



# Non-phosgene synthesis of isocyanates based on CO<sub>2</sub>: Synthesis of methyl *N*-phenyl carbamate through coupling route with lead compound catalysts

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## ABSTRACT

The synthesis of methyl *N*-phenyl carbamate (MPC), the key intermediate for the non-phosgene synthesis of isocyanates based on CO<sub>2</sub>, was studied from the reaction of dimethyl carbonate and *N,N'*-diphenyl urea under pressure. A variety of solid catalysts were screened, which showed lead compounds such as PbO, PbO<sub>2</sub>, PbCO<sub>3</sub>, and 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> had excellent catalytic activity. The characterization of XRD showed that the screened lead compound catalysts after reaction were changed into the same lead compound with the group –PbOH. With the increase of recycling times of the used lead compound catalysts, the selectivity of MPC and conversion of DPU were still about 99%. And the characterization of XRD and FTIR showed that new lead compound, which was produced with the increase of recycling times of the used lead compound catalysts, was also a lead compound with –PbOH. So the above results indicated that the real lead catalyst was the compound containing –PbOH. A possible reaction mechanism was discussed with the lead compound catalysts.

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## 1. Introduction

The control, conversion and utilization of CO<sub>2</sub> have become global challenges and strategies for the sustainable development of human society. To manufacture isocyanates by using CO<sub>2</sub> and CO<sub>2</sub>-derived molecules as carbonylation reagents is one of the important routes for the resource utilization of CO<sub>2</sub>. Isocyanates are important chemicals for the synthesis of polyurethanes, and the commercial method of isocyanates production is via the phosgene route, but it is highly toxic and corrosive. [1,2]

Methyl *N*-phenyl carbamate (MPC) is a key intermediate for the synthesis of isocyanates through non-phosgene routes. The main synthesis methods include oxidative carbonylation of aniline [3], reductive carbonylation of nitrobenzene [4], methoxycarbonylation of aniline [5–7] and alcoholysis of *N,N'*-diphenyl urea [8–9]. Among the two latter methods (see reactions (1) and (2) in Scheme 1), reactants such as dimethyl carbonate (DMC) and *N,N'*-diphenyl urea (DPU) are commercially synthesized indirectly from CO<sub>2</sub>. Because of its simple process, the synthesis of DMC and DPU directly from CO<sub>2</sub> is also attractive (see Scheme 2) [10–13]. Therefore, reactions (1) and (2) will promote the synthesis of important chemicals derived from CO<sub>2</sub> and impulse CO<sub>2</sub> utilization.

However, reactions (1) and (2) produce equal molar amounts of aniline or methanol as byproduct and show poor atom economy (see Scheme 1). To improve it, reaction (3) was obtained by coupling reactions (1) and (2). Reaction (3) was studied under atmospheric pressure, and maximal MPC yield only reached about 80% [14,15]. Since reaction (3) is an endothermic reaction and the boiling point of DMC is only 90 °C under atmospheric pressure, it is necessary for further improving MPC yield to study reaction (3) under pressure. Reaction (3) has been mentioned under pressure [16,17]. But in order to improve MPC yields and promote the commercial process, further research on screening and recycling and separation of catalysts, catalyst characterization and catalytic mechanism is needed under pressure.

In this paper, the screening, recycling, separation and characterization of catalysts for the synthesis of MPC through coupling route (see reaction (3)) were investigated under pressure, and the reaction mechanism was also discussed.

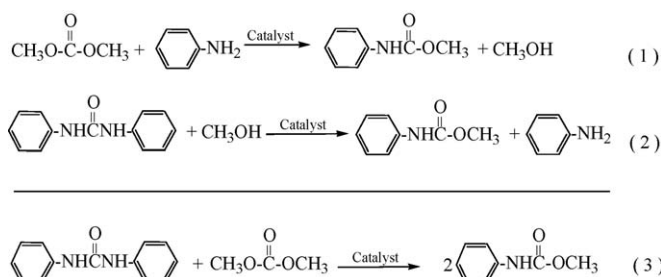
## 2. Experimental

### 2.1. Catalyst preparation and reagents

Catalyst PbO/γ-Al<sub>2</sub>O<sub>3</sub> was prepared by impregnating γ-Al<sub>2</sub>O<sub>3</sub> with Pb(NO<sub>3</sub>)<sub>2</sub> solution containing the desired amount of PbO, then the obtained sample was dried at 120 °C and calcined at 600 °C for 4 h, and the content of PbO was calculated to be 20 wt.% in the final catalyst product. Catalyst PbO/SiO<sub>2</sub> was also prepared by the above

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Scheme 1. Synthesis of MPC through coupling route.

method. Catalyst CaO was prepared by decomposition of calcium carbonate at 900 °C for 2 h.

The Support SiO<sub>2</sub> was purchased from Qingdao Ocean Chemical Factory in Shandong Province of China and its specific surface area is 300 m<sup>2</sup>/g. The support γ-Al<sub>2</sub>O<sub>3</sub> was supplied by Research Institute of Petroleum Processing, China Petroleum & Chemical Corporation and its specific surface area is 245 m<sup>2</sup>/g.

Dimethyl Carbonate was produced by Dongying Hi-tech Spring Chemical Industrial Co., Ltd. in Shandong Province of China (industrial grade, content ≥99.5%). *N,N'*-Diphenyl urea was produced by Beijing Chemical Works In China (chemical pure). PbO, PbO<sub>2</sub>, PbCO<sub>3</sub>, 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> were produced by Beijing Chemical Reagents Company In China (analytical reagent).

Other catalysts and reagents (analytical reagent) were gained directly from market.

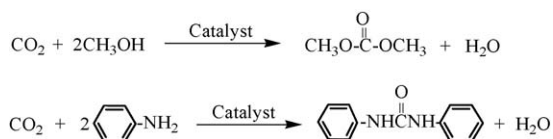
## 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on X'pert Pro MPD X-ray diffractometer from PANalytical with Cu Kα radiation (λ = 0.154187 nm), Generator Settings 40 kV, 30 mA. FT-IR patterns of samples were obtained on SPECTRUM GX II apparatus from PerkinElmer. 2 mg sample and 200 mg KBr were mixed and crushed to a wafer.

The Pb content in the sample was determined using OPTIMA 5300DV Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (PerkinElmer). The sample with known weight was dissolved in nitric acid (HNO<sub>3</sub>). The solution obtained after complete dissolution was diluted to required volume. The samples were analyzed to determine Pb content with the wavelength of 220.253 nm.

## 2.3. Experimental procedure

The reaction between DMC and DPU was carried out in a 100 ml autoclave. In a typical experimental procedure, DMC (0.820 mol), DPU (0.041 mol), and catalyst (2%, based on total mass of reactants) were added, the air in the autoclave was replaced by nitrogen, and the reactions were carried out at 160 °C for 4 h at 1 MPa of nitrogen pressure. The resulting solution was analyzed by HPLC (high performance liquid chromatography, Agilent-1100, column: Agilent ZORBAX Extend-C<sub>18</sub> 2.1 mm × 150 mm 5 μm).

Scheme 2. Synthesis of DMC and DPU directly from CO<sub>2</sub>.

## 3. Results and discussion

### 3.1. Screening of catalysts

#### 3.1.1. Activities of various catalysts

A variety of solid catalysts were chosen and screened for the reaction between DMC and DPU under pressure, and the results were presented in Table 1. Entry 1 showed that a catalyst for the reaction between DMC and DPU was necessary. So it was important to screen catalysts with excellent activity for the reaction under pressure. Because solid acid and base catalysts were often used in many esterification reactions, some of them were chosen for the reaction of DMC and DPU. Typical solid base catalysts such as CaO and K<sub>2</sub>CO<sub>3</sub> were tested for the reaction of DMC and DPU, but showed poor catalytic activity (entries 2–3). Solid acid catalyst SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was also tested, and more poor result was obtained (entry 4). The reaction between DPU and methanol (see reaction (2)) easily took place without catalysts [8,9]. Contrarily, catalysts were necessary for the reaction between DMC and aniline (see reaction (1)) [5–7]. Some catalysts, used in the reaction of DMC with aniline, were also screened for the reaction of DMC and DPU. Catalyst ZnO had good activity in the reaction of DMC with aniline [18], but showed poor activity in reaction (3) under pressure (entry 5). Catalyst PbO was not only used in the reaction of DMC and aniline, but also used in the reaction between diethyl carbonate and DPU [19,20]. When it was used for reaction (3) under pressure, excellent results were obtained (entry 6). Lead compounds such as PbO<sub>2</sub>, PbCO<sub>3</sub>, and 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> were also tested, and all of them showed excellent activity (entries 7–9). Since PbO had simple structure and was easily obtained, supported catalysts PbO/SiO<sub>2</sub> and PbO/γ-Al<sub>2</sub>O<sub>3</sub> were prepared, but both of them showed lower activity than catalyst PbO, and the main reason would be discussed in the catalyst XRD characterization.

From the above results, it could be seen that lead compounds such as PbO, PbO<sub>2</sub>, PbCO<sub>3</sub>, and 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> were excellent catalysts.

#### 3.1.2. XRD characterization of screened lead compound catalysts

During the experimental process, it was found that both yellow catalyst PbO and brown catalyst PbO<sub>2</sub> were changed into white catalyst after reaction, which showed the catalysts might be changed. So XRD characterization of screened lead compound catalysts after reaction was carried out. The results were presented in Fig. 1.

As shown in Fig. 1, the screened lead compound catalysts such as PbO, PbO<sub>2</sub>, PbCO<sub>3</sub>, and 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> after reaction had the

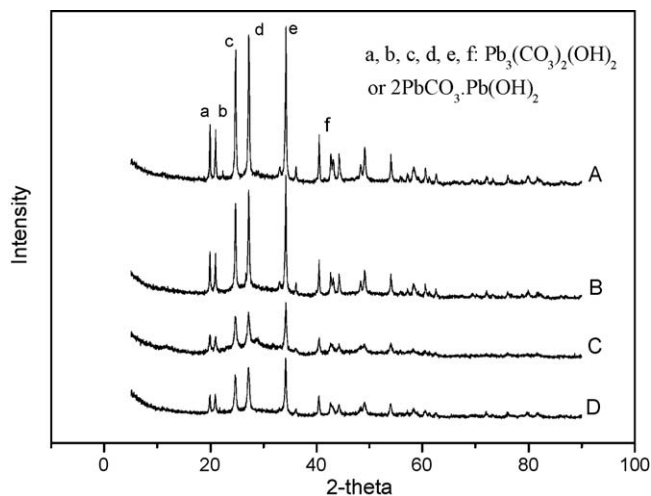
Table 1

Activities of various catalysts for the reactions of dimethyl carbonate and *N,N'*-diphenyl urea.<sup>a</sup>

Entry	Catalyst	DPU conversion (%)	MPC yield (%)
1	None	23.8	5.9
2	CaO	75.2	51.2
3	K <sub>2</sub> CO <sub>3</sub>	94.8	31.3
4	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	71.9	12.0
5	ZnO	54.6	49.2
6	PbO	99.7	96.6
7	PbO <sub>2</sub>	99.6	93.4
8	PbCO <sub>3</sub>	99.5	96.1
9	2PbCO <sub>3</sub> ·Pb(OH) <sub>2</sub>	99.2	97.2
10	PbO/SiO <sub>2</sub> <sup>b</sup>	83.5	65.1
11	PbO/γ-Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	98.2	95.0

<sup>a</sup> Reaction conditions: dimethyl carbonate (0.820 mol), *N,N'*-diphenyl urea (0.041 mol), catalyst (2.0%, based on total mass of reactants), reaction temperature 160 °C, reaction time (4 h).

<sup>b</sup> 10%, based on total mass of reactants.



**Fig. 1.** XRD patterns of screened lead compound catalysts after reaction (A is the patterns of PbO after reaction, B is the patterns of PbO<sub>2</sub> after reaction, C is the patterns of PbCO<sub>3</sub> after reaction, and D is the patterns of 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub> after reaction).

same XRD patterns. The peaks such as a, b, c, d, e and f appeared in each patterns of A, B, C and D. It indicated that the screened lead compound catalysts after reaction were changed into the same lead compound such as Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> or 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>, or their mixture, respectively. The used lead compound catalyst had the group –PbOH, which was similar to Pb catalyst for the reaction between DMC and aniline in the literature [20]. So it could be thought that the real catalyst was the used lead compound catalyst with group –PbOH, and the screened lead compounds were only the precursors of producing it. Since PbO was only a precursor and not the real catalyst, it was reasonable that catalysts PbO/SiO<sub>2</sub> and PbO/γ-Al<sub>2</sub>O<sub>3</sub> showed lower activity than PbO.

Since PbO had simple structure, it was used as the precursor of the used lead compound catalyst for the following study of the reaction between DMC and DPU under pressure.

### 3.2. Recycling of the used lead compound catalyst

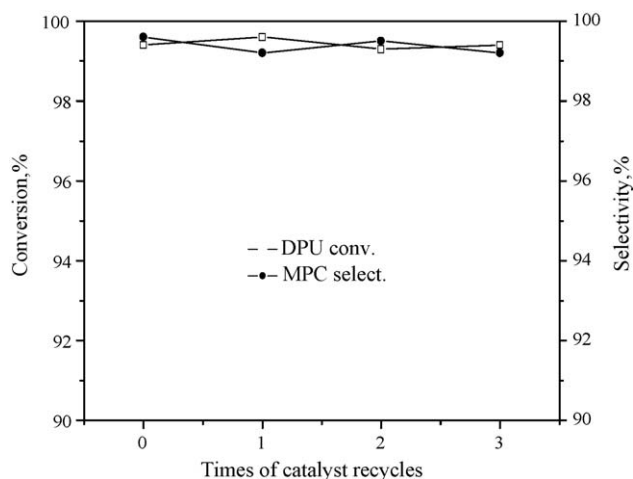
#### 3.2.1. Effect of recycling of the used lead compound catalyst on the reaction

The effect of recycling of the used lead compound catalyst on the reaction between DMC and DPU was studied (see Fig. 2). The experimental procedure was as follows: After each reaction, the filter cake was obtained by filtering the reaction solution and dried at 110 °C for 2 h in a constant temperature oven. Then the dried filter cake was cooled to room temperature in a drier and used as the catalyst for next reaction, or as the sample for the characterization of catalysts.

As shown in Fig. 2, both the selectivity of MPC and conversion of DPU were almost constant with the increase of recycling times of the used lead compound catalyst. When the catalyst was recycled for three times, all of the selectivity of MPC and conversion of DPU were still about 99%. It indicated that the catalytic performance of the used lead compound catalyst was almost constant with the increase of recycling times, which was an excellent catalyst for the reaction of DMC and DPU.

#### 3.2.2. XRD and FTIR characterization of the used lead compound catalyst with recycling times

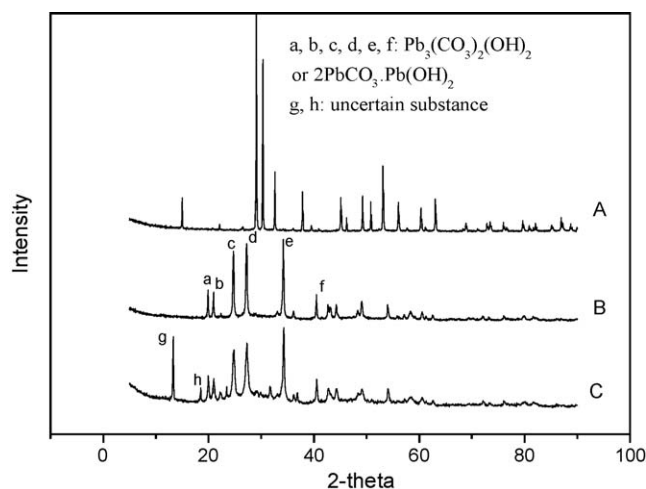
The XRD patterns of the used lead compound catalyst with recycling times are presented in Fig. 3. A is the patterns of PbO, B is the patterns after one reaction, and C is the patterns after four reactions. By the comparison of A and B, PbO was completely



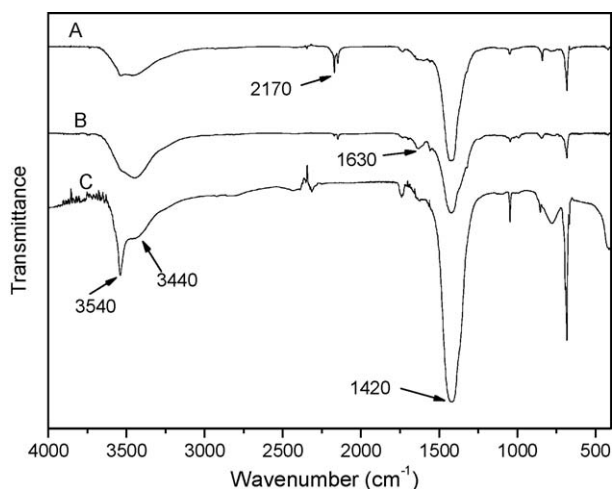
**Fig. 2.** Effect of recycling of the used lead compound catalyst on the reaction between dimethyl carbonate and *N,N'*-diphenyl urea. Reaction conditions: dimethyl carbonate (0.410 mol), *N,N'*-diphenyl urea (0.041 mol), catalyst (1.0%, based on total mass of reactants), reaction temperature 160 °C, reaction time 1 h.

changed into the Pb compound such as Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> or 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>, or their mixture after one reaction. With the increase of recycling times of the used lead compound catalyst, the peaks such as g and h appeared in patterns C after four reactions, which indicated new lead compound was produced. Compared with normal XRD spectra of lead compounds, the new lead compound might be 3PbCO<sub>3</sub>·2Pb(OH)<sub>2</sub>·H<sub>2</sub>O.

FTIR characterization in Fig. 4 was the further analysis of the new lead compound produced with the increase of recycling times of the used lead compound catalyst. A is the spectra of the catalyst after one reaction, B is the spectra of the catalyst after four reactions, and C is the spectra of 2PbCO<sub>3</sub>·Pb(OH)<sub>2</sub>. From spectra A and B, the bands at 2170 and 1630 cm<sup>-1</sup> showed a little difference, which indicated that new lead compound was produced with the increase of catalyst recycling times. By the further comparison with spectra C, the band at 1420 cm<sup>-1</sup> showed the presence of carbonates, the band at 3540 cm<sup>-1</sup> showed the presence of the group –PbOH, and the band at 3440 cm<sup>-1</sup> showed the presence of H<sub>2</sub>O in spectra A, B and C, respectively [21,22]. It indicated that the new compound was also a lead carbonate compound with –PbOH. The band at 3440 cm<sup>-1</sup> in spectra B was the biggest one among the



**Fig. 3.** XRD patterns of the used lead compound catalyst with recycling times (A is the patterns of PbO, B is the patterns after one reaction, and C is the patterns after four reactions).



**Fig. 4.** FTIR spectra of the used lead compound catalyst with recycling times. (A is the spectra after one reaction, B is the spectra after four reactions, and C is the spectra of  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ .)

ones at  $3440\text{ cm}^{-1}$  in spectra A, B and C, which showed that the content of water in samples was also the biggest one. And it was also consistent with the XRD analysis that the new lead compound might be  $3\text{PbCO}_3 \cdot 2\text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (in Fig. 3).

### 3.3. Separation of the used lead compound catalysts

#### 3.3.1. Effect of catalyst recycling on its separation from the reaction solution

With the recycling of catalysts, the separation of the used lead compound catalyst from the reaction solution of DMC and DPU was studied, and the results were shown in Table 2. The experimental procedure was as follows: After each reaction, the catalyst was separated from the reaction solution by vacuum filter. The sample was taken out with known volume respectively from each filtrate, dried, dissolved in nitric acid ( $\text{HNO}_3$ ), diluted to required volume, and analyzed to determine Pb content by ICP-OES.

From Table 2, it could be seen Pb content in the sample was almost constant with the increase of recycling times of catalysts, and there was 0.002 g catalyst (amount of Pb) in each filtrate. It showed that the catalyst was slight soluble in the reaction solution. It also showed that catalyst separation was not affected by the increase of recycling times. Since the catalyst participated in the reaction and produced catalytic intermediate with reactants, the soluble Pb in the reaction solution might be some of the catalytic intermediates (see Scheme 3).

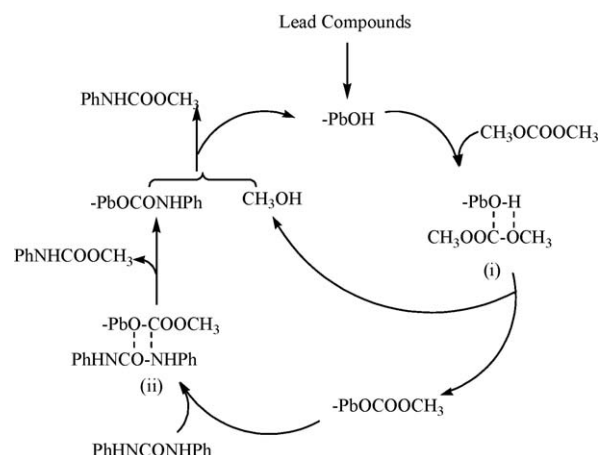
#### 3.3.2. Separation of catalysts from crude product MPC

Since the used lead compound catalyst was slightly soluble in the filtrate, it was necessary to study its separation from crude product MPC. The experimental procedure was as follows: After the reaction solution was filtrated, DMC in the filtrate was removed by distillation, and crude product MPC was obtained. Then crude

**Table 2**  
Effect of recycling of catalyst on its separation from the reaction solution.

Recycling times of catalysts	Concentration of Pb (mg/l)	Amount of Pb (g)
0	0.591	0.002
1	0.477	0.002
2	0.588	0.002
3	0.520	0.002

Reaction conditions: dimethyl carbonate (0.410 mol), *N,N'*-diphenyl urea (0.041 mol), catalyst (1%, based on total mass of reactants), reaction temperature  $160^\circ\text{C}$ , reaction time 1 h.



**Scheme 3.** Mechanism of the reaction between DMC and DPU with lead compound catalysts.

**Table 3**

The analysis of Pb content in product MPC and residue of separation.

Objection of analysis	Concentration of Pb (mg/l)	Content of Pb (% by mass)
MPC <sup>1</sup>	0	0
MPC <sup>2</sup>	0	0
Residue	0.196	0.04

Reaction conditions: dimethyl carbonate (0.410 mol), *N,N'*-diphenyl urea (0.041 mol), catalyst (1%, based on total mass of reactants), reaction temperature  $160^\circ\text{C}$ , reaction time 1 h.

product MPC was purified by recrystallization in cyclohexane, and product MPC<sup>1</sup> and solid residue were obtained. By further recrystallization of product MPC<sup>1</sup>, product MPC<sup>2</sup> was produced, and solid residue was not found. Pb content in crude product MPC, product MPC<sup>1</sup>, and product MPC<sup>2</sup> was analyzed by ICP-OES, respectively. The experimental results were shown in Table 3.

From Table 3, it showed that the content of MPC in product MPC<sup>1</sup> reached 99.5% by the analysis of HPLC. It also showed that Pb could be completely removed from crude product MPC by the first recrystallization, but Pb content in solid residue reached 0.04%. It indicated that the residual catalyst could be easily removed from crude product MPC by recrystallization in cyclohexane, which was also a good method to purify crude product MPC.

### 4. Possible reaction mechanism

The mechanism of the reaction between DMC and DPU was discussed with lead compound catalysts (see Scheme 3). XRD characterization of lead compound catalysts after reaction showed that these catalysts were changed into the same Pb compound such as  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  or  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , or their mixture. And the catalytic performance of the used lead compound catalyst was excellent and almost constant with the increase of recycling times. It also had the group  $-\text{PbOH}$ , which was similar to Pb catalyst for the reaction between DMC and aniline in the literature [20]. It could be thought that the real catalyst was the used lead compound catalyst with group  $-\text{PbOH}$ , which was produced from the screened lead compounds. So based on the above catalyst characterization and literature, the possible mechanism of the reaction between DMC and DPU with lead compound catalysts was as follows: First step was to produce lead compound  $-\text{PbOH}$  with catalytic activity from lead compounds, which was a key step. The following step was to produce  $\text{CH}_3\text{OH}$  and intermediate  $-\text{PbOCOOCH}_3$  by the reaction of  $-\text{PbOH}$  and DMC. Then intermediate  $-\text{PbOCOOCH}_3$  and DPU supplied nucleophiles and electrophilic reagents each other to form transitional compound

(ii), which produced product MPC and intermediate  $\text{-PbOCONHPh}$ . And intermediate  $\text{-PbOCONHPh}$  reacted with methanol to produce product MPC and  $\text{-PbOH}$ . A catalyst cycle was completed.

## 5. Conclusions

A variety of solid catalysts were screened for the synthesis of methyl *N*-phenyl carbamate through the reaction of dimethyl carbonate and *N,N'*-diphenyl urea under pressure. The lead compounds such as  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{PbCO}_3$ , and  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  showed excellent catalytic activity. The XRD characterization indicated that these lead compound catalysts after reaction had the same XRD patterns and were changed into the same lead compound with the group  $\text{-PbOH}$  such as  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$  or  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , or their mixture. With the increase of recycling times, the used lead compound catalyst also showed excellent performance, and all of the selectivity of MPC and conversion of DPU were still about 99%. The characterization of XRD and FTIR indicated new lead compound was produced with the increase of catalyst recycling times and was also a lead compound with  $\text{-PbOH}$ . According to the above results, the real lead catalyst for the reaction of dimethyl carbonate and *N,N'*-diphenyl urea should be the compound containing  $\text{-PbOH}$ . The used lead compound catalyst was slightly soluble in the filtrate, but it could be easily removed from crude product MPC by recrystallization in cyclohexane. Since MPC is the key intermediate for the non-phosgene synthesis of isocyanates based on  $\text{CO}_2$ , the study of synthesis of MPC from DPU and DMC will promote the non-phosgene synthesis of isocyanates and accelerate  $\text{CO}_2$  utilization.

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