Engineering Ni-Co bimetallic interfaces for ambient plasma-catalytic CO_2 hydrogenation to methanol

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Abstract: Plasma catalysis enables CO_2 hydrogenation to methanol under ambient conditions, overcoming thermal catalysis limitations. A bimetallic Ni-Co catalyst achieves 46% methanol selectivity and 25% CO_2 conversion at 35 °C and 0.1 MPa. In situ FTIR and DFT analyses reveal that engineered bimetallic sites reduce steric hindrance, enhancing reaction pathways. This study highlights the potential of bimetallic catalysts for efficient and sustainable CO_2 conversion to fuels.

1. Introduction

Converting CO_2 to methanol is vital for a sustainable net-zero economy, yet conventional thermal methods require high temperatures and pressures with low efficiency. Non-thermal plasma (NTP) enables CO_2 hydrogenation under mild conditions but faces challenges in methanol selectivity. This study introduces a low-cost Ni-Co catalyst achieving efficient plasma-catalytic methanol synthesis at 35 °C and 0.1 MPa. In situ FTIR and DFT analyses reveal Ni-Co interfaces as key active sites, advancing sustainable CO_2 conversion and green fuel production.

2. Materials and Methodology

2.1 Synthesis of Ni-Co Catalysts

Ni-Co/Al_2O_3 catalysts were synthesized via ultrasonic incipient-wetness impregnation. $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in deionized water and mixed with Al_2O_3 support. The slurry was ultrasonically treated at 60 °C for 2 h, aged overnight, dried at 110 °C for 5 h, and calcined at 500 °C for 5 h. Catalysts (40–60 mesh) were reduced in Ar/H_2 (3:2, 50 mL/min) at 550 °C for 5 h, confirmed by H_2-TPR and XRD analyses. Catalysts were labeled as *xNi(10-x)Co* based on Ni/Co ratios.

2.2 Catalytic Test

Catalytic performance was tested in a temperature-controlled DBD reactor at 35 °C with a CO_2/H_2 ratio of 1:3 and a flow rate of 32 mL/min. Plasma conditions included a discharge length of 50 mm, a gap of 1 mm, 30 kV peak voltage, and 9.2 kHz frequency. Tests used 500 mg of catalyst, with stability measured over 14 hours. Products were analyzed by gas chromatography with TCD and FID detectors, with oxygenates quantified via a DB-WAX column. Each measurement was repeated three times with < 4% error.

3. Results and Discussion

Plasma-catalytic CO_2 hydrogenation involves both plasma gas-phase and surface reactions, with surface reactions playing a key role in product distribution. Activity tests showed 7Ni3Co achieved the highest CO_2 conversion and methanol selectivity (~46%), three times higher than 10Ni or 10Co, with a methanol space-time yield of 4.7 mmol g_{cat}^{-1} h^{-1}. In contrast, monometallic catalysts favored RWGS, producing higher CO selectivity. A physical Ni-Co mixture performed similarly to monometallic catalysts, emphasizing the importance of Ni-Co interactions. 7Ni3Co also exhibited the highest

methanol turnover frequency and minimal carbon deposition (< 2%), confirming its superior performance under mild conditions.
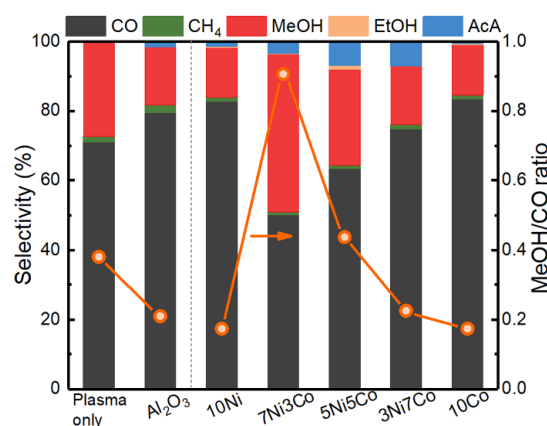
Fig. 1. Product selectivity and MeOH/CO selectivity ratio in CO_2 hydrogenation over Ni-Co catalysts. (SEI 15 kJ L^{-1}, 35 °C, 0.1 MPa, sampling time 1.5 h)

4. Conclusion

This study highlights the significant potential of plasma-catalytic CO_2 hydrogenation to methanol using Ni-Co bimetallic catalysts. The metallic Ni-Co interface, via the E-R mechanism, promotes efficient methanol synthesis with a low energy barrier (0.63 eV), offering critical insights for tailoring catalytic pathways and enhancing selectivity under ambient conditions.

References

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