UNIVERSITI TEKNOLOGI MARA

DIRECT DME PRODUCTION FROM CO_2 HYDROGENATION & MEOH DEHYDRATION OVER CZA & HZSM-5 BIFUNCTIONAL CATALYST BED IN FIXED BED REACTOR

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ABSTRACT

The direct synthesis of dimethyl ether (DME) from carbon dioxide (CO_2) and hydrogen (H_2) offers a promising carbon capture and utilization (CCU) route for clean fuel production. This study evaluates a bifunctional catalyst system comprising commercial CuO-ZnO-Al_2O_3 (CZA) and HZSM-5 pellets in a fixed-bed reactor (FBR). Catalyst characterization was performed using XRD, FESEM, EDX, BET, mercury intrusion, TGA, H_2-TPR, and NH_3-TPD. CZA showed high hydrogen uptake (4900 $\mu mol \cdot g^{-1}$), confirming active Cu^+/Cu^0 surface sites, while HZSM-5 exhibited moderate acidity with NH_3 desorption peaking near 217 °C. Pre-liminary tests compared catalyst form (powder vs pellet), packing structure (mixed vs sequential), and CZA:HZSM-5 mass ratios (1:1 to 4:1) under baseline conditions (200 °C, 40 bar, 500 ml g^{-1} h^{-1} GHSV). The optimal configuration—pellet form, sequential packing, 3:1 ratio—was selected for operating condition optimization. Temperature (150–250 °C), pressure (20–60 bar), and GHSV (250–583 ml g^{-1} h^{-1}) were varied using a one-factor-at-a-time approach. The best performance was achieved at 225 °C, 50 bar, and 500 ml g^{-1} h^{-1}, yielding 85.8% CO_2 conversion, 84.0% DME selectivity, and 97.9% DME yield. Carbon balance validation showed <0.5% deviation. A 12-hour stability test confirmed sustained activity and selectivity. Comparative analysis with literature benchmarks demonstrated superior performance. This study is the first to systematically optimize commercial CZA/HZSM-5 pellet configuration and operating conditions in a single-reactor setup, achieving the highest reported DME yield under non-synthesized catalyst conditions. These findings confirm the viability of commercial bifunctional pellets for scalable, energy-efficient direct DME synthesis.

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CHAPTER 1
INTRODUCTION

1.1 Research Background

Carbon dioxide (CO_2) emissions resulting from human activities, particularly the burning of fossil fuels, deforestation, and industrial processes, have been identified as a significant driver of global warming and climate change. CO_2 contributes 76% of all greenhouse gas emissions as compared to other gasses including methane (CH_4), nitrogen oxide (N_2O), and fluorinated gases, making it the main driver of global climate change (Crippa et al., 2021). As the concentration of CO_2 in the atmosphere continues to rise, there is an urgent need for innovative solutions to mitigate these emissions.

Carbon capture and storage (CCS) technology has been proposed in industrial processes since 1920s as a method to reduce CO_2 emissions by capturing, transporting, and storing it in underground geological formations (IEA, 2016). Capturing, moving, and storing CO_2 in geological formations is considered as a viable way for lowering emissions of CO_2 into the atmosphere. However, CCS faces several challenges that limit its widespread implementation (Raza et al., 2019). The high cost of capturing, transporting, and storing CO_2 remains a major barrier. CCS is also energy-intensive, which reduces the efficiency of power plants and increases operational costs. CO_2 can also interacts with storage reservoirs that can leads to geochemical and mechanical changes, threatening the long-term stability of storage sites. There is also a risk of CO_2 leakage, which could lead to environmental damage and safety concerns. While CCS shows potential for reducing emissions, the significant challenges associated makes this technology less attractive. As a result, increasing attention is being directed towards carbon capture and utilization (CCU).

CCU presents opportunities for converting CO_2 into valuable products, thereby offering both economic incentives and environmental benefits. CCU mitigates financial concerns by converting captured CO_2 into valuable products such as chemicals, building materials, and synthetic fuels, thereby reducing the overall cost of carbon capture while generating new revenue streams. This approach aligns with circular economy principles by promoting the reuse of waste materials, leading to a more resource-efficient and sustainable system. CO_2 can be transformed into a variety of chemical products,