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One-pot sonochemical synthesis of 1,3-thiazolidin-4-ones using nano-$CdZr_4(PO_4)_6$ as a robust heterogeneous catalyst

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ABSTRACT

An efficient three-component synthesis of 1,3-thiazolidin-4-ones is described by one-pot condensation of aldehydes, aniline and thioglycolic acid with nano-$CdZr_4(PO_4)_6$ as a robust heterogeneous catalyst under ultrasonic irradiation. Use of simple and readily available starting materials, experimental simplicity, applying the sonochemical methodology as an efficient method and innocuous means of activation in synthetic chemistry are some advantages of this protocol.

1. Introduction

Thiazolidinones are valuable synthetic scaffolds for both medicinal and synthetic organic chemists. Thiazolidinones exhibit various pharmacological activities such as anti-HIV [1–5], antimicrobials [6,7], antihistaminic [8,9], anti-YFV (Yellow fever virus) [10], anti-cancer [11], antiinflammatory [12] and antioxidant [13]. Therefore, the development of simple and efficient synthetic protocols for the construction of more elaborate and usefully functionalized thiazolidinones are still desirable. Undoubtedly, the synthesis of thiazolidinones through multicomponent reactions (MCR) has been paid much attention due to excellent synthetic efficiency, inherent atom economy, the use of readily available starting materials, experimental simplicity and environmental friendliness [14–16]. The possibility of accomplishing multicomponent reactions with a heterogeneous catalyst under ultrasonic irradiation could improve their effectiveness from cost-effectiveness and environmental points of view. The ultrasound approach offers several advantages, including enhanced organic reaction rates, formation of purer products in high yields, simple experimental conditions, and waste minimization compared with traditional methods [17–19]. Ultrasound irradiation has been utilized to accelerate the chemical reactions proceed through the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation serves as a means of concentrating the dispread energy of sound [20,21]. Recently, ultrasound irradiation was applied for the appropriate and rapid synthesis of 2-aryl-3-(piperonylmethyl)-1,3-thiazolidin-4-ones from piperonilamine [22], synthesis of new 2-imino-1,3-thiazolidin-4-ones [23] and synthesis of thiazolidinones from 2-aminopyridineand 2-picolilamine [24]. Nanocatalysts have been emerged as an alternative approach for the development of many significant organic reactions under ultrasonic irradiations [25,26]. Nanocatalysts are isolated and recovered through filtration or centrifugation methods, and are acknowledged to possess a wide range of specific features including high activity, great selectivity, high stability, efficient recovery and good recyclability.

$MZr_4(PO_4)_6$ structure ceramics have been interested because of their unique properties and potential applications in diverse fields [27,28]. According to the above results we used nano-$CdZr_4(PO_4)_6$ for the synthesis of 1,3-thiazolidin-4-ones. Recently, the synthesis of 1,3-thiazolidin-4-ones has been reported using MCRs in the presence of diverse catalysts including

$HClO_4$-SiO_2 [29], Ionic liquid immobilized on $FeNi_3$ [30], Fe_3O_4/SiO_2/Salen/Mn/IL MNPs [31], $Bi(SCH_2COOH)_3$ [32], and *Saccharomyces cerevisiae* [33]. Many methods for the synthesis of 1,3-thiazolidin-4-ones are known, but some of these methods have certain drawbacks, including long reaction times, use of toxic and non-reusable catalyst and utilize of specific conditions.

In the current work, we disclosed a novel methodology for the synthesis of 1,3-thiazolidin-4-ones by one-pot condensation of aldehydes, aniline and thioglycolic acid with nano-$CdZr_4(PO_4)_6$ as a robust heterogeneous catalyst under ultrasonic irradiation (Scheme 1).

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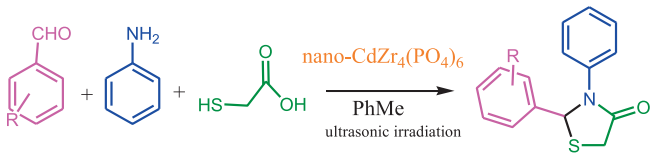

Scheme 1. Synthesis of 1,3-thiazolidin-4-ones using nano-$CdZr_4(PO_4)_6$.

2. Experimental

2.1. Materials and apparatus

All organic materials were purchased commercially from Sigma–Aldrich and Merck and were used without further purification. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 200 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. All melting points are uncorrected and were determined in capillary tube on Boetius melting point microscope. FT-IR spectra were recorded with KBr pellets using a Magna-IR, spectrometer 550 Nicolet. NMR spectra were recorded on a Bruker 400 MHz spectrometer with DMSO-d_6 as solvent and TMS as internal standard. CHN compositions were measured by Carlo ERBA Model EA 1108 analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Zr Kα radiation (λ = 1.5406 Å). In order to investigate the particle size and morphology of the synthesis structures nano-$CdZr_4(PO_4)_6$, FE-SEM images of the products visualized by a HITACHI S4160 Field Emission Scanning Electron Microscope.

2.2. Preparation of nano-$CdZr_4(PO_4)_6$

$ZrOCl_2$ was used as zirconium source. Firstly 1 mmol (322 mg) of $ZrOCl_2{\cdot}8H_2O$ and 1 mmol (266 mg) of $Cd(OAc)_2{\cdot}2H_2O$ were added in 15 mL of $HO(CH_2)_2OH$ and sonicated at 30 W power to completely dissolution. Afterward 0.8 ml H_3PO_4 (85%), 4 mmol of NH_4Cl and 1.4 mL of CH_3NH_2 water solution (25.0–30.0%) were added consecutively and sonicated for 30 min. Then, the reaction mixture was transferred into a Teflon-lined autoclave under autogenous pressure at 200 °C for 5 days. When the reaction was completed, dispersed precipitate was obtained. The solid was filtered and washed with distilled water and ethanol several times. Subsequently product was dried at 50 °C for 5 h and calcined at 700 °C for 2 h. Afterward the solid was added in 20 mL of DMF and sonicated at 95 W power for 2 h. Finally the resulting product was filtered, washed with distilled water and absolute ethanol and dried at 150 °C for 2 h in vacuum to afford pure nano-$CdZr_4(PO_4)_6$ ceramics.

2.3. General procedure for the preparation of 1,3-thiazolidin-4-ones

A mixture of aldehydes (2 mmol), aromatic amine (2 mmol), thioglycolic acid (2 mmol) and 0.50 mol% (12 mg) of nano-$CdZr_4(PO_4)_6$ in PhMe (15 mL) was sonicated at 60 W power. The reaction was monitored by TLC. After completed reaction, hot CH_3OH was added to dilute the reaction mixture after terminating the reaction. The reaction mixture was filtered until heterogeneous catalyst was recovered. The filtrate was evaporated and recrystallized with *n*-hexane/ethyl acetate to get pure product.

2.4. Representative spectral data

2.4.1. 2-(2-chlorophenyl)-3-phenylthiazolidin-4-one (**4a**)

White solid, m.p 120–124 °C, IR (KBr) cm^{-1}: 1683, 1598, 1521, 1455, 732; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.89 (d, 1H, ^2J = 15.6 Hz), 3.96 (d, 1 H, ^2J = 15.6 Hz), 6.76 (s, 1H), 7.12 (m, 1H, J = 7.2 Hz), 7.16–7.45 (m, 4 H), 7.47–7.54 (m, 3 H), 7.61 (d, 1H, J = 7.00 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.20, 60.02, 124.50, 125.20, 126.53, 128.02, 129.10, 129.60, 135.12, 135.72, 137.25, 146.83, 171.10; Anal. calcd for $C_{15}H_{12}ClNOS$: C, 62.17; H, 4.17; N, 4.83; S, 11.07;Found: C, 62.10; H, 4.09; N, 4.71; S, 10.89.

2.4.2. 2-(2-Nitrophenyl)-3-phenylthiazolidin-4-one (**4b**)

Cream Solid; m.p112–114 °C, IR (KBr) cm^{-1}: 1686, 1595, 1521, 1449, 1343; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.84 (d, 1H, ^2J = 16 Hz), 3.97 (d, 1H, ^2J = 16 Hz), 6.78 (s, 1H), 7.12 (m, 1H, J = 7.2 Hz), 7.16–7.27 (m, 4H), 7.47–7.49 (t, 1H, J = 8 Hz), 7.53–7.70 (m, 2H), 7.98–8.00 (d, 1H, J = 8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 32.29, 59.74, 125.53, 127.04, 127.10, 128.05, 129.36, 129.98, 135.02, 135.89, 137.73, 147.40, 171.36; Anal. calcd for $C_{15}H_{12}N_2O_3S$: C, 59.99; H, 4.03; N, 9.33; S, 10.68; Found: C, 59.88; H, 3.95; N, 9.42; S, 10.57.

2.4.3. 3-Phenyl-2-(pyridin-2-yl)thiazolidin-4-one (**4c**)

White solid; m.p 150–152 °C, IR (KBr) cm^{-1}: 1673, 1587, 1524, 1497, 1432; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.80 (d, 1H, ^2J = 15.6 Hz), 4.03 (d, 1H, ^2J = 15.6 Hz), 6.47 (s, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.15–7.40 (m, 5H), 7.52 (m, 1H), 7.72–7.74 (d, J = 7.4 Hz, 1H), 8.49 (d, J = 7.00 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.15, 60.21, 124.69, 127.04, 128.02, 129.30, 130.25, 135.05, 135.93, 147.40, 157.30, 171.36; Anal. calcd for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93; S, 12.51;Found:C, 65.55; H, 4.62; N, 10.99; S, 12.43.

2.4.4. 2-(3-Nitrophenyl)-3-phenylthiazolidin-4-one (**4d**)

Cream solid; m.p 179–181 °C, IR (KBr) cm^{-1}: 1676, 1596, 1529, 1521, 1497, 1386, 1348; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.89 (d, 1H, ^2J = 15 Hz), 4.08 (d, 1H, ^2J = 15 Hz), 6.72 (s, 1H), 7.11 (m, 1H, J = 7.2 Hz), 7.19–7.29 (m, 4H), 7.41–7.52 (t, 1H, J = 8 Hz), 7.51–7.72 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H),7.98–8.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.09, 60.14, 125.62, 127.22, 127.26, 128.15, 129.33, 129.93, 135.15, 135.93, 137.82, 147.42, 171.35; Anal. calcd for$C_{15}H_{12}N_2O_3S$:C, 59.99; H, 4.03; N, 9.33; S, 10.68; Found: C, 59.82; H, 3.93; N, 9.40; S, 10.52.

2.4.5. 3-Phenyl-2-(pyridin-3-yl)thiazolidin-4-one (**4e**)

White solid; m.p 135–137 °C, IR (KBr) cm^{-1}: 1673, 1582, 1495, 1431; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.88 (d, 1H, ^2J = 15.6 Hz), 4.05 (d, 1H, ^2J = 15.6 Hz), 6.57 (s, 1H), 7.13 (d, 1H, J = 6.4 Hz), 7.29–7.60 (m, 5H), 7.83–7.85 (d, J = 8 Hz, 1H), 7.38–7.40 (d, J = 4 Hz, 1H), 8.53 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.19, 60.28, 124.72, 127.05, 128.09, 129.35, 130.29, 135.14, 135.91, 147.47, 157.33, 171.35; Anal. calcd for $C_{14}H_{12}N_2OS$: C, 65.60; H, 4.72; N, 10.93; S, 12.51; Found:C, 65.51; H, 4.65; N, 10.98; S, 12.40.

2.4.6. 2-(4-Chlorophenyl)-3-phenylthiazolidin-4-one (**4f**)

White solid, m.p 125–127 °C, IR (KBr) cm^{-1}: 1675, 1595, 1520, 1453, 730; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.94 (d, 1 H, ^2J = 15 Hz), 4.02 (d, 1H, ^2J = 15 Hz), 6.58 (s, 1H), 7.04–7.45 (m, 7 H), 7.60–7.68 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.10, 59.95, 124.45, 125.22, 126.64, 129.12, 129.60, 135.10, 137.23, 146.81, 171.08; Anal. calcd for $C_{15}H_{12}ClNOS$: C, 62.17; H, 4.17; N, 4.83; S, 11.07; Found: C, 62.09; H, 4.05; N, 4.70; S, 10.87.

2.4.7. 2-(4-Nitrophenyl)-3-phenylthiazolidin-4-one (**4g**)

Yellow Solid; m.p 133–134 °C, IR (KBr) cm^{-1}: 1686, 1598, 1521, 1521, 1455, 1346; ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.89 (d, 1 H, ^2J = 15 Hz), 4.09 (d, 1 H, ^2J = 15 Hz), 6.69 (s, 1H), 7.12–7.15 (t, 1H, J = 7.2 Hz), 7.27–7.35 (m, 4H), 7.66–7.68 (d, 2 H, J = 8 Hz), 8.10–8.12 (d, 2 H, J = 8 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 33.11, 60.18, 125.65, 127.26, 128.15, 129.33, 129.93, 135.93,