Cyclic carbonates through a green route: kinetic and mass transfer modelling

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Highlights

- Cyclic carbonates are needed in green chemical synthesis
- Cyclic carbonates were prepared on a heterogenized catalyst from epoxidized fatty acid ester and carbon dioxide
- Extensive kinetic and mass transfer studies were conducted in a semibatch reactor
- The kinetic and mass transfer data were modelled mathematically

1. Introduction

Cyclic carbonates are used as polymer precursors, fuel additives and solvents. Cyclic carbonates provide an environmentally friendly and non-toxic pathway to the production of polyurethanes, which are still made from polyols and di-isocyanates. The currently applied isocyanate based synthesis route involves the use of a toxic compounds phosgene, so the need for a new and green technology is urgent. Cycloaddition of CO_2 to epoxides in the presence of homogeneous and heterogeneous catalysts gives cyclic carbonates. In the Northern hemisphere, the epoxides obtained from tall oil fatty acids and order vegetable oils are of particular interest, because large amounts of tall oil are obtainable as side streams from the Kraft pulping process. The dominant chemical compounds in tall oil are oleic, linoleic, linolenic and abietic acids which, contain double bonds, which can be epoxidized either by using the classical Prilezhaev concept, heterogeneous catalysts or enzymatic technology. On paper, carbonization of an epoxide is a straightforward process but the reaction rate and the product selectivity are still the major challenges. The carbonation, the cycloaddition reaction $\text{Epoxide} + CO_2 \rightarrow \text{Carbonated product}$, requires the presence of a catalyst. Several homogeneous and heterogeneous catalysts have been screened and the cycloaddition kinetics and product selectivities have varied. This work is devoted to the kinetics and mass transfer in the carbonation of epoxidized methyl oleate on a heterogenized catalyst SBA-15-4PPI. The goal was to obtain a model which comprises the gas solubility, mass transfer and kinetic effects.

2. Methods

The catalytic material used in the carbonation experiments was prepared following a multi-step synthesis procedure. Epoxidized methyl oleate was used as a model molecule and an extensive series of kinetic and mass transfer experiments were conducted in a pressurized autoclave operating under isothermal conditions. Gas-liquid mass transfer experiments were conducted in the same reactor vessel which was utilized for the kinetic studies. Both the reactant (epoxidized methyl oleate, EMO) and the product (carbonated methyl oleate, CMO) were employed in the experiments. The pressure and temperature intervals of the experiments were 20-60 bar and 373-443K. The stirring rate was varied in some experiments to investigate the gas-liquid mass transfer of carbon dioxide.

3. Results and discussion

Based on extensive kinetic experiments, the reaction mechanism displayed in Figure 1 was proposed and rate equations were derived. The rate equations were implemented in three-phase reactor model,

which was solved numerically several times in order to find the optimal set of kinetic and mass transfer parameters. A stiff ODE solver coupled to a merged Simplex-Levenberg-Marquardt algorithm was used in the computational procedure. The quality of the parameters was checked with standard statistical analysis and with the MCMC method [1]. The behavior of the gas phase was described with the Peng-Robinson equation of state. Examples of modelling results are displayed in Figure 2, which shows that the model is able to describe all the essential features in the experimental data. The statistical quality of the model parameters was good and therefore, the model has a perspective in process scale-up.

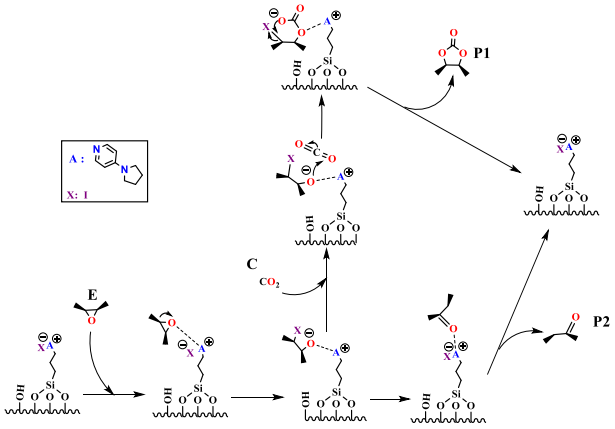

Figure 1. Proposed reaction mechanism for carbonation

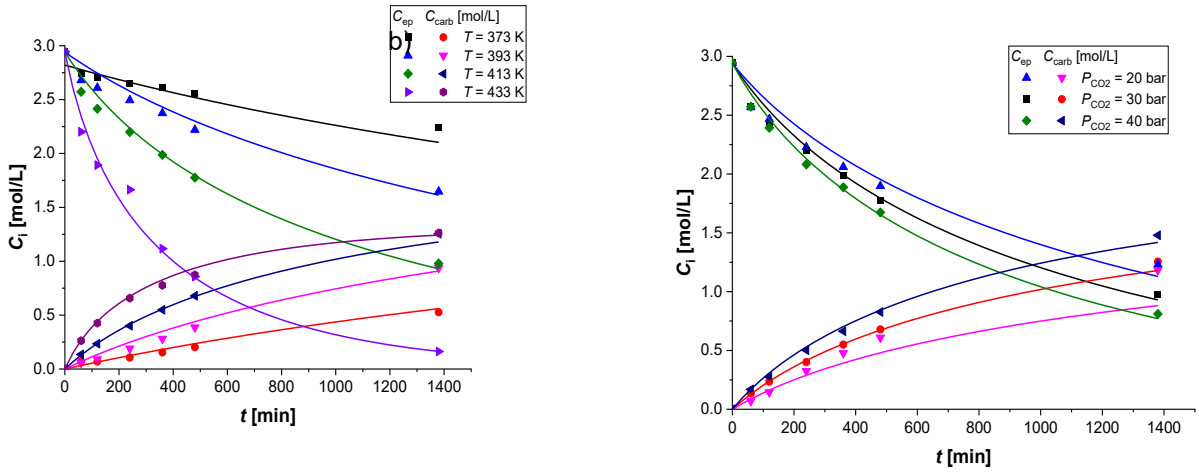

Figure 2. Fit of the model to the experimental data for the mechanism: left) temperature, right: CO_2 pressure.

4. Conclusions

Cycloaddition of epoxidized fatty acid ester was studied from the viewpoints of gas solubility, interfacial mass transfer and intrinsic kinetics. Completely new kinetic models for cycloaddition of carbon dioxide to epoxides were presented and the modelling results were discussed from the viewpoints of reaction mechanisms and reactor technology. The model can in future be used for process scale-up.

References

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Keywords
semibatch reactor, three-phase system, carbonation, mathematical modelling