

Morphological and Electronic Structure of Pt-Re Nanoparticles Supported on Carbon under Activation and Reaction Conditions for Aqueous-Phase Reforming of Bioliquid

Liang Zhang,* Gordon Xia,* Yong Yang,* David Heldebrant,* David King,* Yong Wang* and Lawrence F. Allard**

* Energy and Environment Div., Pacific Northwest National Laboratory, Richland, WA 99352

** Materials Science & Technology Div., Oak Ridge National Laboratory, Oak Ridge, TN 37831

Production of hydrogen and biofuels via reforming of oxygenated hydrocarbons (sugars, sugar alcohols, polyols, etc.) in the aqueous phase (APR) has attracted great interest due to increasing environmental concerns and the national energy security policy [1,2]. Pt-Re/C has proven to be an effective catalyst for the APR process due to its high hydrothermal stability and activity [2]. Efforts have been made to understand the effect of Re on activity enhancement [3]. Formation of a PtRe alloy, or close contact between the Pt and Re phases, have been proposed to account for the effect. However, more definitive evidence is needed to clarify the structure of PtRe nanoparticles and support-particle interaction. Moreover, studies have to date been limited to reduced catalysts; no effort has been reported on catalysts under working conditions. Our present study has focused on investigation of the structure of a PtRe/C catalyst activated and exposed to hydrothermal environments that are close to APR reaction conditions.

Our study of PtRe/C catalysts used aberration-corrected STEM imaging and energy-dispersive spectroscopy (EDS) techniques. It was found the activated carbon helps stabilize the PtRe particles against sintering during in-situ reduction, as shown in Fig.1a and 1b, due to anchoring clusters with oxygen-containing functional groups and confining movement of clusters by the unique physical structure of activated carbon consisting of disordered curved fragments containing hexagonal and non-hexagonal carbon as depicted in Fig.1d. The TEM images of reduced PtRe/C show presence of lots of single atoms, small clusters and particles. After reaction, most of the single atoms or small clusters present in the reduced catalyst disappeared, leaving behind larger nanoparticles, as shown in Fig. 1c. This is possibly due to agglomeration of neighboring clusters facilitated by water interaction or leaching out by liquid. This phenomenon could be one of the reasons, in addition to blocking pores and active sites by polymerized hydrocarbon through aldol condensation, for decline of activity over time. The composition profile of individual PtRe particles obtained by EDS line scans across particles reveals that Pt and Re are distributed uniformly in the bulk of particles, which suggests formation of bimetallic particles instead of close contact between Pt and Re phases. Two types of particles were detected on the carbon surface by EDS analysis: Pt-rich particles and Re-rich particles. To better demonstrate the two types of particles, EDS elemental mapping was performed on larger particles supported on model support (flat carbon film). Because the in-situ H₂ treatment was carried out in a non-purging way, water molecules tend to re-adsorb dissociatively on Re surface. As a result, Fig 1e and 1f clearly shows a Pt-rich particle and a ReOx-rich particle. This suggests the Pt-Re bimetallic bond and/or Pt-O-Re bond might be active sites in the APR reaction, consistent with what we observed in XPS and EXAFS experiments.

The electronic structure of PtRe/C was investigated using in-situ XPS and in-situ EXAFS. After reduction, Pt was found to be slightly positively charged upon addition of Re due to charge transfer through formation of Pt-Re bonds and/or Pt-O-Re bonds. Under a hydrothermal environment similar

to APR reaction conditions, reduced Re is oxidized to various oxidation states. When correlating Pt-Re structure to reaction pathways in APR, it was found that larger amount of ReOx resulted in higher dehydration selectivity relative to decarbonylation selectivity. A tandem reaction pathway is proposed: a Pt surface is required for the first dehydrogenation step, then acidic ReOx facilitates the subsequent dehydration pathway competing with decarbonylation pathway. Partially oxidized Pt increases the dehydrogenation rate, which could be tuned by addition of Re. However, it is unclear at this stage whether the Pt-O-Re or Pt-Re bond is more important for the enhanced effect. The coupled effect on dehydrogenation and dehydration rates enhances the total activity of the catalyst.

References

- [1] Simonetti et al., *J. Catal.* 247 (2007)
- [2] Chheda et al., *Catal. Today* 123 (2007)
- [3] Kunkes et al., *J. Catal.* 260 (2008)
- [4] This work was supported in part by the U.S. DOE Office of Hydrogen, Fuel Cells, and Infrastructure Technologies. Microscopy at Oak Ridge National Laboratory's High Temperature Materials Laboratory was sponsored by the U.S. DOE Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

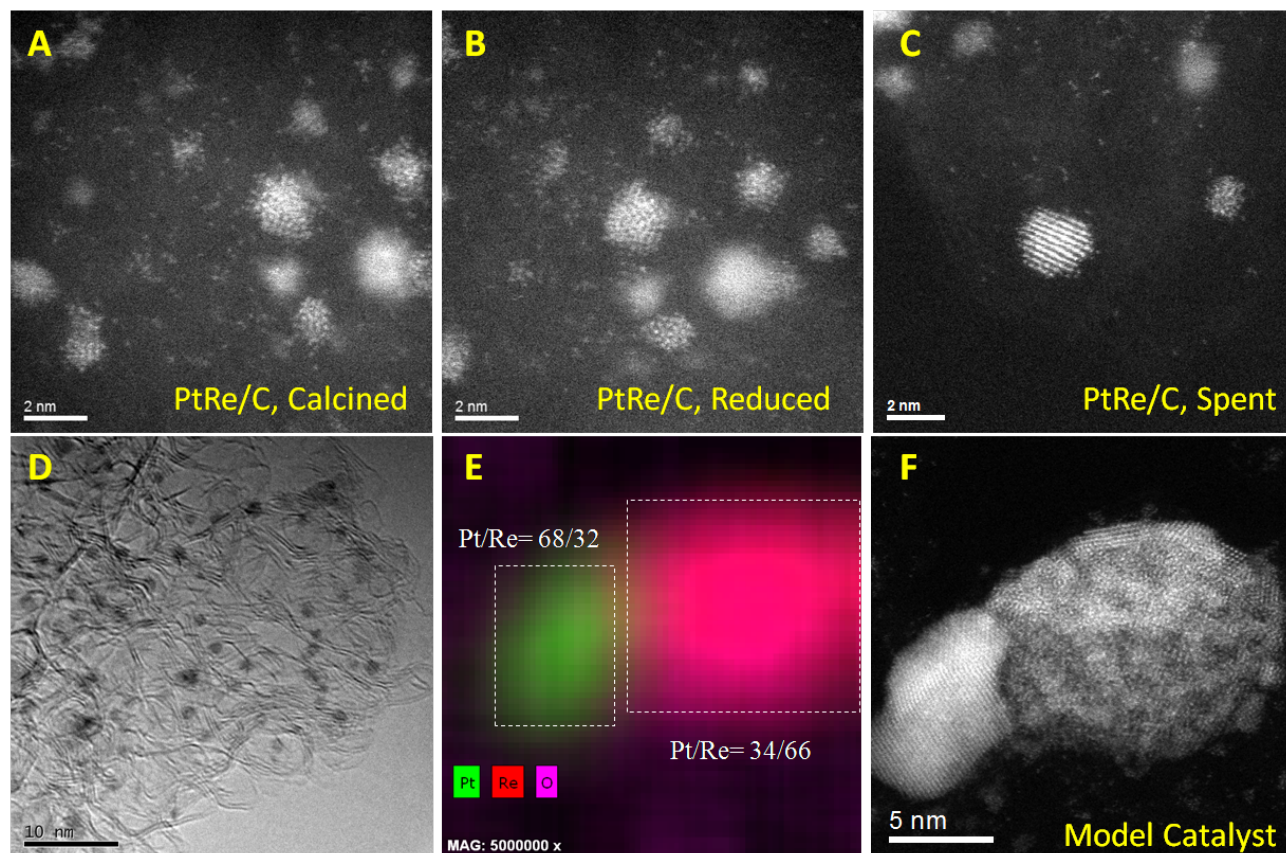


FIG. 1. TEM images of real PtRe/C for APR reaction and model catalyst: a) calcined PtRe/C, b) in-situ reduced PtRe/C in the same area, c) spent PtRe/C, d) BF image of reduced PtRe/C, e) EDS elemental mapping of model PtRe particles, f) PtRe particles supported on model carbon support.