

Contents lists available at ScienceDirect

Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstr

Shape-controlled synthesis of sodium zincate mesoporous structures based on sulfonated melamine formaldehyde and their application as catalysts for Biginelli reaction



Narges Zarnaghash^a, Ramin Rezaei^{a,*}, Payam Hayati^b, Azra Ghiasi Moaser^c, Mohammad Mahdi Doroodmand^d

^a Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Iran

^b Persian Gulf Science and Technology Park, Nano Gostaran Navabegh Fardaye Dashtestan Company, Borazjan, Iran

^c Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO-BOX 55181-83111, Maragheh, Iran

^d Department of Chemistry, College of Sciences, & Nanotechnology Research Center, Shiraz University, Shiraz 71454, Iran

ARTICLE INFO

Article history: Received 25 September 2020 Revised 24 January 2021 Accepted 25 January 2021 Available online 31 January 2021

Keywords: Solvent-free reaction Sodium zincate Ultrasound irradiation Heterogeneous catalysts Biginelli reaction

ABSTRACT

In the current research, two mesoporous structures of sodium zincate $[Na_2Zn(OH)_4]$, spheres and aggregated particles, has been synthesized from sulfonation of melamine-formaldehyde (MF) and then bounding $[Na_2Zn(OH)_4]$ particles onto the surface of sulfonated melamine-formaldehyde (SMF). Furthermore, in the present synthetic methodology the zinc oxide (ZnO) thin films on sulfonated melamine-formaldehyde was formed via the chemical deposition, and thermal treatment techniques of the sodium zincate. Several spectroscopic and analytical methods proved the structural and morphological properties of sodium zincate mesoporous structures based on sulfonated melamine formaldehyde $[SMF/Na_2Zn(OH)_4]$. The experimental studies showed that these catalytic systems showed high activity in the Biginelli reaction for the synthesis of 3,4-dihydropyrimidin-2(1H)-one derivatives and will find recoverable potential application. The obtained results indicated that the synthesized mesoporous structures had a thermal stability near 300 °C, particle-size distribution around of 10–120 nm for spheres and the surface area of 6 and 2 m²/g for spheres and aggregated particles, respectively.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

The applying of heterogeneous acidic catalysts is one of important fields in industrial chemistry, which has been attracting considerable attention in recent years. Disadvantages of homogeneous acid catalysts such as generating waste materials, equipment corrosion, the problems of separating and recycling, high cost, and low yields have limited homogeneous acid catalysts applications [1]. These problems can be overcome by heterogenizing homogeneous acid catalysts via various supports such as polymers [2–8], mesoporous materials [9], metal oxides [10,11], and nano-magnetites [12]. Although the reactants have finite access to the internal active sites of acid catalysts, nanomaterial-based acid catalysts display higher activity and selectivity than their corresponding bulky molecules. This result can be attributed to a considerable increase in surface area of supported system, which enhances the contact of reactant molecules with the catalyst [13]. Recently, the synthesis of

* Corresponding author. E-mail address: rezaieramin@yahoo.com (R. Rezaei). metal oxide nanoparticles has been attracting significant interest in nanotechnology research because of its high demand in industries and medical fields as drug delivery materials, fillers, antimicrobial agents, alternative catalysts, photonic and battery materials [14]. Additionally, many new applications have been developed as a result of controlling particle size and shape of metal oxide nanoparticles [15,16]. Many homogeneous and heterogeneous sulfonated catalysts have been prepared using the direct sulfonation technique, including the addition of chlorosulfonic acid [17]. MF resin has indicated the exceptional potential to enhance numerous properties, such as metal ions chelating [18], anion exchange [19], and composite as well as cells creation [20]. The porosity structure and the clear presence of amino functional groups on the surface of MF lead to distinctive physical, surface-chemical, and catalytic performance [21]. The SMF as a superhydrophilic material was designed and synthesized via self-assembly of a copolymer surfactant (F127) via the reaction of melamine with formaldehyde and NaHSO₃ in an aqueous solution. This material causes increasing the miscibility of the catalyst with the biofuel reactant. The structure of SMF has been fully characterized through electron microscopy methods [22]. Physical and chemical properties of the various nanostructures of ZnO, which are arising from size, morphology, dimensions, shape-controlled synthesis of nanostructures has generated considerable interest in this field [23]. The various nanostructures of ZnO have been used for many applications, so various conditions have been employed for preparing ZnO nanostructure, but in comparison with conventional techniques, the sonochemical method is far more convenient, fast, simple, and easily controlled [24]. Despite extensive surveys in the field of ZnO nanoparticles, limited reports are available on the sodium zincate nanoparticles. Sodium zincate (Na₂ZnO₂) nanostructure has been used as a nanofiller with particle stabilizing PVA films by Subramani et al. [25]. An improved dip-coating approach, applying an ammonium zincate solution, has been used to achieve supported zinc oxide films. The prepared ZnO film on glass or ceramic substrates has been used as photocatalyst [26]. The Italian chemist Pietro Biginelli proved multicomponent reaction of ethyl acetoacetate, benzaldehyde, and urea under strongly acidic conditions is a particularly useful approach for preparation of 3,4-dihydropyrimidin-2(1H)-ones (DH-PMs) [27]. DHPMs and their derivatives have evoked significant interest owing to a wide variety of their biological and pharmacological characteristics, such as antiviral, antitumor, antibacterial, and anti-inflammatory behavior [28–30]. Moreover, some of the marine alkaloids containing the dihydropyrimidinone in the center of their structure with biological activities have been separated from marine sources which can represent the natural properties of these compounds [31]. A wide range of sulfonated acids [32-38], Brönsted acids [39-40], Lewis acids [41,42], nanocatalysts [43,44] and polymers [45] have been effectively applied for preparing Biginelli products. Due to our enthusiasm about synthesis of nanostructure on SMF as a polymer-supported nanocatalysts [46], we have prepared SMF/Na₂Zn(OH)₄ as a novel heterogeneous solid acid catalyst and has been applied for preparation of 3,4 dihydropyrimidin-2(1H)-ones. Also, we proved that the thin film of zinc oxide (ZnO) particles had been formed on sulfonated melamine-formaldehyde by chemical, deposition, and thermal treatment techniques on sodium zincate. The prepared ZnO thin film acts as a photocatalyst for SMF.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were ordered from Merck, Fluka, and applied without more purification. All melting points were taken on a Mettler 9100 melting point instrument. The measurements of Fourier transform infrared spectroscopy (FT-IR) were performed on a 4300 Shimadzu FT-IR spectrometer. Hydrogen nuclear magnetic resonance (¹H NMR) and carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were measured with a Bruker Avance 400 MHz spectrometer in DMSO-d₆ solutions. Elemental analysis was done using Heraeus CHN Rapid analyzer. All products were identified compounds, and their structures were proved by comparison of the obtained physical and spectroscopic data with those of authentic samples. Powder X-ray diffraction (XRD) patterns of the as-prepared particles were performed by XRD (D8 ADVANCE, Bruker, Nederland) at ambient room temperature. Scanning electron microscope (SEM) images were taken with a MIRA III SEM, the Czech Republic, at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were gathered by a JEOL, JEM-2100F transmission electron microscope at a 200 kV accelerating voltage. The Brunauer-Emmett-Teller (BET), specific surface areas, were calculated by nitrogen adsorption-desorption at 77°K with a Belsorp mini II instrument. The Barret-Joyner-Halenda (BJH) technique was utilized to measure the pore size distribution. Energydispersive X-ray (EDX) spectroscopy microanalysis (Bruker XFlash 6130) was used in order to analyzing phase composition and elemental distribution maps of the as-prepared particles. Thermal gravimetric analysis (TGA) of SMF/Na₂Zn(OH)₄ was investigated using TG thermoanalyser (TGA, Mettler system TA 4000) under N₂ environment at a heating rate of 10 °C min⁻¹.

2.2. Synthesis of sodium zincate [Na₂Zn(OH)₄] particles

 $Na_2Zn(OH)_4$ was synthesized, according to the procedures reported previously [47]. The reaction of ZnO (5.50 g, ~67.0 mmol) in a boiling solution of NaOH (20.0 g, ~500.0 mmol) in 20 mL H₂O is an efficient strategy for the preparation of $Na_2Zn(OH)_4$ particles. After the clear solution was cooled within a few hours, the colorless plates of crystal structure appeared. After filtering, the residue was washed with cold water and dried using an oven at 50 °C. Finally, the obtained product was ball milled for ~1 h at ambient temperature.

2.3. Synthesis of sulfonated melamine-formaldehyde (SMF)

MF resin (10.0 g) was slowly added to 50.0 mL stirring CHCl₃ at 0 °C for 2 h. Then under mild stirring, chlorosulfonic acid (20.0 g, ~150.0 mmol) was gently added to the suspension at 0 °C. The resulting mixture was stirred for 24 h to remove HCl. Subsequently, the mixture was filtered, the white crystals were washed with petroleum ether (2 × 15.0 mL), and dried at 50 °C under vacuum conditions for several hours to gain sulfonated melamine-formaldehyde (5.25 g).

2.4. Synthesis of sulfonated melamine-formaldehyde supported structured sodium zincate $[(SMF/Na_2Zn(OH)_4)]$ spheres and aggregated particles

The SMF/Na₂Zn(OH)₄ spheres and aggregated particles were prepared by a simple sonochemical technique using a sonochemical bath. The mentioned method for preparing desired products is as follows: The SMF (0.40 g) was suspended in water (10 mL) and gently refluxed for 12 h, then Na₂Zn(OH)₄ (0.045 g, 0.250 mmol) was added. The reaction mixture was then stirred for ~1 h under ambient temperature, and microwave heating was performed with a power of 800 W for 5.0 min. The SMF/Na₂Zn(OH)₄ spheres and aggregated particles were successfully synthesized in a sonicator at 800 W (freq. 50 MHz), for 4, and ~8 h, respectively. The resulted products, SMF/Na₂Zn(OH)₄ spheres and aggregated particles, were placed in a vacuum oven for ~2 h at 250 °C to get uniform drying.

2.5. Catalytic performances of SMF/Na₂Zn(OH)₄ spheres

In a model reaction for the preparation of 3,4-dihydopyrimidin-2(1H)-ones, a mixture of aromatic aldehyde (1.0 mmol), ethyl ace-toacetate (0.130 g, 1 mmol), urea (0.090 g, 1.5 mmol), and catalyst [SMF/Na₂Zn(OH)₄] spheres (0.10 g, 0.07 wt%) was stirred at 80 °C under solvent-free conditions. The reaction progress was checked by TLC using petroleum ether and ethyl acetate (5:2) as eluent. After completing the reaction, the mixture was allowed to cool and was extracted with hot ethanol (5.0 mL). The purification of products was done by concentration and allowing standing overnight the filtrate. The resultant white crystals of the pure 3,4-dihydropyrimidin-2(1H)-ones were collected by filtration. Melting point, IR, ¹H NMR, ¹³C NMR, and elemental analysis proved the structures of all products.

2.6. General procedure for recycling of SMF/Na₂Zn(OH)₄

The recyclability of SMF/Na₂Zn(OH)₄ was studied in the model Biginelli reaction leading to 3,4-dihydopyrimidin-2(1H)-ones. At

the end of the reaction, the heterogeneous catalyst was filtered via a glass filter, washed thoroughly with hot ethanol (2×15 ml) to eliminate the organic pollutants and dried in a vacuum oven at 80 °C for about 3 h. Moreover, the catalyst has been successfully reused without noticeable loss of activity for subsequent reactions. The results show that the catalyst, even after four cycles afforded a high yield of the desired product.

The spectral data

(5-Ethoxycarbonyl)-6-methyl-4-phenyl-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 1): mp: 196–198 (lit.: 202–204 °C) [39].; IR (KBr): 3240, 3118, 2975, 1725, 1635,1460,1283 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.20 (s, 1H, NH), 7.75 (s, 1H, NH), 7.28–7.15 (m, 5H, ArH), 5.14 (s, 1H, CH), 3.90 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 2.20 (s, 3H, CH₃), 1.12 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.8, 153.4, 147.1, 143.2, 129.6, 125.8, 125.1, 100.9, 60.4, 54.9, 17.9, 14.1; Anal. Calcd for C₁₄H₁₆N₂O₃: C, 64.60; H, 6.20; N, 10.76. Found: C,64.66; H, 6.27; N, 10.95.

(5-Ethoxycarbonyl)-6-methyl-4-(2-chlorophenyl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 2): mp: 218–220 (lit.: 222–224 °C) [**39**].; IR (KBr): 3225, 3152, 2980, 1680, 1620, 1432, 1275 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.22 (s, 1H, NH), 7.70 (s, 1H, NH), 7.35–7.24 (m, 4H, ArH), 5.54 (s, 1H, CH), 3.90 (q, *J* = 7.0 Hz, 2H, OCH₂), 2.30 (s, 3H, CH₃), 1.09 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.2, 151.8, 149.2, 141.1, 130.7, 130.1, 127.1, 126.4, 100.3, 59.5, 51.4, 17.9, 14.1; Anal. Calcd for C₁₄H₁₅N₂O₃Cl: C, 57.03; H, 5.13; N 9.51 .Found: C, 56.90; H, 5.04; N, 9.58.

(5-Ethoxycarbonyl)-6-methyl-4-(3-nitrophenyl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 3): mp: 228–230 (lit.: 229–231 °C) [**39**].; IR (KBr): 3275, 3102, 2965, 1680, 1618, 1535,1450, 1270 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.30 (s, 1H, NH), 7.85 (s, 1H, NH), 8.15–7.57 (m, 4H, ArH), 5.35 (s, 1H, CH), 3.94 (q, J = 7.0 Hz, 2H, OCH₂CH₃), 2.24 (s, 3H, CH₃), 1.10 (t, J = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.1, 151.9, 148.1, 147.1, 147.5, 133.3, 130.1, 122.7, 121.1, 99.3, 59.6, 52.9, 17.8, 14.2; Anal. Calcd for C₁₄H₁₅N₃O₅: C, 55.06; H, 4.96; N, 13.77. Found: C, 54.60; H, 4.85; N, 13.72.

(5-Ethoxycarbonyl)-6-methyl-4-(3-hydroxyphenyl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 4): mp: 159–161 (lit.: 163–165 °C) [39].; IR (KBr): 3515, 3340, 3175, 2980, 1725, 1675, 1633, 1420, 1275 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.35 (s, 1H, OH), 9.10 (s, 1H, NH), 7.75 (s, 1H, NH), 7.15–6.55 (m, 4H, ArH), 5.15 (s, 1H, CH), 3.97 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 2.20 (s, 3H, CH₃), 1.15 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.2, 156.8, 152.6, 148.4, 147.1, 130.2, 116.2, 114.4, 113.3, 101.1, 59.6, 52.8, 17.6, 14.2; Anal. Calcd for C₁₄H₁₆N₂O₄: C, 60.08; H, 5.84; N, 10.14. Found: C, 59.35; H, 5.40; N, 10.88.

(5-Ethoxycarbonyl)–6-methyl-4-(4-methoxyphenyl)–3,4dihydropyrimidin-2(1H)-one (Table 3, entry 5): mp: 206–208 (lit.: 199–201 °C) [40].; IR (KBr): 3240, 1770, 1680, 1625, 1512, 1236 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.15 (s, 1H, NH), 7.70 (s, 1H, NH), 7.25 (d, *J* = 8.0 Hz, 2H, ArH), 6.90 (d, *J* = 8.0 Hz, 2H, ArH), 5.15 (s, 1H, CH), 4.07 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 3.75 (s, 3H, OCH₃), 2.32 (s, 3H, CH₃), 1.18 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.9, 159.4, 153.7, 146.4, 136.2, 128.2, 114.2, 101.8, 59.2, 55.4, 55.2, 18.5, 14.5; Anal. Calcd for C₁₅H₁₈N₂O₄: C, 62.07; H, 6.20; N, 9.66. Found: C, 62.55; H, 6.28; N 9.58.

(5-Ethoxycarbonyl)-6-methyl-4-(4-methylphenyl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 6): mp: 210–212 (lit.: 215–216 °C) [**39**].; IR (KBr): 3255, 3115, 2970, 1724, 1653, 1610, 1544, 1240 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.20 (brs, 1H, NH), 7.75 (brs, 1H, NH), 7.20 (S, 4H, ArH), 5.25 (s, 1H, CH), 4.07 (q, J = 7.0 Hz, 2H, OCH₂CH₃), 2.25 (s, 3H, CH₃), 2.18 (s, 3H, ArCH₃), 1.12 (t, J = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.9, 153.4, 148.7, 141.5, 136.2, 128.2, 125.5, 101.8, 59.2, 53.4, 20. 8,

18.2, 14.3; Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.66; H, 6.62; N, 10.22. Found: C, 65.35; H, 6.75; N, 10.15.

(5-Ethoxycarbonyl)–6-methyl-4-(4-chlorophenyl)–3,4dihydropyrimidin-2(1H)-one (Table 3, entry 7): mp: 210–212 (lit.: 212–214 °C) [40].; IR (KBr): 3240, 3120, 1710, 1655, 1635, 1556, 1268 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.15 (s, 1H, NH), 7.30–7.21 (m, 4H, ArH), 6.30 (s, 1H, NH), 5.50 (s, 1H, CH), 3.90 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 2.52 (s, 3H, CH₃), 1.15 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO–d₆): δ = 165.2, 152.6, 148.1, 142.9, 131.6, 129.8, 129.1, 128.2, 127.4, 98.3, 58.8, 52.6, 17.7, 13. 4; Anal. Calcd for C₁₄H₁₅N₂O₃Cl: C, 57.14; H, 5.10; N, 9.52. Found: C, 56.78; H, 4.90; N, 9.64.

(5-Ethoxycarbonyl)-6-methyl-4-(4-styryl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 8): mp: 218–220 (lit.: 232–235 °C) [40].; IR (KBr): 3248, 3118, 1715, 1650, 1615, 1560, 1265 cm⁻¹; ¹H NMR (DMSO–d₆): δ = 9.13 (s, 1H, NH), 7.45 (s, 1H, NH), 7.35–7.20 (m, 5H, ArH), 6.35 (d, *J* = 12.0 Hz, 1H, =CH), 6.20 (dd, *J* = 12.0, 1H, =CH), 4.70 (S, 1H, CH), 4.15 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 2.20 (s, 3H, CH₃), 1.15 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO-₆): δ = 165.3, 152.7, 148.2, 136.8, 131.1, 128.8, 128.1, 127.5, 126.7, 98.5, 59.1, 51.6, 17.6, 14.3;. Anal. Calcd for C₁₆H₁₈N₂O₃: C, 67.12; H, 6.34; N, 9.78. Found: C, 67.30; H, 6.38; N, 9.70.

(5-Ethoxycarbonyl)-6-methyl-4-(2-furfuryl)-3,4-

dihydropyrimidin-2(1H)-one (Table 3, entry 9): mp: 204–206 (lit.: 209–211 °C) [**3**9].; IR (KBr): 3325, 3215, 3110, 1690, 1645, 1545, 1248 cm⁻¹; ¹H NMR (DMSO-d₆): δ = 9.20 (s, 1H, NH), 7.65 (s, 1H, NH), 7.55 (s, 1H, ArH), 6.45 (s, 1H, ArH), 6.10 (s, 1H, arom CH), 5.25 (s, 1H, CH), 4.10 (q, *J* = 7.0 Hz, 2H, OCH₂CH₃), 2.25 (s, 3H, CH₃), 1.18 (t, *J* = 7.0 Hz, 3H, OCH₂CH₃); ¹³C NMR (DMSO-d₆): δ = 165.1, 155.8, 152.1, 149.5, 142.3, 111.56, 105.4, 97.1, 59.3, 48.5, 18.7, 14.5; Anal. Calcd for C₁₂H₁₄N₂O₄: C, 57.57; H, 5.64; N 11.20

3. Results and discussion

To get insight into the nature of the catalytic activity of the heterogeneous solid acid, we produce $SMF/Na_2Zn(OH)_4$ structures as effective solid acid catalysts. In the first step of catalysts preparation, SMF is formed by adding chlorosulfonic acid to melamineformaldehyde in dry CH_2Cl_2 at 0 °C (Scheme 1).

By modification of SMF with $Na_2Zn(OH)_4$ particles under ultrasonic irradiation, SMF/Na₂Zn(OH)₄ were prepared. Initially, Na₂Zn(OH)₄ nuclei generally evolve into spheres, and then they can be converted into aggregated particles (Scheme 2). The crystal growth in a specific direction has been controlled by changing the duration of ultrasonic irradiation. The conversion of spherical morphology into aggregated particles is because of the adsorption of ultrasound energy by the ionic species generated from water molecules. The growing processes of Na₂Zn(OH)₄ particles are controlled both by the diffusion of Zn^{2+} ions and the ratecontrolling reactions which take place at the surface of polymer [48]. Additionally, charged polymeric materials have various effects on crystallization of $Na_2Zn(OH)_4$ in solution. The aggregation of suspended amorphous clusters leads to formation of homogeneous nucleation which cause minimizing the total surface energy of Na₂Zn(OH)₄. Heterogeneous nucleation of Na₂Zn(OH)₄ causes the amorphous clusters to aggregate into the spherical morphology. Aggregated particles morphology could be achieved by irreversible and oriented attachment of particles by lateral atom-byatom arrangement at the interface of Na₂Zn(OH)₄ particles [49].

3.1. Catalyst characterization

The titration method was used to measure the protic protons of the organized SMF. The titration and its first derivative curves







 $\label{eq:scheme 2} \textbf{Scheme 2.} Preparation of sulfonated melamine-formal dehyde supported Na_2Zn(OH)_4 particles [SMF/Na_2Zn(OH)_4].$





of 0.1 g of SMF in 10 mL water with 0.01 M NaOH show that the surface densities are around 1.3 mmol H^+/g (Fig. 1).

The titration method was used to determine the structure of sodium zincate two proposed modes of Na₂Zn(OH)₄ [47] and Na₂ZnO₂•2H₂O [25]. For this purpose, after preparation and sonication of sodium zincate, this compound was reacted with chlorosulfonic acid to obtain the sulfonated sodium zincate. The asprepared compound was exposed to ultrasonic irradiation at 800 W (freq. 50 MHz), for 8 h. If sodium zincate has Na₂Zn(OH)₄ structure, the following reaction occurs as a result of the sulfonation:

$NaZn(OH)_4 + 4CLSO_3H \rightarrow Na_2Zn(HSO_4) + 4HCL$

In order to determine the basicity character of $Na_2Zn(OH)_4$, the titration and its first derivative curve were drawn up (Fig. 2a). Furthermore, the titration and its first derivative curve corresponding to $Na_2Zn(HSO_4)_4$ indicates its acidity character (Fig. 2b). Thus, it can be concluded that in this case sodium zincate has $Na_2Zn(OH)_4$ structure. $Na_2Zn(HSO_4)_4$ in 10 mL of water were done with 0.01 M HCl and NaOH, respectively.

The FT-IR spectra of $Na_2Zn(OH)_4$, MF, SMF, SMF/ $Na_2Zn(OH)_4$ spheres and SMF/ $Na_2Zn(OH)_4$ aggregated particles are displayed in Fig. 3 respectively. The FT-IR spectrum of pure MF indicates the broad absorption band at 3411 cm⁻¹, which is related to the stretching vibration of N–H and O–H (Fig. 3b) of MF [50]. Ac-



Fig. 3. FT-IR spectra of (a) $Na_2Zn(OH)_4$, (b) MF (c) SMF, (d) SMF/ $Na_2Zn(OH)_4$ spheres and (e) SMF/ $Na_2Zn(OH)_4$ aggregated particles.



Fig. 4. Powder XRD patterns of (a) MF, (b) SMF, (c) SMF/Na_2Zn(OH)_4 aggregated particles and (d) SMF/ Na_2Zn(OH)_4 spheres.

cording to the spectra of SMF (Fig. 3c), SMF/Na₂Zn(OH)₄ spheres (Fig. 3d) and SMF/Na₂Zn(OH)₄ aggregated particles (Fig. 3e), the O = S = O asymmetric and symmetric stretching vibration bands of the sulfonic acid groups (-SO₃H) are appeared at 1342, 1165 cm⁻¹, 1335, 1148 cm⁻¹ and 1334, 1148 cm⁻¹, respectively [51]. A weak absorption band at ~ 486 cm⁻¹ is referred to Zn–O vibration mode of Na₂Zn(OH)₄ sample (Fig. 3a) [52]. Furthermore, in the spectra of SMF/Na₂Zn(OH)₄ spheres (Fig. 3d) and SMF/Na₂Zn(OH)₄ aggregated particles (Fig. 3e), the characteristic stretching vibration of Zn–O bond of Na₂Zn(OH)₄ have appeared at 612 and 604 cm⁻¹ respectively.

The X-ray diffraction (XRD) measurements of the as-prepared samples is indicated in Fig. 4. Two broad diffraction peaks of the



Fig. 5. XRD spectrum of SMF/ZnO from thermal treatment of $SMF/Na_2Zn(OH)_4$ structures.

MF in 2θ range of 5–15° and 15–25° (002 diffractions) shows the amorphous structure for this compound (Fig. 4a). Two equivalent diffraction peaks with equal size are the characteristic peak of MF. After sulfonation the intensity of the 2nd peak of the SMF has been reduced (Fig. 4b). Due to the lack of characteristic peaks in the SMF/Na₂Zn(OH)₄ structures, the composition of these compounds cannot be estimated by XRD patterns (Fig. 4c-d). Furthermore, the XRD pattern has been used to investigate the structural behavior of sodium zincate on sulfonated melamine formaldehyde. It can be seen that after heating several strong reflections appear, which gives a perspective view of the crystal orientations. After heating of SMF/Na₂Zn(OH)₄ at 600 °C for 3 h, its XRD pattern (Fig. 5) exhibited the peaks at $2\theta = 31.75$, 34.45, 36.25, 47.55, 56.60 and 62.85 that could be assigned to (100), (002), (001), (102), (110) and (103) planes of ZnO, respectively. Due to the matching achieved data with previously reported structure of ZnO (JCPDS file No. 80-0074), it seems caused by the ZnO film is deposited by the dipcoating method using zincate [24].

The size, structure/morphology of as-synthesized $Na_2Zn(OH)_4$ were evaluated by the SEM images. As shown in the SEM images, the irregular spherical $Na_2Zn(OH)_4$ particles are aggregated on the wrinkled structures of $Na_2Zn(OH)_4$ (Fig. 6).

The interaction of polymers with the metal ions through complexation or ion-pair formation may improve the optical, electronic and physical properties of pure ZnO particles. In addition, because of the high polarity of water, ZnO is almost insoluble and its agglomeration happens immediately in water during the synthesis. Therefore, using of polymers as capping agents, is a way to overcome these problems. The role of the polymers as a structure directing agent was approved by a comparative study of ZnO particles synthesis with/without using polymers. Furthermore, changes in morphology, crystal orientation and dimensions of the particles were related to various nature of polymers as the capping agents. The pH of the reaction medium is a significant factor affecting the morphology of particles and the action of capping agents. The distribution of Zn(II) species is slightly affected by pH variations in such a way that Zn(OH)₂ at pH 6–9 the dominant species. By increasing the pH around 9-13 the dominant species appear to be $Zn(OH)_4$ ^{- 2}. The SMF as an amphoteric polymer with sufficient free NH and SO_3H groups on its surface, has the ability to adsorb onto the substrate through hydrogen-bond interactions and make a physical barrier to the preferred growth crystal planes. In the first step the interaction of SMF with $Zn(OH)_4 - 2$ ions result into the formation of micro-spherical capsules. Therefore, $Zn(OH)_4 - 2$ species spread towards the surface of the polymer with the assistance water molecules which are present in the reaction medium, lead to formation of spherical micelles. Finally, the growth of the crystals in all directions results into the formation of assembled aggregated particles (Fig. 7) [49].

The SEM images investigated the morphological changes of $Na_2Zn(OH)_4$ spheres and aggregated particles on the SMF surface. It is assumed that the particles have homogeneous mean sizes after the modification. Furthermore, the shape, size, and morphology of the produced SMF/Na₂Zn(OH)₄ characterized by TEM analysis. TEM imaging proves that the structures gained through ultrasonic irradiation within four hours have considerably various morphologies from those obtained within eight hours (Fig. 8).

The surface area, pore volume, and pore size distributions of the SMF/Na₂Zn(OH)₄ particles were analyzed by using the BET and BJH equations (Table 1). The BET surface area measurements indicated that, compared to the SMF/Na₂Zn(OH)₄ spheres, the surface area of the SMF/Na₂Zn(OH)₄ aggregated particles were significantly decreased from 6 m² g⁻¹ to 2 m² g⁻¹ which was attributed to the aggregation effects on the surfaces of the SMF/Na₂Zn(OH)₄ and the random displacement of Na₂Zn(OH)₄ aggregated particles layers.

The N₂ adsorption-desorption isotherms and pore size distributions (PSDs) for both SMF/Na₂Zn(OH)₄ spheres and aggregated particles were shown in Fig. 9. Based on IUPAC classification, both isotherm plots were classified as type III [53], which belonged to the H3 type [54]. The hysteresis loops of SMF/Na₂Zn(OH)₄ spheres which are occurred in the range of $0.30 < P/P_0 < 0.97$, as well as the corresponding pore distribution in the range of 5-10 nm, was the characteristic of mesoporous materials. The SMF/Na₂Zn(OH)₄ aggregated particles demonstrate a type III isotherm with H3 hysteresis loop in the range of 0.30-0.97 P/P₀. Furthermore, as shown in Fig. 9 the pore size distribution is shifted to below 8 nm. This phenomenon suggested that accumulation of slit pores in the obtained aggregated particles composite has been resulted in reduction of surface area, pore volume and pore diameter. According to the BET specific surface area analysis of SMF/Na₂Zn(OH)₄ aggregated particles uncertain the superior uncertain the superior of SMF/Na₂Zn(OH)₄ aggregated particles uncertain the superio



Fig. 6. SEM images of the prepared $Na_2Zn(OH)_4$ particles via hydrolysis and complexation of Zn^{+2} ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. SEM images of the aggregated particles structure of the obtained of composite material SMF/Na₂Zn(OH)₄.

 Table 1

 Surface data of SMF/Na₂Zn(OH)₄ spheres and aggregated particles.

Sample	BET surface area (m ² g^{-1})	Pore volume(cm ³ g^{-1})	Pore diameter (nm)
$SMF/Na_2Zn(OH)_4$ spheres $SMF/Na_2Zn(OH)_4$ aggregated particles	6	0.021	13.01
	2	0.007	11.65

gated particles, the observed aggregation can be referred to sulfonic acid groups in SMF which are successfully grafted onto the $Na_2Zn(OH)_4$ particles.

The EDX of SMF/Na₂Zn(OH)₄ structures demonstrate element composition analysis and all of the C, N, O, S, Zn and Na elements exist in the samples (Fig. 10). Moreover, the Zn content in the SMF/Na₂Zn(OH)₄ shows its amount in the SMF/Na₂Zn(OH)₄ (0.68 wt%).

The EDX elemental mapping shows the uniform dispersion of the carbon, nitrogen, oxygen, zinc, and sodium elements (Fig. 11).

Thermogravimetric analysis (TGA) was carried out to evaluate the thermal stability of both SMF/Na₂Zn(OH)₄ spheres and aggregated particles. According to the TGA curve of the SMF/Na₂Zn(OH)₄ aggregated particles, it can be seen that it is shifted to higher temperatures compared to the TGA curve of the SMF/Na₂Zn(OH)₄ spheres with thermal stability up to 200 °C. For both SMF/Na₂Zn(OH)₄ structures, the first weight loss in the range of at 180–350 °C is related to the removal of formaldehyde. This elimination can be attributed to the loss of ether bonds and the formation of methylene bridges.

Thermal degradation of the triazine-ring begins beyond 390 °C. The second distinct weight loss region is attributed to the deamination reaction, which leads to the formation of HCN [55]. These measurements illustrate that the aggregation effects on the surfaces of the SMF/Na₂Zn(OH)₄ aggregated particles and grafting the sulfonic acid groups in SMF onto the Na₂Zn(OH)₄ particles make higher thermal stability (Fig. 12).

These experimental observations showed that sodium zincate particles were immobilized on the surface of SMF and SMF/Na₂Zn(OH)₄ structures have been successfully synthesized.

3.2. The catalytic performance of SMF/Na2Zn(OH)4 structures for the preparation of 3,4-dihydropyrimidin-2(1H)-ones

After characterization of the catalysts based on the experimental observations, it turned out that the structure of the aggregated particles is not influencing the catalytic activity and not competing with the activity of spherical particles. However, the catalytic performance of SMF/Na₂Zn(OH)₄ spheres was examined in the Biginelli reaction for the synthesis of dihydropyrimidinone derivatives (Scheme 3). The effect of the catalyst amount and solvents in the reaction between benzaldehyde, ethyl acetoacetate, and urea with a building block ratio of 1:1:1.5, respectively, were investigated.

In the first stage, the reaction conditions were investigated and optimized by changing the amount of catalyst. The trace product obtained in the absence of catalyst was evident for the catalytic activity of SMF/Na₂Zn(OH)₄ spheres structure (Table 2, entry 1). It should be mentioned that the optimum amount of catalyst was 7 wt% and the best results were obtained at 30 min, by changing the amount of the catalyst (3, 5, and 7 wt%) (Table 2, entries 2-4). Then the solvent effect was examined in the various solvents such as n-propanol, H₂O, DMF, and toluene (15 mL). Formation of by-products and reduction of reaction rate was observed in the presence of solvents (Table 2, entries 5-8). Various polar and nonpolar solvents evaluation for the catalytic activity of the catalyst indicated, the n-propanol was the most favor solvent because of its considerable efficiency and the environmental benefits. In n-propanol and H₂O the catalyst was not dispersed in the reaction medium, but it was found that n-propanol was the better solvent due to achieve the highest solubility of the reactants. The lower yield of product and higher reaction time in nonpolar solvents may be due to the poor solubility of the reactants. The effect of increasing temperature from 20 to 80 °C has been examined. The results show that the yield of reaction increased by increasing temperature, but there was no significant progress of the reaction above 80 °C. Therefore, in this study, solvent-free conditions with 7 wt% of catalyst at 80 °C were systematically optimized as reaction conditions. All the following experiments were performed under the optimized conditions. The superhydrophilicity of the support is helpful to increase the miscibility of the catalyst with the reactants. The results show that the hydrophilic surface of the catalyst is favorable for the adsorption of polar reactants (benzaldehyde, ethyl acetoacetate and urea) and desorption of the non-polar product (dihydropyrimidinone). This feature would change the reaction balance, leading to a significant enhancement of the catalytic performance. In addition, due to the water formation as a by-product in the Biginelli reaction, we postulated that the water is momentarily adsorbed, giving a swollen surface so it can dissolve the polar reactants. The reaction proceeds by stirring in the presence of the catalyst at 80 °C in solvent free condition [22,56].

In the next step, to explore the generality of the Biginelli reaction, different types of substituted aromatic aldehydes with ethyl acetate and urea have been investigated under the optimized con-



Fig. 8. SEM, TEM and particle size distribution images (obtained from image analysis of SEM and TEM, respectively) of the obtained of samples under ultrasound irradiation for ~4 h (a, c, e, g) and ~8 h (b, d, f, h).



Fig. 9. Nitrogen adsorption-desorption isotherms and pore size distribution curves of SMF/Na₂Zn(OH)₄ spheres and aggregated particles.



Fig. 10. EDX of SMF/Na₂Zn(OH)₄ spheres and aggregated particles.

Tabl	e 2	

Optimization of conditions for preparing of 5-ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyridin-2 (1H)-one catalyzed by SMF/Na $_2$ Zn(OH) $_4$ spheres^a.

Entry	Amount of catalyst (wt%)	Condition/solvent	Time (min)	Yield (%) ^b
1	-	80 °C/solvent-free	180	10
2	3	80 °C/solvent-free	60	60
3	5	80 °C/solvent-free	30	60
4	7	80 °C/solvent-free	30	85
5	7	80 °C/ n-propanol	120	60
6	7	80 °C/water	60	70
7	7	80 °C/DMF	240	55
8	7	80 °C/toluene	240	40

^a Reactions carried out at 1 mmol scales with the molar ratio of benzaldehyde: ethylacetoacetate: urea: 1:1:1.5.

^b isolated yield.





Na Ka

Fig. 11. Elemental mapping analysis of ${\rm SMF}/{\rm Na_2Zn}({\rm OH})_4$ spheres and aggregated particles regions.

ditions (Scheme 3). The results indicate that the aldehydes with sensitive functional groups such as Cl, NO_2 , OCH_3 , and $CH=CH_2$ successfully participated in reactions (Table 3, entries 2, 3, 5, 7 and 8). In the case of furfural as a heterocyclic aromatic aldehyde, SMF/Na₂Zn(OH)₄ structures played a significant catalytic role without making of any side products (Table 3, entry 9). It should be noted that the low boiling points of aliphatic aldehydes may lead



Fig. 12. TGA spectra of (a) $SMF/Na_2Zn(OH)_4$ spheres and (b) $SMF/Na_2Zn(OH)_4$ aggregated particles.

Table 3				
Synthesis	of	3,4-dihydropyrimidinones	catalyzed	by
SMF/Na ₂ Zi	n(OF	I) ₄ spheres under solvent-fr	ree conditio	on ^a .

Entry	R	Time (min)	Yield (%) ^b
1	C ₆ H ₅	30	85
2	2-Cl-C ₆ H ₄	30	80
3	$3 - NO_2 - C_6 H_4$	35	80
4	3-0H-C ₆ H ₄	35	80
5	$4-CH_{3}O-C_{6}H_{4}$	20	95
6	$4-CH_3-C_6H_4$	30	85
7	4-(Cl)-C ₆ H ₄	30	80
8	pH-CH=CH ₂	35	75
9	2-Furyl	60	73
10	$CH(CH_3)_2$	60	-

 a Reaction condition: aldehydes (1 mmol), ethylace-toacetate (1 mmol), urea (1.5 mmol), SMF/Na_2Zn(OH)_4

^b Isolated yield.

to incomplete reactions under solvent-free conditions (Table 3, entry 10).

The better catalytic ability of SMF/Na₂Zn(OH)₄ spheres in compare with Na₂Zn(OH)₄ aggregated particles is due to the grafted sulfonic acid groups on the aggregated particles, which cause the reduction of the catalyst activity [49]. The catalytic efficiency of SMF and Na₂Zn(OH)₄ particles in comparison with SMF/Na₂Zn(OH)₄ spheres, have been investigated separately in the same condition. Comparative data are given in Table 4. The results exhibited yields of 85, 70 and 35% for SMF/Na₂Zn(OH)₄ spheres, SMF and Na₂Zn(OH)₄ particles, respectively. Moreover, the recyclability and stability of the unsupported Na₂Zn(OH)₄ particles was

spheres (7 wt%).



Scheme 3. Synthesis of 3,4-dihydropyrimidinones catalyzed by SMF/Na₂Zn(OH)₄ spheres under optimized conditions.



Scheme 4. The mechanism of 3,4-dihydropyrimidinones synthesis catalyzed by SMF/Na₂Zn(OH)₄ structures.

investigated by the model reaction under optimized condition. The observations illustrated a constant decrease in the isolated yield of the reaction in each run. The obtained results might be due to the aggregation of the unsupported $Na_2Zn(OH)_4$ sphere particles during the reaction [57]. Unlike a vast number of polymer based catalyst like PSSA and PVSA, SMF as an amphoteric polymer has a superhydrophilic and acidic-basic balance with a moderate density of $-SO_3H$ as acidic sites and nitrogen species as Lewis base sites. In this system, SMF acts as the support to increase the miscibility of the composite toward polar reactants [22,56 and 58].

According to the reaction mechanism reported by Kappe [59], the initial step includes the formation of the β -dicarbonyl compound from the Knoevenagel condensation of the activated aldehyde by SMF/Na₂Zn(OH)₄ spheres with enol type of ethyl acetoacetate. In the second step, the interception of the iminium ion by ethyl acetoacetate generates an open-chain ureide that leads to the

production of intermediate. Furthermore, this step is the important rate-limiting step. Finally, cyclization and dehydration produce the 3,4-dihy-dropyrimidin-2(1H)-one (Scheme 4).

Hot filtration studies were performed with the SMF/Na₂Zn(OH)₄ spheres to test true heterogeneity of the reaction. After 30 min of reaction, the SMF/Na₂Zn(OH)₄ spheres were recovered from the reaction system by simple filtration and the reaction was continued with the filtrate in the absence of any solid catalyst. As expected, the results showed that the reaction did not progress in the absence of the catalyst which confirms that the reaction occurs heterogeneously (Fig. 13).

Since the recovery and reusability is one of the most significant benefits of heterogeneous catalysts, after separation of the catalyst by centrifuging, catalyst was washed with hot ethanol and dried in a vacuum oven at 90 °C temperature for 2 h. Although the activity of the recovered catalyst was lost in the 2nd run itself, and 3t



Fig. 13. Hot filtration test for the SMF/Na₂Zn(OH)₄ spheres catalyzed Biginelli reaction for preparing of 5-ethoxycarbonyl-4-phenyl-6-methyl-3,4-dihydropyridin-2 (1H)-one in n-propanol at 80 °C.



Fig. 14. Reusability of the SMF/Na₂Zn(OH)₄ spheres in the Biginelli reaction.

Table 4

Entry	Catalyst (7 wt%)	Time (min)	Yield (%) ^b
1	SMF/ Na ₂ Zn(OH) ₄	30	85
2	SMF	30	70
3	$Na_2Zn(OH)_4$	30	35

 a Reaction condition: aldehydes (1 mmol), ethyl acetoacetate (1 mmol), urea (1.5 mmol) and $SMF/Na_2Zn(OH)_4$ spheres (7 wt%).

Table 5

^b Isolated yield.

obtained for the recovered catalyst (Fig. 14). To show the efficiency of this catalyst, the results of

& 4th run consuming two fold time, but acceptable results were

SMF/Na₂Zn(OH)₄ spheres structure with reported sulfonated catalysts were compared in the preparation of 5-ethoxycarbonyl-4phenyl-6-methyl-3,4-dihydropyridin-2 (1H)-One through the Biginelli reaction. Comparison of the catalytic activity of the SMF/Na₂Zn(OH)₄ spheres with other catalysts showed that yields of SMF/Na₂Zn(OH)₄ spheres was comparable with other compounds however required lower reaction times (Table 5).

Comparative :	study	of th	e results	of th	e SMF/ZnO	spheres	with	several	reported	sulfonated	catalysts	in
Biginelli react	ion.											

Entry	Catalyst	Condition	Time (min)	Yield (%)	Reference
1	Ce(C ₁₂ H ₂₅ SO ₃) ₃	EtOH/80 °C	240	93	32
2	Bentonite/PS-SO ₃ H	Solvent-free/120 °C	30	89	33
3	PS-PEG-SO₃H	Dioxane/80 °C	600	86	34
4	Carbon-SO₃H	CH ₃ CN/80 °C	240	89	35
5	Fe ₃ O ₄ /PAA-SO ₃ H	Solvent-free/rt.	120	90	36
6	nano-γ-Fe ₂ O ₃ -SO ₃ H	Solvent-free/60 °C	180	95	37
7	β -CD-SO ₃ H	Solvent-free/100 °C	120	89	38
8	SMF/Na2Zn(OH)4; spheres	Solvent-free/80 °C	30	85	This work

4. Conclusions

In this study, we have presented an efficient sonochemical method that can control the shape of Na₂Zn(OH)₄ structures. Crystalline Na₂Zn(OH)₄ spheres and aggregated particles were selectively synthesized under ambient conditions. Based on our observations, using the sulfonated melamine-formaldehyde as support not only stabilizes the structures of Na₂Zn(OH)₄ under ultrasonic wave radiation but also makes conversion of spheres to aggregated particles morphology possible. Also, it is possible to convert Na₂Zn(OH)₄ structures on SMF to ZnO by thermal treatment step with a high photocatalytic ability that has some potential and important applications in panel industry, biotechnology, and so on. If the SMF/Na₂Zn(OH)₄ sphere particles are used in the multicomponent Biginelli reaction, it shows to be exactly effective and gives dihydropyrimidinone products in modest to good vields under optimal reaction conditions. Moreover, the application of SMF/Na₂Zn(OH)₄ spheres with strongly -SO₃H groups can be extended to other organic reactions.

Declaration of Competing Interest

We wish to draw the attention of the Editor to the following facts, which may be considered as potential conflicts of interest, and to significant financial contributions to this work.

CRediT authorship contribution statement

Narges Zarnaghash: Writing - original draft. **Ramin Rezaei:** Supervision, Validation. **Payam Hayati:** Visualization, Writing original draft. **Azra Ghiasi Moaser:** Writing - review & editing. **Mohammad Mahdi Doroodmand:** Writing - review & editing.

Acknowledgements

The authors are particularly thankful to Firoozabad University Research Council for being supportive of this work.

References

- K.S. Parthiban, M. Perumalsamy, Nano sized heterogeneous acid catalyst from ceiba pentandra stalks for production of biodiesel using extracted oil from ceiba pentandra seeds, RSC Adv. 5 (2015) 1180–11187, doi:10.1039/ C4RA13328E.
- [2] K. Subodh, K. Prakash, D.T. Chaudhary, Masram, A new triazine-cored covalent organic polymer for catalytic applications, Appl. Catal. A. 593 (2020) 117411, doi:10.1016/j.apcata.2020.117411.
- [3] K.Prakash Subodh, D.T. Masram, Chromogenic covalent organic polymer-based microspheres as solid-state gas sensor, J. Mater. Chem. C. 8 (2020) 9201–9204, doi:10.1039/D0TC02129F.
- [4] K.Prakash Subodh, D.T. Masram, A reversible chromogenic covalent organic polymer for gas sensing applications, Dalton Trans. 49 (2020) 1007–1010, doi:10.1039/C9DT04788C.
- [5] D. Yadav, S.K. Awasthi, Pd confined hierarchically conjugated covalent organic polymer for hydrogenation of nitroaromatics: catalysis, kinetics, thermodynamics and mechanism, Green Chem. 22 (2020) 4295–4303, doi:10.1039/ D0GC01469A.
- [6] D. Yadav, S.K. Awasthi, Pd NPs confined novel covalent organic polymer for catalytic application, New J. Chem. 44 (2020) 1320–1325, doi:10.1039/ C9NJ05827C.
- [7] D. Yadav, S.K. Awasthi, An unsymmetrical covalent organic polymer for catalytic amide synthesis, Dalton Trans. 49 (2020) 179–186, doi:10.1039/ C9DT03931G.
- [8] D. Yadav, A.K. Dixit, S. Raghothama, S.K. Awasthi, Ni nanoparticle-confined covalent organic polymer directed diaryl-selenides synthesis, Dalton Trans. 49 (2020) 12266–12272, doi:10.1039/D0DT01327G.
- [9] S.J. Yuan, X.H. Dai, Facile synthesis of sewage sludge-derived mesoporous material as an efficient and stable heterogeneous catalyst for photo-fenton reaction, Appl. Catal. B. 154 (2014) 252-258, doi:10.1016/j.apcatb.2014.02.031.
- [10] N.K.Mogha Subodh, K. Chaudhary, G. Kumar, D.T. Masram, Fur-iminefunctionalized graphene oxide-immobilized copper oxide nanoparticle catalyst for the synthesis of xanthene derivatives, ACS Omega. 3 (2018) 16377–16385, doi:10.1021/acsomega.8b01781.

- [11] K. Chaudhary, K.Prakash Subodh, N.K. Mogha, D.T. Masram, Fruit waste (Pulp) decorated CuO NFs as promising platform for enhanced catalytic response and its peroxidase mimics evaluation, Arab. J. Chem. 13 (2020) 4869–4881, doi:10. 1016/j.arabjc.2019.09.007.
- [12] M.B. Gawande, P.S. Branco, R.S. Varma, Nano-magnetite (Fe₃O₄) as a support for recyclable catalysts in the development of sustainable methodologies, Chem. Soc. Rev. 42 (2013) 3371–3393, doi:10.1039/C3CS35480F.
- [13] M. Beller, A. Renken, R.A. van Santenin, Catalysis from Principles to Applications, Wiley-VCH, Verlag, 2012.
- [14] M.S. Chavali, M.P. Nikolova, Metal oxide nanoparticles and their applications in nanotechnology, SN. Appl. Sci. (2019) 607, doi:10.1007/s42452-019-0592-3.
- [15] K. Subodh, K. Chaudhary, D.T. Prakash, Masram, TiO₂ nanoparticles immobilized organo-reduced graphene oxide hybrid nanoreactor for catalytic applications, Appl. Surf. Sci. 509 (2020) 144902, doi:10.1016/j.apsusc.2019.144902.
- [16] G. Kumar, N.K. Mogha, M. Kumar, D.T.Masram Subodh, NiO nanocomposites/rGO as heterogeneous catalysis for imidazole scaffolds with their applications in inhibiting DNA binding activity, Dalton Trans. 49 (2020) 1963–1974, doi:10.1039/C9DT04416G.
- [17] K. Nagasawa, H. Yoshidome, Solvent catalytic degradation of sulfamic acid and its N-substituted derivatives, Chem. Pharm. Bull. 17 (1969) 1316–1323, doi:10. 1248/cpb.17.1316.
- [18] A. Baraka, P.J. Hall, M.J. Heslop, Preparation and characterization of melamineformaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater, React. Funct. Polym. 67 (2007) 585–600, doi:10.1016/j.reactfunctpolym.2007.01.015.
- [19] C. Pevida, T.C. Drage, C.E. Snape, Silica-templated melamine-formaldehyde resin derived adsorbents for CO₂ capture, Carbon N Y 46 (2008) 1464–1474, doi:10.1016/j.carbon.2008.06.026.
- [20] R.J. Roberts, P.D. Evans, Effects of manufacturing variables on surface quality and distribution of melamine formaldehyde resin in paper laminates, Compos. Part A, Appl. Sci. Manuf. 36 (2005) 95–104, doi:10.1016/j.compositesa.2003.05. 001.
- [21] G. Nemli, M. Usta, Influences of some manufacturing factors on the important quality properties of melamine-impregnated papers, Build. Environ. 39 (2004) 567–570, doi:10.1016/j.buildenv.2003.12.008.
- [22] Z. Lv, Q. Sun, X. Meng, F.S. Xiao, Superhydrophilic mesoporous sulfonated melamine-formaldehyde resin supported palladium nanoparticles as an efficient catalyst for biofuel upgrade, J. Mater. Chem. A 1 (2013) 8630–8635, doi:10.1039/C3TA10916J.
- [23] J.L. Gomez, O. Tigli, Zinc oxide nanostructures: from growth to application, J. Mater. Sci. 48 (2013) 612–624, doi:10.1007/s10853-012-6938-5.
- [24] X. Zhang, H. Zhao, X. Tao, Y. Zhao, Z. Zhang, Sonochemical method for the preparation of ZnO nanorods and trigonal-shaped ultrafine particles, Mater. Lett. 59 (2005) 1745–1747, doi:10.1016/j.matlet.2005.01.046.
- [25] S. Shivanna, N.K. Subramani, K. Swamy, S.K. Nagaraj, J.R.B. Muthuraj, H. Siddaramaiah, Orange-red fluorescent polymer nanocomposite films with large stokes shift: an opto-electronic exercise, J. Lumin. 208 (2019) 488–494, doi:10. 1016/j.jlumin.2018.12.041.
- [26] A. Akyol, M. Bayramoglu, Preparation and characterization of supported ZnO photocatalyst by zincate method, J. Hazard. Mater. 175 (2010) 484–491, doi:10. 1016/j.jhazmat.2009.10.031.
- [27] P. Biginelli, Aldehyde-urea derivatives of aceto-and oxaloacetic acids, Gazz. Chim. Ital. 23 (1893) 360-413.
- [28] C.O. Kappe, Biologically active dihydropyrimidones of the Biginelli-typea literature survey, Eur. J. Med. Chem. 35 (2000) 1043-1052, doi:10.1016/ S0223-5234(00)01189-2.
- [29] M.M. Ghorab, S.M. Abdel-Gawad, M.S.A. El-Gaby, Synthesis and evaluation of some new fluorinated hydroquinazoline derivatives as antifungal agents, ll Farmaco. 55 (2000) 249–255. doi:10.1016/S0014-827X(00)00029-X.
- [30] B. Shivarama Holla, B. Sooryanarayana Rao, B.K. Sarojini, P.M. Akberali, One pot synthesis of thiazolodihydropyrimidinones and evaluation of their anticancer activity, Eur. J. Med. Chem. 39 (2004) 777–783, doi:10.1016/j.ejmech.2004.06. 001.
- [31] B.B. Snider, Z. Shi, Biomimetic synthesis of (.+.)-crambines A, B, C1, and C2 revision of the structure of crambines B and C1, J. Org. Chem. 58 (1993) 3828– 3839, doi:10.1021/jo00067a014.
- [32] Y. Qiu, H. Sun, Z. Ma, W. Xia, Efficient, stable, and reusable Lewis acidsurfactant-combined catalyst: one-pot Biginelli and solvent-free esterification reactions, J. Mol. Catal.A Chem. 392 (2014) 76–82, doi:10.1016/j.molcata.2014. 04.031.
- [33] R.J. Kalbasi, A.R. Massah, B. Daneshvarnejad, Preparation and characterization of bentonite/PS-SO₃H nanocomposites as an efficient acid catalyst for the Biginelli reaction, Appl. Clay Sci. 55 (2012) 1–9, doi:10.1016/j.clay.2011.05.015.
- [34] Z.-J.J. Quan, Y.-X.X. Da, Z. Zhang, X.-C.C. Wang, PS-PEG-SO₃H as an efficient catalyst for 3,4-dihydropyrimidones via Biginelli reaction, Catal. Commu. 10 (2009) 1146-1148, doi:10.1016/j.catcom.2008.12.017.
- [35] K. Konkala, N.M. Sabbavarapu, R. Katla, N.Y.V. Durga, P.D.B. LA, Revisit to the Biginelli reaction: a novel and recyclable bioglycerol-based sulfonic acid functionalized carbon catalyst for one-pot synthesis of substituted 3,4dihydropyrimidin-2-(1H)-ones, Tetrahedron Lett. 53 (2012) 1968–1973, doi:10. 1016/j.tetlet.2012.02.018.
- [36] F. Zamani, E. Izadi, Synthesis and characterization of sulfonated-phenylacetic acid coated Fe₃O₄ nanoparticles as a novel acid magnetic catalyst for Biginelli reaction, Catal. Commun. 42 (2013) 104–108, doi:10.1016/j.catcom.2013.08.006.
- [37] E. Kolvari, N. Koukabi, O. Armandpour, Simple and efficient synthesis of 3,4-dihydropyrimidin-2-(1H)-ones via Biginelli reaction catalyzed by

nanomagnetic-supported sulfonic acid, Tetrahedron 70 (2014) 1383-1386, doi:10.1016/j.tet.2013.10.085.

- [38] S. Asghari, M. Tajbakhsh, B.J. Kenari, S. Khaksar, Supramolecular synthesis of 3,4-dihydropyrimidine-2(1H)-one/thiones under neat conditions, Chin. Chem. Lett. 22 (2011) 127–130, doi:10.1016/j.cclet.2010.09.030.
- [39] X.H. Chen, X.Y. Xu, H. Liu, L.F. Cun, LZ. Gong, Highly enantioselective organocatalytic Biginelli reaction, J. Am. Chem. Soc. 128 (2006) 14802–14803, doi:10.1021/ja065267y.
- [40] J. Xin, L. Chan, Z. Hou, D. Shang, X. Liu, X. Feng, An enantioselective Biginelli reaction catalyzed by a simple chiral secondary amine and achiral Brønsted acid by a dual-activation route, Chem. Eur. J. 14 (2008) 3177–3181, doi:10.1002/ chem.200701581.
- [41] N.-Y. Fu, Y.-F. Yuan, Z. Cao, S.-W. Wang, J.-T. Wang, C. Peppe, Indium(III) bromide-catalyzed preparation of dihydropyrimidinones: improved protocol conditions for the Biginelli reaction, Tetrahedron 58 (2002) 4801–4807, doi:10. 1016/S0040-4020(02)00455-6.
- [42] Y. Ma, C. Qian, L. Wang, M. Yang, Lanthanide triflate catalyzed Biginelli reaction. One-pot synthesis of dihydropyrimidinones under solvent-free conditions, J. Org. Chem. 65 (2000) 3864–3868, doi:10.1021/jo9919052.
- [43] E. Kolvari, N. Koukabi, M.M. Hosseini, M. Vahidian, E. Ghobadi, Nano-ZrO₂ sulfuric acid: a heterogeneous solid acid nano catalyst for Biginelli reaction under solvent-free conditions, RSC Adv. 6 (2016) 7419–7425, doi:10.1039/ C5RA19350H.
- [44] C.G.S. Lima, S. Silva, R.H. Gonçalves, E.R. Leite, R.S. Schwab, A.G. Corrêa, M.W. Paixão, Highly efficient and magnetically recoverable niobium nanocatalyst for the multicomponent Biginelli reaction, Chem. Cat. Chem 6 (2014) 3455–3463, doi:10.1002/cctc.201402689.
- [45] R.V. Patil, J.U. Chavan, D.S. Dalal, V.S. Shinde, A.G. Beldar, Biginelli reaction: polymer supported catalytic approaches, ACS Comb. Sci. 21 (2019) 105–148, doi:10.1021/acscombsci.8b00120.
- [46] N. Zarnaghash, R. Rezaei, P. Hayati, M.M. Doroodmand, Selective ultrasonic assisted synthesis of iron oxide mesoporous structures based on sulfonated melamine formaldehyde and survey of nanorod/sphere, sphere and core/shell on their catalysts properties for the Biginelli reaction. Mater. Sci. Eng., C. 109975. doi:10.1016/j.msec.2019.109975.
- [47] R. Stahl, R. Niewa, H. Jacobs, Synthesis and crystal structure of Na₂Zn(OH)₄, Z. Anorg. Allg. Chem. 625 (1999) 48–50, doi:10.1002/(SICI)1521-3749(199901) 625:1(48::AID-ZAAC48)3.0.CO;2-L.
- [48] R.S. Yadav, P. Mishra, A.C. Pandey, Growth mechanism and optical property of ZnO nanoparticles synthesized by sonochemical method, Ultrason. Sonochem. 15 (2008) 863–868, doi:10.1016/j.ultsonch.2007.11.003.

- [49 P. Basnet, S. Chatterjee, Structure-directing property and growth mechanism induced by capping agents in nanostructured ZnO during hydrothermal synthesis. A systematic review, Nano-Struct. Nano-Objects. 22 (2020) 100426, doi:10.1016/j.nanoso.2020.100426.
- [50] Z. Jiang, G. Liu, Microencapsulation of ammonium polyphosphate with melamine-formaldehyde-tris(2-hydroxyethyl) isocyanurate resin and its flame retardancy in polypropylene, RSC. Adv. 5 (2015) 88445–88455, doi:10.1039/ C5RA14586D.
- [51] N. Koukabi, E. Kolvari, M.A. Zolfigol, A. Khazaei, B. Shirmardi Shaghasemi, B. Fasahati, Magnetic particle-supported sulfonic acid catalyst: tuning catalytic activity between homogeneous and heterogeneous catalysis, Adv. Synth. Catal. 354 (2012) 2001–2008, doi:10.1002/adsc.201100352.
- [52] S. Jagtap, K.R. Priolkar, Evaluation of ZnO nanoparticles and study of ZnO-TiO₂ composites for lead free humidity sensors, Sens. Actuators, B. 183 (2013) 411–418, doi:10.1016/j.snb.2013.04.010.
- [53] S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, On a theory of the Van der Waals adsorption of gases, J. Am. Chem. Soc. 62 (1940) 1723–1732.
- [54] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, Surface area and pore texture of catalysts, Catal. Today 41 (1998) 207–219, doi:10.1016/S0920-5861(98) 00050-9.
- [55] D.J. Merline, S. Vukusic, A.A. Abdala, Melamine formaldehyde: curing studies and reaction mechanism, Polymer J 45 (2013) 413–419, doi:10.1038/pj.2012. 162.
- [56] S.I. Cheong, B. Kim, H. Lee, J.W. Rhim, Physical adsorption of water-soluble polymers on hydrophobic polymeric membrane surfaces via salting-out effect, Macromol. Res. 21 (2013) 629–635, doi:10.1007/s13233-013-1075-9.
- [57] D. Bhuyan, M. Saikia, L. Saikia, ZnO nanoparticles embedded in SBA-15 as an efficient heterogeneous catalyst for the synthesis of dihydropyrimidinones via Biginelli condensation reaction, Microporous Mesoporous Mater. 256 (2018) 39–48, doi:10.1016/j.micromeso.2017.06.052.
- [58] A. Mobaraki, B. Movassagh, B. Karimi, Hydrophobicity-enhanced magnetic solid sulfonic acid: a simple approach to improve the mass transfer of reaction partners on the surface of the heterogeneous catalyst in water-generating reactions, Appl. Catal., A. 472 (2014) 7201–7204, doi:10.1016/j.apcata.2013.12.018.
- [59] C.O.A. Kappe, A reexamination of the mechanism of the Biginelli dihydropyrimidine synthesis. Support for an N-acyliminium ion intermediate, J. Org. Chem. 62 (1997) 123–133, doi:10.1021/jo971010u.