

Vapor-phase low-temperature methanol synthesis from CO₂-containing syngas via self-catalysis of methanol and Cu/ZnO catalysts prepared by solid-state method

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1. Introduction

Methanol is a kind of clean liquid fuel which can be applied for vehicles or fuel cells.¹⁾ Methanol is also an important feedstock for the production of multiple chemicals such as formic acid, acetic acid, dimethyl ether (DME), dimethoxymethane (DMM), methyl methacrylate, methyl formate (MF), formaldehyde (FA), methyl tert-butyl ether (MTBE) and so on.²⁾ Methanol can also be converted to aromatics, olefins and gasoline.³⁾ Owing to its wide application and demand, it is necessary to develop highly efficient methanol synthesis process and catalyst.

The present work was conducted in two aspects. One was the effect of oxalic acid (H₂C₂O₄) amount on the physicochemical properties and the corresponding catalytic activity of Cu/ZnO catalysts. The other was the influence of various parameters on low-temperature methanol synthesis reaction. The structure-performance relationship was evaluated via detailed characterizations. We found that the oxalic acid amount affected not only specific surface area and Cu⁰ surface area, but also acidic and basic properties, Cu-ZnO interaction, chemical adsorption capability, and amount of CO and H₂. Based on these findings, the correlation among the physicochemical properties, particularly the Cu⁰ surface area, the number of strongly acidic sites and moderately basic sites of Cu/ZnO catalysts, and the catalytic performance was clarified. The present low-temperature methanol synthesis route with methanol as promoter altered the traditional methanol synthesis while the oxalic acid-assisted solid-state method provided a hopeful strategy for producing highly efficient Cu/ZnO catalysts.

2. Experimental

Cu/ZnO catalysts were prepared by a facile solid-state method. 0.01 mol Cu(NO₃)₂•3H₂O, 0.01 mol Zn(NO₃)₂•6H₂O and 0.00-0.12 mol oxalic acid (H₂C₂O₄) were physically mixed in a mortar and ground for 30 min in air. The H₂C₂O₄/(Cu+Zn) molar ratios were 0/1, 1/1, 2/1, 3/1, 4/1, 5/1 and 6/1. The acquired homogeneous metal-oxalic acid complexes were dried at 393 K for 12 h, followed by calcination at 673 K in air for 3 h. Finally, the calcined samples were reduced by H₂/He (5/95, v/v)

at 513 K for 4 h to obtain Cu/ZnO catalysts.

3. Results and Discussion

The performances of various Cu/ZnO catalysts were studied for vapor-phase low-temperature methanol synthesis from syngas, without or with methanol as promoter in a continuous fixed bed reactor. The results are exhibited in Fig. 1. Without the addition of methanol promoter, the total carbon conversion of C₀-Red catalyst was as low as 3.8%. By improving H₂C₂O₄/(Cu+Zn) molar ratio from 0/1 to 4/1, the total carbon conversion had an obvious increase from 3.8% to 45.2%. Further increasing H₂C₂O₄/(Cu+Zn) molar ratio led to decline of total carbon conversion. If 0.003 mL/min methanol was introduced, the total carbon conversion of various Cu/ZnO catalysts clearly increased to 3.9%, 17.7%, 26.2%, 32.0%, 50.7%, 38.4% and 7.5%. This finding clearly implied that methanol synthesis reaction was accelerated by introducing methanol promoter into reaction system even at low temperatures. Among all the catalysts, the C₄-Red prepared with H₂C₂O₄/(Cu+Zn) molar ratio of 4/1 exhibited the best catalytic activity.

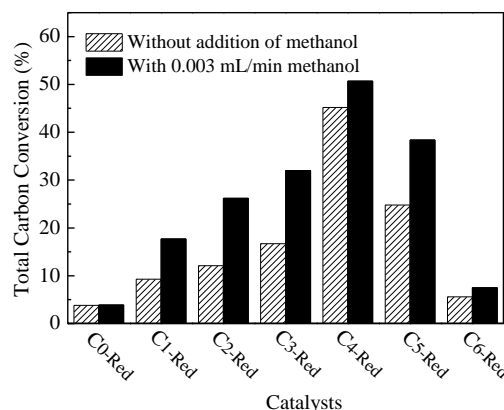


Fig. 1 The fixed-bed reaction results of various Cu/ZnO catalysts. Reaction conditions: temperature = 473 K, total pressure = 7.0 MPa, catalyst weight = 0.5 g, H₂/CO₂/CO/Ar = 59.86/4.90/30.10/5.14 (volume ratio), W/F = 12.4 g · h/mol, GHSV = 1800 ml g_{cat}⁻¹ h⁻¹.

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