Indian Journal of Chemistry
Vol. 57A, Aug-Sept 2018, pp. 1112-1120

Synthesis and characterization of stable ZnO nanoparticles using imidazolium-based ionic liquids and their applications in esterification reaction

S H Kavya, V Vijaya Kumar & C Ramesh Kumar*

Organic Chemistry Laboratory, Department of Chemistry, Vel Tech Rangarajan Dr Sagunthala R&D Institute of Science and Technology, Avadi, Chennai 600 062, Tamil Nadu, India.
Email: nscrameshkumar@gmail.com

Received 4 September 2017; re-revised and accepted 3 August 2018

ZnO nanoparticles have been synthesized from zinc acetate using 1-octyl-3-methylimidazolium hexafluorophosphate as capping agent under microwave irradiation condition in a very short period of time and characterized using UV-visible spectroscopy, powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy and NH_3-TPD analysis. The ZnO NPs have been used as a solid reusable acid catalyst for esterification of carboxylic acids with alcohols.

Keywords: Catalysts, Ionic liquids, Nanoparticles, Solid acid catalysts, capping agents, Esterification, Zinc oxide, Microwave synthesis

Ionic liquids (ILs) are organic salts with low melting points, sometimes as low as –96 °C and have found applications in many areas in chemistry and industry due to their potential as a recyclable alternative to traditional organic solvents[1, 2]. ILs exhibit high thermal stability; up to 400 °C mainly due to the presence of anions in the ILs. The thermal stability of anions is in the order of $[PF_6]^-$ > $[Tf_2N]^-$ > $[BF_4]^-$ > halides. In 1-methylimidazolium ionic liquids, there is no difference in the thermal behaviour with increase in the size of the alkyl chain from butyl to octyl[3]. ILs can be used with catalysts[4], as an inert solvent in electrochemistry[5], for the synthesis of polymer[6, 7], and the shift from enzymatic to organic media[8].

ILs can be used as capping agents and solvents for the synthesis of metal oxide nanoparticles. Capping agents are widely utilized for preventing aggregation during the preparation of nanoparticles. The selection of capping agent depends upon the method of synthesis, nature of the metal oxides and conditions applied for the synthesis. ILs when used as capping agents form a dense layer on the particle surface that stabilizes nanoparticles better and prevents their coagulation or aggregation. Capping agents are always used in the form of solutions and either deionized water or any other solvents is used after the formation of the nanoparticles. The capping agent along with the solvent used must be removed easily to furnish pure metal oxide nanoparticles. PEG[9], oleic acid[10], ionic liquids[11], Polyvinyl pyrrolidone (PVP)[12] and citrate[12,13] are commonly used for capping.

The use of longer alkyl chain effectively decreases the solubility of ionic liquids in aqueous phase and leads to improved yield of the desired product[14]. The advantage of using ILs in an inorganic nanomaterials' synthetic process has been gradually realized due to their unique physical and chemical properties, such as large electrochemical window, high polarity but low interface tension, low interface energies, high thermal stability, and extended hydrogen-bonded system[15-17]. Many reports are available in literature for the synthesis of various metallic NPs, such as palladium[18], iridium[19] and semiconductor NPs using ILs[20].

Microwave heating is regarded as a promising method for rapid volumetric heating, resulting in high reaction rates. Hence, there is a reduction in the reaction time in order of magnitude and an increase in the product yield in comparison with conventional heating method[21,22]. This opens up a pathway for fast synthesis of nanomaterials in a very short time[23]. Ionic liquids have large positive ions with high polarizability at room temperature, making them a good medium for absorbing microwaves, thus enabling very high heating rates. By combining the advantages of both RTILs and microwave heating, it has been possible to achieve a fast and controlled synthetic route for ZnO NPs. Zinc oxide NPs have a wide range of applications in the functional devices, photo-catalysts, pigments, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors and industrial additives[24].

Esterification is an important reaction in the chemical industry where an efficient acid catalyst is required to obtain good yields[25]. Esterification reaction can also be performed using homogeneous catalysts such as H_2SO_4, HF and H_3PO_4, but the use of such catalysts often causes serious issues in product separation, catalyst reuse and disposal[26]. Thus, replacement of homogeneous hazardous mineral acids (H_2SO_4, HF and H_3PO_4) by heterogeneous catalyst (metal oxide) with low corrosiveness, ease in regeneration and reusability nature is required. Zinc oxides exhibit both acidic and basic characteristics, with variations depending upon the method of preparation[27].

In this work, the synthesis of ZnO NPs is reported via microwave irradiation method using 1-octyl-3-methyl imidazolium hexafluorophosphate [OMIM][PF_6] ionic liquid as the capping agent to reduce the agglomeration of the particles as well as a solvent. The ZnO NPs capped with imidazolium-based ionic liquid is used as a solid acid catalyst for the esterification reaction of a series of carboxylic acids with various alcohols in solvent-free condition.

Materials and Methods

AR grade of 1-methylimidazole, bromooctane, potassium hexafluorophosphate, zinc acetate dihydrate, dichloromethane and ethanol were purchased from SD Fine Chemicals, Loba Chemie and Merck and used without further purification. TLC plates were used for monitoring the course of the reaction.

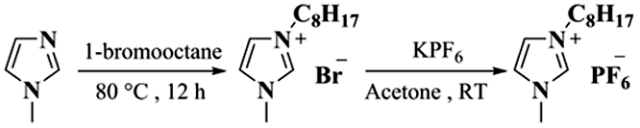
^{1}H NMR and ^{13}C NMR spectra were recorded on the Bruker AVANCE 300 FT-NMR instrument using $CDCl_3$ as NMR solvent. Electrospray Ionization mass spectrophotometry (ESI-MS) was documented on the water Q-TOF Premier mass spectrophotometer. FT-IR spectra of the samples were recorded using Bruker Vector 22 FT-IR spectrometer and the spectra were recorded in the frequency range of 400 to 4000 cm^{-1} using KBr. The crystalline nature of the samples was determined using powder X-ray diffraction using a Philips Xpert X-ray diffractometer with monochromatic Cu-Kα radiation (λ = 1.5418 Å). The samples were recorded over the diffraction angle (2θ) range between 20° and 80°. The surface morphology of the samples was examined using an LEO 1530 FEGSEM. Powder samples were directly used for the analysis. The particle size of the samples was determined on a Philips/FEI CM 200 TEM instrument with an acceleration voltage of 250 kV. The samples were prepared on a copper grid after sonication.

Ammonia temperature programmed desorption (NH_3-TPD) experiments were performed using a Chemisorb 2750 instrument (Micromeritics). ZnO NPs (122 mg) was placed in a quartz reactor and heated to 150 °C at 10 °C/min in 30 mL of high pure helium flow. The temperature was maintained at 150 °C for 30 min. The heated ZnO NPs was then cooled to 100 °C and 10% of NH_3 in helium gas was passed through the samples for 30 min at a flow rate of 30 mL/min. Subsequently, the gas was changed to pure helium (at the rate of 30 mL/min) and the physisorbed ammonia is removed for stable baseline status. The temperature was raised up to 800 °C at a rate of 10 °C/min. A similar experiment was carried out with 150 mg ZnO.

Synthesis and characterization of [OMIM][PF_6] ionic liquid

Synthesis of [OMIM][PF_6] was carried out in two steps. In the first step, 1-octyl-3-methylimidazolium bromide [OMIM][Br] was prepared by adding equal amounts of 1-bromooctane (0.03 mole, 5.79 g) and 1-methylimidazole (0.03 mole, 2.46 g) in a 250 mL round-bottom flask and refluxing at 80 °C to obtain a golden yellow viscous liquid. The viscous liquid was cooled and washed thrice with 50 mL of ethyl acetate. Then the ethyl acetate was evaporated to get [OMIM][Br] as a viscous liquid. In the second step, [OMIM][Br] (0.03 mole, 8.25 g) from the above step was dissolved in acetone (15 mL) and potassium hexafluorophosphate (0.03 mole, 5.03 g) was slowly added over 1 h at room temperature. Then 25 mL of dichloromethane was added and this mixture was washed with water until the washed product (IL) was no longer acidic. The washed IL was dried with anhydrous magnesium sulfate and heated under vacuum at 70 °C to get [OMIM][PF_6] as yellow viscous liquid[28] (Scheme 1).

[OMIM][Br]: Yellow viscous liquid, Yield 92%, ^{1}H-NMR: (300 MHz, $CDCl_3$); δ (ppm), 10.02 (d, 2H), 7.70 (d. 1H), 7.52 (s, 1H), 4.76 (t, 2H), 4.1 (s, 3H), 1.90 (m, 2H), 1.29 (m, 11H) and 0.86 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$); 13.9, 22.5, 26.2, 28.9, 30.2, 31.6, 36.7, 49.9, 122.0, 123.8 and 136.8.



Synthesis of [OMIM][PF_6] ionic liquid

Scheme 1

[OMIM][PF_6]: Yellow viscous liquid, Yield 84%, ^{1}H-NMR: (300 MHz, $CDCl_3$); δ (ppm), 8.53 (s, 2H), 7.34 (d, J = 1.5 Hz, 1H), 7.33 (d, J = 1.5 Hz, 1H), 4.14 (t, 2H), 3.90 (s, 3H), 1.87 (m, 2H), 1.27 (m, 10H) and 0.86 (t, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$); 13.9, 22.5, 26.0, 28.8, 29.9, 30.8, 31.6, 36.0, 49.9, 122.2, 123.7 and 135.7. MM-ES *m/z*: $C_{12}H_{23}N_2$ [PF_6] Calcd: cationic mass 195.34, Found 195.20.

Synthesis of ZnO NPs

NaOH (16 g) was added to a stirred solution of zinc acetate dihydrate (5.5 g) in 50 mL of distilled water when a transparent $Zn(OH)_4^{2-}$ solution was obtained. [OMIM][$PF]_6$ (2 mL) was added to 3 mL of the above solution and the suspension was placed in a microwave oven (2.45 GHz, 850 W). Then, 30% of the output power of the microwave was used for irradiating the mixture for 2-9 min in a cycle mode (on 10 s; off 5 s). The obtained white precipitate was separated by centrifugation, and washed several times with deionized water and ethanol. The pure ZnO NPs was dried under vacuum oven at 50 °C for 10 h[23]. ZnO NPs catalyst so obtained was used for an esterification of acid with alcohol (Scheme 2).

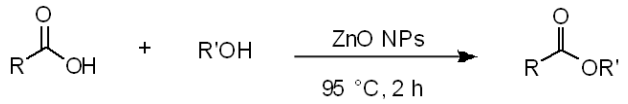
General procedure for esterification

To a stirred solution of carboxylic acid (5 mmol) and alcohol (5 mmol) in a 100 mL RB flask, was added 25 mg of ZnO NPs. The reaction mixture was stirred at 95 °C for 2 h and the course of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was filtered through a filter paper for separating the catalyst and the filtrate was quenched with ice water. The aqueous phase was extracted twice with 50 mL of dichloromethane and the organic layer was washed with 50 mL of aqueous solution of 1 M $NaHCO_3$ followed by 50 mL brine solution. Finally, it was dried over sodium sulfate and the required product was purified by column chromatography using silica gel to get the ester.

Results and Discussion

UV-visible spectrum of ZnO NPs

The UV-vis absorbance spectrum of ZnO NPs shows a broad band with a maxima at 368 nm corresponding to ZnO NPs. There was a slight blue shift relative to the bulk compound (380 nm). The band gap energy (E_{bg}) of ZnO was calculated from the following equation, $E_{bg} = 1240/\lambda$ (eV), where E_{bg} is the band gap energy in eV and λ is the wavelength. The band gap of ZnO was calculated as 3.37 eV, which is in good agreement with the value of 3.42 eV reported by Abiraman *et al.*[29] reported.



General esterification reaction of acid with alcohol

Scheme 2

XRD analysis

The phase, purity and average crystallite size of ZnO NPs were studied using XRD with 2θ values in the range of 25° and 80°. The powder XRD pattern of ZnO NPs in [OMIM][PF_6], shows the main characteristic peaks for ZnO NPs at 31.74°, 34.37°, 36.20°, 56.55°, 62.87°, 67.78° and 69.12° that correspond to (100) (002) (101) (112) (103) and (112) planes respectively (Fig. 1). These data are in good agreement with JCPDS no. 36-1451. The most intense peak was observed for the 101 plane. The strong intensity and narrow width of ZnO diffraction peaks indicate the crystalline nature of the product. The average crystallite particle size of ZnO NPs was calculated using Scherrer equation is 16 nm.

SEM analysis

The morphology of the synthesized ZnO NPs in [OMIM][PF_6] is shown in Fig. 2. The SEM image shows the formation of spherical ZnO NPs. In this study, the formation of spherical shaped ZnO NPs was due to the initial formation of nuclei by the microwave irradiations, and then the subsequent role of the ionic liquid as a growth controller[30].

In general, ZnO acts as a polar compound, where O^{2-} is in hexagonal closest packing and Zn^{2+} lies within a tetrahedral group of four oxygen atoms[31]. The cation of the ionic liquid can be absorbed on the exterior of the O^{2-} terminated by electrostatic force,

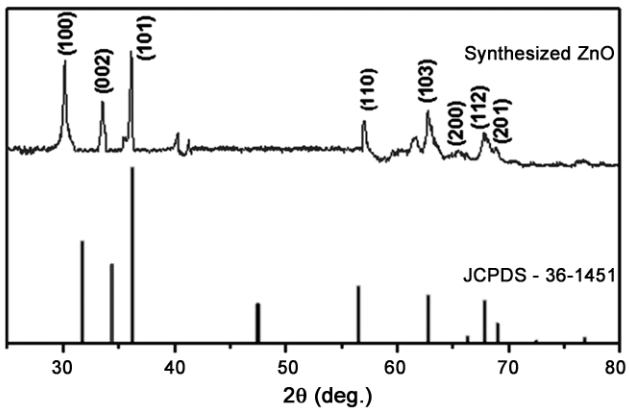


Fig. 1 — Powder XRD pattern of ZnO nanoparticles in [OMIM][PF_6].

and the hydrogen bond formed between the hydrogen atom (at position 2 of the imidazole ring) and the oxygen atom of O-Zn may act as an effective bridge to connect the O^{2-} terminated plane of the nuclei of metal oxide and cations of ionic liquids[30, 32, 33]. Hence, it is proposed that in the presence of ionic liquids, spherical ZnO NPs are formed.

TEM analysis

The shape and size of ZnO NPs were analyzed by TEM. The high magnification HR-TEM image of ZnO NPs shown in Fig. 3(a) clearly indicates the spherical shaped dark parts surrounded by white features, which correspond to ZnO NPs uniformly capped by [OMIM][PF_6]. The mean particle size was predicted to be around 16 nm using the ImageJ software. The TEM image shows the well dispersed ZnO NPs without any agglomeration. The selected area electron diffraction (SAED) pattern of the synthesized ZnO NPs is shown in Fig. 3(b). The TEM analysis is in good agreement with the XRD results.

NH_3-TPD analysis

In general, surface acidic centers can be divided into two groups: Bronsted center (hydroxyl group) and Lewis sites (coordinatively unsaturated cations)[34,35]. The acidic properties (acidic site concentration and strength of acid sites) of ZnO NPs were determined using NH_3-TPD analysis. For comparison, ZnO bulk was also analyzed. It can be clearly seen from Fig. 4 that ZnO NPs showed more intense desorption peaks (at 448.1, 630.0 and 812.7 °C) compared to weak and broad peaks shown by ZnO bulk (at 225.9, 455.2 and 807.2 °C). The peaks at

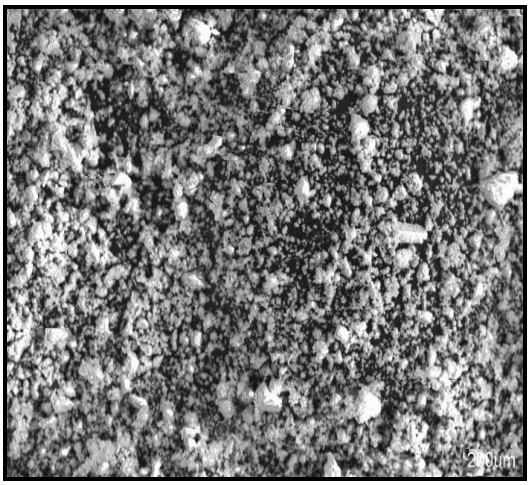


Fig. 2 — SEM image of ZnO nanoparticles in [OMIM][PF_6].

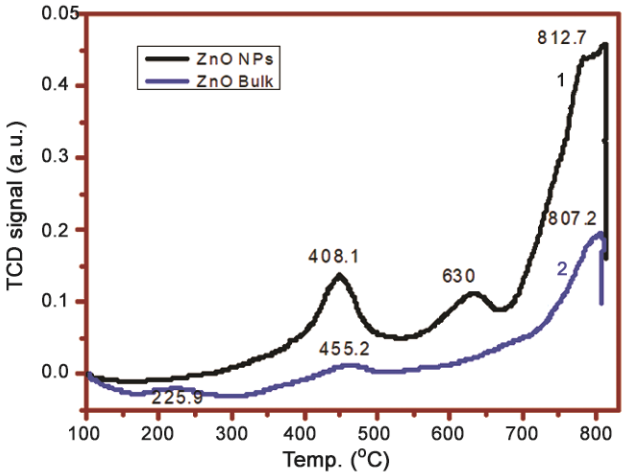


Fig. 4 — NH_3-TPD spectra of ZnO. [1, ZnO NPs; 2, ZnO bulk].

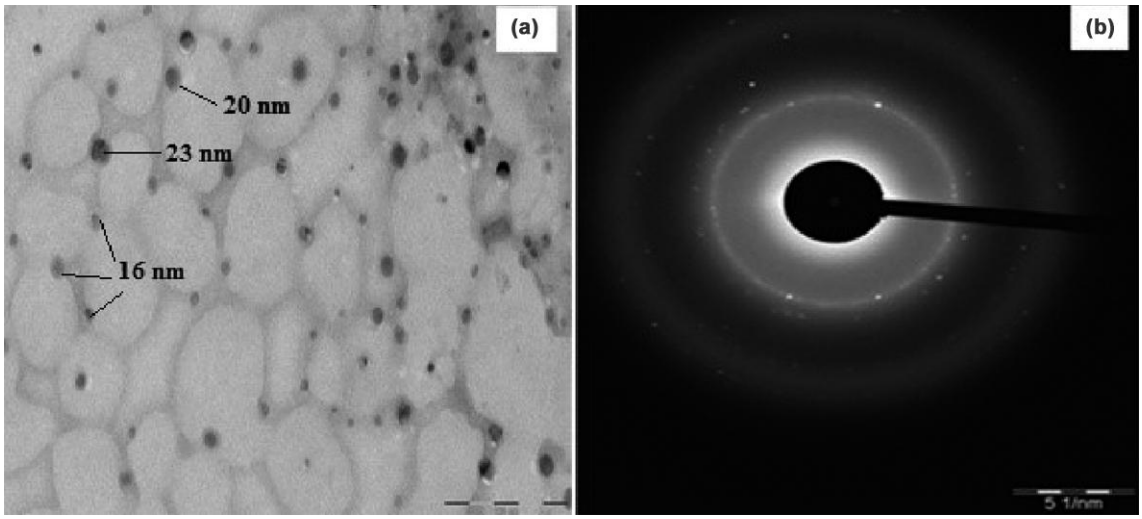


Fig. 3 — (a) TEM image of ZnO NPs in [OMIM][PF_6], and, (b) SAED pattern of ZnO NPs.

225.9 and 448.1 °C respectively for ZnO bulk and ZnO NPs may be assigned to NH_3 bonded with weak Bronsted acid centers (surface hydroxyl groups), whereas the peaks at 455.2 and 630.0 °C respectively of ZnO bulk and ZnO NPs may be attributed to desorption of adsorbed NH_3 from Lewis acid sites. The third peak with maximum at ~800 °C may be attributed to desorption of ammonia decomposition products from the ZnO surface. The results clearly show the presence of higher surface acidity of prepared ZnO NPs, i.e., higher number of acid sites with higher strength, indicating its suitablity as catalyst for esterification reaction.

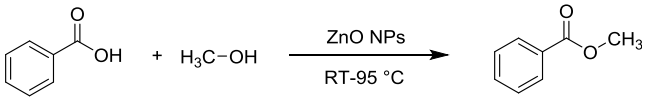
Optimization of esterification reaction

The esterification reaction between benzoic acid (2 mmol) and methanol (2 mmol) was selected as a model reaction for optimizing the reaction conditions (Scheme 3) using ZnO NPs as catalyst. The reaction conditions were optimised by varying the amount of catalyst from 2 mg to 25 mg. The results obtained are listed in Table 1. An increase in the yield of methyl benzoate from 26% to 88% was observed on increasing the amount of catalyst from 2 mg to 12 mg within 2 h of the reaction time at 95 °C. Further increase in the amount of catalyst from 12 mg to 25 mg did not enhance the activity of the catalyst. The esterification reaction progressed well at 95 °C using 5 mol% of ZnO NPs as an acid catalyst and good to excellent yields were observed within 2 h of reaction time.

Increase in reaction temperature is reported to increase the conversion to a significant level[36]. Hence, the effect of temperature on conversion over the catalyst was investigated by varying the temperature from room temperature (25 °C) to 95 °C (Table 2). The yield of methyl benzoate increased significantly with increase in temperature and almost complete conversion was observed at 95 °C within 2 h of reaction time.

Various aliphatic and aromatic acids with primary and secondary alcohols have been successfully screened for the esterification reaction. Good to excellent yields (88-92%) were obtained and the results are summarized in Table 3. In general, primary alcohols gave better yields than secondary alcohols due to its high reactivity. The possible reaction mechanism[40] is shown in Scheme 4.

We also compared the catalytic activity of the synthesized ZnO NPs with ZnO bulk catalyst for the synthesis of methylbenzyl acetate (Table 4). The present ZnO NPs showed higher yield of 92% within 2 h (Entry 6) as compared to ZnO bulk yielding only



Model reaction for the synthesis of methyl benzoate

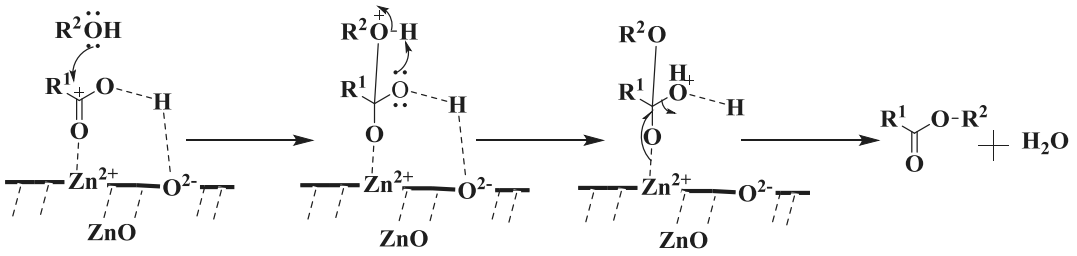
Scheme 3

Table 1 — Effect of ZnO NPs catalyst on esterification of benzoic acid with methanol. [React. cond.: Benzoic acid: 2 mmol; Methanol: 2 mmol; Time: 2 h; Temp.: 95 °C]

Entry	Amt of ZnO NPs catalyst		Yield of methyl benzoate (%)
	(mol%)	(mg)	
1	–	–	No product
2	1	2	26
3	2	5	49
4	5	12	88
5	8	20	88
6	10	25	88

Table 2 — Effect of time and temperature on esterification of benzoic acid with methanol. [React. cond.: Benzoic acid: 2 mmol; Methanol: 2 mmol; ZnO NPs: 5 mol%]

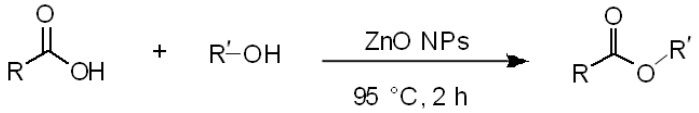
Entry	Temp. (°C)	Time (h)	Yield (%)
1	RT	24	No product
2	40	24	12
3	60	24	59
4	95	2	88
5	95	8	88
6	95	24	88

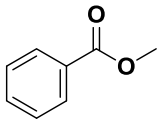
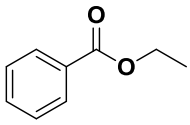
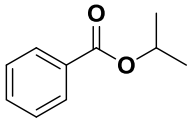
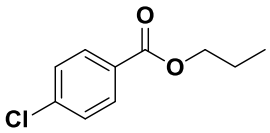
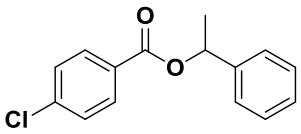
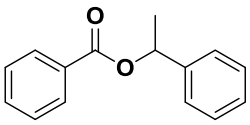
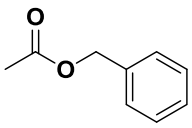
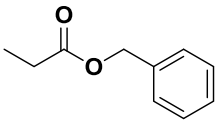
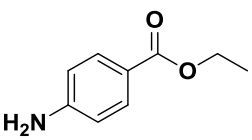


Proposed mechanism (Eley-Rideal) for the esterification of acid with alcohol using ZnO NPs as catalyst

Scheme 4

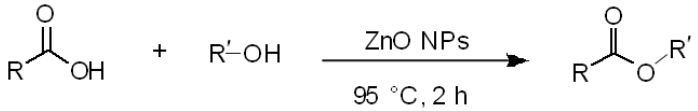
Table 3 — ZnO NPs catalyzed esterification reaction of acids and alcohols[a]

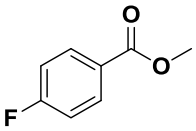
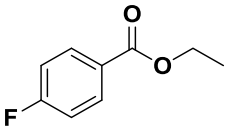
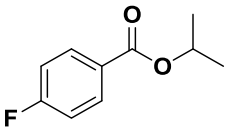
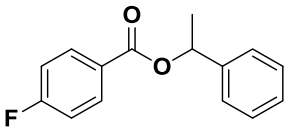
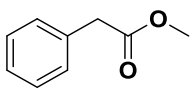
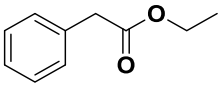
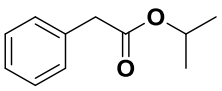


Entry	Acid (R)	Alcohol (R′)	Product	Yield and characterization
1	C_6H_5	CH_3		Yellow liquid, Yield: 88%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.03 (d, J = 5.2 Hz, 2H), 8.03(d, J = 1.2 Hz, 1H), 7.54 (t, 1H), 7.43 (t, 2H), 3.91 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$); 52.1, 128.4, 129.6, 130.2, 132.9, 167.1.
2	C_6H_5	CH_3–CH_2		Yellow liquid, Yield: 87%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.05 (d, J = 6.8 Hz, 2H), 7.55 (s, 1H), 7.43 (t, 2H), 4.38 (q, 2H), 1.39 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 14.3, 60.9, 128.3, 129.6, 132. 8, 166.7.
3	C_6H_5	CH_3–CH–CH_3		Yellow liquid, Yield: 76%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.03 (d, J = 2 Hz, 2H), 7.50 (t, 2H), 7.42 (d, J = 8 Hz, 1H), 7.4 (d, J = 1.6 Hz, 1H), 5.25 (m, 1H), 1.36 (d, J = 6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.9, 68.3, 128.3, 129.5, 130.9, 132.7, 166.1.
4	4–Cl–C_6H_4	CH_3–CH_2–CH_2		Yellow liquid, Yield: 96%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.96 (d, J = 2.4 Hz, 2H), 7.41 (d, J = 2.4 Hz, 2H), 4.2 (t, 2H), 1.78 (m, 2H), 1.02 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 10.5, 22.1, 66.8, 128.7, 129.1, 130.9, 139.3, 165.8.
5	4–Cl–C_6H_4	C_6H_5–CH–CH_3		Yellow liquid, Yield: 80%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.26-7.09 (m, 9H), 6.37 (q, J = 16 Hz, 1H), 1.68 (d, J = 8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.2, 67.0, 126.1, 127.0, 128.2, 135.5, 137.5, 145.6, 164.0.
6	C_6H_5	C_6H_5–CH–CH_3		Yellow liquid, Yield: 90%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.03 (d, J = 1 Hz, 2H), 7.51-7.14 (m, 8H), 6.38 (q, J = 16 Hz, 1H), 1.45 (d, J = 8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.2, 60.9, 125.1, 126.2, 127.0, 128.3, 130.6, 132.8, 135.2, 137.6, 145.6, 166.6.
7	CH_3	C_6H_5–CH_2		Yellow liquid, Yield: 82%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.28 (s, 5H), 5.02 (s, 2H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 20.9, 66.3, 128.3, 135.9, 170.9.
8	CH_3–CH_2	C_6H_5–CH_2		Yellow liquid, Yield: 92%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.33 (s, 5H), 5.11 (s, 2H), 2.38 (q, J = 5.6 Hz, 2H), 1.16 (t, J = 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 9.1, 27.6, 66.2, 128.8, 128.6, 136.2, 174.3.
9	4–NH_2–C_6H_4	CH_3–CH_2		Yellow liquid, Yield: 78%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.71 (d, J = 6.8 Hz, 2H), 6.72 (d, J=6.8 Hz, 2H), 4.38 (q, 2H), 1.39 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 12.3, 59.9, 127.3, 130.6, 148. 8, 167.7.

(*Contd.*)

Table 3 — ZnO NPs catalyzed esterification reaction of acids and alcohols[a] — (*Contd.*)



Entry	Acid (R)	Alcohol (R′)	Product	Yield and characterization
10	4–F–C_6H_4	CH_3		Yellow liquid, Yield: 74%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.07-8.03 (m, 2H), 7.10 (t, 2H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 52.0, 115.2, 115.4, 126.2, 126.2, 131.9, 131.9, 165.9, 166.8.
11	4–F–C_6H_4	CH_3–CH_2		Yellow liquid, Yield: 73%., ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.08-8.04 (m, 2H), 7.09-7.08 (m, 2H), 4.40-4.34 (m, 2H), 1.39 (t, J = 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 14.3, 61.1, 115.5 (2C), 126.7, 132.1 (2C), 165.7, 166.9.
12	4–F–C_6H_4	CH_3–CH–CH_3		Yellow liquid, Yield: 66%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.07-8.03 (m, 2H), 7.12-7.07 (m, 2H), 5.26-5.21 (m, 1H), 1.37 (d, J = 3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.9, 68.5, 115.44 (2C), 127.14, 132.04 (2C), 165.14, 166.88.
13	4–F–C_6H_4	C_6H_5–CH–CH_3		Yellow liquid, Yield: 69%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 8.08-7.99 (m, 2H), 7.56-7.24 (m, 7H), 6.53-6.51 (m, 1H), 1.59 (d, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.4, 42.7, 74.5, 125.7, 127.1, 127.6, 128.0, 129.1, 145.8, 167.7, 168.8.
14	C_6H_5–CH_2	CH_3		Yellow liquid, Yield: 91%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.32-7.26 (m, 5H), 3.68 (s, 2H), 3.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 41.2, 52.0, 127.1, 128.6, 129.2, 133.9, 172.0.
15	C_6H_5–CH_2	CH_3–CH_2		Yellow liquid, Yield: 88%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.34-7.24 (m, 5H), 4.17-4.11 (m, 2H), 3.60 (s, 2H), 1.24 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$); 14.1, 41.4, 60.8, 127.0, 128.5, 129.2, 134.1, 171.6.
16	C_6H_5–CH_2	CH_3–CH–CH_3		Yellow liquid, Yield: 77%. ^{1}H NMR: (300 MHz, $CDCl_3$); δ (ppm) 7.35-7.24 (m, 5H), 5.07-5.00 (m, 1H), 3.59 (s, 2H), 1.30-1.19 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$); 21.6, 41.8, 68.2, 126.7, 129.2 (2C), 130.0 (2C), 134.4, 171.1.

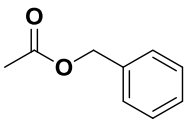
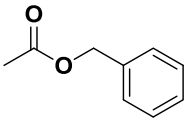
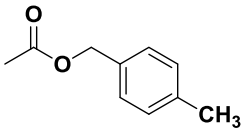
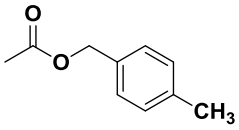
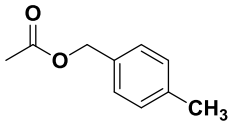
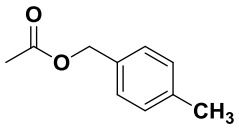
[a]React. cond.: Acid (5 mmol), Alcohol (5 mmol) and ZnO (5 mol%) at 95 °C for 2 h. [b]Isolated yields.

60% yield in 5 h (Entry 5). Javaherian & Sabzi[39] have also reported higher activity of ZnO nanopowder (88%, entry 4) under reflux condition for 3 h as compared to ZnO bulk (59%, entry 3) for the same reaction. The results clearly showed the high activity of presently synthesized ZnO NPs.

Reusability of ZnO NPs catalyst

The catalytic activity and the reusability of the ZnO NPs for esterification of 4-chlorobenzoic acid and *n*-propyl alcohol were studied. After completion of the reaction, the catalyst was filtered, washed and dried under vacuum for 1 h and used under the same conditions for the subsequent reactions. The decrease in yield was insignificant till the fourth cycle (from 96% to 88%), while the recovery of the catalyst was 90% in the fourth cycle. The results indicate that the catalyst can be reused for four cycles without a significant decrease in its catalytic activity.

Table 4 — Comparison of ZnO NPs with ZnO bulk for the synthesis of methylbenzyl acetate

Entry	Catalyst	Acylating agent	Product	Temp. (°C)	Time	Yield (%)
1	Fe- Chemosite-clay	CH_3COOH		100	5 min	99[37]
2	I_2	CH_3COOH		reflux	12 h	90[38]
3	ZnO (Bulk)	CH_3COOH		reflux	3 h	59[39]
4	ZnO-nanopowder	CH_3COOH		reflux	3 h	88[39]
5	ZnO (Bulk)	CH_3COOH		95	5 h	60[a]
6	ZnO NPs	CH_3COOH		95	2 h	92[a]

[a]Present work

Conclusions

The ZnO NPs were synthesized using the microwave conversion method with $[OMIM][PF_6]$ ionic liquid as capping agent as well as solvent. The ZnO NPs were characterized by UV-visible, XRD, SEM, TEM and NH_3-TPD analysis. The resulting ZnO NPs were used as a solid acid catalyst for esterification of carboxylic acids with alcohols. Primary alcohols provide almost 80% of yield and the acid catalyst could be reused for four cycles without loss of catalytic activity. The method offers a simple route for the synthesis of NPs in a very short time with a high yield without using any hazardous solvents. This approach presents a green, safe, and recyclable alternative inorganic acid catalyst for esterification reactions.

Acknowledgment

The authors acknowledge the financial assistance from Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India, under scheme Fast Track Young Scientist Scheme (SB/FT/CS-086/2013).

References

1 Seddon K R, Stark A & Torres M, *Pure Appl Chem*, 72 (2000) 2275.
2 Walton T, *Chem Rev*, 99 (1999) 2071.
3 Kosmulski M, Gustafsson J & Rosenholm J B, *Thermochim Acta*, 357 (2000) 97.
4 Sheldon R, *Chem Commun*, 23 (2001) 2399.
5 Fuller J, Carkin R T & Osteryoung R A, *J Electrochem Soc*, 144 (1997) 3881.
6 Zhao Y L, Zhang J M, Jiang J, Chen C F & Xi F, *J Polym Sci Part A*, 40 (2002) 3360.
7 Kubisa P, *Prog Polym Sci*, 29 (2004) 3.
8 Van Rantwijk F, Lau R M & Sheldon R A, *Trends Biotechnol*, 21 (2003) 131.
9 Tanner E E L, Batchelor-McAuley C & Compton R G, *Chem Eur J*, 22 (2016) 5976.
10 Wang Y & Yang H, *Chem Commun*, (2006) 2545.
11 Irfan M, Moniruzzaman M, Ahmad T, Mandal P C, Abdullah B & Bhattacharjee S, *Arabian J Chem*, (2017) https://doi.org/10.1016/j.arabjc.2017.02.001 (In Press).
12 Thio B J R, Montes M O, Mahmoud M A, Lee D-W, Zhou D & Keller A A, *Environ Sci Technol*, 46 (2012) 6985.
13 Cahyana A H, Pratiwi D & Ardiansah B, *Mater Sci Eng*, 188 (2017) 012008.
14 Williamson C L, Maly K E & MacNeil S L, *J Chem Educ*, 90 (2013) 799.
15 Antonietti M, Kuang D, Smarsly B & Zhou Y, *Angew Chem Int Ed Eng*, 43 (2004) 4988.

16 Taubert A, *Acta Chim Solv*, 52 (2005)168.
17 Ding K, Miao Z, Liu Z, Zang Z, Han B, An G, Miao S & Xie X, *J Am Chem Soc*, 129 (2007) 6362.
18 Deshmukh R, Rajagopal R R & Srinivasan K V, *Chem Commun*, (2001) 1544.
19 Dupont J, Fonseca G S, Umpierre A P, Fichtner P F P & Teixeira X R, *J Am Chem Soc*, 124 (2002) 4228.
20 Endres F & Abedin S Z, *Chem Commun*, 8 (2002) 892.
21 Perreux L & Loupy A, *Tetrahedron*, 57 (2001) 9199.
22 Namboodiri V V & Varma R S, *Green Chem*, 3 (2001) 146.
23 Goharshadi E K, Ding Y & Nancarrow P, *J Phy Chem Solids*, 69 (2008) 2057.
24 Vaezi M R & Sadrnezhaad S K, *Mater Des*, 28 (2007) 515.
25 Nagaraj N, Shamsuddin N & Mohamed S Z, *Indian J Chem*, 44A (2005) 1165.
26 Qiuyun Z, Li Hu, Wenting Q, Liu X, Yuping Z, Wei X & Song Y, *Catal Res*, 15 (2013) 19.
27 James C & Duncan C, *Handbook of Green Chemistry and Technology*, (Blackwell Sci. Ltd, Oxford, London) 2002, p. 321.
28 Vijaya Kumar V & Rajathi K, *J Chem Pharm Res*, 7 (2015) 855.
29 Abiraman T, Kavitha G. Rengasamy R & Balasubramanian S, *RSC Adv*, 6 (2016) 69206.
30
31 Wang L, Chang L, Zhao B, Yuna Y, Shao G & Zheng W, *Inorg Chem*, 47 (2008) 1443.
32 Hu X L, Zhu Y J & Wang S W, *Mater Chem Phy*, 88 (2004) 421.
33 Hu J, Gao F, Shang Y, Peng C, Liu H & Hu Y, *J Microporous Mesoporous Mater*, 142 (2011) 268.
34 Wang Y & Yang H, *J Am Chem Soc*, 127 (2005) 5316.
35 Derouane E G, Vedrine J C, Pinto R R, Borges P M, Costa L, Lemos M A N D A, Lemos F & Ribeiro F R, *Cat Rev Sci Eng*, 55 (2013) 454.
36 Vorobyeva N, Rumyantseva M, Filatova D, Konstantinova E, Grishina D, Abakumov A, Turner S & Gaskov A, *Sensors Actuators, B*, 182 (2013) 555.
37 Varadwaj G B B & Parida K M, *Catal Lett*, 141 (2011) 1476.
38 Sreedhar B, Arundhathi R, Reddy M A & Parthasarathy G, *Appl Clay Sci*, 43 (2009) 425.
39 Ramalinga K, Vijayalakshmi P & Kaimal T N B, *Tetrahedron Lett*, 43 (2002) 879.
40 Javaherian M & Sabzi H E, *Indian J Chem*, 53B (2014) 631.
41 Yang H, Song H, Zhang H, Chen P & Zhao Z, *J Mol Catal: Chem*, 381 (2014) 54.