Chemical fixation of carbon dioxide catalyzed by magnetically recoverable NH₂-MIL-101(Al) as an elegant nanoreactor

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Abstract- A new heterogeneous catalyst, magnetic amino-MIL-101(Al), was synthesized based on the reaction of NH₂-MIL-101(Al) and silica coated magnetic nanoparticles, Fe₃O₄@SiO₂. The prepared catalyst was characterized by UV-vis, FT-IR, X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray (EDX) and inductively coupled plasma (ICP) methods. The catalytic activity of this new catalyst was investigated in the fixation of carbon dioxide with epoxides under atmospheric pressure at 100 °C. Excellent yields, short reaction times and reusability without significant decrease in its initial activity are the advantages of this noble catalyst. Moreover, magnetic property of the catalyst allows easy separation by using an external magnetic field

Keywords: *Metal-organic framework; magnetic amino-MIL-101(Al); Fe₃O₄@SiO₂; CO₂ cycloaddition.*

1. Introduction

Utilization of carbon dioxide, a naturally abundant, inexpensive, non-toxic and non-flammable greenhouse gas, as a C₁ feedstock for the production of useful chemicals has attracted much attention in recent years [1, 2].

One of the invaluable group of compounds which can be synthesized *via* the reaction of epoxides with carbon dioxide as precursor is cyclic carbonates with wide range of applications [3-6].

Due to the inert nature of carbon dioxide, its efficient coupling with epoxides requires a catalytic system to achieve cyclic carbonates. Wide range of catalytic systems have been previously reported for this reaction [4, 7-18], but finding a suitable catalyst which is highly efficient and reusable for chemical fixation of carbon dioxide still remains a significant challenge.

Metal–organic frameworks (MOFs) constructed from an inorganic moiety and organic linkers possess noticeable features such as flexible pore size, shape and structure, high surface area and tuneability which make them unique materials both in adsorption of carbon dioxide [19-21] and catalysis [22-24].

Aluminium aminoterephthalate metal-organic framework, NH₂-MIL-101(Al), built from supertetrahedral building units formed by rigid 2-amino terephthalate ligands and trimeric Al(III) octahedral clusters contains unsaturated metal sites which make it suitable as a mild Lewis acid [25]. Furthermore, high capacity of this MOF for adsorption of carbon dioxide due to amine function in its structure is a plus [26].

Since catalyst recovery and reuse are very important features in many catalytic processes, these days magnetization of metal–organic frameworks has received considerable attention to provide much easier and faster separation of the catalyst from the reaction media by using an external magnetic field instead of performing tedious centrifugation and filtration steps [23, 27-31].

In this paper, we report the preparation of magnetic amino-MIL-101(Al), amino-MIL-101(Al)@Fe₃O₄@SiO₂, by mixing silica-coated iron nanoparticles and amino-MIL-101(Al) under sonication. The resulting new hybrid material has been evaluated as a recoverable catalyst for chemical fixation of carbon dioxide with epoxides at ambient pressure and temperature (Scheme 1).

Scheme 1. Chemical fixation of CO₂ with epoxides catalyzed by amino-MIL-101@Fe₃O₄@SiO₂

2. Experimental

2.1. Materials and methods

All materials were obtained from Merck or Fluka chemical companies. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ on a JASCO 6300 spectrophotometer. The scanning electron micrographs were taken on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). The XRD patterns were recorded using a Bruker D₈ ADVANCE X-ray diffractometer equipped with nickel monochromatized Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The ICP analyses were carried out on a Perkin-Elmer Optima 7300 DV spectrometer. Gas chromatography experiments (GC) were performed by a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M.

2.2. Magnetization of amino-MIL-101(Al) (amino-MIL-101(Al)@Fe₃O₄@SiO₂)

The magnetic nanoparticles, MNPs (Fe₃O₄), were synthesized and silica-coated as reported in the literature [32]. Also, amino-MIL-101(Al) was synthesized according to the procedure reported by Gascon et al. [25, 33]. In the next step, by a very simple method, amino-MIL-101(Al) (0.6 g) and Fe₃O₄@SiO₂ (0.1 g) were placed in a 25 ml glass vial and dispersed in methanol under ultra-sonic vibration for 1.5 h to form amino-MIL-101(Al)@Fe₃O₄@SiO₂ (%88 yield). The magnetic MOF was separated from methanol by using an external magnet and dried overnight in an oven at 75 °C. Fig. 1. show amino-MIL-101(Al) before and after magnetization.

2.3. Catalytic experiment

2.3.1. General procedure for carbon dioxide fixation reaction

First, the reaction parameters including the type of solvent, amount of catalyst, the kind and amount of co-catalyst and temperature were optimized in the reaction of carbon dioxide with 1,2-epoxy octane as a model. Under the optimized reaction condition, the reaction of various epoxides (linear and cyclic)

with CO₂ was investigated in the presence of amino-MIL-101(Al)@Fe₃O₄@SiO₂. To a solution of epoxide (1 mmol) in DMF (3 ml) in a 3-neck round bottom flask, lithium bromide (LiBr) (0.2 mmol) and the catalyst (20 mg, 0.0087) were added. Carbon dioxide gas was bubbled into the solution at atmospheric pressure. The progress of the reaction was monitored by GC. At the end of the reaction, the catalyst was easily separated from the reaction mixture by using an external magnet, and washed with DMF, diethyl ether and ethanol.

2.3.2. Recovery and reuse of magnetic catalyst

The reusability of amino-MIL-101(Al)@Fe₃O₄@SiO₂ catalyst was investigated in the multiple sequential reaction of 1,2-epoxy octane and carbon dioxide, as described above. The amount of Al and Fe leached in the filtrates were determined by ICP.

Fig. 1. The color change during the preparation of amino-MIL-101(Al)@Fe₃O₄@SiO₂

3. Results and discussion

3.1. Preparation and characterization of magnetic catalyst

Magnetic amino-MIL-101(Al) catalyst was easily prepared by dispersion of Fe₃O₄@SiO₂ and MOF under sonication.

The X-ray diffraction pattern (Fig. S1A) and FT-IR spectrum (Fig. S2B) are the same as those of NH₂-MIL-101(Al) in the literatures [25, 33, 34]. As shown in Fig. S2C, the crystallinity of the framework is

retained after magnetization of amino-MIL-101(Al), and the additional peak (around $2\theta=42$) corresponds to $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ (Fig. S1B) which is a strong evidence for successful synthesis of amino-MIL-101(Al) $@ \text{Fe}_3\text{O}_4@ \text{SiO}_2$.

The FT-IR spectrum of the catalyst (Fig. S2C), exhibits characteristic bands of the framework at 1338 cm^{-1} , the C-N stretching absorption of aromatic amines, and the doublet at 3497 and 3385 cm^{-1} corresponds to the asymmetrical and symmetrical stretching of the amine moieties [35]. Also, the stability of the framework is preserved after magnetization, characteristic vibrational bands of the framework $-(\text{O}-\text{C}-\text{O})-$ groups around 1400 cm^{-1} and 1550 cm^{-1} confirm this point. The FT-IR spectrum of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ (Fig. S3A) exhibits characteristic bands at 580 (Fe-O), 950 (Si-OH) and 1091 (Si-O-Si) [36] which is added to NH_2 -MIL-101 spectrum (Fig. S2B) after magnetization reaction and prove successful synthesis of amino-MIL-101(Al) $@ \text{Fe}_3\text{O}_4@ \text{SiO}_2$.

The FE-SEM images (Fig. 2A and B) show that the NH_2 -MIL-101(Al) has retained its nature and not altered during the magnetization reaction. In addition, the energy dispersive X-ray results, obtained from SEM analysis (Fig. 2C) clearly show the presence of Fe, Si and Al in the magnetic catalyst. The presence of magnetic nanoparticles is obviously detectable in the TEM image of NH_2 -MIL-101 after magnetization (Fig S3B). CO_2 adsorption isotherms of the catalyst is presented in Fig S4 at 298 K under CO_2 pressure. The CO_2 adsorption capacity obtained for amino-MIL-101(Al) $@ \text{Fe}_3\text{O}_4@ \text{SiO}_2$ in this study is compared with those previously reported in the literatures [37].

3.2. Catalytic experiments

In order to evaluate the catalytic performance, 1,2-epoxy octane was used as a model substrate for carbon dioxide fixation reaction and all effective parameters were optimized.

First, the effect of catalyst amount on the formation of 1-octene carbonate was investigated using different amounts of amino-MIL-101(Al) $@ \text{Fe}_3\text{O}_4@ \text{SiO}_2$ in the atmospheric pressure of CO_2 at 100°C .

The best result was obtained using 20 mg (0.0087) of the catalyst. As can be seen in Fig 3, no product was obtained in the absence of catalyst, while only 3% of the corresponding carbonate was obtained in

the presence of SiO_2 and 25% in the presence of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ after 7 h. Also, the progress of the reaction was 77% in the presence of amino-MIL-101(Al) which proves that magnetization of the catalyst not only helps the easier reusability but also improves the catalyst activity in preceding the reaction. The selectivity for all reactions was 100% and no by-product was detected by GC analysis.

The effect of different solvents including dichloromethane, acetonitrile, methanol and dimethylformamide (DMF) and temperature was also investigated in model reaction (Table S1). At first for comparison among the employed solvents the reactions were carried out at 40 °C (the lowest boiling point of the used solvents). As can be seen in Table S1, DMF is the best solvent at this temperature. Then the model reaction was carried out at boiling point of solvents except for DMF that maximum yield was achieved at 100 °C. In methanol, only trace amount of 1-octene carbonate was obtained in the presence of amino-MIL-101(Al) $@\text{Fe}_3\text{O}_4@\text{SiO}_2$, while in DMF the reaction yield increased moderately. The positive effect of solvent reported by Aresta et al. which can be attributed to increasing nucleophilicity of the oxygen atom of epoxide or CO_2 in DMF [12]. As shown in Table S1, the highest yield of 1-octene carbonate was obtained at 100 °C, and increasing the temperature up to 120 °C did not decrease the reaction time.

Fig. 2. FE-SEM images of: (A) amino-MIL-101(Al), (B) amino-MIL-101(Al)@Fe₃O₄@SiO₂ and (C) SEM-EDX spectrum of amino-MIL-101(Al)@Fe₃O₄@SiO₂

In chemical fixation of carbon dioxide, both catalyst and co-catalyst as Lewis acid (electrophile) and Lewis base (nucleophile), respectively are necessary for obtaining the highest amount of product [11, 13]. Since, Al is a good Lewis acid [14, 38], different Lewis bases such as tetrabutylphosphonium bromide, tetrabutylammonium bromide, *N*-Methylimidazole, sodium chloride, sodium bromide, lithium iodide and lithium bromide were tested as co-catalyst in the reaction of 1,2- epoxyoctane with CO₂ in the presence of the catalyst (Table S1). LiBr as a co-catalyst showed higher activity than quaternary halide salts (ammonium and phosphonium) in this reaction, probably due to less steric effects. The higher Lewis acidity of lithium bromide compared with sodium salts is due to facile good coordination and ring cleavage of the epoxide and subsequent formation of the cyclic carbonate [39]. Furthermore, lithium bromide has a higher activity (entry 7, 100% yield), compared to lithium iodide (entry 17, 80% yield). One possible reason for that is the fact that bromide (Br) acts both as a good nucleophile and a good leaving group [40].

Fig. 3. Optimization of the catalyst amount after 7 h on the formation of 1-octene carbonate (Reaction conditions: 1,2-epoxyoctane (1 mmol), LiBr (0.2 mmol), catalyst, DMF (3 ml), CO₂ at atmospheric pressure, T=100 °C).

Also, tetrabutylphosphonium bromide showed 92% yield because of improvement of the ionic strength of the solution which in turns increased the reaction rate [41, 42].

The amount of co-catalyst was also optimized. The highest yield was obtained in the presence of 0.2 mmol of co-catalyst after 7 h. The same behavior was observed at higher amount of co-catalyst (Fig. S5). It is noteworthy that when Lithium bromide was used as catalyst, no noticeable product was observed in the reaction mixture.

Under the optimized reaction conditions, the catalytic activity of the amino-MIL-101(Al)@Fe₃O₄@SiO₂ was investigated in the reaction of various epoxides (linear and cyclic) with carbon dioxide. The important point about this catalytic system is the capability of carrying out under atmospheric pressure of CO₂. The results are summarized in Table 1. Epoxides were converted to their corresponding carbonates with the selectivity of 100%. The TOFs for the reaction of linear epoxides are higher than that of cyclic ones. It seems that the less the steric effect, the shorter the reaction time. This catalytic system is highly efficient and active in conversion of carbon dioxide and different epoxides to cyclic carbonates, which is related to the high surface area and the ability of NH₂-MIL-101(Al) for CO₂ adsorption. It has been well documented that due to their high porosity, MOFs are used for storage of different gases. Therefore, they can increase the local concentration of carbon dioxide around active sites of the catalyst which in turns increases their catalytic activity.

3.3. Catalyst recovery and reuse

To assess the reusability of amino-MIL-101(Al)@Fe₃O₄@SiO₂, after carboxylation reaction of 1,2-epoxy octane with carbon dioxide, the catalyst was separated by an external magnet from the reaction mixture, washed and dried. After using the catalyst for four consecutive runs, the yield was 83% (Table S2). Also, the amount of Al leached after four runs is about 1.91% of the initial aluminum, and no Fe was detected in the filtrate by ICP analysis. Also, by considering the XRD patterns and the FT-IR spectra, it is proved that the catalyst has retained its nature during the reaction (Fig. S1D and S2D).

4. Conclusion

In conclusion, we have succeeded in designing a novel catalyst, magnetic amino-MIL-101(Al), as a highly efficient and reusable heterogeneous catalytic system for the coupling reaction of epoxides and CO₂ to generate relevant cyclic carbonate with excellent selectivity. This catalyst which can be easily prepared shows the properties of both magnetic nanoparticles for concise recycling with an external magnet, and MOFs with high surface area, porosity and ability of carbon dioxide adsorption.

Furthermore, extremely mild reaction conditions (temperature and pressure) are unique features of this efficient heterogeneous catalyst.

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Table 1. The coupling results of various epoxides and CO₂ catalyzed by amino-MIL-101(Al)@Fe₃O₄@SiO₂^a

Entry	Epoxide	Cyclic carbonate	Time (h)	Yield (%) ^b	TOF (h ⁻¹)
1			13	100	9
2			2.5	100	46
3			7	100	16.4
4			16	80	5.8
5			9	100	12.8
6			10	95	11
7			14	84	6.9

^a Reaction conditions: 1,2-Epoxyoctane (1 mmol), LiBr (0.2 mmol), amino-MIL-101(Al)@Fe₃O₄@SiO₂ (20 mg), DMF (3 ml), CO₂ atmospheric pressure, T=100°C.

^b GC yield.

Chemical fixation of carbon dioxide to cyclic carbonates catalyzed by magnetically recoverable MIL-101(Al) under mild conditions

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