Sulfonated Carbon Catalyzed Biginelli Reaction for One-Pot Synthesis of 3,4-Dihydropyrimidin-2(1*H*)-ones and -thiones

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Abstract: A sulfonated carbon material was shown to be a highly efficient, eco-friendly, and recyclable solid acid catalyst for the Biginelli reaction of β -ketoester, aldehyde, and urea or thiourea under solvent-free conditions. It gave 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones in good to excellent yields. This method has the advantages of a simple procedure with easy work-up, short reaction time, and high yields. The catalyst can be recycled after a simple work-up and was reused four times without substantial reduction in activity.

Key words: sulfonated carbon; solid acid; Biginelli reaction; heterogeneous catalysis; solvent-free condition

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The Biginelli synthesis is an easy and useful multicomponent reaction that is gaining increasing importance in organic and medicinal chemistry for its generation of multifunctionalized products, including 3,4-dihydropyrimidin-2(1*H*)-ones and their thione analogs and other related heterocyclic compounds [1,2]. Dihydropyrimidinones and thiones are important for their therapeutic and pharmacological properties. They are used in several calcium channel blockers [3], antihypertensive drugs [4], α_{1a} -adrenergic antagonists [5], and neuropeptide antagonists [6]. Recently, dihydropyrimidinones have also been considered for the development of new anticancer drugs [7]. In addition, their special structure has been found in natural marine alkaloid batzelladines, which are the first low molecular weight natural products reported in the literature that inhibits the binding of HIVgp-120 to CD4 cell. This could be a new path for the development of AIDS therapy [8,9]. Thus, the efficient synthesis of these heterocyclic compounds has been of great interest in recent years.

The most straightforward procedure for the preparation of dihydropyrimidinones and thiones is by condensation of β -dicarbonyl compounds with an aromatic aldehyde and urea or thiourea in the presence of Lewis and Brønsted acid promoters such as concentrated H₂SO₄ [10], HEU type zeolite [11], InBr₃ [12], CuI [13], [bmim][FeCl₄] [14], trichloroisocyanuric acid (TCCA) [15], M(NTf₂) (M = Ni, Cu, Yb) [16], Fe(ClO₄)₃ [17], RuCl₃ [18], ZrCl₄ [19,20], ZrOCl₂ [20], H₃PMo₁₂O₄₀ [21], and H₃PW₁₂O₄₀ [21,22]. However,

many of the reported one-pot protocols involved long reaction time and have unsatisfactory yields, cumbersome product isolation procedures, use of harmful organic solvents, expensive reagents, stoichiometric amounts of catalysts, strongly acidic conditions, and environmental pollution. Due to the importance of the Biginelli reaction, the introduction of milder, faster, and greener methods with higher yields is needed.

The replacement of conventional toxic and polluting Brønsted and Lewis acid catalysts with environmentally benign and reusable solid catalysts is an active area of research. Solid acid catalysts have the advantages of ease of product separation, recycling of the catalyst, and environmental compatibility as compared to liquid acid catalysts [23–26]. Sulfonated carbon materials (SCMs) as solid acid catalysts have many advantages. They are insoluble in common organic solvents, hardly cause corrosion, and have environmental compatibility. Also, the products can be easily separated from the reaction mixture and the catalyst is recoverable without loss in activity. They have been successfully used to replace sulfuric acid as catalysts [27–31].

There is no example on the use of SCMs as catalyst for the synthesis of dihydropyrimidinones and thiones. In a continuation of our previous works on the applications of reusable catalysts in the synthesis of organic compounds [32–41], we report here a novel, heavy metal-free, and recyclable catalyst SCM for the efficiently synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones (Scheme 1).

Scheme 1. Biginelli reaction catalyzed by SCM.

1 Experimental

1.1 Preparation of SCM

The SCM was prepared according to the procedure reported by Hara et al. [31]. Naphthalene (20 g) was heated in concentrated sulfuric acid (> 96%, 200 ml) at 250 °C under a flow of N₂. After heating for 15 h, excess sulfuric acid was removed from the dark brown tar by vacuum distillation at 250 °C for 5 h, which resulted in a black solid. The solid was then ground to a powder and was washed repeatedly in boiling water until impurities such as sulfate ions were no longer detected in the wash water. The density of the SO₃H groups was measured using NaOH (0.01 mol/L) as titrant by acid-base potentiometric titration. The amount of SO₃H attached to the polycyclic aromatic carbon was 2.84 mmol/g. The resulting black powder was insoluble in solvents such as water, methanol, ethanol, benzene, and hexane even at their boiling temperatures.

1.2 General procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones

A mixture of β-ketoester (**1**, 4 mmol), an aldehyde (**2**, 4 mmol), urea or thiourea (**3**, 5 mmol), and SCM (0.1 g) was heated in the oil bath at 140 °C for the appropriate time. The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and hot ethanol was added. The catalyst was insoluble in hot ethanol and it could therefore be recycled by simple filtration. The separated catalyst was washed with cold ethanol, dried at 60 °C under vacuum for 1 h, and was re-used. The product was collected from the filtrate after cooling to room temperature and recrystallized from the ethanol to give compounds **4a–4t**.

Melting points were recorded with an electrothermal Type 9100 melting point apparatus. The infrared (IR) spec-

tra were obtained using a 4300 Shimadzu spectrophotometer and KBr disks. The ¹H NMR (500 MHz) spectra were recorded with a Bruker DRX500 spectrometer.

4a (R = Me, R' = 3-BrC₆H₄, X = O). ¹H NMR (500 MHz, DMSO-d₆): δ 1.10 (t, 3H, *J* = 7.0 Hz, CH₃), 2.25 (s, 3H, CH₃), 3.95–4.05 (m, 2H, CH₂), 5.14 (d, 1H, *J* = 3.2 Hz, CH), 7.23 (d, 1H, *J* = 7.7 Hz, arom-H), 7.31 (t, 1H, *J* = 7.8 Hz, arom-H), 7.39 (s, 1H, arom-H), 7.45 (dt, 1H, *J* = 7.9, 0.9 Hz, arom-H), 7.77 (s, 1H, NH), 9.25 (s, 1H, NH); IR (KBr, cm⁻¹): ν 3238 (NH), 3114 (NH), 1706 (C=O), 1654 (C=O).

4c (R = Me, R' = 4-ClC₆H₄, X = O). ¹H NMR (500 MHz, DMSO-d₆): δ 1.09 (t, 3H, *J* = 7.1 Hz, CH₃), 2.25 (s, 3H, CH₃), 3.95–4.05 (m, 2H, CH₂), 5.15 (d, 1H, *J* = 3.2 Hz, CH), 7.25 (d, 2H, *J* = 7.7 Hz, arom-H), 7.39 (d, 2H, *J* = 7.7 Hz, arom-H), 7.75 (s, 1H, NH), 9.22 (s, 1H, NH); IR (KBr, cm⁻¹): ν 3233 (NH), 3114 (NH), 1703 (C=O), 1650 (C=O).

4d (R = Me, R' = 4-FC₆H₄, X = O). ¹H NMR (500 MHz, DMSO-d₆): δ 1.09 (t, 3H, *J* = 7.2 Hz, CH₃), 2.25 (s, 3H, CH₃), 3.95–4.00 (m, 2H, CH₂), 5.14 (d, 1H, *J* = 3.2 Hz, CH), 7.10–7.30 (m, 4H, arom-H), 7.73 (s, 1H, NH), 9.20 (s, 1H, NH); IR (KBr, cm⁻¹): ν 3238 (NH), 3079 (NH), 1703 (C=O), 1650 (C=O).

4g (R = Me, R' = 4-MeOC₆H₄, X = O). ¹H NMR (500 MHz, CDCl₃): δ 1.10 (t, 3H, *J* = 7.1 Hz, CH₃), 2.27 (s, 3H, CH₃), 3.72 (s, 3H, CH₃O), 3.99 (q, 2H, *J* = 7.1 Hz, CH₂), 5.25 (d, 1H, *J* = 2.4 Hz, CH), 6.20 (s, 1H, NH), 6.75 (d, 2H, *J* = 8.7 Hz, arom-H), 7.18 (d, 2H, *J* = 8.7 Hz, arom-H), 8.38 (s, 1H, NH); IR (KBr, cm⁻¹): ν 3247 (NH), 3118 (NH), 1703 (C=O), 1649 (C=O).

4k (R = Me, R' = 4-ClC₆H₄, X = S). ¹H NMR (500 MHz, DMSO-d₆): δ 1.10 (t, 3H, *J* = 7.1 Hz, CH₃), 2.29 (s, 3H, CH₃), 3.95–4.05 (m, 2H, CH₂), 5.17 (s, 1H, CH), 7.22 (d, 2H, *J* = 8.3 Hz, arom-H), 7.42 (d, 2H, *J* = 8.3 Hz, arom-H), 9.65 (s.br., 1H, NH), 10.36 (s.br., 1H, NH); IR (KBr, cm⁻¹): ν 3328 (NH), 3175 (NH), 1673 (C=O).

4m (R = Me, R' = 4-MeOC₆H₄, X = S). ¹H NMR (500 MHz, DMSO-d₆): δ 1.11 (t, 3H, *J* = 7.1 Hz, CH₃), 2.28 (s, 3H, CH₃), 3.72 (s, 3H, CH₃O), 4.00 (q, 2H, *J* = 7.1 Hz, CH₂), 5.11 (d, 1H, *J* = 3.6 Hz, CH), 6.89 (d, 2H, *J* = 8.6 Hz, arom-H), 7.12 (d, 2H, *J* = 8.6 Hz, arom-H), 9.57 (s, 1H, NH), 10.26 (s, 1H, NH); IR (KBr, cm⁻¹): ν 3314 (NH), 3171 (NH), 1667 (C=O).

2 Results and discussion

Solvent-free conditions are especially important for providing an eco-friendly system. The number of publications reporting solvent-free conditions for heterocyclic synthesis has increased rapidly in recent years [42]. One advantage of solvent-free reactions, in comparison to reactions in solvents, is that the compounds formed are often pure enough

to circumvent the need for purification using chromatography. Further, the use of a heterogeneous catalyst is an environmentally clean technique for the synthesis of organic compounds. Therefore, we investigated the efficiency of a SCM as a solid acid catalyst for the synthesis of dihydropyrimidinones and thiones under solvent-free conditions.

To find the optimal conditions, the synthesis of compound **4c** was used as a model reaction (Table 1). The reaction was carried out by heating a mixture of ethyl acetoacetate, 4-chlorobenzaldehyde, and urea in the presence of SCM. The efficiency of the reaction was affected by the amount of SCM (Table 1, entries 1–6)). No product was

Table 1 Effect of SCM amount and temperature on the synthesis of compound **4c** under solvent-free conditions

Entry	Catalyst (g)	Temperature (°C)	Time (min)	Yield* (%)
1	—	140	180	—
2	0.05	140	30	63
3	0.08	140	30	78
4	0.10	140	30	92
5	0.15	140	30	85
6	0.20	140	40	72
7	0.10	25	30	none
8	0.10	60	30	21
9	0.10	100	30	63
10	0.10	120	30	78
11	0.10	150	30	92
12	0.10	150	40	92

Other conditions: ethyl acetoacetate 4 mmol, 4-chlorobenzaldehyde 4 mmol, urea 5 mmol. *Isolated yields.

obtained in the absence of the catalyst (entry 1), indicating that the catalyst was necessary for the reaction. The optimal amount of the catalyst was 0.1 g (entry 4). Larger amounts of the catalyst were found to have an inhibitory effect on formation of the product (entries 5 and 6).

The same reaction in the presence of 0.1 g of the catalyst was carried out at different temperatures under solvent-free conditions to assess the effect of temperature on the reaction yield. The yield increased as the reaction temperature was raised. At 140 °C, product **4c** was obtained in high yield within 30 min. A further increase in temperature and time did not improve the product yield (entries 11 and 12).

For showing the effect of the solvent, the same reaction was also carried out in different solvents including EtOH, CH₃CN, CHCl₃, and tetrahydrofuran (THF) in the presence of 0.1 g of the catalyst. As shown in Table 2, the yield under solvent-free conditions was more, and the reaction time was considerably shorter.

Table 2 Synthesis of compound **4c** in the presence of SCM in different solvents

Solvent	Temperature (°C)	Time (h)	Yield* (%)
EtOH	reflux	6	38
CH ₃ CN	reflux	8	25
CHCl ₃	reflux	10	15
THF	reflux	12	10
Solvent-free	140	0.5	92

Other conditions: ethyl acetoacetate 4 mmol, 4-chlorobenzaldehyde 4 mmol, urea 5 mmol, SCM 0.1 g. *Isolated yields.

Table 3 SCM catalyzed synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and -thiones **4a–4t**

Entry	R	R'	X	Product	Time (min)	Yield* (%)	Melting point (°C)	
							Found	Reported
1	Me	3-BrC ₆ H ₄	O	4a	30	85	195–197	195–196 [14]
2	Me	2-ClC ₆ H ₄	O	4b	30	86	220–222	222–224 [12]
3	Me	4-ClC ₆ H ₄	O	4c	30	92	215–217	212–214 [12]
4	Me	4-FC ₆ H ₄	O	4d	30	88	178–180	173–176 [19]
5	Me	3-HOC ₆ H ₄	O	4e	30	82	168–170	163–165 [12]
6	Me	4-HOC ₆ H ₄	O	4f	30	88	236–238	230–232 [12]
7	Me	4-MeOC ₆ H ₄	O	4g	25	83	203–205	198–200 [19]
8	Me	4-MeC ₆ H ₄	O	4h	15	89	210–212	216–218 [14]
9	Me	3-NO ₂ C ₆ H ₄	O	4i	30	85	223–225	232–234 [14]
10	Me	4-NO ₂ C ₆ H ₄	O	4j	30	82	208–210	206–208 [19]
11	Me	4-ClC ₆ H ₄	S	4k	20	88	192–193	192–194 [12]
12	Me	4-HOC ₆ H ₄	S	4l	20	86	200–202	193–194 [19]
13	Me	4-MeOC ₆ H ₄	S	4m	20	82	158–160	150–152 [12]
14	Me	4-MeC ₆ H ₄	S	4n	20	85	212–214	192–194 [12]
15	Me	Me	O	4o	30	88	192–194	194–195 [12]
16	Me	Et	O	4p	30	90	170–172	171–174 [17]
17	Me	<i>n</i> -Pr	O	4q	30	88	153–155	152–154 [17]
18	Ph	Ph	O	4r	30	81	152–154	152–155 [15]
19	Ph	Ph	S	4s	30	80	185–187	183–185 [20]
20	Ph	4-MeOC ₆ H ₄	S	4t	30	85	150–152	151–152 [20]

Other conditions: β-ketoester 4 mmol, aldehyde 4 mmol, urea or thiourea 5 mmol, SCM 0.1 g, 140 °C. *Isolated yields.

To show the generality of this model reaction, a range of dihydropyrimidinones and thiones were prepared by the reaction of different β -ketoesters, including ethyl acetoacetate and ethyl benzoylacetate, different aliphatic and aromatic aldehydes, and urea or thiourea under optimized reaction conditions. In all cases, the reactions proceeded successfully and gave the expected products in good to high yields in short reaction time (Table 3). The type of β -ketoesters and aliphatic or aromatic aldehydes had no significant effect on the reaction time and yield.

Compared to other methods reported for the synthesis of dihydropyrimidinones and thiones, the present method offers more suitable conditions with good yields. Some of the results are summarized in Table 4, which shows that the reactions under solvent-free conditions gave better results than the reactions in a solvent.

Table 4 Comparison of the efficiency of various catalysts in the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and -thiones

Catalyst	Conditions		Time (h)	Yield (%)	Ref.
	Solvent	$T/^\circ\text{C}$			
HEU type zeolite	AcOH	100	4–12	44–87	[11]
InBr ₃	EtOH	reflux	7–36	68–98	[12]
CuI	CH ₃ CN	reflux	0.75–2	70–87	[13]
CuI	H ₂ O	reflux	4–6	65–73	[13]
[bmim][FeCl ₄]	—	90	2–3	68–92	[14]
TCCA	EtOH	reflux	8–12	46–95	[15]
M(NTf ₂) ₂	H ₂ O, HCl	r.t.	24	25–80	[16]
RuCl ₃	—	100	0.5–1.5	74–93	[18]
H ₃ PMo ₁₂ O ₄₀	CH ₃ CN	reflux	3.5–9	63–97	[21]
H ₃ PW ₁₂ O ₄₀	AcOH	reflux	6–7	40–75	[22]
SCM	—	140	0.25–0.5	80–92	this work

The reusability of the catalyst was also investigated with the same model reaction again studied under the optimized conditions. After the completion of the reaction, the catalyst was recovered according to the procedure described in the experimental section and reused. As shown in Fig. 1, the catalyst could be reused at least four times with only a slight reduction in activity.

Fig. 1. Reusability of SCM for the synthesis of compound **4c**.

A reaction mechanism is proposed in Scheme 2. SCM $\equiv$ HA facilitates the formation of the intermediate **I** by Knoevenagel condensation of β -ketoester **1** and aldehydes **2**, and **I** after dehydration gives the olefin **II**. Nucleophilic attack of the amino group in urea or thiourea at the β -carbon of the α,β -unsaturated carbonyl group followed by cyclization yields the products **4a–4t**. Under these conditions, attempts to isolate the intermediates **I** and **II** failed even after careful monitoring of the reactions.

Scheme 2. Mechanism for the formation of 3,4-dihydropyrimidin-2(1H)-ones and -thiones in the presence of SCM $\equiv$ HA as catalyst.

3 Conclusions

We developed a very simple and efficient method for the synthesis of dihydropyrimidin-2(1*H*)-ones and -thiones by a three-component reaction of β -ketoesters, aldehydes, and urea or thiourea in the presence of a SCM as catalyst under solvent-free conditions. The catalyst can be recycled after a simple work-up, and was reused at least four times without substantial reduction in activity. High yields, short reaction time, easy work-up, and absence of a volatile and hazardous organic solvent are a few advantages of this procedure.

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