



Carbon nanotubes supported by titanium dioxide nanoparticles as recyclable and green catalyst for mild synthesis of dihydropyrimidinones/thiones



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HIGHLIGHTS

- High yields, short reaction times, and simple work-up procedures.
- Ethanol was the best solvent compared to other organic solvents.
- 0.03 g TiO₂-CNTs was the optimum amount in the synthesis of pyrimidinones.

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ABSTRACT

The catalytic activity of titanium dioxide supported on carbon nanotubes has been investigated in a one-pot three components condensation reaction (Biginelli reaction). The TiO₂-CNT nanocomposites as catalyst are highly stable and completely heterogeneous and they can be recycled several times. Compared to the classical Biginelli reaction conditions, the present methodology offers several advantages such as excellent yields, simplicity, fast and clean reactions and short reaction times.

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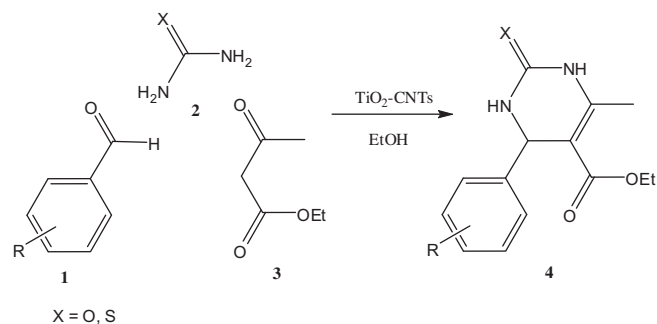
1. Introduction

During the past few years, dihydropyrimidinone (DHPM) has attracted attention as a target skeleton because of its biological significance [1]. Dihydropyrimidinones act as anti-virals [2], antibacterial, antifungal [3], anti-inflammatory [4], antioxidative [5], anticarcinogenic [6], calcium channel Blockers [7], antihypertensive [8], anti-cancer [9] and anti-HIV [10] compounds. In 1893, Italian chemist Pietro Biginelli reported acid catalyzed one-pot three-component condensation of urea, aldehyde and 1,3-ketoester for synthesis of DHPMs [11]. 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 Bronsted acids [12–16], Lewis acids or metal-based catalysts [17–19], ionic liquids [20,21], Ziegler–Natta catalyst [22], heteropoly acids [23], Baker's yeast [24], ion exchange resin [25], polymer support [26], microwave [27,28], ultrasound

irradiations [29], zeolites [30], organocatalysts [31,32], clays [33,34], polyoxometallates [35], solid-phase synthesis [36], L-proline [37] and silica supported on heteropoly acid [38].

Titanium dioxide (TiO₂) is attractive owing to the superior properties such as high photocatalytic activity, excellent stability, super-hydrophilicity, non-toxicity, biological and chemical inertness, semiconductor and optoelectronic properties [39–42]. Due to these effective catalytic, electrical and optical properties, titania (TiO₂) has been extensively employed in many fields such as solar cells [43,44], sensors [45,46], photocatalysis [47,48], photovoltaic cells [49] and photoelectrolysis [50] as well as antibacterial [51], photochemical water purification [52,53], and self-cleaning applications [54]. In particular, the use of carbonaceous nanomaterials to support TiO₂ has attracted much attention because of their unique structural and electrical properties [55]. Carbon nanotubes (CNTs) with unique characteristics such as high-surface area, high quality active sites, one-dimensional electronic structure and retardation of electron–hole recombination could greatly improve the photocatalysis of TiO₂ [56–58]. In addition, the electron-accepting capability and conductivity of the CNTs make them ideal

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Scheme 1. TiO₂-CNTs catalyzed synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones (DHPMs).

to reduce the electron-hole recombination at the TiO₂-C interfaces [59–64]. Therefore, CNTs have been proposed as a promising candidate in the support materials for TiO₂ catalyst composites [65–67]. TiO₂-CNT nanocomposites have been fabricated by many specific methods, which consist of mechanical mixing of TiO₂ and CNTs [68], sol-gel synthesis of TiO₂ in the presence of CNTs [60,69], electrophoretic deposition [70], electro-spinning methods [71–73], physical vapor deposition [74], hydrothermal [75] and chemical vapor deposition [76,77]. The most reported methods for the preparation of CNTs/TiO₂ nanocomposites generally consist of two steps: functionalization of the CNTs and synthesis of nanocomposites. The functional modification of CNTs causes greatly change in electronic properties caused by destruction of original graphite structure of CNTs and introduces different hydrophilic functional groups on the CNT surface providing numerous sites for TiO₂ bonding [78–81]. To introduce more binding sites and surface anchoring groups, surface functionalization of CNTs is generally carried out. Although the catalytic applications of carbon nanotubes have been established for organic synthesis, according to the best of our knowledge, there is no report in the literature on the use of TiO₂-CNTs in Biginelli reaction. Therefore, we disclose a simple, but effective modification of the Biginelli reaction that produces high yields of 3,4-dihydropyrimidinones/thiones using a catalytic amount of titanium dioxide supported on carbon nanotubes while preserves the original one-pot strategy (Scheme 1).

2. Results and discussion

In a novel synthetic research work, the effort has been made to undertake the synthesis of dihydropyrimidine via Biginelli's reaction through one step process. The TiO₂-CNT's excellent catalytic activity encouraged us to explore the potential of this catalytic

Table 3
Three components Biginelli reactions in synthesis of **4a** over TiO₂-CNTs.

Entry	R	X	Product	Mp (°C)		Time (min)	Yield (%)
				Obs.	Lit.		
1	H	O	4a	200–202	201–203 [83]	20	97
2	4-NO ₂	O	4b	208–210	209–210 [84]	30	95
3	4-OMe	O	4c	201–202	202–203 [85]	35	94
4	2,4-Cl ₂	O	4d	248–250	249–250 [86]	40	91
5	4-NMe ₂	O	4e	257–258	255–257 [85]	27	96
6	4-F	O	4f	182–184	183–185 [87]	35	89
7	3-Br	O	4g	184–185	185–186 [86]	30	92
8	H	S	4h	208–210	207–208 [83]	25	90
9	3-NO ₂	S	4i	206–208	206–209 [88]	20	92
10	2-OMe	S	4j	189–190	190–192 [89]	23	96
11	4-Br	S	4k	215–217	216–218 [90]	25	94
12	4-Me	S	4l	191–193	192–194 [91]	30	89

system for the synthesis of various 3,4-dihydropyrimidin-2(1H)-ones/thiones. The discharge of electrons occurs with the placement of CNTs on a metal. Therefore, these nanocomposites show the better Lewis acidic character when they are compared with titanium dioxide. However, combining TiO₂ with CNTs to form metal dioxide/CNT nanocomposites produces synergistic properties from both of the metal dioxide and the CNTs. In fact, TiO₂ nanoparticles on the external walls are easier to make contact with the reactants. Initially, in order to optimize the reaction parameters, we investigated the reaction of benzaldehyde, ethyl acetoacetate and urea in the presence of TiO₂-CNTs under different conditions. We found that the best result obtained with benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol) urea/thiourea (1.5 mmol) and TiO₂-CNTs (0.03 g) as catalyst (Tables 1 and 2).

Thiourea has been used with similar success to provide the corresponding thio-derivatives of dihydropyrimidinones which are also very interesting with respect to their biological activities [82]. In order to explore the scope of this procedure, a series of aldehydes was examined under optimized conditions and the results are shown in Table 3. The results show the generality of the present protocol, which is equally effective for urea and thiourea. Also, both of aromatic aldehydes bearing electron-donating groups such as OMe (entries 3, 10) and electron-withdrawing groups such as NO₂ (entries 2, 9) had excellent yields.

Table 1
Optimization of ratio molar of substrates in the synthesis of **4a**.

Entry	Benzaldehyde: ethyl acetoacetate: urea/thiourea (Molar ratio)	Time (min)	Yield (%)
1	1:1:1.2	75	10
2	1:1:1.3	60	55
3	1:1:1.4	45	70
4	1:1:1.5	30	85
5	1:1:1.6	30	80

Table 2
Optimization of amount of catalyst in the synthesis of **4a**^a.

Entry	Catalyst (g)	Time (min)	Yield (%)
1	0.00	60	15
2	0.01	40	69
3	0.02	35	78
4	0.03	20	97
5	0.04	20	90

^a Molar ratio: benzaldehyde: ethyl acetoacetate: urea (1:1:1.5).

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