

# Imidazolium Chloride Immobilized Fly Ash as a Heterogenized Organocatalyst for Esterification Reaction under Microwave Irradiation Heating

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**ABSTRACT:** An efficient solventless one-pot procedure for the synthesis of imidazolium based ionic liquid under microwave irradiation is described in which 1-methylimidazole was modified by organosilane (3-chloropropyl triethoxysilane). This ionic liquid 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (TMICl) is immobilized on Mechanically activated Fly Ash (MFA) by co-condensation method to develop an active organocatalyst (TMICl/MFA). The mechanical activation has generated significant number of silanol groups suitable for immobilizing ionic liquids. For characterization of various materials, different techniques viz, XRD, FTIR, SEM-EDX, TGA, BET surface area,  $^1\text{H}$ NMR are used. The prepared TMICl/MFA exhibited high catalytic activity for a series of microwave assisted esterification of aliphatic alcohols and salicylic acid for four successive reaction cycles under optimized conditions.

**KEYWORDS** 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride; Solid catalyst; Microwave irradiation; MFA; Esterification; Co-condensation.

## INTRODUCTION

Recent advancements have introduced ionic liquids (ILs) as green and ecofriendly solvents and catalysts towards modern synthetic chemistry [1]. The high thermal stability, high conductivity, low vapour pressure, and structure tuneability make ILs a versatile material for designing innovative catalytic systems for numerous synthetic applications [2-3]. However, widespread applications of ionic liquids are still hampered because of their unendurable viscosity, high cost, and difficulty in recyclability etc. in the homogeneous systems [4].

In order to improve the applicability of ILs at industrial scale a new thought of Supported Ionic Liquid Catalysts (SILCs)

have been adopted. SILCs prepared by fixing the thin film of IL on active solid supports via different methods such as simple impregnation, grafting, polymerization, sol-gel method, encapsulation, or pore trapping [5-11] has achieved high catalytic performance in the field of organic synthesis through green catalytic pathways.

Immobilized ionic liquids have been used as novel heterogeneous catalysts for catalyzing various reactions such as esterification, nitration reactions [12], acetal formation [13], Baeyer-Villiger reaction [14], synthesis of  $\alpha$ -aminonitriles [15] and bis-pyrazolones [16] Knoevenagel condensation reactions [17], cycloaddition

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reaction [18], Henry reaction [19], acetalization reaction [20], hydrogenation of alkynes [21], Suzuki coupling reactions [22], CO<sub>2</sub> cycloaddition reactions [23]. Now a day, microwave dielectric heating has been successfully applied to the synthesis of several imidazolium-based ILs [24]. The imidazolium based ILs are widely used due to structural modifications in both the cation (especially the 1 and 3 positions of the imidazolium ring) and anion can be easily made [25]. Several catalysts have been synthesized by immobilization of number of imidazolium based ILs on various mesoporous materials such as on silica gel [26], SBA-15 [27], magnetic nanoparticles [28] giving highly selective product.

Fly ash (FA), solid waste of thermal power plants contains SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, Mn<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, etc. in varying amounts and inert crystallite phases such as mullite, quartz, and magnetite, etc [29]. Various properties of fly ash such as silica-alumina %, carbon %, porosity, surface area, acidity, etc are important with respect

to their applications in various fields [30-33]. Fly ash based heterogeneous catalysts are efficiently used for synthesis of drug intermediates and fine chemicals under thermal and microwave heating both [32, 34-39] and for waste water treatment [40-42]. Mechanical milling significantly increases surface activity of fly ash [43] to make it an efficient, cost effective catalytic support material for synthesizing green heterogeneous catalysts. The present work elaborates microwave mediated synthesis of TMICl which is further immobilized on mechanically activated FA (MFA) to prepare a heterogeneous organocatalyst, TMICl/MFA, active towards solvent free synthesis of salicylates under dielectric heating. Salicylates are widely used in flavors, fragrances, cosmetics and ultraviolet radiation filters [44].

## EXPERIMENTAL SECTION

### Materials and Apparatus

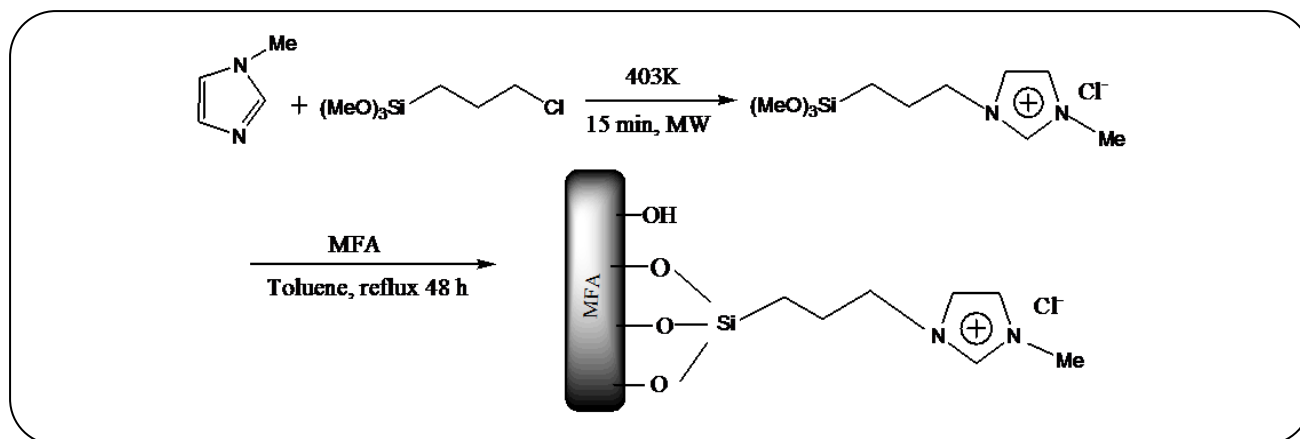
Fly ash [Class F type (SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>) > 70%], collected from Kota Thermal Power Plant (Rajasthan, India) was used as support for the preparation of the supported ionic liquid catalyst. Acids and alcohols were obtained from S.D. Fine Chem. Ltd., India. Ionic liquid precursors 1-methylimidazole (99%), 3-chloropropyltriethoxysilane

(95%) were purchased from Sigma Aldrich. Mechanical activation of FA was performed in high energy planetary ball mill, Retsch PM-100, Germany and thermal activation was carried out using high temperature microwave furnace, CEM USA. The synthesis of ionic liquid and test esterification reactions were performed in microwave synthesis system CEM, USA (Model-Discover) having single mode type, closed Pyrex glass tubes (ca. 10 mL) with Teflon-coated septa and in-built magnetic stirrer. The reaction temperature during the run was monitored with an infrared sensor placed aligned just below the reaction vessel. Variable power was supplied by microprocessor-controlled single-magnetron system. The maximum microwave irradiation power was utilized during 'ramping time' to attain desired temperature. Once the desired temperature is achieved lower power was used to maintain reaction temperature during the 'holding time'. The reaction mixture was cooled to 50°C within the instrument in 'cooling time' using air pump. Removal of solvents and other liquid materials was performed in rotary evaporator (Heidolph G3, Germany). Drying of ionic liquid materials was performed in vacuum oven (Labpro).

As received Fly ash (FA) was washed with distilled water followed by drying at 100°C for 3h, thereafter mechanical activation was performed using high energy planetary ball mill in an agate grinding jar using agate balls of 5 mm ball sizes for 5, 10, 15 and 36 h with 250 rpm to get MFA(5-36). The ball mill was loaded with the ball to Powder Weight Ratio (BPR) of 10:1. All mechanically activated samples were thermally activated by calcination at 800°C for 3h to remove carbonates, sulphates, and other adsorbed moieties. MFA-36 having higher specific surface area (31m<sup>2</sup>/g) was selected for immobilizing ionic liquid.

### Synthesis of imidazolium based ionic liquid

For the synthesis of 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride (TMICl, Scheme 1) mixture of 1-methylimidazole (0.82g, 10mmol) and chloropropyltrimethoxysilane (1.98g, 10mmol) was sealed in stirred closed tube of microwave batch synthesis system under N<sub>2</sub> atmosphere at 120°C for 15 min at 50 psi pressure. The obtained yellowish viscous liquid was brought to room temperature and thoroughly washed three times with diethyl ether (3×20mL). The viscous product was dissolved in methylene chloride and



Scheme 1: The synthesis route of ionic liquid functionalized FA.

subsequently filtered over silica gel and dried overnight in a vacuum at 70 °C. The TMICl was characterized by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 10.80(s,1H), 7.39(s,1H), 7.30(s,1H), 4.37(t,2H), 4.12(s,3H), 3.80(q,6H), 2.02(q,2H), 1.21(t,9H), 0.60(t,2H).

#### Synthesis of TMICl/MFA

Prior to immobilization, MFA-36 was activated at 550°C for 1 h and TMICl was dried at 70°C under vacuum for 1 h. The pretreated MFA-36 (5g) and 2g of TMICl were co-dispersed in 50 ml dry toluene in a refluxing assembly under vacuum. The mixture was refluxed under  $\text{N}_2$  atmosphere at 90°C for 48 h. The toluene solvent was removed by filtration and the solid material was transferred to a rotary evaporator. The excess of physisorbed ionic liquid was removed using rotary evaporator under reduced pressure. Finally the solid was dried under vacuum at 70°C for 24 h to give brown powder of TMICl/MFA to be used as a catalyst (Scheme 1) for esterification reactions.

#### Characterization Techniques

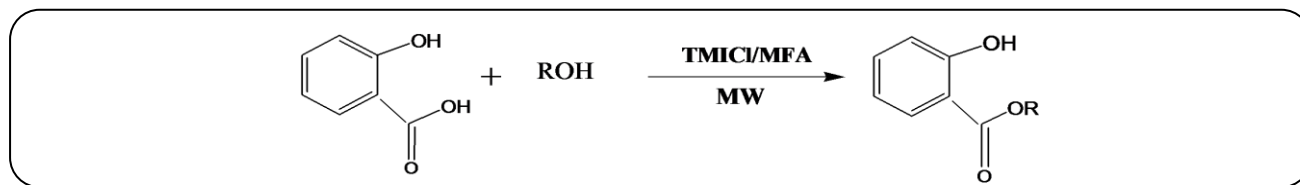
FT-IR spectra of the materials were recorded in the range 550–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  using FT-IR Tensor 27 Bruker with DR (Diffuse Reflectance) accessory. The detailed imaging information about the morphology and surface texture was provided by SEM-EDX (Philips XL30 ESEM TMP). The BET surface area was measured by  $\text{N}_2$  adsorption-desorption isotherm study at liquid nitrogen temperature (77 K) using the Quantachrome NOVA s1000e surface area analyzer. The XRD measurements were carried out using

Bruker D8 Advance X-ray diffractometer with monochromatic  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in a  $2\theta$  range of 5–70°C. The thermal properties were examined by a NETZSCH TG 209F1 Libra thermo gravimetric with a heating rate of 10°C per minute under a dynamic  $\text{N}_2$  atmosphere with temperature range from 33°C to 800°C. The conversion of acid was measured by Gas Chromatograph (GC) with an FID detector (Agilent 7820A, HP-5 capillary column 30m×0.5mm×0.3 $\mu\text{m}$ ).

#### The catalytic activity of TMICl/MFA

In order to evaluate the catalytic behaviors of TMICl/MFA catalyst the microwave assisted solvent free esterification of different alcohols with salicylic acid acid was tested (Scheme 2).

The typical procedure was performed as follows, 20 mmol of aliphatic alcohol, 10 mmol of salicylic acid were filled in the reactor tube. The reaction mixture was fed with preheated (80 °C, 1h) catalyst in acid/catalyst weight ratio of 5:1, the pressurized glass vial with continuous stirring checked the vapor loss during the reaction proceeding at the desired temperature and time. After the reaction the mixture was cooled through air pump before releasing the pressure of the reactor tube. The filtered catalyst is washed with dichloromethane to remove organic impurities. The ester was isolated by transferring into a separatory funnel together with 250 mL brine and basifying the mixture using  $\text{NaHCO}_3$ . The resultant organic layer was dried over anhydrous sodium sulphate and solvent removed under reduced pressure. The desired product was characterized by FT-IR. The reaction conditions were varied to obtain maximum yield and



Scheme 2: Microwave-assisted solvent-free synthesis of ester over TMICl/MFA catalyst.

conversion into an ester. The reactions were analyzed using a GC with an oven temperature range 70-240°C and N<sub>2</sub> (25 mL/min) as a carrier gas. The yield of ester was calculated by selectivity and conversion from GC analysis using following Equation (1).

$$\text{Selectivity}(\%) = \frac{\text{yield}}{\text{conversion}} \times 100 \quad (1)$$

### Catalyst regeneration

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

## RESULTS AND DISCUSSION

### Characterization of catalyst

The effect of mechanical activation on properties of FA is given in Table 1 which indicates that the silica percentage is increased marginally after milling for 5 to 36h but the specific surface area is increased from 9 to 31m<sup>2</sup>/g [30]. As compared with FA, the crystallite size is reduced from 33 to 17 nm as milling time was increase up to 36h.

The FT-IR spectra of FA and MFA-36 in Fig. 1 show a broad band between 3400-3000 cm<sup>-1</sup>, which is attributed to surface -OH groups of Si-OH and adsorbed water molecules on the surface.

The increment in broadness after ball milling for 36h is evidence for the breaking down of the quartz structure and formation of Si-OH groups [30]. A peak at 1650 cm<sup>-1</sup> in the spectra of FA is attributed to bending mode (δO-H) of water molecule. However, FT-IR study clearly shows changes in the broadening of IR peaks corresponding to Si-O-Si asymmetric stretching vibrations (1101, 1090 cm<sup>-1</sup>) indicating structural rearrangement during mechanical milling [30-31].

The FT-IR spectra of TMICl/MFA given in Fig. 2(ii) shows characteristic bands at 1628 cm<sup>-1</sup>, 1570 cm<sup>-1</sup>, 1461 cm<sup>-1</sup>, 1168 cm<sup>-1</sup> which are ascribed to, C=N, C=C and stretching vibrations of the imidazole ring [45]. The adsorption band around 2962 cm<sup>-1</sup>, 2869 cm<sup>-1</sup> assigned to C-H stretching vibration which confirms the presence of propyl groups of ionic liquid [46].

The X-Ray diffraction patterns of the as received FA, as well as MFA, are given in Fig. 3(a,b). show decrement in the crystallinity of fly ash and increase in the amorphous nature as inferred with decrease in the crystalline size of fly ash from 33nm to 17nm on milling. The peaks at 16.4° and 26.2° show mullite (aluminosilicate) phase while quartz(silica) exhibits strong peaks at 20.7°, 26.6°, 40.6° and 49.9° of 2θ values. As a result of ball milling mostly quartz and mullite crystalline phases are reduced [30].

The Energy Dispersive X-ray (EDX) spectrum shows the presence of C, Fe, Si, O, and Al and other metals in FA and MFA samples. However, the presence of high carbon and chloride in TMICl/MFA catalyst confirms the immobilization of TMICl on activated surface of fly ash. On the basis of wt% of C and Cl it results that TMICl grafting is in higher percentage on the surface of MFA than on FA (Table 2).

The SEM photograph of pure fly ash (Fig. 4A) is observed with hollow cenospheres, irregularly shaped unburned carbon particles, mineral aggregates, and agglomerated particles. As a result of mechanical activation the structural break down of larger particles and increased surface roughness are observed (Fig. 4C).

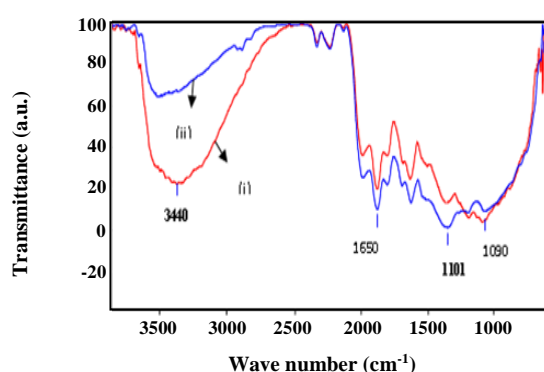
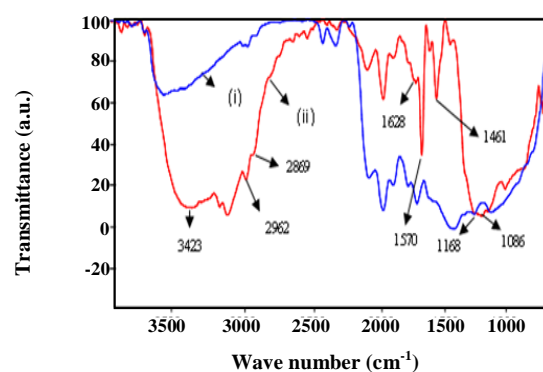
Typical SEM images of TMICl/MFA show that the resulting particles are represented by irregular structures composed of large blocks with many small particles stacked together to form the bigger particles. All particles are wrapped by IL forming a thin layer over the surface of MFA clearly seen in Fig.4 (D, E). In Fig. 4(B) particles are not seen aggregated due to insufficient loading of IL.

**Table 1: Characterization of fly ash before and after mechanical activation.**

Sample	Amount of sample silica, wt %	Crystallite size, Nm	Specific surface area, m <sup>2</sup> /g
FA	62	33	9
MFA-5	62.14	29	11
MFA-10	63.45	25	15
MFA-15	64.27	21	17
MFA-36	65.14	17	31

**Table 2: EDX analysis of FA, MFA, TMIC/FA and TMIC/MFA Catalyst.**

Sample	Amount of O, wt %	Amount of Si, wt %	Amount of Al, wt %	Amount of Ca, wt%	Amount of Fe, wt %	Amount of C, wt %	Amount of Cl, wt %
FA	55.45	25.88	16.11	0.68	0.79	-	-
MFA	55.20	27.01	4.47	0.56	2.81	-	-
TMIC/FA	60.05	35.11	6.41	1.02	2.50	2.15	0.9
TMIC/MFA	95.9	41.88	7.60	1.05	2.72	4.96	2.75

**Fig. 1: FTIR spectra of (i) FA (ii) MFA-36.****Fig. 2: FT-IR spectra of (i) MFA-36 (ii) TMIC/MFA.**

The thermal stability of TMIC/MFA was determined by thermo gravimetric analysis (Fig. 5). The TGA curve indicated initial weight loss within 200° C probably attributed to the removal of physisorbed water and residual solvent toluene [38]. When the temperature further increased to 250°C, the weight of TMIC/MFA decreased rapidly due to removal of IL. Finally, it was observed that the TMIC/MFA catalyst exhibited good thermal stability under 250°C and the residual weight loss of TMIC/MFA was about 10% at around 800°C.

#### **Catalytic activity- microwave assisted the solvent-free synthesis of ester**

In order to evaluate the catalytic activity of synthesized catalysts, the esterification was carried out

with and without a catalyst. The yield of the product in each case is given in Table 3. For uncatalyzed reaction the yield of the product just could reach 15.0%. When reaction was carried out in homogeneous medium, TMICl showed good catalytic activity but separation of pure product was difficult with no possibility of catalyst reuse. However, TMICl supported on FA and MFA, could be easily separated by vacuum filtration and reused. In order to establish the MFA better support for ionic liquid grafting the TMIC/FA and TMIC/MFA both were reused in second cycle. Interestingly regenerated TMIC/FA gave only 25% yield due to leaching of ionic liquid during first cycle of reaction as well as during washing whereas TMIC/MFA showed no significant loss in the yield of ester during second cycle confirming

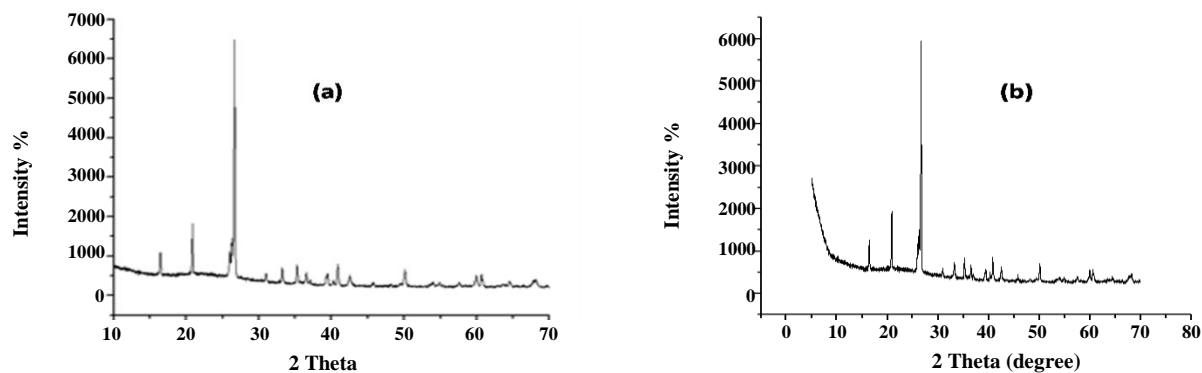


Fig. 3: X-ray diffraction patterns of (a) Pure FA, (b) MFA-36.

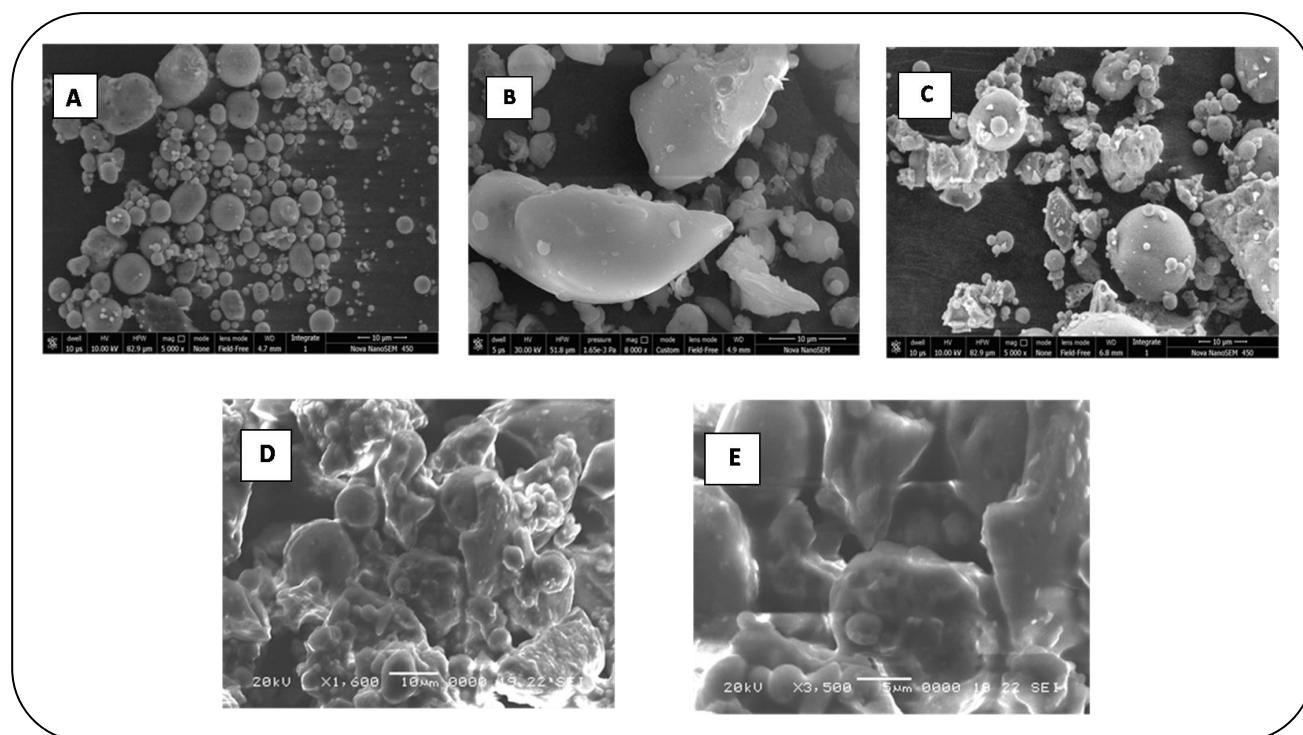


Fig. 4: SEM micrographs (A) pure FA (B) TMICL/FA (C) MFA-36 (D, E) TMICL/MFA and magnified image of TMICL/MFA.

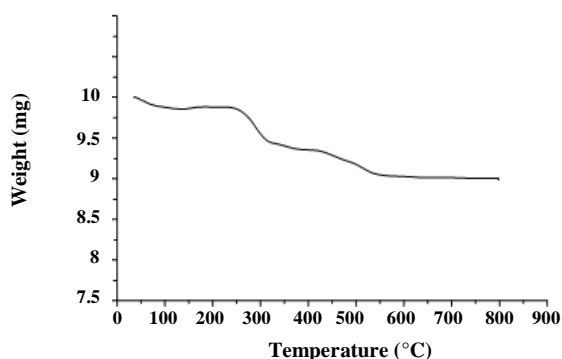


Fig. 5: TGA patterns of TMICL/MFA.

the high stability of catalytic sites. FA and MFA without grafting Ionic Liquid have not shown any catalytic activity for the studied reaction.

Microwave assisted the solvent-free synthesis of ester using different aliphatic alcohols and Salicylic acid as performed in the presence of TMICL/MFA catalysts and result was summarized in Table 4.

Parameters such as reactant molar ratio, amount of catalyst, reaction time and temperature were optimized in order to achieve the maximum catalytic activity and good conversion of desired product.

**Table 3: Esterification reaction between Octanol and Salicylic acid.**

Sample	Catalysts	Temperature, °C	Time, min	Yield, %
1	Blank	110	15	15.04
2	MFA-36	110	15	20.03
3	TMICl	110	15	80
4	TMICl/FA	110	15	50
5	TMICIMFA	110	15	91
6	TMICl/FA (cycle 2)	110	15	25
7	TMICl/MFA (cycle 2)	110	15	90

Salicylic acid(10mmol), Octanol (20 mmol), acid/catalyst weight ratio (5:1)

**Table 4: Microwave assisted esterification reactions catalyzed by TMICl/MFA at T=110°C, Time=15, molar ratio (acid:alcohol) =1:2, P=100W, Pmax. =ON.**

Entry	Acid	Alcohol	Product	Yield, %
1	Salicylic acid	Hexanol	Hexylsalicylate	92
2	Salicylic acid	Heptanol	Heptylsalicylate	94
3	Salicylic acid	Cyclohexanol	Cyclohexylsalicylate	90
4	Salicylic acid	Octanol	Octylsalicylate	92
5	Salicylic acid	Decanol	Decylsalicylate	91

The results of the optimization of operating conditions are given in Table 5. On increasing reaction temperature, conversion % of salicylic acid showed a linear increase up to 100 °C with maximum 89 % conversion and after which remained almost constant up to 110 °C. To optimize reaction time, we carried out the reaction for different reaction times ranging from 3 min to 20 min. In the first 15 min, the conversion of salicylic acid increased linearly up to 89 % which remained constant up to 20 min. The influence of molar ratio of salicylic acid to alcohol on conversion % was monitored at different molar ratios from 1:1 to 1:3 by increasing the amount of alcohol only. The conversion was found maximum at 1:2 M ratio with 89% conversion, which further decreased up to 78% on increasing the molar ratio up to 1:3. The substrate to catalyst weight ratio was varied from 10:1 to 2:1. The maximum 89% conversion was obtained at weight ratio 5:1, which remained constant on increasing the weight ratio up to 2:1. On the basis of above results (Table 5) the optimal conditions were; molar ratio, 1:2 ; reactant to catalyst ratio, 5:1 ; reaction temperature, 100°C ; reaction time, 15min.

#### Catalyst regeneration

The catalyst could be used up to four reaction cycles without any significant loss in product yield (Table 6).

#### CONCLUSION

The present research work provides an energy efficient microwave methodology over traditional thermal refluxing for the synthesis of supported ionic liquids. Synthesized TMICl was successfully grafted over mechanically activated fly ash, the resulting heterogeneous catalyst TMICl/MFA exhibited excellent catalytic activity for microwave assisted esterification of salicylic acid with various alcohols at optimized reaction conditions. In addition the textural property of fly ash has a great influence on stability of grafted ionic liquid during reaction. The mechanical activated FA can replace other costly support materials for synthesis of IL based heterogeneous catalysts for their effective use in atom efficient green chemical processes.

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**Table 5: Optimization of reaction conditions for different ester using TMICl/MFA catalyst.**

S.NO	Molar ratio	Reactant to catalyst weight ratio	Time, min	Temp, °C	Conversion, %	Yield, %
1	1:1	5:1	15	80	35	41
2	1:1.5	5:1	15	90	64	73
3	1:2	5:1	15	100	89	91
4	1:3	5:1	15	110	78	81
5	1:2	10:1	15	100	74	76
6	1:2	2:1	15	100	79	80
7	1:2	5:1	15	80	45	50
8	1:2	5:1	15	90	60	74
9	1:2	5:1	15	110	89	90
10	1:2	5:1	3	100	20	25
11	1:2	5:1	5	100	35	41
12	1:2	5:1	10	100	70	75
13	1:2	5:1	20	100	89	91

**Table 6: The reusability test of TMICl/MFA.**

Entry	Catalysts	Test	Time, min	Conversion, %	Yield, %
1	TMICl/MFA	Fresh	15	89	91
2	TMICl/MFA	1 reuse	15	86	89
3	TMICl/MFA	2 reuse	15	85	88
4	TMICl/MFA	3 reuse	15	84	86

Reaction conditions under microwave irradiation: Temperature = 110 °C; Salicylic acid/catalyst weight ratio=5:1; Power = 100W; Pmax = ON

for XRD conducted at UGC DAE-CSR Lab Indore. TGA and <sup>1</sup>H NMR analyses were conducted at MNIT, Jaipur. The financial support was provided by Fly ash Mission, DST, New Delhi, India. The authors are also thankful to UGC, New Delhi, India for their Junior Research Fellowship Scheme.

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## REFERENCES

- [1] Welton T., Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, *Chem. Rev.*, **99**(8): 2071-2084 (1999).
- [2] Picquet M., Poinot D., Stutzmann S., Tkatchenko I., Tommasi I., Wasserscheid P., Zimmermann J., *Ionic Liquids: Media for Better Molecular Catalysis*, *Top. Catal.*, **29**(3): 139-143 (2004).
- [3] Liu B.Y., Han J., Dong J.F., Wei F., Cheng Y., *Application of Ionic Liquid-Anchored Catalyst or Reagent to Organic Synthesis*, *Chin. J. Org. Chem.*, **27**(10): 1236-1243 (2007).
- [4] Cozzi F., *Immobilization of Organic Catalysts: When, Why, and How*, *Adv. Synth. Catal.*, **348**(12-13): 1367-1390 (2006).
- [5] Li P.H., Li B.L., Hu H.C., Zhao X.N., Zhang Z.H., *Ionic Liquid Supported on Magnetic Nanoparticles as Highly Efficient and Recyclable Catalyst for the Synthesis of  $\beta$ -Keto Enol Ethers*, *Catal. Commun.*, **46**: 118-122 (2014).
- [6] Breitenlechner S., Fleck M., Müller T. E., Suppan A., *Solid Catalysts on the Basis of Supported Ionic Liquids and Their use in Hydroamination Reactions*, *J. Mol. Catal. A: Chem.*, **214**(1): 175-179 (2004).



- [7] Kim D.W., Chi D.Y., [Polymer-Supported Ionic Liquids: Imidazolium Salts as Catalysts for Nucleophilic Substitution Reactions Including Fluorinations](#), *Angew. Chem. Int. Ed.*, **43**(4): 483-485 (2004).
- [8] Riisager A., Fehrmann R., Flicker S., van Hal R., Haumann M., Wasserscheid P., [Very Stable and Highly Regioselective Supported Ionic-Liquid-Phase \(SILP\) Catalysis: Continuous-Flow Fixed-Bed Hydroformylation of Propene](#), *Angew. Chem. Int. Ed.*, **44**(5): 815-819 (2005).
- [9] Mehnert C.P., [Supported Ionic Liquid Catalysis](#), *Chem. Eur. J.*, **11**(1): 50-56 (2005).
- [10] Shi F., Zhang Q., Li D., Deng Y., [Silica-Gel-Confined Ionic Liquids: A New Attempt for the Development of Supported Nanoliquid Catalysis](#), *Chem. Eur. J.*, **11**(18): 5279-5288 (2005).
- [11] Wang F., Zhang Z., Yang J., Wang L., Lin Y., Wei Y., [Immobilization of Room Temperature Ionic Liquid \(RTIL\) on Silica Gel for Adsorption Removal of Thiophenic Sulfur Compounds from Fuel](#), *Fuel*, **107**: 394-399 (2013).
- [12] Qiao K., Hagiwara H., Yokoyama C., [Acidic Ionic Liquid Modified Silica Gel as Novel Solid Catalysts for Esterification and Nitration Reactions](#), *J. Mol. Catal. A: Chem.*, **246**: 65-69 (2006).
- [13] Földes R.S., [The Use of Supported Acidic Ionic Liquids in Organic Synthesis](#), *Mol.*, **19**: 8840-8884 (2014).
- [14] Chrobok A., Baj S., Pudło W., Jarzębski A., [Supported Hydrogensulfate Ionic Liquid Catalysis in Baeyer-Villiger Reaction](#), *Appl. Catal. A: Gen.*, **366**(1): 22-28 (2009).
- [15] Sefat M. N., Saberi D., Niknam K., [Preparation of Silica-Based Ionic Liquid an Efficient and Recyclable Catalyst for One-Pot Synthesis of  \$\alpha\$ -Aminonitriles](#), *Catal. Lett.*, **141**(11): 1713 - (2011).
- [16] Baghernejad M., Niknam K., [Synthesis of 4, 4'-\(Arylmethylene\) bis \(1H-pyrazol-5-ols\) Using Silica-Bonded Ionic Liquid as Recyclable Catalyst](#), *Int. J. of Chem.*, **4**: 52-60 (2012).
- [17] Parvin M.N., Jin H., Ansari M.B., Oh S.M., Park S.E., [Imidazolium Chloride Immobilized SBA-15 as a Heterogenized organocatalyst for Solvent Free Knoevenagel Condensation Using Microwave](#), *Appl. Catal. A: Gen.*, **413**: 205-212 (2012).
- [18] Sun J., Cheng W., Fan W., Wang Y., Meng Z., Zhang S., [Reusable and Efficient Polymer-Supported Task-Specific Ionic Liquid Catalyst for Cycloaddition of Epoxide with CO<sub>2</sub>](#), *Catal. Today*, **148**: 361-367 (2009).
- [19] Burguete M.I., Erythropel H., Garcia-Verdugo E., Luis S.V., Sans V., [Base Supported Ionic Liquid-Like Phases as Catalysts for the Batch and Continuous-Flow Henry Reaction](#), *Green Chem.*, **10**: 401-407 (2008).
- [20] Sugimura R., Qiao K., Tomida D., Yokoyama C., [Immobilization of Acidic Ionic Liquids by Copolymerization with Styrene and Their Catalytic Use for Acetal Formation](#), *Catal. Commun.* **8**: 770-772 (2007).
- [21] Abu-Reziq R., Wang D., Post M., Alper H., [Platinum Nanoparticles Supported on Ionic Liquid-Modified Magnetic Nanoparticles: Selective Hydrogenation Catalysts](#), *Adv. Synth. Catal.*, **349**: 2145-2150 (2007).
- [22] Karimi B., Mansouri F., Vali H., [A Highly Water-Dispersible/Magnetically Separable Palladium Catalyst Based on a Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Anchored TEG-Imidazolium Ionic Liquid for the Suzuki-Miyaura Coupling Reaction in Water](#), *Green Chem.*, **16**: 2587-2596 (2014).
- [23] Sun J., Cheng W., Fan W., Wang Y., Meng Z., Zhang S., [Reusable and Efficient Polymer-Supported Task-Specific Ionic Liquid Catalyst for Cycloaddition of Epoxide with CO<sub>2</sub>](#), *Catal. Today*, **148**: 361-367 (2009).
- [24] Varma R.S., Nambodiri V.V., [Solvent-Free Preparation of Ionic Liquids Using a Household Microwave Oven](#), *Pure Appl. Chem.*, **73**: 1309-1313 (2001).
- [25] Seddon K.R., Stark A., Torres M.J., [Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids](#), *Pure Appl. Chem.* **72** (12): 2275-2287 (2000).
- [26] Miao J., Wan H., Shao Y., Guan G., Xu B., [Acetalization of Carbonyl Compounds Catalyzed by Acidic Ionic Liquid Immobilized on Silica Gel](#), *J. of Mol. Catal. A: Chem.*, **348**: 77-82 (2011).
- [27] Lin Y., Wang F., Zhang Z., Yang J., Wei Y., [Polymer-supported Ionic Liquids: Synthesis, Characterization and Application in Fuel Desulfurization](#), *Fuel*, **116**: 273-280 (2014).

- [28] Li P.H., Li B.L., Hu H. C., Zhao X.N., Zhang Z.H., Ionic Liquid Supported on Magnetic Nanoparticles as Highly Efficient and Recyclable Catalyst for the Synthesis of  $\beta$ -Keto Enol Ethers, *Catal. Commun.*, **46**: 118–122 (2014).
- [29] Mallick D., Khanra S., Chaudhuri S.K., Studies on the Potential of Coal Fly Ash as a Heterogeneous Catalyst in Oxidation of Aqueous Sodium Sulfide Solutions with Hydrogen Peroxide, *J. Chem. Technol. Biotechnol.*, **70**(3): 231-240 (1997).
- [30] Sharma A., Srivastava K., Devra V., Rani A., Modification in Properties of Fly Ash Through Mechanical and Chemical Activation, *Ameri. Chem. Sci. J.*, **2**(4):177-187 (2012).
- [31] Patil G.A., Anandhan S., Ball Milling of Class-F Indian Fly ash Obtained from a Thermal Power Station, *Int. J. Energy Eng.*, **2**: 57-62 (2012).
- [32] Shringi N., Srivastava K., Rani A., Microwave Assisted Acid Activation of Fly Ash: A Green Process for Enhancing its Physico-Chemical Attributes for Esterification under Dielectric Heating, *Chem. Sci. Rev. Lett.*, **4**: 561-570 (2015).
- [33] Styszko-Grochowiak K., Gołaś J., Jankowski H., Koziński S., Characterization of the Coal Fly Ash for the Purpose of Improvement of Industrial on-Line Measurement of Unburned Carbon Content, *Fuel*, **83**(13): 1847-1853 (2004).
- [34] Jain D., Khatri C., Rani A., Fly Ash Supported Calcium Oxide as Recyclable Solid Base Catalyst for Knoevenagel Condensation Reaction, *Fuel Proces. Technol.*, **91**(9): 1015-1021 (2010).
- [35] Jain D., Khatri C., Rani A., Synthesis and characterization of Novel Solid Base Catalyst from Fly Ash, *Fuel*, **90**: 2083–2088 (2011).
- [36] Khatri C., Jain D., Rani A., Fly Ash-Supported Cerium Triflate as an Active Recyclable Solid Acid Catalyst for Friedel–Crafts Acylation Reaction, *Fuel*, **89**(12): 3853-3859 (2010).
- [37] Rani A., Rajoriya P., Supported Imidazolium Based Ionic Liquid as a Green, Highly Effective and Reusable Catalyst for Microwave Assisted Knoevenagel Condensation, *Chem. Sci. Rev. Lett.*, **6**(22): 772-778 (2017).
- [38] Rani A., Khatri C., Hada R., Fly Ash Supported Scandium Triflate as an Active Recyclable Solid Acid Catalyst for Friedel–Crafts Acylation Reaction, *Fuel process. Technol.*, **116**: 366-373 (2013).
- [39] Khatri C., Rani A., Synthesis of a Nano-Crystalline Solid Acid Catalyst from Fly Ash and Its Catalytic Performance, *Fuel*, **87**(13-14): 2886-2892 (2008).
- [40] Styszko K., Szczurowski J., Czuma N., Makowska D., Kistler M., Adsorptive Removal of Pharmaceuticals and Personal Care Products From Aqueous Solutions by Chemically Treated Fly Ash, *Int. J. Environ. Sci. Technol.*, **15**(3): 493-506 (2018).
- [41] Agarwal S., Rani, A., Adsorption of Resorcinol from Aqueous Solution onto CTAB/NaOH/flyash Composites: Equilibrium, Kinetics and Thermodynamics, *J. Environ. Chem. Eng.* **5**(1): 526-538 (2017).
- [42] Agarwal S., Rajoria P., Rani A., Adsorption of Tannic Acid from Aqueous Solution onto Chitosan/NaOH/fly Ash Composites: Equilibrium, Kinetics, Thermodynamics and Modeling, *J. Environ. Chem. Eng.*, **6**: 1486–1499 (2018).
- [43] Marjanović N., Komljenović M., Bašćarević Z., Nikolić V., Improving Reactivity of Fly Ash and Properties of Ensuing Geopolymers Through Mechanical Activation, *Constr. Build. Mater.*, **57**: 151-162. (2014).
- [44] Buckingham J., Macdonald F., “Dictionary of Organic Compounds” [M], 6th ed., Chapman & Hall, London, 1998.
- [45] Sahoo S., Kumar P., Lefebvre F., Halligudi S.B., Oxidative Kinetic Resolution of Alcohols Using Chiral Mn–Salen Complex Immobilized onto Ionic Liquid Modified Silica, *Appl. Catal. A: Gen.*, **354**(1): 17-25 (2009).
- [46] Yuan C., Huang Z., Chen J., Basic Ionic Liquid Supported on Mesoporous SBA-15: an Efficient Heterogeneous Catalyst for Epoxidation of Olefins with H<sub>2</sub>O<sub>2</sub> as Oxidant, *Catal. Commun.*, **24**: 56–60 (2012).