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# Imidazolium-based ionic liquid immobilized on functionalized magnetic hydrotalcite ( $Fe_3O_4$ /HT-IM): as an efficient heterogeneous magnetic nanocatalyst for chemical fixation of carbon dioxide under green conditions

Reza Khalifeh,\*a Zeinab Zarei and Maryam Rajabzadeh a

In this context, a reusable, eco-friendly, long-lived and efficient nanocatalyst, imidazolium-based ionic liquid immobilized on functionalized magnetic hydrotalcite (Fe<sub>3</sub>O<sub>4</sub>/HT-IM), IM is known as imidazolium-based melamine, was successfully introduced. The structure of the synthesized nanocatalyst was characterized by several techniques which revealed a platelike shape with average particle size of approximately 50 nm and also the presence of acidic sites (site density: 12 mmol g 1). The catalytic activity of Fe<sub>3</sub>O<sub>4</sub>/HT-IM was explored in chemical fixation reaction of carbon dioxide towards the preparation of cyclic carbonates under optimized reaction conditions at 100 °C, 0.7 MPa and 1.6 mol% of the nanocatalyst. This reaction was conducted without using any metal, additive, toxic reagents and solvent/co-catalyst which provides a mild and green condition from the standpoint of green chemistry. Owing to having acidic-basic sites which can simultaneously accelerate the ring-opening of the epoxy ring and incorporation of CO2, this catalyst is attractive and suitable for this reaction. In particular, the prepared catalyst can be easily separated using external magnetic field and reused over six times without any significant loss in catalytic performance and selectivity. This proves its great potential to be implemented for industrial purposes as a green catalyst.

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# Introduction

During the last two decades of the twentieth century, in order to mitigate the greenhouse effect and environmental global warming, chemical fixation of carbon dioxide, as the earth's most unfavorable industrial abundant carbon resource and its conversion into valuable, useful, inexhaustible and nontoxic chemical molecules, in modern organic chemistry is among the hottest research topics in both industries and universities. It is a controversial challenge which has attracted continuous attentions from three viewpoints of "environmental problems", "sustainable society" and "atom economy", as far as we are aware.<sup>1, 2</sup> Therefore today, efforts to increase fixation or capture of CO<sub>2</sub> are highly desirable as regards the sustainable chemistry and Green Chemistry.<sup>3, 4</sup> In this regard, conversion route through coupling CO<sub>2</sub> with epoxide as the initial material is a recognized environment-friendly route which has high atom economy without any by-products to afford cyclic carbonates. These are extensively adopted as intermediates, electrolytic elements, monomer of polycarbonates, green polar aprotic solvents and so on.5-8 To the best of our knowledge during past decades, numerous researchers have been enthusiastic to perform various procedures like C-C bond formation of CO<sub>2</sub> with various organo

59 60 compounds, N-formylation and N-methylation of amines using CO<sub>2</sub>, nucleophilic reactions of CO<sub>2</sub> with aziridines or propargylic amines that require harsh reaction condition, supercritical conditions and toxic solvent.<sup>9</sup> Also, till now, various methodologies have been reported using a mixture of hydrogen-bond donors, metal catalysts, zeolites, ionic liquids, transition metal complexes, alkaline metal salts, phosphonium salts, metal oxides, bicyclic guanidines, silver complexes, functional polymers, polyoxometalates, metalloporphyrins, metal-organic frameworks (MOFs), nanoparticles and so on for this transformation reaction.<sup>9-15</sup> Although many of these reactions are highly challenging for researchers and suffer from serious desirable tasks such as low rate of catalyst stability/reactivity, air and moisture sensitivity, the need for a co-solvent/additive, or high pressure, temperature or cost, lack of satisfactory yields, and less green synthesis routes, exhaustive separation of products, their recovery and reutilization, low biodegradability, which confine their applications in many cases. Thus, this has spurred a number of researchers to explore the research on the development of an environmentally benign and effective nanocatalyst which resolves these problems and enables operation in mild conditions and simultaneously culminates in easy product separation and operation simplification. In spite of these advances, some problems have yet to be resolved. It is worth nothing that there have been a lot of reports as regards heterogeneous catalysts or nanocatalysts which catalyze this reaction so far.<sup>16-19</sup> Therefore, it is still in its infancy and it is an attractive subject to focus on this transformation reaction using various nanocatalysts.

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59 60 The layered double hydroxide materials (LDH) like hydrotalcite with general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$  which consist of cation ions such as Al<sup>3+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup> and Mg<sup>+2</sup>, etc, water molecules, anions and layer sheets are a versatile support material due to its structure and acido-basic sites and attracted enormous attention in recent years.<sup>20</sup> In the course of our research, it has been interestingly found that hydrotalcite can also play the most important role in the capture CO<sub>2</sub> which can dramatically promote this reaction owing to (Lewis) acid -base sites. It was proposed that Lewis acid sites (Zn<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup>) can chemically activate the alkoxide intermediate, and surprisingly the base sites will take advantage of the subsequent ring-opening of the epoxide by nucleophile.<sup>21, 22</sup>

Based on literature, it is very interesting to note that chemical fixation of CO<sub>2</sub> has high activation barrier due to its high thermodynamic stability and kinetic inertness of CO2 and need a Lewis acid species and a nucleophile.<sup>23</sup> On the other hand, the presence of special five member ring of imidazole, anions and NH<sub>2</sub>/NH groups could be useful for the further ring opening of epoxide substrates using the hydrogen bond on the oxygen atom of the epoxide which will improve catalytic activity and thus accelerate this transformation reaction.<sup>2, 24-26</sup> Ionic liquids (ILs), as a hot emerging research area, with unique charming features and their outstanding physicochemical properties such as low melting temperature, negligible vapor pressure, low toxicity, suitable solubility, high thermal and chemical stability, good ion conductivity as well as catalytic activity and selectivity, etc, and as a new style of green material and one of most valuable key precursor compounds of catalysts have been extensively discussed and provided new opportunities.<sup>26</sup> Producing a considerable amount of waste materials and removing them is one of the major disadvantages of using ILs directly, which makes the process inappropriate from the environmental point of view. Consequently, immobilization of ILs on different solid supports, as one of the innovative and modern strategies, leads to a combination of the benefits of ILs and heterogeneous support nanomaterials thanks to enhancing the contact surface between ILs and compounds, and making a proper heterogeneous framework.27

In continuation of our works on the synthesis and development of magnetic, and eco-friendly nanocatalyst and their application in organic reactions,<sup>28-41</sup> herein, we were willing to extend preparation of an innovative, highly potential, thermostable, facile and sustainable nanocatalyst based on hydrotalcite as the solid support which exhibits attractive merits for chemical fixation of  $CO_2$  with epoxy (as coupling partner) to give resultant five memberedcarbonate under rather straightforward ambient reaction conditions without any need of solvent/cocatalyst. For this goal, in the present work, we initially synthesized magnetic hydrotalcite, and then modified it chemically with melamine (moieties bearing hydrogenbond-donor), and subsequently an ionic liquid structure with imidazole ring was designed (Scheme 1), with two essential goals to create more powerful catalysts: 1) easy and quick separation of nanocatalyst/ or product, 2) excellent ability to capture carbon dioxide, and accelerate the reaction. We were amazed to realize that because of bifunctional property of obtained nanocatalysts a concerted action on both CO2 and substrates can accelerate this reaction, and result in the cyclic carbonates instead of the

polymerization as may be expected. There is no report regarding ionic liquid immobilized on magnetic hydrotal cite and an application in chemical fixation of CO<sub>2</sub>. Finally, we believe that this catalyst may have great potential for other applications in years to come.

# **Results and discussion**

In this project, the Fe<sub>3</sub>O<sub>4</sub>/HT-IM nanocatalyst was initially synthesized through five steps as shown in Scheme 1. In the first step, the HT (I) (molar ratio Mg/AI = 2) was synthesized using the coprecipitation method.<sup>20</sup> Then, the prepared HT (I) was magnetized by iron salt solutions to achieve Fe<sub>3</sub>O<sub>4</sub>/HT (II). In the following step, the 3-Chloropropyltrimethoxysilane linker was chemically grafted on the surface hydroxyl groups of Fe<sub>3</sub>O<sub>4</sub>/HT (II). Afterward, in order to obtain the nanocatalyst with NH groups (the ability for further hydrogen-bonding), melamine was grafted on the surface of the functionalized Fe<sub>3</sub>O<sub>4</sub>/HT (II). In the final stage, the prepared Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV) was designed as an ionic liquid-bearing imidazolium ring incorporating Br<sup>-</sup> anion. Then, the structure and morphology of the obtained solid material nanocatalyst (Fe<sub>3</sub>O<sub>4</sub>/HT-IM) were fully characterized by FT-IR, XRD, TPR-H<sub>2</sub>, zeta potential, TEM, FESEM, EDX, TPD and TGA techniques.



Scheme 1. An overview on the preparation of the  $Fe_3O_4/HT-IM$  nanocatalyst.

The FT-IR spectra of  $Fe_3O_4/HT$  (II),  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Cl (III),  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Cl (III),  $Fe_3O_4/HT$ -IM (V) nanocatalyst were illustrated and compared, respectively (Figure 1). According to the spectra, Figure 1a exhibited many peaks, a broad band at 3450 – 3400 cm<sup>-1</sup> which was due to the bending vibration mode of

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symmetric stretching vibration of Mg-OH and Al-OH which are on the surface of HT (I). In addition, a peak at 1620 cm<sup>-1</sup> is possibly arisen from stretching vibration of coordinated water molecules in the structure of HT (I). Characteristic adsorption bands at 1367 cm<sup>-1</sup> and 672 cm<sup>-1</sup> correspond to the existence of carbonate ions between layers of hydrotalcite and angular bending mode of carbonate species (Figure 1a). In addition, it was pointed out that the stretching vibrations of Fe-O bonds overlapped with those of Al-O and Mg-O bonds. In the spectrum of Figure 1b, the presence of grafted (3chloropropyl)trimethoxysilane linker was confirmed by the appearance of a slight broad band around 3100- 2850 cm<sup>-1</sup> owing to the C-H stretching vibrations whereas somewhat increasing intensity of band around 1111 cm<sup>-1</sup> was assigned to the C-C stretching vibration of (CH<sub>2</sub>) groups. It is noted that the characteristic peak which is correlating with Si-O stretching vibrations cannot be distinguished (in the range of 680-670 cm<sup>-1</sup>) because of the exhibited broad band of the symmetric stretching vibration of M-O bonds. Also, after covalent anchoring of melamine, in the spectrum of Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV) (Figure 1c), a new absorption band was appeared at 1563 cm<sup>-1</sup>, indicative of the NCN bending of the melamine, suggesting the grafted melamine on the surface of the functionalized  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Cl (III). In Figure 1d, the appearance of a characteristic active strong absorption band at 1206  $\mbox{cm}^{\text{-1}}$ (plausibly due to the bending vibration of C-H bonds), presumably indicated the presence of C-H in-plane of imidazole ring, and also a decrease in the peak intensity in the range of 3445-3400 cm<sup>-1</sup> provided an evidence for grafting 1-methyl imidazole. All of obtained results verify that the structure of the (Fe<sub>3</sub>O<sub>4</sub>/HT-IM) (V) nanocatalyst has truly been proposed (Figure 1d), and also agreed well with data obtained in TGA.



Figure 1. FT-IR spectra of (a)  $Fe_3O_4/HT$  (II), (b)  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Cl (III), (c)  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV), and (d)  $Fe_3O_4/HT$ -IM (V).

In order to evaluate the thermal stability of the obtained materials, TGA analysis was performed under the nitrogen atmosphere with heating rate of 10 °C min<sup>-1</sup> between temperature range from 25 to 800 °C for each sample, as shown in Figure 2. The TGA plot of  $Fe_3O_4/HT-(CH_2)_3-Cl$  (III) exhibited three significant weight loss

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patterns. The first step below 100 °C is related to removal of physically adsorbed water in addition to dehydration 30 the surface OH groups (weight loss 1.84 %). The second weight loss 24.56 % which was because of the organic segment, happened in the range of 100 °C to 500 °C. The appearance of the third step up to 500 °C was related to the last stage of the fully thermal decomposition of the structure (weight loss 7.33 % (Figure 2a). The TGA plot of Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV) also showed three remarkable steps. The first step at 25- 140 °C (due to the removal of the adsorbed water, 2.7%), and second step was observed at 140 - 510 °C with 31.09 % weight loss (consisting of two typical steps related to organic units). Thanks to the cross-linked nature of melamine and intermolecular hydrogen bonding of Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV), it exhibited an enhanced thermal. Hence, the TGA curves also proved the successful grafting of melamine. Above this temperature, the final decomposition step happened at about 510 °C (weight loss 11.14% (Figure 2b). Besides, the TGA analysis of the Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst exhibited three significant patterns. The first mass loss occurred at 50 - 160 °C (owing to the removal of the surface adsorbed water). The second step of the mass loss is owing to the grafted ligand which started to decompose from 160 °C to 580 °C. It consisted of two steps because of the presence of two melamine and imidazoline segments (weight loss 37.66%). Lastly, final decomposition of the catalyst occurred between the temperature ranges of 580 - 800 °C (2.39%). These findings demonstrated good thermal stability of Fe<sub>3</sub>O<sub>4</sub>/HT-IM nanocatalyst up to 160 °C.



Figure 2. TGA thermograms of (a)  $Fe_3O_4/HT-(CH_2)_3$ -Cl (III), (b)  $Fe_3O_4/HT-(CH_2)_3$ -Melamine (IV), and (c)  $Fe_3O_4/HT$ -IM (V) nanocatalyst.

To prove surface modification of  $Fe_3O_4/HT$  (II), zeta potential study was conducted as represented in Figure 3. The zeta potential of  $Fe_3O_4/HT$  (II) was considered to be approximately 0.9 mV as the mean value, while the following modification was -12.6 mV in the  $Fe_3O_4/HT$ -IM (V) nanocatalyst. This decline exhibited the successful modification of the surface of  $Fe_3O_4/HT$  (II). It should be emphasized that the huge negative surface charge owing to the repulsive force among particles can indicate the high stability of the  $Fe_3O_4/HT$ -IM (V) nanocatalyst. This

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Figure 3. Zeta potential analysis for (a)  $Fe_3O_4/HT$  (II), and (b)  $Fe_3O_4/HT$ -IM (V) nanocatalyst.

In order to verify the crystalline structures of Fe<sub>3</sub>O<sub>4</sub>/HT (II) and Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst, X-ray diffraction (XRD) analysis was performed (at  $2\Theta = 0 - 90$ ), as shown in Figure 4. As regards Fe<sub>3</sub>O<sub>4</sub>/HT (II) (Figure 4a), many characteristic diffraction peaks were observed at  $2\theta = 11.2^{\circ}$  (003), 22.6° (006), 34.5° (012), 38.0° (018), 60.3° (110), 61.5° (113), all of which were manifestations of the presence of hydrotalcite. Also, the crystalline peaks occurring at  $2\theta$  = 29.8° (220), 35.4° (311), 43.3° (400), 53.8° (422), 57.3° (511), 62.9° (440), 75.5° (622) demonstrated the cubic structure of  $Fe_3O_4$  MNPs (JCPDS: 19-0629). It is interesting that the XRD pattern of  $Fe_3O_4/HT$ -IM (V) (Figure 4b) is similar to its parent material,  $Fe_3O_4/HT(II)$  that has been used as support, showing no change crystallinity took place after the functionalization of the surface of  $Fe_3O_4/HT$  (II). They match well with each other which indicates the high chemical stability of  $Fe_3O_4/HT(II)$ . The basal spacing d(003) (which is the characteristic of hydrotalcite-like materials) of Fe<sub>3</sub>O<sub>4</sub>/HT (II) was 7.51 nm which increased to 7.61 nm probably due to the placement of bromide ions between the layers of the Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst. This proposal was further confirmed with the increased intensity of the (006) reflection peak relative to (003) in the Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst compared to Fe<sub>3</sub>O<sub>4</sub>/HT(II).

To understand the morphology of the as-synthesized solid materials, FESEM spectrum of the Fe<sub>3</sub>O<sub>4</sub>/HT(II) and Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) at different magnifications have been recorded in Figure 5. It is clear that HT has a plate-like shape, as noticed in Fig. 5a and 5b. Furthermore, the presence of Fe, Mg and Al confirmed the successful preparation of Fe<sub>3</sub>O<sub>4</sub>/HT (II) as EDX analysis shown (Figure 5c). Also clearly shown in Figure 5d, the coexistence of Si strongly approved the covalent grafting of 3-choloropropyltrimethoxysilae linker on the surface of Fe<sub>3</sub>O<sub>4</sub>/HT (II), and well proved that no impurity in the structure of the obtained solid materials was shown.



Figure 4. The XRD patterns of (a)  $Fe_3O_4/HT$  (II), and (b)  $Fe_3O_4/HT$ -IM (V).



Figure 5. FESEM images of (a)  $Fe_3O_4/HT$  (II), and (b)  $Fe_3O_4/HT$ -IM (V) at different magnifications and EDX analysis of (c)  $Fe_3O_4/HT$  (II), and (d) $Fe_3O_4/HT$ -IM (V)

To have a more profound understanding of the structural morphology of synthesized  $Fe_3O_4/HT$ -IM (V) nanocatalyst, the transmission electron microscopic image was performed. As can be seen, the figure 6 displayed the typical layered platelet-like morphology, confirming the presence of HT (I) without any agglomeration while  $Fe_3O_4$  NPs are distributed over the surface of it. Also, it was shown that the average particle size was approximately 50 nm.

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Figure 6. TEM image of  $Fe_3O_4/HT$ -IM (V) nanocatlyst.

In order to study type and strength of the total acid sites, TPD experiments were performed. For this purpose, at first, pure helium was purged on 40 mg of each sample at 300 °C for 1h. Following that, after cooling to 110 °C, 5% NH<sub>3</sub>/He was passed at 110°C for at least 30 min, and finally the active sites of samples were completely removed from loosely bound ammonia by dosing He stream for 30 min at 110 °C, and heated again from 110 to 800 °C at a heating rate of 10 °C/min in a flow of He. As shown in Figure 7a, Fe<sub>3</sub>O<sub>4</sub>/HT (II) curve showed three desorption peaks at around 130-239 °C, 300-500 °C and above 500 °C, which resulted from mostly weak Brønsted acid sites on the surface of HT (due to physisorbed and chemisorbed ammonia). The moderate Lewis acid sites on the surface of HT might be related to the Al<sup>3+</sup>-O<sup>2-</sup>-Mg<sup>2+</sup> species present in the structure of the mixed oxides and Al<sup>3+</sup> cations in octahedral sites and stronger Lewis acid sites which appeared at temperature above 500 °C, respectively. Also as could be seen in Figure 7b, Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst exhibited similar TPD profile accompanied with three NH<sub>3</sub> distinct desorption peaks, while there was a further rise in the intensity of the peak above 500 °C owing to the generation of new strong acid sites (N<sup>+</sup> sites of ionic liquid) and hydrogen bonding of the surface with the adsorbed NH<sub>3</sub>, which are responsible for the increase in acidity. It was highlighted that the total acidity of Fe<sub>3</sub>O<sub>4</sub>/HT (II) and Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalysts were 11 mmol/g and 12 mmol/g, respectively (Table 1).



**Figure 7.**  $NH_3$ -TPD profiles of (a)  $Fe_3O_4/HT$  (II), and (b)  $Fe_3O_4/HT$ -IM (V) nanocatalyst.

Table 1	. Total	quantities	of acid si	tes calcula	ted fron	n∕the₄TPD	Online

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profiles.	DOI: 10.1039/D0NJ05225F
Sample	Total acidity (mmol/g)
Fe <sub>3</sub> O <sub>4</sub> /HT (II)	11
Fe₃O₄/HT-IM (V)	12

Temperature programmed reduction (TPR) was carried out in order to study the reducible metal(s) in the  $Fe_3O_4/HT$  (II) and  $Fe_3O_4/HT$ -IM (V) nanocatalyst. At first, in TPR run, Ar insertion process was performed (on 25 mg of each catalyst) at 300 °C for 1h. Subsequently, under the same atmosphere, samples were lowered to room temperature. Lastly, samples were exposed with 5.0% H<sub>2</sub>/Ar mixture while the temperature ramped from ambient (~35 °C) to 900 °C (at a heating rate of 10 °C/min). After the run, the amount of  $H_2$ consumed (TCD signal) in the reduction process was plotted as a function of temperature, and was determined using calculation under the area under each peak (Table 2). As presented in Figure 8, TPR spectrum obtained for  $Fe_3O_4/HT(II)$  and  $Fe_3O_4/HT-IM$  (V) nanocatalyst are rather similar, and can be deconvoluted into four broad distinct reduction peaks at a wide range from 300 to 342 °C, 500 to 700 °C and above from 800 °C in the structure of both samples. According to the previous studies, a peak between 300-342 °C, could well reflect the reduction of Fe<sup>+3</sup> to Fe<sup>+2</sup> species.<sup>42</sup>More specifically, a broad peak reduction of transformations of magnetite to metallic iron Fe<sub>3</sub>O<sub>4</sub> to FeO/ Fe which consisted of two very broad peaks well spitted reduction peaks, appeared between at 500- 700 °C. Also, the peak centered above 800 °C was attributed to the entire reduction of Fe species in center. Based on previous study, no reduction peak was observed related to HT structure.<sup>43</sup> It should be pointed out that the reduction peak of Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst was moved to higher temperatures towards Fe<sub>3</sub>O<sub>4</sub>/HT(II), which can be probably a result of the presence of imidazoline ring that retarded reduction process. It has been observed that the H<sub>2</sub> consumption of Fe<sub>3</sub>O<sub>4</sub>/HT (II) and  $Fe_3O_4/HT$ -IM (V) nanocatalysts were 3.1 mmol/g and 2.6 mmol/g (Table 2), respectively.



Figure 8. TPR-H<sub>2</sub> profiles of (a)  $Fe_3O_4/HT$  (II), and (b)  $Fe_3O_4/HT-IM$  (V) nanocatalyst.

Table 2. Total amount of H<sub>2</sub> consumed calculated for each peak

from the TPR profiles.

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Sample	Amount of H₂ uptaked (mmol/g)	Ref.
Fe <sub>3</sub> O <sub>4</sub> /HT (II)	3.1	42, 43
Fe <sub>3</sub> O <sub>4</sub> /HT-IM (V)	2.6	-

After successfully synthesizing the  $Fe_3O_4/HT\text{-}IM$  (V) nanocatalyst and conforming its structure properly, the catalytic performance of this

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59 60 nanocatalyst was examined in the coupling reaction of styrene oxide and CO<sub>2</sub>. To explore the optimum conditions to achieve the maximum yield of cyclic carbonates by this catalytic system, initial studies were conducted by performing the model reaction at different conditions. The initial research was performed with respect to the considerable effects of hydrogen bonding and NH/ NH<sub>2</sub> groups on the reaction yield and reaction rate based on literature. We have firstly investigated the catalytic activity of  $Fe_3O_4/HT-(CH_2)_3$ -Melamine (IV) on coupling reaction of styrene oxide and CO<sub>2</sub> which were selected as a model substrate, and the results are outlined in Table 3. Initially, the reaction was studied without the use of any cocatalyst, resulting in the cyclic carbonate in lower yields, only 50% (Table 3, entry 1). Hence, numerous co-catalysts were used in order to raise yield. Under the given conditions, tetrabutyl-n-ammonium tetrafluoroborate (n-BuTA BF<sub>4</sub><sup>-</sup>), heteropolyacid (HPA) and sodium acetate (NaOAc) have proved to be ineffective! By contrast, tetra-FF butylammonium bromide (TBAB) displayed superior activity compared to the other co-catalysts under similar conditions. It was obviously selected as the best option as is shown in Table 3 entries 2-5. As regards green chemistry and in order to continue our efforts to achieve more optimal conditions, we came to conclusion to remove TBAB to improve the reaction conditions. Subsequently, we benefited from the combination of imidazole ring and bromide anion which have remarkably positive synergistic impact on the efficiency of this catalyst system as regards yield. In this regard,  $Fe_3O_4/HT-IM$ (V) nanocatalyst was designed to be as an ionic liquid accomplished by Br<sup>-</sup> anion (Scheme 1).

Table 3. The coupling reaction of styrene oxide and CO <sub>2</sub> in the presence of a Fe <sub>3</sub> O <sub>4</sub> /HT (CH <sub>2</sub> ) <sub>3</sub> Melamine (IV) catalyst under various conditions. $O$ $Fe_3O_4/HT^-(CH_2)_3Melamine + CO_2$ $O$ $Fe_3O_4/HT^-(CH_2)_3Melamine + CO_2$ $O$ $Fe_3O_4/HT^-(CH_2)_3Melamine + CO_2$ $O$							
	Reaction Conditions					Yield	ld
Entry	Catalyst	Press. (MPa)	Temp. (°C)	Amount of catalyst (mol%)	Co catalyst	(%)	Time (h)
1	$Fe_3O_4/HT-(CH_2)_3$ Melamine	1	100	1.6	-	50	8
2	$Fe_3O_4/HT-(CH_2)_3$ Melamine	1	100	1.6	n-BuTA BF <sub>4</sub> -	30	8
3	$Fe_3O_4/HT-(CH_2)_3$ Melamine	1	100	1.6	HPA	-	8
4	$Fe_3O_4/HT-(CH_2)_3$ Melamine	1	100	1.6	NaOAc	60	8
5	$Fe_3O_4/HT-(CH_2)_3$ Melamine	1	100	1.6	TBAB	98	8

In the next stage, different contributing factors to the model reaction such as temperature and pressure of carbon dioxide, which affect the yields of cyclic carbonate, were studied. This nanocatalyst (V) was implemented at different pressures and the results under the same conditions at 100 °C and 1.6 mol% of the nanocatalyst for 8 h indicated that the best pressure was achieved using 0.7 MPa of CO<sub>2</sub> charge. This way the main product was obtained with staggering 96 % yield and 100% selectivity. It is noteworthy that a rise in pressure to 1 MPa had no remarkable impact on the yield of the reaction; while a higher pressure (1.5 MPa) decreased the reaction yield from 96 to 60 % (Figure 9). A possible explanation for this decline might be the fact that excessive pressure of  $CO_2$  may retard the interaction between epoxy styrene and Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst.

Furthermore, under the same conditions at 0.7 MPa and 1.6 mol% of the nanocatalyst for 8 h, the influence of temperature on the model reaction was also investigated in the range of 30–100 °C. The results indicated that a decrease in the temperature to 30 °C would result in a low yield (30 %) (Figure 10), and thus, 100 °C was selected to be the optimal temperature.

Subsequently, the effect of the amount of the catalyst was ascertained on model reaction under the same conditions at 100 °C and 0.7 MPa for 8 h. Considering different figures for the catalyst amount proved that 1.6 mol% of the  $Fe_3O_4/HT$ -IM (V) nanocatalyst will result in extremely excellent yield with 100% selectivity for the cyclic carbonate formation, whereas no further increase was obtained in the reaction yield with raising or lowering amount of catalyst (Figure 11). These results led us to believe that using 100 °C temperature under 0.7 MPa  $CO_2$  pressure with catalyst loading of 1.6 mol% for 8 h, is identified as the best reaction conditions that give maximum yield with 100% selectivity, as can be obviously seen from the Figure 11.



**Figure 9.** The coupling reaction of styrene oxide and  $CO_2$  in the presence of 1.6 mol% of Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst under various pressures at 100 °C for 8 h.

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Figure 10. The coupling reaction of styrene oxide and CO<sub>2</sub> in the presence of 1.6 mol% of Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst under various temperatures at 0.7 MPa for 8 h.



Figure 11. The coupling reaction of styrene oxide and  $CO_2$  in the presence of various amounts of  $Fe_3O_4/HT$ -IM (V) nanocatalyst at 100 °C and 0.7 MPa for 8 h.

The chemical fixation reactions of the other epoxides with carbon dioxide were studied after achieving optimized reaction conditions in order for the substrate scope of the present dual catalyst system to be examined (Scheme 2). The results were mentioned in Table 4. It is obvious that the catalyst system was proved to be practical and appropriate for a variety of epoxides. Moreover, it is noteworthy that without any side products, this system formed the corresponding cyclic carbonates in good to excellent yields and also all reactions proceeded efficiently. As can be seen, transferring to the corresponding cyclic carbonate can be quantitatively done when aromatic epoxide was used in very high yields (96 %) (Table 4, entry 1). In addition, when the aliphatic epoxides were incorporated with both electron-donating and electron-withdrawing groups (Table 4, entries 2-6), a high yield around 95-97 % was achieved. It is

noticeable that the electron withdrawing properties of the chlorine atom led to facilitated nucleophilic attack at the epokide mig Caribon atoms and as a result the corresponding product was obtained at approximately 100% yield (Table 4, entry 7). By contrast, when cyclohexane oxide was used, the related cyclic carbonate required 10 h to reach 60% yield of the corresponding cyclic carbonate (Table 4, entry 8), which can be attributed to the higher hindrance resulting from the two rings (Table 4, entry 8).



Scheme 2. Synthesis of cyclic carbonate derivatives in the presence of Fe $_3O_4$ /HT-IM (V) nanocatlyst.

Table 4. Synthesis of different structurally-cyclic carbonates using the Fe $_3O_4/HT$ -IM nanocatalyst under solvent-free conditions.



## Journal Name



Considering that the reusability of a catalyst is one of the most significant merits of heterogeneous nanocatalysts, the reusability of the Fe<sub>3</sub>O<sub>4</sub>/HT-IM nanocatalyst was also studied under optimized experimental conditions. In this experiment, after the completion of the reaction, the nanocatalyst was easily recovered using an external magnetic field and was subsequently washed with ethylacetate and distilled water. Next, it was dried in a vacuum oven and reused for performing the reaction for 6 times without any considerable loss in the level of activity and selectivity. The results are shown in Figure 12.





It is worth mentioning that a comparison of the FESEM and EDX images of the fresh  $Fe_3O_4/HT$ -IM (V) nanocatalyst (Figure 5b and 5d) and after 6 times of using (Figure 13a and 13b) proved that the morphology did not change considerably, revealing the chemical stability of the synthesized  $Fe_3O_4/HT$ -IM (V) nanocatalyst.



Figure 13. FESEM image of (a)  $6^{th}$  reused Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst and EDX analysis of (b)  $6^{th}$  reused Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst.

To evaluate the heterogeneous nature of the nanocatalyst, a hot filtration test was carried out. The model reaction was firstly done under the optimized reaction condition (for 4 h). Then, the catalyst was magnetically separated from the reaction mixture, and it was seen that the reaction proceeded approximately 40%. Next, the reaction continued and has been monitored (by TLC) for another 4 hours without the presence of any catalyst. It is worth noting that no further proceeding in the reaction was observed after removing the catalyst. Hence, this clearly indicates that no leaching took place during the reaction and it can be concluded that the nanocatalyst is truly heterogeneous and it is stable during the catalytic reaction.

A recommended catalytic mechanism pathway for the chemical fixation catalyzed by Fe3O4/HT-IM (V) nanocatalyst is shown in Scheme 3. According to the literature,<sup>44</sup> the epoxy ring was firstly activated by the Lewis acid sites of nanocatalyst, which coordinated to the O atom of the epoxide and caused the formation of intermediate (I). In the following step, a ring opening of the epoxide took place by the nucleophilic attack of Br- anion, which led to the formation of intermediate (II). Then, the nucleophilicity attack of oxygen atom of intermediate (II) happened to capture CO2, forming the corresponding intermediate (III), which was followed by the removal of Br- anion, and simultaneously eventually afforded the corresponding cyclic carbonate (IV). Finally, the nanocatalyst was released from the product and the catalytic cycle was completed.



Scheme 3. Recommended mechanism pathway for the preparation of cyclic carbonate derivatives using  $Fe_3O_4/HT$ -IM (V) nanocatalyst.

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In this line of work, to prove the merits and catalytic efficiency of the presented catalytic system for model reaction compared to some of the previously reported procedures that have been recently published in the literature, a comparative study was carried out, and the obtained results are listed in Table 5. In spite of the fact that each of these procedures has their own merits, some of them suffer from using toxic solvent (Table 5, entry 1, 2) or additive (co-catalyst/ base) (Table 5, entries 3-12) to achieve the desired product, which can be removed by using this introduced catalytic system. More importantly, our presented catalyst system is superior to the other related reported catalytic systems thanks to its easy separation and reusability using an external magnet (Table 5, entries 13-17).

**Table 5.** Comparison between efficiency of  $Fe_3O_4/HT-IM$  (V) nanocatalyst and some other catalysts for the synthesis of 1,3-dioxolan-2-one.

Entry	Reaction conditions	Time (h)	Yield (%)	Ref.
1	LDH, DMF, 100 °C, 0.1 MPa	24-48	67-92	22
2	Mg-Al mixed oxide, DMF, 100 °C, 0.5 MPa	15	29-90	21
3	Multifunctional MOFs, TBAB, 70 °C, 0.1 MPa	12	73-99	45
4	COF-JLU7, TBAB, 40 °C, 0.1 MPa	48	71-99	46
5	MTpFPC, TBAB, 25-60 °C, 0.1 MPa	8-20	55-98	47
6	ZnO@NPC-Ox-700, TBAB, CH₃CN, 60 °C. 0.1 MPa	48	85-95	48
7	Cu-MOG, TBAB, rt, 0.1 MPa	48	61-80	49
8	Ti-PCP, TBAB,DMF, 100 °C, 0.1-6 MPa	4-24	33-99	49
9	Cationic Zinc-Organic Framework, <i>n</i> Bu₄NBr, 80 °C, 0.1 MPa	1	51-99	50
10	hydroxy-containing imidazole organocatalysts, Bu₄NX, 90 °C, 0.1-1 MPa	2-6	49-99	51
11	NIS, DBU, 60 °C, 0.1 MPa	12	37-99	52
12	[PS-Zn(II)L], Bu₄NBr, rt, 0.1 MPa	8	94-100	53
13	MgO, Bu₄NBr, rt, 0.1 MPa	1-8	42-92	16
14	UiO-66/Cu-BTC, 60 °C , 1.2 MPa	8	76-91	17
15	FJI-C10, 60-80 °C, 0.1 MPa	12-48	38-93	54
16	[TMGH <sup>+</sup> ][O <sub>2</sub> MMIm <sup>+</sup> ][Br <sup>-</sup> ], 30 °C, 1 MPa	12	94-99	55
17	Bifunctional aluminum salen complex, 80 °C, 2 MPa	30	5-95	56
18	Fe <sub>3</sub> O <sub>4</sub> /HT-IM, 100 °C, 0.7 MPa	8	96	This work

### Material characterizations

Experimental

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The FT-IR spectra were obtained using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA). The NMR spectra were obtained in Brucker AMX 300 MHz instruments in CDCl<sub>3</sub>. TGA analysis was carried out on a Shimadzu Thermogravimetric Analyzer (TG-50) in the temperature range of 25-900 °C at a heating rate of 10 °C min<sup>-1</sup> under air atmosphere. The crystalline structure of samples are analyzed using a Bruker (D8 Advance, Germany) powder X-ray diffraction (PXRD) apparatus working with Cu Ka radiation oprerated at 40 kV and 40 mA. The catalyst were analyzed in a step scan mode, using a step size rating of 0.02°/s in the 2O range of 10-80°. The morphology of synthesized sampled was investigated with field-emission scanning electron microscopy (FESEM) using a HITACHI S-4160 instrument. In addition, the elemental analysis of samples is conducted using energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) was applied to investigate the structure of synthesized nanocatalyst using a JEOL, JEM-2100F, 200 KV instrument. TPD experiments were carried out using a NanoSORD NS91 apparatus equipped with a TCD detector which detects the concentration in the gas stream and the adsorbed amount is calculated from the concentration change. H<sub>2</sub>-Temperature Programmed Reduction (H<sub>2</sub>-TPR) experiment were carried out using a NanoSORD NS91 apparatus. The zeta potential of both the samples was analyzed using the HORIBA SZ-100 nanoPartica system. All the yields refer to isolated products after purification by column chromatography.

### Preparation of HT (I), Fe<sub>3</sub>O<sub>4</sub>/HT (II) and Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Cl (III)

HT (I), Fe<sub>3</sub>O<sub>4</sub>/HT (II) and Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Cl (III) were synthesized according to the procedure reported in literature.<sup>20</sup> Briefly, in a typical reaction, following a similar procedure, a mixed solution (60 mL) containing NaOH (4 g, 100 mmol) and NaHCO<sub>3</sub> (2.1 g, 25 mmol) was added drop by drop to 60 mL mixed salt solution (molar ratio Mg/Al : 2/1) with a vigorously-stirring bar and it was heated till 60 °C for 24 h. After this time, the obtained white residue (HT) was filtered and washed three times with water and dried at 100 °C for 12 h. After that, a solution (100 mL) of  $FeCl_3.6H_2O$  (2.1 g, 8 mmol) and FeCl<sub>2</sub>.4H<sub>2</sub>O (1.05 g, 5.2 mmol) was placed in a three-necked 500 mL round-bottom flask equipped with argon gas inlet tube and heated at 80 °C under Ar flow for minutes. Then, 4 g of HT (I) powder and 100 mL NaOH solution (5%) were simultaneously poured in the metal solution and carried out at 80 °C for 24 h. After the reaction was completed, using an external magnet the obtained brown powder was collected and rinsed with distilled water (2 × 100 mL) to give Fe<sub>3</sub>O<sub>4</sub>/HT (II). Then, functionalization of Fe<sub>3</sub>O<sub>4</sub>/HT (II) was carried out by treating dispersed Fe<sub>3</sub>O<sub>4</sub>/HT (II) (2 g in toluene) with 3-Chloropropyltrimethoxysilane (2 g, 8 mmol) under 12 h reflux condition. Successively, after cooling to room temperature, the resultant precipitate was washed with ethanol (20 mL), and dried at 50 °C.

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# Preparation of $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV)

Typically,  $Fe_3O_4/HT$ -(CH<sub>2</sub>)<sub>3</sub>-Cl (III) (0.5 g) and 4 g of melamine were dispersed in 50 mL ethanol. After mixing them together, a solution of NaOH (1 M) was added while being vigorously stirred, refluxed and maintained for 48 h. After that, the solid magnetic residue was collected by an external magnet and washed three times with hot water (200 mL), and dried at 80 °C for 3h.

# Preparation of $Fe_3O_4/HT$ -IM (V) nanocatalyst

Fe<sub>3</sub>O<sub>4</sub>/HT-(CH<sub>2</sub>)<sub>3</sub>-Melamine (IV) (0.25 g), K<sub>2</sub>CO<sub>3</sub> (0.25 g) and 1,6dibromo hexane (1 mL) were poured into a round bottom flask equipped with a magnetic stirrer, and were stirred and heated at 100 °C for 12 h. After that, the final residue was magnetically collected and then washed three times with hexane (100 mL), H<sub>2</sub>O (100 mL) and ethanol (100 mL), respectively, and dried at oven (50 °C). At the next step, the final residue (0.25 g) was added to K<sub>2</sub>CO<sub>3</sub> (0.25 g) and 1-methyl imidazole (1 mL) and stirred continuously at 100 °C for 12 h. At that time, Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) as the final nanocatalyst was also washed (with methanol/H<sub>2</sub>O 50/50), and placed in the oven at 50 °C.

# Representative procedure for the chemical fixation of $CO_2$ with epoxides in the presence of Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst

The cycloaddition reaction of epoxides with carbon dioxide was carried out at a stainless steel high-pressure batch reactor equipped with a magnetic stirrer. Then, epoxide (3 mmol) and the Fe<sub>3</sub>O<sub>4</sub>/HT-IM (V) nanocatalyst (1.6 mol%) were added into the reactor at 0.7 MPa pressure. Subsequently, the mixture was heated for the indicated time at 100 °C. Upon completion, the reactor has been cooled to reach ambient temperature which led to slow release of  $CO_2$  from the vessel. After this, the extraction of the mixture reaction was conducted using ethyl acetate (3 × 10 mL), and the catalyst was readily separated by an external magnetic field. Finally, the concentration and purification of the organic layer was done using column chromatography by eluent ethylacetate and *n*-hexane (2:1).

# Conclusions

In conclusion, we have successfully synthesized and employed a stable, environmentally benign and plate-like Fe<sub>3</sub>O<sub>4</sub>/HT-IM nanocatalyst that can efficiently tolerate reaction of a diverse range of epoxides with  $CO_2$  under green reaction conditions with excellent-to-high yield. It is noticeable that this catalytic system is not sensitive to air and minor moisture. The importance of the synthesized Fe<sub>3</sub>O<sub>4</sub>/HT-IM nanocatalysts with other catalysts and also the reaction plausible mechanism has been revealed in this paper. Although, to further clarify the mechanism of this reaction in detail, efforts are now in progress. Especially, this catalytic system can be easily recovered upon release of CO<sub>2</sub> and reused for six consecutive cycles without obvious loss of activity and selectivity. Importantly, this described nanocatalyst is also unique as it consists both acid and base sites which promotes the cycloaddition reaction of CO2 which is an advantageous point of the presented methodology. It is expected that these characteristics make the proposed protocol an ideal catalyst system that is suitable for the synthesis of a wide range of valuable chemical materials and

# **Conflicts of interest**

There are no conflicts to declare.

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**Graphical abstract** 

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# Imidazolium-based ionic liquid immobilized on functionalized magnetic hydrotalcite (Fe<sub>3</sub>O<sub>4</sub>/HT-IM): as an efficient heterogeneous magnetic nanocatalyst for chemical fixation of carbon dioxide under green conditions

Fe<sub>3</sub>O<sub>4</sub>/HT-IM with plate-like morphology was synthesized as a novel and highly effective magnetic nanocatalyst and applied in the chemical fixation.

