Research Proposal for Bachelor Thesis Project

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Topic: Optimizing the propylene yield of a ZnZrOx/zeolite tandem catalyst system for olefin production from CO2

1 Why this topic is important?

In light of the ever-increasing concentration of CO_2 in the atmosphere and the resulting intensification of the greenhouse effect, it is desirable not only to reduce future CO_2 emissions but also to develop methods for recycling the CO_2 captured from air [1].

For the chemical conversion of CO_2 to light olefins, two main processes are available. Firstly, CO_2 can be reduced to CO via RWGS reaction, which is then hydrogenated to hydrocarbons in the Fischer-Tropsch synthesis. The selectivity towards light olefins of this approach is limited by the Anderson-Schultz-Flory kinetics to approximately 60% in the hydrocarbon fraction [2]. In contrast, the "tandem" methanol-mediated OX-ZEO synthesis directly hydrogenates CO_2 to methanol (MeOH), which is subsequently dehydrated to form olefins. Compared to the Fischer-Tropsch method, the OX-ZEO process offers significantly higher selectivity towards light olefins, with the olefin selectivity within the hydrocarbon fraction reaching up to 95% [3].

The process involves two main steps: first, the hydrogenation of CO_2 to MeOH, and second, the dehydration of MeOH to light olefins. Due to the low energy states of CO_2 and the strong bonds in the MeOH molecule, both reactions require high activation energies, leading to very low reaction rates [4]. To make this process industrially feasible, $ZnZrO_x$-zeolite catalysts have been developed, that demonstrated good performance in facilitating both reactions. The $ZnZrO_x$ component weakens C–O and H-H bonds [5], while the acid sites of the zeolite activate MeOH [6].

2 What has bee done so far? What was observed? What are the research gaps?

In previous studies, a $RhCo_3$/MCM-41 hydroformylation catalyst was investigated as part of a tandem catalyst system for converting CO_2 into higher alcohols (HA). In the first step of this process, the CO_2-to-olefin reaction, various catalysts were tested, with ethylene yield serving as the primary performance indicator. This focus was due to the relatively low selectivity reported for propylene hydroformylation compared to ethylene hydroformylation over $RhCo_3$/MCM-41. The best performance was observed with the $ZnZrO_x$/SAPO-34 catalyst with a Si/Al ratio of 0.30. However, qualitative analysis of the combined catalytic system showed a higher production of 1-butanol compared to 1-propanol, leading to the hypothesis that the high molar ratio of ≈ 1.7 for CO compared to C_2&C_3 olefins resulted in increased CO insertion and enhanced hydroformylation activity for propylene, compared to the hydroformylation of propylene alone [7]. This suggests the need for a tandem catalytic system optimized for propylene yield in the CO_2-to-olefin process. In other studies, the SAPO-14 catalyst was found to outperform SAPO-34 in terms of propylene production, achieving a propylene selectivity of up to 77.3% in the MTO reaction [8]. As a result, the $ZnZrO_x$/SAPO-14 catalyst is a promising candidate for further research on a tandem catalytic system aimed at optimizing propylene yield in the CO_2-to-olefin process. Additionally, former studies show the possibility of increased propylene yield and prolonged catalyst lifetime by

modifying a zeolite structure like ZSM-5 through cation doping with Ca or Mg [9].

3 What will be done? What research gaps am I filling?

This project aims to improve the CO_2-to-olefin reaction in terms of propylene yield and selectivity. In this study, the performance of a $ZnZrO_x$/SAPO-14 catalyst will be investigated and compared to other bifunctional zeolite catalysts (SAPO-18, SAPO34). For this purpose, a series of pure and cation-doped SAPO-14 samples will be synthesized using hydrothermal synthesis and physically mixed with $ZnZrO_x$. To analyze and verify the zeolite structure and correlate it with changes in performance, the synthesized zeolites will be analyzed using powder X-ray diffraction (XRD). The performance of the catalyst will be evaluated by conducting catalytic experiments in a fixed-bed PID reactor and analyzing the outlet gas stream with thermal conductivity detectors and flame ionization detectors. Our goal is to assess the catalytic performance of SAPO-14 in combination with $ZnZrO_x$ and correlate the structural changes imposed by cation doping on its catalytic performance for the CO_2-to-olefin reaction.

This thesis proposal...
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09.10.2024,

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