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Article

Solvent-free thermal decomposition of methylenediphenyl di(phenylcarbamate) catalyzed by nano-Cu_2O

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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_2O catalyst. The preparation of nano-Cu_2O 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_2O. The results show that Cu_2O 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.

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_2O catalyst under solvent-free conditions. The preparation of the nano-Cu_2O 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_2O 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 $AgNO_3$ 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_2O-H.

2.1.2. Preparation of Cu_2O by reduction method [18–21]

CTAB (0.5 g) was dissolved in 100 ml of $Cu(NO_3)_2$ (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 Cu_2O-R.

2.1.3. Preparation of Cu_2O 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_2O-C.

2.2. Catalyst characterization

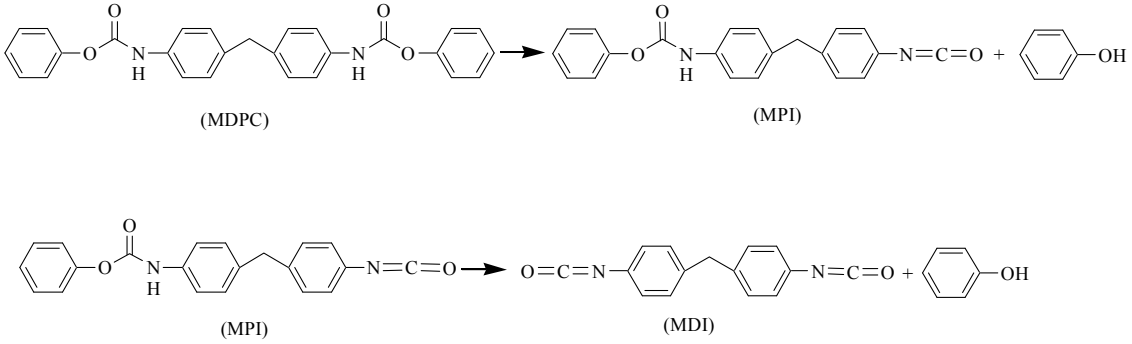
The catalyst was characterized using X-ray diffraction (XRD, X'Pert Pro MPD, Philips), transmission electron microscopy (TEM, JEM-100CX, JEOL) at 80 kV, and scanning electron microscopy (SEM, INSPECT-F, FEI) at 20 kV. The XRD experimental conditions were as follows: 40 kV tube voltage, tube current 35 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: 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.