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Biomass derived β-cyclodextrin-SO_3H as a solid acid catalyst for esterification of carboxylic acids with alcohols†

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A novel β-cyclodextrin-SO_3H carbon based solid acid catalyst was prepared in a convenient and ecofriendly manner and was characterized using FTIR, PXRD, EDAX and NH_3TPD to illustrate that the carbon material has been functionalized with $-SO_3H$, $-COOH$ and $-OH$ groups. The catalyst was studied for esterification of various carboxylic acids and alcohols under solvent free conditions and showed excellent catalytic performance and gave good yields of esters in the range 78–99% at 70 °C. No solvent was used either for catalyst preparation nor for esterification reaction. The catalyst can be easily recovered by simple filtration and reused for subsequent three runs without any significant impact on yields of products. The main advantage of this methodology is easy and ecofriendly catalyst preparation, easy catalyst separation, practical simplicity, safe reaction conditions, recyclable catalyst and high product yields.

Introduction

Esterification is a method of condensing carboxylic groups with alcohols. It is one of the most fundamental yet challenging reactions in organic chemistry.[1] Organic esters are important products or intermediates in the chemical and pharmaceutical industries. Most of these industries use a esterification step in drug synthesis. Traditional liquid acids such as H_2SO_4 have also been used as homogeneous catalyst for esterification reaction. The high acidity of H_2SO_4 resulted in dehydration of alcohols to alkenes, thus decreasing the selectivity and yield of ester formation.[2,3] They also suffer from drawback of corrosion, contamination, have to be neutralized after the reaction and hence the workup is tedious. Such catalysts are difficult to separate from the reaction and they cannot be reused. On contrary, heterogeneous catalyst are more preferred due to their low cost, metal-free composition, easy separation, high stability and high reusability. In recent reports using heterogeneous catalyst for esterification reaction, Zhan *et al.*[4] used GDTCSA catalyst (carbon material functionalized with $-NH_2$ and $-SO_3H$ groups), Minakawa *et al.*[5] used macroporous polymeric acid catalyst, Karimi *et al.*[6] used Bronsted acid ionic liquid, Sakakura *et al.*[7] and Koshikari *et al.*[8] used diarylammonium pyrosulfates in water, Chakraborti *et al.*[9] used $HClO_4$–SiO_2 and Leng *et al.*[10] used heteropolyanion-based ionic liquids for esterification reaction. Though a number of methods have been known for esterification reaction,[11] the use of large amounts of acids, alcohols, expensive reagents and solvents have been used for such type of reactions. Such methods do not promote green synthesis and atom efficiency. Hence there is still a need to develop an efficient process for esterification from both academic and industrial points of view. Herein, we report direct esterification of equimolar amounts of carboxylic acids and alcohols using 10 wt% of β-cyclodextrin-SO_3H catalyst under solvent free conditions.

Results and discussion

An amorphous carbon material consisting of small polycyclic aromatic carbon sheets with a high density of sulfonic acid (SO_3H) sites are especially attractive heterogeneous catalysts now-a-days due to their low cost, metal-free composition, and expected high stability and high reusability. Therefore, we choose readily available β-cyclodextrin as a carbon precursor and *p*-TSA as a sulphonating agent. Naturally occurring β-cyclodextrin can be prepared by enzymatic hydrolysis of starch which comes from biomass.[12] Cyclodextrins are cyclic oligomers of seven D-glucose units linked in a α (1–4) manner and have a pre organized structure. Hence after sulphonation of β-cyclodextrin we expected more polycyclic aromatic sheets to be formed and hence high density of sulphonated sites to be attached on the carbonaceous material ultimately showing more acidic character of the catalyst. In this study, we have prepared β-cyclodextrin-SO_3H catalyst by one step hydrothermal carbonization of β-cyclodextrin and *p*-TSA under mild reaction

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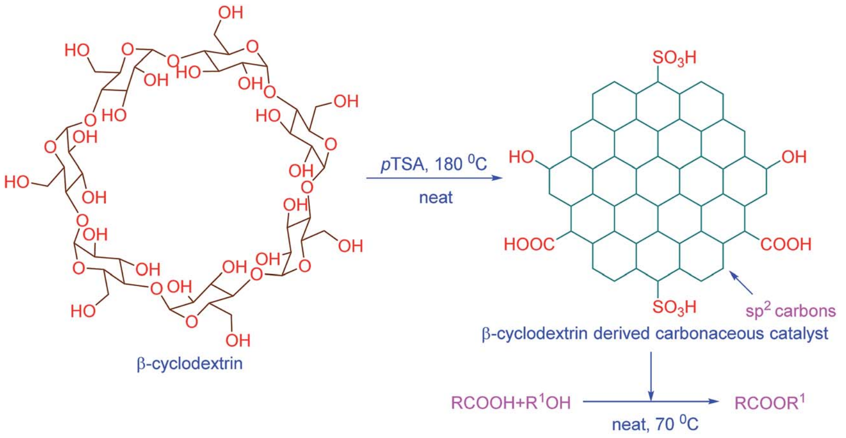


Fig. 1 Preparation of β-cyclodextrin-SO_3H carbonaceous catalyst and its application in esterification reaction.

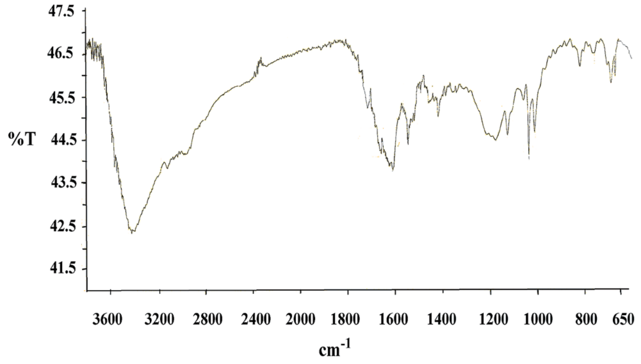


Fig. 2 IR spectra of β-cyclodextrin-SO_3H.

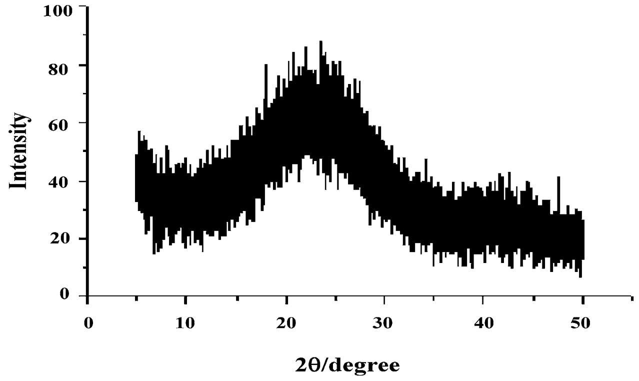


Fig. 3 PXRD spectra of β-cyclodextrin-SO_3H.

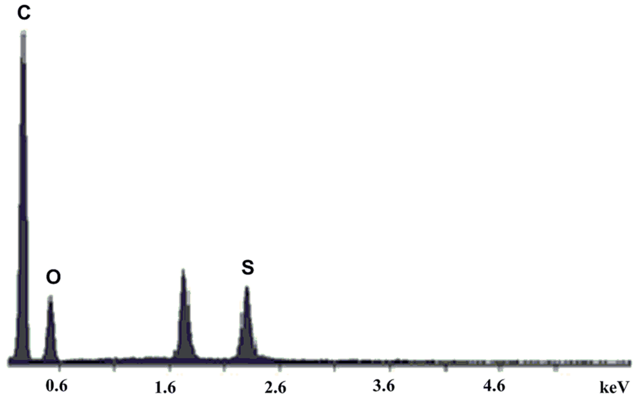


Fig. 4 EDAX analysis of β-cyclodextrin-SO_3H.

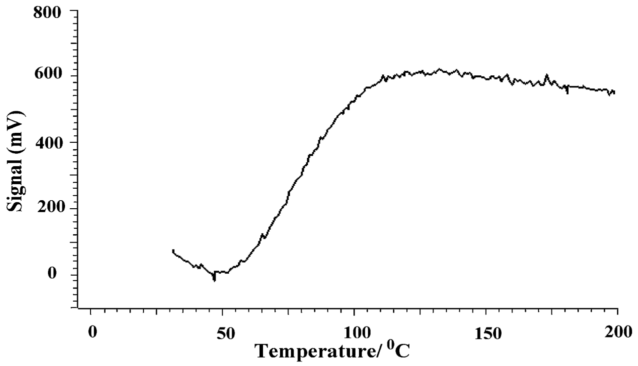


Fig. 5 NH_3TPD curve of β-cyclodextrin-SO_3H.

Table 1 The structure and surface properties of the β-cyclodextrin-SO_3H catalyst

Catalyst	% Sulphur	Surface area ($m^2\ g^{-1}$)	Pore size (Å)	Acid density (mmol g^{-1})	SO_3H amount (mmol g^{-1})
β-Cyclodextrin-SO_3H	2.99	0.18	47.4	3.0	1.24

Table 2 Direct esterification of various alcohols and acids

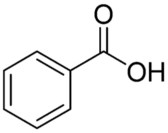
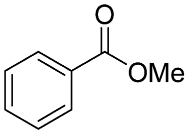
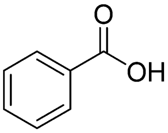
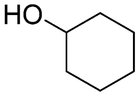
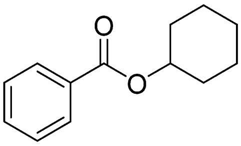
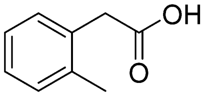
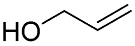
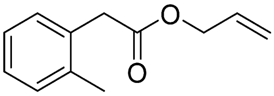
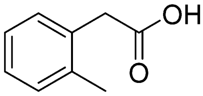
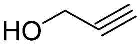
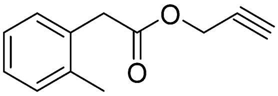
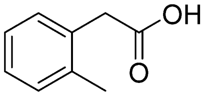
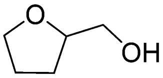
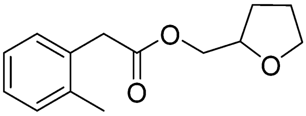
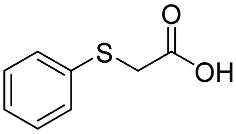
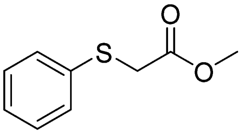
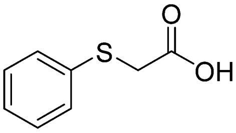
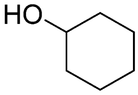
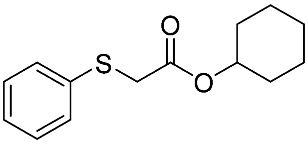
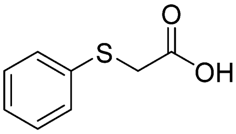
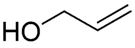
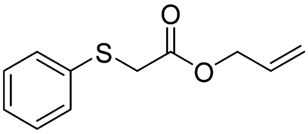
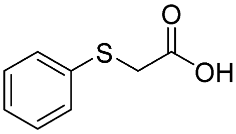
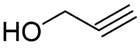
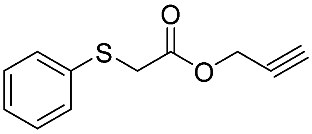
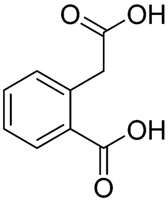
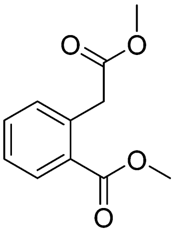
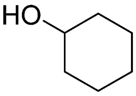
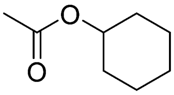
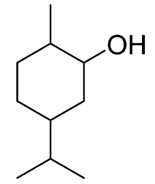
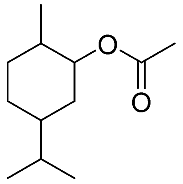
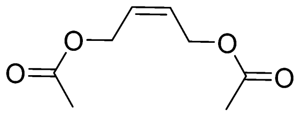
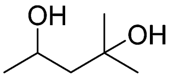
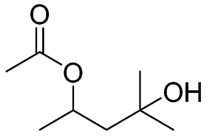
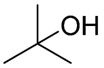
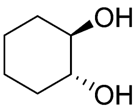
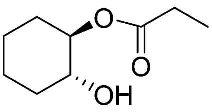
Entry	Acid	Alcohol	Ester	Temp (°C)	Time (h)	Yield^a (%)
1		MeOH		70	3	97
2				70	6	78
3				70	4	91
4				70	4	94
5				70	3	96
6		MeOH		70	3	96
7				70	6	81
8				70	3	94
9				70	3	99
10		MeOH		70	8	94
11	CH_3COOH			70	5	99

Table 2 (*Contd.*)

Entry	Acid	Alcohol	Ester	Temp (°C)	Time (h)	Yield[a] (%)
12	CH_3COOH			70	6	99
13	CH_3COOH			70	7	89
14	CH_3COOH			70	6	99
15	CH_3COOH		No reaction			
16	CH_3CH_2COOH			70	5	79

[a] Isolated yields.

conditions and shown its application in the esterification of various acids and alcohols (Fig. 1). The hydrothermal carbonization promoted the structure to undergo decomposition, hydrolysis, dehydration, and a molecular rearrangement reaction to produce a polycylic aromatic structure embedded with active $-SO_3H$, $-COOH$ and $-OH$ sites.

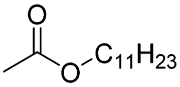
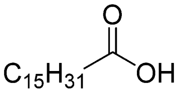
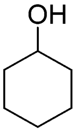
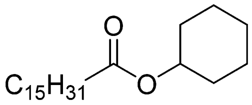
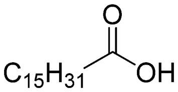
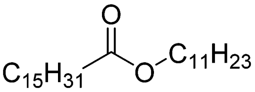
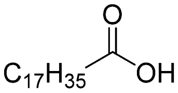
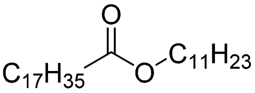
The catalyst thus obtained was characterized with FT-IR (Spectrum 400), PXRD (Panalytical X'Pert Pro), Elemental analysis from EDAX (Quanta 200 3D, FEI), NH_3TPD (Thermo Scientific TPD RO 1100) and BET surface area (Micrometrices ASAP 2020). The acid densities were measured by acid base titration (see ESI†). The FT-IR spectrum (Fig. 2) showed characteristic peaks at 1008 cm^{-1} and 1032 cm^{-1} which are attributed to $O{=}S{=}O$ stretching vibrations in $-SO_3H$ groups and peak at 1174 cm^{-1} for SO_3H stretching. This indicates that the sulfonic acid groups have been successively incorporated on the catalyst surface. Peaks at 1610 cm^{-1} attributed for $C{=}C$ stretching vibrations in aromatic carbons and peak at 1680 cm^{-1} attributed for $C{=}O$ stretching. Peak at 1714 cm^{-1} attributed to presence of $C{=}O$ stretching vibration of $-COOH$ group. Bands at 2950 cm^{-1} to 2875 cm^{-1} attributed for C–H stretching band. Bands due to O–H stretching were observed at 3421 cm^{-1}. The powder X-ray diffraction pattern (Fig. 3) of β-cyclodextrin-SO_3H exhibited a broad diffraction peak ($2\theta = 15°$ to $30°$), which can typically be attributed to amorphous carbon composed of aromatic carbon sheets oriented in considerably random fashion. The energy dispersive X-ray analysis (EDAX) analysis (Fig. 4) showed sulphur composition to be 2.99%. The ammonia desorption studies (Fig. 5) showed the total acid density to be 2.7 mmol g^{-1}.

The total acid density and the sulphonic acid density of β-cyclodextrin-SO_3H based on acid base titration was found to be 3.0 mmol g^{-1} and 1.24 mmol g^{-1} respectively. BET surface areas and pore size were calculated using the standard Brunauer–Emmett–Teller (BET) equation and was found to be 0.18 m^2 g^{-1} and 47.4 Å (Table 1).

The performance of β-cyclodextrin-SO_3H as an acid catalyst was tested for direct esterification reaction of acids and alcohols. Variety of different acids and alcohols were tried for esterification reaction under solvent free condition. In order to optimize the temperature, the reaction with the test substrate (benzoic acid and methanol) was carried out at room temperature, 50 °C, 70 °C and 90 °C. In case of the reaction at room temperature and 50 °C the reaction was found to be very slow. At 70 °C the reaction was clean and good yield of 97% of methyl benzoate was obtained in 3 h (Table 2, entry 1), while at 90 °C not much impact on reaction time and yields was observed. The esterification reaction did not proceed at all in the absence of β-cyclodextrin-SO_3H catalyst.

Inspired by this fact, we then tried to explore the reaction on variety of acids and alcohols using β-cyclodextrin-SO_3H catalyst under solvent free conditions. Benzoic acid was also found to react with cyclohexanol using β-cyclodextrin-SO_3H catalyst at 70 °C in 6 h giving 78% yield of cyclohexyl benzoate (Table 2,

Table 3 Direct esterification of long chain acids and long chain alcohols

Entry	Acid	Alcohol	Ester	Temp (°C)	Time (h)	Yield[a] (%)
1	CH_3COOH	$C_{11}H_{23}OH$		70	3	98
2				70	5	84
3		$C_{11}H_{23}OH$		70	4	93
4		$C_{11}H_{23}OH$		70	4	89

[a] Isolated yields.

entry 2). 2-(*o*-Tolyl) acetic acid reacted with allyl alcohol, propargyl alcohol and cyclopentylmethanol at 70 °C to form the corresponding esters with 91–96% yield (Table 2, entries 3–5). 2-Phenylthioacetic acid also reacted smoothly with MeOH, cyclohexanol, allyl and propargyl alcohols to afford the corresponding esters in 96%, 81%, 94% and 99% yield respectively (Table 2, entries 6–9). 2-(Carboxymethyl)thiobenzoic acid when treated with excess MeOH as a solvent was found to give 94% yield of the diester in 8 h (Table 2, entry 10). Cyclohexanol and menthol when reacted with acetic acid gave about 99% yield of cyclohexyl acetate and menthol acetate (Table 2, entries 11 and 12). 2-Butene diol when condensed with excess acetic acid gave about 89% yield of the corresponding diester (Table 2, entry 13). When a diol containing both secondary and tertiary alcohol functionality was condensed with excess acetic acid, monoester of only secondary hydroxyl was formed in 99% yield (Table 2, entry 14). This method can thus be used for selective esterification of secondary alcohols in presence of tertiary alcohols. Reaction of acetic acid with *t*-butanol gave no ester formation even after keeping for longer reaction time (Table 2, entry 15). 1,2-*trans*-Cyclohexane diol when reacted with one equivalent of propionic acid was found to give monoester of cyclohexane diol in 79% yield (Table 2, entry 16) indicating that selectively one alcohol can be esterified in presence of other.

Esterification was also carried out successively on long chain acids and long chain alcohols under solvent free conditions at 70 °C (Table 3). Esterification of acetic acid with 1-undecanol proceeded smoothly to give 98% of 1-acetylundecanol in 3 h (Table 3, entry 1).

Palmitic acid was found to react with cyclohexanol in 5 h giving 84% yield of cyclohexylpalmitoyl ester (Table 3 entry 2). Both long chain palmitic acid and stearic acid reacted smoothly with long chain 1-undecanol to give the corresponding esters in 93 and 89% yield respectively (Table 3, entries 3 and 4).

As it is very convenient to recover the catalyst at the end of the reaction, the solid catalyst left could be readily reused for the next run. Therefore, the recycled β-cyclodextrin-SO_3H catalyst without any regeneration steps was investigated in the esterification of phenyl thioacetic acid and propargyl alcohol at 70 °C. As shown in Table 4, β-cyclodextrin-SO_3H exhibited a 97% yield of product for the first run, and the catalytic activity showed consistency after repeated use giving 96% yield of the product after 2nd and 3rd run.

Table 4 Reusability of β-cyclodextrin-SO_3H

Entry	Catalyst reuse	Yield[a] (%)
1	1st recycle	97
2	2nd recycle	96
3	3rd recycle	96

[a] Isolated yields.

Conclusion

In conclusion, a carbonaceous β-cyclodextrin-SO_3H catalyst was efficiently prepared and was found to show excellent catalytic activity for esterification of variety of acids and alcohols under mild reaction conditions giving high reactivity and selectivity. No solvent was used for both catalyst preparation and esterification reaction. The yields for the esterification reaction were excellent in the range of 78–99%. The catalyst could also be recovered and reused without any loss of activity. This catalytic system is environmentally green and can be used as an ideal method for esterification in future.

Experimental section

Preparation of catalyst β-cyclodextrin-SO_3H

Typically 4 g of β-cyclodextrin powder was mixed with 18 g of *p*-TSA (18 g of *p*-TSA was used so as to have maximum sulphonation on the β-cyclodextrin surface) and was heated in an oil bath at 180 °C for 24 h under nitrogen. After 24 h, the catalyst was kept open to air and further heated for 24 h to remove all the volatile compounds adsorbed on the surface of the material. Deionised water was added to it and the catalyst was filtered and further washed several times with deionised water to remove the excess sulphate ions and then finally washed with ethanol. The catalyst obtained was called as β-cyclodextrin-SO_3H.

Typical procedure for esterification

The mixture of 0.1 mmol of acid, 0.1 mmol of alcohol and 10 wt% of β-cyclodextrin-SO_3H catalyst in a round bottom flask were stirred magnetically at 70 °C for a stipulated time until the complete consumption of starting material. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and the catalyst was filtered. The filtrate was then washed with saturated solution of $NaHCO_3$, water and dried over Na_2SO_4, concentrated and loaded on silica and purified by column chromatography to obtain the pure ester.

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