Alkali-decorated microenvironments aid Cu single atom catalysts in CO_2 hydrogenation

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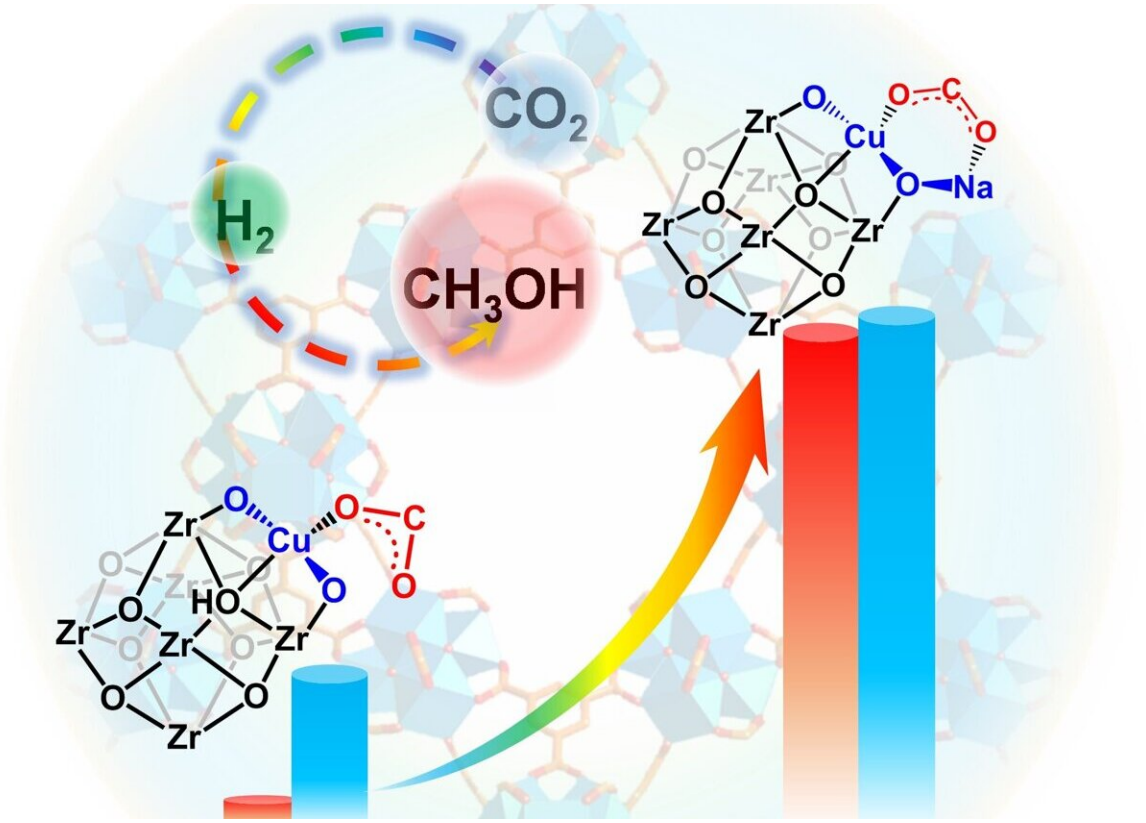

The performance of carbon dioxide hydrogenation using the Cu single atom catalysts without (left) or with (right) the presence of Na^+-decorated microenvironment (reaction conditions: CO_2/H_2 volume ratio of 1/3 with reaction pressure of 3.5 MPa and reaction temperatures from 150 to 275°C.). The red columns represent the space time yield of methanol, while the blue columns represent the selectivity of methanol. Notably, the introduction of Na^+-decorated microenvironment has significantly enhanced the catalytic performance of the Cu single-atom catalysts. Credit: Science China Press

Since the advent of industrial revolution, the accumulation of carbon dioxide (CO_2) in the Earth's atmosphere has raised significant environmental and climate concerns. As a response to this pressing challenge, the conversion of CO_2 into chemicals and/or fuels through direct hydrogenation has emerged as a widely recognized and imperative strategy for mitigating both CO_2 emissions and fossil fuel consumption.

Among the array of catalysts investigated for CO_2 hydrogenation, copper (Cu)-based catalysts have garnered increasing attention for their promising potential in the production of methanol. However, despite the promising catalytic activity exhibited by Cu-based catalysts, their practical application in CO_2 hydrogenation faces a significant difficulty arising from the intrinsic reduction and aggregation tendencies of the Cu-based active centers, particularly at the elevated operating temperatures.

This propensity for reduction and aggregation could potentially result in larger Cu particles, consequently diminishing the CO_2 hydrogenation activity and leading to the generation of undesired CO byproducts. As a result, this pose a considerable impediment to simultaneously achieving the desired high catalytic activity and methanol selectivity, which are beneficial for large-scale industrial applications.

To address these challenges, the research team led by Professor Hai-Long Jiang from the University of Science and Technology of China (USTC) has proposed a novel strategy aimed at immobilizing and stabilizing single-atom Cu sites within a metal-organic framework-based catalyst by creating the Na^+ decorated microenvironment in close proximity. The work is published in the journal *National Science Review*.

Through comprehensive experimental and theoretical calculation investigations, they have uncovered the importance of Na^+-decorated

microenvironment around the single-atom Cu sites. This microenvironment plays a crucial role in maintaining the atomic dispersion of Cu sites during the CO_2 hydrogenation process, even at high temperatures reaching up to 275°C, through the electrostatic interaction between Na^+ and $H^{\delta-}$ species.

This exceptional stabilization effect of single-atom Cu sites has endowed the catalyst with excellent CO_2 hydrogenation activity (306 $g \cdot kg_{cat}^{-1} \cdot h^{-1}$), high selectivity to methanol (93%), and long-term stability, far surpassing its counterpart lacking the presence of Na^+.

This work not only advances the development of Cu-based catalysts for selective CO_2 hydrogenation to methanol, but also introduces an effective strategy for fabricating stable single-atom sites in advanced catalysis by creating alkali-decorated microenvironments in close proximity.

More information: Li-Li Ling et al, Promoted hydrogenation of CO2 to methanol over single-atom Cu sites with Na+ decorated microenvironment, *National Science Review* (2024). DOI: 10.1093/nsr/nwae114

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