

RESEARCH PAPER

Nano-colloidal silica-tethered polyhedral ligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane as a high performance catalyst for the preparation of furan-2(5H)-ones

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ABSTRACT

An efficient and rapid method for the synthesis of 3,4,5-substituted furan-2 (5H)-ones has been achieved through a three-component reaction of aniline, dialkyl acetylenedicarboxylate, and aromatic aldehydes using nano-colloidal silica-tethered polyhedral oligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane (nano-colloidal silica @ APTPOSS) as a superior catalyst under microwave irradiations. Nano-colloidal silica@APTPOSS has been characterized by ¹H NMR spectroscopy, dynamic light scattering (DLS), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA). In this research, microwave irradiation is used as a green and complementary technique for preparation of furan-2 (5H)-ones. The reusability of the catalyst and little catalyst loading, excellent yields, short reaction times, use of the microwave as a green process, and an alternative energy source are some benefits of this method.

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INTRODUCTION

Furan-2(5H)-ones possess many biological properties such as anti-tumor [1], antimicrobial [2], antifungal [3], anti-ulcer [4] and anti-AIDS [5]. Finding effective methods for the preparation of furan-2(5H)-ones is a significant subject. Recently, reports have been developed on the synthesis of furan-2 (5H)-ones using the catalysts such as cyclodextrin [6], Al(HSO₄)₃ [7], (CH₃CH₂CH₂CH₂)₄N(HSO₄) [8], HCOOH [9], Maltose [10], SnCl₂ [11], and Vitamin B12 [12]. Despite the availability of these ways, there remains a need for further new methods for an efficient, high yielding, and mild approach to attain such systems. The use of highly efficient, economic and retrievable catalysts, with low or nil toxicity is required from the green chemistry viewpoint. The

surface of nanoparticles (NPs) can be modified through loading by desirable functionalities such as polyhedral oligomeric silsesquioxanes (POSS). Silsesquioxane is an organosilicon compound with the chemical formula [RSiO_{3/2}]_n (R = H, alkyl, vinyl, aryl, alkoxy), comprised of an inorganic core of oxygen and silicon [13,14]. In continuation of our works on synthesis of nanoparticles [15-18], here, a class of polyhedral oligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane (APTPOSS) is anchored on the surface of colloidal silica nanoparticles. In the current study, we investigate an easy and rapid method for the synthesis of 3,4,5-substituted furan-2 (5H)-ones through a three-component reaction of aniline, dialkyl acetylene dicarboxylate, and aromatic aldehydes using nano-colloidal silica-tethered

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polyhedral oligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane as catalyst under microwave irradiations (Scheme 1). Microwave irradiation (MWI) is utilized for a variety of organic syntheses due to short reaction times, easy workup and good yields [16-19]. The reaction mixture is heated from the inside when the microwave energy is transferred directly to the molecules (catalysts, solvent and reagents). The heterogeneous catalysts absorb microwave irradiation, hence, they can provide an internal heat source for the reactions [20-25].

EXPERIMENTAL SECTION

Materials and Apparatus

All organic materials were purchased commercially from Sigma–Aldrich and Merck and were used without further purification. We used a Milestone microwave (Microwave Labstation, MLS GmbH- ATC-FO 300) for synthesis. CHN compositions were measured by Carlo ERBA Model EA 1108 analyzer. The thermogravimetric analysis (TGA) curves were recorded using a V5.1A DUPONT 2000. The FE-SEM images and EDS spectrum of the products visualized by a Sigma ZEISS, Oxford Instruments Field Emission Scanning Electron Microscope were used to investigate the morphology and particle size of the synthesized NPs.

Preparation of Octakis(3-chloropropyl) octasilsesquioxane (Cl-POSS)

3-chloropropyltrimethoxysilane (80 g) was added to a stirred mixture of methanol (1800 ml) and concentrated hydrochloric acid (90 ml). The

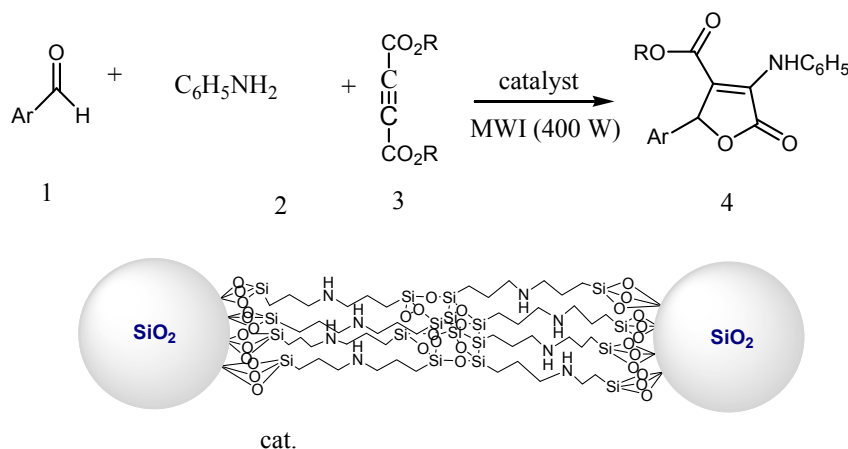
reaction mixture was stirred for 5 weeks at room temperature. Then, the resultant solution was filtered and dried to give a white solid in 42% yield. Anal. Calcd for $\text{Si}_8\text{O}_{12}\text{C}_{24}\text{H}_{48}\text{Cl}_8$ (1036.9): C, 27.80; H, 4.67. Found: C, 27.74; H, 4.60. IR (KBr; ν , cm^{-1}): 2953, 1439, 1104, 810. ^1H NMR (400 MHz, CDCl_3 ; δ , ppm): 0.81 (m, 2H), 1.88 (m, 2H), 3.54 (m, 2H).

Preparation of Octakis[3-(3-aminopropyltriethoxysilane) propyl]octasilsesquioxane (APTPOSS)

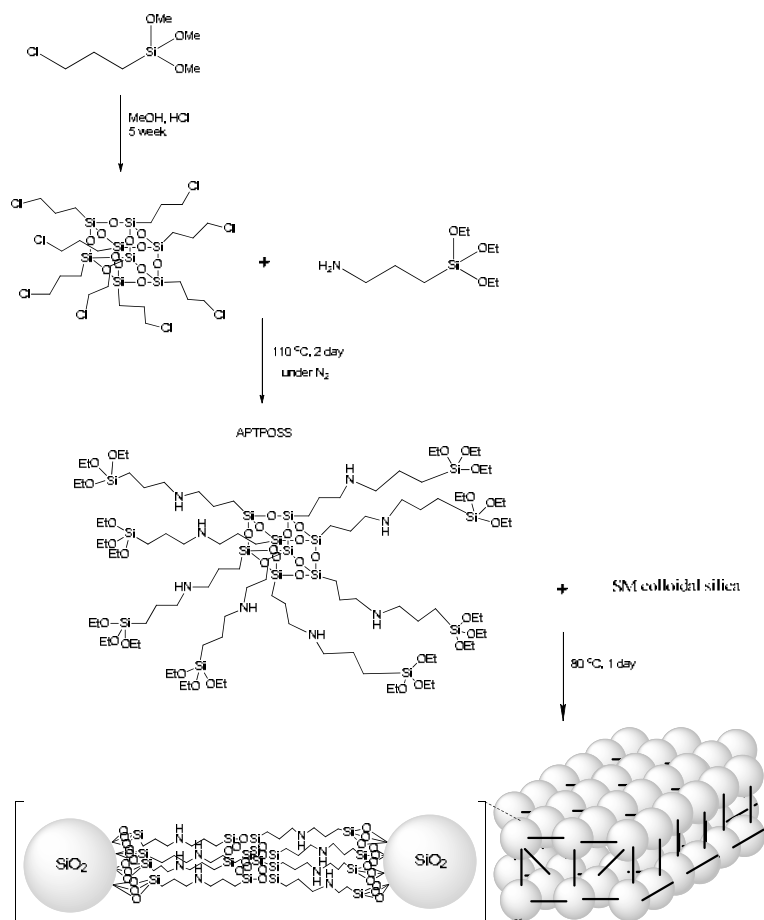
Firstly, 2 mmol (2.07 g) of Cl-POSS was added in 20 mmol (4.43 g) of 3-aminopropyltriethoxysilane. The mixture was transferred to a round-bottom flask under N_2 atmosphere. The mixture was heated in an oil bath at 110 °C for 2 days. After the reaction was completed, the mixture was cooled to room temperature and the mixture was filtered and washed with acetone and methanol to wash the additional reactants. Finally, the resultant pale brown precipitates were dried in a vacuum oven at 70 °C for 12 hours. Anal. Calcd for $\text{C}_{96}\text{H}_{224}\text{N}_8\text{O}_{36}\text{Si}_{16}$ (2516): C, 45.82; H, 8.97; N, 4.45. Found: C, 45.56; H, 8.67; N, 4.32. IR (KBr; ν , cm^{-1}): 2924, 1633, 1112, 1025.

Preparation of nano-colloidal silica @APTPOSS

In a typical procedure, 0.3 mL of colloidal silica nanoparticles (LUDOX SM colloidal silica 30 wt. % suspensions in H_2O) was diluted in 2 mL of deionized water. After that, 0.6 g of APTPOSS was dispersed in 3 mL of deionized water by ultrasonic vibration for 15 min. Then, the suspension was added slowly during one hour to above solution. The mixture was kept at 80 °C for one day (Scheme 2). Finally, the nano-colloidal silica-attached



Scheme 1. Synthesis of 3,4,5-substituted furan-2(5H)-ones under microwave irradiations



Scheme 2. Preparation routes of nano-colloidal silica@APTPOSS.

APTPOSS was separated by centrifugation and washed with acetone and ethanol for several times, then, the mixture was dried in vacuum at 50 °C.

General procedure for the synthesis of furan-2(5H)-ones

A mixture of aldehyde (2 mmol), aniline (2 mmol), dialkyl acetylenedicarboxylate (2 mmol) and 16 mg of nano-colloidal silica@APTPOSS in ethanol (15 mL) was subjected to microwave irradiation (400 W) for the specific time. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted in CH_2Cl_2 ; the catalyst was isolated by simple filtration and the heterogeneous catalyst was recovered. The CH_2Cl_2 was evaporated and the solid separated out was filtered and washed with ethanol to get pure product.

Spectral data

Methyl-(4-bromophenyl)-2,5-dihydro-5-oxo-

4-(phenylamino)furan-3-carboxylate (**4e**) White powder; m.p.: 180–182 °C; IR (KBr): $\bar{\nu} = 3217, 2920, 1684, 1593, 1232, 1138 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 3.75$ (s, 3H, OCH_3), 5.73 (s, 1H, benzylic), 7.12–7.52 (m, 9H, ArH), 8.99 (br s, 1H, NH) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 164.90$ (C=O) and 162.84 (C=OCH_3), 156.06 (C-NH of aromatic), 135.85 (C-NH alkene), 134.22 (C of aromatic), 131.95 (CH of aromatic), 129.10 (CH of aromatic), 126.16 (CH of aromatic), 123.3 (C-Br of aromatic), 122.55 (C of alkene), 122.35 (CH of aromatic), 112.40 (CH of aromatic), 61.04 (OCH_3), 52.15 (CH of benzylic) ppm; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrNO}_4$: C, 55.69; H, 3.63; N, 3.61; Found: C, 55.51; H, 3.50; N, 3.50.

Methyl 2-(2-nitrophenyl)-2,5-dihydro-5-oxo-4-(phenylamino)furan-3-carboxylate (**4g**) White powder; m.p.: 200–202 °C; IR (KBr): $\bar{\nu} = 3174, 2952, 1684, 1530, 1465, 1384, 1359, 748 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, $\text{CDCl}_3 + \text{DMSO}-d_6$): $\delta = 3.72$ (s,

3H, OCH₃), 5.75 (s, 1H, benzylic), 7.08-7.92 (m, 9H, ArH), 8.97 (br s, 1H, NH) ppm; ¹³C NMR (100 MHz, CDCl₃+ DMSO-*d*₆): δ = 164.50 (C=O), 162.64 (COOCH₃), 154.02 (C-NH of aromatic), 150.35 (C-NO₂ of aromatic), 136.34 (C-NH alkene), 133.50 (C of aromatic), 131.25 (CH of aromatic), 129.15 (CH of aromatic), 129.15 (CH of aromatic), 126.90 (CH of aromatic), 125.67 (CH of aromatic), 124.90 (C of alkene), 121.45 (CH of aromatic), 111.78 (CH of aromatic), 54.65 (OCH₃), 51.60 (CH of benzylic) ppm; Anal. Calcd for C₁₈H₁₄N₂O₆: C, 61.02; H, 3.98; N, 7.91; Found: C, 59.97; H, 3.92; N, 7.82.

Ethyl 2-(4-chlorophenyl)-2,5-dihydro-5-oxo-4-(phenylamino) furan-3-carboxylate (4j): White powder; m.p.: 181-184 °C; IR (KBr): $\bar{\nu}$ = 3220, 2922, 1687, 1596, 1239, 11368 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.20 (t, 3 H, *J* = 7.2 Hz, CH₃), 4.05 (m, 2H, *J* = 7.2 Hz, OCH₂), 5.73 (s, 1H, benzylic), 7.12-7.52 (m, 9H, ArH), 8.95 (br s, 1H, NH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 168.95 (C=O), and 165.04 (COOCH₂), 156.07 (C-NH of aromatic), 137.85 (C-NH alkene), 135.22 (C of aromatic), 134.96 (C-Cl of aromatic), 133.22 (CH of aromatic), 129.16 (CH of aromatic), 126.19 (CH of aromatic), 123.22 (C of alkene), 122.54 (CH of aromatic), 114.48 (CH of aromatic), 60.92 (OCH₂), 52.18 (CH of benzylic), 14.32 (CH₃) ppm; Anal. Calcd for C₁₉H₁₆ClNO₄: C, 63.78; H, 4.51; N, 3.91; Found: C, 63.72; H, 4.45; N, 3.84.

Ethyl 2,5-dihydro-2-(4-nitrophenyl)-5-oxo-4-(phenylamino) furan-3-carboxylate (4k):

White powder; m.p.: 250-252 °C; IR (KBr): $\bar{\nu}$ = 3305, 2927, 2843, 1722, 1665, 1508, 1339, 1225 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 1.22 (t, 3 H, *J* = 7.2 Hz, CH₃), 4.07 (m, 2H, *J* = 7.2 Hz, OCH₂),

5.82 (s, 1H, benzylic), 7.22-8.32 (m, 9H, ArH), 9.12 (br s, 1H, NH) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 165.2 (C=O), and 163.2 (COOCH₃), 155.4 (C-NH of aromatic), 144.2 (C-NO₂ of aromatic), 142.1 (C-NH alkene), 134.1 (C of aromatic), 130.2 (CH of aromatic), 129.0 (CH of aromatic), 127.10 (CH of aromatic), 124.75 (CH of aromatic), 120.72 (C of alkene), 113.9 (CH of aromatic), 61.3 (OCH₂), 52.1 (benzylic), 14.32 (CH₃) ppm; Anal. Calcd for C₁₉H₁₆N₂O₆: C, 61.95; H, 4.38; N, 7.61; Found: C, 61.82; H, 4.25; N, 7.52.

RESULTS AND DISCUSSION

Characterization of the nanocatalyst

The preparation steps of nano-colloidal silica-tethered polyhedral oligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane are illustrated in Scheme 2. In the first step, Cl-POSS was synthesized by the hydrolysis of 3-chloropropyltrimethoxysilane under acidic conditions. Afterwards, reaction of 3-aminopropyltriethoxysilane with Cl-POSS yields APTPOSS. Then, reaction of nano-colloidal silica with APTPOSS afforded nano-colloidal silica @ APTPOSS.

Fig. 1 shows the ¹H NMR spectra for octakis(3-chloropropyl)octasilsesquioxane (Cl-POSS) in CDCl₃. The NMR spectra of Cl-POSS are consistent with the expected results.

Fig. 2 shows FE-SEM image of nano-colloidal silica @ APTPOSS (nanocatalyst). The SEM images show the particles with diameters in the nanometer range. It is observed that the particles are strongly aggregated and glued with very large and continuous aggregates.

The components of the APTPOSS and silica @ APTPOSS were analysed using EDS (Fig. 3).

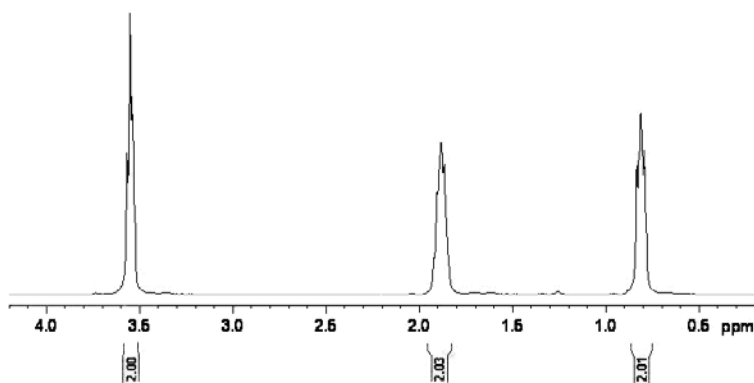


Fig. 1. ¹H NMR spectrum of Cl-POSS

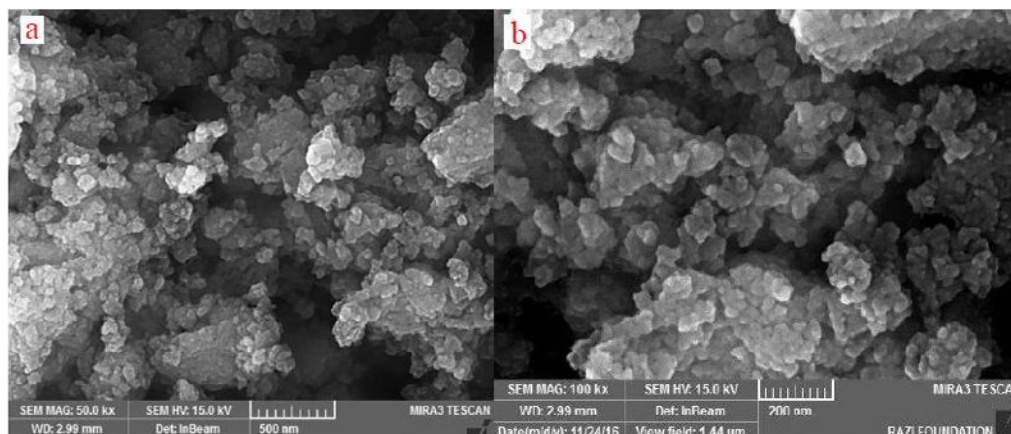


Fig. 2. (a) FE-SEM image of nano-colloidal silica@APTPOSS (b) SEM image of nanocatalyst after six times reuse

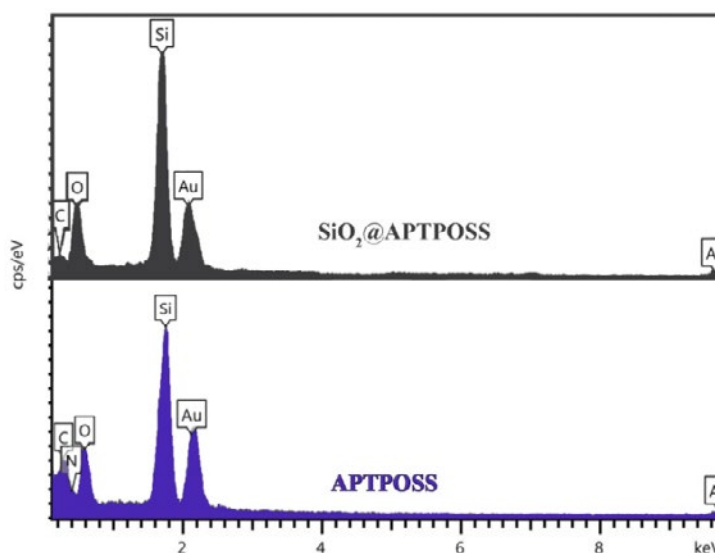


Fig. 3. Energy dispersive spectroscopy for APTPOSS and nano-colloidal silica@APTPOSS

EDS confirmed the presence of C, N, O and Si in the compounds. The higher intensity of Si peak compared with C peak in the nanocatalyst indicates that SiO₂ is loaded with APTPOSS.

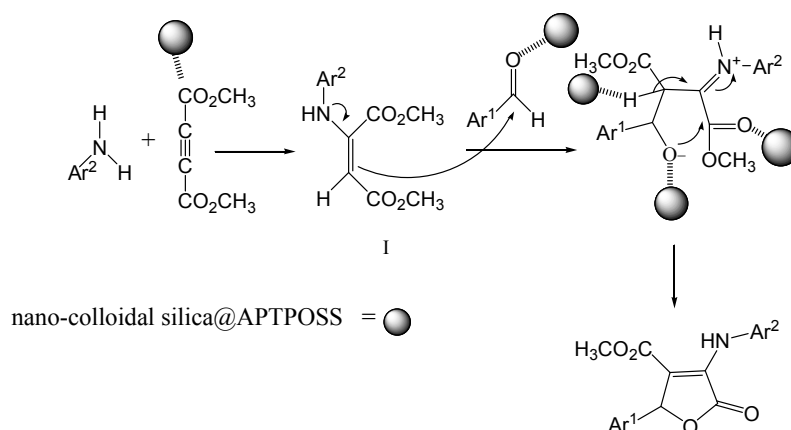
Thermogravimetric analysis (TGA) evaluates the thermal stability of the nano-colloidal silica-tethered APTPOSS. The curve shows a weight loss lower than 210 °C related to desorption of physically adsorbed water, while a weight loss at the temperature from 210 to 560 °C could be due to the decomposition of organic spacer attaching to the silica nanoparticles. Thus, the nano-catalyst was stable up to 210 °C.

In order to study the size distribution of nanocatalyst, DLS (dynamic light scattering)

measurements of the nanoparticles are shown in Fig. 5. This size distribution is centered at a value of 35.6 nm. The dispersion for DLS analysis (2.5 g nanocatalyst at 50 mL ethanol) was prepared using an ultrasonic bath (60 W) for 30 min. This analysis is in accordance with the previous SEM picture.

Catalytic behaviors of nanocatalyst for the synthesis of furan-2 (5H)-ones

We commenced our investigation by testing the reaction of dimethyl acetylene dicarboxylate, aniline, and 4-chlorobenzaldehyde as model reaction for the synthesis of furan-2 (5H)-ones. To obtain the ideal reaction conditions for the synthesis of compound **4a**, we studied the various catalysts,



Scheme 3. Possible mechanism for the synthesis of 3,4,5-substituted furan-2(5H)-ones in the presence of nano-colloidal silica@APTPOSS under microwave irradiation

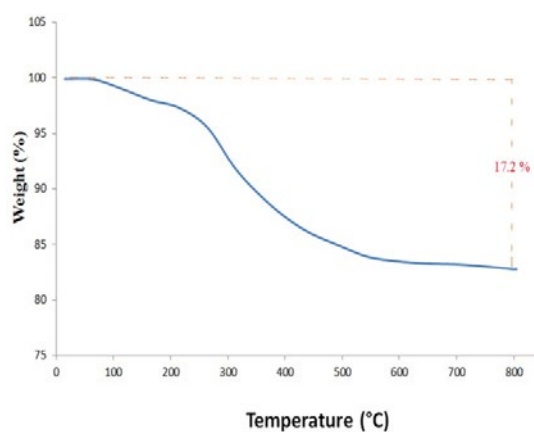


Fig. 4. TGA of nano-colloidal silica@APTPOSS

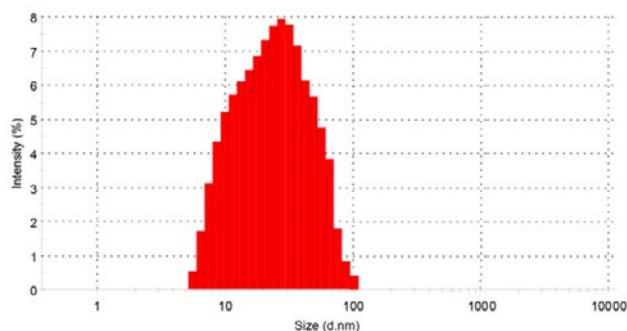


Fig. 5. DLS (dynamic light scattering) of nano-colloidal silica@APTPOSS

and solvents which are shown in Table 1. Screening of different catalysts such as $ZrOCl_2 \cdot 8H_2O$, nano-NiO, $NaHSO_4$, nano- Fe_3O_4 , APTPOSS and nano-colloidal silica@APTPOSS revealed nano-colloidal silica@APTPOSS (16 mg) as the most effective catalyst to perform this reaction under

microwave irradiations (400 W) (Table 1). In order to investigate the effect of intensity of microwave power on reaction, the reaction was also performed at different powers of the microwave irradiation (Table 1, entry 14-16). The best results were obtained under microwave irradiation (400 W) in

ethanol and the reaction gave satisfying results in the presence of nano-colloidal silica@APTPOSS as catalyst. When the catalysis was performed under microwave irradiations, the reaction rate increased considerably. While longer reaction times were required under conventional heating, microwave irradiation improved the yields of the reactions and shortening the reaction times. We explored the feasibility of the reaction by choosing some representative substrates (Table 2). It has been considered that better yields are achieved with substrates having electron-withdrawing groups. In addition, we examined isatin instead of benzaldehydes in the reaction, however, we could not find a considerable amount of the title product from isatin. This reaction could not be observed when the isatins were used as a substrate.

We also checked reusability of nano-colloidal silica @APTPOSS as an efficient catalyst; its

reusability was achieved by the reaction of dimethyl acetylene dicarboxylate, aniline, and 4-chlorobenzaldehyde and 16 mg of nano-colloidal silica@APTPOSS under microwave irradiations. After completion of the reaction, the catalyst was washed with water and acetone and used with new substrates under the same conditions. The results showed that the nano-colloidal silica @APTPOSS can be reused several times (Yields 92 to 90%) in Fig. 6. The morphology of nanoparticle was investigated by scanning electron microscopy (SEM) before use and after reuse of six times with images shown in Fig. 2 (b). Interestingly, the shape and size of the nanoparticles remained unchanged before and after reaction. This could be also the possible reason for the extreme stability of the nanoparticles presented herein.

To compare the efficiency of nano-colloidal silica@APTPOSS with the reported catalysts for

Table 1. Optimization of the reaction conditions using different catalysts under different conditions ^a

Entry	Solvent (conditions)	Catalyst	Time (min)	Yield ^c %
1	EtOH (reflux)	No catalyst	700	trace
2	EtOH (reflux)	ZrOCl ₂ .8H ₂ O (3 mol%)	500	42
3	CH ₃ CN (reflux)	nano-NiO (3 mol%)	500	34
4	DMF (reflux)	NaHSO ₄ (10 mol%)	400	43
5	EtOH (reflux)	nano-Fe ₃ O ₄ (4 mol%)	350	28
6	CH ₃ CN (reflux)	APTPOSS (10 mol%)	120	45
7	DMF (reflux)	nano-colloidal silica@APTPOSS (16 mg)	120	46
8	H ₂ O (reflux)	nano-colloidal silica@APTPOSS (16 mg)	120	52
9	CH ₃ CN (reflux)	nano-colloidal silica@APTPOSS (16 mg)	120	57
10	EtOH (reflux)	nano-colloidal silica@APTPOSS (16 mg)	120	74
11	DMF (MWI: 400 W) ^b	nano-colloidal silica@APTPOSS (16 mg)	15	63
12	H ₂ O (MWI: 400 W)	nano-colloidal silica@APTPOSS (16 mg)	15	69
13	CH ₃ CN (MWI: 400 W)	nano-colloidal silica@APTPOSS (16 mg)	10	72
14	EtOH (MWI: 300 W)	nano-colloidal silica@APTPOSS (16mg)	10	82
15	EtOH (MWI: 400 W)	nano-colloidal silica@APTPOSS (16 mg)	10	92
16	EtOH (MWI: 500 W)	nano-colloidal silica@APTPOSS (16 mg)	10	92
17	EtOH (MWI: 400 W)	nano-colloidal silica@APTPOSS (14 mg)	10	85
18	EtOH (MWI: 400 W)	nano-colloidal silica@APTPOSS (18 mg)	10	92

^a 4-Chlorobenzaldehyde (2 mmol), aniline (2 mmol), dimethyl acetylenedicarboxylate (2 mmol)

^b Microwave irradiations

^c Isolated yield

Table 2. Synthesis of 3,4,5-substituted furan-2(5H)-ones using nano-colloidal silica@APTPOSS (16 mg) under microwave irradiations (400 W) in ethanol

Entry	Aldehyde	R	Product	Time (min)	Yield ^a %	m.p ^o C ^{ref}
1	4-Cl-C ₆ H ₄	CH ₃	4a	10	92	148-151 [11]
2	C ₆ H ₅	CH ₃	4b	10	89	160-163 [11]
3	4-O-Me-C ₆ H ₄	CH ₃	4c	15	83	240-243 [11]
4	2-Cl-C ₆ H ₄	CH ₃	4d	10	89	274-276 [11]
5	4-Br-C ₆ H ₄	CH ₃	4e	10	92	180-181 [12]
6	4-NO ₂ -C ₆ H ₄	CH ₃	4f	10	93	176-179 [10]
7	2-NO ₂ -C ₆ H ₄	CH ₃	4g	10	90	200-201 [12]
8	3-NO ₂ -C ₆ H ₄	CH ₃	4h	10	88	199-202 [12]
9	4-CH(CH ₃) ₂ -C ₆ H ₄	CH ₃	4i	15	85	202-204 [12]
10	4-Cl-C ₆ H ₄	CH ₃ CH ₂	4j	10	89	181-184
12	4-NO ₂ -C ₆ H ₅	CH ₃ CH ₂	4k	10	90	250-252

^aIsolated yield

Table 3. Comparison of catalytic activity of nanocatalyst with other reported catalysts for the synthesis of furan-2(5H)-one (4a)

Entry	Catalyst (condition)	Time (min)	Yield, ^a %	[Ref]
1	β -cyclodextrin, 10 mol%	800	80	[6]
2	$[\text{Al}(\text{HSO}_4)_3]$, 50 mg	600	75	[7]
3	$[\text{Bu}_4\text{N}][\text{HSO}_4]$, 10 mol%	500	72	[8]
4	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 3 mol%	420	87	[11]
5	vitamin B12, 10 mol%	120	75	[12]
6	nano-colloidal silica@APTPOSS (16 mg)	10	92	This work

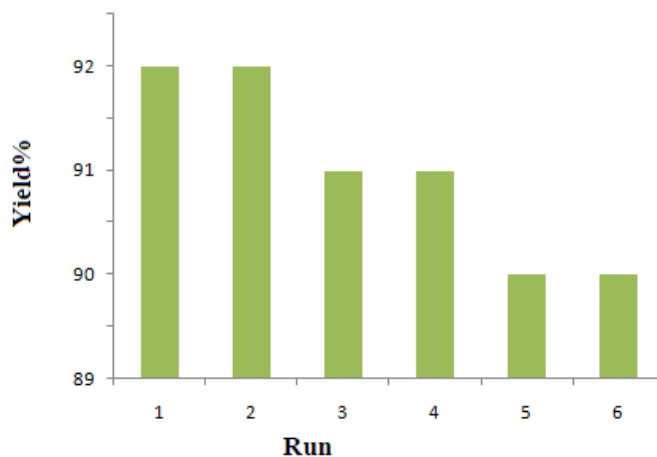
^a Isolated yield

Fig. 6. Reusability of nano-colloidal silica@APTPOSS for the preparation of 4a

the synthesis of furan-2 (5H)-ones, the results are collected in Table 3. As Table 3 indicates, nano-colloidal silica@APTPOSS is superior with respect to the reported catalysts in terms of reaction time, yield and conditions. In addition, our catalyst was recyclable for six times. The reaction mixture is heated from the inside since the microwave energy is transferred directly to the reagents. The solid catalysts absorb microwave irradiation, thus they can serve as an internal heat source for the reactions. High catalytic activity and ease of recovery from the reaction mixture through filtration or centrifugation methods, and several reuse times without significant losses in performance are additional eco-friendly attributes of this catalytic system. As expected, the increased surface area due to small particle size increased reactivity of catalyst. This factor is responsible for the accessibility of the substrate molecules on the catalyst surface.

The proposed reaction mechanism

A proposed mechanism for the formation of 4 is shown in Scheme 3. An initial condensation of dimethyl acetylenedicarboxylate and aromatic amine generated intermediate I. Subsequently, the

reaction of aromatic aldehyde and intermediate I and then cyclodehydration produced furan-2(5H)-ones. In this mechanism, nano-colloidal silica@APTPOSS acts as a highly efficient and green catalyst activating the C=O, COO groups for better reaction with nucleophiles.

CONCLUSION

In this study we introduced an efficient method for the preparation of 3,4,5-substituted furan-2 (5H)-ones through a three-component reaction of aniline, dialkyl acetylenedicarboxylate, and aromatic aldehydes using nano-colloidal silica-tethered polyhedral oligomeric silsesquioxanes with eight branches of 3-aminopropyltriethoxysilane as a superior catalyst under microwave irradiations. High yields, short reaction times, atom economy, reusability of the catalyst, low catalyst loading, and use of microwave as clean method are some of the remarkable advantages of the present protocol.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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