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Chitosan grafted polymer matrix/$ZnCl_2$/1,8-diazabicycloundec-7-ene catalytic system for efficient catalytic fixation of CO_2 into valuable fuel additives

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HIGHLIGHTS

- Dimethyl carbonates synthesis from CO_2 and methanol in mild reaction conditions.
- Novel chitosan based matrix/$ZnCl_2$/DBU catalyst system were used and characterized.
- Reaction mechanism was proposed and CO_2 absorption studied.
- Catalyst system shows excellent catalytic activity for DMC production.

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ABSTRACT

The chitosan grafted polymer matrix/$ZnCl_2$/1,8-diazabicycloundec-7-ene (DBU) novel catalytic system was developed. It was found out that the microwave assisted technique was efficient for chitosan grafting compared to conventional chemical method. The morphology, thermal stability, functional groups, crystalline nature of grafted polymer matrix were investigated using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and wide angle X-ray diffraction (WAXRD) techniques, respectively. SEM images revealed that the surface of chitosan became rough and cross-linked after grafting with amine derivatives. The prepared sorbent showed good CO_2 absorption capacity i.e. ~0.35 mmol/g-catalyst, due to the presence of amines and hydroxyl CO_2 philic functional groups which shows an obvious positive effect on its CO_2 capture capacity. These properties enable this sorbent to be a promising catalyst for dimethyl carbonate (DMC) synthesis from methanol and CO_2. DBU was used as a super base for methanol activation by abstracting acidic proton and $ZnCl_2$ for the activation of CO_2. Remarkably, the excellent methanol conversion up to ~23% and ~99% DMC selectivity were achieved by Ch-g-PEI/$ZnCl_2$/DBU catalysts system at ambient reaction conditions. Catalytic synthesis of organic carbonates is of significant interest both conceptually and practically because this can produce compounds from CO_2. This synthesis can provide mild alternative approaches to the direct conversion of CO_2 to organic carbonates, an important fuel and building block for organic synthesis.

1. Introduction

The most challenging environmental policy arguably faced by all countries is the control of greenhouse gases (GHG). This has led to a widespread gain of interest for CO_2 emissions control by capturing and storage of CO_2 from fossil-fuel combustion sources. The main advantage of this approach is that fossil fuels can be use in future without contributing significantly to greenhouse warming. CO_2 is the second most contributor (9–26%) among GHG that absorbs and emits harmful infrared radiations from earth's surface which increase the atmospheric temperature that lead to significant effects on ecosystem, biodiversity and everyday life of living organisms [1,2]. It has been demonstrated that atmospheric CO_2 concentration and the GHG effect in global warming are account for environmental effects such as continuous rise of sea water-level, ocean storms and floods [3–5]. From this perspective, CO_2 capture or chemical fixation becomes more and more important from the ecological and economic points of view. Also, the commission on climate change and the global climate change initiative has taken important steps towards this issue by

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considering critical points and suggests an urgent need in the development of methodologies for CO_2 capture and storage (CCS) [6,7]. This would be an advance and essential account for climate change mitigation with eliminating or severely limiting the use of fossil fuels.

Presently, pre-combustion capture, post-combustion capture and oxy-fuel combustion are the dominant processes for CO_2 capture [8]. Among them, the post-combustion capture method is considered as an ideal process in which amine-based CO_2 wet scrubbing is promising method; however, it is associated with efficiency loss and demands high capital and operational costs [9]. From this regards, several research groups all over the world have been paying significant attention towards designing suitable materials such as supported ionic liquids, graphite/graphene based materials, boron nitrides, clay-based sorbents, zirconium phosphates, and metal oxides for effective CO_2 capture/storage [10]. Interestingly, zeolites have been widely reported as a good physical adsorbent for CO_2 capture in patents and journals [11]. Adsorption studies with carbon based compounds, metal organic frameworks (MOFs) and organic salts have also been extensively investigated for CO_2 capture [12–15]. However, alkanol amine is the most promising candidates for decades in industrial CO_2 capture and separation [16,17].

Recently, task specific ionic liquids (TSILs) came forward, in which the cations are modified with attaching amino functionalized moieties having ability to form chemical bonding with CO_2 [18]. This report drew considerable attention and inspired extensive work regarding the replacement of amine group with the easily available, bio-compatible, bio-degradable amino acid anions to achieve rapid, reversible and equimolar CO_2 absorption (i.e. mole of CO_2 capture by per mole of amine). In addition, unlike amino functionalized ILs, some of the ILs showed a decrease in viscosity upon uptake of CO_2 which might be related to the absence of strong hydrogen bonded networks in it. Our goal was to design such a CO_2 sorbent material which possesses large number of amino groups to increase the amount of CO_2 and amine/CO_2 ratio of catalyst. Therefore, we have considered chitosan as a suitable catalytic material which contains very high number of CO_2 philic amine groups.

Once the CO_2 is captured, the next important step should be its secure storage (sequestration). So far a number of approaches are applied such as deep saline reservoirs, depleted oil and gas wells, and storing CO_2 in coal seams are some of the potentially attractive options. On the other hand ocean disposal option is also reported. However, the economic costs of CO_2 storage and its social and political acceptability are not yet clear, particularly with regard to ocean sequestration. Therefore, CO_2 fixation into organic valuables becomes a most promising route to mitigate GHG effect. Because of their favorable distribution in gasoline/H_2O, high oxygen content (53 wt%), excellent octane number, good blending properties, and fast biodegradation, DMC is one of the most promising CO_2 derived product. These has led to an explosion in their use for various applications such as fuel additive, green chemical intermediate to substitute toxic dimethyl sulfate and phosgene in industrial processes such as carbonization and methylation [19–22]. To date, several catalysts like Ni-acetate, ZrO_2, polyphosphoric acid-ZrO_2, ZrO_2-MgO, CeO_2, Ce-ZrO_2, zeolites, ILs, etc. have been investigated for the direct synthesis route of DMC but the issue of DMC yield remains challenging [23–32].

The objectives of the present work are to synthesize a new synthetic CO_2 sorbent from chitosan and amine derivatives using non-conventional microwave assisted method and investigate their catalytic performance for the production of fuel additive such as DMC. Moreover, the use of chitosan grafted material has not been investigated for either CO_2 capture or DMC synthesis.

2. Experimental

2.1. Materials and characterization of chitosan grafted polymer matrix

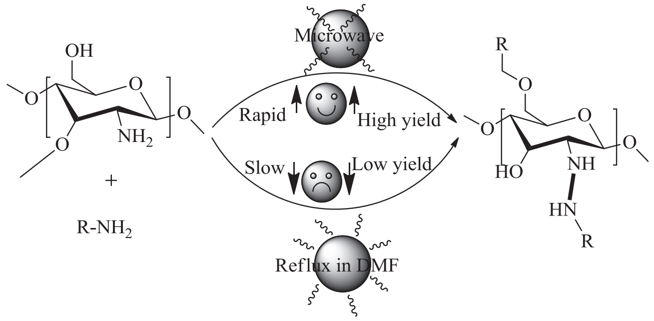
All chemicals were purchased from Sigma Aldrich, USA were used without further purification. A 99.99% pure AR grade CO_2 was purchased from Green Tech. Ltd. (South Korea) and used without further purification.

Fourier Transform Infrared Spectrometer spectra (KBr) of the grafted samples, chitosan and the amine derivatives were recorded on a Varian 2000 spectrophotometer. A wide angle X-ray diffraction analyzed on a Rigaku Miniflex, Rigaku Corporation, Japan. Scanning electron microscopy (SEM) was used to investigate the morphology of the grafted samples with Hitachi, S-3500N. TGA (model SETARAM-92-16-18) was used to check the thermal stability of samples and spectra were collected using Q600 Software (TA Instruments).

2.2. Synthesis of chitosan grafted samples by chemical method and under microwave irradiation

Scheme 1 represents the schematic of grafting procedure. Chitosan solution was prepared by dissolving 0.1 g of chitosan in 25 mL of 1% aqueous acetic acid. The respective amine derivatives (1.6×10^{-3} M) were thoroughly mixed with previously prepared chitosan solution. Chitosan grafted amine samples were prepared using domestic microwave oven (AR 7008) by polymerization reaction. The irradiation reaction was carried out in a 150 mL open necked flask using domestic microwave oven by 80% MW power for 20 min. After completion of irradiation reaction, the reaction flask was allowed to cool at room temperature and methanol was added to obtain the white precipitate chitosan-graft-amines. The obtained precipitate was dialyzed for 3 days, and the H_2O/methanol was refreshed every day. The purified product were dried in vacuum oven at 60 °C and activated at 110 °C before used as catalyst. An excellent percentage grafting and grafting efficiency was achieved by this method. The amine grafted derivatives of acryl amide, polyethylenimine, allyl amine and polyaniline are denoted as Ch-g-AC, Ch-g-PEI, Ch-g-AA and Ch-g-PA respectively.

The graft copolymerization of amine derivatives onto chitosan was carried out by amine derivatives and chitosan dissolving in 25 mL of DMF solvent. Further, 30 mg of AIBN was added as a radical initiator and the mixture was subjected to continuous stirring till forming a homogeneous solution. The glass vessel was placed in a thermostatic water bath to control the reaction temperature (80–90 °C). When the reaction temperature was attained, the reactants were subjected to continuous stirring for 24 h. Observed yield



Where, R = Polyethylimine, Polyallyl amine, Polyacryl amide, Polyaniline

Scheme 1. Grafting of amines on chitosan backbone using microwave and conventional method.