Understanding Catalytic Clusters under Operando Conditions by XANES.

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Subnanometer metal clusters composed of only a few atoms exhibit unique properties that make them highly attractive for catalytic applications. In this presentation, we discuss recent advances in the study of five-atom copper and silver clusters (Cu_5 and Ag_5), with an emphasis on their catalytic performance as revealed by operando X-ray absorption near-edge structure (XANES) spectroscopy. Ag_5 clusters have demonstrated remarkable activity in the complete oxidation of sulfur-containing compounds, including dibenzothiophene and other highly refractory thiophenes, under ambient conditions, offering a simple and environmentally benign route for fuel desulfurization. Additionally, Cu_5 clusters supported on TiO_2 display exceptional selectivity and efficiency in CO_2 methanation, achieving 100% selectivity toward CH_4 at temperatures as low as 300 °C and exhibiting low activation energy. Their performance has been rationalized through a combined operando XANES and density functional theory (DFT) approach. In both systems, XANES spectroscopy provides crucial insights into oxidation-state dynamics and reaction pathways, revealing the reversible redox behavior of Cu_5 during CO_2 hydrogenation and the oxidation routes promoted by Ag_5 in sulfur removal. Together, these results highlight the potential of subnanometer clusters as efficient, stable, and environmentally relevant catalysts, while underscoring the power of operando XANES to elucidate structure–activity relationships under working conditions.