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A non-phosgene route for synthesis of methylene diphenyl dicarbamate from methylene dianiline and methyl carbamate

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ABSTRACT

This paper proposes a non-phosgene route for the synthesis of methylene diphenyl dicarbamate (MDC) by the methoxycarbonylation of methylene dianiline (MDA) with methyl carbamate (MC). Effects of catalysts, reaction temperature, reaction time, catalyst content and the molar ratio of reactants were investigated in the presence of methanol. The results showed that methanol-pretreated PbO catalyst exhibited high catalytic activity for this reaction. Under the condition of 433 K for 3 h, near-complete conversion of MDA and 83.1% selectivity of MDC were obtained. A possible reaction mechanism for the methoxycarbonylation reaction was proposed based on product distribution.

1. Introduction

Methylene diphenyl diisocyanate (MDI), one of the most important raw materials for synthesizing polyurethanes, is commercially manufactured by phosgenation of methylene dianiline (MDA). Due to the extreme toxicity of phosgene and serious pollution of the co-product HCl in the phosgene route, significant attempts have been made to develop non-phosgene routes [1–4], among which, thermal decomposition of methylene diphenyl dicarbamate (MDC) to obtain MDI is thought to be one of the most attractive ways [5,6].

In recent years, studies on MDC synthesis have been mainly focused on the condensation of methyl phenyl carbamate (MPC) [7,8], which can be efficiently synthesized by many methods [9,10]. However, the condensation of MPC is complex and the separation of MPC is difficult because of its thermal instability [11], thus hindering the industrialization of this route. Methoxycarbonylation of MDA is another promising way of synthesizing MDC [12,13]. Dimethyl carbonate (DMC) has attracted many attentions as the reactant with MDA [14,15] and the reaction was demonstrated in Eq. (1) of Scheme 1. However, it involves the separation of methanol-DMC azeotrope, which calls for high energy consumption.

We propose an alternate clean route to synthesize MDC by the reaction of MDA with methyl carbamate (MC), which was another methoxycarbonylation agent of amines [16,17], as demonstrated in Eq. (2) of Scheme 1. The reaction of MDA and MC avoids the formation of azeotropes, thus following the easier removal of the co-product as compared to Eq. (1), and also making this route attractive from the viewpoint of “green chemistry”. Reactant MC can be produced with high yield by urea mono-methanolysis without catalyst [18] and the co-product NH_3 can be easily separated and recycled to synthesize urea by fixing greenhouse gas CO_2 at the front end of the process. Synthesis of chemicals by using CO_2 and CO_2-derived materials is an important aspect for the utilization of CO_2 [19]. So the route proposed in present work may provide a promising way for the non-phosgene synthesis of MDC as well as simultaneous utilization of CO_2.

2. Experimental

Reactant MDA was purified by recrystallization in cyclohexane. Zinc acetate $Zn(OAc)_2$ and lead acetate $Pb(OAc)_2$, as catalysts used in this work, were obtained by removal of crystal water from $Zn(OAc)_2{\cdot}2H_2O$ and $Pb(OAc)_2{\cdot}3H_2O$ at 373 K for 4 h. Methanol-pretreated PbO catalyst (denoted as P-PbO) was prepared by treating PbO in methanol at 423 K for 4 h and then drying in accordance to Wang et al. [20]. Other reagents were commercial A.R.-purity products and were used as received.

In a typical procedure for MDC synthesis, MDA (3.96 g, 0.02 mol), MC (9.0 g, 0.12 mol), methanol (24 mL, 0.6 mol) and catalyst (0.15 g) were charged into a 100 mL stainless steel autoclave. After purging with nitrogen, the reactor was heated to 433 K with stirring and then kept at 433 K for 4 h. After cooling to room temperature, the obtained solid–liquid mixture was

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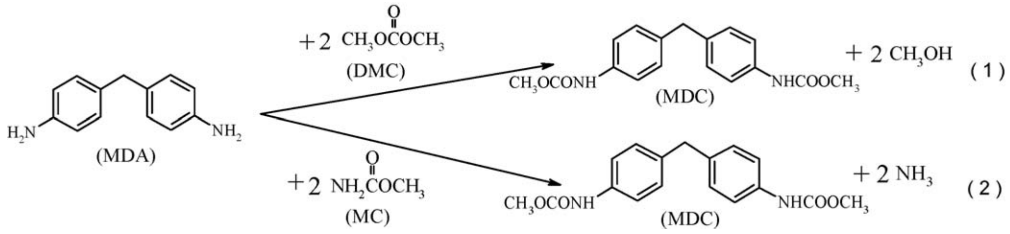


Scheme 1. Equations for the methoxycarbonylation of MDA.

filtered to separate solid from liquid and both were analyzed by High Performance Liquid Chromatography (HPLC, Agilent 1100 series) equipped with a UV detector and ZORBAX Extented-C18. FTIR analysis was carried out on SPECTRUM GX II (Perkin-Elmer). Gas Chromatography coupled with mass spectrometry (GC–MS) was run on a GC (Agilent 6890 series)/MS system with EI ion source and Mass Selective Detector (Agilent 5975C).

3. Results and discussion

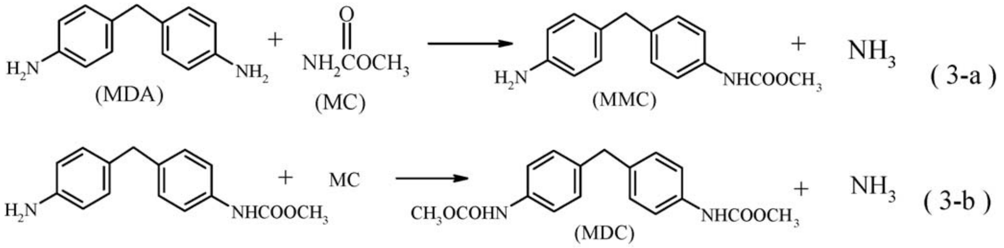
To investigate the component of products in the reaction of MDA and MC, preliminary experiments were carried out in methanol. Mono-carbamate methyl-4-(4′-aminobenzyl) phenylcarbamate (MMC), an intermediate product in the methoxycarbonylation of MDA [12], was also identified besides MDC in the products, indicating that MDC was formed by two steps *via* reactions (3-a) and (3-b), as represented in the following Scheme 2.

The IR spectra of by-products exhibited the a peak at 1653 cm^{-1}, which contributes to the characteristic absorption peak of carbonyl C=O in –NH–CO–NH_2, suggesting ureas to be among by-products, though neither detailed structure nor quantification was possible. Moreover, compounds of N-methylated MDA and MMC were also detected by GC–MS analysis, though not yet quantified.

3.1. Activities of catalysts

It was reported that Zn [21,22] and Pb compounds [23,24] could catalyze the methoxycarbonylation of aromatic amines to produce the corresponding carbamates. To choose the appropriate catalyst for the reaction of MDA with MC, experiments were therefore carried out over a series of catalysts in methanol, leading to the results of Table 1.

Without catalyst, MDA showed complete conversion while the selectivity of MDC and MMC were 51.4 and 4.3%, respectively (Table 1, Entry 1). Catalysts containing Zn (Entries 2–5), as well as the basic catalyst $NaOCH_3$ (Entries 6), have negative effect on this reaction. Both conversion of MDA and selectivity of MDC decline with zinc acetate catalyst containing water of crystallization (Entries 4). Amphoteric metal oxides such as Al_2O_3 and Pb-containing compounds exhibited good catalytic activity (Entries 7–13), especially P-PbO. Water of crystallization seems to have no interference in the catalytic activity of the lead-acetate catalyst (Entries 7, 8). Although the reaction between MDA and MC could proceed in the absence of a catalyst, catalyst is essential for higher MDC yield, thus leading to P-PbO as the catalyst of choice in further investigation.



Scheme 2. Process in the methoxycarbonylation of MDA with MC.

Table 1
Catalytic activity of different catalysts for reaction between MDA and MC.

Entry	Catalyst	Conversion of MDA (%)	Yield[a] of MDC (%)	Selectivity[a] (%)		
				MDC	MMC	Others[b]
1	None	~100	51.4	51.4	4.3	44.3
2	$ZnCl_2$	99.4	35.1	35.3	6.0	58.7
3	$Zn(OAc)_2$	99.3	27.3	37.5	9.5	53.0
4	$Zn(OAc)_2 \cdot 2H_2O$	85.7	13.0	15.2	8.9	75.9
5	ZnO	99.7	28.5	28.6	7.3	64.1
6	$NaOCH_3$	96.3	43.4	45.1	5.5	49.4
7	Al_2O_3	99.9	60.0	60.1	4.2	35.6
8	$Pb(OAc)_2$	99.9	74.5	74.6	5.6	19.8
9	$Pb(OAc)_2 \cdot 3H_2O$	99.6	76.9	77.2	3.8	19.0
10	P-PbO	~100	79.9	79.9	6.0	14.1
11	PbO_2	99.2	72.3	72.8	6.4	20.8
12	PbO	99.9	66.9	66.9	1.3	31.8
13	$Pb(CO_3)_2 \cdot Pb(OH)_2$	99.9	67.1	67.2	3.6	29.2

Reaction conditions: methyl carbamate (0.12 mol), methylene dianiline (0.02 mol), methanol (15 mL); catalyst (0.2 g), reaction time (3 h), reaction temperature (423 K).

[a] Based on moles of MDA added.

[b] "Others" mainly include urea derivatives, as well as a few compounds of N-methylated MDA and MMC.

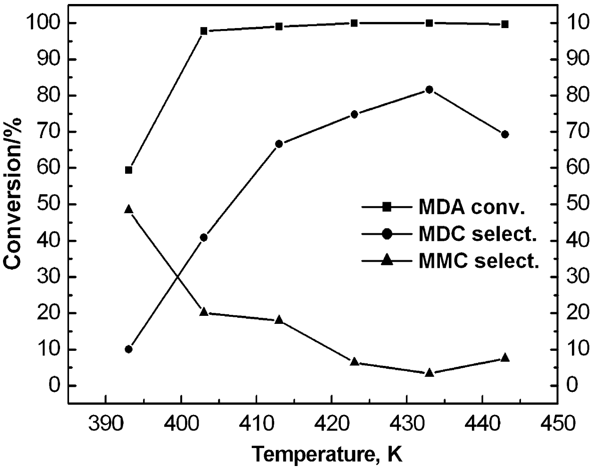


Fig. 1. Effect of temperature on reaction between MDA and MC. Reaction conditions: molar ratio of MC to MDA 6:1, catalyst content 5% (based on MDA, by mass), and reaction time 3 h.

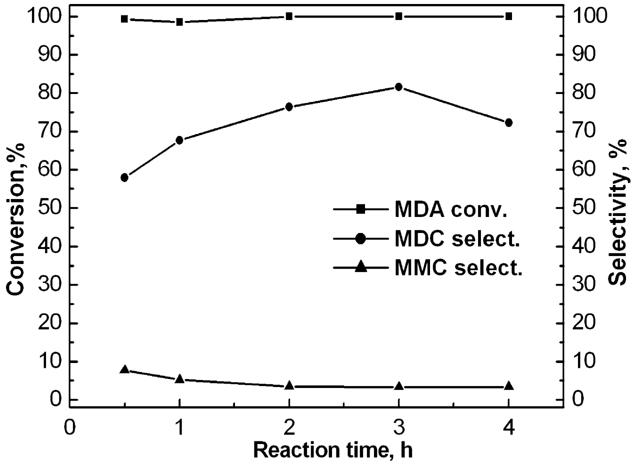


Fig. 2. Effect of reaction time on reaction between MDA and MC. Reaction conditions: molar ratio of MC to MDA 6:1, catalyst content 5% (based on MDA, by mass), and reaction temperature 433 K.

3.2. *Effect of reaction temperature*

The effect of reaction temperature was investigated firstly. Fig. 1 indicates that the conversion of MDA is low below 403 K, with the intermediate MMC as main product, but it increases sharply to 97.3% at 403 K. The selectivity of MMC decreases but the selectivity of MDC increases with temperature rise. At 433 K, conversion of MDA reaches almost 100% and the selectivity of MDC reaches 81.6%, indicating that high temperature favors the conversion of MMC to produce MDC. With further increasing of the temperature beyond 433 K, selectivity of MDC decreases because the dimerization of aromatic amines could take place easily at higher temperature. The other reason might be related to the N-methylation of MDA and MMC. It is concluded that the optimum temperature for this reaction is 433 K.

3.3. *Effect of reaction time*

The investigation of reaction time on the methoxycarboxylation of MDA with MC was performed in presence of methanol over P-PbO catalyst as illustrated in Fig. 2. The MDA conversion is near to 100% after 0.5 h, while the selectivity of MDC is only 57.8%, which increases with the prolonging time to reach a maximum of 81.6% after 3 h. With further prolonging of reaction time, selectivity of MDC decreases because of side reactions such as dimerization of aromatic amines. Meanwhile, the selectivity of MMC shows a slight downward trend with time to attain final constancy, suggesting eventual balance in the reaction (3-b), possibly due to the existence of NH_3 in the system. The conversion of MMC is incomplete which might be related to the concentration of ammonia produced in methanol.

3.4. *Effect of catalyst content*

Fig. 3 shows that the conversion of MDA is independent of the content of catalyst, and that complete conversion is achieved under the reaction condition chosen. The selectivity for MMC shows a rather inconspicuous downward trend at first, followed a rising trend, while the selectivity of MDC increases obviously with increasing content of catalyst to reach maximum at catalyst content of 5% (based on MDA, by mass). However when the catalyst content is more than 8%, the selectivity of MDC decreases to constancy at catalyst content above 12 wt.%. It is likely that the catalyst and reagents form a homogeneous system since the catalyst content does not affect the reactivity significantly, which means that the mass transportation is nearly negligible. The decline of the selectivity of MDC might be related to the concentration of indiscerptible catalyst in the reaction system. So the best content of P-PbO catalyst is about 5 wt.%.

3.5. *Effect of MC to MDA molar ratio*

Fig. 4 shows that conversion of MDA increases with increasing molar ratio of MC to MDA and remains almost constant when the molar ratio is more than 4. While the selectivity of MDC increases sharply, with the increase of molar ratio (MC to MDA) below 6, to reach a maximum of 83.1% at the molar ratio of 8. It also can be observed that selectivity of MMC decreases with the increase of molar ratio below 4 but a rising trend appears above 8. It can be explained by the concentration of MC in the system. In low concentration, the methyl carbamate molecules were encircled tightly by methanol molecules, which retarded the main reaction (3-b). When the molar ratio was above 8, the concentration of MC was high and the probability of the trimerization of MC increased, which inhibited the further methoxycarboxylation of MMC.

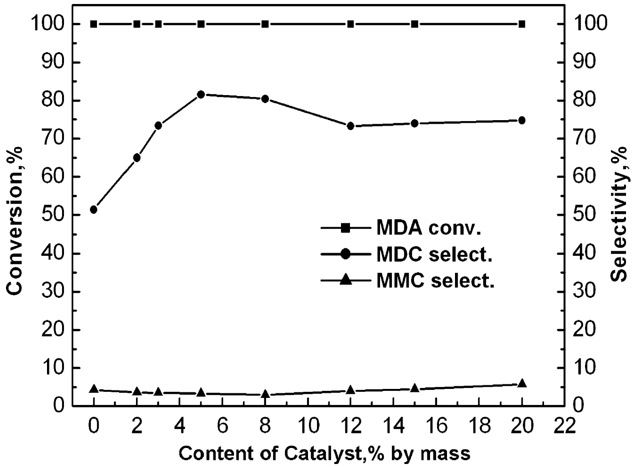
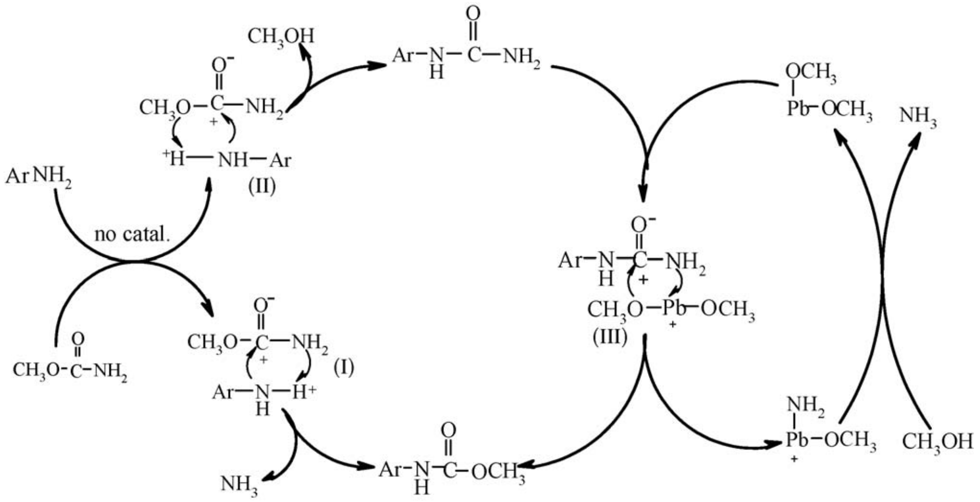
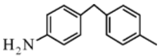
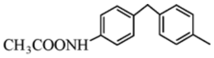


Fig. 3. Effect of catalyst content on reaction between MDA and MC. Reaction conditions: molar ratio of MC to MDA is 6:1, reaction temperature 433 K, and reaction time 3 h.



Scheme 3. Possible mechanism for the methoxycarbonylation of MDA with MC over P-PbO catalyst in the presence of methanol (Ar =  in the process of MDA to MMC; Ar =  in the process of MMC to MDC).

3.6. *A possible mechanism for methoxycarbonylation of MDA in presence of P-PbO*

As described in Scheme 2, MDC was formed by two similar steps (reactions 3-a and 3-b). Here, we mainly discuss the process of MDA to MMC, Eq. (3-a) of Scheme 2, since the formation of MDC from MMC is the same methoxycarbonylation process. A possible reaction mechanism is proposed based on the products distribution and the structure of P-PbO catalyst, as illustrated in the following Scheme 3.

The methoxycarbonylation of amines with MC is presumed as an addition–elimination mechanism. First, MDA attacks the carbenium of methyl carbamate as an nucleophile reagent in the absence of catalyst. There is a competition between intermediates I and II. According to the electron distribution of MC, the electron density at the $–NH_2$ is higher than $–OCH_3$. In a general sense, proton of amine would mainly combine with $–NH_2$ and corresponding carbamate (MMC) is formed by the elimination of NH_3 *via* the tetrahedral intermediate I. Because of geometrical barrier of benzene ring of MDA, the proton of aromatic amine could combined with methoxy of MC to form another intermediate II and part of MDA is transformed into corresponding methanol and urea derivatives, which are presumed to exist in the system by identification of $–NHCONH_2$ through FTIR analysis.

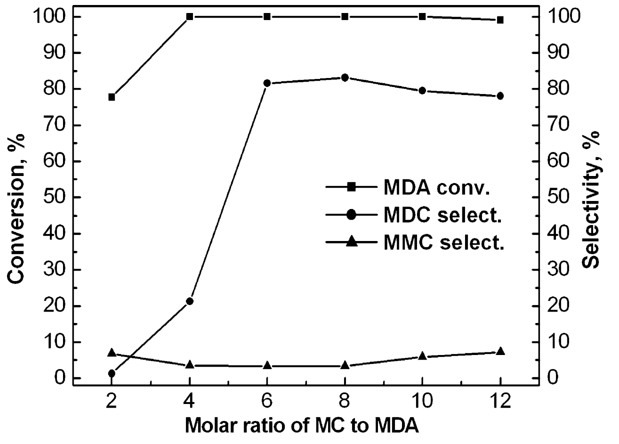


Fig. 4. Effect of MC to MDA molar ratio on the synthesis of MDC. Reaction conditions: catalyst content 5% (based on MDA, by mass), reaction temperature 433 K and reaction time 3 h.

The structure of P-PbO catalyst was reported as $Pb(OCH_3)_2$ [20]. As an nucleophilic group, $CH_3O–$ could attack the carbonyl carbon of urea derivatives and $(Pb–OCH_3)^+$ could combine with the nitrogen atom in $–NH_2$. So urea derivatives convert to a tetrahedral intermediate III over P-PbO catalyst. Then target-carbamate (MMC) is produced by detaching of $(NH_2–PbOCH_3)^+$ from intermediate (III). The P-PbO catalyst is restored by further reaction of methanol with $(NH_2–PbOCH_3)^+$. The combination of $(Pb–OCH_3)^+$ with nitrogen atom in –NH might happen also, but the probability is little due to the geometrical barrier of benzene ring. Therefore, MMC and NH_3 are the main product in the first step of MDA-methoxycarbonylation.

Then MMC recycles to the next methoxycarbonylation process in the same way and MDC is produced as a final product.

4. Conclusions

A non-phosgene route for MDC synthesis *via* the reaction between MDA and MC was proposed in this work. A series of catalysts were screened and P-PbO catalyst exhibited high catalytic activity in the presence of methanol. Reaction temperature, reaction time, catalyst content and the molar ratio of reactants were investigated over P-PbO catalyst. The results showed that MDA conversion mainly related to the temperature and molar ratio of MC to MDA. Under the temperature of 403 K, main product was intermediate MMC. MDC selectivity reached 83.1% when the reaction was carried out at 433 K for 3 h with molar ratio (MC to MDA) of 8. Based on the product distribution, an addition–elimination reaction mechanism for the methoxycarbonylation of amines with MC over P-PbO catalyst was proposed. In a typical methoxycarbonylation process, there was a competition between the target carbamate and by-product urea derivatives in the absence of catalyst. The urea derivatives can be transformed into the target carbamate over P-PbO catalyst in the presence of methanol, therefore the yield of the target products was enhanced.

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