



Synthesis of sulfonic acid functionalized carbon catalyst from glycerol pitch and its application for tetrahydropyranyl protection/deprotection of alcohols and phenols

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ABSTRACT

A novel carbon catalyst with $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ functional groups was prepared from glycerol pitch by *in situ* partial carbonization and sulfonation with sulfuric acid. The activity of the catalyst was investigated through tetrahydropyranlation and dehydropyranlation of a wide variety of alcohols and phenols at room temperature by changing the solvent medium from dichloromethane to methanol. Excellent yields, short reaction times, easy and quick isolation of the products and reusability of the catalyst are the main attractions of this method. The novel carbon catalyst holds great potential in the green chemical processes.

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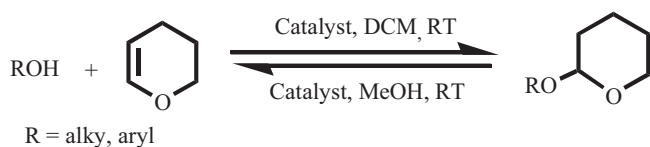
1. Introduction

The green approach to chemical processes has stimulated the use of recyclable heterogeneous solid acids as replacements for corrosive, non-recyclable liquid acid catalysts [1–5]. The use of heterogeneous catalysts offers several intrinsic advantages like insolubility of catalyst in the product enabling ease of product separation, catalyst reuse and additional process advantages through reactor operation in continuous flow versus batch configuration over their homogeneous counterparts. However, a major obstacle to such progress is the lack of a suitable solid acid that is as active, stable, and inexpensive as sulfuric acid. Sulfonated ($-\text{SO}_3\text{H}$ -bearing) materials have been reported as strong solid acid catalysts. The first such sulfonated catalyst was prepared in two steps via carbonization followed by the sulfonation of polycyclic aromatic hydrocarbons [6]. Some of the stability problems of these catalysts were overcome by saccharide-based carbon catalysts employing a controlled carbonization and sulfonation [7–12]. Initially, incomplete carbonization of the saccharide/sugar/cellulose was carried out at high temperature (about 400 °C) under nitrogen atmosphere for 15 h to form the polycyclic aromatic carbon sheets. The incom-

plete carbonized materials were sulfonated by treating with large volumes of sulfuric acid (1:20 wt/vol) at 150 °C for 15 h to produce the carbon based sulfonated solid acids. Recently, we have reported a similar carbon catalyst with a high density of sulfonic acid groups ($-\text{SO}_3\text{H}$) from crude glycerol with very good esterification activity and reusability employing rapid *in situ* carbonization and sulfonation [13] using considerably lower amounts of sulfuric acid (1:4 wt/vol) without separate carbonization at higher temperature. In continuation of this study, glycerol pitch is employed as carbon precursor for the preparation of carbon catalyst. Glycerol pitch is generated from fat splitting units during the refining of sweet water to pure glycerol. Presently, the industry is struggling to dispose off glycerol pitch as it does not have any commercial value. The glycerol pitch is a semi-solid material containing a major portion of diglycerol and salts along with minor amounts of glycerol, triglycerol, tetraglycerol and polyglycerol. Here, we wish to report a novel use of glycerol pitch by the way of developing a method for the preparation of sulfonic acid functionalized carbon catalyst. The activity of the carbon catalyst was investigated through the protection and deprotection of hydroxyl groups with 3,4-dihydro-2H-pyran (DHP) and the results showed that the catalyst was very efficient for this purpose.

3,4-Dihydro-2H-pyran (DHP) has been widely utilized as a protective group of hydroxy compounds as they are stable under a variety of reaction conditions [14]. THP groups are also the

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Scheme 1. Carbon-based solid acid catalyzed tetrahydropyranylation and depyranylation of alcohols and phenols.

protective groups of choice in peptide, nucleotide, carbohydrate and steroid chemistry [15–17]. This transformation has been generally achieved using both Brønsted acid as well as Lewis acid catalysts [18–20]. Recently the tetrahydropyranylation process (THP ether synthesis) has been performed under environmentally friendly conditions with concomitant minimum purification requirements [21–37]. Deprotection of THP ethers for the regeneration of hydroxyl compounds usually entails rather harsh acidic conditions, which are rarely compatible with sensitive substrates [38,39]. Heterogeneous catalysts [40] and ion-exchange resins like amberlyst, nafion and dowex [41–44], that are used extensively in protection/deprotection processes in organic synthesis, are of considerable help in this direction. Taking into account the increasing demand for new and cleaner chemical processes, here we report a novel carbon-based solid acid catalyzed methodology for effective tetrahydropyranylation of alcohols and phenols and their deprotection (Scheme 1) at room temperature by changing solvent medium from dichloromethane to methanol.

2. Experimental

Chemicals were purchased from S.d. Fine Chemicals Ltd., Mumbai, India. All other reagents and solvents used were of analytical grade. Elemental composition of the sulfonic acid functionalized carbon catalyst was estimated using the equipment Elementar (Model; Vario EL). TG/DTA was carried out on a Mettler-Toledo 851E instrument. XRD pattern was recorded on a Rigaku, D-5000 diffractometer, using Ni-filtered Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). X-Ray Photoelectron Spectroscopy (XPS) measurements were conducted with a KRATOS AXIX 165 with a DUAL anode (Mg and Al) apparatus using the MgK α anode. The specific surface area of the catalyst was estimated using N $_2$ adsorption at -196°C by the single point BET method using Quantachrome Antosorb-1. ^{13}C Magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of solid catalyst was recorded on a Bruker Spectrometer. The acidity of the carbon catalyst was measured by the potentiometric titration method using an automatic titrator, Schott GmbH, Germany. The acid strength of the catalyst was measured by employing a saturated calomel electrode. Catalyst (about 0.1 g) was suspended in acetonitrile and stirred for about 3 h. Later, the suspension was titrated with a solution of 0.05 N n-butyl amine in acetonitrile at a flow rate of 0.5 mL/min. The variation in electrode potential, while adding the n-butyl amine solution, was recorded using a double junction electrode. ^1H NMR spectra were recorded on a 300 (Varian, Palo Alto, USA) spectrometer in CDCl_3 solution with tetramethylsilane as the internal standard. Chemical shift values (δ) are given in parts per million. GC-MS spectra were recorded on Agilent 5973 GC-mass spectrometer (Agilent, USA) in the EI mode and are given in mass units (m/z). IR spectra were recorded on a Perkin Elmer (model: spectrum BX) FT-IR Spectrometer using CH_2Cl_2 or KBr.

2.1. General procedure for the preparation of sulfonated carbon catalyst from glycerol pitch

The hard mass of glycerol pitch obtained from a local fat splitting industry was used as such without any purification. A mixture of glycerol pitch (10 g) and conc. sulfuric acid (40 g) was gently heated

from ambient temperature to 250°C for 20 min to facilitate *in situ* partial carbonization and sulfonation under static air condition at atmospheric pressure without any nitrogen/air flow. The reaction mixture was allowed at that temperature for about 10 min till the foaming ceased to obtain the carbon compound. The resultant product was cooled to ambient temperature and washed with hot water under agitation till the wash water became neutral to pH. The partially crystalline product was filtered and dried in the oven at 120°C for 2 h till it was moisture-free to obtain carbon catalyst (4.0 g).

2.2. General procedure for tetrahydropyranylation of hydroxy compounds: tetrahydropyranylation of 1-decanol (Table 1, Entry 1)

A mixture of 1-decanol (0.790 g, 5 mmol), DHP (0.420 g, 5 mmol) and carbon catalyst (0.080 g, 10 wt% of substrate) was stirred in dichloromethane (5 mL) at room temperature for 2 h. The progress of the reaction was monitored by TLC (eluant, n-hexane/ethyl acetate, 9:1). After completion of the reaction, the catalyst was filtered out and the product was passed through a column of silica gel eluting with hexane/ethyl acetate (9:1) to afford pure 2-decyloxy-tetrahydro-pyran (1.18 g, 98% yield). IR 2927, 2856, 1462, 1075, 1031 cm^{-1} ; ^1H NMR δ 0.88 (3H, t); 1.25–1.90 (22H, m); 3.30–3.35 (1H, m), 3.4–3.5 (1H, m), 3.62–3.7 (1H, m), 3.75–3.8 (1H, m); 4.55 (1H, br, s); GC-MS: m/z [M^+] 242. The recovered catalyst was washed with water, dried at 120°C in oven and reused for eight cycles of THP protection reaction of 1-decanol for determining its stability and activity. Control reaction of tetrahydropyranylation of 1-decanol was carried out employing glycerol-based sulfonic acid functionalized carbon catalyst [13] for comparing the activity with glycerol pitch based catalyst. In both the cases the reaction was found to be completed within 2 h resulting the product in 95% yield.

2.3. 2-(4-Methoxy benzyloxy)-tetrahydro-pyran (Table 1, Entry 10)

IR 2943, 1248, 1030, 756 cm^{-1} ; ^1H NMR δ 1.05–1.90 (6H, m); 3.42–3.55 (1H, m); 3.77 (3H, s); 3.80–3.90 (1H, m); 4.35–4.40 (2H, m); 4.60 (1H, br, s); 6.8–7.25 (4H, m); GC-MS: m/z [M^+] 222.

2.4. General procedure for deprotection of THP ethers

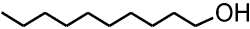

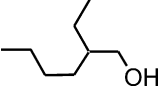


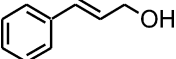


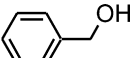
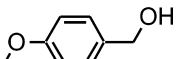
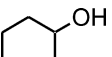

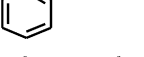
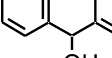
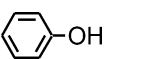
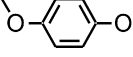
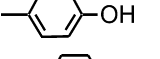
THP ether (5 mmol) and carbon catalyst (10 wt% of substrate) were stirred in methanol (5 mL) at room temperature for 30 min. The cleavage of THP ethers was monitored by TLC (eluant, n-hexane/ethyl acetate, 9:1). After completion of the reaction, the catalyst was filtered and washed with methanol. The filtrate was concentrated under reduced pressure to obtain the corresponding pure hydroxy compound in quantitative yield. The recovered catalyst was washed with water, dried at 120°C in an oven and reused for eight cycles of reaction for determining its stability and activity.

3. Results and discussion

3.1. Preparation and characterization of sulfonic acid functionalized carbon catalyst from glycerol pitch

Sulfonic acid functionalized polycyclic aromatic carbon catalyst was prepared by employing *in situ* partial carbonization and sulfonation protocol by heating the mixture of glycerol pitch (procured from a local industry) and sulfuric acid in the ratio of 1:4 (wt/vol) to 250°C for 20 min. The yield of the carbon catalyst obtained was about 40% by the weight of glycerol pitch taken for the reaction. A thorough characterization of the carbon catalyst was carried out to establish its physico-chemical characteristics. The catalyst was

Table 1
Carbon-based solid acid catalyzed tetrahydropyranylation and depyranylation of alcohols and phenols.

Entry	Substrate	THP protection ^a	Deprotection ^a
		Yield (%) ^b	Yield (%) ^b
1		95	98
2		95	99
3		98	98
4		90	97
5		90	98
6		90	98
7		98	95
8		98	99
9		96	98
10		98	98
11		95	95
12		87	95
13		80	96
14		90	95
15		90	95
16		90	98
17		88	97

^a Reaction conditions: (i) alcohol/phenol (5 mmol), DHP (5 mmol), carbon catalyst (10 wt.%), dichloromethane (5 mL), room temperature, 2 h. (ii) carbon catalyst (10 wt.%), methanol (5 mL), room temperature, 30 min.

^b Isolated yield.

insoluble in water and organic solvents like methanol, ethanol, chloroform, benzene, hexane, and pyridine. The carbon catalyst was found to have an elemental composition of $\text{CH}_{0.87}\text{S}_{0.02}\text{O}_{0.46}$. The X-ray diffraction pattern (Fig. 1) of the catalyst showed weak diffraction peaks at 2θ values between 10–30 and 35–50°, due to its amorphous nature. The non-porous nature of the catalyst is confirmed by the low surface area of 0.96 m²/g obtained by nitrogen adsorption. The FTIR spectrum (Fig. 2) showed peaks at 3430, 1702 and 1660 cm⁻¹ corresponding to the stretching modes of –OH, –COOH and –SO₃H groups, respectively. ¹³C magic angle spinning (MAS) nuclear magnetic resonance (NMR) analysis (Fig. 3) showed the resonance peaks at 137, 151, and 166 ppm attributable

to aromatic carbon attached with OH, COOH and SO₃H groups, respectively. The peaks at δ 19, 51 and 86 ppm are related to the spinning side bands of the polycyclic aromatic carbon. The XPS spectrum (Fig. 4) of the catalyst exhibited the S_{2p} peak at 168.47 eV, which can be assigned to –SO₃H groups and this observation supports the data obtained by FTIR. Potentiometric titration method is used for the estimation of the total acid density of the catalyst and was found to be 1.9 mmol/g. The physico-chemical characterization thus indicates that the carbon catalyst is a partially crystalline material consisting of polycyclic aromatic carbon sheets with –SO₃H, –COOH and –OH functional groups as proposed for the sugar catalyst [7–12].

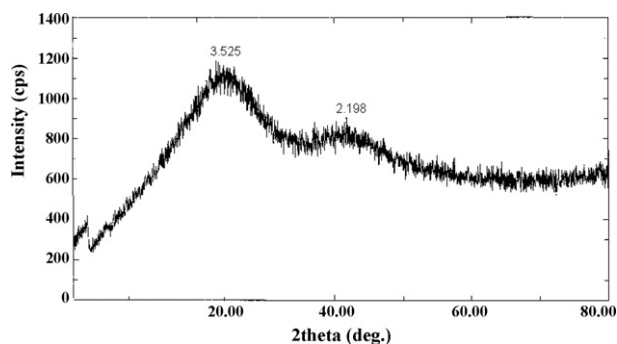


Fig. 1. The powder XRD pattern of the carbon catalyst.

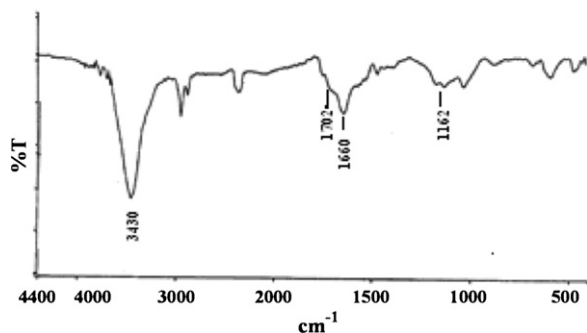


Fig. 2. The FTIR spectrum of the carbon catalyst.

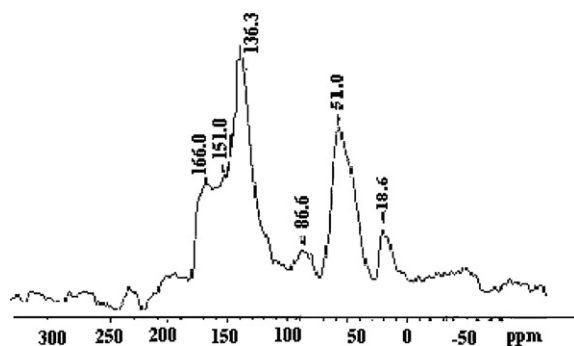


Fig. 3. The ^{13}C MAS NMR spectrum of the carbon catalyst.

3.2. Tetrahydropyranlation of alcohols and phenols catalyzed by carbon catalyst

Several types of alcohols (primary, secondary, aliphatic, benzylic, cyclic, allylic and propargylic) and phenols with different substituents were converted to their corresponding THP ethers by

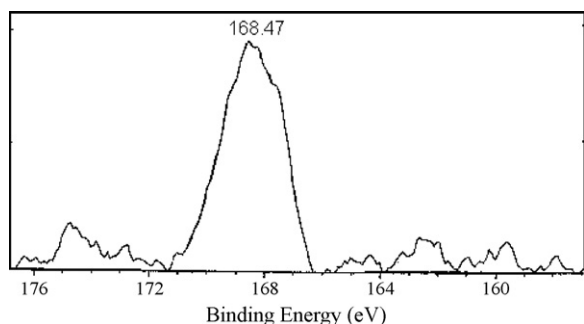


Fig. 4. The XPS spectrum of the carbon catalyst.

the treatment of 3,4-dihydro-2H-pyran with glycerol-pitch based carbon catalyst in dichloromethane medium at room temperature in good to excellent yields (80–98%), as shown in Table 1. Lower reactivity of phenols as compared to alcohols, is attributed to the decreased nucleophilic character of the phenolic oxygen. The same is evident in terms of higher yields of THP ethers of alcohols (90–98%, entries 1–11) compared to THP ethers of phenols (80–90%, entries 14–17). Allylic and propargylic alcohols (entries 5–7) are also converted to their corresponding THP ethers in 90–98% yields without formation of any elimination products or isomerization of the double bond. The THP protection of solketal took place efficiently and gave excellent yield (98%) without affecting the isopropylidene protected group (entry 8). Control reaction of 1-decanol with DHP was carried out employing glycerol-based carbon catalyst [13] for comparing the activity with glycerol-pitch based catalyst and found that the activity of the both the catalysts was almost same resulting the product in 95% yield.

3.3. Deprotection of THP ethers catalyzed by carbon catalyst

The deprotection of THP ethers by merely changing the solvent system has been effected by several reagents [44–47]. We have now found that the same carbon catalyst also to be an efficient deprotection catalyst for THP ethers in the presence of methanol at room temperature to provide the corresponding free alcohols in consistently excellent yields (95–99%, Table 1), irrespective of structural variations. It is interesting to note that the deprotection of all the compounds reported in the present study was completed within 30 min. After completion of the reaction, the catalyst was removed by filtration and washed with dichloromethane. The solvent was evaporated under reduced pressure and the residue was further purified by passing through silica gel column. The reusability of the catalyst was studied for both protection and deprotection of 1-decanol and obtained almost similar results at the same reaction conditions even after 8 cycles without any pretreatment for reactivation. The notable feature of this method is that anhydrous conditions and high temperatures are not required as reported previously [44,47], to effect similar deprotections indicating that the present method to be milder. All the products were characterized by ^1H NMR, IR and GC–MS analysis by comparison with those of reported authentic samples [21–37].

4. Conclusion

In conclusion, a novel and versatile method for the synthesis of highly active and stable sulfonic acid functionalized carbon catalyst from glycerol pitch by *in situ* partial carbonization and sulfonation was developed. The study revealed that the carbon catalyst has an excellent capability for the preparation of THP ethers, as well as for their cleavage to the corresponding alcohols at room temperature. In addition, the catalyst has the added advantage of its simple preparation, reusability, operational simplicity and high yields. This is the first example of carbon catalyst employed for both protection and deprotection of hydroxyl groups by changing the solvent medium from dichloromethane to methanol and obtaining higher yields at room temperature. We believe that the present methodology employing carbon catalyst could be an important addition to the existing methodologies in organic reactions to replace corrosive acids.

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