Methanol Synthesis from CO_2 and Hydrogenation over Cu-ZnO-black TiO_2 Catalysts: Effect of Copper Loading and ZnO Promotion

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Abstract

The thesis focused on methanol synthesis from CO_2 and H_2 over Cu-ZnO-black TiO_2 catalysts with two different copper loadings (15 and 30 wt%). Additionally, the effect of ZnO addition on one of the catalysts was studied, evaluating its activity and selectivity under reaction conditions (WHSV:10h^{-1}, Temperature: 180-300°C, Pressure:20 bar)

Introduction

The global need for sustainable energy solutions has surged in response to the escalating impacts of climate change, largely driven by anthropogenic greenhouse gas (GHG) emissions [1]. Carbon dioxide (CO_2), the predominant GHG, is responsible for nearly 75% of global emissions, primarily arising from fossil fuel combustion in energy production, industrial operations, and transportation sectors [3]. Meeting the targets of the Paris Agreement—which seeks to limit global temperature rise to well below 2°C above pre-industrial levels—requires significant reductions in CO_2 emissions and a transition toward carbon-neutral energy systems.In this context, renewable and low-carbon fuels, such as methanol produced via CO_2 hydrogenation, are gaining strategic importance [3]. Methanol is a versatile chemical feedstock and energy carrier, increasingly viewed as a promising green fuel [3]. Traditionally synthesized from fossil-based sources like natural gas and coal, methanol production has contributed substantially to GHG emissions. However, a shift toward using CO_2 as a carbon source for methanol synthesis offers a compelling route to closing the carbon loop [3]. This process, known as CO_2 hydrogenation, involves the catalytic conversion of CO_2 and green hydrogen (H_2) into methanol. The principal advantage of this approach is the ability to generate methanol with a low carbon footprint, effectively turning CO_2 from a waste product into a valuable resource [3]. Catalyst selection is critical to achieving high selectivity and efficiency in this process. Research has extensively focused on optimizing catalytic formulations to improve CO_2 conversion, methanol selectivity, and catalyst longevity. Among the catalysts investigated, copper-based systems are the most widely studied for CO_2 hydrogenation. In particular, Cu-ZnO/Al_2O_3—historically used for methanol synthesis from syngas (CO and H_2)—remains a reference catalyst due to its robust activity and industrial relevance []. Recent advances have aimed at strengthening the interaction between copper and the oxide support to enhance CO_2 adsorption and activation. Numerous studies have demonstrated that supports rich in oxygen vacancies exhibit high activity for CO_2 hydrogenation. Accordingly, this study focuses on the use of Cu-ZnO catalysts supported on black titania, which possesses a high concentration of surface oxygen vacancies that enhance CO_2 adsorption and activation efficiency[4].

Experimental and Discussion

The experiments were conducted in a tubular stainless steel reactor (inner diameter: 20 mm) using a CO_2 and H_2 feed with a molar ratio of 30:70. All tests were performed under identical conditions: a weight hourly space velocity (WHSV) of 10 h^{-1}, a pressure of 20 bar, and a temperature range of 180–300°C. The catalysts evaluated in this study include 15Cu-bTiO_2 (15 wt.% Cu on black TiO_2), 30Cu-bTiO_2, and 15Cu-ZnO-bTiO_2. Initial tests were carried out on 15Cu-bTiO_2 and 30Cu-bTiO_2 to investigate the effect of copper loading on CO_2 conversion and methanol selectivity. CO_2 conversion was comparable for both samples at lower temperatures (180–200°C); however, the 30Cu-bTiO_2 catalyst exhibited higher conversion at elevated temperatures (250°C and 300°C), attributable to its higher copper content (Figure 1). In contrast, methanol selectivity was not significantly affected by copper loading. As shown in Figure 2, both catalysts exhibited similar selectivity profiles across the entire temperature range. Subsequently,

the effect of ZnO addition was studied by testing the 15Cu-ZnO-bTiO$_2$ catalyst. A reduction in CO_2 conversion was observed at 250°C and 300°C, while conversion remained comparable to the previous catalysts at lower temperatures. Notably, methanol selectivity differed from the unpromoted catalysts. The ZnO-promoted sample maintained high selectivity at low temperatures and demonstrated significantly enhanced selectivity at 250°C and 300°C. These results suggest that ZnO addition improves methanol selectivity by suppressing undesired side reactions, such as the reverse water-gas shift (RWGS) reaction.

Conclusion

In this study, Cu-ZnO-bTiO$_2$ catalyst was tested, in particular, it was studied how Cu-loading and ZnO addition influence the CO_2 conversion and methanol selectivity. Cu-loading results to influencing only the conversion, which increases with the Cu-content, but not the selectivity that remains the same. ZnO addition influences both the CO_2 conversion and the methanol selectivity. Compared to the sample without ZnO, it shows lower CO_2 conversion at higher temperatures and higher methanol selectivity.

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Referencies

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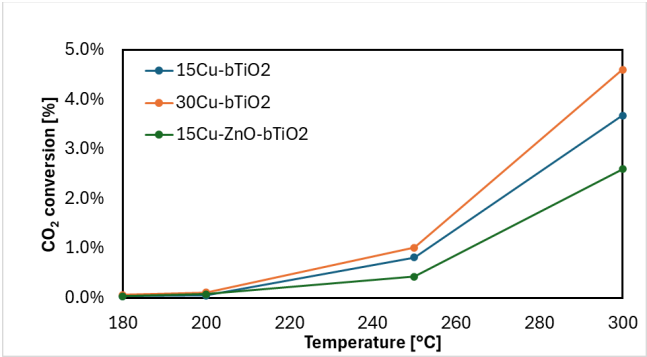

Figure 1 CO2 conversion for the three tested catalysts

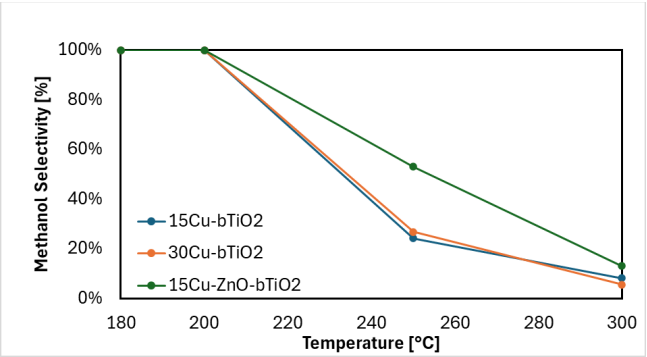

Figure 2 methanol selectivity for the three tested catalysts