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# The Induction Period and Novel Active Species in $Zn(OAc)_2$ Catalyzed Synthesis of Aromatic Carbamates

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**Abstract** $Zn(OAc)_2$ is known to exhibit excellent catalytic activity for aromatic carbamate synthesis by the reaction of aromatic amine and dimethyl carbonate (DMC). It is determined that an induction period exists during the synthesis of dimethyl-4,4′-methylenediphenyl dicarbamate (MDC) and methyl *N*-phenyl carbamate (MPC), although this period is more evident in the case of MDC. $Zn(OAc)_2$ is able to catalyze the reaction of amine and DMC, but also react with DMC to form $Zn_4O(OAc)_6$, which also shows excellent catalytic activity for carbamate synthesis. As for MDC synthesis, $Zn_4O(OAc)_6$ plays the important role. However, $Zn(OAc)_2$ plays the leading role in MPC synthesis. The deactivation of $Zn_4O(OAc)_6$ was also investigated. $Zn_4O(OAc)_6$ was initially transformed into $Zn_5(OH)_8(OAc)_2{\cdot}2H_2O$ (LHZA) and then into ZnO.

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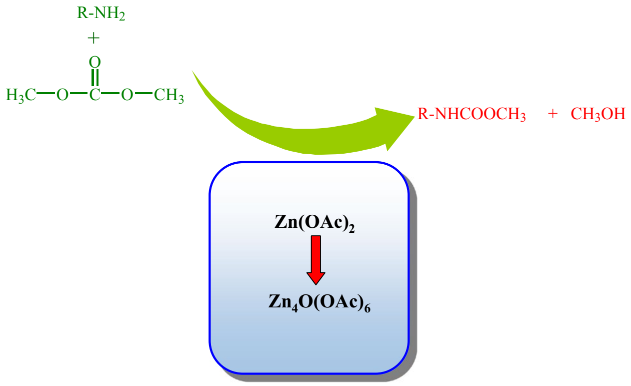
## Graphical Abstract



**Keywords** $Zn(OAc)_2$ · Dimethyl carbonate · Methyl *N*-phenyl carbamate · Dimethyl-4,4′-methylenediphenyl dicarbamate · $Zn_4O(OAc)_6$ · Induction period

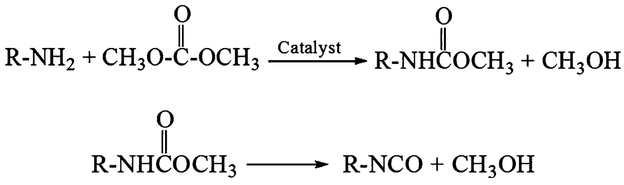
## 1 Introduction

Organic carbamates are widely used as important intermediates in the synthesis of agrochemicals, dyestuffs and pharmaceuticals. They also play a key role in synthetic chemistry in the protection of amino groups [1–4] and, in addition, are important intermediates in isocyanates production by their thermal decomposition [5]. Isocyanates can be divided into aromatic and aliphatic types and several of the aromatic isocyanates, such as 4,4′-diphenyl-methane diisocyanate and 2,4-toluene diisocyanate, are widely used in polyurethane production.

The most common method of synthesizing aromatic isocyanates begins with phosgene. Phosgene, however, is very hazardous and its use in large scale production entails risks related to worker exposure, equipment corrosion and environmental damage upon the release of waste streams. Owing to the environmental hazards of phosgene, efforts are being made to develop non-phosgene synthetic routes to isocyanates. Among the non-phosgene routes, the synthesis of carbamates by aminolysis of dimethyl carbonate (DMC) followed by the thermal decomposition of these carbamates to generate isocyanates is becoming more attractive [6]. The reaction scheme for the synthesis of isocyanates from DMC is described in Scheme 1. In this process, the only by-product is methanol. In addition, the methanol generated as a by-product may be used as the raw material for the subsequent production of DMC by oxidative carbonylation, thus reducing the overall production costs.

In the first step of Scheme 1, a catalyst is required to achieve a suitably high aromatic carbamate yield. At present, lead [7–10] or zinc [11–17] compounds and other catalysts [18–22] are often applied in this reaction. Among these catalysts, zinc compounds, especially $Zn(OAc)_2$, often give the best activity for aromatic carbamate synthesis. As an example, Gurgiolo [11] prepared methyl *N*-phenyl carbamate (MPC) using DMC and aniline as raw ingredients over a $Zn(OAc)_2$ catalyst, and the selectivity for MPC from aniline was found to be 99.8% at 140 °C. Additionally, Baba [13] investigated the methoxycarbonylation of 2,4-toluene diamine (TDA) and 4,4′-diphenylmethane diamine (MDA) with DMC to their corresponding dicarbamates using $Zn(OAc)_2$ as a catalyst at 180 °C for 2 h. The yield of dimethyl toluene-2,4-dicarbamate was 96% while the yield of dimethyl-4,4′-methylenediphenylcarbamate (MDC) was 98%. $Zn(OAc)_2$ also shows excellent catalytic activity for the reaction of TDA or MDA with diethyl carbonate, generating yield of the corresponding carbamate greater than 93% [15]. Other zinc compounds, such as *N,N*-substituted carbamate complexes of zinc [12] and $Zn_4O(OAc)_6$ [16], actually exhibit superior catalytic performance for the reaction of aromatic amines and DMC, but are challenging to prepare and thus more expensive.

During the $Zn(OAc)_2$-catalyzed reaction of *m*-phenylenediamine or 2,4-toluene diamine with DMC, an induction period existed [13]. Whether this induction period also exists in the reaction of MDA or aniline with DMC and what may cause the induction period? Additionally, we have determined that, during the catalytic process, $Zn(OAc)_2$ can react with DMC to form a new compound that shows better catalytic performance, and so which plays the important role in the catalytic reaction: $Zn(OAc)_2$ or the new compound? To investigate this catalytic process in more detail, the present study examined the reactions of DMC with aniline and MDA over a $Zn(OAc)_2$ catalyst and the associated reaction mechanism is discussed herein.



$$\text{R-NH}_2 + \text{CH}_3\text{O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OCH}_3 \xrightarrow{\text{Catalyst}} \text{R-NH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OCH}_3 + \text{CH}_3\text{OH}$$

$$\text{R-NH}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OCH}_3 \longrightarrow \text{R-NCO} + \text{CH}_3\text{OH}$$

**Scheme 1** General synthesis of isocyanates from DMC and amines 113×63 mm

## 2 Experimental

### 2.1 Chemicals and Materials

Dimethyl carbonate (99.5%) was purchased from Tangshan Chaoyang Chemical Co. Ltd. Aniline (99.5%) and zinc acetate (99.5%) was purchased from Sinopharm Chemical Reagent Co. Ltd. MPC (>98.0%) and MDI (>98.0%) was purchased from Tokyo Chemical Industry Co. Ltd. MDA(>97.0%) was purchased from Acros.

4,4′-MDC standard was prepared by the reaction of 4,4′-MDI (>97.0%) and excessive methanol (>99.9%), then by recyrstallization using ethanol as solvent.

### 2.2 Catalytic Evaluation

The reactions to generate either MPC or MDC were carried out in a stainless steel autoclave. In this process, the aromatic amine, DMC and $Zn(OAc)_2$ (prepared by the dehydration of $Zn(OAc)_2{\cdot}H_2O$ at 120 °C) were added to the autoclave and allowed to react at the desired temperature for the desired time span. Owing to the different solubility of MPC or MDC in DMC, the two reaction mixtures were treated differently. Following MPC synthesis, the reaction mixture was simply filtered to separate the catalyst, and the filtrate was analyzed by high performance liquid chromatography (HPLC). Following MDC synthesis, the reaction mixture was also filtrated but, owing to the poor solubility of MDC in DMC, some MDC that had precipitated from the DMC was contained in the filter cake along with the catalyst. In order to separate the MDC from the catalyst, the filter cake was washed with acetone and both the resulting acetone solution and the filtrate were analyzed by HPLC.

A Mettler Toledo Labmax system equipped with a 1L glass reactor was used to observe the solubility of $Zn(OAc)_2$ in DMC and also to prepare $Zn_4O(OAc)_6$.

### 2.3 Product Analysis

Waters HPLC was used to analyze the reaction liquid. The analytical conditions for MPC synthesis were as follows: A Kromasil C-18 (Φ4.6 mm × 150 mm, 5 μm) chromatographic column was used at a flow rate of 0.4 mL/min. $CH_3OH/H_2O$ (70/30, V/V) was used as the mobile phase and the detection wavelength was 254 nm. A quantitative analysis was carried out using nitrobenzene as the internal standard. The analytical conditions for MDC synthesis were the same as that of MPC, except the mobile phase and the flow rate. $CH_3OH/H_2O$ (60/40, V/V) was used as the mobile phase and the flow rate was 0.8 mL/min for MDC analysis.

### 2.4 Catalyst Characterization

X-ray diffraction patterns were recorded on a Rigaku D/MAX2500 with Cu $K\alpha$ radiation at 40 kV and 100 mA. The scanning range was 3°–90°.

FTIR spectra were obtained with a NICOLET NEXUS-470 spectrometer. A DTGS detector was used and 32 scans were accumulated at a spectral resolution of 4 $cm^{-1}$.

Element analysis was performed for carbon and hydrogen with a Thermo Scientific Flash EA 1112 elemental analyzer.

NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature ($^1H$ 400 MHz, $^{13}C$ 100 MHz).

## 3 Results and Discussion

### 3.1 Induction Period in $Zn(OAc)_2$ Catalyzed MDC or MPC Synthesis

Effect of reaction time on the catalytic activity of $Zn(OAc)_2$ was shown in Table 1. During the reaction of aniline with DMC, aniline conversion was 68% at a reaction time of 1 h and reached to 97% at 2 h. Accordingly, MPC yield increased from 68 to 97%. With regard to the MDC synthesis, MDA conversion and MDC yield also increased with reaction time. The MDA conversion of 47% and the MDC yield of 2% at a reaction time of 2 h increased to 100 and 84% at a reaction time of 3 h, respectively. Thus the induction period existed in the reactions of MDA and aniline with DMC.

It was also observed that the induction period was shortened by pretreatment of the $Zn(OAc)_2$ with DMC, based on the results shown in Table 1 (Entry 2), especially for MDC synthesis. The MDC yield reached 92% at a reaction time of 2 h, following pretreatment of the $Zn(OAc)_2$ with DMC at 130 °C for 1 h. In contrast, the original MDC yield was only 2% at a reaction time of 2 h when the $Zn(OAc)_2$ was not pretreated with DMC. As for MPC synthesis, MPC yield was 68% at a reaction time of 1 h without the treatment of $Zn(OAc)_2$ with DMC. After the pretreatment,

**Table 1** Effect of the DMC pretreatment on the catalytic performance of $Zn(OAc)_2$

| Entry | Catalyst | Reaction of DMC and aniline | | | Reaction of DMC and MDA | | |
|---|---|---|---|---|---|---|---|
| | | Time (h) | Aniline conversion (%) | MPC yield (%) | Time (h) | MDA conversion (%) | MDC yield (%) |
| 1 | $Zn(OAc)_2$ | 1[a] | 68 | 68 | 1[b] | 36 | 0 |
| | | 2[a] | 97 | 97 | 2[b] | 47 | 2 |
| | | 3[a] | 98 | 97 | 3[b] | 100 | 84 |
| 2 | $Zn(OAc)_2$ pretreated | 1[c] | 80 | 80 | 1[d] | 66 | 7 |
| | | 2[c] | 98 | 98 | 2[d] | 100 | 92 |
| 3 | The acquired solid[c] | 0.5[e] | 67 | 59 | 1[f] | 46 | 2 |
| | | 1[e] | 98 | 94 | 2[f] | 100 | 86 |
| | | 2[e] | 99 | 99 | 3[f] | 100 | 89 |

[a] Reaction conditions: $Zn(OAc)_2$ 0.56 g (3 mmol), aniline 2 mL (22 mmol), DMC 40 mL (475 mmol), 130 °C

[b] Reaction conditions: $Zn(OAc)_2$ 0.20 g (1 mmol), MDA 0.82 g (4 mmol), DMC 14 mL (166 mmol), 130 °C

[c] 0.56 g (3 mmol) $Zn(OAc)_2$ was pretreated with 40 mL DMC (475 mmol) at 130 °C for 1 h, then cool to room temperature and 2 mL aniline (22 mmol) was added to continue the reaction

[d] 0.20 g (1 mmol) $Zn(OAc)_2$ was pretreated with 14 mL (166 mmol) DMC at 130 °C for 1h, then cool to room temperature and 0.82 g MDA (4 mmol) was added to continue the reaction

[e] Reaction conditions: the acquired solid 0.56 g (0.9 mmol), aniline 2 mL (22 mmol), DMC 40 mL (475 mmol), 130 °C

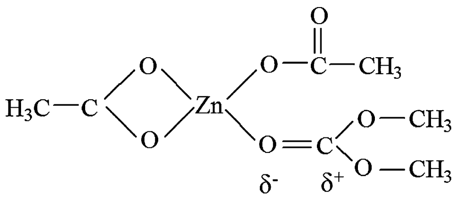
[f] Reaction conditions: the acquired solid 0.20 g (0.3 mmol), MDA 0.82 g (4 mmol), DMC 14 mL (166 mmol), 130 °C

MPC yield reached 80% at a reaction time of 1 h. It can be seen that the pretreatment of the $Zn(OAc)_2$ with DMC can shorten the reaction time.

In order to find the cause for the induction period, 4.3 g of $Zn(OAc)_2$ was pretreated with 300 mL DMC at 130 °C for 1 h ($n_{DMC}$:$n_{Zn(OAc)2}$ = 151:1) in a 1 L glass reactor. It was found that $Zn(OAc)_2$ could not completely dissolve in DMC during the pretreatment, which indicates that the solubility of $Zn(OAc)_2$ in DMC was limited at this temperature. Thus it is presumed that the possible cause of the induction period might be the time required for $Zn(OAc)_2$ dissolution in the DMC at 130 °C. Due to the limited solubility of $Zn(OAc)_2$ in the DMC, $Zn(OAc)_2$ exists in two forms at the start of the reaction; homogeneous $Zn(OAc)_2$ and heterogeneous $Zn(OAc)_2$, with the latter present in a large proportion. Both the homogeneous and heterogeneous $Zn(OAc)_2$ exhibit good catalytic performance for MPC or MDC synthesis. In the case of the heterogeneous catalyst, the reactants must diffuse and adsorb on the catalyst surface before the reaction can occur, which leads to an induction period.

Furthermore, the induction period is more obvious during the reaction of MDA with DMC compared with that of aniline with DMC, possibly owing to the reaction mechanism associated with using $Zn(OAc)_2$ as the catalyst. The reaction of an amine with DMC is nucleophilic, since the carbonyl group of DMC will attract nucleophiles owing to its positive polarization and the $sp^2$ hybridization of the C atom [23, 24]. When $Zn(OAc)_2$ is used as the catalyst, the $d^{10}$ electrons of $Zn^{2+}$ can coordinate with the oxygen atom of the carbonyl to form an intermediate (Scheme 2) that can activate the carbonyl group of DMC by the nucleophilic attack of amine [14].

As for heterogeneous $Zn(OAc)_2$, DMC must diffuse to and adsorb on the heterogeneous $Zn(OAc)_2$ surface. And this is not the case for homogeneous $Zn(OAc)_2$. As noted, however, aniline has one amino group, while MDA has two. The difference between these two species, therefore, occurs owing to the lower probability of the two MDA amino groups simultaneously attacking the carbonyl group of DMC during catalysis by the heterogeneous $Zn(OAc)_2$. Thus the two amino groups in MDA cannot be esterified simultaneously, but are rather successively catalyzed by heterogeneous $Zn(OAc)_2$. When homogeneous $Zn(OAc)_2$ is present, however, the probability of the two amino groups simultaneously being esterified is increased, owing to the reduced steric hindrance. The aforementioned factors result in the different induction periods observed for the reactions of MDA and aniline with DMC.



**Scheme 2** The intermediate in $Zn(OAc)_2$ catalyzed the reaction of DMC with amine 92 × 42 mm

Additionally, it is possible that the above pretreatment step could promote the transformation of $Zn(OAc)_2$ to other catalytic species. To assess this possibility, the aforementioned pretreatment reaction mixture was cooled to room temperature and filtered under vacuum. The filtrate was distilled under vacuum and a white solid precipitated after the distillation. This solid was evaluated for the reaction of DMC with aniline and MDA, with the result shown in Table 1 (Entry 3). The solid exhibited excellent catalytic activity for MPC synthesis, giving a MPC yield of 94% at a reaction time of 1 h. Similarly, this solid exhibited excellent catalytic performance for MDC synthesis, generating an MDC yield of 86% at a reaction time of 2 h.

The white solid was subsequently characterized by Fourier Transform Infrared (FTIR) spectroscopy and the results were shown in Fig. 1. The absorption bands (Fig. 1a) at 1559 and 1447 $cm^{-1}$ are attributed to the asymmetric and symmetric stretching vibration of $COO^-$, while the band at 697 $cm^{-1}$ is attributed to the deformation vibration of $COO^-$. Figure 1b shows the

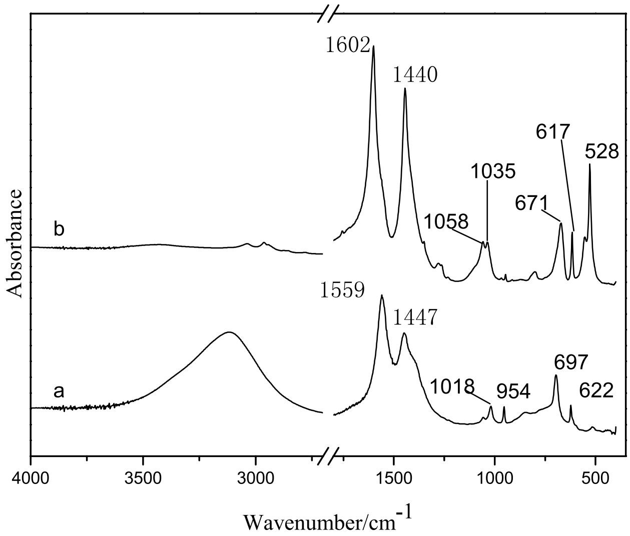


**Fig. 1** FTIR spectrum of *a* $Zn(OAc)_2$ and *b* the acquired solid 210 × 148 mm

FTIR spectrum of the acquired solid, which matches that of $Zn_4O(OAc)_6$ [16, 25]. The bands at 1602 and 1440 $cm^{-1}$ correspond to the asymmetric and symmetric stretching vibrations of $COO^-$, while those at 1058 and 1035 $cm^{-1}$ are attributed to C–C stretching. The bands at 617 and 671 $cm^{-1}$ are assigned to the deformation vibration of $COO^-$ and that at 528 $cm^{-1}$ is due to the asymmetric stretching vibration of $Zn_4O^-$. Additionally, the white solid was also characterized by $^1H$ NMR, $^{13}C$ NMR and elemental analyses. The results are as follows: $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 1.878 ($CH_3$); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 23.1 ($CH_3$), 178.5(CO). Anal. Calcd for $Zn_4O(OAc)_6$: C, 22.81; H, 2.87. Found: C, 22.86; H, 2.82. Thus it can be seen that after the pretreatment of $Zn(OAc)_2$ with DMC part of the $Zn(OAc)_2$ is transformed into $Zn_4O(OAc)_6$, which has a tetrahedral $Zn_4O^-$ center with bridging carboxyl groups along each of the six edges of the tetrahedron [26].

The above results noted an induction period during the synthesis of MDC or MPC using $Zn(OAc)_2$ as the catalyst. However, after the pretreatment of $Zn(OAc)_2$ with DMC, this induction period was significantly shortened. Owing to the limited solubility of $Zn(OAc)_2$ in DMC, the amount of dissolved $Zn(OAc)_2$ increases as the reaction time is prolonged. The dissolved $Zn(OAc)_2$ will catalyze the reaction, but also react with DMC to form $Zn_4O(OAc)_6$. Therefore, the joint catalytic effects of the dissolved $Zn(OAc)_2$ and the $Zn_4O(OAc)_6$ rapidly increase the MDC yield. Then, which compound plays the important role in the catalytic reaction: $Zn(OAc)_2$ or $Zn_4O(OAc)_6$. As for MDC synthesis (shown in Table 1, Entry 1), MDA conversion and MDC yield were found to be 36 and 0% at 1 h, respectively. As aforementioned, part of $Zn(OAc)_2$ could be transformed into $Zn_4O(OAc)_6$ when $Zn(OAc)_2$ was pretreated with DMC for 1 h at 130 °C. MDA conversion and MDC yield increased promptly to 100 and 84%, respectively, at 3 h. So it is reasonable to presume that $Zn_4O(OAc)_6$ plays the major role in MDC synthesis. However, with regard to the MPC synthesis, MPC yield was 68% at a reaction time of 1 h and it increased to 97% at 2 h. So $Zn(OAc)_2$ plays the leading role in MPC synthesis.

Additionally, the effects of reaction conditions on the induction period of $Zn(OAc)_2$ in MDC synthesis were evaluated and the results are shown in Fig. 2. There was a distinct induction period within 3 h when the reaction temperature was 130 °C, as shown in Fig. 2a, b. However, the induction period didn't appear at 110 °C. When the temperature was 110 °C, MDA conversion and MDC yield were only 27 and 1% for 3 h, respectively. It meant that the induction period was probably prolonged at lower temperature. When the temperature increased to 150 °C, MDA conversion and MDC yield reached 100 and 83% even at 1 h. This indicated that the induction period was shortened. The cause is that, at higher temperature, the solubility of $Zn(OAc)_2$ in DMC increased and the formation of $Zn_4O(OAc)_6$ is accelerated. Moreover, higher temperature can also promote the reaction rate of MDC synthesis. Therefore, higher temperature shortens the induction period. Unlike the temperature, the molar ratio of $Zn(OAc)_2$/MDA and DMC/MDA showed less influence on the induction period of $Zn(OAc)_2$ within 3 h. This could be also explained by the fact that they had less influence on the reaction rate and the solubility of $Zn(OAc)_2$ in DMC.

### 3.2 Catalytic Stability of $Zn_4O(OAc)_6$

The stability of $Zn_4O(OAc)_6$ in MDC and MPC synthesis was studied, with the results shown in Table 2. After the second use, the catalytic performance of $Zn_4O(OAc)_6$ for MDC and MPC synthesis decreased significantly. To investigate the deactivation, $Zn_4O(OAc)_6$ was characterized after the first and second uses by XRD. Figure 3 shows the XRD patterns of deactivated $Zn_4O(OAc)_6$ in MDC synthesis. Weak ZnO diffraction peaks are seen in Fig. 3a, indicating the presence of a small amount of ZnO after the initial usage of the $Zn_4O(OAc)_6$. Additionally, diffraction peaks appear at 2θ values of 5.8°, 33.2° and 59.6° in the XRD pattern of $Zn_4O(OAc)_6$ after its first use. These can be assigned to the (001), (100) and (110) reflections of layered basic zinc acetate, $Zn_5(OH)_8(OAc)_2{\cdot}2H_2O$ (LHZA) [27–29]. Figure 3b presents the XRD pattern of $Zn_4O(OAc)_6$ after its second use. It can be seen that the intensities of the LHZA diffraction peaks are obviously weakened while the ZnO peaks are strengthened, demonstrating that the majority of the LHZA was transformed into ZnO. Figure 4 shows the XRD patterns of deactivated $Zn_4O(OAc)_6$ in MPC synthesis. Similarly, the diffraction peaks of LHZA appear (shown in Fig. 4a) after the first use of $Zn_4O(OAc)_6$. After its second use, the diffraction peaks of LHZA disappear and the diffraction peaks of ZnO appear. Therefore, the deactivation of $Zn_4O(OAc)_6$ is evidently due to the formation of ZnO. During the formation of ZnO, $Zn_4O(OAc)_6$ is initially transformed into LHZA and then the LHZA is transformed into ZnO.

## 4 Conclusion

(1) An induction period exists during the synthesis of MDC and MPC, possibly owing to the time lag associated with dissolution of $Zn(OAc)_2$ in DMC.

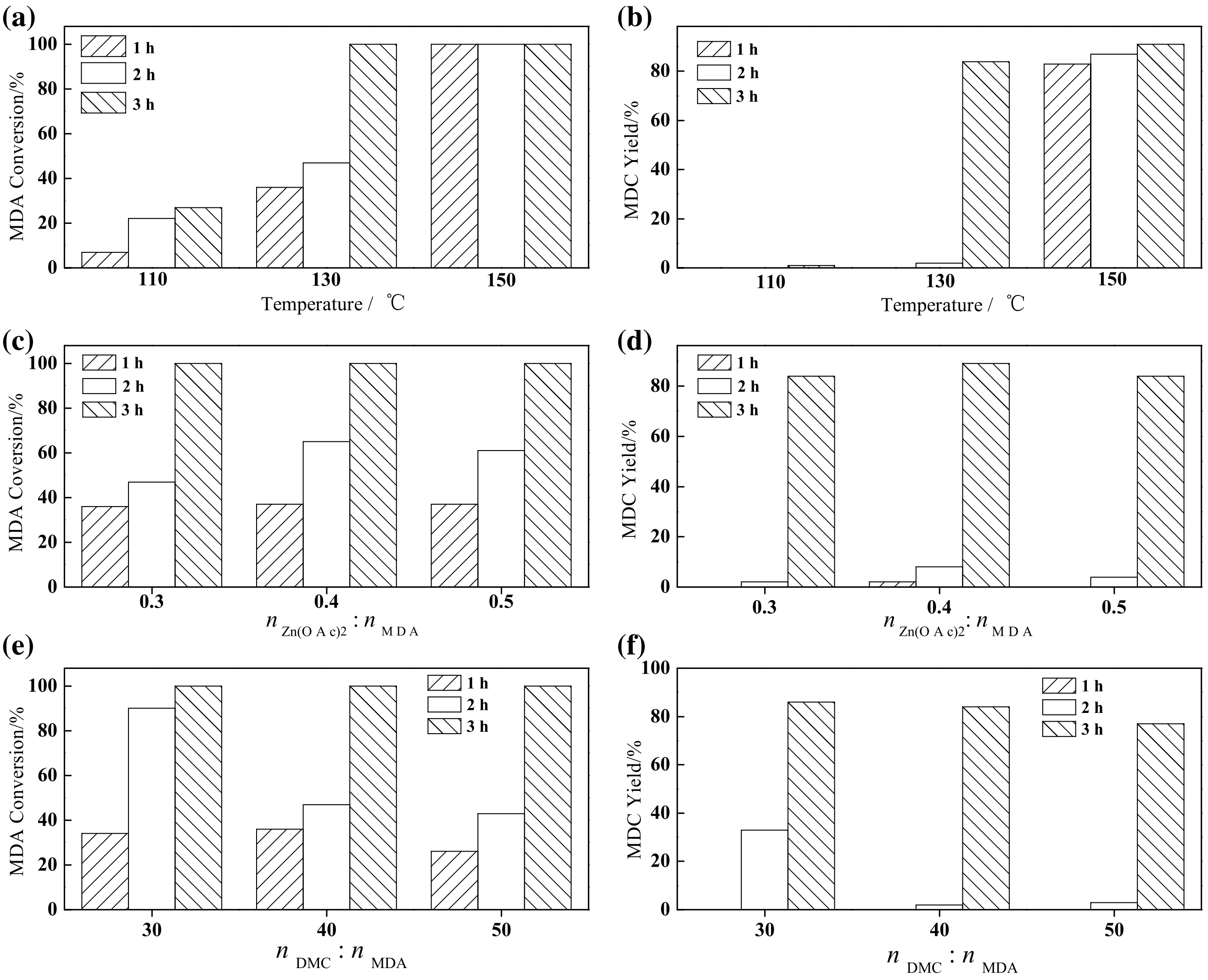


**Fig. 2** Effects of reaction conditions on induction period in MDC synthesis reaction conditions: **a, b** $n_{\mathrm{DMC}}$: $n_{\mathrm{MDA}} = 40$, $n_{\mathrm{Zn(OAc)_2}}$: $n_{\mathrm{MDA}} = 0.3$; **c, d** $n_{\mathrm{DMC}}$: $n_{\mathrm{MDA}} = 40$, 130 °C; **e, f** $n_{\mathrm{Zn(OAc)_2}}$: $n_{\mathrm{MDA}} = 0.3$, 130 °C 206 × 158 mm

**Table 2** Stability of $Zn_4O(OAc)_6$ for MDC and MPC synthesis

| Times | Reaction of DMC and aniline[a] | | Reaction of DMC and MDA[b] | |
|---|---|---|---|---|
| | Aniline conversion (%) | MPC yield (%) | MDA conversion (%) | MDC yield (%) |
| 1 | 99 | 99 | 100 | 89 |
| 2 | 2 | 2 | 50 | 3 |

[a] Reaction conditions: catalyst 0.56 g (0.9 mmol), aniline 2 mL (22 mmol), DMC 40 mL (475 mmol), 130 °C, 2 h

[b] Reaction conditions: catalyst 0.20 g (0.3 mmol), MDA 0.82 g (4 mmol), DMC 14 mL (166 mmol), 130 °C, 3 h

(2) $Zn(OAc)_2$ can react with DMC to form $Zn_4O(OAc)_6$, which also shows excellent catalytic activity for carbamate synthesis. As for MDC synthesis, $Zn_4O(OAc)_6$ plays the important role in the catalytic reaction. However, $Zn(OAc)_2$ plays the leading role in MPC synthesis.

(3) During the catalytic synthesis of aromatic carbamate $Zn_4O(OAc)_6$ initially transforms into LHZA and then into ZnO.

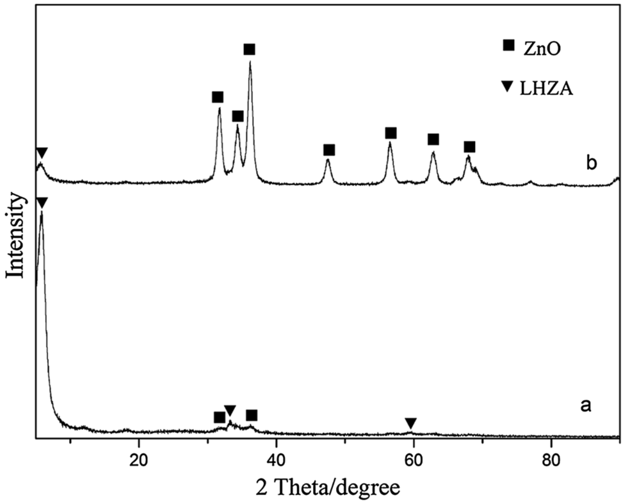


**Fig. 3** XRD patterns of deactivated $Zn_4O(OAc)_6$ in MDC synthesis. *a* After first use of $Zn_4O(OAc)_6$; *b* after second use of $Zn_4O(OAc)_6$. 103 × 73 mm

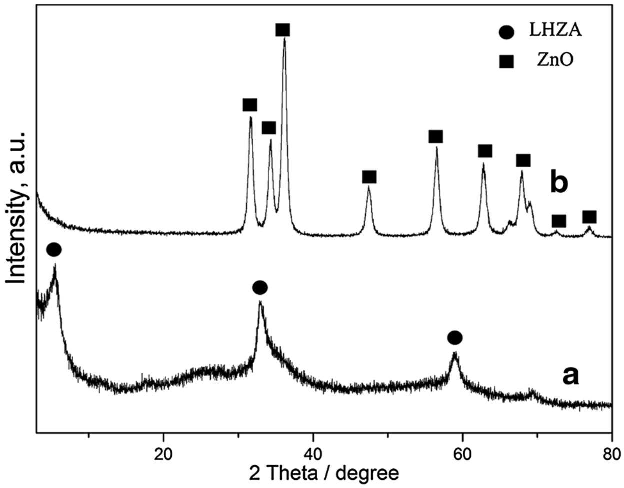


**Fig. 4** XRD patterns of deactivated $Zn_4O(OAc)_6$ in MPC synthesis. *a* After first use of $Zn_4O(OAc)_6$; *b* after second use of $Zn_4O(OAc)_6$.103 × 73 mm

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## References

1. Ray S, Pathak SR, Chaturvedi D (2005) Drugs Future 30:161
2. Gupta RC (ed) (2006) Toxicology of organophosphate and carbamate compounds. Elsevier, Burlington
3. Litjens REJN, van den Bos LJ, Codée JDC, Overkleeft HS, van der Marel GA (2007) Carbohydr Res 342:419
4. Wuts PGM, Greene TW (2007) Greene's protective groups in organic synthesis. Wiley, New Jersey
5. Valli VLK, Alper H (1995) J Org Chem 60:257
6. Kreye O, Mutlu H, Meier MAR (2013) Green Chem 15:1431
7. Li F, Wang YJ, Xue W, Zhao XQ (2009) J Chem Technol Biotechnol 84:48
8. Fu ZH, Ono Y (1994) J Mol Catal A 91:399
9. Wang SP, Zhang GL, Ma XB, Gong JL (2007) Ind Eng Chem Res 46:6858
10. Pei YX, Li HQ, Liu HT, Zhang Y (2011) Ind Eng Chem Res 50:1955
11. Gurgiolo AE (1981) US Patent 4,268,683, 19 May 1981
12. Bosetti A, Cesti P, Calderazzo F (1997) US Patent 5,698,731, 16 Dec 1997
13. Baba T, Kobayashi A, Yamauchi T, Tanaka H, Aso S, Inomata M, Kawanami Y (2002) Catal Lett 82:193
14. Baba T, Kobayashi A, Kawanami Y, Inazu K, Ishikawa A, Echizenn T, Murai K, Aso S, Inomata M (2005) Green Chem 71:59
15. Reixach E, Bonet N, Rius-Ruiz FX, Wershofen S, Vidal-Ferran A (2010) Ind Eng Chem Res 49:6362
16. Reixach E, Haak RM, Wershofen S, Vidal-Ferran A (2012) Ind Eng Chem Res 51:16165
17. Wang YJ, Zhang WH (1999) Acta Pet Sin 15:9
18. Li F, Miao J, Wang YJ, Zhao XQ (2006) Ind Eng Chem Res 45:4892
19. Li QF, Wang JW, Dong WS (2003) Chin J Catal 24:639
20. Juárez R, Pennemann H, García H (2011) Catal Today 159:25
21. Katada N, Fujinaga H, Nakamura Y, Okumura K, Nishigaki K, Niwa M (2002) Catal Lett 80:47
22. Lucas N, Amrute AP, Palraj K, Shanbhag GV, Vinu A, Halligudi SB (2008) J Mol Catal A 295:29
23. Tundo P, Rossi L, Loris A (2005) J Org Chem 70:2219
24. Tundo P, Bressanello S, Loris A, Sathicq G (2005) Pure Appl Chem 77:1719
25. Berkesi O, Berenji P, Dreveni I, Körtvélyesi T, Andor JA, Mink J, Goggin PL (2007) Vib Spectrosc 43:227
26. Johnson MK, Powell DB, Cannon RD (1982) Spectrochim Acta Part A 38:125
27. Xia ZB, Wang YW, Fang YJ, Wan YT, Xia WW, Sha J (2011) J Phys Chem C 115:14576
28. Poul L, Jouini N, Fiévet F (2000) Chem Mater 12:3123
29. Hosono E, Fujihara S, Kimura T, Imai H (2004) J Colloid Interface Sci 272:391