New functionalized 8-hydroxyquinoline-5-sulfonic acid mesoporous silica (HQS-SBA-15) as an efficient catalyst for the synthesis of 2-thiohydantoin derivatives

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Article Info
Article history:
Received 12 April 2016
Received in revised form 3 July 2016
Accepted 7 July 2016
Available online 16 July 2016

Dedicated to Professor Majid Jafarian on the occasion of his birthday

A R T I C L E  I N F O
Article history:
Received 12 April 2016
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Accepted 7 July 2016
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Keywords:
SBA-15
Mesoporous silica
8-Hydroxyquinoline-5-sulfonic acid
2-Thiohydantoin

A B S T R A C T
Mesoporous silica SBA-15 functionalized with 8-hydroxyquinoline-5-sulfonic acid (HQS-SBA-15) was used as a new recyclable nanocatalyst for the one-pot synthesis of 2-thiohydantoin derivatives under solvent-free conditions. The catalyst exhibited excellent recyclability at least for 3 times with a high catalytic activity.

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1. Introduction

Acidic reaction conditions are essential to perform some of the named organic reactions such as condensations and esterifications, Aldol reactions, alcohol dehydrodimerizations and some of multicomponent reactions. Considering the drawbacks of homogeneous acid catalysts including difficult separations, need for neutralizing the chemical wastes, reactor corrosion, and so on; preparation and application of solid acid catalysts have long been a subject of immense interest.

Santa Barbara Amorphous (SBA-15), a new nonporous silica with a hexagonal structure, large pore size, high surface area, and high thermal stability, opens a new window towards promising solid acids. Up to now, SBA-15 was used in different fields of study, for example, as a support for the delivery of natural and synthetic drugs. However, integration of the acidic functional groups (e.g., –SO3H) into the SBA-15’s pores has only been recently explored. Some studies have been reported for applying several types of sulfonic acid functionalized SBA-15 (SBA–Pr–SO3H) in chemical transformations. For example, it has been used in the synthesis of isoindigo derivatives, the Pechmann reaction and one-pot synthesis of spiromiquazolinones.

Immobilization of acidic compounds onto the pores of SBA-15 is an interesting demand in the field of solid phase organic synthesis due to its higher acidic character.

Development of heterocycles synthesis is one of the most important areas in organic chemistry since these compounds exhibit different biological activities. Among them, anomic spiromucosides have been identified to display a wide range of biological activities (Fig. 1). For example, phenytoin is an

Fig. 1. Examples of medicinally interesting hydantoin analogs.
antiarrhythmic, anticonvulsant, antineuralgic, and trigeminal neuralgia agent and skeletal muscle relaxant. It was reported that glucopyranosylidene-spirothiohydantoin is as an efficient inhibitor of muscle and liver glycogen phosphorylases.

Fused thiohydantoin derivatives also exhibit weak antioxidant activity. Though, hydantoin and thiohydantoin derivatives have diverse therapeutic applications, the biological mechanisms of these compounds have not been fully elucidated. So far, different types of thiohydantoin derivatives were obtained by intermolecular reaction of N-alkyl amines and thiocyanato sugars, or intramolecular reaction of amino acids (thio) urea. Additionally, microwave irradiation and/or the use of polyethylene glycol as solvent in the presence of K₂CO₃ were successful methods for this aim. However, these methods are time-consuming and require a large amount of toxic solvents, and reagents. Thus, developing a more green and efficient method for the synthesis of these compounds, from readily available reagents, remains one of the major challenges in organic synthesis.

Hence, for the first time the present work illustrates the immobilization of 8-hydroxyquinoline-5-sulphonic acid groups onto the pores of SBA-15 (HQS-SBA-15) (Scheme 1) for its use as recyclable solid acid catalyst for the synthesis of 2-thiohydantoin derivatives through the reaction of amino acid methyl esters and isothiocyanates in solvent-free reaction conditions (Scheme 2).

2. Results and discussion

At first the SBA-15 was prepared according to the reported method in the literature. Then, the iodo-functionalized SBA-15 was reacted with 8-hydroxyquinoline-5-sulphonic acid 2 to prepare the (HQS-SBA-15) as a new silica-based catalyst. TEM, TGA, XRD and N₂ adsorption–desorption isotherms were used to characterize the prepared HQS-SBA-15.

In FTIR spectra of SBA-15, I-SBA-15 and HQS-SBA-15 (Fig. 2), a series of characteristic bands located around 800, 960, 1100, 1640 and 3434 cm⁻¹ are related to the symmetric stretching vibrations of Si-O, symmetric stretching vibration of Si-OH, asymmetric stretching vibrations of Si-O-Si, physically absorbed water molecules, and stretching vibrations of -OH, respectively. The new appeared band around 2890 cm⁻¹ in I-SBA-15 spectrum is due to the stretching vibrations of the CH₂ units of the propyl chains while in HQS-SBA-15, two new bands around 1405 and 1475 cm⁻¹ are related to the C=N and C=C aromatic stretching vibrations, respectively.

In order to analyze the structure of SBA-15 after functionalization steps, XRD patterns of original SBA-15 and HQS-SBA-15 were obtained. Generally, mesoporous silica materials exhibit three characteristic diffractions including a high intensity diffraction around 2θ=1° originated from the (100) plane and two weak diffractions originated from the (110) and (200) planes indicating the long-range periodic order and two-dimensional hexagonal (p6mm) mesostructured, respectively. As can be seen in Fig. 3a,b, both SBA-15 and HQS-SBA-15 samples showed these diffractions confirming the original structure of SBA-15 was preserved after functionalization steps. However, the decrease in the intensities of the 100, 110 and 200 planes in HQS-SBA-15 was due to the incorporation of organic moieties onto the pore walls which leads to a partial lowering of the crystallinity. TEM image (inset of Fig. 3) of SBA-15 particles showed the uniform channels, which were open along the particles.

For further insight into the functionalized SBA-15 structure, N₂ adsorption–desorption technique was used. The HQS-SBA-15 isotherm showed a type IV isotherm based on standard IUPAC
categories with a H1 type hysteresis loop indicating ordered structure of the mesoporous materials (Fig. 4). The pore-size distribution has its maximum at 3.5 nm, as shown in BJH pore size distribution curve of HQS-SBA-15 (the inset of Fig. 4).

Thermogravimetric analysis was conducted to assess the amount of the attached organic moieties. For both samples (Fig. 5), the weight loss up to 150 °C can be related to the elimination of trapped water molecules within the pores of the SBA-15 channels. Moreover, a major weight loss within the range of 150–600 °C were due to the degradation of organic moieties which were estimated to be about 8% and 18% for I-SBA-15 and HQS-SBA-15 samples, respectively. Therefore, the amount of the attached propyl chains and 8-hydroxyquinoline-5-sulphonic acid groups was estimated to be 0.48 and 0.45 mmol g⁻¹, respectively.

To optimize the reaction conditions, methyl thiazolidine-4-carboxylate 4b (1.0 mmol), and phenylisothiocyanate 5a (1.0 mmol) were used as the model reactants under solvent-free conditions (Scheme 3).

To optimize the reaction conditions, the effect of solvent was studied as shown in Table 1. Accordingly, among the tested conditions, solvent-free condition was the best which gave the product with the highest yield in the shortest reaction time. Additionally,
the effect of catalyst in this reaction was investigated (Table 1, Entry 6), it was found that the efficiency of this catalyst is due to the strong acidic feature of HQS anchored onto the pores of the modified SBA-15 as well as its high surface area.

Following the obtained results, we explored the scope of our methodology using a variety of α-amino esters 4a–b and isothiocyanates 5a–e (Table 2). There was a general difference in the yield of products between the cyclic and non-cyclic α-amino esters. That is, cyclic amino esters were relatively more active than the others which can be definitely attributed to the closer functional groups (amine and ester) and leads to increasing the rate of intramolecular reaction and reducing the reaction times.

The plausible mechanism is shown in Scheme 4. Because of the high surface area of the acidic nanocatalyst, accompanied by the inherent Brønsted acidity of −SO3H, which is capable of bonding with the N atom of thiocyanate moiety the reactants are absorbed easily. Afterwards, nucleophilic addition of the α-amino ester (4a–b) to the activated thiocyanate (5a–e) results in the formation of the intermediate 7. Subsequently, through intramolecular cyclization, the product (6a–i) is formed. In the other words, ionic intermediate (7) is generated inside the nanocatalyst because of the strong polarity of the −SO3H groups.

The reusability of the catalyst was determined under optimized conditions for the preparation of compound 6a. The process of recycling was performed three times and no significant decrease in activity was observed. The yields for the four runs were found to be 90, 83, 81, and 80%, respectively. The results showed the catalyst was efficient without any significant reduce the yield was collected effectively and the recovered catalyst was used in subsequent runs without observation of any significant reduction yield (Table 3).

3. Conclusion

In summary, a new sulfonic acid–based nanocatalyst was used as a solid Brønsted acid for the one-pot synthesis of 2-thiohydantoin derivatives under solvent-free conditions. This heterogeneous catalyst has various advantages, such as: easy handling and recovery, high recyclability and low amount use of the catalyst (0.02 g). Thus, a mild and green approach for this reaction through the catalysis of HQS-SBA-15 was developed in this paper.

4. Experimental

4.1. General procedure

Commercially available chemicals were bought and used. Melting points were recorded on an Electrothermal 9100 apparatus. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded using an ABB FTIR (FTLA 2000) on KBr plates. High resolution mass spectra were recorded on Jeol-JMS-700 mass spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained through a BRUKER AVANCE DRX-500 (for 1H NMR) and DRX-125 MHz (for 13C NMR) in CDCl3 using tetramethylsilane (TMS) as an internal standard. Transmission electron microscopy (TEM) was performed using a Zeiss EM900 instrument at an accelerating voltage of 80 kV. Low-angle X-ray scattering measurements were performed by an X’Pert Pro MPD diffractometer using Cu Ka radiation (λ=1.5418 Å). N2 adsorption–desorption isotherms were obtained using a Belsorp-mini II instrument at liquid nitrogen temperature (−196 °C). Thermogravimetric analysis (TGA) was carried out using a TGA Q50 V6.3 Build 189 instrument from ambient temperature to 800 °C with a ramp rate of 10 °C min⁻¹ in air.

4.2. Synthesis of HQS-SBA-15

SBA-15 was prepared according to our previous published procedure. 3-(Iodopropyl)-trimethoxysilane (10 mmol) was slowly added to SBA-15 (2 g) dispersed in toluene while vigorous stirring followed by refluxing for 24 h. Then, the resulted iodo-functionalized SBA-15 (denoted as I-SBA-15) was filtered, washed with toluene and dried overnight. Afterwards, a mixture of I-SBA-15 (1 g), 8-hydroxyquinoline-5-sulfonic acid (2.5 mmol in 100 mL of MeOH:H2O with a ratio of 3:1), and triethylamine (10 mmol) was refluxed for 24 h. The final light yellow product (denoted as HQS-SBA-15) was filtered, washed with an excess amount of ethanol and water and dried overnight. The amount of the grafted propyl chains and HQS groups was estimated to be 0.48 ± 0.05 mmol g⁻¹, respectively. Scheme 1 exhibits the overall synthetic procedure of HQS-SBA-15.

4.3. General procedure for the synthesis of α-amino ester derivatives 4a–b

In a 50-mL round bottom flask, a solution of L-phenyl alanine 3a (826 mg, 5 mmol) and/or L-thiazolidine-4-carboxylic acid 3b (665 mg, 5 mmol) in MeOH (10 mL) was stirred over a salty iced-water bath until the temperature reached to ~10 °C, then followed by slowly addition of thionyl chloride (SOCl2) (1.5 mL, 20 mmol). The reaction was completed about 24 h, then, the solvent was evaporated under reduced pressure and the obtained product was recrystallized in MeOH and Et2O.

4.4. General procedure for the synthesis of 2-thiohydantoin derivatives 6a–i

To a mixture of α-amino ester 4a–b (1 mmol) and isothiocyanate 5a–e (1 mmol) derivatives, HQS-SBA-15 (0.02 g) was added; it was then stirred for 1 h at 60 °C. After completion of the reaction (monitored by TLC), the solid precipitate was dissolved in hot EtOH to remove the heterogeneous catalyst then, the pure product was obtained from the filtrate.

4.4.1. Tetrahydro-6-phenyl-5-thioximidazo[1,5-c]thiazol-7(3H)-one (6a).

Colorless solid (0.245 g, 98%); mp: 168–170 °C; FTIR (KBr, cm⁻¹): ν=1110, 1755; 1H NMR (500 MHz, CDCl3; δppm=3.19 (dd, 1H, J=11.1, 9.0 Hz, −CH2CH3), 3.40 (dd, 1H, J=11.1, 7.7 Hz, −CH2CH=CH2), 4.52 (d, 1H, J=9.5 Hz, −CH), 4.68 (t, 1H, J=8.1 Hz, −CH2CH2), 5.43 (d, 1H, J=9.5 Hz, −CH'), 7.31 (d, 2H, J=7.9 Hz, ArH), 7.45–7.53 (m, 3H, ArH); 13C NMR (125 MHz, CDCl3; δppm=31.2, 50.0, 66.4, 95.2, 128.1, 129.4, 131.2, 140.0, 149.5, 150.7).
4.4.2. Tetrahydro-6-(4-methoxyphenyl)-5-thioxoimidazo[1,5-c]thiazol-7(3H)-one (6b).

Colorless solid (0.224 g, 80%); mp: 185–188°C.

FTIR (KBr, cm⁻¹): ν = 1111, 1750; ¹H NMR (500 MHz, CDCl₃): δ ppm = 3.17 (dd, 1H, J = 11.1, 8.9 Hz, –CH₂CH), 3.39 (dd, 1H, J = 11.1, 7.6 Hz, –CH₂CH), 3.84 (s, 3H, –OMe), 4.52 (d, 1H, J = 9.5 Hz, –SCH), 4.66 (t, 1H, J = 8.1 Hz, –CH₂CH), 5.42 (d, 1H, J = 9.5 Hz, –SCH), 7.02 (d, 2H, J = 8.8 Hz, H₆), 7.21 (d, 2H, J = 8.8 Hz, H₆); ¹³C NMR (125 MHz, CDCl₃): δ ppm = 31.2, 50.0, 55.5, 66.3, 114.6, 125.5, 129.2, 160.1, 170.9, 185.7; Mass: HR-EI: calcd for C₁₂H₁₂N₂O₂S₂ [M]+ 280.3400, found 280.3570.

4.4.3. 6-(4-Chlorophenyl)-tetrahydro-5-thioxoimidazo[1,5-c]thiazol-7(3H)-one (6c).

Colorless solid (0.252 g, 89%); mp: 140–144°C.

FTIR (KBr, cm⁻¹): ν = 1091, 1762; ¹H NMR (500 MHz, CDCl₃): δ ppm = 31.2, 50.0, 55.5, 66.3, 114.6, 125.5, 129.2, 160.1, 170.9, 185.7; Mass: HR-EI: calcd for C₁₂H₁₀N₂O₂S₂ [M]+ 280.3400, found 280.3570.

### Table 2

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<td>198–200</td>
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* Reaction condition: α-amino ester 4a–b (1.0 mmol) and isothiocyanate 5a–e (1.0 mmol) were reacted using 0.02 g of catalyst for 1 h under solvent-free system at 60°C.
δ<sub>ppm</sub> = 3.18 (dd, 1H, J = 11.1, 8.9 Hz, -CH<sub>2</sub>CH), 3.39 (dd, 1H, J = 11.1, 7.6 Hz, -CH<sub>2</sub>CH), 4.52 (dd, 1H, J = 9.5 Hz, -SCH), 4.68 (t, 1H, J = 8.1 Hz, -CH<sub>2</sub>H), 5.41 (d, 1H, J = 9.5 Hz, -SCH), 7.27 (d, 2H, J = 8.4 Hz, H<sub>Ar</sub>), 7.47 (d, 2H, J = 8.4 Hz, H<sub>Ar</sub>); 13C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 31.2, 50.0, 66.3, 129.4, 129.5, 131.3, 135.4, 170.4, 184.7; Mass: HR-EI: calcd for C<sub>11</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub> [M+Cl]<sup>+</sup> 285.9845, found 285.9828; calcd for C<sub>11</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub> [M+2]<sup>+</sup> 285.9815, found 285.9790.

4.4.4. Tetrahydro-6-(4-nitrophenoxy)-5-thioxoimidazo[1,5-c]thiazol-7(3H)-one (6d). Colorless solid (0.266 g, 91%); mp: 206–209 °C; FTIR (KBr, cm<sup>-1</sup>): v = 1107, 1771, 3211; 1H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 3.22 (dd, 1H, J = 11.2, 8.8 Hz, -CH<sub>2</sub>CH), 3.42 (dd, 1H, J = 11.2, 7.6 Hz, -CH<sub>2</sub>CH), 4.54 (d, 1H, J = 9.6 Hz, -SCH), 4.73 (t, 1H, J = 8.1 Hz, -CH<sub>2</sub>H), 5.42 (d, 1H, J = 9.6 Hz, -SCH), 7.58 (d, 2H, J = 9.0 Hz, H<sub>Ar</sub>), 8.35 (d, 2H, J = 9 Hz, H<sub>Ar</sub>); 13C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 31.2, 50.0, 66.4, 124.4, 129.0, 138.2, 147.7, 169.9, 183.5; Mass: HRMS (EI): calcd for C<sub>11</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>2</sub>[M+H]<sup>+</sup> 295.0086, found 295.0097.

4.4.5. Tetrahydro-5-thioxo-6-m-tolylimidazo[1,5-c]thiazol-7(3H)-one (6e). Colorless solid (0.252 g, 95%); mp: 139–141 °C; FTIR (KBr, cm<sup>-1</sup>): v = 1096, 1767, 3049; 1H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 2.41 (s, 3H, -CH<sub>3</sub>), 3.18 (dd, 1H, J = 11.1, 8.9 Hz, -CH<sub>2</sub>CH), 3.39 (dd, 1H, J = 11.1, 7.6 Hz, -CH<sub>2</sub>CH), 4.52 (d, 1H, J = 9.5 Hz, -SCH), 4.67 (t, 1H, J = 8.1 Hz, -CH<sub>2</sub>H), 5.43 (d, 1H, J = 9.5 Hz, -SCH), 7.10 (s, 2H, H<sub>Ar</sub>), 7.27 (d, 1H, J = 8.2 Hz, H<sub>Ar</sub>), 7.39 (t, 1H, J = 8.0 Hz, H<sub>Ar</sub>); 13C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 21.4, 31.2, 50.0, 66.4, 125.1, 128.6, 129.1, 130.4, 132.9, 139.4, 170.8, 185.4; Mass: HRMS (EI): calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>[M+H]<sup>+</sup> 264.0932, found 264.0403.

4.4.6. 5-Benzyl-3-phenyl-2-thioxoimidazolidin-4-one (6f). Colorless solid (0.244 g, 87%); mp: 171–174 °C; FTIR (KBr, cm<sup>-1</sup>): v = 1099, 1753, 3159; 1H NMR (500 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 3.1 (d, 2H, J = 4.1 Hz, -CH<sub>2</sub>CH), 4.8 (t, 1H, J = 4.1 Hz, -CH<sub>2</sub>CH), 6.76 (d, 2H, J = 6.6 Hz, H<sub>Ar</sub>), 7.2 (d, 2H, J = 6.4 Hz, H<sub>Ar</sub>), 7.29–7.37 (m, 6H, H<sub>Ar</sub>), 10.61 (s, 1H, -NH);

δ<sub>ppm</sub> = 31 (d, 2H, J = 4.1 Hz, -CH<sub>2</sub>CH), 4.8 (t, 1H, J = 4.1 Hz, -CH<sub>2</sub>CH), 6.76 (d, 2H, J = 6.6 Hz, H<sub>Ar</sub>), 7.2 (d, 2H, J = 6.4 Hz, H<sub>Ar</sub>), 7.29–7.37 (m, 6H, H<sub>Ar</sub>), 10.61 (s, 1H, -NH);

δ<sub>ppm</sub> = 3.18 (dd, 1H, J = 11.1, 8.9 Hz, -CH<sub>2</sub>CH), 3.39 (dd, 1H, J = 11.1, 7.6 Hz, -CH<sub>2</sub>CH), 4.52 (d, 1H, J = 9.5 Hz, -SCH), 4.67 (t, 1H, J = 8.1 Hz, -CH<sub>2</sub>H), 5.43 (d, 1H, J = 9.5 Hz, -SCH), 7.10 (s, 2H, H<sub>Ar</sub>), 7.27 (d, 1H, J = 8.2 Hz, H<sub>Ar</sub>), 7.39 (t, 1H, J = 8.0 Hz, H<sub>Ar</sub>); 13C NMR (125 MHz, CDCl<sub>3</sub>): δ<sub>ppm</sub> = 21.4, 31.2, 50.0, 66.4, 125.1, 128.6, 129.1, 130.4, 132.9, 139.4, 170.8, 185.4; Mass: HRMS (EI): calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>[M+H]<sup>+</sup> 264.0932, found 264.0403.

Table 3

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<th>Entry</th>
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Supplementary data associated with this article can be found in the online version, at [http://dx.doi.org/10.1016/j.tet.2016.07.034](http://dx.doi.org/10.1016/j.tet.2016.07.034).
These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes


