Combustion Derived Nanocrystalline-ZrO₂ and Its Catalytic Activity for Biginelli Condensation under Microwave Irradiation

Bhojegowd, Madhusudana Reddy M.   Siddaramanna, Ashoka

Siddappa, Anandakumar B.   Thimmanna, Chandrappa G.*   Pasha, Mohamed A.*

Department of Studies in Chemistry, Central College Campus, Bangalore University, Bengaluru-560001, India

Nanocrystalline zirconium(IV) oxide (nc-ZrO₂) possessing high surface area was synthesized by a low temperature eco-friendly solution combustion method using a new organic fuel alanine. The powder XRD, SEM and surface area measurements were carried out for characterization of nc-ZrO₂. The powder XRD results revealed that, the nc-ZrO₂ has the pure tetragonal phase. The crystallite size calculated by Scherrer's formula and BET surface area were found to be *ca.* 53—57 nm and *ca.* 275 m²/g, respectively. SEM micrograph exhibited the macroporous nature of the powder. nc-ZrO₂ has been employed as a catalyst for the solvent-free synthesis of 3,4-dihydro-pyrimidin-2-ones (DHPMs) by a microwave (MW) assisted one-pot, multicomponent Biginelli condensation reaction of araldehydes, ethylacetoacetate and urea or thiourea. DHPMs are obtained in good to excellent yields (85%—96%) under this reaction condition within short interval of time (10—20 min).

Keywords nanocrystalline-ZrO₂, solution combustion, araldehydes, ethylaceto acetate, nano materials, green chemistry, catalysis, 3,4-dihydropyrimidinones

Introduction

In recent years, multi-component domino coupling reactions (MCDCRs) have attracted industrial as well as academic interest owing to their increased efficiency and practicability.[1] In addition MCDCRs usually exhibit a higher atom economy and selectivity, with minimum level of byproduct formation as compared to classical multistep synthetic routes.[2] Further, in many cases MCDCRs have simpler experimental procedures, involve lower costs, require lesser time and consume less energy.[3]

The Biginelli-reaction,[4] developed in 1893 by Biginelli is a three-component, one-pot condensation reaction to obtain DHPMs from readily available aldehydes, β-ketoesters, and urea (or thiourea) in the presence of HCl. The DHPMs are known to exhibit a wide range of biological activities such as antiviral, antitumor, antibacterial, and anti-inflammatory properties.[5] These compounds have emerged as potential calcium channel blockers, as antihypertensive agents, and as α1a-adrenergic antagonists and neuropeptide antagonists.[6] Further, the 2-oxo-3,4-dihydropyrimidine-5-carboxylate unit is found in many marine natural products, including the batzelladine alkaloids, which are found to be potent HIV gp-120-CD4 inhibitors.[7]

Methods reported for the synthesis of DHPMs have one or more advantages as well as disadvantages such as involvement of expensive reagents, formation of side products, thermal instability, use of toxic solvents, requirement of excess of reagents/catalysts, laborious work-up procedures and difficult accessibility to reagents. Thus, a mild, convenient, reusable and high yield procedure using inexpensive catalyst would be valuable.

On the other hand, there is a strong need to develop new green catalysts that should be efficient, and involve an easy work-up procedure and afford greater yields of desired products in shorter reaction times.[8] In recent years, nanoparticles have attracted a great deal of attention as effective catalysts in synthetic organic chemistry, due to their high efficiency and selectivity which has led to development of greener and waste-minimized processes. For example, Pd-nanoparticles are found to be efficient catalysts for the Mizoroki-Heck reaction,[9] Suzuki cross-coupling,[10] Stille type reactions,[11] Sonogashira coupling reaction,[12] Tsuji-Trost allylation,[13] Pauson-Khand reactions,[14] and aza-Michael reactions.[15] Cu-nanoparticles are proved to be good catalysts in the oxidative cyclization of Schiffs' bases,[16] and for one-pot three-component synthesis of thiazolidine-2,4-dione derivatives.[17] A chemoselective reduction of aldehydes using Ni-nanoparticles as an efficient green catalyst is also recorded in the literature.[18] Very recently, nano-metal oxides have been used in organic synthesis and these include copper(II) oxide in the synthesis of 1,4-dihydropyridines,[19] and as an effective catalyst for the CO and NO oxidation, as well as in the oxidation of volatile organic pollutants.[20] Similarly, nano ZnO in

Knoevenagel condensation,[21] and nano MgO in the synthesis of 2-amino-2-chromenes[22] have been reported.

Over the past two decades, several methods have been developed for the preparation of nc-ZrO_2, including sol-gel,[23] hydrothermal/solvothermal,[24] emulsion precipitation,[25] and microwave/sonication-assisted co-precipitation[26] methods. All the above methods require high quality chemicals, high temperature, high pressure, sintering and long time. In recent years, the solution combustion synthesis has drawn a considerable attention due to its unique combination of technologically relevant characteristics. Solution combustion synthesis is an attractive technique for the production of nanocrystalline metal oxides. The advantages of this method are rapid synthesis at normal atmosphere, low cost with a great potential scale up and eco-friendly *i.e.* complete conversion to non-toxic gases. This method is also useful for producing homogeneous, porous and crystalline fine powders. Present technology needs a simple and large scale production with improved properties like surface area in a short duration (*ca.* 5 min) without requiring sophisticated apparatus. Hence, we explored the possibility of using a simple solution combustion method for the successful preparation of nc-ZrO_2.

In continuation of our work on the synthesis of nano materials and their use as catalysts in organic synthesis, we herein report a combustion derived synthesis of nano crystalline-ZrO_2 powder with large surface area. Alanine has been used as a fuel for the first time and employed as an efficient catalyst for the synthesis of crystalline-ZrO_2.

We have recently reported the synthesis and characterization of MgO nano particles, and its application in the synthesis of formamides from amines with formic acid.[27] Organic reactions catalysed by nc-ZrO_2 are very less and to the best of our knowledge there are no reports available on the synthesis of DHPMs in the literature using ZrO_2. It was therefore desirable to use this new recyclable green catalyst that could enhance the rate of the chemical reactions.

To examine the catalytic behaviour of nc-ZrO_2 in the Biginelli reaction, a mixture of *p*-anisaldehyde (2 mmol), ethylacetoacetate (2 mmol) and urea (2.5 mmol) was irradiated in a microwave reactor at 110 ℃ in the presence of 123 mg (1 mol%) of nc-ZrO_2 for 10 min under solvent-free condition (Scheme 1), to get the product in 95% yield, the structure of which was elucidated by IR, ^{1}H NMR and Mass spectral analysis.

Experimental

General procedure

The chemicals used were commercial reagents. All the reactions were carried out in a MILESTONE microwave reactor at 300 W (110 ℃). Melting points were determined using a Raaga, Chennai, Indian-made apparatus. Nuclear magnetic resonance spectra were obtained on a 400 MHz Bruker AMX spectrometer in DMSO-d_6 using TMS as the standard. GC-Mass spectra were obtained using a Shimadzu GC-MS QP 5050A instrument equipped with a 30 m length and 0.32 mm diameter BP-5 column with the column temperature programme 80—15—250 ℃. Infrared spectra were recorded using Shimadzu FT-IR-8400s spectrometer as KBr pellets for solids and as thin films between NaCl plates in case of liquids. Powder X-ray diffraction data were obtained using Philips X'pert PRO X-ray diffractometer using Cu Kα radiation. Morphology of the ZrO_2 was examined by JEOL (JSM-840 A) scanning electron microscope. Surface area and porosity of nc-ZrO_2 were determined using gas sorption analyzer Quanta Chrome Corporation NOVA 1000. Photoluminescence spectra were measured at room temperature using Perkin Elmer spectrometer employing He-Cd laser with an excitation wavelength of 254 nm.

Synthesis of catalyst

nc-ZrO_2 was prepared by the combustion of aqueous solutions containing stoichiometric amounts of zirconium nitrate and alanine. Stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valencies of the oxidizer and the fuel keeping their ratio unity.[28] The aqueous solution of the redox mixture was taken in a pyrex dish, the excess water was allowed to evaporate by heating on a hot plate until a viscous gel was formed. The pyrex dish was then placed in a muffle furnace maintained at (300 ± 10) ℃. Initially the reaction mixture underwent dehydration followed by smoldering (low flame) combustion. The product, ZrO_2 left behind is found to be in porous and voluminous form. The theoretical equation for the formation of ZrO_2 with alanine can be formulated as follows,

$$3Zr(NO_3)_4 + 4C_3H_7O_2N \xrightarrow{300 \pm 10\ ^oC} 3ZrO_2 + 8N_2 + 12CO_3 + 14H_2O$$
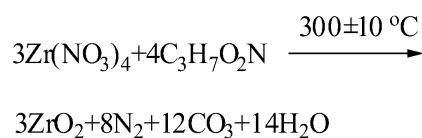
Characterization of catalyst

X-ray powder diffraction (XRD) studies Powdered XRD pattern of combustion derived nc-ZrO_2 (Figure 1) shows all the peaks for the pure tetragonal phase of ZrO_2. The crystallite size was calculated using the Scherrer's formula[29] and found to be *ca.* 53—57 nm, which indicates the nanocrystalline nature of the powder.

FT-IR spectroscopic studies The formation of pure zirconium oxide was further confirmed by FT-IR studies and the FT-IR spectrum is shown in Figure 2. The broad band around 500 cm^{-1} corresponds to v_{Zr-O} vibration. The bands observed at 3442 and 1627 cm^{-1} are due to adsorbed water on the surface of the zirconium oxide.[30]
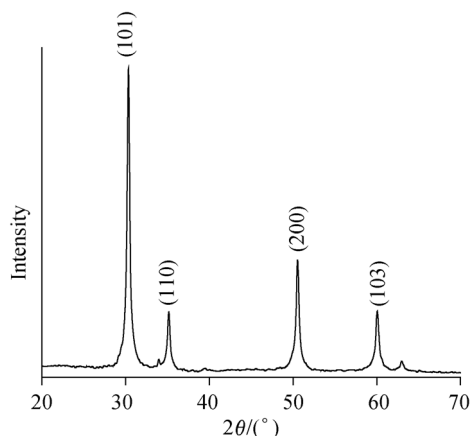
Figure 1 Powder XRD pattern of nanocrystalline zirconium oxide.
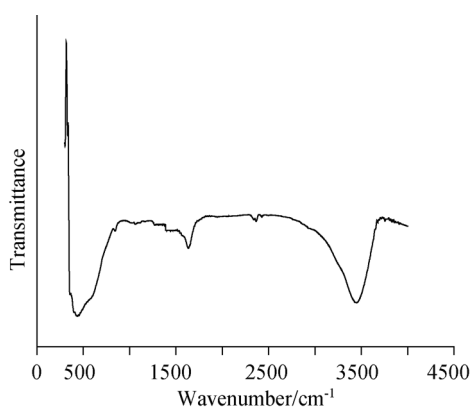
Figure 2 FT-IR spectrum of nanocrystalline zirconium.

Figure 3 Nitrogen adsorption-desorption isotherm of nanocrystalline zirconium oxide.

Figure 4 SEM images of nanocrystalline zirconium oxide.
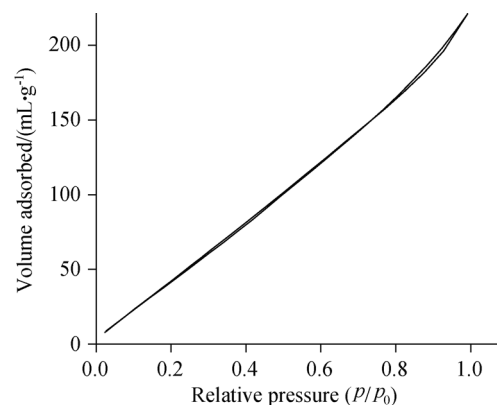
Surface area analysis

Surface area of nc-ZrO$_2$ was studied from nitrogen adsorption/desorption isotherm by BET method as shown in Figure 3. The isotherm of zirconium oxide shows type III characteristics. The prepared nc-ZrO$_2$ has large surface area of 275 m^2/g which is *ca*. 16 times larger than the earlier combustion derived ZrO$_2$ using glycine as fuel.[31] The higher surface area in the latter case is attributed to the liberation of gaseous products such as H$_2$O, CO$_2$ and N$_2$ during combustion. The agglomerates disintegrate and most of the heat is carried away from the system, thereby hindering the particle growth. This high surface area is important for catalytic/adsorbent applications, because the small size particles maximize the surface area when exposed to the reactants.[32]
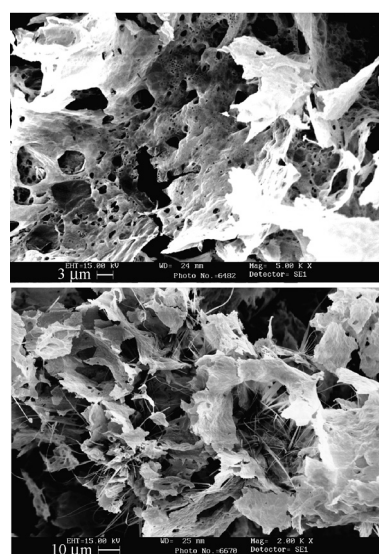
SEM studies

Figure 4 shows a typical SEM images of nc-ZrO$_2$ prepared at (300 ± 10) ℃. It also shows the high porous nature of ZrO$_2$ powder. Fiber like structure observed in SEM images may be due to the voluminous eruption of the product during combustion.

Photoluminescent properties

The photoluminescence (PL) spectrum of nc-ZrO$_2$ (Figure 5) exhibits a strong UV band at 385 nm; and blue and green bands at 420 and 488 nm respectively. UV emission originates from the band edge excitation recombination.[33] Blue and green emissions originate from the mid-gap trap states, such as surface defects and oxygen vacancy defects.[34] The combustion process produces large number of oxygen vacancy defects in nc-ZrO$_2$ powder. This provides an opportunity for the association among oxygen vacancy defects. Therefore, it is reasonable to assume that, the blue and green emissions arise from the singly ionized associated oxygen vacancy defects. These crystal defects are important parameters for the nano materials to exhibit good catalytic activity.[35]

Catalytic activity, microwave-induced cyclocondensation of ethylacetoacetate, benzaldehyde and thiourea under solvent-free condition

To a microwave process vial equipped with a magnetic stirrer, was added benzaldehyde (2 mmol), ethylacetoacetate (2 mmol), thiourea (2.5 mmol), and nc-ZrO$_2$ (1 mol%) as the catalyst. The contents were
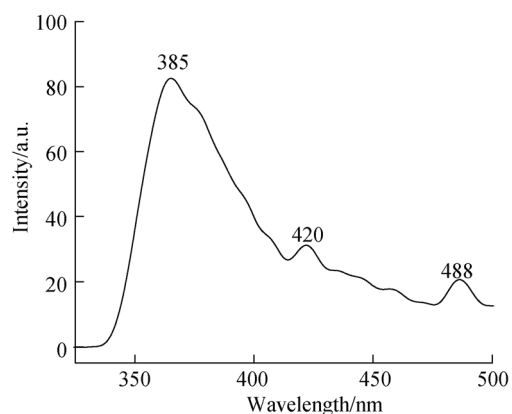
Figure 5 Room temperature PL nanocrystalline zirconium oxide.

mixed thoroughly and irradiated in a microwave reactor (300 W) at 110 ℃ for 15 min. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature; then, ethanol (5 mL) was added to it. The reaction mixture was filtered to remove nc-ZrO$_2$, and the filtrate was poured into cold water. The solid thus separated was filtered and recrystallized from ethanol to obtain the pure 5-ethoxycarbonyl-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-thione as yellow crystals (yield 90%, m.p. 203—204 ℃).

Characterization of DHPMs

All the compounds synthesized were characterized using IR, mass, ^{1}H NMR spectral analysis. In the mass spectra, the molecular ion peaks were in agreement with the molecular weights of the respective compounds. In the ^{1}H NMR spectra, two characteristic peaks of NH of the dihydropyrimidine ring were observed between δ 8.5 and 10. The chiral proton at the C-4 position showed a singlet between δ 5—5.5. The IR spectra showed N—H stretching between 3200 and 3400 cm^{-1} and the carbonyl (C=O) group stretching near 1690 cm^{-1}.

Results and discussion

Initially, solvent-free cyclocondensation reaction of benzaldehyde as a representative substrate with ethylacetoacetate and urea under microwave irradiation was carried out by varying the temperature from 80 to 120 ℃, and microwave output from 150 to 350 W using nc-ZrO$_2$ as the catalyst (Table 1, Entries 1—5). Increasing the temperature to 100 from 80 ℃ improved the yield of **4a** from 15% to 75% (Table 1, Entry 3). Improvement occurred by raising the reaction temperature to 110 ℃. There was no improvement in the yields of the product by either increasing the temperature above 110 ℃ or by increasing the amount of the nc-ZrO$_2$ (Table 1, Entries 5, 6). On heating to 120 ℃, about 57% yield was obtained after 30 min (Table 1, Entry 9). Further, when the same reaction was carried out in the absence of nc-ZrO$_2$ under microwave irradia-

tion only 10% product was obtained (Table 1, Entry 7), demonstrating that the catalyst is necessary for the reaction to proceed. When the reaction was carried out at 25 ℃, no product was obtained even after longer duration of time (60 min, Table 1, Entry 8).

Table 1 Optimization of reaction condition for Biginelli condensation of benzaldehydes, ethylacetoacetate and urea^a

Entry	Condition	$T/$℃	$t/$min	Yield^b/%
1	MW/150W/nc-ZrO$_2$ (1 mol%)	80	25	15
2	MW/200W/nc-ZrO$_2$ (1 mol%)	90	20	40
3	MW/250W/nc-ZrO$_2$ (1 mol%)	100	15	75
4	MW/300W/nc-ZrO$_2$ (1 mol%)	110	10	96
5	MW/300W/nc-ZrO$_2$ (2 mol%)	110	10	90
6	MW/350W/nc-ZrO$_2$ (1 mol%)	120	10	88
7	MW/350W/Neat	110	30	10
8	RT/nc-ZrO$_2$ (1 mol%)	25	60	ND^c
9	Heating/solventfree/nc-ZrO$_2$ (1 mol%)	120	30	57
10	MW/300W/commercial-ZrO$_2$ (1 mol%)	110	20	65

^{a} Reaction condition, 1 mol% nc-ZrO$_2$; ^{b} isolated yield; ^{c} not detected.

To show the merits of nc-ZrO$_2$, the yield of the product formed in the presence of nc-ZrO$_2$ under optimized condition was compared with the commercial-ZrO$_2$ (Table 1, Entry 10). As can be seen from Table 1, nc-ZrO$_2$ can serve as an efficient catalyst in the formation of DHPM with high yields in shorter reaction times, and the method is more efficient than with commercial-ZrO$_2$ under MWI.

Results recorded in Table 1 also reveal that, 110 ℃ temperature and MW irradiation at 300 W were optimum (Table 1, Entry 4) to give the best catalytic activity in terms of product yields within 10 min.

Following the above results, we utilized nc-ZrO$_2$ as a catalyst for the conversion of a wide range of aromatic aldehydes as well as cinnamaldehyde under optimum conditions into DHPMs (Table 2, Entries a—j). An important feature of this procedure is the survival of a variety of functional groups such as halide, nitro, hydroxy and methoxy groups. Interestingly, acid sensitive aldehyde like 2-furaldehyde worked well without the formation of side products, and cinnamaldehyde also gave good yield of the desired product.

It is worthwhile to note that, the same procedure can be applied employing thiourea to obtain the corresponding thio-derivatives of DHPMs (Table 2, Entries k—p), which are also of interest due to their biological activity.

Recyclability of the catalyst

Reusability of the catalyst was examined employing the reaction between **1a**, **2** and **3** to obtain **4a** under identical reaction conditions (Scheme 1). The catalyst could easily be recovered from the mixture by filtration;

Table 2 Biginelli condensation of aldehyde, ethylacetoacetate and urea or thiourea[a]

Entry	**1** (R)	**3** (X)	Time/min	Product[b] (**4**)	Yield[c]/%	m.p. (Lit. m.p.)/℃
a	Ph	O	10	**4a**	96	201 (200—202)
b	4-F-Ph	O	12	**4b**	93	181 (182—184)
c	2-Cl-Ph	O	15	**4c**	90	215 (216—218)
d	4-Cl-Ph	O	10	**4d**	89	210—211 (212—213)
e	4-CH$_3$O-Ph	O	10	**4e**	87	199 (200—201)
f	4-HO-Ph	O	17	**4f**	85	226—228 (227—229)
g	2-furyl	O	15	**4g**	91	204 (203—205)
h	4-(CH$_3$)$_2$N-Ph	O	16	**4h**	89	253—255 (257—258)
i	4-NO$_2$-Ph	O	14	**4i**	90	205—207 (207—209)
j	Ph-CH=CH	O	20	**4j**	91	230—231 (232—235)
k	Ph	S	15	**4k**	90	206—207 (208—210)
l	2-Cl-Ph	S	18	**4l**	93	165 (164—165)
m	4-Cl-Ph	S	15	**4m**	92	183 (184)
n	4-CH$_3$O-Ph	S	18	**4n**	90	153 (154—155)
o	4-NO$_2$-Ph	S	20	**4o**	88	107—108 (109—111)
p	4-(CH$_3$)$_2$N-Ph	S	18	**4p**	86	200 (202—205)

[a] All reactions were performed using an aldehyde (2 mmol), ethylacetoacetate (2 mmol), urea or thiourea (2.5 mmol) and 1 mol% of nc-ZrO$_2$. [b] All the compounds are known and physical properties agree with the reported values; ^{1}H NMR, IR and Mass spectral data matched with the reported spectral data. [c] Isolated yields.

Scheme 1 Synthesis of 3,4-dihydropyrimidin-2-ones
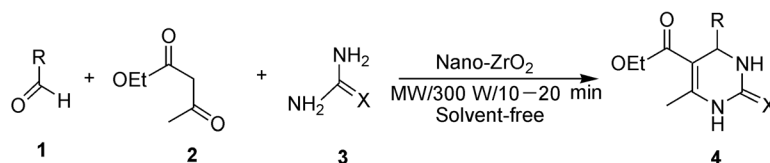
washed with distilled water and ethanol repeatedly, and dried for 2—3 h under vacuum before re-use. The recycled catalyst was used for five times to obtain 5-ethoxycarbonyl-4-(phenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one without appreciable decrease in the yield. The yields were 96%, 93%, 93%, 90% and 89% respectively for 1—5 cycles, the decrease of yield may be due to adsorption of substrates on the active sites. After every reaction, the catalyst was recovered from the reaction mixture by filtration and regenerated as described above.

Conclusions

Nanocrystalline zirconium oxide with high surface area has been synthesized by using alanine as a fuel by the solution combustion method for the first time; and has been employed in the synthesis of DHPMs using a MW reactor under solvent-free condition. By this novel procedure 3,4-dihydropyrimidin-2(1*H*)-ones/-thiones with varied substitution pattern could be synthesized in very high yields. Reactions are rapid and the catalyst can be recycled for five cycles without any appreciable change in its activity.

Acknowledgements

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