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Article

Cycloaddition of CO₂ with epoxides by using an amino-acid-based Cu(II)–tryptophan MOF catalyst

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ABSTRACT

Metal organic frameworks (MOFs) constructed from natural/biological units (amino acids) are prospective candidates as catalysts in CO₂ chemistry owing to their natural origin and high abundance of Lewis acid/base sites and functional groups. Herein, we report the catalytic efficiency of an amino-acid-based Cu-containing MOF, denoted as CuTrp (Trp = L-tryptophan). The CuTrp catalyst was synthesized by direct mixing at room temperature using methanol as a solvent—a synthetic route with notable energy efficiency. The catalyst was characterized using various physicochemical techniques, including XRD, FT-IR, TGA, XPS, ICP-OES, FE-SEM, and BET analysis. The catalytic activity of CuTrp was assessed in the synthesis of cyclic carbonates from epoxides and CO₂. The CuTrp operated in synergy with the co-catalyst tetrabutylammonium bromide under solvent-free conditions. Several reaction parameters were studied to identify the optimal reaction conditions and a reaction mechanism was proposed based on experimental evidence and previous density functional theory studies. The CuTrp also exhibited satisfactory stability in water and could be reused more than three times without any significant loss of activity.

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1. Introduction

With the increase in greenhouse gas emissions, CO₂ pollution has become a major concern because it is the main cause of global warming. Many researchers have reported promising methodologies for the removal and re-use of anthropogenic CO₂, which is a nonpoisonous and abundant thermodynamically stable C1 feedstock. In many industries, captured CO₂ has been used for producing food, plastics, refrigerants, carbonates, fire extinguishers, and diverse chemicals. Among the several approaches for CO₂ utilization [1–3], the production of five-membered cyclic carbonates as valuable chemicals has been particularly promising owing to the quadrupole moment

and high polarizability of CO₂. Five-membered cyclic carbonates are used in a wide range of applications as solvents, precursors in the synthesis of polycarbonates, or intermediates in the production of many organic materials, surfactants, and plasticizers [4–6].

A large pool of catalysts is available for use in the cycloaddition reaction of epoxides and CO₂ [7–14]; however, these catalysts present certain drawbacks. Homogeneous catalysts, such as quaternary ammonium salts or ionic liquids, show very high performance under mild conditions and are capable of numerous transformations; however, they require cumbersome recovery steps after the reaction is completed. Therefore, bulk scale and commercial production often demands the use of

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heterogeneous catalysts because of easy separation of the catalyst or to setup continuous flow processes. Unfortunately, many pure heterogeneous catalytic phases show lower activity than their homogeneous counterparts and harsher reaction conditions are required. Therefore, the development of efficient heterogeneous catalytic systems involving heterogeneous analogues of efficient homogeneous species is in high demand for cycloaddition reactions. Metal organic frameworks (MOFs) [15–22], which consist of metal ions or clusters linked by organic ligands expanding from one-dimensional to three-dimensional structures, provide excellent candidates for use in gas storage/separation [23–26], drug delivery [27], and catalysis [28–32].

MOFs are popular for their guest-inclusion capacity because their pore size can be easily tuned. MOFs can be designed with large internal surface areas, good thermal stability, mechanical strength, and crystallinity [33–36]. MOFs possess a large capacity to absorb CO₂ for carbon capture and utilization. To lower the cost of the synthesis of MOFs and obtain high-quality catalysts, several synthetic methodologies, such as solvothermal, electrochemical, slow evaporation, microwave, and direct-mixing synthesis, have been developed [37]. Exodentate carboxylate and pyridyl terminal ligands are the most common ligands in MOF chemistry. Amino acids, which are biologically important natural and biocompatible materials, consist of aminocarboxylate terminals and sidechains containing functional groups, which provide multiple metal binding sites for coordination [38–42]. The amine and carboxylate ends have been reported to catalytically activate epoxides.

Herein, we report the catalytic properties of an amino acid coordination framework (CuTrp), in which copper centers are connected by L-tryptophan units. The CuTrp catalyst was synthesized by an economic and ecofriendly route at room temperature. The copper centers are penta-coordinated as CuO₃N₂ with L-tryptophan units. The N-atoms of the heterocyclic rings in L-tryptophan are potentially active species in CO₂ chemistry because they act as Lewis bases and favor chemical interactions with CO₂ [43].

2. Experimental

2.1. Synthesis of the catalyst

The CuTrp catalyst was prepared according to a reported procedure [43]. The amino acid (0.2 g L-TrpH) was dissolved in 10 mL aqueous solution of trimethylamine (0.05 mol L⁻¹). Methanol was added (10 mL) and the mixture was stirred until the amino acid was completely dissolved. An aqueous solution (5 mL) of the metal salt (0.5 mmol = 0.1 g Cu(NO₃)₂·2.5H₂O) was added dropwise to the above amino acid solution and stirred for 6 h. The obtained precipitate was separated from the solution using a sintered funnel, and then washed sequentially with water (2×5 mL), ethanol (5 mL), and diethyl ether (5 mL). After drying in an oven at 50 °C for 12 h, a pale blue solid was obtained.

2.2. Characterization of the catalyst

The X-ray diffraction (XRD) patterns were analyzed in a Rigaku Ultima IV diffractometer using Cu K_α radiation (40 kV, 40 mA). Step size 2θ = 0.02°, time per step = 4 s. The diffractograms were recorded in the 2θ range of 5–50°. The morphology studies of CuTrp were performed with a S-4200 field emission scanning electron microscope (FE-SEM, Hitachi-3500N). The surface area and pore volume of CuTrp was analyzed using the BET model equation (analyzed by recording an N₂ adsorption isotherm at –196 °C with a BET apparatus (Micromeritics ASAP 2020). The infrared (FTIR) analysis was performed with an Avatar 370 Thermo Nicolet spectrophotometer at a resolution of 4 cm⁻¹. The elemental analysis of the catalyst was performed with a Vario EL III analyzer. Inductively coupled plasma-optical emission (ICP-OES) analysis was carried out by using an ULTIMA2 CHR (1.5 kW, 40.68 MHz, 130–800 mm) with a monochromator HDD and a polychromator PMT detector to obtain the metal content of both catalysts. Thermogravimetric analysis (TGA) was performed with an AutoTGA 2950 apparatus under a nitrogen flow of 100 mL min⁻¹ while heating from room temperature to 600 °C at a rate of 10 °C min⁻¹.

2.3. Cycloaddition of CO₂ and epichlorohydrin

Epichlorohydrin (ECH) (2.0 mL, 25.5 mmol), CuTrp (0.1 g, 0.212 mmol), and tetrabutylammonium bromide (TBAB) (0.0683 g, 0.212 mmol) were placed in a 25-mL stainless steel autoclave reactor with a magnetic bar. The pressure and temperature were adjusted with a controller. The reactor was purged with CO₂ before the reaction was started. The reaction was carried out at the desired temperature with continuous stirring at 600 r min⁻¹ under semi-batch conditions, under which the reactor pressure was maintained constant by using a back-pressure regulator. After the reaction was complete, the reactor was cooled and the remaining CO₂ was vented off slowly through an outlet. The reaction mixture was centrifuged and the liquid product was separated and then mixed with dichloromethane as an internal standard and analyzed by gas chromatography (Agilent HP 6890 A, HP-5, 30 m × 0.25 μm) with a flame ionization detector to determine the conversion of epichlorohydrin, the selectivity, and the yield of the desired product epichlorohydrin carbonate 4-(chloromethyl)-1,3-dioxolan-2-one (ECHC). Recyclability studies of CuTrp were performed under the same procedures by adding fresh TBAB to a mixture of recycled CuTrp MOF and ECH in each cycle. After each reaction run, the separated CuTrp MOF was washed with ethanol and dried in an oven at 100 °C.

3. Results and discussion

3.1. Characterization of the catalyst

As shown in Fig. 1, the XRD peaks of CuTrp were consistent with the simulated peaks generated from crystallographic information in the literature, thereby validating the formation of CuTrp. The FT-IR spectra of CuTrp and the L-tryptophan ligand are shown in Fig. 2. A sharp ν(N–H) stretching band at 3408 cm⁻¹ in the L-tryptophan was attributed to the indole group on

Fig. 1. XRD patterns of the synthesized and simulated CuTrp.

Fig. 2. FT-IR spectra of Tryptophan (a) and CuTrp (b).

the sidechain. The FT-IR also exhibited two $\nu(\text{N-H})$ bending bands between 1670 and 1450 cm^{-1} and two bands in the 1580–1670 and 1345–1420 cm^{-1} regions from the asymmetric and symmetric $\nu(\text{COO}^-)$ stretching vibrations, respectively. In the FT-IR spectrum of CuTrp, these bands slightly shifted to lower wavenumbers owing to the bidentate coordination with copper. Furthermore, the shift of the broad $\nu(\text{NH}^3^+)$ stretching band in the 2915–3145 cm^{-1} region to higher wavenumbers (3300–3180 cm^{-1}) was attributed to the binding between the nitrogen atom of the amino group and the copper centers. The presence of aromatic groups in the complex was also confirmed by the presence of peaks in the 2900–3150 cm^{-1} region. The thermal stability of the material was assessed by TGA. The copper tryptophan complex was stable up to approximately 266 °C without any notable weight loss, indicating that the catalyst could participate in cycloaddition reactions, which are typically performed at temperatures below 120 °C (Fig. 3). The oxidation state of the Cu(II) metal centers was verified by XPS analysis, which showed copper $2p_{1/2}$ and $2p_{3/2}$ peaks at 955.4 and 935.1 eV, respectively, in accordance with the literature (Fig. 4). Moreover, the ICP-OES analysis revealed that the copper content was 13.85 wt%, which was consistent with the corresponding theoretical calculation (13.47 wt%). The

Fig. 3. TGA curve of CuTrp.

Fig. 4. XPS Cu 2p spectra of CuTrp.

FE-SEM image in Fig. 5 shows that the synthesized copper tryptophan complex exhibited a plate-like sheet morphology. The BET isotherm plot indicated that the CuTrp was a nonporous solid material with a multilayer structure, which explained the low surface area of 4.2 $\text{m}^2 \text{g}^{-1}$ (Fig. 6).

Fig. 5. FE-SEM image of CuTrp.

Fig. 6. Nitrogen adsorption-desorption isotherm of CuTrp.

3.2. Cycloaddition of CO₂ with epichlorohydrin

A control reaction without the catalyst was first carried out, which proved that the catalyst was vital for transforming the epoxide to the cyclic carbonate (Table 1, entry 1). The catalyst components (L-tryptophan, Cu(NO₃)₂·5H₂O) (Table 1, entries 2 and 3) alone did not show any catalytic activity. CuTrp alone at 80 °C showed no ECH conversion (Table 1, entry 5), but it exhibited 68.1% conversion at 120 °C and 12 h. The TBAB alone showed 86.7% of ECH conversion (Table 1, entry 6). However, a higher conversion of 95.1% (Table 1, entry 7) was obtained using CuTrp together with the co-catalyst TBAB, pointing to a synergistic effect between the MOF and TBAB in this cycloaddition reaction. Other quaternary ammonium salts (tetrabutylammonium chloride (TBAC) and tetrabutylammonium iodide (TBAI)), were also investigated; the bromide anion (Table 1, entry 7) showed the best catalytic performance, followed by the iodide and chloride anions (Table 1, entries 10 and 9). The order of nucleophilicity of these anions is I[−] > Br[−] > Cl[−], whereas the leaving ability of the anions is in the reverse order. This suggested that the cycloaddition reaction was affected by the combination of nucleophilicity and leaving ability of the co-catalyst. Moreover, the presence of water molecules seemed to have a favorable effect on the cycloaddition, because a higher

Table 1
Cycloaddition of CO₂ with epichlorohydrin for different catalysts.

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	None	0	—
2	Cu(NO ₃) ₂ ·5H ₂ O	0	—
3	L-Tryptophan	0	—
4	CuTrp	0	—
5	CuTrp ^a	68.1	99.0
6	TBAB	60.7	98.8
7	CuTrp/TBAB	95.1	99.2
8	CuTrp/TBAB ^b	97.6	99.3
9	CuTrp/TBAC	85.4	97.2
10	CuTrp/TBAI	91.6	98.5

Reaction conditions: Epichlorohydrin = 25.5 mmol, CuTrp = 0.83 mol%, TBAB = 0.83 mol%, T = 80 °C, t = 9 h, P_{CO2} = 1.2 MPa.

^a T = 120 °C, t = 12 h.

^b Reactions with 30 μL of water.

Table 2

Effect of CuTrp: TBAB ratio on the synthesis of epichlorohydrin carbonate.

Entry	CuTrp (mol%)	TBAB (mol%)	Ratio of CuTrp/TBAB	Conversion (%)	Selectivity (%)
1	0.83	0.83	1:1	95.1	99.2
2	0.415	0.83	1:2	93.0	98.9
3	0.83	0.415	2:1	86.3	98.8
4	0.83	0.2075	4:1	69.0	99.0

Reaction conditions: Epichlorohydrin = 25.5 mmol, T = 80 °C, t = 9 h, P_{CO2} = 1.2 MPa.

conversion was obtained after the addition of 30 μL of water to the reaction system (Table 1, entry 8). This effect may be owing to hydrogen bonding between the water and epoxide oxygen [21].

The results after varying the catalyst/co-catalyst ratio are shown in Table 2. The conversion was 95.1% with 0.83 mol% of each CuTrp and TBAB (Table 2, entry 1). Only a slight decrease in ECH conversion was observed (Table 2, entry 2) when the content of CuTrp was halved (0.415 mol%), while the same co-catalyst TBAB loading was maintained (0.83 mol%). Meanwhile, at a CuTrp loading of 0.83% and a reduced TBAB loading of 0.415 mol%, the conversion modestly decreased to 86.3% (Table 2, entry 3). When the TBAB loading was further reduced to 0.2075 mol% at a constant CuTrp loading of 0.83 mol%, the ECH conversion decreased to 69% (Table 2, entry 4). The system with a 1:1 ratio of catalyst/co-catalyst was chosen for the subsequent cycloaddition experiments.

The reaction parameters of the CuTrp-catalyzed cycloaddition reaction were optimized through experiments under semi-batch conditions. Fig. 7(a) illustrates the effect of temperature on the cycloaddition reaction of ECH in the range from 40 to 100 °C; the conversion of ECH steadily increased from 25.3% to 95.1% as the temperature increased up to 80 °C, whereas the ECHC selectivity remained at approximately 98%. Moreover, almost 99% conversion of ECH was obtained at 100 °C. Because the increase in conversion was modest, 80 °C was chosen as the optimum temperature for the reaction. Subsequently, the effect of the reaction time on the cycloaddition reaction was studied at 80 °C. Notably, the conversion of ECH increased with increasing reaction time from 1 to 12 h. The optimum reaction time was 9 h; however, the highest conversion was obtained after 12 h, at which the ECH conversion was only 0.5% higher than the 95.1% conversion after 9 h, whereas the selectivity was maintained at 99% (Fig. 7(b)). Fig. 7(c) depicts the effect of CO₂ pressure on the reactivity of the catalyst. The enhancement of the ECH conversion coincided with increasing CO₂ pressure in the range from 0.1 to 1.2 MPa. Thereafter, the activity of the catalyst slightly decreased owing to mass transport limitations, which indicated that excess CO₂ hampered the efficient contact between ECH and the catalyst [44–47]. However, the catalyst exhibited activity even under atmospheric pressure, showing a relatively high ECH conversion of 83.5%. Consequently, the optimized cycloaddition reaction conditions were 80 °C for 9 h and 1.2 MPa of CO₂ pressure, at which the ECH conversion was

Fig. 7. (a) Effect of reaction temperature on the reactivity of CuTrp. Reaction conditions: ECH = 25.5 mmol, Cat. = 0.83 mol%, t = 6 h, CO₂ pressure = 1.2 MPa, Semi-batch. (b) Effect of reaction time on the reactivity of CuTrp. Reaction conditions: ECH = 25.5 mmol, Cat. = 0.83 mol%, T = 80 °C, CO₂ pressure = 1.2 MPa, Semi-batch. (c) Effect of CO₂ pressure on the reactivity of CuTrp. Reaction conditions: ECH = 25.5 mmol, Cat. = 0.83 mol%, T = 80 °C, t = 9 h, Semi-batch.

95.1% and the selectivity towards ECHC was 99%.

Several epoxides were tested for the conversion of CO₂ into cyclic carbonates using the CuTrp catalyst and TBAB under the optimized conditions (80 °C, 9 h, 1.2 MPa), as shown in Table 3. Although the conversion of the terminal aliphatic epoxides was very effective, with excellent selectivity of no less than 98% to their corresponding cyclic carbonates, the internal epoxide, cyclohexene oxide, was difficult to convert to its cyclic carbonate under the employed reaction conditions. This has been the case for most of the reported catalysts for the CO₂-epoxide cycloaddition reaction and has widely been ascribed to the steric hindrance caused by the cyclohexene ring [44,47].

3.3. Structure of CuTrp and mechanism of cycloaddition with the TBAB co-catalyst

The coordination environment around Cu in CuTrp is shown in Fig. 8. The Cu(II) atom was coordinated to L-tryptophan through Cu–N and Cu–O bonds with the N and O atoms of the amine and carboxylate groups of tryptophan, respectively. The N atoms of the indole group in this molecule (N2 and N4) did not participate in the coordination to Cu. The 5th coordination site of Cu was satisfied by binding to the O2 atom from an adjacent tryptophan unit. This O2 atom of tryptophan coordinated to another Cu center at the other end of the amino acid sequence, thus serving as a bridge between Cu centers and creating a one-dimensional polymer. Noticeably, O4, a carboxylate oxygen not coordinated to any metal center, formed H-bonding interactions with the H-atoms of NH₂ (N1···H···O4). The O1 atom also formed H-bonding interactions with the amino group

at the other end, N1···H···O1, which resulted in an unsaturated penta-coordinated Cu(II) center that was active in cycloaddition reactions. Moreover, the role of these unbound O4 and N4 atoms was beneficial for cycloaddition reactions as they were electron-rich Lewis base sites. Structural details are provided in the supporting information.

Scheme 1 describes a plausible mechanism for the cycloaddition reaction of an epoxide and CO₂ using CuTrp and TBAB. The reaction begins with the activation of the epoxide oxygen by the active Lewis acidic Cu(II) center of CuTrp. Concomitant-

Table 3
Catalytic activity of CuTrp for various epoxides.

Entry	Epoxide	Conversion (%)	Selectivity (%)
1	Epichlorohydrin	98.6	99.1
2	Allylglycidyl ether	89.6	97.6
3	Propylene oxide	96.8	98.6
4	Styrene oxide	83.6	97.5
5	Cyclohexene oxide	35.0	96.7

Reaction conditions: CuTrp = 0.83 mol%, TBAB = 0.83 mol%, Epoxide = 25.5 mmol, T = 100 °C, t = 9 h, P_{CO_2} = 1.2 MPa.

Fig. 8. (a) Representation of coordination around Cu in mercury structure visualization software (brown: copper, red: oxygen, blue: nitrogen, grey: carbon, white: hydrogen) and (b) The 1-D polymer growing as a helix (repeating Cu–O1–C1–O2–Cu linkages).

Scheme 1. Plausible mechanism of cycloaddition reaction catalyzed by CuTrp and TBAB.

ly, the Br[−] ion of TBAB attacks the least-hindered β-carbon of the epoxide, leading to epoxide ring opening. Subsequently, the O[−] of the opened-ring intermediate attacks the carbon atom of CO₂, forming a carbonate complex intermediate. At this point, the nitrogen atom of the indole group can facilitate the polarization of CO₂. Consequently, the intramolecular carbonate–O[−] attack on the carbon atom bonded to the bromide atom results in ring closure, thereby affording a cyclic carbonate with the concomitant regeneration of the original form and geometry of CuTrp and TBAB.

3.4. Hydrothermal stability and reusability

To investigate the hydrothermal stability of the catalyst in water, 0.5 g catalyst and 50 mL water were placed in a 100-mL

Fig. 10. Reusability studies of CuTrp. Reaction conditions: ECH = 25.5 mmol, Cat. = CuTrp (0.212 mmol), Co-cat. = TBAB (0.212 mmol), $T = 80\text{ }^{\circ}\text{C}$, $t = 9\text{ h}$, CO₂ pressure = 1.2 MPa, Semi-batch.

Teflon autoclave vessel and then heated at 100 °C in an oven for a week. This mixture was subsequently filtered and dried. The obtained sample exhibited similar patterns to fresh CuTrp in its XRD and FT-IR spectra (Fig. 9), which demonstrated that the structure of the catalyst was stable under hot water conditions.

The CuTrp catalyst was recovered after a catalytic run by centrifugation and subsequently washed with ethanol and dried in an oven at 100 °C. Thereafter, the catalyst was recycled in three catalytic cycles. The catalyst did not lose any activity, as shown in Fig. 10, and exhibited a similar performance in the cycloaddition reaction even after three catalytic runs, with only a 2% reduction in the conversion of ECH. The XRD and FT-IR spectra of the recycled catalyst (Fig. 11) displayed the same features as those of the fresh catalyst. The ICP-OES analysis of the reaction mixture after recovery of the catalyst revealed only 40 ppm of Cu ions in the product mixture (i.e., catalyst leaching of only 0.08%).

Fig. 9. XRD patterns (a) and FT-IR spectra (b) of fresh CuTrp and after hydrothermal treatment.

Fig. 11. XRD patterns (a) and FT-IR spectra (b) of fresh CuTrp and recovered CuTrp after 3rd reuse.

4. Conclusions

An amino-acid-based copper-tryptophan complex CuTrp MOF was synthesized by an efficient direct-mixing method under mild conditions and characterized using several analytical methods (XRD, FT-IR, TGA, XPS, FE-SEM, ICP-OES). In a synergistic manner, the CuTrp catalyst and a quaternary ammonium salt cocatalyst (TBAB) were employed for the synthesis of cyclic carbonates from epoxides and CO₂. The optimal conditions for the cycloaddition reaction were 80 °C for 9 h and 1.2 MPa of CO₂ pressure, which resulted in excellent ECH conversion and ECHC selectivity. A plausible mechanism involves the penta-coordinated Cu center of CuTrp complex as an active Lewis acidic site, whereas the nucleophilic bromide anion from TBAB assists in the ring-opening of the epoxide. The catalyst also exhibited good hydrothermal stability and a slight improvement in the catalytic activity upon the addition of water. Furthermore, the catalyst retained its activity even after three cycles with only 0.08% leaching of Cu ions.

Supporting Information

The details of Cu-Trp structure is included in the supporting information.

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Graphical Abstract

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Cycloaddition of CO₂ with epoxides by using an amino-acid-based Cu(II)-tryptophan MOF catalyst

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An amino-acid-based Cu-containing MOF, CuTrp (Trp = L-tryptophan) was synthesized by direct mixing in methanol. The CuTrp showed good catalytic activity and recyclability in the synthesis of cyclic carbonates from epoxides and CO₂.

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基于氨基酸的Cu(II)-色氨酸MOF催化剂上环氧化物与CO₂环加成反应

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摘要: 由天然的/生物单元(氨基酸)构成的金属有机框架材料(MOFs)具有自然属性和丰富的酸/碱位和官能团,因而可用于CO₂化学中。本文报道了氨基酸系含铜 MOF(CuTrp, Trp = L-色氨酸)的催化效率。以甲醇为溶剂,在室温采用直接混合法合成了 CuTrp 催化剂,该方法具有很高的能量效率。采用 X 射线衍射、红外光谱、热重分析、电感耦合等离子体发射光谱法、扫描电镜和 BET 分析等手段对该催化剂进行了表征。采用环氧化物与 CO₂ 环加成制备环状碳酸酯反应评价了 CuTrp 催化剂活性。结果表明,在无溶剂条件下, CuTrp 催化剂可与四丁基溴化铵助催化剂发生协同作用。通过条件实验确定了优化的反应条件,并基于该实验结果和前期的密度泛函理论计算结果提出了反应机理。另外, CuTrp 催化剂在水中也表现出令人满意的稳定性,可重复使用三次以上而活性无明显下降。

关键词: 金属有机框架材料; 氨基酸; 铜-色氨酸; 直接混合; 二氧化碳; 环状碳酸酯

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