

Sodium alginate beads as catalyst support on scalable cycloaddition of CO₂ to propylene oxide

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Resumo/Abstract

RESUMO – A presença de CO₂ na atmosfera só será reduzida com um esforço concentrado de diversas áreas. Uma dessas áreas é conversão do CO₂ em outros produtos, como na cicloadição dele ao Óxido de Propileno. A catálise dessa reação pode ser realizada com um par funcional de ácido e base de Lewis. O presente trabalho introduz o estudo do uso de sítios de Fe(III) como ácido de Lewis, bem como a Polietileno Imina (PEI) como base de Lewis. Esferas a base de alginato de sódio foram sintetizadas como suporte para o par catalítico, afim de estudar esse sistema com possível síntese simples e escalonável. A síntese do catalisador foi alcançada, embora otimizações estejam em andamento. Ajustes na pressão e temperatura do sistema serão estudados para facilitar o fluxo de massa dentro do reator e através das esferas, bem como manter a integridade física do catalisador. Os autores esperam que o material possa potencialmente ser utilizado similarmente a recheios em reatores de leito empacotado.

Palavras-chave: dióxido de carbono, catálise heterogênea, alginato de sódio, cicloadição.

ABSTRACT – CO₂ presence in the atmosphere can only be reduced with a concentrated effort from several areas. One such area is the conversion of CO₂ into other products, as in the cycloaddition of it to Propylene Oxide. This reaction's catalysis can be carried by a functional pair of both acidic and basic Lewis sites. The present work introduces the study of the use of Fe(III) as Lewis acid sites, as well as Polyethyleneimine (PEI) as Lewis basic sites. Sodium alginate beads were synthesized as a support for the catalytic pair, aiming to facilitate simple synthesis and scalability of the studied system. Catalyst synthesis was accomplished, although optimizations are being carried out. Adjustments to reaction pressure and temperature will be studied, to aid mass flux inside the reactor and through the beads, as well as maintaining the catalysts physical integrity. The authors expect the material to potentially be usable similarly to packings in a packed bed reactor.

Keywords: carbon dioxide, heterogeneous catalysis, sodium alginate, cycloaddition.

Introduction

CO₂ is a greenhouse effect contributing gas – its concentration reduction in the atmosphere can only be achieved with coordinated efforts from several areas (1). One such area is the catalytic conversion of CO₂ into value-added products, such as the cycloaddition to Propylene Oxide (PO) with the formation of Propylene Carbonate (PC). The claimed catalytic sites for this reaction are a pair of Lewis acid-base (2). Though recent research efforts focus on multifunctional catalysts (3, 4), the use of this acid-base catalytic pair is the approach of the present work. Lewis acid functions can be performed by several metallic ions, such as Fe³⁺ (5), which will be the studied as part of the catalytic pair on the present work.

Sodium alginate is a natural polymer, occurring in algae, and its research as a catalyst support is already reported on the literature (6,7). Its chains can cross-link with each other producing an “egg-box-like” structure, behaving macroscopically as a gel, and trapping metallic ions within in the process of reticulation, generating alginate-metal beads in a relatively simple synthesis (8). Several treatments

can be applied to this material, such as lyophilization (6), drying or pyrolysis (7), for improvement of its properties.

Therefore, the present work will introduce an ongoing project on the use of sodium alginate as a support for Fe(III) sites, as part of a catalytic pair for the cycloaddition of CO₂ to PO, for a potentially simple to implement, scalable methodology. Tetra-n-butylammonium Bromide (TBAB) is one of the studied co-catalysts to perform the Lewis basic function (9,10). Alongside TBAB, the present work will also analyze Polyethyleneimine (PEI) as a potential candidate, due to the presence of amine nucleophilic regions in its structure (11).

Experimental

Catalyst Synthesis

Sodium alginate was purchased from Sigma-Aldrich (Lot #SHB2247). FeCl₃·6H₂O (97.0 – 102.0%) was purchased from Vetec. PEI (50 % w/w H₂O, MW 1300 g/mol) was purchased from Sigma-Aldrich. The beads were synthesized according to Bahsis *et al.* (7) methodology. When the insertion of PEI was desired, the beads were soaked in a 0.2 mol/L PEI solution for 2 h previously to lyophilization.

Fe(III)-Alginate and PEI-Fe(III)-Alginate beads were characterized through XRD and N₂ adsorption techniques.

Catalyst Evaluation

Propylene Oxide ($\geq 99\%$) was purchased from Sigma-Aldrich. CO₂ was pressurized from an Air Liquide CO₂ cylinder. 100 mg of the catalyst and 1.0 mL of PO were inserted into the reactor, and after this, 10 bar of CO₂, measured at RT, were added. The catalytic system was submitted to 100 °C for 24h in an oil bath, with agitation, then allowed to cool down to RT, then depressurized. After that, the liquid products were filtered. Selectivity and conversion were selected as performance indicators, but yield (Y) was measured in this first step as an indirect performance indicator. The yield was calculated as the ratio between the mols of liquid product, while initially estimating 100% selectivity, and the initial mols of PO.

Results and Discussion

XRD analysis indicates an amorphous structure on the supported catalyst, which is expected from the alginate chains. BET analysis of N₂ adsorption-desorption isotherms indicates a surface area of 78.9 m²·g⁻¹. Synthesis of Fe(III)-Alginate was done successfully, producing solid, even if fragile, beads. Figure 1 shows the synthesized Fe(III)-Alginate beads. The addition of PEI proved to be more difficult, due to the apparent interaction with Fe³⁺ ions. When both are solubilized together, precipitation of a brown flocculated solid occurs, indicating the formation of a solid complex.

If PEI is added to the alginate solution during the reticulation process, the formation of a rubber-like material takes place. Such material does not resist pressures or temperatures required for CO₂ cycloaddition to PO, though it seems to prevent changes in coloration when stored at RT. The only feasible way found by the authors to incorporate PEI into the beads was via soaking the wet gel Fe(III)-Alginate beads in a PEI solution, which maintains their structure intact, but could potentially only attach PEI sites to the surface of the catalyst, leaving most of the porous regions without the required nucleophilicity.

Furthermore, exposure of the catalyst to reaction pressure and temperature conditions darkens the beads, indicating a possible reduction process. Moreover, the use of a different co-catalyst, not supported by alginate, but added alongside it to the reaction, must also be studied. Yields upwards of 40% were found, but products were cloudy even after filtration, requiring further cleaning for proper characterization and selectivity/conversion calculation. Physical separation of the solid catalyst from the agitator was applied, but resulted in near-zero yields, indicating an optimization path towards better matter flux inside the reactor, enabling possible future design of a packed bed reactor for the utilization of developed materials.



Figure 1. Photo of the synthesized Fe(III)-Alginate beads.

Conclusions

Fe(III)-Alginate beads were successfully prepared by a simple methodology. However, the catalytic system still needs improvements to increase reaction yield and selectivity towards Propylene Carbonate. Modifications such as the addition of a co-catalyst to the system, e. g. TBAB, will be explored. To further expand the ease of industrial potential applicability, the phase homogenization of reactants, via pressure and temperature manipulation are to be considered, while keeping products in the liquid state. This could aid the matter flux inside the reactor, as well as allow the design relatively easy separation of the products and reactants, with the beads to be used akin to packings in a packed bed reactor.

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