

Nano-silica supported ethane-sulfonic acid: An efficient heterogeneous solid acid catalyst for one-pot synthesis of xanthene and acridine derivatives

Zohreh Loghemani Jahromi*, Hassan Zare

Department of Chemistry, Islamic Azad University, Firoozabad Branch, P.O.Box 74715-117, Firoozabad, Fars, Iran.

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ABSTRACT

In this study, silica nanoparticles were used as support to prepare a new heterogeneous catalyst system for application in organic reactions. The reaction of silica nanoparticles with sodium 2-bromoethane-1-sulfonate resulted in the connection of a sulfonic acid group on the surface of silica nanoparticles (NSESAs). The synthetic catalyst system was characterized using different microscopic and spectroscopic techniques. After characterization of NSESAs, its catalytic activity was evaluated in a multicomponent reaction for one-pot synthesis of xanthene and acridine derivatives. Results of this study show that this catalyst system is effective in this reaction so that a range of xanthenes and acridines were obtained in high isolated yields under optimized conditions. The catalyst system was reusable at least for 7 times without significant decreasing in its catalytic activity.

Keywords: Nano-Silica, Heterogeneous catalyst, Solid acids, Xanthene, Acridine.

1. Introduction

Synthesis of organic compounds under mild conditions and using new approaches for the efficient synthesis of them is one of the main subjects in organic chemistry [1,2]. To achieve this goal, catalysis has a key role and many research groups focused on design, synthesis and development of catalyst systems. Catalysis systems used in organic chemistry divided into two important branches homogeneous and heterogeneous in classic [3-5]. The heterogeneous catalyst systems usually have more activity and selectivity in organic transformations. However, many problems associated with these catalyst systems caused that both academic and industrial researches followed developments on heterogeneous catalysis [6,7]. Although, heterogeneous catalysis may have less selectivity and activity in comparison with homogeneous counterparts but they are reusable and work with them are simple [8]. In order to increase the activity and selectivity of heterogeneous catalysts, nanomaterials were used as supports [9]. In this way, nanocatalysts become one of the most considerable heterogeneous catalysts in recent

years and there are many research groups that work in this field. Silica is a very promising support for the synthesis of heterogeneous catalysts due to the excellent feature of this material including stability and possibility of the connection of functional groups on its surface to generate catalytic sites [10-12]. Nano-silica has all of the characteristics of silica and also has a small particle size which resulted in the high activity and selectivity of nano-silica supported heterogeneous catalysts [13,14].

Acid catalysts are important in organic synthesis for the preparation of many fine chemical materials. However, the uses of mineral acid catalyst in organic reactions have many drawbacks including, non-reusability, being corrosive and difficulty in their using and the work up process. Thus solid acids have been considered in organic synthesis which possesses many advantages in comparison with mineral acids [15-17]. Sulfonic acid functionalized solid acids are an important class of heterogeneous acid catalyst which has been widely used in organic transformations [18-20].

In this study, we want to introduce an efficient heterogeneous solid acid catalyst to be used in organic reactions. The reaction route to synthesize nano-silica-

*Corresponding author email: zloghemani@yahoo.com
Tel.: +98 71 5437 2002; Fax: +98 71 5437 2010

functionalized ethane-sulfonic acid (NSESAs) catalyst system is simple. It can be prepared using the reaction of nano-silica and sodium 2-bromoethane-1-sulfonate as cheap and available starting materials (NSESAs). The nano nature of this catalyst system caused that it has high activity in organic reactions. To the best of our knowledge, there is no report in the literature on the stabilization of ethane-sulfonic acid on silica nanoparticles by this method. In this work, NSESAs catalyst was applied in a multicomponent reaction for one-pot synthesis of xanthene and acridine derivatives [21]. These classes of organic compounds have many biological activities and physical properties, thus their simple and efficient preparation is important [22-29]. Xanthene compounds have been synthesized using the reaction of dimedone and aldehyde in the presence of acid catalyst. For the synthesis of acridines in addition to dimedone and aldehyde amine should be used. There are several methodologies on the synthesis of these categories of compounds, but most of them suffer from drawbacks and there is a requirement on the introduction of a new catalyst for synthesis of these compounds [30-37]. NSESAs catalyst showed good reactivity in synthesis of xanthene and acridine derivatives and the result of this study is provided below.

2. Experimental

2.1. General

Chemicals were purchased from Merck and Aldrich Chemical companies and used without further purification. The nano-silica was provided from the US Research Nanomaterials company with the following information: Purity= 99%; APS= 20-30 nm; SSA= 180-600 m²/g; Color= white; Bulk density= <0.10 g/cm³; True density= 2.4 g/cm³. For the recorded ¹HNMR and ¹³CNMR spectra we used a Bruker (250 MHz) Advance DRX in pure deuterated DMSO-d₆ and CDCl₃ solvents with tetramethylsilane (TMS) as the internal standards. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer), was employed for characterization of the compounds. The transmission electron microscopy (TEM) images were obtained using TEM apparatus (CM-10-philips, 100 kV) for characterization of the ligand. The scanning electron micrograph (SEM) for the PAFMNP ligand was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). The thermogravimetric analysis (TGA) of the samples was analyzed using a lab-made TGA instrument. X-ray diffraction (XRD, D8, Advance, Bruker, axis) was employed for the characterization of the catalyst. Melting points were determined in open capillary tubes in a Barnstead

Electrothermal 9100 BZ circulating oil melting point apparatus. Reaction monitoring was accomplished using TLC on silica gel PolyGram SILG/UV254 plates.

2.2. Synthesis of nano-silica-functionalized ethane-sulfonic acid (NSESAs) catalyst

In a 100 mL conical flask, a mixture of nano-silica (3 g), sodium 2-bromoethane-1-sulfonate (3 mmol, 0.64 g) and K₂CO₃ (6 mmol, 0.825 g) was added in 50 mL of toluene. The reaction mixture was stirred at room temperature for 1h. Subsequently, the reaction temperature was increased to 110 °C and the solution was stirred for 24 h at this temperature. Then, the reaction temperature was decreased to room temperature and the solid was filtered and washed several times with ethanol and water. The solid was dried in an oven and then dissolved in a 50 mL 0.01M HCl in order to exchange proton be completed. The filtration of solid and washing with water and drying resulted in the production of NSESAs catalyst.

2.3. General procedure for synthesis of xanthenes using NSESAs catalyst

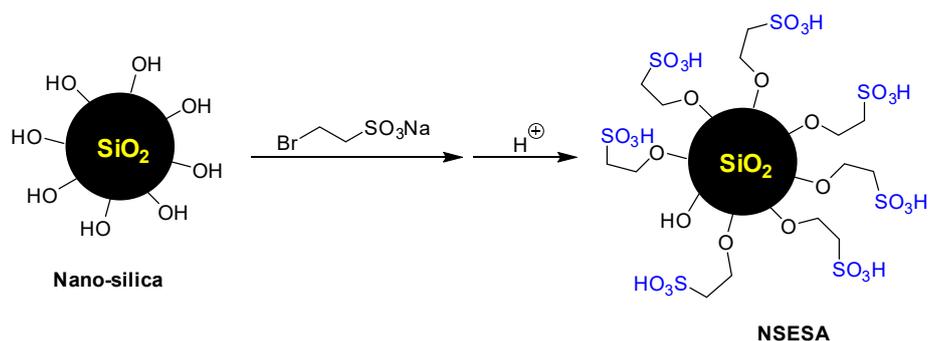
In a typical experiment, the NSESAs catalyst (0.1 g) was added to a mixture of aldehyde (1 mmol) and dimedone (2 mmol) in 5 mL EtOH, and heated in an oil bath at 80 °C. The reaction was followed by TLC. After the completion of the reaction, hot filtration was accomplished and the catalyst was separated from the reaction mixture and washed with EtOH (2 × 5 mL). The catalyst was dried for the next run. The organic phase after separation of the catalyst was evaporated to obtain the product. For further purification recrystallization in hot ethanol was employed.

2.4. General procedure for synthesis of xanthenes and acridines using NSESAs catalyst

The procedure for the synthesis of acridines is same to xanthenes with this different that amine component (1 mmol) was used in the reaction. The progress of the reaction was monitored by TLC.

3. Results and Discussion

First, we start to prepare the NSESAs catalyst according to the reaction route showed in Scheme 1. Nano-silica in the range of 20-30 nm was used for the synthesis of this catalyst system. It was reacted with sodium 2-bromoethane-1-sulfonate under conditions showed in Scheme 1. The acidifying the prepared material in the previous step resulted in the synthesis of NSESAs catalyst, successfully. Afterward the NSESAs catalyst was characterized using some different techniques including FT-IR, TGA, XRD and TEM analysis.



Scheme 1. Synthesis of NSESA catalyst using the reaction of nano-silica and 2-bromoethane-1-sulfonate.

The FT-IR of purchased nano-silica, sodium 2-bromoethane-1-sulfonate and NSESA catalyst are shown in Fig. 1. According to the FT-IR spectrum of nano-silica, the broad peak at 3448 cm^{-1} is due to the stretching vibration of H_2O molecules. The band at 1643 cm^{-1} is due to the bending vibration of H_2O molecules. The shoulder at 3300 cm^{-1} could be assigned to the stretching vibrations of Si-OH groups in the structure of SiO_2 . Also, the weak band around 950 cm^{-1} can be assigned to silanol groups. The peak at 1103 cm^{-1} with a shoulder at 1190 cm^{-1} is usually assigned to the Si-O-Si asymmetric stretching vibrations. Furthermore, the peak at 802 cm^{-1} can be assigned to Si-O-Si symmetric stretching vibrations. The band at 471 cm^{-1} is due to O-Si-O bending vibrations [38]. The FT-IR spectrum of sodium 2-bromoethane-1-sulfonate shows characteristic peaks positioned at 3603 , 1620 , 1203 , 1190 , 1050 , 795 , 571

and 521 cm^{-1} . The peaks appeared at 1203 and 1190 is attributed to stretching vibrations of O=S=O group [39,40]. Also the band at 795 cm^{-1} is referred to stretching vibration of S-O bond [41]. It should be mentioned that the peak positioned at 521 cm^{-1} is assigned to C-Br bond. The comparison of starting materials FT-IR spectra and NSESA catalyst clearly show the presence of ethane sulfonic moiety in the structure of nano-silica. For example the peaks appeared at 1103 , 802 and 471 cm^{-1} show the presence of Si-O-Si bond in the material. Also, peaks at 1205 and 1195 cm^{-1} show the existence of O=S=O bond and a weak peak at 790 show the S-O bond, representing the $-\text{SO}_3\text{H}$ group in the structure of NSESA catalyst. The disappearance of the peak at 521 cm^{-1} confirms the connection of ethane sulfonic acid moiety to the silica via C-O bond formation.

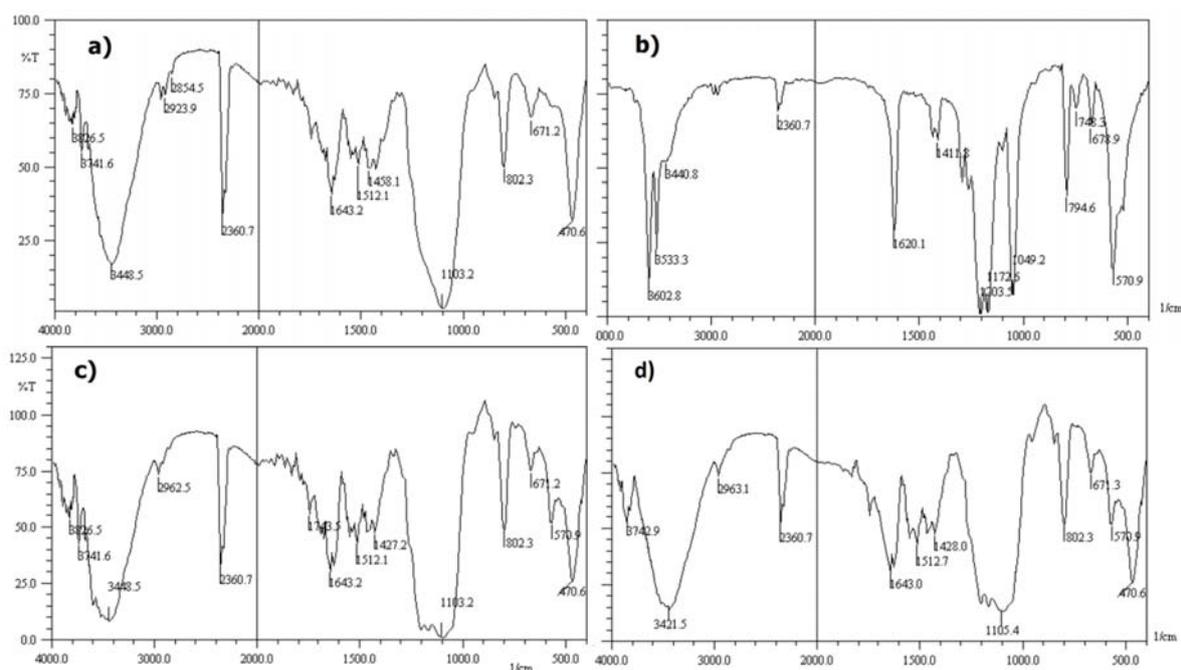


Fig. 1. The FT-IR spectra of nano-silica (a), sodium 2-bromoethane-1-sulfonate (b) and NSESA (c) reused NSESA catalyst (d).

The NSESA catalyst was also characterized by thermal gravimetric analysis (TGA), in order to investigate its thermal behavior and stability. The TGA curve of NSESA catalyst, show two main weight losses. The first was occurs approximately at 180 °C, which is attributed to the absorbed water in the structure of the catalyst (~4%). The next one, which is the main losses, observed at 210-320 degree, showing the decomposition of organic moiety connected to the nano silica surface (~14%). Also, it is possible to calculate the amount of grafted ethane sulfonic acid to the nano-silica surface using TGA (~1.27 mmol/g). Thus, TGA demonstrates the high stability of catalyst and strong connection of ethane sulfonic acid to the silica surface via covalent bonding.

The nanostructure of the NSESA catalyst was investigated using transmission electron microscopy (TEM) and it confirms the nano feature of the material. The TEM images of the catalyst are shown in Fig. 3. It seems that NSESA catalyst particles are formed regularly in a spherical shape and with good monodispersity. The average size of nanoparticles was

obtained about 24 nm according to dynamic light scattering (DLS) analysis.

The x-ray powder diffraction (XRD) pattern of NSESA catalyst is shown in Fig. 4. The XRD pattern of catalyst show the strongest peaks at $2\theta = 22$ degree which corresponds to the nano-silica [42,43].

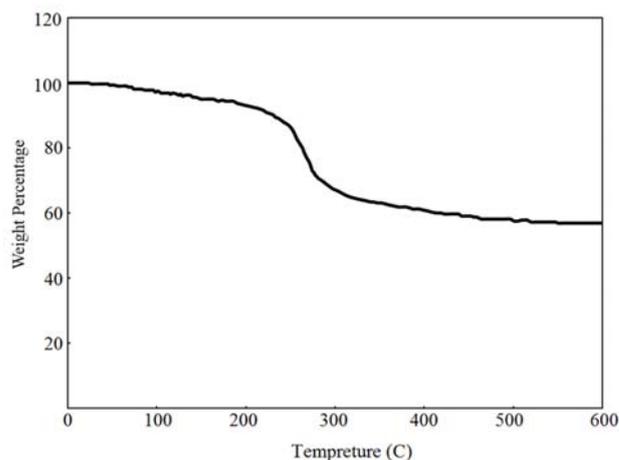


Fig. 2. The TGA analysis of NSESA catalyst.

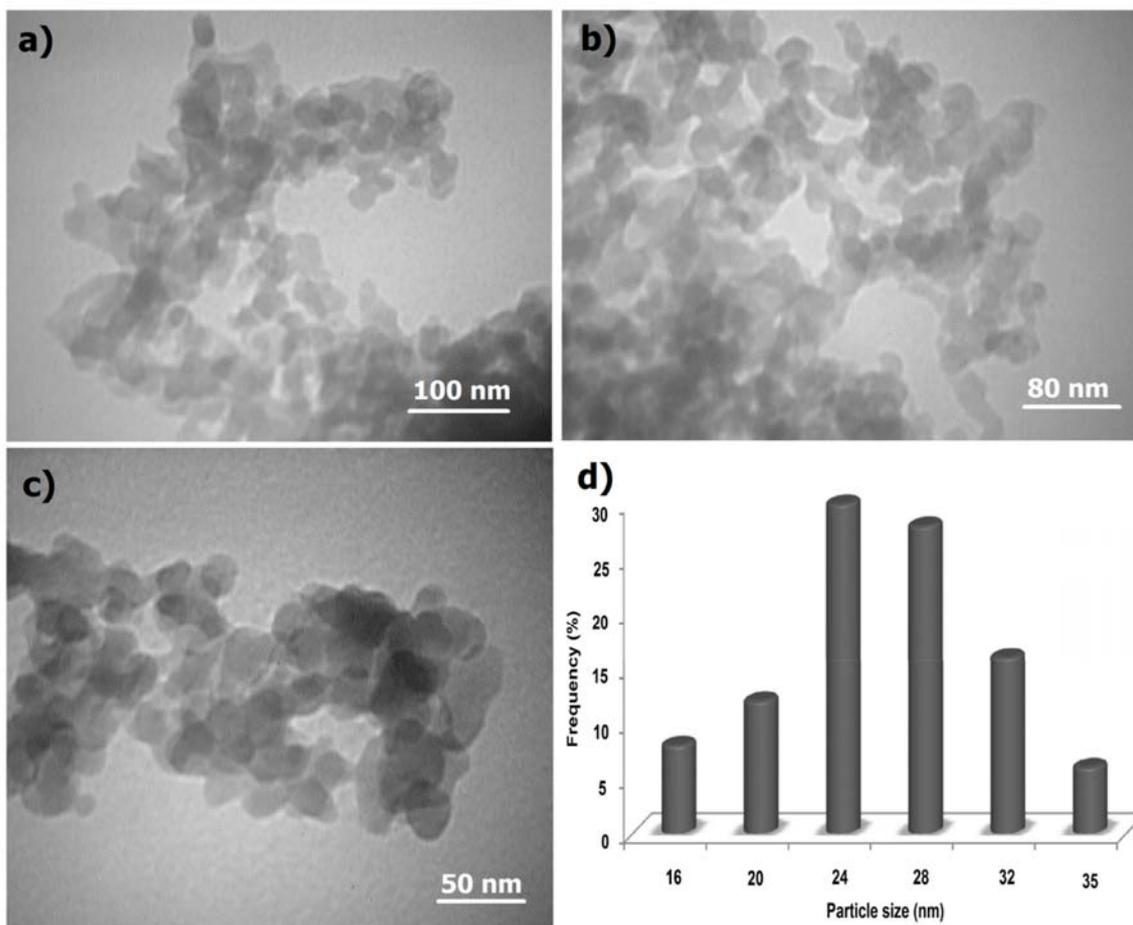


Fig. 3. The TEM images of NSESA catalyst from different positions and different magnifications (a-c). DLS analysis of NSESA catalyst which representing the size distribution of particles.

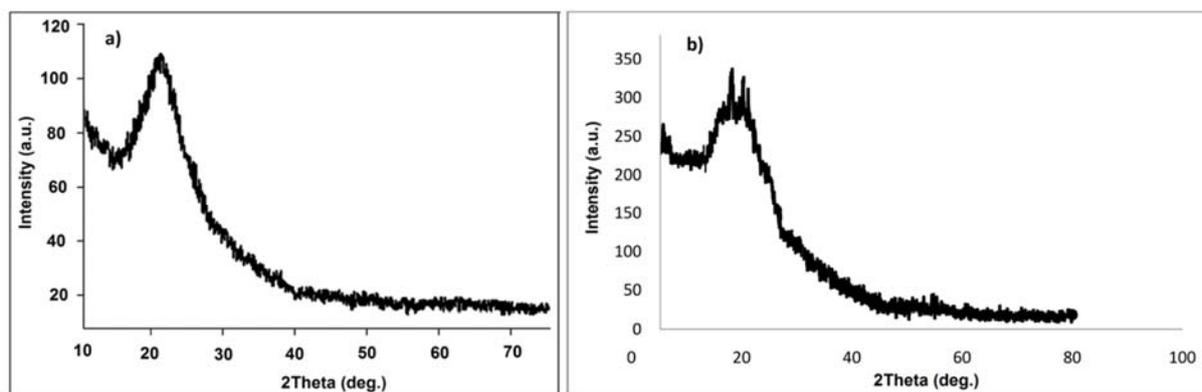


Fig. 4. The XRD pattern of fresh NSESA catalyst (a) and reused NSESA catalyst (b).

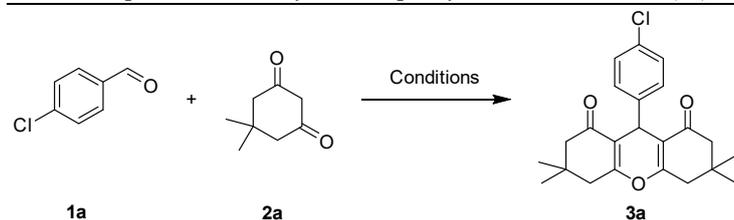
The elemental analysis of the catalyst shows that the percentage of sulfur is 4.1. Accordingly, we can calculate the amount of grafted sulfonic acid moiety on the surface of nano silica (1.3 mmol/g) which is in good agreement with TGA analysis.

After synthesis and characterization of NSESA catalyst, in order to show its catalytic applicability in organic transformations, the multicomponent synthesis of xanthenes and acridine derivatives was evaluated with this catalyst. The reaction between 4-Cl-benzaldehyde and dimedone was selected as a model

reaction and synthesis of correspond xanthenes was evaluated in the presence of NSESA catalyst. The result of optimization study is shown in Table 1.

Different conditions were checked in order to find optimized conditions for this reaction using NSESA catalyst. In the absence of catalyst a trace amount of product was obtained (Table 1, entry 1). Nano-silica was used as a catalyst and only 30% of product was isolated after 6h (Table 1, entry 2). Interestingly, in the presence of NSESA catalyst about 93% of product was produced after only 1h (Table 1, entry 3).

Table 1. Optimization study for one-pot synthesis of xanthenes (3a) in the presence of NSESA catalyst.^a



Entry	Catalyst (loading)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	None	EtOH	78	12	Trace
2	Nano-silica (0.1 g)	EtOH	78	6	30
3	NSESA (0.1 g)	EtOH	78	1	93
4	NSESA (0.1 g)	None	80	1	81
5	NSESA (0.1 g)	Toluene	100	5	70
6	NSESA (0.1 g)	H ₂ O	80	5	72
7	NSESA (0.1 g)	CH ₃ CN	70	5	65
8	NSESA (0.075 g)	EtOH	78	1	89
9	NSESA (0.05 g)	EtOH	78	3	80
10	NSESA (0.125 g)	EtOH	78	1	94
11	NSESA (0.1 g)	EtOH	50	3	70
12	NSESA (0.1 g)	EtOH	rt	6	45

^aReaction conditions: 4-Cl-benzaldehyde (1 mmol), dimedone (2 mmol), solvent (5 mL).

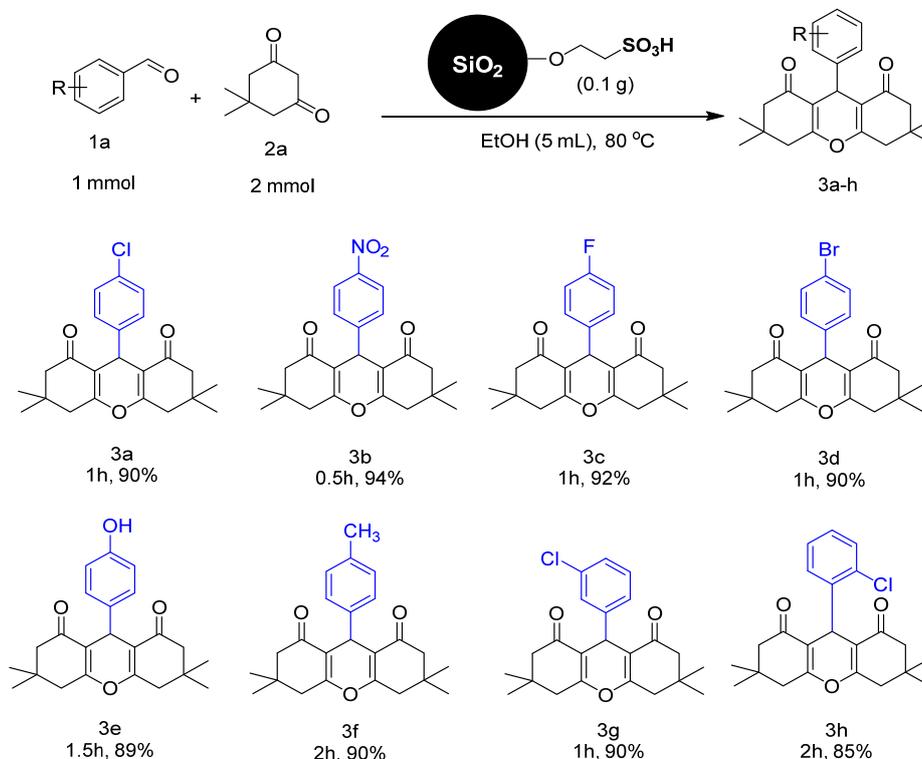
^bIsolated yield.

Then, the type of solvent was changed and among different tested solvents ethanol was recognized as best one (Table 1, entries 4-7). Then the amount of catalyst was optimized and 0.1 gram of catalyst was selected as optimum (Table 1, entries 8-10). The reaction yield by decreasing of temperature was decreased and the reflux temperature of ethanol as the optimized temperature was chosen (Table 1, entries 11 & 12). In this way, the entry 3 of Table 1 as the best conditions for synthesis of xanthenes was selected.

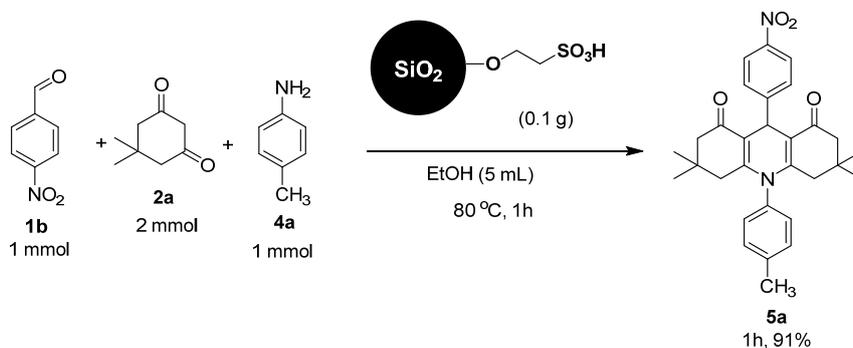
In order to show the generality and applicability of the NSESA catalyst in preparation of xanthenes derivatives, some other compounds were also synthesized under optimized conditions (Scheme 2). As shown in Scheme

2, different aldehydes have been used to synthesize diverse xanthenes using NSESA catalyst under optimized conditions. Electron-poor aldehydes gave corresponding xanthenes in less reaction times and high yields (**3b**). The reaction yield was decreased to some extent for electron-rich aldehydes along with more reaction time (**3e** & **3f**). Halogen substituted aldehydes were produced corresponding products in high yields (**3a**, **d**, **c** & **g**).

The synthesis of acridine derivatives under optimized conditions for xanthenes synthesis is done and reaction promoted with a high yield of acridine. For example, acridine **5a** was obtained in 91% yield using optimized conditions for synthesis of xanthenes (Scheme 3).



Scheme 2. Synthesis of diverse xanthenes using NSESA catalyst.



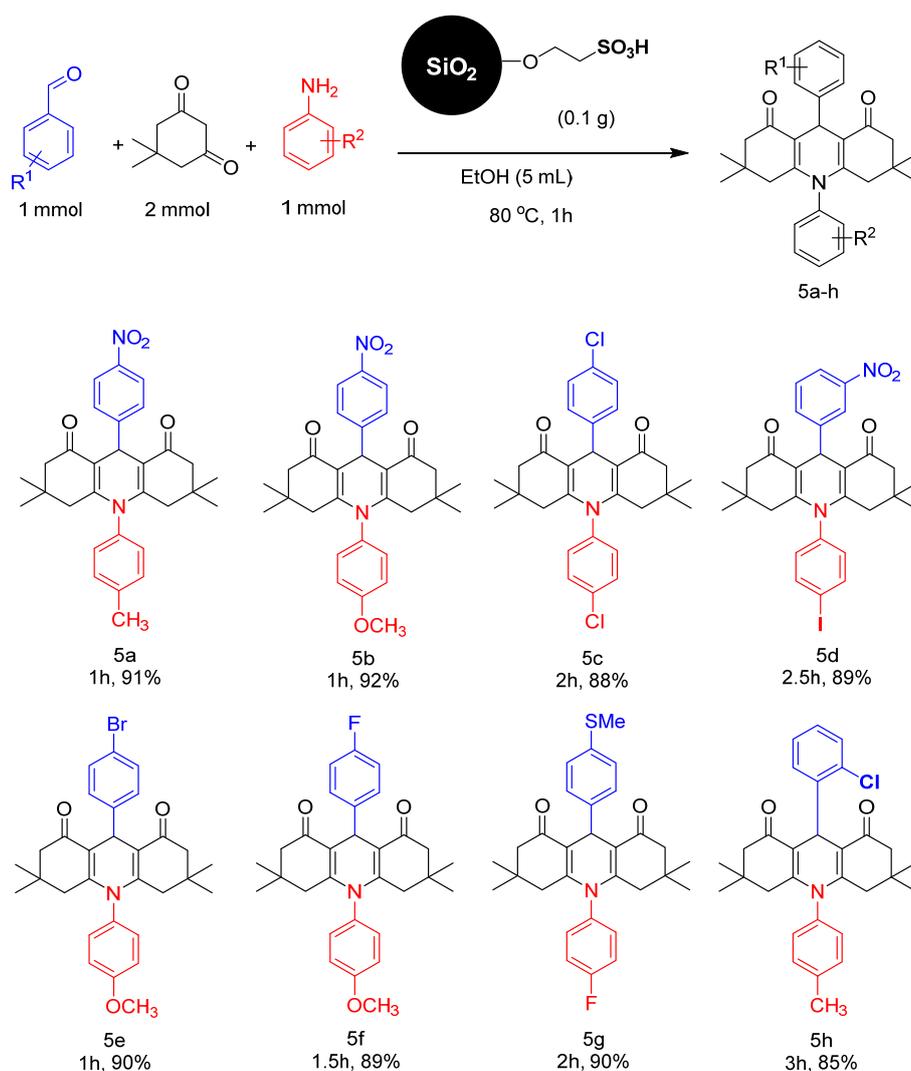
Scheme 3. Synthesis of acridine using NSESA catalyst.

The generality of this methodology was evaluated in the synthesis of diverse acridine derivatives as shown in Scheme 4. As shown in Scheme 4, different acridine derivatives could be synthesized under optimized conditions by selection of different amine and aldehyde components. It seems that the reaction yield is high for choices that amine component has electron donating group and aldehyde component has electron withdrawing group. All of the acridine products showed in Scheme 4 were obtained less than 3h with an isolated yield of more than 89%.

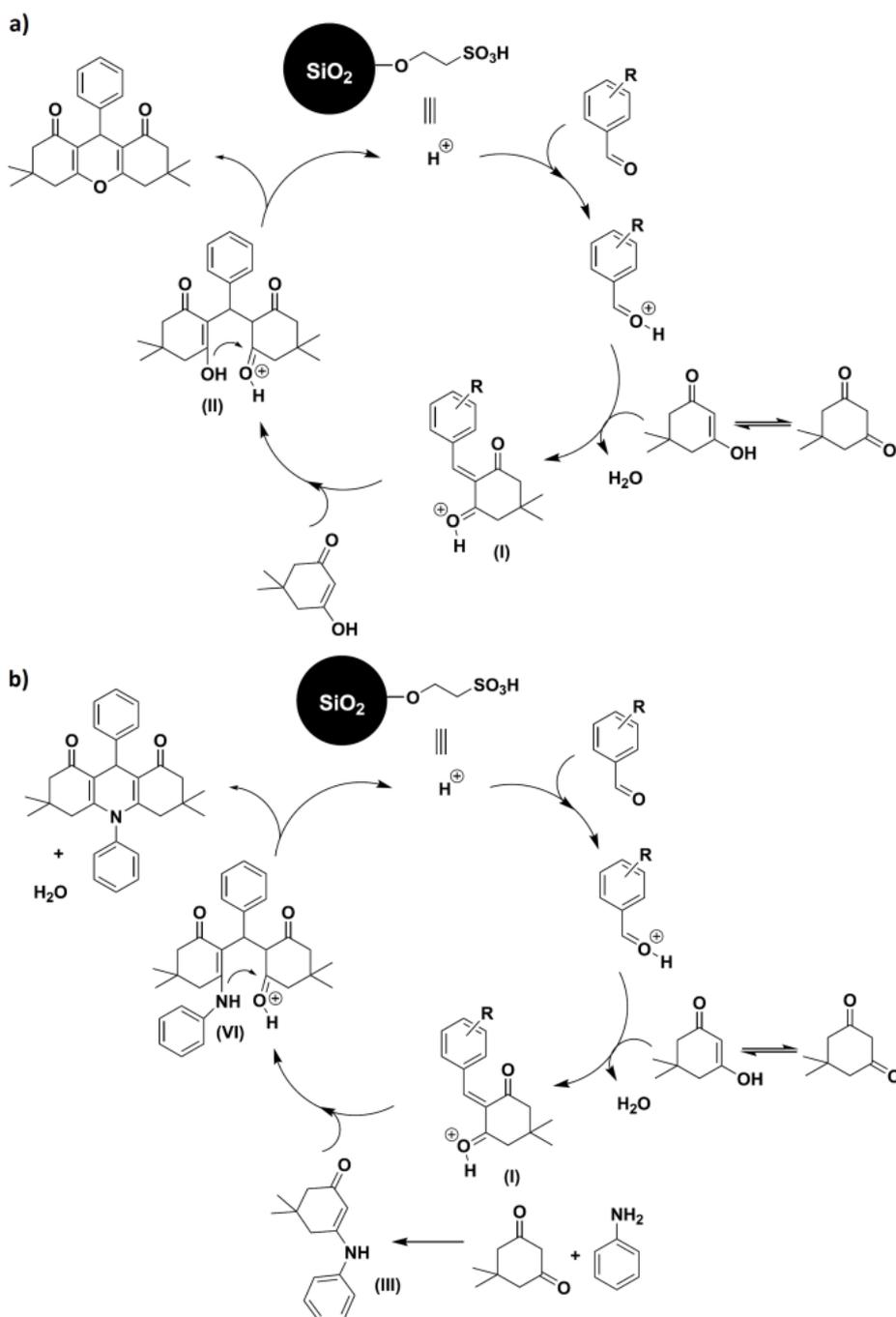
In this way, NSESA is proposed as an efficient nanocatalyst for one-pot synthesis of different xanthene and acridine derivative in high yields and short reaction time. Another feature of the NSESA is that it acts as a heterogeneous catalyst in this transformation. After completion of the reaction, hot filtration was done and the catalyst was reusable from the reaction mixture. The crude product was

recrystallized in hot ethanol to obtain the pure product. The reaction mechanism for this reaction is same to other reported pathway in the literature [32,37]. Accordingly, a reaction mechanism was proposed and it was depicted in Scheme 5.

The reusable capability of the NSESA catalyst was evaluated using model reaction for synthesis of xanthene **3a** under optimized conditions. It was observed that the catalyst system is reusable for 7 times (The yields were 93, 92, 91, 90, 89, 88 and 87 %, respectively). No remarkable decreasing activity was observed for this catalyst system in the reaction, demonstrating that it acts heterogeneously in practice in this protocol. The sulfur content of the catalyst after 7 times of reusability was investigated using elemental analysis and it was demonstrated that less than 1% of a sulfonic moiety was removed from the nano-silica surface during these stages.



Scheme 4. One-pot synthesis of various acridine derivatives using NSESA catalyst



Scheme 5. The proposed mechanism for synthesis of xanthenes (a) and acridines (b) in the presence of NSESA catalyst.

This information clarifies that NSESA catalyst is an efficient heterogeneous catalyst for synthesis of xanthene and acridine derivatives and it has high potential application to be used in other acid-catalyzed organic transformations. The FT-IR (Fig. 1d) and XRD pattern (Fig. 4b) of reused catalyst was shown that the structure of catalysts was not changed remarkably during reaction process. The TEM images of the catalyst after reusability also illustrate that the morphology and size of catalyst

not changed significantly, demonstrating high stability and practicality of this catalyst system (Fig. 5). In order to show the merit and applicability of this catalyst system for synthesis of xanthenes and acridines in comparison with reported catalysts a Table of comparison was provided (Table 2). This comparison showed that our catalyst system is superior in terms of activity, reaction conditions and yield related that previously reported catalysts.

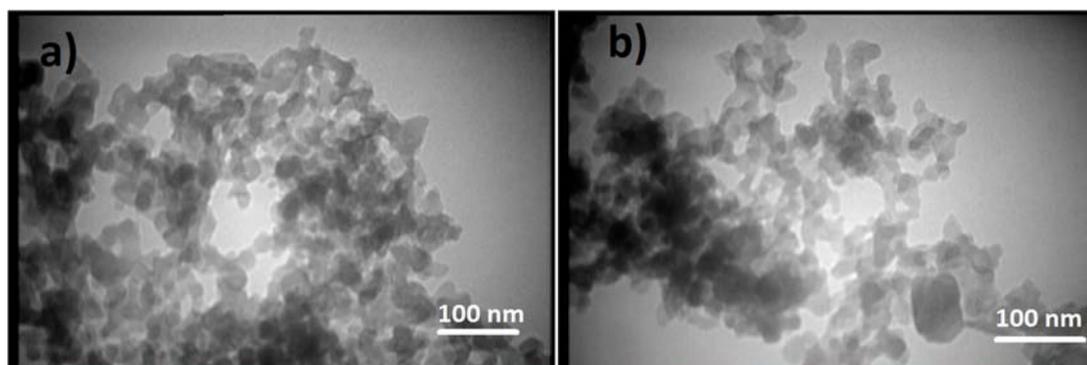
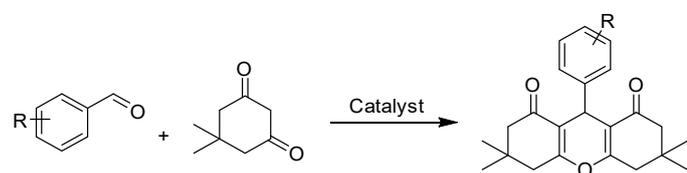


Fig. 5. The TEM image of reused NSESA catalyst.

Table 2. Comparison of the efficiencies of different catalysts for the synthesis of 1,8-dioxo-octahydroxanthenes.



Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref.
1	NSESA	EtOH	80	0.5-2	85-94	This work
2	Amberlyst-15	CH ₃ CN	reflux	5	91-96	[30]
3	SBSSA	EtOH	reflux	2-10	87-98	[31]
4	Mg(BF ₄) ₂	neat	80	15-30 min	81-97	[33]
5	SBSAN	None	50	1-4	73-94	[35]
6	[PVP-SO ₃ H]Cl	None	120	3-20 min	91-96	[36]
7	[Hmim]TFA	None	80	2.5-4	82-94	[45]
8	Silica sulfuric acid	None	80	1-2.5	88-97	[46]

4. Conclusion

In conclusion, we have introduced a new nano solid acid for application as a heterogeneous catalyst in organic transformations using a simple method and available and cheap starting materials. The nano feature of the substrate caused that this catalyst has high activity in organic transformations. The catalytic activity of this catalyst system was evaluated in the one-pot synthesis of xanthene and acridine derivatives using an acid-catalyzed multicomponent reaction. The NSESA catalyst showed high catalytic activity in this reaction and a range of acridine and xanthenes were obtained in good to excellent yield. The catalyst was reusable at least for 7 times in this protocol without significant decreasing in its catalytic activities. This catalyst system has great promise to be used in other organic transformations in future.

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