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- Nano-WO_3-supported sulfonic acid has been reported.
- The n-WSA works very well for different organic reactions with excellent yields.
- The advantages of n-WSA are high efficiently, reusability and operational simplicity.
- The n-WSA was easily separated and reused for several runs without loss activity.

Nano-WO_3-supported sulfonic acid: New, efficient and high recyclable heterogeneous nano catalyst

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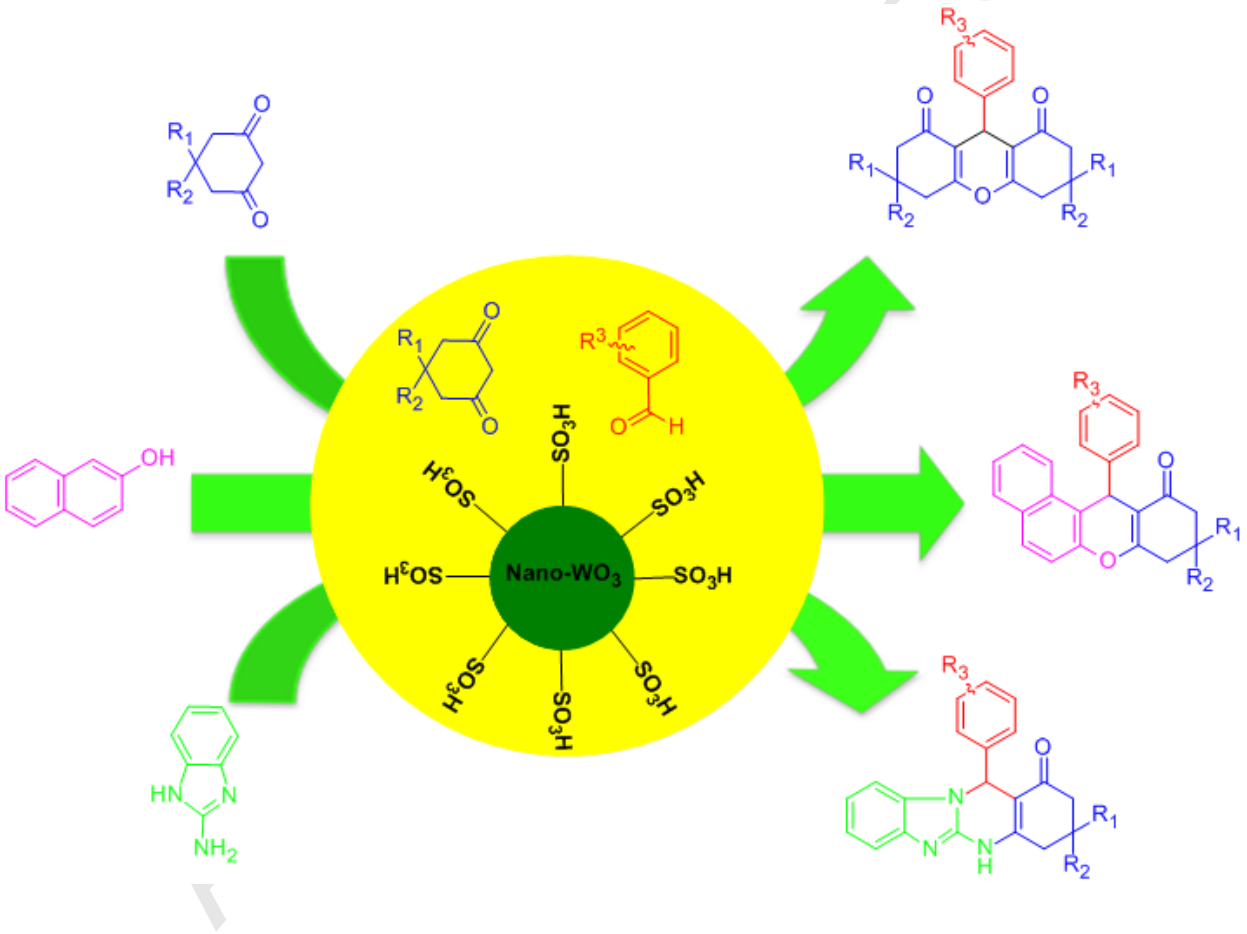

Nano-WO_3-supportedsulfonic acid:New, efficient andhighreusable heterogeneous nanocatalyst

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Abstract

Nano-WO_3-supported sulfonic acid [n-WO_3-SO_3H (n-WSA)]is easily prepared from the reaction of nanoWO_3 with chlorosulfonic acid as sulfonating agent.This new catalystis characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), FT-IR spectroscopy, thermal gravimetric analysis (TGA), pH analysis and Hammett acidity function. Nano-WO_3-supported sulfonic acid is used as an efficient and recyclable catalyst forsome organic reactions such as synthesis of1,8-dioxo-octahydroxanthene, tetrahydrobenzoxanthene and benzimidazoloquinazolinone derivatives. All of the reactions are very fast and the yields are excellent. The used catalyst was easily separated and reused for 10 runs without appreciable loss of its catalytic activity.

Keywords: Nano-WO_3-supported sulfonic acid, Heterogeneous nano catalyst, Multi component reaction, Green chemistry.

1. Introduction

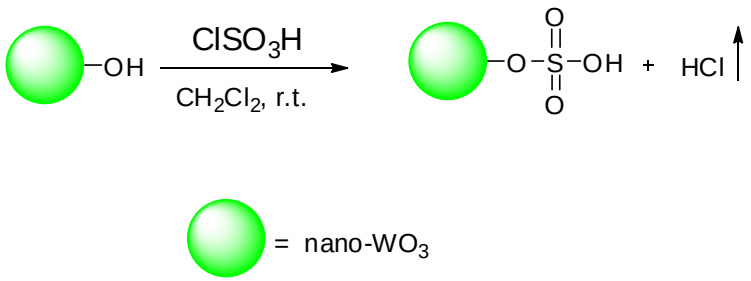
The “green chemistry” principles of chemical reactions have encouraged the use of reusable strong solid acids as alternatives for such unrecyclable “liquid acids” catalysts such as sulfuric acid, nitric acid,*etc*. Though the use of new solid acid catalystshas been widely developed, there is still a need to discover new methodologies for the immobilization of sulfonic acid.These solid acids are suitable options economically and industrially because of their special properties such as using less toxicity and readily available

precursors, simple and non-energy-intensive methods for recovery and reuse of catalyst[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]. In addition, the application of transition metal nanoparticles as catalysts for organic reactions has been attracting wide interest as nanoparticle-based catalytic systems can exhibit superior catalytic activities than the corresponding bulk materials. Transition metal oxides have been efficiently played an important role as catalysts in organic reactions. These high reactivities are due to high surface areas combined with unusually reactive morphologies.

Among various transition metals, tungsten is one of the important metals on our globe, and consequently, one of the most economical and environmentally well-suited ones.Moreover, tungsten is not toxic and additionally, the tungsten trioxide is commercially available.

The tungsten trioxide (WO_3) is commonly regarded as a material for many promising applications, in several research fields, due to their multiple potential applications such as catalytic activity for water purification[4], metathesis between ethene and 2-butene[5], esterification of propionic acid[6], photocatalytic activity[7], NO_2 sensing[8], photocatalytic O_2 production[9], oxidation of cyclopentene to glutaraldehyde[10], gas sensing properties [11] and adsorption of methylene blue from water [12] and other application such as heterogeneous catalysts, chromogenic devices, solar-energy devices, field electron emission. In spite of the aforementioned advantages, unpredictably, in comparison with some other transition metals until lately, tungsten has been comparatively unheeded as a catalyst in the organic synthesis.

Based on the mentioned facts, it has been decided to improve the catalytic properties of nano-WO_3 by reacting it with chlorosulfonic acid to produce nano-WO_3-supported sulfonic acid (n-WSA) (Scheme 1).Sulfonation with chlorosulfonic acid is convenient, fast and efficient method for heterogenization of homogeneous catalysts[13-15] that has attracted more much attention after Zolfigol's report on the preparation of silica sulfuric acid (SSA) [16].



Scheme 1. Preparation of nano-WO_3-SO_3H (n-WSA).

2. Experimental

2.1. Materials and Instruments

Chemicals were purchased from the Merck chemical companies. Thin-Layer Chromatography (TLC) on commercial plates of silica gel 60 F254 was used to monitor the progress of reactions. The products were characterized by FT-IR spectra, ^{1}HNMR, ^{13}CNMR and CHN analyzer. ^{1}H and ^{13}CNMR spectra which were recorded on Bruker Advance Spectrometer 400 & 500 MHz using $CDCl_3$-*d* and DMSO-d_6 as solvent. The chemical shifts are expressed in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Elemental analyses were performed by Perkin Elmer CHN analyzer, 2400 series II. Melting points were recorded on a THERMO SCIENTIFIC 9100 apparatus.

2.2. Characterization methods of nano-WO_3-SO_3H (n-WSA)

2.2.1. X-ray diffraction spectrum

Wide angle X-ray diffraction spectrum for the n-WSA powder sample was obtained using a Siemens D5000 (Siemens AG, Munich, Germany) X-ray diffractometer using Cu-Ka radiation of wavelength 1.54 Å.

2.2.2. Filed emission scanning electron microscopy

A particle size study of n-WSA sample was carried out using Philips XL30 field emission scanning electron microscope (Royal Philips Electronics, Amsterdam, The Netherlands) 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.

2.2.3. Infrared spectra

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

2.2.4. 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 °C/min.

2.3. Preparation of nano-WO_3

10 mL of ammonia solution (25 wt%) was added to the CTAB solutions while stirring. After getting a homogenous solution, 0.117 mol of WCl_6 1000 mL^{-1} of CTAB solution was added with vigorous stirring. After stirring for 4 h, the products were aged at ambient temperature for 72 h. The final product was filtered, washed with deionized water and absolute ethanol in order to remove surfactant, residual reactants and by products and then calcinated at 500°C for 2 h[17].

2.4. Preparation of nano-WO_3-SO_3H (n-WSA)

A suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an adsorbing solution (i.e., water) was used, charged with the nano-WO_3 (4 g, 17 mmol) in dry CH_2Cl_2 (20 ml). Then chlorosulfonic acid (1 ml, 15 mmol) (CAUTION: a highly corrosive and water absorbant. Be careful when using this liquid. Protective gloves, protective clothing and eye and face protection equipment are also needed.)was added dropwisely over a period of 30 min at room temperature. HCl gas immediately evolved from the reaction vessel. Stirring was continueduntilHCl evolution was seized. After the addition was completed, the mixture was shaken for 30 min. A darkgreen powder of nano-tungsten trioxide-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 prepared n-WSA stored in vacuum desiccator over anhydrous silica gel, then, was dried in 120 °C for 6 hours. The mmol of H^+ per gram of catalyst (3.7 mmol/ gram of n-WSA) was determined by the titration of 0.1 gram of sample with a standard solution of NaOH (0.1 N). For this purpose, the surface acidic protons of nano-WO_3-SO_3H (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 obtained solution was titrated by NaOH (0.1 M) solution in presence of phenol red indicator solution or pH meter.

2.5. General procedure for synthesis of 1,8-dioxo-octahydroxanthene derivatives

In a typical experiment, various aromatic aldehyde (1 mmol), 1,3-cyclic diketon (2mmol) and catalyst (0.019 g) in solvent free condition were taken in a 25 ml round bottomed flask.The flask was stirred at 100 ^{o}C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL), centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure 1,8-dioxo-octahydroxanthene derivatives.

2.6. General procedure for synthesis of tetrahydrobenzoxanthene derivatives

In a typical experiment, various aromatic aldehyde (1 mmol), 1,3-cyclic diketon (1 mmol), β-naphtol (1 mmol) and catalyst (0.019 g) in solvent free condition were taken in a 25 ml round bottomed flask.The flask was stirred at 100 ^{o}C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL), centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure tetrahydrobenzoxanthene derivatives.

2.7. General procedure for synthesis of benzimidazoloquinazolinone derivatives

In a typical experiment, different aromatic aldehyde (1 mmol), 1,3-cyclic diketon (1 mmol), 2-amino-benzimidazole (1 mmol) and catalyst (0.019 g) in solvent free condition were taken in a 25 ml round bottomed flask.The flask was stirred at 100 ^{o}C for an appropriate time. The reaction mixture was cooled, eluted with hot ethanol (5 mL), centrifuged and filtrated to collect the formed precipitate. The crude product was recrystallized from ethanol to yield pure benzimidazoloquinazolinone derivatives.

3. Results and Discussion

3.1. Characterization of nano-WO_3-SO_3H

3.1.1. X-ray diffraction spectra

The nano-WO_3 powder can be easily synthesized by reported procedure[17].Fig. 1a shows the XRD patterns of nano-WO_3 powder before modification.The following peak signals with miler indices (001),

(020), (200), (120), (111),(021), (201), (220), (221), (320), (131), (002), (040), (400), (140), (022), (202), (240), (420), (222), (240) and (430) in Fig. 1a confirm the formation ofnano tungsten trioxide crystal phase which coincides with JCPD 201324 standard. The crystal size of the nanoWO_3 powder was also determined from X-ray pattern using the Debye-Scherrer formula given as $t=0.9\lambda/B_{1/2}\cos\theta$, that t is the average crystal size, λ the X-ray wavelength used (1.54 Å), $B_{1/2}$ the angular line width at half maximum intensity and θ the Bragg′s angle. The average crystal size of the nano-WO_3 powder for2θ = 24.32 ºis calculated to be around 21.67nm.Fig.1b illustrates XRD patterns of the samples of modifiednanoWO_3. As shown in Fig.1b, the peak intensities of nano-WO_3-SO_3H (n-WSA) are almost the same as those ofnanoWO_3(Fig. 1a) and sulfonate modification dose not change the phase ofnanoWO_3.

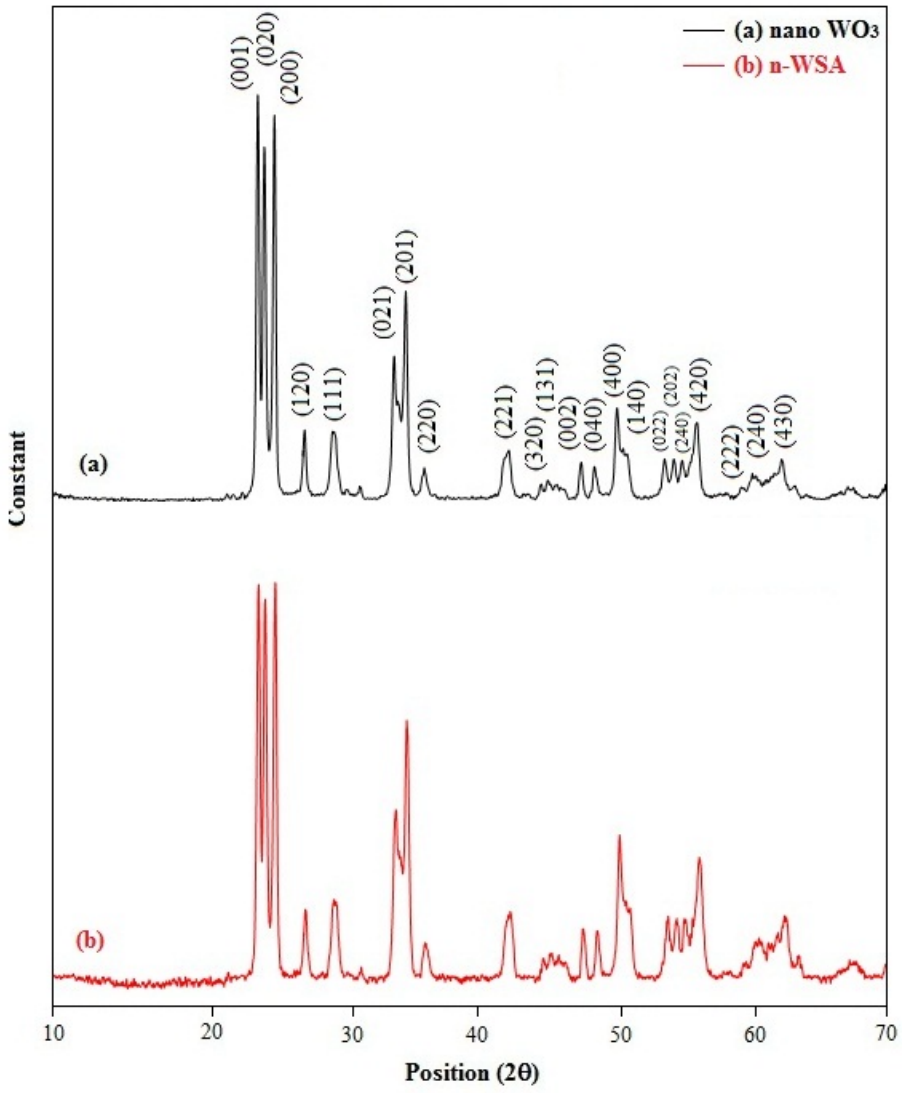


Fig.1. The X-ray diffraction pattern of (a) the nano-WO_3 powder and (b) n-WSA.

3.1.2. Field emission scanning electron microscopy

The field emission scanning electron microscopy (FE-SEM) images of nano-WO_3 powder reveals thespherical nano-WO_3 powder with average particle sizes of about75-80 nm(Fig.2).

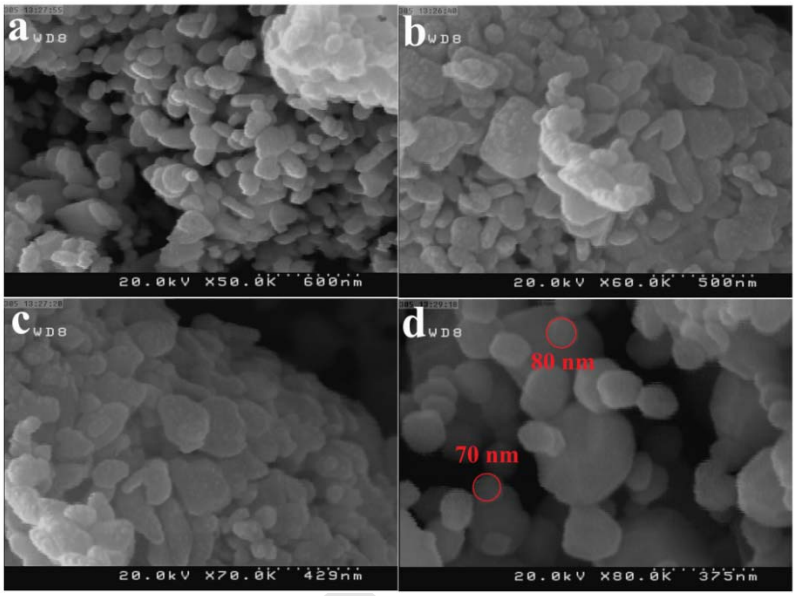


Fig.2. The FE-SEM image of nano-WO_3.

It was revealed by the FE-SEM images of n-WSAthat the spherical n-WSA powder average particle sizes was about60-75 nm (Fig. 3). Compared to Fig. 2, as shown in Fig. 3, its cleared that the surface of the as-synthesized n-WSA are not smoothed indicating that the modification process has performed successfully.

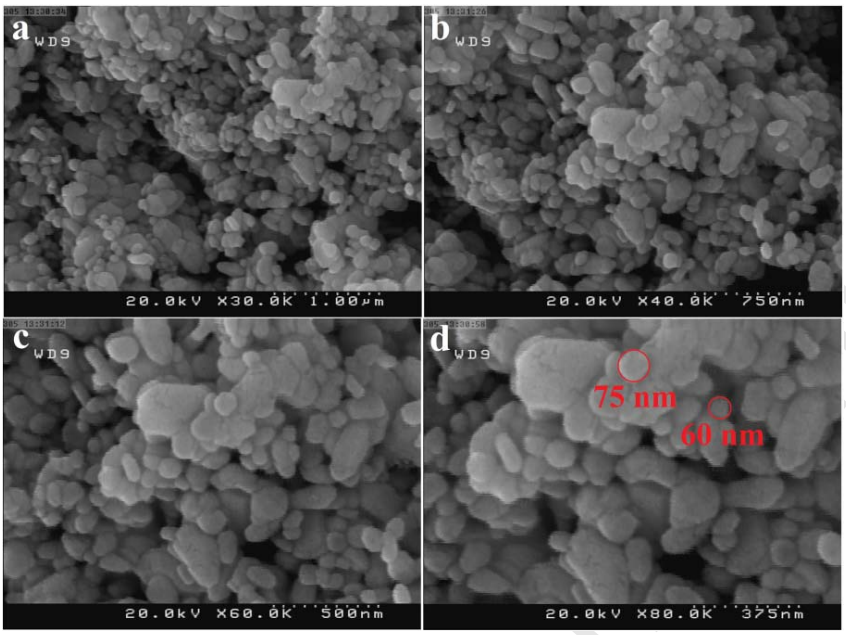


Fig.3. The FE-SEM image of n-WSA.

3.1.3. FT-IR spectra

The FT-IR spectra of nano-WO_3 powder and n-WSA are shown in Figure4. In the graph **a** of Fig. 4, the absorbance bands at around 777 and 838 cm^{-1} is due to W-O-W vibration, 1629 cm^{-1} W-OH vibrationand the absorbance bands at around 3400-3500 cm^{-1} was certified to the adsorbed water (Fig. 4, graph a and b) which is consistent with the reported IR spectra for nano-WO_3[7]. In the graph **b** of Fig. 4, the absorption range in 1177-1284 and 1012-1070 cm^{-1} was certified the O=S=O asymmetric and symmetric stretching modes lies respectively and the S-O stretching mode lies in 577-615 cm^{-1} showing the presence of sulfonic acid functional group which is consistent with the reported IR spectra for -SO_3H[18].

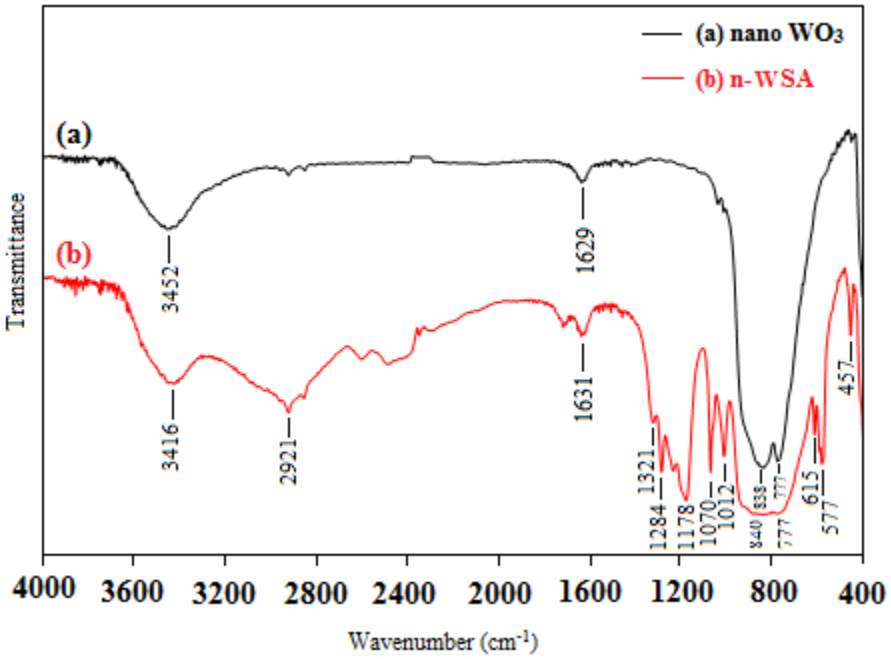


Fig. 4. The FT-IR spectra of (a) The nano WO_3 powder and (b) n-WSA.

3.1.4. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) of n-WSA in comparison with nano WO_3 is shown in Fig. 5. The TGA curve of WO_3 (Fig. 5a) displays a weight loss (5 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 WO_3.

In the TGA curve of n-WSA (Fig. 5b) exist two regions corresponding to different mass lose ranges. In the first region,a mass loss approximately 4% weight occurred below 140 °C that displayed that was attributable to the loss of trapped water from the catalyst. A mass loss of approximately 16% weight occurred between 140 and 250 °C that was related to the sudden mass loss of SO_3H groups[18, 19]. Also, from the TGA, it can be understood that n-WO_3-SO_3H has a greater thermal stability (up 150 °C) confirming that it could be safely used in organic reactions at temperatures in the range of 80-130 °C.

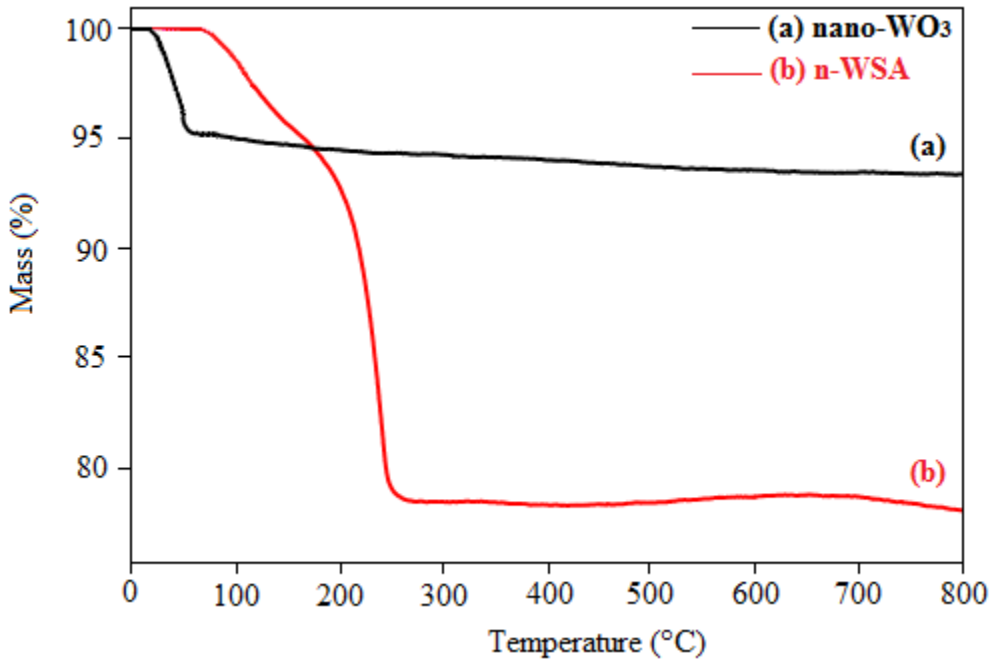


Fig.5. TGA cure of (a) nano-$WO_3$and (b) n-WSA.

3.1.5. Surface acidity studies

The Hammett acidity function (H_0) can effectively express the acidity strength of an acid in organic solvents[20]. It can be calculated using the following equation:

$$H_0 = pK(I)_{aq} + \log([I]_s/[IH^+]_s),$$

Here, 'I' represents the indicator base (mainly substituted nitroanilines) and $[IH^+]_s$ 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 the Lambert-Beerlaw, the value of $[I]_s/[IH^+]_s$ can be determined and calculated using the UV-visible spectrum. In this experiment, 4-nitroaniline was chosen as the basic indicator, and CCl_4 was chosen as the solvent because of its aprotic property. The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 329 nm in CCl_4. As Fig. 6 shows, the absorbance of the unprotonated form of the indicator in n-WO_3-SO_3H was weak as compared to the sample of the indicator in CCl_4, which indicated that the indicator was partially in the form of $[IH^+]$.

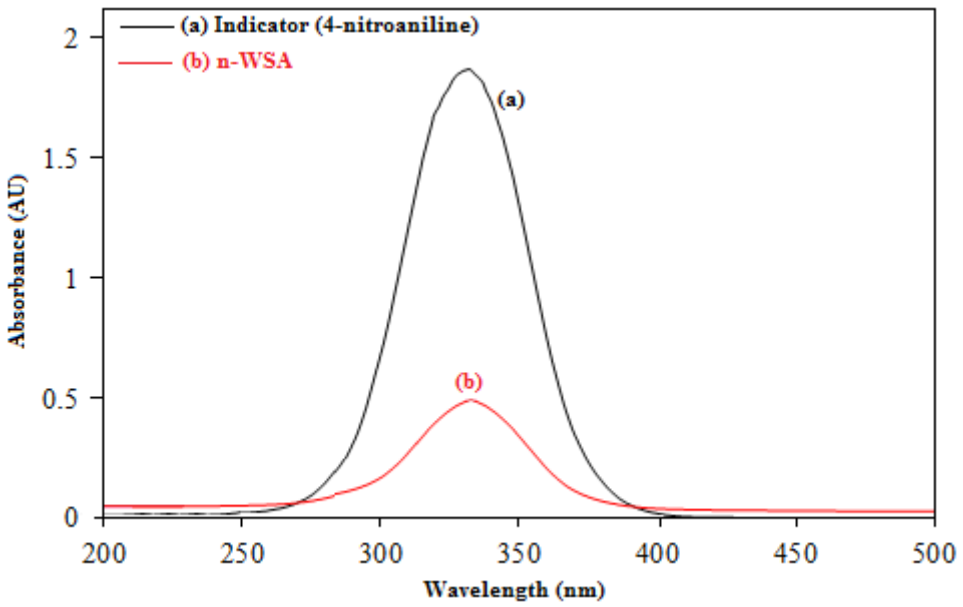


Fig.6. Absorption spectra of (a) 4-nitroaniline (indicator) and (b) n-WSA (catalyst) in CCl_4.

The obtained results are listed in Table 1, which shows the acidity strength of nano-WO_3-SO_3H. These results of the Hammett acidity function (H_0) also confirm the synthesis of nano-WO_3-SO_3H with a high density of acid sites (-SO_3H groups)on the surface of nano-WO_3-SO_3H (Table 1).

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

Entry	Catalyst	A_{max}	$[I]_s$ (%)	$[IH^+]_s$ (%)	H_0
1	-	1.83	100	0	-
2	n-WSA	0.512	27.17	72.83	1.13

Condition for UV-visible spectrum measurement: solvent, CCl_4;
indicator, 4-nitroaniline ($pK(I)_{aq}$= 0.99), $1.44*10^{-4}$mol/L; catalyst, n-WSA (20 mg), 25 °C.

To compoare the relative acidity of n-WSA, Hammet acidity of various amount of n-WSA (0-25 mg) was compared with sulfuric acid at 50 mM concentration (by the methodology described in the literature [21]). The obtained results were shown in the Fig. 7. From Fig. 7 it is clear that the n-WSA prossess similar acidity as sulfuric acid. Also,from the obtained results, we can investigated the contributed supported sulfonic acid for reactions.

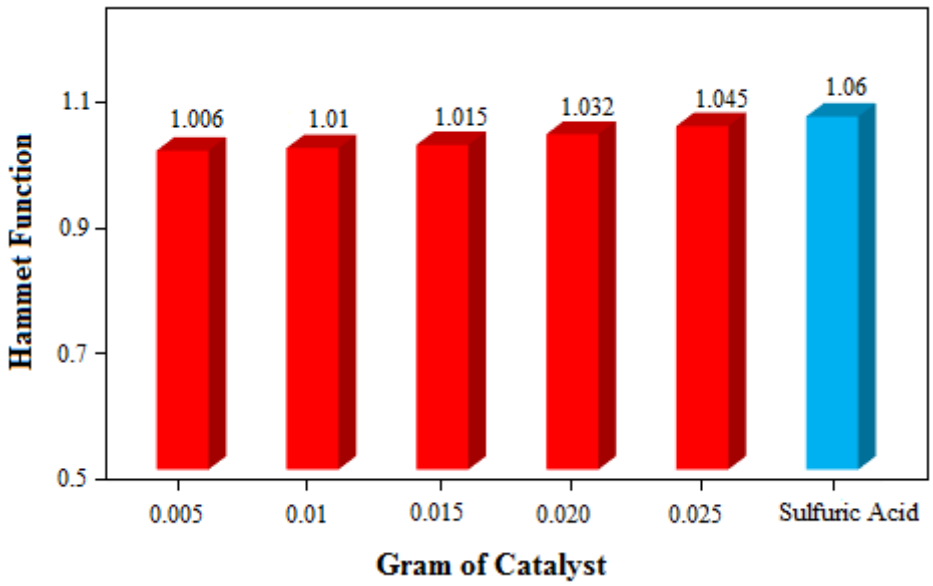


Fig. 7. Comparison of Hammett functions of various amount of n-WSA in water with Sulfuric Acid (50 mM) (4-nitroaniline (44.8 mM) as indicator pK_a= 0.99, A_{max}= 380 nm).

The obtained results of characterization methods showed that the nano-WO_3-supported sulfonic acid is prepared and different characterization methodsalso show that the sulfunic acid groups (-SO_3H) have been supported on the surface of nano-WO_3. Indeed, nano-WO_3 functions as a Lewis acid and sulfonic acids functions as the Brønsted. Brønsted acids could usually provide a hydrogen bond which can initiate the catalytic procedure. In our new solid acid supported catalyst, we have conserved both of these properties.Based on the obtained results,we expected better catalytic activity for nano-WO_3-supported sulfonic acid comparing with nano-WO_3. Toconfirm this hypothisis, the catalytic ability of nano-WO_3-supported sulfonic acid is tested in some of organic reactions.

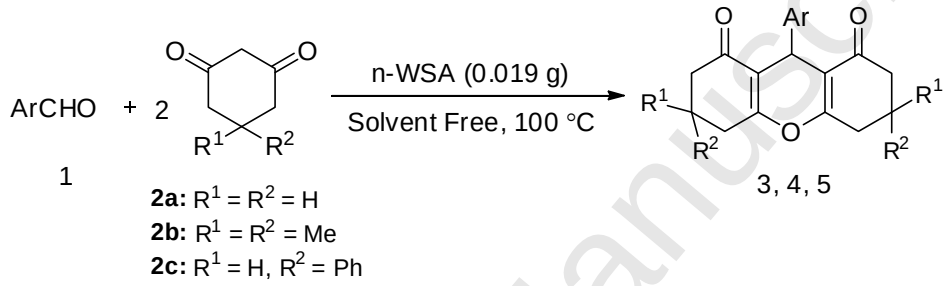
3.2. Using nano-WO_3-SO_3H in some organic reactions

In continuation of our studies on developing inexpensive and environmentally benign methodologies for organic reactions [22, 23],nano-titania-supported sulfonic acid[13]as heterogeneous solid acid nano catalyst was studied where the results were also very satisfactory.

In thepresent work, nano-WO_3-supported sulfonic acid was easily prepared andused as a highly efficient, heterogeneous, reusable and inexpensive solid acid catalystfor synthesis of 1,8-dioxo-octahydroxanthene, tetrahydro-benzoxanthene and benzimidazolo-quinazolinone derivatives.

3.2.1. Synthesis of 1,8-dioxo-octahydroxanthene derivatives

The synthesis of xanthenes, especially dioxo-octahydroxanthenes, has emerged as a powerful tool in organic synthesis due to their broad applications in different fields[24-27].The prepared n-WSA has been tested for the synthesis of 1,8-dioxo-octahydroxanthene derivatives by condensation between *para*-chlorobenzaldehyde (**1**) (1 mmol) and dimedone (**2**) (2 mmol) under solvent free condition as a model reaction (Scheme 2).



Scheme 2. Synthesis of 1,8-Octahydroxanthene derivatives.

To justify the efficiency of the n-WSA, the model reaction was carried out in presence of different amount of n-WSA in solvent free condition at 90 ºC and compared it by nano-WO_3 (Table 2).

Table 2. Optimization of catalyst amount for the synthesis of 1,8-dioxo-octahydroxanthene[a].

Entry	Catalyst	Amount of catalyst (g)	Yield[b] (%)
1	-	-	21
2	Nano-WO_3-SO_3H	0.011	49
	Nano-WO_3-SO_3H	0.013	62
3	Nano-WO_3-SO_3H	0.015	75
4	Nano-WO_3-SO_3H	0.017	81
5	Nano-WO_3-SO_3H	0.019	89
6	Nano-WO_3-SO_3H	0.021	89
7	Nano-WO_3	0.019	25

[a]Reaction condition: **1** (1 mmol), **2** (2mmol), reaction time: 1 h, under solvent free condition at 90 ºC.
[b]Isolated yield.

The obtained results showed that n-WSA performed well to give desired product within 60 min in 89% yield at 90 ºC under solvent free condition (Table 2, entry 5) and is a more suitable option than tungsten trioxide (Table 2, entry 7). The greater catalytic activity of n-WSA was most likely related to the SO_3H groups of the catalyst, which could provide efficient acidic sites.

In the next step, the effect of temperature in presence of 0.019 g of n-WSA was investigated. The results showed that the best temperature was 100 ºC (Table 3, entry 7). By increasing the temperature to 110 °C, the achieved yield was decreased to 92% (Table 3, entry 8), so the experiences were followed at 100°C.

Table 3. Optimization of other conditions for the synthesis of 1,8-dioxo-octahydroxanthene[a].

Entry	Temperature (ºC)	Solvent	Yield[b] (%)
1	RT	-	Trace
2	40	-	21
3	60	-	39
4	70	-	64
5	80	-	83
6	90	-	89
7	100	-	93
8	110	-	92
9	100	EtOH	58
10	100	PEG	63
11	100	MeOH	50
12	100	CH_3CN	42
13	100	Toluen	37
14	100	CH_2Cl_2	21
15	100	H_2O	12

[a]Reaction condition: **1** (1 mmol), **2** (1 mmol), n-WSA (0.019 g), reaction time: 1 h.
[b]Isolated yield.

Eventually to making sure that the solvent free condition is appropriate, it has been decided to investigate the effect of different classical solvents such as EtOH, PEG, MeOH, CH_3CN, Toluene, CH_2Cl_2 and H_2O at 100 °C (Table 3, entries 9-15). As it is shown in Table 3, using these solvents gave significantly lower yields and longer reaction times. Increasing the reaction times did not improve the yields. So the best yield of product was provided in solvent free conditions.

After optimizing the conditions, the scope of method was successfully studied by using a various aromatic aldehydes (including aldehydes with electron-releasing substituents, electron-withdrawing substituents and halogens on the aromatic ring) and cyclic 1,3-diketone compounds. The results aresummarized in Table 4.

Table 4. Synthesis of 1,8-dioxo-octahydroxanthene derivatives by n-WSA[a].

Entry	Ar	R^1	R^2	Product	Time (h)	Yield[b] (%)	Melting point (◦C)	
							Found	Reported
1	$-C_6H_5$	H	H	**3a**	1.05	90	213-215	[28]
2	$4\text{-}O_2N\text{-}C_6H_4$	H	H	**3b**	0.85	94	234-236	[28]
3	$4\text{-Br-}C_6H_4$	H	H	**3c**	0.9	92	222-225	-
4	$4\text{-}H_3C\text{-}C_6H_4$	H	H	**3d**	1.05	89	244-246	-
5	$4\text{-}H_3CO\text{-}C_6H_4$	H	H	**3e**	1.1	88	190-191	190-192[29]

6	-C_6H_5	CH_3	CH_3	**4a**	1.1	92	203-204	205-206 [30]
7	2-O_2N-C_6H_4	CH_3	CH_3	**4b**	0.85	90	244-245	246-248 [31]
8	3-O_2N-C_6H_4	CH_3	CH_3	**4c**	0.8	93	168-169	167-168 [30]
9	4-O_2N-C_6H_4	CH_3	CH_3	**4d**	0.8	94	222-224	221-223 [30]
10	4-F-C_6H_4	CH_3	CH_3	**4e**	0.9	92	206-207	208-209 [31]
11	4-Cl-C_6H_4	CH_3	CH_3	**4f**	1	93	237-239	236-237 [32]
12	4-Br-C_6H_4	CH_3	CH_3	**4g**	1	91	264-267	263-265 [33]
13	2-H_3C-C_6H_4	CH_3	CH_3	**4h**	1.2	89	230-232	-
14	4-H_3C-C_6H_4	CH_3	CH_3	**4i**	1.25	89	212-214	216-217 [33]
15	4-H_3CO-C_6H_4	CH_3	CH_3	**4j**	1.3	90	242-244	241-243 [33]
16	4-HO-C_6H_4	CH_3	CH_3	**4k**	1.25	87	246-247	246-248 [31]
17	2-Naphtaldehyde	CH_3	CH_3	**4l**	1.05	92	234	234-235 [34]
18	2-OH-5-BrC_6H_3	CH_3	CH_3	**4m**	1.3	86	268-271	-
19	C_6H_5-CH=CH-	CH_3	CH_3	**4n**	1.25	85	256-258	-
20	-C_6H_5	H	Ph	**5a**	1.2	91	196-198	-
21	4-H_3C-C_6H_4	H	Ph	**5b**	1.25	90	204-208	-
22	4-H_3CO-C_6H_4	H	Ph	**5c**	1.25	90	212-215	-
23	4-Cl-C_6H_4	H	Ph	**5d**	1.05	93	234-236	-

[a]Reaction conditions: aromatic aldehyde (1 mmol), cyclic-diketone (2mmol), n-WSA (0.019 g)under solvent-free at 100 ^oC.
[b]Isolated yield.

The present method not only affords the products in excellent yields but also avoids the problems associated with catalyst cost, handing, safety and pollution.

As indicated in Table 4, the reaction works easily for a vast variety of aromatic aldehydes with both electron-donating and electron-withdrawing groups and different cyclic diketone to give corresponding 1,8-dioxo-octahydroxanthene derivatives in good to excellent yields. In almost all cases, the reactions proceeded smoothly within 50-80 min. However, it is notable that substituted aromatic aldehydes with electron-withdrawing groups increase the rate of reaction (Table 2 entries **2**, **3**, **7-12** and **23**) probably by activating the carbonyl group as electrophile center. Contrarily in the case of electron-donating groups, the reaction was more slowly (Table 2, entries **3**, **5**, **13-19**, **21** and **22**).

A plausible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenesin presence of n-WSA as catalystis shown in Fig. 8.

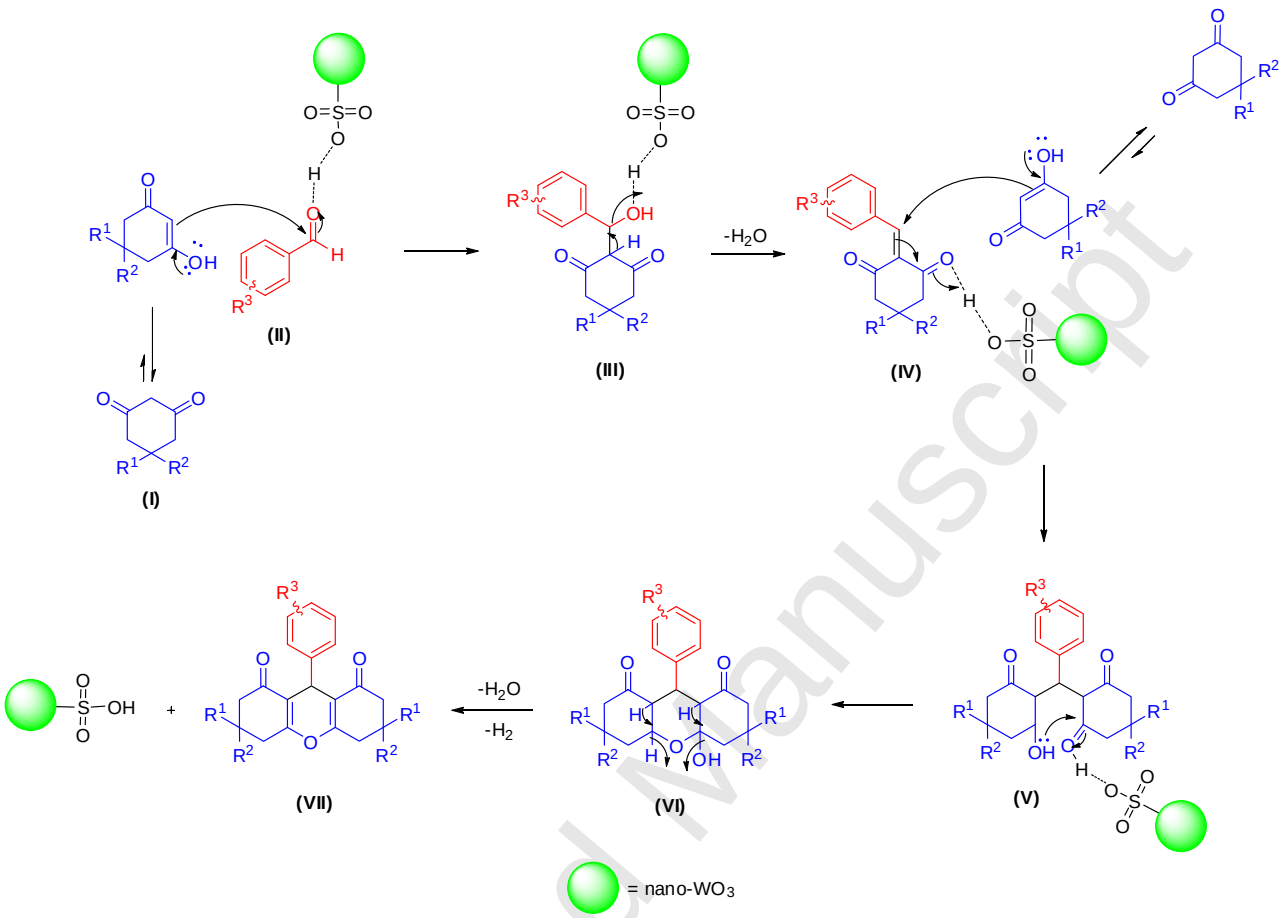


Fig. 8. Possible mechanism for the synthesis of 1,8-dioxo-octahydroxanthene derivatives in presence of n-WSA as catalyst.

In the proposed mechanism, initially, the carbonyl group of aromatic aldehyde is activated by SO_3H groups of nano-WO_3-SO_3H to give intermediate**II**. Then, 1,3-cyclic diketone attacksthe activated aldehyde and affords intermediate **III**. Following, by removing H_2O from intermediate **III**, the **IV** as a Mickel acceptor is prepared. One more time, the SO_3H group of nano-WO_3-SO_3H activates intermediate **IV**. Then, Michael addition of dimedone with intermediate **IV** gives **V**. Intermediate **V** changes to **VI** after ring closing reaction and removing catalyst. Finally by removing H_2O from compound **VI**, final 1,8-dioxo-octahydroxanthene derivatives**VII**is produced. The proposed mechanism illustrate clearelythe catalytic role of nano-WO_3SO_3H. As indicated in the Figure 8, the SO_3H groups play important role in the catalytic activity of nano-WO_3-SO_3H.

Reusability of the catalyst was checked by recovered n-WSA and reused for eight consecutive reactions and obtained the yield 90-93%. This indicates that as -SO_3H groups has fixed on the surface of nano-WO_3, it does not lose its activity and could be recycled 10 times(Fig. 9).Further, pH analysis of the recovered catalyst showed loading of 3.35 mmol H^+/g. This result suggests that the nature of the catalyst remains intact after each run and leaching of the acid species did not occur during the course of the reaction.

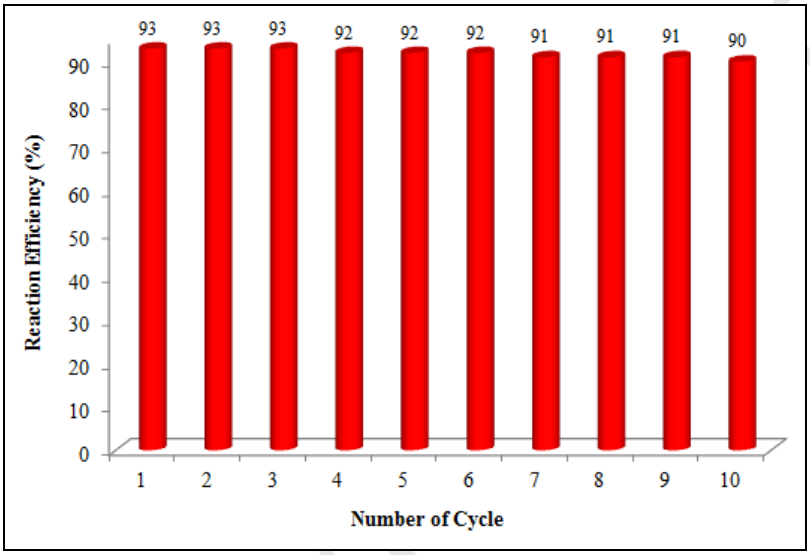


Fig. 9. Reusability of n-WSA for the synthesis of 1,8-dioxo-octahydroxanthenes, Reaction conditions:*para*-chlorobenzaldehyde (1 mmol), dimedone (2mmol), reaction time: 1 h at 100 ºC in solvent free condition.

Various methods have been reported for the synthesis of 1,8-dioxo-octahydroxanthenes, including, condensation of aromatic aldehydes and 1,3-cyclic diketones in presence of different catalysts. A comparison between the result of the proposed catalyst and some of the recently used catalysts for synthesis of octahydroxanthene derivatives is summarized in Table 5.

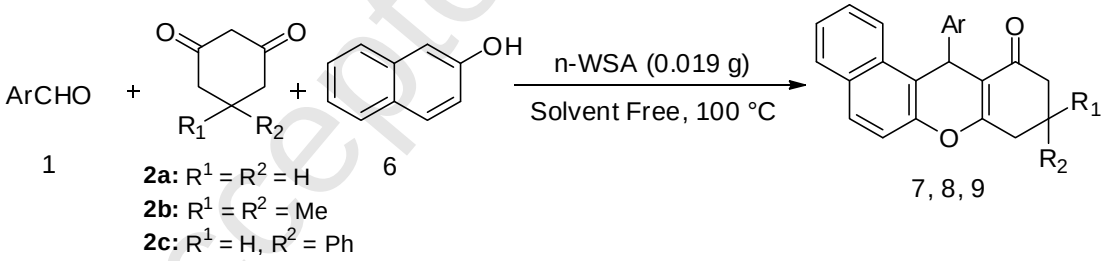
Table 5. Comparison of the characteristic of new synthesized catalyst with some reported catalysts.

Entry	Catalyst	Amount of Catalyst	Time (h)	Condition	Solvent	Yield (%)
1	Nano-ZnO	10 mol%	2	100 ºC	-	Trace
2	Nano-NiO	10 mol%	2	100 ºC	-	Trace
3	[CMIM][HSO_4] [35]	10 mol%	2.5	70	H_2O	95
4	$NaHSO_4.SiO_2$[36]	0.1 g	6.5	Reflux	CH_3CN	90
5	MCM-41-SO_3H [32]	0.2 g	1	Ultrasonic	H_2O	95
6	[Hmim]TFA [37]	0.1 g	3	80 ºC	-	91
7	[cmmim][BF_4] [38]	0.2 g	2.5	80 ºC	-	87
8	CAN/HY-Zeolite [39]	0.1 g	1.5	80 ºC	-	88
9	Dowex-50W [40]	0.4 g	1.5	100 ºC	-	78
10	Amberlyst-15 [41]	0.2 g	5	Reflux	CH_3CN	92
11	Fe^{+3}-montmorillonite [42]	0.05 g	6	100 ºC	Et-OH	94
12	Proposed catalyst	0.019 g	1	100 ºC	-	93

Although, some of these methods have convenient protocols with good to high yields, the majority of these methods suffer at least from one of the following disadvantages such as the use of toxic organic solvents, excess reagents, long reaction time and harsh reaction conditions. Table 5 shows that the heterogeneous solid acid catalyst of nano-WO_3-SO_3H is the best in comparison to the other mentioned catalysts. The proposed new catalyst has some advantages in comparison with the other catalyst including shorter reaction time, easy separation, low consumption of organic solvents, reusability and ability to perform reactions in solvent free conditions. It is a stable solid acid catalyst with high densities of sulfuric acid groups that can be easily synthesized in the laboratory and can be reused for several times.

3.2.2. Synthesis of tetrahydrobenzoxanthene derivatives

As Xanthenes and compounds based on these core templates are important heterocycles that are known to possess multiple biological, pharmaceutical and other activities [43, 44],it was decided to develope the catalytic activity of n-WSA by investigating their synthesis. For this purpose,tetrahydrobenzoxanthene was synthesized by condensation between benzaldehyde (**1**) (1 mmol), dimedone (**2**) (1 mmol) and β-naphtole (**6**) (1 mmol) under solvent free condition as a model reaction (Scheme 3).



Scheme 3. Synthesis of tetrahydrobenzoxanthene derivatives.

In table 6, the activity of n-WSA is compared with the nano-WO_3 and other catalyst.

Table 6. Comparison of nano-WO_3-SO_3H with some reported catalysts.

Entry	Catalyst	Amount of Catalyst	Condition	Time (min)	Solvent	Yield (%)
1	-	-	100 ºC	90	-	15
2	Nano-WO_3	0.019 g	100 ºC	85	-	31
3	Nano-WO_3-SO_3H	0.019 g	100 ºC	85	-	91
4	Nano-ZnO	10 mol%	100 ºC	85	-	Trace
5	Nano-NiO	10 mol%	100 ºC	85	-	Trace
6	Trityl Chloride [45]	7 mol%	110 ºC	50	-	89
7	$CeCl_3.7H_2O$-NaI [46]	5 mol%	50 ºC	120	CH_3OH	93

8	NH_2SO_3H [47]	20 mol%	120 ºC	150	-	85
9	$H_{14}[NaP_5W_{30}O_{110}]$[48]	0.4 mol%	120 ºC	120	-	88
10	TCT [49]	5 mol%	80 ºC	60	-	92
11	$InCl_3$[50]	30 mol%	120 ºC	30	-	84
12	P_2O_5[50]	20 mol%	120 ºC	40	-	76
13	$HClO_4$-SiO_2[51]	0.1 g	80 ºC	60	-	95
14	$Sr(OTf)_2$[52]	10 mol%	80 ºC	300	$ClCH_2CH_2Cl$	85
15	pTSA/[bmim]BF_4[53]	10 mol%	80 ºC	180	-	90

The obtained results showed that the n-WSA (91%,yield) was a more suitable option rather than the nano-WO_3 (31%, yield).In comparison with the other mentioned catalysts, the presence new catalyst has some advantages including shorter reaction time, easy preparation and separation, low consumption of organic solvents, lower temperature of reaction and amount of catalyst, reusability and ability to perform reactions in solvent free conditions and high yield of products. It is a useful solid acid nanocatalyst with high densities of sulfuric acid groups that can be easily prepareded.

To examine the limitation and the scope of the reaction, the synthesis of different tetrahydrobenzoxanthene derivatives heve been investigated. The obtained results are summarizedin Table 7.

Table 7. Synthesis of tetrahydrobenzoxanthene derivatives by n-WSA[a].

Entry	Ar	R^1	R^2	Product	Time (min)	Yield[b] (%)	Melting point (◦C)	
							Found	Reported
1	-C_6H_5	H	H	**7a**	90	90	190-192	192-193 [54]
2	4-H_3C-C_6H_4	H	H	**7b**	95	88	205-207	206-207 [54]
3	4-H_3CO-C_6H_4	H	H	**7c**	100	89	182-184	181-182 [54]
4	2-Cl-C_6H_4	H	H	**7d**	88	90	244-246	243-245 [54]
5	4-Cl-C_6H_4	H	H	**7e**	85	91	207-209	208-209 [54]
6	4-F-C_6H_4	H	H	**7f**	85	92	208-210	209-211 [54]
7	4-Br-C_6H_4	H	H	**7g**	85	91	212-214	214-215 [54]
8	3-O_2N-C_6H_4	H	H	**7h**	80	94	235-236	234-235 [54]
9	4-O_2N-C_6H_4	H	H	**7i**	80	94	237-238	236-237 [54]
10	2-Naphtyl	H	H	**7j**	80	87	190-191	-
11	-C_6H_5	CH_3	CH_3	**8a**	85	91	148-150	151-153 [55]
12	2-Cl-C_6H_4	CH_3	CH_3	**8b**	80	92	178-180	179-180 [55]
13	2-O_2N-C_6H_4	CH_3	CH_3	**8c**	80	92	222-224	223-225[55]
14	3-O_2N-C_6H_4	CH_3	CH_3	**8d**	75	93	169-171	168-170 [55]
15	4-O_2N-C_6H_4	CH_3	CH_3	**8e**	75	94	177-179	178-180 [55]
16	4-F-C_6H_4	CH_3	CH_3	**8f**	80	93	182-184	184-185 [56]
17	4-Cl-C_6H_4	CH_3	CH_3	**8g**	80	92	180-181	180-182 [55]
18	4-Br-C_6H_4	CH_3	CH_3	**8h**	80	92	186-188	186-187 [57]
19	4-H_3C-C_6H_4	CH_3	CH_3	**8i**	85	88	177-178	176-188 [55]
20	4-H_3CO-C_6H_4	CH_3	CH_3	**8j**	90	86	202-204	204-205[55]
21	4-HO-C_6H_4	CH_3	CH_3	**8k**	90	85	222-225	223-225[55]
22	2-Naphtyl	CH_3	CH_3	**8l**	80	83	228-230	228-230 [56]
23	-C_6H_5	H	Ph	**9a**	85	88	118-124	-
24	4-F-C_6H_4	H	Ph	**9b**	80	90	181-183	-
25	4-Cl-C_6H_4	H	Ph	**9c**	80	90	234-235	-

26	4- O_2N-C_6H_4	H	Ph	**9d**	75	92	183-186	-
27	4-H_3C-C_6H_4	H	Ph	**9e**	85	85	198-200	-
28	4-H_3CO-C_6H_4	H	Ph	**9f**	85	83	191-192	-

[a]Reaction conditions: **1** (1 mmol), **2** (1mmol), **6** (1 mmol) and n-WSA (0.019 g) in solvent-free at 100 °C.
[b]Isolated yield.

As indicated in Table 7, the new conditions are very suitable for a vast varity of tetrahydrobenzoxanthene derivatives.

A plossible mechanism for thesynthesis of tetrahydrobenzoxanthenes is shown in Fig. 10.

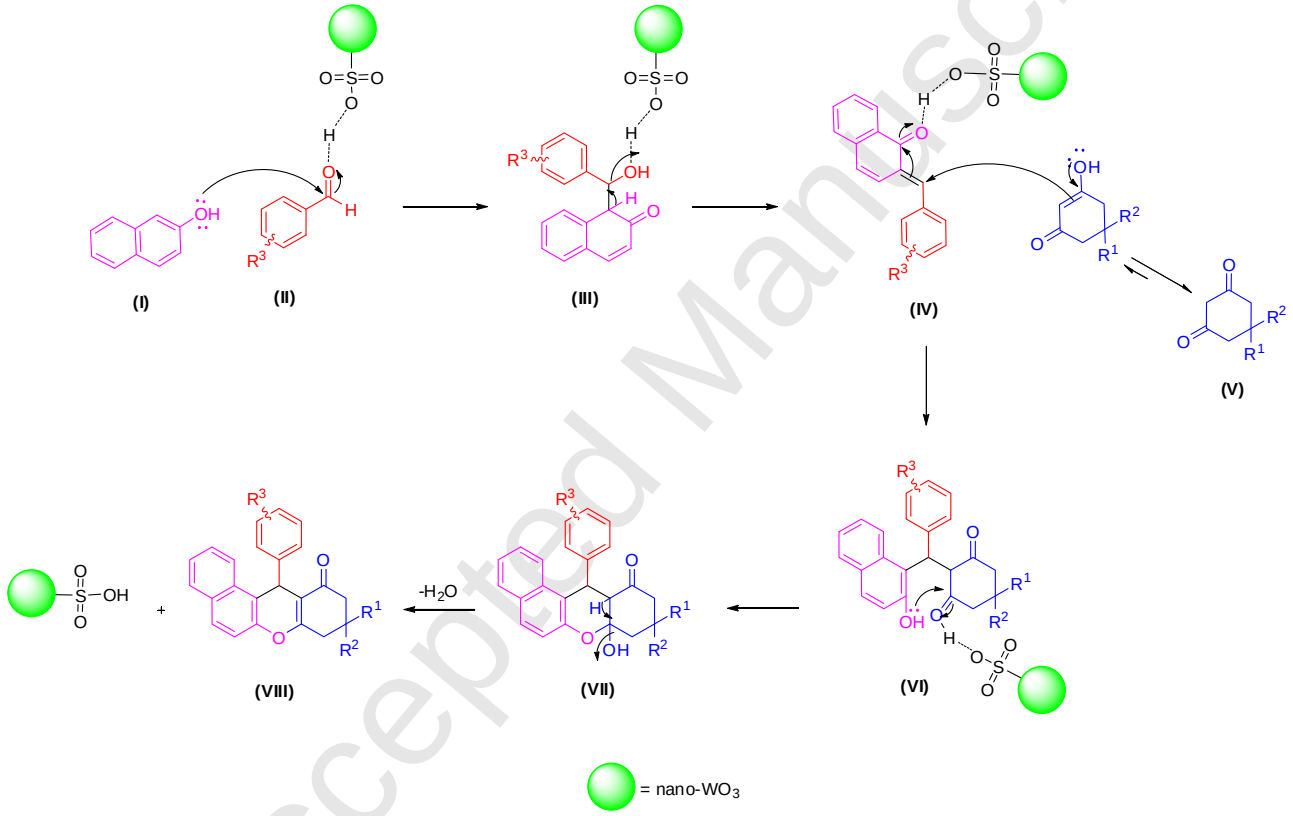


Fig. 10. Proposed mechanism for the synthesis of tetrahydrobenzoxanthenes in presence n-WSA.

In the possible mechanism (Fig. 10), initially, activated carbonyl group of aromatic aldehyde (**II**) is attacked by B naphtol (i) to afford intermediate **III**.Dehydration of **III**, provides chalkon**IV** as a Mickel acceptor. The intermediate **IV** is activated by SO_3H groups of nano-WO_3-SO_3H. Then, Michael addition of dimedone (V) with intermediate **IV** gives intermediate**VI** which could be changed to **VII** after ring closing reaction and removing catalyst. Finally by removing H_2O from **VII**, product **VIII** is produced. The proposed mechanism illustrate the catalytic role of nano-WO_3SO_3H. As indicated in the Figure 9, the SO_3H groups of nano-WO_3-SO_3H plays principal role in the catalytic activity of nano-WO_3-SO_3H.

The recyclability of the catalyst was tested with five consecutive synthesis of tetrahydrobenzoxanthene by using recovered n-WSA and desired product obtained in 89-91% yield(Fig.11).

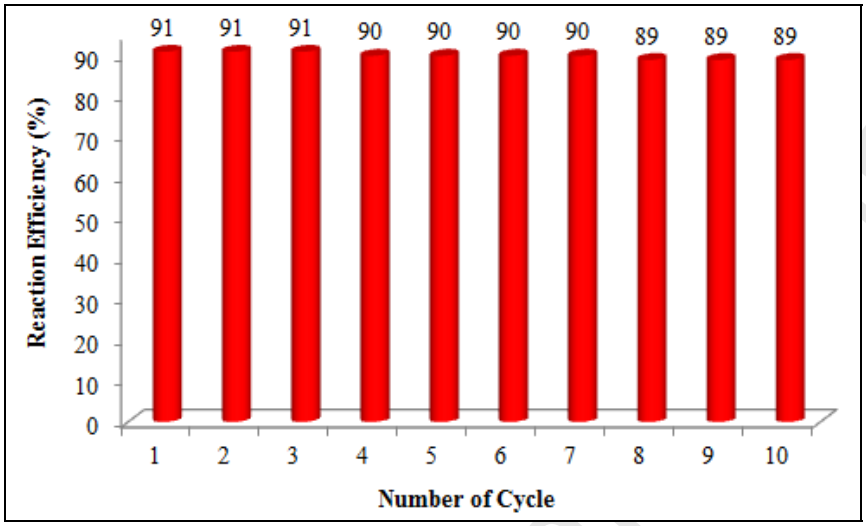
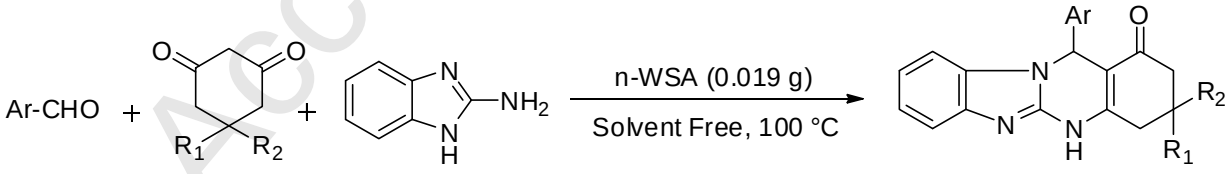


Fig. 11. Reusability of n-WSA for the synthesis of tetrahydrobenzoxanthenes, Reaction conditions:benzaldehyde (1 mmol), dimedone (1 mmol), β-naphtole (1 mmol), reaction time: 85 min at 100 ºC in solvent free condition.

3.2.3. Synthesis of benzoimidazoloquinazolinone derivatives

As benzoimidazoloquinazolinones are important because of their wide range of biological activities, application in medicinal chemistry, agrochemicals and pharmaceutical industry as herbicides and active pharmaceuticals[58-60] and to explore the efficiency of n-WSA, it wastested it for their synthesis by condensation between benzaldehyde (**1**) (1 mmol), dimedone (**2**) (1 mmol) and 2-amino benzimidazole (**10**) (1 mmol) under solvent free condition as a model reaction (Scheme 4).



Scheme 4. Synthesis of 3,3-dimethyl-12-phenyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-b]quinazolin-1(2H)-one derivatives.

One more time the activity of n-WSA was compared with the nano-$WO_3$and some other catalyst (Table 8).

Table 8. Comparison of nano-WO_3-SO_3H with some reported catalysts.

Entry	Catalyst	Condition	Time (min)	Solvent	Yield (%)
1	-	100 ºC	15	-	12
2	Nano-WO_3	100 ºC	15	-	34
3	Nano-WO_3-SO_3H	100 ºC	15	-	94
4	Nano-ZnO	100 ºC	15	-	Trace
5	Nano-NiO	100 ºC	15	-	Trace
6	- [61]	Reflux	360	DMF	64
7	I_2[62]	Reflux	10	CH_3CN	84.6
8	Silica gel [63]	Microwave 120 ºC-100 psi	3	-	95
9	SBA-Pr-SO_3H [64]		10	-	90
10	$H_6P_2W_{18}O_{62}$[65]	Reflux	15	CH_3CN	91
11	NH_2SO_3H [66]	Reflux	20	CH_3CN	90
12	Ionic Liquid [67]	Heating	360	-	84
13	- [68, 69]	Reflux	5	DMF	58
14	- [61]	Microwave	5	DMF	89

The obtained results showed that the n-WSA (94%, yield) works better than the nano-WO_3 (34%, yield).One more time, our new catalyst has some advantages in comparison with the other catalyst such as easy preparationand separation, low consumption of organic solvents, recoverability and reusability, operational simplicity and solvent free conditions.

To examine the limitation and the scope of the reaction, the synthesis of benzoimidazoloquinazolin derivatives have been investigated. The obtained results are summarized in Table 9.

Table 9. Synthesis of benzoimidazoloquinazolinderivatives by n-WSA[a].

Entry	Ar	R^1	R^2	Product	Time (min)	Yield[b] (%)	Melting point (◦C)	
							Found	Reported
1	-C_6H_5	CH_3	CH_3	**11a**	15	94	318-319	>300[62]
2	4-H_3C-C_6H_4	CH_3	CH_3	**11b**	18	92	328-330	330-332 [61]
3	4-H_3CO-C_6H_4	CH_3	CH_3	**11c**	20	90	317-318	318-320[61]
4	4-O_2N-C_6H_4	CH_3	CH_3	**11d**	12	95	334-336	>300 [62]
5	4-F-C_6H_4	CH_3	CH_3	**11e**	12	94	324-326	-
6	4-Cl-C_6H_4	CH_3	CH_3	**11f**	14	95	337-339	340 [61]
7	4-Br-C_6H_4	CH_3	CH_3	**11g**	14	95	312-314	>300 [62]
8	4-HO-C_6H_4	CH_3	CH_3	**11h**	16	91	332-334	330-332 [64]
9	-C_6H_5	H	H	**12**	15	92	312-313	-
10	-C_6H_5	H	Ph	**13**	15	93	335-336	-

[a]Reaction conditions: **1** (1 mmol), **2** (1mmol), 2-amino benzimidazole (1 mmol), n-WSA (0.019 g)under solvent-free conditions at 100 ^oC.
[b]Isolated yield.

As showed in Table 8, fortunately the new catalyst also works very well for a vast varity of benzoimidazoloquinazolin derivatives.

A proposed mechanism for the synthesis of benzoimidazoloquinazolins is shown in Fig. 12.

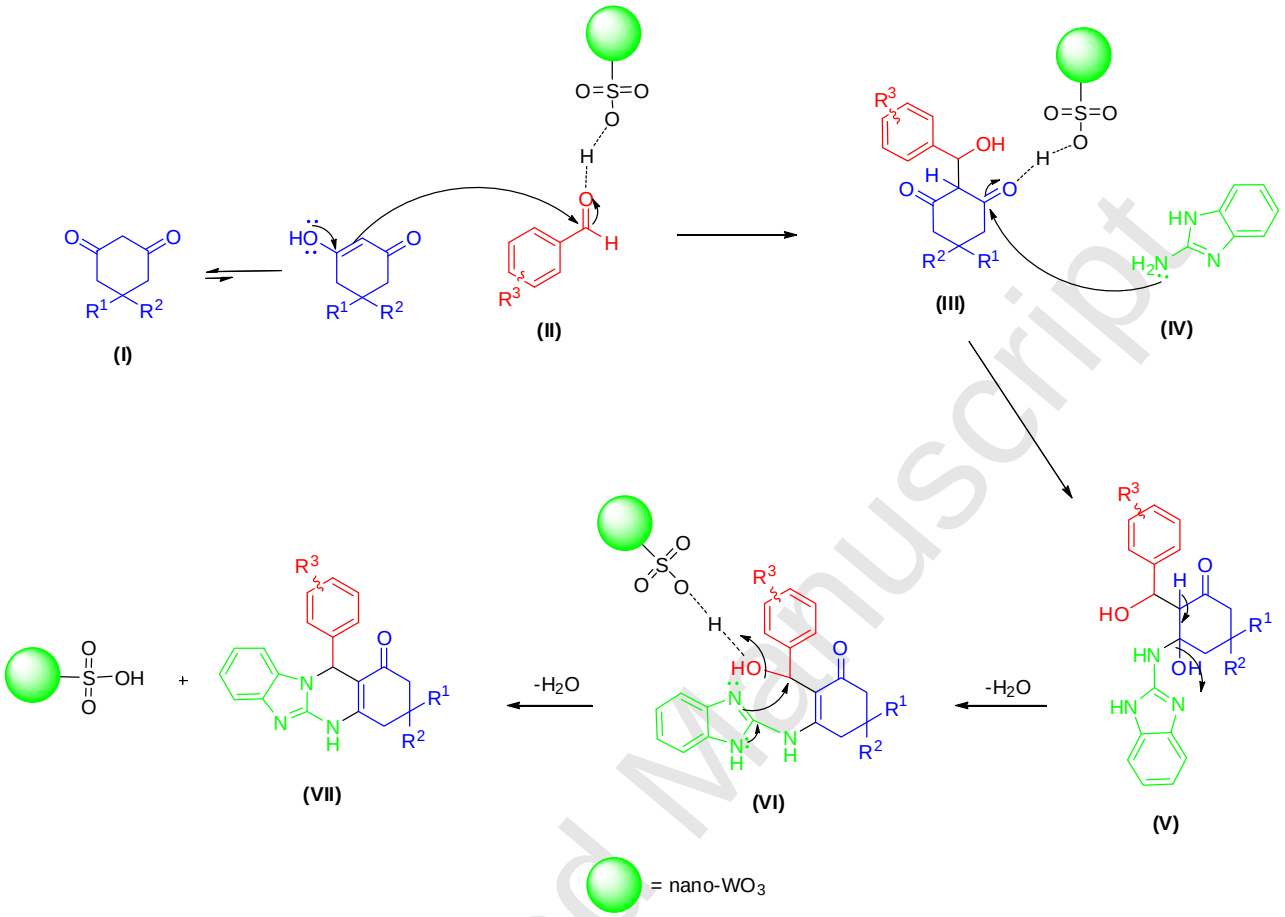


Fig. 12. Proposed Mechanism for the synthesis of benzoimidazoloquinazolins by n-WSA.

The reusability of the catalyst was tested with five consecutive synthesis of benzoimidazoloquinazolin by using recovered n-WSA and desired product obtained in 91-94% yield(Fig.13).

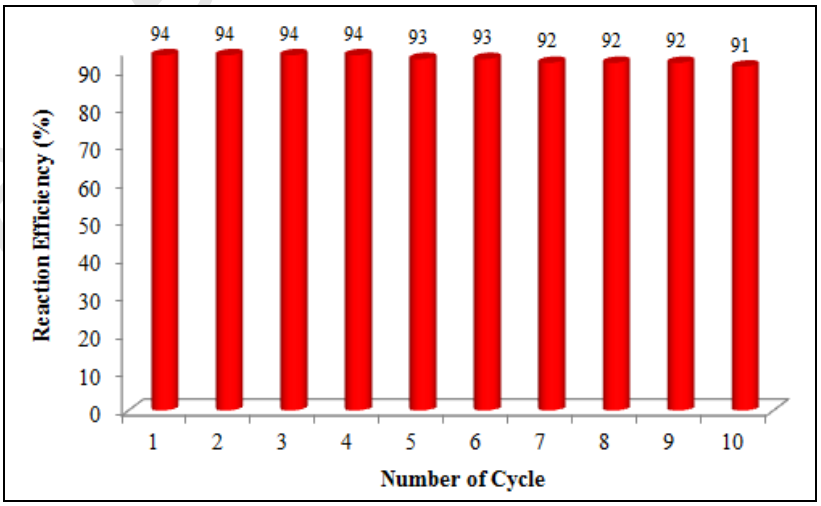


Fig.13. Reusability of n-WSA for the synthesis of benzimidazoloquinozoline,Reaction conditions: benzaldehyde (1 mmol), dimedone (1mmol), 2-amino benzimidazole (1 mmol),reaction time: 15 min at 100 ºC in solvent free condition.

4. Conclusion

In summary, for the first timenano-WO_3-supported sulfonic acid was introduced as a new heterogeneous solid acid nano catalyst. This new catalyst has been efficiently used for the synthesis of 1,8-dioxo-octahydroxanthenes, tetrahydrobenzoxanthene and benzoimidazoloquinazolinin multi component reactionsunder solvent-free conditions. Allthe reactions works easily for a variety of aldehydes with both electron-donating and electron-withdrawing groups to give corresponding products in excellent yields. The catalyst was reused for 10 consecutive cycles with consistent activity. The excellent catalytic performance, easy preparation and separation of the catalyst make it a good heterogeneous solid acid nano catalyst for organic synthesis and transformations.

Acknowledgements

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