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Metal-free catalytic systems based on imidazolium chloride and strong bases for selective oxidative esterification of furfural to methyl furoate

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ABSTRACT

Homogeneous and heterogeneous catalytic systems based on 1-benzyl-3-methylimidazolium chloride (BzmimCl) assisted by strong bases (Cs_2CO_3 or 1, 8-diazabicyclo [5.4.0] under-7-ene (DBU)) were applied in the oxidative esterification of furfural, to obtain 2-methyl-furoate (MF). The reaction was carried out in one step, using oxygen as a unique source of oxidation and methanol as an esterification reagent. Commercial BzmimCl was used as a homogeneous ionic catalyst whereas the heterogeneous ionic one (HCP-BzmimCl) was prepared through a Friedel-Crafts reaction between biphenyl and BzmimCl.

The catalytic systems here reported yield MF with a selectivity > 92% and furfural conversions > 82% after 24 h. The homogeneous catalyst systems have better catalytic activity than the similar ionic liquid systems assisted by bases published so far. Besides, HCP-BzmimCl is the first heterogeneous metal-free catalyst containing imidazole chloride groups for this reaction. HCP-BzmimCl can be recycled up to 5 times using both bases, obtaining quantitatively methyl furoate.

1. Introduction

2-Methyl furoate (MF) is a biobased molecule, largely applicable in fine chemicals and its use ranges from being an explosion-proof additive in gasoline to an antitumor drug [1]. Thus, MF can be used for example in the synthesis of renewable hydrophilic polyesters, fuels or fuels additives, as an intermediate for the synthesis of compounds with medical applications such as N-hydroxy-2-furamide or as well as adjusting the activity thresholds of aroma components in cigarette smoke and grape wine [2–5]. In addition to its natural abundance in certain plants such as peanuts, cocoa and coffee, MF can be synthesized from furfural, which is a very interesting renewable raw material as it is derived mainly from lignocellulosic biomass. Moreover, furfural is a versatile platform compound for the synthesis of other chemicals, biofuels and additives [3, 6–8].

There have been many reports on the synthesis of MF from furfural via oxidative esterification with methanol. In most of these studies, mono- or bimetallic catalysts containing elements such as Au, Pd, Zr and Ce have been used. For instance, in the presence of oxygen, catalysts such as Au/ZrO_2[9–12], Au/CeO_2,[13] Au/TiO_2,[9,11,14–16], Au-MgO [17], $Au-K_2CO_3$ [18], Au/CMK-3 [19], AuPd/HAP-T[20] have been used to obtain MF in high yield. Except for some example that catalyzes the reaction at room temperature, such as Au/TiO_2 assisted by $NaOCH_3$ [14], these processes rely completely on expensive chemical catalysts (precious metals) and high temperatures (100–120 °C),

In 2013, Chiarotto et al. reported the oxidative esterification of furfural to obtain 2-ethyl furoate (EF) in moderated yield (25%) using an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) as precatalyst in the presence of a mixture of 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU) and cesium carbonate (Cs_2CO_3) and using MnO_2 as an oxidizing agent, Fig. 1. The reaction was maintained at room temperature for 24 h [21]. In the same year, Kiran et al. reported a metal-free catalyst based on an ionic liquid (1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride) and the same strong base, DBU (Fig. 1) using oxygen as a source of oxidation. The MF yield, in this case, was 63% and 24 h of reaction was also necessary [22].

Recently, Song et. al proposed a two-step process which involves the use of the same ionic liquid in the first step and enzymes in the second to obtain MF in higher yield (80.6%) at 50 °C after 24 h of reaction (Fig. 1) [23].

The possibility of having a supported ionic liquid is extremely interesting to have a heterogeneous catalyst that is reusable. Thus, for example, polymers containing imidazolium salts have received wide attention as they have potential applications in the fields of catalysis

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[24]. Among the different types of polymers, hypercrosslinked polymers (HCPs) can be facilely synthesized by Friedel–Crafts alkylation from a broad range of easily available monomers. Moreover, some HCPs incorporating IL-like ionic modules into their structure have been proven be excellent catalysts in the conversion of CO_2 into cyclic carbonates [25,26]. However, as far as we know, these types of networks have not been explored as heterogeneous catalysts in the oxidative esterification of furfural.

Thus, in this work, we reported the use of 1-benzyl-3-methyl imidazolium chloride (BzmimCl) as homogeneous ionic liquid catalyst assisted by strong bases (Cs_2CO_3 or DBU) to produce 2-methyl furoate from furfural in higher yield that the imidazolium-based catalytic systems previously reported for this reaction (Fig. 1). Besides, the heterogenization of BzmimCl to obtain the corresponding hyper-cross-linked ionic polymer (HCP-BzmimCl) (Fig. 1) is also reported. HCP-BzmimCl was also used as catalyst, assisted by the same bases in this reaction, obtaining excellent yield and possibility of recycling. Thus, the first example of an imidazolium chloride -based heterogeneous catalyst is reported for this reaction.

2. Methods

2.1. Materials

All reagents and solvents from commercial sources were used as received. Solvents were purchased from JT Baker.

Oxygen (99.9% of purity) was supplied by air liquide; Furfural (F, 99.0%), Cesium carbonate (Cs_2CO_3, 99.5%), Biphenyl (99.0%) and anhydrous dichloromethane (DCM, 99.8%) were purchased from Across Organics; 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98.0%) was supplied by Sigma-Aldrich; anhydrous Aluminum chloride ($AlCl_3$, 99.9%), 1-Butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) (98%) was purchased from Across Organics. 1-Benzyl-3-methylimidazolium chloride (BzmimCl, 97.0%) was supplied by Alfa Aesar.

2.2. Synthesis of HCP-BzmimCl

Biphenyl (0.37 mmol) and BzmimCl (1.50 mmol) were dissolved in DCM (25 mL), and N_2 was bubbled for 20 min under stirring. Then, $AlCl_3$ (14.06 mmol) was added and the mixture was stirred at 50 °C for 48 h. The solid was isolated by filtration, washed with HCl 0.005 M, washed with water and then purified by Soxhlet extraction with methanol. The brown solid obtained was dried in a vacuum oven at 100 °C for 12 h.

2.3. Catalytic activity

2.3.1. General procedure using Cs_2CO_3 as base

Furfural (1.0 mmol), ionic-based catalyst (1.0 mmol), Cs_2CO_3 (0.5 mmol) and MeOH (2 mL) were placed into a glass reactor. The reactor was sealed, evacuated, backfilled with O_2 three times, charged with 5.0 bar of O_2, and heated at 50 °C. After 24 h, the reactor was cooled to room temperature, depressurized and opened. CH_2Cl_2 (10 mL) was added and the resulting mixture was subsequently washed with water (2 ×10 mL) and saturated NaCl aqueous solution (1 ×10 mL). The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to obtain MF as a yellow oil.

2.3.2. General procedure using DBU as base

Furfural (1.0 mmol), ionic-based catalyst (0.4 mmol), DBU (1.2 mmol) and MeOH (2 mL) were placed into a glass reactor. The reactor was sealed, evacuated, backfilled with O_2 three times and finally charged with 5.0 bar of O_2 and heated at 60 °C. After 4 h, the reactor was cooled to room temperature, depressurized and opened. CH_2Cl_2 (10 mL) was added and the resulting mixture was treated as in the previous case, obtaining MF as a yellow oil. All catalytic experiments were followed by ^{1}H NMR.

The conversion of furfural and selectivity of 2-methyl-Furoate was determined by ^{1}H NMR. The spectrum of furfural (Fig. S1) shows a characteristic peak at 9.55 ppm (d) attributed to the proton of the aldehyde group whose integral is 1. The integration of this signal in the corresponding runs, allows calculating that is being transformed (conversion). The ^{1}H NMR of 2-methyl -furoate (MF) (Fig. S1) shows as more characteristic peak a singlet at 3.88 ppm attributed at the methyl group of the ester group (h), integrating by three protons. The rest of the signals (e, f and g) correspond to the protons of the furan ring and are

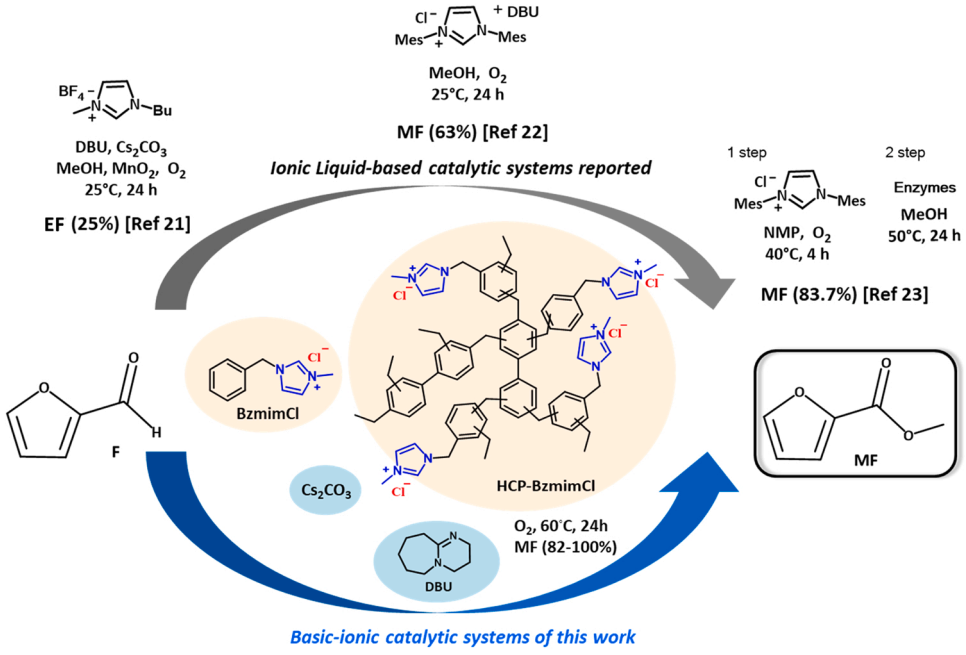


Fig. 1. (up) Ionic Liquid based systems reported for the oxidative esterification of furfural to obtain 2-Ethy-Furoate (EF) or 2-Methyl Furoate (MF) and (down) basic-ionic liquid catalytic systems used in this work.

similar in displacement, and show the same integrations as the signals of furfural (a, b and c).

2.3.3. Recycling experiments

After each reaction is complete, the polymer HCP-BzmimCl was separated from the reaction media by filtration. In the case of using Cs_2CO_3 as a base, the catalyst was washed with CH_2Cl_2 and dried in an oven at 100 °C for 12 h. When DBU was used as a base, the catalyst was washed with diluted HCl, water, and methanol and dried in an oven at 100 °C for 12 h. After that, it was used in a fresh reaction.

2.4. Measurements

FTIR were recorded at room temperature in a Perkin-Elmer RX1 spectrometer operating with Fourier transforms in terms of absorption (cm^{-1}).

Microanalysis was made with a Carlo Erba EA1108 elemental analyzer (C, H, N).

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker AVANCE 300 spectrometer at r.t.

Scanning electron microscopy (SEM) analysis was performed on a Hitachi SU-8000 microscope operating at 0.5 kV.

The solid-state ^{13}C NMR spectrum was taken in a Bruker AV-400-WB using a 4 mm triple channel probe with ZrO rotors and Ke1-F plug a room temperature and at 100.32 MHz.

The thermal stability was evaluated by thermogravimetric analysis using a TQ-500 apparatus from TA Instruments. The experiments were carried out under an oxidizing atmosphere at the heating rate of 10 °C min^{-1} to a final temperature of 800 °C.

3. Results and discussion

3.1. Synthesis and characterization of HCP-BzmimCl

The hypercrosslinked ionic polymer, HCP-BzmimCl was obtained in a single synthetic step (Fig. 2) through a Friedel-Crafts reaction following the procedure previously reported for polyphenylene networks [27]. Recently a similar strategy has been employed for the synthesis of an ionic liquid-based hypercrosslinked network using 1-benzyl-3-ethylimidazolium bromide as an ionic liquid monomer [25]. Thus, 1-benzyl-3-methylimidazolium chloride (BzmimCl) and biphenyl were used as monomers, $AlCl_3$ as catalyst and dichloromethane as solvent and linker between the monomers. Since the reactivity of biphenyl is greater than that of most monomers with which it has been copolymerized [28–30], to have enough imidazolium centers, the reaction was carried out with a small amount of biphenyl. The elemental analysis (Table S1) showed a ratio BzmimCl /biphenyl = 2. Due to the difficulty to completely burn the crosslinked polymeric networks, the percentages of C, H and N obtained are lower than the theoretical ones, but the C/H and N/H ratios are maintained.

The ^{13}C NMR (Fig. 3) showed the characteristic broad signals

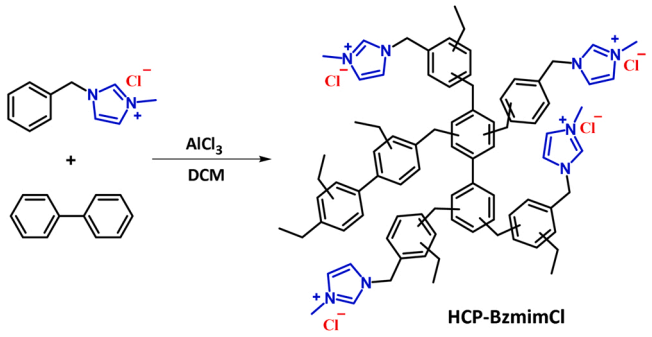


Fig. 2. Synthesis of HCP-BzmimCl.

attributed to the aromatic protons of the polymeric network between 110 and 150 pm and the characteristic signals of the methylene and methyl groups of the imidazolium moieties at 50 and 35 ppm respectively which were not observed in the ^{13}C NMR of the polymeric network containing only biphenyl units previously reported by us [28].

The FTIR spectrum (Fig. 4a) confirmed also the incorporation of the imidazolium moieties into the network due to the appearance of two characteristic bands of the imidazolium ring at 1559 and 1155 cm^{-1} [31] which were also observed in the spectrum of the commercial BzmimCl monomer (Fig. 4a).

The thermogravimetric analysis (Fig. 4**b**) indicated excellent thermal stability with an initial degradation temperature close to 300 °C. The polymer showed a decomposition pattern in two steps, the first one (around 17% of weight loss) could be attributed to the loss of the chlorine anions and methyl groups of the imidazolium units and the second one to the generalized degradation of the network. The absence of residue confirmed that the polymer purification removed the excess aluminum trichloride used during the synthesis.

The wax diffractogram indicated that the synthesized polymer is amorphous, which is attributed to the absence of regularly stacked structures along the polymer network (Fig. S2).

SEM images showed that HCP-BzmimCl is composed of irregular particles on the micrometre scale (Fig. 5).

3.2. Catalytic activity

3.2.1. BzmimCl or HCP-BzmimCl catalytic systems assisted by Cs_2CO_3

Taking into account the conditions reported [21] our first attempt to obtain the target compound involved the use of MnO_2 and O_2 as oxidizing agents and Cs_2CO_3 as a base and 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) as catalyst (Table 1, entry 1). When the reaction was carried out at 80 °C, no product was formed. This fact is most likely due to the fact that this temperature exceeds the melting point of BzmimCl (70 °C). However, when lowering the temperature to 60 °C, a 71% yield of MF was achieved in 4 h (entry 2), and increasing the amount of ionic catalyst (entry 3) a higher yield (93%) was obtained. By using 1-benzyl-3-methylimidazolium chloride (BzmimCl) in the same conditions (entry 4), the target compound was also obtained. When the reaction was done in absence of MnO_2, increasing the amount of this IL, base and the reaction time (entry 5), the reaction also took place, although a decrease in the yield of MF was observed. This result pointed out that the reaction can take place using only O_2 as the oxidizing agent. Thus, some experiments free of MnO_2 were carried out to optimize the reaction, obtaining 82% of MF (entry 6) using half amount of Cs_2CO_3 that IL. Thus, in these conditions and using only O_2 as an oxidizing agent, it was possible to obtain MF in a higher yield than the ionic liquids catalysts previously reported [21,22]. Moreover, the reaction was scaled to 12 mmol of FA (entry 7) obtaining also a high yield of the target compound.

The catalytic activity of the hypercrosslinked ionic polymer, HCP-BzmimCl was studied in the same conditions of entry 6 that is using O_2 as the only oxidizing agent and half the amount of Cs_2CO_3 that polymeric catalyst, getting 50% yield of MF in 24 h (Fig. S3, entry 8). Increasing the amount of base until equal to the amount of catalyst (1:1) it was possible to obtain MF also in excellent yield (Fig. S4, entry 10). This result could be attributed to the less accessibility of the base to the imidazolium groups of HCP-BzmimCl compared with the BzmimCl molecule. In fact, some accessibility difficulties to imidazolium chloride groups in polymer networks have been previously reported [32–34].

In the absence of base (entry 11), the furfural was converted into 2-(dimethoxymethyl) furfural in 67% of yield. Fig. S5 shows the ^1H NMR spectrum of this reaction where the signal at 3.35 ppm shows the formation of the mentioned acetal.

When the reaction was carried out using only Cs_2CO_3 (entry 12) no reaction took place since the ^1H NMR spectrum (Fig. S6) showed furfural as main product. Some impurities were observed which did not

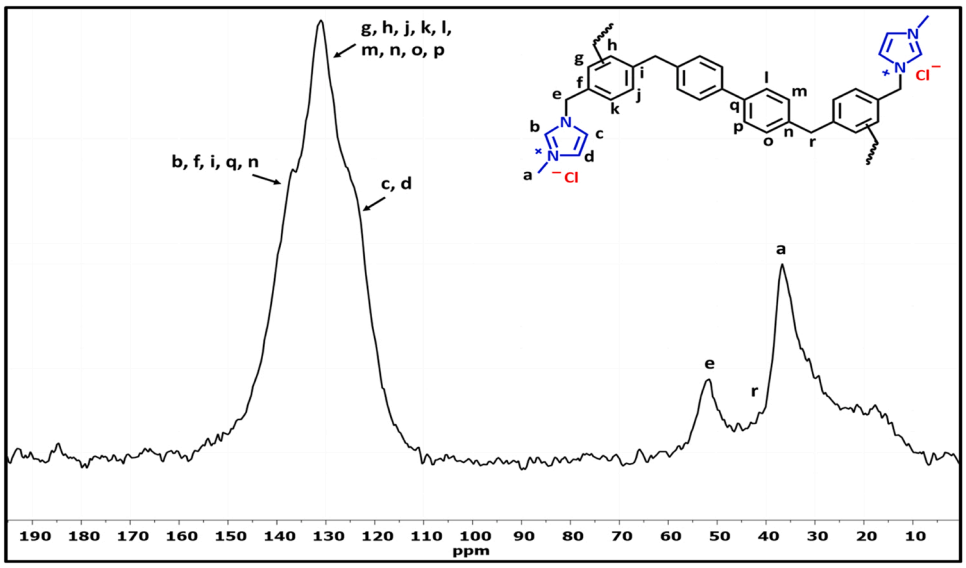


Fig. 3. ^{13}C NMR spectrum of HCP-BzmimCl.

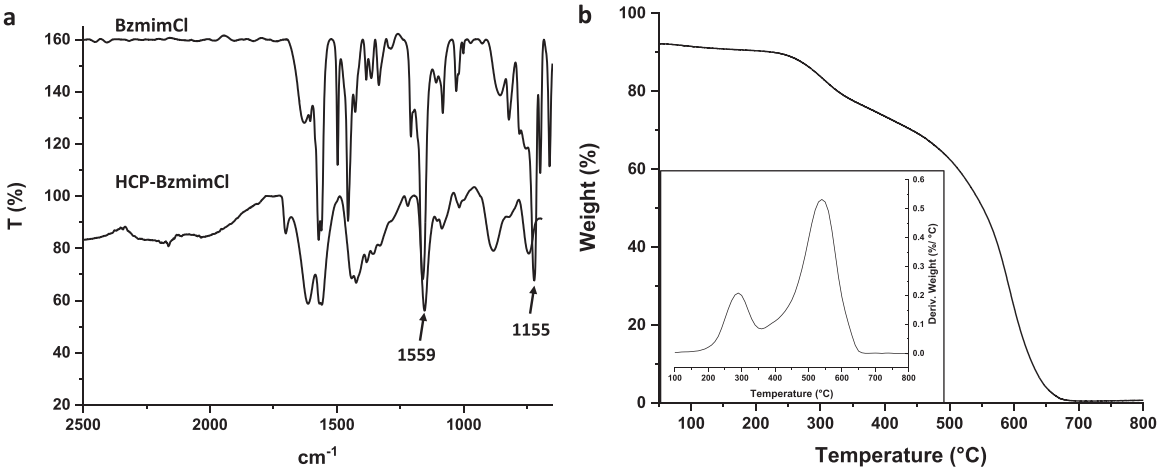


Fig. 4. a) FT-IR spectra of BzmimCl and HCP-BzmimCl. **b)** Thermogravimetric analysis (TGA-DTGA) of HCP-BzmimCl.

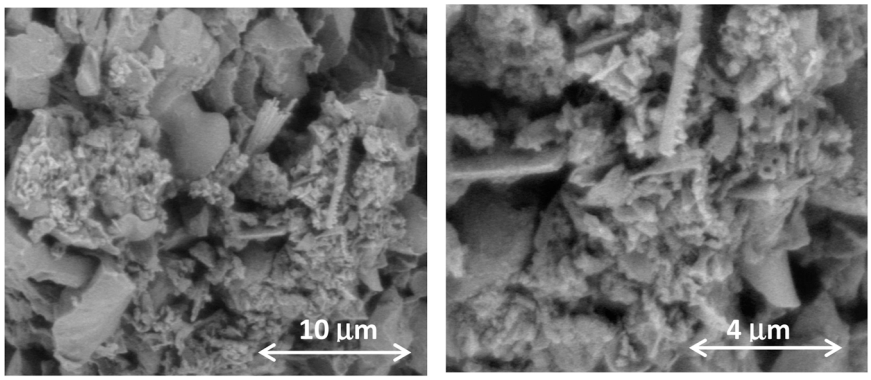


Fig. 5. SEM images of HCP-BzmimCl.

correspond to possible intermediates as furfuryl alcohol or furoic acid. Thus, the results in absence of imidazole chloride-based catalysts or Cs_2CO_3 (entries 11 and 12) demonstrate the synergic effect between the two components to obtain the target compound.

To prove the O_2 activation in this reaction, a control experiment was run in absence of this oxidant (Entry 13). The ^1H NMR spectrum (Fig. S7) confirmed the role of oxygen in the reaction since no oxidized species was detected obtaining only the starting furfural.

An important aspect concerning the heterogeneous catalytic system is the possibility of being recycled. Thus, after the first run using the

Table 1
Study of oxidative esterification of furfural to obtain MF using BzmimCl/Cs_2CO_3 or HCP BzmimCl/Cs_2CO_3 as catalytic systems.[a].

Entry	MnO_2 (mmol)	Ionic Catatyst (IC) (mmol)	Cs_2CO_3 (mmol)	T (°C)	Time (h)	F Conv. (%)	MF Yield (%)	MF (select.)
1	0.25	$BmimBF_4$ (0.20)	0.25	80	4	-	-	-
2	0.25	$BmimBF_4$ (0.20)	0.25	60	4	71	71	100
3	0.25	$BmimBF_4$ (0.40)	0.25	60	4	93	93	100
4	0.25	BzmimCl (0.40)	0.25	60	4	85	85	100
5	-	BzmimCl (0.80)	0.50	60	24	68	68	100
6	-	**BzmimCl (1.00)**	**0.50**	**60**	**24**	**82**	**82**	**100**
7[b]	-	BzmimCl (12.0)	6.00	60	24	90	90	100
8	-	HCP-BzmimCl (1.0)	0.50	60	24	50	50	100
9	-	HCP-BzmimCl (1.0)	0.75	60	24	76	76	100
10	-	**HCP-BzmimCl (1.0)**	**1.00**	**60**	**24**	**94**	**94**	**100**
11	-	HCP-BzmimCl (1.0)	none	60	24	67	0	0
12	-	-	1.00	60	24	2	-	-
13[c]	-	HCP-BzmimCl (1.0)	1.00	60	24	0	-	-

[a] Conditions: $P(O_2)$ = 5 bar, MeOH = 2 mL, F (Furfural) = 1 mmol, [b] Furfural= 12 mmol, [c] $P(N_2)$= 2 bar.

conditions of entry 10, the catalyst HCP-BzmimCl was separated by simple filtration, washed with methanol and dichloromethane, and finally dried in a vacuum oven at 100 °C for 12 h. The polymer was then reused with a fresh reaction mixture, repeating the process to four more runs. The results showed good recyclability (Fig. 6), even increasing the yield of the reaction in some cases.

Recovered catalyst was analyzed by FTIR (Fig. S8) and thermogravimetric analysis (Fig. S9) observing differences between the materials before and after recycling although did not affect the catalytic activity.

3.2.2. *HCP-BzmimCl or BzmimCl catalytic systems assisted by DBU*

In order to explore an entirely organic catalytic system, the strong organic base DBU was used as an alternative to the Cs_2CO_3, optimizing the reaction conditions with the hypercrosslinked ionic polymer (HCP-BzmimCl) due to the possibility of recycling that it offers.

The use of the same ratio HCP-BzmimCl: base of the above study and the same reaction time, 24 h, MF was obtained with moderate yield (Table 2, entry 1) but increasing the amount of this base led to the formation of MF with high yield and selectivity (entry 2). However, an attempt to reduce the amount of catalyst maintaining the amount of DBU caused the formation of a small amount of a secondary product, furan-2-carboxylic anhydride (FCA) (entry 3). The formation of this by-product was attributed to an excess base. In fact, when the amount of DBU increases a lot, this undesired FCA was obtained as the main product in 60% of the yield (entry 4). However, diminishing the reaction time to 4 h (entry 5), less amount of FCA was obtained (15%). Fig. S10 shows the ^{1}H NMR spectrum of this reaction in which can be observed the new signals at 6.70, 7.49 and 8.15 ppm attributed to the by-product.

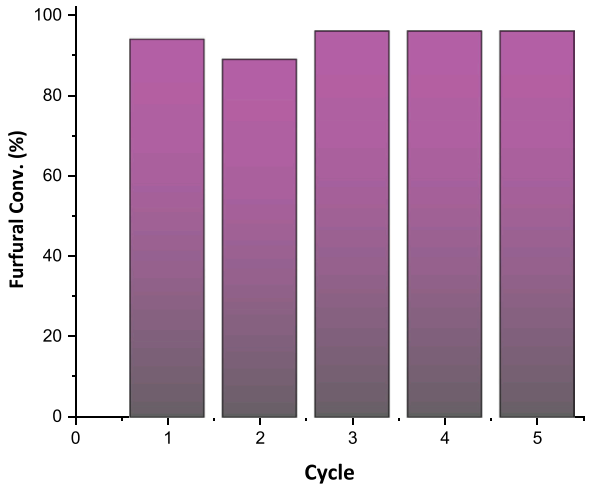


Fig. 6. Recycling experiments using the HCP-BzmimCl (1.0 mmol) and Cs_2CO_3 (1.0 mmol) as catalytic system.

The chromatogram of this reaction (Fig. S11) shows the peaks of the three compounds detected, furfural (F), 2-methyl furoate (MF) and furan-2-carboxylic anhydride (FCA).

As the best result was obtained using 1.2 mmol of DBU per mmol of HCP-BzmimCl (entry 2), the reaction was scaled using these conditions (entry 6), obtaining also excellent yield and selectivity towards the target compound.

Finally, BzmimCl was used as a homogeneous ionic catalyst assisted by DBU in the conditions of entry 5, observing worse catalytic performance than the heterogeneous catalyst since the target compound was obtained with a lower yield. By using more amount of the ionic catalyst and a longer reaction time, the MF was obtained with 81% of selectivity observing the formation of 19% of FCA (entry 8). Only, by using half amount of base that ionic catalyst, as happened when Cs_2CO_3 was used as a base, a good selectivity towards the MF was obtained with complete furfural conversion (entry 9).

By using of DBU as unique component of the catalytic system (entry 10) no traces of 2-methyl furoate was observed. The ^{1}H NMR spectrum (Fig. S12) showed signals of furfural and furan-2-carboxylic anhydride (FCA). This result confirms again the synergic effect between the two components to obtain the target compound MF.

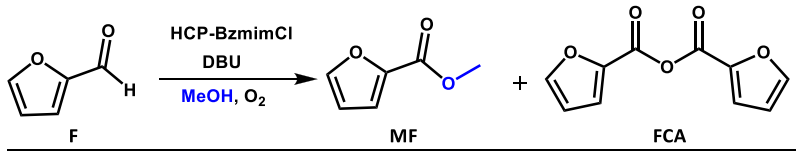
Just as in the previous catalytic system, the recyclability of the polymer HCP-BzmimCl was studied in conditions of run 2 (Fig. 7). After the first run, HCP-BzmimCl was used in a fresh reaction observing a decrease in the catalytic activity. For these reason, the catalyst was treated with diluted HCl observing the recovering of the activity. We attributed this result to a partial deactivation of the network during the reaction. Thus, a regeneration of the catalyst after each run was required by treatment of the recovered catalyst with diluted HCl. From the third run, a small amount of FCA was observed which indicated worse recyclability when DBU was used as a base.

The recycling of the heterogeneous catalyst was studied also using an excess of base (conditions of run 5) observing similar results that the first run. MF was obtained in yields up to 85% in 4 h of reaction with similar ratios between the target compound (MF)and the secondary product (FCA) (Fig. 8).

The reaction mechanism for oxidative esterification of furfural to obtain MF in the presence of strong bases and using O_2 as an oxidant was proposed in Fig. 9, based on other previously reported oxidation mechanisms [35–38]. First, a carbene intermediate can be formed from BzmimCl in the presence of the base (2). Then, this carbene species reacts with furfural to form a highly reactive intermediate (3) which reacts with O_2 to form the peroxy anion (4) which upon decomposition results in the formation of the acyl intermediate (5). Finally, the alkoxide ion formed from the alcohol reacts with (5) to give MF with the liberation of the carbene (2).

The formation of carbene species on the HCP-BzmimCl catalyst is more hindered, probably being the cause of the need to add more base to activate this catalyst and also that the conversion of furfural was slightly

Table 2
Study of oxidative esterification of furfural (F) to obtain 2-methyl furoate (MF) using DBU/HCP-BzmimCl or BzmimCl as catalytic systems.[a].



Entry	Ionic catalyst (mmol)	DBU (mmol)	Time (h)	F Conv. (%)	Selectivity MF (%)	FCA (%)
1	HCP-BzmimCl (1.0)	0.5	24	50	100	-
2	**HCP-BzmimCl (1.0)**	**1.2**	**24**	**98**	**100**	**-**
3	HCP-BzmimCl (0.8)	1.2	24	95	94	6
4	HCP-BzmimCl (0.5)	1.2	24	100	40	60
5	HCP-BzmimCl (O.5)	1.2	4	100	85	15
6[b]	HCP-BzmimCl (6)	7.2	24	95	100	0
7	BzmimCl (0.5)	1.2	4	87	64	36
8	BzmimCl (1.0)	1.2	24	92	81	19
9	**BzmimCl (1.0)**	**0.5**	**24**	**100**	**92**	**8**
10	-	1.2	24	18	-	18

[a] Conditions: $P(O_2) = 5$ bar, MeOH = 2 mL, Furfural (F) = 1 mmol, [b] Furfural (F) 12 mmol.

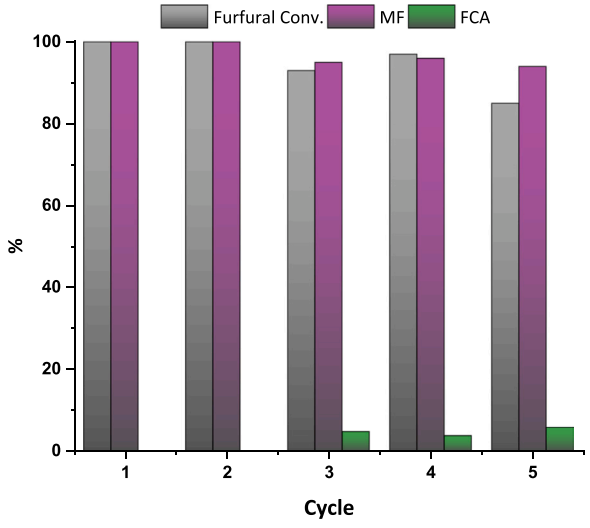


Fig. 7. Recycling experiments of HCP-BzmimCl in the oxidative esterification of F using the HCP-BzmimCl (1.0 mmol) and DBU (1.2 mmol) as catalytic system.

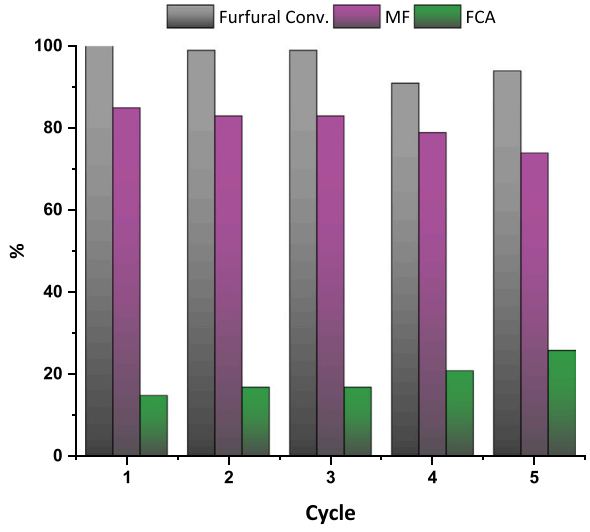


Fig. 8. Recycling experiments in the oxidative esterification of F using of HCP-BzmimCl (0.5) mmol) and excess of DBU (1.2 mmol).

lower than with the soluble catalyst, BzmimCl.

To give a perspective of the catalytic performance of the systems reported here, a comparative study has been carried out with most of the metal catalysts mentioned in the introduction that also use oxygen as an oxidation source and selectively produce methyl furoate (Table S2). As can be seen, the catalytic systems based on imidazolium chloride and strong bases reported here are metal-free alternatives to the metal catalysts since they produce MF with high selectivity working at lower temperatures than most of metal catalysts. Comparing with the imidazolium based catalysts previously reported (Table S2), the catalytic systems here reported have much better catalytic activity.

4. Conclusions

The development of efficient and eco-friendly catalytic systems is an important goal to advance in sustainable chemical production from biomass resources. In this work, we have studied the oxidative esterification of furfural to obtain 2-methyl-furoate (MF) using four sustainable catalytic systems based on imidazolium chloride and strong bases. The ionic components were 1-benzyl-3-methylimidazolium chloride (BzmimCl) or a hypercrosslinked ionic polymer prepared from it (HCP-

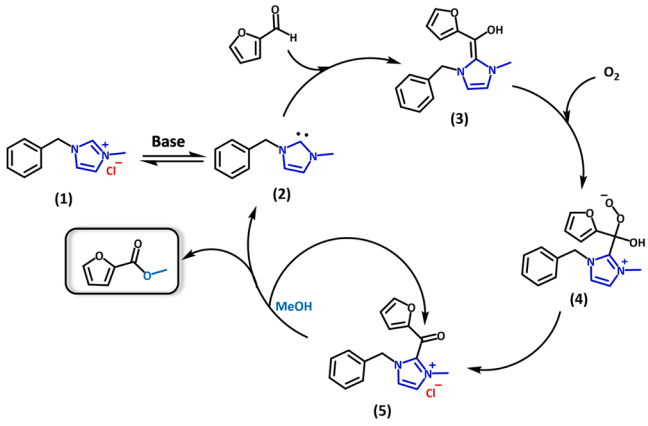


Fig. 9. Proposed reaction pathway for the oxidative esterification of FA using the basic-ionic catalytic systems.

BzmimCl) and the bases were Cs_2CO_3 or 1, 8-diazabicyclo [5.4.0] under-7-ene (DBU). All catalytic systems were used in presence of O_2 as a unique oxidant agent, at 60 °C with reaction times of 24 h. The homogeneous catalytic systems, with half amount of both bases that ionic component (BzmimCl) produced MF with a yield above 92% and furfural conversions between 82% and 100%, improving the catalytic activity of other similar systems previously published. The heterogeneous catalyst (HCP-BzmimCl) needs an equal or more amount of base, yielding MF with 100% of selectivity and almost complete furfural conversion. In addition, the systems were used on a larger scale, maintaining the catalytic performance. HCP-BzmimCl combined with strong bases becomes the first example of an ionic heterogeneous catalyst for this reaction offering high MF yields, although it showed better recyclability when Cs_2CO_3 was used as a base.

CRediT authorship contribution statement

E.M Maya and E.Rangel-Rangel have been the authors who have conceived the original idea of this work, designing all the experiments, catalytic systems and carrying out the writing of the article. B. Fuerte has carried out a large part of the experimental development of this work and M. Iglesias has contributed to the discussion of the catalytic activity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcata.2023.119088.

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