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Short Communication

# Nano titania-supported sulfonic acid: An efficient and reusable catalyst for a range of organic reactions under solvent free conditions



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#### ARTICLE INFO

#### ABSTRACT

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#### 1. Introduction

In accordance with the principles of green chemistry, the design of easily separable, reusable, non-toxic, low cost, and insoluble acidic catalysts has become an important area of research in chemistry [1]. In this context, the use of nanoparticles as heterogeneous catalysts has attracted considerable attention because of the interesting structural features and high levels of catalytic activity associated with these materials [2]. Furthermore, nanoparticle materials are considered to be a bridge between homogeneous and heterogeneous catalysts [3]. The application of nanoparticles has extended to almost all possible fields of science ranging from medicine to rocketry.

Among various nanoparticles, nano  $TiO_2$  has been widely investigated over the past few decades due to its multiple potential applications such as catalytic activity for esterification [4], catalyst support for proton exchange membrane fuel cells [5], sono catalytic degradation of methyl parathion [6], photodecomposition of methylene-blue by highly dispersed on Ag [7], catalyst for rhodamine B degradation [8], synthesis of dibenzo[a,j]xanthenes [9], polyhydroquinoline [10], 1,8-dioxooctahydroxanthenes [11], crosslinking of cotton cellulose with succinic acid under UV [12] and synthesis of  $\beta$ -acetamido ketones [13].

Based on the above, we decided to improve the catalytic properties of nano-TiO<sub>2</sub> by reacting it with chlorosulfonic acid to produce nano-titania sulfonic acid (n-TSA) (Scheme 1). Sulfonation with chlorosulfonic acid is a convenient, fast and efficient method for Brønsted acid fictionalization

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of different compounds [2,14,15] that has attracted much attention after Zolfigol's report on the preparation of silica sulfuric acid [16].

#### 2. Experimental section

arated and reused for several runs without appreciable loss of its catalytic activity.

#### 2.1. Characterization methods of nano-TiO<sub>2</sub>-SO<sub>3</sub>H (n-TSA)

#### 2.1.1. X-ray diffraction spectrum

Nano titania-supported sulfonic acid (n-TSA) has been easily prepared from the reaction of nano titania (titanium

oxide) with chlorosulfonic acid as sulfonating agent and characterized by the FT-IR spectroscopy, scanning elec-

tron microscopy (SEM), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA). The catalytic activity of

n-TSA was investigated in the synthesis of important organic derivatives such as pyrimidones, benzothiazoles

and chalcones. All of the reactions are very fast and the yields are good to excellent. The catalyst was easily sep-

Wide angle X-ray diffraction spectrum for the n-TSA powder sample was obtained utilizing a Bruker D8 X-ray diffractometer using Cu-Ka radiation of wavelength 1.54 Å.

#### 2.1.2. Scanning electron microscopy

The particle size study of n-TSA samples was carried out using BAL-TEC SCD 005 scanning electron microscope instrument operating at 10 kV. The sample was mounted on a double sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample charging problems.

#### 2.1.3. Infrared spectra

The n-TSA sample was mixed with KBr powder and compressed into pellet, wherein, the n-TSA powder was evenly dispersed. Fourier transform infrared spectrum was recorded on Shimadzu FT-IR 8400 instrument.

#### 2.1.4. Thermo gravimetric analyses

Thermo gravimetric analyses (TGA) were conducted on a Du Pont 2000 thermal analysis apparatus under air atmosphere at a heating rate of 5  $^{\circ}$ C/min.





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nano-TiO<sub>2</sub> + CISO<sub>3</sub>H 
$$\longrightarrow$$
 nano-TiO<sub>2</sub>-SO<sub>3</sub>H

Scheme 1. Preparation of n-TSA.



Fig. 1. The X-ray diffraction patterns of the (a) nano-TiO<sub>2</sub> powder, (b) n-TSA.

#### 2.2. Preparation of nano-TiO<sub>2</sub>-SO<sub>3</sub>H (n-TSA)

A suspension of titania nanoparticles (4 g) in dry  $CH_2Cl_2$  (20 mL) was added to a suction flask that was equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water). Then chlorosulfonic acid (CAUTION: a highly corrosive and water-absorbent. Be careful when using this liquid. Protective gloves, protective clothing and eye and face protection equipment are also needed.) (1 mL, 15 mmol) was added dropwisely over a period of 30 min at room temperature while the mixture was stirred slowly in an ice bath. HCl gas immediately evolved from the reaction vessel. Stirring was continued until HCl evolution was seized. After the addition was completed, the mixture was stirred for 30 min. A white solid of nano titania-supported sulfonic acid was obtained. Then, the  $CH_2Cl_2$  was removed under reduced pressure and the solid powder was washed with ethanol (10 mL) and dried at 70 °C.

The n-TSA was stored in vacuum desiccator over anhydrous silica gel. Then, it was dried at 120 °C for 6 h. The mmol of  $H^+$  per gram of catalyst (4.5 mmol/g of n-TSA) was determined by the methodology

described in the literature [17]. For this purpose, the surface acidic protons of nano-TiO<sub>2</sub>–SO<sub>3</sub>H (100 mg) were ion-exchanged with a saturated solution of NaCl (10 mL) by sonication. This process was repeated twice more, yielding 30 mL of proton-exchanged brine solution. Therefore, to determine the loading of acid sites on the synthesized catalyst, the solution obtained was titrated with NaOH (0.1 M) solution in presence of phenol red indicator solution or by using a pH meter.

#### 2.3. General procedure for synthesis of pyrimidinone derivatives

In a typical experiment, aromatic aldehyde (1 mmol), cyclopentanone (1 mmol), urea or thiourea (1.2 mmol) and n-TSA (0.032 g) under solvent free conditions were taken in a 25 mL round bottomed flask and was stirred at 70 °C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL) and was centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure pyrimidinone derivatives.

#### 2.4. General procedure for preparation of benzothiazole derivatives

In a typical experiment, aromatic aldehyde (1 mmol), 2aminothiophenol(1 mmol) and n-TSA (0.032 g) under solvent free conditions were taken in a 25 mL round bottomed flask and were stirred at 70 °C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL) and was filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure benzothiazole derivatives.

#### 2.5. General procedure for preparation of chalcone derivatives

In a typical experiment, aromatic aldehyde (1 mmol), acetophenone (1 mmol) and n-TSA (0.032 g) under solvent free conditions were taken in a 25 mL round bottomed flask and were stirred at 70 °C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL) and was filtrated to collect the precipitate. The crude product was recrystallized from ethanol to yield pure chalcone derivatives.

#### 3. Results and discussion

#### 3.1. Characterization of nano-TiO<sub>2</sub>-SO<sub>3</sub>H

#### 3.1.1. X-ray diffraction spectra

The nano-TiO<sub>2</sub> powder can be easily synthesized by a hydrothermal method as reported in the literature [18]. Fig. 1a shows the XRD patterns of nano-TiO<sub>2</sub> powder before modification. The following signals at (101), (103), (004), (112), (200), (105), (211), (204), (220), (215) and (224) in Fig. 1a planes confirm that only the anatase crystal phase



Fig. 2. The SEM image of the (a) nano-TiO<sub>2</sub> powder, (b) n-TSA.



Fig. 3. The FT-IR spectra of (a) nano-TiO<sub>2</sub> powder and (b) n-TSA.

is formed, which conforms with the JCPD 89-4921 standard. The estimated crystalline size of titanium dioxide nanoparticles was also determined from X-ray line broad using the Debye-Scherrer formula given as  $t = 0.9\lambda/B_{1/2}\cos\theta$ , where t is the average crystalline size,  $\lambda$  is the X-ray wavelength used (1.54 Å), B is the angular line width at half maximum intensity and  $\theta$  is the Bragg's angle. The average size of the nano-TiO<sub>2</sub> powder for  $2\theta = 25.303^{\circ}$  is estimated to be around 21.88 nm. Fig. 1b illustrates XRD patterns of the samples of modified nano TiO<sub>2</sub>. As shown in Fig. 1b, the main peaks of modified nano TiO<sub>2</sub> are the same as nano  $TiO_2$  (Fig. 1a) i.e. the main phase of the XRD pattern has not been changed and it indicates that chlorosulfonic acid has not influenced the crystallinity phase of TiO<sub>2</sub>. As it was expected, the reaction between chlorosulfonic acid and nano-TiO<sub>2</sub> for modification by SO<sub>3</sub>H groups was carried out on the surface of nano-TiO<sub>2</sub> and the crystallinity of nano-TiO<sub>2</sub> has not been changed. This fact is illustrated by comparison between XRD pattern of nano-TiO<sub>2</sub> and n-TSA.

#### 3.1.2. Scanning electron microscopy

The scanning electron microscopy (SEM) analysis of nano  $TiO_2$  powder reveals the spherical nano  $TiO_2$  powder with average size 20–30 nm (Fig. 2a). As shown, the SEM analysis of n-TSA reveals the spherical n-TSA powder with average size 35–60 nm (Fig. 2b).

#### 3.1.3. FT-IR spectra

The FT-IR spectra of nano  $TiO_2$  powder and n-TSA are shown in Fig. 3. The absorbance bands at around 3200–3500 cm<sup>-1</sup> were attributed to the adsorbed water in nano  $TiO_2$  (Fig. 3a) and n-TSA (Fig. 3b). The broad intense band below 1200 cm<sup>-1</sup> is due to Ti-O-Ti vibration which is consistent with the reported IR spectra for nano  $TiO_2$  [19]



Fig. 4. TGA curve of (a) nano-TiO<sub>2</sub> and (b) n-TSA.



Fig. 5. Absorption spectra of (a) 4-nitroaniline (indicator) and (b) n-TSA (catalyst) in CCl<sub>4</sub>.

(Fig. 3a). In Fig. 3b, the absorption range in 1176–1284 and 1006–1088 cm<sup>-1</sup> was certified the O=S=O asymmetric and symmetric stretching modes lies respectively and the S–O stretching mode lies in 675–852 cm<sup>-1</sup> showing the presence of sulfonic acid functional group which is consistent with the reported IR spectra for -SO<sub>3</sub>H [20].

#### 3.1.4. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) of n-TSA in comparison with nano TiO<sub>2</sub> is shown in Fig. 4. The TGA curve of TiO<sub>2</sub> (Fig. 4a) displays a weight loss (4 wt.%) below 100 °C which corresponds to the loss of the physically adsorbed water. Also, there is a slight weight loss (1 wt.%) between 100 °C and 800 °C, which possibly corresponds to the dehydroxylation of TiO<sub>2</sub> as has already been reported in the literature for similar case [21].

In the TGA curve of n-TSA (Fig. 4b), three regions corresponding to different mass lose ranges exist. The first region is below 150 °C that displayed a mass loss that was attributable to the loss of trapped water from the catalyst. A mass loss of approximately 5% weight occurred between 150 and 400 °C that is related to the slow mass loss of SO<sub>3</sub>H groups. Finally, a mass loss of approximately 10% weight occurred between 400 and 570 °C that is related to the sudden mass loss of SO<sub>3</sub>H groups [20,22,23]. Also, from the TGA, it is understood that n-TiO<sub>2</sub>–SO<sub>3</sub>H has a greater thermal stability (until 300 °C) confirming that it can be safely used in organic reactions at temperatures in the range of 80–150 °C.

#### 3.1.5. Surface acidity studies

The Hammett acidity function  $(H_0)$  can effectively express the acidity strength of an acid in organic solvents [24]. It can be calculated using the following equation:

$$\mathbf{H}_{0} = \mathbf{p}\mathbf{K}(I)_{aq} + \log\left([\mathbf{I}]_{s}/[\mathbf{I}\mathbf{H}^{+}]_{s}\right).$$

'I' represents the indicator base and  $[I]_s$  and  $[IH^+]_s$  are respectively the molar concentrations of the unprotonated and protonated 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 the Lambert–Beerlaw, the value of  $[I]_s/[IH^+]_s$  can be determined and calculated using the UV–visible spectrum. In the present experiment, 4-nitroaniline was chosen as the

Table 1Calculation of Hammett acidity function  $(H_0)$  of n-TSA.

Entry	Catalyst	A <sub>max</sub>	[I] <sub>s</sub> (%)	$[IH^{+}]_{s}$ (%)	Ho
1	-	1.83	100	0	-
2	n-TSA	0.473	25.35	74.65	1.12

Condition for UV–visible spectrum measurement: solvent, CCl<sub>4</sub>; indicator, 4-nitroaniline (pK(I)<sub>*aq*</sub> = 0.99), 1.44 \* 10<sup>-4</sup> mol/L; catalyst, n-TSA (20 mg), 25 °C.



Scheme 2. Synthesis of pyrimidinone derivatives.

basic indicator and CCl<sub>4</sub> was chosen as the solvent because of its aprotic nature. The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 329 nm in CCl<sub>4</sub>. As Fig. 5 shows, the absorbance of the unprotonated form of the indicator in n-TiO<sub>2</sub>–SO<sub>3</sub>H was weak as compared to the sample of the indicator in CCl<sub>4</sub>, which indicated that the indicator was partially in the form of [IH<sup>+</sup>]. The results obtained are listed in Table 1, which shows the acidity strength of n-TiO<sub>2</sub>–SO<sub>3</sub>H.

## 3.2. Using nano-TiO<sub>2</sub>–SO<sub>3</sub>H as a new heterogeneous solid acid nano catalyst in some organic reaction

In the present study, to justify the efficiency of the new catalyst and in continuation of the studies on developing inexpensive and environmentally benign methodologies for synthesis of heterocyclic compounds and organic reactions [25,26], it has been decided to investigate the possibility of synthesizing some of organic reactions by one-pot condensation reaction strategy in presence of n-TSA under solvent free conditions.

#### 3.2.1. Biginelli reaction for synthesis of pyrimidinone derivatives

In this study, to justify the efficiency of the new catalyst for synthesis of pyrimidinones (Scheme 2), it was compared by some other titanium dioxide base such as nano TiO<sub>2</sub>, bulk TiO<sub>2</sub> and modified bulk TiO<sub>2</sub> (prepared by reported procedure [27]) which gave the desired product in 25–78% yield, respectively. The results obtained indicate clearly that n-TSA performed well to give the desired product within 0.75 h in 91% yield at 90 °C in solvent free condition. The greater catalytic activity of n-TSA was most likely related to the SO<sub>3</sub>H groups of the catalyst, which could provide efficient acidic sites.

The achieved results of optimization of other conditions showed that the best yield was obtained at 70 °C and under solvent free conditions. Synthesis of pyrimidinone derivatives was also studied (Table 2). All

#### Table 2

Synthesis of pyrimidinone derivatives by n-TSA<sup>a</sup>.

Entry	Ar	Х	Product	Time (h)	Yield <sup>b</sup> (%)
1	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	0	4a	0.75	95
2	3b: 2-Cl-C <sub>6</sub> H <sub>4</sub>	0	4b	1.5	86
3	3c: 4-Cl-C <sub>6</sub> H <sub>4</sub>	0	4c	1.25	84
4	<b>3f</b> : 4–F–C <sub>6</sub> H <sub>4</sub>	0	4d	1.25	83
5	3g: 4-Br-C <sub>6</sub> H <sub>4</sub>	0	4e	1.25	89
6	<b>3h</b> : 4-Me-C <sub>6</sub> H <sub>4</sub>	0	4f	1	94
7	3i: 4-MeO-C <sub>6</sub> H <sub>4</sub>	0	4g	1	93
8	3k: 3-02N-C6H4	0	4h	2.5	83
9	3m: 2-Naphthyl	0	<b>4</b> i	1.5	82
10	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	S	4j	1	96
11	3b: 2-Cl-C <sub>6</sub> H <sub>4</sub>	S	4k	2	86
12	3c: 4-Cl-C <sub>6</sub> H <sub>4</sub>	S	41	1.5	92
13	<b>3f</b> : 4–F–C <sub>6</sub> H <sub>4</sub>	S	4m	1.6	86
14	3g: 4-Br-C <sub>6</sub> H <sub>4</sub>	S	4n	1.4	89
15	<b>3h</b> : 4–Me–C <sub>6</sub> H <sub>4</sub>	S	40	1	91
16	3i: 4-MeO-C <sub>6</sub> H <sub>4</sub>	S	4p	1	93
17	3k: 3-02N-C6H4	S	4q	3.5	79
18	31: 4-0 <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub>	S	4r	3	91
19	<b>3m</b> : 2-Naphthyl	S	4s	1.5	87

Bold values indicate that the 3a-3m identify different aldehydes and 4a-4s identify the pyrimidinone derivatives.

<sup>a</sup> Reaction conditions: aromatic aldehyde (1 mmol), cyclopentanone (1 mmol), urea or thiourea (1.2 mmol) in solvent-free at 70 °C.
 <sup>b</sup> Isolated yield.



Scheme 3. Synthesis of benzothiazole derivatives.

the products were identified by the comparison of the melting point data with those reported in literature [28,29].

Reusability of the catalyst was checked by recovered n-TSA and reused for a five consecutive reactions and obtained the yield 90–95%. It indicates that n-TSA does not lose its activity and can be recycled.

#### 3.2.2. Cyclo condensation for synthesis benzothiazole derivatives

The efficiency of n-TSA for the synthesis of benzothiazoles (Scheme 3) was compared by other titanium dioxide base such as unmodified nano TiO<sub>2</sub>, unmodified bulk TiO<sub>2</sub> and bulk-modified TiO<sub>2</sub>. The best yield achieved by n-TSA (90% yield), whereas bulk-modified TiO<sub>2</sub> provides 65% yield. Synthesis of benzothiazole derivatives was also studied (Table 3). All the products were identified by the comparison of the melting point data with those reported in literature [30–32].

The recyclability of the catalyst was tested with five consecutive synthesis of benzothiazole by using recovered n-TSA and the desired product was obtained in 88–90% yield.

#### 3.2.3. Cyclo condensation for synthesis chalcone derivatives

To determine the productivity of n-TSA for synthesis of chalcones (Scheme 4), it was compared with the titanium dioxide base. Obtained results show that n-TSA (88% yield) is a better option in comparison to the other titanium dioxide base (0–62% yield). Synthesis of different chalcone derivatives were also studied (Table 4). All the products were identified by the comparison of the melting point data with those reported in literature [33–35].

The recyclability of the catalyst was tested with five consecutive synthesis of chalcone by using recovered n-TSA and the desired product was obtained in 86–88% yield.

#### 4. Conclusion

In summary, nano titania-supported sulfonic acid was efficiently used as a heterogeneous catalyst for synthesis of pyrimidinones, benzothiazoles and chalcones under solvent-free conditions. The catalyst was reused for 5 consecutive cycles with consistent activity. The excellent catalytic performance, the easy preparation and

Table 3		
Synthesis of benzothiszole derivatives	hy n	TSA

Entry	Ar	Product	Time (min)	Yield <sup>b</sup> (%)
1	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	6a	30	90
2	3b: 2-Cl-C <sub>6</sub> H <sub>4</sub>	6b	50	84
3	3c: 4-Cl-C <sub>6</sub> H <sub>4</sub>	6c	40	86
4	3d: 2-OH-C <sub>6</sub> H <sub>4</sub>	6d	20	82
5	3e: 4-OH-C <sub>6</sub> H <sub>4</sub>	6e	15	83
6	3f: 4-F-C <sub>6</sub> H <sub>4</sub>	6f	15	86
7	3g: 4-Br-C <sub>6</sub> H <sub>4</sub>	6g	20	86
8	<b>3h</b> : 4–Me–C <sub>6</sub> H <sub>4</sub>	6h	45	90
9	3i: 4-0Me-C <sub>6</sub> H <sub>4</sub>	6i	25	93
10	3j: 2-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	6j	20	81
11	3k: 3-NO2-C6H4	6k	15	86
12	31: 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	61	10	89
13	3m: 2-Naphtyl	6m	20	90
14	3n: Furyl	6n	20	79

Bold values indicate that 3a-3m identify different aldehydes, 7a-7c identify different acetophenones and 8a-8q identify the chalcone derivatives.

<sup>a</sup> Reaction condition: aldehyde (1 mmol), 2-aminothiophenol (1 mmol) and catalyst (0.032 g) in solvent free condition at 70 °C.
 <sup>b</sup> Isolated yield.



Scheme 4. Synthesis of chalcone derivatives.

**Table 4**Synthesis of chalcone derivatives by n-TSA<sup>a</sup>.

Entry	Ar	R(7)	Product	Time (h)	Yield <sup>b</sup> (%)
1	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	7a	8a	1.5	88
2	3b: 2-Cl-C <sub>6</sub> H <sub>4</sub>	7a	8b	2	85
3	3c: 4-Cl-C <sub>6</sub> H <sub>4</sub>	7a	8c	1.8	90
4	3d: 2-OH-C <sub>6</sub> H <sub>4</sub>	7a	8d	1.2	90
5	3e: 4-0H-C <sub>6</sub> H <sub>4</sub>	7a	8e	1	95
6	3f: 4-F-C <sub>6</sub> H <sub>4</sub>	7a	8f	1.8	95
7	3g: 4-Br-C <sub>6</sub> H <sub>4</sub>	7a	8g	1.5	92
8	<b>3h</b> : 4–Me–C <sub>6</sub> H <sub>4</sub>	7a	8h	1	90
9	3i: 4-0Me-C <sub>6</sub> H <sub>4</sub>	7a	8i	.0.75	92
10	3j: 2-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	7a	8j	2	83
11	3k: 3-NO2-C6H4	7a	8k	1.8	85
12	31: 4-NO2-C6H4	7a	81	1.7	89
13	3m: 2-Naphtyl	7a	8 m	1.4	92
14	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	7b	8n	2	90
15	3i: 4-0Me-C <sub>6</sub> H <sub>4</sub>	7b	80	1	91
16	<b>3a</b> : – C <sub>6</sub> H <sub>5</sub>	7c	8p	1.2	86
17	3e: 4-OH-C <sub>6</sub> H <sub>4</sub>	7c	8q	0.8	93

Bold values indicate that 3a-3m identify different aldehydes, 7a-7c identify different acetophenones and 8a-8q identify the chalcone derivatives.

<sup>a</sup> Reaction condition: different aromatic aldehydes (1 mmol), different acetophenones (1 mmol) and catalysts (0.032 g) in solvent free condition at 70 °C.

<sup>b</sup> Isolated yield.

separation of the catalyst make it a good heterogeneous solid acid for organic synthesis and transformations.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.07.002.

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