Support-dependent evolution of oxidation state and nanoassembly formation of subnanometer copper clusters under carbon dioxide conversion conditions

AVIK HALDER, BING YANG, KARTHIKA L. KOLIPAKA, MICHAEL PELLIN, SOENKE SEIFERT, STEFAN VAJDA, Argonne National Laboratory, MATERIALS SCIENCE DIVISION TEAM — Size- and support-dependence of the properties of copper clusters have been investigated during carbon dioxide conversion with hydrogen at high reactant concentrations and atmospheric pressure. The model catalyst systems were prepared by depositing size-selected Cu$_n$ clusters ($n = 3, 4, 12$ and $20$) on various amorphous metal oxide ($\text{Al}_2\text{O}_3$, $\text{ZnO}$, and $\text{ZrO}_2$), and carbon-based (UNCD = ultrananocrystalline diamond) supports. During the temperature ramp, the evolution of the chemical state and size of the particles were characterized by in situ grazing incidence X-ray absorption near edge structure (GIXANES), and grazing incidence small angle X-ray scattering (GISAXS) respectively. Under reaction conditions the initially oxidized Cu clusters reduced at various temperatures depending on cluster size and support. Clusters supported on ZnO and UNCD were found to be sinter-resistant under reactive gases at elevated temperatures and atmospheric pressures, whereas on ZrO$_2$ support the clusters formed stable aggregates. Clusters on Al$_2$O$_3$ support demonstrated unique properties, where a formation of a nanostructure was observed during heating, which then disintegrated during the cool down. Under applied conditions, Cu$_4$ clusters on Al$_2$O$_3$ were found to be the most efficient in methanol formation.

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