Nano-whisker-functionalized SiC foams coated with structured $CuO/ZnO/Al_2O_3$ catalysts for efficient CO_2 hydrogenation to methanol

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Highlights

- CZAC-E@SNW/SiC achieves 32 mol_{MeOH} kg_{cat}^{-1} h^{-1} STY and >97% selectivity under optimal conditions.
- CTAB reduced CuO crystal size from 4.7 to 2.6 nm and improved copper dispersion.
- DRIFTS confirms pathway shift from formate to CO hydrogenation on CTAB catalyst.
- The catalyst retains >94% methanol selectivity over 100 h with excellent stability.

1. Introduction

CO_2 hydrogenation to methanol is a pivotal Carbon Capture and Utilization (CCU) route. However, it is hindered by the poor mass/heat transfer and rapid deactivation of traditional $CuO/ZnO/Al_2O_3$ (CZA) powder catalysts in packed-bed reactors.

To overcome these limitations, we employ an unconventional design strategy that combines structured catalysis with reactor-adapted engineering. Specifically, we use a hierarchical SiC nano-whisker-modified SiC foam (SNW/SiC) as a monolithic support to enhance transfer properties, coupled with CTAB-assisted ethanolic impregnation to achieve optimal active site dispersion. This synergistic approach is designed to create a more efficient and robust catalytic system, directly contributing to the development of innovative applications for advancing carbon neutrality solutions.

2. Methods

SiC and SNW/SiC supports were prepared as reported [1]. $Cu(NO_3)_2/Zn(NO_3)_2/Al(NO_3)_3$ (6:3:1) precursors dissolved in water/ethanol; CTAB added for modified samples. Supports: dip-coating, ultrasonication, drying (150 °C, 5 min), calcination (350 °C, 5 min), annealing (400 °C, 2 h). Catalysts denoted by solvent (W=water, E=ethanol), CTAB (CZAC), support (SiC/SNW/SiC); powder: CZAC-E. Characterization includes ICP-OES, XRD (5–90°), SEM-EDS, H_2-TPR, XPS, N_2O chemisorption and in situ DRIFTS (H_2/D_2 tracing). Tests were conducted in a high-pressure fixed-bed reactor. Monolithic (7.5 g) or powder (1.5 g, mixed with 6 g SiC) catalysts were reduced (H_2, 275 °C, 2 h) prior to reaction. Reaction conditions: 3 MPa, $H_2/CO_2/N_2$=30:10:10 sccm, 175–300 °C. Products were analyzed via online GC (TCD/FID). CO_2 conversion, product selectivity, and methanol space-time yield (STY) were calculated.

3. Results and discussion

Ethanol solvent (low surface tension, ~22.1 mN m^{-1}) enabled higher CZA loading (23%) than water (8%). CTAB addition further increased loading to 26% for CZAC-E@SNW/SiC (vs. 21% for CZAC-E@SiC), attributed to SNW's high surface area and capillary forces (Figure 1a). XRD (Figure 1b) showed CTAB reduced CuO crystallite size from 4.7 nm (CZA-E) to 2.6 nm (CZAC-E). SEM-EDS revealed CZAC-E formed uniform ~100 nm particles with homogeneous Cu/Zn/Al distribution (vs. ~200 nm microrods in CZA-E). XPS confirmed CZAC-E had higher surface Cu/Zn ratio (0.72 vs. 0.11) and enhanced metal-support interactions. H_2-TPR and N_2O chemisorption showed CZAC-E had stronger CuO-support interaction and higher Cu dispersion (0.68% vs. 0.40%).

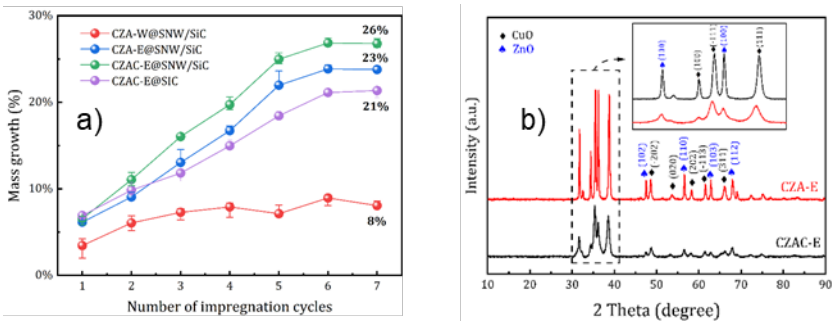

Figure 1. a) Mass growth of the CZA catalysts on SiC foam composites; b) Comparative XRD patterns of the CZA-E and CTAB-modified CZAC-E catalysts.

CZAC-E@SNW/SiC exhibited optimal performance: 15% X_{CO2}, >97% methanol selectivity, and 32 mol_{MeOH} kg_{cat}^{-1} h^{-1} STY at 275 °C (Figure 2). Structured catalysts outperformed powder CZAC-E due to SiC foam's superior mass/heat transfer. SNW suppressed RWGS, delaying CO formation to higher temperatures. Long-term stability tests showed negligible deactivation: X_{CO2} remained ~15% and methanol selectivity >95% over 100 h.

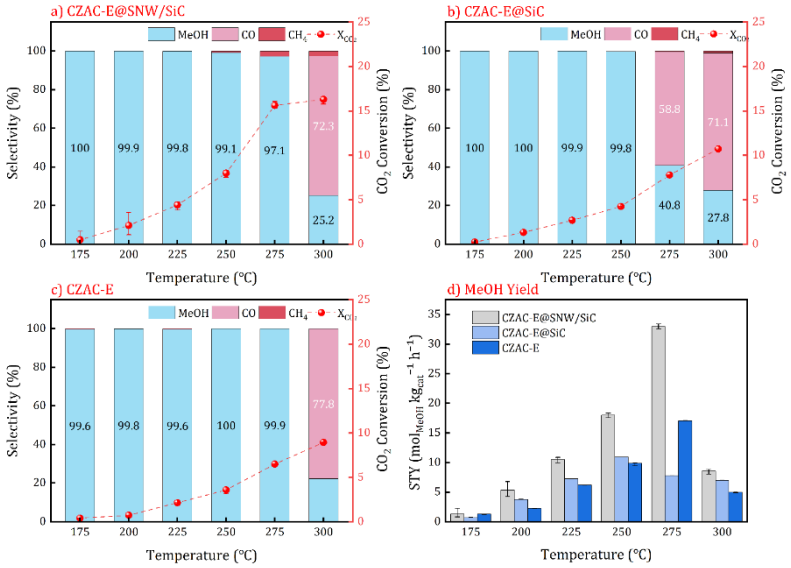

Figure 2. Catalytic performance of the synthesized catalysts in CO_2 hydrogenation to methanol. CO_2 conversion and product selectivity for a) CZAC-E@SNW/SiC, b) CZAC-E@SiC, c) CZAC-E, and d) the STY of MeOH over different catalysts

In situ DRIFTS showed CZA-E followed the formate pathway (HCOO* intermediates). CZAC-E shifted to the CO hydrogenation pathway, with strong CO* signals and weak HCOO* peaks. Isotopic tracing ($H_2 \rightarrow D_2$) confirmed HCOO* as active intermediate for CZA-E, while CZAC-E showed no isotopic shift, supporting transient intermediates (e.g., HCO*) in CO hydrogenation.

4. Conclusions

A high-performance CZAC-E@SNW/SiC catalyst was developed via CTAB-assisted ethanolic impregnation. The dual-scale design (macro SiC foam for mass/heat transfer; micro SNW/CTAB for active site regulation) achieved 32 mol_{MeOH} kg_{cat}^{-1} h^{-1} STY, >97% selectivity, and excellent long-term stability. CTAB reduced CuO crystal size and enriched surface Cu, shifting the reaction pathway from formate to CO hydrogenation. This catalyst offers great potential for industrial CO_2-to-methanol conversion, providing a practical CCU solution.

References

[1] Y. Jiao, X. Yang, C. Jiang, C. Tian , Z. Yang, J. Zhang, J Catal. 332 (2015) 70-76

Keywords
Structured catalyst; SiC foam; CO_2 hydrogenation; methanol synthesis