In situ X-ray absorption spectroscopy (XAS) measurements, at the Pt L3 edge (XANES and EXAFS), were carried out on carbon-supported Pt, Mo, and PtSn electrocatalysts in an electrochemical cell in 1 M HClO4 with 0.3 M methanol. The CO, OH, and H relative adsorbate coverages on Pt are determined as a function of the applied potential via the ΔXANES technique and compared with comparable data previously reported for Pt-Ru. The more reactive Sn and Mo atoms on the Pt surface form the oxide over the potentials of interest, while Ru has variable oxide content depending on Ru island size and potential. The strength of the electronic ligand effect appears to increase in the order Ru < MoO4n < SnO2n < RuO4n, where the Pt−CO bond strength is found to decrease and the Pt−OH bond strength increase with ligand effect. In the Sn and Mo bimetallics, the ligand effect is found to be sufficiently strong to allow CO replacement by H2 at low potentials. These widely different ligand effects may provide a straightforward explanation for the previously observed anode behavior in fuel cells: Pt, Mo better in reformate but Ptω,Ru better in methanol.

1. Introduction

Improvement in the performance of proton exchange membrane (PEM) fuel cell performance is an area of great interest in the race to produce efficient, economic alternative power sources. Currently, due to H2 storage and other issues, PEM fuel cells are often more conveniently fed either with reformed H2 generated at the fuel cell or with liquid fuel such as methanol. Both reformate and methanol introduce CO, the main poison of fuel cells. As little as 10 ppm CO is known to poison Pt catalysts irreversibly. Therefore, the development of more CO-tolerant catalyst materials is crucial to the advancement of fuel cell technology.

One method that has been explored to increase the CO tolerance of catalytic material is to incorporate a second transition metal with the traditional Pt. This method has the added advantage of reducing the amount of costly Pt needed for the catalyst. A variety of Pt−M bimetallic nanocrystals and M-decorated Pt single crystals have been investigated, with the second metal being Ru, Mo, and other transition metals. The catalytic enhancement from the addition of the second metal is generally accepted to derive from two mechanisms. In the bifunctional (BF) mechanism, water activation,

\[ M + H_2O \rightarrow OH/M + e^- + H^+ \]  

occurs more readily at the second metal surface, yielding bound OH/M, to which CO can then migrate and be oxidized, as in

\[ CO/Pt + OH/Pt \rightarrow Pt + M + CO_2 + e^- + H^+ \]
islands also affect the nearby Pt, and if so how and to what extent? That is a question we consider in this work. We examine the effect of changing the adatom identity by comparing our previous results on three different PtRu electrocatalysts with three new catalysts; two Pt3Mo and a PtSn electrocatalyst. We determine and compare CO, O(H), and Hupd (under potential deposited) coverages as a function of potential on the Pt surface utilizing in situ Pt L3 edge X-ray absorption data with the Δµ analysis technique, as well as the EXAFS analysis technique to gain information on the size and morphologies of the clusters.

2. Experimental Section

Materials. Three types of carbon-supported Pt-based electrocatalysts were used for preparation of the anodes. 30% PtMo (3:1 and 4:1) and 50% PtSn (1:1) were obtained from DeNora N.A. ETEK Division (Somerset, NJ), hereafter referred to as Pt3Mo, Pt4Mo, and PtSn, respectively. The anode (working) electrodes were prepared in-house with a metal loading of ~45 mg/cm² by a standard vacuum table paper making technique. The metal loading was chosen on the basis of absorption cross sections for Pt and Ru to ensure a step height of close to 1 for the XAS measurements. The electrodes were soaked in 1 M HClO4 for 48 h, followed by vacuum impregnation. 

The sealed compression cell used to obtain in situ XAS data has been described in detail elsewhere. The membrane electrode assembly (MEA) was made by sandwiching a Nafion 1135 (1100 MW, 3.5 mm thick) membrane between the prepared anode and a Grafost (carbon/graphite foil) counter electrode. The electrolyte used in these experiments was 1 M HClO4 with the addition of 0.3 M methanol. The reference electrode was a reversible hydrogen electrode (RHE). These MEAs were prepared by Dr. R. Craig Urian.

X-ray Absorption. An Eco Chemie Autolab PGSTAT-30 potentiostat/galvanostat was used for potential control of the electrodes for XAS experiments. X-ray absorption data were taken at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory at beamlines X23A2 and X11A in transmission mode with a three-detector setup. The NSLS storage ring operated at 2.8 GeV and a current between 120 and 350 mA. The three detectors collected incident (I0), sample (I), and foil transmission data (Iref), i.e., the electrochemical cell was placed between the first and second detector, and a reference foil of the metal of interest was placed between the second and third detectors. The transmission data of the reference foil was used for alignment, as described later. The Si(111) crystal monochromator was detuned by 15% for the Pt edges to exclude higher harmonics. Measurements were taken at the Pt L3 and L2 edges at the following potentials in time sequence—PtSn: 0.0, 0.24, 0.40, 0.54, 0.70, and 0.40 V (returning); Pt3Mo: 0.0, 0.24, 0.54, 0.84, and 1.14 V (with respect to RHE)—however, only the L3 edges were analyzed.

3. Data Analysis

XANES Analysis. Analysis of the XANES (near-edge) region of the XAS data was carried out using the Δµ technique, previously applied to adsorption of H, O, and OH on Pt57 and Pt−M (M = Cr, Fe, Co, and Ni) cathodes54 and Pt−Ru anodes53 in an electrochemical cell, and even to Pt and PtRu anodes in an operating direct methanol fuel cell. A brief summary is given here for clarity and to highlight slight differences from the previous method. The absorption coefficient, μ, was obtained from the raw data using the ATHENA code of Ravel and Newville. After linear combination of appropriate channels of the raw data, the pre-edge background is removed using the AUTOBK algorithm, described more fully elsewhere,67 followed by normalization over the 20–150 eV (relative to the edge) range for XANES analysis. This procedure was carried out for both the sample data (ln I/I0) and the reference foil data (ln I/Iref). The foil data were then aligned with each other using a group-developed code, and the resultant energy differences were transferred to the sample data, i.e., the ΔE determined for the foil at x potential is added to the energy of the data at the same x potential. This energy calibration corrects for shifts due to photon beam drift and other possible effects. This energy calibration is crucial for the success of the Δµ technique to ensure full cancellation of the atomic contribution in the XANES, which dominates the spectrum, i.e., Δµ is typically only about 1–5% of the total µ signal.

The difference Δµ = µ(V) − µ(Vref) is generally determined by subtracting the µ at an appropriate reference potential, Vref, (usually taken to be that potential at which the electrode is relatively free of most adsorbates) from other potentials to highlight the effect of these adsorbates. However, the choice of reference can change on the basis of the sample, the adsorption edge, and the operating conditions. In this work, 0.54 V in 1 M HClO4 without methanol was used as the reference to determine CO and Hupd coverages for the PtMo samples. However, in the case of the PtSn, the samples in and out of methanol were not comparable, and therefore, 0.40 V on the return in methanol was used as reference, as in our previous work with PtRu catalysts. This potential has been determined to contain the least amount of CO, as most of the CO has been oxidized off and only a comparably smaller amount adsorbed, and neither H nor O(H) are heavily adsorbed in this potential region. Therefore, the CO signal, as well as the Hupd signal, can be obtained from the difference,

\[ \Delta \mu(x, CO, H) = \mu(x, Me) - \mu(0.40, Me) \]  

for Pt3Mo and

\[ \Delta \mu(x, CO, H) = \mu(x, Me) - \mu(0.54) \]  

for PtSn. As will be shown in Figure 2, CO and Hupd (i.e., under potential deposited H in a 3-fold site)53 were visible as two distinct features by this method, allowing for simultaneous determination of their coverages.

Because CO and O(H) have been shown to coadsorb53 and because their signals contain areas of overlap, a more complex method was used to extract the O(H) (i.e., O or OH) signal. In this case, 0.24 (Pt3Mo, PtSn) or 0.54 V (Pt4Mo) in methanol was used as the reference. At both these potentials, neither H nor O(H) should be contributing significantly to the signal. As the reference in this case does contain contributions from CO, it is necessary to add a scaled portion of the CO signal \( \Delta \mu(0.24, CO) \) from eq 3a back in, to remove this CO contribution to the signal. The scale factor, a, is chosen to minimize \( \Delta \mu \) in the positive CO region (~7.5–11 eV relative to the Pt edge). Thus,

\[ \Delta \mu(x, O) = \mu(x, Me) - \mu(0.24, V, Me) + a \Delta \mu(0.24 V, CO) \]  

for Pt3Mo and PtSn and
4. Results

Adsorbate atom to allow for different surroundings of each atom. In FEFF 8.0, a unique potential was calculated for each Pt, M, and O. This prefers to be singly coordinated, and O doubly or triply. In FEFF 8.0, it is not expected that a differentiation can be made between OHnear and OHaway in a FEFF 8.0 calculation of a PtM2 “Janin cluster” (Figure 1), it is not expected that a differentiation can be made between OHnear and OHaway in a FEFF 8.0 calculation of a PtM2 “Janin cluster” (Figure 1). The bond distances used in the clusters were the same as those in our previous FEFF 8.0 calculations. Oxygen in the atop position was treated as OH (since the scattering from H is negligible), while oxygen in an n-fold position was treated as O. This is consistent with chemical intuition and density functional theory (DFT) calculations, which show that OH prefers to be singly coordinated, and O doubly or triply. In FEFF 8.0, a unique potential was calculated for each Pt, M, and adsorbate atom to allow for different surroundings of each atom.

FEFF 8.0 Calculations. The FEFF 8.0 code was also used to model the adsorbate Δμ signatures. The Δμ(Ads) was determined by subtracting the μ of a cluster containing an adsorbate molecule in the atop, bridged, or n-fold position (Figure 1), i.e., Δμ = μ(O/PtM2) − μ(PtM2). The “Janin cluster”, used in much but not all of our previous work, was chosen here because it is about the smallest cluster that contains atop, bridged, fcc, and hcp sites. The bond distances used in the clusters were the same as those in our previous FEFF 8.0 calculations. Oxygen in the atop position was treated as OH (since the scattering from H is negligible), while oxygen in an n-fold position was treated as O. This is consistent with chemical intuition and density functional theory (DFT) calculations, which show that OH prefers to be singly coordinated, and O doubly or triply. In FEFF 8.0, a unique potential was calculated for each Pt, M, and adsorbate atom to allow for different surroundings of each atom.

4. Results

XANES Analysis. Figure 2a shows typical Pt L3 edge Δμ spectra emphasizing the CO and H fcc (Hupd) signals, compared with the theoretical atop signal for CO and the fcc signal for H, calculated using FEFF 8.0. The magnitude of each peak (negative for Hupd and positive for CO) in the highlighted region was evaluated to determine the relative amounts of H and CO in the indicated highlighted regions, in order to estimate coverage, as will be described more fully later.

Figure 2b shows representative Pt L3 edge Δμ spectra in this case emphasizing the contribution of oxygen to the spectra, which was partially hidden (although evident as negative features) in Figure 2a by the negative portion of the CO peak in the -2 to 7 eV range. As seen previously, three peaks are visible in the oxygen region, corresponding to (in increasing energy) OH atop “near” an M island, OH atop “away from” an M island, and O in an n-fold position (referred to in this work as OHnear, OHaway, and O). Due to the small size of the “Janin cluster” (Figure 1), it is not expected that a differentiation can be made between OHnear and OHaway in a FEFF 8.0 calculation on a small PtM2 cluster, as necessarily all atoms are “close” to each other. However, we can mimic the effect of OHaway by modeling O(H) on a simple Pt6 Janin cluster (i.e., without any M atoms present). Although a single FEFF 8.0 calculation does not reproduce the three peak structure seen in the data, nor reproduce the full shift, FEFF 8.0 does predict twice the gap in energy between the atop and n-fold positions in the PtM2 cluster compared to the Pt6 cluster. Figure 2b shows the FEFF 8.0 calculated individual Δμ signals in which the OHnear result has been moved down to mimic the doubled energy gap between the atop and n-fold positions.

The relative shift in the energy positions of OHnear and OHaway has been seen before in bimetallics when some M (M = Cr, Fe, Co, Ni, and Ru) atoms are at the surface, but not when they are absent. This shift is believed to arise in part from a Pt L3 core level shift occurring as a result of charge transfer between the M and nearby Pt atom (i.e., a ligand effect). Further, XANES analysis of pure Pt samples does not show the lowest energy OHnear peak, giving further evidence that this peak is the result of the mixed metal morphology. The height of each experimental Δμ peak in the indicated highlighted regions was used to determine the relative coverage of O(H) species at each potential.

Figure 3 shows the relative coverage change for each indicated adsorbate species determined from the Δμ amplitudes...
in the shaded regions, as shown in Figure 2 and similar plots of $\Delta\mu$ for the other catalyst but scaled by factors as discussed below to yield coverages in monolayers (ML) per accessible Pt atom. To arrive at these results, corrections were included to allow for overlap of the coadsorbate signatures. For example Figure 2a shows that a significant contribution from $\Delta\mu$(Hupd) will appear in the experimental $\Delta\mu$ at 10 eV, where the magnitude for estimating the CO coverage is made. This overlap between $\Delta\mu$(Hupd) and $\Delta\mu$(CO) is accounted for by subtracting out the $\Delta\mu$(Hupd) contribution before estimating the CO coverage; the $\Delta\mu$(Hupd) magnitude determined at 0 eV, where the $\Delta\mu$(CO) is nearly negligible, and the $\Delta\mu$(Hupd) line shape determined from the theory. Much stronger overlap exists between the 3 different O(H) signatures in Figure 2b, particularly at high potential (above 0.8 V) when the $\Delta\mu$(O$_{h\text{-fold}}$) dominates and the $\Delta\mu$(OH$_{\text{ave}}$) introduces just a small feature on top of this larger one. Resolution of these three contributions might possibly be improved by fitting two or three Gaussian-type functions to the experimental $\Delta\mu$, but this was not attempted in this work.

Figure 3 shows that Hupd in the fcc sites is present at 0.0 V, and at slightly lower coverage at 0.24 V, before being oxidized off by around 0.35 V. CO is also present at low potentials reaching a significant level in most cases around 0.5 V, when the Hupd and OH coverages are at a minimum. In general, the CO coverage decreases as the OH coverage increases, reflecting the reaction between adsorbed CO and OH (i.e., via either the bifunctional or ligand mechanism). Differences between the onset for OH$_{\text{ave}}$ will be discussed below.

**EXAFS Analysis.** The EXAFS analyses of the three electrocatalysts at the Pt L$_3$ edge are summarized in Table 1. In all cases, the Debye–Waller factor, $\sigma^2$, was held at 0.005 Å$^2$, exactly as done previously for the Pt$_5$Ru catalysts$^{53}$ to allow meaningful comparison of N for all cases. The magnitudes of $N_{\text{Ttot}}$ at the platinum edge indicate particle sizes ranging from about 1.3 to 2.3 nm, on the basis of model cluster calculations assuming spherical clusters.$^{71,72}$ Although it is not claimed that these are perfectly spherical clusters, this does illustrate the difference in size (1.3–2.3 nm) and dispersion (0.56–0.90) of the catalysts.

**Converting $\Delta\mu$ Magnitudes to Absolute Coverage.** The magnitudes of the various $\Delta\mu$ features of interest were measured, as indicated in Figure 2. These magnitudes were then divided by the absolute height of the relevant FEFF 8.0 calculation, shown also in Figure 2. Since the Janin cluster (Figure 1) used for the FEFF 8.0 calculations has a Pt–Ad coordination number of 1 (i.e., the photon absorber Pt atom is always placed next to the adsorbate (Ad)), after applying these scale factors $S_{\text{ad}}$ (i.e., $\Delta\theta_{\text{ad}} = \Delta\theta_{\text{ad}}/S_{\text{ad}}$),$^{73}$ one obtains a reasonable measure of the coverage change from the reference (i.e., $\Delta\theta_{\text{ad}}$) in units of ML adsorbate per total absorber atom ($M_{\text{tot}}$, where 1 indicates one adsorbate atom for each Pt atom). This coverage change is relative to $M_{\text{tot}}$ because the XAS spectra are normalized to one and the XAS samples all atoms present in the beam cross-sectional area. Using this method, we obtain at 0.0 V RHE, CO coverages for PtSn, Pt$_3$Mo, and Pt$_5$Mo, of approximately 0.025, 0.06, and 0.05 ML/$M_{\text{tot}}$, respectively, and $\Delta\theta_{\text{CO}}$ coverages of 0.14, 0.17, and 0.37 ML/$M_{\text{tot}}$, respectively. As discussed previously, these estimates are only semiquantitatively correct because the conversion factors may vary with coverage (e.g., each surface CO in an fcc binding site is coordinated to three Pt atoms, while at a different coverage the CO may prefer a corner/edge atop site, which is coordinated to just one Pt atom).$^{68}$

Further, the FEFF8 $\Delta\mu$ amplitudes, although normally quite reliable, are particularly suspect for the very light H atom where the single 1s orbital can become highly distorted by bonding with the Pt, and hence not be reproduced accurately by the muffin-tin calculations done in FEFF8. Nevertheless, we have previously calibrated the $\Delta\mu$ scale factors for H using gas-phase H$_2$ chemisorption results at different temperatures and pressures to determine the absolute H coverages,$^{74}$ and found the coverages estimated from $\Delta\mu$ amplitudes to be quite reliable. Thus the estimated adsorbate coverages are semiquantitatively correct, and these can be very helpful in understanding the relative activity of the different CO oxidation mechanisms. Further, estimating coverages on these samples makes possible comparison with the previous Pt$_5$Ru samples.

Although these magnitudes represent actual change in coverage ($\Delta\theta_{\text{ad}}$) from the reference potential, they essentially indicate absolute coverage ($\theta_{\text{ad}}$) for all but the CO/PtSn case. Recall, for the determination of CO and H fcc on Pt$_3$Mo, the $\mu$ at 0.54 V in 1.0 M HClO$_4$ with no methanol was used as the reference. CO should not be present in the reference, as no methanol is present, and fcc H is known to be removed from the surface by 0.54 V. The reference used for O(H) determination was either 0.24 or 0.54 V, where no O(H) is found or believed to be present on the relevant samples either. The only reference, therefore, which contains an adsorbate species of interest is 0.40 V on the return, used to determine CO coverage on PtSn. Rough estimates of the CO coverage on PtSn at 0.40 V on the return can be obtained from the $\Delta\mu$ signals. Although, as mentioned above, the samples in solution without methanol were not found to be directly comparable to those in methanol for the PtSn case (i.e., the Pt clusters appeared to experience shape or morphological changes so that the large Pt–Pt EXAFS contributions did not cancel completely upon taking the difference), they were similar enough to allow for some comparison of the CO coverages. Using the 0.54 V ‘clean’ (i.e., no methanol) spectrum as a reference, the ratio [CO$_\text{PtSn}$(0.24 V) − clean]/[CO$_\text{PtSn}$(0.24 V) − CO$_\text{PtSn}$(0.40 V)] determined from the relative size of the $\Delta\mu$ amplitudes was found to be 3 ± 0.3. Assuming full coverage at 0.24 V is 0.20 ML (see below), means 0.20(0.20 − θ(0.40 V)) = 3, or θ(0.40 V) = 0.13; that is, ~2/3 of the maximum coverage is still present at 0.40 V on the return.

**Catalysts Utilization.** In our previous work with the Pt$_5$Ru catalysts,$^{53}$ it was shown that the number of electrochemically accessible Pt absorber atoms (Pt$_{\text{acc}}$), and thus their coverage by adsorbate, could be related to the total number of Pt atoms (Pt$_{\text{tot}}$), by accounting for several factors, including the dispersion $D$.
Assuming most of the M atoms are on the Pt surface core, PtM/\(\text{Pt}_{\text{surf}}\) is related to the electrochemical surface area (ECSA) typically reported in m\(^2\) Pt/gPt, but now as a unitless number representing fractional loss.

We can estimate the fractional loss by making a few assumptions. It has been previously shown that the maximum number representing fractional loss.

The estimated diameter assuming spherical particles and these \(N_{\text{cov}}\) values are given along with the dispersion (fraction of atoms at the surface). Having the estimated dispersion we can estimate \(F_{\text{cont}F_{\text{cov}}}\), which is tabulated in Table 2 and plotted in Figure 4 along with the ratio \(nN_{\text{Pd}}/N_{\text{Pd}}\), as a function of \(n\), the Pt/Pt molar ratio.

Figure 4 clearly shows that \(F_{\text{cont}F_{\text{cov}}}\) decreases sharply with the M/Pt molar ratio, but a large scatter exist with \(nN_{\text{Pd}}/N_{\text{Pd}}\), a factor that one might expect would reflect the morphology of the cluster. The continuous decrease in \(F_{\text{cont}F_{\text{cov}}}\) with M/Pt suggests that the M atoms exist primarily at the surface of the Pt core, and as M/Pt increases more of the Pt sites are covered by the M atoms. Further, the absence of a correlation between \(F_{\text{cont}F_{\text{cov}}}\) and \(nN_{\text{Pd}}/N_{\text{Pd}}\) suggest that the latter does not in fact indicate the morphology of the cluster (i.e., the distribution of M in the cluster), but rather the oxidation level of the M atoms on the surface, since oxidation of the surface islands, including insertion of O between Pt and M atoms, will decrease the Pt−M coordination. In our previous work we indeed showed from the Ru K-edge EXAFS data that the PtRuE and PtRuW clusters had a significant fraction of oxidized Ru on their surfaces, and the PtRuW islands were smaller and less oxidized, consistent with the relative sizes of \(nN_{\text{Pd}}/N_{\text{Pd}}\). For PtSn, consistent with the Sn at the surface being heavily oxidized. The much larger values for PtMo (0.7−0.9) seem to suggest that the Mo islands are not islands so easily, with the oxide layer more on the outer surface in contrast to that for Ru and Sn that have a weaker interaction with Pt. However, this is only conjecture.

Assuming most of the M atoms are on the Pt surface core, one can then estimate \(F_{\text{cov}}\) (fraction of surface atoms not covered by M islands) with the simple expression, \(F_{\text{cov}} = 1 - \theta_{\text{H}2} - \theta_{\text{O}}\). We note again that although the final estimated adsorbate coverages, \(\theta_{\text{M}}\) or \(\theta_{\text{H}2}\), represent reasonable estimates of the coverage in situ on real supported Pt catalysts, they are still only slightly better than qualitative for the reasons discussed above, but even such estimates are difficult to obtain by other means.

Table 2 also gives a summary of the total Pt EXAFS coordination, \(N_{\text{cov}} = N_{\text{Pd}} + N_{\text{Pd}}\), for the three Pt/M catalysts in this work and the three PtRu catalysts considered previously.

### Table 2: Comparison of Various Properties of the Six Electrocatalysts Considered

<table>
<thead>
<tr>
<th>Property</th>
<th>PtRuW</th>
<th>PtMo</th>
<th>PtSn</th>
<th>PtRuW</th>
<th>PtRuE</th>
<th>PtMo</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{cov}})</td>
<td>7.2</td>
<td>7.6</td>
<td>7.7</td>
<td>8.3</td>
<td>8.6</td>
<td>9.4</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>1.3</td>
<td>1.4</td>
<td>1.4</td>
<td>1.6</td>
<td>1.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Dispersion</td>
<td>0.90</td>
<td>0.83</td>
<td>0.82</td>
<td>0.74</td>
<td>0.7</td>
<td>0.56</td>
</tr>
<tr>
<td>(nN_{\text{Pd}}/N_{\text{Pd}})</td>
<td>0.64</td>
<td>0.87</td>
<td>0.22</td>
<td>0.30</td>
<td>0.42</td>
<td>0.71</td>
</tr>
<tr>
<td>(\text{thres}(\text{O}/\text{P}))</td>
<td>0.3 (0.5)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.4</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>(DF_{\text{cont}F_{\text{cov}}})</td>
<td>0.19</td>
<td>0.22</td>
<td>0.17</td>
<td>0.27</td>
<td>0.19</td>
<td>0.42</td>
</tr>
<tr>
<td>(F_{\text{cont}F_{\text{cov}}})</td>
<td>0.21</td>
<td>0.27</td>
<td>0.21</td>
<td>0.36</td>
<td>0.27</td>
<td>0.75</td>
</tr>
</tbody>
</table>

\(a\) Calculated assuming spherical particles with uncertainty = ±0.2. In general EXAFS gives particles sizes about 50% smaller than that from XRD or TEM. \(N_{\text{Pd}}\) from Table 1 and similar results for PtRu reported elsewhere. \(b\) Based on particle diameters indicated. \(c\) Threshold potential (V, RHE) for \(nN_{\text{Ru}}/N_{\text{Ru}}\) from Figure 2 and similar results for PtRu reported elsewhere. \(d\) Relative uncertainty = 40%.

### Table 1: Summary of in Situ EXAFS Results from Pt L\(_2\) Edge at 0.54 V RHE (Pt\(_x\)Mo) and 0.58 V RHE (PtSn) in 1 M HClO\(_4\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(N_{\text{Pd}})</th>
<th>(R_{\text{Pd}}) (Å) ± 0.02</th>
<th>(\sigma^2) (Å(^2))</th>
<th>(E_0) (eV) ± 1 eV</th>
<th>(N_{\text{Pt}})</th>
<th>(R_{\text{Pt}}) (Å) ± 0.02</th>
<th>(\sigma^2) (Å(^2))</th>
<th>(E_0) (eV) ± 1 eV</th>
<th>(N_{\text{Ru}})</th>
<th>(N_{\text{Pd}}/N_{\text{Pd}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSn</td>
<td>6.3</td>
<td>2.79</td>
<td>0.005</td>
<td>−0.678</td>
<td>1.4</td>
<td>2.76</td>
<td>0.005</td>
<td>−0.504</td>
<td>7.7</td>
<td>0.2</td>
</tr>
<tr>
<td>PtMo</td>
<td>5.9</td>
<td>2.76</td>
<td>0.005</td>
<td>1.588</td>
<td>1.7</td>
<td>2.76</td>
<td>0.005</td>
<td>5.535</td>
<td>7.6</td>
<td>0.3</td>
</tr>
<tr>
<td>PtMo</td>
<td>7.9</td>
<td>2.77</td>
<td>0.005</td>
<td>1.303</td>
<td>1.8</td>
<td>2.77</td>
<td>0.005</td>
<td>5.995</td>
<td>9.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(a\) Although the absolute errors are of the order of 20%, the changes with catalysts are expected to be meaningful to 0.1 because of the fixed \(\sigma^2\).

### Figure 4. Plot of several parameters from Table 2 as discussed in the text with the M/Pt mole ratio.
estimated particle diameter indicated in Table 2. Figure 4 shows that $F_{\text{cont}}$ (fraction of surface Pt atoms still accessible after support and neighboring cluster contact) varies roughly as $0.4d$ until it reaches 1.0, i.e., small particles suffer a large contact reduction as expected, and this factor goes to 1 as the particle size goes above 2.5 nm.

The estimate above that only one out of every three or four surface Pt atoms is actually electrochemically accessible for catalysis/adsorption on particles less than 1 nm is not surprising considering the relatively high loading utilized here for XAS analysis. Wang et al. suggested a contact factor of 0.7 for much larger 13-nm particles and much lower loading than in this work (both factors should increase $F_{\text{cont}}$). Earlier electrochemical and microscopy catalysts utilization studies indicated that much of the Pt might be inaccessible due to particle agglomeration and other ionic/electronic isolation mechanisms, and found it to depend on the Pt/Nafion ratios, composition, processing techniques, electrolyte, etc. as one might expect. The ECSA in m$^2$ Pt/g Pt can easily change by a factor of 2 or more even for 20 wt % E-tek Pt/VC (Vulcan carbon) electrodes (i.e., without a second M) just by varying the electrolyte.

**Effect of the Metal M on the Dominant Mechanism.** Figure 5a compares the estimated CO/Pt coverages ($\Delta \theta$ in ML/Pt$_{\text{acc}}$) for PtSn, Pt$_3$Mo, and Pt$_4$Mo, as well as for the three Pt$_n$Ru samples previously examined. This figure also indicates the effective experimental ranges previously determined for each of the CO oxidation mechanisms; i.e., the BF mechanism is dominant from 0 to 0.25 V, and the direct ligand (DL) effect is dominant from around 0.25 to 0.75 V. As CO is oxidized by OH above 0.7 V on pure Pt, any decrease in CO coverage above this potential is presumed to be independent of the second alloying metal. Figure 5b provides a similar comparison for fcc Hupd. Figure 6 for OH$_{\text{near}}$ and OH$_{\text{away}}$, and Figure 7 for $n$-fold O.

One can condense all of this data, and better understand it, by estimating the threshold potential for each adsorbate (i.e., for O, OH$_{\text{away}}$, and OH$_{\text{near}}$), as well as the threshold potential for CO oxidation. This is shown in Figure 8 as a function of $N_{\text{PtPt}}$, which reflects the Pt particle sizes. Also included in Figure 8 is a result reported elsewhere for catalysts with large pure Pt particles. Error bars give the estimated uncertainty in these threshold estimates, which are somewhat large because of the paucity of data points.

Figure 8 shows the systematic increase in the adsorbate threshold values with particle size. Note the merging of the threshold for OH and O with particle size, completely consistent with the known near absence of OH on SC Pt(111), and recent theoretical calculations showing the OH and O thresholds
essentially the same for Pt(111).83 Note that for PtRuW, having the smallest average particle size, the O threshold falls off of the linear trend line. However, the data in Figure 7 reveal two thresholds, which we believe arise from O adsorption near (lower) and removed (higher) from the Ru islands, and the higher threshold (indicated by the blue shaded square in Figure 8) clearly falls on the trend line. The data for PtRuW in Figure 8 do not actually reveal a second threshold, but the nature of the curve suggests that one would also exist in this case if the data were extended, and clearly the first threshold is reflecting a ligand effect from the Ru. Finally, note the gradual loss of the M atom ligand effect on Pt with particle size, as expected, and the unexpectedly large ligand effect for the PtRuE catalyst.

These comparisons reveal some interesting observations:

(a) The agreement in Figure 8, to within experimental uncertainty, between the CO oxidation and OHnear adsorption thresholds clearly establishes the direct ligand mechanism as dominant between 0.25 and 0.75 V, and this ligand effect is strongly dependent on particle size.

(b) The most striking difference in the CO coverage between the six catalysts is the large CO coverage on the PtRu catalysts and the dramatically lower CO coverage below 0.3 V for the PtMo and PtSn catalysts. We attribute this to a hydrogen replacement (HR) mechanism, whereby the CO–Pt bond is sufficiently weakened by the M atom ligand effect enabling Hupd to replace CO at low potentials. In our previous work, Hupd was not seen on the PtRu samples in methanol, suggesting that Hupd was unable to displace CO for the PtRu catalysts. We have previously seen88 where hydrogen replaces CO at low currents (potentials) in reformate for some PtRu catalysts, so that the Ru ligand effect does weaken the CO bond sufficiently to allow some H replacement of the CO in the presence of H2 gas and weak concentrations of CO2; however, apparently not enough to allow this to occur in methanol.

(c) We have noted previously that the BF mechanism is active in the PtRu catalysts when the Ru islands are relatively small. When the islands are small, a reverse ligand effect by the Pt keeps the Ru islands from being fully oxidized, enabling OH adsorption on the Ru (i.e., for the two PtRu catalysts). In the PtRuE catalysts the islands are bigger and more oxidized, making the BF mechanism inactive but exerting a very strong ligand effect at 0.5 V. Sn and Mo are expected to be more reactive to oxygen than Ru making the BF mechanism inactive in these cases regardless of island size; but this is not important because the HR mechanism below 0.3 is active anyway.

(d) Figure 8 shows that the OHnear and O thresholds for PtRuE do not fall on the trend lines but are much lower. We have previously observed the strong ligand effect exhibited by the oxidized Ru islands for this PtRuE catalyst (point c above) and will discuss this further below.

(e) All catalysts have essentially zero CO coverage beyond 0.75 V except for PtMo; it apparently requires some OH adsorption directly on the Pt (i.e., the OH must come to the CO, rather then the CO coming to the OH on or near the MoO3 islands). The fraction of CO able to migrate to the M islands will be determined by both the density of M islands (presumably inversely proportional to n, the Pt/M ratio) and perhaps cluster size. Cluster size enters because only the CO on the Pt(111) faces is expected to be mobile (as opposed to those on the corner/edges), and the fraction of Pt atoms on the faces increases as the cluster size increases. The PtMo catalyst has a large n and relatively small particles both consistent with the low fraction of CO able to migrate to the M islands.

### 5. Discussion

#### Performance in Reformate versus Methanol

The results reported above suggest that the Mo and Sn islands are oxidized at all relevant potentials and exert a strong ligand effect on the Pt, while the Ru ligand effect is strongly dependent on the island size, large for the big Ru islands and smaller for the smaller ones. The ligand effects exhibited by Sn, Mo, and Ru for both hydrogen oxidation (HOR) in reformate, and methanol and CO oxidation have been extensively studied previously, so we compare the current results with those found in the literature.

The literature results are summarized in Table 3. These results generally show that PtMo (and perhaps PtSn) catalysts are more effective fuel cell catalysts in reformate than PtRu; however, PtRu is more effective in a direct methanol fuel cell. This difference has been attributed to a number of factors, some noted in Table 3. We discuss these factors in light of the three different mechanisms for CO oxidation listed above, namely the BF, DL, and HR mechanisms. For example, Mukerjee’s group (as well as others) have noted that CO can compete for adsorption with OH on Ru, but not on Mo or Sn, similar to that suggested above, ruling out the BF mechanisms for PtMo and PtSn.18,19

A second difference between the PtM catalysts has consistently been noted when studying CO oxidation, and that is the difference in the nature of the CO participating in the reaction. Wang et al.41 have noted that two types of CO exist on PtSn, a “high coverage” CO and a “low coverage” CO, the former bonded much weaker to the surface, and arising only from direct adsorption of CO, (i.e., it cannot be formed from methanol oxidation because methanol requires more than one site to oxidize, and neighboring multiple sites do not exist when the “low coverage” CO already poisons the Pt for methanol oxidation). Therefore, Wang et al. attribute the strong enhancement (factor of 1000) for CO stripping currents in PtSn to oxidation of this “high coverage” CO, which apparently only exists on PtSn during CO exposure.85 It is probable that the COhi and its contribution to the oxidation stripping current does not relate directly to the effectiveness of PtSn in reformate and methanol, because the COlow will primarily determine this. We suggest that the COhi is linearly bonded CO, and COlow is bridged (or even 3-fold) bonded CO. CO is believed to bond in atop sites, and then at higher coverage, because of lateral interactions, some CO is pushed into bridge (and n-fold) bonded sites. SFG studies suggest that CO may even be lying nearly flat at lower coverage.84 The bridged/linear binding ratio is

| Table 3: Summary of Previously Reported Pt, PtRu, PtMo, and PtSn Electrocatalysts Properties |
|-----------------------------------------|---------|---------|---------|---------|
| characteristic | Pt | PtRu | PtMo | PtSn |
| rel. CO tol. in H2/CO | 1 | 1.3 | 4 | 1.2 |
| rel. eff. in methanol | ~5 | 1 | 1 |
| CO/M | yes | yes | no | no |
| CO react. order | 0.39 | 0.46 | 0.38 |
| CO ox pot. (V @ thr and pk, 85 °C) | 0.4 | 0.22 | <0.18 | 0.18 |
| H2/100 ppm CO | 0.52 | 0.38 | 0.39 | 0.48 |
| CO binding sites | CObridge | COlow | CObridge | COlow |
| CO ox. pot. (V) | 0.6 | 0.35 | <0.1, 0.5 |
| CO ox. pot. (V) sat. CO | 0.85 | 0.60 | 0.3 |

a CO tolerance based on limiting current at steady state anode polarization in a 1 cm2 PEMFC under 100 ppm CO in H2 at 85 °C. b Based on limiting current for methanol oxidation at 90 °C with 1 M MeOH and Naion 117 membrane.
highly dependent on coverage, particle size, and even Pt particle support (i.e., acidic or basic). The different order in CO for PtSn observed by Mukerjee et al. (Table 3) may arise from this different CO binding site.

Mukerjee’s group has also measured the activation energy for releasing CO from Pt sites during the HOR as summarized in Table 3. Because \( E_a \) is related to the removal of CO to create active sites for the HOR, it in some sense reflects the nature of the Pt–CO bond strength. These results suggest then that the Pt–CO bond on PtSn and PtMo has a much weaker Pt–CO bond strength compared to that on Pt and PtRu; however, at lower temperature, when the CO coverage is higher, a weaker bonded CO participates also on PtRu. All of these results suggest that the adatom islands weaken the Pt–CO bond in the order, Ru1 < Mo < Sn ≈ Ru2. Here the second \( E_a \) for PtRu is interpreted as arising from two different Ru environments (Ru1 vs Ru2) rather than two different CO binding sites on Pt (e.g., linear vs bridged as suggested by Lee et al.21). As we suggested previously, Ru can exert two widely different or varying ligand effects, depending on the oxidation state of the RuOx islands, the later determined in part by the Ru island size. Therefore, we suggest that the ligand effect weakening the Pt–CO bonding increases in the order Ru < MoOx ≈ SnOx < RuOx.

Comparison of the threshold potentials for CO oxidation in reformate (Table 3) indeed suggests they are all in the range of 20–48 mV consistent with the DL mechanism and Figure 8, but in general they are slightly lower for Mo and Sn than for Ru, suggesting a ligand effect in the order Ru < SnOx ≈ MoOx. Combining these results with those in this work, where we find a very strong ligand effect for RuOx, we find the methanol oxidation and HOR in reformate results suggest similar trends; namely that the ligand effect increases in the order Ru < MoOx ≈ SnOx < RuOx.

The results above suggest that the ligand effect weakens the Pt–CO bond, that MoOx and SnOx exert a particularly strong ligand effect compared to Ru, and this is most directly confirmed in Figure 5 by the different coverages of CO in methanol. Previously reported results summarized in Figure 9 directly confirm this difference between PtRu vs PtMo catalysts also in CO stripping. Here CV curves for Pt are compared with the PtRuE and PtMo catalyst after dosing with CO at 0.0 V for 1 h, and for PtMo without exposure to CO (only N2 for 1 h). Comparison of the two CV curves for PtMo in the Hupd region below 0.3 V does show some CO poisoning, but not near as much as for the Pt and PtRu catalysts. The bottom part of Figure 9 shows the CO electro-oxidation charge reported by Russell et al.86 as determined from CV curves similar to those above, as a function of the CO dosing potential. The dramatic difference in CO coverage behavior between Pt and PtRu vs PtMo confirms the very different mechanisms acting in PtMo. The CO coverage decreases with dosing potential for both Pt and PtRu, obviously because of increasing water activation producing OH on the surface to oxidize the CO. This occurs much more dramatically in PtRu because of the ligand mechanism increasing the strength of the Pt–OH bond and lowering the CO oxidation peak for PtRu compared to Pt in the CVs above. However, on PtMo the CO coverage increases with dosing potential. This is exactly as expected when the hydrogen replacement mechanism is dominating, since as the dosing potential is increased, less Hupd is present, allowing for more CO to adsorb. Although this data was reported previously, the previously proposed mechanism invoked the Mo (IV/VI) redox couple without further specificity on how this mechanism worked.18,86

We do not suggest that the ligand effect is the same for Sn and oxidized Sn (or Mo and oxidized Mo), only that both Sn and Mo are normally oxidized above 0.2 V when existing as islands on Pt. Other evidence for the importance of the oxidation state of the second metal in PtM bimetallics, and we believe the source of conflicting conclusions on the effect of the second metal is abundant in the literature. For example, consider the PtMo literature first. DFT calculations on a PtMo cluster mimicking the PtMo(111) surface showed very little weakening of the CO–Pt bond, and the reduced barrier to CO oxidation was therefore attributed to a subtle geometric effect of the transition state.87 On the other hand, similar DFT calculations on a water covered Pt(111) surface (i.e., essentially oxidized Mo) showed a drop in the CO–Pt binding energy by a factor of 3 compared to CO/Pt(111) surface.88 This again reflects the strong dependence on the oxidation state of the Mo. Direct experimental proof for the lower Pt–CO binding in PtMo catalysts was obtained from temperature programmed desorption (TPD) experiments that showed that the linearly adsorbed CO species on a PtMo/TiO2 sample desorbs at temperatures below 375 K, which is almost 100 K below the COx species desorption from Pt/TiO2.89 This low desorption temperature of CO/PtMo was attributed to the chemical oxidation at the boundaries of the MoOx oxide nanoclusters that were detected by XPS as the most abundant oxidation state. Finally recent studies of methanol oxidation over MoOx@Pt core–shell nanoparticles (1–2 ML of Pt over a MoOx core) revealed incredible CO tolerance, and a threshold for CO oxidation much lower than even traditional PtMo/C catalysts. The authors suggest that a different mechanism other than the bifunctional must be at work in this case and suggest a dramatic weakening of the Pt–CO bond to allow
such a dramatic lowering of the methanol oxidation overpotential.\textsuperscript{90} It should be mentioned that the weakened Pt–CO bond for PtMo catalysts is not necessarily the only mechanism for the enhanced CO tolerance, as many papers show a CO reduction peak in the CV curves around 0.4 V, which has been attributed to a bifunctional type mechanism\textsuperscript{18,86} but clearly oxidized Mo exhibits a much stronger ligand effect on the Pt–CO binding, and it is probably the dominant role.

Similar apparently conflicting but now understood results have been found for PtSn bimetallic catalysts. For example DFT calculations for Pt\textsubscript{x}Sn(111)\textsuperscript{91,92} show that the Sn has a relative weak effect on the Pt–CO binding, (only 10% reduction)\textsuperscript{93}. Experimental IR data examining the CO vibrational stretch frequency region also suggest that on Pt\textsubscript{x}Sn(111) the CO stretch is only slightly decreased relative to that for CO/Pt(111)\textsuperscript{94}. Stamenkovic et al. even attribute this small decrease to a coverage effect (i.e., higher) on the Pt\textsubscript{x}Sn(111) and therefore appear in this case not to invoke any ligand effect from the Sn on the CO binding to Pt. In these two cases the Sn exists in a reduced state primarily alloyed with the Pt. In contrast, when Sn is added as an adatom on the Pt surface, and therefore existing in an oxidized state, very strong ligand effects have been noted. Nearly 20 years ago, Haner and Ross\textsuperscript{84} observed that dissolved Sn species interacting with the surface greatly enhanced methanol oxidation, while PtSn alloys did not. It is well known that SnO\textsubscript{x} islands on Pt also dramatically enhance acetaldehyde formation in ethanol oxidation and DFT calculations indicate acetaldehyde formation occurs because of a weakened Pt–C interaction.\textsuperscript{94} In work studying the effect of the alloying degree in PtSn/C catalyst on its catalytic behavior for ethanol oxidation, it was found that a PtSn/C catalyst with low alloying degree (i.e., oxidized Sn) enhanced the yield of acetaldehyde products, but a PtSn/C catalyst with high alloying degree (nonoxidized Sn) promoted the overall activity for ethanol oxidation (i.e., enhanced the rate in a different fashion, mostly like CO oxidation via a bifunctional mechanism) but did not decrease the Pt–C bond strength.\textsuperscript{95} It seems clear that Mo and Sn show the same varied electronic (ligand) effect on the Pt–C or Pt–CO bond, depending on oxidation state, as Ru, but as will be discussed below, Sn and Mo are mostly oxidized when existing as polyatomic surface islands.

We must carefully distinguish between the ligand effect on the Pt–CO bond and that on the Pt–OH bond (i.e., water activation). The BF and DL CO oxidation mechanisms distinguish the source of the OH involved in eq 3a, i.e., either on the M or near the M island, and the threshold potential for these mechanisms are due to the production of OH via water activation. In Figure 8, no systematic difference with M is found in this threshold, except for the PtRuE catalysts; rather, it shows that the ligand effect is more dependent on particle size. However a significant and systematic trend does appear in the tabulated $E_a$ in Table 3, reflecting the Pt–CO bond strength: Ru > MoO\textsubscript{2} λ = SnO\textsubscript{2} > RuO\textsubscript{2} λ, and this is also reflected in the HR mechanism observed for PtSn and Pt\textsubscript{2}Mo catalysts. Thus, our results in Figure 8 and previous results in Table 3 are generally consistent; however, this does introduce two puzzling questions:

1. Why does the ligand effect by these MO\textsubscript{x} islands strengthen the Pt–OH bond but weaken the Pt–CO bond?
2. Why is the HR mechanism not active for the PtRuE catalysts, if the RuO\textsubscript{2} λ ligand effect is the strongest, as exhibited by the water activation?

The answers to these questions are given in Figures 9 and 10, respectively.

Figure 9 illustrates the Norskov\textsuperscript{96} bonding model for O/Pt and the well-known Blyholder\textsuperscript{97} model for CO/Pt. According to the Norskov model for O/Pt, a raising of the Pt d band raises the antibonding Pt–O orbital, which causes charge transfer out of this orbital and hence an increase in the Pt–O bond strength. Thus, first-row transition metals such as Fe, Co, Ni, and Cr, when mixed with Pt generally push down the Pt d band, decrease the Pt–O bond strength, thereby decreasing OH poisoning and increasing the oxidation reaction rate (ORR). In contrast metals such as Mo, Ru, and Sn raise the Pt d band (as shown in Figure 9a), increase the Pt–O bond strength and thereby increase the oxophilicity of the bimetallic cluster and hence water activation. In contrast, a similar raising of the Pt d band makes the Pt–CO bond less covalent and weakens the Pt–C bond as illustrated by the Blyholder model,\textsuperscript{97} particularly for linearly bonded CO (dominating at higher coverage) when the 5σ orbital dominates the bonding with Pt as discussed above. The Pt–CO antibonding band is sufficiently high that significant charge transfer does not occur for O, and this accounts for the reverse direction in binding with raising of the Pt d band. Indeed even the Pt–O bond can weaken with raising of the d band if the Pt particle is sufficiently small and the Pt–O antibonding band is sufficiently high (the strong coupling limit). Experimental results reported by Koningsberger et al.\textsuperscript{98} and DFT results do indeed show this opposite trend for the Pt–OH coverage for small Pt particles. Further evidence for the reversal of the Pt–OH bond strength on small particles is clearly evident from the recent work examining monolayers of PtM on various metals M′ (i.e., ternary systems PtM/M′ with one metal M in the outer monolayer and another M′ as the substrate)\textsuperscript{99}. In this case the M′ metal reduced the Pt–OH bond strength and coverage by a small amount, and...
the M metal by a very large amount. Note the M metal reduced the Pt−OH coverage, not increased it as we find above. Calculations suggest that the MOH−PtOH repulsion was the dominant factor keeping the OH off of the Pt, but a “reverse” electronic ligand effect in the strong coupling limit (single-atom particles) could also be playing a significant role.

Figure 10 provides an answer to question 2 above regarding the absence of the HR mechanism in PtRuE, when the water activation suggests a very strong ligand effect. Mo and Sn are more reactive metals than Pt and oxidize well below 0.2 V, indeed Sn goes to Sn⁴⁺ already at −0.16 V RHE.⁹⁰ In the potential region above 0.0 V, Sn⁴⁺ even goes to Sn⁶⁺, so the Sn islands are always oxidized in the potential region of interest here.⁹⁰ The same goes for Mo, indeed Mukerjee et al.¹⁰⁸ et al. have found that around 0.43−0.50 V, Mo⁴⁺ goes to Mo⁶⁺. However, Figure 10 suggest that an O(H) layer forms in the range of 0.2−0.5 V consistent with CV plots for Ru electrodes, which show oxidation or OH adsorption over the range 0.3 and higher.¹⁰¹ Thus, Mo and Sn islands are oxidized and exert a strong ligand effect on the Pt throughout the potential range, but Ru is oxidized only above 0.45 V. This explains the lack of the HR mechanism for PtRuE in region a) of the figure, when the RuO₂ is already significantly reduced, but a strong ligand effect in region b where the threshold for CO oxidation by adsorbed OH in methanol appears.

This difference between Mo and Ru is revealed very clearly by in situ XAS data reported by Mylswamy et al.¹⁰² on PtMo/C and PtRu/M catalysts. Their Ru K-edge data show oxidation of the Ru with potential in the range 0.1−1.0 V, with the average oxidation level intermediate between Ru and RuO₂ samples. In contrast, their Mo K-edge data shows the Mo to be mostly oxidized and thus compares more with that for MoO₂. Finally, their white line of Pt L₃-edge data shows an increase of intensity with increased M composition. The white line intensity increases nearly linearly with Mo atomic fraction but very slow initially with Ru atomic fraction until about 50% Ru when it increased sharply. Assuming this increase results from OH adsorption, it demonstrates again that the electronic ligand effect dramatically increases only when the Ru islands get larger and become oxidized, exactly as expected from the above discussion.

The above emphasizes the importance of the oxidation state of the alloying metal and its effect on Pt. Many studies of Pt on various supports have illustrated the dramatic effect that the acidity of the support can have on the nature of Pt and its reactivity with H, O, and other adsorbates.¹⁰³ In general, an acidic (covalent oxide) support causes the bond with H to get weaker and that with O to get stronger (in the strong coupling and small particle limit), and vice versa for basic supports (ionic oxides). Therefore the effect of oxidation of the metal islands in electrocatalysts on Pt has a strong similarity with that established previously in the gas phase where the charge on the O anions of the oxide is the critical parameter.⁹⁸,¹⁰³ By why should RuO₂ give a stronger ligand effect than MoO₂ and SnO₂ at 0.5 V? The electronegativities of the metals (Mo = 1.8, Sn = 2.0, Ru = 2.2)¹⁰⁴ suggest that the full RuO₂ oxide should be the least ionic of these three (hence the O anion have the smallest negative charge); however, as illustrated in Figure 10, the RuO₂ is only partially oxidized in this potential region and the character of the oxide becomes more covalent with oxidation level (i.e., the oxide ionic character decreases with oxidation level as the metal valence increases). Therefore, the partially oxidized RuO₂ (when the oxides is quite ionic) exerts the strongest ligand effect of the three oxides at 0.5 V, but at potentials below 0.2 V this oxide is nearly totally reduced (i.e., RuO₂ has returned to OH/Ru or even just Ru when the islands are very small).

Finally, the results reported here easily explain why Pt₈,Mo is better for HOR in reformate and Pt₈Ru for methanol oxidation as exhibited in Table 3. The striking difference in Figure 5a between the CO coverage below 0.3 V for PtSn, PtMo and that for Pt₈Ru gives the answer. At low potentials where the HOR occurs, the HR mechanism active with Pt₈Mo keeps the catalysts relatively free of CO. However, in methanol, the potential generally rises to 0.3−0.4 V where the strong DL mechanism becomes active, and this mechanism is even better at freeing Pt from CO at this potential. Here it is useful to quote from a paper by Koper,³⁸ with regard to the different mechanisms at work for CO vs methanol oxidation; “The bifunctional effect is thought to be the dominant mechanism in the catalytic methanol electro-oxidation. However, in relation to CO tolerance of the hydrogen oxidation, the current consensus in the electrochemical surface science community seems to shift towards the electronic effect as the dominant mechanism.” The results in this work confirm this statement; the electronic weakening of the Pt−CO bond is critical for HOR in reformate, but the bifunctional mechanism, which involves CO oxidation by the OH existing on the second metal or nearby Pt (the latter also as a result of an electronic ligand effect) becomes more important for the MOR.

6. Conclusions

The coverages of CO, Hupd, and O(H) on Pt in two different Pt₈Mo anodes and a PtSn anode are compared with that previously obtained for three Pt₈Ru anodes. The importance of island size and M oxidation state appears to be critical factors in catalyst performance only for PtRu as Sn and Mo islands on the surface (as opposed to Sn and Mo alloyed with Pt) are essentially fully oxidized at all relevant potentials. The ligand effect appears to follow the order Ru < MoO₂ < SnO₂ < RuO₂ with the Pt−OH bond getting stronger and the Pt−CO bond weaker with increasing ligand effect, i.e., oxidation state of the metal M. In retrospect, this should not be surprising, since Ru, a Pt-group metal, shares common properties with Pt, and therefore, an isolated Ru atom shares relatively weak ligand interaction effects with Pt. However, after the formation of larger islands, the metallic-like Ru islands oxidize and have very different properties. Mo and Sn islands on the other hand are very different from Ru, oxidizing at lower potentials and exerting a relatively strong ligand effect at all potentials.

Finally, the data suggest that the catalyst effectiveness in methanol is determined primarily by the bifunctional mechanism enhanced by the MO₂ direct ligand effect increasing Pt−OH binding; however, CO tolerance in reformate is determined primarily by the hydrogen replacement mechanism, the latter enhanced by the MO₂ ligand effect weakening the Pt−CO binding.

References and Notes

Pt₅M Electro catalysts in Methanol Studied by XANES

JP908582R