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Lignin modified by deep eutectic solvents as green, reusable, and bio-based catalysts for efficient chemical fixation of CO₂

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Abstract: Lignin is a biodegradable, abundant and rene vable natural polymer on earth. In this study, deep eutectic solvents (DESs)-moining lignin heterogeneous catalysts were prepared for the first time *via* a facile ac.1-base interaction between choline chloride (ChCl) and *p*-aminobenzoic acid (PABA) or its derivatives, which were used to efficiently catalyze the cycloaddition of CO₂ and terminal epoxides under green and mild conditions. Among them, lignin-ChCl-PABA was found to exhibit the highest catalytic activity for the cycloaddition of epoxides in the presence of 1.0 MPa of CO₂ while retaining high selectivity, which far outperformed those achieved on the homogeneous ELSs catalytic system. A series of cyclic carbonates could be obtained in high yiekle (90-99%), and lignin-ChCl-PABA was stable and reusable for the cycloaddition (84% yield after 5 recycles). The attaching DES of ChCl/PABA one the functional lignin increased the catalytic activity and also made the catalyst eacier to recycle from the reaction mixture. The -OH and -NH₂ groups on the surface of lignin-ChCl-PABA played a very important role in the acceleration of the cycloaddition reaction under solvent free conditions.

Keywords: Lignin; Bio-based catalyst; Deep eutectic solvents; CO₂; Cyclic Carbonates

1. Introduction

Climate change and global warming became major issues for society in the last few years. CO_2 is a major greenhouse gas and the increasing emission of CO_2 related to global warming. Although CO_2 is a major cause of global warming, it is a renewable, abundant, non-toxic, easily available C1 resource to produce valuable chemicals,

which promotes the carbon cycle in nature [1-4].Chemical conversion and utilization of CO_2 has become an important part of green and sustainable chemistry and has attracted worldwide attention in recent years [5-10]. Up to now, a series of valuable chemicals have been synthesized from CO_2 [11-15], such as cyclic carbonates, alkynyl acids, carboxylic acid and its derivatives, carbonyl compounds, formic acid, and others. Among them, cyclic carbonates are important chemical products with good biodegradability, solubility and other physical properties. Nowadays, cyclic carbonates have been widely applied as clean polar solvents, monomers for synthesis of polymeric materials, chemical intermediates, electrolytes in lithium-ion batteries with high energy density [16-18].



Scheme 1. General methods for synthesis of cyclic carbonates.

In general, the a^{n} the following methods to synthesize cyclic carbonates: (1) cyclization of diols $ah CO_2$; (2) oxidative carbonylation of olefins; (3) cyclization of diols with urea; (4) cycloaddition of epoxides with CO_2 (**Scheme 1**). CO_2 has many advantages, such as abundant reserves, low cost, easy availability and environment friendliness. Therefore, cycloaddition reaction using epoxides as starting material and CO_2 as C1 building block is an important method to synthesize cyclic carbonates [19]. Because of its high atom economy and no by-products, cycloaddition of epoxides with CO_2 meets the requirements of green chemistry and sustainable social development, so it has been widely studied in chemical synthesis. However, CO_2 has

high catalytic activity are needed to promote the efficient conversion of CO_2 .

Over the past decades, numerous homogeneous and heterogeneous catalysts have been used to perform the cycloaddition reaction, such as ionic liquids [20-25] or ionic polymers [26-28], metal oxides [29, 30], organometallic complexes [31-34], metal organic frameworks [35-41], porous materials [42-48], etc. Unfortunately, some heterogeneous catalysts are made from non-renewable sources and composed of non-biodegradable materials, which will result in environmental and security issues. In addition, traditional ionic liquids homogeneous catalytic systems still show shortcomings, such as high cost and low biodegradebingy, which limit their applications in real chemical and large scale industria¹. Therefore, a highly efficient, environmental and easily prepared catalytic system is still highly desirable for chemical fixation of CO_2 to cyclic carbonates.

In recent years, DESs have been widely used as a novel class of ILs owing to some prominent environmentally benign features [49-57]. DESs not only retain the similar physicochemical properties of ILs, but caso have some excellent nature, such as being easy to prepare from cheap and easily available components, low cost, environmentally benign and good chemical stability. As far as we knew, only few articles on the cycloadditic $n \rightarrow f CO_2$ with epoxides to produce cyclic carbonates in DESs catalytic system wer tound [58-61]. For example, Lü et al. have studied the cycloaddition of CO when epoxides in ChCl-based DESs catalytic system [58]. It was found that ChCl-ba ed DESs catalytic system exhibited good activity in the cycloaddition reaction in the absence of any additives under solvent- and metal-free conditions. In addition, the same group had prepared L-proline/propanedioic acid/ZnBr₂ DESs system to catalyze the cycloaddition reaction of CO₂ with epoxides [59]. The results showed that the DESs system exhibited good activity and selectivity for the cycloaddition reaction. However, this catalytic system contained toxic metal, which could cause environmental pollution. Furthermore, in the above homogeneous catalytic systems, EDSs and ZnBr2 were difficult to separate from the products and more cumbersome separation procedures were needed. To sum up, an ideal solution is to use renewable and biodegradable support materials as carriers and load DESs as

green and efficient catalysts for the chemical conversion of CO₂.

It has been reported that hydrogen bonding between functional groups, such as hydroxyl [62], carboxyl [63], or amino groups [64] and epoxides plays an important role in the chemical fixation of CO_2 into cyclic carbonates, which was helpful for the further ring opening of epoxide substrates. Therefore, the introducing these functional groups into the support of heterogeneous catalysts can effectively improve their catalytic activity towards the cycloaddition reaction. Lignin is one of the most abundant natural resource on earth. It is amorphous in structure and contains a large number of phenolic hydroxyl groups, which can be further cubmically modified [65, 66]. Because of the biocompatibility, nontoxicity, biouegradability, lignin-based functional materials have been widely applied in many research areas, such as bioadsorbents, thermoset polymers, etc [67-72].

In this study, DESs-modified lignin heterogeneous catalysts were prepared for the first time *via* a facile acid-base interaction between ChCl and PABA or its derivatives, which were used to efficiently catalore the cycloaddition of CO₂ and terminal epoxides under green and mild conditions (Figure 1). Because there are lots of hydroxyl and amino groups, the obtained lignin-ChCl-PABA was found to act as an efficient and reusable catalyst in the cycloaddition of terminal epoxides in the presence of 1.0 MPa of CO while retaining high selectivity, which far outperformed those achieved on the homogeneous EDSs catalytic system [53,54]. A series of cyclic carbonates could be obtained in high yields (90-99%), and lignin-ChCl-PABA was stable and reusable for the cycloaddition reaction (84% yield after 5 recycles). The attaching DES of ChCl/PABA onto the functional lignin increased the catalytic activity and also made the catalyst easier to recycle from the reaction mixture. The -OH and -NH₂ groups on the surface of lignin-ChCl-PABA played a very important role in the acceleration of the cycloaddition reaction under solvent free conditions.



Fig. 1. An illustration for the preparation of DE modified lignin-ChCl-PABA catalyst and its application in heterogeneous catalysis of CO₂ chemical fixation.



Scheme 2. Synthetic route of DESs-modified lignin heterogeneous catalysts through hydrogen bonds interaction.

2. Experimental

2.1 Chemicals and reagents

Lignin was purchased from Macklin Reagent Company (dealkaline, product number: MFCD00147441). Epichlorohydrin, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), NaOH, choline chloride, benzoic acid and its derivatives were obtained from Aladdin Reagent Company. Dichloromethane, ethyl acetate, and tetrahydrofuran were obtained from Xiamen Lvyin Reagent Company. All chemicals were obtained commercially and used as received, without further purification. CO₂ (99.99%) was purchased from Xiamen Kongfente Gas Co., Ltd.

2.2. Instruments

The chemical fixation of CO_2 with different eporticles was monitored by TLC method. FT-IR spectra were registered on a Nicolet Nexus FT-IR instrument at 4 cm⁻¹ resolution and 32 scans and samples for FT-IR a valy is were prepared using the KBr press disc method. ¹H NMR spectra were circle on a Bruker AVANCE III-500 spectrometer. TGA was run on TG instructents DTG-60H, samples were heated from 25 to 800°C at a heating rate of 20 ° min⁻¹ under an Ar atmosphere. SEM images were obtained using a SU8020 (Huechi, Japan) scanning electron microscope.

2.3. Preparation of epoxy-functions fized lignin-EPI

Lignin (5.0 g), NaOH (4.3 \gtrsim 107 mmol), and distilled water (25.0 mL) were added into a 3-neck round botton. flask, and then epichlorohydrin (50.0 mL) was add to the mixture, and then reacted for 3 hours at 80°C under nitrogen condition. The black solid product could up obtained after simple filtration and washed with water. The purified product was dried under vacuum at 50°C for 8 hours for further application.

2.4. Synthesis of ChCl-functionalized lignin-ChCl

ChCl (8.0 g) was added into 100.0 mL of aqueous solution containing 4.0 g of lignin-EPI and the mixture was magnetically stirred at 30°C for 24 hours. Next, DBU (1.0 g) was added to the dispersion and continued for 6 hours at 30°C. The obtained lignin-ChCl were washed two times with EtOH and water to remove the excess choline chloride and DBU, and then dried in vacuo for 12 hours.

2.5. Synthesis of lignin-based catalysts

The obtained product lignin-ChCl was mixed with benzoic acid or its derivative in

a mass ratio of 1:1 and placed in a 250 mL round bottom flask. After the reaction for two hours at 80°C, 100.0 mL de-ionized (DI) water was added and then the mixture was magnetically stirred at 80°C for 24 hours. After simple filtration and washing with EtOH, the desired lignin-acid catalysts dried at 60°C for further use.

2.6. A general and green procedure for the synthesis of cyclic carbonates

All the chemical fixation of CO_2 into cyclic carbonate were carried out in a Teflon-lined stainless-steel reactor (20 mL) equipped with a pressure gauge and a magnetic stirrer. In the typical procedure, epoxide (10.0 mmol), lignin-DES catalyst (100 mg), and the co-catalyst TBABr (1.0 mmol) were placed into the reactor. Then the reactor was purged 3 times with CO_2 . Subsequently, the reactor was heated to the desired temperature and pressure. After completion of the reaction, the reactor was placed into the reaction mixture, and the the lignin-DES catalyst was recovered by filtration. Subsequently, the obtained the two times with EtOH and dried under vacuum for the further. The further the second states the further the furt

2.7 Spectroscopic data of the obtained products

4-(Phenoxymethyl)-1,3-dievol.vr.-2-one (Table 2, entry 1): FT-IR (KBr disc) cm⁻¹: 1788 (C=O), 1167 (C-O), 052(C-O), 754, 692; ¹H NMR (500 MHz, CDCl₃) δ : 7.33 (m, 2H), 7.04 (t, *J*=7.6 Чz, H), 6.93 (d, *J* =7.8 Hz, 2H), 5.05 (m, 1H), 4.63 (t, *J*=8.3 Hz, 1H), 4.56 (dd J= 5.8. 8.6 Hz, 1H), 4.26 (dd, *J*=4.3, 10.5 Hz, 1H), 4.17 (dd, *J*=3.6, 10.5 Hz, 1H).

4-((O-tolyloxy)methyl)-1,3-dioxolan-2-one (Table 2, entry 2): FT-IR (KBr disc) cm⁻¹: 1789 (C=O), 1163 (C-O), 1049 (C-O), 732, 703; ¹H NMR (500 MHz, CDCl₃) δ: 7.19 (m, 2H), 6.95 (t, *J*=7.0 Hz, 1H), 6.80 (d, *J* =8.6 Hz, 2H), 5.08 (m, 1H), 4.66 (t, *J*=8.3 Hz, 1H), 4.60 (dd, *J*=5.3, 8.4 Hz, 1H), 4.29 (dd, *J*=3.6, 10.7 Hz, 1H), 4.16 (dd, *J*=3.0, 10.6 Hz, 1H), 2.24 (s, 3H).

4-(Hydroxymethyl)-1,3-dioxolan-2-one (Table 2, entry 3): FT-IR (KBr disc) cm⁻¹: 3416 (OH), 1770 (C=O), 1170 (C-O), 1048 (C-O), 732, 715; ¹H NMR (500 MHz, CDCl₃) δ: 4.83 (m, 1H), 4.54-4.49 (m, 2H), 3.84-3.73 (m, 2H).

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4-((Allyloxy)methyl)-1,3-dioxolan-2-one (Table 2, entry 4): FT-IR (KBr disc) cm⁻¹: 1794 (C=O), 1735 (C=C), 1163 (C-O), 1046 (C-O), 734, 714; ¹H NMR (500 MHz, CDCl₃) δ: 5.86 (m, 1H), 5.28-5.21 (m, 2H), 4.83 (m, 1H), 4.50-4.39 (m, 2H), 4.05 (m, 2H), 3.69-3.61(m, 2H).

4-(Butoxymethyl)-1,3-dioxolan-2-one (Table 2, entry 5): FT-IR (KBr disc) cm⁻¹: 1789 (C=O), 1166 (C-O), 1047 (C-O), 734, 714; ¹H NMR (500 MHz, CDCl₃) δ: 4.81 (m, 1H), 4.50-4.40 (m, 2H), 3.68-3.61 (m, 2H), 3.51 (m, 2H), 1.56 (m, 2H), 1.37 (m, 2H), 0.92 (t, *J*=7.39, 3H).

4-(((2-Ethylhexyl)oxy)methyl)-1,3-dioxolan-2-one (Tabla 2, entry 6): FT-IR (KBr disc) cm⁻¹: 1788 (C=O), 1166 (C-O), 1043 (C-O), 722 7.14; ¹H NMR (500 MHz, CDCl₃) δ: 4.81 (m, 1H), 4.49-4.39 (m, 2H), 3.66-3.5 (m, 2H), 3.39 (m, 2H), 1.50 (m, 1H), 1.42-1.19 (m, 8H), 0.92 (m, 6H).

4-(Chloromethyl)-1,3-dioxolan-2-one (Tz'z': 2, entry 7): FT-IR (KBr disc) cm⁻¹: 1812 (C=O), 1264, 1162 (C-O), 1073 (C-C), 751, 702; ¹H NMR (500 MHz, CDCl₃) δ: 4.99 (m, 1H), 4.58 (t, *J*=8.6 Hz, 1H), ¹ ? J (m, 1H), 3.81-3.72 (m, 2H).

4,4'-((Ethane-1,2-diylbis(oxy)), 's(methylene))bis(1,3-dioxolan-2-one) (Table 2, entry 8): FT-IR (KBr disc) cm⁻¹. '7;,4 (C=O), 1170 (C-O), 1048 (C-O), 733, 714; ¹H NMR (500 MHz, CDCl₃) δ . 4.85 (m, 2H), 4.53-4.44 (m, 4H), 3.76-3.58 (m, 6H).

4,4'-(1,3-Phenylenebis(, 'hane-2,1-diyl))bis(1,3-dioxolan-2-one) (Table 2, entry 9): FT-IR (KBr disc) cm⁻¹: 1790 (C=O), 1158 (C-O), 1051 (C-O), 731, 702; ¹H NMR (500 MHz, CDCl₃) ⁵: 7.22 (t, *J*=8.2 Hz, 2H), 6.59-6.47 (m, 3H), 5.04 (m, 2H), 4.62-4.52 (m, 4H), 4.24 (m, 2H), 4.12 (m, 2H).

4-Phenyl-1,3-dioxolan-2-one (Table 2, entry 10): FT-IR (KBr disc) cm⁻¹: 1789 (C=O), 1163 (C-O), 1065 (C-O), 732, 697; ¹H NMR (500 MHz, CDCl₃) δ : 7.45-7.37 (m, Ar-H, 5H), 5.69 (t, *J*=8.4 Hz, 1H), 4.81 (t, *J*=8.2 Hz, 1H), 4.35 (t, *J*=8.2 Hz, 1H).

3. Results and Discussion

3.1 Synthesis and characterization of lignin-ChCl-PABA catalyst

The detailed preparation route of the catalyst is shown in Scheme 2. For the synthesis of epoxy-modified lignin, lignin was reacted with epichlorohydrin to

produce the lignin-EPI. In the next step, the lignin-ChCl were prepared by reaction of lignin-EPI with ChCl in the presence of DBU in aqueous solution at room temperature. The lignin-ChCl was then reacted with PABA or its derivatives to yield lignin-based heterogeneous catalysts.

The properties of the prepared lignin-ChCl-PABA heterogeneous catalyst were characterized by FT-IR, SEM, TGA, and elemental analysis. The FT-IR spectra of original lignin, ChCl, and lignin-ChCl are shown in Figure 2. The FT-IR spectra of original lignin, PABA, and the lignin-ChCl-PABA catalyst are shown in Figure 3. The FT-IR spectra of lignin, EPI, and lignin-EPI are shown in Figure S1. In the FT-IR spectrum of Figure 2a, original lignin sample exhibited a broad peak around 3351 cm⁻¹, attributed to the aliphatic and phenolic hydrox 'l groups on the surface of lignin sample. As shown in Figure S1b, characteristic bso ption peaks of epoxy appear at 1265, 905, 852 cm⁻¹ in epichlorohydrin molecule. In the FT-IR spectrum of Figure S1c, the lignin-ChCl-PABA catalyst exhil 'ted characteristic absorption peaks at 1263, 905, 859 cm⁻¹, which proved that $e_{p_v} x^{-1}$ groups had been grafted onto the surface of lignin successfully. As could be seen, characteristic absorption peaks of ChCl molecule appear at 3259, 2895, 1.35 cm⁻¹ (Figure 2b). Compared to the FT-IR spectrum of original lignin (Figure 2a), some new absorption peaks at 3259, 2896, and 1140 cm⁻¹ appears (Figure ?c), which belong to the stretching vibration of C–H bond and the bending vibration of C-N bond of the grafted ChCl, respectively. It was an obvious indication to: the presence of ChCl grafted onto the surface of lignin-ChCl. In the FT-IR spectrum (Figure 3d), characteristic absorption peaks appear at 1663, 1601, 1521, 842, and 771 cm⁻¹ in PABA molecule. After the acid-base interaction between PABA and ChCl-modified lignin, the characteristic absorption bands of PABA (1603, 1508, 844, and 775 cm⁻¹) appeared in the spectrums of the lignin-ChCl-PABA catalyst (Figure 3e). These results suggest that PABA had been grafted onto the surface of lignin-ChCl successfully.



Fig. 2. FT-IR spectra of (a) lignin, (b) CnCl, and (c) lignin-ChCl.



Fig. 3. FT-IR spectra of (a) lignin; (d) PABA; (e) lignin-ChCl-PABA.

The TGA curves of original lignin, lignin-ChCl-PABA, and the recycled lignin-ChCl-PABA catalyst, are shown in Figure 4. Experiments were performed at heating rate of 10°C/min in N₂ atmosphere up to 800°C. It was clear that the above three samples showed similar thermal stability. The TGA curves show the first weight losses around 3.5% at 100°C, which correspond to the loss of the physical adsorbed water molecules from the samples. At the same time, Figure 4 demonstrates all

lignin-based products show a two-step degradation profile in the range of 200–300 and 300–500°C. An obvious weight loss between 200 and 300°C is associated with the breaking of aliphatic chains in the lignin-based samples. While the second broad mass loss between 300 and 500°C is the breaking of aromatic C–C bonds. Fortunately, the obtained lignin-ChCl-PABA catalyst is thermally stable up to 200°C, which could meet the application requirements in heterogeneous catalysis for CO₂ chemical fixation with epoxides. Even after five cycles of recycling, the thermal stability of the recycled catalyst is still good, and there is no significant difference with the newly prepared catalyst under 200°C. However, the weight loss on the catalyst after five times recycling is obvious above 300°C, which may here the loss of lignin and other components in the catalyst during recycling.



Fig. 4. TGA of (a) original lignin; (b) lignin-ChCl-PABA; (c) lignin-ChCl-PABA after five cycles.

The morphology of original lignin and the obtained lignin-ChCl-PABA catalyst was characterized by SEM (Figure 5). As could be seen, the original lignin exhibited as irregular plates but the lignin-ChCl-PABA catalyst exhibited layered structure with rough surfaces in micrometer scale. Lignin-ChCl-PABA showed much looser layered structure indicating the chemical modification decreased the irregular plates size of lignin and could improve its dispersibility. The looser layered structure with rough

surfaces would be helpful to improve the catalytic activity of the catalyst for CO_2 chemical fixation with epoxides.



Fig. 5. The SEM images of original lignin (A) and the lignin-ChCl-PABA catalyst (B).

3.2 Catalytic performance of DESs-modified lignin catalysts

We then examined the catalytic activity of the different DESs-modified lignin catalysts by performing the CO₂ chemical fixation with glycidyl phenyl ether (Table 1). We used glycidyl phenyl ether is a starting substrate to produce the corresponding carbonate with CO₂ (1.0 M⁺a) at 110°C in the presence of DESs-modified lignin catalyst (100 mg). Low yields were observed when CO₂ chemical fixation was performed by using either ¹¹gnin-ChCl/TBABr, or TBABr as catalyst (<59%, entries 1 and 2, Table 1). Nowmer, CO₂ chemical fixation proceeded smoothly when using lignin-ChCl-acid as catalyst and TBABr as co-catalyst. As shown in Table 1, the moderate to good carbonate yields of 67-87% were obtained by the catalyst lignin-ChCl-BA, lignin-ChCl-PMBA, lignin-ChCl-PEBA, lignin-ChCl-PNBA, or lignin-ChCl-PABA (100 mg) after 2 hours by using TBABr as co-catalyst.

Among these heterogeneous catalysts, lignin-ChCl-PABA showed the highest catalytic activity, which was mainly due to the positive role of PABA supported by acid-base interaction between ChCl and PABA on the surface of lignin-ChCl-PABA. Due to the presence of amine groups on lignin-ChCl-PABA catalyst, chemically inert CO₂ molecules can be activated. The detailed reaction mechanism is shown in the

later mechanism section. As shown in Table 1 (entries 8 and 9), increasing the amount of lignin-ChCl-PMBA from 50 to 100 mg increased the cycloaddition yield from 81% to 99%. Obviously, the yield of styrene carbonate rose with increasing catalyst amount. However, further increase in catalyst amount did not enhance the yield of styrene carbonate apparently. Under the same experimental conditions, when the amount of catalyst was increased to 150 mg, the yield still remained 99% (entry 10).

 Table 1. Effect of different time, co-catalyst and temperature on the synthesis of cyclic carbonate.



			·R/Br			Isolated
Entry	Catalyst	Cat. mg	(mmol)	Time (h)	Temp (°C)	Yield
						(%)
1	None	N ne	1	2	110	28
2	Lignin-ChCl	100	1	2	110	59
3	Lignin-ChCl-B.	100	1	2	110	72
4	Lignin-ChC ¹ PML	100	1	2	110	70
5	Lignin-C. Cl-1 டீBA	100	1	2	110	67
6	Lignin-ChCI-PNBA	100	1	2	110	75
7	Lignin-ChCl-PABA	100	1	2	110	87
8	Lignin-ChCl-PABA	50	1	3	110	81
9	Lignin-ChCl-PABA	100	1	3	110	99
10	Lignin-ChCl-PABA	150	1	3	110	99

^a Reaction conditions: glycidyl phenyl ether (10.0 mmol), CO₂ (1.0 MPa).

3.3 Effects of reaction conditions

From the data in Table 1, we can know that the catalyst lignin-ChCl-PABA with TBABr showed the highest catalytic activity among the tested catalysts. Therefore,

lignin-ChCl-PABA was further investigated to get the optimized reaction conditions. In detail, the effects of the reaction temperature and reaction time on the yields were then discussed, and the obtained results were shown in Figure 6. As shown in Figure 6a, the reaction temperature had a positive impact on the yield of the corresponding carbonate. The yield of the carbonate product increased with the increasing reaction temperature in the range of 70–110°C (65%-87%) and levels off upon further increasing temperature to 120°C (87%). The impact of reaction time under the condition of 110°C and 1.0 MPa of CO₂ could also be obtained in Figure 5b. As shown in Figure 6b, increasing the reaction time from 1 to 2, 3, 4, and 5 hours increased the yield of the carbonate product from 77% 229%. Obviously, glycidyl phenyl ether was almost completely converted int. the desired carbonate within 3 hours.



Fig. 6. Effect of reaction parameters on CO_2 chemical fixation over the lignin-ChCl-PABA caulyst: (a) temperature on yield; (b) reaction time on yield. Reaction conditions. epoxide (10.0 mmol), CO_2 (1.0 MPa), TBABr (1.0 mmol), weight of lignin-ChCl-PABA (100 mg).

3.4 Cycloaddition of CO₂ with various epoxides

A promising heterogeneous catalyst not only has high catalytic activity but also has a broad substrate scope. To demonstrate the practicality and extensiveness of this lignin-ChCl-PABA catalyst, the cyclization of different terminal epoxides with CO_2 was investigated under the optimum reaction conditions. The corresponding results are summarized in Table 2. As shown in Table 2, all of the mono-substituted terminal epoxide substrates underwent the transformation smoothly with excellent yields of

isolated cyclic carbonates (entries 1–10, 90-99% yields). Even for the epoxides with long alkyl chain, the reaction could also proceed smoothly with excellent yields (91 and 96% yields, entries 5 and 6). The excellent yields are likely due to the presence of highly electron withdrawing atoms, such as oxygen and chlorine atoms. However, for cyclohexane oxide, due to its steric hindrance around the epoxide ring, the reaction activity is not high, resulting in a moderate yield (entry 11, 59% yield). Aside from its broad substrate scope and excellent catalytic performance, good tolerance towards various functional groups (such as hydroxyl, alkenyl, halogen, alkoxy, etc.) are remarkable features of this bio-based lignin-ChCl-PABA catalyst, which exhibiting its potential applicability in scaled-up production of cyclic carbonates.

Table 2. CO₂ fixation into cyclic carbonates catalyze ' by ngnin-ChCl-PABA.^a

Entry	Substrate	Prc Juc'	Selectivity (%)	Isolated Yield (%)
1			> 99	99
2			> 99	99
3	но	но	> 99	96
4	~O		> 99	94
5	H ₃ C ⁰	H ₃ C O O O O	> 99	96
6	H ₃ C O O	H ₃ C CH ₃ C CH ₃ C	> 99	91
7	CI		> 99	98

Q	+ 00-	TBABr	o~(
R	. 002	Lignin-ChOI-PABA	R



^a Reaction conditions: epoxide (10.0 mmol), CO₂ (1.0 MP₂), TBABr (1.0 mmol), lignin-ChCl-PABA (100 mg).

3.5 Recyclability of the bio-based lignin-ChCl-P^BA catalyst

A promising heterogeneous catalyst not only has the outstanding catalytic activity but also has good reusability. Recycling Cype iments were conducted in order to investigate the reusability of lignin-ChC'-Pr-BA in the chemical fixation of CO₂ into cyclic carbonate with glycidyl phenyl ether under 110°C and 1.0 MPa. Obviously, the catalytic activity of lignin-ChC' PALA was well retained during the recycling test after separated from the reaction mixture through simple filtration. As shown in Figure 7, the catalytic activity of lignin-ChCl-PABA was not decreased after it was used after five times with the corresponding cyclic carbonate yield around 84%. At the same time, the selectivity of cycloaddition reaction remained constant after five cycles, which showed lignin-ChCl-PABA have a quite stable catalytic performance.



Fig. 7. Recyclability and selectivity of lignin-ChCI-PABA. Reaction conditions: glycidyl phenyl ether (10.0 mmol), lignin-ChCI-PABA (100 mg), TBABr (1.0 mmol), CO₂ pressure (1.0 MPa), reaction time (3 h) and ten perature (110 $^{\circ}$ C).

Chemical stability of heterogeneous values is an important aspect in most chemical processes. In order to eviluate the stability of the lignin-ChCl-PABA catalyst after five times of recycling unt, reused catalyst has been characterized by FT-IR and TGA techniques. FT-IR prectra of the fresh lignin-ChCl-PABA catalyst (Figure 8a) and the reused lightin-CnCl-PABA catalyst after five times recycling are shown in Figure 8b. As shown in Figure 8b, the characteristic absorption bands of 4-aminobenzoic acid (1(93, 1508, 844, and 775 cm⁻¹) still appeared in the spectrum of the reused lignin-ChC) PABA catalyst, which indicates excellent stability of lignin-ChCl-PABA fire five times recycling. Compared with the fresh lignin-ChCl-PABA catalyst, the new absorption band at 1805 cm⁻¹ appeared, which belongs to the bending vibration of C=O bond in cyclic carbonate product (adsorbed in lignin-ChCl-PABA). The other FT-IR peaks of the reused catalyst were in good agreement with the fresh catalyst. After five cycles of recycling, the FT-IR spectrum of the recycled lignin-ChCl-PABA did not change obviously, indicating that lignin-ChCl-PABA was very stable. Additionally, the thermal stability of the reused lignin-ChCl-PABA catalyst after five times recycling was as good as that of the fresh catalyst under 200°C (Figure 4b and 4c). Therefore, it did not affect its practical

application when used at 110°C.



Fig. 8. FT-IR spectra of lignin-ChCl-PABA (a) and the reused lignin-ChCl-PABA after five cycles (b).

3.6 Scale-up procedure for the synthes is of cyclic carbonate

In order to further study the procleability of the bio-based heterogeneous catalyst lignin-ChCl-PABA, the multigeneous catalyst eraction on the lignin-ChCl-PABA mediated model cycloaddition of glyciayl phenyl ether with CO₂ was also conducted. The procedure was carried out with lignin-ChCl-PABA in a Teflon-lined stainless-steel reactor, and the reaction substrates were magnified 2, 4, 6, and 8 times, respectively. The obtained results showed that the reactions proceeded smoothly without any extension of reaction time or additional catalyst dosage, to afford an excellent product yield (80 mmol, product 14.5 g in 93% yield, Table 3). Combining the results of the scaled-up experiment and the advantages of the lignin-ChCl-PABA catalyst itself, such as high catalytic activity, simple preparation method, renewable and degradable performance, it is obvious that lignin-ChCl-PABA is expected to be applied in industrial production.

Table 3. The results of scaled-up experiment.^a

		<ĭ + co₂ —	TBABr		
Entry	Scale (mmol) ^b	TBABr (mmol)	Catalyst (g)	Yield (%) ^c	Product (g)
1	10	1	0.1	99	1.9
2	20	2	0.2	97	3.8
3	40	4	0.4	94	7.3
4	60	6	0.6	93	10.9
5	80	8	0.8	93	14.5

^a Reaction conditions: 1.0 MPa CO₂ initial pressure, comperature 110 °C, 3 h; ^b glycidyl phenyl ether; ^c Isolated yield.

In order to examine the activity and capacitity of the present catalytic system, we compared the catalytic activities of 'gn a-ChCl-PABA in the CO₂ chemical fixation into cyclic carbonate with other reported catalysts (Table 4). As shown in Table 4, the previously reported synthetic m the 4 s suffer from one or more shortcomings, such as longer reaction time (6 h), higher reaction temperature and pressure (150° C, >1.0 MPa), lower yield of product (< 90%). Furthermore, the homogeneous properties of the catalytic systems 1.3 in table 4 make them difficult to separate from the product, limiting their application in industry. It is obvious that our present catalyst lignin-ChCl-PABA snows promising features in terms of high activity (3 h), excellent yield (90%), and mild reaction conditions (110° C, 1.0 MPa).

 Table 4. Comparison of catalytic activity of lignin-ChCl-PABA with several known catalysts.

Entry	Catalyst	Condition	Yield (%)	Ref.
1	EDS (L-pro/PA/ZnBr ₂)	150°C/5 h/1.2MPa	57	73
2	EDS (ChCl-PEG200)	150°C/5 h/0.8MPa	82	74

3	$(EMIL)_2 ZnBr_4$	100°C/1.0 h/3.5 MPa	81	75
4	[HTEA]I	110°C/6 h/2.0 MPa	84	76
5	Lignin-ChCl-PABA	110°C/3 h/1.0MPa	90	This work

3.7 Reaction mechanism

Combining the mechanism reported in previous literatures [62-64] and the structural characteristics of the bio-based lignin-ChCl-PABA catalyst itself, a plausible mechanism for the CO₂ chemical fixation with epoxides over was proposed (Scheme 3). Initially, the hydrogen bond was formed between the oxygen atom in ring of the epoxide compound and the -OH group on the surface of lignin-ChCl-PABA, which was obtained from the ring-opening reaction between epoxide-modified lignin and choline chloride (Scheme 3). In the next step, the nucleophilic reagent bromine anion attacked the β -carbon atom with low steric hindrance of epoxide, which had been activated by hydrogen bond. Beca. se of the presence of the $-NH_2$ group on the surface of lignin-ChCl-PABA, Co, could be adsorbed and activated, resulting in easy insertion of CO₂ into the mermediate to form the corresponding carbonate intermediate. Finally, the acsired cyclic carbonate is generated by the simultaneous intramolecular ring closure and release of bromine anion with regeneration of the lignin-ChCl-PABA catalyst. Thus, the -OH and -NH₂ groups on the surface of lignin-ChCl-PABA played a very important role in the acceleration of the cycloaddition reaction under solvent free conditions.



Scheme 3. A plausible reaction mechanism for CO_2 hemical fixation with epoxide co-catalyzed by lignin-ChCl-PABA and TB. Pc.

4. Conclusions

In conclusion, we have firstly reported several heterogeneous lignin-acid catalysts through the acid-base interaction of ween ChCl on the surface of functional lignin and benzoic acid derivatives, for CC₂ chemical fixation into cyclic carbonates. These lignin-based catalysts exhabited good catalytic activity for the chemical fixation of CO₂ with epoxides under mild conditions, especially for lignin-ChCl-PABA, with excellent catalytic contribution of lignine catalyst amount for 3 hours. A series of cyclic carbonates could be obtained in high yields (90-99%), and lignin-ChCl-PABA catalyst showed good recyclability with little loss in activity even after five catalytic runs (84% yield after 5 recycles). The present methodology provides prominent advantages to previously reported similar catalytic systems for chemical fixation of CO₂ with epoxides including economic viability. The attaching DES of ChCl/PABA onto the functional lignin has increased the catalytic activity and also has made the catalyst easier to recycle from the reaction mixture. The -OH and -NH₂ groups on the

surface of lignin-ChCl-PABA played a very important role in the acceleration of the cycloaddition reaction under solvent free conditions.

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