Chinese Chemical Letters xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

$SnCl_2$/nano SiO_2: A green and reusable heterogeneous catalyst for the synthesis of polyfunctionalized 4*H*-pyrans

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ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 4 June 2013
Accepted 6 June 2013
Available online xxx

Keywords:
Nano silica supported tin (II) chloride
Polyfunctionalized 4*H*-pyrans
Multicomponent reactions
Heterogeneous catalyst

ABSTRACT

A highly efficient and general method for the synthesis of polyfunctionalized 4*H*-pyrans is established through a one-pot multicomponent cyclocondensation of aromatic aldehydes with CH acids, malononitrile and ethyl acetoacetate using nano silica supported tin (II) chloride as a catalyst. In this method $SnCl_2$/nano SiO_2 was used as green and reusable catalyst. Excellent yields, short reaction times, simple workup, and inexpensiveness and commercially availability of the catalyst are the advantages of this method.

1. Introduction

Polyfunctionalized 4*H*-pyrans have a unique role in medicinal chemistry due to their wide range of biological and pharmacological activities [1,2]. These compounds are utilized as anticancer agents, anti-coagulants, spasmolytics, and anti-anaphylactics [3,4]. 4*H*-Pyran derivatives containing heterocyclic rings are extensively used for their pharmacological activities [5,6]. Furthermore, 4-phenyl-4*H*-pyrans have been identified as potent and specific IK_{Ca} channel blockers [7]. In addition, a number of 2-amino-4H-pyrans are valuable photoactive materials [8].

On the other hand, multicomponent reactions (MCRs) are efficient methods in heterocyclic scaffolds for the construction of diverse chemical libraries of drug-like molecules [9]. Synthetic strategies consisting MCRs have established themselves as a useful tool for the rapid introduction and development of molecular diversity [10]. MCRs increase the efficiency by combining several operational steps without isolation of intermediates or changing the reaction conditions [11,12]. Because of their convergence and productivity, the MCRs have attracted noticeable attention from the combinatorial chemistry community [13].

Previously, 2-amino-4*H*-pyrans were produced by the cyclization of arylidenemalononitriles with β-dicarbonyl compounds in the presence of bases such as piperidine [14], triethylamine [15], magnesium oxide [16], Mg/La [17], PEG1000-DAIL/EM [18], and nano ZnO [19]. Furthermore, diethyl 2,6-dimethyl-4-aryl-4*H*-pyran-3,5-dicarboxylates was synthesized with a low yield, utilizing $ZnCl_2$ as a catalyst, acetic anhydride as the solvent, and column chromatography as the purification method [20,21].

However, many of these methods require expensive reagents, acidic conditions, long reaction times, excess of reagents/catalyst, or toxic organic solvents and tedious workup, yet the yields are sometimes not ideal. In recent years, the use of heterogeneous catalysts has provided significant advantages in organic synthesis, for example, environmental compatibility, operational simplicity; also they are low cost, nontoxic, and easy to separate from the reaction mixtures [22,23]. Furthermore, heterogeneous solid acids and especially those based on silica gel and other mesoporous high surface area support materials are beginning to show an influential role in the greening of fine and speciality chemicals manufacturing procedures [24–26]. In continuation of our recent work using heterogeneous solid acid nanoparticles in organic reactions [27–29], we decided to investigate nano silica supported tin (II) chloride ($SnCl_2$/nano SiO_2) as a green catalyst for the practical and environmentally benign one-pot multicomponent synthesis of diethyl 2,6-dimethyl-4-aryl-4*H*-pyran-3,5-dicarboxylates and 6-amino-5-cyano-2-methyl-4-aryl-4*H*-pyran-3-carboxylic acid ethylester (Scheme 1).

2. Experimental

2.1. Preparation of $SnCl_2$/nano SiO_2 catalyst

Nano silica gel supported tin (II) chloride was prepared according to the procedure reported in the literatures with some modification [30,31]. In a typical procedure, tin (II) chloride

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http://dx.doi.org/10.1016/j.cclet.2013.06.021

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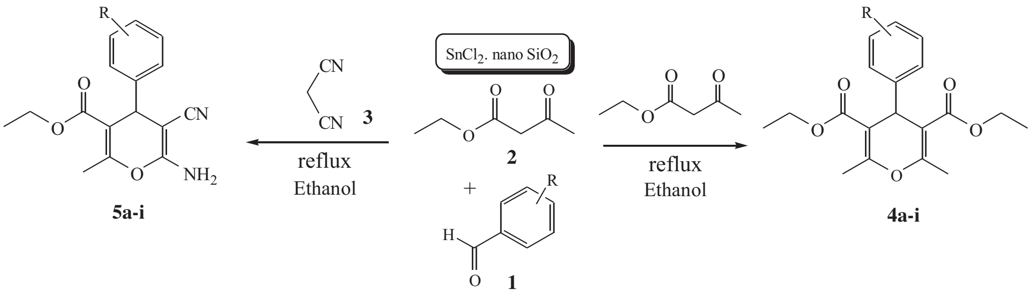


Scheme 1. $SnCl_2$/nano SiO_2 catalyzed synthesis of polyfunctionalized 4*H*-pyrans.

dihydrate (0.28 g) was added to a suspension of nano particles of silica gel (3.075 g) in dichloromethane (DCM) (25.0 mL). The mixture was stirred at room temperature overnight. Then the solvent was removed under reduced pressure and the residue was heated at 100 °C under vacuum for 5 h to furnish $SnCl_2$/nano SiO_2. The prepared $SnCl_2$/nano SiO_2 has been structurally characterized by EDAX and SEM analysis.

*2.2. General procedure for the preparation of diethyl 4-aryl-2,6-dimethl-4H-pyran-3,5-dicarboxylate (**4a–i**)*

A mixture of aldehyde (2 mmol), ethyl acetoacetate (4 mmol), and nano silica supported tin (II) chloride (0.15 mol%) was refluxed in ethanol (10 mL) for the appropriate time (monitored by TLC analysis). The hot reaction mixture was filtered to separate the catalyst and filtrate was solidified after cooling to room temperature. Then, ice water was added to mixture. The organic phase was extracted with dichloromethane, washed with water and dried with Na_2SO_4. The solvent was removed under reduced pressure. The crude products were purified by recrystallization (ethanol and water) with sufficient purity for spectral analysis.

*2.3. General procedure for the preparation of ethyl-6-amino-5-cyano-4-aryl-2-methyl-4H-pyran-3-carboxylate (**5a–i**)*

A mixture of aldehyde (2 mmol), malononitrile (2 mmol), ethyl acetoacetate (2 mmol), and nano silica supported tin (II) chloride (0.15 mol%) was refluxed in ethanol (5 mL) for the appropriate time (monitored by TLC analysis). The hot reaction mixture was filtered to separate the catalyst and filtrate was solidified after cooling to room temperature. The solid product was consecutively washed with hexane (2 mL), ethyl acetate (2× 0.5 mL), and dried.

*Diethyl 4-(3-methoxyphenyl)-2,6-dimethl-4H-pyran-3,5-dicarboxylate (**4h**):* Yellow crystal; 85%; mp: 91–94 °C, FT-IR (KBr, cm^{-1}): ν 3020 (C–H), 1682 (C═O); ^1H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, 3H, J = 6.8 Hz), 1.72 (s, 3H), 3.81 (s, 2H), 3.90 (s, 1H), 4.10 (q, 2H, J = 6.8 Hz), 6.58–7.17 (CH aromatic); ^{13}C NMR (400 MHz, $CDCl_3$): δ 14.5, 17.6, 48.1, 52.8, 64.2, 106.4, 112.5, 116.7, 120.7, 128.8, 141.1, 155.6, 162.3, 166.9. Anal. calcd. for $C_{20}H_{23}O_6$: C, 66.85; H, 6.40. Found: C, 66.79; H, 6.48.

*Ethyl-6-amino-5-cyano-4-(4-bromophenyl)-2-methyl-4H-pyran-3-carboxylate (**5e**):* Orange crystal; 95%; mp: 264–265 °C, FT-IR (KBr, cm^{-1}): ν 3401, 3319 (NH_2), 2210 (CN), 1692(C═O); ^1H NMR (400 MHz, DMSO-d_6): δ 1.10 (t, 3H, J = 7.2 Hz), 2.28 (s, 3H), 2.48 (s, 1H), 3.94 (q, 2H, J = 7.2 Hz), 4.27 (s, NH_2), 6.93–7.4 (CH aromatic); ^{13}C NMR (400 MHz, DMSO-d_6): δ 15.3, 18.6, 36.6, 60.9, 63.4, 111.5, 116.8, 120.6, 133.9, 135.8, 156.7, 159.1, 160.3, 165.9. Anal. calcd. for $C_{16}H_{16}O_4N_2$: C, 53.03; H, 4.14; N, 7.73. Found: C, 52.91; H, 4.10; N, 7.80.

*Ethyl-6-amino-5-cyano-4-(3-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (**5h**):* Yellow crystal; 83%, mp: 264–265 °C, FT-IR (KBr, cm^{-1}): ν 3405, 3315 (NH_2), 2206 (CN), 1706 (C═O); ^1H NMR (400 MHz, DMSO-d_6): δ 1.61 (t, 3H, J = 6.8 Hz), 2.12 (s, 3H), 3.83 (s, 3H), 3.97 (s, 1H), 4.10 (s, NH_2), 4.45 (q, 2H, J = 6.8 Hz), 6.51–7.85 (CH aromatic); ^{13}C NMR (400 MHz, DMSO-d_6): δ 11.2, 17.2, 40.1, 57.9, 61.1, 63.8, 105.5, 111.2, 117.9, 119.8, 123.4, 130.7, 141.8, 158.2, 159.9, 162.5, 170.2. Anal. calcd. for $C_{17}H_{18}O_4N_2$: C, 64.96; H, 5.73; N, 8.91. Found: C, 64.87; H, 5.66; N, 8.97.

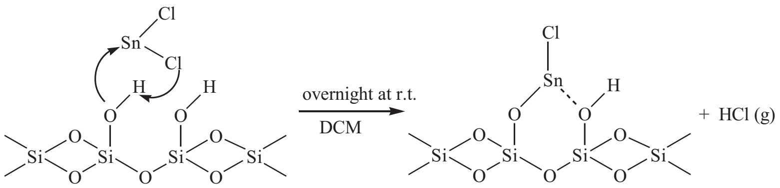
3. Results and discussion

According to literature reports, utilities of the heterogeneous solid-supported materials as new environmentally friendly catalysts for the synthesis of biologically active molecules have increased. Hence, we describe a simple and efficient method for the synthesis of polyfunctionalized 4*H*-pyrans using the environmental friendly and reusable nano silica supported tin (II) chloride as a catalyst herein. The catalyst was prepared by reacting of tin (II) chloride with silica under favorable conditions (Scheme 2). In order to study the morphology and dimension of $SnCl_2$/nano SiO_2, SEM image of $SnCl_2$/nano SiO_2 was obtained and shown in Fig. 1.

These results show that the size of commercial silicagel and synthesized $SnCl_2$/nano SiO_2 are till about 20 nm (Fig. 1). In the EDAX pattern of $SnCl_2$/nano SiO_2 (Fig. 2), Sn, Cl, Si and O elements are indicated. This analysis is detecting that $SnCl_2$ is supported in nano silicagel.

To identify the structure of this catalyst, we studied IR spectra of $SnCl_2$/nano SiO_2 (Fig. 3). In the IR spectrum of $SnCl_2$/nano SiO_2, the Sn–Cl, Sn–O, Si–OH and Si–O–Si resonances were observed in 1559, 563, 3347 and 1061 cm^{-1}, respectively. Based on these results, we suggest the following structure for $SnCl_2$/nano SiO_2.

We would like to report the preparation of polyfunctionalized 4*H*-pyran using reactions involving arylaldehydes, ethylacetoacetate, and malononitrile (Scheme 1). We chose the reaction of



Scheme 2. Reaction of $SnCl_2$ with silicagel.

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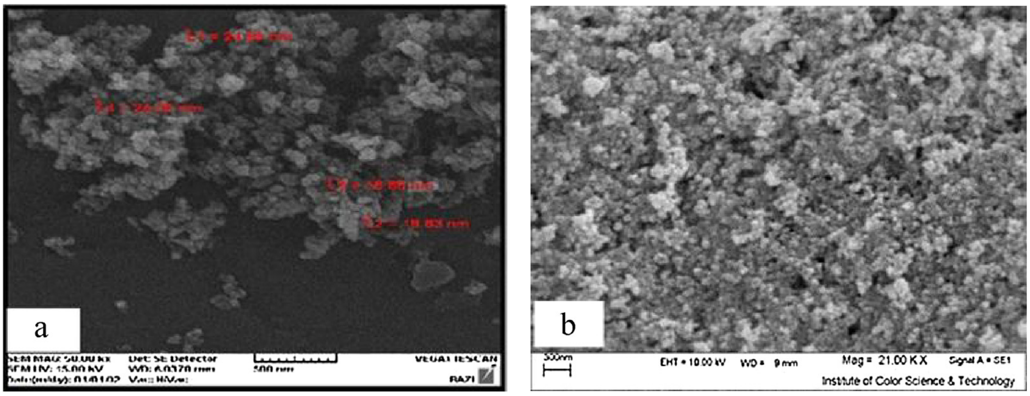

Fig. 1. SEM photograph of (a) nano-SiO_2 and (b) $SnCl_2$/nano SiO_2.

benzaldehyde **1**, ethylacetoacetate **2** and malononitrile **3** as a model system for the optimization study.

Initially, a series of comparative experiments were performed to compare the effectiveness of $SnCl_2$/nano SiO_2 versus other catalysts in the formation of polyfunctionalized 4*H*-pyran. In some cases, data for other catalysts were taken from the literature. The results are shown in Table 1. $SnCl_2$/nano SiO_2 was assessed to be the most efficient of all tested catalysts, in terms of reaction time and yield (Table 1, entry 11). As shown in Table 1, the yield for products **4a** and **5a** is high in the presence of $SnCl_2/SiO_2$ as a catalyst (Table 1, entry 9). Also it indicates the yields of products in the presence of $SnCl_2$/nano SiO_2 (Table 1, entry 10) are higher than those catalyzed by $SnCl_2/SiO_2$. We believe that the heterogeneous nanoparticles have higher surface-to-volume ratio, which provides a larger number of active sites per unit area in comparison to their heterogeneous counterparts. Also, as shown in Table 1 no product was obtained in the absence of the catalyst (Table 1, entry 13).

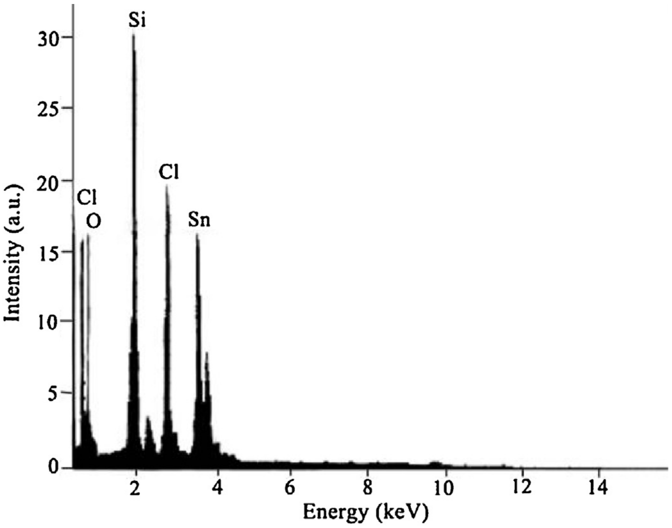

Fig. 2. The EDAX spectrum of $SnCl_2$/nano SiO_2.

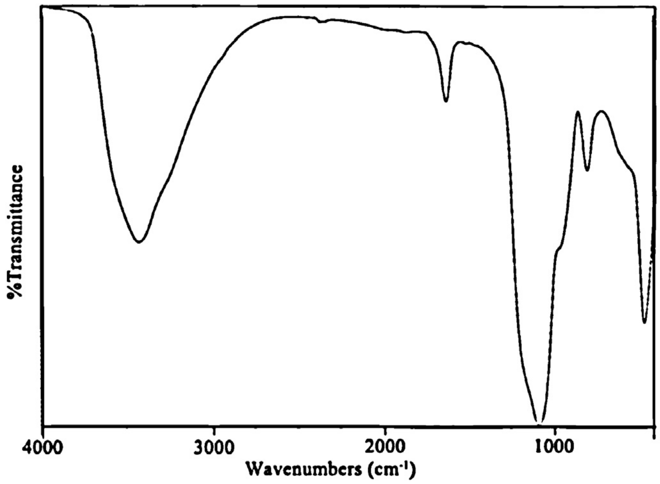

Fig. 3. The IR spectrum of $SnCl_2$/nano SiO_2.

In the next step, the synthesis of **4a** and **5a** was separately carried out in different solvents such as water, ethanol, methanol, tetrahydrofuran (THF), acetonitrile and dichloromethane (DCM) under stirring and reflux. The results are summarized in Fig. 4. In the presence of water the products were obtained in low yield 55%–60%.

Unfortunately, when the reactions were carried out in THF and DCM, the desired product was only obtained in 30%, 25% yields respectively. Obviously, the protic solvents such as ethanol were more suitable than aprotic solvents (Fig. 4). In solvent-free conditions the reaction did not give the desired product.

In continuation of our research, we used a diverse of aldehydes to investigate these three-component reactions under the optimized conditions. We observed various aldehydes could be introduced with high efficiency and produced products in high yields. Also aldehydes bearing electron-withdrawing group such as NO_2, Cl in the *para*-position reacted very smoothly, while reactants with electron-donating group decreased both the rate of reaction and yield of the corresponding products as shown in Table 2.

Table 1
Literature results for the synthesis of **4a** and **5a** with various catalysts.

Entry	Catalyst	Yield (%)[a] **4a/5a**	Ref **4a/5a**
1	Piperidine	–/60	–/[14]
2	Triethylamine	–/63	–/[15]
3	MgO	–/77	–/[16]
4	Cu(II) oxymetasilicate	–/88	–/[32]
5	Baker's yeast	–/65	–/[33]
6	$ZnCl_2$	35/–	[20]/–
7	Nano SiO_2	–/85	–/[34]
8	$SnCl_2{\cdot}2H_2O$	82/83	This work
9	$SnCl_2/SiO_2$	84/84	This work
10	$SnCl_2$/nano SiO_2 (0.10 mol%)	88/89	This work
11	$SnCl_2$/nano SiO_2 (0.15 mol%)	90/93	This work
12	$SnCl_2$/nano SiO_2 (0.20 mol%)	90/91	This work
13	None	Trace	This work

[a] Isolated yield.

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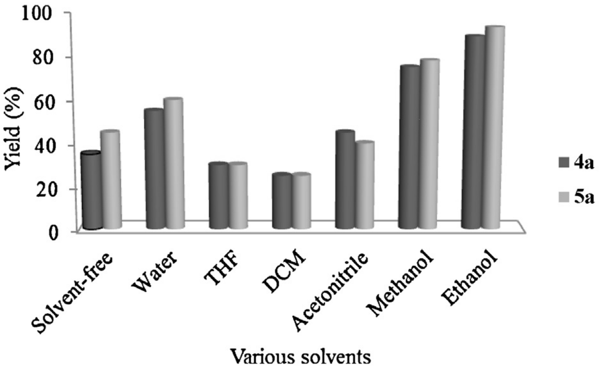

Fig. 4. Effect of solvents on the activity of $SnCl_2$/nano SiO_2 catalyst.

As an environmentally-friendly methodology, the reuse and recovery of the $SnCl_2$/nano SiO_2 are highly desirable. In order to study the reusability of nano silicagel supported tin (II) chloride as a catalyst, eight batches of the experiments were carried out for the preparation of products **4a** and **5a** (Fig. 5). The catalyst was filtered off and washed with an excess of ethanol and reused in a new reaction.

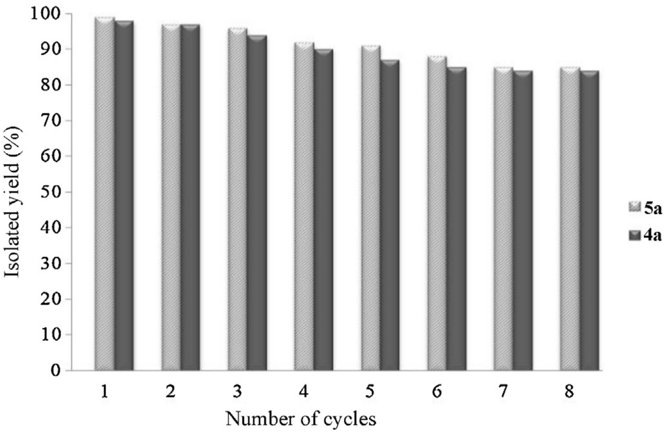

Fig. 5. Repeated use of $SnCl_2$/nano SiO_2 for the synthesis of 4*H*-pyran derivetives **4a** and **5a**.

The characterization of the fresh $SnCl_2$/nano SiO_2 and after eight times of reuse showed the same particle size by SEM (Fig. 6). Interestingly, the shape and size of the nanoparticles remained unchanged before and after reaction. We believe that, this is also the possible reason for the extreme stability of the $SnCl_2$/nano SiO_2 presented herein.

Table 2
Synthesis of polyfunctionalized 4*H*-pyrans catalyzed by $SnCl_2$/nano SiO_2 (0.15 mol%)[a].

Entry	*R*	Products[b]	*T* (min)	Yield (%)[c]	mp (°C)	
					Found	Ref
1	H	**4a**	25	90	72–73	[35]
2	4-NO_2	**4b**	35	95	83–85	[35]
3	3-NO_2	**4c**	40	93	87–89	[35]
4	4-Cl	**4d**	22	95	61–63	[21]
5	4-Br	**4e**	30	92	81–83	[21]
6	4-CH_3	**4f**	40	88	76–78	[21]
7	4-OCH_3	**4g**	45	86	82–83	[35]
8	3-OCH_3	**4h**	45	85	91–94	–
9	4-OH	**4i**	45	82	104–107	[35]
10	H	**5a**	22	93	189–191	[16]
11	4-NO_2	**5b**	25	95	180–182	[16]
12	3-NO_2	**5c**	30	93	181–183	[16]
13	4-Cl	**5d**	20	96	171–173	[16]
14	4-Br	**5e**	25	95	174–175	–
15	4-CH_3	**5f**	28	90	175–178	[16]
16	4-OCH_3	**5g**	35	87	141–144	[16]
17	3-OCH_3	**5h**	35	83	145–147	–
18	3-OH	**5i**	40	82	162–164	[16]

[a] Reaction conditions: aryl aldehyde (2 mmol), malononitrile (2 mmol), ethyl acetoacetate (2 mmol) in ethanol (5 mL), reflux (**4a–i**) and aryl aldehyde (2 mmol), ethyl acetoacetate (2 mmol) in ethanol (5 mL), reflux (**5a–i**).

[b] Products are well characterized by the comparison of their spectral (^{1}H NMR, ^{13}C NMR and IR) and physical data with those reported in literature.

[c] Isolated yields.

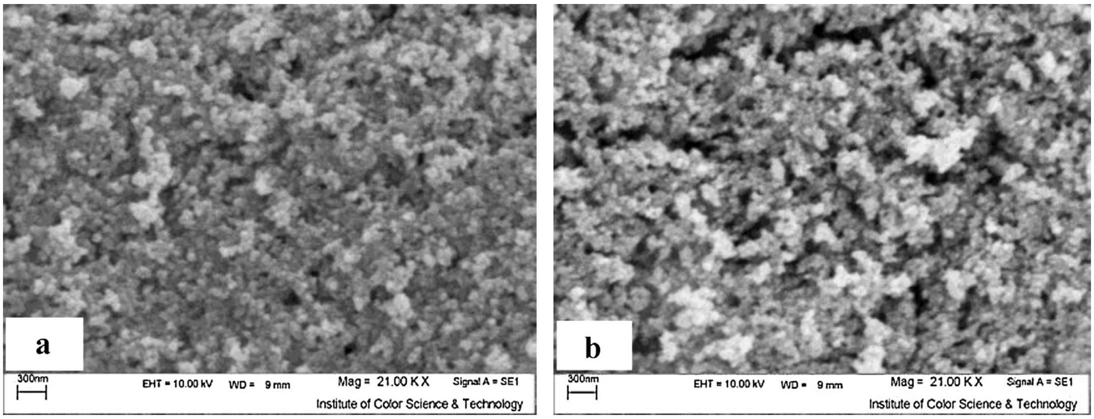

Fig. 6. SEM images of $SnCl_2$/nano SiO_2 before use (a) and after eight times reuse (b).

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4. Conclusion

This paper describes $SnCl_2$/nano SiO_2 as a heterogeneous, easy to prepare, inexpensive, and efficient catalyst for the synthesis of polyfunctionalized 4*H*-pyrans. The distinguished advantages of this procedure are novelty, operational simplicity, high yields and the ease of isolation. The products were obtained in excellent yields and the reaction times were significantly shorter than the available methods. The present approach demonstrates a simple and effective method using $SnCl_2$/nano SiO_2 as novel nano-scale materials.

Acknowledgment

The authors are grateful to University of Kashan for supporting this work by Grant No. 159196/XV.

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Please cite this article in press as: J. Safaei-Ghomi, et al., $SnCl_2$/nano SiO_2: A green and reusable heterogeneous catalyst for the synthesis of polyfunctionalized 4*H*-pyrans, Chin. Chem. Lett. (2013), http://dx.doi.org/10.1016/j.cclet.2013.06.021