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ORIGINAL PAPER

# Sulfonated Honeycomb Coral (HC-$SO_3H$): a new, green and highly efficient heterogeneous catalyst for the rapid one-pot pseudo-five component synthesis of 4,4′-(aryl methylene) bis(3-methyl-1*H*-pyrazol-5-ol)s

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**Abstract** Sulfonated Honeycomb Coral (HC-$SO_3H$), has been synthesized from the reaction of Honeycomb Coral with chlorosulfonic acid as sulfonating agent. The as-synthesized catalyst was characterized via XRF, FT-IR, TGA, SEM–EDS, XRD, BET and pH analysis. The superior catalytic activity of HC-$SO_3H$ was investigated for the synthesis of 4,4′-(aryl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) derivatives through the one-pot pseudo-five component reactions. The main advantages of this protocol include simple procedure, excellent yields and short reaction times besides the non-toxicity, high stability and reusability of the catalyst.

**Keywords** Sulfonated Honeycomb Coral (HC-$SO_3H$) · 4,4′-(Aryl methylene)bis(3-methyl-1*H*-pyrazol-5-ol)s · One-pot pseudo-five component reaction · Heterogeneous catalysis · Green chemistry

## Introduction

According to the "green and sustainable chemistry", one of the most appealing developments in the synthetic organic chemistry is applying the environmentally benign reagents and reaction conditions (Anastas and Williamson 1998). Since catalysis organizes the basis of chemical industry nowadays, the development of novel, eco-friendly, non-toxic, inexpensive, stable, selective and recyclable catalysts with improved efficiency has attracted a great deal of interest, regarding to the green chemistry demands (Haile et al. 2001; Shylesh et al. 2009; Dabral et al. 2014; Pagadala et al. 2014; Ahmed and Siddiqui 2014).

During the past decades, acid-catalyzed chemical processes have been the subject of immense investigations, with respect to the widespread applications in chemical industries (Hosseini et al. 2016). However, although the conventional homogeneous acid catalysts such as sulfuric acid, hydrofluoric acid, hydrochloric acid and phosphoric acid are commonly used in the large-scale production of industrially important chemicals (Melero et al. 2006; Hara et al. 2004; González et al. 2012; Armstrong and Glover 1908), they suffer from several drawbacks. For instance, these homogeneous acids are associated with corrosive nature, high toxicity, hazardous handling and difficulty in separation from the reaction products (Hosseini et al. 2016). These disadvantages lead to wasting energy, besides the formation of immense amounts of waste products, which are far from the concept of ''Green Chemistry''. In this context, to overcome the problems caused by such catalysts, heterogenization of these homogeneous catalysts through their immobilization on various solid supports has been developed (Parella et al. 2012; Siddiqui and Ahmed 2013; Zolfigol et al. 2013; Kuo et al. 2014; Mobaraki et al. 2014). This process leads to improve the aspects of environmental compatibility, as well as economic, in numerous industrial manufacturing.

Sulfonation with chlorosulfonic acid has been received considerable attention due to the suitable, convenient, fast and efficient approach involved in the heterogenization

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process of the corresponding homogeneous catalysts (Kolvari et al. 2015).

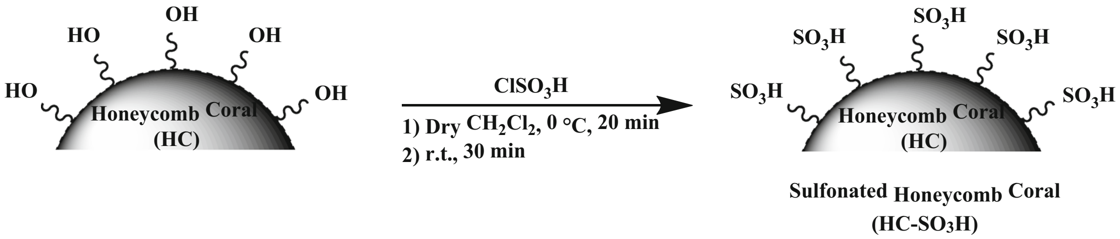
In recent years, multi-component reactions (MCRs) have played crucial role in the combinatorial chemistry to assemble complex target structures with attractive biological aspects using simple and readily available starting materials, through a one-pot process. The one-pot character delivers fewer by-products, besides the lower costs, time and energy involved, in comparison with classical stepwise synthetic routes and leads to the formation of interesting heterocyclic scaffolds (Zhu and Bienayme 2005).

Synthesis of pyrazolone derivatives has attracted great attention recently in synthetic organic chemistry due to their therapeutic and pharmacological features (Elguero 1996). Among these significant class of heterocyclic compounds, 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s have numerous biological activities including anti-inflammatory (Sugiura et al. 1977), antinociceptive (Carlsson and Jurna 1987), antipyretic (Behr et al. 1967), antidepressant (Bailey et al. 1985), antimalarial (Acharya et al. 2010), antitumor (Antre et al. 2012), antiviral (Sujatha et al. 2009) and bactericidal (Mahajan et al. 1991) activities. In addition to these, 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s are widely used as insecticides (Lecher 1955), pesticides (Londershausen 1996), fungicides (Singh and Singh Singh and Singh 1991), dyestuffs (Uzoukwu 1993), bis-Schiff bases (Ren et al. 2012), ligands (Abbasi-Tarighat et al. 2013) and important intermediates in organic synthesis (Hamama 2001). The most common route for the synthesis of 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s is the one-pot pseudo three-component reaction of aldehydes with the initially formed 3-methyl-5-pyrazolone derivatives from the condensation reaction of hydrazine/aryl hydrazine and ethyl acetoacetate, in the presence of various catalytic systems (Sujatha et al. 2009; Singh and Singh 1984; Wang et al. 2005; Shi et al. 2005; Niknam et al. 2010; Hasaninejad et al. 2011a, b; Elinson et al. 2008). However, most of these synthetic approaches have restrictions including the utilization of intense acidic or basic conditions, toxic or expensive catalysts or reagents, lower yields of the products and prolonged reaction times. Nevertheless, limited methods have been described for the synthesis of these compounds through the one-pot pseudo-five component condensation reactions in the presence of a variety of catalyst such as pyridine trifluoroacetate (Soleimani et al. 2012), 2-hydroxyethylammonium propionate (2-HEAP) (Zhou and Zhang 2014), sulfonated rice husk ash (RHA-$SO_3H$) (Seddighi et al. 2013), *N*,2-dibromo-6-chloro-3,4-dihydro-2*H* benzo[*e*][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide (DCDBTSD) (Khazaei et al. 2014), silica-bonded *N*-propylpiperazine sulfamic acid (SBPPSA) (Tayebi and Niknam 2012), ultrasonic irradiation (Hasaninejad et al. 2013) and sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH$_2$-$SO_3H$) (Zarghani and Akhlaghinia 2015a).

Considering the above points and as part of our continued interest in the development of efficient and environmentally benign heterogeneous catalysts (Zarghani and Akhlaghinia 2015a, b, 2016a, b; Razavi and Akhlaghinia 2015, 2016; Ghodsinia and Akhlaghinia 2015; Zarei and Akhlaghinia 2015; Jahanshahi and Akhlaghinia 2015, 2016; Yousefi Siavashi et al. 2016; Karimian et al. 2016; Ghodsinia et al. 2016), herein, we are willing to report a novel, green and efficient heterogeneous catalyst which was prepared through the immobilization of chlorosulfonic acid on Honeycomb Coral (HC) as a new, sustainable, green and natural platform (Scheme 1). The superior catalytic activity of sulfonated Honeycomb Coral (HC-$SO_3H$) was proved for the synthesis of 4,4′-(aryl methylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s via a one-pot pseudo-five component condensation reaction (see Scheme 2).

## Experimental

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. Honeycomb Coral was obtained from the Persian Gulf in Iran. The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer



**Scheme 1** Preparation of sulfonated Honeycomb Coral (HC-$SO_3H$)

(Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 $cm^{-1}$ with a resolution of 4 $cm^{-1}$, and each spectrum was the average of 32 scans. NMR spectra were recorded on an NMR Bruker Avance spectrometer at 400 and 300 MHz in DMSO-$d_6$ as solvent in the presence of tetramethylsilane as internal standard and the coupling constants (*J* values) are given in Hz. Elemental analysis was performed using a Thermo Finnigan Flash EA 1112 Series instrument (furnace 900 °C, oven: 65 °C, flow carrier 140 mL $min^{-1}$, flow reference 100 mL $min^{-1}$). Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in *m*/*z* (rel %). The chemical compositions of the Honeycomb Coral were specified with X-ray fluorescence spectroscopy (XRF), using BRUKER axs-S4 EXPLORER spectrometer. The crystal structure of the catalyst was analyzed by XRD using a D8 ADVANCE-Bruker diffractometer operated at 40 kV and 30 mA, utilizing CuKα radiation ($\lambda = 0.154$ Å), at a step size of 0.040° and step time of 1.5 s. The diffraction angles ($2\theta$) were scanned from 10° to 80°. Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620 energy dispersive spectrometer (SEM–EDS) presenting a 133 eV resolution at 20 kV. Thermogravimetric analysis (TGA) was carried out using a Shimadzu Thermogravimetric Analyzer (TG-50) in the temperature range of 25–900 °C at a heating rate of 10 °C $min^{-1}$, under air atmosphere. Nitrogen adsorption–desorption isotherms and BET analysis results were obtained using a Belsorp mini II system at −196 °C utilizing $N_2$ as adsorbate. All yields refer to the isolated products after purification by recrystallization.

### Pre-preparation of Honeycomb Coral

To remove the probable contaminants trapped inside the Honeycomb Coral structure, it was powdered thoroughly, followed by washing with distilled water several times and air-dried for 24 h.

### Preparation of sulfonated Honeycomb Coral (HC-$SO_3H$)

Chlorosulfonic acid 0.4 mL (6.5 mmol) was added dropwise to a magnetically stirred mixture of Honeycomb Coral (1 g) in dry dichloromethane (20 mL), in an ice bath (0 °C). After a period of 20 min, the mixture was stirred for an additional 30 min at room temperature. Afterward, the suspension was filtered and washed with dichloromethane (2 × 15 mL) and dried at 50 °C for 1 h to afford the HC-$SO_3H$ as a pale brown powder.

### Typical procedure for preparation of 4,4′-(phenyl methylene) bis(3-methyl-1 phenyl-1*H*-pyrazol-5-ol)

A mixture of phenylhydrazine (2 mmol, 0.216 g), ethyl acetoacetate (2 mmol, 0.260 g) and HC-$SO_3H$ (0.04 g) was stirred at 70 °C for 1 min. Then, benzaldehyde (1 mmol, 0.106 g) was added to the reaction mixture. The reaction was completed in less than 1 min, as monitored by TLC. After that, hot ethanol (2 × 5 mL) was poured to the reaction mixture and the mixture was stirred for additional 3 min. The resultant hot suspension was filtered off. The filtrate was cooled to room temperature and the crude product was precipitated. Thereafter, the crude product was purified by recrystallization from ethanol (0.42 g, 98%). In the following, to reuse the catalyst in the next runs, the solid residue (HC-$SO_3H$) was refluxed in EtOAc (3 × 10 mL) for 15 min and centrifuged consecutively. The recovered catalyst was then dried at 50 °C under vacuum for 2 h and reused for several times without significant loss of activity.

## Results and discussion

Corals are marine invertebrates of the class Anthozoa, which are known as unique natural solids that can efficiently catalyze organic reactions (Roschat et al. 2012; Bigdeli et al. 2015), as well as have beneficial applications in medical (Hamza et al. 2013). The principal components of Corals are calcium carbonate ($CaCO_3$) and also chitin (Bennett et al. 2016; Juárez-de la Rosa et al. 2015). They are mostly found in clear tropical oceans such as the Indian Ocean, the Red Sea, the Gulf of Aden, the Persian Gulf, the East China Sea and the West and Central Pacific Oceans. The Coral species used in the present study is Honeycomb Coral (Fig. 1).

### Characterization of the catalyst

HC-$SO_3H$ as a novel potent and stable solid acid heterogeneous catalyst was synthesized according to Scheme 1. The chemical composition of Honeycomb Coral was determined by X-ray fluorescence analysis (XRF). Likewise, the structure and morphology of the newly synthesized catalyst were fully characterized by different techniques such as Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric (TGA) analysis, scanning electron microscopy equipped with an energy dispersive spectrometry (SEM–EDS), X-ray powder diffraction (XRD), Brunauer, Emmett and Teller (BET) surface area analysis and pH analysis. The results obtained from these

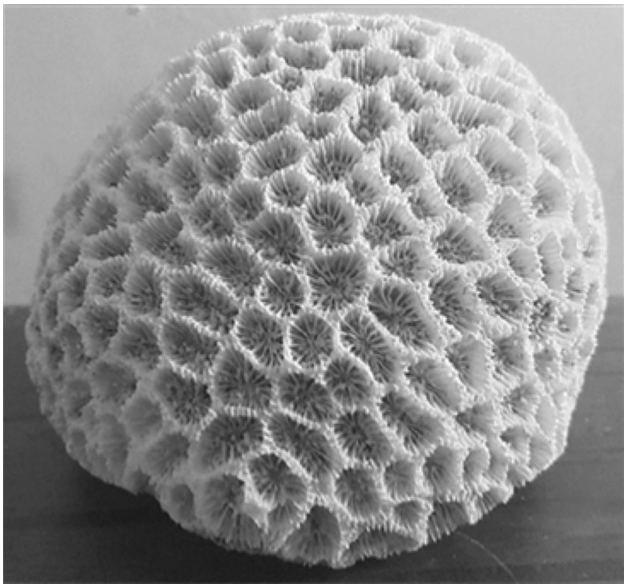


**Fig. 1** The Honeycomb Coral image

techniques, confirmed the successful preparation of the new catalyst.

## XRF analysis

The elemental composition analysis of Honeycomb Coral was determined by XRF spectroscopy (see electronic supplementary information). The obtained results showed that the predominant composition of Honeycomb Coral is CaO. Accordingly, the principal inorganic component of Honeycomb Coral is considered to be a natural calcium carbonate ($CaCO_3$).

## FT-IR spectroscopy

To evaluate the incorporation of sulfonic groups on the Honeycomb Coral structure, FT-IR spectra of the respective Honeycomb Coral and HC-$SO_3H$ have been investigated (Fig. 2). As can be clearly inferred from spectroscopic data, calcium carbonate and chitin are the main Honeycomb Coral components (Bennett et al. 2016; Juárez-de la Rosa et al. 2015). The FT-IR spectrum of Honeycomb Coral, shown in Fig. 2a exhibits the characteristic absorptions bands for aragonite phase (calcium carbonate) in the Honeycomb Coral structure, which are related to the planar $CO_3^{2-}$ ions. There are four vibrational modes in the free $CO_3^{-2}$ ions (Plavsic et al. 1999), which were established by the following absorption bands: $\nu_1$ (for the split in-plane bending vibrations at about 711 cm$^{-1}$); $\nu_2$ (for the out-of-plane bending absorption at about 852 cm$^{-1}$); $\nu_3$ (for the symmetric stretching vibration of the carbonate ion at about 1082 cm$^{-1}$); $\nu_4$ (for the asymmetric stretching vibrations at about 1400–1500 cm$^{-1}$).

In the case of the chitin segment of Honeycomb Coral, a broad peak centered at 3421 cm$^{-1}$ represented the combined O–H and N–H stretching vibrations. Moreover, the adsorption band centered at 2922 cm$^{-1}$ was attributed to the C–H stretching vibrations of $CH_2$ and $CH_3$ groups (Rwei and Lien 2014). The indicative absorption bands regarding to amide groups in the chitin structure are usually observed at 1662 cm$^{-1}$ (amide I), 1550 cm$^{-1}$ (amide II) and 1315 cm$^{-1}$ (amide III) (Zarghani and Akhlaghinia 2016a). However, these absorption bands were covered by broad and strong asymmetric stretching vibrations of $CO_3^{2-}$ ions ($\nu_4$).

In the FT-IR spectrum of HC-$SO_3H$ (Fig. 2b), the absorption bands at 593, 617 and 674 cm$^{-1}$ can be assigned to the asymmetric bending vibrations of sulfate ions (Liu et al. 2009) that have been created as a result of ion exchange during the sulfonation process. In the other words, the appropriate exchange of carbonate ions with sulfate ions has occurred.

In addition, the FT-IR spectrum of HC-$SO_3H$ shows the appearance of new absorption bands at about 1012, 1112, 1151 and 1174, which are attributed to the symmetric and asymmetric stretching frequencies of S=O in the sulfonated chitin. The spectrum also demonstrates a relatively broad band at around 3200–3600 cm$^{-1}$ due to the OH stretching absorption of $SO_3H$ groups. Furthermore, the stretching vibration band of C–N (related to the chitin groups), was observed around 1470 cm$^{-1}$ (Zarghani and Akhlaghinia 2016a). Besides, the other strong chitin band at 858 cm$^{-1}$ (related to –$CH_3$ in acetylamide groups) (Skołucka-Szary et al. 2016; Ehrlich et al. 2007) can be evidently perceived in Fig. 2b, c.

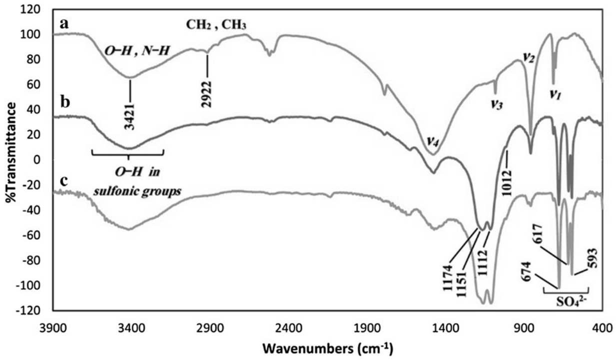


**Fig. 2** FT-IR spectrum of **a** Honeycomb Coral; **b** HC-$SO_3H$ and **c** 7th recovered HC-$SO_3H$

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of bare Honeycomb Coral and the as-synthesized acidic catalyst (Fig. 3). As it is evident in Fig. 3a, TGA thermogram of Honeycomb Coral exhibited a weight loss of about 0.5% at temperatures below 100 °C corresponding to the removal of physically adsorbed water. The next weight loss of about 2.5% at 300 °C, is relating to the elimination of $CO_2$ from the Honeycomb Coral structure (Cuif et al. 2004). Also, the simultaneous release of $H_2O$ in this temperature can be explained either by the decomposition of hydrated chitin or by water molecules strongly bound to the skeletal matrix which cannot be released at lower temperatures (Cuif et al. 2004). The most prominent weight loss starting at approximately 650 °C, is related to the decomposition of $CaCO_3$ to CaO (Cuif et al. 2004).

For HC-$SO_3H$, it is clear that there are three steps of weight loss (Fig. 3b). (1) Below 150 °C, the representative mass loss is ascribed to the removal of physically adsorbed water (about 3%). (2) Around 150–550 °C, a large weight loss occurred, which can be predominantly attributed to decomposition of $SO_3H$ groups (Naeimi and Mohamadabadi 2014) (about 9%). (3) Above 550 °C, the occurrence of further mass losses at higher temperature resulted from the decomposition of the Honeycomb Coral structure (about 19%). According to the TGA thermogram, it can be estimated that the amount of sulfonic acid groups delivered to the Honeycomb Coral structure is about 0.82 mmol $g^{-1}$.

### PH analysis

The total number concentrations of acidic sites of the HC-$SO_3H$ were determined by acid–base back potentiometric titration of the catalyst. For this purpose, 100 mg of catalyst was added to an aqueous solution of sodium hydroxide (0.1 N, 15 mL). Then, the resulting mixture was stirred at room temperature for 12 h. Finally, the leftover basic solution was filtered and the filtrate was neutralized using a standard solution of HCl (0.1 M). According to the consumed volume of HCl (14.2 mL), the number of acidic sites for HC-$SO_3H$ was found to be 0.80 mmol $g^{-1}$. This result was in a good agreement with those obtained from TGA.

### SEM–EDS analysis

Figure 4 depicts the scanning electron microscopy (SEM) images of non-powdered Honeycomb Coral (Fig. 4a), finely powdered Honeycomb Coral (Fig. 4b) and HC-$SO_3H$ catalyst (Fig. 4c, d). Interestingly, SEM image of the cross-sectional disc of non-powdered Honeycomb Coral reveals a structure that looks like a honeycomb (Fig. 4a). In comparing Fig. 4b with Fig. 4c, d, the surface morphological changes were clearly observed on the material due to the modification process. In the other words, while the finely powdered Honeycomb Coral has a smoothed morphology (Fig. 4b), the surface of HC-$SO_3H$ is rough to a certain extent. Accordingly, it can be concluded that the functionalization procedure has been accomplished successfully.

Energy dispersive spectrum (EDS) of HC-$SO_3H$ (Fig. 5) indicates the presence of Ca, S and O as the main elements of HC-$SO_3H$ structure. Beside these, a few other minerals were also found in low contents (Cl, Na, Mg and Si). This analysis approves the successful functionalization of the Honeycomb Coral (see also XRF results in electronic supplementary information).

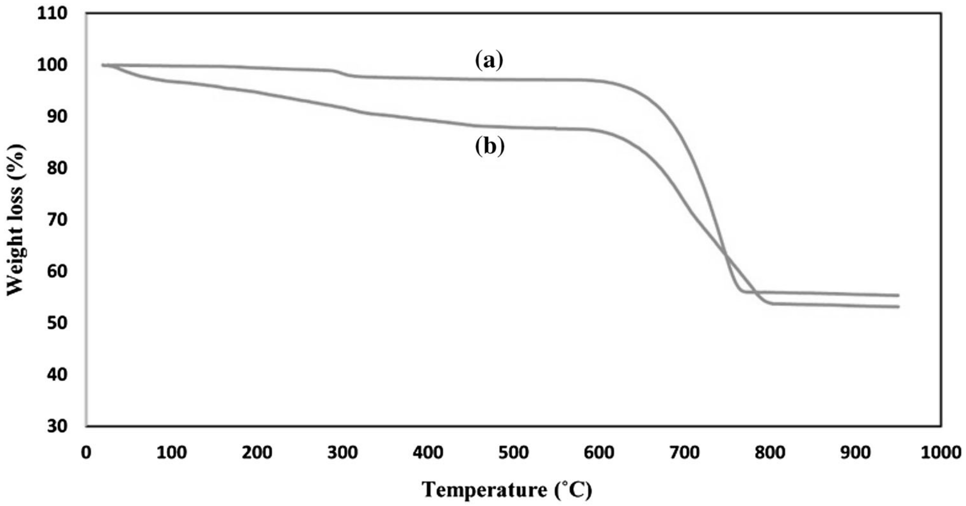


**Fig. 3** TGA thermograms of **a** Honeycomb Coral and **b** HC-$SO_3H$

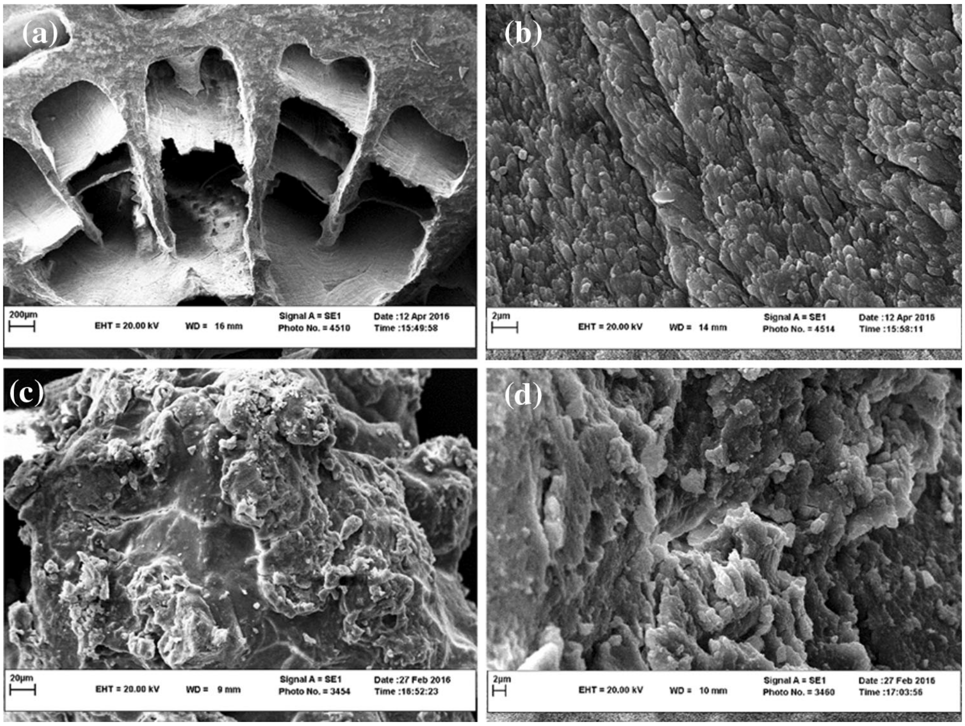


**Fig. 4** SEM images of a cross-sectional disc of **a** non-powdered Honeycomb Coral; **b** finely powdered Honeycomb Coral and **c**, **d** HC-$SO_3H$

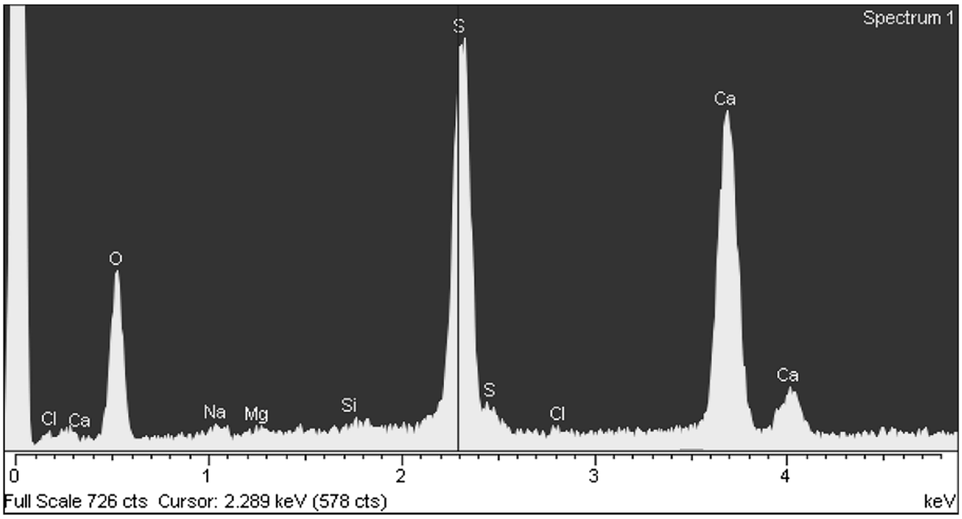


**Fig. 5** EDS analysis of HC-$SO_3H$

## X-ray powder diffraction analysis

The crystallinity and phase identification of Honeycomb Coral and HC-$SO_3H$ were determined using XRD. As illustrated in Fig. 6a, the most intense diffraction peaks appearing at angles corresponding to (1 1 1), (0 2 1), (0 1 2), (2 0 0), (1 1 2), (1 3 0), (2 1 1), (2 2 0), (2 2 1), (0 4 1), (1 3 2), (1 1 3) and (2 3 1) reflections were in good agreement with the standard pattern for crystalline aragonite ($CaCO_3$) with orthorhombic structure (JCPDS: 05-0453). In addition, weak diffraction peaks appeared at angles attributing to (1 0 4) and (1 1 3) crystallographic faces, could be assigned to calcite ($CaCO_3$) XRD diffraction peaks (JCPDS: 05-0586). However, XRD analysis of HC-$SO_3H$ (Fig. 6b) revealed that $CaCO_3$ with the orthorhombic crystalline structure was converted to $CaSO_4$ with preserving the orthorhombic crystalline structure (JCPDS: 37-1496). The results confirm that although the bona fide exchange of carbonate ions with sulfate ions has occurred, the crystalline structure of catalyst was maintained, under the conditions used for the modification process.

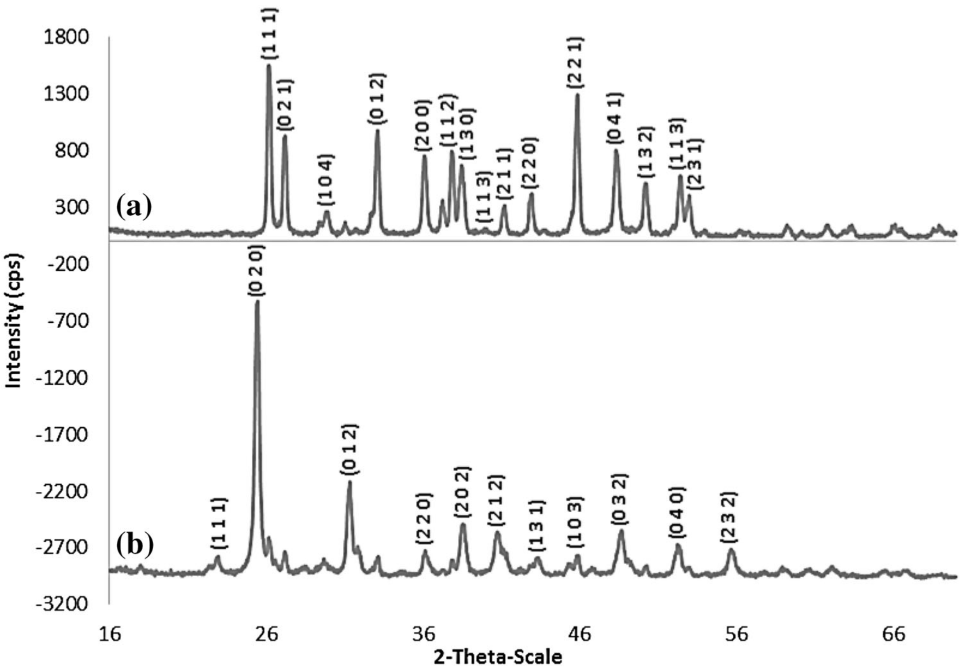


**Fig. 6** XRD patterns of **a** Honeycomb Coral and **b** HC-$SO_3H$

## BET analysis

The BET surface area measurement was conducted for Honeycomb Coral (HC) and sulfonated Honeycomb Coral (HC-$SO_3H$) (see electronic supplementary information). Table 1 illustrates the respective average surface area, pore volume and mean pore diameter of both HC and HC-$SO_3H$. The BET surface area, pore volume and pore diameter of HC are 120.25, 1.006 and 14.27, respectively. According to the obtained data from Table 1, it can be concluded that the introduction of sulfonic acid to the HC structure, shifted the pore diameter to the smaller amounts and also decreased the surface area and pore volume. These results confirm the successful modification of HC with chlorosulfonic acid.

## Catalytic synthesis of 4,4′-(aryl methylene) bis(3-methyl-1*H*-pyrazol-5-ol)s

On the basis of the information obtained from the studies on the natural Honeycomb Coral, we anticipated that this marine coral can be used as an efficient and green platform for heterogenization of sulfonic acid, to prepare a superlative solid acid catalyst which would promote the reactions that need an acidic catalyst to speed-up. So, we have investigated the applicability of HC-$SO_3H$ in developing the rapid one-pot pseudo-five component synthesis of 4,4′-(aryl methylene)-bis-(3-methyl-1-phenyl-1*H*pyrazol-5-ols) from phenylhydrazine/or hydrazine hydrate, ethyl acetoacetate and aldehydes (Scheme 2).

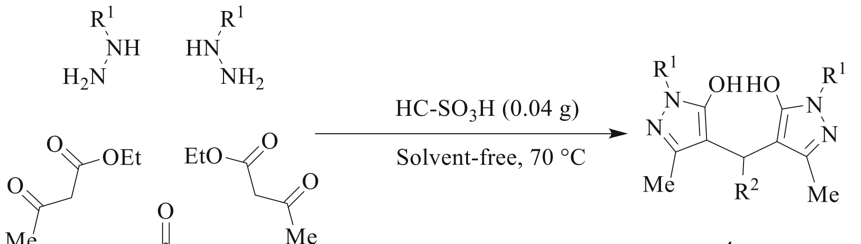
**Table 1** Specific surface area ($S_{\mathrm{BET}}$), pore volume and mean pore diameter of Honeycomb Coral (HC) and sulfonated Honeycomb Coral (HC-$SO_3H$)

| Sample | $S_{\mathrm{BET}}$ ($m^2\ g^{-1}$) | Pore volume ($cm^3\ g^{-1}$) | Mean pore diameter (nm) |
|---|---|---|---|
| HC | 120.25 | 1.006 | 14.27 |
| HC-$SO_3H$ | 90.38 | 0.504 | 12.67 |

To find an appropriate reaction medium for the synthesis of these compounds in the presence of the catalytic amount of HC-$SO_3H$, one-pot pseudo-five component reaction between phenylhydrazine (2 mmol), ethyl acetoacetate (2 mmol) and benzaldehyde (1 mmol) was selected as a model reaction.

Various reaction conditions including different solvents, temperatures and amount of the catalyst were examined and the results are listed in Table 2. When the model reaction was carried out in the absence of catalyst, either in solvent-free condition or in $H_2O$, at temperature ranging from 70 to 90 °C, the progress of the reaction was sluggish, even after a long reaction time (Table 2, entry 1–4). Interestingly, by applying the model reaction at 70 °C, in the presence of 0.05 g of the HC-$SO_3H$, the desired product was obtained with excellent yield, in less than 1 min (Table 2, entry 5). This result denotes to the essential role of HC-$SO_3H$ in the synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol). Furthermore, the results show that the lower the reaction temperature, the less efficiently the reaction could proceed (Table 2, entries 6–8). However, any further increase in the temperature did not improve the reaction progress (Table 2, entry 9). To determine the optimal amount of catalyst, we have explored the model reaction at lower catalytic amounts of HC-$SO_3H$ (0.04 and 0.03 g), under solvent-free conditions

**Scheme 2** One-pot pseudo-five component synthesis of 4,4′-(aryl methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s in the presence of HC-$SO_3H$



**4a-x**

$R^1$ = H, $C_6H_5$

$R^2$ = $C_6H_5$, 4-(F)$C_6H_4$, 4-(Cl)$C_6H_4$, 2-(Cl)$C_6H_4$, 2,4-$(Cl)_2C_6H_3$, 4-(Br)$C_6H_4$, 3-$(NO_2)C_6H_4$, 2-$(NO_2)C_6H_4$, 4-(OH)$C_6H_4$, 3-(OH)$C_6H_4$, 2-(OH)$C_6H_4$, 4-(OMe)$C_6H_4$, 3-(OMe)$C_6H_4$, 4-(Me)$C_6H_4$, 3-(Me)$C_6H_4$, 5-(Br)-2-(OH)$C_6H_3$, 4-($^i$Pr)$C_6H_4$, 1-Naphthyl, 3-Pyridyl, 2-Pyridyl, $C_6H_5CH{=}CH$

**Table 2** Synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) in the presence of HC-$SO_3H$, under different reaction conditions

| Entry | Catalyst (g) | Solvent | Temperature (°C) | Time (min) | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 | – | Solvent-free | 70 | 36 h | 15 |
| 2 | – | Solvent-free | 90 | 36 h | 15 |
| 3 | – | $H_2O$ | 70 | 36 h | 15 |
| 4 | – | $H_2O$ | 90 | 36 h | 15 |
| 5 | 0.05 | Solvent-free | 70 | <1 | 98 |
| 6 | 0.05 | Solvent-free | 60 | 10 | 90 |
| 7 | 0.05 | Solvent-free | 40 | 20 | 65 |
| 8 | 0.05 | Solvent-free | r.t. | 4 h | 40 |
| 9 | 0.05 | Solvent-free | 80 | <1 | 98 |
| 10 | 0.04 | Solvent-free | **70** | **<1** | **98** |
| 11 | 0.03 | Solvent-free | 70 | 10 | 94 |
| 12 | 0.04 | $H_2O$ | 70 | 15 | 78 |
| 13 | 0.04 | EtOH | 70 | 25 | 72 |
| 14 | 0.04 | $H_2O$/EtOH (1:1) | 70 | 25 | 68 |
| 15[a] | 0.04 | Solvent-free | 70 | 5 h | 25 |
| 16[b] | 0.04 | Solvent-free | 70 | 5 h | 15 |
| 17[c] | 0.04 | Solvent-free | 70 | 2 h | 79 |
| 18[d] | 0.04 | Solvent-free | 70 | 7 h | 15 |

[a] The reaction was performed in the presence of the thoroughly powdered Honeycomb Coral

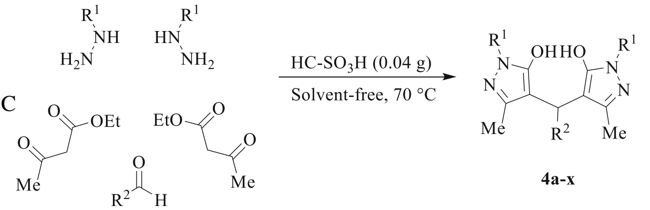
[b] The reaction was performed in the presence of the non-powdered Honeycomb Coral

[c] The reaction was performed in the presence of the non-powdered sulfonated Honeycomb Coral

[d] The reaction was performed in the presence of the $CaCO_3$

at 70 °C (Table 2, entries 10, 11). The results revealed that 0.04 g of HC-$SO_3H$ was found to be the optimum amount of catalyst in terms of yield and reaction time (Table 2, entry 10). Likewise, the reaction was carried out in solvents such as $H_2O$, EtOH and $H_2O$/EtOH (1:1). The slow rate of such a transformation in the presence of these solvents (maybe due to the solvation effects), offered that the solvent-free condition is more appropriate to improve the reaction rate, in this protocol (Table 2, entry 10). In another experiment, the activity of the intact Honeycomb Coral both in the thoroughly powdered form (as we have utilized it in our study) and also the non-powdered form was tested for the same reaction condition and only a scant yield of the product was obtained (Table 2, entry 15, 16). To get more insight into the impact of the structural form of the prime Honeycomb Coral on the final catalyst activity, the sulfonation process was implemented on the non-powdered form of the Honeycomb Coral (exactly based on the mentioned procedure in the experimental section) and next the model reaction was conducted in the presence of the non-powdered HC-$SO_3H$ as catalyst. As it is clear in Table 2, the results were far from satisfactory in this context (Table 2, entry 17). These findings suggested that

**Table 3** Preparation of 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s catalyzed by HC-$SO_3H$ under solvent-free conditions at 70 °C



| Entry | $R^1$ | $R^2$ | Product | Time (min) | Isolated yield (%) | M.p. (°C) Found reported (references) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $C_6H_5$ | **4a** | <1 | 98 | 173–174 171–172 (Hasaninejad et al. 2011a) |
| 2 | $C_6H_5$ | 4-$FC_6H_4$ | **4b** | <1 | 98 | 180–181 180–182 (Keshavarz and Vafaei-Nezhad 2016) |
| 3 | $C_6H_5$ | 4-$ClC_6H_4$ | **4c** | <1 | 97 | 205–207 207–209 (Hasaninejad et al. 2011a) |
| 4 | $C_6H_5$ | 2-$ClC_6H_4$ | **4d** | 18 | 84 | 235–237 236–237 (Hasaninejad et al. 2011a) |
| 5 | $C_6H_5$ | 2,4-$(Cl)_2C_6H_3$ | **4e** | 5 | 82 | 227–229 229–231 (Keshavarz and Vafaei-Nezhad 2016) |
| 6 | $C_6H_5$ | 4-$BrC_6H_4$ | **4f** | <1 | 95 | 181–183 183–185 (Hasaninejad et al. 2011a) |
| 7 | $C_6H_5$ | 3-$NO_2C_6H_4$ | **4g** | 5 | 83 | 148–149 150–151 (Zolfigol et al. 2015) |
| 8 | $C_6H_5$ | 2-$NO_2C_6H_4$ | **4h** | 8 | 83 | 219–221 222–224 (Zolfigol et al. 2015) |
| 9 | $C_6H_5$ | 4-$OHC_6H_4$ | **4i** | 2 | 96 | 159–160 160–162 (Thummar et al. 2014) |
| 10 | $C_6H_5$ | 3-$OHC_6H_4$ | **4j** | 3 | 96 | 166–167 165–168 (Niknam et al. 2010) |
| 11 | $C_6H_5$ | 2-$OHC_6H_4$ | **4k** | 7 | 92 | 225–226 227–228 (Zolfigol et al. 2015) |
| 12 | $C_6H_5$ | 4-$OMeC_6H_4$ | **4l** | <1 | 97 | 172–174 171–173 (Nader Ghaffari et al. 2016) |
| 13 | $C_6H_5$ | 3-$OMeC_6H_4$ | **4m** | 10 | 95 | 179–181 180–182 (Phatangare et al. 2012) |
| 14 | $C_6H_5$ | 4-$MeC_6H_4$ | **4n** | 8 | 95 | 202–204 203–205 (Keshavarz and Vafaei-Nezhad 2016) |
| 15 | $C_6H_5$ | 3-$MeC_6H_4$ | **4o** | 12 | 87 | 236–237 238–241 (Karimi-Jaberi et al. 2012) |
| 16 | $C_6H_5$ | 5-Br-2-$OHC_6H_3$ | **4p** | 10 | 91 | 265–267 266–268 (Baghernejad and Niknam 2012) |
| 17 | $C_6H_5$ | 4-$^{i}PrC_6H_4$ | **4q** | 15 | 83 | 134–136 132–134 (Keshavarz and Vafaei-Nezhad 2016) |
| 18 | $C_6H_5$ | 1-Naphthyl | **4r** | 5 | 93 | 210–212 213–215 (Zolfigol et al. 2015) |
| 19 | $C_6H_5$ | 3-Pyridyl | **4s** | 7 | 90 | 238–239 238–240 (Niknam et al. 2013) |
| 20 | $C_6H_5$ | 2-Pyridyl | **4t** | 4 | 95 | 230–233 228–231 (Moosavi-Zare et al. 2013) |
| 21 | $C_6H_5$ | $C_6H_5CH = CH_2$ | **4u** | 10 | 88 | 217–219 220–222 (Zarghani and Akhlaghinia 2015a) |
| 22 | H | $C_6H_5$ | **4v** | 12 | 95 | 231–233 228–230 (Nader Ghaffari et al. 2016) |
| 23 | H | 4-$ClC_6H_4$ | **4w** | 7 | 94 | 223–225 224–226 (Nader Ghaffari et al. 2016) |
| 24 | H | 4-$MeC_6H_4$ | **4x** | 15 | 89 | 197–199 202–204 (Nader Ghaffari et al. 2016) |

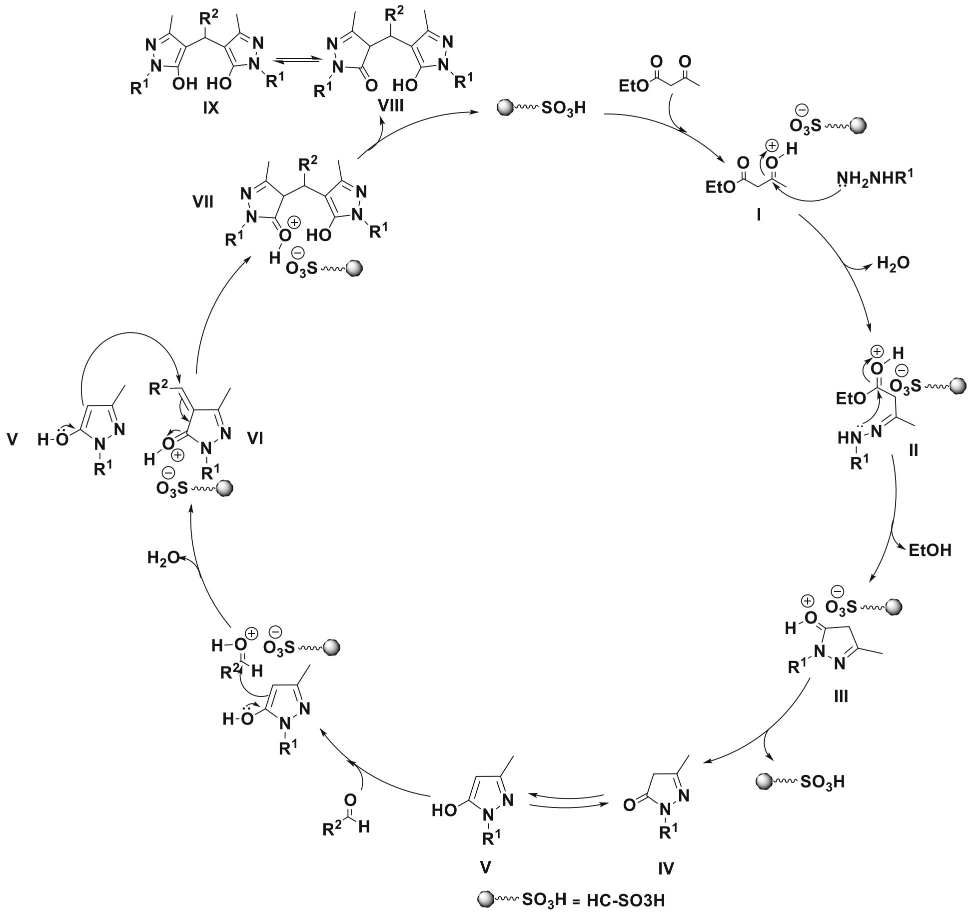
the sulfonation process was much better done for the thoroughly powdered Honeycomb Coral. This might be due to the more available surface area and also porosity of the thoroughly powdered Honeycomb Coral (see BET analysis results in Table 1), in comparison with the non-powdered one, that improves the successful incorporation of the sulfonic groups on its structure. In continuing our study, by considering calcium carbonate as the main inorganic component of Honeycomb Coral (see XRF results in electronic supplementary information), we decided to probe the reactivity of $CaCO_3$ as catalyst in this transformation. As demonstrated in Table 2, the desired product was poorly obtained in the presence of $CaCO_3$ under solvent-free conditions at 70 °C (Table 2, entry 18). These results confirm the superior catalytic performance of the sulfonated Honeycomb Coral (HC-$SO_3H$), in this protocol. Afterward, in a separate experiment, to compare the catalytic activity of HC-$SO_3H$ with its homogenous counterparts, the model reaction was performed under the optimized conditions in the presence of chlorosulfonic acid, *p*-toluene sulfonic acid and methane-sulfonic acid, respectively. It was observed that the catalytic activity of $ClSO_3H$, PTSA and $MeSO_3H$ was very close to HC-$SO_3H$ and the corresponding product was obtained in less than one minute, in excellent isolated yield (98%). However, as previously mentioned, the main challenging problems in using such catalysts are their homogeneous feature which leads to difficult and expensive catalyst recovery process, along with their corrosive nature that makes a troublesome handling. Nevertheless, these problems have been eliminated in the HC-$SO_3H$ as a new heterogeneous catalytic system.

Using the optimized reaction conditions, the activity of HC-$SO_3H$ as catalyst was further confirmed in the green and efficient preparation of 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s (Table 3). For this purpose, phenyl hydrazine/or hydrazine (2 mmol) and ethyl acetoacetate (2 mmol) were treated with a broad range of structurally diverse aromatic aldehydes (1 mmol) in the presence of HC-$SO_3H$ to achieve the intended products. This study showed that both electron poor (Table 3, entries 2–8) and electron rich (Table 3, entries 9–18) aromatic aldehydes afforded the corresponding products rapidly, in excellent isolated yields. It is noteworthy that heteroaromatic aldehydes such as pyridine carboxaldehydes and allylic aldehydes such as cinnamaldehyde led to the desired products, as well (Table 3, entries 19–21). Satisfactorily, we found that utilizing hydrazine instead of phenylhydrazine in this transformation also resulted in the rapid formation of the intended products, in high yields (Table 3, entries 22–24).

All of the synthesized products (**4a–x**) were known compounds and their structures were confirmed by comparison of their melting points, FT-IR spectroscopy and $^1$H NMR spectroscopy with those of authentic compounds. Likewise, the selected compounds were further identified by $^{13}$C NMR spectroscopy, mass spectrometry and elemental analysis (see electronic supplementary information). It is noteworthy that in the FT-IR spectrum of all purified products the appearance of absorption bands at about 3450–2500, 1600 and 1499 cm$^{-1}$ was assigned to OH, C=N and C=C bonds, respectively. Moreover, the $^1$H NMR spectra displayed a sharp singlet resonating at around 5.50–4.89 ppm attributed to aryl methylene proton and also two broad peaks around 13.91 and 12.40 ppm, that revealed two –OH groups. Besides, the existence of a signal at 32 ppm in $^{13}$C NMR spectra of the products, is allocated to aryl methylene carbon. The elemental analysis of the synthesized compounds was also in a very good conformity with the presented structures. To more clarification of the products structures, mass spectrometry was carefully evaluated. As can be seen in the mass spectra, molecular ion was not obvious in some cases which was related to the very facile cleavage of C–C bond between aryl methylene carbon and pyrazole ring. However, some useful fragmentation information for each compound has been found, which can be beneficial for the verification of the desired products.

By analogy with our investigation, a plausible mechanism for the synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) derivatives in the presence of HC-$SO_3H$ catalyst is proposed in Scheme 3.

According to this mechanism, the initial condensation reaction between phenylhydrazine/hydrazine and protonated form of ethyl acetoacetate (**I**), eventually leads to the



**Scheme 3** Plausible mechanism for the one-pot pseudo-five component synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) using HC-$SO_3H$ catalyst

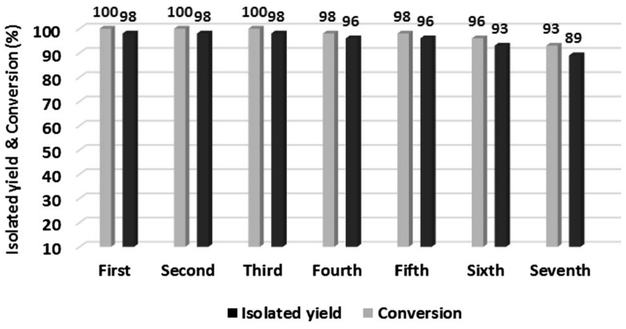


**Fig. 7** Synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) in the presence of the reused HC-$SO_3H$

formation of pyrazolone (**IV**), which is in equilibrium with its tautomeric form (**V**). In the next step, the condensation reaction between intermediate **V** and aldehyde in the acidic condition, followed by dehydration, affords intermediate **VI**. Thereupon, a Michael addition reaction between **V** and **VI** happens to furnish the product **VIII** which undergoes a tautomeric proton shift to deliver the desired product (**IX**). Afterward, the released acidic catalyst re-enters the catalytic cycle. It is assumed that the main catalytic performance of catalyst was implemented through the sulfonated active sites on the chitin matrix and the calcium sulfate groups exciting in its inorganic matrix, as well. Further studies to elucidate the details of the mechanism are ongoing.

The reusability of the catalyst is a very important subject, particularly for commercial and industrial applications. Therefore, the recovery and reusability of HC-$SO_3H$ were scrutinized for the synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol), under the optimized reaction conditions. Upon completion of the reaction, the heterogeneous catalyst was easily separated from the reaction mixture by vacuum filtration, followed by washing with ethanol sequentially to remove the organic compounds and dried at 70 °C for 1 h. Next, the recovered catalyst was reused in the consecutive runs, under the same reaction conditions. The catalyst was successfully used in seven subsequent reactions with undiminished efficiency (Fig. 7). The average isolated yield of the product for seven consecutive runs was 93.8%, which clearly proves the outstanding practical reusability of the present catalyst.

According to the FT-IR spectrum of the 7th recovered HC-$SO_3H$ (Fig. 2c), all of the characteristic peaks are well preserved in terms of shape, position and relative intensity, which is another evidence that demonstrates no substantial changes occurred in the chemical structure of functional groups and hydrogen bonding network of the catalyst.

The catalytic efficiency of HC-$SO_3H$ was compared with the previously reported catalysts in literature that have been employed for the one-pot pseudo-five component preparation of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol) and the related results are listed in Table 4. Although, each of these methods has their own advantages, but they often suffer from one or more of the following drawbacks, such as higher temperatures (Zhou and Zhang 2014; Seddighi et al. 2013; Khazaei et al. 2014; Tayebi and Niknam 2012; Zarghani and Akhlaghinia 2015a), certain and difficult reaction conditions as ultrasonic irradiation along with using organic solvent (Hasaninejad et al. 2013), require longer reaction times to achieve reasonable yield of the product (Zhou and Zhang 2014; Seddighi et al. 2013; Khazaei et al. 2014; Tayebi and Niknam 2012; Hasaninejad et al. 2013; Zarghani and Akhlaghinia 2015a) and most importantly, the necessity of applying strict condition (Zhou and Zhang 2014; Seddighi et al. 2013; Khazaei et al. 2014; Tayebi and Niknam 2012; Hasaninejad et al. 2013; Zarghani and Akhlaghinia 2015a) and expensive precursors (Zhou and Zhang 2014; Khazaei et al. 2014; Tayebi and Niknam 2012; Hasaninejad et al. 2013; Zarghani and Akhlaghinia 2015a) to prepare the corresponding catalysts.

**Table 4** A comparative study regarding the catalytic efficiency of HC-$SO_3H$ and some previously reported catalytic systems, in the one-pot pseudo-five component synthesis of 4,4′-(phenyl methylene)bis(3-methyl-1*H*-pyrazol-5-ol)

| Entry | Catalyst | Reaction conditions | Yield (%) | References |
|---|---|---|---|---|
| 1 | 2-HEAP[a] | Solvent-free, 90 °C, 30 min | 91 | Zhou and Zhang (2014) |
| 2 | RHA-$SO_3H$ | Solvent-free, 80 °C, 3 min | 91 | Seddighi et al. (2013) |
| 3 | DCDBTSD[b] | Solvent-free, 80 °C, 100 min | 74 | Khazaei et al. (2014) |
| 4 | SBPPSA[c] | Solvent-free, 80 °C, 45 min | 93 | Tayebi and Niknam (2012) |
| 5 | – | Ultrasonic irradiation, $H_2O$/EtOH (1:1), r.t., 15 min | 98 | Hasaninejad et al. (2013) |
| 6 | HAP@AEP$H_2$-$SO_3H$[d] | Solvent-free, 80 °C, 3 min | 98 | Zarghani and Akhlaghinia (2015a) |
| **7** | HC-$SO_3H$ | Solvent-free, 70 °C, <1 min | 98 | Present study |

[a] 2-Hydroxy ethylammonium propionate

[b] *N*,2-Dibromo-6-chloro-3,4-dihydro-2*H* benzo[*e*][1,2,4]thiadiazine-7-sulfonamide 1,1-dioxide

[c] Silica-bonded *N*-propylpiperazine sulfamic acid

[d] Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate

However, compared with these catalytic systems, the current work shows unique advantages such as simplification of the catalyst system and its synthesis and the application of inexpensive natural, nontoxic and available precursor for the preparation of a green and highly efficient heterogeneous catalyst with ease of handling, as well as the fast and clean synthetic route and also the milder reaction conditions.

## Conclusions

In conclusion, we have introduced HC-$SO_3H$ as a novel, green and highly powerful heterogeneous and recoverable solid acid catalyst. The as-synthesized catalyst was fully characterized by XRF, FT-IR, TGA, SEM–EDS, XRD and pH analysis and then was utilized for simple, efficient and rapid one-pot pseudo-five component synthesis of 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s. The promising features that have distinguished this approach from other reported methods regarding this transformation are using the highly efficient, green, inexpensive, easy handling and recoverable catalyst, as well as simple reaction work-up, which make the present methodology more economical and industrially important. Furthermore, excellent yields, quick reaction times and non-toxicity of the catalyst, besides the solvent-free conditions are the other advantages that support the present method towards the green chemistry, as well.

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