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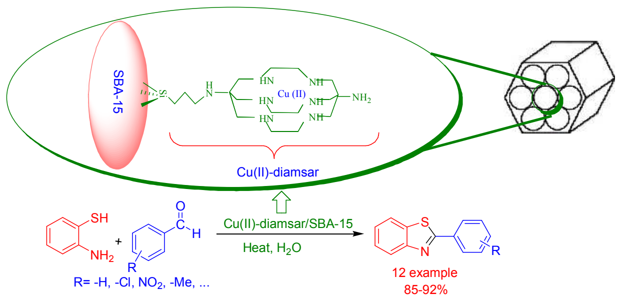

Cu(II)-diamsar/SBA-15 was prepared and used as an efficient heterogeneous catalysts for the synthesis of benzothiazole heterocycles in water media.

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A novel method for the synthesis of benzothiazole heterocycles catalyzed by copper-diamsar complex loaded on SBA-15 in water media

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Cu(II)-diamsar complex functionalized mesoporous SBA-15 silica supports was employed for the synthesis of benzothiazole heterocycles in water media as a green solvent with excellent yields. The resulting novel catalyst is extraordinarily stable and inhibits leaching of the metal ions from the SBA-15 support. Furthermore, it showed good heterogeneous catalytic activity in the synthesis of the aforementioned heterocycles and moreover could be recycled from the reaction mixture and used again for 6 times. The nature of the support after the anchoring of Cu(II)-diamsar complex on the surface of SBA-15 nanochannels and successful anchoring were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen physical adsorption (BET), Fourier transform infrared (FT-IR) studies and thermogravimetric analysis (TGA).

1. Introduction

Mesoporous materials, such as M41s, FSM and SBA families with pore sizes between 2 and 50 nm have got plenty of attention in catalysis and other areas because of their features such as high surface areas (up to 1200 m^2/g), uniform and tuneable pore sizes, organic solvent tolerance and great diversity in surface functionalization.[1-3]

The entitled nanomaterials have been widely used as useful and versatile solid supports for constructing various hybrid materials for heterogeneous catalysis, adsorbing agents, drug delivery and other fields. The larger pore sizes and high thermal and physical stability of SBA-15 makes it as one of the most interesting supports in the family of mesoporous materials.[4-6] SBA-15 is not directly utilized as a catalyst in reactions, therefore, functionalization of SBA-15 nanomaterials by organic frameworks or complexes containing transition metal ions is applied. The covalent linkage between support and the active site is a desirable way to avoid the leaching of metal ions. Therefore, encapsulation of the metal, especially with diamine-sarcophagines ligands (diamsar) which are covalently anchored[7-9] into the pores of mesoporous materials is worthy of examination. Furthermore, heterogeneous catalysts are very effective from a green chemistry viewpoint, because, the applied catalyst can be easily recycled and separated.[10-12]

Diamsar ligands are very appropriate for encapsulations of different metal ions, including radioisotopes and transition metals, which make them particularly well suited for radiopharmaceutical applications, diagnostic positron emission tomography (PET) imaging, and highly active in catalytic systems.[13,14] Diamsar can also conjugate to peptides, antibodies and biologically compatible polymers via its amine functionality and can be radiolabelled with a number of PET isotopes such as ^{64}Cu(II) in order to imaging interactions between molecular excavators and biological targets.[15,16]

Molecules containing benzothiazole moiety are of great interest in synthesis, because of their various biological activities; including anti-HIV,[17] antibacterial,[18] antitumor,[19] and neuroprotective effects.[20] There are also some pharmaceutical drugs such as Riluzole **1** (used in the treatment of amyotrophic lateral sclerosis),[21] Ethoxzolamide **2** (used for glaucoma, duodenal ulcers and as a diuretic) and dyes such as Thioflavin **3** (for histology staining) which have benzothiazole building blocks (Fig. 1). Because these heterocycles are important in medicinal and synthetic chemistry,[22] a range of approaches have been reported for preparation of 2-substituted benzothiazoles. Most commonly these routes involve condensation reactions of 2-aminothiophenol with carbonyl derivatives such as aldehydes,[23] carboxylic acids,[24] acid chlorides[25] and esters.[26] However, currently reported methods suffer from one or more drawbacks such as the use of strongly oxidizing or toxic reagents. Consequently, the development of a simple, convenient and eco-friendly method would be interesting. In this study, we introduce a novel, environmentally friendly and highly active Cu(II)-diamsar/SBA-15 as a heterogeneous reusable catalyst and investigate its application in the synthesis of benzothiazole derivatives in water.

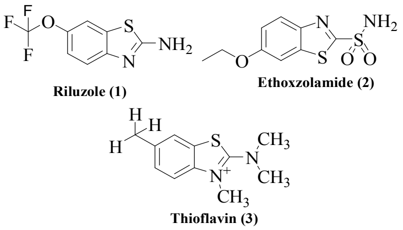


Fig. 1 Drug and dye products contain benzothiazol moieties.

2. Experimental

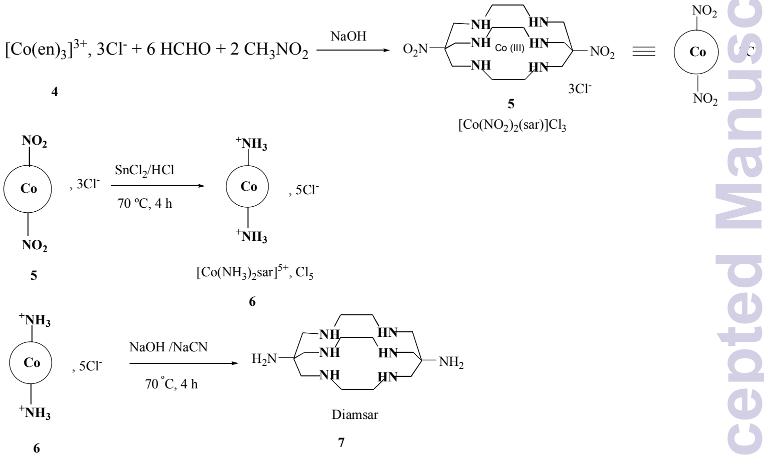
2.1. Materials

Acetonitrile, ethanol, formaldehyde, sodium hydroxide, hydrochloric acid, methanol, stannous chloride dihydrate, cobalt (II) chloride 6-hydrate, sodium cyanide, nitromethane, ethylanediamine, commercial grade of 2-aminothiophenol (*ortho*-aminothiophenol), aldehydes, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer (P123), (3-chloropropyl)trimethoxysilane (CPTMS), copper (II) acetate monohydrate, tetraethyl orthosilicate (TEOS), HNO_3 and HCl were purchased from Sigma-Aldrich, Merck and Acros chemical companies. Double distilled water was used when necessary. All materials were used without further purification. The solvents used for the synthesis were of analytical grade and were used as received. Silica gel (Merck, grade 9385, 230-400 mesh, 60 A°) for column chromatography was used as received. All other reagents were purchased from Merck and used as received unless otherwise noted. The course of the synthesis of heterocycles was followed by TLC on silica gel plates (Merck, silica gel 60 F_{254}, ready to use), using n-hexane: ethyl acetate (4:1) as eluents. The eluent for column chromatography was the same as TLC eluent.

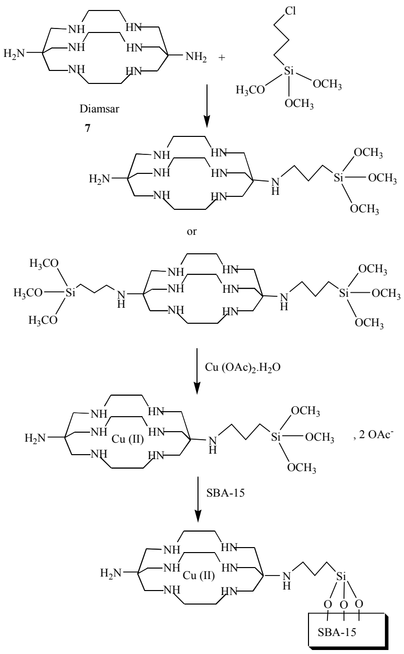
2.2. Synthetic procedures

2.2.1. Preparation of Cu(II)-diamsar complex anchored onto SBA-15 (Cu(II)-diamsar/SBA-15) (Scheme 2)

SBA-15 was prepared by the procedure previously explained by Zhao et al.[27]. The syntheses of diamsar **7** -(Scheme 1) is reported elsewhere (see also the detailed procedure on preparation in Electronic Supplementary Material section).[28,29] Diamsar **7** (0.0318 mmol, 0.01 g) and methanol (20 mL) were added in a flask and stirred at room temperature for an hour. Then (3-Chloropropyl)trimethoxysilane (0.0318 mmol, 0.006 g) was added to the solution and solution was stirred at room temperature for 24 hours, afterwards copper (II) acetate monohydrate (0.0318 mmol, 0.006 g) was added and the–solution was heated at 80 ºC for a further 6 hours. Finally, activated SBA-15 was added and the resulting solution was heated for 24 hours. The solvent was evaporated by a rotary evaporator, and obtained blue solid dried overnight at 80 °C. The product was washed with MeOH and deionized water until it became colorless. Further drying was carried out in an oven at 80 °C for 8 hours.



Scheme 1 Preparation of diamsar.



Scheme 2 Preparation of Cu(II)-diamsar complex anchored on SBA-15 (Cu(II)-diamsar/SBA-15).

2.2.2. General procedure for preparation of 2-substituted benzothiazole heterocycles in water

A round-bottomed flask equipped with a magnet and condenser was charged with 2-aminothiophenol **8** (1.0 mmol), substituted benzaldehyde (1.0 mmol), catalyst Cu(II)-diamsar/SBA-15 (0.005 g) and water (2 mL). The resulting mixture was stirred and heated at reflux for the appropriate times. After the reaction was completed (monitored by TLC), the reaction mass was cooled to room temperature. Finally, the crude mixture was purified by column chromatography or recrystallization in toluene to obtain the desired products. Spectral and physical data for all heterocycles are reported in Electronic Supplementary Material section.[30-32]

2.3. Characterizations

TEM observation was performed with a Hitachi H-700 CTEM. FT-IR spectra were recorded on KBr pellets by a Jasco 4200 FT-IR spectrophotometer. X-ray diffraction experiments (XRD; Bruker D8ADVANCE with Ni-filtered Cu Kα radiation at 1.5406 Å) were recorded with a speed of 2° min^{-1} and a step of 0.05°. ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 300, 400 and 500 MHz spectrometers using $CDCl_3$ or DMSO-d_6 as the NMR solvents. ^1H NMR spectra are referenced to tetramethylsilane (0.00 ppm) and ^{13}C NMR spectra are referenced from the solvent central peak (for example, 77.23 ppm for $CDCl_3$). Chemical shifts are given in ppm. N_2 adsorption/desorption isotherms were obtained at 77.35 °K with a Quantachrome Autosorb-1 apparatus. Before measurements, the samples were outgassed at 120 ºC for 12 h. The specific surface area and the pores size distributions were obtained from the desorption branch of the isotherms, respectively, using the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) analyses. A Shimadzu AA-6300 flame atomic absorption spectrometer was used to obtain the concentration of metal ions. For this purpose, 0.1 g of the catalyst was digested by HNO_3 with stirring at room temperature for a week. Then the mixture was filtered and the solid was washed several times with water to gain a colourless filtrate solution for metal measurements. The concentration of Cu(II) in the immobilized SBA-15 was 0.016 mmol/g. Thermogravimetric analysis was carried out with a TGA/DTA Shimadzu-50 instrument equipped with a platinum pan. The samples were heated in air from 25 to 1000 ºC with a heating rate of 10 ºC/min. The weight loss was recorded as a function of temperature. Melting points were recorded using a Buchi B540 melting point apparatus and are uncorrected.

3. Results and discussion

3.1. Characterization of Cu(II)-diamsar complex anchored onto SBA-15

Cu(II)-diamsar complex grafted on SBA-15 (Cu(II)-diamsar/SBA-15) was prepared according to Scheme 2. First, (3-chloropropyl)trimethoxysilane entity was introduced to dimasar amine functional groups. This moiety was immobilized onto SBA-15 after complexing with copper salt, using 3-chloropropyltrimethoxysilane as a reactive surface modifier through silylation reaction.

The successful anchoring of the Cu(II)-diamsar complex onto SBA-15 was characterized by using various physico-chemical techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), FT-IR and N_2 adsorption/desorption (BET) techniques to study the morphology, pore dimensions, functional group analysis and catalyst loading in the mesoporous material.

The quality and structural ordering of Cu(II)-diamsar/SBA-15 were measured by XRD. Fig. 2 shows XRD patterns of SBA-15 and Cu(II)-diamsar/SBA-15 samples. The X-ray diffraction scheme of both SBA-15 and Cu(II)-diamsar/SBA-15 exhibited a high intensity basal (100) peaks at (110) and (200) peaks, therefore confirming that the mesophase had hexagonal (p6mm) pore channels ordering and more over suggesting that the structure of mesoporous SBA-15 did not collapse by immobilization.[33] The XRD peaks of Cu(II)-diamsar/SBA-15 not only shows lower intensities but also have slightly lower angles than SBA-15 peaks. These losses in the intensities of the peaks were observed after the attachment of Cu(II)-diamsar revealing that silylation had indeed occurred inside the mesoporous of SBA-15. These results are consistent with the TEM images (Fig. 3) which also showed a hexagonal mesostructure.

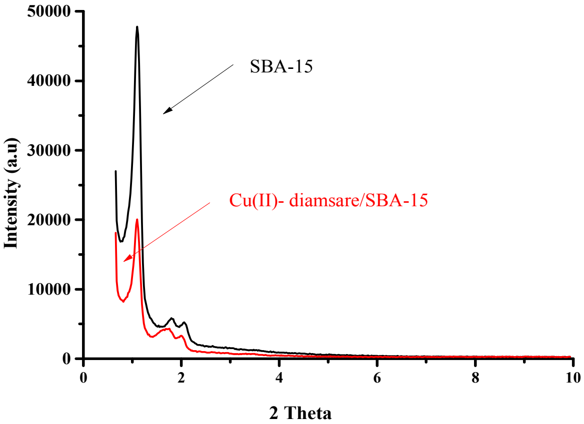


Fig. 2 XRD patterns of SBA-15 and Cu(II)-diamsar/SBA-15.

The TEM images of Cu(II)-diamsar/SBA-15 are presented in Fig. 3, (a) in the direction of the pore axis and (b) perpendicular direction to the pore axis of Cu(II)-diamsar/SBA-15, respectively. The preservation of the cylindrical shape of the pores and the retaining of hexagonal arrays of uniform channels indicates that the channel structure of SBA-15 is not destroyed after anchoring of Cu(II)-diamsar.

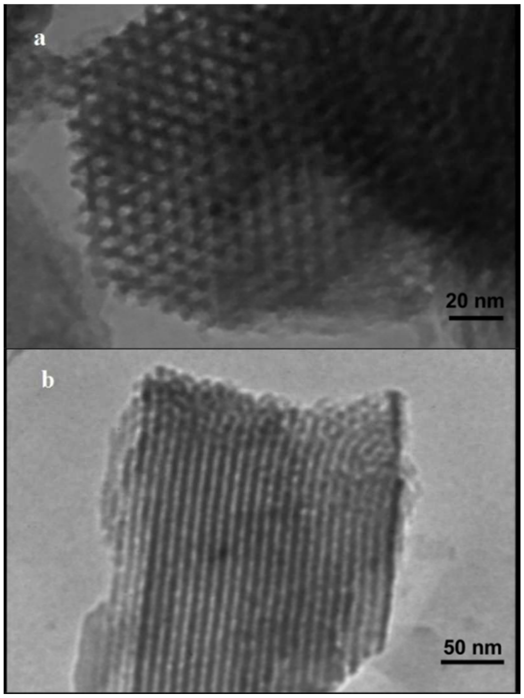


Fig. 3 TEM images of Cu(II)-diamsar/SBA-15: (a) in the direction of the pore axis and (b) in the perpendicular direction to the pore axis.

Thermogravimetric analysis is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature.[34] TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition. Here, thermogravimetric analysis was used for determination of thermal stability of the catalyst (Fig. 4). Pure siliceous SBA-15 shows a mass loss below 100 °C through the loss of adsorbed water from the surface of SBA-15. Surface condensation of hydroxyl groups occurs typically above 200-250 °C (and more). The weight losses observed for Cu(II)-diamsar/SBA-15 are at two temperatures: the minor weight loss was observed at 100 °C, which is due to physically adsorbed water molecules on the surface of the SBA-15. The major weight loss between 200 and 700 °C (Fig. 4) is due to the thermal decomposition of anchored Cu(II)-diamsar moieties. According to TGA data, the grafting amount of diamsar on SBA-15 was 62 wt.% (based on the initial amount of diamsar which was used for the anchoring).

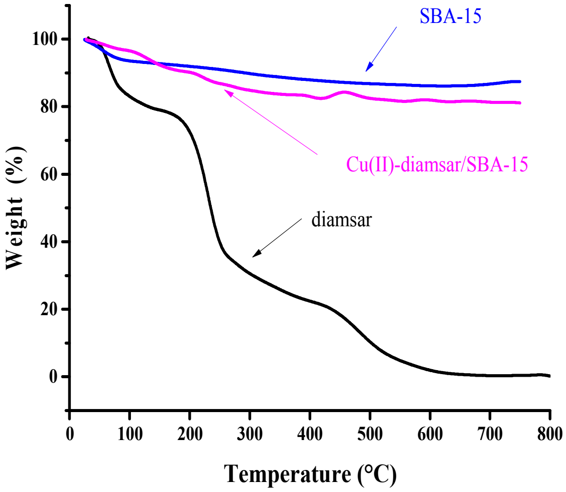


Fig. 4 Thermogravimetric analysis results of: (a) SBA-15, (b) Cu(II)-diamsar/SBA-15 and (c) diamsar.

The FT-IR spectrums of the SBA-15 and Cu(II)-diamsar/SBA-15 are shown in Fig. 5. The constitution of the immobilized complex was demonstrated by the strongly absorbing region of 1000-1200 cm^{-1} which is due to stretch vibrations of (Si-O-Si) bonds. The FT-IR spectrum of the Cu(II)-diamsar/SBA-15 shows a broad band between 3000 and 3700 cm^{-1}, which can be attributed to the stretching vibration absorption of NH and OH groups. The medium band observed in the 2935 cm^{-1} was assigned to stretching vibrations of CH_2. The peak at 1640 and 1400-1450 cm^{-1} in the Cu(II)-diamsar/SBA-15 was due to absorption peaks of C-N groups. These results confirmed the successful anchoring of Cu(II)-diamsar complex on SBA-15 surface.

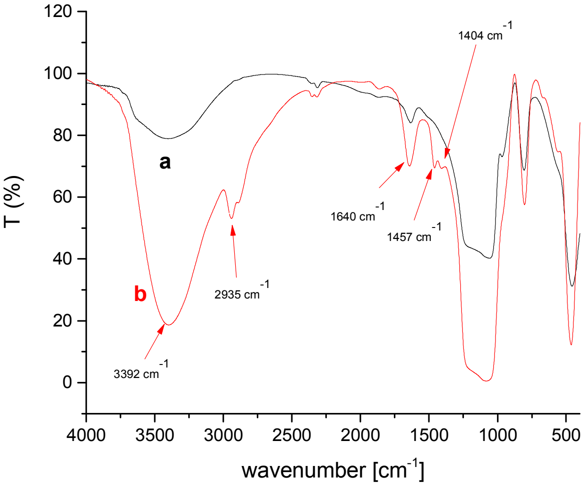


Fig. 5 IR spectra of (a) SBA-15 and (b) Cu(II)-diamsar/SBA-15.

The nitrogen adsorption-desorption isotherms and pore size distributions of corresponding samples are depicted in Fig. 6. Both SBA-15 and Cu(II)-diamsar/SBA-15 exhibit type IV isotherm patterns with a small H_1 hysteresis loop, showing that the cage liked structure of SBA-15 was maintained even after anchoring with Cu(II)-diamsar.[35] According to nitrogen adsorption and desorption experiment and BJH analysis, the textural parameters of samples were collected in Table 1. It can be seen that the decreases in BET surface area and pore volume were observed for Cu(II)-diamsar/SBA-15. This shows that Cu(II)-diamsar was immobilized inside the mesoporous of SBA-15.

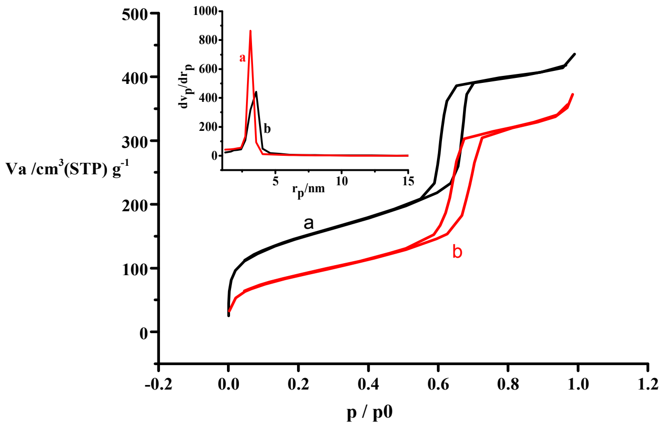


Fig. 6 Nitrogen adsorption/desorption isotherms and corresponding pore size distribution profile (inset) of (a) SBA-15 and (b) Cu(II)-diamsar/SBA-15.

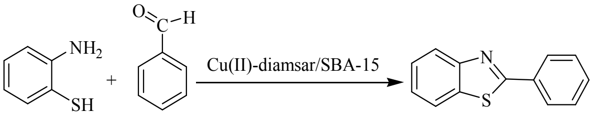
Table 1 Textural properties of the SBA-15 and Cu(II)-diamsar/SBA-15 (S_{BET}, specific surface area (m^2g^{-1}); V_{BJH}, pore volume (cm^3g^{-1}); D_{BJH}, Pore diameter (calculated from the adsorption branch) (nm)).

Materials	S_{BET}	V_{BJH}	D_{BJH}
SBA-15	532	0.600	6.24
Cu(II)-diamsar/SBA-15	317	0.560	7.1

3.2. Synthesis of heterocyclic derivatives in water

To test the applicability of our catalyst in organic synthesis under green conditions, the reaction of 2-aminothiophenol **8** and benzaldehyde **9a** in water and in the presence of Cu(II)-diamsar/SBA-15 was selected as the model reaction. Greener conditions selected to study the reaction and satisfying results of the reaction in water inspired us to further investigate this transformation. Some parameters such as the amount of the catalyst and the temperature were examined to determine the efficiency of the model reaction (Table 2). At first attempt, we examined the reaction at room temperature without the catalyst and it gave no yield of product. The best yield was obtained in the presence of 8 × 10^{-5} mmol of the catalyst, under reflux conditions (Table 2, entry 6).

Table 2 Screening of the reaction conditions for the reaction of 2-aminothiophenol **8** and benzaldehyde **9a**



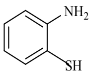
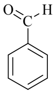
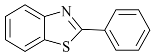
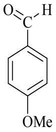
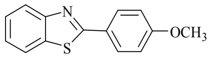
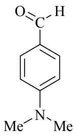
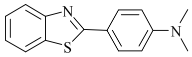
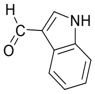
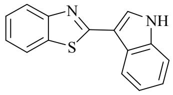
8 **9a** **10a**

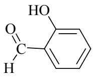
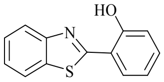
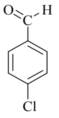
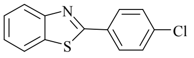
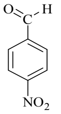
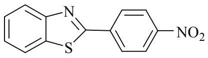
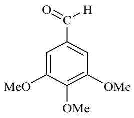
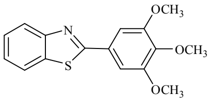
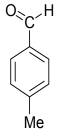
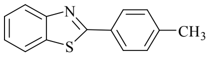
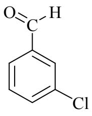
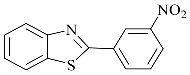
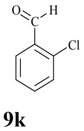
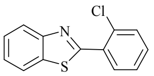
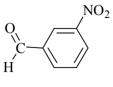
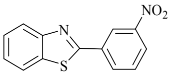
Entry	Catalyst (mol %)	Temperature. (°C)	Time (min)	Yield (%)[b]
1	0	rt	60	—
2	0.00008	rt	60	30
3	0.00016	rt	60	30
4	0.000008	rt	60	30
5	0.0008	60	60	50
6	**0.00008**	**95**	**20**	**90 (89)[c,d]**
7	0.00008	80	60	65

[a] All reactions were runing under the following conditions: 2-aminothiophenol **8** (1 mmol, 1 equiv), benzaldehyde **9a** (1.0 mmol, 1 equiv) and catalyst (0-0.00016 mmol of only Cu(II) ions or 0-0.05 g of Cu(II)-diamsar/SBA-15) in water (2 mL) were heated for appropriate time. [b] GC yields. [c] Optimum conditions. [d] Isolated yield in parentheses.

With the optimized conditions in hand, the reaction was evaluated by using various bennzaldehyde derivatives (Table 3, entries 1-12). As can be seen, most of the examined substrates provided good to excellent yields with short reaction times.

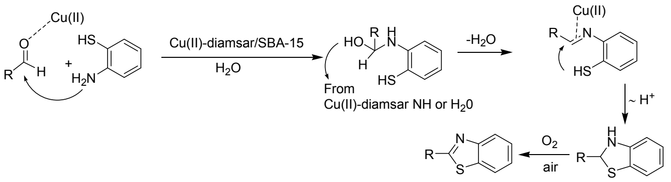
Table 3 Synthesis of benzothiazole based heterocycles catalyzed by Cu(II)-diamsar/SBA-15 in water[a].

Entry	Amine **8**	Aldehyde **9**	Product	Yield (%)[b]
1	 **8**	 **9a**	 **10a**	90
2	**8**	 **9b**	 **10b**	90
3	**8**	 **9c**	 **10c**	85
4	**8**	 **9d**	 **10d**	85

5	**8**	 **9e**	 **10e**	88
6	**8**	 **9f**	 **10f**	90
7	**8**	 **9g**	 **10g**	88
8	**8**	 **9h**	 **10h**	92
9	**8**	 **9i**	 **10i**	88
10	**8**	 **9g**	 **10j**	89
11	**8**	 **9k**	 **10k**	87
12	**8**	 **9l**	 **10l**	88

[a] All reactions were runing under the following conditions: 2-aminothiophenol **8** (1 mmol, 1 equiv), benzaldehyde **9a** (1.0 mmol, 1 equiv) and catalyst (0.005 g of Cu(II)-diamsar/SBA-15 or 0.00008 mmol of only Cu(II) ions) in water (2 mL) were heated for 20 min. [b] Isolated yield.

As one can see from Table 3, very electron-rich aldehydes such as 4-methoxybenzaldehyde and 3,4,5-trimethoxybenzaldehyde took part in this event with a high yield of the desired product (Table 3, entries 2 and 8). The proposed mechanism for the synthesis of benzothiazole derivatives can be presented as follo (Scheme 3):



Scheme 3 Proposed mechanism for the synthesis of benzothiazoles in the presence of Cu(II)-diamsar/SBA-15.

After examining the general scope of the reaction, our attention turned to recycling of the catalyst. It turned out that Cu(II)-diamsar/SBA-15 could be reused directly for a new cycle after the catalyst was first filtered, then washed with ethanol and dried at 80°C for 60 min. The recovered catalyst was recycled and reused for six times (Table 4).

Table 4 Investigation on the reusability of the catalyst for the preparation of 2-(phenyl)benzothiazole **10a**.

Run	1	2	3	4	5	6
Yeild (%)[a]	90	90	90	89	89	89

[a] Isolated yield.

4. Conclusions

In conclusion, we have shown that functionalization of silica with diamine-sarcophagus and subsequent complexation with copper creates an easily recoverable heterogeneous catalyst. The catalyst affords good activity in water for the synthesis of benzothiazole derivatives.

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Notes and references

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