

# Effect of Pt-Re Interaction on the Aqueous Phase Reforming of Glycerol over Pt-Re/C Catalysts

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## Introduction

Driven by increasing environmental concern and energy security policy, thermochemical production of hydrogen and chemical intermediates from renewable biomass feedstocks is of increasing interest.<sup>1</sup> Reforming of oxygenated hydrocarbons (sugars, sugar alcohols, polyols, etc.) in the aqueous phase (APR) offers a promising alternative to conventional production methods.<sup>2</sup> Encouraging progress has been made in developing and moving APR technology toward commercialization. Nevertheless, the reaction mechanisms and the relation between catalyst structure and function are not fully understood. Therefore, an increased focus is being directed toward fundamental understanding of the interfacial reactions in the APR process in order to make the technology more efficient and cost-effective.

The present study has focused primarily on investigating the role of Re in Pt-Re/C catalysts for aqueous phase reforming of glycerol. As a model chemical with similar reaction pathways as sugar alcohols, glycerol provides a more tractable aqueous phase product set for clearer delineation of these pathways. Reaction kinetics were studied on a series of catalysts with varying Pt/Re ratios to identify effect of Re addition on reaction pathways. The kinetic data were further correlated to structural information deduced from a combination of characterization techniques including BET, TPR, chemisorption, EXAFS/XANES, isotopic transient kinetic analysis, XPS and TEM. These results help elucidate the specific Pt-Re interaction accounting for the improved catalytic performance compared with Pt/C catalyst.

## Materials and Methods

Coconut shell-based activated carbon-supported catalysts were prepared by incipient wetness impregnation with aqueous solutions of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  and perrenic acid ( $\text{HReO}_4$ ). Pt loading was held at 3wt.% and Re loadings varied from 0 to 4.5wt.%. About 200mg of calcined catalyst was loaded into a small microchannel fixed bed reactor<sup>3</sup> and reduced in flowing  $\text{H}_2$  at 280°C. Following reduction, the catalyst was cooled to reaction temperature and an aqueous mixture of glycerol (10 wt.%) flowed over the catalyst using a HPLC pump. Operating temperature was typically 225-230°C with an operating pressure of 30 bar and a WHSV (glycerol) of 5.6h<sup>-1</sup>. Agilent micro GC and HPLC were utilized to analyze gas phase and liquid phase products respectively. Mass balance was typically 90+%.

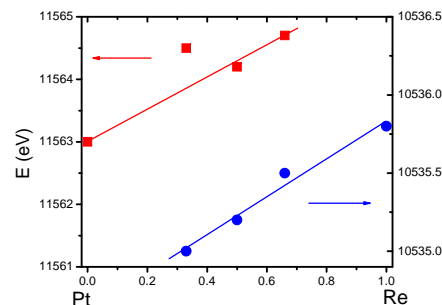
Catalyst BET surface area was measured with Quantachrome Autosorb II. Metal dispersion and reducibility of catalysts were determined by CO chemisorption and temperature programmed reduction on Micromeritics Autochem II. Oxidation states and local chemical environment of metal atoms were identified by X-ray absorption and photoelectron spectroscopy (XAS and XPS). XAS data were collected on beamline X19A at the National Synchrotron Light Source, Brookhaven National Laboratory. XPS was performed with PHI Quantum 2000. Structures of bimetallic clusters were imaged by high-resolution TEM.

## Results and Discussion

As summarized in Table 1, our test results indicate that the addition of Re to Pt significantly increases the glycerol conversion at the expense of somewhat higher selectivity toward gas phase hydrocarbons relative to hydrogen. In addition, liquid phase product analysis shows a trend toward greater production of monohydric alcohols and carboxylic acids with the addition of Re, whereas 3%Pt/C catalyst produces mainly glycols. Such selectivity suggests that reaction pathways involving sequential dehydration and hydrogenation are occurring with greater prevalence as a result of Re addition. Since the water gas shift reaction is highly favored (CO production was not observed regardless of the Pt-Re ratio), the declining ratio of  $\text{H}_2$  to  $\text{CO}_2$  with addition of Re also indicates that Re promotes the cleavage of the C-O bond compared to C-C bond scission. We believe the effect of Re on the selectivity of bond cleavage can be attributed to the strong interaction of Re with Pt. This interaction will be described by TPR and CO chemisorption results, which indicate that Re modifies the Pt surface for CO adsorption. XAS and XPS data further suggest that the nature of this interaction may be through modification of the Pt electronic structure by Re by electron transfer as shown in Figure 1. We will also show direct evidence of Pt-Re interaction in the bimetallic clusters by *in situ* observation of model catalyst with high-resolution TEM.

**Table 1. Chemisorption and reaction data on catalysts with varying Pt-Re ratio**

Catalyst	CO uptake (μmol/g)	Conversion Of Glycerol	TOF to $\text{H}_2$ (min <sup>-1</sup> )	$\text{H}_2$ Selectivity (%)	Alkane Selectivity (%)	$\text{H}_2/\text{CO}_2$
3%Pt/C	116	0.045	2	0.662	0.100	2.85
3%Pt 1%Re/C	70	0.524	28	0.308	0.113	1.72
3%Pt 3%Re/C	67	0.912	26	0.267	0.139	1.55



**Figure 1. Change of X-ray absorption edge as function of Pt-Re ratio.**

## Significance

Our results point to the importance of understanding the nature of Pt-Re interaction and its effect on product selectivity and yield for APR of glycerol and related sugar alcohols.

## References

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