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ORIGINAL ARTICLE

# Covalently anchored chlorosulfonyl-calix[4]arene onto silica gel as an efficient and reusable heterogeneous system for reduction of ketones using $NaBH_4$

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## Abstract

The catalytic activities of chlorosulfonyl-calix[4]arene-bonded silica gel (CSC[4]A-SG) as a novel heterogeneous catalyst was illustrated by efficient reduction of various ketones to their corresponding alcohols. To illustrate the promoting effect of the catalyst in the reaction, two more series of parallel experiments were also carried out using bare silica gel and no catalyst. The study suggests that this newly synthesized solid catalyst has high binding tendency toward sodium cations through ion- pair interactions and is consequently effective for the reduction of ketones to alcohols using $NaBH_4$ as a hydrogen donor. Also to demonstrate the high affinity and strong trap capacity of CSC[4]A-SG toward sodium cation, atomic absorption spectrometric measurements were performed. As a result, quantitative reduction of ketones was observed in short time periods, while the catalyst shows high thermal stability (up to 300 °C) and can be recovered and reused for at least five times in a row without loss of its catalytic performance. This is the first report about the application of CSC[4]A-SG as a catalyst in the chemical reactions.

**Keywords** Chlorosulfonyl-Calix[4]arene-bonded silica gel · Ketone reduction · Sodium borohydride · Heterogeneous catalytic system

## Introduction

Synthesis of novel heterogeneous catalytic systems has become a fascinating area of chemical research due to numerous applications these systems have found in both academia [1] and industries [2]. Heterogeneous catalyzed reactions are widely accepted as environmentally friendly alternatives to conventional homogeneous counterparts for the synthesis of fine chemicals [3], natural products, and pharmaceuticals [4], since they usually end up with more convenient workup procedures, higher selectivities, and easier recycling of catalysts.

Calix[n]arenes (usually n = 4, 5, 6, 8) and their related compounds have received increasing attention in recent years from theoretical and practical points of view [5]. They are considered as a new class of cavity-shaped macrocycles composed of phenolic units linked via alkylidene groups [6] and have been widely used as platforms to build receptors for binding to ions and molecules with important biological and environmental features [7, 8]. The ion binding properties of these molecules appear to be highly dependent on the nature and the number of donor groups and also on the conformation of the calix[n]arene moiety [9–15]. Among the calix[n]arene family, calix[4]arenes present significant advantages over the other homologs since calix[n]arene derivatives with the n higher than 4, (i.e. 6, 8, 10, …) exhibit different conformational orientations and not all the aromatic rings can arrange in the same direction, therefore, giving deformed macrocycles.

The chemical immobilization of calix[n]arenes moities to the surface of particular porous materials can produce new classes of heterogeneous systems with many academic and technological applications in catalysis [16, 17], adsorption [8, 18–21], separation [22–33] and sensors [34–37]. Among

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various porous materials, silica gel deserves special attention due to the presence of very reactive silanol groups on its surface which considerably increase the chemical reactivity of this adsorbent [28, 38, 39].

Ordinarily, the chemistry of attaching organic functionalities to the silica surface is carried out using standard grafting methods [40], where the reaction of a suitable organosilan ($R_{4-n}SiX_n$ with n = 1–3, X = Cl, OMe, OEt and R = a spacer) as a coupling agent with surface silanol groups of silica gel occurs [41]. In the case of calixarenes, the use of any coupling agent and spacer may increase conformational flexibility of the anchored site and, as a result, the maximum attainable site density would be diminished. In fact, chemical bonding of calix[n]arenes on silica surface without using any flexible spacer is a very useful approach for ion binding and sorption. This is due to the rigid structures that are attainable in this way [42, 43]. For this reason, *p*-*t*ert-butyl calix[4]arene was first functionalized with chlorosulfonic acid at the upper rim to get chlorosulfonyl-calix[4]arene (CSC[4]A). Then CSC[4]A was loaded onto activated silica gel to cause direct esterification between Si–OH and the chlorosulfonyl groups to yield CSC[4]A-bonded silica gel (CSC[4]A-SG) as a heterogeneous system (Fig. 1).

Recently, we have reported the preparation and full characterization of chlorosulfonyl-calix[4]arene-bonded silica gel (CSC[4]A-SG) and used it as a selective and reusable sorbent for rubber chemical additives [44, 45]. To evaluate the catalytic behavior of CSC[4]A-SG, we decided to employ it for the reduction of ketones, a reaction which is one of the most common and useful synthetic transformations in organic chemistry [46] and has been carried out so far using various methods [47, 48]. Among different hydrogen donors [47–59], $NaBH_4$ is especially interesting, since it demonstrates high selectivity towards C=O groups in the presence of other reducible functionalities, while it is inexpensive, safe to handle, and environmentally friendly. However, $NaBH_4$ requires long reaction times and does not reduce ketones efficiently in the absence of activators [60]. This background and the fact that calixarenes are efficient and selective sodium ionophores [61–63] persuaded us to investigate the catalytic effect of CSC[4]A-SG in the reduction of carbonyl groups. It should be mentioned that increased interest in organocatalyst is due to its operational simplicity, low toxicity and cost. Nowadays, calixarenes and its derivatives are easily synthesized in large scale and also the immobilization of them onto the surface of various solid supports were done by simple methods. Despite the attractiveness of this reagent, to the best our knowledge, there is no report on the catalytic behavior of this catalyst in the various chemical reactions.

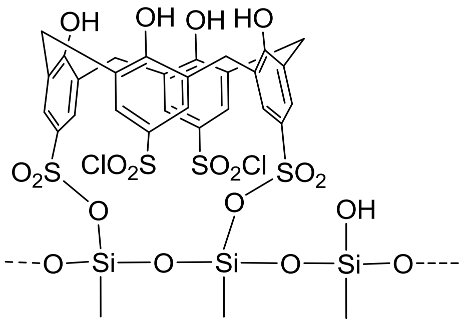


**Fig. 1** Structural representation of CSC[4]A-SG

## Experimental

### Apparatus and chemicals

$Na^+$ in the aqeous phase was analysed by using atomic absorption spectrophotometer (AAS, VARIAN 240) at 589.0 nm of wavelength. Mesoporous amorphous silica gel 60 (irregular particles with particle size 220–440 mesh) was purchased from Fluka and use as support material. All reagents used for the synthesis of p-tertbutyl calix[4]arene and chlorosulfonylated calix[4]arene were obtained from various commercial sources and were analytical pure grade. All the solvents were analytical grades and were purchased from Merck. Generally, they have been dried according to the standard procedures and then stored over molecular sieves. The doubly distilled water was obtained from GSL system (German). All ketone compounds used for the catalytic studies were purchased from Fluka. Analytical thin layer chromatography was performed for monitoring of the reduction process using Merck prepared plates (silica gel 60 $F_{254}$ on Aluminium). Since the synthesis of CSC[4]A-bonded silica gel carried out under a dry nitrogen gas, all glassware was flame dried before use.

### Synthesis of CSC[4]A-SG

The method for the synthesis of CSC[4]A (2) was followed as previously reported [64]. After initial activation of silica gel, CSC[4]A-SG (4) was prepared in two steps according to the our reported method [44]. The preparation scheme of CSC[4]A-SG was shown in Fig. 5.

### Typical procedure for reduction of ketones

To a mixture of methanol (10 mL), a ketone (1 mmol), and 50 mg of freshly prepared CAC[4]-SG (containing 0.005 mmol CSC[4]A) at 0 °C, was slowly added 200 mg $NaBH_4$. The reaction mixture was stirred until TLC showed the ketone is consumed. At this point, the reaction mixture was vacuum filtered using a sintered glass funnel and the filtrate was quenched with diionized water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and the volatiles were evaporated at reduced pressure to obtain the corresponding alcohol. In all cases, products were characterized by comparison of their spectroscopic data (IR and $^1$H-NMR spectra) and melting points with those of authentic samples. The solid catalyst which was separated from the reaction mixture by filtration was then washed consecutively with dichloromethane, diethyl ether, methanol, and hexane and dried for 12 h at 150 °C. The recycled catalyst was reused in next reactions without loosing its activity. Elemental analysis showed no significant changes in chemical composition of the catalyst after recovery.

## Results and discussion

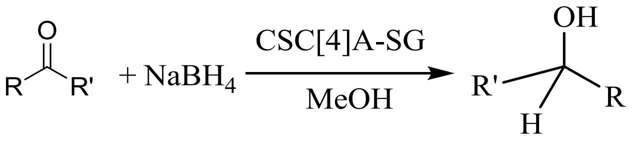
### Preparation and characterization of CSC[4]A-SG

The procedure was described briefly as follows: a mixture of *p*-*t*ert-butyl calix[4]arene (2 mmol)(1) and anhydrous dichloromethane (25 mL) was placed in a three necked 100 mL round- bottom flask equipped with a magnetic stirrer, reflux condenser and septum. The mixture was stirred for 15 min at room temperature in an inert atmosphere of nitrogen gas. To this mixture, chlorosufonic acid (5 mL) was slowly added by syringe at a rate to keep the temperature between 0 and 5 °C. When the addition of chlorosulfonic acid was finished, the solution mixture was refluxed for 2 h under vigorous stirring. After cooling, dry ether (30 mL) was added and the resulting oil after separating was triturated several times with methanol. CSC[4]A as a tan powder was prepared first. yield 50%; mp > 230 dec; $^1$H NMR: (500 MHz, DMSO-d6, TMS), δ(ppm), 3.94 (8H, s, $ArCH_2Ar$), 7.39 (8H, s, Ar–H) and 11.39 (4H, s, 8OH) ; $^{13}$C NMR: (125 MHz, DMSO-$d_6$), δ(ppm), 138.3 (ArC–$SO_2$), 30.4 ($ArCH_2Ar$); MS-FAB: m/z 817.0 ($M^+$, calcd 817.5).

Subsequently, 100 mL round-bottom flask, equipped with a reflux condenser, a gas inlet tube for conducting of HCl gas over silver nitrate solution was charged with 50 mL anhydrous xylene, 1.5 g of activated silica gel and 1 g of CSC[4]A. The mixture was allowed to reflux under continuous stirring and a dry nitrogen atmosphere at 140 °C for 72 h. After carrying out the reaction, the suspension was vacuum filtered using a sintered glass funnel (porosity 3) and CAC[4]-SG was obtained .The final product was dried in an oven at 150 °C for 12 h and kept in the desiccator. Quantitative determination of the organic functional group covalently anchored onto the surface of silica gel was performed with elemental analysis and titration. The percentage of carbon, sulfur, hydrogen which was obtained from elemental analysis and resulting acidic properties of CSC[4]A-SG are listed in the following Table 1. The carbon and sulfur content were assigned to the loading of CSC[4]A over silica gel. The bonded amount was found to be 92.82 µmol/gr (0.17 µmol/m$^2$) according to the carbon content shown in Table 1. Further, the sulfur content of CSC[4]A-SG was 0.36 mmol/gr. The number of $H^+$ determined by acid-base titration was 0.17 mmol/gr in the hydrolyzed sample. This value is half of the sulfur content, indicating that only two ester units took place onto CSC[4]A-SG and two acidic sites exit on the surface.

**Table 1** The results of elemental analysis and titration of CSC[4]-bonded silica gel

| Compound | Elemental analysis | | | | Titration |
|---|---|---|---|---|---|
| | %C | %H | %S | Bonded amount (µmol/gr) | Acid capacity (mmol $H^+$/g) |
| CSC[4] A-bonded silica gel | 3.11 | 6.14 | 1.11 | 92.82 | 0.17 |



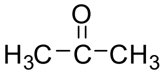
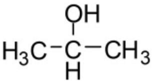
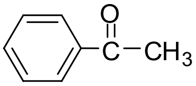
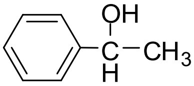
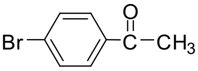
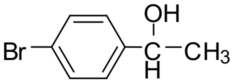
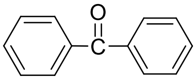
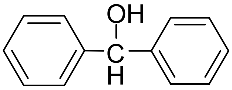
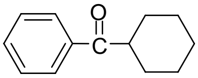
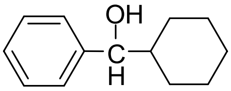
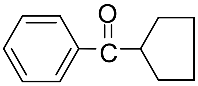
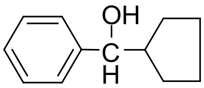
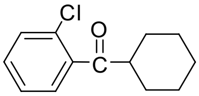
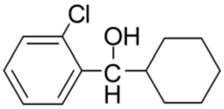
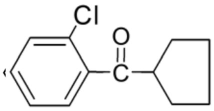
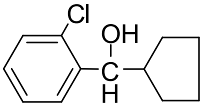
**Scheme 1** Typical reduction of ketone

### Catalytic evaluation

The scope and failure of CSC[4]A-SG as a heterogeneous catalyst in reduction of various ketones using $NaBH_4$ as a hydrogen donor was evaluated (Scheme 1). To illustrate the promoting effect of the catalyst in the reactions, two more series of parallel experiments were also carried out using bare silica gel and no catalyst. The results (Table 2; Fig. 2) clearly show that reductions performed in the presence of catalytic amounts of CSC[4]A-SG reach to completion in much shorter time periods than those carried out using bare silica gel or no catalyst. Sodium borohydride is used in stoichiometric ratio and the completion of the reactions was monitored by TLC. The yields which are reported in Table 2, are only related to the series of experiments which used catalytic amounts of CSC[4]A-SG as a heterogeneous catalyst and it is specified under the “yield column”.

Overall, a major advantage of the present protocol is the relative low reaction times required for the reactions to completion. It should be noted that phenolic oxygen at the lower rim of CSC[4]A-SG have high binding affinity toward sodium cations through ion-pair interactions (Fig. 3) [65]. To indicate the cooperation of sodium cations in the catalytic mechanisms, the reduction of acetone (Table 2, entry 1) was selected as a model. The reaction was carried out

**Table 2** Catalytic investigation of CSC[4]A-SG in the reduction of various ketones with $NaBH_4$

| Entry | Ketone | Product[a] | Reaction time (min) | | | Yield |
|---|---|---|---|---|---|---|
| | | | None | Activated silica | CSC[4]A-SG | CSC[4]A-SG (%) |
| 1 |  |  | 140 | 90 | 10 | 90 |
| 2 |  |  | 120 | 80 | 7 | 98 |
| 3 |  |  | 110 | 80 | 10 | 100 |
| 4 |  |  | 120 | 85 | 12,11[b],10[c],10[d],9[e] | 77 |
| 5 |  |  | 90 | 70 | 5 | 62 |
| 6 |  |  | 90 | 70 | 5 | 76 |
| 7 |  |  | 100 | 75 | 5 | 88 |
| 8 |  |  | 130 | 90 | 12 | 85 |

[a] Products were identified by comparison of the physical and spectral data with those of authentic samples

[b] Second cycle

[c] Third cycle

[d] Fourth cycle

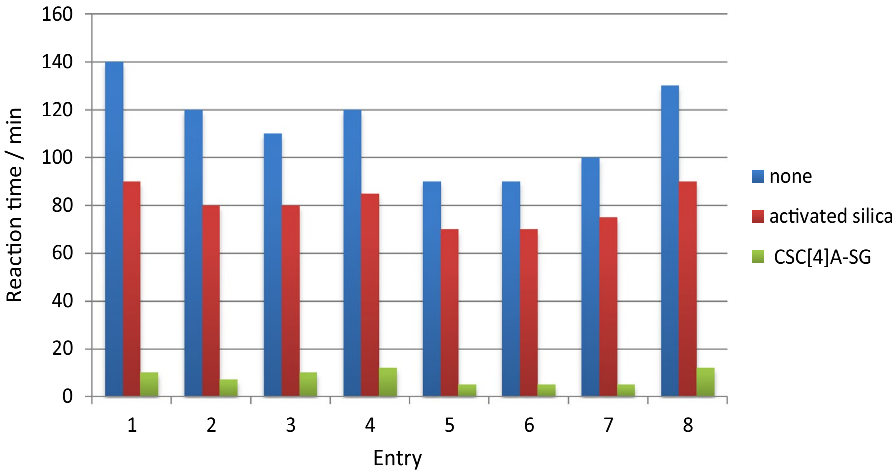


**Fig. 2** The catalytic activity of CSC[A]-SG in the reduction of ketones

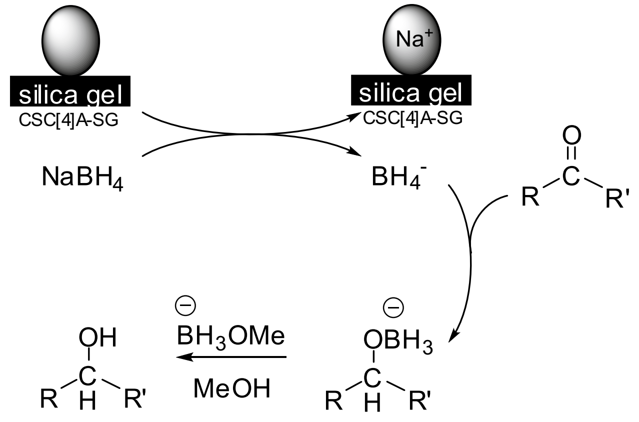


**Fig. 3** The proposed mechanism

using CSC[4]A-SG in the high concentration of sodium cations under similar reaction conditions. As expected, the catalytic activities of catalyst were affected by the presence of large excesses of $Na^+$. The reaction time was considerably increased and were almost equal to that one carried out in the absence of CSC[4]A-SG. This is due to the fact that phenoxide ions of CSC[4]A-SG show more binding abilities toward sodium cations in the aqueous solution. Consequently, the catalytic activities of CSC[4]A-SG in the reduction of various ketones to their corresponding alcohols can be attributed to the high affinity of CSC[4]A-SG toward sodium cations in the presence of $NaBH_4$ as a hydrogen donor. This phenomenon plays a key role in catalytic performance of CSC[4]A-SG in the reduction of ketones. As a result, while $Na^+$ ions coordinate to calix[4]arene moieties, the negatively charged hydride complex i.e. $BH_4^-$ (the counter ion) can freely react with the carbonyl group. On the other hand, the alcohol (the solvent) facilitates the reduction by hydrogen bonding interactions between the carbonyl oxygen and the acidic hydroxyl group of the alcohol. The resulting $[BH_3OMe]^-$ anion is still reactive and can cause further reduction cycles.

In order to demonstrate the high affinity and strong trap capacity of CSC[4]A-SG toward sodium cations, atomic absorption spectrometric measurements were performed. For this procedure, 50 mg of CSC[4]A-SG was suspended in a 10 mL aqueous solution of sodium ions with concentrations varying from 50–400 mg $L^{-1}$. The samples were mechanically shaken at 175 rpm for 1 h, after which the solid was separated by vacuum filtration using a sinter glass funnel. The results of the analysis of the supernatant at 589 nm are presented in Fig. 4 and Table 3.

The % adsoption of sodium ions was then calculated as shown in Eq. 1, where $C_i$ and $C_f$ (mg $L^{-1}$) is the initial and the final concentrations of sodium cation solutions before and after sorption, respectively. The adsorption capacity was calculated as shown in Eq. 2, where $q_e$ is the adsorption capacity (mg $g^{-1}$), $C_i$ and $C_e$ are the initial and equilibrium concentrations (mg $L^{-1}$), respectively, V is the volume (mL) of the solution, and m is the mass (mg) of the adsorbent.

**Table 3** The ability of CSC[4]A-SG for removal of $Na^+$

| Entry | Initial $[Na^+]$ (ppm) | Final $[Na^+]$(ppm)[a] | % Sorption | Sorption capacity (mg $g^{-1}$) |
|---|---|---|---|---|
| 1 | 50 | 17.71 | 64.58 | 6.45 |
| 2 | 100 | 36.93 | 63.07 | 12.72 |
| 3 | 200 | 81.09 | 59.45 | 23.78 |
| 4 | 300 | 155.48 | 48.17 | 28.90 |
| 5 | 400 | 218.84 | 45.29 | 36.23 |

[a] Solid phase, CSC[4]A-SG = 50 mg, Aqueos phase, NaCl solution = 10 mL at 25 °C for 1 h

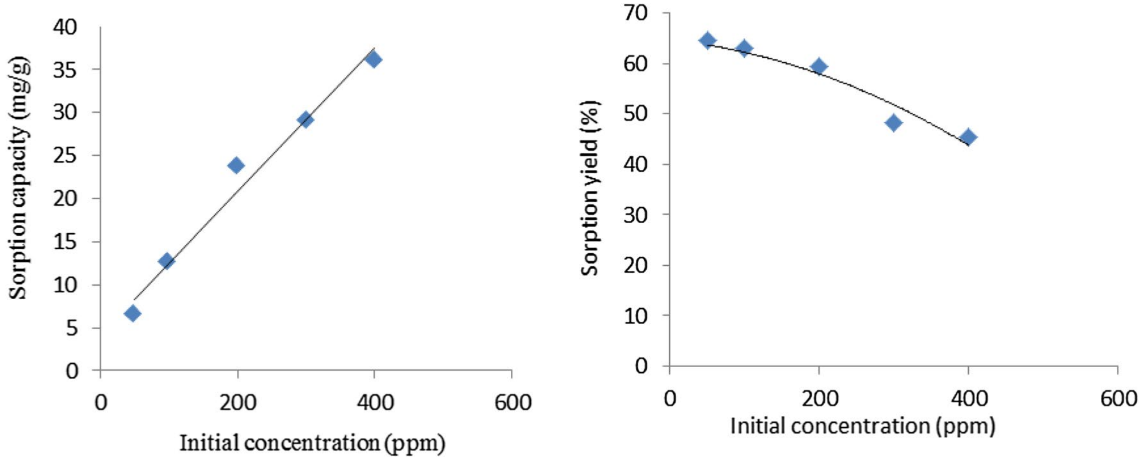


**Fig. 4** Initial concentration effect of $Na^+$ sorption on CSC[4]A-SG

$$\% \text{ Sorption} = \left(C_i - C_f/C_f\right) \times 100 \quad (1)$$

$$qe = \left(C_i - C_e\right) v/m \quad (2)$$

The results show that the ion sorption capacity increases with the increase in initial concentration of $Na^+$. As reported in the literature [66], at lower concentrations, all metal ions in solution could react with the binding sites and thus the percentage of the sorption would be higher than what is observed for higher initial metal ion concentrations. At higher concentration, lower sorption percentage is due to the saturation of binding sites. These results are not only in support of the high affinity of CSC[4]A-SG toward sodium ions but can also justify the high reactivity of the catalyst in reduction of carbonyl compounds to their corresponding alcohols in the presence of $NaBH_4$. Figure 5 summaries the achievement of the present work.

Since the reusability of heterogeneous systems is of high importance from commercial points of view, we therefore investigated the possibility of recovery and reusability of CSC[4]A-SG in the synthesis of benzhydrol from benzophenone (Table 2, Entry 4). The catalyst was recovered after each run, washed consecutively with dichloromethane, diethyl ether, methanol, and hexane and dried at 150 °C for 12 h prior to next use. The recovery and reusability experiments showed the catalyst efficiency was not compromised after several usage-regeneration cycles (Fig. 6). Furthermore, elemental analysis confirmed that both carbon and sulfur contents of CSC[4]A-SG do not change significantly after each cycle under the employed conditions, indicating that the recovered CSC[4]A-SG is as reactive as the fresh catalyst.

## Conclusions

In conclusion, this work shows that CSC[4]A-SG is a remarkably efficient heterogeneous system for the reduction of carbonyl compounds using $NaBH_4$. The catalytic activity of CSC[4]A-SG in reduction of ketones was shown to be directly due to high affinity of the catalyst for sodium ions. The present protocol is associated with several advantages such as mild conditions, short reaction time periods, simple experimental procedure and reusability of the catalyst. The

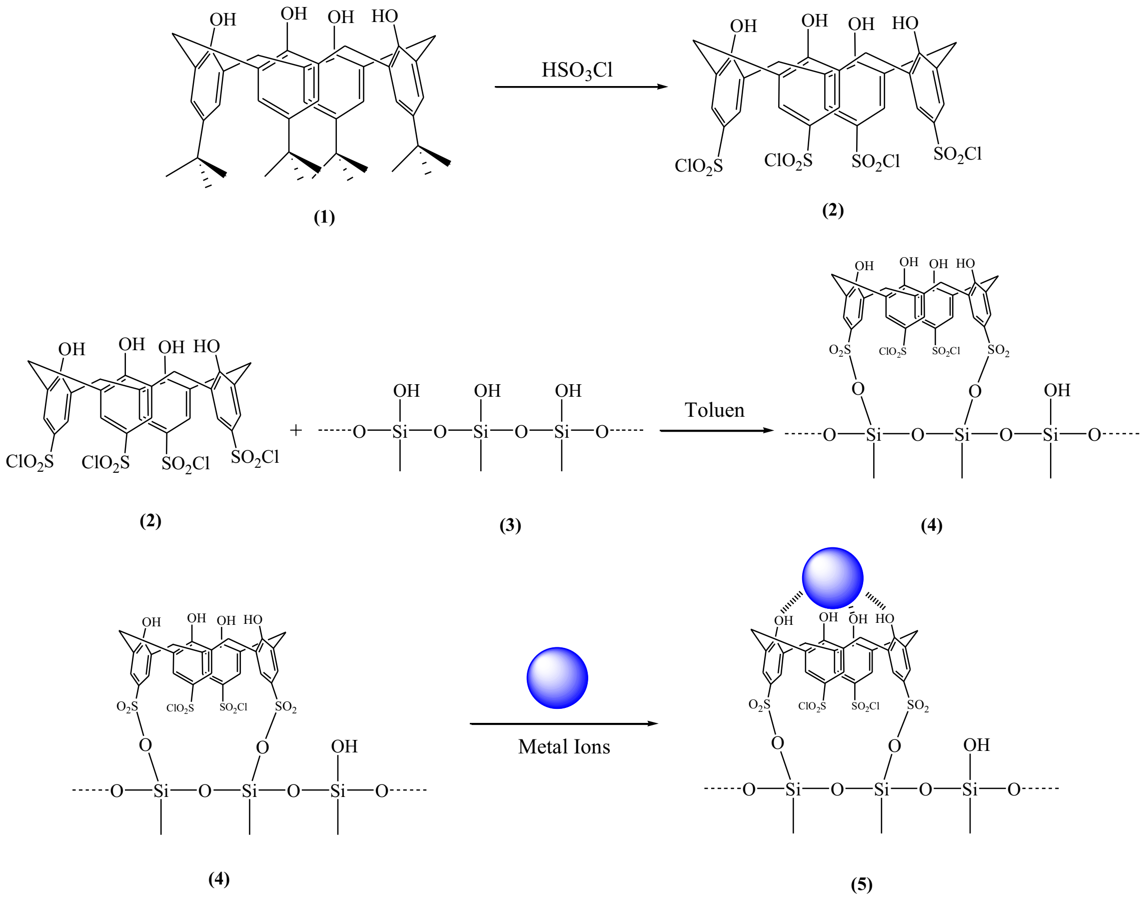


**Fig. 5** The route of preparation of CSC[4]A-SG (suggested on the basis of elemental analysis) and their ability to trap metal ions

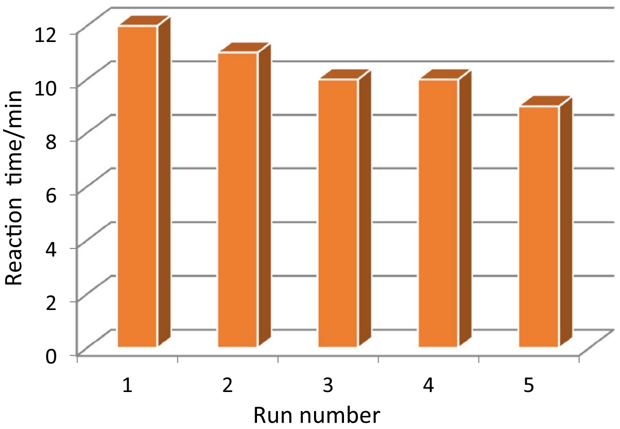


**Fig. 6** The reusability of CSC[4]A-SG in the synthesis of benzhydrol

catalyst shows high thermal stability (up to 300 °C according to TGA curves), while it can be recovered and reused over several cycles without remarkable loss of activity. Moreover, $NaBH_4$ is used in stoichiometric amounts which is very important from atom economic and green chemistry perspectives and minimizes the overall cost and waste production. Other applications of the present method to various functional group transformations are under investigation in our laboratory.

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