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CO_2 valorization through methyl *N*-phenylcarbamate synthesis

XUN Jia-yao[1]，SONG Qing-wen[1,*]，ZHANG Qian-xia[1]，HAN Li-hua[1]，
ZHANG Kan[1]，ZHANG Jian-li[2]，LIU Ping[1,*]
（1. *State Key Laboratory of Coal Conversion*, *Institute of Coal Chemistry*, *Chinese Academy of Sciences*,
Taiyuan 030001, *China*;
2. *State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering*,
Ningxia University, *Yinchuan* 750021, *China*）

Abstract: Methyl *N*-phenylcarbamate (MPC) is an important intermediate for the synthesis of diphenylmethane diisocyanate (MDI), and its preparation using CO_2 or its equivalents/derivatives as carbon source represents a green and sustainable manner for fine chemicals synthesis. This review will highlight the development of MPC synthetic methods from the viewpoint of chemical fixation of CO_2. The contents mainly include the introduction of MPC synthesis through CO_2 equivalents (urea or phenyl urea) alcoholysis, dimethyl carbonate (DMC) aminolysis, and the coupling of DMC and diphenyl urea. Furthermore, one-pot synthesis of carbamates/MPC from aliphatic amines/aniline, CO_2 and alcohols is highlighted which represents one of the most promising schemes in direct CO_2 utilization. What is more, the reaction mechanisms and selection of catalysts are also discussed in detail. The advances will provide important theories on further improving the efficiency of green catalysis and sustainable chemical processes.

Key words: carbon dioxide; CO_2 equivalent; methyl *N*-phenylcarbamate; catalysis; synthetic method
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For a long time, a large amount of CO_2 from the consumption of fossil fuels is emitted which continuously increases the greenhouse effect. Meanwhile, CO_2 is also a safe, abundant and inexpensive carbon resource. Considering environmental protection and resource utilization, it is of great significance to launch the study on the synthesis of highly value-added chemicals using CO_2 as the raw material [1,2]. As a green building block, CO_2 has been widely used in the synthesis of urea, carbonates, carboxylic acids, formamides, hydrocarbons and so on[3−5]. Among them, the synthesis of methyl *N*-phenylcarbamate (MPC) through the coupling of aniline with CO_2 or its equivalents and derivatives has attracted great attention.

MPC is one kind of methyl carbamate being widely used in synthesis of diphenylmethane diisocyanate (MDI) which is the main raw material for polyurethane (PU) production[6]. In 2019, the total production capacity of isocyanates in the world was about 12.7 million t/a, and that of MDI was about 9.2 million t/a. China is the largest MDI producer in the world at present, and the production capacity reaches 3.7 million t/a accounting for around 68.9% of the world's total production capacity[7]. In recent years, with the increasing global demand of PU and the awareness of energy conservation, the demand for MDI is also increasing. Besides, MPC is also used as an important organic intermediate in the synthesis of non-toxic polyurethane, isocyanate, polyvinyl amine, etc.[8]

At present, industrial production of MDI is from the phosgene method, namely the two-step reaction from aniline, formaldehyde and phosgene. In the process, the phosgene is highly toxic, and the by-product hydrogen chloride is corrosive which can cause many potential environmental problems[9]. In recent years, much attention is paid to the non-phosgene synthesis technology of MDI. As shown in Figure 1, the traditional non-phosgene route to MDI contains aniline oxidation carbonyl method[10], Hofmann rearrangement method[11] and nitrobenzene carbonyl reduction carbonyl method, etc.[12]. In these methods,

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[*] Corresponding author. Tel: 0351-4040510, E-mail: songqingwen@sxicc.ac.cn, pingliu@sxicc.ac.cn.

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the use of precious metals as catalyst, harsh reaction conditions and the generated by-products are inevitable. Therefore, these non-phosgene protocols for MDI synthesis only stay in the theoretical stage. In the further, the green, economic and efficient routes will be indispensable and urgently needed.

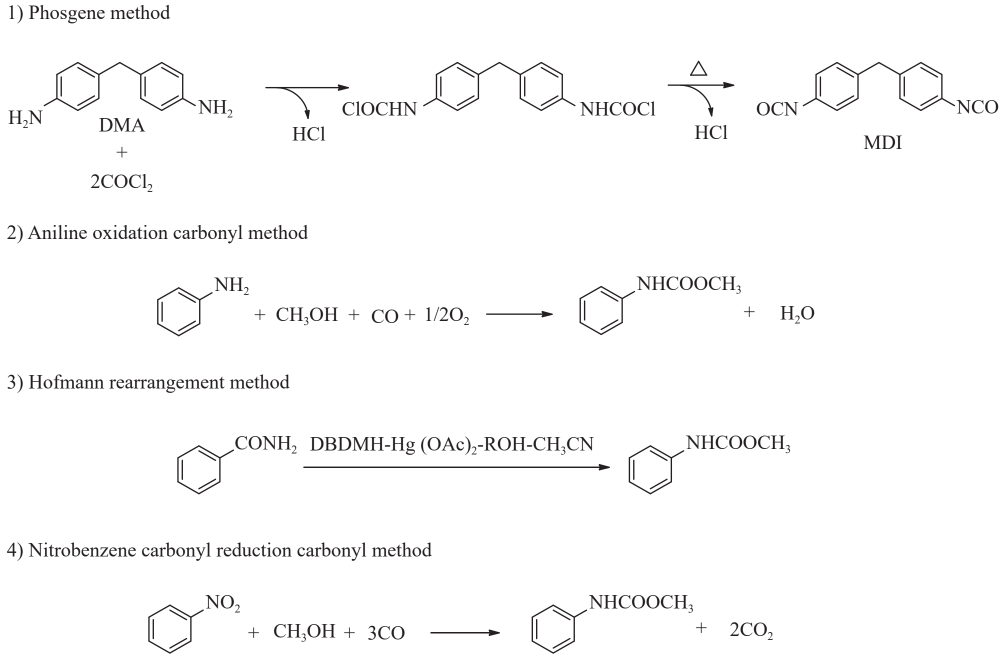


Figure 1 Traditional MDI synthetic methods

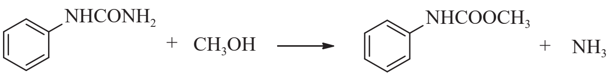
The synthesis of MDI using CO_2 or its equivalents and derivatives as carbon source represents the green and sustainable method with high atom economy under mild reaction conditions. Herein, the advances on the synthesis of methyl *N*-phenylcarbamate, the key intermediate for the preparation of MDI, through CO_2 or its equivalents and derivatives as C_1 source are summarized. The highlights of synthetic methods, catalytic processes and reaction mechanism are introduced, and the results under different reaction conditions and catalysts are compared and discussed, which will provide the guidance for fundamental research and application exploration.

1 Synthesis of MPC through CO_2 equivalents and derivatives

1.1 Phenyl urea alcoholysis

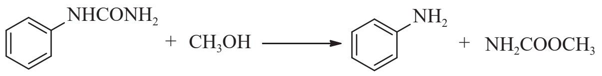
Industrial process for the synthesis of urea is via the reaction of CO_2 with ammonia. Moreover, phenyl urea and diphenyl urea can be easily synthesized through the reaction of urea and aniline in equal or excessive amount. As the equivalents of CO_2, phenyl urea and diphenyl urea also play an important role in the synthesis of MPC[13]. MPC can be formed via an exchange reaction between phenyl urea and methanol along with the generation of NH_3 (eq. (1)). Simultaneously, a competitive side reaction of phenyl urea and methanol occurs to give the aniline and methyl carbamate (eq. (2)). Besides, *N*-methylaniline can also be generated by the subsequent methylation reaction of aniline and methanol (eq. (3)).

Main reaction

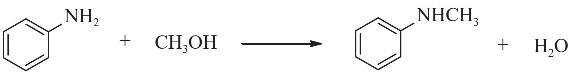


(1)

Side reaction



(2)



(3)

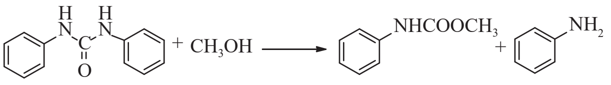
In the previous work, $Pb(OCH_3)_2$ was demonstrated to be the active species and showed good catalytic activity among the catalysts tested in the reaction of phenyl urea and methanol. In addition, the reaction conditions (including reaction temperature, time and methanol/phenyl urea mole ratio) also strongly affected the synthetic efficiency of MPC. Specially, the influence of methanol-pretreated PbO catalyst in the reaction of phenyl urea and methanol was studied[14]. Comparing with the system without any catalyst, the conversion of phenyl urea and the selectivity of MPC increased after introducing Pb-based catalysts such as PbO, Pb_3O_4 or methanol-pretreated PbO, and meanwhile the selectivity of the byproduct aniline reduced. Using methanol-pretreated PbO catalyst under the same conditions, the selectivities of aniline, methyl carbamate and *N*-methylaniline were 14.51%, 11.32% and 0.64%, respectively. After the pretreatment via methanol, PbO was transferred into the $Pb(OCH_3)_2$ bearing better catalytic activity, and therefore the reactivity of phenyl urea was enhanced. Finally, a new addition-elimination reaction mechanism was proposed on the basis of the experimental results. In the presence of methanol-pretreated PbO catalyst ($Pb(OCH_3)_2$ species), the nucleophilic species CH_3O^- attacks the carbonyl carbon and meanwhile $(Pb\text{-}OCH_3)^+$ combines with the nitrogen atom in $-NH_2$. As a result, a tetrahedral transition state forms through the reaction of phenyl urea with $Pb(OCH_3)_2$), and then $(NH_2\text{-}PbOCH_3)^+$ detaches from the process with the generation of MPC. Meanwhile, the reaction of methanol with the intermediate $NH_2\text{-}PbOCH_3$ regenerates $Pb(OCH_3)_2$ and releases NH_3. Due to the large diameter of $Pb(OCH_3)_2$ and the geometrical barrier of benzene ring unit, the combination of $(Pb\text{-}OCH_3)^+$ with nitrogen atom in $-NH$ is suppressed. Therefore, MPC and ammonia are mainly produced. In addition, methanol can be activated via $Pb(OCH_3)_2$, which facilitates the transformation of phenyl urea.

Furthermore, solid alkaline catalysts, being prepared through supporting KF on metallic oxide (Al_2O_3, Nd_2O_3, La_2O_3, CeO_2, Pr_6O_{11} or SiO_2), were also demonstrated enable to promote the methanolysis of phenyl urea to MPC. As seen from the result, KF/Al_2O_3 catalyst displayed good catalytic performance, and the conversion of phenyl urea reached 96.5% with MPC selectivity of 86.3%[15]. There is a strong interaction between KF and Al_2O_3, and K_3A1F_6 forms in the calcination process. KF is beneficial to the activation of methanol, while K_3A1F_6 is conducive to the formation of MPC. Thus, the synergistic catalysis promotes the conversion of phenyl urea to MPC.

Methanol is used as both reactant and solvent in phenyl urea alcoholysis method, and the excess of methanol (e.g. the molar ratio of phenyl urea/methanol up to 1:40) is unfavorable to industrial production. Due to the equivalent amount of NH_3 generated during the reaction, the atom economy is relatively low, and meanwhile there is much difficulty in the separation process of methanol. Additionally, the competitive reaction in this system results in the formation of aniline and carbamate, which leads to the difficulty in separation and simplification of equipment. At the same time, the production cost increases. In the process of phenyl urea alcoholysis, the efficiency of $Pb(OCH_3)_2$ catalyst is very high, but the metal used is not friendly to the environment. In addition, the cost of the raw material phenyl urea is also high, and now the method only stays in the laboratory stage and is reported rarely.

1.2 Diphenyl urea alcoholysis

MPC can also be synthesized through the reaction of diphenyl urea and methanol in the presence of suitable catalyst (eq. (4)), and fortunately diphenyl urea is easily obtained through the reaction of aniline with CO_2[16,17]. In addition, it is worth noting that the yield of diphenyl urea is enhanced after the introduction of CO_2 into the system. Firstly, aniline can react with CO_2 and give diphenyl urea (eq. (5)). Secondly, the removing of the aniline in eq. (4) through eq. (5) will promote the equilibrium shifting to the direction of MPC generation. At last, the synergistic effect further stimulates the conversion of methanol, and as a result, both the conversion of diphenyl urea and the selectivity of MPC are greatly improved.



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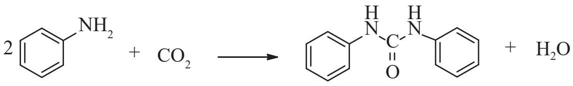


(5)

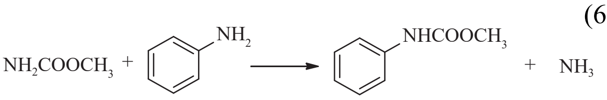
Comparing with the system without any catalyst, both the conversion of diphenyl urea and selectivity of MPC increased in the presence of metal catalyst[18]. As for the mechanism, the MPC is formed through the exchange reaction between phenylamino group of diphenyl urea and $-CH_3O$ of methanol along with the generation of by-product aniline. In this work, the catalysts supported on various metal compounds including Pb, Zn, Al, Fe or Mo were investigated successively. In the absence of catalysts, diphenyl urea conversion, MPC yield and selectivity reached 70.21%, 40.32% and 57.43%, respectively. However, after introducing the Mo catalyst, the conversion of diphenyl urea, the yield and selectivity of MPC correspondingly increased to 85.36%, 73.92% and 86.60%. With the addition of PbO, the catalytic activity was enhanced, and the conversion of diphenyl urea and the selectivity of MPC significantly increased. The conversion of diphenyl urea was higher than that of the other catalytic species screened when PbO/Al_2O_3 was used as the catalyst. Comparing with PbO catalyst, the selectivity of MPC from PbO/Al_2O_3 catalytic system was slightly lower. Nevertheless, the PbO/Al_2O_3 catalyst was more easily recovered from the reaction system than that of PbO catalyst, which was favorable for the technology exploration. Under the conditions of 180 °C for 3 h, the mass ratio of m(methanol)/m(diphenyl urea) being 10∶1, the conversion of diphenyl urea reached up to 95.68%, and the selectivity of MPC reached 88.16% in presence of PbO/Al_2O_3 catalyst. To inhibit the *N*-methylation reaction of aniline with methanol to produce *N*-methylaniline, CO_2 was introduced into the reaction for consuming the aniline. The activation energy of CO_2 reacting with aniline to produce diphenylurea is relatively low, however, the methylation reaction of methanol with aniline requires higher activation energy. As a result, no *N*-methylaniline formation is observed in the product, indicating that the introduction of CO_2 inhibits the methylation reaction between methanol and aniline. By adjusting the conditions, the further *N*-methylaniline reaction between aniline and methanol was inhibited leading to an improved yield and selectivity of MPC, and a new and effective method for the synthesis of MPC was opened up.

Totally, MPC is obtained through the reaction of diphenyl urea and methanol under relatively mild conditions. The main side reaction is methylation of aniline. The introduction of high pressure of CO_2 contributes to an improved selectivity of MPC but leads to the new by-product i.e. dimethyl carbonate (DMC) which can also accelerate the formation of *N*-methylaniline. As a result, the separation process can also become complicated and the production cost also increases.

1.3 Urea alcoholysis

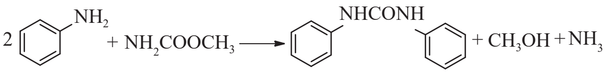
The urea alcoholysis route contains two steps. Firstly, the reaction of urea with methanol gives a methyl carbamate (eq. (6)). Secondly, methyl carbamate reacts with aniline to form MPC (eq. (7)). Both of them afford a stoichiometric ammonia. In fact, the first step of this route has been widely used, and the yield of methyl carbamate can reach more than 90%[19]. Herein, the second step is studied[20], and on the basis of the distribution of products, the main and side reactions occurring in the reaction system are also proposed (eqs. (3) and (4)).

$$(NH_2)_2CO + CH_3OH \longrightarrow NH_2COOCH_3 + NH_3 \tag{6}$$



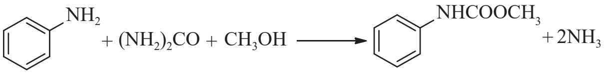
(7)

Using $ZnCl_2$ as catalyst, MPC was synthesized with high selectivity by the reaction of aniline and methyl carbamate under methanol medium[20]. The introduction of excess methanol in the reaction system significantly increased the MPC selectivity. Methanol is beneficial to promoting the eq. (4) shifting to the right side. By contrast, short of methanol, the side eq. (8) is enhanced, and meanwhile DPU and ammonia are also generated. At 160 °C for 4 h, the aniline conversion and MPC selectivity can reach 90.1% and 99.7%, respectively.



(8)

Urea alcoholysis method can be used to synthesize MPC conveniently due to the abundant raw materials and simple processes. However, the separation process is relatively complicated and the efficiency is urgently needed to be improved. In addition, coupling the two steps, MPC can be obtained in “one pot” pattern as seen in eq. (9).



(9)

Wang et al.[21] reported an effective route to synthesize *N*-substituted carbamates from amines, urea and alcohols, and in the work, the developed TiO_2-Cr_2O_3/SiO_2 catalyst performed the excellent catalytic activity. Several different aliphatic amines (butylamine, cyclohexylamine, isophorone diamine, 4,4'-diaminodicyclohexyl methane and 1,4-butanediamine) and various aromatic amines were tested, and meanwhile the alcohols bearing different chain length (from methanol to butanol) were also examined. Under the optimized reaction conditions (n(amine)∶n(urea)∶n(alcohol) being 1∶1.2∶15, 0.1 g catalyst, 190 °C, 8 h), several important *N*-substituted carbamates were successfully synthesized in good yields. Under the optimized reaction conditions, the conversions of various aromatic amines are 73%−99% along with

70%−97% yields of the corresponding *N*-substituted carbamates. The aromatic amines behave a little weaker basicity and nucleophilicity than those of aliphatic amines due to the conjugate effect, thus showing a lower reactivity.

The catalytic performances of some metal oxides (PbO, MgO, CaO, ZnO and γ-Al_2O_3) and Lewis acids ($AlCl_3$, $ZnCl_2$, $Zn(OAc)_2$, $Pb(OAc)_2$ and $Pb(NO_3)_2$) on the one-step synthesis of MPC from aniline, urea and methanol were investigated as well as the effects on the generation of by-products DPU, phenyl urea (PU), *N*-methylbenzourea (NMA), and *N*,*N*-dimethylbenzourea (DMA)[22]. Under the conditions of 180 °C, 0.6 MPa, 2 h, n(aniline)∶n(catalyst)∶n(urea)∶n(MeOH) being 1∶0.12∶5∶75, all of the metal oxides had certain catalytic effect on the reaction. Among them, only γ-Al_2O_3 calcined at 400 °C for 2 h improved aniline conversion as well as MPC selectivity up to 88.4% and 84.6%, respectively. Among the investigated Lewis acid catalysts, only in the presence of $Zn(OAc)_2$, the conversion of aniline and the selectivity of MPC reached up to 82.2% and 81.1%, respectively. The catalytic performance of γ-Al_2O_3 had no obvious change after reusing for five times. Afterwards, a reaction mechanism referring to five possible reaction paths namely via DMC, methyl carbamate (MC), 1-phenyl biuret (PBU), PU or DPU intermediates was conjectured. In order to verify the feasibility of these pathways, thermodynamic analysis and experimental studies were carried out on the reactions involved in these pathways. The results revealed that in the absence of catalyst, the reaction through PU intermediate was mainly taken place. While in the presence of γ-Al_2O_3 catalyst, the synthesis of MPC went through the MC intermediate[23].

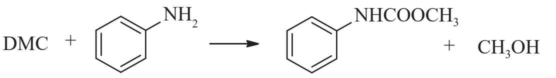
Qin et al.[24] carried out one-step reaction of aniline, urea and methanol to synthesize MPC in a high-pressure reaction kettle, and HY catalyst was screened out with good catalytic performance. Under the conditions of n(AN)∶n(urea)∶n(MeOH) being 1∶5∶15, 180 °C for 5 h, the yield of MPC was 66.5%, and the catalyst retained high catalytic activity after recycling 4 times. They prepared catalysts by impregnating alkaline metals and alkaline earth metals on HY, and found that KNO_3/HY showed the best catalytic performance. The aniline conversion and MPC selectivity reached 93.5% and 83.5% respectively under the condition of 180 °C for 5 h[25]. In the first step, urea interacts with active surface site of HY and carbonyl group is activated. In the second step, aniline and methanol molecules react with carbonyl of urea and give methyl *N*-phenylcarbamate. This step can occur via two reaction pathways, one goes through a MC intermediate, and another undergoes a phenyl urea intermediate. In detail, methanol or aniline exerts the nucleophilic attack on the urea and gets rid of a NH_3 at first to form MC or phenyl urea, and then aniline or methanol nucleophilically attacks the intermediate and gets rid of a NH_3 to form MPC.

1.4 Aminolysis of DMC

DMC being a widely used building block and green chemical has attracted considerable attention in recent years. The mainstream synthetic route to DMC is from sustainable CO_2 and methanol, and water is the only byproduct (eq. (10))[26]. As one of the most important derivatives of CO_2, DMC has many advantages as a feedstock to react with aniline for the synthesis of MPC. Comparing with the traditional routes, the avoidance of highly toxic phosgene represents one of the most promising and green methods.

In view of the environmentally friendly advantage, MPC can be directly synthesized through the reaction of DMC and aniline with the assistance of suitable catalysts (eq. (11))[27−29].

$$CO_2 + 2CH_3OH \longrightarrow DMC + H_2O \quad (10)$$



(11)

Thermodynamic calculation on the synthesis of MPC was carried out through the non-phosgene method from DMC and aniline, and the results showed that it is a spontaneous exothermic reaction. Therefore, the reaction is favorable for the synthesis of MPC under low reaction temperature. With the decrease of reaction temperature, the reaction rate also slows down. In practical application, the synthetic reaction is generally carried out at about 150 °C under the catalytic condition[30].

Zinc acetate catalyst supported on activated carbon (AC) or γ-Al_2O_3 showed good catalytic properties in the reaction of aniline and DMC (Table 1, entry 1). The MPC was obtained in up to 78% yield and 98% selectivity in the $Zn(OAc)_2$/AC catalyst system. The study revealed that the acidic supporter can promote the *N*-methylation of aniline while the alkaline supporter benefits for the formation of diphenyl urea[31]. Baba et al.[32] reported the methoxy carbonylation of 2,4-toluene diamine with DMC using

$Zn(OAc)_2 \cdot 2H_2O$ as a catalyst. Under the condition of 180 °C for 2 h, dimethyltoluene-2,4-dicarbamate was produced in a yield of 98%. During the study, an induction period was observed in the reaction of aromatic amines with DMC. However, with the addition of methanol, the methoxy carbonylation of aniline with DMC was accelerated. Notably, after pretreating the catalyst with methanol, the induction period was almost completely eliminated. A series of inorganic and organic zinc compounds e.g. ZnX_2 (X = CH_3COO, Cl, SO_4, Br or NO_3), Zn-MOF and so on were screened[33]. Among them, $Zn(CH_3COO)_2$ showed the best catalytic activity (Table 1, entry 2). In the optimized reaction conditions of molar ratio of DMC to aniline being 9 at 170 °C for 2 h, the conversion of aniline reached 99% and the selectivity of MPC was over 90%.

Table 1 Metal catalysts for MPC synthesis from aniline and DMC

Entry	Catalyst	Supporter	Conditions			Results			Ref.
			t /°C	p /MPa	t /h	conv. /%	sel. /%	y /%	
1	$Zn(OAc)_2$	AC	150	0.1	4	−	98	78	[31]
2	$Zn(OAc)_2$	−	170	0.1	2	99	90	−	[33]
3	$Zn(OAc)_2$	SiO_2	190	0.1	5	97.2	89.4	−	[34]
4	$Zn(OAc)_2$	−	130	0.1	3	98	−	97	[35]
5	zinc alkyl carboxylate	silica	170	0.1	1	94.6	96.8	91.6	[36]
6	Zn/Al/Ce mixed oxide	−	200	0.1	7	95.8	81.6	78.2	[37]
7	$ZnO-TiO_2$	SiO_2	170	0.1	7	49.9	52.3	−	[38]
8	ZrO_2	SiO_2	170	0.1	7	79.2	80.1	−	[39]
9	PbO	SiO_2	150	0.1	2	91.08	90.37	82.31	[40]
10	In_2O_3	SiO_2	150	0.1	2	75.98	78.24	59.45	[40]
11	PbO	SiO_2	160	0.1	4	99.7	99.8	99.5	[41]
12	PbO	−	170	0.1	4	81	−	−	[42]

Note: conversion (conv.), selectivity (sel.), yield (y), (−: mark indicates no available information in the reference)

$Zn(OAc)_2/SiO_2$ catalyst was prepared through solvothermal impregnation with DMC as the solvent (Table 1, entry 3) [34]. Under the conditions of 190 °C for 5 h, n(DMC): n(aniline) being 20:1 and m(aniline): $m(Zn(OAc)_2/SiO_2)$ being 0.2, the aniline conversion and MPC selectivity reached 97.2% and 89.4%, respectively. $Zn(OAc)_2/SiO_2$ catalyst showed good stability. After reusing 7 times, the aniline conversion and MPC selectivity correspondingly decreased to 79.19% and 79.29%. The explanation is that DMC as the solvent is easily hydrolyzed during the process of solvothermal impregnation. Furthermore, the presence of $Zn(OAc)_2$ will accelerate the hydrolysis of DMC. Moreover, the adsorbed water on the surface of SiO_2 will be hydrolyzed thus releasing a large number of free silica hydroxyl group, which is conducive to the dispersion of the active component on the SiO_2. As the dispersion of $Zn(OAc)_2$ on SiO_2 surface increases, the density of Si−O−Zn bonds on SiO_2 supporter rises. Meanwhile, the steric-hindrance effect of Zn^{2+} enhances, which inhibits the reaction of $Zn(OAc)_2$ with methanol and avoids the conversion of $Zn(OAc)_2$ into invalid ZnO.

Furthermore, in the $Zn(OAc)_2$-catalyzed reaction of aniline and DMC (Table 1, entry 4), $Zn(OAc)_2$ could be converted into $Zn_4O(OAc)_6$ which also showed excellent catalytic activity for carbamate synthesis[35]. Besides, some other catalysts containing Zn components also displayed good catalytic performance. For example, a new type of heterogeneous salt catalyst was designed and prepared through zinc alkyl carboxylate covalently bonding on silica by a special grafting method in aqueous media[36], and it was demonstrated highly active and recyclable for MPC synthesis from aniline and DMC (Table 1, entry 5). In addition, Zn/Al/Ce mixed oxide was also acting as an effective and recoverable heterogeneous catalyst for MPC synthesis via DMC aminolysis[37]. The introduction of appropriate amount of cerium could form the strong interaction within the mixed oxide. Thus, $Zn/Al/Ce_{2.5}$ oxide showed high catalytic activity with 95.8% conversion of aniline and 78.2% yield of MPC (Table 1, entry 6). Moreover, the catalyst also exhibited a good stability with retained nanoplate structure after five cycles. During the 5 repeated runs, the conversion of aniline was kept at about 95%, but the selectivity of MPC decreased slowly. Factually, the supporter acted as a key role on the catalytic activity improvement of metal species. Comparing with ZnO-TiO_2 catalyst in synthesis of MPC, MPC selectivity obtained through ZnO-TiO_2/SiO_2 catalyst was improved (Table 1, entry 7)[38]. In addition, the ZnO-TiO_2/SiO_2 showed higher MPC selectivity than ZnO-TiO_2/HZSM-5 and ZnO-TiO_2/γ-Al_2O_3. Aniline conversion and MPC selectivity reached 49.9% and 52.3% under conditions of n(aniline)∶n(DMC) = 1∶20 and m(catalyst)∶m(DMC) = 0.013, respectively. The catalytic activity of ZrO_2 and ZrO_2/SiO_2 were also investigated. As a result, ZrO_2 supported on SiO_2 could greatly improve the catalytic performance (Table 1, entry 8)[39]. This attributes to the formation of Zr−O−Si bond through the interaction between ZrO_2 and SiO_2, which significantly increases the proportion of weak acid sites on ZrO_2/SiO_2 surface, and the weak Lewis acid sites are in favor of MPC synthesis.

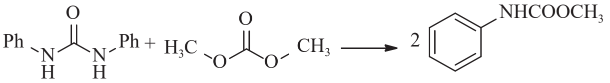
Based on the systematic study on the catalytic performance of PbO catalyst for the synthesis of MPC through the reaction of aniline and DMC, the catalytic performance of the supported PbO catalysts with different carriers was investigated[40,41]. Among them, the SiO_2 carrier is demonstrated with the highest catalytic performance (Table 1, entry 9). Subsequently, the catalytic ability of potential active components for MPC synthesis was investigated using SiO_2 as the supporter, and finally the In_2O_3/SiO_2 catalyst exhibits the highest catalytic activity among the selected candidates. Under the conditions of Pb compound (PbO/SiO_2) catalyst with 5∶1 molar ratio of DMC/aniline, 10% Pb (based on aniline) at 150 °C for 2 h, the conversion of aniline reaches 91.08%, and the yield of MPC is 82.31% with 90.37% selectivity. Considering the toxicity of Pb compounds and the easy deactivation of PbO catalyst, In_2O_3/SiO_2 catalyst is selected as a substitute. Under the same reaction conditions, the catalyst also shows good catalytic activity, and the aniline conversion, MPC yield and selectivity are 75.98%, 59.45% and 78.24%, respectively (Table 1, entry 10). With the increased numbers of catalyst recycling experiments, the aniline conversion and MPC selectivity show a downward trend. Totally, In_2O_3/SiO_2 catalyst shows a relatively long lifetime and its deactivation is not significant after recycling 8 times. Meanwhile, the complex post-treatment process is avoided during the catalyst regeneration stage.

The catalytic activity of Sn-, Ti-, Zn- and Pb-based catalysts for the reaction of DMC and aniline was investigated, and the PbO catalyst displayed the outstanding catalytic activity (Table 1, entry 12)[42]. Under the reflux condition at 170 °C for 4 h with 7.5% PbO, the conversion of aniline reaches 81%. In addition, the study also reveals the catalytic activity of Pb_3O_4-ZnO composite catalyst is higher than that of Pb_3O_4 or ZnO alone, which indicates a certain synergistic effect.

In summary, on the one hand, this synthetic method leads to the generation of equivalent methanol, which reduces the atom economy and increases the complexity of product separation. On the other hand, methanol can easily react with aniline to generate by-product *N*-methylaniline which reduces the chemoselectivity and meanwhile increases the difficulty of separation. Therefore, the development of highly efficient catalyst is indispensable to obtain the specificity of the reaction.

1.5 The coupling of DMC and diphenyl urea

Among the above-mentioned methods, aminolysis of DMC and alcoholysis of diphenyl urea are the relatively better methods that focusing on the synthesis of carbamate by non-phosgene method with good industrial prospects. However, equal mole of methanol or aniline is generated as by-products in both methods, and therefore, the atom economy of the reaction is very low. Delightedly, the synthesis of MPC is achieved by the coupling reaction of DMC and diphenyl urea (eq. (12)). This process is much simpler than the previous routes. In this transformation, only the target product MPC is afforded, which greatly increases the utilization ratio of raw materials and meanwhile reduces the difficulty of the separation procedure. The method represents a very promising non-phosgene route featuring as environmentally friendly and high atom economy[43].



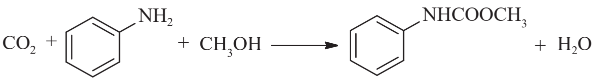
(12)

Di-*n*-butyltin oxide (DBTO) was reported as a catalyst for the synthesis of carbamates from substituted urea and organic carbonates. The results verify that basic homogeneous catalysts such as tin complexes, particularly DBTO show excellent catalytic activity towards carbamate synthesis. In aminolysis of substituted carbonates, the reactivity depends upon the basicity of nucleophilic amine. Aliphatic ureas show higher reactivity than aromatic ureas. Till now, the reports on the route to MPC from DMC and diphenyl urea are few, and the study still stays in the laboratory stage.

Based on the previous reports on the role of PbO species, the supported PbO catalyst was investigated in the reaction of diphenyl urea and DMC[44]. After the screening of different supporters, Al_2O_3 is found to be the potential high activity supporter. Under the conditions of 160 °C for 4 h with 4% catalyst relative to diphenyl urea as well as the mass ratio of DMC and DPU being 15, MPC is afforded in up to 98.2% yield. Liu et al.[45] prepared a new alcoholic Pb catalyst HO-Pb-OCH_3. For the synthesis of MPC from DMC and DPU, the alcoholic Pb catalyst shows good catalytic activity under the reaction pressure of 0.5 MPa, and the catalytic activity remains stable after four cycles. Under the conditions of 120 °C for 2 h, the raw material ratio *n*(DMC) and *n*(DPU) being 5, catalyst dosage being 1.0%, both DPU conversion and MPC selectivity reach 99%. There is a −PbOH group in this catalyst which performs high catalytic activity. Moreover, the catalyst reacts with DMC and trace water from the system to obtain basic lead carbonate $2PbCO_3\cdot Pb(OH)_2$ with the same good catalytic performance. The nucleophilic group −PbOH in $2PbCO_3\cdot Pb(OH)_2$ attacks the carbonyl carbon of DMC, causing demethylation of DMC and subsequently forming −$PbOCOOCH_3$. Then, this unit interacts with DPU via $(Ph\text{-}NH\text{-}PbOCH_3)^+$ intermediate to give the target product MPC. In addition, $NaOCH_3$ is also demonstrated to be an excellent catalyst in a non-phosgene route for the synthesis of MPC from DMC and *N*,*N*'-diphenyl urea, and the reaction proceeds smoothly at atmospheric pressure[46]. At 90 °C, the yield of MPC exceeds 80%. By comparison, under the conditions of 3.4 MPa and 150 °C, the yield of MPC only exceeds 77% using highly poisonous homogenous Bu_2SnO catalyst. For this route, there is nearly no side reaction happening, and meanwhile the target product is single which is convenient for products separation, purification and industrial production. The emphasis of this path is to develop the powerful catalysts to boost the efficiency and the easily recovered catalysts to facilitate the catalyst separation and recycling from the reaction system.

2 Direct CO_2 route to carbamates and MPC: one-pot reaction of various amines, CO_2 and alcohols

Indirect methods such as CO_2 equivalents and derivatives used for preparation of MPC with special advantages especially bearing thermodynamic favorable process have been introduced above, however, the most ideal route to MPC is the direct method using CO_2 as a carbon resource. One-pot cascade reaction of aniline, CO_2 and methanol represents the most simple and green route to MPC, which uses the widely available commercial raw materials. Currently, most of the carbamates synthesized by this method are limited to the aliphatic carbamates from aliphatic amines and CO_2. The reactivity of aromatic amine substrates is very low. Therefore, one-pot synthesis of MPC from aniline, methanol and CO_2 is generally confronted with very low reactivity (eq. (13)), which makes this method face a great challenge. Herein, the advances on insights into efficient methods to carbamates/MPC direct from aliphatic amines/aniline and CO_2 in the past several years are reviewed[47]. Especially, the CeO_2-catalyzed effective scheme for MPC synthesis from aniline, CO_2 and CH_3OH with the assistance of 2-cyanopyridine as dehydrating agent is highlighted here.



(13)

Firstly, thermodynamic calculations were carried out for the reaction of aniline, CO_2 and methanol. The results showed that the three-component reaction is exothermic ($\Delta_r H$ = −35.27 kJ/mol) but it is non-spontaneous ($\Delta_r G$ = 12.53 kJ/mol)[48,49]. In addition, three routes via the intermediates of DPU, DMC and DPU/DMC, respectively, were proposed (Figure 2). Among the routes, the route via DPU intermediate was demonstrated to be the most favorable manner[50].

A series of alkaline catalysts were examined for the synthesis of MPC through aniline, CO_2 and methanol[51]. As seen from the results, the bicyclic amidine DBU showed outstanding catalytic ability in acetonitrile which contributed to the good solubility of CO_2. Besides, acetonitrile also acted as a dehydrating agent to shift the reaction equilibrium to the right. Under the conditions of initial 1 MPa CO_2 at 180 °C for

5 h, volume ratio of methanol to aniline being 1:4, and volume ratio of acetonitrile to aniline being 1:1, the conversion of aniline and the selectivity of MPC were 7.1% and 25.3%, respectively. Similarly, in the presence of DBU and CH_2Br_2 as both solvent and indirect dehydrating agent, carbamates were obtained from aromatic amines, CO_2, and CH_3OH under mild conditions[52]. Two possible routes referring to the amine or alcohol activation through DBU were proposed. The active [$DBUH^+$][$ROCO_2^-$] and [$DBUH^+$][$RNHCO_2^-$] intermediates were converted into the target products through reacting with the corresponding amines and alcohols with the assistance of CH_2Br_2. In the metal-contained system, Cu-Fe/ZrO_2-SiO_2 catalyst was investigated and showed catalytic activity in the synthesis of MPC using acetonitrile as a dehydrating agent[53]. Under 10% metal loading, 14% conversion of aniline and 65.7% selectivity of MPC were obtained, which were much higher than the values reported. Nevertheless, there remain some shortcomings being confronted in these systems. Firstly, both the reactivity of aniline and selectivity of MPC are very low. Additionally, the chemical dehydrating method adopted still brings much byproduct and increases the complexity in the separation procedure.

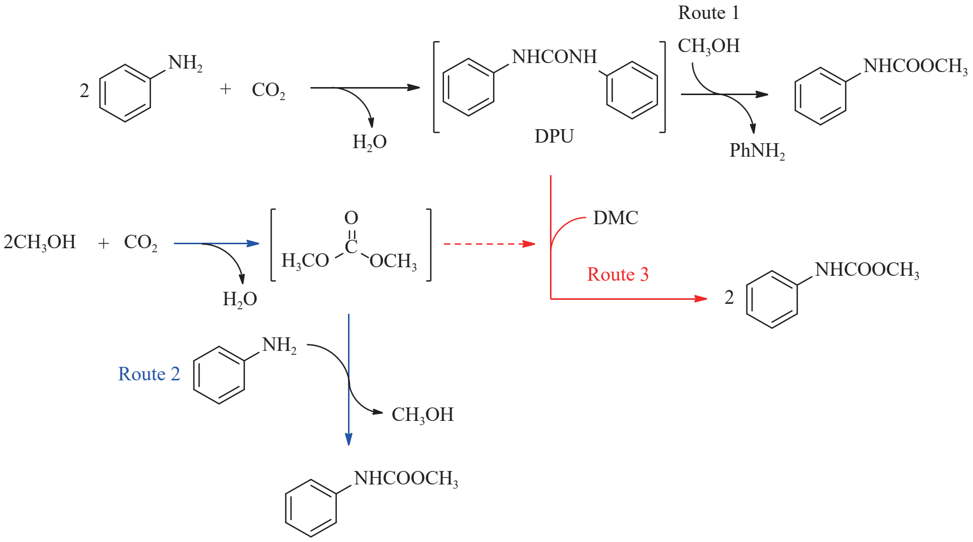


Figure 2　Proposed routes to MPC via three different processes[50]

In 2018, Tomishige's group[54] reported a CeO_2-catalyzed scheme for MPC synthesis from aniline, CO_2 and CH_3OH with the assistance of 2-cyanopyridine as dehydrating agent (Figure 3). To date, this is the best example reported for highly efficient MPC synthesis using CO_2 as direct carbon source. The reaction proceeds smoothly, and the MPC is afforded in more than 99% conversion and 98% selectivity under the mild conditions.

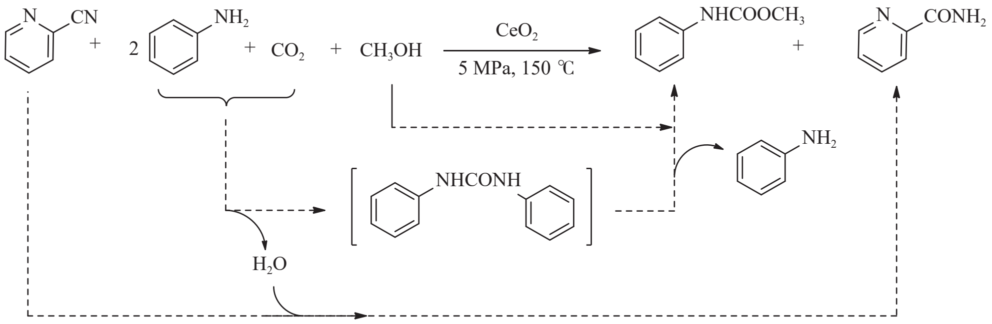


Figure 3　Possible route of CeO_2-catalyzed four-component reaction

In this work, various metal oxides and nitrile dehydrating agents were investigated, and CeO_2 combining with 2-cyanopyridine was demonstrated to be the best protocol. Based on the experimental study, the synthetic mechanism of MPC via DPU intermediate was proposed. Initially, aniline reacts with CO_2 to form DPU and H_2O, and meanwhile the H_2O molecule is consumed through hydration reaction of 2-

cyanopyridine. Moreover, the intermediate DPU reacts with methanol to produce the target product MPC with the generation of aniline. In the system, CeO_2 offering the active catalytic species can catalyze both the coupling reaction for MPC synthesis and hydration of 2-cyanopyrdine under the same reaction conditions[55].

At present, the reports on the synthesis of carbamates/MPC by one-pot method from amines, CO_2 and alcohols are relatively few, and the target products are mostly concentrated on aliphatic carbamates. Under the conditions of 30 MPa CO_2 at 200 °C for 24 h, the reaction of tert-butylamine (t-$BuNH_2$), ethyl alcohol and CO_2 can take place smoothly in the presence of Bu_2SnO and two equivalents of 2,2-diethoxypropane with 100% conversion of t-$BuNH_2$ and 84% selectivity of urethane[56]. Under the same conditions, using $Ni(OAc)_2$ as catalyst, 4,4-dimethyldipyridine as additive and dimethylacetal as dehydrant, the conversion of t-$BuNH_2$ reaches 49% and the selectivity of *tert*-butylcarbamate is up to 98%[57].

Basic catalysts were found suitable to convert a broad variety of amines and alcohols into the corresponding carbamates using CO_2 as a carbonyl source. Under the conditions of 2.5 MPa CO_2 at 200 °C for 24 h, Cs_2CO_3 acting as catalyst, and the molar ratio of *n*-octylamine to *n*-PrOH being 1∶15, the conversion of amine and the selectivity of carbamate reached 56% and 79%, respectively[58]. The catalytic scheme is able to convert both linear and branched aliphatic amines into their corresponding carbamates under mild reaction conditions. For the amine substrate with steric hindrance such as t-$BuNH_2$, the introduction of added dehydrating agents such as dimethoxypropane or diethoxypropane is required, and as a result the corresponding carbamate is obtained with over 90% selectivity.

Using CeO_2 as a heterogeneous catalyst, one-pot synthesis of aliphatic carbamates from CO_2, benzylamine and alcohols was also achieved[59]. In the absence of any dehydrating agent, the reactivity of different amines was detailedly investigated. Under the CeO_2-catalyzed reaction conditions of initial 5 MPa CO_2 at 150 °C for 2 h, *n*(amine)∶*n*(alcohol) being 5∶900, the amine conversion and carbamate selectivity were up to 99% and 89%, respectively. The protocol was also compatible with the other aliphatic amines (e.g. benzylamine, amino methylcyclohexane and methylamine) and alcohols (e.g. methanol, ethanol, 1-propanol and 2-propanol) in good yields and high selectivity. Nevertheless, the reactivity of aniline is still very low. During the process, the CeO_2 catalyst is deactivated because of the poisonous adsorption of the products. Delightedly, the experimental results show that the CeO_2 catalyst can be reused after the calcination at 600 °C.

Based on the previous study[54], Tomishige et al.[60] continued to expand the research on synthesis of alkyl *N*-alkylcarbamates from anilines, CO_2 and various alcohols through CeO_2 and 2-cyanopyridine system. In the work, alcohol substrates were extended to the branched alcohols such as 2-propanol and cyclohexanol. As a result, the undesirable side reaction of alcohols with CO_2 to dialkyl carbonates was remarkably suppressed probably due to the steric effect of branched alcohols, and the formation of picolinamide was minimized. High conversion of aniline (97%) and yield of isopropyl *N*-phenylcarbamate (94%) were obtained under 1 MPa CO_2, and low CO_2 pressure (0.5 MPa) was also applicable in 90% yield of isopropyl *N*-phenylcarbamate. In this study, various alkyl *N*-alkylcarbamates could be synthesized from CO_2, anilines, and alcohols in good product yield and high selectivity.

Comparing with aliphatic carbamates, the synthesis of methyl *N*-phenylcarbamate by one-pot reaction of aniline, methanol and CO_2 has many disadvantages e.g. low reactivity and poor selectivity. This may be due to the hyper conjugation effect of the aromatic ring, which reduces the electron density of N atom in the amino group and subsequently weakens its alkalinity and nucleophilicity. Therefore, it is necessary to improve the yield of MPC prepared by one-pot reaction of aniline, methanol and CO_2 from two aspects: one is to develop a robust catalyst enable to activate the substrates and CO_2, the other is to remove the water generated from the reaction in time to break the chemical equilibrium and promote the reaction to take place in the direction of product generation.

3 Summary and outlook

With the continuous increase of diphenylmethane diisocyanate requirement during recent years, the synthesis of methyl *N*-phenylcarbamate, a key raw material for the synthesis of MDI, is becoming more and more important, and the green and sustainable preparation methods are urgently needed. Currently, the effectively indirect routes to MPC are dependent on the coupling of methanol with CO_2 equivalents or derivatives acting as carbon/nitrogen source. These efforts contribute to much important foundation in the process of technology exploration. Although great advances are made, most of the catalysts rely on the limited metal species e.g. Pb compounds. In addition, the selectivity is still very low in most systems, and the process is also complicated which restricts the exploration of industrial technology. Moreover, the thermal stability of the current supported catalysts is not well enough to meet the practical production. In particular, the most ideal route to MPC is the reaction of commercial aniline, methanol and CO_2 used as carbonyl group source. However, the thermodynamic limitation bottleneck is confronted, thus leading to very low efficiency. At present, the effective schemes are still depended on a great deal of chemical dehydrating agents which produces much waste. At the same time, the reactivity and selectivity are still insufficient.

In the near further, to solve the problems in the synthesis of MPC, the development of new and efficient catalysts is inevitable. Firstly, expanding the newly efficient and non-toxic metal catalyst in place of Pb and the other metal species is needed to boost the efficiency of the process. Secondly, it is necessary to develop the heterogeneous catalysts e.g. supported catalysts with high catalytic activity and stability. Furthermore, although the great challenge confronted in the direct method for CO_2 conversion to MPC, the breakthrough is urgently needed to make and it is one of the most promising trends from the viewpoint of green and sustainable chemistry. The hopeful fields refer to the exploration of functional catalytic materials in combination with the water removal process and the highly efficient technology on the regeneration of dehydration agent. Last but not least, the exploration of the simple and efficient separation methods is indispensable for the economic industrial technology.

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二氧化碳高值利用合成苯氨基甲酸甲酯

荀家瑶[1]，宋清文[1,*]，张乾霞[1]，韩丽华[1]，张侃[1]，张建利[2]，刘平[1,*]

（1. 中国科学院山西煤炭化学研究所 煤转化国家重点实验室, 山西 太原, 030001;

2. 宁夏大学 省部共建煤炭高效利用与绿色化工国家重点实验室, 宁夏 银川, 750021）

摘　要: 苯氨基甲酸甲酯（MPC）是合成二苯甲烷二异氰酸酯（MDI）的关键原料。以二氧化碳（CO_2）及其等价物或衍生物作为碳源合成 MPC 代表了绿色和可持续的精细化学品合成方法。基于该领域研究, 概述了基于 CO_2 转化合成苯氨基甲酸甲酯的研究方法进展。合成路线包括研究较多的 CO_2 等价物（尿素或苯基脲）醇解法, 碳酸二甲酯（DMC）氨解法以及二苯基脲和 DMC 耦合反应法。另外, 最理想的合成方法是近几年发展的苯胺、CO_2 和甲醇三组分“一锅”反应法, 以及使用脂肪胺类原料构建氨基甲酸烷基酯类化合物, 其代表了最有前景的 CO_2 利用途径之一。详细探讨了反应机理和催化剂选择等问题。研究进展将为进一步提升绿色催化和可持续化学过程效率提供重要理论支持。

关键词: 二氧化碳; CO_2 等价物; 苯氨基甲酸甲酯; 催化; 合成方法

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