

# A phosgene-free process for the synthesis of methyl *N*-phenyl carbamate by the reaction of aniline with methyl carbamate

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## Abstract

A phosgene-free route for the synthesis of methyl *N*-phenyl carbamate (MPC) by the reaction of aniline with methyl carbamate in the presence of methanol was studied. Effects of catalysts, reaction temperature, reaction time, and catalyst content, the molar ratio of reactants and the content of water on the reaction were investigated. The results demonstrated that an aniline conversion of 90.1% and MPC selectivity of 99.7% were achieved when the reaction was carried out at 433 K for 4 h using ZnCl<sub>2</sub> as a catalyst. A possible reaction mechanism was proposed based on the product distribution.

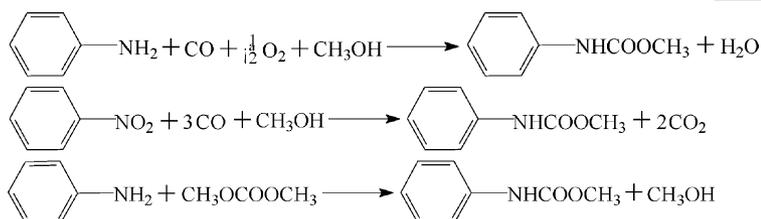
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**Keywords:** Aniline; Methyl carbamate; Carbonylation; Methyl *N*-phenyl carbamate; ZnCl<sub>2</sub>

## 1. Introduction

Isocyanates are important intermediates for the manufacture of polyurethanes and pesticides. Commercially, isocyanates are synthesized by the reaction of phosgene and primary amines. Due to the environmental problems of the phosgene route, significant attempts [1] have been made to explore phosgene-free synthesis of isocyanates.

Methyl *N*-phenyl carbamate (MPC) is an important precursor for preparing isocyanates, since it produces isocyanates and alcohols in good yields by thermal decomposition. Presently, the studies on phosgene-free synthesis of MPC are mainly focused on oxidative carbonylation of aromatic amines [2–6], reductive carbonylation of nitro derivatives [7–10], and methoxycarbonylation of amines [11,12], which can be summarized in the following equations:



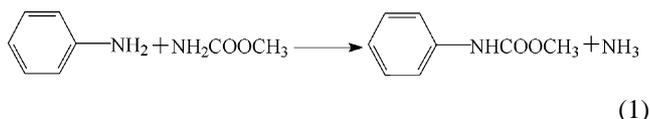
In the oxidative carbonylation process, the reaction is a costly process together with safety problem. While in the reductive carbonylation reaction, only one-third of CO could be used efficiently, and the separation of CO from CO<sub>2</sub> would increase the operation cost. Additionally, the presence of cocatalysts gives rise to the corrosion problems and makes recovery of the catalyst difficult [9].

Methoxycarbonylation of amines gives high selectivity and yield of MPC in the presence of Pb catalyst [11,12]. This route seems promising, but it involves separation of methanol-dimethyl carbonate (DMC) azeotrope, and DMC is relatively expensive.

In addition to above-mentioned routes, MPC can also be synthesized by the reaction of aniline with methyl carbamate [13]. This method is of significance since methyl carbamate can be produced from urea and methanol.

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This reaction can proceed under relatively mild conditions. Previously, a MPC yield of 82.3% from aniline and methyl carbamate has been reported at 463 K for 6.5 h in the presence of methanol over  $\text{ZnCl}_2$  catalyst [13]. However, there is no further report regarding the detailed investigation of the role of methanol, the effect of reaction conditions, product distribution, and the possible reaction mechanism, which prompted us to undertake the present work. The products were identified by GC–MS, and a possible reaction mechanism was proposed in the presence of  $\text{ZnCl}_2$  catalyst.

## 2. Experimental

The reactants including aniline, methyl carbamate, methanol and the catalysts such as  $\text{ZnCl}_2$ , HZSM5,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$  and  $\text{NaOH}$  were commercial products.  $\text{Zn}(\text{OAc})_2$  was obtained by heating  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  at 323 K for 2 h under vacuum.  $\text{CH}_3\text{OK}$  was obtained by dissolving potassium in methanol.  $\text{Pd/C}$  was prepared by impregnating active carbon with  $\text{PdCl}_2/\text{HCl}$  solution, followed by drying at 393 K for 12 h, and calcining at 773 K for 2 h under nitrogen atmosphere. They were dried at 303 K again under vacuum for 40 min prior to use.

MPC was synthesized in a stainless steel autoclave. Aniline, methyl carbamate, methanol and a catalyst were charged into a 100  $\text{cm}^3$  autoclave. After purging with nitrogen for a few minutes, the reactor was heated to the reaction temperature at a rate of 5 K/min with aptotic magnetic stirring. After the reaction, the reactor was cooled down quickly to room temperature by ice water. Biphenyl as internal standard was added into the reaction mixture under stirring.

The products were analyzed by a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a PEG20M capillary column. The distribution of products was identified by GC–MS. The selectivity of products

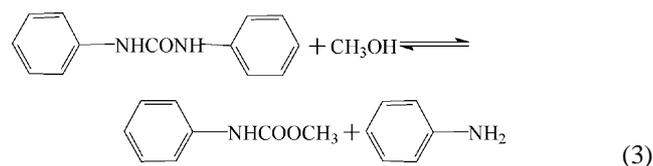
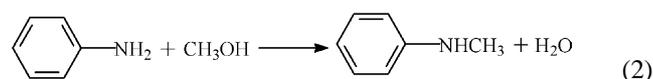
was calculated based on the conversion of aniline as described below:

$$S(x) = \frac{M_x}{M_{\text{MPC}} + M_{\text{NMA}} + M_{\text{DPU}}} \times 100\%$$

where  $S$  refers to selectivity;  $M$  to the molar number; NMA to *N*-methyl aniline; DPU to diphenyl urea; and  $x$  refers to MPC, NMA, or DPU.

## 3. Results and discussion

From the GC–MS data, it was shown that the products in the final system contained MPC, ammonia, NMA and DPU. Based on the distribution of products, besides the aimed reaction, the side-reactions taking place in the reaction system were proposed as follows:



### 3.1. Effects of catalysts

The results of MPC synthesis by the reaction of aniline, methyl carbamate and methanol over various catalysts were shown in Table 1. In the absence of catalyst, aniline conversion was 67.4% and MPC yield was less than 40%. The conversion was increased to 90.1% with a MPC yield of 89.8% when the  $\text{ZnCl}_2$  catalyst was introduced. This result was better than that reported in the literature [13]. Table 1 also indicated that all catalysts tested improved aniline conversion and MPC selectivity to some extent, and it seemed that the catalytic performance of acidic catalysts was better than that of basic catalysts and Lewis acidity was better

Table 1  
Effects of different catalysts on the synthesis of MPC

Sample number	Catalyst	Reaction temperature (K)	Aniline conversion (%)	MPC selectivity (%)	NMA selectivity (%)	DPU selectivity (%)	MPC yield (%)
0	–	433	67.4	58.6	10.3	31.1	39.5
1	$\text{ZnCl}_2$	433	90.1	99.7	0.16	0.14	89.8
2	$\text{Zn}(\text{OAc})_2$	433	87.5	77.9	7.2	14.9	68.2
3	HZSM5	433	82.3	72.2	11.9	15.9	59.4
4	$\text{PbO}$	433	80.4	75.5	8.4	16.1	60.7
5	$\text{Pb}_3\text{O}_4$	433	80.5	76.2	8.2	15.6	61.3
6	$\text{Pd/C}$	433	71.7	68.3	7.2	24.5	49.0
7	$\text{CH}_3\text{OK}$	433	81.1	78.2	6.6	15.2	63.4
8	$\text{NaOH}$	433	72.6	73.8	6.1	20.1	53.6

Reaction conditions: molar ratio of methyl carbamate, methanol to aniline is 8:5:1, catalyst content is 6% (based on aniline), and reaction time is 4 h. NMA: *N*-methyl aniline.

than Bronsted one. As to the Pd/C catalyst employed in the reaction system, it is not easy to strictly classify it into acidic, basic, or redox catalyst here, but the  $\text{NH}_3$ -TPD curve of it clearly showed one desorption peak appeared at about 503 K; so we consider it as a comparatively weak acid.

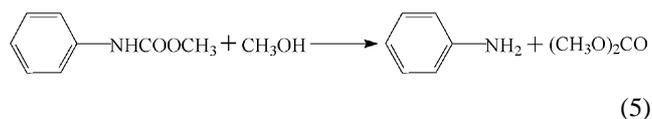
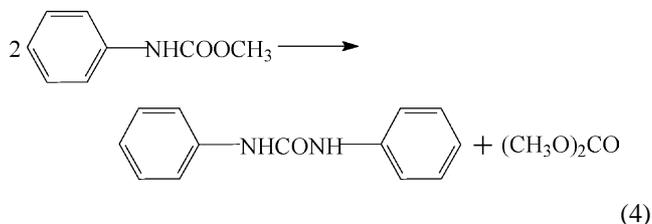
But on the strong acidic catalyst such as HZSM-5, MPC selectivity was obviously lower than that on  $\text{ZnCl}_2$  catalyst, which might be caused by the occurrence of side reaction (2). Too strong acidity of HZSM5 catalyst enhanced the *N*-methylated reaction of aniline [14], which produced a large amount of NMA.

### 3.2. Effect of reaction temperature

The effect of reaction temperature on the synthesis of MPC was shown in Fig. 1. Aniline conversion and MPC selectivity increased with the increase of reaction temperature from 373 to 433 K, and the yield of MPC reached the maximum of 89.8% at 433 K. With further increase of reaction temperature, aniline conversion and MPC selectivity decreased apparently. Meanwhile, a gradual increase of NMA and DPU were detected in the reaction products.

These might be due to the conversion equilibrium between DPU and MPC in the course of the reaction, as shown in reaction (3). With the increase of reaction temperature, this equilibrium leaned to the right side and produced a large amount of MPC and aniline [15,16]. Meanwhile, the reaction (4), which produced DPU and DMC, showed that the dimerization of MPC would be enhanced at higher temperature [14]. In general, it becomes a methanolizing reaction of MPC as shown in reaction (5), which produces aniline and DMC, and causes the decrease of aniline conversion. Additionally, the decreased MPC selectivity might be caused by the *N*-methylated reaction of aniline,

the reaction (2), which could easily take place at higher temperature [14].



### 3.3. Effect of reaction time

The effect of reaction time on the synthesis of MPC was shown in Fig. 2. It was observed that MPC selectivity increased initially and then decreased while aniline conversion changed slightly with reaction time. MPC yield achieved maximum at 4 h run.

The decrease of MPC selectivity with the reaction time might be caused by two reasons. One is the dimerization of MPC, the side reaction (4), which was enhanced with the reaction time [14]. The other reason might be related to the decomposition of MPC. The corresponding investigation was performed in the presence of MPC and methanol under the same reaction conditions. It was found that MPC decomposed partly and transformed into aniline and methyl carbamate.

### 3.4. Effect of catalyst content

The effect of catalyst content on the synthesis of MPC was shown in Fig. 3. Aniline conversion and MPC selectivity

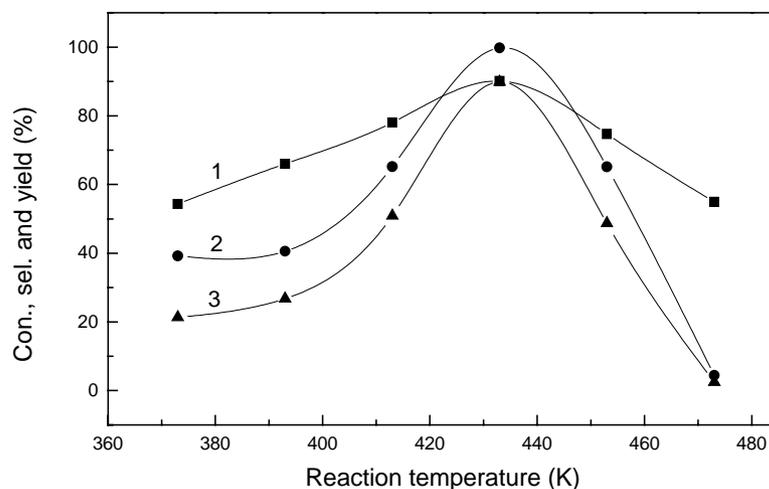


Fig. 1. Effect of temperature on the synthesis of MPC: (1) aniline conversion; (2) selectivity to MPC; and (3) MPC yield. Reaction conditions: molar ratio of methyl carbamate, methanol to aniline is 8:5:1, zinc chloride content is 6% (based on aniline), and reaction time is 4 h.

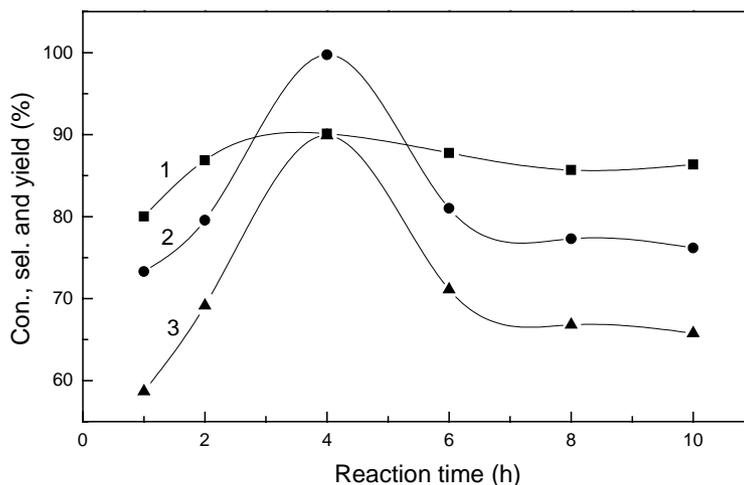


Fig. 2. Effect of time on the synthesis of MPC: (1) aniline conversion; (2) selectivity to MPC; and (3) MPC yield. Reaction conditions: molar ratio of methyl carbamate, methanol to aniline is 8:5:1, zinc chloride content is 6% (based on aniline), and reaction temperature is 433 K.

increased as catalyst content is below 6% (based on aniline), and then decreased with the increase of catalyst content. MPC yield achieved maximum when the catalyst content reached about 6% (based on aniline).

The decreasing trend of aniline conversion and MPC selectivity might be related to the solubility of the catalyst in the reaction system. The dispersion of catalyst in the system was influenced by the increase of catalyst content, too high concentration of catalyst led to the aggregation of catalyst, which maybe switched the reaction from homogeneous catalytic to heterogeneous catalytic, and hence the reduction of effective active centers. Additionally, with the increase of catalyst content, the decrease of MPC selectivity might be caused by the *N*-methylated reaction of aniline, the reaction (2), which could be proceeded easily in the acidic environment [14].

### 3.5. Effect of methyl carbamate to aniline molar ratio

The effect of methyl carbamate to aniline molar ratio on the synthesis of MPC in the absence of methanol was shown in Fig. 4. Aniline conversion and MPC selectivity increased with the increase of methyl carbamate to aniline molar ratio, and they achieved maximum when the molar ratio reached 8.

### 3.6. Effect of methanol to aniline molar ratio

The effect of methanol to aniline molar ratio on the synthesis of MPC was shown in Fig. 5. In the presence of methanol, the decrease of aniline conversion was accompanied by the increase of MPC selectivity at the molar ratio of methanol to aniline below 5. With further increase of methanol content,

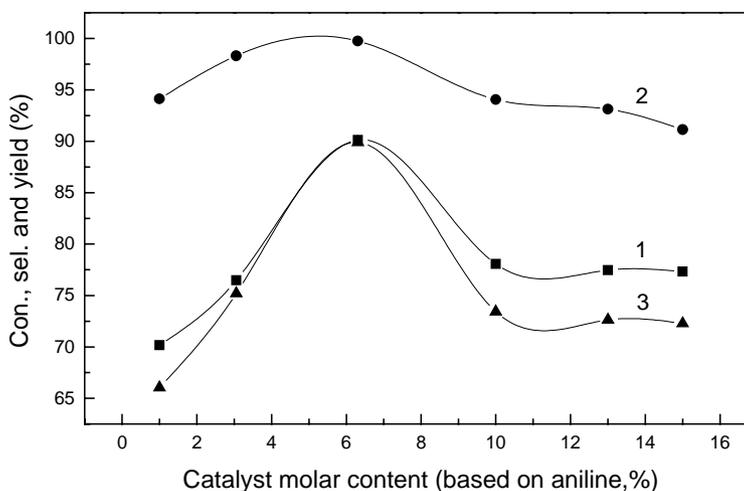


Fig. 3. Effect of catalyst content on the synthesis of MPC: (1) aniline conversion; (2) selectivity to MPC; and (3) MPC yield. Reaction conditions: molar ratio of methyl carbamate, methanol to aniline is 8:5:1, reaction temperature is 433 K, and reaction time is 4 h.

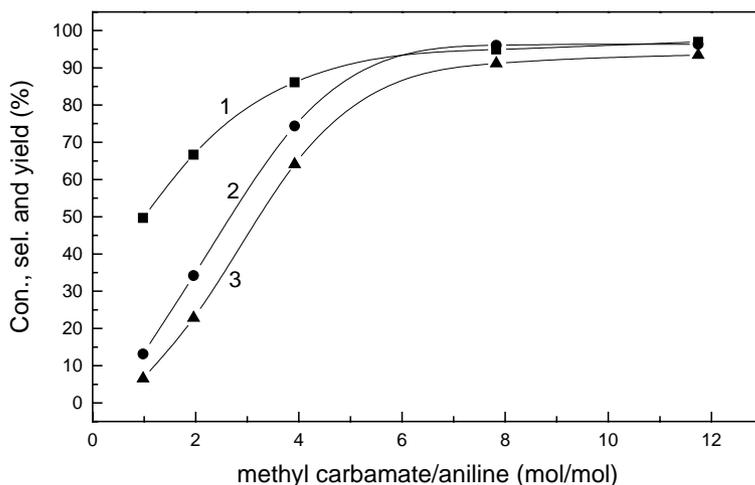


Fig. 4. Effect of molar ratio of methyl carbamate to aniline on the synthesis of MPC: (1) aniline conversion; (2) selectivity to MPC; and (3) MPC yield. Reaction conditions: zinc chloride content is 6% (based on aniline), reaction temperature is 433 K, and reaction time is 4 h.

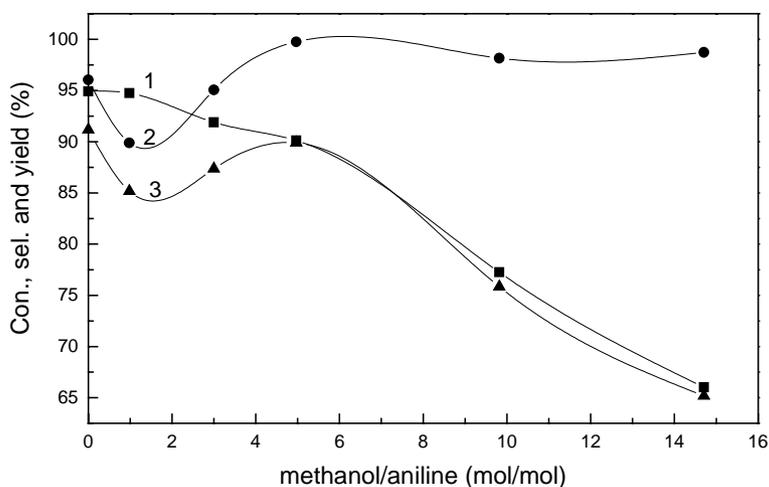


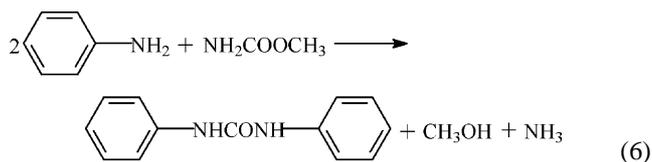
Fig. 5. Effect of molar ratio of methanol to aniline on the synthesis of MPC: (1) aniline conversion; (2) selectivity to MPC; and (3) MPC yield. Reaction conditions: molar ratio of methyl carbamate to aniline is 8:1, zinc chloride content is 6% (based on aniline), reaction temperature is 433 K, and reaction time is 4 h.

aniline conversion decreased sharply while MPC selectivity remained.

With the increase of methanol content, the concentrations of the other molecules in the reaction system were all decreased and they were encircled tightly by methanol molecules, which led to the decline of occurring probability of main reaction and then the decrease of aniline conversion. Also, the increase of MPC selectivity might be caused by the decline of occurring probability of certain side reaction, such as dimerization of MPC.

From Fig. 5, it can also be observed that, higher aniline conversion and lower MPC selectivity were obtained in the absence of methanol than that methanol existed. Based on these results, it can be deduced that the incorporation of methanol in the reaction system not only significantly increased the MPC selectivity but also facilitated the separation and transfer of the products. In the absence of methanol, the side reaction (6) was enhanced and DPU and ammonia

were produced, whereas the existence of methanol promoted the reaction equilibrium (3) shifting to the right side and led to the increase of MPC selectivity.



### 3.7. Effect of water content

In order to reveal how water influences products distribution, the effect of water content on the synthesis of MPC was investigated and shown in Table 2. Aniline conversion and MPC selectivity decreased sharply when trace amount of water existed in the system. The higher water content was, the lower conversion and MPC selectivity were.

Table 2  
Effect of water content on the synthesis of MPC

Sample number	ZnCl <sub>2</sub> content (%)	H <sub>2</sub> O content (%)	Aniline conversion (%)	MPC selectivity (%)	NMA selectivity (%)	DPU selectivity (%)	MPC yield (%)
0	6	0	90.1	99.7	0.16	0.14	89.8
1	6	0.14	72.3	84.6	12.4	3.0	61.2
2	6	0.48	70.5	80.4	16.2	3.4	56.7
3	6	1.2	65.6	78.8	17.5	3.7	51.7
4	6	2	62.4	73.6	20.1	6.3	45.9
5	6	5	46.8	56.4	35.4	8.2	26.4
6	6	10	15.3	44.5	43.5	12.0	6.8
7	0	0	67.4	58.6	10.3	31.1	39.5
8	0	1.2	67.5	73.1	12.1	14.8	49.3

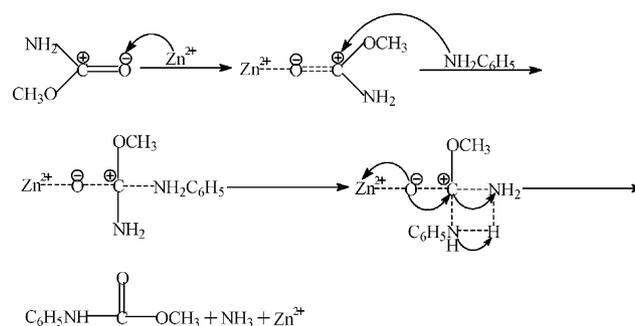
Reaction conditions: molar ratio of methyl carbamate, methanol to aniline is 8:5:1, reaction temperature is 433 K, and reaction time is 4 h. NMA: *N*-methyl aniline.

With the increase of water content, the combination with aniline and the hydrolyzation of methyl carbamate might be occurred easily, which led to the decrease of aniline conversion and MPC selectivity. Meanwhile, the probability of *N*-methylated reaction of aniline increased which can lead to the decrease of MPC selectivity. Moreover, the existence of water may results in the deactivation of ZnCl<sub>2</sub> catalyst and the decomposition of methyl carbamate and MPC.

### 3.8. A possible reaction mechanism for synthesis of MPC

It was shown in literature [17–19] that partial of Lewis acid catalysts has higher catalytic activity in the methoxy-carbonylation of amines to produce the corresponding carbamates and methyl carbamate can also be methanolized to form DMC at certain conditions. In order to clarify whether the reaction is via a DMC intermediate, the corresponding investigation was carried out in the presence of aniline, DMC and ZnCl<sub>2</sub> catalyst. The result showed that ZnCl<sub>2</sub> catalyst has basically no catalytic activity in this reaction. In addition, the relevant study in the reaction of methyl carbamate and methanol at the same reaction conditions also indicated that there was no DMC formation. So, it was concluded that the reaction was not via a DMC intermediate.

Previously, Zhao and Jiang [20] reported that the reaction of dimethyl carbonate with organic amines gave the corresponding carbamates in the presence of metal compounds such as CaCl<sub>2</sub> and proposed a possible reaction mechanism. As to the reaction system, we discussed, based on the experimental analysis and the product distribution, a possible mechanism was proposed as follows: as an electrophilic reagent Zn<sup>2+</sup> exert an electrophilic attack on the methyl carbamate, followed by the nucleophilic attack of aniline on the intermediate and a molecular rearrangement of the intermediate, as shown in Scheme 1. It should be noted that in Scheme 1 we simplified the catalyst as Zn<sup>2+</sup>. In fact, the catalyst was not an isolated cation in the reaction system, and it was surrounded by the electronegative ions such as Cl<sup>-</sup>.



Scheme 1. A possible mechanism for synthesis of MPC over ZnCl<sub>2</sub> catalyst.

## 4. Conclusions

MPC was synthesized with high selectivity through a phosgene-free route by the reaction of aniline and methyl carbamate in the presence of methanol over ZnCl<sub>2</sub> catalyst. Effects of catalysts, reaction temperature, reaction time, and catalyst content, the molar ratio of reactants and the content of water on the reaction were investigated. The results showed that aniline conversion and MPC selectivity reached 90.1 and 99.7% respectively when the reaction was carried out at 433 K for 4 h by using ZnCl<sub>2</sub> as a catalyst. A possible reaction mechanism was proposed based on the product distribution.

## Acknowledgements

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