

Efficient DMF-assisted synthesis of formamides from amines using CO₂ catalyzed by heterogeneous metal-free imidazolium-hypercrosslinked polymers

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ABSTRACT

CO₂ emissions are constantly increasing, so it is necessary to continue working to mitigate the excess of CO₂ in the atmosphere and reduce the effects it has on the environment. In this regard, we have developed novel catalysts by synthesizing ionic liquids based on imidazolium chloride, supported on hyper-crosslinked polymers (HCP-BzmimCl and HCP-Bis(BzmimCl)). These catalysts enable the highly selective N-formylation of secondary amines, utilizing CO₂ as a carbon source, phenylsilane as a hydrogen donor, and DMF as a crucial polar additive. The reactions were carried out under mild conditions, with CO₂ pressure at 5 bar and a temperature of 35°C, yielding formamides in excellent yields. HCP-Bis(BzmimCl) has emerged as a particularly promising catalyst, boasting shorter reaction times, exceptional recyclability, and scalability for potential industrial applications.

1. Introduction

The utilization of CO₂ as a raw material for the synthesis of chemicals is an opportunity to convert a harmful gas for the environment into an added-value compound. Formamides can be prepared from CO₂ and are a clear example of very versatile industrial chemicals since they can be used in the synthesis of drug molecules, agrochemicals or nitrogen-based heterocycles [1]. Several noble metals such as Ir, Pt, Pd, Ru or Rh or non-noble metals such as Fe, Ni, Co, Cu, Mb or Zn have been proved to be excellent catalyst in the N-formylation of amines with CO₂ using reducing agents such as H₂, silanes or even boranes [2]. Except a few examples, most of these metallic catalysts need PCO₂ above 10 bars, temperatures above 100°C and long reaction times, between 16 and 24 h to obtain high formamides yields [2–5].

In 2015, Liu et al. reported the use of ionic liquid based on 1-alkyl-3-methylimidazolium salts as excellent catalysts for catalyzing the formylation of amines using 1 atm of CO₂ and phenylsilane at room temperature, producing the corresponding formamides in excellent yields [6]. From this moment, the use of ionic liquid as metal-free catalysts for this conversion has gained great interest since it allows the reaction to be carried out in mild conditions: room temperature and moderated CO₂ pressure (1–10 bar) [7–10]. The possibility of having a supported ionic liquid is a great opportunity since having a heterogeneous catalyst that

can be recyclable would make the N-formylation much more sustainable. Thus, some ionic liquids have been supported in COFs [11,12], MOFs [13,14], ZIFs [15,16] and POPs [17–19] mainly by post-functionalization of the corresponding support with an ionic liquid. Most of these catalysts work at room temperature and low CO₂ pressures (1–5 bar) but they need 24 h to achieve conversions above 85% of the corresponding amines, and showed good recyclability up to 5 times. Although some supported ionic liquid in hypercrosslinked polymers have been employed as heterogeneous catalysts to obtain cyclic carbonates using CO₂ as raw material [20–22], there is only one example of an ionic-liquid-based hypercrosslinked polymer reported to catalyze the synthesis of formamides from CO₂, PIP@QP in Fig. 1a. This catalyst was prepared by post-functionalization of a preformed binaphthol-based porous polymer network through a Williamson ether reaction with quaternary ammonium bromide and it exhibited moderate catalytic performance (58% yield) for the solvent-free N-formylation of N-methylaniline using CO₂, and phenylsilane as reducing agent under 35 °C and 5 bar for 8 h. Increasing the reaction time to 16 h, 99% of the yield was reached [19].

Herein, we report the use of imidazolium chloride-based hypercrosslinked polymers (HCP-BzmimCl and HCP-Bis-BzmimCl, Fig. 1b) prepared in one step, directly from the corresponding ionic-liquid supported monomers, as heterogeneous catalysts in the formylation of

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different amines with CO₂ and phenylsilane to obtain the corresponding formamides in high yield (99%) using stoichiometric amounts of DMF that allow faster formylation reactions (4–16 h).

2. Experimental section

2.1. Materials and methods

1-Benzyl-3-methylimidazolium chloride (BzmimCl, 97.0%) was supplied by Alfa Aesar.

1-Benzylimidazole was purchased by TCI with a purity $\geq 98\%$. Biphenyl was supplied by Fluka with a purity $> 98\%$; AlCl₃ (anhydrous) and CH₂Cl₂ (extra dry) were supplied by Acros Organics with purities $> 98.5\%$ and $> 99.8\%$ respectively. The other reagents and solvents were supplied by Aldrich with analytical grade and were used as received.

3,3'-methylenebis(1-benzyl-1 H-imidazol-3-ium) dichloride (Bis(BzmimCl)) was prepared according with literature [23]. The synthetic procedure and the characterization data are included in the [supplementary information](#).

HCP-BzmimCl was prepared using 1-benzyl-3-methylimidazolium chloride according to the procedure previously reported by us [24] and it is reproduced in the [supporting information](#).

2.2. Measurements

Fourier Transform Infrared Spectra (FTIR) were recorded on a Perkin-Elmer RX-1 instrument.

The solid-state ¹³C NMR spectra were taken in a Bruker AV-400-WB using a 4 mm triple channel probe with ZrO rotors and Kel-F plug at room temperature and 100.32 MHz. The speed of rotation is set at 10 KHz in all cases. ¹³C NMR CP-MAS spectra were recorded using a spectral width of 35 kHz and the chemical shift refers to the CH₂ signal of adamantane (29.5 ppm) as a secondary reference to TMS as the primary reference.

Microanalyses were made with a LECO CHNS-932 elemental analyzer (C, H, N). Residual aluminum contents were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

on a Perkin Elmer OPTIMA 2100 DV. Specific surface area measurements and porosity analysis were performed using N₂ adsorption isotherms on a Micromeritics, ASAP 2020 MICROPOROUS DRY Analyzer (P/P₀ 0.01–1.0) using the BET theory, BJH and DFT methods. Before, the samples were degassed at 110 °C for 12 h. Thermogravimetric analysis (TGA) data were obtained on a TGA-DSC1600 Setsys Evolution under an air atmosphere, using approximately 5 mg of the sample under a flow of 50 mL/min. The samples were heated from 50 to 850 °C at 5 °C/min. Scanning electron microscopy (SEM) micrographs were obtained with a Hitachi SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface. Transmission electron microscopy (TEM) micrographs were recorded with a JEM2100F electron microscope (JEOL Ltd., Tokyo, Japan) operating at 200 keV. High-resolution isotherms of CO₂ were obtained at a series of temperatures in a Micromeritics ASAP 2010 volumetric instrument, using ~150 mg of powder sample. The sample was placed in a sample holder that was immersed into a liquid recirculating thermostatic bath (Julabo FP40-HL) able to control the adsorption temperature from 273 to 333 K. Before adsorption experiments, samples were outgassed at 423 K for 6 h under turbo-molecular high vacuum. The adsorption heat was estimated using the Clausius-Clapeyron equation from the CO₂ isotherms obtained at different temperatures.

X-ray Photoelectron Spectroscopy (XPS) data were obtained with a SPECS GmbH system equipped with a hemispherical energy analyzer PHOIBOS 150 9MCD. A non-monochromatic Mg X-ray source was used with a power of 200 W and voltage of 12 kV. Samples were placed first in the pre-chamber at room temperature and degassed for several hours before being transferred to the analysis chamber. Pass energies of 50 and 20 eV were used for acquiring both survey and high resolution spectra, respectively.

2.3. Synthesis of HCP-Bis(BzmimCl)

Biphenyl (57 mg, 0.37 mmol) and Bis(BzmimCl) (599 mg, 1.50 mmol) were dissolved in CH₂Cl₂ (25 mL), and N₂ was bubbled for 20 min under stirring. Then, AlCl₃ (14.06 mmol) was added and the mixture was stirred at 50 °C for 48 h. The solid was isolated by filtration,

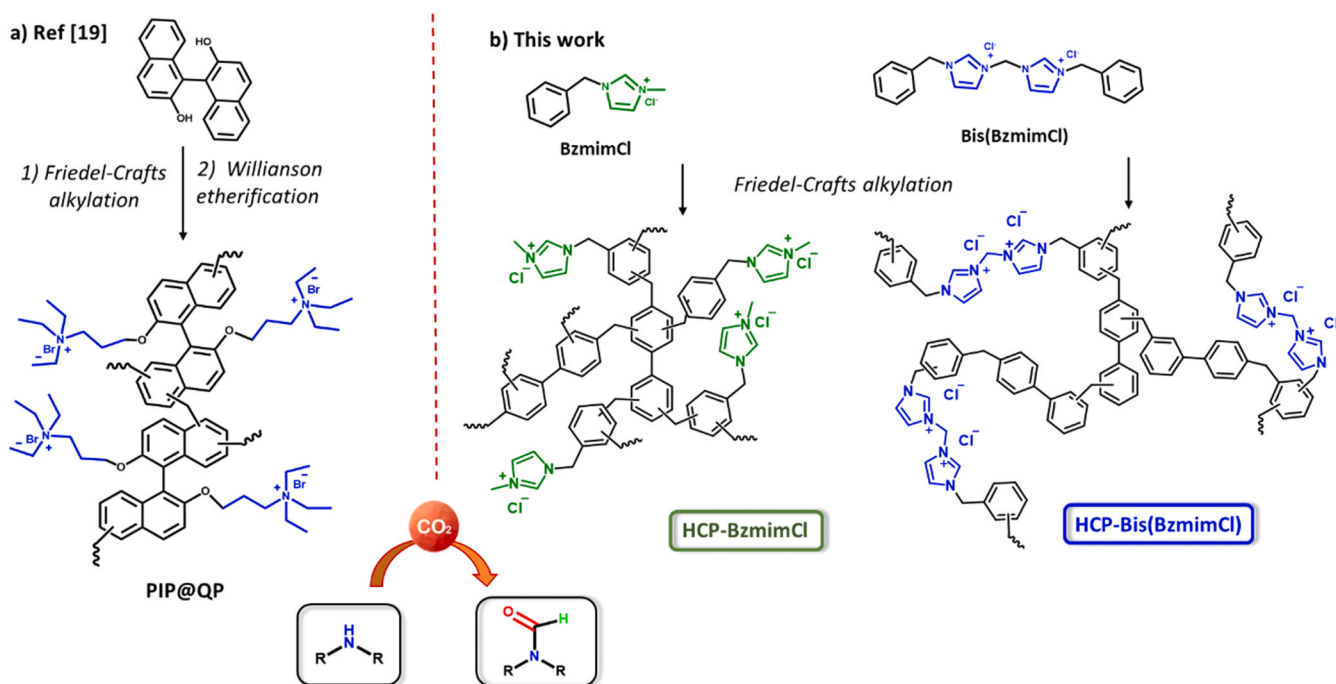


Fig. 1. Synthesis of ionic-liquid-based hypercrosslinked polymers used as catalysts in the synthesis of formamides from CO₂.

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.

2.4. Catalytic performance

In a glass reactor, the corresponding amine substrate (0.1 mmol), the phenylsilane (1 mmol), dimethylformamide (2 mmol) and the catalyst (10% molar N) are added. The suspension is charged with CO₂ (5 bar) and heated at 35 °C with magnetic stirring the time indicated in Tables 1 and 2. The reactor was cooled to room temperature, depressurized and opened. The catalyst was separated from the reaction by filtration and washing with CH₂Cl₂. 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 MgSO₄, and the solvent was removed under reduced pressure. The reactions were monitored by ¹H NMR. Each spectrum is compared with the spectrum of the starting amine. The amine conversion is determined by the integration of a characteristic signal which does not appear between the signal of the protons of the formamide. This signal is noted in each example of the supporting information. If no sign of the precursor amine is observed, a 100% conversion is attributed.

The selectivity of the formamide is estimated by integrating the signal of the methyl group of the corresponding methylamine (2b) if had been formed, a secondary product of this reaction.

2.4.1. Recycling experiment

After the reaction was complete, the polymer was separated from the reaction by filtration, washed with CH₂Cl₂ and methanol and dried in an

oven at 100 °C for 12 h. Then it was used in a fresh run.

3. Results and discussion

3.1. Synthesis and characterization of HCP-Bis(BzmimCl)

The synthesis of the novel hypercrosslinked polymer, HCP-Bis(BzmimCl) is depicted in Fig. 1. It was obtained following the same procedure previously reported by us for the synthesis of HCP-BzmimCl [24] which involves a Friedel-Crafts reaction between Bis(BzmimCl) and biphenyl using AlCl₃ as catalyst and dichloromethane as solvent and linker between the monomers. Due to the high reactivity of biphenyl in Friedel-Craft couplings, to ensure enough imidazolium centres, the reaction was carried out with using an excess of Bis(BzmimCl) monomer respect to biphenyl, as in the synthesis of HCP-BzmimCl and other hypercrosslinked networks which biphenyl has been copolymerized [25–27]. The bis(imidazolium chloride) based monomer, Bis(BzmimCl), was prepared according to the literature from 1-benzylimidazole [23]. The monomer was obtained with good yield and the characterization data (Analysis Elemental (Table S1), ¹H NMR (Fig. S1) and ¹³C NMR (Fig. S2) and FTIR (Fig. 2a) were consistent with published data for this monomer [23].

The elemental analysis (Table S2) showed a ratio between benzene and imidazolium rings of 2, as showed the HCP-BzmimCl [24] which indicates that both networks had the same imidazolium centres content. Due to the difficulty of completely burn the crosslinked polymeric networks, the percentages of C were lower than the theoretical ones.

The FTIR spectroscopy (Fig. 2a) showed the two characteristics bands of the imidazolium ring at 1550 cm⁻¹ and 1150 cm⁻¹ [28] as it

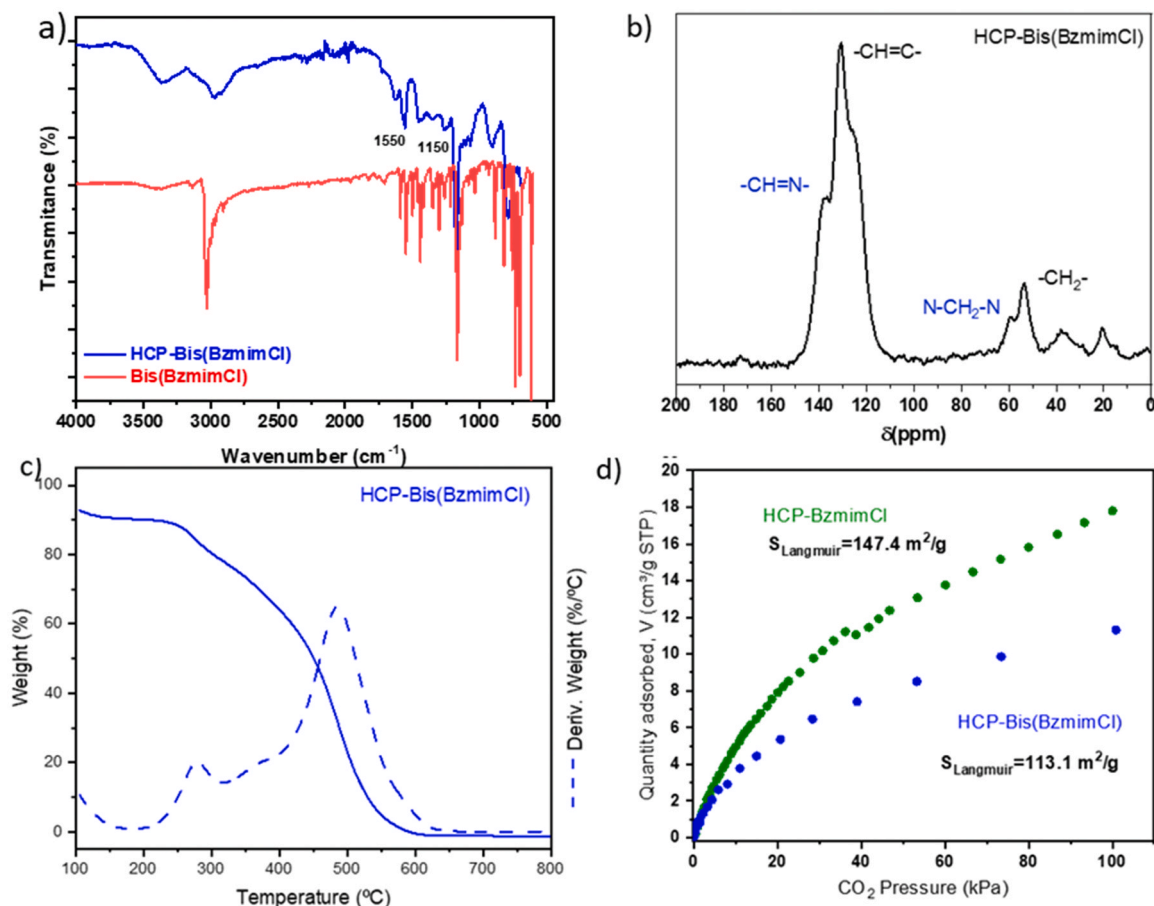


Fig. 2. a) FT-IR spectra of Bis(BzmimCl) monomer and HCP-Bis(BzmimCl); b) ¹³C NMR spectrum of HCP-Bis(BzmimCl); c) TGA (DGTA) of HCP-Bis(BzmimCl); d) CO₂ uptake isotherms of HCP-BzmimCl and HCP-Bis(BzmimCl).

was also observed in the IR spectrum of the precursor monomer Bis (BzmimCl) or in the IR spectrum of HCP-BzmimCl [24]. The ¹³C NMR spectrum (Fig. 2b) showed an intense and broad signal between 110 and 130 ppm attributed to the aromatic carbons of the benzene rings. This signal is accompanied by a shoulder around 140 ppm that was attributed to the aromatic carbons of the benzimidazolium rings. The characteristic signals of the methylene groups appeared between 35 and 50 ppm whereas the signal at 60 ppm was attributed to the methyl groups between the imidazolium moieties.

The thermogravimetric analysis (Fig. 2c) showed good thermal stability with a degradation pattern in two steps. The first one has an initial degradation temperature of 250 °C and a weight loss of 12% which was attributed to the loss of the chlorine anions of the imidazolium units. The second step has a degradation temperature of 500 °C ascribed to the generalized degradation of the network. The absence of residue confirmed the full elimination of aluminum trichloride used during the synthesis of the polymer.

The XPS survey spectra of both catalysts confirmed the presence of C, N and Cl elements in both structures (Figs. S3 and S4). The Cl1s spectra of both catalysts exhibited a predominant peak at 285 eV attributed to the C-C bonds. Besides, the spectra of HCP-BzmimCl show a second peak at slightly high energy at 287.2 due to de energy binding of C-N bonds. The appearance of an intense peak at 402 eV in the N1s spectra confirmed the presence of quaternary nitrogen (N⁺) [29,30]. The characteristic Cl 2p_{3/2} peak is found at 197 eV and as it was expected it appears accompanied by a second peak at 199 eV due to the spin-orbit coupling [31]. The spectrum of HCP-Bis(BzmimCl) shows an additional peak at 200 eV characteristic of covalent chlorine species [32] that could be attributed to dichloromethane trapped within the network.

The porosity was investigated by N₂ adsorption/desorption isotherms (Fig. S5). The specific surface areas of both polymers (HCP-BzmimCl and HCP-Bis(BzmimCl)), were low (4.5 m²/g and 16.9 m²/g) which indicated low porosity for both catalysts. The pore size distribution pointed out an average pore diameter of 7 and 8 nm respectively (Fig. S6).

The SEM images (Fig. S7) showed that HCP-Bis (BzmimCl) is formed by aggregates of irregular particles on the micrometer scale, similar to what was observed in the SEM images of HCP-BzmimCl [24]. In the TEM images of both catalysts (Fig. S8), a lot of disorder can be observed and in some, a certain microporosity is detected, also in a disordered way.

The CO₂ isotherms recorded for HCP-BzmimCl and HCP-Bis (BzmimCl) (Fig. 2d) indicated moderated CO₂ uptake, 0.795 mmol/g

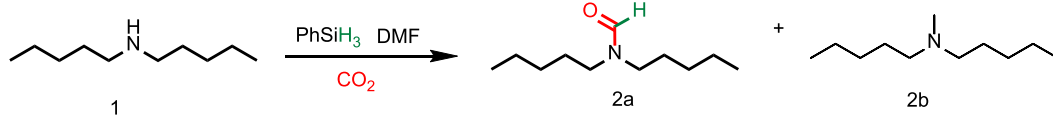
(3.49%) and 0.506 mmol/g (2.26%) respectively and therefore moderate Langmuir surface areas, 147 and 131 m²/g respectively. These values were lower than those reported for another imidazolium-based hypercrosslinked polymers [33–38] and can be attributed to the absence of porosity in both structures. The higher values in HCP-BzmimCl with respect to HCP-Bis(BzmimCl) could indicate that the first structure is more open and the accessibility of CO₂ to the imidazolium rings in the structure is more favoured.

3.2. Catalytic activity

For the synthesis of formamides, optimization was first performed using dipentylamine as a model substrate and 10% of HCP-BzmimCl as a catalyst (based on N content) with respect to the amine (Table 1). Initially, a study was carried out with different pressures, temperatures and times. Starting at 5 bar of CO₂ pressure, room temperature and using phenylsilane as a reducing agent, a 60% amine conversion was obtained in 24 h of reaction (Table 1, entry 1) and increasing the temperature to 35 °C, the complete conversion was achieved (entry 2). By decreasing the pressure (entry 3) or increasing the temperature and therefore reducing the reaction time, (entry 4) complete conversion was not achieved in no case, so a temperature of 35 °C, 5 bar of CO₂ and 24 h of reaction were established as the best initial conditions to carry out this reaction. Control experiments in the presence of different reducing agents such as Ph(CH₃)₂SiH, Ph₂SiH₂ or NaBH₄ (entries 5–7) yielded less amount of formamide which indicated the need for the phenylsilane to achieve good conversions in this reaction.

In order to shorten the reaction time, a strong polar additive DMF was added to the reaction. It was reported that 2 equivalents of DMF promoted the N-formylation of amines in excellent yields and selectivity at room temperature playing an important role in the activation of the amines and PhSiH₃ favoring also the insertion of CO₂ [39]. Thus, in the presence of 2 equivalents of DMF (entry 8) the time of reaction was shortened to four hours obtaining excellent conversion and selectivity towards the formamide (Fig. S9). As DMF has moderate toxicity, the amount of DMF was reduced to 1 mmol. However, the conversion of the amine was low (entry 9). The use of 1.5 mmol of DMF also did not lead to high amine conversion (entry 10). Thus, 2 mmol of DMF was established as the optimal amount to carry out this reaction. A control experiment in the absence of the catalyst and using only DMF was carried out (entry 11) leading to only 20% of the product confirming the necessity of both components in the reaction mixture. Moreover, in

Table 1
Optimization of reaction conditions N-formylation of dipentylamine using HCP-BzmimCl as catalyst.^a



	Reducing agent	DMF	T (°C)	P (bar)	t (h)	Conv (%)	Sel. (%)
1	PhSiH ₃	-	r.t	5	24	60	98
2	PhSiH ₃	-	35	5	24	100	99
3	PhSiH ₃	-	35	1	24	25	99
4	PhSiH ₃	-	90	5	4	50	99
5	Ph(CH ₃) ₂ SiH	-	35	5	24	4	99
6	(Ph) ₂ SiH ₂	-	35	5	24	10	98
7	NaBH ₄	-	35	5	24	50	98
8	PhSiH ₃	2 mmol	35	5	4	100	99
9	PhSiH ₃	1 mmol	35	5	4	25	99
10	PhSiH ₃	1.5 mmol	35	5	4	60	99
11 ^b	PhSiH ₃	2 mmol	35	5	4	20	99
12	PhSiH ₃	-	35	5	4	20	98

^a Reaction conditions: amine (1 mmol), reducing agent (1 mmol), catalyst (10% molar based on N content).

^b without catalyst.

absence of DMF gives low conversion confirming also the positive effect of DMF (entry 12).

The use of the second catalyst under the most favourable conditions (Table 2, entry 1) yield also the expected formamide in 4 h with excellent conversion and selectivity. The reaction was extended to the synthesis of other formamides using both imidazolium chloride- catalysts (Table 2).

By using an aliphatic-aromatic amine such as N-methylphenylamine (entries 4 and 5), more reaction time (10 h) was required with both catalysts, although the times used for other catalysts based on liquid ions for this same substrate are higher (16–24 h) [11,12,17–19]. These results were attributed to the higher steric hindrance of this amine compared with the dipentylamine. When cyclic amines such piperidine or morpholine were used (entries 6–9), the reaction times ranged from 9 to 16 h. Again, HCP-Bis(BzmimCl) was more effective, obtaining the corresponding formamides in less time, 14 and 9 h, respectively. These results could be attributed to the pKa of the two amines: 9.73 for piperidine and 8.36 for morpholine. Thus, the lower pKa of morpholine could facilitate the removal of the proton and therefore the reaction complete in less time.

Finally, the use of bis(1-phenylethyl)amine (entries 10 and 11) yielded the desired formamide with both catalysts although the amine conversion reached only 60% and 65%, respectively. This result was attributed to the high steric hindrance of this diamine which makes difficult the deprotonation as well as the insertion of CO₂ molecule. Selected ¹H NMR of these experiments are recorded in Figs. S10-S13.

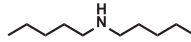
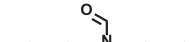
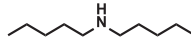
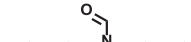
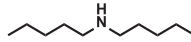
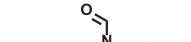












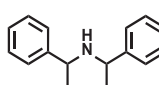
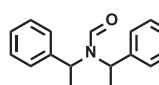
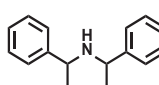
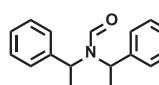
To further evaluate the practicability of HCP-Bis(BzmimCl), the reaction was scale-up by using dipentylamine as substrate in higher amounts (10 times more). The corresponding formamide was quantitatively after 6 h (Table 2, entry 2). This result showed the potential industrial application of the developed catalytic system.

Once the generality of both catalysts was demonstrated in the N-formylation reaction, their heterogeneity was evaluated using dipentylamine as substrate. The recyclability of HCP-BzmimCl was limited to five cycles, observing a progressive decrease in the conversion of the diamine, although the selectivity towards the formation of the corresponding formamide was maintained (Fig. 3a). However, HCP-Bis(BzmimCl) showed excellent recyclability maintaining the amine conversion and formamide selectivity at least 10 cycles (Fig. 3b). The better recyclability of HCP-Bis(BzmimCl) relative to HCP-BzmimCl can be attributed to higher stability of the imidazolium chloride groups within the HCP-Bis(BzmimCl) network, while the imidazolium chloride groups in HCP-BzmimCl are terminal groups of the network and are more exposed.

We could attribute this fact to the starting monomer, Bis(BzmimCl) which maintains two imidazolium chloride groups linked to each other providing higher structural stability of these groups while the monomer BzmimCl disperses the imidazolium chloride groups in the network. Besides, a partial blocking of the micropores in this catalyst could be contributing to the lack of recyclability of this catalyst. The FTIR spectra and TGA after the corresponding reuses (Figs. S14 and S15) showed some structural changes in the recycled HCP-BzmimCl. The characteristic bands of the imidazolium ring at 1550 and 1150 cm⁻¹ are maintained in the spectrum of HCP-Bis(BzmimCl), while in the case of HCP-BzmimCl, these bands have shifted and split. The TGA of the recycled HCP-BzmimCl showed also lower thermal stability than HCP-Bis(BzmimCl) and some amount of solvent trapped within the network after the recycling experiments.

To confirm the heterogeneity of HCP-Bis(BzmimCl), a hot filtration experiment was also carried out removing the catalyst after three hours of reaction. At this time the conversion of dipentylamine was 51% and as shown in Fig. S16 it does not increase significantly after 5 h which

Table 2
N-formylation of amines with CO₂ using and imidazolium based hypercrosslinked polymers as catalysts^a.

Entry	Amine	Catalyst	Product	t (h)	Conv. (%)	Sel. (%)
1		HCP-Bis(BzmimCl)		4	100	99
2 ^b		HCP-Bis(BzmimCl) ^b		6	100	99
3		HCP-BzmimCl		5	100	99
4		HCP-Bis(BzmimCl)		10	95	98
5		HCP-BzmimCl		10	90	98
6		HCP-Bis(BzmimCl)		14	98	98
7		HCP-BzmimCl		16	98	96
8		HCP-Bis(BzmimCl)		9	98	94
9		HCP-BzmimCl		10	98	98
10		HCP-Bis(BzmimCl)		24	65	92
11		HCP-BzmimCl		24	60	90

^a Amine (1 mmol), PhSiH₃ (1 mmol), DMF (2 mmol), Catalyst (10 mol% based on N content), P(CO₂) = 5 bar, T = 35°C;

^b 10 mmol of amine

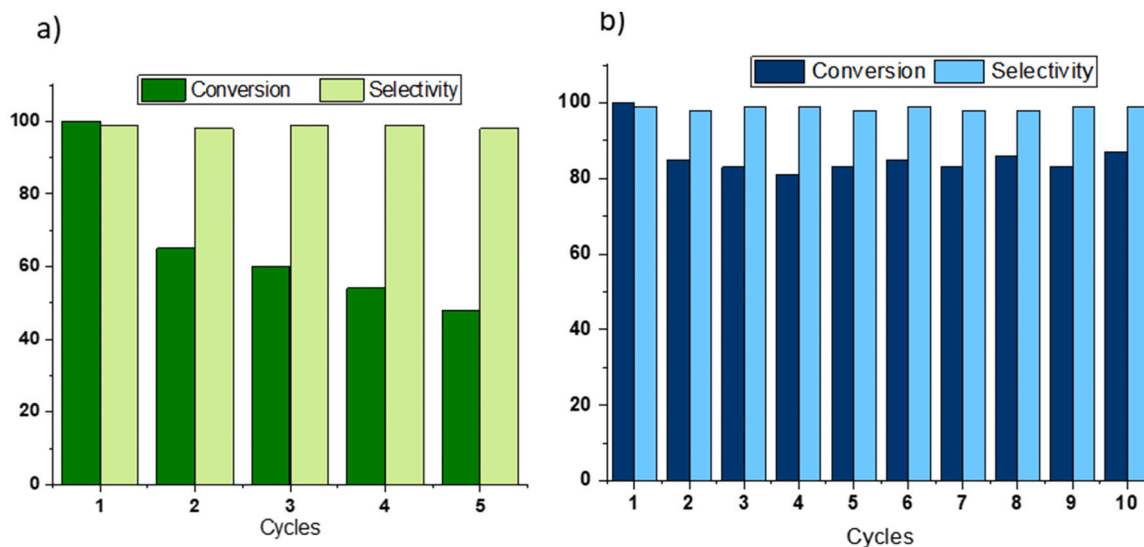


Fig. 3. Recyclability of a) HCP-BzmimCl and b) HCP-Bis(BzmimCl) in the DMF-assisted synthesis of N,N-dipentylformamide from dipentylamine and CO₂.

confirms that there is no release of catalytic species to the reaction medium.

3.3. Proposed mechanism

The proposed reported mechanisms for the reaction of amines with CO₂ using PhSiH₃ as reducing agent are shown in Scheme S2 [17,40].

The *route 1* is a direct reaction between the amine and PhSiH₃, generating H₂ and a silylamine, which can react with CO₂ to give silylcarbamate. In *route 2* the catalyst interacts with PhSiH₃ to form an active intermediate, which promotes CO₂ hydrosilylation leading to a silyl formate. Then the formamide was formed by the formylation of the amine with the formate. Finally, the route 3 yield the methylated products. This route involves the hydrosilylation of silyl formates to

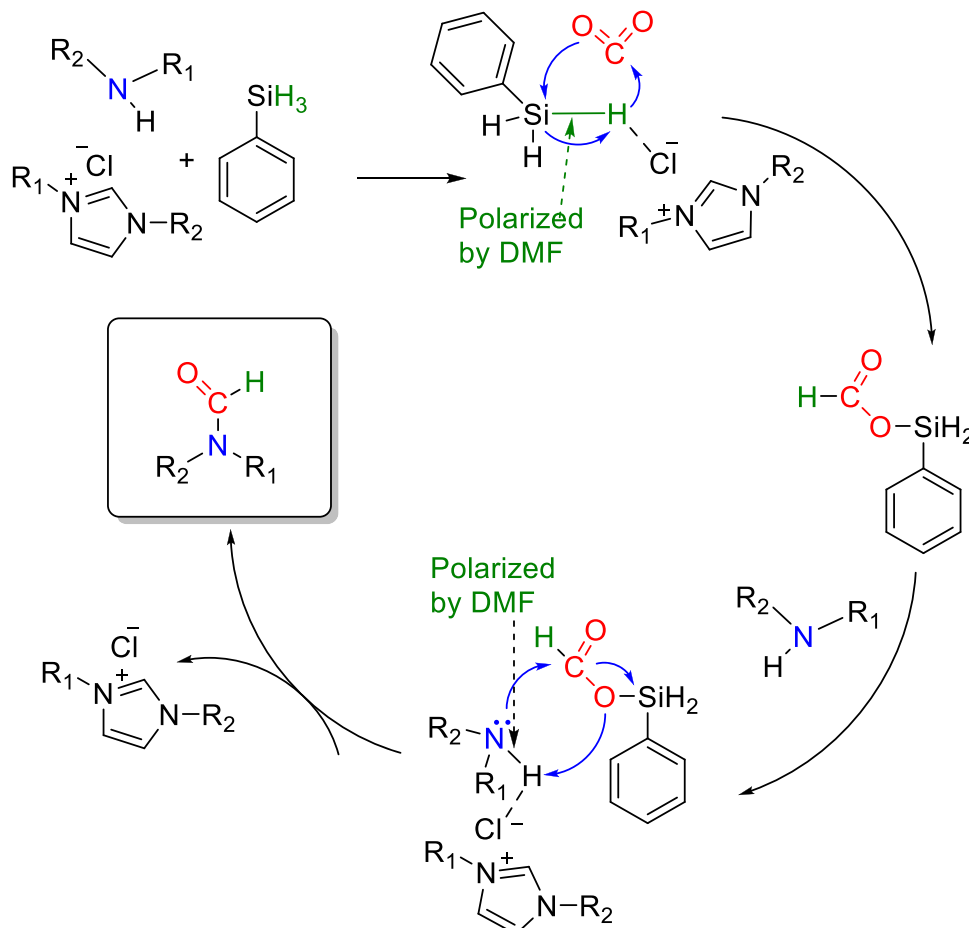


Fig. 4. Proposed reaction mechanism for the N-formylation of amines with CO₂ and PhSiH₃ assisted by DMF.

form silyl acetals follow by intermolecular hydrosilylation to form silylmethoxide species, and finally methylation of amines with silylmethoxide to yield the methylated products.

According to the results obtained in our experiments, *route 3* was the first to be ruled out because we did not detect N-methyldipentylamine in any of our experiments. Despite this, we did a control experiment adding an excess of PhSiH₃ to force the formation of the tertiary amine. The ¹H NMR spectrum (Fig. S17) shows a small signal characteristic of the methyl of the corresponding amine, therefore, even if phenylsilane is added in excess, the reaction is selective towards the corresponding formamide.

To check if the mechanism develops through *route 1*, an experiment reacting PhSiH₃ with dipentylamine in absence of CO₂ was carried out to force the formation of the silyl formate intermediate. As it can be observed ¹H NMR spectrum (Fig. S18) a mixture of the two reagents without signals from the N,N-dipentyl-1-phenylsilanamine was obtained, therefore this route was also discarded.

Thus, based on the results obtained, the above control experiments and in combination with previous reported work [17,40], the proposed reaction mechanism for the N-formylation-of-amine with CO₂ and PhSiH₃ over the imidazolium-based catalysts were deduced as described in Fig. 4. The Si-H bond in PhSiH₃ was first activated by Cl⁻ of the catalyst and tuned by DMF which polarizes the Si-H bond. The enriched CO₂ molecule was then inserted into the activated Si-H bond, affording a highly active pivotal silyl formate intermediate. Meanwhile, the coordination occurred between the Cl⁻ of HCP and the H atom of the secondary amino group, which is also polarised by the DMF, through intermolecular hydrogen bonding to form an activated substrate containing a nucleophilic nitrogen atom. Subsequently, a new C-N bond formed through a nucleophilic attack of nitrogen atom on the electron-deficient carbon atom of silyl formate intermediate, thus producing the final targeted formamide.

3.4. Catalytic performance

To establish the catalytic performance of the HCP-Bis(BzmimCl), a comparison has been carried out with the metal-free ionic liquid-based heterogeneous catalysts found in the literature that have been used in this reaction. Specifically, the comparison has been made using N-methyl aniline as a common substrate to all the reported works. As can be observed in Table 3, all of the reported catalysts need 16–24 h to achieve a high conversion of the amine into the corresponding formamide which is also necessary in most of the cases, a solvent to carry out the reaction. However, by using HCP-Bis(BzmimCl) as a catalyst in a solvent-free reaction assisted by DMF, a very high yield of the

corresponding formamide was achieved in 10 h. Besides, the recyclability of our catalyst was also higher than those reported. Thus, in terms of time and recyclability, our catalyst presents better catalytic performance than the mentioned reference catalysts.

4. Conclusions

Imidazolium chloride-based hypercrosslinked polymers (HCP-BzmimCl and HCP-Bis(BzmimCl)) directly prepared from imidazolium chloride-based monomers, are excellent catalyst candidates to obtain formamides from amines and CO₂ using PhSiH₃ as reducing agent and DMF as a key polar additive which activates the N-H and Si-H bonds in reaction times shorter than the published conversions for this reaction using other ionic-liquid-based heterogeneous catalysts. The reactions take place in the absence of solvent, at moderate pressures of CO₂ (5 bar) and mild temperatures (35°C). Despite HCP-Bis(BzmimCl) showing less CO₂ capture capacity than HCP-BzmimCl, it has positioned itself as one of the most efficient metal-free catalysts, in terms of reaction time and recyclability because the reaction occurs between 4 and 16 h, depending of the amine used, and the catalyst can be recycled up to 10 times. We attributed this excellent result to the fact that the imidazolium rings are very stabilized within this network, which affords a highly recyclable catalyst. However, in HCP-BzmimCl, although the imidazolium rings are more accessible to interact with CO₂, yielding higher CO₂ uptake capacity, at the same time more exposure increases its lability and therefore decreases the stability of this catalyst.

Author statement

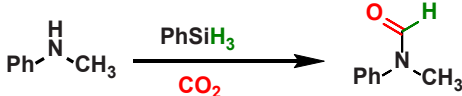
B. Fuerte has carried out the experimental work; **E. Rangel Rangel** has contributed to the experimental work; **M. Iglesias** has participated in the corrections and validation of the experimental work and **E.M. Maya** is responsible of the work (conceptualization, funding acquisition, supervision and writing-original draft).

CRediT authorship contribution statement

Maya Eva M: Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition, Conceptualization. **Fuerte-Diez Beatriz:** Methodology, Investigation. **Rangel Elizabeth:** Investigation. **Iglesias Marta:** Writing – review & editing, Validation, Supervision.

Table 3

Metal-free ionic liquid based heterogeneous catalysts in the formylation of N-methylaniline with CO₂.^a



Catalyst	Mol (%)	Ph ₃ SiH (mmol)	Solvent	T (°)	P (CO ₂) (bar)	t (h)	Yield (%)	Catalyst Recyclability	Ref
[Et ₄ NBr] _{50%} -Py-COF	5	2	DMF, 1 mL	30	1	24	94	4 cycles	[11]
[BE]X%-TD-COF	3.4	2	CH ₃ CN, 2 mL	30	5	24	99	4 cycles	[12]
FIP-Im@QA	6	1	none	35	10	24	99	6 cycles	[17]
IPOP-3	10	4	1 mL, CH ₃ CN	r.t	AFG ^b	24	71	5 cycles ^c	[18]
PIP@QA	5	1	none	35	5	8 (16)	58 (99)	6 cycles	[19]
HCP-Bis(Bzmim)Cl	10	1 ^d	none	35	5	10	95	10 cycles ^e	This work

^a N-methylaniline (1 mmol),

^b AFG: CO₂ in anaerobic fermentation gas,

^c *p*-methoxyaniline as substrate,

^d with 2 mmol of DMF,

^e dipentylamine as substrate.

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.jcou.2024.102679](https://doi.org/10.1016/j.jcou.2024.102679).

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