

## Synthesis of Heteroatom Rh–ReO<sub>x</sub> Atomically Dispersed Species on Al<sub>2</sub>O<sub>3</sub> and Their Tunable Catalytic Reactivity in Ethylene Hydroformylation

Mingjie Xu<sup>1</sup>, Insoo Ro<sup>2</sup>, George Graham<sup>3</sup>, Xiaoqing Pan<sup>4</sup> and Phillip Christopher<sup>2</sup>

<sup>1</sup>UCI, United States, <sup>2</sup>UCSB, United States, <sup>3</sup>UM, United States, <sup>4</sup>Department of Physics and Astronomy, University of California, Irvine, CA 92697, Irvine, California, United States

Atomically dispersed late-transition-metal catalysts exhibit distinct catalytic reactivity and selectivity compared to metal clusters in many reactions. Realizing the potential benefits of these catalysts requires active site uniformity and control of their local environment. Here, we propose a catalyst synthesis route for manipulating the local environment of atomically dispersed metal-active sites. This was achieved via the targeted deposition of Rh precursors near atomically dispersed ReO<sub>x</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> using electrostatic interactions. CO probe molecule infrared spectroscopy and aberration-corrected scanning transmission electron microscopy suggested that Rh could be preferentially located near a single ReO<sub>x</sub> species or multiple ReO<sub>x</sub> species by controlling ReO<sub>x</sub> loading. Rh–ReO<sub>x</sub> interactions promoted catalytic reactivity and selectivity for ethylene hydroformylation. Kinetic measurements suggested that ReO<sub>x</sub> species withdrew charge from Rh, weakening Rh–CO interactions, which promoted the concentration of vacant sites under reaction conditions and in turn catalytic reactivity. This work demonstrates a general synthetic approach for creating atomically dispersed heteroatom species consisting of oxophilic and late-transition metals and the importance of regulating the local environment of atomically dispersed metals for maximizing catalytic performance.

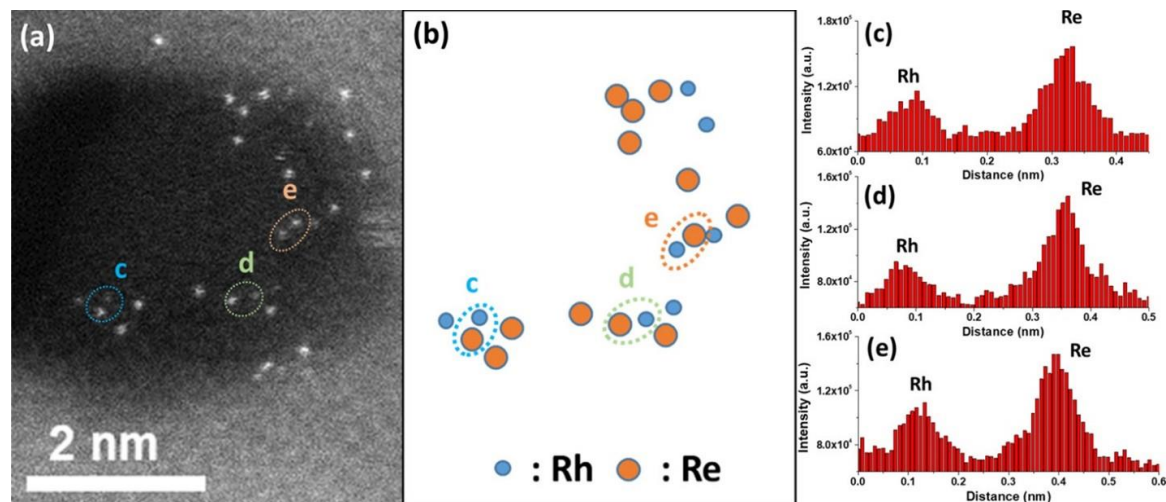
High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEOL Grand ARM300CF microscope at 300 kV. The HAADF-STEM images of Rh/ReO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> sample enables the direct observation of co-localized atomically dispersed Rh and Re species distinguished by Z contrast (Figure 1).

In conclusion, we demonstrated a synthetic approach for tuning the local environment of atomically dispersed Rh species through the targeted deposition of Rh near atomically dispersed ReO<sub>x</sub> species using electrostatic interactions. The charge states of dispersed Rh species were systematically controlled by varying the local coverage of ReO<sub>x</sub> around Rh. Correlations between the CO stretching frequency of Rh(CO)<sub>2</sub> species and the catalytic properties indicate that the charge state of Rh strongly influenced the reactivity and selectivity in ethylene hydroformylation. Catalytic activity was promoted via interactions between dispersed Rh–ReO<sub>x</sub> species (ReO<sub>x</sub> withdrawing charge from Rh), rendering a higher concentration of vacant sites because of a decrease in the CO binding energy. This work demonstrates how the local environment of atomically dispersed late transition metals can be systematically controlled to tune catalytic reactivity. The synthetic protocols employed here should be generally useful for the systematic engineering of the local environment of atomically dispersed metal species and could be employed to probe electronic structure–reactivity relationships.

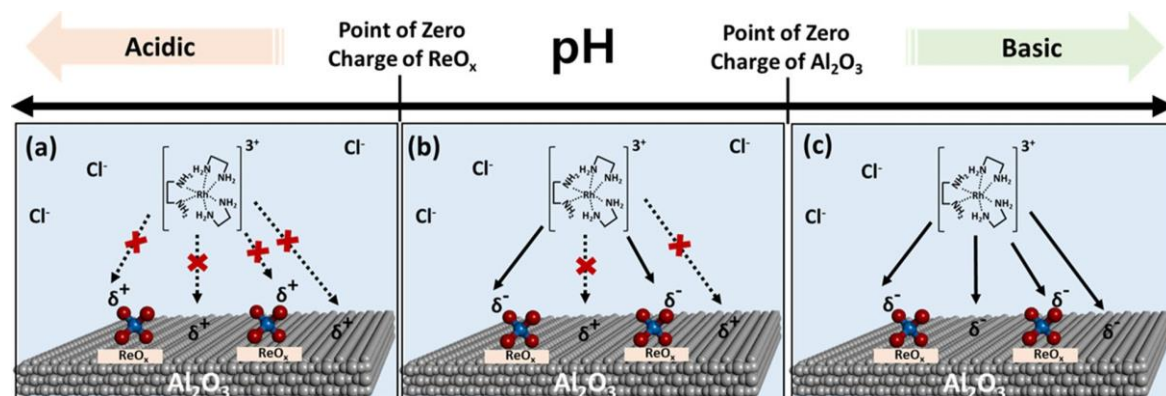
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**Figure 1.** Figure 1 (a) HAADF-STEM image of Rh/1ReO<sub>x</sub>-Al<sub>2</sub>O<sub>3</sub> after ex situ calcination at 623 K. (b) Using the different scattering intensities of Rh and Re, a schematic was created identifying Rh and Re species in (a). (c–e) Corresponding line scan intensity analysis of the three selected dimers shown in (a,b).



**Figure 2.** Schematic of the SEA-based synthetic protocol allowing selective deposition of the cationic Rh precursor ( $[(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3\text{Rh}]^{3+}$ ) near ReO<sub>x</sub> domains via electrostatic attraction between metal oxide surfaces and charged precursors in solution at three different pH regions. The charge state shown in the figure represents a net charge of ReO<sub>x</sub> and the Al<sub>2</sub>O<sub>3</sub> surface after protonation/deprotonation depending on the pH. (a) At a pH below the PZC of ReO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>, the positively charged ReO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub> surface after protonation do not interact with the cationic Rh precursor, resulting in negligible Rh deposition on the metal oxide surface. (b) At a pH between the PZC of ReO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>, only hydroxyl groups on ReO<sub>x</sub> are deprotonated and create negatively charged oxygen species, leading to a potential for selective deposition of Rh precursor near negatively charged ReO<sub>x</sub>. (c) At a pH above the PZC of ReO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>, hydroxyl groups on the ReO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub> surface are deprotonated, creating negatively charged oxygen species that both induce electrostatic interactions with cationic Rh precursor.

## References

Ro, I., Xu, M., Graham, G. W., Pan, X. & Christopher, P. Synthesis of Heteroatom Rh–ReO<sub>x</sub> Atomically Dispersed Species on Al<sub>2</sub>O<sub>3</sub> and Their Tunable Catalytic Reactivity in Ethylene Hydroformylation. *ACS Catalysis* **9**, 10899–10912, doi:10.1021/acscatal.9b02111 (2019)