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One Step Dimethyl Ether Synthesis from CO₂ Hydrogenation over Hybrid Cu-ZnO-Al₂O₃/ desilicated ZSM-5 Catalysts

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Introduction

The direct synthesis of dimethyl ether (DME) from CO₂ hydrogenation is an attractive approach to CO₂ utilization, contributing to the decarbonization of the energy matrix and supporting the transition to a more sustainable economy. DME is a cleaner fuel with higher combustion efficiency than traditional diesel, helping reduce CO₂ emissions. For the direct synthesis of DME, a hybrid catalyst with both metal and acidic sites is required to facilitate CO₂ hydrogenation to methanol and methanol dehydration to DME, respectively. However, a key challenge in this technology is developing catalysts that are active, selective, and stable. The effectiveness of these catalysts relies on the proximity of metal and acidic sites [1]. Hierarchical zeolites are promising as catalyst supports due to their high surface area and mesoporosity, which help prevent metal particle sintering and promote interactions between acid and metal sites. Alkaline desilication treatment is a post-synthesis method considered simple and effective for producing mesoporous zeolites. Desilicated ZSM-5 zeolites exhibited higher activity at low temperature and lower coke formation for methanol dehydration to DME [2]. Thus, the objective of this work is to evaluate the performance of Hybrid Cu-ZnO-Al₂O₃/desilicated ZSM-5 catalysts in the CO₂ hydrogenation reaction for DME production.

Materials and Methods

HZSM-5 zeolite used as support was synthesized according to the procedure disclosed in patent EP1707533 (A1). The desilicated ZSM-5 zeolites were prepared using a method previously reported in the literature [3]. For the metal phase, metal nitrates (Cu, Zn, Al) were precipitated using sodium carbonate at 70 °C. The precipitate was calcined at 325°C. The Cu:Zn:Al ratios were 4.5:4.5:1 and 6:3:1. After that, the zeolite was dispersed in water, and metal phase was added. The mixture was stirred, dried, and calcined at 325 °C. Then, two catalysts were obtained: 4.5CZA/ZSM-5 and 6CZA/ZSM-5. The catalysts were characterized by X-ray diffraction (XRD), N₂ physisorption, Scanning Electron Microscopy (SEM), Temperature-Programmed Reduction (TPR), Infrared Spectroscopy (IR) and NH₃ Temperature Programmed Desorption (NH₃-TPD). CO₂ hydrogenation was performed at 240–280°C and pressures of 28 and 40 bar, with a different value of space velocity (GHSV) of 2,400–14,400 mL h⁻¹ g⁻¹ and CO₂/H₂ = 3.0. Prior to reaction, the catalysts were reduced at 320 °C for 1 h under H₂.

Results and Discussion

XRD results of desilicated samples showed the lines corresponding to the MFI structure, indicating that the crystalline structure of the zeolite was preserved after alkaline

treatment. Characteristic lines of aluminum, copper, and copper-zinc oxides were also observed. The Cu metallic particle size was similar for 4.5CZA/ZSM-5 and 6CZA/ZSM-5 (18–20 nm). Nitrogen adsorption-desorption isotherms of the supports showed the appearance of hysteresis loops indicating the formation of mesopores, corresponding to type IV. Catalytic tests at 240°C, 28 bar, and 3600 mL h⁻¹ g⁻¹ showed that 6CZA/ZSM-5 achieved the highest CO₂ conversion and DME selectivity, attributed to its greater number of weak and medium acidic sites, as indicated by NH₃-TPD analysis. The effect of reaction conditions was studied in more detail for this sample. Increasing reaction temperature, increased CO₂ conversion and CO selectivity but resulted in a decrease in DME selectivity (Figure 1). The reverse water gas shift reaction, responsible for CO synthesis, is an endothermic reaction, making CO formation more favorable at high temperatures. At 240°C, raising the pressure to 40 bar did not significantly affect CO₂ conversion but slightly decreased CO formation while increasing DME selectivity. The reduction in the space velocity improved the CO₂ conversion and DME selectivity. The reaction temperature and GHSV had a more pronounced impact on the catalytic performance compared to the effect of pressure. The best performance was obtained at 240°C, 2,400 mL h⁻¹ g⁻¹ and 28 bar, achieving a DME selectivity of 68 %.

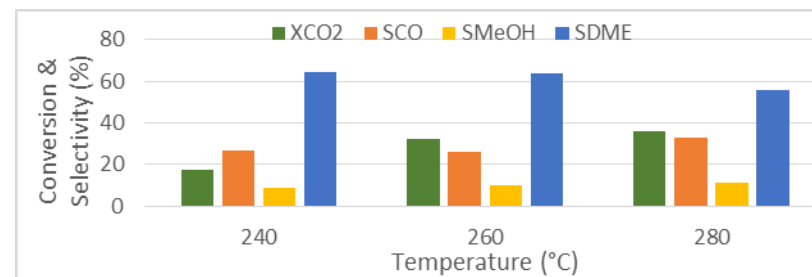


Figure 1. Catalytic performance of 6CZA/ZSM-5 (28 bar and GHSV = 3,600 mL h⁻¹ g⁻¹)

Significance

This study highlights that desilicated ZSM-5 zeolite combined with the Cu-ZnO-Al₂O₃ phase is a highly effective catalyst for CO₂ hydrogenation to DME. It achieves superior CO₂ conversion and DME selectivity compared to literature-reported results under similar reaction conditions, offering a valuable contribution to overcoming one of the primary challenges in CO₂ utilization.

References

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