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Continuous esterification in organic solvents as a step in the valorization of CO2.

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PURPOSE OF THE ABSTRACT

Introduction

As part of the Carbon2Chem project [1], the aim of the SynAlk subproject is the production of C2+-alcohols from steel mill furnace gases. Their use is important to reduce carbon emissions and close the carbon cycle. So far, heterogeneous catalysts have dominated the field of CO2 utilization and are well established in many large scale chemical processes. Homogeneous catalysis has made great progress, however, and can reach the results of its heterogeneous counterpart.

Overview

In this context, a continuous multi-step synthesis for the utilization of CO2 is being developed as a telescope reaction. As part of the multi-step synthesis a continuous esterification is investigated in a coiled PFTR setup. [2] Continuous flow reactions have known advantages when it comes to reaction engineering as well as scale-up. [3]

Objective

The aim is to transfer the reaction from lab scale to pilot plant. For further process development the potential of homogeneous catalysis is evaluated. Different triflates are tested as homogeneous molecular catalysts which have so far been used as co-catalysts in homogeneous hydrogenation with sophisticated noble metal, or transition metal, catalysts. With the use of triflates multiple consecutive reactions can be carried out without separation steps allowing telescope reactions to produce higher alcohols directly from CO2.

Experimental setup

In a PFTR setup, the kinetics is determined for different homogeneous catalysts in organic solvents. The reactor is automatically fed with HPLC pumps with the corresponding reactants. The conversion and product yield are measured using GC analysis, NMR spectroscopy and inline mid-IR spectroscopy.

Results

The homogeneous catalysts have shown very good performance in the continuous flow set-up, reaching equilibrium concentration in less than seven minutes, as shown in Figure 1. Figure 1 shows the promising capability of one of the tested catalysts, in this case aluminum trifluoromethanesulfonate (Al(OTf)3), for the continuous esterification. The applicability of this catalyst for telescope reactions has also been proven. However flow phenomena are prohibiting the determination of the real kinetic data making a kinetic analysis difficult. This leads to bad predictions of the concentration when the conversion is low. This is strongly represented by the 363 K curve. However the kinetic values determined so far are in good accordance with literature.

Figure 1 - Experimental and predicted concentration-time profiles of ethyl acetate at different reaction temperatures.

Further understanding of the flow pattern as well as the comparison with known flow phenomena is the aim of current investigations. [4], [5] The aim is the determination of a more accurate kinetics for a reliable prediction of the reactor system independently of the observed flow regime while allowing kinetic investigations independently of the flow conditions. Increasing the reactor size over several orders of magnitude towards an industrial-size application is the final step in this research.

Acknowledgements
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FIGURES

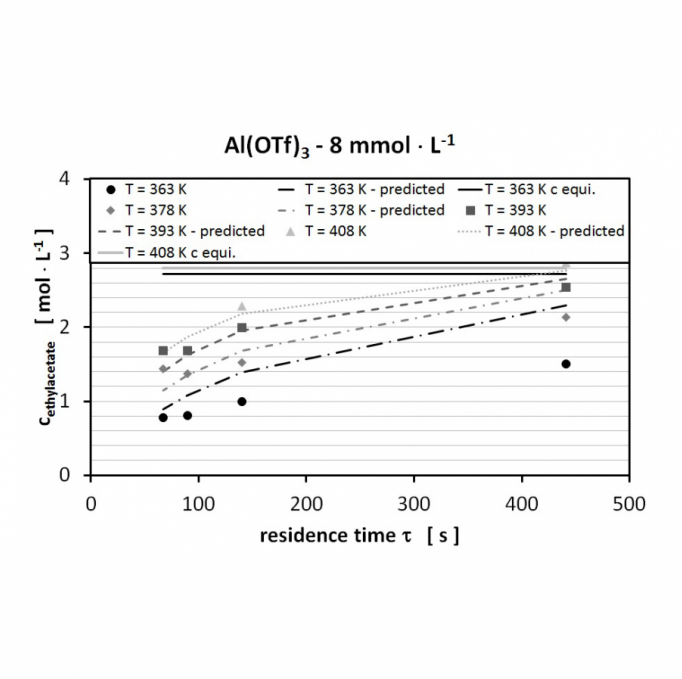

FIGURE 1

Experimental and predicted concentration-time profiles of ethyl acetate at different reaction temperatures.

included

FIGURE 2

KEYWORDS

flow chemistry | esterification | homogeneous catalysis | Carbon2Chem

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