

Impact of oxidation state on copper nanoparticle stability in industrial Cu/ZnO/Al₂O₃ hydrogenation catalyst

Xiansheng Li¹, Henrik Eliasson¹, Rolf Erni¹

¹Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, CH

Background

The escalating concentrations of atmospheric CO₂ represent an urgent challenge for the global climate system, driving intensive research efforts aimed at mitigating this trend through innovative strategies for CO₂ reduction, conversion, and sequestration. The catalytic conversion of CO₂ into liquid fuels and high-value chemicals emerges as a pivotal area of focus within the realm of environmental stewardship and energy efficiency. Among these strategies, the hydrogenation of CO₂ to methanol stands out as a particularly promising avenue for the effective large-scale deployment of CO₂ utilization technologies. The production of methanol through the conversion of CO₂ using green hydrogen obtained from sustainable energy sources like wind, solar, and biomass, serves the dual purpose of CO₂ utilization and the storage of renewable energy into chemical compounds.

The standard methanol catalyst Cu/ZnO/Al₂O₃ has been industrially applied for more than 50 years. Still, its efficacy is marred by exceeding 50% decline in activity within the initial weeks of operation, primarily due to thermal sintering and structural reconfigurations. It underscores the critical need for an in-depth exploration into the mechanisms underlying catalyst deactivation, with the ultimate goal of engineering more resilient catalyst systems. Previous studies attribute this deactivation to the sintering of copper, a process intimately linked to the dynamics and stability of Cu nanoparticles (NPs).

In the quest to elucidate the dynamic behaviors and migration patterns of NPs, electron microscopy stands as the method of choice. Specifically, in situ Transmission Electron Microscopy (TEM) offers unparalleled insights into catalyst structures under near-industrial operational conditions, including the intricate dynamics of nanoparticulate entities. This study, therefore, harnesses the power of in situ TEM to meticulously examine the behaviors of Cu NPs on industrial Cu/ZnO/Al₂O₃ catalysts throughout the entire CO₂ hydrogenation lifecycle, spanning activation, steady-state operation, and eventual deactivation. By focusing on the oxidation state of copper under varying operational conditions, this investigation seeks to unravel the complex interplay between the chemical state and the mobility of Cu NPs, with the overarching aim of fostering advancements in catalyst design and CO₂ conversion technologies.

Methods

In situ TEM experiments were carried out using a windowed gas cell nanoreactor (Climate, DENS solutions) comprising of two electron-transparent Si₃N₄ windowed chips. Commercial Cu/ZnO/Al₂O₃ catalyst (Alfa Aesar, 45776) was dispersed in ethanol and deposited on the bottom climate chip before constructing the climate holder and sealing the nanoreactor. The nanoreactor consists of a top and bottom chip of 50 nm and 30 nm thickness respectively. The internal temperature of the microreactor was accurately controlled by a 4-point probe method.

Microscopy measurements were conducted using a probe aberration-corrected FEI Titan Themis microscope operating at 300 kV. The beam convergence angle was set to approximately 26 mrad. EEL spectra were recorded with an ELA hybrid pixel direct electron detector from Dectris that was retrofitted with a CEFID energy filter from CEOS. The energy dispersion of the ELA detector was 0.747 eV per channel, and the dwell time was set to 1 s.

Results

Upon careful reduction following standard industrial procedures, the catalyst was activated, demonstrating significant changes in the behavior of Cu NPs across various stages of treatment, as monitored by in situ STEM and complemented by EDS and EELS analyses. Initially, under high vacuum at room temperature, Cu NPs exhibited stability with no discernible movement; the only observable change was the slight contraction of the overall catalyst structure. EELS indicated a pronounced white line, suggesting an oxidized state of copper.

Heating to 180°C under a 1 bar N₂ atmosphere triggered dynamics within Cu NPs, extending them towards the sample's edge to form larger entities. EDS data revealed Cu's segregation from Zn, highlighting Cu's higher mobility. This segregation could contribute to deactivation, as the Cu-Zn synergy is deemed crucial for catalytic activity. Notably, areas not subjected to electron beam exposure did not exhibit similar changes, suggesting that temperature or gas composition, in conjunction with beam interaction, might facilitate these dynamics. Post-sintering, EELS data suggested a reduction in Cu, with a diminished white line intensity and reduced mobility.

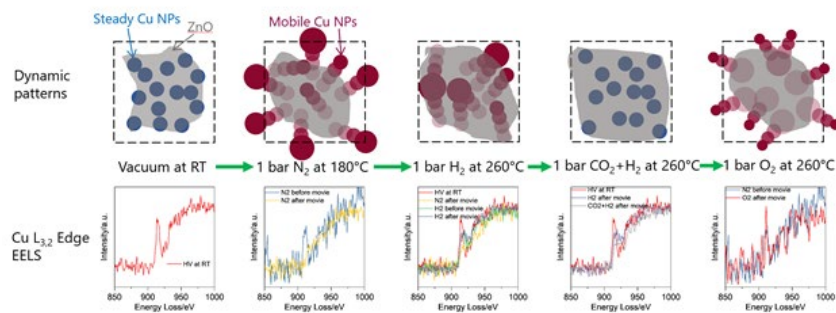
At 260°C in a 1 bar H₂ atmosphere, Cu NPs demonstrated sintering with no alteration in the white line intensity of Cu EELS before and after observation, indicating a stable oxidation state that was reduced compared to the initial state but more oxidized than beam-induced sintered NPs. Some level of dynamic behavior was still observed, albeit less than in N₂. Significant movements, such as approaching beyond the edge of the specimen, are indiscernible, suggesting that the beam-damage is minimized in H₂ atmosphere. Exposure to a 1 bar CO₂+H₂ atmosphere at 260°C resulted in immediate stabilization of Cu NPs, with EELS revealing a lower white line intensity, approaching that of beam induced sintered NPs.

Finally, under a 1 bar O₂ atmosphere at 260°C, Cu NPs were re-oxidized, regaining high mobility. The presence of O₂ also facilitates the redispersion of Cu NPs.

Conclusions

The comprehensive investigation delineates the nuanced mobility hierarchy within the catalytic system, conclusively establishing that the mobility of copper is positively related to its oxidized state. The discovery holds significant importance within the realm of Cu/ZnO/Al₂O₃ deactivation, as corroborated empirically that deactivated Cu/ZnO/Al₂O₃ catalysts exhibit the presence of partially oxidized copper. The study further corroborates the role of oxygen in facilitating the reoxidation of Cu to CuO, a process that significantly contributes to the sintering, underscoring the detrimental impact of oxidation processes on catalyst longevity and performance. The mobility difference between copper and zinc could potentially cause their segregation and contribute to deactivation, as the Cu-Zn synergy is deemed crucial for catalytic activity. Moreover, the addition of CO₂ to the hydrogen flow enhances the reduction power, likely through the formation of CO by Reverse water gas shift. Collectively, these insights not only advance our understanding of the dynamic interplay between catalytic components under varying environmental conditions but also pave the way for the development of more resilient and robust hydrogenation catalyst systems.

Graphic:



Keywords:

Cu/ZnO/Al₂O₃, In-situ-TEM, Gas-Cell, Sintering, Stability

Reference:

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