

Nano perlite sulfuric acid: an inexpensive heterogeneous acid catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes and tetrahydrobenzoxanthenes under solvent-free conditions

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Abstract

Nano perlite sulfuric acid (n-PeSA) as an inexpensive powerful solid acid nanocatalyst has been successfully applied for the efficient and green synthesis of 1,8-dioxo-octahydroxanthenes and tetrahydrobenzoxanthenes under solvent free condition in excellent yield. These new procedures offer many advantages including ease of preparation and handling, low cost and low toxicity of catalyst, environmental friendliness reaction conditions, short reaction time and absence of any tedious workup or purification. Furthermore, the catalyst could be recycled and reused at least five times without appreciable deterioration in catalytic activity, confirming the stability of the covalent bonding of acidic centers.

Keywords: Nano perlite sulfuric acid, 1,8-dioxo-octahydroxanthenes, tetrahydrobenzoxanthenes, green chemistry, recyclability.

1. Introduction

One of the most prominent challenges in modern world is the sufficient and sustainable supply of clean energy [1]. Equipment corrosion, serious environmental contamination through producing a large amount of hazardous wastes and tedious catalyst separation cause that the use of homogeneous acid-catalysis in chemistry is not economical and environmentally friendly.. In this respect, heterogeneous acid catalysts were introduced owing to their unique properties such as low toxicity, non-corrosive nature and ease of separation and recovery from the viewpoint of green chemistry [2, 3]. The use of nanomaterial as heterogeneous catalysts is a current topic of research because of their wonderful structural features and high levels of their catalytic activity [4-6].

Multi-component reactions (MCRs) along with advantages of efficiency, selectivity, atom economy, and simplicity are arguably one of the most important protocols in organic and medicinal chemistry that have attracted considerable attention in many years [7]. Therefore, synthesis of heterocyclic compounds through multicomponent reactions via environmentally benign procedures and utilizing green reusable catalysts is a prominent subject of interest [8]. Xanthenes and benzoxanthenes are noteworthy biologically active heterocyclic compounds along with a broad range of biological activities such as antibacterial, antiviral, antidepressant and anti-inflammatory [9-12]. Additionally, they have been widely used as dyes, photodynamic therapy, laser technologies and pH sensitive fluorescent materials [13-16]. Several synthetic methods have been reported

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up to now for the preparation of xanthenes derivatives through multicomponent condensation reaction of aryl aldehydes and dimedone for the synthesis of 1,8-dioxo-octahydroxanthenes and condensation of aryl aldehydes, dimedone and β -naphthols for the synthesis of tetrahydrobenzo xanthenes [17-20]. However, the discovery of efficient, green and simple methods for the preparation of these compounds is of prime interest. Recently, we have introduced perlite sulfuric acid (PeSA) as an efficient and inexpensive heterogeneous solid acid catalyst for the promotion of a wide range of organic reactions [21]. The ease of handling, ease of preparation, low cost, low toxicity and recyclability are the main superiorities of this catalyst.

Considering the above facts and in continuing our efforts towards the development of efficient and environmentally benign heterogeneous catalysts in organic transformations [22-26], we now wish to report nano perlite sulfuric acid can be catalyzed efficient and green synthesis of 1,8-dioxo-octahydroxanthenes and tetrahydrobenzoxanthenes under mild and eco-friendly conditions. Mild reaction conditions, short reaction times, simple work-up procedures and ease of purification, are the main superiorities of this procedure.

2. Experimental procedure

2.1. Materials and Methods

Chemical materials and solvents were purchased from Merck and Aldrich chemical companies. n-PeSA nanoparticles were dispersed in water and the sizes and morphology of the particles was determined using TEM (Transmission Electron Microscopy) analysis on a Philips – CM300 - 150 KV microscope. ^1H NMR and ^{13}C NMR spectra were measured in pure deuteriated chloroform on a Bruker Avance 300 MHz instruments (^1H NMR 300 MHz). The chemical shifts are raised in parts per million (ppm) and tetramethylsilane (TMS) was used as an internal reference. Fourier transform infrared spectroscopy (FT-IR) was recorded using KBr pressed powder discs on a Shimadzu 8400s spectrometer. Melting points

were designated using a THERMO SCIENTIFIC 9100 apparatus. The progress of reactions and the purity of products were evaluated by thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using hexane/ethyl acetate mixture as mobile phase.

2.2. Preparation of n-PeSA

A suction flask charged with 1.0 g of perlite and dry CH_2Cl_2 (20 ml) equipped with a invariant-pressure dropping funnel comprising chlorosulfonic acid (0.3856 g, 3.3 mmol) and a gas inlet tube for transferring HCl gas toward an adsorbing solution (i.e., water) was used. Then chlorosulfonic acid was added dropwise over a period of 30 min in an ice bath. HCl gas immediately evolved from the reaction vessel followed by stirring at room temperature for 1 hour to complete removal of HCl. After that, the CH_2Cl_2 was decanted and the white solid powder was washed with water (10 mL) and dried at 100 °C. In this step, n-PeSA (1.44 g) was collected as a white solid powder [21].

The mmol of H^+ per gram of catalyst was also evaluated by acid-base titration of the suspension of the 1g of n-PeSA dispersed in 20 ml H_2O with standard NaOH solution (0.08 N). The amounts of acidic protons found to be 3.8 mmol.g⁻¹ of n-PeSA.

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

In a typical experimental reaction procedure, aromatic aldehyde (1 mmol), dimedone (2 mmol) and n-PeSA (0.026g, 10 mol%) were taken in a 10 mL round-bottomed flask, the resulting mixture was stirred under solvent-free condition at 110 °C for an appropriate time. After the completion of the reaction (monitored by TLC), the reaction mixture was eluted with hot ethanol (5 mL) and was centrifuged to filter the catalyst. Then, solid products were obtained by recrystallization of ethanol solution.

2.4. General procedure for synthesis of tetrahydrobenzoxanthene derivatives

In a typical experimental reaction procedure, aromatic aldehyde (1 mmol), dimedone (1 mmol), β -naphthol (1 mmol) and n-PeSA (0.013g, 5 mol%) were taken in a

10 mL round-bottomed flask, the resulting mixture was stirred under solvent-free condition at 80 °C for an appropriate time. After the completion of the reaction (monitored by TLC), the reaction mixture was eluted with hot ethanol (5 mL) and was centrifuged to filter the catalyst. Then, solid products were obtained by recrystallization of ethanol solution.

3. Results and discussion

Considering our research toward evaluating the catalytic activity of PeSA as an inexpensive and environmentally catalyst for the synthesis of heterocyclic compounds [21], in this work we have investigated the performance of this nanocatalyst in the synthesis of 1,8-dioxo-octahydroxanthenes and tetrahydrobenzoxanthene under solvent-free conditions. The catalyst was already characterized by the thermal gravimetric analysis (TGA), X-ray diffraction (XRD), FT-IR spectroscopy, field emission scanning electron microscopy (FE-SEM) and the acid strength of n-PeSA was determined by the Hammett acidic function too. The shape and size of the particles is determined by TEM analysis.

3.1 TEM analysis of catalyst

Figs. 1a-d show TEM images of nano-perlite sulfuric acid (n-PeSA). The average particle size and the layer thickness were carried out using image software. The images show layer structures along with spherical fine perlite particles on them which are formed by the reaction of perlite with chlorosulfonic acid. It is evident from Fig. 1a and d that the morphology size and distribution of the particles located on the layer are almost homogeneous. As could be seen from Fig. 4b, the layer thickness size is 10-20 nm and the particles diameter sizes are about 50-60 nm according to the Fig. 4d.

3.2 Catalytic activity of nano perlite sulfuric acid in one-pot multicomponent reactions

After characterization, catalytic activity of the nanocatalyst was examined for the one-pot synthesis of 1,8-dioxo-octahydroxanthene and tetrahydrobenzoxanthene derivatives. Final compounds

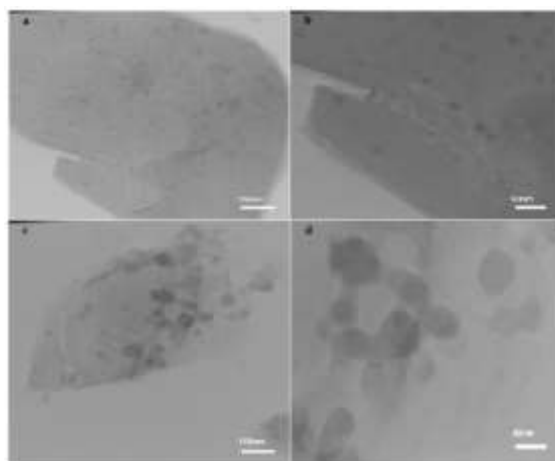


Figure 1. TEM images of n-PeSA.

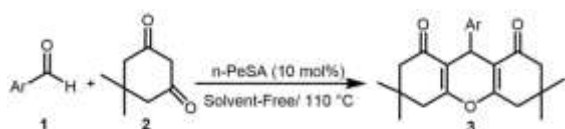
were well characterized by spectral data and compared with their physical data with the literature.

3.2.1 Synthesis of 1,8-dioxo-octahydroxanthene derivatives

In order to establish the best reaction conditions with respect to catalytic efficiency of n-PeSA for the synthesis of 1,8-dioxo-octahydroxanthenes, the reaction of benzaldehyde 1 (1 mmol) and dimedone 2 (2 mmol) in different sets of reaction conditions was used as a model reaction (Scheme 1). We investigated the effects of various amounts of catalyst, different solvents and temperatures on the model reaction yields (Table 1). To select an appropriate amount of catalyst on the catalytic performance, the reaction was optimized by varying the amount of catalyst (Table 1, entries 1-5). Therefore, it was found that the use of 10 mol% of the catalyst was sufficient to promote the reaction. (Table 1, entry 3). The usage of larger amounts of nanocatalyst did not have any dramatic effect on the product yield of reaction. The results show clearly that catalyst is effective for this reaction and in the absence of it, the reaction did not occur in any way (Table 1, entry 1). The reaction was also carried out in MeOH, EtOH, CH₃CN, and water to examine the solvent effect, (Table 1, entry 6-9). As can be seen the reaction proceeded under solvent-free condition to generate the corresponding product in excellent yields in short reaction time in comparison with solvent conditions (Table 1, entry 3). To find out the best operative reaction temperature, the same

reaction in the presence of 10 mol% of catalyst was carried out at different temperatures (60, 90, 110, 140 °C) in the presence of 10 mol% of n-PeSA under solvent-free conditions to appraisement the effect of temperature on the reaction yield (Table 1, entries 3, 10–12) and the best results were obtained at 110 °C.

Based on the optimized reaction conditions, in order to explore the scope and generality of this protocol, a series of aromatic aldehydes with the electron-donating and electron withdrawing groups were reacted with dimedone under the optimized conditions (Scheme 1). As is observable, by using this catalyst, the aromatic aldehydes containing both electron-donating and electron-withdrawing groups afforded the corresponding 1,8-dioxo-octahydroxanthenes **3** with excellent yield (Table 2, entries 1–17).



Scheme 1. Synthesis of 1,8-octahydroxanthenes using of n-PeSA. Physical and spectroscopic data for selected compounds

9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**3f**): ¹H NMR (CDCl₃) δ (ppm): 6.07 (q, 4H), 3.58 (s, 1H), 1.34 (s, 4 H), 1.06 (q, 4 H), 0.14 (s, 6 H), 0.03 (s, 6 H). ¹³C NMR (CDCl₃) δ (ppm): 27.25, 29.27, 31.47, 32.19, 40.78, 50.68, 115.17, 115.20, 128.17, 129.79, 131.93, 142.78, 162.54. FT-IR (KBr) cm⁻¹: 2951, 1660, 1512, 1373, 1333, 1218, 1191, 1135, 1008, 832, 733.

3,3,6,6-tetramethyl-9-(*p*-tolyl)-3,4,5,6,7,9-hexahydro-¹H-xanthene-1,8(2*H*)-dione (**3i**): ¹H NMR (CDCl₃) δ (ppm): 7.16-7.26 (m, 2H), 7.005-7.025 (d, 2H), 4.70 (s, 1H), 2.17-2.45 (m, 4H), 2.13 (s, 3H), 1.66-1.72(m, 4 H), 1.095 (s, 6 H), 0.99 (s, 6 H). FT-IR (KBr) cm⁻¹: 2958, 1664, 1620, 1512, 1373, 1333, 1200, 1160, 1020, 853.

3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**3k**): ¹H NMR (CDCl₃) δ (ppm): 8.10-8.11 (m, 2H), 7.47-7.49 (m, 2H), 4.62 (s, 1H), 2.50 (m, 4H), 2.24-2.28 (d, 2H), 2.15-2.17 (d, 2H), 1.12 (s, 6H), 0.99 (s, 6H). ¹³C

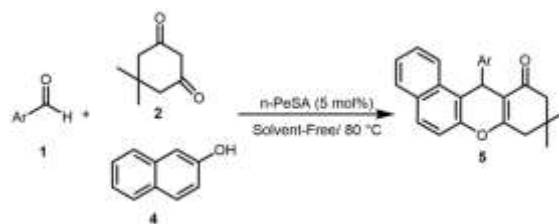
NMR (CDCl₃) δ (ppm): 27.26, 28.46, 28.96, 32.07, 40.79, 50.59, 114.19, 124.59, 127.14, 132.07, 138.17, 149.77, 163.06, 196.37. FT-IR (KBr) cm⁻¹: 2958, 1662, 1614, 1532, 1514, 1361, 1201, 1196, 1160, 1136.

9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**3m**): ¹H NMR (CDCl₃) δ (ppm): 7.32-7.34 (d, 2H), 7.16-7.29 (t, 2H), 4.69 (s, 1H), 2.46 (s, 4 H), 2.14-2.25 (q, 4 H), 1.10 (s, 6 H), 0.98 (s, 6 H). ¹³C NMR (CDCl₃) δ (ppm): 27.27, 29.28, 31.57, 32.11, 32.18, 40.71, 40.77, 50.68, 115.00, 115.07, 120.15, 130.21, 131.01, 143.32, 162.57, 169.37. FT-IR (KBr) cm⁻¹: 2951, 1660, 1512, 1373, 1333, 1218, 1191, 1135, 1008, 832, 733.

9-(3-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**3p**): ¹H NMR (CDCl₃) δ (ppm): 6.01 (m, 4H), 3.59 (s, 1H), 1.32 (s, 4 H), 1.07 (q, 4 H), 0.12 (s, 6 H), 0.02 (s, 6 H). ¹³C NMR (CDCl₃) δ (ppm): 27.33, 29.21, 31.73, 32.21, 40.79, 50.69, 115.02, 126.59, 126.89, 128.40, 129.23, 133.80, 146.16, 162.65, 196.31. FT-IR (KBr) cm⁻¹: 2951, 1660, 1512, 1373, 1333, 1218, 1191, 1135, 1008, 832, 733.

3.2.2 Synthesis of tetrahydrobenzoxanthene derivatives

The as-prepared n-PeSA has been tested as catalyst for the synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-one derivatives by condensation of aromatic aldehydes **1** (1 mmol) with β-naphthol **4** (1 mmol) and dimedone **2** (1 mmol) under optimal conditions (5 mol% of catalyst at 80 °C under solvent-free condition) (Scheme 2). The obtained results showed the efficiency of this method in the synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones **5** (Table 3, entries 1-16).



Scheme 2. Synthesis of 12-aryl-tetrahydrobenzo[*a*]xanthene-11-ones using n-PeSA

Table 1. Optimization of synthesis of 1,8-octahydroxanthenes^a

Entry	Solvent	Condition	Amount of Catalyst		Time (min)	Yield (%) ^b
			(mol %)			
1	Solvent-free	110 °C	-		30	trace
2	Solvent-free	110 °C	5		30	80
3	Solvent-free	110 °C	10		10	98
4	Solvent-free	110 °C	15		10	92
5	Solvent-free	110 °C	20		10	83
6	H ₂ O	Reflux	10		30	76
7	CH ₃ CN	Reflux	10		30	79
8	MeOH	Reflux	10		30	82
9	EtOH	Reflux	10		30	86
10	Solvent-free	60 °C	10		30	83
11	Solvent-free	90 °C	10		30	85
12	Solvent-free	140 °C	10		10	98

^a Reaction condition: benzaldehyde (1 mmol), dimedone (2 mmol). ^b Isolated yields

Table 2. n-PeSA-catalyzed one-pot synthesis of 1,8-octahydroxanthenes^a

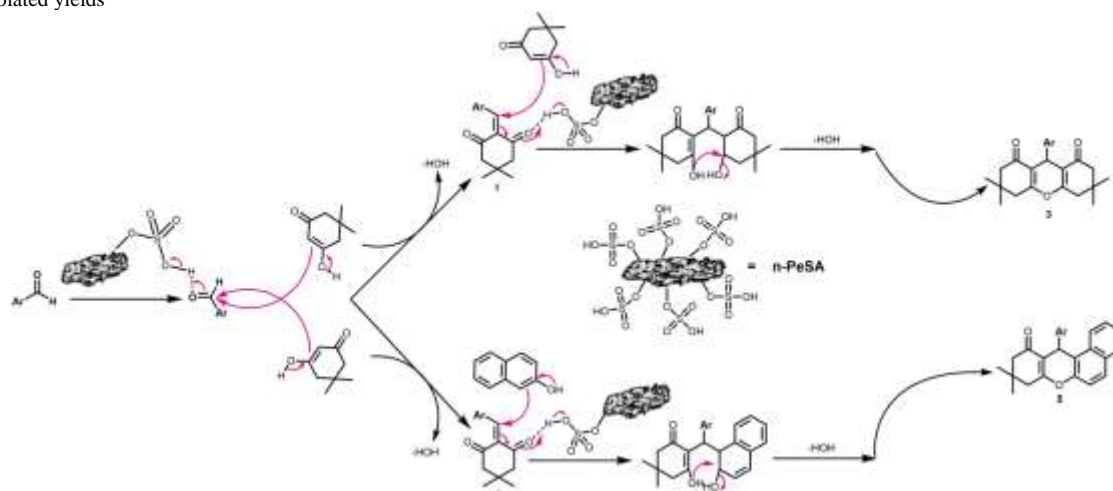
Entry	Ar	Product	Time (min)	Yield ^b (%)	mp (°C)	
					Found	Reported (ref.)
1	Ph	3a	10	98	203-204	203-205[27]
2	2-O ₂ NC ₆ H ₄	3b	20	91	255-257	256-257[27]
3	2-MeOC ₆ H ₄	3c	50	85	208-211	209-210[28]
4	2-ClC ₆ H ₄	3d	18	96	227-229	226-228[27]
5	2,6-(Cl) ₂ C ₆ H ₃	3e	35	82	318-320	319-320[29]
6	4-ClC ₆ H ₄	3f	10	98	228-230	227-229[28]
7	4-HOC ₆ H ₄	3g	30	90	246-248	246-247[30]
8	4-MeOC ₆ H ₄	3h	45	88	243-245	243-245[28]
9	4-MeC ₆ H ₄	3i	22	93	215-217	216-217[30]
10	4-(CH ₃) ₂ NC ₆ H ₄	3j	53	79	220-224	222-225[31]
11	4-O ₂ NC ₆ H ₄	3k	8	96	225-226	223-224[28]
12	4-FC ₆ H ₄	3l	5	98	258-260	259-260[28]
13	4-BrC ₆ H ₄	3m	7	97	238-241	239-240[29]
14	3-O ₂ NC ₆ H ₄	3n	16	89	172-175	173-174[27]
15	3-HOC ₆ H ₄	3o	19	86	215-216	214-215[29]
16	3-ClC ₆ H ₄	3p	17	88	193-195	192-193[27]
17	3,4-(MeO) ₂ C ₆ H ₃	3q	60	80	175-177	176-177[29]

^aReaction condition aromatic aldehyde (1 mmol), dimedone (2 mmol), n-PeSA (10 mol%), solvent-free, 110 °C. ^b Isolated yields

Table 3. n-PeSA-catalyzed one-pot synthesis of 12-aryl-tetrahydrobenzo[a]xanthene-11-ones^a

Entry	Ar	Product	Time (min)	Yield (%)	mp (°C)	
					Found	Reported (ref.)
1	Ph	5a	60	96	149-151	148-150[32]
2	2-O ₂ NC ₆ H ₄	5b	40	80	222-224	222-224[32]
3	2-OH C ₆ H ₄	5c	10	80	226-228	227-228[33]
4	2-ClC ₆ H ₄	5d	35	92	178-180	178-180[32]
5	4-ClC ₆ H ₄	5e	50	94	178-179	178-179[34]
6	4-HOC ₆ H ₄	5f	40	82	221-222	220-222[32]
7	4-MeOC ₆ H ₄	5g	30	84	204-205	202-204[32]
8	4-MeC ₆ H ₄	5h	60	89	174-176	175-176[32]
9	4-O ₂ NC ₆ H ₄	5i	70	86	176-178	176-178[32]
10	4-(CH ₃) ₂ CHC ₆ H ₄	5j	30	85	215-217	215-216[28]
11	4-FC ₆ H ₄	5k	30	95	184-186	185-186[35]
12	4-BrC ₆ H ₄	5l	50	95	184-185	184-186[32]
13	3-HOC ₆ H ₄	5m	40	85	238-240	238-240[34]
14	3,4-(MeO) ₂ C ₆ H ₃	5n	20	98	202-204	201-204[36]
15	3-O ₂ NC ₆ H ₄	5o	45	82	170-172	170-172[35]
16	3-OEt-4-OHC ₆ H ₃	5p	60	85	203-205	-

^aReaction condition aromatic aldehyde (1 mmol), dimedone (1 mmol), β -naphthole (1 mmol), n-PeSA (5 mol%), solvent-free, 80 °C. ^b Isolated yields



Scheme 3. A plausible mechanism for the synthesis of xanthene derivatives in the presence of n-PeSA under solvent-free conditions

Physical and spectroscopic data for selected compounds

12-(2-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (**5c**): ¹H NMR (CDCl₃-d) δ (ppm): 6.58-7.78 (m, 12H), 5.76 (s, 1H), 2.59 (s, 2H), 2.34-2.43 (m, 2H), 1.14 (s, 3H), 0.98 (s, 3H). FT-IR (KBr) cm⁻¹: 3200, 2950, 1631, 1593, 1532, 1232, 1196, 1160, 1135, 835, 738.

12-(3-ethoxy-4-hydroxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-11H-benzo[a]xanthen-11-one (**5p**): ¹H NMR (CDCl₃-d) δ (ppm): 6.6-7.98 (m, 11H), 5.62 (s, 1H), 5.56 (s, 1H), 4 (m, 2H), 2.5 (s, 2H), 2.22-2.31 (d.d, 2H), 1.33-1.37 (t, 3H), 1.09 (s, 3H), 0.96 (s, 3H). FT-IR (KBr) cm⁻¹: 3546, 2950, 1643, 1595, 1532, 1226, 1196, 1160, 1135, 835, 738.

From a mechanistic point of view, aromatic aldehyde is first activated by n-PeSA and the carbonyl carbon is attacked by the nucleophilic dimedone to form the Knoevenagel products (I). The Subsequent Michael addition of dimedone or β-naphthol to I, gives the acyclic adduct intermediate, which undergoes intramolecular cyclization with participation of two hydroxyl groups to give the corresponding products 3 and 5 (Scheme 3).

The efficiency of n-PeSA for the synthesis of 1,8-dioxo-octahydroxanthenes and 12-aryl-tetrahydrobenzo[a]xanthen-11-ones was compared with some other published works in literature (Table 4 and 5). As can be seen in these tables, the present nanocatalyst was found to be the more efficient catalyst among all of the catalysts in these reactions with respect to reaction condition, time and yield.

Table 4. Comparing the efficiency of n-PeSA with some different reported catalysts for the synthesis of 1,8-dioxo-octahydroxanthenes

Entry	1,8-dioxo-octahydroxanthenes			
	Catalysts	Condition	Time (min)	Yield (%)
1	n-WSA ^a [30]	Solvent-free/ 100 °C	85	91
2	TCCA ^b [37]	Solvent-free/ 110 °C	20	86
3	SSA ^c [39]	Solvent-free/ 80 °C	60	97
4	CSA ^d [40]	Solvent-free/ 110 °C	300	94
5	PSA ^e [41]	Solvent-free/ 80 °C	50	86
6	n-PeSA	Solvent-free/ 110 °C	10	98

^aNano-WO₃-supported sulfonic acid. ^b1,3,5-trichloro-2,4,6-triazinetriion (trichloroisocyanuric acid). ^cSilica sulfuric acid. ^dCellulose sulfuric acid. ^ePhospho sulfonic acid

Table 5. Comparing the efficiency of n-PeSA with some different reported catalysts for the synthesis of tetrahydrobenzo[a]xanthen-11-ones

Entry	tetrahydrobenzo[a]xanthen-11-ones			
	Catalysts	Condition	Time (min)	Yield (%)
1	n-WSA[30]	Solvent-free/ 100 °C	70	92
2	TCCA[37]	Solvent-free/ 110 °C	40	80
3	Ce(SO ₄) ₂ .4H ₂ O[35]	Solvent-free/ 120 °C	15	91
4	P-TSA ^a [38]	[bmim]BF ₄ / 80 °C	180	90
5	Sr(OTf) ₂	CH ₂ Cl ₂ /80 °C	300	85
6	n-PeSA	Solvent-free/ 80 °C	60	96

3.3 Reusability of the catalyst

The recovery and reuse of catalyst without loss of activity is one of the most important advantages of heterogeneous catalyst from the viewpoint of atom economy and green chemistry. In this regard, reusability of this nanocatalyst was evaluated in the one-pot synthesis of 1,8-octahydroxanthenes under optimized conditions. After completing the reaction, n-PeSA was recovered from the reaction mixture via centrifuge, washed with hot ethanol and water to

ensure the organic reagents do not remain on the surface of nanocatalyst and dried in oven at 110 °C and was reused for another batch of the reaction. The results of six consecutive runs showed that the catalyst can be reused 5 times without any appreciable loss of its activity suggesting that the nature of the catalyst remains intact after each run.

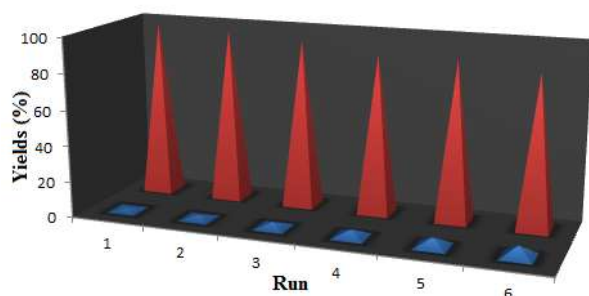


Figure 2. Reusability of n-PeSA in the one-pot synthesis of 1,8-octahydroxanthenes

4. Conclusion

To sum up, nano perlite sulfuric acid (n-PeSA) as an efficient and powerful nanocatalyst for the one-pot synthesis of 1,8-octahydroxanthenes and 12-aryl-tetrahydrobenzo[a]xanthene-11-ones was presented for the first time. Furthermore, the application of n-PeSA as a highly efficient, inexpensive, accessible and eco-friendly catalyst makes all process more industrially and economical important. In addition, good yields, short reaction times, low-cost, solvent-free conditions and a recyclable catalyst lead toward the green chemistry.

Acknowledgments

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