 Immediately, 97% Ref: [38]	 Immediately, 95% Ref: [39]
 Immediately, 94% Ref: [40]	 Immediately, 96% Ref: [36]	 Immediately, 95% Ref: [33]
 Immediately, 97% Ref: [17]	 Immediately, 95% Ref: [41]	 Immediately, 94% Ref: [42]
 Immediately, 92% Ref: [43]	 Immediately, 95% Ref: [44]	 5 min., 95% Ref: [36]

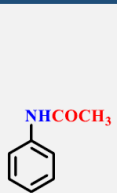
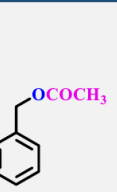
^[a] Immediately means ≤ 3 min.^[b] Yields refer to the isolated pure products.**Table 3.** Optimization experiments for the *O*-acetylation of benzylalcohol in the presence of TiO₂-Bis [TMS-NH₂⁺C(NO₂)₃⁻].

Entry	Catalyst (g)	CH ₃ COCl (mmol)	Temperature (°C)	Solvent	Time (min.)	Yields (%)
1	-	1	-	-	15	30
2	0.012	1	-	-	15	50
3	0.020	1	-	-	15	70
4	0.020	1.5	-	-	5	85
5	0.020	1.5	50	-	2	95
6	0.020	1.5	-	H ₂ O	10	70
7	0.020	1.5	-	EtOH	10	70

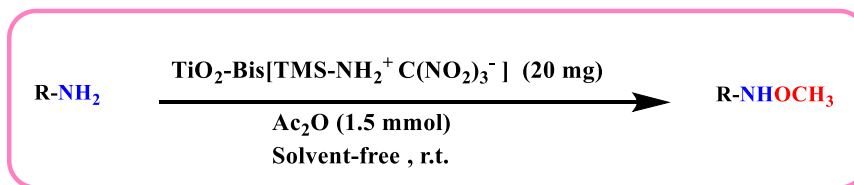
Table 4. *O*-Acetylation of various alcohols with CH₃COCl in the presence of TiO₂-Bis [TMS-NH₂⁺C(NO₂)₃⁻]^{[a][b]}.

 Immediately, 95% Ref: [33]	 5 min., 95% Ref: [33]	 Immediately, 96% Ref: [45]
 Immediately, 95% Ref: [46]	 Immediately, 98% Ref: [33]	 Immediately, 95% Ref: [46]
 Immediately, 98% Ref: [47]	 Immediately, 93% Ref: [48]	 Immediately, 95% Ref: [49]
 4 min., 94% Ref: [33]	 Immediately, 92% Ref: [17]	 Immediately, 95% Ref: [17]

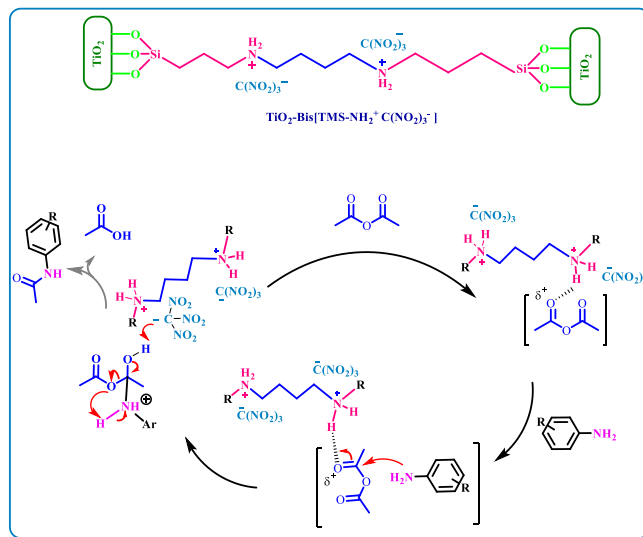
^[a] Immediately means ≤ 3 min.^[b] Yields refer to the isolated pure products.**Table 5.** Comparison of the reduction of *N*-acetylation of aniline and *O*-acetylation of benzyl alcohol by TiO₂-Bis[TMS-NH₂⁺C(NO₂)₃⁻] and other reported catalyst systems.

Product	Catalyst (amounts)	Molar ratio	Reaction conditions	Time (min.)	Yield (%) ^[a]	[Ref.]
	SiO ₂ /PDA-SO ₃ H (1 mol %)	(1:2)	Solvent-free/r.t.	60	96	[33]
	AgNPs (1 mmol)	(1:1/2)	Solvent-free/50 °C	60	94	[34]
	nano γ-Fe ₂ O ₃ (5 mol %)	(1:1/5)	Solvent-free/r.t./U.S.	60	95	[35]
	Fe ₃ O ₄ @PDA-SO ₃ H (2 mol %)	(1:1/5)	Solvent-free/r.t.	30	96	[36]
	Gd(OTf) ₃ (0.1 mol %)	(1:1/2)	CH ₃ CN/r.t.	15	88	[37]
	TiO ₂ (0.020 g)	(1:1/5)	Solvent-free/r.t.	4	95	[This work]
	TiO ₂ -Bis[TMS-NH ₂ ⁺ C(NO ₂) ₃ ⁻] (0.020 g)	(1:1/5)	Solvent-free/r.t.	1	98	[This work]
	nano γ-Fe ₂ O ₃ (5 mol %)	(1:1/5)	Solvent-free/r.t./U.S.	40	64	[35]
	ZnO (10 mol %)	(1:1/2)	Solvent-free/r.t.	10	93	[36]
	ZrOCl ₂ ·8H ₂ O (0.5 mol %)	(1:2)	CH ₂ Cl ₂ /r.t.	5	95	[38]
	BiFeO ₃ (100 mg)	(1:1)	Solvent-free/r.t.	12	92	[39]
	TiO ₂ (0.020 g)	(1:1/5)	Solvent-free/50 °C	5	90	[This work]
TiO ₂ -Bis[TMS-NH ₂ ⁺ C(NO ₂) ₃ ⁻] (0.020 g)	(1:1/5)	Solvent-free/50 °C	2	95	[This work]	

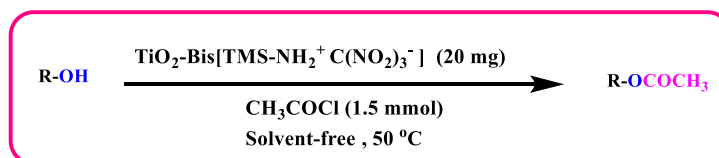
^[a] Isolated yields.



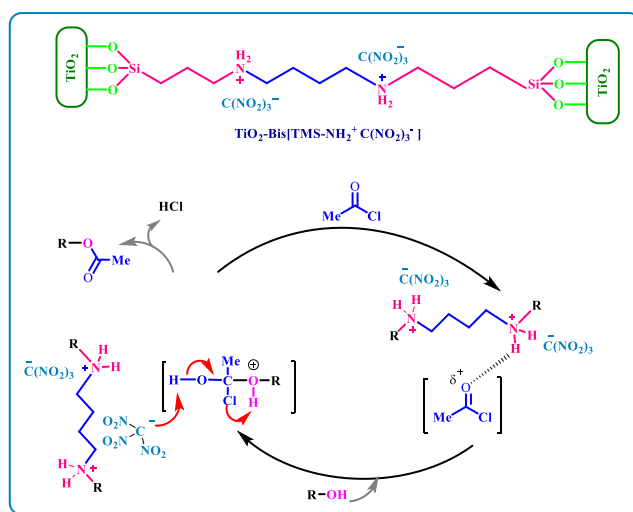
Scheme 2. *N*-Acetylation of anilines with Ac₂O in the presence of TiO₂-Bis[TMS-NH₂⁺ C(NO₂)₂]⁻.



Scheme 3. The proposed mechanism for acetylation of amines utilizing TiO₂-Bis [TMS-NH₂⁺ C(NO₂)₃⁻].



Scheme 4. The proposed mechanism for acetylation of alcohols utilizing TiO₂-Bis [TMS-NH₂⁺ C(NO₂)₃⁻].



Scheme 5. The proposed mechanism for acetylation of alcohols utilizing TiO₂-Bis [TMS-NH₂⁺ C(NO₂)₃⁻].

4. Conclusion

In the present study, N^1-N^4 -bis (3-(trimethoxysilyl) propyl) butane-1,4-diammonium trinitromethanide on titanium dioxide employed as a new efficient nano catalyst for the acetylation of amines and alcohols. All reactions are performed under mild conditions in short reaction times with good to high yields in the absence of solvent. High catalytic activity, easy work-up, easy separation, and the reusability of the catalyst are the other significant advantages of the proposed method.

Acknowledgments

The authors are thankful to the University of Guilan Research Council for helping to do this work.

Authors Contributions

All authors have contributed equally to prepare the paper.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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