

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. 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. In-situ x-ray photoelectron spectroscopy (XPS) and in-situ extended x-ray absorption fine structure (EXAFS) techniques have also been used after exposing the catalyst to water and water/H₂ vapor at reaction temperatures. The physicochemical and electronic structures of PtRe nanoparticles have been correlated to reaction data expressed with the ratio of dehydration selectivity and decarbonylation selectivity to provide insight on Pt-Re interactions and the effect of Re on reaction pathways in the APR process.

The TEM images of PtRe/C activated in-situ with hydrogen demonstrated that the carbon support stabilizes the PtRe particles against sintering during reduction. After reaction, most of the single atoms or small clusters present in the reduced catalyst disappeared, and the average particle size increased, as shown in Fig. 1. This is possibly due to agglomeration during reaction or leaching out by liquid. 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. Two types of particles were detected on the carbon surface by EDS analysis. EDS elemental mapping of the model catalyst clearly shows a Pt-rich particle and a ReOx-rich particle (Fig. 2), which suggests the Pt-Re bimetallic bond and/or Pt-O-Re bond might be active sites in the APR reaction.

The electronic structure of PtRe/C was investigated using in-situ XPS and in-situ EXAFS. After reduction, Pt was found to be 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 Pt is partially oxidized, and reduced Re is oxidized to various oxidation states. The radial distribution function obtained from the EXAFS spectrum of the Pt LIII edge in the Pt-Re catalyst reveals the presence of both a Pt-Re bond and a Pt-O-Re bond.

By using the new definition of dehydration selectivity and decarbonylation selectivity, the Pt-Re ratio is correlated to the competitive reaction pathways. It was found that more Re addition to Pt resulted in higher dehydration selectivity relative to decarbonylation selectivity. A tandem dehydrogenation-decarbonylation/dehydration reaction pathway is proposed: a Pt surface is required for the first dehydrogenation step, then ReOx facilitates the dehydration 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. Unsaturated ReOx of various oxidation states exhibits some Lewis acidity, and facilitates electrophilic elimination of H₂O from polyols to form lower alcohols and C²⁺ alkanes. 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. XAS data were collected on beamline X19A at the National Synchrotron Light Source, Brookhaven National Laboratory. XPS was performed with PHI Quantum 2000 at the Environmental and Molecular Science Laboratory, Pacific Northwest National Laboratory.

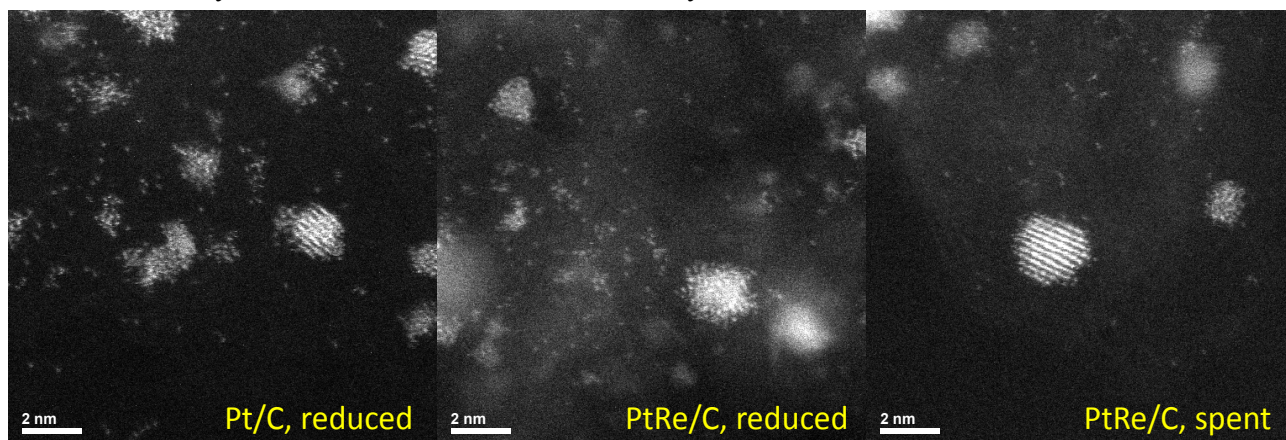


FIG. 1. HA-ADF STEM images of reduced and spent PtRe/C.

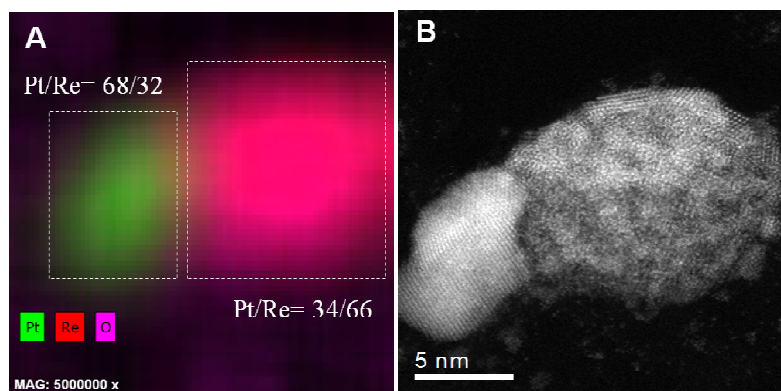


FIG. 2. EDS element map and STEM image of model PtRe/C catalyst.