

Structure-activity relationships of Au-Pd single-atom alloys for selective oxidation studied by EXAFS

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Introduction

The splitting of hydrogen is a limiting step both in selective hydrogenation and selective oxidation reactions on coinage metals such as Au or Cu [1], which show promise for the purification of ethylene or the production of propylene oxide. Single-atom alloys (SAA) of platinum-group metals in coinage metals have superior activity and selectivity for selective hydrogenation reactions, where single platinum-group atoms split the hydrogen. Likewise, selective oxidation, e.g. of propylene to propylene oxide over Au/TiO₂ [2] can potentially be improved by implementing SAA to split hydrogen from a co-feed of hydrogen and oxygen to create peroxide intermediates. In this work, we correlate the nuclearity of Pd-Au SAA nanoparticles studied by EXAFS to performance in selective oxidation of isopropanol to acetone as a probe reaction for the formation of peroxide intermediates.

Methods

Pd-Au SAA nanoparticles (Pd:Au ratios 1:70 and 1:13) and monometallic Au and Pd nanoparticles were synthesized using an Au seed-mediated colloidal technique, loaded onto TiO₂ and heat-treated to remove ligands remaining from synthesis. Conversion of isopropanol to acetone with oxygen was tested with and without hydrogen. EXAFS spectra were recorded at SSRL at wiggler beamline 9-3 at the Pd K-edge (24350 eV) and Au L₃-edge (11919 eV) in fluorescence mode, using a 100-element Ge detector (Canberra). Samples were loosely pressed inside an *in situ* XAS flow cell [3] with Kapton windows. Heating up to 350°C by two cartridge heaters was controlled using a thermocouple near the catalyst.

Results and discussion

The catalytic conversion of isopropanol to acetone increased with increasing Pd in the absence of hydrogen at temperatures below 150°C. In the presence of hydrogen, conversion increased over all catalysts, likely due to the creation of peroxide intermediates. This increase was greatest for Pd-Au SAA nanoparticles, which also showed superior selectivity to monometallic Pd and Au. EXAFS has revealed that a Pd:Au molar ratio of 1:13 led to isolated Pd atoms in the Au matrix, correlating to a high oxidation selectivity. With higher ratios, Pd_x entities segregated within the Au matrix, causing a loss of reaction selectivity.

Conclusion

The superior activity of Pd-Au SAA nanoparticles towards oxidation of isopropanol to acetone suggests a synergy between single Pd atoms to split hydrogen, and Au nanoparticles to create peroxides. This work brought us further to understanding selective oxidation over SAA systems.

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