UNIVERSITI TEKNOLOGI MARA

PREPARATION OF Cu-Zn BASED CATALYSTS VIA ULTRASONIC SPRAY PRECIPITATION METHOD FOR METHANOL SYNTHESIS

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The potential of various Cu-Zn-based catalysts in a form of non-hybrid (triple and quadruple metallic) as well as hybrid (multi-metallic with ZSM-5 zeolite) catalyst formulation are being explored for converting CO_2 into methanol. The application of the new preparation method, namely, Ultrasonic Spray Precipitation (USP) is advantageous in improving physicochemical properties of catalysts. This is based on the fact that the spraying action generates microdroplets of catalyst precursors, providing higher surface area contact during the precipitation stage. Meanwhile, the incorporation of an ultrasonic effect can physically alter the surface morphology of the catalyst. This produces much finer and more uniform particles, which also improve the overall physicochemical characteristics. Study on the effect of different preparation methods have shown that the USP-prepared catalyst outperformed the conventionally prepared (CP) catalyst for CO_2 conversion by 20.9% and also improved the methanol selectivity and yield by 2.7% and 27%, respectively. In terms of the elemental composition aspect, the quadruple metallic formulation (CZAZ catalyst) has shown an enhanced characteristics, particularly in reducibility, Cu metal dispersion and total basic sites. These qualities have translated into the highest CO_2 conversion at 20.1% as well as methanol yield at 0.45 $g.ml^{-1}.h^{-1}$ in CO_2 hydrogenation reaction. On the other hand, by adding zeolite (ZSM-5) in the multi-metallic component in a form of hybrid-catalyst formulation, it improves characteristics such as particle size distribution and its uniformity, bulk surface area and total acid sites, which have reflected the catalyst selectivity, especially in reducing the undesired by-product of CO. These results had proven the role of zeolite in retarding the reverse water gas shift (RWGS) reaction had instead facilitated the consecutive third reaction to shift the equilibrium back into the direction of methanol synthesis and other related hydrocarbons. The influence of reaction condition of temperature and pressure has also aligned with the thermodynamics theoretical calculations. Both non-hybrid (CZAZ) and hybrid (CZAZ-Z) catalysts have exhibited an identical trend in relation to temperature and pressure variations during CO_2 hydrogenation reaction at a fixed gas hourly space velocity (GHSV). The CO_2 conversion and methanol yield increased significantly with increasing pressure but decreased strongly at temperature beyond 520 K. This trend is in-line with the thermodynamic principle that methanol synthesis via CO_2 hydrogenation reaction is exothermic, thus favouring high pressure and low temperature condition. As a conclusion, application of the USP method during preparation stage has proven to enhance the overall physicochemical properties of Cu-Zn based catalysts. These enhancements have promoted better catalytic performance of the catalysts in methanol synthesis with improved CO_2 conversion, methanol selectivity and yield as compared to those of conventional method.

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