Revealing The Dynamic Surface State of Cu-based Single-Atom Alloys Using Ambient Pressure X-ray Photoelectron Spectroscopy

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Single-atom catalysts (SACs) have emerged as a transformative class of catalysts, combining the atomic efficiency of isolated active sites with unique chemical and electronic properties that distinguish them from traditional bulk or nanoparticle-based catalysts. A type of SAC called singleatom alloy (SAA) is typically composed of a small amount of a catalytically active noble metal (e.g. Pd, Pt, Rh, Ir) atomically dispersed in the surface of a more inert host metal (e.g. Cu, Ag, Au). The reactivity of the dopant metal and the selectivity of the host metal work synergistically, yielding bifunctional catalysts that deviate from the typical scaling relationships that govern catalytic activity. Research efforts on SAAs exemplify the oft-mentioned "pressure gap" existing between the abundance of recent research performed under ultra-high vacuum conditions and catalytic reactor studies at high pressures. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is the ideal technique for bridging this gap by providing an understanding of how the surface chemical and electronic states of SAAs dynamically evolve under reaction conditions, thus revealing property-structure-reactivity relationships important in catalysis. We have studied SAA model systems with copper as the host metal and compared the effects of three different dopants: Pt, Rh, and Ir. Differences in CO adsorption properties as well as CO-induced atomic mobility were revealed using AP-XPS, with Pt showing the weakest binding to CO and Ir the strongest. Under oxidizing and reducing conditions, we also discovered significant differences in how the different dopants either promote or hinder O₂ dissociation and H₂ activation depending on the structural arrangements of the dopant with respect to the host. In addition, structural heterogeneities of the Cu host metal surface were found to significantly impact the dopant alloying sites, which subsequently alter surface chemical reactivity. Overall, our in situ research using AP-XPS revealed how such a small amount of dopant metal can have an outsize impact on reactivity, with important implications in various catalytic reactions.

Keywords: ambient pressure X-ray photoelectron spectroscopy, single-atom catalyst, singleatom alloy, copper, noble metals

Acknowledgement: This research used resources of the 23-ID-2 (IOS) beamline of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704