



# Synthesis of Starch Derived Sulfonated Carbon-based Solid Acid as a Novel and Efficient Nanocatalyst for the Synthesis of Dihydropyrimidinones

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## ABSTRACT

Novel Carbon-based solid-acid nanocatalyst (SCP-SO<sub>3</sub>H) has been synthesized via one-step hydrothermal carbonization and sulfonation of starch, citric acid, and p-toluenesulfonic acid at 180 °C in a sealed autoclave. The novel nanocatalyst had an acidity of 6.4 mmol/g which was characterized by IR, EDX, TEM, FESEM, and XRD analyses. The catalytic activity of the carbonaceous material as an efficient and reusable catalyst was investigated by the condensation reaction of ethyl acetoacetate, aldehyde and urea for the synthesis of Dihydropyrimidinones. The condensation reaction was carried out under solvent-free conditions at 100 °C to produced Dihydropyrimidinones in good to high yields. The mild conditions, eco-friendly, excellent yields, short reaction times and using an inexpensive and reusable catalyst are important features of this method.

**Keywords:** multicomponent reaction, carbonaceous nanocatalyst, starch, hydrothermal carbonization, dihydropyrimidinone

## 1. INTRODUCTION

Reactions whereby three or more different components are combined in one reaction vessel, leading to the formation of a single product, are summarized under the term multicomponent reactions (MCRs) [1-4]. Recently, MCRs have Multicomponent reactions (MCRs) promote the formation of several bonds in one operation with remarkable advantages, such as simple procedure, multiple-bond-forming efficiency, time and energy savings, easy extraction and

purification processes, and minimized waste generation [5]. The Biginelli reaction is ranked as one of the most powerful MCRs for the synthesis of the dihydropyrimidinone (DHPM) scaffold.

The Biginelli reaction was first reported more than a century ago and recently reviewed; [6] it involves the synthesis of 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) by multicomponent cyclocondensation reaction of ethyl acetoacetate, benzaldehyde,

and urea. They possess a broad spectrum of pharmacological activities such as antiviral, anti-inflammatory, antibacterial, anticarcinogenic, antihypertensive, antagonists, neuropeptide Y (NPY) antagonist, and calcium channel blockers [7]. In order to improve the efficiency of Biginelli reaction, several new and modified procedures in the presence of various catalysts have been studied including of Lewis acid catalysts such as  $\text{BF}_3 \cdot \text{OEt}$  [8], tetrabutylammonium bromide (TBAB) [9], In (III) halides [10], solid phase [11],  $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$  [12], ionic liquids [13], polymer support [14], polystyrene poly(ethylene glycol) sulfuric acid (PS-PEG- $\text{SO}_3\text{H}$ ) [15], phenyl phosphonic acid [16],  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  [17],  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  [18],  $\text{ZrCl}_4$  [19],  $\text{LiBr}$  [20],  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  [21],  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  [22],  $\text{FeCl}_3/\text{Si}(\text{OEt})_4$  [23], BPMO-IL- $\text{SO}_3\text{H}$  [24], bentonite/PS- $\text{SO}_3\text{H}$  [25], p-sulfonic acid calixarenes [26], Nafion-Ga [27], metal triates such as  $\text{Zn}(\text{OTf})_2$  [28],  $\text{Cu}(\text{OTf})_2$  [29],  $\text{Yb}(\text{OTf})_2$  [30] and  $\text{Bi}(\text{OTf})_2$  [31], TMSI [32], Polyoxometalates (POMs) [33],  $\text{SbCl}_3$  [34],  $\text{HClO}_4\text{-SiO}_2$  [7], Im-MNPs [6],  $\text{TiO-CNTs}$  [35], HPAILs-MWI [5], ASA NPs [36]. Most of these available protocols suffer from several drawbacks such as a long reaction times, low product yields, an excess of organic solvent, harsh reaction conditions, occurrence of several side products and difficulty in recovery and reusability of the catalysts. Due to these problems, the development of novel, efficient, and versatile catalytic systems for the Biginelli reaction is an active ongoing research area. Hence, there is a scope for exploration of synthetic methodology to achieve milder reaction conditions, variations of substituents in all three components, and better yields.

The solid acid catalysts have received much attention for the potential substitution of the homogeneous acids with the advantages of easy separation and reusability [37]. Integration of acidic functional groups

(e.g.,  $-\text{SO}_3\text{H}$ ) into solid surface, e.g. carbonaceous or silica-based materials, has been explored to produce promising solid acids [38]. Among them, the sulfonated carbon materials have received much attention due to their low costs, high stability, and high activities. Sulfonated ( $\text{SO}_3\text{H}$ -bearing) carbon materials have been reported to act as strong solid acid catalysts [39]. In recent years, carbon material has become a hot research area, and carbon-based sulfonated catalysts (CBSCs) are developing rapidly. All of the CBSCs contain carbon skeleton and  $-\text{SO}_3\text{H}$  group, and the carbon skeleton is stable and insoluble in most acidic/basic conditions as well as organic solvents. Here, for the first time, we report a facile procedure for the synthesis of novel carbon-based nanocatalyst through hydrothermal process. Starch, citric acid, and p-toluenesulfonic acid (PTSA) were used as the raw materials. Since the use of PTSA, great amount of  $-\text{SO}_3\text{H}$  groups were introduced into the resulted carbon based solid acid. Thus the prepared acidic carbon was denoted as SCP- $\text{SO}_3\text{H}$ . The catalytic activity of SCP- $\text{SO}_3\text{H}$  was investigated in the synthesis of DHPMs through the Biginelli three-component condensation.

## 2. MATERIALS AND METHODS

### 2.1 Materials and Instruments

All chemicals were purchased from Merck Chemical Companies. All the reagents and chemicals were obtained from Merck and used without further purification. The development of the reactions was monitored by TLC on Merck pre-coated silica gel 60 F254 aluminum sheets, visualized by UV light. IR spectra was recorded on a Shimadzu FT-IR 8300 Spectrophotometer using the KBr pellets technique. The known products were identified by comparison of their melting points and spectral data with

those reported in the literature.  $^1\text{H}$  NMR spectra was recorded at ambient temperature on a BRUKER AVANCE DRX-400 MHz spectrophotometer using  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. XRD patterns were recorded by the X-ray diffractometer (Philips-PW1800). The particles size and external morphology of the catalyst were studied by a field emission scanning electron microscope (FESEM, Mira 3-XMU) with an accelerating voltage at 10 Kv and Transmission Electron Microscope (TEM, Zice EM900). Using the EDX system, one can calculate the elemental analysis, such as, the weight and atomic percent of the existing elements.

## 2.2 Synthesis of the SCP-SO<sub>3</sub>H

A mixture of starch (5 g), citric acid (2.5 g) and p-toluenesulfonic acid (2 g) in deionized water (40 mL) was placed in a 100 mL Teflon-sealed autoclave and maintained at 180 °C for 9 h. The resulting black-brown reaction mixture was cooled to room temperature. Distilled water (10 mL) and methanol (10 mL) were added to the black-brown suspension, and the suspension was filtered to remove the supernatant. The residue was washed with methanol (30 mL  $\times$  3 times) to provide black-brown carbon sphere and then oven-dried at 90 °C overnight. As a comparison, 2 g of starch was also treated in the similar way and was denoted as Sta-180.

## 2.3 General Procedure for the Synthesis of Dihydropyrimidinones

To a mixture of ethyl acetoacetate (1 mmol), aldehyde (1 mmol) and urea (1.5 mmol) was added SCP-SO<sub>3</sub>H nanocatalyst (0.07 g). The reaction mixture were stirred at room temperature. After the reaction was completed, as indicated by TLC analysis (Cyclohexane-Ethyl acetate (3:1) as

eluent), the reaction mixture was treated with hot EtOH and filtered. The filtrate was crystallized in EtOH/H<sub>2</sub>O to afford the desired dihydropyrimidinone product. All products were characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data and by comparison with melting points of the reported compounds.

## 3. RESULTS AND DISCUSSION

Carbon-based materials include sulfonic acid (SO<sub>3</sub>H) groups as solid acid catalysts are especially attractive catalysts due to their low cost, metal-free composition, and expected high stability and strong acidity.

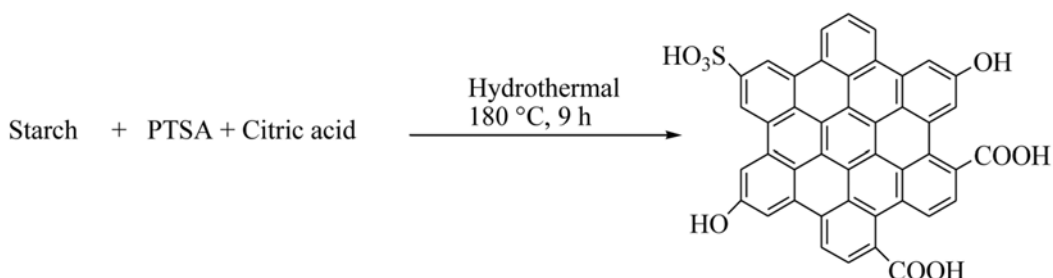
In the following, in according to application of heterogeneous catalyst [37, 40-43], we will disclose our preliminary investigation on the synthesis of a novel carbon-based solid acid (SCP-SO<sub>3</sub>H) nanocatalyst and its application in the multicomponent and solvent-free preparation of various dihydropyrimidinone derivatives.

### 3.1 Characterization of SCP-SO<sub>3</sub>H

SCP-SO<sub>3</sub>H was prepared by simultaneously carbonization and sulfonation of starch via hydrothermal-treated (180 C, 9 hr) in the presence of PTSA and citric acid. Acid-base back titration was used for determination of acidity of SCP-SO<sub>3</sub>H. The total acidity was 6.4 mmol/g. The elemental analysis presented the results: C 67.77%; H 3.666%; S 0.406%. The results have indicated that almost all the elements S existed in the catalyst, in the form of sulfonic groups. If all sulfur elements in the catalyst were assumed as -SO<sub>3</sub>H groups, the acid site densities of the catalyst were 0.5-2 mmol H<sup>+</sup>/g depending on the synthetic conditions. But the acid titration experiments demonstrated much higher acid site densities than the estimations based on the sulfur elemental analysis. The reason is that abundant phenolic -OH and -COOH groups were

generated in the process of partial oxidation of starch. According to the reported carbon-based solid acid, the proposed carbon

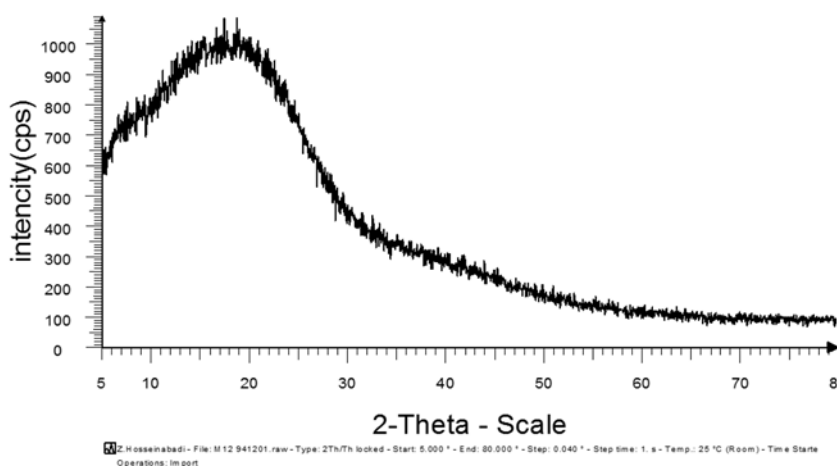
structure is schematically illustrated in Scheme 1 [44].



**Scheme 1.** Synthesis of SCP- $\text{SO}_3\text{H}$  and proposed structure for the catalyst.

The SCP- $\text{SO}_3\text{H}$  sample has a broad and so weak XRD pattern (shown in Figure 1), confirming that the SCP- $\text{SO}_3\text{H}$  is still amorphous and far from the graphitic carbon [45]. Two broad and diffuse peaks at 2 angles of 20-30° and 40-50° are due to carbon (0 0 2) and (1 0 0) reflections, respectively. These diffraction patterns reflect that SCP- $\text{SO}_3\text{H}$  is an amorphous carbon composed of aromatic carbon sheets oriented

in a considerably random fashion. Structurally, the carbon framework of SCP- $\text{SO}_3\text{H}$  is approximately consistent with the others reported in the literature [46, 47]. Nevertheless, the peaks of the 0 0 2 and 1 0 0 reflections are changed slightly in their position and shape. This may be due to the differences in carbonization mechanisms of starch and other carbohydrates, which impact the size and orientation degree of graphite crystallite.



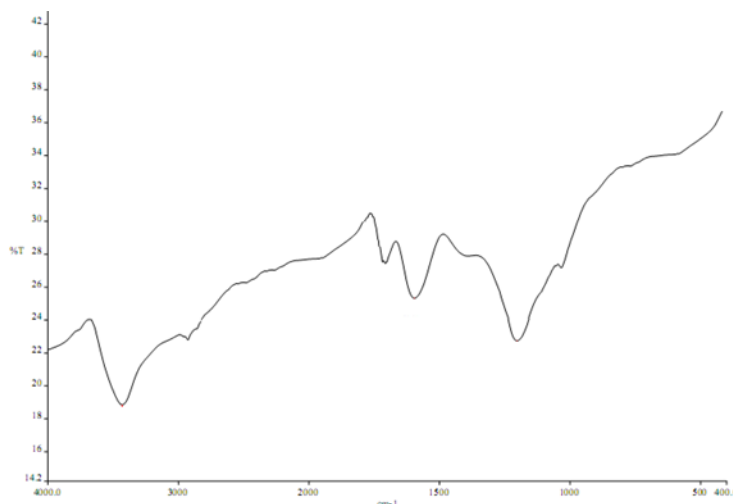
**Figure 1.** XRD patterns of the SCP- $\text{SO}_3\text{H}$  nanocatalyst.

The IR spectrum of the SCP- $\text{SO}_3\text{H}$  is shown in Figure 2. Compared to the carbon from the single Starch, the absorbance at  $1046\text{ cm}^{-1}$  confirmed the existence of the sulfonic acid groups. This indicates that the

$\text{SO}_3\text{H}$  groups were successfully incorporated into the carbon framework by adding p-toluenesulfonic acid in the synthesis system. The strong absorbance at  $1704\text{ cm}^{-1}$  indicated the existence of carboxylic acid

groups. Therefore, both the sulfonic acid and carboxylic acid groups existed in carbon. On the other hand, the bands due to -OH stretching at  $3420\text{ cm}^{-1}$ , C=O stretching at

$1710\text{ cm}^{-1}$  and C=C bonds stretching at  $1620\text{ cm}^{-1}$  were observed for both SCP-SO<sub>3</sub>H and Sta-180 samples independent of the sulfonation.

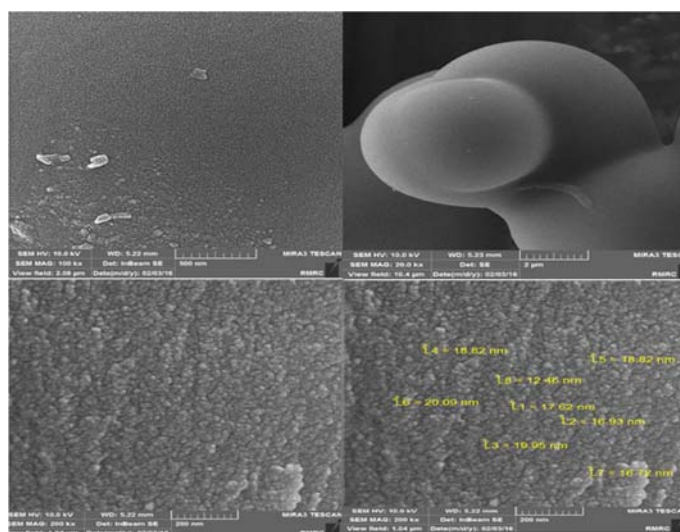


**Figure 2.** The IR spectrum of the SCP-SO<sub>3</sub>H (top) and the Sta-180 (bottom).

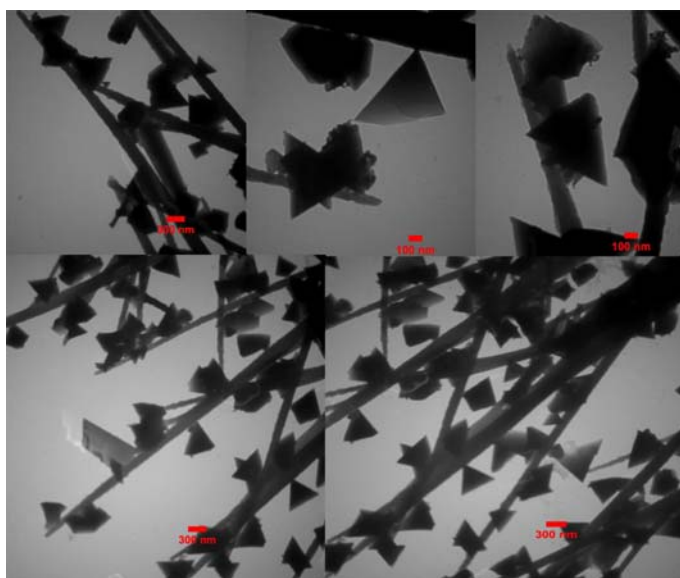
Figure 3 and 4 have shown the TEM and FESEM images of the novel acid carbon. The morphology of the novel solid acid was characterized by FESEM and representative images are illustrated in Figure 3. The sample was gold coated before scanning. As shown in Figure 4, the images of TEM show the particle size at the micro-level. But when the images of the FESEM are examined, it is observed that SCP-SO<sub>3</sub>H surface was found to be composed of nonspherical and irregular grains of <20-nm size and there are many bumps on the surface of the catalyst particles on the nanoscale, in which bumps

increase the surface-to-volume ratio. In fact, the catalyst surface can be considered as a Nano-pattern. According to this description, it can be said that this nanoscale model increases the speed required to carry out for the reaction and reduce the time required.

Figure 3 also shows the morphologies of the materials, micrometer-sized, microporous carbon spheres with the smooth surface, which was quite different from the amorphous structures of the sulfonated carbonaceous materials. The carbon spheres structure also made the recycle of the material very simple and the filtration was enough without suspension in the reaction mixture [48].



**Figure 3.** FESEM image of SCP-SO<sub>3</sub>H nanocatalyst.



**Figure 4.** TEM images of SCP-SO<sub>3</sub>H nanocatalyst.

Figure 5 shows the EDX images of the catalyst. These images are used to obtain the percentage of elements in the sample. As shown in the table 1, the presence of

sulfur and oxygen in the corresponding catalyst confirms the presence of SO<sub>3</sub>H and COOH acid groups.

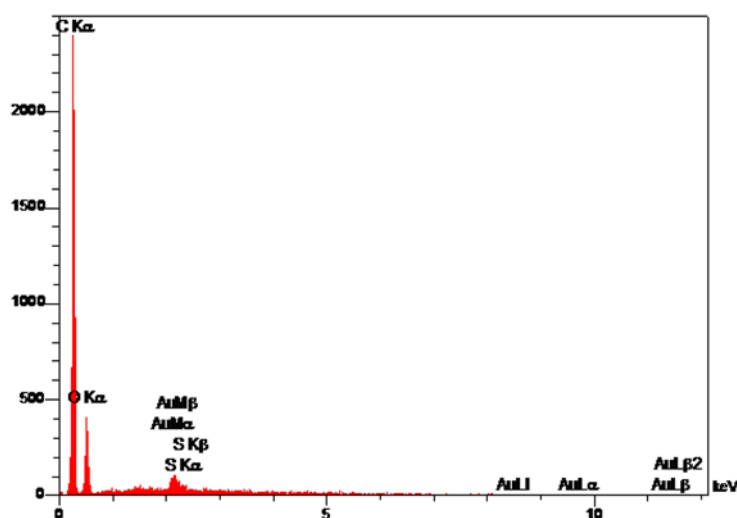


Figure 5. EDX image of SCP-SO<sub>3</sub>H nanocatalyst.

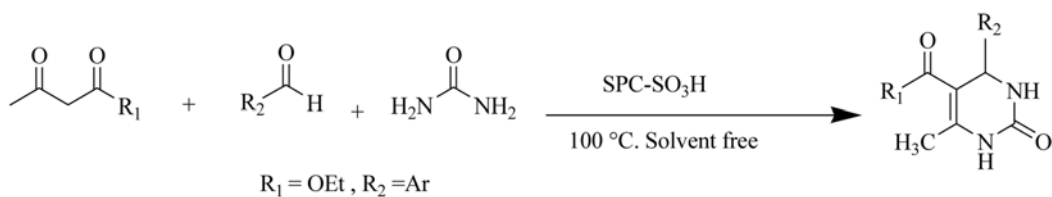
Table 1. Percentage of the elements in the catalyst using the EDX analysis.

Entry	C Wt%	O Wt%	S Wt%	Au Wt%
1	69.94	24.12	0.29	5.65

### 3.2 Catalytic Studies

Characterizations showed that the acid site densities of the novel carbon-based nanocatalyst were 6.4 mmol H<sup>+</sup>/g. The excellent acidity encouraged us to explore

the potential of this catalytic system for the synthesis of various 3,4-dihydropyrimidin-2(1H)-ones using ethyl acetoacetate, aldehyde and urea under solvent free conditions (Scheme 2).



Scheme 2. Synthesis of dihydropyrimidinones.

A series of trial reactions were performed with a combination of ethyl acetoacetate, aldehyde and urea to obtain reaction conditions. Initially, the cyclocondensation under solvent-free conditions was considered as a standard model reaction to determine the optimum conditions (Table 2). First, when the reaction was carried out in the absence of the catalyst at 100 °C for 3 h, only 10% yield of desired dihydropyrimidinone was obtained (Table 2,

entry 1), whereas the rate and yield of the reaction both increased dramatically in the presence of SCP-SO<sub>3</sub>H (Table 2, entry 2). The results revealed that the catalyst can be essential for the Biginelli reaction. At the same time it was shown that the yield of the reaction increased when heating at 100 °C (Table 2, entry 2), but there was no appreciable change at higher temperature (120 °C) (Table 2, entry 3).



**Table 2.** Optimization of the reaction conditions for the synthesis of dihydropyrimidinones.<sup>a</sup>

Entry	Solvent	Catalyst (gr)	Temperature	Time (min)	Yield (%)
1	-	-	100	180	10
2	-	0.05	100	120	69
3	-	0.05	120	120	69
4	-	0.05	80	120	60
5	-	0.05	R.T	120	25
6	-	0.07	100	120	78
7	-	0.1	100	120	78
7	-	0.03	100	120	50
8	H <sub>2</sub> O	0.07	reflux	120	55
9	ETOH	0.07	reflux	120	53
10	Ethyl acetate	0.07	reflux	120	52
11	<i>n</i> -Hexane	0.07	reflux	120	45

<sup>a</sup> Conditions: benzaldehyde (1 mmol), urea (1.5 mmol), and ethyl acetoacetate (1 mmol).

In the screening test of optimum catalyst concentration, it was found that using 0.07 gr of Nanocatalyst (Table 2, entry 6) could present the best result in which greater amount of the catalyst did not obviously improve the result (Table 2, entry 7).

Using the optimal reaction conditions, several solvents were screened prior to conclude in which reactions carry out without any solvent (Table 2).

Thus, the optimum conditions for

the synthesis of highly substituted dihydropyrimidinone were achieved by treatment of aldehyde (1 mmol), urea (1.5 mmol), and ethyl acetoacetate (1 mmol) in the presence of nanocatalyst (0.07 g) at 100 °C under solvent-free conditions.

To examine the substrate scope of this catalyzed Biginelli reaction, a variety of aromatic aldehydes were subjected to react with 1, 3-dicarbonyl compounds and urea under these optimized reaction conditions.

The results are summarized in Table 3.

**Table 3.** Synthesis of dihydropyrimidinones using SCP-SO<sub>3</sub>H Nanocatalyst. <sup>a</sup>

Entry	R <sub>1</sub>	R <sub>2</sub>	Time (min)	Yield <sup>c</sup> (%)	m.p. □C	
					Found	Reported [Ref.]
1	OEt	C <sub>6</sub> H <sub>5</sub>	120	78	202-204	206 [49]
2	OEt	4-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	120	90	200-202	201-202 [35]
3	OEt	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	120	89	192-194	191-193 [35]
4	OEt	4-Cl-C <sub>6</sub> H <sub>4</sub>	130	82	210-212	214-216 [50]
5	OEt	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	130	75	209-211	208-210 [35]
6	OEt	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	130	78	205-209	206-208 [35]
7	OEt	3,4-di-CH <sub>3</sub> O-C <sub>6</sub> H <sub>3</sub>	120	84	173-175	174-176 [49]
8	OEt	2,4-di-Cl-C <sub>6</sub> H <sub>3</sub>	120	77	249-250	248-250 [35]
9	OEt	4-F-C <sub>6</sub> H <sub>3</sub>	130	80	183-185	182-184 [35]

<sup>a</sup> Conditions: aldehyde (1 mmol), urea (1.5 mmol), ethyl acetoacetate (1 mmol), SCP-SO<sub>3</sub>H (0.07 gr), at 100 °C under solvent free conditions. <sup>b</sup> All compounds were characterized by 1H-NMR, 13C-NMR, IR. <sup>c</sup> Isolated yield.



In all cases, the reaction proceeded smoothly to afford the corresponding DHPMs in good to excellent yields (75-90%). A wide range of aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents at different positions afforded good yields of DHPMs in high purity (Table 3, entries 2-9). Meanwhile, condensation was compatible with a variety of functional groups including methoxy, methyl, chloro, fluoro, and nitro. Also, both of aromatic aldehydes bearing electron-donating groups such as OMe

(entries 2) and electron-withdrawing groups such as NO<sub>2</sub> (entries 5, 6) had excellent yields.

In order to show the merit of the present work in comparison with recently reported protocols, we compared the results of the reaction of ethyl acetoacetate (1 mmol), 4-Methoxybenzaldehyde (1 mmol) and urea (1.5 mmol) in the presence of various catalysts (Table 4). The results show that SCP-SO<sub>3</sub>H promotes the reactions effectively as far the amount of catalyst and reaction times are concerned.

**Table 4.** Comparison of different catalysts for synthesis of dihydropyrimidinones.

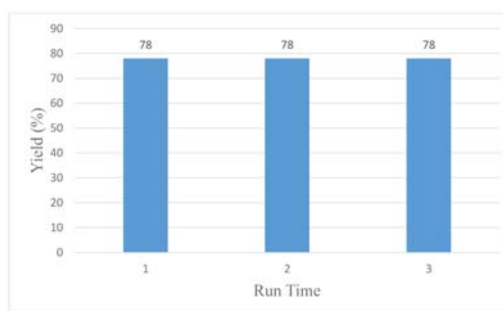
Entry	Catalyst	Solvent/ Temperature	Reaction time	% Yield <sup>ref.</sup>
1	SCP-SO <sub>3</sub> H	None/ 100	120 min	90
2	Cu(OTf) <sub>2</sub> -MW	EtOH/ 100	60 min	Quantitative [51]
3	SG-NH <sub>2</sub> -AcPy-Ni-MW	None / rt	5 min	94 [52]
4	HClO <sub>4</sub> -SiO <sub>2</sub>	None / rt	90 min	90 [7]
5	Im-MNPs	None / 80	30 min	91 [6]
6	TiO-CNTs	EtOH/ 100	35 min	94 [35]
7	HPAILS-MWI	None / 120	5 min	96 [5]
8	ASA NPs	None / 120	25 min	94 [36]

<sup>a</sup> Reaction conditions: Conditions: 4-Methoxybenzaldehyde (1 mmol), urea (1.5 mmol), ethyl acetoacetate (1 mmol).

<sup>b</sup> Isolated yields

The reusability of the catalyst is one of the most important element for commercial feasibility; therefore, the recovery and reusability of Sta-SO<sub>3</sub>H was investigated in the reaction of ethyl acetoacetate, benzaldehyde and urea for 120 min, at 100 °C under solvent-free conditions, and the results are shown in Figure 6. The separated catalyst can be reused after washing with ethyl acetate and drying at 80 °C. The catalyst was recovered in good yields and it was used in the mentioned reaction for three

successive reactions without significant loss of activity (Figure 5).



**Figure 6.** The reuse of the catalyst.

#### 4. CONCLUSIONS

The novel carbonaceous nanocatalyst (SCP-SO<sub>3</sub>H) has been synthesized via one-step hydrothermal carbonization and sulfonation of starch, citric acid and PTSA just for 9 h. The carbon had high acidity with both sulfonic and carboxylic acid groups. The novel process was more environmental friendly in the mild conditions with little waste emission and high yields. Here, we have found that the formation of dihydropyrimidinones is possible in the presence of this carbonaceous materials a nanocatalyst by the condensation reaction of ethyl acetoacetate, aldehyde and urea under solvent free conditions at 100 °C in good to high yields. Operational simplicity, low cost of the catalyst used, high stability, high activity, and reusability are the key features of the novel acid carbon, which indicated that carbon holds great potential for green processes.

#### Spectral data of some selected products:

**Ethyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (Table 2, entry 1)** White solid. Mp: 202-204 °C; IR (KBr): 3244, 3109, 2933, 1710, 1650, 1222, 1089 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 9.20 (s, 1H), 7.74 (s, 1H), 7.35-7.30 (m, 2H), 7.25-7.21 (m, 3H), 5.15 (d, J=3.0 Hz, 1H), 3.98 (q, J=7.0 Hz, 2H), 2.25 (s, 3H), 1.09 (t, J=7.0 Hz, 3H).

**Ethyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 1)** Mp: 202-204 °C; IR (KBr): 3230, 3120, 1730, 1710, 1650 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 1.11 (t, J = 7.5 Hz, 3H), 2.29 (s, 3H), 4.00 (q, J = 7.5 Hz, 2H), 5.29 (d, J = 3.0 Hz, 1H), 7.51 (d, J = 10 Hz, 2H), 7.91 (s, 1H), 8.23 (d, J = 8.76 Hz, 2H, ArH CH), 9.37 (s, 1H, NH).

**Ethyl-6-methyl-4-(4-methylphenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 1)** Mp: 202-204 °C; IR (KBr): 3326, 3152, 1691, 1562, 1232, 1051, 783 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 1.12 (t, J = 7.5 Hz, 3H), 2.28, 2.30 (s, 3H), 4.00 (q, J = 7.5 Hz, 2H), 5.11 (d, J = 3.0 Hz, 1H), 7.25 (m, 4H), 7.70 (br s, 1H, NH), 9.19 (br s, 1H, NH).

**Ethyl-6-methyl-4-(4-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 2, entry 1)**

Mp: 202-204 °C; IR (KBr): 3220, 3100, 1720, 1700 cm<sup>-1</sup>; <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ: 1.10 (t, J = 7.2 Hz, 3H), 2.22 (s, 3H), 3.96 (q, J = 7.2 Hz, 2H), 5.02 (s, J = 3.2 Hz, 1H), 6.64 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 7.57 (s, 1H), 9.07 (s, 1H).

#### ACKNOWLEDGEMENTS

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