Catalytic CO_2 hydrogenation to methanol over encapsulated Cu/ZnO based catalysts: Synthesis, characterization and in situ mechanism determination

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Combustion of carbonaceous fuels like coal, oil and natural gas cause atmospheric concentrations of CO_2 to continue to rise. CO_2 could be utilized as starting material in a catalytic process to produce valuable chemicals and fuels such as synthesis gas (CO and H_2 mixture), oxygenates (alcohols, ethers), or hydrocarbons. The development of an appropriate heterogeneous catalyst that will actively and selectively convert mixtures of CO_2 and H_2 to methanol as a liquid fuel additive or surrogate, can significantly contribute to a more widespread large scale utilization of CO_2 and renewable energy. The most active catalyst for methanol production is copper-zinc-based materials which are widely used for syngas transformation to methanol. These catalysts also show promising results in CO_2 hydrogenation, however, their activity value is still far from commercial utilization and further catalyst improvement is still required [1-3].

The main goal of this research project was to investigate mechanism of direct selective hydrogenation of CO_2 into CH_3OH over Cu/ZnO based catalyst. During catalyst design, attention was focused on maintaining a high dispersion and intimate contact between Cu and ZnO phases for highest possible number of active sites and consequently highest activity. For this reason nanosized Cu/ZnO clasters were encapsulated into zeolite framework. CuO and ZnO phases were introduced by ion exchange and precipitation methods. Influence of precipitation agent (Na_2CO_3/Na_2S) during preparation step was carefully investigated. It was found that precipitation with 0.05 M Na_2CO_3 results in superior catalytic properties. Furthermore, several zeolite structures (FAU and LTA) with different Si/Al ratio were investigated. Synthesized catalyst samples were further examined by a variety of relevant characterization techniques in order to determine their morphological and surface properties, as well as mechanism of CO_2 hydrogenation to methanol. Accordingly to results of *operando* XRD investigation, encapsulation of CuO and ZnO into zeolite framework prevents nano-particles sinthering and aggregation during catalytic test. It was confirmed that reducibility of ZnO (*operando* XAS) and formation of Cu-Zn alloy (*operando* XRD) play a crucial role in investigated process. The higher the amount of reduced Zn^0 species were presented in the catalyst during reaction conditions, the higher the overall activity and selectivity to methanol were.

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