

TRANSESTERIFICATION OF PROPYLENE CARBONATE WITH METHANOL TO DIMETHYL CARBONATE OVER CALCIUM OXIDE CATALYST: EFFECTS OF CATALYST PRE-TREATMENT

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Abstract

Transesterification of cyclic carbonate is an important process for the manufacture of dimethyl carbonate (DMC), which involves a reversible catalytic reaction in a slurry phase. In this work, catalyst pre-treatment effects in transesterification using CaO catalyst will be presented. Initial catalyst evaluation revealed that CaO pre-treatment by reactants has a strong influence on the rate of transesterification. It was observed that CaO pre-treated with methanol significantly enhances the catalytic activity while pre-treatment with cyclic carbonate such as propylene carbonate (PC) inhibits the rate of reaction. The effects of pre-treatment conditions and possible reaction pathway will be discussed. Further, a detailed kinetics of transesterification of propylene carbonate (PC) to dimethyl carbonate (DMC) was studied. Concentration-time profiles were obtained at different catalyst loadings, substrate concentrations (PC and methanol) and temperatures. Several rate models were evaluated to fit the integral batch reactor data following a rigorous model discrimination approach to develop a rate equation and determine rate parameters.

Keywords

Transesterification, Kinetics, Pre-treatment.

Introduction

Transesterification of cyclic carbonates such as ethylene carbonate (EC) and propylene carbonate (PC) with methanol to dimethyl carbonate (DMC) is a key step in the non-phosgene routes for polycarbonates and polyurethane monomers (Osamu et al, 1998). Synthesis of DMC by transesterification also has several advantages over the conventional routes based on oxidative carbonylation and phosgenation and hence is recognized as an atom efficient and environmentally greener route. Transesterification of cyclic carbonates involves a reversible reaction carried out in the presence of homogeneous or heterogeneous catalyst. Typical homogeneous catalysts used are alkali metal methoxides, carbonates, tertiary phosphines, arsines or

selenium compounds. Homogeneous catalysts are usually used below 100 °C. For example, sodium methoxide was reported to give 53.9% PC conversion at 60 °C (Johannes et al, 2013). Although the homogeneous catalysts give high DMC yields under mild conditions, they are difficult to separate and recover from products. Among reported heterogeneous catalysts, metal oxides, ion exchange resins, supported metal catalysts, molecular sieves were investigated. From the metal oxide group, CaO was reported to give 83% PC conversion and 97% DMC selectivity at 50 °C (Wei et al, 2004). Strong basic quaternary ammonium ion exchange resins with hydroxide counter ion was reported to show a 55-65% PC conversion

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and 97% DMC selectivity at 40 °C (Pyrlík et al, 2012). In none of these studies, the reaction mechanism, role of catalyst pre-treatment and kinetics of the transesterification have been addressed.

In this report, it is shown that CaO was the best heterogeneous catalyst based on evaluation of several metal oxide catalysts. Also, the pre-treatment of CaO with methanol showed a significant enhancement in transesterification rate without loss of DMC selectivity. Therefore, effects of pre-treatment of CaO catalyst with methanol and PC were first investigated to determine conditions for kinetic study. Further, effects of catalyst loading, PC and methanol concentrations and temperature on concentration-time profiles in a batch slurry reactor were studied to develop rate equations and intrinsic kinetic parameters.

Experimental Section

Experimental Procedure

Transesterification experiments were carried out in a stirred batch reactor with provision for temperature control, variable agitation speeds and sampling. In each experiment, concentration-time profiles were obtained in which, PC, DMC, methanol and propylene glycol were analyzed using GC. Catalyst pre-treatment experiments were carried out by varying the order of addition of the reactants, while for kinetic study, methanol-pretreated catalysts were used.

Results

Catalyst Evaluation

Metal oxides, such as CaO, MgO, BaO, SrO and CeO₂ were first tested in transesterification of PC to DMC. The results presented in Figure 1 show that CaO gives the highest yield (81%) of DMC (PC conversion: 88.09%, DMC selectivity: 92.04%). Therefore, CaO was chosen for further studies.

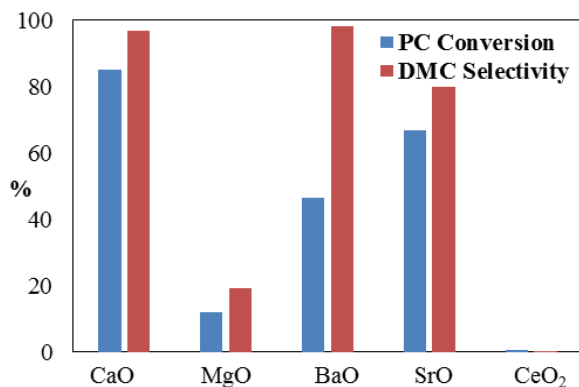


Figure 1. Catalyst Screening. Reaction conditions: PC: 1.07kmol/m³, methanol: 21.4kmol/m³, Catalyst: 5.35kg/m³ at 50 °C

Methanol Pre-treatment Effect

In order to understand the pre-treatment effects, fresh CaO and methanol pre-treated CaO were evaluated for transesterification. It was observed (see Figure 2) that for reactions with no pre-treatment (fresh CaO catalyst), 20 min induction period was observed while, with methanol pre-treated CaO several fold increase in catalytic activity was observed with no induction time. The experiments for kinetic study were carried out using methanol pre-treated catalyst in which the effects of CaO loading, PC concentration and temperature were investigated. The analysis of these results using Langmuir-Hinshelwood type rate models will be presented considering different possible mechanisms for the fresh and pre-treated catalysts.

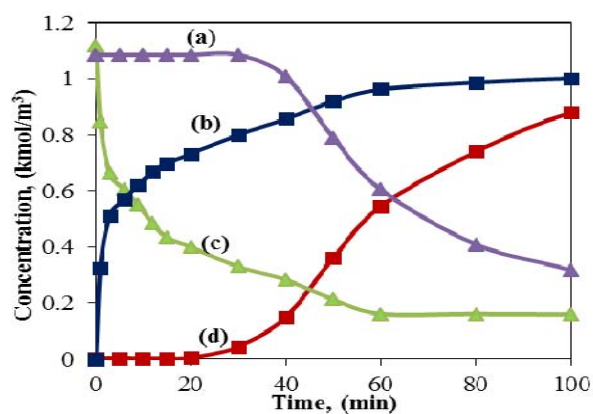


Figure 2. Concentration-time profile for (a). PC for fresh CaO, (b). DMC for methanol pretreated CaO, (c). PC for methanol pretreated CaO, (d). DMC for fresh CaO. Reaction conditions: PC: 1.07kmol/m³, methanol: 21.4kmol/m³, CaO: 1.07kg/m³ at 20 °C under 100 psi N²

Acknowledgments

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