

Synthesis, Characterization and Investigation of Catalytic Activity of a Highly Sulfonated Carbon Solid Acid in the Synthesis of Dihydropyrimidinones under Solvent-Free Conditions

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A highly sulfonated carbon as an efficient, recyclable, nontoxic and green solid acid catalyst was synthesized readily by simultaneous sulfonation, dehydration and carbonization of sucrose $C_{12}H_{22}O_{11}$ in sulfuric acid and was characterized with Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric and differential thermal gravimetric analysis (TG-DTG), X-ray diffraction (XRD), carbon-hydrogen-nitrogen-sulfur analysis (CHNS), neutralization potentiometric titration and scanning electron microscopy (SEM). This new catalyst was used in one pot three-component condensation reaction of various aromatic aldehydes with β -ketoester and urea under solvent-free conditions to afford the corresponding dihydropyrimidinones (DHPMs). This catalyst can be reused several times without loss of its activity.

Keywords: Solid acid catalyst, Sulfonated carbon, Dihydropyrimidinones, Solvent-free conditions

INTRODUCTION

The dihydropyrimidinone (DHPMs) derivatives have attracted considerable interest in recent years due to promising activities as calcium channel blockers, and as antihypertensive, antibacterial, antitumor and anti-inflammatory agents [1-6]. Additionally, their particular structure have been found in natural marine alkaloid Batzelladine A and B, which are natural products reported in the literature to inhibit the binding of HIV gp-120 to CD4 cells, so disclosing a new field towards the development of AIDS therapy [7]. The original procedure for the preparation of this type of compounds was reported by Biginelli [8], involving one-pot condensation of ethyl acetoacetate, aromatic aldehydes and urea under strongly acidic conditions.

However, this reaction suffers from the harsh conditions,

long reaction times and frequently low yields. In recent years, new methods for preparation of dihydropyrimidinones have been the subject of research for chemists. A number of synthetic procedures based on the modifications of the classical Biginelli's approach have been developed during past few years. Basically, these methods are all similar, using different Lewis acid catalysts. The replacement of environmental hazardous solvents (by solvent free conditions) and catalysts (by the use of solid acid catalysts) are the innovative trends.

In the other hand the preparation of cheap, recyclable and nontoxic strong solid acids also is an attractive area in green chemistry. This kind of solid acids must be as strong, active and stable as sulfuric acid [9-14]. A good material for this purpose should have high stability and numerous strong protonic acid sites. Most commonly used Lewis acids are $BF_3 \cdot OEt_2/CuCl$, $InCl_3$, $NbCl_5$, vanadium(III) chloride, cupric chloride, $LiBr$, $SnCl_2 \cdot CdCl_2$, *N*-bromosuccinimide under

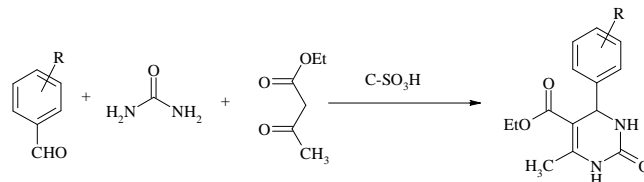
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microwave irradiation, polymer-supported ytterbium(II) reagent, polyphosphate ester, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, BiCl_3 , ZrCl_4 , $\text{La}(\text{OTf})_3$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Bi}(\text{OTf})_3$, natural clays, HEU-type zeolite and HY-zeolite, lithium perchlorate, $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$, RuCl_3 , ferric chloride/tetraethyl orthosilicate, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, iodine-alumina, trimethylchlorosilane, heteropoly acids (HPAs), silica gel supported-sodium hydrogen sulfate, silica sulfuric acid, KHSO_4 as well as Bronsted acids, such as *p*-toluene sulfonic acid, montmorillonite KSF, and methanesulfonic acid [15-55]. Obviously, many of these catalysts are not acceptable in the context of green synthesis. Although many inorganic-oxide solid acids (such as zeolites and niobic acid that provide acidic OH groups) and organic acids (such as cationic exchange resins and perfluorosulfonated ionomers with SO_3H groups as strong acidic sites) have been studied extensively but these materials are expensive and the activity of acidic sites are much lower than liquid inorganic acids. Therefore, the adequate performance in acid-catalyzed reactions, in aqueous media, has not been obtained [56-60].

Highly sulfonated carbon material is a promising solid acid catalyst. However, sulfonation of carbon in concentrated sulfuric acid is very difficult and finally mellitic acid, $[\text{C}_6(\text{COOH})_6]$, is produced. Therefore, the sulfonation of carbon nanotubes has been investigated for preparation of sulfonated carbon, but carbon nanotubes are very expensive and the degree of sulfonation is very low [9]. Okamura *et al.* used *D*-glucose for preparation of sulfonated carbon as a solid acid. First, they pyrolyzed the *D*-glucose and polycyclic aromatic carbon sheets were obtained by heating and then sulfonation was carried out in sulfuric acid under N_2 . This process produces a low density of sulfonic acid groups on carbon sheets [10]. Hara *et al.* used sulfonated naphthalene as starting material and then carbonized the naphthalene sulfonic acid under N_2 . This process is very tedious and time consuming and releases a lot of SO_2 as by-product [11].

Here, we introduce a highly sulfonated carbon material by simultaneous sulfonation, dehydration and carbonization of sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in one step. The obtained catalyst is a highly sulfonated carbon solid acid ($\text{CH}_{0.43}\text{O}_{0.65}\text{S}_{0.22}$) with an amorphous structure.

Due to the importance of Biginelli reaction products, the discovery and introduction of better and milder conditions



Scheme 1. Synthesis of dihydropyrimidinones

using new catalysts has been under attention. Here, we wish to report the use of a highly sulfonated carbon material as a promising alternate solid acid catalyst for preparation of dihydropyrimidinones in the Biginelli-type reactions in one-pot condensation of ethyl acetoacetate, benzaldehyde and urea under solvent free reactions (Scheme 1).

EXPERIMENTAL

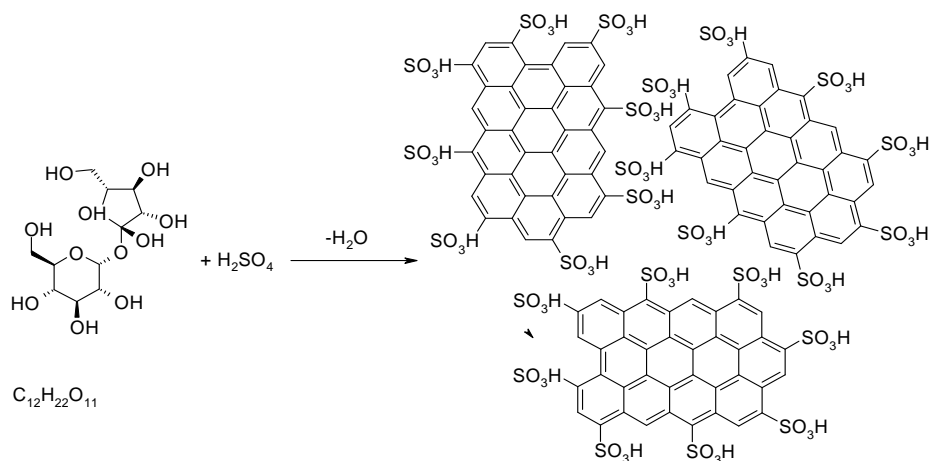
Instruments

Melting points were measured on an Elecrtothermal 9100 apparatus. ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer using TMS as an internal standard (CDCl_3 solution). Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet IMACT 400D instrument. Thermal gravimetric and differential thermal gravimetric analyses (TG-DTG) were carried out using a METTLER TG 50 instrument. X-ray diffraction patterns (XRD) were obtained on a Bruker D8 ADVANCE instrument. Scanning electron microscopy images (SEM) were taken on SEM Philips XL30. The specific surface area and mean pore diameter (dp) were calculated from adsorption isotherms of nitrogen at 77 °K using the standard Brunauer-Emmett-Teller (BET) equation and were obtained on a NOVA 2200, Quantachrome Corporation, Version 7.11 instrument.

Typical Procedure for Preparation of Solid Acid

In a typical procedure for the preparation of highly sulfonated carbon solid acid, 25 g sucrose was ground and gradually added to 75 ml of concentrated H_2SO_4 (98 wt%). The solution was stirred violently and then was heated for 2 h in 523 K. Some of the carbon atoms in hot sulfuric acid were oxidized to CO_2 and a lot of foam was made during heating of mixture, but heating was necessary for decomposition of C-O- SO_3H esters which were produced during the catalyst

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Scheme 2. Preparation of sulfonated carbon

preparation. After then, the product was dried in an oven at 373 K and then heated at 623 K (350 °C) for removing trapped sulfuric acid. After cooling to room temperature, the mixture was filtered on a sintered glass and the solid was washed with distilled water until no sulfate ion was detected in the filtrates by BaCl_2 . The product was dried in an oven at 373 °K and then heated at 623 °K (350 °C) for removing any trapped sulfuric acid. The highly sulfonated carbon solid acid was an amorphous material. The sample was characterized with FT-IR spectrum, TG-DTG analysis, neutralization potentiometric titration, carbon-hydrogen-nitrogen-sulfur analysis (CHNS). A speculative structure of sulfonated carbon sheets have been proposed in Scheme 2.

General Procedure for Preparation of DHPMs under Solvent-Free Conditions

In the solvent-free procedure, a mixture of aromatic aldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea (15 mmol) and sulfonated carbon (50 mg) was heated and stirred at 120 °C in an oil bath for appropriate time according to Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, hot ethanol (10 ml) was added and the reaction mixture was filtrated. The filtrate was poured onto crushed ice and a yellow to white solid was produced, the solid was filtered, washed with cold water and finally crystallized from EtOH or EtOAc:petroleum ether to

afford the pure product.

RESULTS AND DISCUSSION

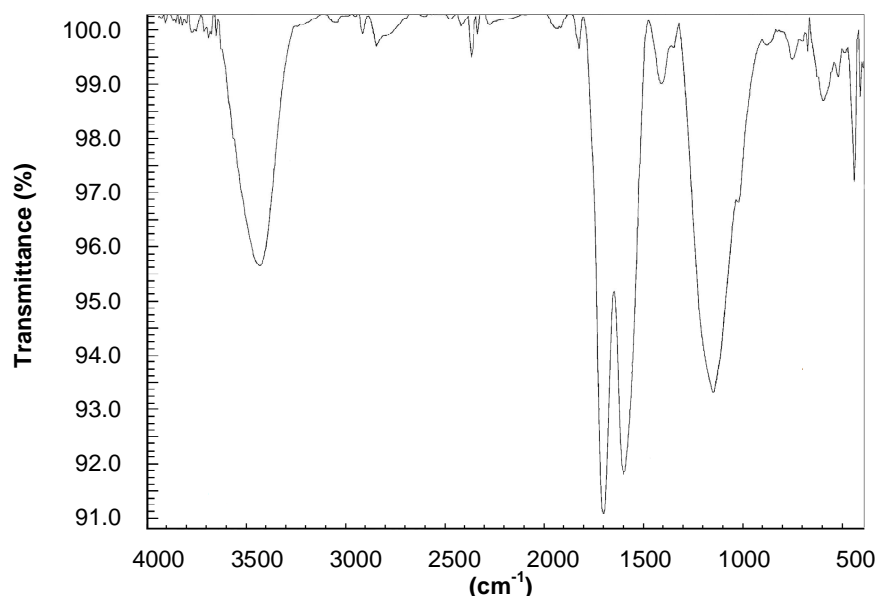
Characterization of Highly Sulfonated Carbon

The FT-IR spectrum of H_2SO_4 -treated sucrose (Fig. 1) shows a broad band at 3300-3500 cm^{-1} , which is assigned to OH groups (3442 cm^{-1}). The strong and sharp bands at 1719, 1613 cm^{-1} and broad band at 1164 cm^{-1} are attributed to the stretching vibration modes of sulfate groups. The strong and sharp bands indicate that sucrose can be easily sulfonated, dehydrated and carbonized for attaching $-\text{SO}_3\text{H}$ groups to geraphen rings with a high density of acid sites.

The density of $-\text{SO}_3\text{H}$ groups on sulfonated carbon was determined by potentiometric titration by NaOH (0.01 N) and it was in agreement with CHNS analysis ($\text{CH}_{0.43}\text{O}_{0.65}\text{S}_{0.22}$). The neutralization titration showed that the amount of SO_3H which is attached to carbon is 7.23 mmol g^{-1} . The BET was 9.25 $\text{m}^2 \text{g}^{-1}$ and the dp was 56 Å. The thermal stability of sulfonated carbon was examined by TG and DTG under a flow of nitrogen at a heating rate of 10 K min^{-1} (Figs. 2 and 3). The results showed that the sample weight decreases as temperature increases. The weight loss of sample is about 94% in the temperature range of 673-804 °K (400-531 °C, peak temperature at 421 °C). These results indicate that the weight loss can be attributed to thermal decomposition of sulfonated

Table 1. Highly Sulfonated Carbon Catalyzed Synthesis of Dihydropyrimidin-2(1H)-ones (DHPMs) under Solvent Free Conditions

Entry	R	Time (min)	Yield (%) ^a	m.p. (°C)	
				Recorded	Reported
1	H	25	95	204	202-203
2	4-Cl	30	96	211	213-215
3	4-NO ₂	30	95	210	209-211
4	2- NO ₂	30	94	218	218-220
5	2-MeO	25	96	258	259-260
6	3-MeO	30	95	207	207-209
7	4-MeO	25	95	203	201-203
8	4-Me	25	96	213	214-215
9	4-Br	30	94	214	213-215
10	4-F	30	93	184	185-186

^aIsolated yields.**Fig. 1.** FT-IR spectrum of sulfonated carbon.

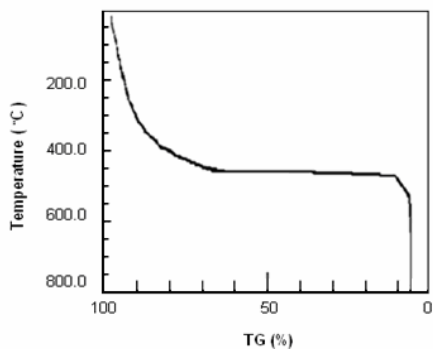


Fig. 2. TG of sulfonated carbon.

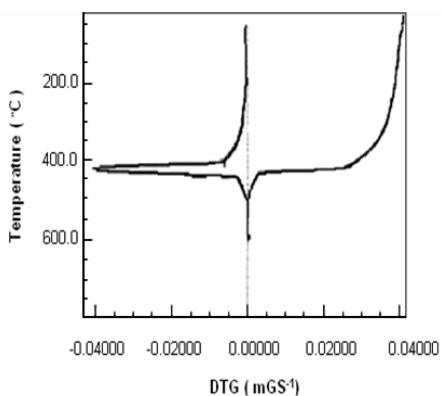
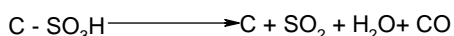


Fig. 3. DTG of sulfonated carbon.



Scheme 3. Thermal decomposition of sulfonated carbon

carbon to C, SO₂, H₂O and CO as shown in Scheme 3.

The XRD pattern (Fig. 4) exhibits two broad and weak diffraction peaks (2θ = 10-30°, 35-50°), which is attributed to amorphous carbon. The X-ray diffractogram is similar to char because the sulfonic acid groups were attached to edges of isotropic carbon sheets and the solid acid exhibits broad diffraction peaks of amorphous carbon.

The SEM image of H₂SO₄-treated sucrose (Fig. 5) reveals the morphology and structure of amorphous carbon. Sample was gold coated prior to scanning.

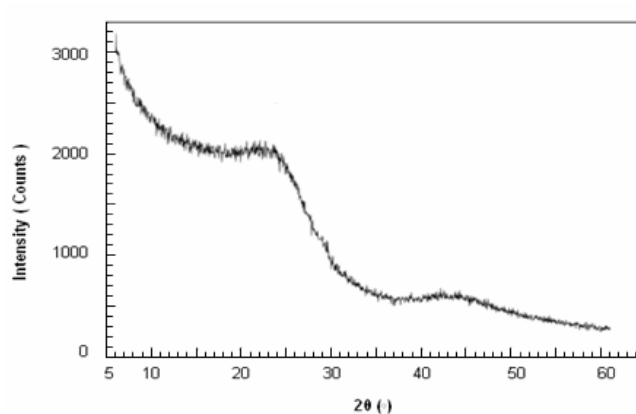


Fig. 4. XRD pattern of sulfonated carbon.

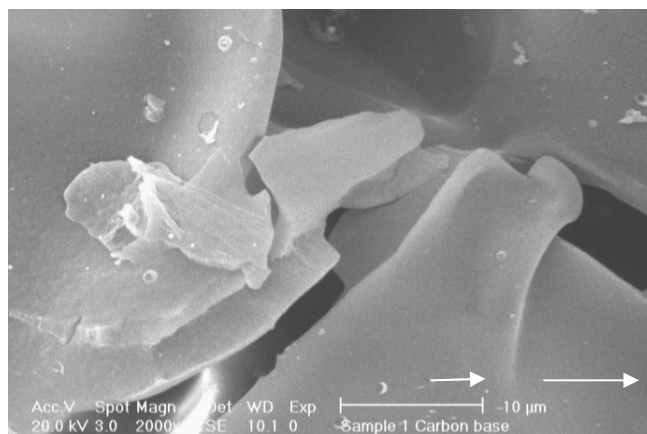


Fig. 5. SEM of sulfonated carbon.

Typical Procedure for Preparation of DHPMs in the Presence of Highly Sulfonated Carbon

First, the catalytic activity of highly sulfonated carbon for synthesis of DHPMs was investigated in the reaction of benzaldehyde with ethyl acetoacetate and urea under solvent free conditions. So a mixture of benzaldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea (15 mmol) and sulfonated carbon (50 mg) was prepared and heated at 120 °C in an oil bath for appropriate time according to Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, hot ethanol (10 ml) was added and the reaction mixture was filtrated. The filtrate was poured onto crushed ice

and a yellow to white solid was produced, the solid was filtered, washed with cold water and finally crystallized from EtOH or EtOAc: petroleum ether to afford the pure product. The results showed that the reaction was completed in 25 min and in the presence of 50 mg of catalyst at 120 °C. No product was obtained when the reaction was carried out at room temperature for a long time. In the absence of catalyst, the reaction did not proceed even at high temperature. Therefore, the reaction of different aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents with ethyl acetoacetate and urea was carried out and the corresponding DHPMs were obtained in excellent yields (Table 1). The results showed that the nature of substituent has no significant effect on the product yield. However, when the aliphatic aldehydes were used as the starting materials, DHPMs were produced in lower yield. A proposed reaction pathway is shown in Scheme 4.

The products were identified by ¹H NMR, and physical data with those reported in the literature [14,15,17,22,24,25, 26-31,52].

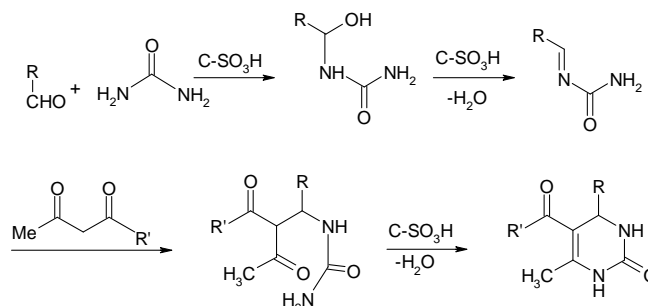
In order to show the versatility and generality of this method, acetylacetone was used instead of ethyl acetoacetate. The results showed that the corresponding DHPMs were obtained in high yield (Table 1, entries 12 and 13).

Reusability of the Catalyst

We found that carbon-based solid acid shows high catalytic activity and could be recovered and recycled several times without significant loss of activity. At the end of each reaction, the catalyst was filtered, washed with hot ethanol and diethyl ether, successively, dried at 180 °C for 1 h, and reused in another reaction. The results showed that this solid acid catalyst can be reused several times (5 times was checked) without loss of its catalytic activity or leaching (Table 2).

Experimental studies about leaching in the beginning were done by boiling carbon-based solid acid in various organic solvents and hot filtration after boiling. In all of these experiments no weight loss or leaching were observed and we confided the carbon-based solid acid is insoluble in organic solvents and no catalyst leaching was detected.

Comparison of this highly sulfonated carbon solid with previously reported acid catalysts in the synthesis of DHPMs showed that the present method is superior in terms of reaction times or product yields and catalyst reusability (Table 3).



Scheme 4. Suggested mechanism

Table 2. The Reusability of the Highly Sulfonated Carbon Catalyst in Solvent-Free Synthesis of DHPMs^a

Recycling No.	1	2	3	4
Yield (%) ^b	95	95	94	95

^aReaction conditions: benzaldehyde (10 mmol), ethyl acetoacetate (10 mmol), urea (15 mmol), catalyst (50 mg), time (24 min). ^bIsolated yield.

CONCLUSIONS

In comparison with other solid acid catalysts, this sulfonated carbon showed very high density of acidic sites on the amorphous carbon. Our procedure is very easy and simple that produces stable, cheap, insoluble, recyclable and environmentally friendly strong solid acid. The sulfonated carbon has a good potential replacement for sulfuric acid in catalytic reactions which can be attributed to high density of SO₃H groups with strong acidity. In the other hand, carbon-based solid acid is superior in term of toxicity [LD₅₀]. The LD₅₀ (Lethal Dose, 50%) for carbon-based solid acid is comparable with cationic exchange resins with sulfonic acid functional groups. This catalyst can be an effective catalyst for the formation of DHPMs with excellent yields. The uses of this inexpensive and easily available catalyst under solvent free conditions make this protocol practical and economically attractive. The simple workup procedure, mild reaction conditions, excellent yields make our methodology a valid contribution to the existing processes in the field of DHPMs derivatives synthesis.

Table 3. Comparison of Catalytic Activity of other Lewis Acids with Carbon-Based Solid Acid under Various Conditions^a

Lewis acid	Time (h)	Yield (%) ^b	Solvent	Ref.
Carbon-based solid acid	0.45	95	-	Present work
<i>p</i> -Toluenesulfonic acid	0.05	93	-	[34]
Sr(NO ₃) ₂	6	77.8	AcOH	[24]
HBF ₄	0.6	95	-	[50]
Silica sulfuric acid	6	91	EtOH	[51]
Natural HEU Zeolite	5	75	AcOH	[48]
HCl	24	50	EtOH	[54]
Phenylboronic acid	18	87	Acetonitrile	[16]
12-Molybdophosphoric acid	5	80	AcOH	[55]
12-Tungstophosphoric acid	6	75	AcOH	[20]
Iodine	4	95	Toluene	[39]
Nano CeO ₂ /Vinylpyridine	4.5	92	H ₂ O	[36]
Anchored sulfonic acid on SiO ₂	8	90	Acetonitrile	[50]
FeCl ₃ /Si(OEt) ₄	3	88	Isopropanol	[41]
Nafion NR-50	3	96	Acetonitrile	[48]

^aReaction mixture: benzaldehyde, ethyl acetoacetate, urea and catalyst. ^bIsolated yield.

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