available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Solvent-free thermal decomposition of methylenediphenyl di(phenylcarbamate) catalyzed by nano-Cu₂O

WANG Qingyin^{a,b}, KANG Wukui^c, ZHANG Yi^{a,b}, YANG Xiangui^a, YAO Jie^a, CHEN Tong^a,
WANG Gongying^{a,*}

^a Chengdu Institute of Organic Chemistry, the Chinese Academy of Sciences, Chengdu 610041, Sichuan, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, Shandong, China

ARTICLE INFO

Article history:

Received 18 September 2012

Accepted 26 November 2012

Published 20 March 2013

Keywords:

Nano cuprous oxide

Methylene-di(phenylisocyanate)

Catalytic thermal decomposition

Methylenediphenyldi(phenylcarbamate)

Isocyanate

Methylene-di(phenylene carbamate)

ABSTRACT

Methylene di(phenylisocyanate) (MDI) was prepared by thermal decomposition of methylenediphenyl di(phenylcarbamate) (MDPC) under solvent-free conditions with a nano-Cu₂O catalyst. The preparation of nano-Cu₂O 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-Cu₂O. The results show that Cu₂O 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 6.0×10^{-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.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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-

* Corresponding author. Tel: +86-28-85215405; Fax: +86-28-85220713; E-mail: gywang@cioc.ac.cn

This work was supported by the National Key Technology R&D Program (2006BAC02A08); Knowledge Innovation Project of the Chinese Academy of Sciences (KGCX2-YW-215-2).

DOI: 10.1016/S1872-2067(11)60494-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 3, March 2013

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-Cu₂O catalyst under solvent-free conditions. The preparation of the nano-Cu₂O 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 Cu₂O 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 Na₃PO₄ (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 AgNO₃ 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 Cu₂O-H.

2.1.2. Preparation of Cu₂O by reduction method [18–21]

CTAB (0.5 g) was dissolved in 100 ml of Cu(NO₃)₂ (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 Cu₂O-R.

2.1.3. Preparation of Cu₂O 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 Cu₂O-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 2θ = 25°–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: N₂ 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 × 150 mm, 5 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 α -Al₂O₃ 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 Bi₂O₃ [23] or amphoteric oxides such as Cu₂O, ZnO [9,11], and ZrO₂ [24] are used, the MDPC conversions and MDI selectivities are high. Cu₂O was the best catalyst.

3.3. Effect of preparation conditions on catalytic activity of Cu₂O

3.3.1. Effect of preparation method

The catalytic activities under similar reaction conditions of Cu₂O prepared by three different methods were compared, and the results are shown in Table 2. The catalytic performance of Cu₂O-H is obviously better than those of Cu₂O-R and Cu₂O-C, based on MDPC conversion and MDI selectivity, i.e., the catalytic efficiencies are in the following order of Cu₂O-H > Cu₂O-R > Cu₂O-C. The XRD patterns of the three types of Cu₂O are shown in Fig. 2. The characteristic diffraction peaks of Cu₂O 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 Cu₂O-C was mixed with a small amount of CuO, mainly because CuO was not completely transformed into Cu₂O, but this was not observed for the other catalysts [19]. The order of the integrities of the crystalline phases is Cu₂O-C > Cu₂O-H > Cu₂O-R, which suggests that a high temperature contributes to the formation of a crystalline phase. The SEM images of these Cu₂O catalysts are shown in Fig. 3. The

Fig. 1. DTA-TG curves of MDPC.

Table 1

Performance of different metal oxides in catalytic decomposition of MDPC to MDI.

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

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

Table 2Catalytic performance of Cu₂O prepared by different methods.

Sample	MDPC conversion (%)	Selectivity (%)	
		MDI	MPI
Cu ₂ O-C	52.8	6.3	51.5
Cu ₂ O-H	76.3	19.1	38.9
Cu ₂ 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 Cu₂O samples prepared by different methods.

Cu₂O-C particles are largest in diameter, those of Cu₂O-R are the second largest, and those of Cu₂O-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 Cu₂O-H > Cu₂O-R > Cu₂O-C. Cu₂O-H is therefore the best catalyst, and the hydrolysis method was selected for Cu₂O preparation.

3.3.2. Influence of calcination atmosphere on Cu₂O-H catalytic activity

The influence of the calcination atmosphere needs to be further investigated to improve the catalytic activity of Cu₂O prepared by the hydrolysis method. Cu₂O is susceptible to both oxidizing and reducing atmospheres, so an inert gas is the best choice. After calcining Cu₂O-H samples at 200 °C in N₂ and Ar atmospheres, respectively, the catalytic activities of Cu₂O-H in thermal decomposition was studied and the experimental results are shown in Table 3. The results show that Cu₂O-H calcined in an Ar atmosphere had better catalytic activity than that of the sample calcined under N₂.

Table 3Catalytic performance of Cu₂O-H calcined in different atmospheres.

Atmosphere	MDPC conversion (%)	Selectivity (%)	
		MDI	MPI
N ₂	78.9	20.3	50.8
Ar	80.4	22.7	56.1

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 Cu₂O. A Cu spot emerges in Cu₂O powder calcined under N₂, which can be attributed to the reduction of Cu₂O to Cu by impurities in the N₂. The Cu₂O calcined under Ar remains comparatively pure and the catalytic activity is also improved. The particle diameters of Cu₂O samples calcined in Ar and N₂ 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 N₂ atmosphere because the obtained Cu₂O has a favorable crystalline microstructure, active catalytic properties, and high purity.

3.3.3. Effect of calcination temperature on catalytic properties of Cu₂O-H

The temperatures for calcination of Cu₂O-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 Cu₂O-H samples pretreated in different atmospheres. **Fig. 3.** SEM images of Cu₂O samples prepared by different methods. (a) Cu₂O-H; (b) Cu₂O-R; (c) Cu₂O-C.

Table 4Effect of calcination temperature on Cu₂O-H activity.

Calcination temperature (°C)	MDPC conversion (%)	Selectivity (%)	
		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 Cu₂O-H powders calcined at different temperatures was performed. As seen in Fig. 5, diffraction peaks of Cu are not seen in the patterns 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, Cu₂O 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 Cu₂O-H to Cu by reductive gas impurities in the Ar.

The SEM (Fig. 6(a)) and TEM (Fig. 6(b)) images of Cu₂O-H calcined at 300 °C for 2 h are shown in Figs. 6. The SEM(a) image shows that the Cu₂O-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 Cu₂O is therefore 300 °C.

3.3.4. Effect of calcination time on catalytic activity of Cu₂O-H

The calcination time, as well as the temperature and atmosphere, needs to be studied. The catalytic activities of Cu₂O-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 Cu₂O-H samples calcined at different temperatures. **Fig. 6.** SEM (a) and TEM(b) images of Cu₂O-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° . This is consistent with the pattern for a calcination temperature of 400 °C. The reaction between Cu₂O 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 Cu₂O-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 Cu₂O-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 Cu₂O-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-Cu₂O prepared by hydrolysis, exhibit su-

perior 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.

References

- [1] Xu P L, Zhang Sh Q. Handbook of Polyurethane Materials. Beijing: Chem Ind Press (徐培林, 张淑琴. 聚氨酯材料手册. 北京: 化学工业出版社), 2002. 35
- [2] Yu L M, Zheng B Sh. *Chem Ind* (余黎明, 郑宝山. 化学工业), 2008, 26(7): 46
- [3] Xia M, Tang J X. *J Zhuzhou Inst Technol* (夏敏, 唐建新. 株洲工学院学报), 2000, 14(3): 1
- [4] Dong Y W, Sun J M, Zhai J, Zhang Zh G, Wang J M. *Tianjin Chem Ind* (东玉武, 孙建梅, 翟江, 张兆贵, 王景明. 天津化工), 2002, (6): 41
- [5] Mango F D. US Patent 4 163 019. 1979
- [6] Hammen G, Knoefel H, Friedrichs W. EP Patent 0 396 977. 1990
- [7] Wang G Y, Chen D, Feng X L, Wang Q Y, Yao J, Wang Y, Zeng Y (王公应, 陈东, 冯秀丽, 王庆印, 姚洁, 王越, 曾毅). CN Patent 1721060. 2005
- [8] Rosenthal R, Zajacek J G. US Patent 3 919 279. 1975
- [9] Chen D, Liu L M, Wang Y, Yao J, Wang G Y, Li Sh X, Xue Y, Zhan J H. *Chin J Catal* (陈东, 刘良明, 王越, 姚洁, 王公应, 李石新, 薛援, 展江红. 催化学报), 2005, 26: 987
- [10] Deng Y Q, Guo X G, Shi F, Zhang Q H, Ma X Y, Lu L J, Li J, Tian X, Ma Y B, Shang J P, Cui X J, Wang L G, Zhang H Z. US Patent 0 021 810. 2011
- [11] Guan X, Li H Q, Liu H T, Guo F, Yao X X. *J Beijing Univ Chem Technol (Nat Sci)* (关雪, 李会泉, 刘海涛, 郭奋, 姚星星. 北京化工大学学报 (自然科学版)), 2009, 36(4): 12
- [12] Wang J G, Guo X C, Qin Zh F, Wang G F (王建国, 郭星翠, 秦张峰, 王国富). CN Patent 101 269 342. 2008
- [13] Wang G Y, Dai Y Sh, Wang Q Y, Liu L M, Wang Y, Yao J, Zeng Y (王公应, 戴云生, 王庆印, 刘良明, 王越, 姚洁, 曾毅). CN Patent 101 011 657. 2007
- [14] Uriz P, Serra M, Salagre P, Castillon S, Claver C, Fernandez E. *Tetrahedron Lett*, 2002, 43: 1673

Graphical Abstract

Chin. J. Catal., 2013, 34: 548–558 doi: 10.1016/S1872-2067(11)60494-4

Solvent-free thermal decomposition of methylenediphenyl di(phenylcarbamate) catalyzed by nano-Cu₂O

WANG Qingyin, KANG Wukui, ZHANG Yi, YANG Xiangui, YAO Jie, CHEN Tong, WANG Gongying*
Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences;
University of Chinese Academy of Sciences; Qingdao Agricultural University

Nano-Cu₂O shows high catalytic activity for the thermal decomposition of methylenediphenyl di(phenylcarbamate) under solvent-free conditions. Solvent-free thermal decomposition is a green synthetic route to methylene di(phenylisocyanate).

- [15] Hammen G, Knofel H, Friederichs W. US Patent 5 043 471. 1991
- [16] Zhao X Q, Wang Y J, Wang S F, Yang H J, Zhang J Y. *Ind Eng Chem Res*, 2002, 41: 5139
- [17] Bosman J K P, Mangos Jostes N (博斯曼 J K P, 曼格斯乔特斯 N). CN Patent 1 406 224. 2003
- [18] Mei G J, Shi W, Xie K F, Xia Y. *Resources Environ Eng* (梅光军, 师伟, 解科峰, 夏洋. 资源环境与工程), 2007, 21: 335
- [19] Yamada Y, Yano K, Fukuzumi S. *Energy Environ Sci*, 2012, 5: 5356
- [20] Zhang Z L, Che H W, Gao J J, Wang Y L, She X L, Sun J, Gunawan P, Zhong Z Y, Su F B. *Catal Sci Technol*, 2012, 2: 1207
- [21] Xu Y, Wang H, Yu Y F, Tian L, Zhao W W, Zhang B. *J Phys Chem C*, 2011, 115: 15288
- [22] Bai Zh H, Luo B H, Jin X H. *Mining Metall Eng* (柏振海, 罗兵辉, 金晓鸿. 矿业工程), 2001, 21(4): 67
- [23] Dai Y Sh, Wang Y, Yao J, Wang Q Y, Liu L M, Wei Ch, Wang G Y. *Catal Lett*, 2008, 123: 307
- [24] Ruan Ch X, Chen Ch Q, Zhang Y J, Lin X Y, Zhan Y Y, Zheng Q. *Chin J Catal* (阮春晓, 陈崇启, 张燕杰, 林性怡, 詹瑛瑛, 郑起. 催化学报), 2012, 33: 842
- [25] Zhang Q H, Li H Q, Liu H T, Pei Y X. *Chem J Chin Univ* (张琴花, 李会泉, 刘海涛, 裴义霞. 高等学校化学学报), 2011, 32: 1106

纳米Cu₂O催化二苯甲烷二氨基甲酸苯酯无溶剂热分解制备二苯甲烷二异氰酸酯

王庆印^{a,b}, 康武魁^c, 张毅^{a,b}, 杨先贵^a, 姚洁^a, 陈彤^a, 王公应^{a,*}

^a中国科学院成都有机化学研究所, 四川成都 610041

^b中国科学院大学, 北京 100049

^c中青岛农业大学化学与药学院, 山东青岛 266109

摘要: 研究了无溶剂条件下纳米Cu₂O催化二苯甲烷二氨基甲酸苯酯(MDPC)热分解制备二苯甲烷二异氰酸酯(MDI), 考察了纳米Cu₂O的制备条件与反应条件对MDPC热分解反应性能的影响。结果表明, 水解法制备的纳米Cu₂O在Ar中于300 °C焙烧2 h, 其催化性能最佳; 最佳的反应条件为Cu₂O用量为原料总重的0.06%, 反应温度220 °C, 反应压力0.6 kPa, 反应时间12 min, 此时MDPC转化率达到99.8%, MDI选择性86.2%。

关键词: 纳米氧化亚铜; 二苯甲烷二异氰酸酯; 催化热分解; 二苯甲烷二氨基甲酸苯酯; 异氰酸酯; 二苯甲烷二氨基甲酸甲酯

收稿日期: 2012-09-18. 接受日期: 2012-11-26. 出版日期: 2013-03-20.

*通讯联系人. 电话: (028)85215405; 传真: (028)85220713; 电子信箱: gywang@cioc.ac.cn

基金来源: 国家科技支撑计划(2006BAC02A08); 中国科学院知识创新工程重要方向项目(KGCX2-YW-215-2).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

二苯甲烷二异氰酸酯(MDI)是一种极其重要的有机异氰酸酯。它比甲苯二异氰酸酯(TDI)挥发性小, 对人体的毒性相对较小, 有利于安全生产。目前聚氨酯泡沫主要使用的异氰酸酯已由TDI和TDI-MDI混用向全MDI体系转变, MDI已广泛用于生产各类聚氨酯产品, 成为目前世界上产量最大、用途最广的异氰酸酯^[1,2]。MDI的生产主要采用光气法, 但光气易挥发, 剧毒, 环境污染大, 产品中含氯化物不易分离, 因此业界逐渐开展环境友好的MDI非光气合成工艺, 如三光气法^[3,4]、酯交换法^[5]和氨基甲酸酯分解法^[6-16]。三光气法虽然原料比较安全, 但生产过程中仍会产生大量的盐酸, 腐蚀设备, 产品中仍含有氯化物; 酯交换法副产物多, 难工业化。氨基甲酸酯分解法避免了上述两种方法的不足, 是目前研究的热点, 它主要是溶剂法热分解二苯甲烷二氨基甲酸甲(乙)酯脱除小分子醇类物质制备MDI, 其原料浓度低于5%。陈东等^[9]以超细ZnO为催化剂, 以邻苯二甲酸二丁

酯为溶剂, 研究了260 °C时3%二苯甲烷二氨基甲酸甲酯(MDC)的热分解反应, MDI产率为52.1%。关雪等^[11]以ZnO/Zn为催化剂, 以邻苯二甲酸二丁酯为溶剂, 将2.5%MDC溶液在250 °C进行热分解, MDI产率为67.3%。Zhao等^[16]以锌粉为催化剂, 以“硝基苯与四氢呋喃”为混合溶剂, 在280 °C下2%MDC热分解生成的MDI产率为87.3%。博斯曼等^[17]公开了一种有机多氨基甲酸酯分解成有机多异氰酸酯和苯酚的方法, 该法在低温下可以高产率地获得有机多异氰酸酯。溶剂法虽然产率较高, 且能抑制聚合反应的发生, 但由于在反应过程中加入了大量高沸点溶剂, 产物浓度低, 造成MDI后续分离提纯工艺复杂, 效率低且高温能耗高。因此, 降低反应温度, 提高产物浓度及产率是目前热分解制备MDI急需解决的问题。

本文采用自制的纳米Cu₂O在无溶剂条件下催化二苯甲烷二氨基甲酸苯酯(MDPC)热分解制备MDI, 考察了催化剂制备条件以及反应条件对热分解反应性能的影响。

2. 实验部分

2.1. 催化剂的制备

2.1.1. 水解法制备 Cu_2O ^[18–21]

于25 °C下在200 ml NaCl (AR, 广州市金华大化学试剂有限公司) 溶液(5 mol/L)中加入2 g CuCl (AR, 成都科龙化工试剂厂)和1g十六烷基三甲基溴化铵(CTAB; AR, 广州市金华大化学试剂有限公司), 超声分散, 然后加入20 ml Na_3PO_4 (AR, 成都科龙化工试剂厂)溶液(1 mol/L), 得到黄色悬浊液, 抽滤水洗直至无氯离子(AgNO_3 检测), 再用丙酮、乙醚各洗一次, 于70 °C真空干燥3 h, 备用, 记为 $\text{Cu}_2\text{O-H}$.

2.1.2. 还原法制备 Cu_2O ^[18–21]

于25 °C下将0.5 g CTAB溶于100 ml $\text{Cu}(\text{NO}_3)_2$ (AR, 上海三爱思试剂有限公司) 溶液(0.1 mol/L)中; 将该溶液快速加入到10 ml NaOH (AR, 广州市金华大化学试剂有限公司)水溶液(0.1 mol/L)中, 超声分散, 生成蓝色沉淀, 再逐滴加入水合肼(AR, 广州市金华大化学试剂有限公司)水溶液(50%), 生成红色沉淀, 抽滤, 水洗, 再分别用丙酮和乙醚各洗一次, 于70 °C下真空干燥3 h, 备用, 记为 $\text{Cu}_2\text{O-R}$.

2.1.3. 粉末冶金烧结法制备 Cu_2O ^[22]

将一定量的CuO (AR, 成都科龙化工试剂厂)和Cu (AR, 成都科龙化工试剂厂)粉混合, 于1100 °C下焙烧2 h, 备用, 记为 $\text{Cu}_2\text{O-C}$.

2.2. 催化剂的表征

X射线衍射(XRD)测试在飞利浦公司的X'Pert pro MPD型X射线仪上进行. Cu靶($\lambda = 0.1540$ nm), 管电压40 kV, 管电流35 mA, 石墨单色滤光片, 连续扫描, 扫描范围 $2\theta = 25^\circ \sim 80^\circ$, 扫描速度 $0.2^\circ/\text{s}$. 透射电镜(TEM)表征采用日本电子公司(JEOL)的JEM-100CX型透射电镜, 工作电压80 kV. 扫描电镜(SEM)表征采用FEI公司的INSPECT-F型扫描电镜, 工作电压20 kV.

2.3. MDPC热分解反应

称取一定量的反应物MDPC(自制)和催化剂放入三颈瓶中, 依次安装温度计、蒸馏头、冷凝管、尾接管和接收瓶, 连接真空系统. 升至220 °C, 抽真空至0.6 kPa, 反应12 min(反应式见图式1).

取反应后的釜液, 乙醇衍生(图式2), 用Waters e2695型高效液相色谱仪检测衍生产物, Waters 2998紫外检测器, 色谱柱为Waters Symmetry C18 (4.6×150 mm, 5 μm), 流动相为甲醇-水(体积比为70:30), 流速为1.0 ml/min, 紫外检测波长为260 nm, 柱温40 °C, 外标法定量

分析.

3. 结果与讨论

3.1. MDPC热重分析

对MDPC进行热重(TG)分析, 采用EXSTAR 6000热重分析仪(日本精工公司), N_2 气氛, 以10 °C/min由室温升至300 °C. 图1为MDPC样品的TG曲线.

由图可见, MDPC在160~255 °C失重明显, 至255 °C时, 趋于平缓, 分解结束. 其中215.4 °C时分解速率最快. 关雪等^[11]报道的MDC在280 °C分解速率最快. 两者相比, 在较低温度下, MDPC更易于热分解生成目标产物MDI.

3.2. 不同金属氧化物催化性能比较

金属氧化物是一类重要的催化剂. 戴云生等^[23]在研究氨基甲酸酯热分解反应中提出酸碱协同催化机理. 根据金属氧化物的酸碱性, 选择了几种市售金属氧化物, 并在相同条件下考察了其催化MDPC热分解制备MDI的反应性能, 结果列于表1. 可以看出以酸性或碱性很强的金属氧化物, 如CaO, $\alpha\text{-Al}_2\text{O}_3$ 等为催化剂时, MDPC的转化率和MDI的选择性都较低; 而酸性或碱性较弱的金属氧化物, 如 Bi_2O_3 ^[23]等, 尤其是具有酸碱两性的氧化物, 如 Cu_2O , ZnO ^[9,11]或 ZrO_2 ^[24]等为催化剂时, MDPC的转化率和MDI的选择性相对较高. 其中以 Cu_2O 的催化效果最好, MDPC的转化率和MDI选择性分别达63.6%和13.1%.

3.3. 制备条件对 Cu_2O 催化性能的影响

3.3.1. 制备方法的影响

在相同反应条件下, 考察了三种方法制备的 Cu_2O 的催化性能, 结果列于表2. 可以看出, 各 Cu_2O 样品催化性能的顺序为 $\text{Cu}_2\text{O-H} > \text{Cu}_2\text{O-R} > \text{Cu}_2\text{O-C}$. 可见, 水解法制备的 $\text{Cu}_2\text{O-H}$ 催化效果明显好于还原法和粉末冶金烧结法制备的.

图2为这三个 Cu_2O 样品的XRD谱. 由图可见, 仅 $\text{Cu}_2\text{O-C}$ 样品中出现CuO的衍射峰(35.6° , 38.8° , 48.7°), 这主要是由于CuO在高温焙烧过程中没有完全反应, 残留在 Cu_2O 中^[22]. Cu_2O 晶相衍射峰(36.5° , 42.4° , 61.5°), Cu_2O 结晶度大小顺序为 $\text{Cu}_2\text{O-C} > \text{Cu}_2\text{O-H} > \text{Cu}_2\text{O-R}$. 可见高温有利于晶相结构的生成.

图3为各 Cu_2O 样品的SEM照片. 可以看出, $\text{Cu}_2\text{O-C}$ 样品的粒径远大于 $\text{Cu}_2\text{O-R}$ 和 $\text{Cu}_2\text{O-H}$, $\text{Cu}_2\text{O-H}$ 的最小. 颗粒越大, 催化活性位相对就越少, 其催化性能也就越低, 这较好地解释了这三个样品催化性能的差异. 因此,

采用水解法制备 Cu_2O 较为适宜,下文均以 Cu_2O -H为例说明其催化性能。

3.3.2. 焙烧气氛的影响

为了进一步提高 Cu_2O -H催化剂活性,考察了不同焙烧气氛对其性能的影响。 Cu_2O 在空气气氛中焙烧易氧化生成 CuO ,而在还原性气氛中则易生成单质 Cu 。因此,将 Cu_2O -H分别在 N_2 (成都金克星气体有限公司)和 Ar (成都金克星气体有限公司)中于 $200\text{ }^\circ\text{C}$ 焙烧后,在相同反应条件下考察了它们的催化性能,结果列于表3。可以看出,在 Ar 中焙烧时, Cu_2O -H催化性能略好。

图4为这两个 Cu_2O 样品的XRD谱。可以看出, Cu_2O 在 N_2 中焙烧后有 Cu 出现,是由于 N_2 中杂质气体的还原所致。在 Ar 中焙烧的 Cu 物种仍为 Cu_2O ,因此催化性能较好。通过Scherrer公式估算,在 Ar 和 N_2 中焙烧的 Cu_2O 晶粒尺寸分别为22.6和25.7 nm。由此可见,在 Ar 中焙烧的 Cu_2O 晶相结构保持较好,活性物种 Cu_2O 未发生变化,因此其催化性能较好。

3.3.3. 焙烧温度的影响

表4为在 Ar 中焙烧温度对所制 Cu_2O -H样品催化性能的影响。可以看出, $200\text{ }^\circ\text{C}$ 焙烧的催化剂上,MDPC转化率即可达80.4%,但MDI选择性仅为22.7%,较多生成了MPI;至 $300\text{ }^\circ\text{C}$ 时,MDPC转化率和MDI分别增至90.5%和25.9%;至 $400\text{ }^\circ\text{C}$ 时,催化剂性能开始下降,MDPC转化率为85.5%,MDI的选择性仅为18.1%。

图5为不同温度下焙烧的 Cu_2O -H样品的XRD谱。由图可见,在 200 和 $300\text{ }^\circ\text{C}$ 焙烧时未出现单质 Cu 的衍射峰;至 $400\text{ }^\circ\text{C}$ 时样品中出现单质 Cu 的衍射峰,高温使得 Cu_2O 部分转变为单质 Cu ,结合表4可知,单质 Cu 不是活性物种。单质 Cu 的生成可能是由于 Ar 中含有极少量还原性气体还原所致。

图6是 $300\text{ }^\circ\text{C}$ 焙烧2 h所制 Cu_2O -H样品的SEM和TEM照片。由图6(a)可见,催化剂颗粒分散均匀,形貌近似球形。另外,样品的颗粒大小相对比较均匀,平均粒径在25 nm左右(见图6(b))。

综合考虑, Cu_2O 的适宜焙烧温度为 $300\text{ }^\circ\text{C}$ 。

3.3.4. 焙烧时间的影响

图7为焙烧时间对制得 Cu_2O -H催化剂性能的影响。可以看出,催化剂于 $300\text{ }^\circ\text{C}$ 焙烧1 h后其催化活性较高;至2~3 h时,MDPC的转化率从90.5%略增至92.1%;继续延长至5 h时,MDPC转化率降至87.3%。而对于MDI选择性,焙烧2 h时MDI选择性达最高,为25.9%;继续延长焙烧时间则下降。综合考虑,催化剂焙烧时间以2 h为宜。

图8为上述 Cu_2O -H催化剂的XRD谱。由图可见,焙烧1~3 h时,样品的晶相均未发生变化;至4 h时开始出现单质 Cu 的晶相;到5 h时该衍射峰(43.4° 和 50.5°)更加明显。这也是由于 Ar 中含有的极少量还原性气体与 Cu_2O 反应所致;单质 Cu 生成量随焙烧时间的延长而逐渐增加,因而其催化活性降低。

3.4. 反应条件对MDPC热分解反应的影响

3.4.1. 反应温度的影响

反应温度是热分解反应的决定性因素^[11]。图9考察了反应温度对 Cu_2O -H催化剂上MDPC转化率和MDI选择性的影响。由图可见,随着反应温度的升高,MDPC转化率和MDI选择性逐渐增大;至 $220\text{ }^\circ\text{C}$ 时分别为97.5%和35.1%。继续升高反应温度,MDPC被蒸汽带出进入馏分中,导致MDPC转化率下降。由于该反应为吸热过程,因此高温有利于MDI的生成^[25],选择性增加;但同时由于MDI属于温敏性物质^[9],高温加剧了聚合反应的发生。因此,适宜的反应温度为 $220\text{ }^\circ\text{C}$ 。

3.4.2. 真空度的影响

如图式1所示,该热分解反应属于平衡可逆反应,抽真空降低反应压力,移走副产物苯酚,可促进反应正向进行,提高MDI的产率。图10考察了真空度对催化热分解反应的影响。由图可见,随着真空度的提高,MDPC转化率变化不明显,稳定在98%左右,但是MDI的选择性明显增加,至0.6 kPa时达63.2%。真空度提高时不但有利于平衡正向移动,增大产率,而且促进了MPI进一步转化成MDI。继续提高真空度,MDPC未反应就被蒸出。因此,真空度宜为0.6 kPa。

3.4.3. 反应时间的影响

图11为反应时间对热分解反应的影响。由图可见,随着反应时间从5 min 延长至15 min,MDPC的转化率变化不明显,但MDI的选择性先增加后减少;至12 min 时达最大,为64.4%。反应时间的延长有利于MPI继续分解生成MDI,因此MDI选择性增加。由于MDI分子中的异氰酸根($-\text{NCO}$)是热敏性基团,因此,继续延长反应时间处于高温环境中的MDI会发生聚合反应,使其选择性下降。可见,反应时间宜为12 min。

3.4.4. 催化剂用量的影响

图12为催化剂用量对热分解反应的影响。由图可见,随着催化剂用量的增加,MDPC转化率和MDI选择性逐渐增加,当催化剂用量为原料总重的0.06%时,MDPC转化率和MDI选择性均达最大,分别为99.8%和86.2%,继续增加催化剂用量,MDI选择性开始下降,而MDPC转

化率趋于稳定。这可能主要是由于过量的催化剂加速热分解,同时也促进了MDI聚合反应的发生^[1]。因此,合适的催化剂用量为原料总量的0.06%。

4. 结论

通过对不同金属氧化物催化性能的比较,发现具有酸碱两性的金属氧化物对氨基甲酸酯热分解反应有较

好的催化性能。其中以采用水解法制备的纳米Cu₂O的催化性能最好,MDPC的转化率达到99.8%,MDI的选择性为86.2%。虽然目前无溶剂条件下MDI的选择性比有溶剂条件下的稍低,但采用无溶剂条件催化MDPC热分解制备MDI,避免使用大量高沸点溶剂,产物浓度高,简化工艺,降低能耗,利于MDI的纯化,为非光气法合成MDI提供了一条新的途径。

第十三届全国均相催化学术讨论会第一轮通知

时间: 2013年9月25~27日 地点: 江苏省苏州市

承办单位: 中国科学院兰州化学物理研究所 苏州大学材料与化学化工学部

一、会议介绍

由中国化学会催化委员会均相催化专业委员会主办,中国科学院兰州化学物理研究所和苏州大学材料与化学化工学部联合承办的第十三届全国均相催化学术讨论会定于2013年9月25~27日在美丽的城市苏州举行。本届会议是全国均相催化和相关领域专家学者的一次聚会,将全面展示两年来我国在这些领域取得的研究成果,交流和讨论均相催化发展的新趋势和所面临的机遇与挑战,以推动我国均相催化领域的研究和相关产业向更高的目标迈进。

会议拟邀请著名专家学者与会,会议组委会热忱欢迎从事均相催化科学研究与技术开发的专家、同行及在读研究生积极投稿,并莅临本届盛会。会议期间将颁发第二届“中国均相催化青年奖”和第十三届全国均相催化学术讨论会“优秀墙报奖”。

二、会议主办单位: 均相催化专业委员会

主 任: 夏春谷

副主任: 丁奎岭 李贤均

秘书长: 孙伟

委 员: 包明 陈静 范青华 龚流柱 郭灿城 贺德华 胡信全 华瑞茂 江焕峰 金国新 雷爱文 李光兴 梁永民 陆维敏 施章杰 王公应 王向宇 吴鹏 吴静 徐杰 夏清华 游书力 袁友珠 周永贵

三、征文范围

1. 均相催化剂的设计、合成和表征; 2. 均相酸碱催化反应; 3. 不对称催化反应; 4. 小分子催化; 5. 生物催化与仿生催化反应; 6. 胶束和胶体催化以及微乳催化反应; 7. 纳米催化剂的制备、表征和催化反应; 8. 光、电催化反应; 9. 生物质催化转化;

10. 均相催化剂的多相化; 11. 均相催化的工业应用; 12. 与均相催化相关的反应机理、理论和计算化学等。

四、投稿要求及日期

关于详细论文摘要的格式要求请登录会议网站查看: <http://13nchc.csp.escience.cn/dct/pag>。论文经评审录用后发出录用通知。被录用的论文一般不再退回修改,作者在寄论文摘要时应做好一次性定稿准备,文责自负。论文录用与否,一概不退,请作者自留底稿。征文截止日期为2013年6月30日,请登陆会议网站进行在线投稿或通过E-mail (13nchc@licp.cas.cn) 发送征文电子版。

五、会议承办单位及联系人

中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室

地址: 甘肃省兰州市天水中路18号 邮编: 730000

联系人: 李福伟 牛建中

电话: (0931)4968528; (0931)4968126

传真: (0931)4968129

E-mail: fuweili@licp.cas.cn; njz@licp.cas.cn

苏州大学材料与化学化工学部

地址: 江苏省苏州市工业园区仁爱路199号907栋

邮编: 215123

联系人: 王兴旺

电话: (0512)65880378

E-mail: wangxw@suda.edu.cn

(第十三届全国均相催化学术讨论会组委会)