Elucidation of the Roles of Rhenium in Vapor-Phase Reformsing of
Glycerol over Pt-Re/C Catalyst

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Introduction
Catalytic reforming of glycerol with water has been extensively studied to produce
either synthesis gas in vapor phase (steam reforming, or SR) [1] or hydrogen in condensed
phase (aqueous-phase reforming, or APR) reactions [2]. Pt/C catalyst has been identified to
provide good hydrogen selective although its activity is low at moderate reaction temperatures
(below 300 °C). Addition of rhenium significantly enhances the catalyst activity. Both
weakened CO adsorption on PtRe alloy surface [2] and enhanced CO adsorption on supported
Pt-Re [3] have been reported, and the definitive roles of rhenium are still unclear.
In the present study, we investigated glycerol SR over Pt/C and Pt-Re/C catalysts
and employed a suite of complementary in situ spectroscopic tools to elucidate the roles of Re
under working reaction conditions.

Materials and Methods
Catalysts samples were prepared by impregnating platinum and rhenium precursors
onto activated carbon support following by drying (110 °C, 2 h) and calcination (260 °C, 2 h).
In situ reduction (280 °C, 1 h) was performed prior to reaction or characterization. Reaction
testing was carried out using fixed-bed reactors [4]. In situ spectroscopic studies, including X-
ray absorption spectroscopy (XAS), Raman, and attenuated total reflection infrared
spectroscopy (ATR-IRS), employed home-made reaction cells [5] for high temperature and/or
high pressure application.

Results and Discussion
We have previously reported that adding Re to Pt/C dramatically improved its activity in glycerol reforming with water in condensed phase [6]. According to Simonetti et al.,
such improvement also applies to vapor-phase reforming, and PtRe alloy was believed to be
involved in the active site. Due to the oxophilic nature of rhenium metal, it is highly possible that
rhenium can be readily oxidized under reaction condition as we previously reported [6]. To
further elucidate the roles of Re, we employ in situ X-ray absorption near edge spectroscopy
(XANES) to study the Pt L3 edge, and by comparing the fractional change in the total
number of unfilled d-band states of Pt in reduced Pt/C and Pt-Re/C, the effect of Re on the
electronic property of Pt is found to be negligible. The narrowing of d density of state (DOS) is
supposed to result in more electron back-donation from Pt to adsorb over Pt-Re/C catalyst.
Thus, on the contrary to the previous viewpoint [2], stronger CO adsorption on PtRe/C than
that on Pt/C is expected.
In situ ATR-IRS with CO probe molecule also suggests that the charge transfer is
minimal on PtRe/C. Temperature-programmed CO desorption recorded by ATR-IRS indicates
that CO adsorption is actually stronger on reduced PtRe/C than Pt/C. Further results with steam
reform treatment, which is more representative of the steam reforming condition, evidences that steam
has little effect on the CO adsorption on Pt/C, whereas on PtRe/C CO desorption is greatly
facilitated. In situ Raman and XANES clearly indicate that oxidized rhenium species is formed
under steam environment on PtRe/C catalyst surface. Steam exposure can cause further
oxidation of rhenium, while CO could indirectly interact with the oxidized rhenium species via
redox cycle. Such indirect interaction is made possible via CO spillover from neighboring
platinum to such oxidized rhenium. This is likely the reason for the facile desorption of CO,
which could further react with oxidized rhenium via redox or water via water-gas shift (WGS)
reaction to form CO2. Such facile CO desorption leads to the enhanced activity in glycerol
steam reforming and WGS over PtRe/C catalyst. A scheme of the catalyst structure under
steam condition is also provided and discussed.

Compared to monometallic Pt/C catalyst, bimetallic PtRe/C catalyst exhibits
significantly enhanced activity; improved H2/CO ratio and CO2 selectivity are also observed
over PtRe/C in glycerol steam reforming.

Figure 1. CO ATR-IRS with respect to desorption
Figure 2. Re L3 XANES of PtRe/C
temperatures (25, 50, 100, 150 and 200 °C) on (left)
Pt/C and (right) PtRe/C

inset showing enlarged view of the
white line.

Significance
Using a suite of complementary in situ techniques, including XAS, Raman, and ATR-IR, we
are able to provide better understanding of the catalyst surface structures and their correlation
with catalytic performances, particularly under hydrothermal environments including steam
and aqueous phase, and using carbon material as the catalyst support. Oxidation of rhenium
and CO spillover from platinum to oxidized rhenium are unambiguously attributed to the
enhanced activity over PtRe/C catalysts.

References