

### Article

# Solvent-free thermal decomposition of methylenediphenyl di(phenylcarbamate) catalyzed by nano-Cu<sub>2</sub>O

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#### ABSTRACT

Methylene di(phenylisocyanate) (MDI) was prepared by thermal decomposition of methylenediphenyl di(phenylcarbamate) (MDPC) under solvent-free conditions with a nano-Cu<sub>2</sub>O catalyst. The preparation of nano-Cu<sub>2</sub>O was investigated in detail to obtain the optimal catalytic performance. The thermal decomposition reaction conditions, including reaction temperature, reaction pressure, and reaction time, were studied in the presence of nano-Cu<sub>2</sub>O. The results show that Cu<sub>2</sub>O prepared using a hydrolysis method and then calcined at 300 °C in Ar atmosphere for 2 h exhibited the optimal catalytic activity. The optimal reaction conditions were as follows: mass ratio of catalyst to MDPC  $6.0 \times 10^{-4}$ , reaction temperature 220 °C, reaction time 12 min, and reaction pressure 0.6 kPa. Under these conditions, the conversion of MDPC reached 99.8% and 86.2% MDI selectivity was achieved.

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#### 1. Introduction

Methylene di(phenylisocyanate) (MDI) is an important isocyanate and plays a major role in industrial applications. MDI is preferable to(tolylene diisocyanate) TDI because it is less volatile, which avoids potential toxic pollution, and is safer to handle and use. As a result, the feedstock for polyurethane has been changed from the conventional pure TDI or TDI-MDI mixture to pure MDI. MDI is predominant in polyurethane production and has become the most important isocyanate [1,2]. However, the current methods for the preparation of MDI usually involve the use of phosgene; phosgene is highly volatile, extremely toxic, causes serious pollution, and produces chloride as a byproduct. Phosgene-free, environmentally friendly techniques are preferable. Three main non-phosgene processes have been developed, namely the triphosgene method [3,4], the transesterification method [5], and carbamic ester decomposition [6–16]. Although the raw materials for the triphosgene method are safe, the large amounts of hydrochloric acid released during the production process severely corrode the equipment, and the chloride byproduct is difficult to remove from the product. The transesterification process yields various byproducts, and this has prevented further industrial use of this method. Because they do not suffer from these defects, carbamic ester decomposition techniques have been extensively studied in recent years. MDI is prepared by thermal decomposition of methylene di(phenylenecarbamate) (MDC), using a solvent method, accompanied by removal of low alco-

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hols. The concentration of the raw material in the reaction is usually no more than 5 wt%. Chen et al. [9] investigated the thermal decomposition of 3% MDC in dibutyl phthalate at 260 °C, using ultrafine ZnO as a catalyst, yielding 52.1% MDI. Guan et al. [11] performed a similar study using 2.5% MDC at 250 °C catalyzed by ZnO/Zn in dibutyl phthalate; the yield was 67.3%. When Zhao et al. [16] used Zn as the catalyst and a mixed nitrobenzene-tetrahydrofuran solvent in the thermal decomposition of 2% MDC, the yield of MDI was 87.3%. Bosman et al. [17] reported a method that gave high yields of isocyanate at low temperatures by the decomposition of polymethylene-polyphenylene-poly(dialkylurea). Although the solvent method can reduce polymerization side-reactions to give high yields, the use of a large amount of high-boiling-point solvent during the reaction reduces the concentration of the reaction product to an extremely low level, and makes the separation and purification of MDI necessary. Consequently, there is an urgent need to develop methods of preparing MDI by thermal decomposition without the use of large amounts of high-boiling-point solvents, to reduce the reaction temperature and enhance product concentration.

In the present paper, MDI was prepared by the thermal decomposition of methylenediphenyl di(phenylcarbamate) (MDPC) in the presence of a synthesized nano-Cu<sub>2</sub>O catalyst under solvent-free conditions. The preparation of the nano-Cu<sub>2</sub>O was investigated in detail, and the influence of the reaction conditions on thermal decomposition was also examined to optimize the results.

#### 2. Experimental

#### 2.1. Catalyst preparation

#### 2.1.1. Preparation of Cu<sub>2</sub>O by hydrolysis method [18–21]

Na CuCl (2 g) and hexadecyltrimethylammonium bromide (CTAB, 1 g) were added to 200 ml of NaCl (5 mol/L) solution, followed by sonic oscillation. On addition of 20 ml of  $Na_3PO_4$  (1 mol/L) solution, a yellow suspension was observed. To eliminate chloride ions, suction filtration followed by water scrubbing was repeated several times until no chloride ions were detected via AgNO<sub>3</sub> titration. The sample was further washed once with pure acetone and once with pure diethyl ether, and then dried under vacuum at 70 °C for 3 h. The end product was denoted by Cu<sub>2</sub>O-H.

#### 2.1.2. Preparation of Cu<sub>2</sub>O by reduction method [18-21]

CTAB (0.5 g) was dissolved in 100 ml of Cu(NO<sub>3</sub>)<sub>2</sub> (0.1 mol/L) solution, which was labeled as solution A. Solution A was poured into 10 ml of NaOH (0.1 mol/L) solution, and, after sonic dispersion, a blue precipitate, B, was observed. Then 50% hydrazine hydrate was added dropwise to B and a red precipitate, C, was formed. Suction filtration and water scrubbing were each performed once on C. The sample was further washed using pure acetone and pure diethyl ether, and then dried at 70 °C under vacuum for 3 h. The end product was denoted by Cu<sub>2</sub>O-R.

### 2.1.3. Preparation of Cu<sub>2</sub>O by powder metallurgy sintering process [22]

A mixed CuO/Cu powder was calcined at 1100 °C for 2 h, and the final product was denoted by Cu<sub>2</sub>O-C.

#### 2.2. Catalyst characterization

The catalyst was characterized using X-ray diffraction (XRD, X'Pert Pro MPD, Philips), transmission electron microscopy (TEM, JEM-100CX, JEOL) at 80 kV, and scanning electron microscopy (SEM, INSPECT-F, FEI) at 20 kV. The XRD experimental conditions were as follows: 40 kV tube voltage, tube current 35 mA, graphite single-filter, scanning range  $2\theta = 25^{\circ}$ -80°, and scanning velocity 0.2°/s.

The decomposition of MDPC was examined using thermogravimetric analysis (TG, EXSTAR 6000, NSK LED); the experimental parameters were set as follows:  $N_2$  atmosphere, temperature range 25–300 °C, and heating rate 10 °C/min.

## 2.3. Thermal decomposition of methylenediphenyl di(phenylcarbamate) (MDPC)

A certain amount of MDPC and catalyst were placed in a three-necked bottle, and other instruments were put in place, i.e., a thermometer, distillation head, condensate pipes, tail pipe, receiving flask, and vacuum system. The temperature was set at 220 °C, the pressure was 0.6 kPa, and the reaction time was 12 min. The reactions are shown in Scheme 1.

The reaction products were derivatized with ethanol, and the derivatives were determined using high-performance liquid chromatography (Waters e2695). The derivatization reactions are shown in Scheme 2. The operating conditions were as fol-



Scheme 1. Thermal decomposition of MDPC to MDI and phenol.



Scheme 2. MDI and MPI were derivatized with ethanol.

lows: a Waters Symmetry C18 ( $4.6 \times 150 \text{ mm}, 5 \text{ m}$ ) chromatographic column, a Waters 2998 UV detector, methanol (70:30 volume ratio) as the mobile phase, flow rate 1.0 ml/min, UV adsorption wavelength 260 nm, and column temperature 40 °C, calibrated using an external standard.

#### 3. Results and discussion

#### 3.1. TG curve of MDPC

The TG results are shown in Fig. 1. As shown in Fig. 1, the TG curve of MDPC declines sharply from 160 °C, and levels off after 255 °C, signifying the completion of decomposition. It is worth noting that the fastest decomposition occurs at 215.4 °C, which is much lower than the temperature of 280 °C reported by Guan et al. [11]. It follows that a lower temperature facilitates MDPC decomposition.

#### 3.2. Catalytic performance of metal oxide catalyst

Metal oxides are important catalysts with a large range of applications. As a result of an investigation of the thermal decomposition of carbamic esters, Dai et al. [23] proposed a synergistic acid-base catalysis mechanism. Based on the properties of metal oxides, several representative commercial oxides were selected and their catalytic activities were compared, as shown in Table 1. When a strong acidic or alkaline metal oxide such as acidic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or CaO is used in the thermal decomposition of



MDPC, the MDPC conversion and MDI selectivity are both low. When weak acidic or alkaline metal oxides such as  $Bi_2O_3$  [23] or amphoteric oxides such as  $Cu_2O$ , ZnO [9,11], and ZrO<sub>2</sub>[24] are used, the MDPC conversions and MDI selectivities are high.  $Cu_2O$  was the best catalyst.

### 3.3. Effect of preparation conditions on catalytic activity of Cu<sub>2</sub>O

#### 3.3.1. Effect of preparation method

The catalytic activities under similar reaction conditions of Cu<sub>2</sub>O prepared by three different methods were compared, and the results are shown in Table 2. The catalytic performance of Cu<sub>2</sub>O-H is obviously better than those of Cu<sub>2</sub>O-R and Cu<sub>2</sub>O-C, based on MDPC conversion and MDI selectivity, i.e., the catalytic efficiencies are in the following order of Cu<sub>2</sub>O-H > Cu<sub>2</sub>O-R > Cu<sub>2</sub>O-C. The XRD patterns of the three types of Cu<sub>2</sub>O are shown in Fig. 2. The characteristic diffraction peaks of Cu<sub>2</sub>O are 36.5°, 42.4°, and 61.5°, and the characteristic peaks of CuO are 35.6°, 38.8°, and 48.7°. Figure 2 shows that Cu<sub>2</sub>O-C was mixed with a small amount of CuO, mainly because CuO was not completely transformed into Cu<sub>2</sub>O, but this was not observed for the other catalysts [19]. The order of the integrities of the crystalline phases is Cu<sub>2</sub>O-C > Cu<sub>2</sub>O-H > Cu<sub>2</sub>O-R, which suggests that a high temperature contributes to the formation of a crystalline phase. The SEM images of these Cu<sub>2</sub>O catalysts are shown in Fig. 3. The

Table 1	Та	bl	е	1
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Performance of different metal oxides in catalytic decomposition of MDPC to MDI.

Metal oxides	MDPC	Selectivity (%)	
	conversion (%)	MDI	MPI
MgO	45.9	5.9	42.2
CaO	43.1	3.7	45.9
CuO	47.0	5.4	57.3
CeO <sub>2</sub>	39.8	3.4	51.9
Y <sub>2</sub> O <sub>3</sub>	44.1	5.1	60.1
acid α-Al <sub>2</sub> O <sub>3</sub>	41.5	4.9	43.0
CrO <sub>3</sub>	46.3	4.1	31.7
Bi <sub>2</sub> O <sub>3</sub>	55.6	9.2	40.8
ZnO	50.4	8.9	39.5
ZrO <sub>2</sub>	50.8	9.6	45.9
BeO	52.8	9.3	45.6
$Sb_2O_3$	59.3	11.9	44.7
Cu <sub>2</sub> O	63.6	13.1	48.4

Reaction conditions: 210 °C, 15 min, 5 kPa, the catalyst amount 0.5% of MDPC.

 Table 2

 Catalytic performance of Cu<sub>2</sub>O prepared by different methods.

Sample	MDPC	Selectivity (%)	
	conversion (%)	MDI	MPI
Cu <sub>2</sub> O-C	52.8	6.3	51.5
Cu <sub>2</sub> O-H	76.3	19.1	38.9
Cu <sub>2</sub> O-R	68.5	12.5	31.7

Reaction conditions: 210 °C, 5 kPa, 15 min, the catalyst amount 0.5% of MDPC.



Fig. 2. XRD patterns of Cu<sub>2</sub>O samples prepared by different methods.

Cu<sub>2</sub>O-C particles are largest in diameter, those of Cu<sub>2</sub>O-R are the second largest, and those of Cu<sub>2</sub>O-H are the smallest. The larger the particles are, the smaller the number of active sites, and the weaker the catalytic activity. The conclusions drawn from the SEM observations are consistent with the other experimental results, i.e., the sequence of catalytic activity is Cu<sub>2</sub>O-H > Cu<sub>2</sub>O-R > Cu<sub>2</sub>O-C. Cu<sub>2</sub>O-H is therefore the best catalyst, and the hydrolysis method was selected for Cu<sub>2</sub>O preparation.

### *3.3.2.* Influence of calcination atmosphere on Cu<sub>2</sub>O-H catalytic activity

The influence of the calcination atmosphere needs to be further investigated to improve the catalytic activity of  $Cu_2O$ prepared by the hydrolysis method.  $Cu_2O$  is susceptible to both oxidizing and reducing atmospheres, so an inert gas is the best choice. After calcining  $Cu_2O$ -H samples at 200 °C in N<sub>2</sub> and Ar atmospheres, respectively, the catalytic activities of  $Cu_2O$ -H in thermal decomposition was studied and the experimental results are shown in Table 3. The results show that  $Cu_2O$ -H calcined in an Ar atmosphere had better catalytic activity than that of the sample calcined under N<sub>2</sub>.

Catalytic performance of Cu<sub>2</sub>O-H calcined in different atmospheres.

Atmosphere	MDPC	Selectivity (%)	
	conversion (%)	MDI	MPI
N <sub>2</sub>	78.9	20.3	50.8
Ar	80.4	22.7	56.1
Position conditions, 210 °C 15 min 5 kps the satabut amount 0 504 of			

Reaction conditions: 210 °C, 15 min, 5 kPa, the catalyst amount 0.5% of MDPC.

The XRD patterns (Fig. 4) also verified that the calcination atmosphere has an effect on the preparation of Cu<sub>2</sub>O. A Cu spot emerges in Cu<sub>2</sub>O powder calcined under N<sub>2</sub>, which can be attributed to the reduction of Cu<sub>2</sub>O to Cu by impurities in the N<sub>2</sub>. The Cu<sub>2</sub>O calcined under Ar remains comparatively pure and the catalytic activity is also improved. The particle diameters of Cu<sub>2</sub>O samples calcined in Ar and N<sub>2</sub> atmospheres, calculated using the Scherrer equation, are 22.6 nm and 25.7 nm, respectively. This indicates that the Ar atmosphere contributes to the formation of smaller granules. In summary, calcination in an Ar atmosphere is preferable to calcination in a N<sub>2</sub> atmosphere because the obtained Cu<sub>2</sub>O has a favorable crystalline microstructure, active catalytic properties, and high purity.

### *3.3.3. Effect of calcination temperature on catalytic properties of Cu<sub>2</sub>O-H*

The temperatures for calcination of Cu<sub>2</sub>O-H under Ar were investigated to optimize the catalytic properties. The experimental results are shown in Table 4. The catalyst calcined at 200 °C showed good activity, with MDPC conversion of 80.4%, but the MDI selectivity was only 22.7%, because the remaining MDPC was transformed into the monoisocyanate (MPI) by-



Fig. 4. XRD patterns of  $Cu_2O$ -H samples pretreated in different atmospheres.



Fig. 3. SEM images of Cu<sub>2</sub>O samples prepared by different methods. (a) Cu<sub>2</sub>O-H; (b) Cu<sub>2</sub>O-R; (c) Cu<sub>2</sub>O-C.

Table 4
Effect of calcination temperature on Cu <sub>2</sub> O-H activity

Calcination	MDPC	Selectivity (%)	
temperature (°C)	conversion (%)	MDI	MPI
200	80.4	22.7	56.1
300	90.5	25.9	40.2
400	85.5	18.1	42.8
-			

Reaction conditions: 210 °C, 15 min, 5 kPa, the catalyst amount 0.5% of MDPC.

product. The MDI selectivity and MDPC conversion both increased, i.e., to 25.9% and 90.5%, respectively, when the calcination temperature was 300 °C. When the temperature was increased to 400 °C, the catalytic activity began to decline. The MDPC conversion fell to 85.5% and the MDI selectivity dropped sharply to 18.1%.

XRD characterization of Cu<sub>2</sub>O-H powders calcined at different temperatures was performed. As seen in Fig. 5, diffraction peaks of Cu are not seen in the patters for the catalysts calcined at 200 °C and 300 °C, but the Cu peak is present in the pattern for the catalyst calcined at 400 °C. At the higher temperature of 400 °C, Cu<sub>2</sub>O was partly converted to Cu, and its catalytic activity dropped, which signifies that Cu is not the active component. The presence of Cu at high temperature may be caused by the conversion of Cu<sub>2</sub>O-H to Cu by reductive gas impurities in the Ar.

The SEM (Fig. 6(a)) and TEM (Fig. 6(b)) images of Cu<sub>2</sub>-H calcined at 300 °C for 2 h are shown in Figs. 6. The SEM(a) image shows that the Cu<sub>2</sub>O-H particles are of uniform size and are approximately spherical. The TEM(b) results verify that the granules are well proportioned and that the average diameter is 25 nm. The best calcination temperature for Cu<sub>2</sub>O is therefore 300 °C.

#### 3.3.4. Effect of calcination time on catalytic activity of Cu<sub>2</sub>O-H

The calcination time, as well as the temperature and atmosphere, needs to be studied. The catalytic activities of Cu<sub>2</sub>O-H calcined at 300 °C in an Ar atmosphere for different times are shown in Fig. 7. The catalytic activity improves at 1 h, deduced from the values for MDPC conversion and MDI selectivity. The MDPC conversion increases from 90.5% to 92.1%



Fig. 5. XRD patterns of  $Cu_2O$ -H samples calcined at different temperatures.



Fig. 6. SEM (a) and TEM(b) images of Cu<sub>2</sub>O-H calcined at 300 °C.

during 2–3 h, and decreases to 87.3% during 3–5 h. For the MDI selectivity, a different tendency from that of MDPC conversion is observed. The value of MDI selectivity peaks at 25.9% at 2 h and then drops. The combined MDPC conversion and MDI selectivity results show that the best calcination time is 2 h.

XRD was used to further investigate the influence of calcination time, and the results are shown in Fig. 8. It is obvious that new species are hardly observed when the calcination time is less than 3 h. The presence of a Cu crystalline phase occurs at 4 h, and becomes noticeable at 5 h,  $2\theta = 43.4^{\circ}$  and  $50.5^{\circ}$ . This is consistent with the pattern for a calcination temperature of 400 °C. The reaction between Cu<sub>2</sub>O and reductive gas impurities in Ar increased with increasing calcination time, and the generation of Cu reduced the catalytic activity as a result of the change in the catalyst composition.

#### 3.4. Effects of reaction conditions on thermal decomposition of



**Fig. 7.** Effect of calcination time on  $Cu_2O$ -H activity. Reaction conditions: 210 °C, 15 min, 5 kPa, the catalyst amount 0.5% of MDPC. (1) MDPC conversion; (2) MPI selectivity; (3) MDI selectivity.



Fig. 8. XRD patterns of Cu<sub>2</sub>O-H samples calcined for different time.

#### **MDPC**

### 3.4.1. Effect of reaction temperature on thermal decomposition of MDPC

It is well known that temperature has a major influence on decomposition reactions [11]. High temperatures are favorable for the formation and polymerization of MDI because of the endothermic decomposition reaction and thermosensitivity of MDI [9,25]. Selection of the appropriate temperature is therefore one of the decisive factors in enhancing MDI production. The effects of temperature on MDPC conversion and MDI selectivity using the Cu<sub>2</sub>O-H catalyst were investigated, and the results are shown in Fig. 9. MDPC conversion and MDI selectivity initially increase with increasing temperature. When the temperature is raised to 220 °C, MDPC conversion is 97.5% and MDI selectivity is 35.1%. If the temperature continues to increase, MDPC vapor is removed, which reduces MDPC conversion. Although a high temperature is favorable for the decomposition reaction and the production of MDI from MPI, thereby increasing MDI selectivity, it also promotes MDI polymerization. The optimal temperature is therefore 220 °C.



**Fig. 9.** Effect of reaction temperature on MDPC pyrolysis. Reaction conditions: 15 min, 5 kPa, the catalyst amount 0.5% of MDPC. (1) MDPC conversion; (2) MDI selectivity; (3) MPI selectivity.



**Fig. 10.** Effect of reaction pressure on MDPC pyrolysis. Reaction conditions: 220 °C, 15 min, the catalyst amount 0.5% of MDPC. (1) MDPC conversion; (2) MDI selectivity; (3) MPI selectivity.

### *3.4.2. Effect of vacuum degree on thermal decomposition of MDPC*

The decomposition reactions (Scheme 1) are reversible, and the reactions can be pushed in the positive direction by reducing the pressure using a vacuum pump. As a result, the phenol byproduct can be removed and the MDI productivity can be enhanced. It is therefore necessary to investigate the effect of the vacuum degree on the catalytic thermal decomposition. As shown in Fig. 10, with increasing vacuum degree, the MDPC conversion fluctuates almost negligibly and remains stable at about 98%. However, the MDI selectivity increases progressively with increasing vacuum degree and reaches 63.2% at a pressure of 0.6 kPa. Enhancement of the vacuum degree not only facilitates byproduct removal, it also promotes conversion of MPI to MDI. However, if the pressure is reduced below 0.6 kPa, MDPC will be removed from the reactor by distillation. Consequently, a pressure of 0.6 kPa is chosen.

### 3.4.3. Effect of reaction time on thermal decomposition of MDPC

Figure 11 shows the effect of reaction time on thermal de-



**Fig. 11.** Effect of reaction time on MDPC pyrolysis. Reaction conditions: 220 °C, 0.6 kPa, the catalyst amount 0.5% of MDPC. (1) MDPC conversion; (2) MDI selectivity; (3) MPI selectivity.



**Fig. 12.** Effect of catalyst amount on MDPC pyrolysis. Reaction conditions: 12 min, 0.6 kPa, 220 °C. (1) MDPC conversion; (2) MDI selectivity; (3) MPI selectivity.

composition. MDPC conversion remains almost constant with increasing reaction time, whereas the MDI selectivity reached its highest value (64.4%) at 12 min. Increasing the reaction time promotes decomposition of MPI to MDI. The –NCO group on MDI is thermally sensitive, and exposure to high temperature for a long time will facilitate polymerization. Here, the reaction time is fixed at 12 min.

### *3.4.4. Effect of catalyst amount on thermal decomposition of MDPC*

Figure 12 shows the effect of catalyst amount on MDPC decomposition. The maximum values of MDPC conversion and MDI selectivity are both obtained at a catalyst amount of 0.06% (wt%) of the total amount of raw materials. The MDI selectivity is 86.2% and the MDPC conversion is 99.8%. The drop in MDI selectivity with increasing catalyst amount may be attributed to accelerated thermal decomposition and polymerization of MDI as a result of the presence of excess catalyst. The catalyst content is therefore fixed at 0.06% of the total amount of raw materials.

#### 4. Conclusions

Among various investigated metal oxides, amphoteric oxides, especially nano-Cu<sub>2</sub>O prepared by hydrolysis, exhibit superior catalytic activities in the thermal decomposition of carbamic esters. An MDPC conversion of 99.8% and MDI selectivity of 86.2% were achieved. Although the MDI selectivity achieved using a solvent-free method is slightly lower than that using a solvent, the preparation of MDI by catalytic thermal decomposition of MDPC under solvent-free conditions avoids the use of large amounts of high-boiling-point solvents. Moreover, the process is much simpler, which is more favorable for purifying MDI. Industrialization of MDI using a non-phosgene process can be achieved by developing catalysts with improved activities and enhanced MDI selectivities.

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