Fine-Tuning Copper-Based Nanocatalysts for Optimized CO_2 Conversion

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INTRODUCTION. Over the past few decades, nanomaterials have gained significant attention due to their unique physicochemical properties at the nanoscale, which differ from bulk materials and enhance functionalities. Copper-based nanocatalysts, in particular, are attractive in catalysis because of their abundance, low cost, and effective catalytic properties. Unlike noble metals like platinum or palladium, copper offers a more economical alternative and plays a key role in catalytic processes such as CO_2 hydrogenation, which is crucial for reducing CO_2 emissions and producing valuable chemicals like methanol. The $Cu/ZnO/Al_2O_3$ catalyst has been used for this reaction since the early 20th century, but factors like particle shape, size, and crystallinity remain underexplored [1]. The difficulty in synthesizing copper nanoparticles due to its high oxidation potential complicates the control over size and morphology [2]. In this study, we report the synthesis of Cu NPs with various shapes and crystallinity, as well as Cu@ZnO core-shell nanoparticles, using a seed-mediated growth method. We also present initial findings on the catalytic activity of these systems for CO_2 hydrogenation to methanol.

EXPERIMENTAL. In this study, Cu NPs with controlled morphologies, were synthesized from copper (I) halide precursors like CuBr and CuCl. The synthesis parameters, including reaction temperature, heating rate, precursor concentration, and ligand type (TOP, TOPO etc)), were carefully controlled [3]. The NPs were characterized using high-resolution TEM, STEM-HAADF, and EELS mapping to assess morphology and crystallinity, while XPS was used to analyze the ligands. Cu@ZnO NPs were then synthesized using a seed-mediated growth method with varying ZnO coverage. These core-shell NPs were further evaluated for their catalytic performance.

RESULTS AND DISCUSSION. The synthesis of Cu NPs with controlled morphologies—ranging from cubic to spherical to octahedral—was successfully achieved with particle sizes between 30 and 60 nm. XPS analysis revealed the nature of the ligands, providing insights into their role in stabilizing the nanoparticles. The Cu@ZnO core-shell nanoparticles were then synthesized, with the ZnO coverage ratio varying in the seed-mediated growth process. When tested under real conditions for the CO_2 hydrogenation reaction, at high temperatures (200-270°C) and high pressures (31 bar), the Cu@ZnO nanoparticles exhibited promising catalytic properties. The study revealed that the crystallinity and morphology of the copper nanoparticles significantly influenced the reactivity and selectivity of the reaction. Specifically, the exposed crystalline faces of the copper nanoparticles were found to promote higher selectivity, reducing the formation of undesired by-products. Moreover, a greater number of Cu-ZnO interfaces contributed to higher yields of methanol and methanol-derived products, such as dimethyl ether (DME) and methyl formate (MF). These findings underline the importance of nanoparticle structure in enhancing the catalytic performance of copper-based catalysts for CO_2 hydrogenation**.**

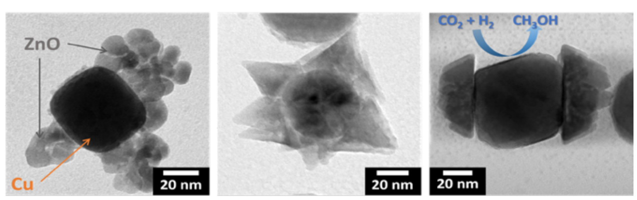

Fig. 1 TEM images of (left to right) cubic, quasi spherical and octahedral copper NPs covered by zinc oxide shell.

CONCLUSION. The knowledge gained from this study can be extended to other catalytic systems, such as $Cu@ZrO_2$ or $Cu@TiO_2$, by adjusting synthesis parameters (precursors, temperature, reaction duration). These materials will take advantage of the ZrO_2 selectivity for methanol and the reactivity of TiO2 in reduction processes, thus optimizing CO_2 conversion.

REFERENCES

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