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Short Communication

The synthesis of organic carbonates over nanocrystalline CaO prepared via microemulsion technique

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ABSTRACT

A new method, combining microemulsion, ultrasonication and ultracentrifugation with the addition of polyethylene glycol was developed to synthesize nanocrystalline CaCO₃. Calcination of the CaCO₃ resulted in nanocrystalline CaO. Physical characterization by XRD indicated that the material had high purity of nanocrystalline CaCO₃ and CaO particles respectively. TEM images showed that the material was composed of non-agglomerated, single nanoparticles with a size range of 10–30 nm. The CaO was used as a catalyst in the solvent free direct condensation of diethyl carbonate with benzyl alcohol. The catalytic reaction resulted in 99.7% conversion and 100% selectivity for benzyl ethyl carbonate in 3 h.

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1. Introduction

Organic carbonates have found numerous applications as important intermediates for the synthesis of fine chemicals [1,2], pharmaceuticals [3], plasticizers, synthetic lubricants [4], monomers for organic glasses and solvents [5,6]. These are also used as linkers and tagging moieties [7]. However, most of the catalytic systems for the synthesis of carbonates require the toxic and hazardous phosgene as reagent [1,2]. The use of phosgene may cause safety and environmental problems. In order to address this problem, dimethyl carbonate (DMC) or diethyl carbonate (DEC) has attracted considerable attention as a substitute for phosgene [8]. The preparation of organic carbonates has been reviewed by Shaik and Sivaram [9]. Several authors have reported the solvent free preparation of alkyl carbonates using supported solid catalysts [10–12].

To the best of our knowledge, there are only a few reports on the direct condensation of an alcohol and diethyl carbonate using various catalysts such as Y- and X-faujasties [13] and several study on heterogeneous basic catalysts such as nanocrystalline magnesium oxide [12], KF/ α -Al₂O₃, MCM-41-TBD, Mg-La metal oxide [14]. These afforded unsymmetrical organic carbonates from the reaction of DEC with various alcohols or amines at 125 °C, but these reactions are time consuming. Various metal salts, organometallics, and hafnium (IV) salts were used as catalyst for the direct condensation of carboxylic acid with alcohols [15]. Considering the various studies related to the

direct condensation, we herein report an efficient nanocrystalline CaO for the synthesis of organic carbonate in yield.

Microemulsion technique has found its way into a wide range of applications, such as in catalysis, in high-performance ceramic materials, in microelectronic devices, in high-density magnetic recording and in drug delivery [16]. Currently, controlled morphology studies in nanocrystalline materials have received much attention as size and shape can significantly influence various properties [17].

Metal oxide has been used as catalysts for many organic reactions [18,19]. Calcium oxide (CaO) is promising as a solid base catalyst under mild conditions. Solid base catalysts has great potential leading to processes featuring fast reaction rates [20]. Besides the O^{2-} sites, hydroxyl groups also act as basic sites and have been shown to promote basic reactions [21,22]. CaO find applications in a wide range of materials such as insulators to semiconductors and conducting materials, catalysts, electronics, ferroelectrics, cosmetics and superconductor materials [20,23]. Hitherto, CaO had been utilized in various catalytic applications such as transesterification [20], aldol condensation [21], dimerization of ethanol [24], cyanoethylation of alcohols [25], synthesis of DMC [26], reduction of benzaldehyde [27], adsorption of CO₂ and SO₂[28], and in oxidative coupling of methane [29].

In this work, we describe an improved microemulsion technique to synthesize nanocrystalline CaO particles redispersed by ultrasonication to form homogeneous and non-agglomerated nanocrystalline CaO. To the best of our knowledge, this is the first report of the synthesis of nanocrystalline CaO by reverse microemulsion technique with novel hierarchical structure and used as solid base catalysts for the direct condensation of benzyl alcohol with DEC (Scheme 1).

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2. Experimental

2.1. Catalyst preparation

CaCO₃ was synthesized by reverse microemulsion using cetyltrimethylammonium bromide (CTAB) as the templating agent. In a typical procedure, a mixture of toluene (200 mL) and CaCl₂ solution (0.2 M, 200 mL) was taken in a 500 mL round bottom flask and sonicated for 0.5 h at ambient temperature. The CTAB solution (27 g in 110 mL distilled water) was added into the solution and sonicated to form a turbid mixture and refluxed at 80 °C for 1.5 h. Then, 100 mL (0.54 M) of sodium bicarbonate solution was added dropwise. After 30 min of sonication, 80 mL of polyethylene glycol 200 (PEG) was added into this hot suspension. The system was refluxed at 80 °C for 5 h. The colloidal suspension was aged and collected by ultracentrifugation at 8000 rpm for 10 min followed by washing with 200 mL of distilled water. 200 mL of absolute ethanol and 200 mL of acetone to remove traces of surfactant. The collected sample was sonicated for 10 min and dried at 60 °C for overnight. Finally, CaO was obtained after calcination at 900 °C for 1.5 h.

2.2. Catalyst characterization

The samples were characterized by powder X-ray diffractometry (Siemens Diffractometer D5000, Kristalloflex), transmission electron microscopy (Philips CM12), scanning electron microscopy (Leica Cambridge S360), BET surface area analysis (Micromeritics Instrument Corporation Model ASAP 2000, Norcross). The product was analyzed by GC (PerkinElmer Clarus 500 equipped with a capillary wax column and FID detector), GC-MS (PerkinElmer Clarus 600 equipped with same column), NMR spectroscopy (Bruker 300 MHz) and FT-IR spectroscopy (PerkinElmer System 2000, KBr pellet method).

2.3. Catalytic studies

For activity studies of direct condensation of benzyl alcohol with DEC (Scheme 1), DEC (66 mmol, 8 mL), benzyl alcohol (4 mmol) (the molar ratio of DEC/benzyl alcohol = 16.5:1) and catalyst (0.25 g) were charged into a round bottom flask, equipped with a magnetic stirrer and a reflux condenser. The mixture was stirred at 140 °C until completion of the reaction. Aliquots of samples were withdrawn for analysis by GC and GC-MS. 10 μ L of dodecane was added as internal standard before the analysis.

2.3.1. Product analysis by GC and GC-MS

Reaction mixture obtained from the catalytic reaction was analyzed using GC (PerkinElmer Clarus 500 with FID detector and a 30 m capillary wax column) and GC-MS (PerkinElmer Clarus 600 with the same column). The temperature programs used for the analysis were the following: initial temperature:60 °C; initial time: 0 min; Ramp 1: 10 °C/min; Temp 2: 90 °C; Ramp 2: 20 °C/min; final temperature: 180 °C; hold: 2 min; injector port temperature: 250 °C; detector temperature: 250 °C. GC analysis was used to determine the conversion percentage of the reactant and the selectivity percentages of the product. GC-MS was used to identify the organic product.



Scheme 1. The direct condensation of DEC and benzyl alcohol using nanocrystalline CaO.

2.3.2. Purifications

After completion of the reaction, the combined organic layers were dried over Na_2SO_4 and the excess reactant was removed under reduced pressure [12]. The crude products were purified by column chromatography and monitored by TLC, GC-MS, NMR and FT-IR.

4. Results and discussion

Powder XRD pattern of the as-prepared CaCO₃ powder and CaO obtained after calcination at 900 °C are shown in Fig. 1a and Fig. 1b. Intensities of CaCO₃ peaks and the cell parameter obtained clearly confirm that the phases belong to calcite and match well with the phase reported in the powder diffraction database (JCPDS No. 71-3699). Fig. 1b shows the main characteristic peaks of (111), (200), (220), (311), (222), (400) and (331), corresponding to 2-Theta values of 32.2°, 37.35°, 53.85°, 64.15° 67.35°, 79.65° and 88.55° respectively of CaO. These diffractions correspond to the face-centered cubic (space group: Fm-3m (225), *a* = 4.81) structure and very close to the reported pattern as given in JCPDS No. 43-1001. XRD pattern of CaCO₃ and CaO are very sharp, intense and no impurity peaks were observed, indicating the complete formation of crystalline phase. The BET result showed surface area of CaO synthesized was 13.94 m² g⁻¹ and pore volume was found to be 0.02 cc g⁻¹.

The TEM and SEM images of CaO nanoparticles are shown in Fig. 2. The micrograph (Fig. 2a) shows CaO to be composed of elementary particles with uniform particle-size distribution with low agglomeration of primary particles. Inset (Fig. 2a) shows the particles size distribution



Fig. 1. (a) The XRD pattern of the synthesized $CaCO_3$ matching (JCPDS No. 01-071-3699) and (b) the synthesized CaO matching (JCPDS No. 00-043-1001).



Fig. 2. The TEM and SEM images if CaO nanoparticle. (a) The TEM image of CaO with ultrasonication and added PEG. Inset: nanoparticles size distribution, (b) The TEM image of single particle CaO with ultrasonication and added PEG, Inset: nanoparticles size distribution, (d) TEM image of CaO with ultrasonication and without added PEG, Inset: nanoparticles size distribution, (d) TEM image of CaO with ultrasonication and without added PEG, and corresponding SEM images of CaO with ultrasonication and added PEG of (e).

of 10–30 nm in diameter. The micrograph of CaO under ultrasonication with added PEG (Fig. 2b) shows that the particles are spherical. In contrast, Fig. 2c shows the micrograph of CaO prepared under ultrasonication without PEG 200, reveals pronounced agglomeration of the particles. Inset (Fig. 2c) shows the particles size distribution of 40–90 nm which is larger than the CaO prepared with the addition of PEG. Interestingly, the addition of PEG stabilizes the colloidal particles and thus suppresses the formation of aggregates. The micrograph of CaO without ultrasonication (Fig. 2d) shows much agglomeration and the diameter of the particles is indistinguishable. It should be noted that the effect of ultrasonication results in homogeneous and non-agglomerated materials. Fig. 2e presents a typical SEM image of CaO powder obtained by microemulsion under ultrasonication with added PEG showing monodispersed irregular spheres.

The reaction of DEC and benzyl alcohol over CaO resulted in a conversion of 99.7% in 3 h. The CaO obtained from commercial CaCO₃ only gave 33.5% in 3 h under the same reaction condition. The conversion was based on benzyl alcohol with dodecane as the internal standard. These results are much better than that reported by Kantam et al. [12] (97% in 4 h) and Veldurthy and Figueras [30] (98% in 6 h).

The turn over frequency (TOF) for the nano CaO synthesized in this work was 1.07×10^5 s⁻¹, while the TOF for the commercially derived CaO was found to be 3.61×10^4 s⁻¹. There is a threefold increase in TOF for the nano CaO. The benzyl alcohol and DEC undergo a nucleophilic and an electrophilic activation respectively [13]. However, the reaction could take place via a four-membered ring transition state as shown in Fig. 3. The Lewis base site (O²⁻) activate benzyl alcohol by hydrogen bonding to form an alcoholate-like nucleophile species that can engage the DEC [12]. Then, the addition and elimination mechanism takes place with the help of the carbonyl group [31]. All four atoms involved in the transition state are aligned on the same plane which reduces steric hindrance. This stabilizes the transition state and leads to product formation. The analytical data of the product using ¹H NMR (Sup. 1.), ¹³C NMR (Sup. 2.), GC-MS (Sup. 3.) and FT-IR (Sup. 4.) are shown in the supplement.

Conclusion

Nanocrystalline CaO was successfully synthesized through a new method combining microemulsion, ultrasonication, ultracentrifugation



Catalyst

Fig. 3. The plausible mechanism for the formation of benzyl ethyl carbonate over CaO catalyst. The reaction could take place via the four membered ring transition state.

and PEG. The nanocrystalline CaO showed high catalytic activity for the direct condensation of benzyl alcohol with DEC to give exclusively benzyl ethyl carbonate.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.06.023.

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