

Melem based multifunctional catalyst for chemical fixation of carbon dioxide into cyclic carbonate

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ABSTRACT

In the present work, melem based catalysts with various functional groups were developed by the modification of melem oligomers and tested for the chemical fixation of CO₂ into cyclic carbonates. The characterization of these catalysts, by means of SEM, BET, XRD, IR, TG and XPS, verified the functional groups are successfully incorporated into the melem oligomers structure. Activity test demonstrated that melem oligomers grafted with both hydroxyl and quaternary ammonium groups (MOSB) presented the best catalytic performance. A propylene oxide conversion of 97.4% and propylene carbonate selectivity of 97.8% were obtained under the optimal reaction conditions. The simultaneous existence of edge defects, hydroxyl groups and quaternary ammonium groups in the structure of the catalyst are responsible for the high performance of MOSB. These three groups synergistically catalyzed the chemical fixation of CO₂ to proceed with high efficiency. Moreover, moderate yield could still be obtained after five cycles. A possible reaction mechanism was proposed for the cycloaddition of CO₂ with epoxides to form cyclic carbonates.

1. Instruction

The ever increasing industrial waste gas carbon dioxide (CO₂) in atmosphere, due to the burning of fossil fuels and biofuels, can also serve as an abundant, cheap, nontoxic, and renewable carbon resource for various industrial products [1–3]. Therefore, conversion of CO₂ into value added fine chemicals has become a hot topic in the past few years and drawn much research attention [4–6]. Among all the conversions of CO₂, the cycloaddition of CO₂ with epoxides to afford cyclic carbonates is one of the most promising reactions for its high atom economy. Besides, cyclic carbonates are widely used as polar aprotic solvents, fuel additives, electrolytes for lithium batteries, and intermediates for medicines and materials [7–9].

Over the past few decades, a wide variety of catalysts have been developed to catalyze the cycloaddition of CO₂ with epoxides to prepare cyclic carbonates. According to literature, metal related catalysts, including metal oxides [10], metal-salen complexes [11,12], alkali metal halides [13], were active for this reaction. Later, ammonium salts [14,15], phosphonium salts [16], were developed for the cycloaddition reaction. Besides, organic base [17], and ionic liquids [18–20] were also reported to exhibit high performance for CO₂ fixation. Recently, ZIF materials were found to be active for this reaction [21]. Besides, when carbocation and polyol were applied to the fixation of CO₂, the reaction can be performed at mild conditions (50 °C, 5 MPa) [22].

Moreover, when Ca²⁺-crown ether complex was used as the catalyst, the cycloaddition reaction could be carried out at room temperature (23 °C, 1 atm) [23].

Graphitic carbon nitride (g-C₃N₄) materials as metal-free catalysts have received increasing attentions due to their higher thermal stability and easily adjustable functional groups in the structure [24–26]. Over the past few years, carbon nitride as catalysts have been utilized to catalyze the cycloaddition of CO₂ with epoxides. Ansari et al. was the first to apply carbon nitride as catalyst in the catalytic conversion of CO₂ [27]. Then, Su et al. reported their work of using urea-derived g-C₃N₄ as catalyst for CO₂ conversion [28]. The incompletely condensed nitrogen atoms, also known as edge defects, in g-C₃N₄ of low polymerization degree were suggested to be active center for CO₂ activation [28,29]. Hydroxyl groups were presumed to facilitate the reaction through hydrogen bonds. Therefore, more active amino- and hydroxyl-rich g-C₃N₄ was developed to catalyze the reaction [30]. However, due to the limitation of the material itself, new active groups need to be introduced to further improve the catalytic performance of carbon nitride. In this regard, phosphorous-modified g-C₃N₄ [31], boron-doped carbon nitrides [32], mesoporous carbon nitride grafted with n-bromobutane [33], and bifunctional metallophthalocyanine-carbon nitride hybrid [34] were developed to catalyze CO₂ transformation.

Although many carbon nitride materials have been developed for CO₂ chemical fixation, the catalytic performance of these catalysts is

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moderate. The development of carbon nitride catalysts with better catalytic activity is still of significance. In the previous work, we found g-C₃N₄ exhibits superior activity towards epichlorohydrin in cycloaddition with CO₂, and proposed a possible reaction mechanism [35]. However, g-C₃N₄ itself showed poor activity towards other epoxides. Because the combination of the groups useful for CO₂ capturing/activation allows, in principle, for synergistic effects. For example the combination of phosphonium salts and hydroxyl groups showed high activity for the chemical fixation of CO₂ [36]. Besides, the immobilized amine (imidazole) and quaternary ammonium chlorides bound to multi-walled carbon nanotubes were also reported to be active for this kind of reaction [37,38]. Thus, in this work, we tried to develop a new C/N based catalyst, incorporating amino, hydroxyl and quaternary ammonium groups simultaneously into the C/N catalysts structure, which is active for a wide range of epoxides. As is well known to all, carbon nitride with low polycondensation degree possesses more edge defects (–NH, –NH₂). Besides, carbon nitride can be prepared from melamine at elevated temperature. However, intermediates, such as melem, melam, or melem oligomers, for carbon nitride may be formed when melamine was treated at lower temperature, as illustrated in Scheme 1. [39–41] Compared with carbon nitride, melem oligomers possesses more edge defects which is active for CO₂ activation. Besides, the amino groups of melem oligomers are more reactive compared with the carbon nitride edge defects, and can be easily modified. In this work, hydroxyl and quaternary ammonium groups are successfully introduced into the melem oligomers structure through the modification of the incompletely condensed melamine. The new catalyst exhibits good catalytic activity towards the cycloaddition of CO₂ with epoxides to form cyclic carbonate. The co-existence of multi active groups is the main reason for the high activity of the catalyst.

2. Experimental section

2.1. Raw materials

All chemicals were used as received without further purification. Melamine (99%), 3-aminopropyltriethoxysilane (APTES) (99%), and 1-bromobutane (AR) were obtained from Aladdin Industrial Inc. (Shanghai, China). Formaldehyde (37% aqueous solution) was purchased from Xilong Chemical Co., Ltd. Toluene, Propylene oxide (99.5%) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Propylene carbonate (99%) and 2-butoxy ethanol (99%) were purchased from Heowns Biochem Technologies. Carbon

dioxide (CO₂ > 99.9%) was supplied by Nanjing Special Gas Factory Co., Ltd.

2.2. Catalyst preparation

2.2.1. Preparation of melem oligomers

The melem oligomers were prepared by treatment of melamine at high temperature in N₂ atmosphere. In a typical synthetic procedure, melamine (10.17 g) was placed into a quartz boat and heated in a tube furnace at 450 °C for 4 h with a heating rate of 2.5 °C min^{−1} in N₂ atmosphere. The obtained solid product (4.86 g) was grounded into fine powder for further use. The obtained melem oligomers were marked as CN-450.

2.2.2. Preparation of hydroxyl group functionalized CN-450

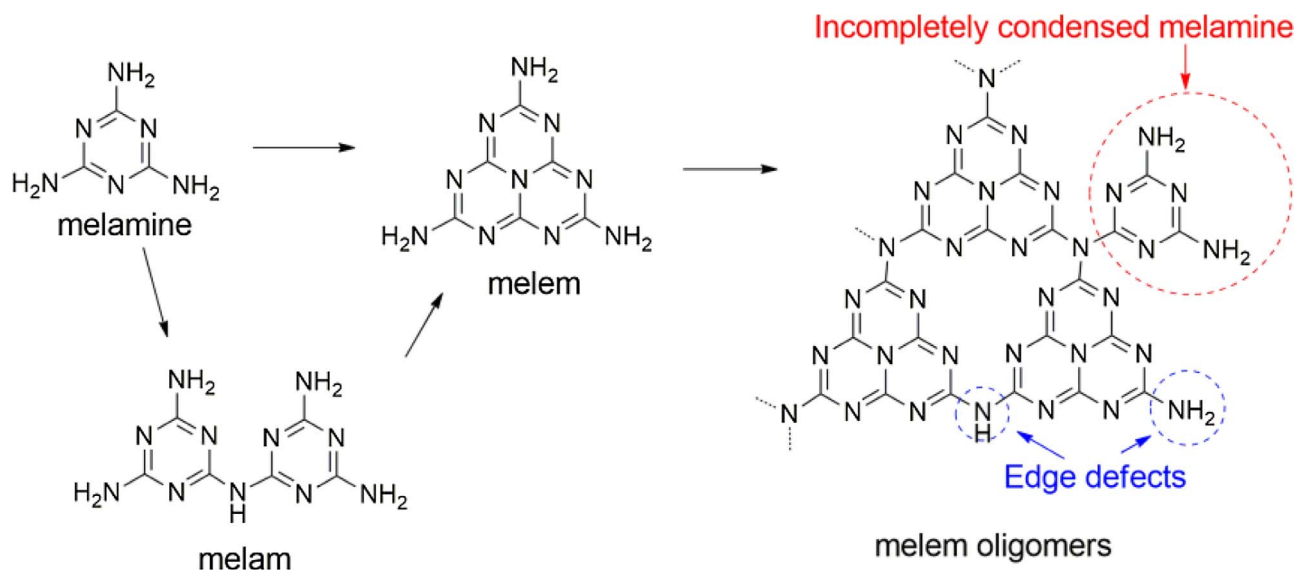
The hydroxyl group functionalized CN-450 was prepared according to literature with some modifications [42]. Typically, CN-450 (4.01 g) and 37% aqueous formaldehyde (0.26 mol, 19.52 g) with a pH value of about 7.5 were placed into a 100 mL three neck flask. The resulting mixture was stirred and heated on water bath at 70 °C for 2 h, and then the reaction mixture was cooled to room temperature. The resulting solid was filtered, washed with ethanol (2 × 5 mL), and dried at 80 °C. And 3.27 g of slight yellowish product was obtained. The catalyst was denoted as MO.

2.2.3. Preparation of MOS

MOS was synthesized following the published method [43]. MO (1.01 g) was dispersed in 20 mL toluene and subject to ultrasonication for 2 h. After the addition of APTES (1.0 g), the reaction system was heated to 110 °C and refluxed for 24 h under N₂ atmosphere. After cooling to room temperature, the solid was separated by filtration, followed by washing with toluene for three times, ethanol for three times. The obtained yellowish solid was dried at 60 °C for 12 h. About 1.11 g product was obtained. There is only slight increase in the weight of product after modification, indicating only a few groups are modified.

2.2.4. Preparation of MOSB

The catalyst MOSB was prepared according to the reported literature [44]. In a typical procedure, MOS (1.01 g) and 1-bromobutane (1.02 g) were dispersed in 20 mL toluene. The resulting mixture was heated to reflux and kept at this temperature for 24 h under N₂ atmosphere. The solid was obtained by filtration and washed with H₂O and



Scheme 1. Possible products from melamine annealed at lower temperature.

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