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Direct Synthesis of Diallyl Carbonate Via Urea Transesterification with Allyl Alcohol Over Metal Chlorides

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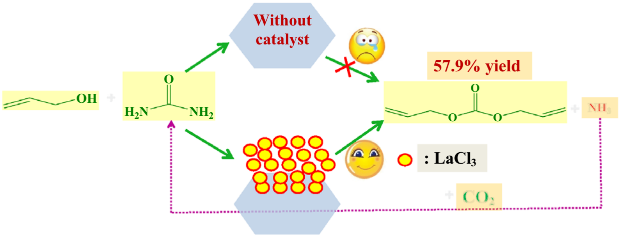
Abstract

A promising technique was studied towards diallyl carbonate (DAC) manufacture via urea transesterification with allyl alcohol over several metallic chlorides. It was revealed that the intermediate allyl carbamate (AC) was first generated via urea mono-alcoholysis with high yield, and subsequently AC further reacted with another allyl alcohol molecule to produce DAC. All the metal halides were evaluated for the overall reaction and the reaction of AC and allyl alcohol, respectively. This work found that the catalytic ability of catalysts originated from metal ions. Importantly, the highest yield of DAC could be achieved using $LaCl_3$ as catalyst. In addition, the activation patterns of reactants were investigated using in situ FT-IR measurement. Based on the characterization results of X-ray power diffraction and elemental analysis of the lanthanum species, separated from the reaction conduced over $LaCl_3$, a possible reaction mechanism was speculated.

Graphical Abstract



Keywords Dially carbonate · Urea · Allyl alcohol · $LaCl_3$

1 Introduction

Recently, owing to the continuous depletion of fossil based resources and increasing CO_2 concentration in the atmosphere, it is highly desirable to explore a novel strategy to produce more renewable fuels and chemicals [1–3]. In this aspect, organic carbonates that could be synthesized using CO_2 as starting feedstock, have attracted increasing attention from researchers [4, 5]. To date, several methodologies for the synthesis of organic carbonates have been proposed. As the oldest method, the process based on the use of phosgene was phased out owing to high toxicity of phosgene [6]. Oxidative carbonylation of alcohol [7] and transesterification alcohol with alkyl carbonate [8–10] were well known routes with high selectivity to the target product. However, they were limited severely by corresponding disadvantages such as hash reaction conditions or high investment cost which inhibit their expansion of production to desired scale. Currently, an attractive method that synthesis of organic carbonates using CO_2 as carbonylation agent is investigated widely because that CO_2 is a readily available and environmentally acceptable material with low-price [11]. Nevertheless, this process was far from industrial application owing

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to its poor thermodynamics because of highly stable structure of CO_2 [2]. In order to avoid such negative effect, an alternative route is the transesterification urea with alcohol. Urea was mainly produced by the reaction of CO_2 and NH_3, namely Bosch–Meiser process [12]. Therefore, it is generally reported that the production of organic carbonate by urea alcoholysis is a green process of indirect utilization CO_2. Furthermore, the by-product NH_3 can be recycled for the production of urea via reaction with CO_2, which renders urea alcoholysis an atom-efficient technique [5, 13]. So far, the manufacture of various kinds of alkyl and cyclic carbonates like dimethyl carbonate (DMC) [14], diethyl carbonate (DEC) [15], ethylene carbonate [16], propylene carbonate [17] and glycerol carbonate [18] has been successfully achieved via this method. Unfortunately, there is very few document reported on the green synthesis of dially carbonate (DAC), including several active basic groups such as $CH_2{=}CH{-}CH_2{-}$, $CH_2{=}CH{-}CH_2{-}O{-}$, and $-CO-$. Thus, DAC could be acted as green agent for manufacture of polycarbonates and nontoxic intermediates for organic synthesis. Moreover, its potential application in solvent, agrochemical and pharmaceutical industry has been extensively demonstrated [19]. In addition, thanks to its higher flash point and larger molecular weight than that of DMC and DEC, DAC can be applied as an ideal electrolyte for lithium ion batteries at relative high temperature [20]. Considering these aspects and the advantage of urea alcoholysis, it is of great importance to explore catalyst to promote the DAC production from urea and allyl alcohol effectively.

In recent years, several heterogonous catalytic procedures have been employed to realize the effective synthesis of organic carbonates with pure metal oxides [21], mixed oxides [22] and supported zinc catalysts [23]. On the other hand, it was also reported that the urea alcoholysis towards organic carbonates synthesis took place in two steps. In the first step, the carbamate was generated fast; nevertheless, the further reaction to the carbonate was very difficult [21, 24]. To the best of our knowledge, the process for production of DAC via trasesterification between urea and allyl alcohol was not clarified yet. Furthermore, the reaction mechanism and characterization of the active species, especially in homogeneous catalytic systems for the DAC production was still unknown.

Herein, we experimentally studied the homogeneous synthesis of DAC from urea and allyl alcohol using various metal chlorides as catalysts. The reaction process was confirmed over $LaCl_3$ owing to its high catalytic ability. Then, the model catalyst before and after the reactions was characterized by X-ray power diffraction (XRD) and elemental analysis techniques. To gain precise insights into the role of $LaCl_3$ in this reaction, the in situ FT-IR experiments were conducted. Finally, a possible reaction mechanism was disclosed. Therefore, this work not only open a new way for green and effective synthesis of DAC with low-price, but also make the catalytic mechanism of urea alcoholysis over $LaCl_3$ clear.

2 Experimental

2.1 Catalyst Preparation

$MgCl_2$, $CuCl_2$, $Cu(NO_3)_2$, $LaCl_3$, $CeCl_3$ and $La(NO_3)_3$ catalysts were acquired by evacuating $MgCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}6H_2O$, $LaCl_3{\cdot}7H_2O$, $CeCl_3{\cdot}7H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ at 80 °C in vacuum oven under 5 kPa overnight, respectively. Other catalytic samples were bought commercially without pre-treatment.

2.2 Catalytic Activity Test

The reaction of allyl alcohol and urea were evaluated in a 50 mL autoclave with a reflux column. Typically, after 1.0 mol allyl alcohol, 0.1 mol urea and 0.2 g catalyst were charged into the reactor, the system was heated to 180 °C in a short time and the reaction was conducted for 6 h under magnetically stirring. When the reaction was finished, the product was taken out from the autoclave. Finally, after the catalyst was separated by centrifugation, the liquid product was analyzed on a GC-950 gas chromatograph with an FID detector and a capillary column. Moreover, the chemical structures of the liquid product were measured using a GC–MS (Agilent 7890-700B) with HP-5MS capillary column (30 m). Here, the yields of DAC (or AC) were calculated by the following formulas, respectively:

$$DAC\ yield = \frac{DAC\ (mol)}{starting\ urea\ (mol)} \times 100\%$$

$$AC\ yield = \frac{AC\ (mol)}{starting\ urea\ (mol)} \times 100\%$$

In case of the reaction between allyl carbamate (AC) and allyl alcohol, 0.2 g catalyst, 1.0 mol allyl alcohol and 0.1 mol AC were added into the reactor. The reaction procedure was similar to that of reaction between urea and allyl alcohol. After the desired time of reaction, the liquid products were determined on GC. Accordingly, the AC conversion and DAC yield were determined by these two equations, separately:

$$AC\ convertion = \frac{(starting\ AC - AC)\ (mol)}{starting\ AC\ (mol)} \times 100\%$$

$$DAC\ yield = \frac{DAC\ (mol)}{starting\ AC\ (mol)} \times 100\%$$

2.3 Characterization

XRD patterns were collected using a Rigaku Miniflex diffractiometer at 40 kV and 30 mA with Cu Kα radiation.

The quantitative analysis of lanthanum was performed on an inductively coupled plasma (ICP) emission spectroscopy (Perkin-Elmer ICP OPTIMA-3000). With the respect to the nitrogen and hydrogen content in catalyst, the data was acquired on an Elemental Analyzer (Vario EL III).

The in situ FT-IR measurements were conducted using a closed stainless steel FT-IR cell. The spectra were obtained using a Nicolet Magna 550 Fourier-transform infrared spectrometer. The scanning region was 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Here, four kinds of experiments were conducted, described as follows, respectively: a), allyl alcohol adsorption on $LaCl_3$: 5 mg $LaCl_3$ and 100 mg KBr were ground finely, and then 4 mg of mixing sample was pressed into 13 mm discs and placed into the cell. Subsequently, 20 μL allyl alcohol was added into the cell. In advance, the sample should be pre-treated in vacuum for 2 h to eliminate the adsorbed gaseous impurities. The cell was heated to the desired temperature for FT-IR characterization. b), urea decomposition on $LaCl_3$: first, 13 mg $LaCl_3$ and 2 mg urea were mixed together. Then, 5 mg of mixture was made into a ϕ 13 mm pellet with 100 mg KBr, and finally put into the apparatus. The FT-IR spectra were obtained as the cell was heated from room temperature to 180 °C. c), AC adsorption on $LaCl_3$: the analysis method and procedure of AC adsorption was similar to that of urea, except that AC was used instead of urea. d), co-adsorption of AC and allyl alcohol on $LaCl_3$: 13 g catalyst and 2 mg AC were mixed together. Afterwards, a disc with 13 mm was obtained by grounding 5 mg such mixture and 100 mg fresh dried KBr. Subsequently, the sample was placed into the FT-IR cell and pretreated under vacuum for 3 h. After various volumes of allyl alcohol were introduced into the apparatus, the FT-IR spectra were recorded at 180 °C.

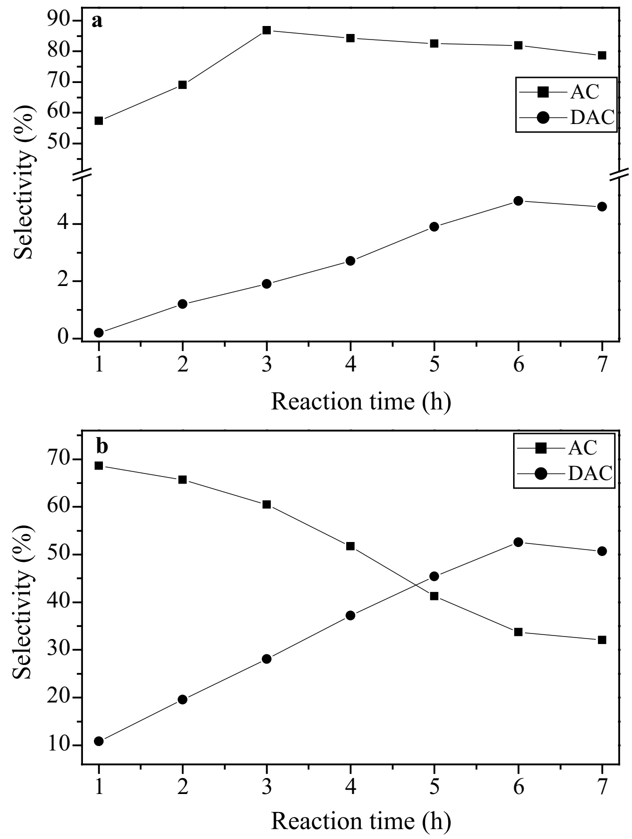


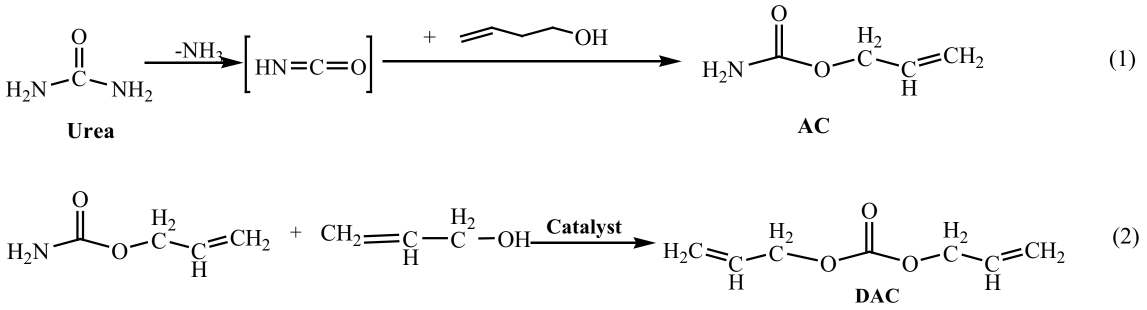
Fig. 1 Influence of reaction time without (**a**), and with $LaCl_3$ catalyst (**b**). Reaction conditions: 0.1 mol urea, 1 mol allyl alcohol; catalyst amount 0.2 g; 180 °C; 6 h. Product selectivies were based on urea

3 Results and Disscusion

3.1 Catalytic Test

Here, the products in liquid phase were measured using GC–MS and quantified by means of GC. The experimental results displayed that the major components were allyl alcohol, AC and DAC. In order to identify the reaction pathway between urea and allyl alcohol, the effect of reaction time was evaluated without and with $LaCl_3$, respectively, and the comparative results are shown in Fig. 1. Evidently, AC could be synthesized fast from urea and allyl alcohol even without catalyst. By contrast, only trace amount of desired product of DAC was generated although the reaction proceeded more than 6 h. When the reaction was catalyzed by $LaCl_3$, the selectivity of AC decreased rapidly. During this procedure, the selectivity of DAC rose sharply at the cost of AC consumption. Therefore, it was reasonable to state that the production of DAC between urea and allyl alcohol could be divided into two steps (Scheme 1). Initially, a large amount of the intermediate AC was formed, and this step was fast. Nevertheless, the conversion of AC to DAC was difficult, and it only occurred efficiently over proper catalyst. Herein, the second step was the rate-control step for the DAC synthesis. The remarkable catalytic performance of $LaCl_3$ could be ascribed to its high ability towards conversion of AC to DAC.

Table 1 summarizes the reactivity comparison of various samples for the DAC manufacture from urea or from AC. Only trace amount of DAC was formed in absence of catalyst no matter the staring material was urea or AC. For all the catalysts, the deviation of DAC yield from transesterification of urea and that from AC alcoholysis could be neglected. As a result, the following discussion regarding these catalysts was based on their catalytic performance towards DAC synthesis from AC and allyl alcohol. It was important to note that the DAC yield differed significantly among these metal chlorides after 6 h reaction. NaCl, KCl, $MgCl_2$, $CaCl_2$ and $CuCl_2$ showed rather low activity. At the same reaction conditions, the DAC yield increased sharply



Scheme 1 The reaction procedure for the synthesis of DAC from thansesterification between urea and allyl alcohol

Table 1 Yield comparison of DAC synthesized from urea and that from AC

Entry	Catalyst	AC conversion/ yield (%)	DAC yield (%)
1	None[a]	81.9	4.8
2	None[b]	6.2	5.3
3	$NaCl$[a]	80.2	6.2
4	$NaCl$[b]	8.4	6.9
5	KCl[a]	83.1	5.2
6	KCl[b]	6.8	5.7
7	$MgCl_2$[a]	69.2	12.4
8	$MgCl_2$[b]	19.3	15.5
9	$CaCl_2$[a]	66.3	10.4
10	$CaCl_2$[b]	14.5	11.8
11	$CuCl_2$[a]	77.6	6.8
12	$CuCl_2$[b]	9.4	7.2
13	$ZnCl_2$[a]	53.7	28.5
14	$ZnCl_2$[b]	48.4	34.9
15	$CeCl_3$[a]	43.2	45.8
16	$CeCl_3$[b]	64.6	49.0
17	$LaCl_3$[a]	32.8	57.9
18	$LaCl_3$[b]	74.1	60.7
19	$La(NO_3)_3$[a]	33.7	52.6
20	$La(NO_3)_3$[b]	70.5	54.8
21	$NaNO_3$[a]	77.4	3.6
22	$NaNO_3$[b]	4.3	3.7
23	$Cu(NO_3)_2$[a]	75.7	5.3
24	$Cu(NO_3)_2$[b]	7.4	6.0
25	Precipitate[a]	26.5	59.1
26	Precipitate[b]	76.2	61.6

[a] Reaction conditions: 0.1 mol urea, 1 mol allyl alcohol; catalyst amount 0.2 g; 180 °C; 6 h. DAC yields were based on urea

[b] Reaction conditions: 0.1 mol AC, 1 mol allyl alcohol; catalyst amount 0.2 g; 180 °C; 6 h. DAC yields were based on AC

to 34.9% and 49.0%, when $ZnCl_2$ and $CeCl_3$ were separately applied as catalyst (Entries 14, 16). Notably, $LaCl_3$ gave the best catalytic performance with 60.7% of DAC yield (Entry 18). So, these catalytic test results indicated that the reactivity of these homogeneous catalysts closely depended on their metal cations. To verify this hypothesis, the catalytic abilities of $La(NO_3)_3$ were further investigated. As expected, this compound also gave a rather high yield of DAC (54.8%). Meanwhile, the possibility of NO_3^- devotion to the reactivity was also ruled out because that both $NaNO_3$ and $Cu(NO_3)_2$ were inactive for the DAC synthesis (Entries 21–24). Therefore, it was ascertained that the reactivity of these La-containing samples only stemmed from trivalent lanthanum ions, and the reaction hardly took place without La^{3+} species.

3.2 FT-IR Spectra of Product of Interaction Between Reactants and $LaCl_3$

To explore the possible reaction mechanism of the transesterification between urea and allyl alcohol over $LaCl_3$ catalyst, in situ FT-IR experiments were performed under different conditions (see Fig. 2).

3.2.1 Allyl Alcohol Absorption Over $LaCl_3$

At first, the adsorption of allyl alcohol over $LaCl_3$ was investigated and the FT-IR spectra are given in Fig. 2a. It was showed that there was no obvious change for allyl alcohol at various temperatures, implying that allyl alcohol did not seem to interact with $LaCl_3$. Allyl alcohol gave its characteristic bands at 3310 cm^{-1}, which was associated with O–H stretching vibration. The bands at 2810 and 1646 cm^{-1} were ascribed to the C–H stretching vibrations. Besides, the deformation vibrations attributed to $–CH_3$ could be seen at 1420 and 1115 cm^{-1}. The C–O starching vibration at 1025 cm^{-1}, as well as the bands attributed to the vinyl groups (3086, 992 and 920 cm^{-1}) were all in line well with the standard infrared spectrum of allyl alcohol [25]. Therefore, it was likely that allyl alcohol could not be activated over $LaCl_3$ in the present case.

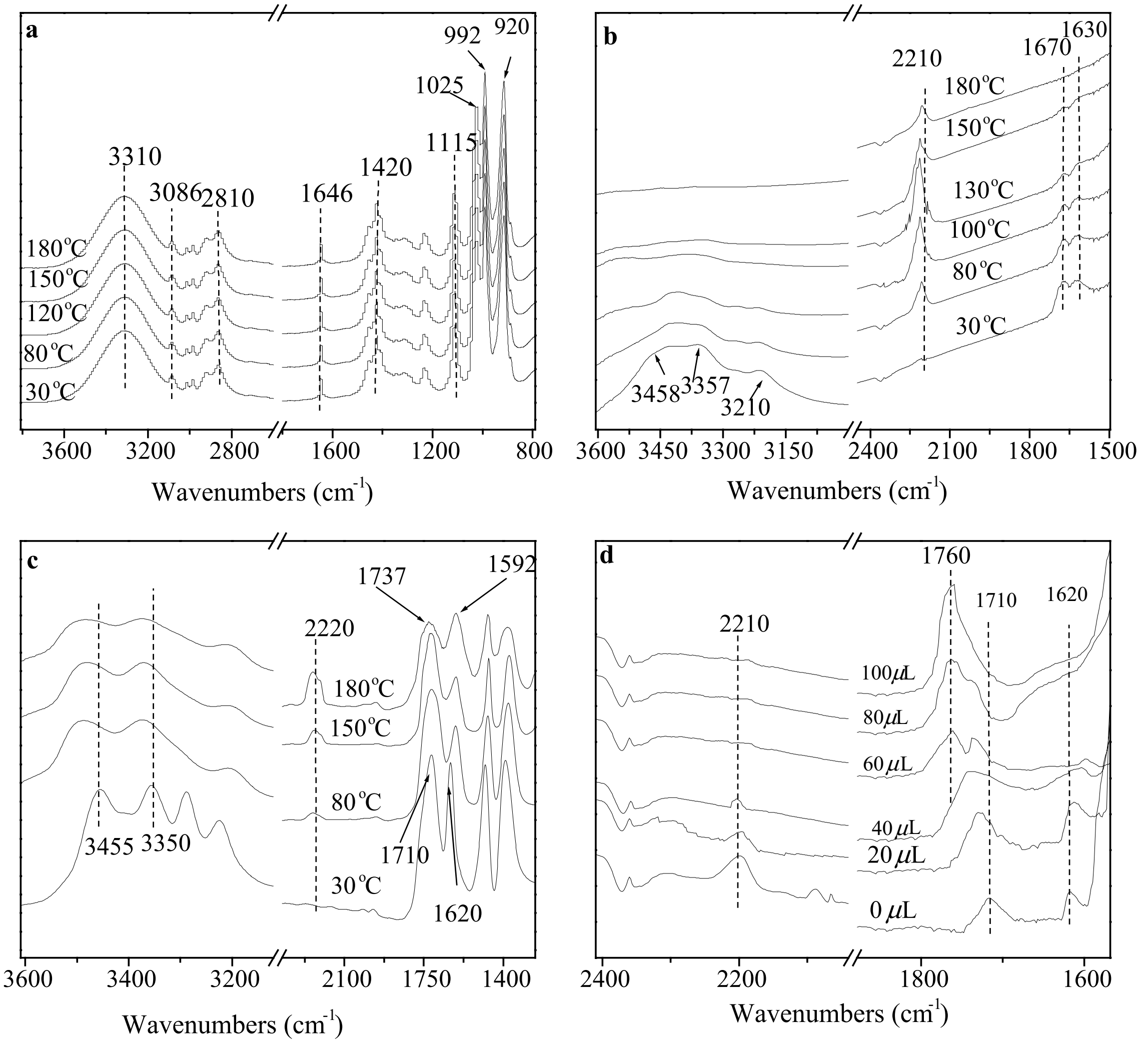


Fig. 2 FT-IR spectra evolution of allyl alcohol absorbed on $LaCl_3$ (**a**), urea absorbed on $LaCl_3$ (**b**), AC absorbed on $LaCl_3$ (**c**) at different temperatures; and AC with different amounts of allyl alcohol co-adsorbed on $LaCl_3$ at 180 °C (**d**)

3.2.2 Urea Decomposition

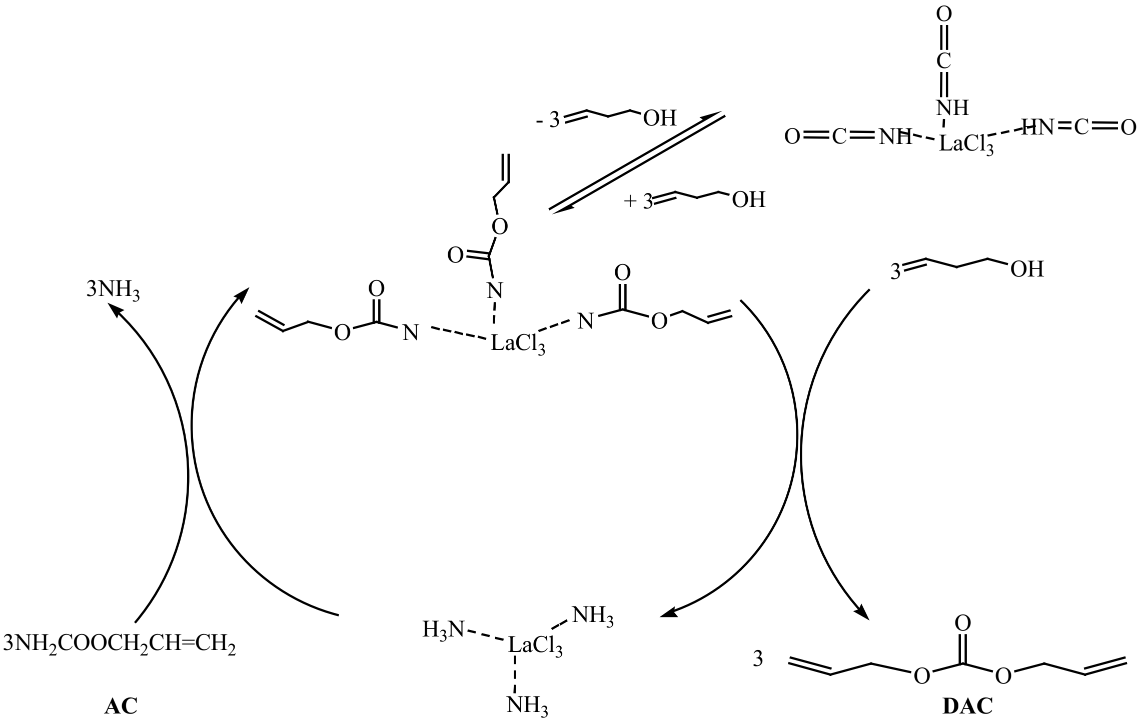
To figure out how the reactant of urea was activated over $LaCl_3$, the FT-IR spectra of urea alternation over $LaCl_3$ were collected (see Fig. 2b). At the room temperature, the feature bands of urea could be seen at 3458, 3357 and 3210 cm^{-1}, which were ascribed to N–H symmetry and anti-symmetry stretching vibration, respectively. Moreover, the bands assigned to C=O stretching and N–H bending vibration were separately observed at 1670 and 1630 cm^{-1} [26, 27]. With the rise of temperature, the intensities of aforementioned bands tended to be weaker and weaker. Interestingly, a new band related to N=C=O asymmetric stretching vibration of isocyanate species, appeared at around 2210 cm^{-1} [28]. Moreover, its intensity increased gradually with the increasing temperature. When the temperature reached 150 °C, the band of isocyanate species reached its peak value, while that of urea almost disappeared. Considering the structure of urea, it was reasonable to state that urea could be activated and decomposition into isocyanic acid, releasing a NH_3 molecule over $LaCl_3$ (See Scheme 1). The similar discovery and conclusion were also proposed by other researchers [28]. In addition, it should be mentioned that with further increase temperature, the intensity of HN=C=O decreased, implying that it was decomposed at a relative higher temperature.

3.2.3 Interaction of AC and $LaCl_3$

Figure 2c illustrates the FT-IR spectra of AC adsorption over $LaCl_3$ with increasing temperature. For pure AC, it exhibited the absorptions at 3455 and 3350 cm^{-1}, which were ascribed to N–H antisymmetry and symmetry stretching vibrations, respectively [29]. Because that some AC dimer could be formed through connection of hydrogen bonds of monomer, they showed red shifts to 3285 and 3220 cm^{-1}, respectively [30]. Besides, the C=O stretching vibration, denoted as amide I band, was found at 1710 cm^{-1}. Amide II band, caused by NH_2 bending vibration, appeared at 1620 cm^{-1}. As the temperature increased, blue shifts towards 3490 and 3370 cm^{-1} occurred for N–H stretching vibrations antisymmetry and symmetry stretching vibrations, respectively. At the same time, the bands attributed to AC dimer decreased, which was an indicator of break of intermolecular hydrogen bonds. More importantly, the amide I and II bands had a clearly blue shift towards 1737 cm^{-1} and a red shift to 1592 cm^{-1}, respectively. These changes suggested that the La^{3+} had coordinated with the nitrogen atom of AC [14, 31, 32]. In addition, it was interesting to see that a new absorption corresponding to isocyanate species was detected at about 2220 cm^{-1} [28], accompanying a gradual increase in intensity with increasing temperature. Meanwhile, the feature bands above-mentioned attributed to pure AC all showed a gradual decrease in intensity. All these phenomena provided evidences that AC could be activated and decomposed into isocyanic acid over $LaCl_3$ (see Scheme 2).

3.2.4 Co-Adsorption of AC and Allyl Alcohol on $LaCl_3$ Catalyst

The above results confirmed that the reaction of AC and allyl alcohol was the rate-control step. Thus, the co-adsorption of them over $LaCl_3$ was also studied to elucidate the reaction procedure more clearly and reasonably. Here, we mainly focused on the evolution of the band belonged to N=C=O coordinated to $LaCl_3$, the absorption at around 1760 cm^{-1} corresponding to the C=O stretching vibration of carbonate [33], as well as the amide I and II bands of AC. Absence of allyl alcohol, AC was decomposed into isocyanic acid species at 180 °C to some extent. Upon the addition of allyl alcohol, some obvious alternations could be observed. The absorption of La–N=C=O decreased rapidly with the increasing amount of allyl alcohol, and vanished as it reached 60 μL. Interestingly, the bands attributed to AC at 1710 and 1620 cm^{-1} also appeared. Thus, it was likely that the reaction for AC conversion to isocyanic acid was reversible [14]. Therefore, allyl alcohol would easily react with isocyanic acid to regenerate AC because that there was a large amount of allyl alcohol available in the system. Besides, amide I and of amide II showed a red shift and a blue shift, respectively, unambiguously demonstrating that the AC amino group had be coordinated with La^{3+} via nitrogen atom [14, 31, 32]. Importantly, it was noteworthy that the characteristic band of DAC appeared at around 1760 cm^{-1} when 60 μL allyl alcohol was introduced into system. As the amount of allyl alcohol further increased to 100 μL, the intensity of DAC always monotonically rose, whereas that of AC



Scheme 2 The possible reaction mechanism for the DAC synthesis from AC and allyl alcohol over $LaCl_3$

consistently decreased, revealing the manufacture of DAC from AC and allyl alcohol over the $LaCl_3$ catalytic sample.

3.3 Structure Change of $LaCl_3$ Before and After Reaction

It should be mentioned that $LaCl_3$ could not dissolved into alcohol solution completely at room temperate. Surprisingly, it could dissolve into reaction system and the mixture solution became transparent when reaction temperature was over 100 °C. However, some yellow crystals were generated when the reactor was put in the ice bath. To gain the clue on the nature of active species, the yellow crystal was recovered by centrifugation, and then washed with ethanol several times to eliminate the organic species. Figure 3 demonstrates the XRD patterns of the fresh and recovered $LaCl_3$. To our surprise, after one reaction run, $LaCl_3$ had converted to another species, which was proved to be $La(NH_3)Cl_3$, according to the standard XRD data base (PDF# 32-0429). Additionally, it was found that this precipitant possessed greater quality than that of fresh $LaCl_3$. Furthermore, the experiment data of element analysis of this sample was highly in agreement with the standard result based on the chemical formula (see Table 2). The catalytic test showed that this yellow sample was also active for the DAC synthesis (see Table 1, Entries 25, 26). Thus, the above results was strong evidenced that $LaCl_3$ had changed to $La(NH_3)Cl_3$ completely, and it might be the active intermediate during the catalysis.

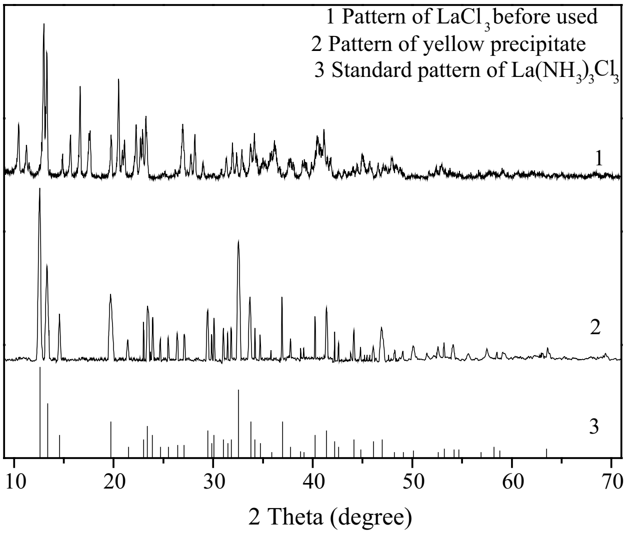


Fig. 3 XRD patterns of the fresh $LaCl_3$ catalyst and the precipitant obtained after one reaction

Table 2 Element analysis of the precipitate from the transesterification of urea and allyl alcohol over $LaCl_3$

	La	N	H
Determined (%)	47.2	14.1	2.9
Formula of $La(NH_3)_3Cl_3$ (%)	46.8	14.2	3.0

3.4 Possible Reaction Mechanism for Transesterification of Urea and Allyl Alcohol

According to the experimental results and forgoing discussion, the production of DAC from urea and allyl alcohol over $LaCl_3$ could be divided into two steps. It was obviously showed that the conversion of urea to AC was easier than the second step. The in situ FT-IR characterization meant that isocyanic acid was generated from urea decomposition. It was generally considered that this compound was an active intermediate species and it could not exist in nature separately [21]. When there was abundant alcohol present in system, it would react with allyl alcohol to form AC very easily [14]. Herein, AC could be obtained with high yield without catalyst. However, although AC could be converted into isocyanic acid over $LaCl_3$, the generation of DAC via the isocyanic acid from AC was proved to be hardly achieved. The reason might be as follows: as the discussion abovementioned, the decomposition of AC into allyl alcohol and isocyanic acid could be reversible. Considering that the allyl alcohol/AC molar ratio was 10 in the reaction system, the excessive allyl alcohol would drive the reaction equilibrium towards the AC production. Simultaneously, NH_2^- was a stronger nucleophile compared to $CH_2{=}CH{-}CH_2{-}O^-$, therefore, it was required high energy for replacement of amino group by allyl group. This made the reaction of AC and allyl alcohol thermodynamically unfavorable [21]. Furthermore, the NH_3 accumulated in the reactor due to the conversion of urea to AC unambiguously prevented the generation of DAC, for this side-product also produced in the reaction of AC and allyl alcohol. Thus, the conversion of AC to DAC was very difficult and hardly occurred without catalyst.

In the other hand, it was well known that $LaCl_3$ was a hard Lewis acid, and it could be easily coordinated to nitrogen or oxygen atom with lone pair electrons. In the present case, AC molecule had one nitrogen atom in amino group, two oxygen atoms in allyl and carbonyl group. All of these hetero atoms were likely to be coordinated with La^{3+} [34]. Zhao et al. proposed that the electron densities of nitrogen were higher than that of oxygen atom in the carbamate molecule [30], implying that the former more likely bound to $LaCl_3$. Indeed, this conclusion was strongly proved by the measurement of FT-IR, which showed that AC bounded La^{3+} via the nitrogen atom of amino group. So, a plausible catalytic mechanism is depicted in Scheme 2 for the synthesis of DAC from AC and allyl alcohol over $LaCl_3$. First, a coordination complex was generated as the result of three equiv AC bound to one equiv $LaCl_3$ via nitrogen atom in AC. Consequently, the La^{3+} ion reached a 6-coordinated stable state (the three chloride atom would give one pair of electrons, respectively). Meanwhile, as the nitrogen atom bounded with La^{3+}, its hybridized orbital might altered from sp^2 to sp^3. As the result, the π-delocalized bond of amide would disappear completely. This undoubtedly led to the weakness of amino bond of AC, which was in turn benefit for the attack of allyl alcohol. Subsequently, the lone pair of oxygen of allyl alcohol could attack the carbonyl carbon of the activated AC. During this process, the proton of O–H in allyl alcohol would bind to nitrogen atom, giving rise to the break of C–N bond. At the same time, the target product DAC and the active intermediate species $La(NH)_3Cl_3$ was produced. Finally, due to the liberation of NH_3, AC, which possessed high nucleophilic ability, would replace the NH_3 in this complex to start next catalytic circle.

4 Conclusion

In summary, we have investigated the catalytic ability of various metal chlorides for the green production of DAC via transesterification of urea and allyl alcohol. A highest DAC yield of 57.9% was obtained applying $LaCl_3$ as catalyst. Importantly, it was demonstrated that this process was a two-step reaction, and the second step difficulty occurred in the absence of catalysts. The excellent catalytic ability of $LaCl_3$ could be ascribed the fact that AC could be activated by coordination of La^{3+} via its nitrogen atom. In addition, we discovered that $LaCl_3$ had been changed to $La(NH_3)_3Cl_3$, which was might the active intermediate for the efficient conversion of AC to DAC. Considering the variety application of organic carbonates, this new findings may provide a new way to achieve green synthesis of DAC with high yield and low-price.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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