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Efficient preparation of boehmite silica dopamine sulfamic acid as novel nanostructured compound and its application as catalyst in some organic reactions

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A novel type of boehmite-recoverable nanocatalyst was prepared *via* immobilization of dopamine on the surface of boehmite followed by coating with silica, then reaction with chlorosulfunic acid to obtain boehmite silica dopamine sulfamic acid (boehmite-Si-DSA). This compound was characterized by FT-IR spectroscopy, TGA, XRD, TEM and SEM techniques. Boehmite-Si-DSA used as an efficient, recoverable and thermally stable heterogeneous nanocatalyst for the preparation of 2,3-dihydroquinazolin-4(1*H*)-one, sulfoxides and disulfides. The catalyst was recovered by simple filtration and reused for several times without significant loss of its catalytic efficiency.

1 Introduction

In recent years, supported catalysts on the nanoparticles have attracted much attention in organic reactions.[1] Because, when the size of the support is decreased to the nanometer scale, the surface area is substantially increased and the support can be evenly dispersed in solution, forming a homogenous emulsion.[2] Some nanomaterial such as magnetic iron oxide,[3] mesoporous silica material,[4] graphene oxide,[5] molecular sieve[6] and etc. were applied as support. But preparation of many supports required a lot of time or N_2 atmosphere, also mesoporous silica required high temperature for calcination. While nanoboehmite is rarely employed as a heterogeneous support. Boehmite is an aluminum oxide hydroxide (γ-AlOOH) particles, has the orthorhombic structure, which the surface of boehmite nanoparticles covered with hydroxyl groups, which existence of many hydroxyl groups on the nanoboehmite surface leads to reaction with dopamine, alkoxysilane and other reagents which support terminal functional groups available for immobilization of other substances.[7] Nanoboehmite has several advantages, such as non-toxicity, readily available, high dispersion of the active phases, thermal and mechanical stability and high-surface-area resulting in high catalysts loading capacity.[8, 9]

2,3-Dihydroquinazolinone derivatives are important bicyclic heterocycles which have been reported to possess a wide range of biological properties and pharmaceutical activities such as vasodilating, diuretic, tranquilizing, Antibacterial, antitumor, antidefibrillatory, antihistaminic, anticonvulsant, anticancer, antihistaminic, herbicidal activity, plant growth regulation ability and antihypertensive agents.[10-12] In addition, these compounds can be oxidized to their quinazolin-4(3*H*)-one analogues, which also are important pharmacologically active compounds.[13] For example, based Fluorescence property of quinazolinone, 2-(2-hydroxyphenyl)-4(3*H*)-quinazolinone was utilized in the detection of metal ions.[14] Generally, 2,3-dihydroquinazolin-4(1*H*)-ones were prepared using the cyclization of carbonyl groups with anthranilamide or one pot three-component reaction of isatoic anhydride, aldehydes and amines in the presence of acid catalysts.[15, 16]

Besides, the oxidation of sulfides to sulfoxides and oxidative coupling of thiols into disulfides are useful in the synthesis of new products, which play an important role in various medical and biological applications.[17, 18] Some of biologically active sulfoxides play an important role as therapeutic agents such as antifungal, antibacterial, antihypertensive and anti-atherosclerotic as well as psychotropics and vasodilators.[18, 19] Sulfoxides are also valuable in the C-C bond formation and molecular rearrangements.[20] Additionally, Omeprazole, and the pesticide fipronil are two typical examples of the extensive application of these intermediates in pharmaceutical and fine chemical industries.[17-19] Likewise, disulfide bond formation is important in peptides, in bioactive molecules as well as oil sweetening processes.[20] Disulfides are used in synthesis of organo-sulfur compounds via C–S bond formation and sulfonylation of enolates and other anions while some disulfides have been found to be useful as vulcanizing agents for rubber and elastomers imparting them suitable tensile strength[21, 22] and they are also essential moieties of biologically active compounds for peptide

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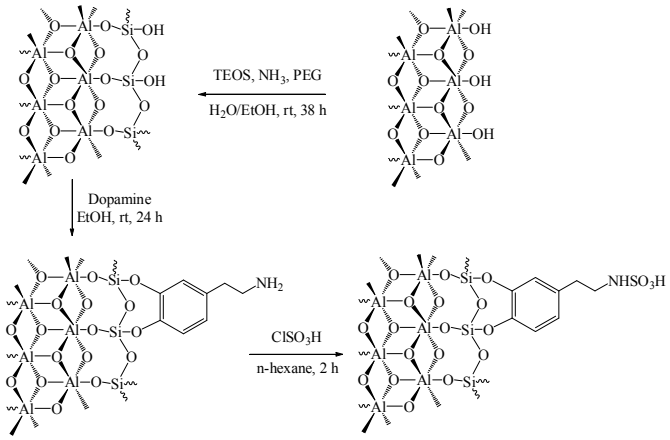
and protein stabilization anions.[23] For these reasons, oxidation of sulfides and thiols has been reported using a variety of reagents in the presence of different catalyst.[17-28] Hydrogen peroxide (with only H_2O as a byproduct) has been applied for these transformations as an inexpensive and environmentally benign oxidant.[29]

2 Results and discussion

2.1 Catalyst preparation

The boehmite-Si-DSA was prepared by the concise route outlined in Scheme 1. Initially, boehmite nanoparticles have been prepared on addition of NaOH to the solution of $Al(NO_3)_3.9H_2O$ as the source of aluminum at room temperature. After coating of boehmite nanoparticles with silica using tetraethyl orthosilicate (TEOS), the silanol groups were functionalized with dopamine. Ultimately, the functionalization of terminal amines with chlorosulfunic acid led to the boehmite dopamine sulfamic acid (boehmite-Si-DSA). The crystalline structure of synthesized samples was examined by X-ray diffraction using GBC-Difftech MMA diffractometer. The nickel filtered Cu Kα (λ= 1.54A˚) radiation was used at acceleration voltage of 35 kV and current of 34.2 mA. The diffraction angle was scanned from 1˚ to 80˚, 2θ at a rate of 1˚/min. Fourier transform infrared spectroscopy (FTIR) analyses were carried in KBr on FTIR, spectrophotometer (Bruker, Germany) Vertex 70 in the range of 400–4000 cm^{-1}. A thermogravimetric analysis (TGA) was carried out (PerkinElmer Pyris Diamond, U.K.) from an ambient temperature to 840 ˚C and at N_2 atmosphere, using a ramp rate of 10˚C/min. TEM analysis of catalyst was recorded using a Zeiss-EM10C-80KV TEM. Also the catalyst morphology was examined by measuring SEM and EDX study with accelerating voltage of 10 kV were using FESEM-TESCAN MIRA3.



Scheme 1. Synthesis of boehmite-Si-DSA.

2.2 Catalyst characterization

The size and morphology of boehmite nanoparticles and boehmite-Si-DSA were obtained by SEM and TEM. As shown in Figure 1, the particle sizes of boehmite-Si-DSA were about 86 and 30 nm in the long and short dimension respectively. Also, the SEM image of the boehmite and boehmite-silica showed that particles have a regular geometric shape in comparison with nanoboehmite (Figure 2).

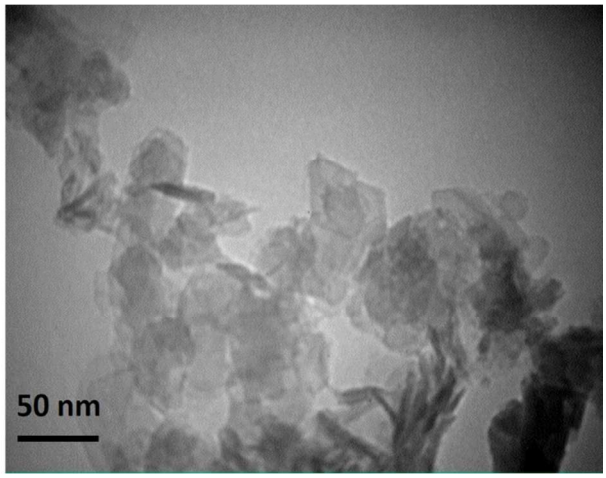


Figure 1. TEM image of boehmite-Si-DSA.

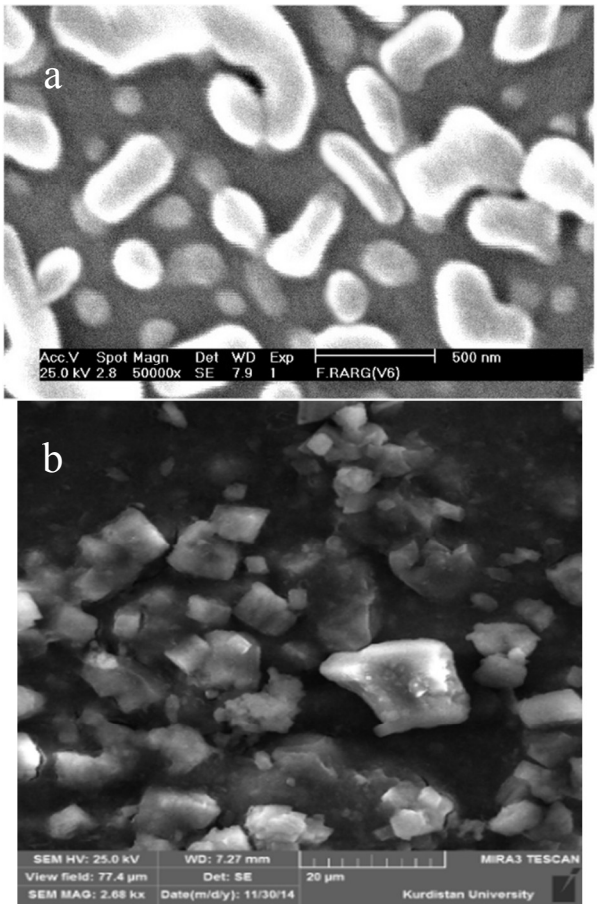


Figure 2. SEM image of boehmite-Si-DSA (a) and boehmite (b).

The XRD patterns of boehmite nanoparticles (red line) and boehmite-Si-DSA (green line) are shown in Figure 3. As seen in Figure 3, the boehmite phase was identified from the XRD patterns by the peak positions at 14.40 (0 2 0), 28.41 (1 2 0), 38.55 (0 3 1), 46.45 (1 3 1), 49.55 (0 5 1), 51.94 (2 0 0), 56.02 (1 5 1), 59.35 (0 8 0), 65.04 (2 3 1), 65.56 (0 0 2), 68.09 (1 7 1), and 72.38 (2 5 1), which all the peaks can be confirmed the crystallization of boehmite with an orthorhombic structures.[8, 30] Also sharp peaks around 2θ=20-30 in boehmite-Si-DSA XRD pattern, which is typical for dopamine and in boehmite itself can't be seen.[31,32]

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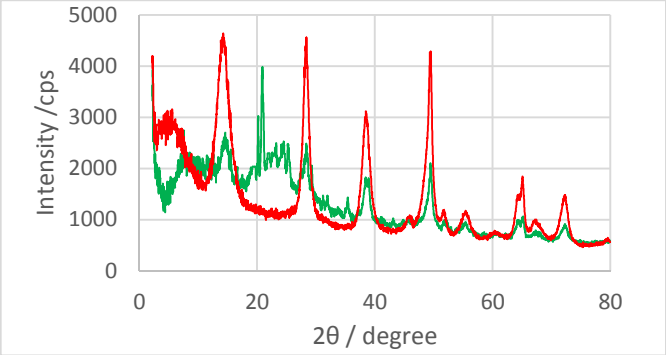

Figure 3. The XRD pattern of boehmite (red line) and boehmite-Si-DSA (green line).

The TGA was used to determine the percent of functional groups chemisorbed onto the surface of boehmite nanoparticles. Figure 4 shows the TGA curves for bare boehmite nanoparticles (black curve), boehmite coated with silica (boehmite-silica) (red curve), boehmite functionalized with dopamine (boehmite-Si-dopamine) (blue curve) and boehmite-Si-DSA (green curve). The initial weight loss at below 110 ºC in the all samples, was caused by the removal of the adsorbed water, as well as the endothermic weight loss at 300 ºC is attributed to water loss from structural hydroxyl groups in the precursor.[33] In the profile of boehmite-Si-DSA, organic groups have been reported to desorb at temperatures above 250 °C (about 85%). Meanwhile, weight loss about 45% from 250 to 650 °C is occurred for boehmite-Si-dopamine. On the basis of this result, the well grafting of dopamine sulfamic acid on the boehmite nanoparticles is verified.Thermal stability of the catalyst was also determined, since synthesis of many organic compound were usually carried out at high temperature. As shown in Figure 4, boehmite-Si-DSA catalyst was stable even at 220 ºC.

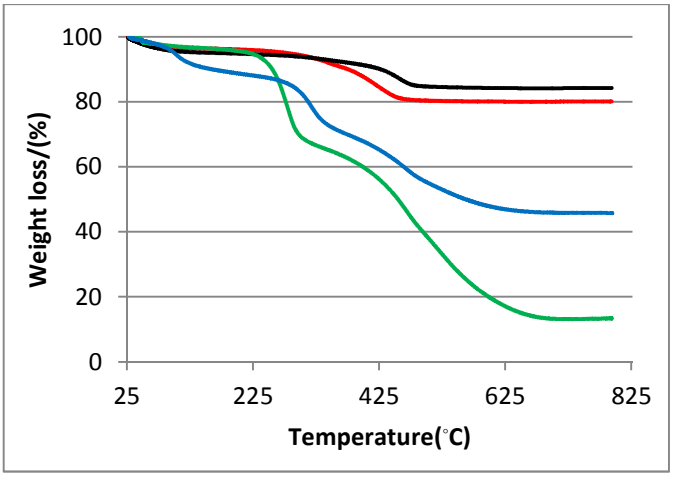

Figure 4. TGA diagram of (black line) boehmite nanoparticles, (red line) boehmite-silica, (blue line) boehmite-Si-dopamine and boehmite-Si-DSA (green line).

The FT-IR spectrum for boehmite nanoparticles (a), boehmite-silica (b), boehmite-Si-dopamine (c) and boehmite-Si-DSA (c) are shown in figure 5.
The FT-IR spectrum of the boehmite nanoparticles shows two strong bands at 3086 and 3308 cm^{-1} which incorporates the contributions from both symmetrical and asymmetrical modes of the O-H bonds which are attached to the surface boehmite nanoparticles.[3, 7, 8] Several peaks in FT-IR spectrum of boehmite nanoparticles at 477, 613 and 735 cm^{-1} can be attributed to the characteristic absorption of Al-O bonds.[7] Also, the nitrate impurity vibration at 1650 cm^{-1} and the vibrations of hydrogen bands OH…OH by two strong absorption bands at 1164 and 1069 cm^{-1} were observed in FT-IR spectrum [7, 34]. In the 1072 and 770 cm^{-1} spectral region of the FT-IR spectra (Figure 5b-d): an overlap of the asymmetric and symmetric stretching vibration of the Si-O-Si bonds with Al-O and OH…OH stretching vibration leads to band broading.[35] In the FT-IR spectra of boehmite-Si-dopamine (Figure 5c), The presence of the anchored dopamine groups are confirmed by C–H stretching vibrations that appear at 2961 cm^{-1} and also N-H stretching vibration modes as a broad band that appear at 3080-3343 cm^{-1}. Also, vibrations in the range of 1100-1600 cm^{-1} are attributed to the aromatic ring, C-C, C-O and C-N. Reaction of boehmite-Si-dopamine with chlorosufonic acid produces boehmite-Si-DSA in which the presence of SO_3H moiety is asserted with 938-1220 cm^{-1} bands in FT-IR spectra. Also, vibrations in the range of 3000-3400 cm^{-1} are attributed to the SO_3-H groups.

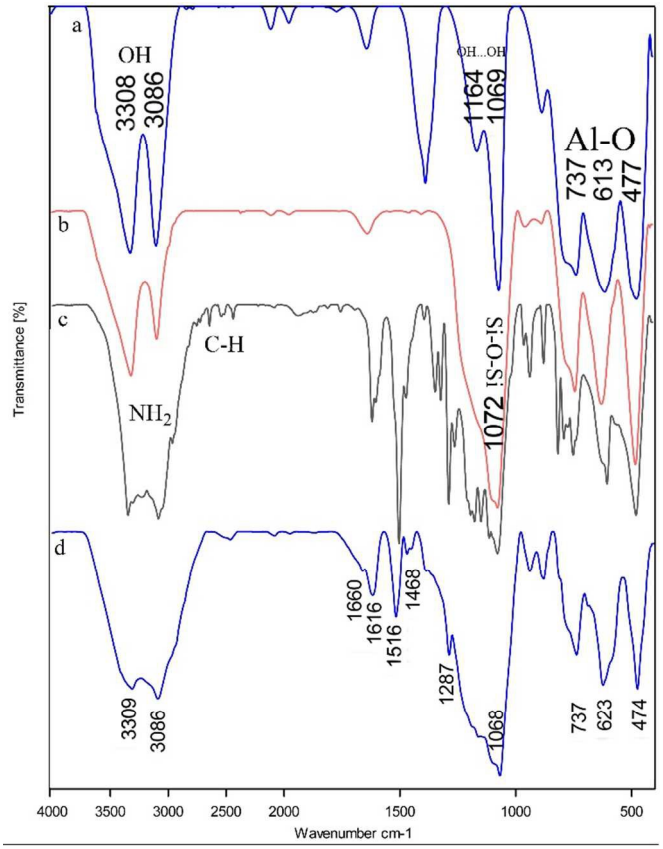

Figure 5. FT-IR spectra of (a) boehmite nanoparticles, (b) boehmite-silica, (c) boehmite-Si-dopamine and (d) boehmite-Si-DSA.

The energy dispersive X-ray spectrum (EDX) of boehmite-Si-DSA in Figure 6 displayed that the mass percent of C, N, O, Si and Al are 17.0, 4.7, 52.3, 10.4 and 15.6, respectively and the Si/Al ratio is 0.67. Also to determine the amount of acid in catalyst according to the literature,[13] the 0.1 g of catalyst was added to an aqueous NaCl solution (1 mol/L, 10 mL) with an initial PH 6.89. The mixture was stirred for 30 min until the PH of solution decreased to 2.62 that indicating an ion exchange between sulfamic acid protons and sodium ions and this is equal to a loading of 0.53 $mmol.g^{-1}$ of sulfamic acid group.

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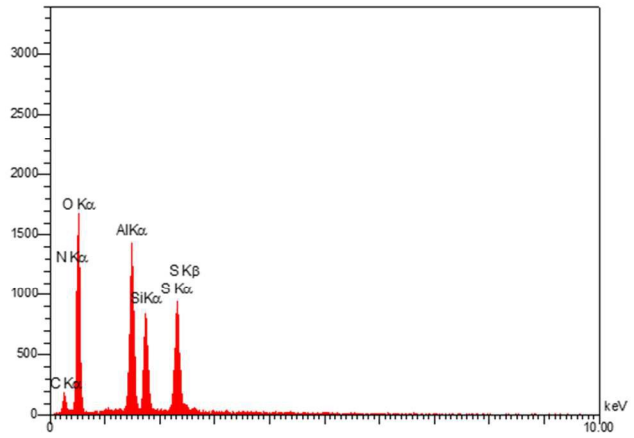
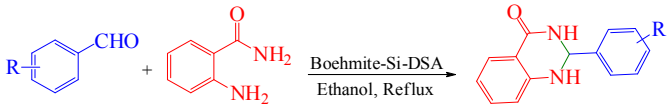


Figure 6. EDX spectra of boehmite-Si-DSA

2.3 Catalytic study

Herein we examined the catalytic activity of boehmite-Si-DSA in some organic reactions such as synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives, oxidation of sulfides and oxidative coupling thiols into sulfoxides and disulfides respectively. Synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives using cyclocondensation reaction of aldehydes and anthranilamide in the present of boehmite-Si-DSA was shown in Scheme 2.



Scheme 2. boehmite-Si-DSA catalyzed the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives.

The reaction condition for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives was optimized by cyclocondensation reaction of anthranilamide and 4-chlorobenzaldehyde in the presence of different amounts of boehmite-Si-DSA (Table 1, entries 1-6) and in various solvents such as Acetonitrile, Acetone, Ethyl acetate, n-hexane and Dichloromethane were used (Table 1, entries 6-11). As shown in Table 1, the best results were obtained in ethanol using 0.03 gr of boehmite-Si-DSA (Table 1, entry 6).

Table 1. Optimization for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one conditions for the cyclocondensation of 4-chlorobenzaldehyde and anthranilamide as a model compound at 80 ºC for 150 min.

Entry	Solvent	Catalyst (mg)	Yielde (%)[a]
1	Ethanol	5	35
2	Ethanol	10	46
3	Ethanol	15	58
4	Ethanol	20	80
5	Ethanol	25	89
6	Ethanol	30	97
7	Acetonitrile	30	75
8	Acetone	30	35
9	Ethyl acetate	30	76
10	n-hexane	30	62
11	Dichloromethane	30	57

[a] Isolated yield.

After the obtimumization of the reaction condition, the various aldehydes including aromatic aldehydes (Table 2, entries 1-13), aliphatic aldehydes (Table 2, entries 15 and 16) and alylic aldehyde (Table 2, entry 14) have been described in optimum condition and the products were obtained in good to excellent yields (Table 2). The experimental procedure is very simple and convenient, and has the ability to tolerate a variety of aldehydes contain electron-donating (Table 2, entries 2-5) and electron-withdrawing (Table 2, entries 6-11) functional groups. Also, terephthaldehyde and isophthaldehyde (Table 2, entries 12 and 13) were successfully employed to prepare the corresponding products in excellent yields. Therefore, the results revealed that this methodology is effective for a wide range of aldehydes.

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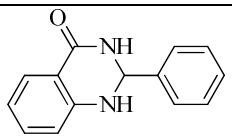
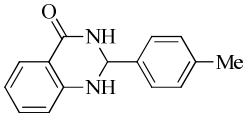
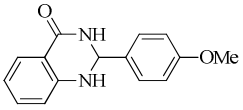
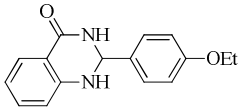
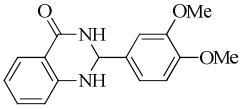
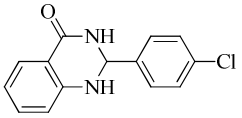
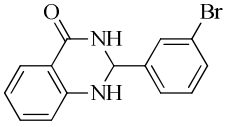
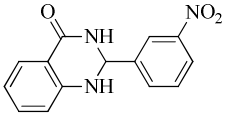
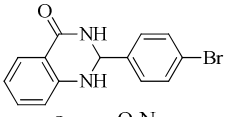
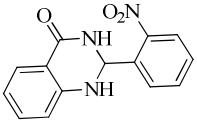
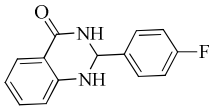
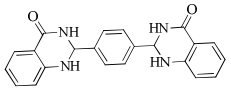
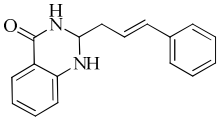
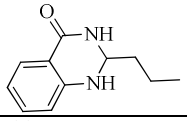
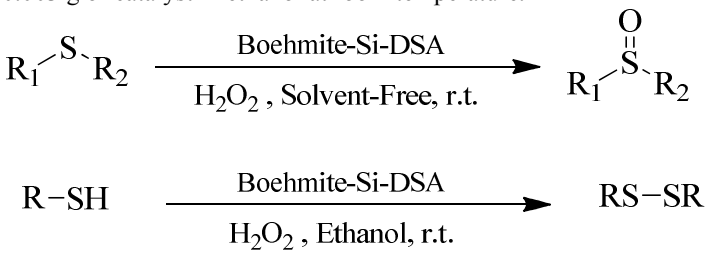
Table 2. Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones catalyzed by boehmite-Si-DSA in ethanol and at 80 ºC.

Entry	Product	Time (min)	Yield (%)[a]	Melting point (ºC)	Reference
1		60	96	219-221	[13]
2		30	98	224-226	[35]
3		45	98	177-179	[13]
4		50	97	163-165	[13]
5		60	96	212-215	[35]
6		150	97	199-200	[16]
7		75	98	174-176	[35]
8		155	94	214-216	[13]
9		110	95	197-199	[16, 35]
10		190	93	181-183	[13]
11		105	97	195-197	[13, 35]
12		30	98	244-246	[16]
13		55	92	200-203	[35]
14		50	95	175-178	[35]

[a] Isolated yield.

Also, we tested the catalytic activity of boehmite-Si-DSA in the oxidation of sulfides to sulfoxides and oxidative coupling of thiols into disulfides using H_2O_2 (Scheme 3). In order to choose the reaction condition, we examined the oxidation of methylphenyl sulfide as a model compound in the presence of different amounts of boehmite-Si-DSA (Table 3, entries 1-7) and in various solvents (Table 3, entries 7-14). As shown in Table 3, the best results for sulfoxidation were found under solvent-free condition using 0.03 g of boehmite-Si-DSA at room temperature (Table 3, entry 6). The optimum reaction conditions for the oxidative coupling of thiols were found to be 0.003 g of catalyst in ethanol at room temperature.



Scheme 3. The oxidation of sulfides into sulfoxides and oxidative coupling of thiols into disulfides using H_2O_2 in the presence of boehmite-Si-DSA.

Table 3. Optimization of the reaction conditions for the oxidation of methylphenyl sulfide (1 mmol) as a model compound.

Entry	Solvent	Catalyst (mg)	Time (min)	Yield (%)[a]
1	Solvent-Free	0	20	-[b]
2	Solvent-Free	10	20	40
3	Solvent-Free	15	20	51
4	Solvent-Free	20	20	65
5	Solvent-Free	25	20	78
6	Solvent-Free	30	20	98
7	Solvent-Free	40	20	95
8	Dichloromethane	30	285	94
9	Acetone	30	275	95
10	n-hexane	30	420	95
11	Acetonitrile	30	120	93
12	Water	30	95	97
13	Ethanol	30	60	98
14	Ethyl acetate	30	600	94

[a] Isolated yield, [b] No reaction.

In obtained optimum condition, the wide range of sulfides and thiols with different functional groups were converted to their corresponding products in the present of boehmite-Si-DSA as catalyst at room temperature under solvent-free condition. The products were obtained in high to excellent yields in a short reaction time. The result of this study was shown in table 4 and 5. These oxidizing systems allowed the chemoselective oxidation of 2-(phenylthio)ethanol, 2-(methylthio)ethanol and 2-mercaptoethanol to the corresponding sulfoxides and disulfide. Interestingly primary hydroxyl groups in these substrates remained intact during the oxidation reactions (Table 4, entries 3, 4 and Table 5, entry 3). The all products were obtained in high to excellent yields without any byproducts such as sulfone (for oxidation of sulfides) or thiosulfinates, disulfoxides, sulfinyl sulfones or disulfones (for the oxidative

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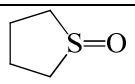
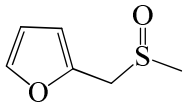
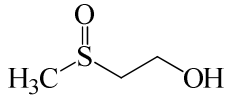
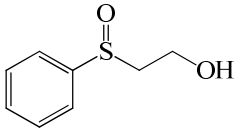
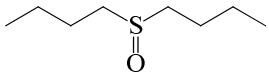
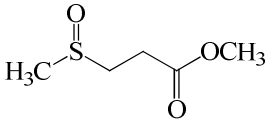
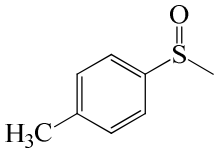
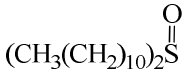
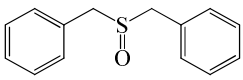
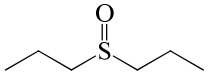
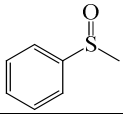
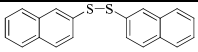
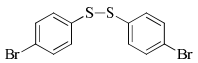
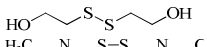
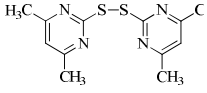
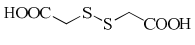
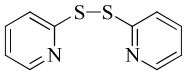
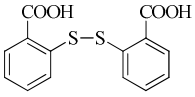
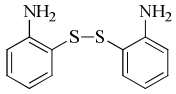
coupling of thiols). Therefore, the results revealed that this methodology is effective for a wide range of sulfides.

Table 4. Oxidation of sulfides into sulfoxides using H_2O_2 in the presence of boehmite-Si-DSA at room temperature.

Entry	Product	Time (min)	Yield (%)[a]
1		5	83
2		25	80
3		30	80
4		10	80
5		55	85
6		10	98
7		45	98
8		65	98
9		100	98
10		15	91
11		20	98

[a] Isolated yield.

Table 5. Oxidative coupling of sulfides into disulfides using H_2O_2 in the presence of boehmite-Si-DSA at room temperature.

Entry	Product	Time (min)	Yield (%)[a]	Melting point (ºC)	Ref.
1		5	97	130-132	[17]
2		120	98	85-87	[17]
3		20	95	Oil	[17]
4		10	97	160-163	[36]
5		10	97	Oil	[17]
6		20	98	55-56	[4]
7		120	97	267-269	[17]
8		15	96	85-87	[17]

[a]Isolated yield.

In another study, to better clarify the importance of Boehmite as support, we functionalized MCM-41 mesoporous with dopamine sulfamic acid and also supported dopamine sulfamic acid on silica as new catalysts and examined the reactions at the same conditions. First of all we prepared MCM-41-Si-DSA. In this light mesoporous Si–MCM-41 was prepared according to the literature procedure.[37] Deionized water was added to 2 M NaOH and cetyltrimethylammoniumbromide (CTAB) as a surfactant template and stirred intense at 80 °C, after clarification tetraethylorthosilicate (TEOS) was added slowly and continuously. After 2 h stirring, the synthetic solution obtained with molar composition TEOS/CTAB/NaOH/H_2O: 60/3.0/1.0/1. After cooling to room temperature, the resulting solid was gathered by filtration, washed with deionized water, and dried at 343 K. Then followed by calcination at 823 K for 5 h with rate of 2˚C/min to remove the residual surfactant. Then dopamine (1.5 g) was added to the 1 g of Si-MCM-41in ethanol. The reaction mixture was stirred at room temperature for 24 h. Then, the dopamine-Si-MCM-41 was separated by simple filtration and washed with ethanol and dried at room temperature. Chlorosulfunic acid (0.75 mL) was added drop wise over a period of 30 min to the obtained dopamine-Si-MCM-41 (0.5 g) in n-hexane (5 mL) and the mixture was stirred for 5 h at room temperature. Then, the final product was filtered and washed by dry n-hexane, ethanol to remove the unattached substrates. The product (MCM-41-DSA) dried at room temperature.

In another effort, we immobilized sulfamic acid on silica in the absence of boehmite. The procedures are the same as that reported in 4.1. Preparation of the boehmite-DSA but without the first step related to boehmite synthesis. Then we examined the synthesis of 2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one and oxidation of methylphenyl sulfide using mesoporous catalyst (MCM-41-DSA) and Si-DSA at the same condition of boehmite-DSA. The results are presented in table 6.

Table 6. Immobilization of sulfamic acid on defferent supports

Entry	Substrate	Catalyst	Time (min)	Yield (%)[a]
1	4-methylbenzaldehyde	MCM-41-DSA	30 (200)	38 (65)
2	4-methylbenzaldehyde	Si-DSA	30 (200)	25 (60)
3	4-methylbenzaldehyde	boehmite-DSA	30	98[b]

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4	methylphenyl sulfide	MCM-41-DSA	20 (180)	42 (92)[b]
5	methylphenyl sulfide	Si-DSA	20 (150)	30 (95)[b]
6	methylphenyl sulfide	boehmite-DSA	20	98

[a] Purification by preparative TLC. [b] Isolated yield.

As shown in table 6, in the synthesis of 2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one, after 30 min the reaction did not completed and the yields of 38% in the presence of MCM-41-DSA and 25% in the presence of Si-DSA obtained by purification with preparative TLC. Even after a longer time, 200 min, reaction did not completed and product purification performed by preparative TLC. In the oxidation of methylphenyl sulfide, similar behavior occurred, but with much more time (8 × compared to boehmite-DSA) the reaction have been completed.

2.4 Recyclability of the catalyst

In order to examine ability of the catalyst recycling, the reusability of the boehmite-Si-DSA was examined for the oxidation of methylphenyl sulfide and synthesis of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one. For this issue, after the completion of the reaction, the mixture was filtered and washed with ethylacetate to remove the residual product. The recovered catalyst was dried and subjected to the next without any significant activation. As shown in figure 7, the catalyst can be reused up to 5 runs without any significant loss of activity. The average isolated yield for several successive runs was obtained in 96 and 97%, for methylphenyl sulfoxide and 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one, respectively.

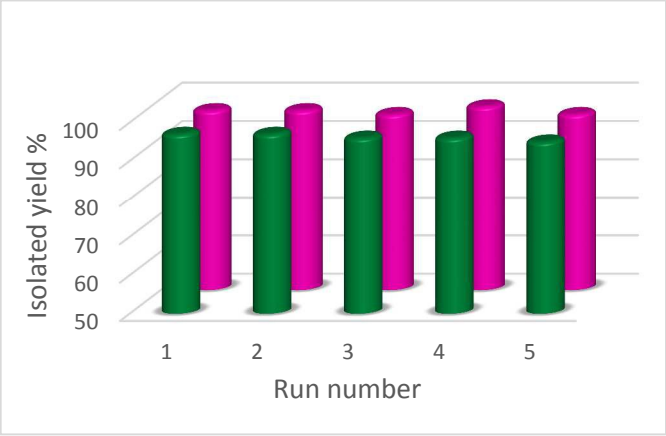

Fig 7. The recycling experiment of boehmite-DSA in oxidation of methylphenyl sulfide (green column) and synthesis of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one (red column).

2.5 Comparison of the catalyst

In order to describe the catalytic activity of boehmite-Si-DSA, we compared the results of the synthesis of 2-(p-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (Table 2, entry 2) and also oxidation of methyl(phenyl)sulfide (Table 4, entry 11) and oxidative coupling of naphthalene-2-thiol (Table 5, entry 1) in the presence of this catalyst with the previous methods in the literatures. This catalyst afford good reaction time and higher yield than other catalysts (Table 7). Also comparison of activity based on turnover frequency (TOF) showed excellent results for boehmite-Si-DSA in all three kinds of reactions. More importance, in compared than other catalyst, boehmite-Si-DSA has been easily prepared using cheap and commercially materials in short time, and can be reused for 5 times without any significant loss of activity.

Table 7. Comparison results of boehmite-Si-DSA with other catalysts

Entry	Substrate	Catalyst	Time (min)	Yield (%)[a]	TOF (min^{-1})	Ref.
1	4-methylbenzaldehyde	2-morpholinoethanesulfonic acid	180	91	0.05	[38]
2	4-methylbenzaldehyde	p-SAC	20	92	4.6	[39]
3	4-methylbenzaldehyde	$ZrCl_4$.	15	97	3.23	[40]
4	4-methylbenzaldehyde	[hnmp][HSO4]	28	75	0.54	[41]
5	4-methylbenzaldehyde	boehmite-Si-DSA	30	98	2.05	This work
6	methyl(phenyl)sulfane	Ru^{II}(TMP)(CO)	100	90	4.5	[20]
7	methyl(phenyl)sulfane	SiO_2–2-ImSiO_2–2-Im	150	86	0.38	[42]
8	methyl(phenyl)sulfane	Mn(III)–salphen	32	95	2.97	[43]
9	methyl(phenyl)sulfane	boehmite-Si-DSA	20	98	3.08	This work
10	naphthalene-2-thiol	Fe@SBA-15	10	95	9.5	[44]
11	naphthalene-2-thiol	nickel nanoparticles	8	93	0.78	[45]
12	naphthalene-2-thiol	boehmite-Si-DSA	5	97	12.2	This work

3 Conclusions

In summary, we have demonstrated that boehmite-DSA can be used as a green, efficient and reusable nanocatalyst for the synthesis of a

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wide range of 2,3-dihydroquinazolin-4(1*H*)-one derivatives in ethanol under reflux condition. Also, oxidation of sulfides to sulfoxides and oxidative coupling of thiols into disulfides was reported at room temperature in the present of boehmite-DSA as an efficient nanocatalyst. The advantages of these protocol are the use of a commercially available, eco-friendly, cheap and chemically stable materials, the simple methodology, practicability, easy work up and high products yields. The product separation and catalyst recycling are easy by simple filtration. The catalyst can be reused for 5 times without any significant loss of activity.

4 Experimental

4.1. Preparation of the boehmite-DSA

The solutions of 6.490 g NaOH in 50 ml of distilled water was added to solutions of 20 g $Al(NO_3)_3 \cdot 9H_2O$ in 30 ml distilled water as drop to drop under vigorous stirring. The resulting milky mixture was subjected to mixing in the ultrasonic bath for 3 h at 25 ºC. The resulted nanoboehmite was filtered and washed by distilled water and were kept in the oven at 220 ºC for 4 h.
The obtained boehmite nanoparticles (1 g) was dispersed in water (10 mL) and ethanol (50 mL) by sonication for 30 min. Under continuous stirring, PEG (5.36 g), ammonia solution (10 mL) and TEOS (2 mL) were respectively added into the suspension, and continuously reacted for 38 h at room temperature. Then, the product (boehmite-silica) was filtered and washed with ethanol and distilled water, the obtained boehmite-silica was dried at room temperature.
The obtained boehmite-silica (1 g) was dispersed in 25 mL ethanol, and solution by ultrasonic bath for 30 min, and then dopamine (1.5 gr) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h. Then, the nanoparticles was separated by simple filtration and washed with ethanol. The obtained boehmite-Si-dopamine was dried at room temperature.
The obtained boehmite-Si-dopamine (0.5 g) were dispersed in dry n-hexane (5 mL) by ultrasonic bath for 20 min. Subsequently, chlorosulfunic acid (0.75 mL) was added drop wise over a period of 30 min and the mixture was stirred for 2h at room temperature. Then, the final product was filtered and washed by dry n-hexane, ethanol and n-hexane respectively to remove the unattached substrates. The product (boehmite-DSA) dried at room temperature and stored in a refrigerator to use.

4.2 General procedure for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones derivatives

A mixture of boehmite-Si-DSA (0.03 g), anthranilamide (1 mmol) and aldehyde (1 mmol) was stirred at 80 ºC in ethanol (2 mL). The progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. CH_2Cl_2 (2 ×5 mL) was added and the catalyst was separated using simple filtration. CH_2Cl_2 was evaporated and all products was recrystalized in ethanol for further purification.

4.3 General procedure for the oxidation of sulfides to sulfoxides using H_2O_2 in the presence of boehmite-Si-DSA

A mixture of sulfide (1 mmol), H_2O_2 (0.4 mL) and boehmite-Si-DSA (0.03 g) was stirred at room temperature under solvent-free condition and the progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated using simple filtration and washed with ethyl acetate, and next, the product was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Finally, the organic solvents were evaporated, and products were obtained in good to high yield.

4.4 General procedure for the oxidative coupling of thiols into disulfides using H_2O_2 in the presence of boehmite-Si-DSA

Boehmite-Si-DSA (0.03 g) was added to a mixture of thiol (1 mmol) and H_2O_2 (0.4 mL) in ethanol (5 mL). Then the mixture was stirred for the appropriate time at room temperature. The progress was monitored by TLC. After completion of the reaction, the catalyst was separated by simple filtration and the mixture was washed with ethyl acetate. The product was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). In some cases, the product was recrystallized from ethanol for further purification and products were obtained in good to high yield.

4.5 Selected Spectral data

2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (Table 2, entry 2):

Mp: 224-226 °C. IR (KBr) cm^{-1}: 3313, 1658, 1611, 1439. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.20 (s, 1H), 7.63-7.60 (d, *J*=7.5, 1H), 7.40-7.37 (d, *J*=7.5, 2H), 7.25-7.13 (m, 3H), 7.03 (s, 1H), 6.74-6.63 (m, 2H), 5.71 (s, 1H), 2.50-2.43 (s, 3H) ppm.

2-(4-Ethoxyphenyl)-2,3-dihydoquinazolin-4(1*H*)-one (Table 2, entry 4):

Mp: 163-165 °C. IR (KBr) cm^{-1}: 3301, 1650, 1613, 1443. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 7.96-7.95 (b, 1H), 7.51-7.49 (m, 2H), 7.34 (s, 1H), 7.25 (s, 1H), 6.94-6.89 (m, 3H), 6.67-6.66 (m, 1H), 5.84 (s, 1H), 5.75 (s, 1H), 4.08-4.06 (q, *J*=4, 2H), 1.47-1.45 (s, 3H) ppm.

2-(3,4-Dimethoxyphenyl)-2,3-dihydoquinazolin-4(1*H*)-one (Table 2, entry 5):

Mp: 212-215 °C. IR (KBr) cm^{-1}: 3335, 1671, 1610, 1436. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.20 (s, 1H), 7.65-7.63 (d, *J*=7.6, 1H), 7.29-7.25 (t, *J*=0.8, 1H), 7.16 (d, *J*=1.6, 1H), 7.03-6.96 (m, 2H), 6.94 (s, 1H), 6.79-6.78 (d, *J*=8, 1H), 6.73-6.68 (t, *J*=1.2, 1H), 5.71 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H) ppm.

2-(4-Chlorophenyl)-2,3-dihydoquinazolin-4(1*H*)-one (Table 2, entry 6):

Mp: 199-200 °C. IR (KBr) cm^{-1}: 3309, 1655, 1611, 1435. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.30 (s, 1H), 7.60-7.41 (m, 5H), 7.25-7.19 (t, *J*=7.5, 1H), 7.11 (s, 1H), 6.76-6.64 (m, 2H), 5.76 (s, 1H) ppm.

2-(4-Bromophenyl)-2,3-dihydoquinazolin-4(1*H*)-one (Table 2, entry 9):

Mp: 197-199 °C. IR (KBr) cm^{-1}: 3310, 1656, 1608, 1433. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.18-8.15 (m, 1H), 7.79-7.77 (m, 1H), 7.62-7.60 (m, 3H), 7.48-7.45 (m, 2H), 7.29-7.23 (m, 1H), 6.78-6.73 (d, *J*=19.2, 1H), 6.70-6.67 (m, 1H), 5.77 (s, 1H) ppm.

Tetrahydrothiophene 1-oxide (Table 4, entry 1): ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (t, *J*= 7.6 Hz, 2H), 3.05 (t, *J*= 7.6 Hz, 2H) ppm.

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2-((Methylsulfinyl)methyl)furan (Table 4, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.58 (s, 3H), 4.06 (d, *J*= 14 Hz,1H), 4.15 (d, *J*= 14 Hz,1H), 6.43 (d, *J*= 3.2 Hz,1H), 7.14-7.57 (m, 2H) ppm.

Methyl(p-tolyl)sulfane (Table 4, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 2.56 (s, 3H), 7.18 (d, *J*= 3.2 Hz, 2H), 7.40 (d, *J*= 3.2 Hz, 2H) ppm.

1-(Propylsulfinyl)propane (Table 4, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (t, *J*= 6 Hz, 6H), 1.85-1.94 (m, 4H), 2.64-2.96 (m, 4H) ppm.

1,2-di(naphthalen-2-yl)disulfane (Table 5, entry 1): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (m, 4H), 7.64 (m, 2H), 7.75 (m, 2H), 7.80 (m, 4H), 8.1 (s, 2H) ppm.

1,2-bis(4-bromophenyl)disulfane (Table 5, entry 2): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J*= 8.2 Hz, 4H), 7.43 (t, *J*= 8.2 Hz, 4H) ppm.

2,2'-Disulfanediyldiethanol (Table 5, entry 3): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (br, 2H), 2.90 (t, *J*= 5.6 Hz, 4H), 3.92 (t, *J*= 5.6 Hz, 4H) ppm.

1,2-bis(4,6-dimethylpyrimidin-2-yl)disulfane (Table 5, entry 4): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 12H), 6.75 (s, 2H) ppm.

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Notes and references

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1. G. R. Patzke, Y. Zhou, R. Kontic and F. Conrad, *Angew. Chem. Int. Ed*., 2011, **50**, 826.
2. Y. Zhu, L. P. Stubbs, F. Ho, R. Liu, C. P. Ship, J. A. Maguire and N. S. Hosmane, *ChemCatChem*., 2010, **2**, 365.
3. B. Atashkar, A. Rostami and B. Tahmasbi, *Catal. Sci. Technol*., 2013, **3**, 2140.
4. M. Nikoorazm, A. Ghorbani-Choghamarani, F. Ghorbani, H. Mahdavi and Z. Karamshahi, *J. Porous Mater*., 2015, **22**, 261.
5. Y. S. Feng, X. Y. Lin, J. Hao and H. J. Xu, *Tetrahedron,* 2014, **70**, 5249.
6. A. Fodor, Z. Hella and L. Pirault-Roy, *Appl. Catal. A: Gen*., 2014, **484**, 39.
7. V. Vatanpour, S. S. Madaenia, L. Rajabi, S. Zinadini and A. A. Derakhshan, *J. Membr. Sci*., 2012, **401**, 132.
8. K. Bahrami, M. M. Khodaei and M. Roostaei, *New J. Chem*., 2014, **38**, 5515.
9. E. Carbonell, E. Delgado-Pinar, J. Pitarch-Jarque, J. Alarcón and E. García-Españ, *J. Phys. Chem*., 2013, **117**, 14325.
10. S. D. Dindulkar, J. Oh, V. M. Arole and Y. T. Jeong, *C. R. Chimie,* 2014, **17**, 971.
11. B. H. Chen, J. T. Li and G. F. Chen, *Ultrason. Sonochem*., 2015, **23**, 59.
12. J. Zhang, D. Ren, Y. Ma, W. Wang and H. Wu, *Tetrahedron,* 2014, **70**, 5274.
13. A. Rostami, B. Tahmasbi, H. Gholami and H. Taymorian, *Chinese Chem. Lett*., 2013, **24**, 211.
14. M. Waibel and J. Hasserodt, *Tetrahedron Lett*., 2009, **50**, 2767.
15. M. Narasimhulu and Y. R. Lee, *Tetrahedron,* 2011, **67**, 9627.
16. A. Ghorbani-Choghamarani and G. Azadi, *RSC Adv*., 2015, **5**, 9752.
17. Y. Chen, J. Zhuo, D. Zheng, S. Tian and Z. Li, *J. Mol. Catal. B: Enzym*., 2014, **106**, 100.
18. A. Ghorbani-Choghamarani, Z. Darvishnejad and M. Norouzi, *Appl. Organometal. Chem*., 2015, **29**, 170.
19. T. H. Chen, Z. Yuan, A. Carver and R. Zhang, *Appl. Catal. A: Gen*., 2014, **478**, 275.
20. D. Habibi, M. A. Zolfigol, M. Safaiee, A. Shamsian and A. Ghorbani-Choghamarani, *Catal. Commun*., 2009, **10**, 1257.
21. Y. Liu, H. Wang, C. Wang, J. P. Wan and C. Wen, *RSC Adv*., 2013, **3**, 21369.
22. D. Singh, F. Z. Galetto, L. C. Soares, O. E. D. Rodrigues and A. L. Braga, *Eur. J. Org. Chem*., 2010, **2010**, 2661.
23. A. K. Patra, A. Dutta, M. Pramanik, M. Nandi, H. Uyama and A. Bhaumik, *ChemCatChem*., 2014, **6**, 220.
24. A. A. Elkin, T. I. Kylosova, V. V. Grishkoc and I. B. Ivshina, *J. Mol. Catal. B: Enzym*., 2013, **89**, 82.
25. G. P. Romanelli, P. I. Villabrille, C. V. Cáceres, P. G. Vázquez and P. Tundo, *Catal. Commun*., 2011, **12**, 726.
26. L. Villalobos and T. Ren, Inorg. *Chem. Commun*., 2013, **28**, 52.
27. S. Thurow, V. A. Pereira, D. M. Martinez, D. Alves, G. Perin, R. G. Jacob and E. J. Lenardão, *Tetrahedron Lett*., 2011, **52**, 640.
28. M. Abbasi and D. Khalili, *J. Iran. Chem. Soc*., 2015, **12**, 1425.
29. H. Zhang and G. Wang, *Tetrahedron Lett*., 2014, **55**, 56.
30. H. Liu, J. Deng and W. Li, *Catal. Lett*., 2010, **137**, 261.
31. M. Safari, M. Ghiaci, M. Jafari-Asl and A. A. Ensafi, *Appl. Surf. Sci*., 2015, **342**, 26.
32. K. Farhadi and N. Farnad, *J. Iran. Chem. Soc*., 2015, **12**, 347.
33. P. Liu, Y. Zhu, J. Ma, S. Yang, J. Gong and J. Xu, *Prog. Nat. Sci.: Mat. Int*., 2013, **23**, 145.
34. L. Rajabi and A. A. Derakhshan, *Sci. Adv. Mater*., 2010, **2**, 163.
35. A. Ghorbani-Choghamarani and M. Norouzi, *J. Mol. Catal. A: Chem*., 2014, **395**, 172.
36. A. Ghorbani-Choghamarani, B. Ghasemi, Z. Safari and G. Azadi, *Catal. Commun*., 2015, **60**, 70.
37. M. Hajjami, L. Shiri and A. Jahanbakhshi, *Appl. Organomet. Chem*., 2015, **29**, 668.
38. V. B. Labade, P. V. Shinde and M. S. Shingare, *Tetrahedron Lett*., 2013, **54**, 5778.
39. M. Rahman, I. Ling, N. Abdullah, R. Hashim and A. Hajra, *Rsc Adv*., 2015, **5**, 7755.
40. M. Abdollahi-Alibeik and E. Shabani, *Chinese Chem. Lett*., 2011, **22**, 1163.
41. H. R. Shaterian and M. Aghakhanizadeh, *Res. Chem. Intermed*., 2014, 40, 1655.
42. X. -Y. Shi and J. -F. Wei, *J. Mol. Catal. A: Chem*., 2008, **280**, 142.
43. A. Abdolmaleki and S. Malek-Ahmadi, *J. Iran. Chem. Soc*., 2012, **9**, 1015.
44. F. Rajabi, T. Kakeshpour and M. R. Saidi, *Catal. Commun*., 2013, **40**, 13.
45. A. Saxena, A. Kumar and S. Mozumdar, *J. Mol. Catal. A: Chem*., 2007, **269**, 35.

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Graphical Abstract

Efficient preparation of boehmite silica dopamine sulfamic acid as novel nanostructured compound and its application as catalyst in some organic reactions

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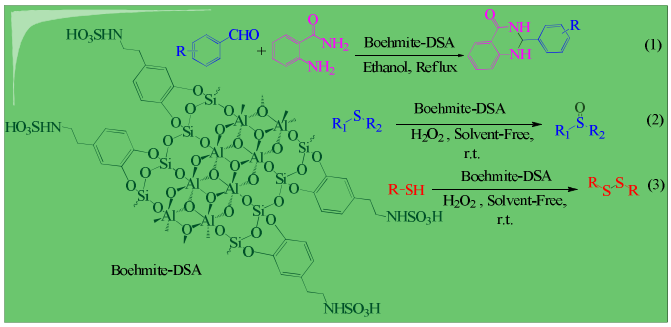

Nanoboehmite was prepared in water at room temperature using commercially materials and applied as support for preparation of new catalyst.