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 recycling of CO_2 to light olefins, two main processes are available. The Fischer-Tropsch synthesis uses the RWGS reaction to reduce CO_2 to CO, which is then hydrogenated to hydrocarbons. The selectivity for light olefins of this approach is limited by the Anderson-Schultz-Flory kinetics to approximately 60% in the hydrocarbon fraction. 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 for light olefins, with selectivity within the hydrocarbon fraction reaching up to 95%.

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 MeOH, both reactions require high activation energies, leading to very low reaction rates. To make this process industrailly feasable, $ZnZrO_x$-zeolite catalysts have been developed, that demonstrated good performance in facilitating both reactions. The $ZnZrO_x$ component weakens C–O and H-H bonds, while the Brønsted acid sites of the zeolite activate MeOH. Additionally, the small pore size of the zeolite enhances the selectivity for light olefins.

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 additional CO resulted in increased CO insertion and enhanced hydroformylation activity for propylene, compared to the hydroformylation of propylene alone. This suggests the need for a tandem catalytic system optimized for propylene yield in the CO_2-to-olefin process. In subsequent studies, the SSZ-13(100) catalyst was found to outperform SAPO-34 in terms of propylene production, achieving a propylene selectivity of up to 52%. As a result, the $ZnZrO_x$/SSZ-13 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.

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