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One Pot Synthesis of Methyl *N*-Phenyl Carbamate from Aniline, Urea and Methanol

Fei Qin · Qifeng Li · Junwei Wang · Yuelan Feng · Maoqing Kang · Yulei Zhu · Xinkui Wang

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Abstract Methyl *N*-phenyl carbamate (MPC) was synthesized from aniline, urea and methanol. The effects of catalysts, loading amounts, preparation condition of catalyst and reaction condition on the synthesis of MPC were investigated. It was shown that KNO_3 modified zeolite HY gave the best performance to MPC formation among the evaluated catalysts, over which 93.1% aniline conversion and 82.6% MPC selectivity were obtained under the optimum reaction condition. Additionally, a possible catalytic mechanism to the formation of MPC in this reaction was proposed.

Keywords Methyl *N*-phenyl carbamate · Aniline · Urea · Methanol · Modified HY

1 Introduction

Synthesis of isocyanate via a phosgene free route has attracted much interest of researchers due to the drawbacks originated by phosgene [1]. Preparing isocyanate by a decomposition method from carbamate is commended as a promising way among the reported nonphosgene routes. As a simplest aryl carbamate, Methyl *N*-phenyl carbamate (MPC) has been prepared through various methods [2, 3], such as oxidative carbonylation of aniline [4–6], reductive carbonylation of nitro benzene [7, 8], alcoholysis of 1,3-diphenyl urea [9], methoxy carboxylation of aniline [10] and reaction of aniline with methyl carbamate [11]. However, different shortcomings of above routes to MPC limited their industrial application, e.g., hazardous operating condition, high cost of catalyst and separation, expensive material and others [12].

Besides above routes, MPC can also be prepared directly from aniline, urea and methanol by an one pot reaction. Since both urea and methanol are abundant and commercially produced, and this reaction can be carried out under relatively mild condition, it avoided almost acute problems mentioned above. Additionally, the formed ammonia could be collected and reused for the preparation of urea. Therefore, the synthesis of MPC from urea will promote CO_2 utilization and the synthesis of important chemicals derived from CO_2.

So far, one pot reaction to MPC was disclosed by several patents, BASF had reported the similar route to synthesize aryl carbamate. While, the used homogeneous catalysts also brought out some drawbacks, such as the severe reaction condition, separation and recovery of catalyst etc. Therefore, developing a new heterogeneous catalyst with high activity and selectivity to MPC formation is of great significance.

In the present work, The effects of catalysts, preparation condition of catalyst and reaction conditions on the synthesis of MPC were investigated. Finally, the products were identified by GC-MS, and a possible MPC formation mechanism in the presence of KNO_3 modified zeolite HY catalyst was suggested based on the product distribution.

F. Qin (✉) · Q. Li · J. Wang · Y. Feng · M. Kang · Y. Zhu · X. Wang
Institute of Coal Chemistry,
Chinese Academy of Sciences,
Taiyuan 030001, China
e-mail: qinfei1982@gmail.com

F. Qin
Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

2 Experimental

2.1 Raw Materials and Reagents

The reactant including aniline (≥99.5%), urea (≥99.0%), methanol (≥99.5%) and used catalysts in this work were analytical grade and were used as received without further purification.

2.2 Catalyst Preparation

Zeolite HY was got by calcining zeolite NH_4Y at 773 K for 4 h. KNO_3/HY was prepared by incipient impregnation process: Appropriate amounts of KNO_3 were dissolved into distilled water. The solution was impregnated on zeolite HY. The impregnated samples were kept overnight at room temperature, then calcined. The other nitrate modified zeolite HY was made by the same method.

2.3 Catalyst Evaluation

MPC was synthesized in a stainless steel autoclave equipped with a cooling condenser. Aniline, urea, methanol and catalyst were charged into a 100 mL autoclave. In order to get rid of air in the autoclave, purging with nitrogen for 5 min, then sealed the reactor and heated to the reaction temperature in 30 min with electro-magnetic stirring, NH_3 was released twice during the reacting process. After 5 h reaction, the reactor was cooled down quickly to room temperature. Biphenyl was added into the reaction mixture as internal standard.

2.4 Product Analysis

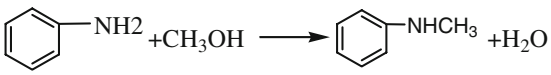
The products were analyzed by a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector and a PEG20M column. The molecular structure of products was identified by GC-MS.

3 Results and Discussion

According to the GC-MS analysis, it is clear that MPC, ammonia, NMA and DPU are consist of the final mixture. Based on the distribution of products, the side-reactions were proposed as follows (Schemes 1, 2).

3.1 Effect of Catalysts on the Synthesis of MPC

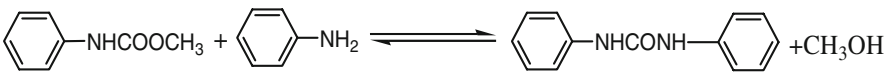
The various catalysts were applied to the synthesis of MPC. The result listed in Table 1 reveals that MPC could be formed in the absence of catalyst, while the conversion of aniline was low. With the introduction of catalysts, aniline conversion was enhanced markedly. Meanwhile, the selectivity of DPU increased too. It might be ascribed to the further reaction between formed MPC and aniline. The formed NMA should be related to the reaction between aniline and methanol. Similar phenomenon was



(1)

Scheme 1 The *N*-methylated reaction of aniline

Scheme 2 The ammonolysis reaction of MPC



(2)

Table 1 Effects of different catalysts on the synthesis of MPC

Catalyst	Aniline conversion (%)	MPC selectivity (%)	NMA selectivity (%)	DPU selectivity (%)	MPC yield (%)
–	50.5	72.5	18.4	9.1	36.6
$ZnCl_2$	86.2	66.7	17.4	15.9	57.5
$Zn(OAc)_2$	86.3	66.6	18.4	15.0	57.4
PbO	87.3	60.2	17.4	22.4	52.6
Pb_3O_4	89.1	62.0	10.7	13.6	55.2
SiO_2	84.0	68.3	15.5	16.2	57.4
Al_2O_3	77.3	70.7	15.1	14.2	54.7
NaX	77.0	75.1	12.8	12.1	57.8
HY(5.0)	85.5	70.5	16.2	13.3	60.3
HZSM-5(50)	55.4	59.9	21.7	18.4	33.2

Reaction conditions: molar ratio of methanol, urea to aniline, 1:5:15; catalyst content, 10.7% (based on aniline); reaction time, 5 h; reaction temperature, 453 K; NMA, *N*-methyl aniline; DPU, diphenylurea

reported by other researchers [13, 14]. Among these evaluated catalysts, $ZnCl_2$ and $Zn(OAc)_2$, as typical Lewis acid catalysts, possess high catalytic activity. However, both of them could be dissolved by methanol. This indicated that it is difficult to be separated from reacted mixture. The catalysts with weak acidity and basicity such as PbO, Pb_3O_4, SiO_2 and Al_2O_3 were not satisfactory because of the low yield of MPC. HY and HZSM-5 with strong acidic sites also showed high activity, and the highest MPC yield was acquired over HY catalyst. Moreover, all of the tested catalysts showed lower selectivity to MPC than that obtained without catalyst except NaX. It seems that suitable basicity of the catalyst might be helpful to the formation of MPC.

3.2 Effect of Metal Nitrate Modified HY Zeolite on the Synthesis of MPC

Above work showed that HY could promote the conversion of aniline efficiently, and the basicity of catalyst might be helpful to the increase of MPC selectivity. Therefore, it is reasonable that base modified HY might enhance MPC formation more efficiently. Based on this, series of alkali metal and alkali earth metal ions were introduced onto HY.

The influence of zeolite HY treated with different metal nitrates on the synthesis of MPC was shown in Table 2. It was found that aniline conversion and MPC selectivity increased obviously with the strengthened electronegativity of the alkali metal ion and the highest value was obtained over KNO_3 modified HY catalyst. Meanwhile, similar tendency was observed over alkali earth metal modified ones. These further proved that suitable basicity of the catalyst could promote the formation of MPC efficiently. Among the tested catalysts, KNO_3 modified zeolite HY showed best performance to MPC preparation, the related aniline conversion and MPC yield attained 91.2 and 67.6%, respectively.

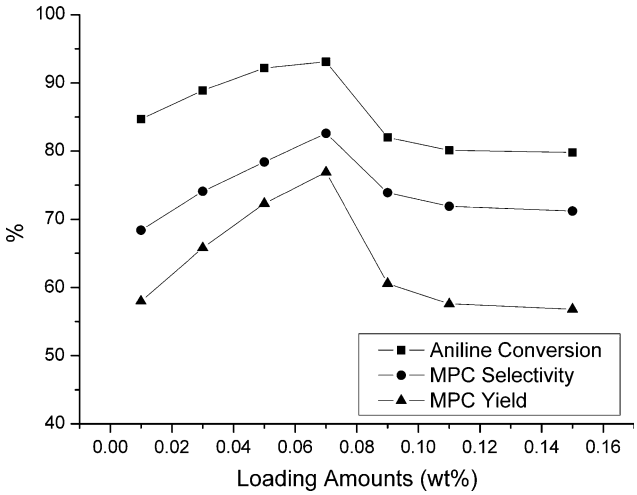


Fig. 1 Effect of loading amounts on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; catalyst content, 10.7% (based on aniline); calcination temperature, 773 K; calcination time, 4 h; reaction temperature, 453 K; reaction time, 5 h

3.3 Effect of Loading Amounts on the Performance of K/HY Catalyst

Previous work showed that KNO_3 modified HY catalyst could promote MPC formation more efficiently than others. Based on this, the influence of KNO_3 loading amounts on the performance of K/HY catalyst was then investigated and the result was exhibited in Fig. 1.

As Fig. 1 revealed, aniline conversion, MPC selectivity and yield smoothly increased with the increase of KNO_3 loading amounts and attained the highest value at 7 wt% KNO_3 loading. The increasing trend might be related to the number of active centers which increased with the loading amounts. However, higher KNO_3 loadings led to the decrease of those markedly. That might be ascribed the excessive KNO_3 blocked the pore of the carrier (HY) and reduced the active surface area of the catalyst [15]. Moreover, decomposition products from overmany KNO_3

Table 2 Effect of metal nitrate supported zeolite HY on the synthesis of MPC

Metal nitrate	Aniline conversion (%)	MPC selectivity (%)	NMA selectivity (%)	DPU selectivity (%)	MPC yield (%)
HY	85.5	70.5	16.2	13.3	60.3
$LiNO_3$/HY	85.4	65.5	14.8	19.7	56.0
$NaNO_3$/HY	90.6	71.5	12.2	16.3	64.8
KNO_3/HY	91.2	74.1	11.7	14.2	67.6
$CsNO_3$/HY	87.3	71.1	12.9	16.0	62.0
$Mg(NO_3)_2$/HY	81.5	60.8	17.4	21.8	49.6
$Ca(NO_3)_2$/HY	86.4	63.0	15.1	21.9	54.4
$Sr(NO_3)_2$/HY	87.7	68.3	13.4	18.3	60.0
$Ba(NO_3)_2$/HY	80.8	67.3	15.0	17.7	55.6

Reaction conditions: molar ratio of methanol, urea to aniline, 1:5:15; loading amounts, 3 wt%; catalyst content, 10.7% (based on aniline); reaction time, 5 h; reaction temperature, 453 K; NMA, *N*-methyl aniline; DPU, diphenylurea

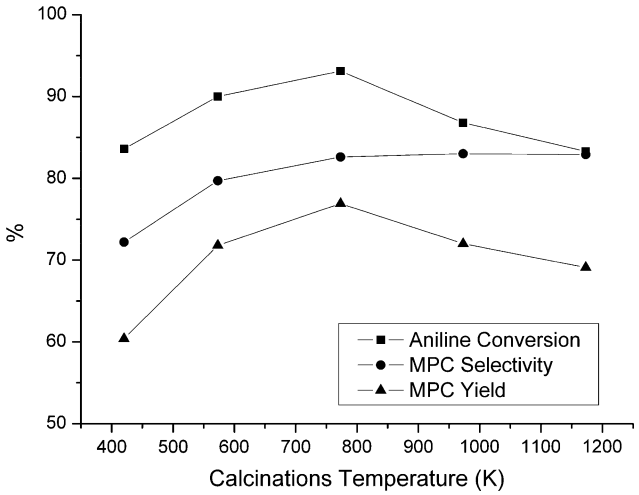


Fig. 2 Effect of calcination temperature on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; catalyst content, 10.7% (based on aniline); loading amount, 7 wt%; calcination time, 4 h; reaction temperature, 453 K; reaction time, 5 h

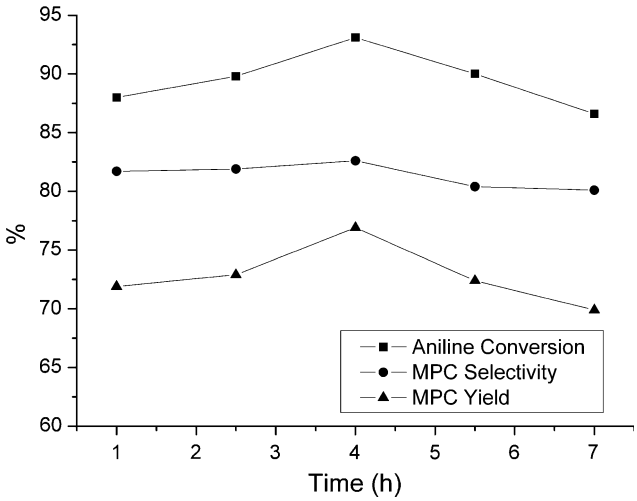


Fig. 3 Effect of calcination time on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; catalyst content, 10.7% (based on aniline); loading amounts, 7 wt%; calcination temperature, 773 K; reaction temperature, 453 K; reaction time, 5 h

will cover active centers of the catalyst. It will change the ratio between acidic centers and basic ones and then affect the catalytic performance to MPC formation negatively. Considering MPC selectivity and yield, 7 wt% KNO_3 loading should be a commendable choice.

3.4 Effect of Calcination Temperature on the Performance of K/HY Catalyst

Figure 2 provided the influence of calcination temperature on the synthesis of MPC. Aniline conversion and MPC selectivity gradually increased at first and then decreased with calcination temperature. MPC selectivity was enhanced when the calcination temperature below 773 K. It is noteworthiness that the effect of calcination temperature is unconspicuous with the more augment of calcination temperature. The decreasing trend may be related to the amount of active center, higher temperatures might cause the excessive dehydroxide of HY and destroy the structure of zeolite, which lead to the tunnel collapse and surface area reduction, and result in the decrease of catalytic performance of the catalyst.

3.5 Effect of Calcination Time on the Performance of K/HY Catalyst

The effect of calcination time on the synthesis of MPC was presented in Fig. 3. Aniline conversion and MPC yield increased when the calcination time below 4 h and then decreased with the further prolongation of calcination time. The reason for this trend might be similar to that caused by calcination temperature mentioned above.

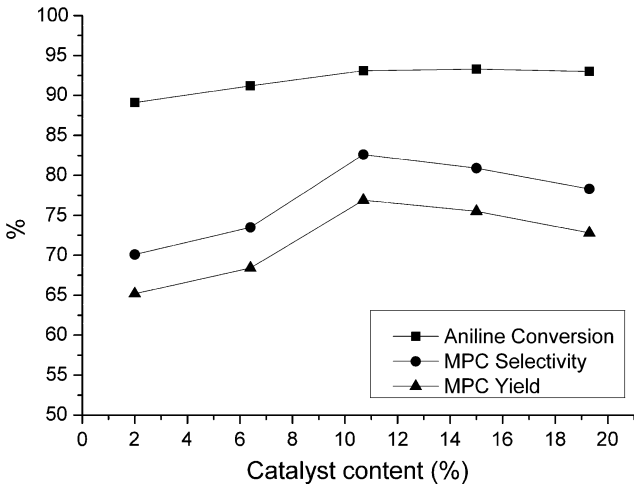


Fig. 4 Effect of catalyst content on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; loading amounts, 7 wt%; calcination temperature, 773 K; calcination time, 4 h; reaction time, 5 h; reaction temperature, 453 K

3.6 Effect of Catalyst Content on the Synthesis of MPC

The effect of catalyst content on the synthesis of MPC was shown in Fig. 4. Aniline conversion was strengthened by the increased catalyst content and attained stable at 10.7% (based on aniline) charging. Further increase of catalyst amount cannot bring out obvious increase. MPC selectivity and yield gradually increased when catalyst content below 10.7%, and then decreased when the content exceed 10.7%. Considering the activity and selectivity of catalyst, 10.7% charging content should be a better choice for MPC formation.

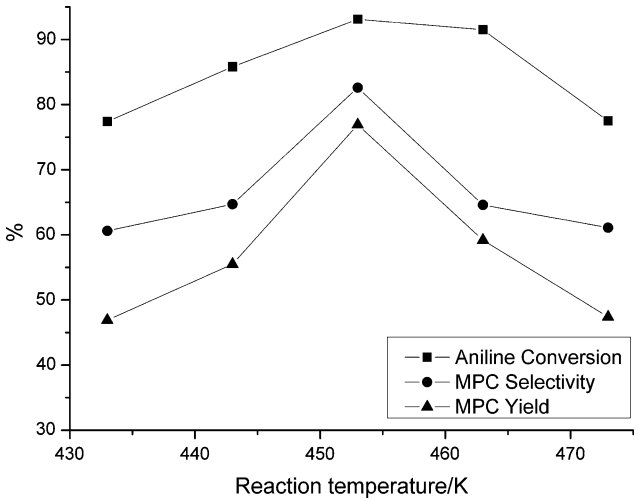


Fig. 5 Effect of reaction temperature on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; catalyst content, 10.7% (based on aniline); loading amounts, 7 wt%; calcination temperature, 773 K; calcination time, 4 h; reaction time, 5 h

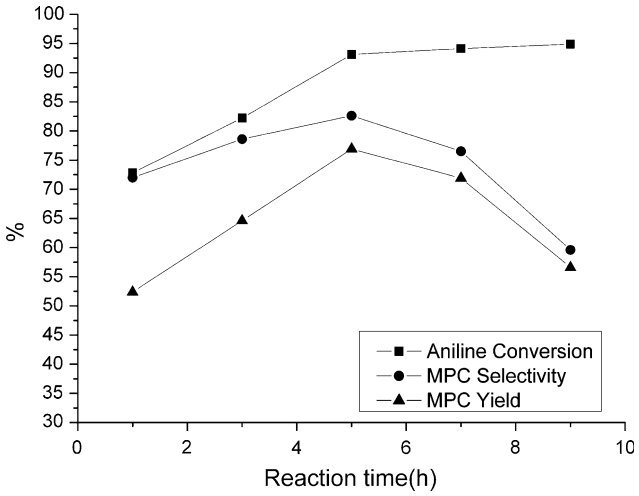


Fig. 6 Effect of reaction time on the synthesis of MPC. Reaction conditions: molar ratio of aniline, urea and methanol, 1:5:15; catalyst content, 10.7% (based on aniline); loading amounts, 7 wt%; calcination temperature, 773 K; calcination time, 4 h; reaction temperature, 453 K

3.7 Effect of Reaction Temperature on the Synthesis of MPC

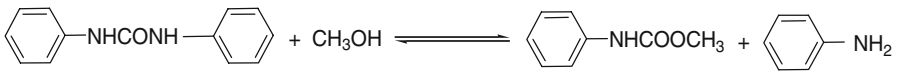
Figure 5 demonstrated the effect of reaction temperature on the synthesis of MPC. Aniline conversion, MPC selectivity and yield gradually increased at first and then decreased with reaction temperature. The maximum of MPC selectivity of 82.6% and yield of 76.9% was obtained at the temperature of 453 K.

Due to the conversion equilibrium between DPU and MPC in the course of the reaction, as shown in reaction (3). The increase of reaction temperature make the equilibrium lean to the right side and produced a mass of MPC and aniline [16, 17]. At the same time, DPU, the byproduct were produced by the reaction (4). And the higher temperature enhanced the dimerization of MPC [18]. Base on the side reaction of this reaction system, it was proposed that aniline conversion lied on reaction (5), which decreased aniline conversion. Additionally, the decreased MPC selectivity might be caused by the *N*-methylated reaction of aniline, the reaction (1), which could easily take place at higher temperature (Schemes 3, 4, 5).

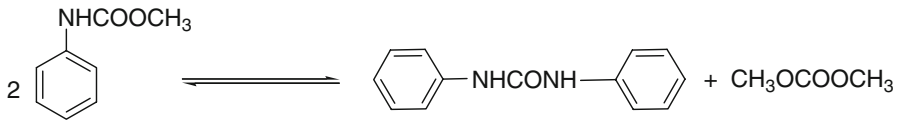
3.8 Effect of Reaction Time on the Synthesis of MPC

The effect of reaction time on the synthesis of MPC was illustrated in Fig. 6. Aniline conversion, MPC selectivity and yield increased when reaction time below 5 h. With the further increase of reaction time, MPC selectivity and yield gradually decreased, but aniline conversion changed slightly.

Scheme 3 The alcoholysis reaction of DPU



Scheme 4 The dimerization of MPC



Scheme 5 The alcoholysis of MPC

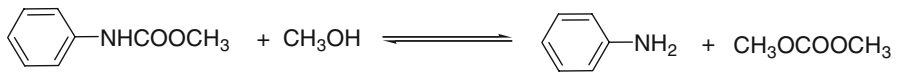


Table 3 Reusability of K-HY for the reaction of aniline, urea and methanol

Recycle times	Aniline	MPC	
	Conversion (%)	Selectivity (%)	Yield (%)
1	93.1	82.6	76.9
2	91.6	81.7	74.8
3	90.1	80.8	72.9
4	88.3	81.0	71.5
5	87.0	81.1	70.6

Reaction conditions: molar ratio of methanol, urea to aniline, 1:5:15; catalyst content, 10.7% (based on aniline); reaction time, 5 h; reaction temperature, 453 K

Based on the equilibrium of reaction, aniline conversion increased to a certain level and did not changed along with the increase of reaction time. There are two reasons for the decrease trend of MPC selectivity and yield. First, the dimerization of MPC which produced DPU and was enhanced with reaction time decreased MPC selectivity and yield [18]. Second, the decomposition of MPC might be another main reason for the decrease of MPC selectivity and yield.

3.9 Reusability of KNO_3/HY Catalyst

To investigate the stability of KNO_3/HY catalyst, the catalyst was used repeatedly after pretreatment. Activity of catalyst was first performed at 180°C for 5 h with 0.5 g of KNO_3/HY. After each reaction, KNO_3/HY was separated by filtration and washed with 20 mL of methanol for three times, and then used for the next run. As shown in Table 3, the KNO_3/HY catalyst could be used five times without remarkable deactivation. This indicated that KNO_3/HY had satisfactory stability for this reaction.

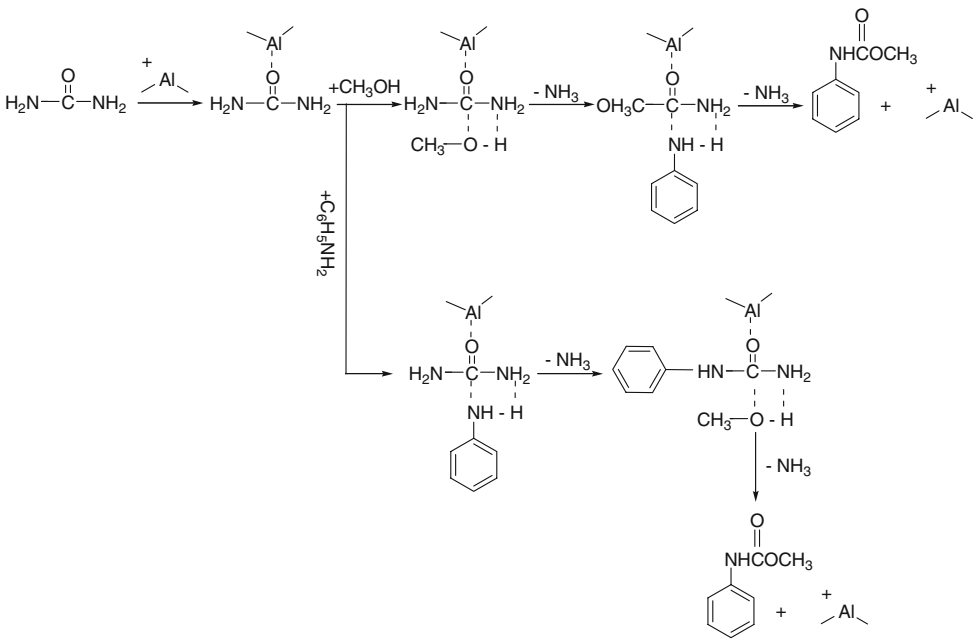
3.10 The Possible Synthesis Mechanism of MPC from Aniline, Urea and Methanol

It was shown in literature [19, 20] that a high yield of MC could be achieved from urea and methanol, even in the absence of a catalyst, but it hardly converted to DMC.

Previously, Li and Wang et al. [11] reported that the reaction of MC with aniline gave the corresponding carbamates in the presence of $ZnCl_2$ and proposed a possible reaction mechanism. As to the reaction system, a possible mechanism was proposed based on the experimental analysis and the product distribution. As described by Scheme 6, the urea molecules are adsorbed on the Lewis acid sites of the catalyst and occupy most of these sites at first. A small part of methanol and aniline molecules reacts with free Brønsted acid sites to form *N*-methyl aniline [21]. The remainders are present as methanol and aniline molecules with high mobility. In the first step, urea reacts with the zeolite surface to activate carbonyl group.

In the second step of the reaction, aniline and methanol molecules react with carbonyl of urea to give methyl *N*-phenyl carbamate. This reaction may occur via two reaction pathways, the first pathway is via a MC intermediate, another pathway is via a phenyl urea intermediate. Namely methanol or aniline exerts the nucleophilic attack on the urea and get rid of a NH_3 at first to form MC or phenyl

Scheme 6 The possible mechanism of the synthesis of MPC from aniline, urea and methanol



urea and then aniline or methanol nucleophilic attacks the intermediate and get rid of a NH_3 to form MPC.

4 Conclusions

MPC was synthesized with high selectivity through a phosgene-free route by the reaction of aniline and urea in the presence of methanol over KNO_3/HY catalyst. The examination of the effect of preparation condition on the catalyst performance revealed that 7 wt% KNO_3 loaded on HY and calcined at 773 K for 4 h could promote MPC formation more efficiently than that prepared under other conditions. And over this catalyst, the influence of reaction condition on MPC preparation was investigated. The result showed that aniline conversion and MPC selectivity reached 93.5 and 83.5%, respectively, under optimized condition as 453 K for 5 h.

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