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Stability and Properties of Small Atomic Clusters: Complementarity Between In Situ X-ray Absorption Experiments and Simulations.

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The geometry and electronic structure of transition-metal nanoparticles change drastically when their size is reduced below 1-1.5 nm (i.e., fewer than 100 - 150 atoms) due to quantum confinement effects.[1][2] In this size regime, the metallic band structure transforms into a series of discrete electronic levels, giving rise to novel properties distinct from those of larger nanomaterials or bulk metals. The discretization of energy levels causes sub-nanometer-sized metal clusters to behave like atomic-scale semiconductors, preventing collective phenomena such as localized surface plasmon resonance (LSPR), which is typically observed in larger metallic nanoparticles.[3] When clusters consist of only a few atoms, a network of d-orbitals interconnects the metal atoms, with inter-atomic distances comparable to chemical bonds (1–2$\mathring{A}$). The "floppy"; nature of these structures results in structural fluxionality,[4] a characteristic that has the potential to enhance catalytic activity. Recently, these sub-nanometer-scale materials have garnered significant interest in the field of catalysis, particularly as catalysts composed of only a small number of atoms, providing unique properties and new catalytic mechanisms.[5]

For characterization, X-ray absorption near-edge structure (XANES) spectroscopy and near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) are employed as powerful, noninvasive methods to directly determine the structural and electronic state of each chemical element in the clusters. When used in "in situ"; or "operando"; modes, these techniques offer direct visualization of the system under realistic conditions, i.e., under thermodynamic equilibrium with its environment.[6]

In this work, we demonstrate the sensitivity of these experimental techniques in determining both structural and chemical aspects of Cu atomic clusters, even under sub-nanometric conditions. These measurements also provide a foundation for subsequent simulations, enabling us to describe the origin of the stability and properties of these systems, particularly in relation to oxygen, as a function of concentration and temperature when supported on HOPG.

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