

The synthesis of spherical polymeric ionic liquid catalyst and its catalysis for CO₂ to dimethyl carbonate

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Abstract

Spherical particle catalysts (PILs-XSS) were synthesized by suspension polymerization, which was characterized by SEM-EDS, FT-IR, TG, and BET-BJH. The characterization results showed that PILs-XSS had a specific core structure, a certain pore size (14.3nm), and surface area size (71.5m²/g), and remained stable at 293.4 °C. The catalyst performance was evaluated by a one-pot synthesis of dimethyl carbonate. The process conditions were optimized in detail. The optimal reaction conditions were as follows: the dosage of PILs-XSS was 2.5 wt %, the CO₂ pressure was 1.5 MPa, the reaction temperature was 100 °C, the reaction time was 4 h, the molar ratio of methanol to propylene oxide (PO) was 3: 1, and the dosage of cocatalyst Na₂CO₃ was 3 wt %. Under the optimum conditions, the conversion of PO was up to 98.8 % and the yield of DMC reached 53.7 %.

The synthesis of spherical polymeric ionic liquid catalyst and its catalysis for CO₂ to dimethyl carbonate by one-pot methods

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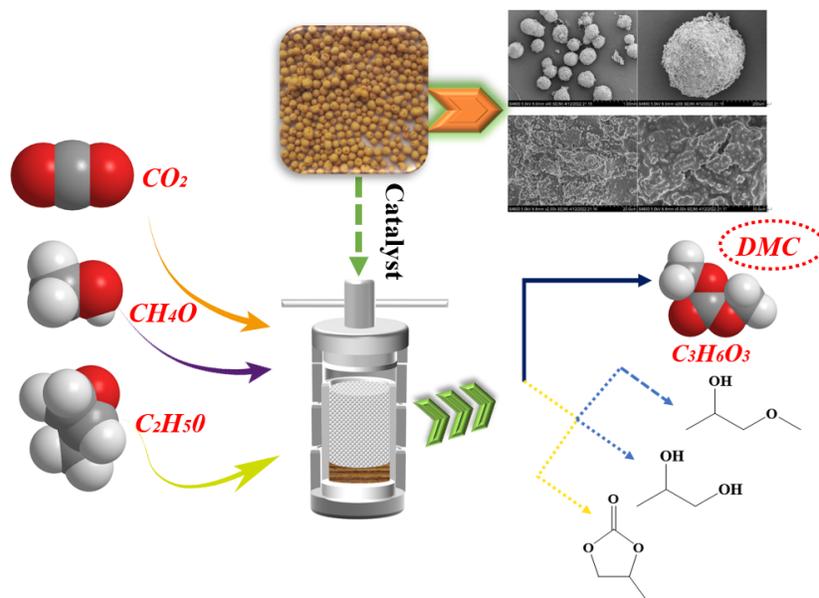
Abstract: Dimethyl carbonate (DMC) is widely used and nontoxic and can replace more dangerous materials such as dimethyl sulfate or methyl chloride. Spherical particle catalysts (PILs-XSS) were synthesized by suspension polymerization, which was characterized by SEM-EDS, FT-IR, TG, and BET-BJH. The characterization results showed that PILs-XSS had a specific core structure, a certain pore size (14.3nm), and surface area size (71.5m²/g), and remained stable at 293.4 °C. The catalyst performance was evaluated by a one-pot synthesis of dimethyl carbonate. The process conditions were optimized in detail. The optimal reaction conditions were as follows: the dosage of PILs-XSS was 2.5 wt %, the CO₂ pressure was 1.5 MPa, the reaction temperature was 100 °C, the reaction time was 4 h, the molar ratio of methanol to propylene oxide (PO) was 3: 1, and the dosage of cocatalyst Na₂CO₃ was 3 wt %. Under the optimum conditions, the conversion of PO was up to 98.8 % and the yield of DMC reached 53.7 %. In addition, the combined catalyst PILs-Na₂CO₃ was easily recovered by filtration in the reaction system. After five times of repeated use, the activity and the shape of the catalyst were almost unchanged, which meant that the catalyst had amazing mechanical strength. This study found that the transesterification catalyst Na₂CO₃ not only had good transesterification efficiency but also promoted the reaction of CO₂.

Keywords: Poly-ionic liquid, CO₂, Dimethyl carbonate, Propylene oxide

Highlights

1. The spherical polymer ionic liquid catalyst was synthesized by suspension polymerization.
2. The particle size of the catalyst is controllable.
3. The catalyst for one-pot synthesis of dimethyl carbonate, the yield is 53.7%.
4. The catalytic activity does not decrease after repeated use for 5 times.

Graphic



Introduction

In recent years, the global temperature has been rising, and the melting of bipolar icebergs has appeared in front of us. CO_2 is considered to be the main reason for these problems. Despite the corresponding measures taken by most countries around the world, CO_2 emissions are increasing year by year [2-3]. Therefore, it is a cutting-edge remedy to achieve carbon neutralization and capture and utilize the emission of CO_2 [4-8].

The special properties of dimethyl carbonate (DMC) determine its wide range of applications. Compared with traditional chemical products, DMC has low toxicity, and high oxygen content makes it appear in fuel oil additives and can be used as a green solvent. With the rapid development of lithium batteries, DMC can be used as an electrolyte for battery additives. Therefore, the wide application of DMC in the chemical industry can be determined. There are many methods for the production of DMC. Some have achieved large-scale applications, such as the phosgene method, but they have obvious shortcomings, such as the generation of harmful substances. Conversion of CO_2 to DMC is a typical carbon neutralization pathway [14-17]. Since CO_2 is abundant, non-toxic, environmentally friendly, and cheap, the direct synthesis of DMC from CO_2 and methanol is a front-end reaction system, but the reaction system absorbs more energy, so it is greatly affected by the conversion rate, and the effect is difficult to make people satisfied [18]. On this basis, the method of introducing an alkylene oxide (ethylene oxide or propylene oxide) for a two-step reaction can largely solve this problem, thereby improving the methanol conversion rate and the yield of DMC. One-pot synthesis of DMC involves two steps: ring addition and transesterification. Cycloaddition is the reaction of CO_2 with propylene oxide to generate propylene carbonate (PC), and transesterification is the transesterification of methanol with propylene carbonate to synthesize DMC and 1,2 - propanediol. Propylene glycol methyl ether as a by-product is produced by dehydration of 1,2-propanediol and methanol.

Methanol is excessive. The consumption of 1,2-propanediol in the product has a certain role in promoting the yield of DMC.

The screening of catalysts is the most important part of the successful activation of CO₂. CO₂ is extremely stable, and electrophilicity is an important way to activate it. In the past, the catalyst is divided into homogeneous and heterogeneous two parts to study. Homogeneous catalysts are mainly ionic liquids for the direct synthesis of DMC from methanol and CO₂. For example, Ashif H. Tamboli et al. [20] synthesized a 10 wt % chitosan/ionic liquid (IL)-catalyst system with hydroxyl and amine groups as nucleophilic and carbon dioxide absorption centers, with a methanol conversion rate of 16.90% and DMC selectivity 98.72%, the catalyst has good catalytic activity, selectivity, and stability, but requires higher pressure to improve the conversion rate and yield, which is a challenge for large-scale production. Heterogeneous catalysts include many: alkali metals, transition metal hydroxides, and supported catalysts [21], such as Ming Liu et al. [22] using K₂CO₃NaBr-ZnO catalyst system, methanol, propylene oxide, and CO₂ one-pot synthesis DMC. The addition of Zn powder improves the selectivity of DMC, but the final selectivity is only 40.2%, which is unfavorable for production. awad Al-Darwish et al. [23] synthesized cerium oxide (CeO₂) with three different shapes (nano-octahedron, nanocube, nanorod) by hydrothermal method, and activated carbonylation reaction of CO₂ and methanol to dimethyl carbonate. ester (DMC), the results show that the shape of the nanostructured ceria affects the yield of DMC, and the catalytic effect is general.

Ionic liquids are commonly used in green production in recent years. For the activated CO₂ reaction, alkali metal halides use the nucleophilic attack of halide ions to perform the first addition reaction [24]. Carrying halide ions in ionic liquids should also have the same effect [25], but for homogeneous reactions, ionic liquid catalysts are too troublesome to recycle and reuse. The emergence of polymeric ionic liquids solves this dispute. It not only inherited the strong catalytic activity, thermal stability, and chemical stability of ionic liquids, but also added the advantages of inorganic catalysts, such as certain mechanical strength, modifiability, and corrosion resistance.

The purpose of this study is to activate CO₂ by one-pot method, conduct a cycloaddition reaction with propylene oxide, and then transesterify to synthesize DMC. The nucleophilic attack of halide ions in the polymerized ionic liquid is used to complete the first step, and the second step uses sodium carbonate as a catalyst for the transesterification of propylene carbonate and methanol. As we know, there are no similar papers in the literature, the polymer ionic liquid catalyst can be easily separated after the reaction. Results from material characterization and reaction testing allowed us to better understand the catalyst's effect on the final conversion of CO₂ to DMC. The resulting products are analyzed by gas chromatography (GC) for detailed optimization of the influencing factors in the catalytic process.

Experimental

2.1 Material

1 - vinylimidazole (99.0 %), 1,2 - dibromoethane (99.0 %), 1,3 - dibromopropane (99.0 %), 1,4 - dibromobutane (99.0 %), 1,5 - dibromopentane (99.0 %), 1,6 - dibromohexane (99.0 %), N, N ' -methylenebisacrylamide, sodium carbonate (98 %), 2, 2 ' -azobisisobutyronitrile (AIBN, 98.0 %), anhydrous ethanol (AR, [?] 99.7 %), ethyl acetate (AR, [?] 99.5) methanol (AR, [?] 99.5 %), propylene carbonate (GC, > 99.0 %), dimethyl carbonate (GC, > 99.0 %), 1,2-propanediol (GC, [?] 99.5 %), propylene glycol methyl ether (GC, [?] 99.5 %), propylene oxide (GC, [?] 99.5 %) were purchased from ALADDIN-E.com. Solvents (methanol, ethanol, etc.) were obtained from Tianjin Chemical Reagent Co. Ltd.

2.2 Catalyst preparation

The preparation of polymeric ionic liquid catalysts is shown in Fig. 1.

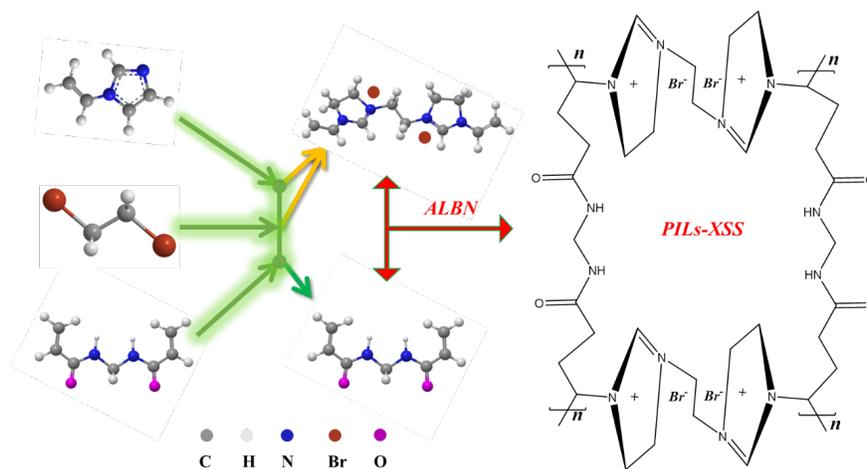


Figure 1 Synthetic route of polymer ionic liquids

2.2.1 Synthesis of ionic liquid monomer

1 - vinyl imidazole, 1,2 - dibromoethane, and N, N ' -methylene bisacrylamide were mixed in a ratio of 2: 1: 1 with anhydrous ethanol as solvent. The mixture was reacted at 80 °C for 36 hours.

2.2.2 Synthesis of Polymeric Ionic Liquids

The obtained ionic liquid monomer was cooled to room temperature, and the initiator 2,2 - azobisisobutyronitrile with 0.5 % mass fraction of mixture was added. The initiator and ionic liquid monomer were mixed evenly. The petroleum ether was added to the three-necks flask with magnetic stirring at 65 °C. Then, the mixture was added to the three-necks flask, and nitrogen was filled in the reaction process. After two hours, the temperature was raised to 75 °C, and the temperature was raised to 85 °C in the next two hours, The polymerization was continued for six hours at 85 °C. After the reaction, yellow spherical particles were obtained by precipitation, filtration, washing, and drying. The diameter was about 4 mm. The polymerization ionic liquid catalyst was prepared and named PILs-XSS.

Catalytic characterization\

Nicolet6700 / FT was used to analyze the functional groups of catalysts. The surface area of the catalyst was measured by Brunauer-Emmett-Teller (Brunauer-Emmett-Teller) method using Quantachrome (NO-VA2000). The pore size distribution is measured by BJH (Barrett-Joyner-Halenda) method. The TEM (transmission electron microscopy) instrument model running at 200 kV was JEM-2100 to observe the surface of the catalyst. Thermogravimetric analysis (TG) was performed using the STD-2960 instrument in an N₂ atmosphere with a heating rate (10 °C / min) from 25 °C to 800 °C.

2.4 Catalytic Synthesis and Product Analysis of DMC

One-pot synthesis of DMC was carried out in a rust steel reactor equipped with a heating outer layer and a thermometer with magnetic stirring. In the typical reaction, 0.15 mol propylene oxide, 0.4 mol methanol, 0.3 g PILs-XSS, and 0.3 g Na₂CO₃ were added to the reactor. At room temperature, the air in the reactor was removed by CO₂, and then the reactor was pressurized to 15 bar by CO₂, heated to 100 °C for 3 h. The pressure of the reactor was measured by a pressure gauge equipped with a pressure-reducing valve. After the reaction, the reactor was quickly cooled to 15 °C in an ice water bath, and the supernatant was taken to the centrifuge tube. The internal standard method was used for detection by GC-FID. The products were detected by gas chromatography-mass spectrometry, and the by-products were propylene carbonate, 1,2-propanediol, and propylene glycol methyl ether.

3 Results and discussion

3.1 Characterization of catalysts

3.1.1 FT-IR analysis

To verify the reaction and polymerization of 1,2-dibromoethane, N,N'-methylenebisacrylamide, and 1-vinylimidazole, the four samples were identified by FT-IR in the range of 500-4000cm⁻¹. structure. As shown in Figure 2, first, the characteristic peak at 1670cm⁻¹ (C=O vibration) [25], a special functional group in N,N'-methylenebisacrylamide. 2850cm⁻¹ and 3040cm⁻¹ (saturated C-H and unsaturated C-H) [26], 1020cm⁻¹ is the C-N characteristic peak vibration in the imidazole ring [27], 590cm⁻¹ is the C-Br vibration peak [28]. Tthe above The analysis results preliminarily judged that PILs-XSS was synthesized successfully.

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Fig. 2 FT-IR spectra : (a) 1-vinylimidazole, (b) 1,2-dibromoethane, (c) PILs-XSS, (d) N, N ' -methylenebisacrylamide

3.1.2 BET-BJH analysis of PILs-XSS

BET-BJH analysis was performed on the structure of the sample, as shown in Figure 3, showing the specific surface area and pore size test curve of the material. First of all, the test chart of BET-specific surface area consists of two curves of adsorption and analysis. It can be seen from the figure that the adsorption hysteresis loop in the middle represents the type IV isotherm [29], and the specific surface area reaches 71.5m²/g, The average pore size of FILs-XSS is greater than 14.8 nm, which is an important sign of mesoporous materials [30]. The CO₂ molecule can fully contact with propylene oxide on the catalyst, which is very favorable for the first step of the reaction between CO₂ and propylene oxide, and the average pore size of PILs-FL has reached the basic requirement [31]. According to the situation analysis, PILs-FL has a high-quality specific surface area (71.5m²/g) and pore size (14.8nm), which can show good performance in the process of one-pot production of DMC.

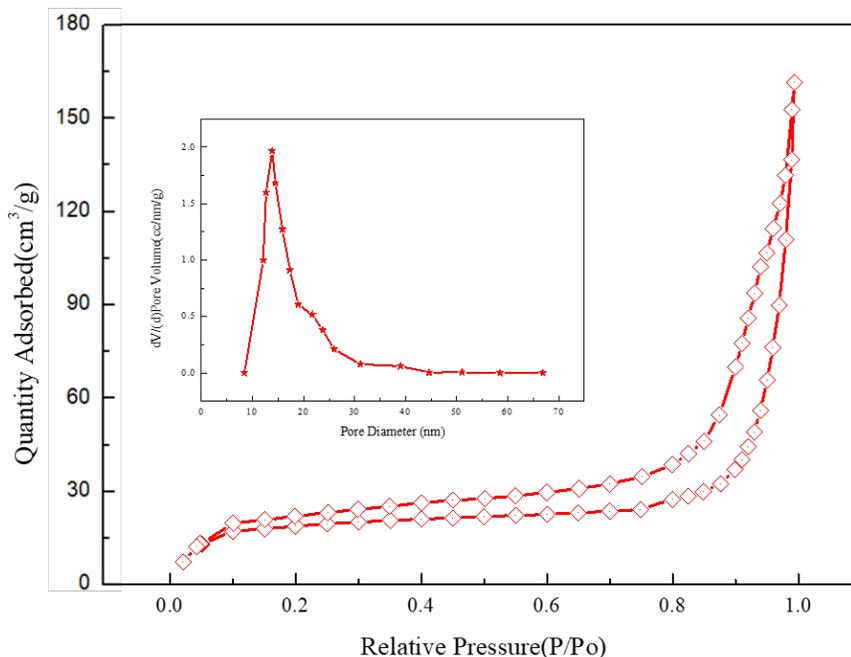


Fig. 3 BET-BJH analysis curve of PILs-XSS

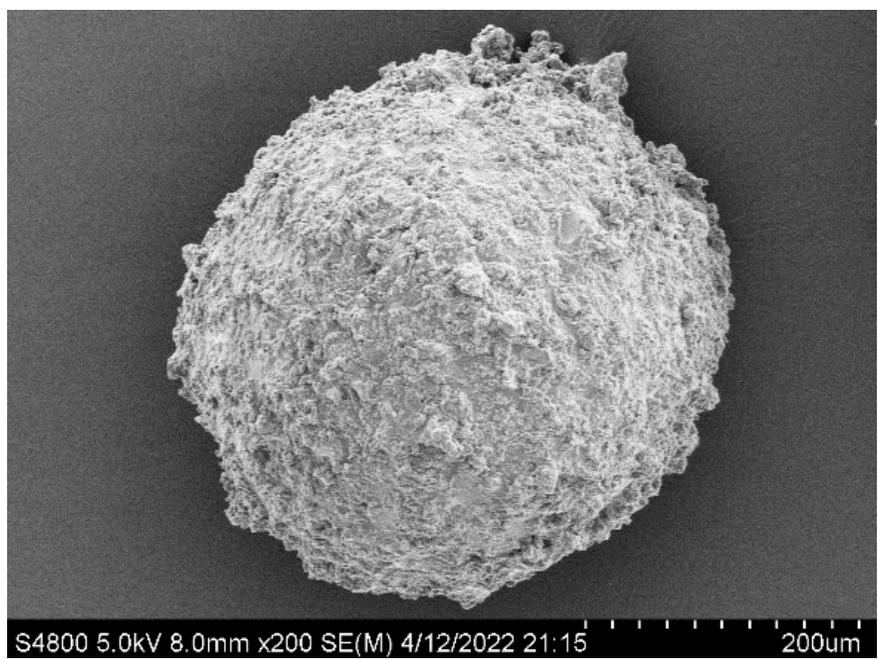
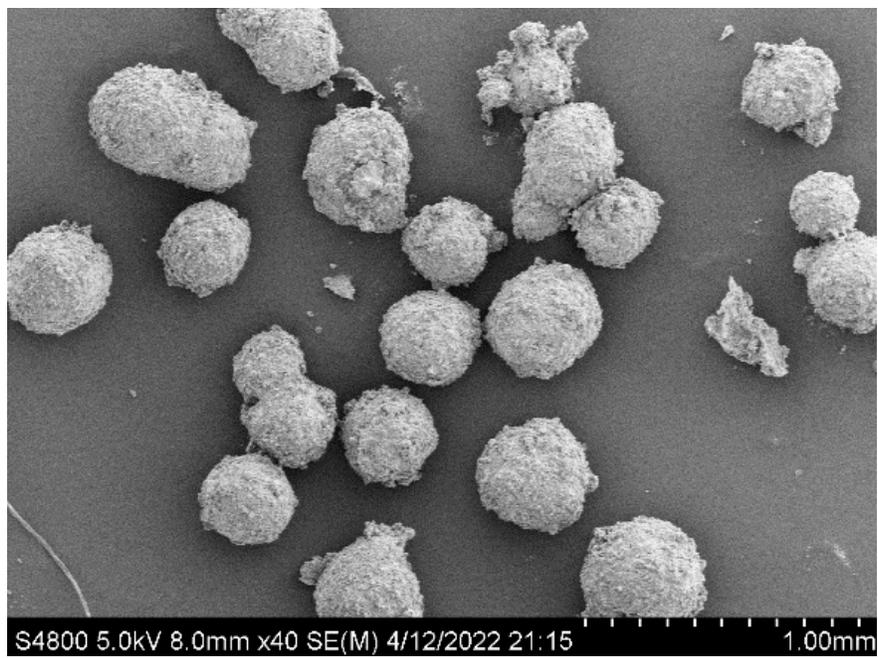
3.1.3 SEM and EDS analysis

The structural characteristics and the surface morphology of the samples were observed by SEM. The spherical PILs-XSS was ground for SEM analysis, as shown in Figure 4, which shows the SEM picture of the sample. We can see that PILs-XSS has a fluffy pore-like structure, which is consistent with the high surface area ($71.5\text{m}^2/\text{g}$) and the mesoporous material (14.8nm), which well explains the special advantages of the catalyst PILs-XSS in the reaction[32].

The samples were characterized and analyzed by EDS to study their composition, distribution. The EDS analysis of the samples is shown in Table 1. It can be seen from the table 1 that bromine was detected in the catalyst PILs-XSS, which is important for the addition reaction of CO_2 and propylene oxide. For EDS detection, the results are similar to the theoretical ratio. It was further proved that PILs-XSS was synthesized successfully.

Table 1 EDS analysis of PILs-XSS

Element percentage (%)	C	N	O	Br
1-Vinylimidazole	66.67	33.33	0	0
1,2-Dibromoethane	13.06	0	0	86.94
N,N'-Methylenebisacrylamide	58.33	19.44	22.23	0
PILs-XSS	45.26	16.67	31.72	6.35



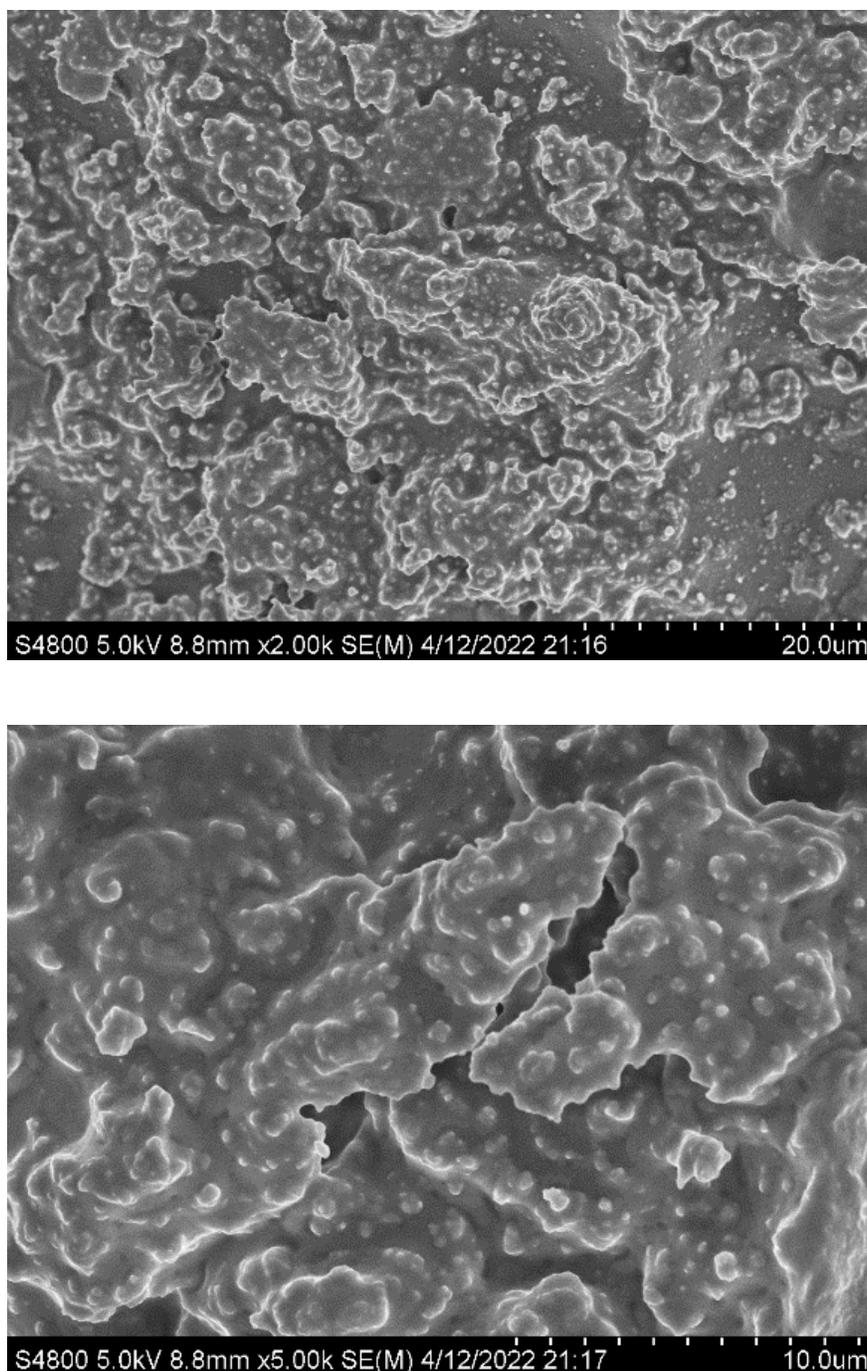
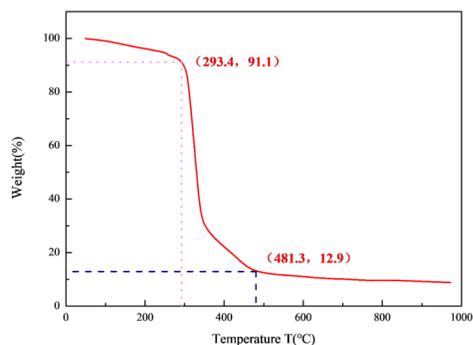


Fig 4 SEM analysis of PILs-XSS

3.1.4 TG analysis



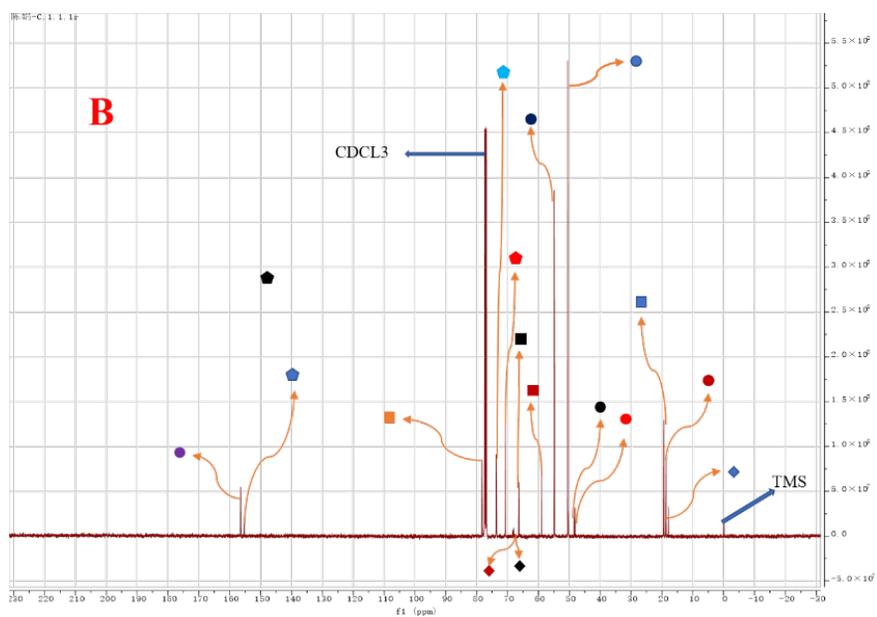
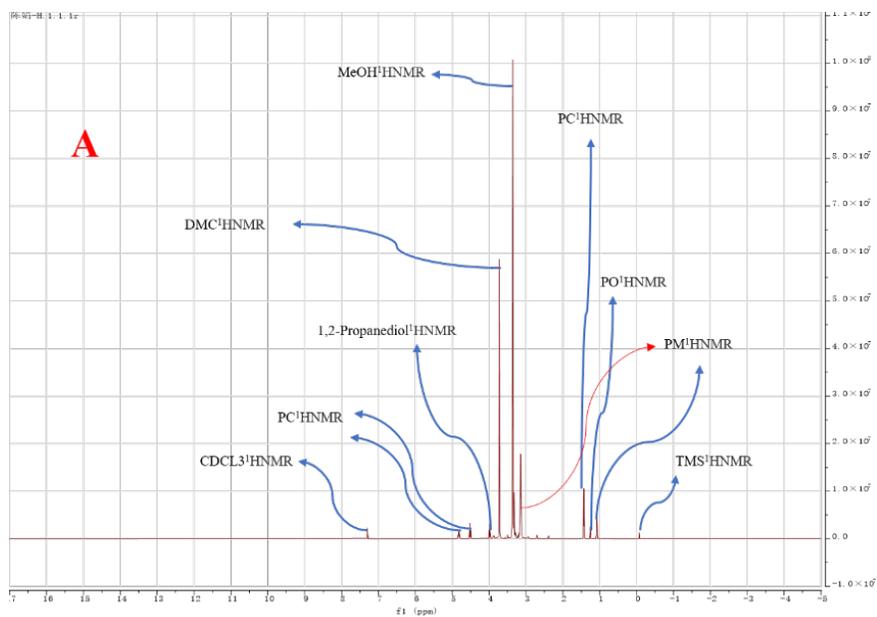
To measure the thermal stability of PILs-XSS, TG curves were recorded in flowing dry N₂. As shown in Figure 5, the initial weight loss at 293.4 °C was 8.9%, which was due to the adsorption of organic solvents and water on the surface of the catalyst PILs-XSS during washing. A complete loss of all covalently attached organic structures was observed in the temperature range of 293.4–481.3 °C [33], and the final amount of remaining organic components was approximately 12.9% of the total solid catalyst. Therefore, PILs-XSS is thermally stable below 293.4 °C, proving the feasibility of this catalyst as a solid catalyst basis for catalyzing CO₂ to DMC by one-pot method.

Fig. 5 TG analysis of PILs-XSS

3.2 The synthesis of DMC by one-pot method

3.2.1 Hydrocarbon spectrum analysis products

To detect the presence of dimethyl carbonate in the product, we performed nuclear magnetic resonance on the product after the reaction. Fig. 6 (A) was the ¹HNMR spectrum, Fig. 6 (B) was the ¹³CNMR spectrum, and Fig. 6 (C) was the marker of the carbon vibration peak of each substance in the carbon spectrum. Combined with gas chromatography and nuclear magnetic resonance spectroscopy, all substances in the reaction were analyzed.



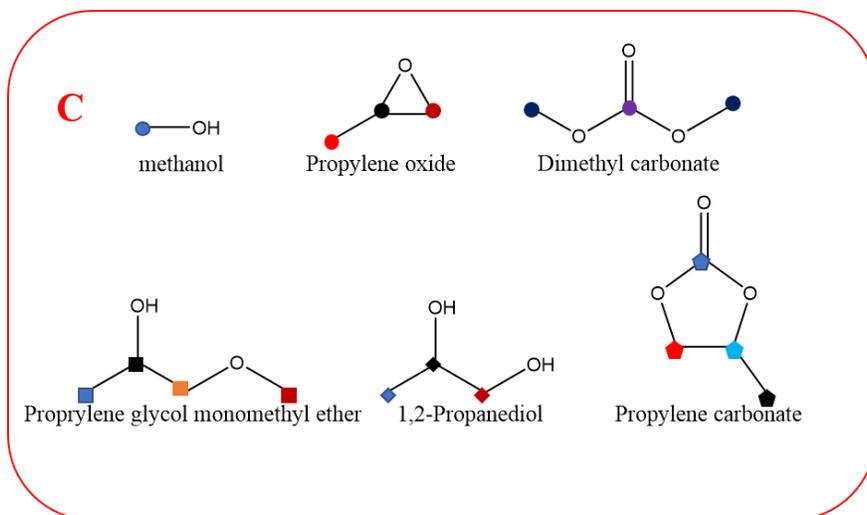


Fig. 6 (A) ^1H NMR spectra of the reaction system ; (B) ^{13}C NMR spectra of the reaction system ; (C) Determination of carbon position at each position in the ^{13}C NMR spectrum.

From Fig. 6, we can see that DMC was detected in the product, which proved that the catalyst prepared by us is effective by the one-pot method with CO_2 , methanol, and propylene oxide. At the same time, there were also by-products. The by-products were propylene carbonate, 1,2 - propanediol, and propylene glycol methyl ether.

The next step was process optimization. The effects of pressure, time, alcohol/alkyl ratio, temperature, catalyst dosage, and other variables on the yield of DMC were investigated.

3.2.2 Single-factor experiment of one-pot synthesis of DMC

In this experiment, the effects of single factors such as the amount of catalyst PILs-XSS (1 wt % – 3 wt %), the amount of cocatalyst Na_2CO_3 (1 wt % – 5 wt %), the pressure of CO_2 (0.9 MPa – 1.7 MPa), the reaction temperature (90 °C – 110 °C), the reaction time (2 h – 6 h), and the molar ratio of methanol to propylene oxide (2 : 1 – 4 : 1) on the conversion of propylene oxide and the yield of dimethyl carbonate were studied.

Amount of catalyst PILs-XSS. Figure 7(A) shows the effect of PILs-XSS on the conversion of propylene oxide and the yield of DMC. The reaction conditions were as follows: reaction time 3 h, 1.0 MPa, reaction temperature 95 °C, methanol / PO molar ratio 4: 1, and 5 wt % Na_2CO_3 , respectively. When the amount of catalyst PILs-XSS increased from 1 wt % to 3 wt %, the conversion rate of PO and the yield of DMC increased continuously. When the amount was 2.5 wt %, the conversion rate of PO reached 86.8 % and the yield of DMC reached 41.2 %. When the catalyst dosage was increased again, the PO conversion and DMC yield did not increase, indicating that the catalyst PILs-XSS had the highest catalytic effect at this time. Therefore, the optimal dosage of PILs-XSS was 2.5 wt % for this reaction.

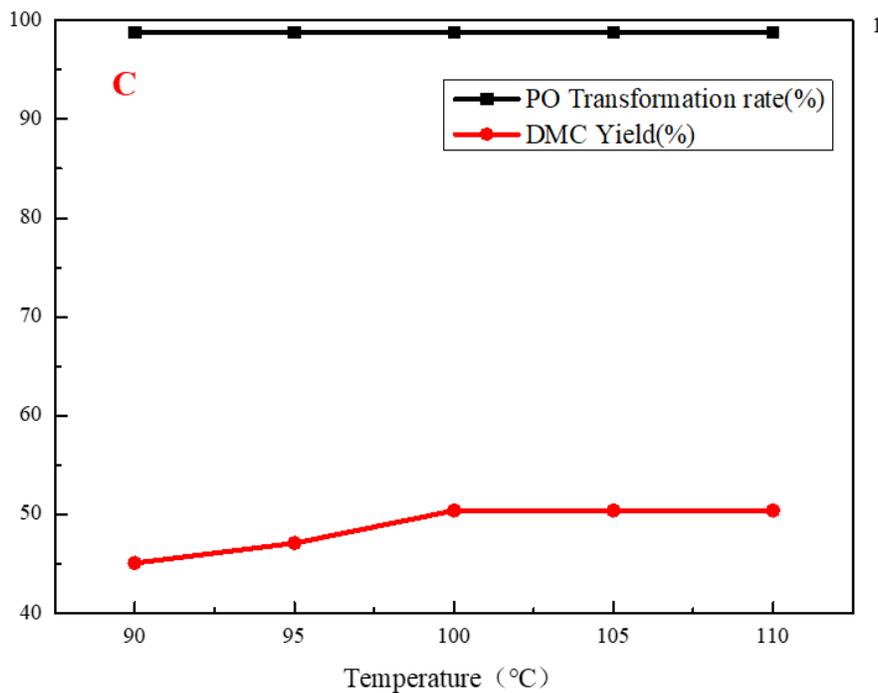
Pressure. The CO_2 pressure had a decisive influence on the reaction. As shown in Fig. 7(B), the pressure gradually increased from 0.9 MPa to 1.7 MPa. The conditions were as follows: the amount of catalyst PILs-XSS was 2.5 wt %, the reaction time was 3 h, the reaction temperature was 95 °C, and the molar ratio of methanol to PO was 4: 1, and the amount of Na_2CO_3 was 5 wt %. Under the pressure of 1.5 MPa, the conversion rate of PO reached the highest 98.8 % and the yield of DMC reached the highest 47.1 %. So the best pressure condition is 1.5MPa.

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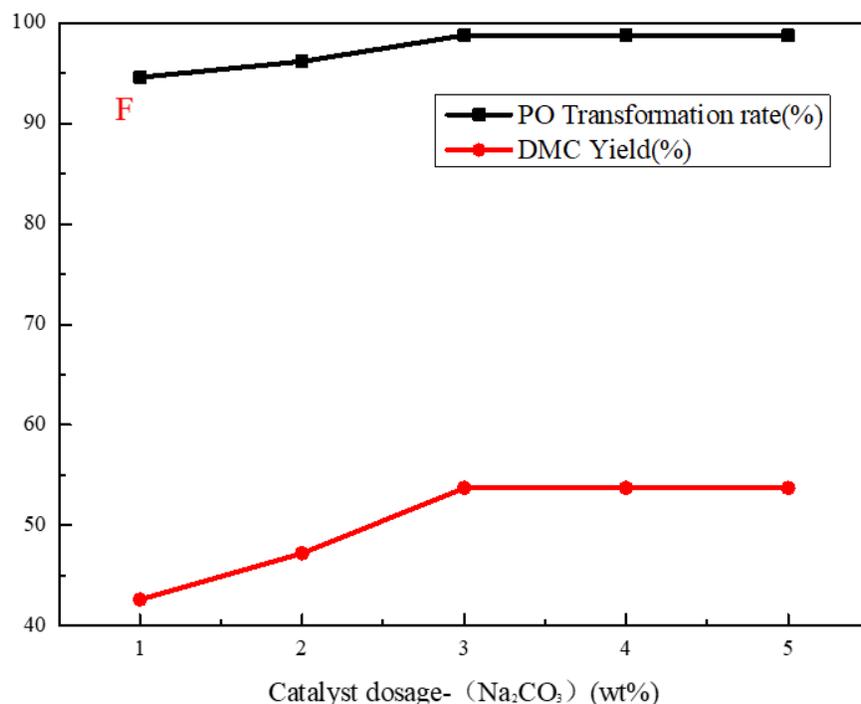


Fig. 7 Single-factor optimization of one-pot synthesis of DMC catalyzed by PILs-XSS/ Na_2CO_3 : (A) catalyst dosage, (B) reaction pressure, (C) reaction temperature, (D) reaction time, (E) methanol / PO molar ratio, (F) Na_2CO_3 dosage

Reaction temperature. The effects of reaction temperature on PO conversion and DMC yield are shown in Fig. 7(C). Other conditions are as follows: the optimum amount of catalyst PILs-XSS is 2.5 wt %, and the pressure is 1.5 MPa, and the undetermined reaction time is 3 h. The molar ratio of methanol to PO is 4: 1, and 5 wt % Na_2CO_3 . It can be seen that with the increase in temperature, the conversion rate of PO did not change, and the yield of DMC increased continuously until 100 °C reached the highest 50.4 %. It indicated that the reaction between PO and CO_2 had reached the highest conversion rate of 98.8 % at 90 °C. Therefore, 100 °C is the best temperature for this reaction.

Reaction time. The effect of reaction time on this reaction is shown in figure 7(D). Other conditions are as follows : catalyst PILs-XSS dosage 2.5wt %, 1.5 MPa, 100 °C, methanol / PO molar ratio 4 : 1, 5wt % Na_2CO_3 . In the reaction time of 2-6h, the conversion of PO first increased and then remained unchanged, reaching the highest 98.8 % at 3h, DMC yield reached the highest 53.7 % at 4h, continuing to extend the reaction time, and DMC yield remained unchanged. Therefore, the optimal reaction time was 4h.

The molar ratio of methanol to PO. As shown in figure 7(E), the other conditions are catalyst PILs-XSS dosage 2.5wt %, 1.5MPa, 100 °C, reaction time 4h, 5wt % Na_2CO_3 . The reaction process was studied by changing the molar ratio of methanol to PO. It was found that the conversion of PO remained unchanged, indicating that the first step of the ring-opening reaction was not affected by the amount of methanol when the amount of PO and CO_2 was constant. With the increase in methanol / PO molar ratio, the yield of DMC first increased and then stabilized. The yield of DMC reached the highest 53.7 %, when the molar ratio was 3: 1. Therefore, the optima molar ratio of 1 methanol to PO was 3: 1.

Na_2CO_3 dosage. The effect of Na_2CO_3 as cocatalyst on the reaction is shown in Fig.7 (F). The optimized conditions are as follows: the amount of catalyst PILs-XSS 2.5 wt %, 1.5 MPa, 100 °C, reaction time 4 h, and methanol / PO molar ratio 3: 1. We found that the conversion rate of PO increased with the increase of Na_2CO_3 content, which was a special phenomenon, indicating that Na_2CO_3 played a certain role in promoting

the catalytic reaction of CO₂. When the dosage was 3 wt %, the yield of DMC reached the highest 53.7 %. Therefore, the best dosage of Na₂CO₃ is 3wt %.

In summary, the optimum conditions were as follows: catalyst PILs-XSS 2.5wt %, CO₂ pressure 1.5MPa, reaction temperature 100 °C, reaction time 4h, methanol / PO molar ratio 3: 1, Na₂CO₃ dosage 3wt %. Under these conditions, the conversion rate of PO reached 98.8 % and the yield of DMC was 53.7 %. Of course, after exploration, the first step of the addition reaction was rapid and the conversion rate was high. The transesterification reaction took a long time in the series and the conversion rate was relatively low, but it had little effect on the overall reaction.

3.3 Comparison of catalytic activity of the same series of PILs/Na₂CO₃

Table 2 Comparison of catalytic activity for DMC synthesis

Entry	Catalyst	PO conversion (%)	DMC yield (%)	Conversion rates	
				PC	1,2-Propanediol
I	PILs-XSS/Na ₂ CO ₃	98.8	53.7	45.1	40.2
II	PILs-XST/Na ₂ CO ₃	94.2	50.1	44.1	39.3
III	PILs-XSO/Na ₂ CO ₃ -	90.5	47.6	42.9	38.5
IV	PILs-XSP/Na ₂ CO ₃	89.6	46.5	43.1	38.7
V	PILs-XSQ/Na ₂ CO ₃	88.2	46.1	42.1	37.2

PILs-XSS : 1,2-dibromoethane ; PILs-XST : 1,3-dibromopropane ; PILs-XSO : 1,4-dibromobutane ; PILs-XSP : 1,5-dibromopentane ; PILs-XSQ : 1,6-dibromohexane ;

Reaction conditions : catalyst PILs dosage 2.5wt %, CO₂ pressure 1.5MPa, reaction temperature 100 °C, reaction time 4h, methanol / PO molar ratio 3 : 1, transesterification catalyst Na₂CO₃ dosage 3wt %.

The activities of a series of PILs/Na₂CO₃ catalysts are compared in Table 2. By comparing the catalytic activities of the same series of bromides, it was found that the chain was longer, the catalytic activity was lower. In the process of producing catalysts, it was found that the chain was longer, the hardness of the synthesized spherical particles was lower. Therefore, 1,2 - dibromoethane was reasonable as a raw material.

3.4 Investigation of reusability

In addition to the high requirements for the catalytic activity of organic catalysts, sustainable utilization is equally important in production, which determines whether continuous production can be achieved. Therefore, the reusability of PILs-XSS was evaluated under the optimal conditions (PILs-XSS dosage 2.5wt %, CO₂ pressure 1.5MPa, reaction temperature 100 °C, reaction time 4h, methanol / PO molar ratio 3: 1, Na₂CO₃ dosage 3wt %). As shown in Fig. 8, The catalytic activity of PILs-XSS was not significantly decreased after five consecutive cycles. The spherical state of the catalyst did not also changed. This indicated that the catalyst had a strong mechanical strength and recyclability.

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Fig. 8 Study on the reuse of PILs-XSS catalyst. The reaction conditions were as follows: catalyst PILs-XSS dosage 2.5 wt %, CO₂ pressure 1.5 MPa, reaction temperature 100 °C, reaction time 4 h, methanol / PO molar ratio 3: 1, and ester exchange catalyst Na₂CO₃ dosage 3 wt %.

3.4 Effect of Na₂CO₃ on conversion

For transesterification catalysts, the strength of the alkali determines the efficiency of transesterification, but too strong an alkali will lead to side reactions. For example, strong alkalis such as NaOH and KOH cannot

be used as transesterification catalysts in this study. They are not only easily contaminated by CO_2 , but also can directly react with methanol. Catalysts with relatively strong basicity can only be used. Sodium methoxide is a strong base and does not react with CO_2 and methanol. The basicity is much stronger than that of Na_2CO_3 . Under the same conditions, the transesterification catalyst is replaced by sodium methoxide. The yield of DMC does not increase, but the conversion of PO is reduced to 86.7 %. In this regard, we carried out the corresponding research. After comparing several common transesterification catalysts, we found that carbonate had a certain promoting effect on CO_2 and propylene oxide.

4. Conclusions

In summary, PILs-XSS/ Na_2CO_3 has been used as a catalyst for the one-pot synthesis of DMC from methanol, propylene oxide, and carbon dioxide. The catalyst is synthesized by suspension polymerization. The polymerization ionic liquid catalyst PILs-XSS has a certain pore size, specific surface area, and certain heat resistance by characterization.

The optimal reaction conditions were as follows: the dosage of PILs-XSS was 2.5 wt %, the CO_2 pressure was 1.5 MPa, the reaction temperature was 100 °C, the reaction time was 4 h, the molar ratio of methanol to propylene oxide (PO) was 3: 1, and the dosage of cocatalyst Na_2CO_3 was 3 wt %. Under the optimum conditions, the conversion of PO was up to 98.8 % and the yield of DMC reached 53.7 %. In addition, the combined catalyst PILs- Na_2CO_3 was easily recovered by filtration in the reaction system. After five times of repeated use, the activity and the shape of the catalyst were almost unchanged, which meant that the catalyst had amazing mechanical strength. It has a spherical shape and good repeatability, which is a special breakthrough for the continuous production of DMC. This catalyst(PILs-XSS) is a very promising catalyst in for CO_2 development.

Conflict of interest

The authors declare that they have no conflict of interest.

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