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Zinc grafted to magnetic nanostarch for cyclic carbonate synthesis from propargylic alcohols and CO_2 at room temperature

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ABSTRACT

A novel, cost effective and magnetically separable nanocrystalline starch zinc catalyst was developed for the synthesis of α-alkylidene cyclic carbonates from propargylic alcohols and CO_2 at room temperature under solvent-free conditions. The synthesized nanocomposite along with triethylamine played excellent synergistic roles in activating both CO_2 and propargylic alcohols and afforded desired products in moderate to excellent yields. The salient features such as the use of renewable, inexpensive support matrix, facile separation of the catalyst by an external magnet, mild reaction conditions, excellent product yields and heterogeneous nature of the catalyst without any detectable leaching make the developed methodology promising for the synthesis of α-alkylidene cyclic carbonates.

1. Introduction

Carbon dioxide is a green house gas (GHG) and the concentration of CO_2 in the atmosphere has increased significantly in the last few decades [1]. Owing to the increasing concerns about global warming, continuous efforts are being made towards reducing the emissions of carbon dioxide in the atmosphere [2]. The chemical fixation and transformation of carbon dioxide (CO_2) to high-value chemicals is an attractive and important approach from both environmental and economical viewpoints as CO_2 is not only a greenhouse gas but also can be used as a cheap, non-toxic, renewable and easily available C_1 resource [3–7]. Significant efforts have been devoted to developing methods and technologies to transform CO_2 into various high-value chemicals, such as formic acid [8], alcohol [9,10], cyclic carbonates [11,12], oxazolidinone [13–17] and others. However, harsh and severe reaction conditions are often required due to its high thermodynamic stability and kinetic inertness [18]. Therefore, the development of an efficient catalyst system for CO_2 utilization under mild conditions, especially at room temperature, is highly desired.

Among the several known CO_2 conversions, synthesis of α-alkylidene cyclic carbonates resulting from the reaction of CO_2 with propargylic alcohols is an important transformation due to their wide spread applicability in organic synthesis [19]. For example, they can be utilized as building blocks in the formation of α-hydroxy ketones [20] and 5-methyleneoxazolidin- 2-one derivatives [21]. Numerous transition metal based including Ru, [22,23], Co [24], Fe [25], Cu [24–29], Pd [30], Ag [31–34], tungstate [35] and metal-free catalytic systems such as phosphine [36] bicyclic guanidines [37] crown ethers [38] *N*-heterocyclic carbenes [39] and alkoxide-functionalized imidazolium betaines [40,41] have been reported for the synthesis of these heterocyclic carbonates. Recently silver catalysts such as AgOAc/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [42] Ag_2WO_4/Ph_3P [43] and $[(PPh_3)_2Ag]_2CO_3$ [44] have been acknowledged as potential catalysts for this transformation. However, harsh and severe reaction conditions such as higher temperature/ pressure, inefficient recovery using traditional filtration, toxic and expensive metals are the prime limitations associated with most of the reported systems. Therefore, the exploration of cost effective, easily recoverable and the safer catalytic system is highly desired for this important transformation.

In the recent years, utilization of biopolymers as a support matrix for immobilizing metal salts/ complexes to transform them into heterogeneous forms is gaining tremendous importance [45]. There are several functional groups in the structure of these biopolymers being able to provide remarkable affinities with metal as well as can stimulate the reactivity and selectivity of the catalyst [46,47]. Among the different biopolymers known, starch materials, more particularly nanocrystalline starch owing to its higher abundance, non-toxicity, higher surface area, biocompatibility and low cost has increasingly being used as support for developing heterogeneous catalytic materials [48–51]. Furthermore, functionalization of the immobilized catalyst with magnetic nanoparticles not only facilitates the recovery of the catalyst by an external magnet but also the developed magnetic nanostructured catalyst can serve as a more active sustainable catalyst for chemical synthesis.

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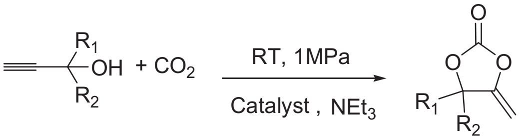

Scheme 1. Synthesis of cyclic carbonates from propargylic alcohols and CO_2.

Herein, we report for the first time a simple, efficient and reusable Zn grafted to magnetic nanostarch for the synthesis of α-alkylidene cyclic carbonates from the reaction of carbon dioxide and propargylic alcohols at room temperature in the presence of triethylamine as a base (Scheme 1).

2. Experimental

2.1. Materials

Corn starch (CS), ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), ammonium hydroxide (NH_4OH, 25% of ammonia), zinc acetate dihydrate ($Zn(O_2CCH_3)_2$ (≥99.99%), zinc nitrate ($Zn(NO_3)_2$) (≥98%), zinc carbonate ($ZnCO_3$) (≥58%), zinc bromide ($ZnBr_2$) (≥98%), zinc chloride ($ZnCl_2$), sodium sulfate (Na_2SO_4) and triethylamine (Et_3N) (≥99.5%) were purchased from Sigma Aldrich. All were of analytical grade and used without further purification. All the solvents such as acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (C_2H_5OH) and dichloromethane (CH_2Cl_2) were of analytical grade and used as received. Hydrogen peroxide (H_2O_2) (35%) and ethanol (C_2H_5OH) used were of analytical grade and procured from Alfa Aesar.

2.2. Techniques used

The FTIR spectra were recorded on a Nicolet 8700 FTIR spectrometer, with beam slitter XT-KBr and using a DTGS TEC detector in the region of 4000–400 cm^{-1}. The running conditions were as follows: 4 cm^{-1} spectral resolution, 36 kHz scan speed. The samples were prepared using KBr pellets. Phase structure and crystalline state of the material was determined on Bruker D8 Advance diffractometer at 40 kV and 40 mA with Cu K_α radiation ($\lambda = 0.15418$ nm). For XRD, samples were prepared on a glass slide by adding well-dispersed catalyst slot and drying properly. Scanning electron microscopy (SEM) was done using FESEM, Quanta 200 F (Netherland) at a voltage of 10–30 kV using tungsten filament doped with lanthanum hexaboride(LaB6) as an X-ray source fitted with an ETD (Everhart Thornley Detector). The sample for SEM was mounted on an adhesive coated carbon paper followed by gold coating. Inner fine structure of samples was determined by high-resolution transmission electron microscopy using FEI-Tecnai G2 S-Twin TEM instrument operated at 200 kV. The samples for TEM analysis were made by depositing very dilute aqueous suspension of samples on carbon coated TEM grid. Nitrogen adsorption desorption isotherm was used for calculating surface properties like Brunauer–Emmet–Teller (SBET) surface area, Barret–Joiner–Halenda (BJH) porosity (rp), pore volume (VP)of samples at 77 K by using VP; Micromeritics ASAP2010. Thermo gravimetric analyses (TGA) was obtained on Perkin Elmer TG/DTA diamond under N_2 atmosphere within temperature range 50–900 °C with the scan of 5 °C per min.

^1H NMR spectra were recorded on Bruker Avance III 500 MHz NMR spectrometer operating at 500.13 and 125.7 MHz resonance frequencies for ^1H and ^{13}C respectively, using 5 mm broad band probe. Approximately 10 mL (w/v %) of the purified samples was prepared in $CDCl_3$ (Merck, 99.8% containing 0.03 v% for ^1H TMS) for acquiring NMR spectra. ^1H spectra were recorded at 500 MHz using 13.40 μs 90° pulse, 7 kHz spectral width, 32 transients, 4.7 s acquition time and 5 s relaxation delay for quantitative analysis.^{13}C spectra were acquired in inverse gated decoupling mode using WALTZ-16 with 9.90 μs 90° ^{13}C pulse, 37 kHz spectral window, 2 k transients, 0.86 s acquition time, 5 s relaxation time, 64k points.

2.3. Preparation of expanded corn starch (ECS)

Expanded corn starch (ECS) was prepared by following the literature published elsewhere [52]. In a typical procedure, 8 g corn starch (CS) was added into distilled water (150 mL) and reflux the mixture for 1 h at 90 °C under constant stirring for complete gelatinization of CS. Then, ethanol (150 mL) was added drop wise to the above-gelatinized mixture, and the resulting product was cooled to room temperature. Again, 150 mL of ethanol was added drop wise for about 50 min at constant stirring. The finally obtained solid (ECS) was separated by centrifugation and thoroughly washed with ethanol, dried under vacuum for 12 h.

2.4. Synthesis of magnetic nanocrystalline starch (Fe_3O_4/ ECS)

Magnetically separable nanocrystalline starch was prepared by a slightly modified method according to the reported literature. Expanded corn starch (3 g dissolved in 250 mL deionized water), $FeCl_2{\cdot}4H_2O$ (3.9 g dissolved in 250 mL of deionized water) and $FeCl_3{\cdot}6H_2O$ (3.9 g dissolved in 250 mL of deionized water) were mixed and stirred vigorously at room temperature. A solution of sodium hydroxide (2 mol/L NaOH) was added dropwise to the resulting solution, and the mixture was kept under stirring at 50 °C for 12–14 h to adjust the pH of the solution to 11. The black colored solid thus obtained was separated by an external magnet and washed several times with deionized water until pH 7 was obtained. The as-prepared Fe_3O_4/ECS was dried in vacuum at 60 °C for 12 h.

2.5. Synthesis of Zn grafted magnetic nanostarch (Zn/Fe_3O_4/ECS)

Magnetic nanocrystalline starch (2 g) was added to 100 mL of deionized water to make a homogeneous dispersion under ultrasonication. In a subsequent step, an aqueous solution zinc iodide (20 wt %, 10 mL) was added to the resulting dispersion under constant stirring at room temperature for 24 h. The resulting solid was separated from the solution by using an external magnet and washed successively with deionized water, ethanol thoroughly to get the desired Zn grafted magnetic nanocrystalline starch (Zn/Fe_3O_4/ECS).

2.6. General experimental procedure for synthesis of α-alkylidene carbonates from propargylic alcohols and CO_2

The experiments were performed in a high-pressure stainless steel 25 cc autoclave equipped with magnetic stirrer. At first, the autoclave was purged with CO_2 for 10 min to evacuate air. After that triethylamine (1.5 mmol), propargylic alcohol (1.5 mmol) and catalyst (200 mg) were loaded. The pressure of CO_2 was kept the constant at 1.0 MPa and the reaction mixture was stirred for 12 h at room temperature. After completion of the reaction, the vessel was cooled down in an ice bath and the pressure was released slowly to prevent the loss of reactant and product along with CO_2. The resulting mixture was diluted with dichloromethane and transferred to a beaker. The catalyst was recovered by an external magnet and the recovered catalyst was washed with water, dried for subsequent runs. The organic layer was washed with water and then dried over Na_2SO_4 and filtered. The solvent was removed under vacuum to afford the product.

3. Results and discussions

3.1. Synthesis and characterization of the catalyst

Nanocrystalline starch has plenty of –OH groups on the surface and higher surface area were prepared via gelatinization of amorphous corn