Structure-Performance Relationship of Cu-Nb Catalysts Supported on MOF-Derived CeO_2 Prepared by Different Methods for the Low-Temperature Water-Gas Shift Reaction

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ABSTRACT

The development of highly active and stable catalysts is essential for improving the low-temperature water-gas shift (LTS-WGS) reaction for hydrogen production. The effect of Cu and Nb incorporation sequence on the physicochemical properties and catalytic performance of Cu-Nb catalysts supported on MOF-derived CeO_2 was systematically investigated. Five catalysts with different preparation routes, including Cu/MDNC, Cu-Nb/MDC, Nb/MDCC, MDCNC, and a conventional prepared Cu-Nb/CeO_2, were synthesized and characterized using N_2 physisorption, XRD, H_2-TPR, XPS, SEM-EDS, oxygen storage capacity (OSC/OSCC), and N_2O chemisorption. The catalytic performance was evaluated in the LTS-WGS reaction over the temperature range of 200-400 °C at a gas hourly space velocity (GHSV) of 22,097 $mL \cdot gcat^{-1} \cdot h^{-1}$. The preparation sequence substantially affected the Cu crystalline structure, reducibility, surface chemical states, morphology, and oxygen-related properties. Among the catalysts, Cu/MDNC, prepared by pre-incorporating Nb during MOF synthesis followed by Cu impregnation, exhibited the highest CO conversion, reaching 74.3% at 350 °C. Its superior performance was associated with the lowest dominant H_2-TPR temperature (164.2 °C), the highest low-temperature reducible Cu fraction (91%), and the highest Cu^+ fraction (79.96%), together with relatively stable Cu crystallites and low coke formation after reaction. However, no single parameter, including BET surface area, Cu^0 dispersion, oxygen-defect concentration, or total oxygen storage capacity, was sufficient to explain the catalytic performance. Instead, the observed activity was governed by the combined effects of Cu reducibility, surface Cu oxidation state, interfacial accessibility, oxygen-related properties, and structural stability. Notably, Cu/MDNC maintained a stabilized CO conversion of approximately 60% after 200 h on stream, demonstrating sustained catalytic performance under prolonged LTS-WGS operation. Overall, these results demonstrate that the sequence of metal incorporation is an important synthesis parameter for controlling the Cu-Nb-CeO_2 structure and redox properties, with Nb pre-incorporation into the MOF-derived framework followed by Cu deposition providing the most favorable combination of properties for LTS-WGS.

Keywords: Cu-Nb catalyst/ MOF-derived CeO_2/ Cu-Nb incorporation sequence/ Low-temperature water-gas shift/ Structure-performance relationship