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Research Article

Supported Imidazolium Based Ionic Liquid as a Green, Highly Effective and Reusable Catalyst for Microwave Assisted Knoevenagel Condensation

Priyanka Rajoriya and Ashu Rani*

Department of Pure and Applied Chemistry, University of Kota, Kota, 324005, Rajasthan, India

Abstract

Imidazolium chloride is synthesized by direct alkylation of 1-methyl imidazole under dielectric heating and grafted on chemically activated fly ash (CFA) using impregnation method to develop an efficient heterogeneous catalyst. The catalyst is characterized with various techniques viz. FTIR, SEM and ^{1}HNMR and used as environmentally benign catalysts for Knoevenagel condensations of benzaldehyde and ethyl cyanoacetate giving high product yield up to four reaction cycles without any significant loss of its catalytic activity.

Keywords: Imidazolium hloride, Direct alkylation, Knoevenagel Condensation, Impregnation method, CFA

***Correspondence**
Author: Ashu Rani
Email: ashu.uok@gmail.com

Introduction

Knoevenagel condensations of aldehydes with active methylene compounds are extensively used in the synthesis of pharmaceutical and fine chemical intermediates [1]. A wide range of homogeneous bases such as piperidine, amines, ammonia, and ammonium salts [2] and solid bases such as KF/Al_2O_3, hydrotalcite, KNH_2/Al_2O_3 and immines/SiO_2 [3-6] have been reported for catalyzing Knoevenagel condensation although have disadvantages such as difficulty in separation and reuse in case of homogeneous base and high mass transfer resistance and easy to deactivation in case of heterogeneous. Recently, Ionic liquid (IL) technology has become a need of green and sustainable chemistry, due to the remarkable properties of IL viz. nonvolatility, immiscibility with regular organic/inorganic solvents and non inflammability responsible for wide applications [7-8]. In synthetic organic chemistry ionic liquids are used as dual reagent (solvent and catalyst) in various catalytic processes [9-10]. In addition to homogeneous applications of IL, supported ionic liquid (SIL) catalysts in which thin layer of ionic liquid is immobilized on solid support material has been employed in various synthetic applications such as esterification, nitration [11], Baeyer-Villiger reaction [12], Knoevenagel condensation [13] acetalization reaction[14] Friedel-Crafts alkylation reactions [15] carbonylation [16], hydrogenation [17], Heck reactions [18], hydroaminations [19], epoxidation [20], asymmetric aldol condensation[21]. Many mesoporous materials, such as silica [22], polymers [23], and magnetic nano particles [24] etc. are popularly used as support for immobilizing ILs. In continuation, we have synthesized an innovative catalyst by immobilizing 1-butyl-3-methyl imidazolium chloride[bmim]Cl on chemically activated fly ash (FA) and used in microwave assisted Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate giving industrially important product ethyl 2-cyano-3-phenylacrylate up to four reaction cycles . In previous years our laboratory has already reported several fly ash based solid acids [25-29], solid base [30] and oxidation catalysts[31] for organic transformations. This report is novel as firstly presenting chemically activated fly ash based supported ionic liquid catalyst.

Experimental

Materials and Apparatus

Ionic liquid precursors, 1-methylimidazole (99%), chlorobutane were purchased from Sigma Aldrich. Benzaldehyde and ethyl cyanoacetate were obtained from S.D. Fine Chem. Ltd., India. Coal Fly ash [Class F type (SiO_2 + Al_2O_3) > 70%] was collected from Kota Thermal Power Plant (Rajasthan, India). The knoevenagel condensatsation was carried out in microwave synthesis system CEM, USA (Model-Discover) single mode type, closed Pyrex glass tubes (ca. 10 ml) with Teflon-coated septa. The removal of solvents was performed in rotary evaporator (Heidolph G3, Germany).

Synthesis of [bmim]Cl/CFA

A mixture of 1-methylimidazole (1.23gm, 15mmol) and chlorobutane (1.38 gm, 15mmol) was placed in microwave reactor tube and irradiated at 110 °C for 20 min at 50 psi pressure. After cooling to room temperature, the obtained yellow viscous [bmim]Cl, was thoroughly washed with diethyl ether and the solvent was removed by rotatory evaporator and dried overnight in a vacuum oven at 70 ºC. The chemical activation of FA was carried out in a stirred reactor by stirring 5M aqueous solution of H_2SO_4 in the ratio of 1:2 (FA: H_2SO_4) for 24h at 110 ^oC. Filtered fly ash was then washed with distilled water till complete removal of soluble ionic species (Cl^-, NO^{3-}, SO_4^{2-}, ClO_4^- further dried at 110 ^oC for 24h. Prior to the grafting, CFA was activated at 550 ºC for 1 h and [bmim]Cl was dried at 70ºC under vacuum for 1 h. The pretreated CFA (5gm) was dispersed in 50 ml anhydrous toluene, followed by taking 2gm of [bmim]Cl in a refluxing assembly under vacuum. The mixture was refluxed under N_2 atmosphere at 90 °C for 48 h. After cooling to room temperature the product was filtrated, washed with dry dichloromethane to remove the excess of ionic liquid and dried under vacuum at 70 ºC for 24 h to give brown powder. The resultant solid powder is denoted as [bmim]Cl/CFA to be used as a catalyst for Knoevenagel condensation.

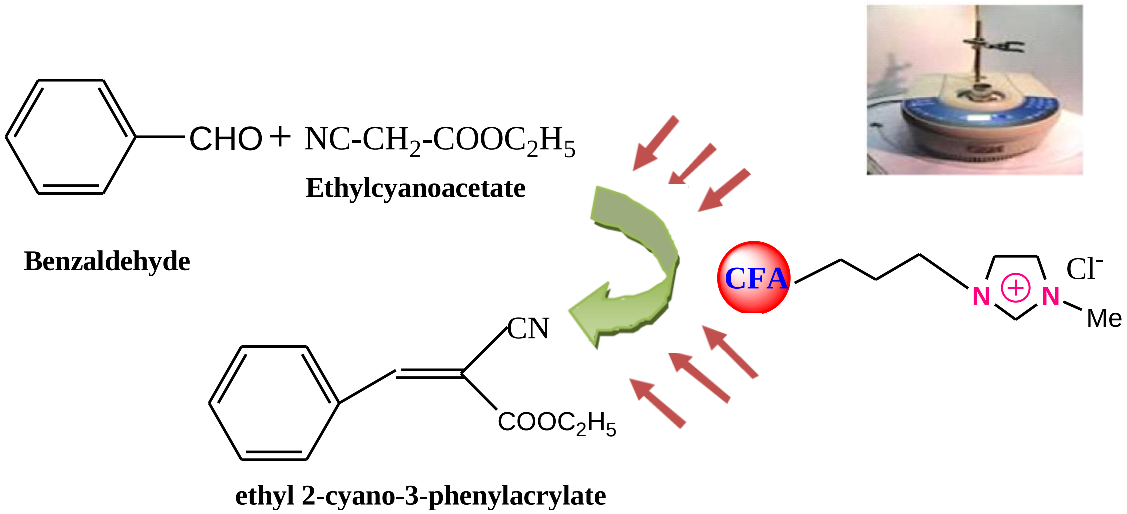
The [bmim]Cl was characterized by ^1H NMR ($CDCl_3$): d = 0.71–0.78 (m, 2H), 1.25–1.33 (t, 9H), 1.85–1.91 (m, 2H), 3.40–3.52 (m, 6H), 4.11 (s, 3H), 8.26 (d, 1H), 8.34 (d, 1H), 8.53 (s, 1H)

Characterization Techniques

FTIR spectra of the materials were recorded in the range 550 – 4000 cm^{-1} with a resolution of 4 cm^{-1} using FTIR Tensor 27 Brucker with DR (Diffuse Reflectance) accessory. The detailed imaging information about the morphology and surface texture was provided by SEM-EDX (Philips XL30 ESEM TMP). Conversion of benzaldehyde was measured by Gas Chromatograph with an FID detector (Agilent 7820 A, HP-5 capillary column 30m×0.5mm×0.3μm).

Catalytic activity of [bmim]Cl /CFA

The catalytic activity of [bmim]Cl /CFA catalytic system was investigated by microwave assisted solvent free Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate (**Scheme 1**) as a test reaction in microwave reactor. 20 mmol of benzaldehyde and 20 mmol of ethyl cyanoacetate were taken in the reactor tube. The catalyst (benzaldyhde to catalyst weight ratio = 5), activated at 70 °C for 1 h prior to the reaction in vacuum, was added in the reaction mixture and the pressurized glass vial with continuous stirring checked the vapor loss during the reaction proceeding at desired temperature and time. After completion of the reaction, the mixture was cooled at room temperature through air pump before releasing the pressure of the reactor tube.



Scheme 1 The Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate

The filtered catalyst was washed with dichloromethane to remove organic impurities. The product was separated by ether. The reaction conditions were varied to obtain maximum yield and conversion to ester. The reactions were analyzed using a GC with oven temperature range 70-240 °C and N_2 (25 ml/min) as a carrier gas. The conversion of benzaldehyde and yield of product was calculated by using weight percent method [28]

Catalyst regeneration

For catalytic reusability test the spent catalyst was recovered by filtration from the initial run, washed thoroughly with dichloromethane and dried in vacuum oven at 80 ºC for 24 h followed by activation at 70 ºC for 1 h in vacuum oven. The regenerated catalyst was used in next reaction cycles under the same reaction conditions following the procedure described as above.

Results and Discussion

Characterization of catalyst

After chemical activation the silica content in CFA is significantly enhanced (55% to 81%) showing the loss of other components during the activation with higher concentration of H_2SO_4 [28, 29]. The FT-IR spectra of FA shows broad band in –OH region (3800–2700 cm^{-1}), which is attributed to surface OH groups, particularly of silica and the water molecules adsorbed on the surface **(Figure 1(i))**. The FT-IR spectrum of CFA **(Figure 1(ii))** shows a significant increase in peak intensity of the band for -OH group due to increased silanol groups and adsorbed water molecules on the surface [29]. The increased amorphous silica in the activated fly ash can be characterized by an intense band in the range 1000–1300 cm^{-1}, corresponding to the valence vibrations of the silicate oxygen skeleton [32]. The main absorption band of the valence oscillations of the groups Si-O-Si in quartz appears with a main absorption maximum at 1100 cm^{-1} [27]. Increase in silica content results in increase in the surface free silanol groups, enhancing strong hydrogen bonding between anions of IL and surface free silanols groups which stabilized thin layer of IL on the surface of CFA [33].

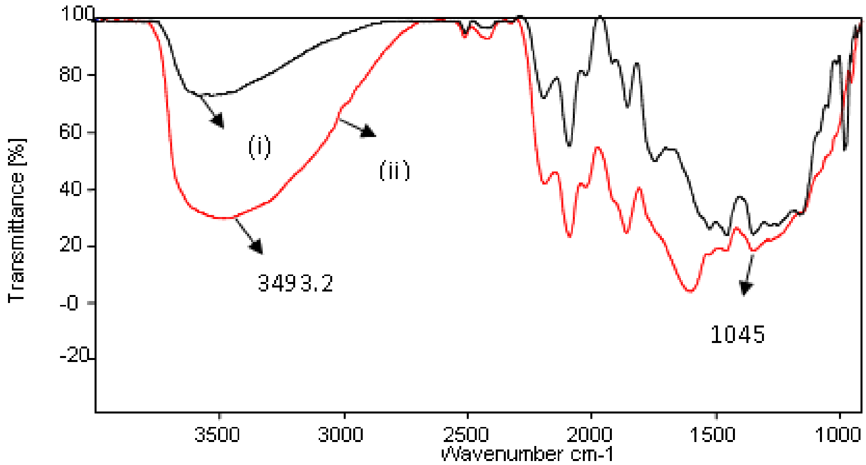


Figure1 FTIR spectra of (i) FA (ii) CFA

The FT-IR spectrum of [bmim]Cl/CFA in **Figure 2** shows the typical strong peak corresponding to OH stretching frequency centered at about 3410 cm^{-1}, and characteristic bands observed at1094 cm^{-1}, 1571.7 cm^{-1}, and 1636 cm^{-1} associated with stretching frequencies of the imidazolium ring [34]. The adsorption band around 2970 cm^{-1} assigned to C–H stretching vibration which confirms the presence of alkyl groups of ionic liquid [35].

SEM micrographs of raw FA in **Figure 3A** revealed different shaped, relatively smooth hollow cenospheres. In CFA shown in Figure 3B the crystalline and spherical particles break down into amorphous ones and get agglomerated. The agglomerated particles are scattered conferring the increase in surface area, which is due to increase in silica content after acid leaching. The SEM images of [bmim]Cl /CFA showed that the resulting particles are represented by irregular structures composed of large blocks with many small particles stacked together to form the bigger particles. All particles are covered by IL forming a thin layer over the surface of CFA clearly seen in Figure 3 (D).The energy dispersive spectrum (EDX) shows the presence of C, Fe, Si, O, and Al and other metals in

FA and CFA samples. However the presence of high carbon (4.96%) and chloride (2.75%) in [bmim]Cl/CFA catalyst confirms immobilization of [bmim]Cl on activated surface of fly ash.

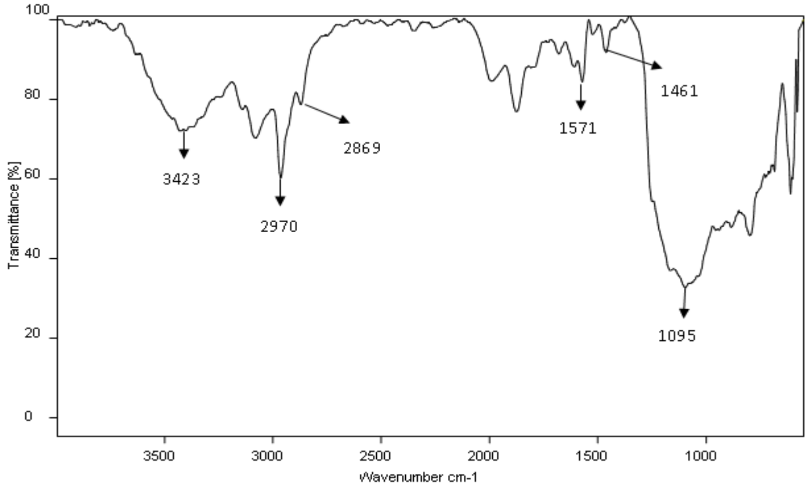


Figure 2 FTIR spectra of [bmim]Cl/CFA

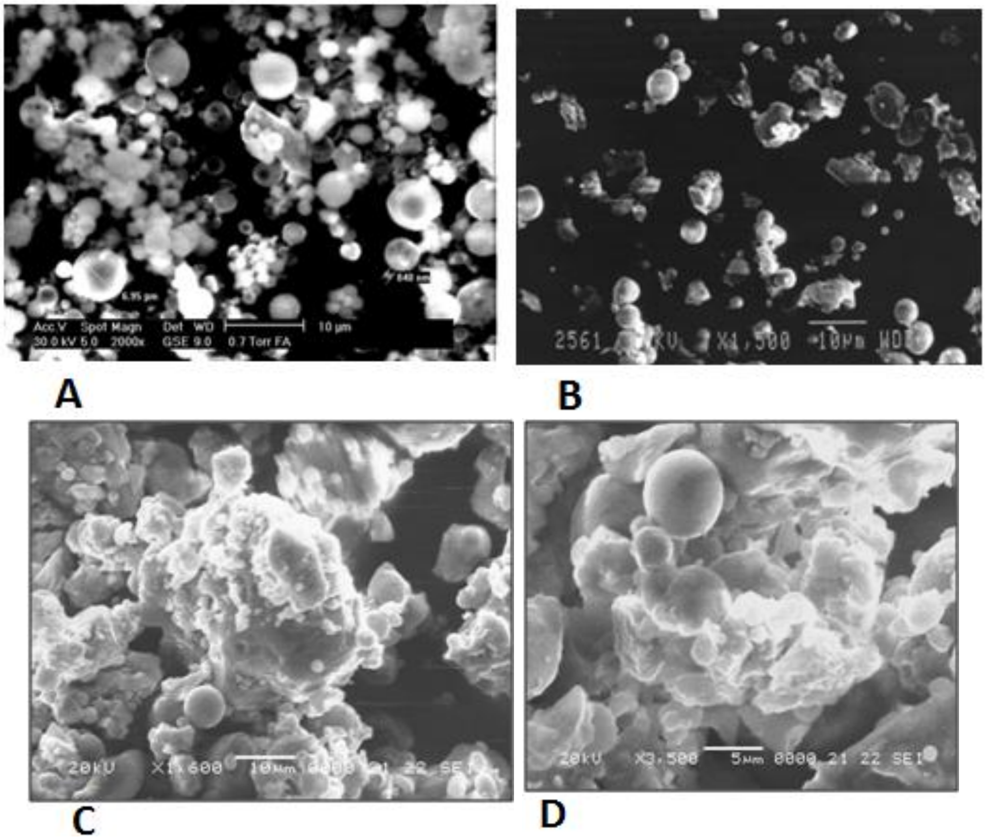


Figure 3 SEM micrographs (A) pure FA (B) CFA (C, D) [bmim]Cl /CFA and magnified image of [bmim]Cl/CFA

To evaluate the catalytic activity of synthesized catalyst, Knoevenagel condensation was performed with pure FA and CFA also, both have not shown any catalytic activity for studied reaction. [bmim]Cl/CFA catalyst showed high catalytic activity for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate resulting conversion to ethyl 2-cyano-3-phenylacrylate maximum up to 88%.

Microwave assisted Knoevenagel condensation was performed at different temperatures ranging 90 °C to 130 °C for 5 to 20 min. to optimize the reaction temperature, time, catalyst and reactants molar ratio . The results of optimization of reaction conditions for studied reaction are given in **Table 1**.On the basis of table 1 the optimal conditions were; molar ratio, 1:1 ; reactant to catalyst ratio, 5:1 ; reaction temperature, 120ºC ; reaction time, 15min.

Table 1 Optimization of reaction conditions for synthesis of ethyl 2-cyano-3-phenylacrylate using [bmim]Cl/CFA as catalyst

S.NO	Molar ratio	Reactant to catalyst weight ratio	Time, min.	T/ ºC	Conversion, %	Yield, %
1	1:1	5:1	15	90	61	64
2	1:1	5:1	15	100	75	78
3	**1:1**	**5:1**	**15**	**120**	**88**	**90**
4	1:1	5:1	15	130	87	89
5	1:1.5	5:1	15	120	74	76
6	1:2	5:1	15	120	60	62
8	1:3	5:1	15	120	55	57
9	1:1	5:1	5	120	45	47
10	1:1	5:1	10	120	56	59
11	1:1	5:1	20	130	88	89
12	1:1	10:1	15	120	62	67
13	1:1	2:1	15	120	74	77
14	1:1	2:1	20	130	75	78

Reusability of catalyst

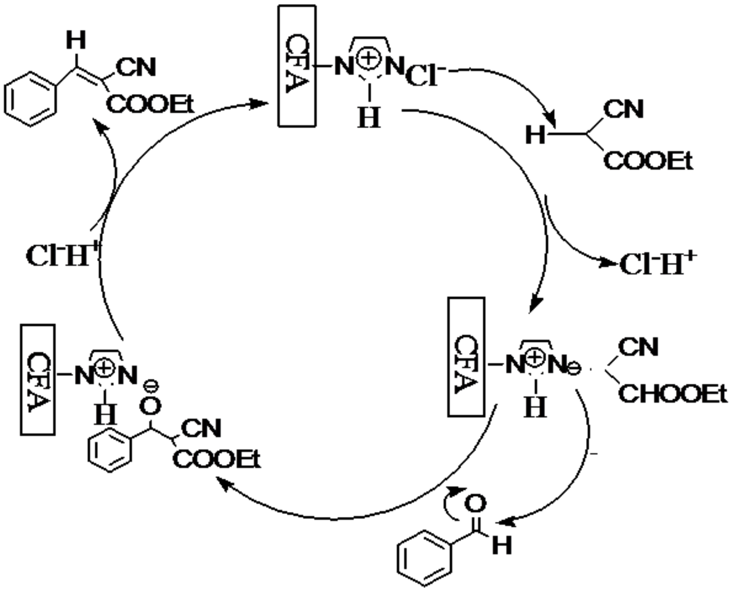
The catalyst [bmim]Cl/CFA could be used up to four reaction cycles to catalyze the reaction in high product yield (**Table 2**). The product yield was slightly decreased with increasing reuse run, which may be due to the deposition of significant amount of carbonaceous material on the surface of used catalyst that may block the catalyst active sites.

Table 2 The reusability test of [bmim]Cl/CFA catalyst

S.No.	Run	Conversion (%)	Yield (%)
1	Fresh catalyst	88	91
2	First cycle	86	88
3	Second cycle	84	86
4	Third cycle	80	84

Proposed mechanism

Reaction mechanism is based on the experimental results with reference to previous findings [36]. The plausible mechanism is schematically presented in **Scheme 2**.



Scheme 2 Proposed mechanistic pathway of microwave-assisted condensation of benzaldehyde and ethyl cyanoacetate reaction over [bmim]Cl/CFA catalyst

The chloride anion of [bmim]Cl/CFA initiate reaction by accepting a proton from the active methylene group of ethyl cyanoacetate leading to formation of carbanion. The formed carbanion of ethyl cyanoacetate makes nucleophilic attack to the carbonyl carbon atom of aromatic aldehydes, followed by loss of water molecule to form α β unsaturated carbonyl compound.

Conclusion

The present work introduces a new, efficient and recyclable heterogeneous organocatalyst prepared by immobilization of ionic liquid on the active sites of CFA. An energy efficient elegant and fast microwave technology was employed for synthesis of ionic liquid. The resulting heterogeneous catalyst [bmim]Cl/CFA exhibited excellent catalytic activity for microwave assisted condensation reaction at optimized reaction conditions. The CFA posses high silica content and surface roughness and high concentration of free silanol groups, giving an effective solid support for immobilization of ionic liquid. This heterogeneous catalyst can be recovered and reused up to four reaction cycles giving high yield of desired product without significant loss of its catalytic activity.

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