

Green Synthesis of Catalyst and Biodegradable Polymer by Using Dense Gas Technology

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The aim of this study is to apply dense gas CO₂ for the synthesis of zinc glutarate that is broadly used in manufacturing aliphatic polycarbonate, polyglycidol and other types of polymer. Zinc glutarate is currently produced by dispersion of reactants in an organic solvent such as toluene. The effects of temperature, pressure and time on the yield, degree of crystallinity and surface area of the catalyst synthesized in dense gas CO₂ were determined. The yield and catalyst characteristics achieved in high pressure CO₂ system were comparable with the one in toluene system. The process variables such as temperature, pressure and time have significant impact on the zinc glutarate conversion. The activity of the catalyst processed in dense gas CO₂ for the synthesis of biodegradable propylene oxide - ε-caprolactone copolymer was significantly increased.

INTRODUCTION

The use of organic solvents is extremely widespread in industry. While the degree of hazard may vary, all solvents should be considered harmful to the environment. The recent drive within society towards the use of green-technology in conjunction with the hazardous nature of organic solvents has deemed the research into finding alternative solvents for industry.

The use of organic solvents in a range of industries is associated with a generation of large amounts of liquid waste and solvent emissions, which are a cause of environmental and economic burden. It has been estimated that organic solvent in industrial processing operations release about 20 million tonnes of volatile organic solvents (VOCs) per year [1]. The amount of liquid waste created in many branches of the chemical industry is often far greater than the mass of the products, in some cases hundreds times, as in the case of the pharmaceutical industry[1]. Across the board, solvents make up two third of all industrial emissions and one thirds of all VOC emissions in US.

For more than 30 years, researchers have looked for ways to minimise solvents consumption and to replace them with benign alternatives such as supercritical CO₂ (scCO₂) [2], supercritical water [2], CO₂ expanded liquids and ionic liquids, and switchable solvents [3]. Particular attention was given to (scCO₂) because of the widespread view that it satisfies several green chemistry and engineering principles and has been used as a media for reaction. Carbon dioxide is nontoxic, nonflammable, inexpensive and easily separated from the product. Dense gas CO₂ has been used as a monomer, carrier and reagent in synthesis of polymers since it was first discovered by Inoue et al in production of aliphatic poly(alkylene carbonate) from CO₂ and epoxides in 1969 [4-6].

The relatively high thermal stability of CO₂ impedes its application as a cheap and abundant carbon source in polymerisation. A catalyst with very high activity is required for initiation and progression of the reaction for CO₂ polymerisation. The copolymerization of CO₂ and

epoxides to produce polycarbonates is one of the most practical applications of chemical fixation of CO₂. In the past decades, various types of catalysts have been fabricated to enhance the conversion of CO₂ into polymer chain [7, 8]. Zinc glutarate is one of the most effective and cost effective heterogenous catalyst for the reaction between CO₂ and epoxide monomer that can be prepared easily [9]. This catalyst is found to be active in the synthesis of other biodegradable polymers such as terpolymer poly(propylene carbonate-co-ε-caprolactone) [10] and polyglycidol [11].

Zinc glutarate is commonly produced by mixing the reactants in a solvent such as toluene at a desired temperature for a certain period of time. Glutaric acid dissolves in toluene and reacts with ZnO suspended particles in slurry solution to yield the catalyst [6, 9, 12]. The yield of 90% with a catalytic activity of 64 g polymer/g catalyst has been achieved at 60°C within 4 hours [6, 13].

In this study we assess the feasibility of using dense gas CO₂ as a benign solvent for the synthesis of organometallic catalyst zinc glutarate (ZnGA), which can be used for the production of polymers or nutrients. The processing conditions were optimised to promote the yield and activity of the catalysts for the synthesis of polymers such as polycarbonates and biodegradable polymers. Our hypothesis is that the elimination of toxic organic solvent in the synthesis of the catalyst will enhance the activity of the catalyst, minimise the number of stages, consequently the processing period, and allow us to design a one pot polymerisation process.

MATERIALS AND METHODS

Preparation of catalyst

Zinc oxide nanopowder and glutaric acid with purity 99% were purchased from Aldrich. Before reaction, glutaric acid was ground up to the fine powders. Food grade carbon dioxide (>99.9% purity) was obtained from BOC Company. Solvents used in this study were all analytical grades. Toluene, methanol, dichloromethane were supplied by Aldrich, acetone and absolute ethanol were purchased from Ajax Finechem and Merck chemical company, respectively. Propylene oxide (PO) with 99.5% purity and ε-Caprolactone (ε-CL) monomer with 99% purity were obtained from Fluka.

Synthesis of ZnGA

Prior to conducting the high pressure experiment ZnGA was prepared according to the conventional method as described by Meng et al [12]. In the dense gas process, known amounts of GA and ZnO were added into a controlled- temperature high- pressure stirred-reactor. A high pressure pump (Thar Model 50P) was used to gradually pressurise the vessel and then the system was isolated. Prior to pressurisation, the system was first purged with CO₂ to remove air and water residues. The humidity may have a negative effect on particle size of the catalyst and hence its activity. After a desired period of time, the stirring was ceased, the reactor was gradually depressurised, and the product was collected. The residues of reactants were removed by washing the product with acetone, water and ethanol, subsequently, followed by drying under vacuum to dry powder. The catalyst was then stored at ambient temperature in a desiccator.

Copolymerization

Prior to the polymerisation reaction ZnGA was dried at 100°C under vacuum to remove traces of water from the catalyst. The known amount of PO and ϵ -CL was added into the stirred vessel, the reactor was purged with nitrogen before heating and then sealed. The temperature of the vessel was adjusted above the boiling points of both reactants (e.g. > 90°C). After certain period of time the heater was turned off, and the system was cooled down to condense the residues of reactants in the vessel. The catalyst was then removed from the product according to the procedure described by Wang et al [6].

Characterization

FTIR spectroscopic analysis was conducted to identify the bonding. An Attenuated Total Reflectance (ATR) FTIR spectrometer (Varian 660-IR) was used with a resolution of 4 cm⁻¹. The particle size and distribution of the catalyst suspended in chloroform were determined using Malvern Mastersizer 2000. Surface area was measured by the Brunauer-Emmet-Teller (BET) technique using a Quantachrome Autosorb-1 analyzer using nitrogen as an absorbing gas. Scanning Electron Microscopy (SEM) was used to assess the surface morphologies of the catalysts. The samples were coated with gold and imaged with a Zeiss Ultra Plus field emission scanning electron microscope. Wide-angle X-ray diffraction (WXR) measurements with step size of 0.02° over the range of 4-90° were performed using a Siemens D5000 diffractometer with copper (Cu) k-alpha radiation with a wavelength of 1.5418 Angstroms. Nuclear Magnetic Resonance (NMR) spectroscopic measurement was conducted by using a Bruker NMR spectrometer (DPX 400) for analysing the polymer product. Chloroform-*d*₁ and benzene-*d*₆ were used to calibrate the chemical shifts.

RESULTS AND DISCUSSION

Synthesis of Zinc Glutarate

A preliminary study was undertaken to determine the optimum temperature for the synthesis of ZnGA at both atmospheric pressure using toluene and high pressure CO₂. In both systems increasing the temperature from 25°C to 60° C promoted the yield of the reaction. At 60° the yield of the reaction was 95% and 80% in toluene and CO₂, respectively as depicted in Table 1. The higher yield in toluene compared with the dense gas system may have resulted from the differences in the solubility of glutaric acid in both solvents. The GA was soluble in toluene, while it has negligible solubility in CO₂. Consequently, the concentration of GA on the surface of ZnO solid particles was higher in toluene system, promoting the yield of the reaction. The yield of the reaction in the CO₂ system was slightly increased, when the pressure heighten from 50 bar (subcritical) to 100 bar (supercritical). The time has a significant impact on the yield of the reaction for the production of ZnGA in toluene system; the yield was dramatically reduced, when the reaction time was decreased from 4 to 2 hrs. However, in CO₂ the yield of 80% was achievable within even two hrs. Further research is underway to investigate the effect of process variables in CO₂ system. The particle size of the catalyst was slightly decreased in CO₂ system at supercritical conditions. Our results corroborated that the purification protocol was also a major factor in the particle size of the catalyst. Care must be taken during the purification and drying to minimise the degree of particle agglomeration. The residual water, method of suspending the catalysts in a purifying solvent will affect their particle size.

Table 1. Yields and particle sizes of the synthesized catalysts

Catalyst*	Reaction Pressure (CO ₂ , bar)	Reaction Time (h)	Yield (%)	Particle size (µm)
T (toluene)	N/A	4	95.38	5.609
1	50	4	81.31	5.984
2	100	4	83.33	4.902
3	150	2	80.70	4.764

*The synthesis was conducted at 60°C using 1:1 molar ratio of reactants.

Characterisation of ZnGA

The FTIR spectrum of the catalyst is presented in Figure 1 and was consistent with the one in the literature [6, 13]. As can be seen the three vibrational stretching frequencies 1,585 cm⁻¹ (COO⁻, antisymmetric stretching), 1,536 cm⁻¹ (COO⁻, antisymmetric stretching), 1,405 cm⁻¹ (COO⁻, symmetric stretching) demonstrates the successful formation of zinc-carboxyl bond. Moreover, CH stretching and CH₂ scissoring peaks were observed at 2,957cm⁻¹ and 1458cm⁻¹, respectively. In contrast, vibrational characteristic peak of GA which is carbonyl (C=O) stretching of 1,697 cm⁻¹ was not detected in the IR spectrum, indicating no residual GA in the final product.

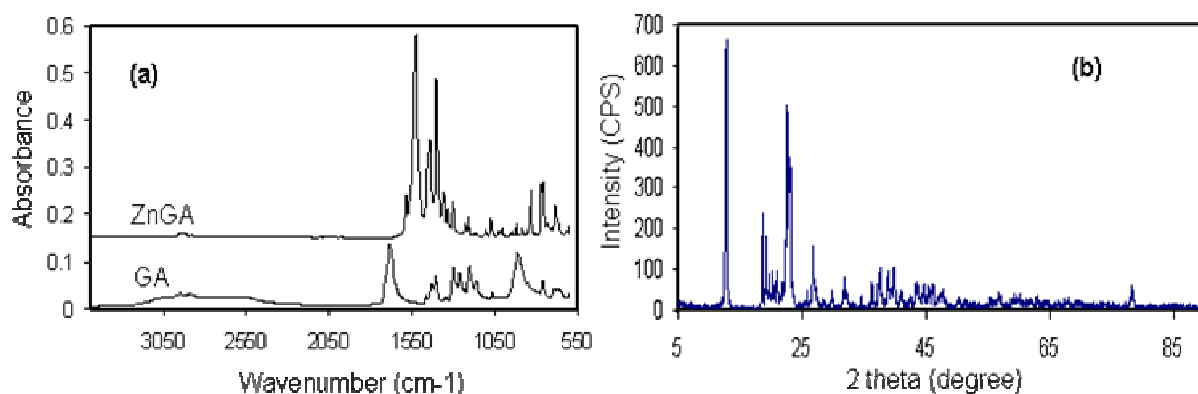


Figure 1. (a) FTIR spectrum of Catalyst ZnGA and glutaric acid (b) WAXD pattern of ZnGA at various conditions

The results of the WAXD analysis in Figure 1 demonstrate that crystalline structures of ZnGA were identical, regardless of the fabrication procedure used. However, the peak intensity and widths at each angle was slightly different. In general, peak intensities represent the overall crystallinity and crystal quality (namely, size and perfectness of crystal) of a specimen. Sharper peaks and higher intensities are two factors that are correlated to the higher crystallinity. The result reveals that the crystallinity level of ZnGA is promoted by dense gas process as depicted in Table 2. Increasing the CO₂ pressure promoted both the degree of crystallinity and the size of ZnGA crystals. More regular shape crystals were also formed at higher pressures.

From the SEM images in Figure 2(a, b), it can be seen that ZnGA catalyst has rectangular plate morphology. Larger crystals with lower degree of aggregation were formed at higher degree of crystallinity. Kim et al investigated the effect of different characteristics of a solid phase on the catalyst activity. It was suggested that the morphological structure of ZnGA

including the degree of crystallinity, crystal size and shape play critical roles in catalytic activity [6, 9, 14]. Based on this conclusion and our experiment results, it was expected that the catalyst synthesised in the dense gas CO₂ system possessed superior catalytic activity or at least equivalent to the one fabricated in toluene.

Table 2. Relative crystallinity and surface area of the synthesized catalysts

Zinc Glutarate	Sum of sample NPH (peak a-d)	Relative crystallinity (%)	Surface area (m ² /g)
Cat. T	61,927	83.30	22.05
Cat. 1	62,860	84.56	12.05
Cat. 2	67,976	91.44	13.63
Cat. 3	74,337	100	13.21

Copolymerization of PO and ϵ -CL

The activity of the catalyst was assessed by conducting the reaction for the synthesis of a biodegradable alkylene oxide-lactone copolymer poly(propylene oxide-co- ϵ -Caprolactone). Ree et al reported that ZnGA has no catalytic activity in the homopolymerization of CL but highly active to polymerize PO [15]. The mechanism proposed is that the nucleophilic oxygen atom of the PO monomer can insert into the zinc-carboxyl bond, then activating the zinc metal center of ZnGA for the continuous reaction[15]. Our hypothesis was that the presence of PO in the reaction system can make ZnGA active to polymerize CL to produce a copolymer of PO and CL. Compared with poly(propylene oxide) homopolymer, the presence of lactones (e.g. CL) units in the polyether chain can enhance its overall biodegradability, hence improve its applications in biomedical field [16].

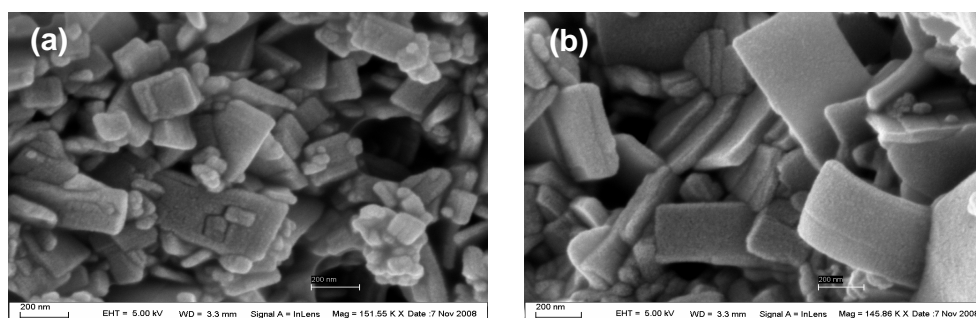


Figure 2. (a) SEM image of Cat. T; (b) SEM image of Cat. 3.

The yield of the reaction for copolymerisation of PO-CL (molar ratio 60:40) at 90°C and 24 hours was 60.1(g/g.cat) and 86.2(g/g.cat), when using ZnGA synthesised in toluene and CO₂, respectively. The enhancement in yield achieved, using ZnGA processed by CO₂, may be due to the higher degree of crystallinity of the catalyst.

The chemical compositions of the methanol insoluble polymer product were characterized by ¹H-NMR and ¹³C-NMR. The representative NMR spectra are shown in Figure 3, confirming the reaction between PO and CL. It can be concluded that in presence of PO, the catalyst ZnGA was efficient for the polymerisation between CL monomers. Future study will be carried out to investigate the effect of different molar ratio and reaction conditions on the extension of the reaction and polymer molecular structure.

CONCLUSION

For the first time the potential of dense gas CO₂ as an alternative solvent for the fabrication of

solid-based organometallic catalyst was demonstrated. The yield of the process for the synthesis of ZnGA was slightly lower in CO₂ than in organic solvent. However, the reaction time was dramatically decreased in supercritical CO₂ system. It was demonstrated that ZnGA activity for the synthesis of PCL based polymer substantially enhanced in the presence of PO. The activity of the catalyst fabricated in CO₂ system was remarkably higher than the one produced from toluene system. This study will open an avenue for removing the organic solvents in synthesis of organometallic catalysts that broadly used in production of many polymers such as polycarbonates in commercial scale.

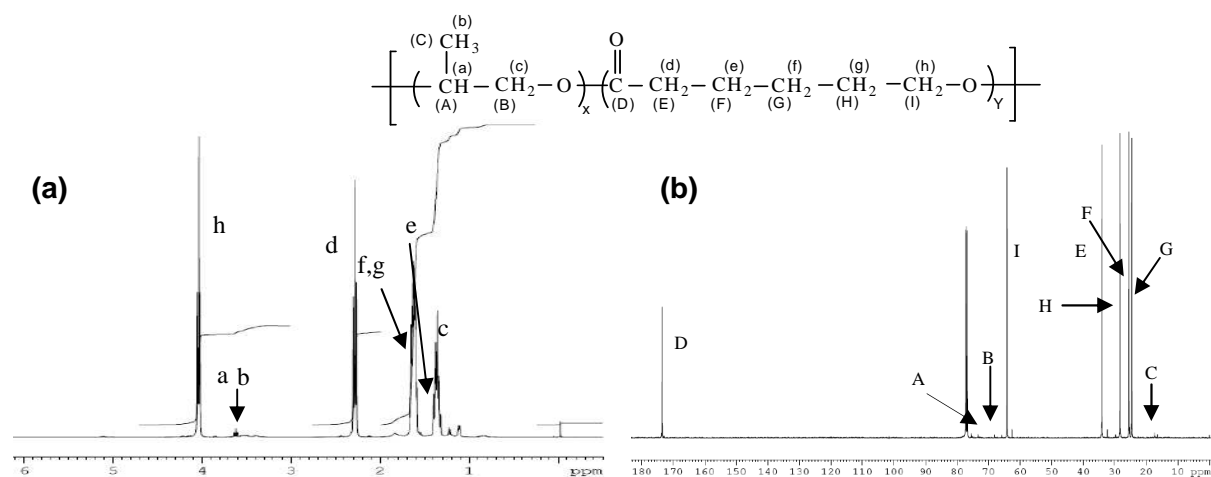


Figure 3. (a) ¹H NMR spectra; (b) ¹³C NMR spectra.

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