Experimental Study of Cu-ZnO-ZrO₂/Hydrotalcite Catalyst for Sorption-Enhanced Hydrogenation of CO₂ to Methanol

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Abstract

CO₂ utilization is increasingly seen as a potential mitigating component of CO₂ emissions control, in addition to carbon capture and storage (CCS). Specifically, a novel carbon cycle was put forward recently centred on methanol and dimethyl ether (DME) so that the generated CO₂ can be converted to clean energy, easing the climate crisis and energy shortage at the same time. However, methanol synthesis via CO₂ hydrogenation remains a challenge industrially due to the restricted CO₂ conversion and methanol selectivity, though great efforts have been paid to enhance the properties of catalysts, e.g., importing additive elements, promoting active site dispersions, elevating surface areas, etc. Among those modifications, the sorption-enhanced strategy attracts our special interests as a consequence of its remarkable promotion by breaking the original thermodynamic equilibrium in reaction systems. It occurs because the adsorption effect will help drive reactant molecules onto active sites and, meanwhile, removing products as they are made. This provides a novel idea to introduce adsorbents to catalysts to obtain better properties, so hydrotalcite-like compounds (HTLCs) are expected to be beneficial in CO₂ hydrogenation processes as efficient high-temperature binary adsorbents of CO₂ and water vapor. Herein, Cu-ZnO-ZrO₂ (CZZ), prepared by the common co-precipitation method, and commercial hydrotalcite (HT) were physically mixed varying the CZZ/HT ratios to explore their interactions and thus impact on catalysis performance, which were then analyzed on the micro-reactor apparatus equipped with an Agilent GC. Crystals of single CZZ and HT were confirmed by characteristic peaks in the XRD spectrum. The former has an average particle diameter of approximately 20 nm according to XRD results, which is essential for efficient catalysis. Nevertheless, the CZZ-HTs simply show as overlays of single CZZ and HT without other peaks. The BET surface areas of CZZ and activated HT are 35.8 and 175.6 m²/g, respectively, and a linear trend is also observed in CZZ-HTs between BET surface area and CZZ/HT ratio. The aforementioned results both demonstrate that the CZZ and HT still remained separate at the nanoscale after mixing. Isolated as they seemed, however, excellent catalytic performance were achieved. In a typical process, the CO₂ conversion scores the same level as single component Cu-ZnO-ZrO₂ catalyst, yet the methanol selectivity is 50 % higher, reaching over 80 % at 250 C, 30 bars. The reason results from synergies between CZZ and HT. The former provides active sites for CO₂ hydrogenation, while the later provides sites for CO₂ and H₂O adsorption. Accordingly, CO₂ molecules are easily caught and react on copper sites, and produced H₂O molecules are then quickly removed from the copper surface,
providing the CZZ-HTs with considerable CO$_2$ conversion and methanol selectivity even at high space velocities. The present work provides a simple method to elevate catalytic performance of traditional copper based catalysts by introducing hydrotalcites, promoting the catalytic properties in aspects of methanol selectivity. Since the as-obtained catalyst can also be easily fine-tuned by changing the CZZ/HT ratio, it exhibits promising applications in methanol synthesis by CO$_2$ hydrogenation.