Characterization and Theory of Re films on Pt(111) grown by UHV-CVD

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ABSTRACT

Changes in surface chemistry and morphology of Re-Pt surfaces synthesized by ultra-high vacuum chemical vapor deposition (UHV-CVD) of Re on Pt(111) were studied by a combination of experiment and density functional theory (DFT) modeling. A Re oxide formed following exposure of the as-deposited Re to 1×10^{-6} mbar oxygen at 600-673 K. Subsequent annealing at 973 K resulted in oxygen desorption and a decrease in Re coverage, as calculated by XPS and as observed by STM. This observation was explained by DFT calculations which showed that a clean Pt surface slab with subsurface Re is thermodynamically more favorable than Pt(111) with Re on the surface. DFT calculations also predicted weaker O and CO binding on this surface compared to both monometallic Pt and Re, and HREELS and temperature desorption measurements suggested that O binds weakly to the Pt skin surface, with oxygen on the Pt skin

desorbing from this surface following annealing at 373 K. Trends in adsorption energies were consistent with DFT calculated d-band centers of surface atoms for model Pt-Re structures. Comparison of HREELS data and STM images with DFT calculated vibrational frequencies have been used to understand the structure of rhenium oxide on Pt(111).

1. Introduction

Pt-Re catalysts have been used for hydrocarbon reforming since their invention in the 1960s [1]. Investigators have discovered many benefits of using bimetallic Pt-Re catalysts over monometallic catalyst systems, most recently for aqueous phase reforming (APR) of model polyol compounds [2-7]. Improved turnover rates for glycerol conversion to syngas for Pt-Re/C catalysts were reported by Simonetti et al. [7], and Kunkes et al. [6] discovered that the addition of Re to a Pt/C catalyst promoted the overall rates of glycerol APR and the water-gas shift reactions by weakening CO binding to the surface. They also found that Re prevents sintering of Pt nanoparticles. Daniel et al. [5] similarly found that the addition of Re to Pt increased glycerol hydrogenolysis rates and leads to measured selectivity toward 1,3-propanediol as high as 34%. Multiple groups have found that adding Re to Pt catalysts promotes Pt reduction [4, 5].

Understanding the nature of the active sites on Pt-Re surfaces responsible for improvements in APR reaction rate and selectivity remains a challenge given the range of surface configurations possible. Surface sensitive studies in controlled ultra-high vacuum (UHV) environments have been used to better understand the interaction between Pt and Re using model systems on single crystal and foil surfaces [8-17]. Bimetallic systems

have been prepared on flat samples by evaporation of Pt on Re(0001) [11-13], by evaporation of Pt on Re foil [10, 18, 19], by evaporation of Re on Pt foil [16], and by evaporation of Re on Pt(111) [8, 9, 12-15, 17] and Pt(100) [12]. The resulting surfaces have been subjected to a variety of treatments including heating, oxidation, and exposure to small probe molecules. Of special interest are properties of Re films on Pt and alloyed Pt-Re systems, formed by annealing a surface containing Re and Pt to temperatures ≥ 900 K [8, 9, 12, 16, 17]. In one study, CO was found to bind more weakly to this alloy surface than monometallic Pt or Re, and O interaction with this surface was not detected by XPS [8]. Similarly, Duke et al. found that Pt-Re alloy surfaces on Pt(111) produced more CO₂ from CO oxidation than monometallic Pt(111) and that the alloy surface was more resistant to oxidation [17]. The unique properties of Pt-Re alloy surfaces have been attributed to electronic effects associated with this bimetallic system [9].

In this study, we synthesized bimetallic Pt-Re surfaces by UHV chemical vapor deposition (UHV-CVD) of Re onto Pt(111) and followed chemical and morphological changes to the surfaces after annealing and oxidative treatments using surface sensitive experiments. DFT modeling aided interpretation of the experimental results. Briefly, two types of surfaces were synthesized: first, as-deposited Re formed a sub-monolayer surface oxide, ReO_x ($0.5 \leq x \leq 1$), upon exposure to 1×10^{-6} mbar O₂ at temperatures ≥ 673 K. Annealing to about 1000 K desorbed this oxygen and caused Re diffusion into the near surface region, forming the second surface type, a Pt skin. We found that O and CO binding energies on Pt-skin surfaces were much weaker than on a monometallic Pt(111). This type of adsorption behavior, predicted in the past based on relative metal-metal bond strengths for bimetallic systems [20], can also be explained on the basis of calculated d-

band centers of Pt-Re systems. This work shows the power of coupling surface sensitive characterization experiments with DFT modeling, which together can predict thermodynamics of adsorption processes and surface structures for the complicated Pt-Re bimetallic system.

2. Experimental Materials and Methods

Experiments were performed in an Omicron Surface Analysis Cluster at the Birck Nanotechnology Center, Purdue University. This system has been described in detail elsewhere [21]. Briefly, it consists of a preparation chamber and μ -metal analysis chamber with base pressures of 1×10^{-9} and 5×10^{-11} mbar, respectively. The preparation chamber contains an Ar^+ sputter gun, resistive sample heating, and leak valves connected to gas dosing manifolds for precursor and gas dosing. The analysis chamber is equipped with instrumentation for X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), high resolution electron energy loss (HREELS), and low energy electron diffraction (LEED).

A Pt(111) single crystal (MaTecK) with 9.0 mm diameter, 1.0 mm thickness, and orientation accuracy $< 0.5^\circ$ was used. Repeated cycles of Ar^+ sputtering and annealing at 1000 K were used to clean the crystal, as monitored by XPS, LEED, HREELS, and STM. Re was deposited on Pt(111) by UHV-CVD using $\text{Re}_2(\text{CO})_{10}$ as the precursor (98%, Strem Chemicals Inc.). $\text{Re}_2(\text{CO})_{10}$ was pumped through the dosing manifold for several minutes prior to sample dosing in the preparation chamber through a leak valve at a pressure of approximately 5×10^{-6} mbar. To have sufficient and stable pressure during precursor exposure, a mini-cylinder with $\text{Re}_2(\text{CO})_{10}$ was heated in a hot water bath.

Crystal temperatures, controlled by resistive heating, precursor temperatures, controlled by a hot water bath, and exposure times are reported in Table SI-1 in the Supplementary Information. For annealing treatments in oxygen, the crystal was cooled in oxygen following heating. Oxygen was pumped from the system once the crystal was cooled for transfer from the preparation to the analysis chamber, which took approximately ~5 min. At this time, the pressures of each chamber were close to the base pressures reported above.

HREELS data were acquired with an ELS5000 (LK Technologies). Electrons were collected in the specular direction with primary beam energies of 5 or 7 eV. The FWHM of the elastic peak was roughly 3 meV (24 cm^{-1}) and the peak had intensity above 10^5 cps. All HREELS spectra have been normalized to the elastic peak intensity.

XPS data were collected using non-monochromatic Mg $K\alpha$ X-rays (1253.6 eV) at an X-ray gun power of 150 W. High-resolution core level spectra were obtained at constant pass energy of 20 eV with an energy spacing of 0.05 eV. XPS resolution, expressed as the FWHM of the Pt4f_{7/2} peak, was approximately 1.2 eV. Electrons were collected at a 45° photoemission angle with respect to the surface normal. No energy scale correction was foreseen by the analyzer manufacturer (the electron energy analyzer - Omicron EAC 125 and the analyzer controller - Omicron EAC 2000); therefore, it was possible only to set the Au 4f_{7/2} peak at 84.0 eV by changing the spectrometer work function.

XPS data were analyzed using CasaXPS (version 2313Dev64) software. Metallic Re 4f and Pt 4f components were fit with an asymmetric line-shape with both Gaussian

(10%) and Lorentzian (90%) components and tail dampening (CasaXPS Line-shape = LF(1, x, y, 90); x = 2 for Pt 4f and x = 1.5 for Re 4f; y = 50 for Pt 4f and y = 10 for Re 4f.) The superficial Re oxide and O 1s peaks were fit using a symmetric line-shape with both Gaussian (70%) and Lorentzian (30%) components (CasaXPS Line-shape = GL(30)). Spin orbit doublets for the Pt 4f and Re 4f regions were subject to spacing constraints of 3.33 and 2.43 eV, respectively. Areas of spin orbit doublets were also constrained to their expected ratios. Coverages for Re, C, and O reported in this work have been calculated using Fadley's approach [22], which assumes fractional coverage of a non-attenuating overlayer on a semi-infinite substrate. Coverage is expressed in monolayers (ML), and is the ratio of the number of adsorbed species per surface Pt atom on Pt(111). This model has been described in detail elsewhere [21].

STM images were collected with an Omicron ambient temperature UHV STM/AFM in constant current mode. W tips were made via electrochemical etching followed by electron bombardment in UHV. Images were analyzed using WSxM software [23]. LEED patterns were acquired using an Omicron rear-view LEED optics with primary electron energies between 63-261 eV.

3. Computational Details

DFT calculations were performed using plane wave-based VASP (Vienna Ab initio Simulation Package) code. Exchange correlation energies were described using GGA-PW91 treatment. Ionic cores were represented using the PAW (Projector Augmented Wave) method. The as-deposited Re on Pt was modeled using a Re film of 1 ML coverage on the Pt(111) surface. Different coverages of subsurface Re were

investigated to model the Pt-Re structure after annealing. (111) surfaces were modeled using 2×2 unit cells with 5 layers, with the bottom two layers fixed at bulk atomic distances. The vacuum layer between the slabs was fixed at 13 – 14 Å. The surface Brillouin zone was sampled using Monkhorst scheme with a $4 \times 4 \times 1$ k point grid. The energy cutoff was fixed at 400 eV. Self-consistent electronic iteration steps were converged to 1.0×10^{-4} and ionic forces were converged to $0.02 \text{ eV} \text{Å}^{-1}$. Gas phase calculations were performed in $13 \times 14 \times 15$ Å unit cells. Methfessel Paxton smearing of 0.1 eV for surface slabs and Gaussian smearing of 0.01 eV for gas phase molecules was applied in the calculations. The binding energy of atomic oxygen was referenced to gas phase molecular oxygen. The DFT calculated lattice constant for Pt was 3.99 Å. This is close to the experimentally reported value of 3.92 Å [24].

4. Results and Discussion

The experimental results outline three stages of the preparation and characterization of the Pt-Re bimetallic system on Pt(111): (1) preparation via UHV-CVD, (2) oxygen exposure for carbon removal and Re oxidation, and (3) subsequent annealing in UHV to reduce Re_xO_y . All Re/Pt(111) surfaces were characterized by XPS, HREELS and STM. The use of theory for interpretation of these results follows.

4.1 Deposition of Re Using UHV-CVD

Figure 1. XPS O 1s (left) and Re 4f (right) core-level regions. Bottom spectra: after dosing $\text{Re}_2(\text{CO})_{10}$ on Pt(111) at approximately 5×10^{-6} mbar, sample temperature = 573 K, temperature of precursor miniature cylinder ≈ 353 K. Middle: after heating at 673 K in 1×10^{-6} mbar O_2 for 20 min. Top: after subsequent stepwise annealing to 973 K. Open circles: raw data after background subtraction, grey line: peak envelope from sum of components. In the O 1s region, blue dashed line: O_{ads} component, red dashed line: CO_{ads} component. In the Re 4f region, blue dashed line: Re^0 component, red dashed line: Re_xO_y component.

$\text{Re}_2(\text{CO})_{10}$ was dosed on clean Pt(111) surfaces and on Re/Pt(111) surfaces (coverage of subsurface Re ≤ 0.1 ML). Dosing conditions and XPS results for the four separate experiments are summarized in the supplemental information in Table SI-1. To the best of our knowledge, CVD has been used previously for deposition of Re onto a variety of substrates [25-28], but not for deposition of Re onto Pt in UHV for surface sensitive studies. The Re coverage calculated from XPS data varied between 0.4 and 1.0 ML using a variety of dosing conditions. The Pt(111) sample temperature varied between 410 and 573 K, and precursor temperatures varied between 313 and 353 K. Immediately after all precursor exposures carbon contamination with coverage ranging between 1.9 to 5.3 ML was detected. Otherwise, oxygen coverage was very low (< 0.1 ML) in all cases, indicating that adsorbed carbon was not in the form of CO. The absence of CO was confirmed by a single C 1s peak at ca. 284.0 eV. Deposited carbon might form through CO dissociation on a Pt-Re center.

A typical Re 4f spectrum after dosing $\text{Re}_2(\text{CO})_{10}$ is shown in Figure 1. On the as-dosed surface, the Re 4f_{7/2} binding energy (BE) varied between 40.5 and 40.8 eV. The measured Re 4f_{7/2} BEs are 0.2-0.5 eV higher than the bulk metallic reference BE of 40.3 eV [29]. This range of BEs is similar to that observed by Ramstad et al. [9] for sub-monolayer coverages of Re islands deposited on Pt(111) by evaporation. They fit the Re 4f_{7/2} peak with two components: one at 40.6 eV, assigned to Re surrounded by Re in a Re 2D island, and another at 40.8 eV assigned to Re on the edge of an island. Duke et al. observed a Re 4f_{7/2} BE of 40.9 eV following evaporation of 2.9 ML of Re onto Pt(111) [17].

An STM image of the surface exposed to $\text{Re}_2(\text{CO})_{10}$ is shown in Figure SI-1. Imaging of this surface was difficult because it was very rough, and the tip was most likely dragging carbon. Bright features cover the majority of the surface and are assigned to Re or C clusters. The presence of carbon likely affects the morphology of the as-deposited Re. This carbon might be responsible for the 3D particle growth observed in STM by blocking adsorption sites on Pt. The carbon might also poison the surface, limiting the amount of Re deposited at a time by this technique.

4.2 Rhenium Oxide Formation

Oxygen treatments were used to remove carbon from the surface exposed to $\text{Re}_2(\text{CO})_{10}$. Oxygen was dosed at 1×10^{-6} mbar for a total of 20 minutes at 673 K. The resulting Re 4f and O 1s core level regions for the sample with initial $\theta_{\text{Re}} = 0.8$ ML are shown in Figure 1. Following this treatment, 87% of the Re 4f envelope could be fitted with a Re 4f_{7/2} component at 41.3 eV assigned to a rhenium surface oxide, Re_xO_y . The remainder of the 4f_{7/2} peak was the metallic/alloy Re component at 40.7 eV. Following the oxygen treatment, the Re coverage decreased from 0.8 to 0.6 ML, carbon coverage decreased from 3.4 to 0.1 ML, and oxygen appeared on the surface with coverage of 0.4 ML. The O 1s region was fitted with two components: a dominant feature at 530.6 eV and a weak feature at 532.2 eV assigned to O adsorbed on Re and CO adsorbed on Pt, respectively. Literature reports have assigned peaks at ~530.0 eV to O on both Pt and Re, and peaks at ~532 eV to CO on both Pt and Re. The justification for our assignment is discussed below in the presentation of HREELS results. From XPS, the ratio between oxygen and oxidized Re was 0.6. In a separate experiment, when Pt(111) with initial θ_{Re}

= 1.0 ML was exposed to O₂ at 1×10^{-6} mbar at 598 K, the oxygen/oxidized rhenium ratio was 0.8. The oxidized Re 4f_{7/2} component, Re_xO_y, was still located at 41.3 eV.

Based on comparison to literature, the Re 4f_{7/2} component attributed to Re_xO_y likely did not arise from a rhenium oxide with bulk stoichiometry. Tysoe et al. [16] measured the Re 4f_{7/2} BEs of various Re oxides prepared by evaporating approximately 10 ML of Re on a Pt ribbon and then oxidizing these surfaces in 1 atm of oxygen at various temperatures. They reported Re 4f_{7/2} BEs of 42.5, 44.9, and 46.7 eV for ReO₂, ReO₃, and Re₂O₇, respectively. Binding energies of 41.3 to 41.4 eV have been attributed previously to a superficial rhenium oxide with stoichiometry ReO [17, 30-33]. The Re 4f_{7/2} peaks with similar BEs were assigned by other groups to ReO_x, $0.5 \leq x \leq 1$ [34], (BE = 41.2 eV) and to superficial oxide stoichiometries of ReO_{1/3} (BE = 41.1 eV) and ReO_{2/3} (BE = 41.5 eV) [8]. Based on these BE assignments and the ReO_x stoichiometry of $0.6 \leq x \leq 0.8$ calculated using XPS data, the superficial Re oxide stoichiometry was between ReO_{1/2} and ReO in our experiments.

Figure 2: HREELS spectra of superficial oxide surface and subsequent annealing in UHV at the specified temperatures for 5 min. The original superficial oxide surface was prepared by dosing Re/Pt(111) to 1×10^{-6} mbar O₂ for 20 min at 673 K (left panel) and for 10 min at 723 K (right panel) followed by cooling in O₂ to 373 K and 343 K, respectively.

Vibrational Mode	Frequency, cm ⁻¹	
	Re(0001)	Pt(111)
$\nu(\text{M-CO})$ (on top)	415 [35], 405±15 [36], 428 [37]	470 [38], 466*
$\nu(\text{C=O})$ (on top)	1990-2050 [35], 2010 ± 15 [36], 2054 [37]	2100 [38], 2059*
$\nu(\text{M-CO})$ (bridge)		380 [38]
$\nu(\text{C=O})$ (bridge)		1850 [38]
$\nu(\text{M-O})$	560-585 [35], 550 [36], 540 [37]	490 [39], 480 [40], 466*
$\nu(\text{M-O})$ (oxide)		760 [39]
$\nu(\text{M-C})$	495 [35], 709 (hcp) [37]	

Table 1. Summary of vibration frequencies for O and CO adsorbed on Pt(111) and Re(0001). * = This work, DFT calculation.

The superficial oxide surface was also investigated by HREELS (Figure 2). The $\text{Re}_2(\text{CO})_{10}$ -exposed Pt(111) surface was treated in 1×10^{-6} mbar oxygen at 673 (Figure 2, left panel) and at 723 K (Figure 2, right panel). Initial coverages of Re on these surfaces were 0.6 and 0.8 ML, respectively. HREELS revealed a feature at 670 cm⁻¹ which was

assigned to a Re-O loss in the rhenium superficial oxide. A summary of HREELS literature with assignments for adsorbed CO, O, and C is given in Table 1. Ducros et al. observed an Re-O vibration at 580 cm^{-1} after oxygen adsorption on Re(0001) [35], and Asscher et al. [36] observed a band at $585\pm 20\text{ cm}^{-1}$ assigned to the Re-O bond on Re(0001) for co-adsorbed CO and O. The frequency of the vibration here is higher than references for O adsorbed on various Re surfaces in the literature. This is likely caused by clusters of ReO_x on Pt(111), which are predicted to have higher frequencies than O adsorbed on monometallic Re (see DFT calculations below). The identity of the weak loss peak at ca. 970 likely also results from O adsorbed on Re single atoms or very small clusters, as per the DFT calculations. The assignment of the broad, weak loss peak at approximately 1100 cm^{-1} is unclear, but similar frequencies have been reported for graphitic or carbidic carbon on Pt(111) [41]. On the other hand, XPS did not detect much carbon but the losses due to the graphitic structure became visible at graphite coverage of $\sim 0.8\text{ ML}$ [42]. No loss peak at 1100 cm^{-1} was detected on the Re/Pt(111) surface treated in O_2 at 723 K confirming that graphitic and/or carbidic carbon could be efficiently removed. On this surface, weak linear CO stretching was present at 2080 cm^{-1} as a result of CO adsorption on Pt from vacuum residual gas.

4.3 Subsurface Pt-Re Alloy

Figure 3: Re 4f_{7/2} BE plotted as a function of Re coverage calculated from the XPS data. Filled shapes (green and blue triangles, black squares, and red circles) are from this work, with each shape representing a different experimental series. The first point for each experimental series was obtained after (1) exposure of Pt(111) to Re₂(CO)₁₀; (2) treatment in O₂; and (3) heating in UHV at 923 K or higher. Open black squares are coverages calculated from linear interpolations of Re concentrations taken from Reference [9].

The superficial oxide surfaces were subsequently annealed in UHV in 100 K steps for 5 min. at each temperature (Figure 2). The Re-O peak attenuated at each temperature, and all vibrations involving O disappeared by 973-1023 K. The oxygen atoms coordinated single Re atom/small cluster characterized by the loss peak at 970 cm⁻¹ showed slightly lower thermal stability and this species was present until heated above 723 K. No Pt-O vibrations at ~490 cm⁻¹ were detected (see Figure SI-2 for a larger image of this region).

Upon decomposition of the superficial Re oxide, the Re coverage decreased regardless of sample history or initial Re coverage. For the experiments above, the sample with initial $\theta_{\text{Re}}=0.8$ ML had a drop in Re coverage to 0.6 ML following annealing to 973 K. In fact, through the course of characterizing Re films in this paper, calculated Re coverage dropped continuously as the result of annealing and oxidative treatments. The amount by which Re coverage dropped was not correlated with the specific annealing or oxidative procedure; however, the Re 4f_{7/2} BE increased linearly with the decrease in Re coverage as plotted in Figure 3 for all treatments. The Re 4f_{7/2} BE as a function of Re concentration has been reported previously, and these Re coverages interpolated from concentration values in reference [9] are also plotted in Figure 3 for comparison.

The drop in Re coverage could be due to two factors: 1) evaporation of Re, or 2) diffusion of Re into the Pt bulk. Though we could not eliminate the possibility of Re evaporation, it is unlikely occurring under the experimental conditions used here. Tysoe et al. [16] observed depletion of surface Re on a Pt foil following oxidation in 700 Torr O₂ at 625 K. They attributed this loss of Re to the formation of the volatile Re₂O₇ species. Following this treatment, some Re₂O₇ remained on the surface, which was detected by XPS. However, we observed no evidence of the formation of Re₂O₇ from XPS, and our oxygen pressure was ~9 orders of magnitude lower. Oxygen also desorbs from Re(0001) as ReO₂ or ReO₃ above 1700 K [43], but temperatures used in the present study did not exceed 1100 K. Likely, diffusion of Re into the Pt bulk resulted in the attenuation of the Re 4f XPS signal by platinum and increasing of the Re 4f BE was

indicative of Re alloying with Pt [9, 12]. The possible Re-Pt alloy structures are discussed in the DFT section.

An STM image taken of the Pt-skin surface is shown in Figure SI-3. The amount of bright features on the surface in these images is much less than on the as-dosed surface shown in Figure SI-1. Some surface features are one atomic Pt or Re step high and others are approximately two atomic steps high. Though measuring the exact lateral dimensions of the features was not possible due to thermal drift, the image revealed that the bright features, likely Re that has not diffused into the Pt subsurface, are of two sizes: small clusters and much larger agglomerates.

4.4 Oxygen Adsorption on Re-Pt Surface Alloy

Figure 4: HREELS spectra obtained from the Re-Pt surface alloy exposed to 1×10^{-6} mbar O_2 at 373 K for 5 min (top panel), and at 723 K for 10 min. (bottom panel). In both experiments, the sample was cooled in O_2 to 273 K. Following O_2 dosing, each sample was heated in UHV at 373 K for 5 min.

Figure 5: HREELS spectra obtained from Pt(111) exposed to 1×10^{-6} mbar O_2 at 673 K followed by annealing at 373 K and 473 K in UHV for 5 min.

The Re-Pt surface alloy interacted with oxygen very differently than the surface exposed to $Re_2(CO)_{10}$. Figure 4 shows the HREELS spectra obtained following O_2 dosing and subsequent annealing to 373 K in UHV for 5 min for two similar Re-Pt surface alloys, which were prepared by the oxidative treatment of $Re_2(CO)_{10}$ exposed Pt(111) followed annealing to 973 K or higher in UHV. For all experiments, the Re-Pt surface

alloy was exposed to 1×10^{-6} mbar O_2 while heating the sample to temperatures between 373-723 K and while cooling to 273 K. Regardless of dosing conditions, all HREELS spectra following O_2 dosing revealed energy loss features at approximately $460\text{-}465\text{ cm}^{-1}$ and $2080\text{-}2085\text{ cm}^{-1}$, which could be assigned to Pt-CO and C-O stretching vibrations of CO adsorbed in the on-top configuration on Pt(111). Literature values for these assignments are given in Table 1. This CO originated from vacuum residual gas and, judging from the $\nu(\text{C-O})$ intensity and frequency, the CO coverage was very similar in all these experiments and did not exceed 0.05 ML. Only the Pt-O vibration appeared at 455 cm^{-1} when a pure Pt(111) surface (no rhenium) was exposed to O_2 under similar conditions (Figure 5); no C-O stretching vibration was detected. This led to the conclusion that the feature at 465 cm^{-1} observed after O_2 exposure to the Re-Pt surface alloy (Figure 4) contained the contribution of the Pt-O vibration. Indeed, in a control experiment, when the Pt(111) surface was exposed to CO up to saturation, the ratio between the intensities of $\nu(\text{C-O})$ and $\nu(\text{Pt-CO})$ was 1.6. For the Re-Pt surface alloy (Figure 4), the ratio between the intensities of the peak at approximately 465 cm^{-1} and $\nu(\text{C-O})$ at 2085 cm^{-1} was 1.1 and 0.5 for O_2 adsorption temperature of 373 and 723 K, respectively. This trend was confirmed in the other experiments and it demonstrated that the amount of oxygen adsorbed on the platinum surface increased with the O_2 adsorption temperature. On the other hand, estimating from the relative intensity of $\nu(\text{Pt-O})$, the oxygen coverage was more than 5 times less following O_2 adsorption on the Re-Pt surface alloy at 723 K (maximum amount of O_{ads}) compared to Pt(111). It is clear that HREELS is an inferior technique for quantification of adsorbates compared to temperature programmed desorption (TPD). Unfortunately, our STM sample holder is not

compatible with TPD, and TPD was not done. In conclusion, very little O adsorbed on the Re-Pt surface alloy during O₂ exposure or CO reacted very quickly with O_{ads} during transfer to the HREELS stage and data acquisition (total time was ~1 hour). This is in agreement with the XPS study by Alnot et al. [10] which showed that CO partially reacted with adsorbed O on a Pt-Re alloy surface.

We also note that adsorption of oxygen on other Pt-bimetallic systems has resulted in surface segregation of the second metal, as has been observed for Pt-Ni [44, 45] and Pt-Co [44]. Given the trend in O binding energies calculated below (see DFT section), this seems likely for Pt with Re in the subsurface, given the observed correlation of surface segregation of 3d metals with O binding energies [44]. While we cannot eliminate the possibility of this happening with Re, we did not see any direct evidence to suggest Re is segregating on the surface. The drop in Re coverage and lack of strongly-bound O on Re in HREELS suggests that Re does not surface segregate.

Several other vibrations not discussed above appeared on alloy surfaces and were difficult to assign. It is interesting that after annealing of the Re-Pt alloy surfaces at 373 K in UHV, all vibrations assigned to CO_{ads}, $\nu(\text{C-O})$ at 2085 cm⁻¹ and $\nu(\text{Pt-CO})$ at 465 cm⁻¹, and to O_{ads}/Pt(111), Pt-O at 460 cm⁻¹, disappeared completely (Figure 4), while the other vibrations were still detectable. The DFT calculation helped to understand the nature of these vibrations. Peaks in the range 630 – 990 cm⁻¹ could be due to Re-O stretching vibrations for varying Re coverages and Re cluster sizes (see DFT section below). The assignment of low frequency features at 275 and 365 cm⁻¹ and high frequency feature at 1190 cm⁻¹ are unclear, but may be related to vibrational modes of

oxygen atoms coordinated with platinum and rhenium atoms. It should be noted that the Re 4f peaks were unaffected by O adsorption on the Re-Pt surface alloys.

Once again, we must underline that O_{ads} thermal stability changed on the Re-Pt surface alloys compared with Pt(111) and Re monometallic surfaces. On Pt(111), oxygen desorbs between 600-1100 K (see reference [46] and references therein). O desorbs from Re(0001) [47] and from polycrystalline Re [48] at about 1700 K. In our case, $ReO_x/Pt(111)$ decomposed between 923 and 973 K as shown by HREELS (Figure 2). However, it is not very fair to compare the decomposition/desorption temperatures obtained in TPD and HREELS experiments. In our case, cooling in UHV was slow and O_{ads} could react on a warm surface with residual gases, resulting in an apparent lowering of the desorption temperature. In a control experiment, O desorbed from the clean Pt(111) surface at 473 K as shown in Figure 5. This desorption temperature is lower than those reported in the literature (reference [46] and references therein) due to reaction with residual gas, however, this temperature is higher than what was observed on the Re-Pt surface alloy where O_{ads} desorbed at 373 K. This confirmed that O_{ads} was destabilized by the presence of rhenium.

4.5 DFT Calculations

Oxygen binding energies were computed on different surfaces as shown in Figure 6. The as-dosed Re on Pt(111) was modeled using a pseudomorphic film of Re on Pt(111) (Figure 6b). Segregation of Re into the bulk of Pt was modelled by assuming a Re sublayer in Pt with different coverages of Re (Figures 6c to 6f). While the real system would most likely have Re both on surface as well as subsurface, the models considered

here serve as first approximations to give us useful insights into the behavior of Pt-Re system. Calculation of energetics showed that the structure in 6f, with a full monolayer of Re in the subsurface, was more stable than that in Figure 6b, with Re on surface, by 3.39 eV per unit cell. The tendency of Pt to segregate to the surface can be understood in terms of the higher cohesive energy of Re as compared to Pt, making Re inside the Pt bulk more energetically favorable than on the surface. This result is in agreement with other theoretical studies where Pt surface segregation was found to be favorable in Pt-Re bimetallic systems [49, 50].

Figure 6 : Close packed surface structures used in DFT calculation: (a) Monometallic Pt(111) (b) Re film on Pt (c):(f) Re sub layer of coverage (c) 0.25 (d) 0.5 (e) 0.75 and (f) 1.0 ML.

<i>Structure</i>	<i>O adsorption</i>		<i>CO adsorption</i>	
	<i>adsorption site</i>	<i>Adsorption energy (eV)</i>	<i>adsorption site</i>	<i>Adsorption energy (eV)</i>

A	Fcc	-1.28	Fcc	-1.72
B	Hcp	-3.73	Top	-2.15
C	Fcc	-1.07	Fcc	-1.57
D	Fcc	-0.99	Top	-1.51
E	Fcc	-0.90	Top	-1.48
F	Fcc	-0.89	Top	-1.51

Table 2 : DFT calculation results. Oxygen adsorption energies refereced to a gas phase oxygen molecule.

The results of the calculations of O adsorption on these structures have been summarized in Table 2. The Re-film-on-Pt binds O more strongly than does monometallic Pt. However, the structures with Re present in the subsurface are found to bind O much more weakly than monometallic Pt. Increased Re coverage in the subsurface increases the degree of weakening. The DFT calculated trend in O adsorption energy is consistent with experimental measurements where as-dosed Re on Pt was found to bind O more strongly than pure Pt, but Pt-Re alloys formed after annealing and desorption of oxygen bound O more weakly than pure Pt. These results indicate that one possible reason for the alloy weakly adsorbing oxygen may be due to segregation of Pt to the top layer with concomittant Re segregation into the bulk of Pt. Structures having sub surface Re also adsorb CO more weakly than monometallic Pt.

<i>Structure</i>	<i>O adsorption energy (eV)</i>	<i>d-band center (eV)</i>
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A	-1.28	-1.94
B	-3.73	-1.18
C	-1.07	-2.12
D	-0.99	-2.34
E	-0.90	-2.56
F	-0.89	-2.67

Table 3 : Comparison of O adsorption energies with d-band center.

Since the lattice constant of all structures in the calculations was held constant at the optimum lattice constant of monometallic Pt, the change in O binding energy in the different structures can be attributed to electronic effects. To understand the effect of electronic structure on the adsorption energies, we calculated the d-band centers of the surface atoms of the structures shown in Figure 6. The results are shown in Table 3. We find that the presence of subsurface Re in Pt (structures c through f) lowers the d-band center of surface Pt atoms, resulting in weaker binding of O as compared to monometallic Pt (structure a). The structure with a Re film on Pt (structure b) adsorbs O more strongly than pure Pt. This can be attributed to the fact that Re, with fewer d electrons than Pt, is less noble than Pt and binds O more strongly. In addition, even though we cannot quantitatively relate the d-band centers of these two structures to the respective oxygen binding energies, since the coupling matrix elements (V_{ad}) of Pt and Re differ [51], we suggest that the very large magnitude of the difference in d-band centers between the surfaces (-1.18 vs. -1.94 eV) is qualitatively consistent with the calculated trends in binding energies.

DFT-calculated vibrational frequencies for adsorbed O and CO on monometallic Pt, a Re film on Pt, and a Re sublayer in Pt with monolayer Re coverage are shown in Table 4. The calculated frequencies agree with literature values reported in Table 1. The trend in the M-adsorbate frequency is consistent with the trend in binding energies of the adsorbates. This is not surprising as an increased stretching frequency could be associated with stronger binding. Quite different from these results, however, HREELS performed on the superficial rhenium oxide discussed in section 4.2 was exhibited peaks at much higher frequencies of 670 cm^{-1} and 970 cm^{-1} , which are assigned to Re-O bonds of rhenium oxide. The exact structure of the oxide surface is difficult to ascertain, however, and in order to gain some insight into the effect of oxide structure on the stretching frequency of oxygen, we performed DFT calculations on some model oxide structures, as shown in Figure 7. A rhenium oxide structure is expected to have different physical and chemical characteristics than that of a simple chemisorbed O on Re, in that the Re in an oxide should be more cationic, with O bond more strongly to Re and, therefore, exhibit a different vibrational frequency than an adsorbed O on Re. A Bader charge analysis revealed that the Re in Fig. 8(a) was in a +1 oxidation state, while that in Fig. 7(b) was nearly zero valent. When present in the form of a cluster, modelled as shown in Fig. 8(c), the Re was found to be even more cationic than the film structure of 8(a). These results confirm the presence of more complicated oxide structures. This agrees with our XPS result.

We have additionally used pseudomorphic ReO and ReO₂ film models to investigate the effect of oxidation state and structure on oxygen vibrational frequencies (we have also analyzed the stability of these films in different non-pseudomorphic

configurations on the Pt substrate, but the conclusions are not significantly affected by these considerations, and we therefore defer the details of the study, and the associated phase diagrams, to a future publication). The stretching frequencies of oxygen in these structures are reported in Table 5. The stretching frequencies of oxygen in the oxide are, in general, higher than that of an oxygen adsorbed on Re, as reported in Table 4. For a uniform rhenium oxide film on Pt(111), the frequency is 570 cm^{-1} for ReO and 563 cm^{-1} for ReO₂. However, the frequency is much higher if the oxide is present in the form of a cluster, even if it has same oxidation state as an oxide film. The calculated stretching frequency for a single ReO cluster is 982 cm^{-1} while for ReO₂ it is 909 cm^{-1} . These trends indicate that the superficial oxide experimentally observed, with a peak at 670 cm^{-1} , is possibly a cluster bigger than the single Re atom clusters considered in the calculations, but it is not quite a uniform oxide film. The HREELS peaks observed at 970 cm^{-1} , however, can be due to the presence of additional Re-O clusters on the Pt surface. This analysis is consistent with the STM image shown in the supplementary information (Figure SI-3), which reveals a distribution of Re cluster sizes.

<i>Structure</i>	$\nu (M-O)\text{ cm}^{-1}$	$\nu (M-CO)\text{ cm}^{-1}$	$\nu (C-O)\text{ cm}^{-1}$
A	436	466	2059
B	486	460	1983
F	425	431	2040

Table 4: DFT calculated vibrational frequencies for adsorbed oxygen.

<i>Structure</i>	<i>ν (Re-O) cm^{-1}</i>
A	570
B	Upper O – 563 Lower O – 493
C	982
D	909

Table 5: DFT calculated vibrational frequencies for oxygen in rhenium oxide on Pt(111).

Figure 7: Rhenium oxide structures on Pt(111). (a) ReO film (b) ReO₂ film (c) single ReO islands, and (d) single ReO₂ islands.

The lack of evidence for oxygen adsorption on the Pt-Re alloy surface, predicted to contain a Pt skin by DFT, as observed by experiment and confirmed by DFT calculations, is in agreement with observations in Reference [8], where dosing O₂ on a Re/Pt(111) surface following annealing did not result in formation of a superficial oxide

as detected by XPS. Pt-Re alloy systems are also known to bond CO more weakly than either monometallic Pt or Re [6, 8]. Furthermore, CO oxidation activity is enhanced on Pt-Re alloy surfaces, resulting in more CO₂ produced compared to monometallic Pt(111) [17]. Therefore, even if O did adsorb on the Pt-skin surface, it may have reacted with residual CO in the vacuum chamber at room temperature during the ~5 minute transfer to the HREELS stage. Further, Pt skin formation is consistent with experiments which show Re coverage dropping following annealing. The results for O/CO binding are consistent with our HREELS data, showing no evidence of O or CO binding on Re sites on the annealed surface. Our analysis of the d-band centers further shows that the lower adsorption energies on Pt skin surfaces can be correlated to a decrease in the d-band center of the surface Pt atoms. Finally, vibrational frequency calculations are consistent with both literature and experimental observations and indicate that the superficial rhenium oxide on the Pt(111) surface could be present in the form of rhenium oxide islands on Pt, in agreement with STM images.

5. Conclusions

Studying changes to the Re/Pt(111) system using surface sensitive experiments in UHV and DFT modeling provided detailed information on the morphology of this system and how it interacts with adsorbates. Major findings are:

- UHV-CVD is able to deposit sub-monolayer amounts of Re on Pt(111) using Re₂(CO)₁₀ as a precursor.
- A superficial oxide can be formed dosing the Re₂(CO)₁₀ exposed Pt(111) to 1×10^{-6} mbar oxygen at temperatures greater than 573 K. The stoichiometry of this

surface oxide is between $\text{ReO}_{0.5}$ and ReO . The superficial oxide, $\text{ReO}_x/\text{Pt}(111)$, decomposes at approximately 973 K.

- Annealing the superficial oxide surface to 973 K in UHV results in the decrease of the calculated surface coverage of Re from XPS. Subsequent annealing treatments reduce the Re coverage further and increase the Re 4f BE relative to the $\text{Re}_2(\text{CO})_{10}$ dosed surface, indicating greater alloying of Re with Pt.
- STM indicates that the Re surface coverage decreases during these conditions.
- The annealed Pt-Re alloy surface likely forms at least a partial Pt skin. Oxygen adsorption on Re sites is hindered, and oxygen binding to Pt sites is weaker compared to Pt(111). CO from vacuum residual gas can adsorb the Pt-Re surface alloy exposed to O_2 , which does not occur on $\text{O}_{\text{ads}}/\text{Pt}(111)$.
- DFT predicts that a Pt substrate with a monolayer of subsurface Re is more stable than one with a monolayer of Re on top of Pt.
- DFT predicted O/CO binding on Pt skin surfaces are much weaker than that on monometallic Pt or on a monolayer of Re deposited on Pt.
- The trends in binding energy can be explained on the basis of d-band centers of Pt-Re systems. The DFT calculated trend in vibrational frequencies for adsorbed oxygen is consistent with binding energies. Vibrational frequency calculations for rhenium oxide indicate the oxide could be present in the form of islands on the Pt, some of which might be ReO clusters.

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REFERENCES

- [1] H.E. Kluksdahl, Reforming a sulfur-free naphtha with a platinum-rhenium catalyst, in, United States, 1968.
- [2] L. Zhang, A.M. Karim, M.H. Engelhard, Z.H. Wei, D.L. King, Y. Wang, Correlation of Pt-Re surface properties with reaction pathways for the aqueous-phase reforming of glycerol, *J. Catal.*, 287 (2012) 37-43.
- [3] D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Bimetallic catalysts for upgrading of biomass to fuels and chemicals, *Chem. Soc. Rev.*, 41 (2012) 8075-8098.
- [4] C.H. Deng, X.Z. Duan, J.H. Zhou, D. Chen, X.G. Zhou, W.K. Yuan, Size effects of Pt-Re bimetallic catalysts for glycerol hydrogenolysis, *Catal. Today*, 234 (2014) 208-214.
- [5] O.M. Daniel, A. DeLaRiva, E.L. Kunkes, A.K. Datye, J.A. Dumesic, R.J. Davis, X-ray Absorption Spectroscopy of Bimetallic Pt-Re Catalysts for Hydrogenolysis of Glycerol to Propanediols, *ChemCatChem*, 2 (2010) 1107-1114.
- [6] E.L. Kunkes, D.A. Simonetti, J.A. Dumesic, W.D. Pyrz, L.E. Murillo, J.G.G. Chen, D.J. Buttrey, The role of rhenium in the conversion of glycerol to synthesis gas over carbon supported platinum-rhenium catalysts, *J. Catal.*, 260 (2008) 164-177.
- [7] D.A. Simonetti, E.L. Kunkes, J.A. Dumesic, Gas-phase conversion of glycerol to synthesis gas over carbon-supported platinum and platinum-rhenium catalysts, *J. Catal.*, 247 (2007) 298-306.
- [8] A. Ramstad, F. Strisland, S. Raaen, A. Borg, C. Berg, CO and O₂ adsorption on the Re/Pt(111) surface studied by photoemission and thermal desorption., *Surf. Sci.*, 440 (1999) 290-300.
- [9] A. Ramstad, F. Strisland, S. Raaen, T. Worren, A. Borg, C. Berg, Growth and alloy formation studied by photoelectron spectroscopy and STM, *Surf. Sci.*, 425 (1999) 57-67.
- [10] M. Alnot, A. Cassuto, R. Ducros, J.J. Ehrhardt, B. Weber, XPS and UPS Study of the Reaction of Carbon-Monoxide with Oxygen and Nitrogen Monoxide on Platinum-Rhenium Alloy, *Surf. Sci.*, 114 (1982) L48-L56.
- [11] M. Alnot, V. Gorodetskii, A. Cassuto, J.J. Ehrhardt, Auger-Electron Spectroscopy, X-Ray Photoelectron-Spectroscopy, Work Function Measurements and Photoemission of Adsorbed Xenon on Thin-Films of Pt-Re(111) Alloys, *Thin Solid Films*, 151 (1987) 251-262.

- [12] D.J. Godbey, G.A. Somorjai, The Preparation and Characterization of Rhenium Modified Pt(111) and Pt(100), and Platinum Modified Re(0001) Single-Crystal Surfaces, *Surf. Sci.*, 202 (1988) 204-226.
- [13] D.J. Godbey, F. Garin, G.A. Somorjai, The Hydrogenolysis of Ethane over Re-Pt(111) and Pt-Re(0001) Bimetallic Crystal-Surfaces, *J. Catal.*, 117 (1989) 144-154.
- [14] D.J. Godbey, G.A. Somorjai, The Adsorption and Desorption of Hydrogen and Carbon-Monoxide on Bimetallic Re-Pt(111) Surfaces, *Surf. Sci.*, 204 (1988) 301-318.
- [15] C.M. Kim, G.A. Somorjai, The Effects of Rhenium and Sulfur on the Reactivity and Selectivity of Pt Single-Crystal Catalysts, *J. Catal.*, 134 (1992) 179-185.
- [16] W.T. Tysoe, F. Zaera, G.A. Somorjai, An XPS Study of the Oxidation and Reduction of the Rhenium Platinum System under Atmospheric Conditions, *Surf. Sci.*, 200 (1988) 1-14.
- [17] A.S. Duke, R.P. Galhenage, S.A. Tenney, P. Sutter, D.A. Chen, In Situ Studies of Carbon Monoxide Oxidation on Platinum and Platinum-Rhenium Alloy Surfaces, *J. Phys. Chem. C*, 119 (2015) 381-391.
- [18] M. Alnot, A. Cassuto, J.J. Ehrhardt, A. Slavin, B. Weber, Growth of Platinum on Rhenium and Evolution of the Interface under Thermal-Treatment, *Appl. Surf. Sci.*, 10 (1982) 85-99.
- [19] N. Mesboua, B. Weber, A. Cassuto, The Stationary Oxidation of Rhenium in the Presence of Platinum Atoms - a Mass-Spectrometry Study under Low Oxygen Pressures, *Surf. Sci.*, 231 (1990) 356-360.
- [20] C.T. Campbell, Bimetallic Surface-Chemistry, *Annu. Rev. Phys. Chem.*, 41 (1990) 775-837.
- [21] A. Gharachorlou, M.D. Detwiler, A.V. Nartova, Y. Lei, J. Lu, J.W. Elam, W.N. Delgass, F.H. Ribeiro, D.Y. Zemlyanov, Palladium Nanoparticle Formation on TiO₂(110) by Thermal Decomposition of Palladium(II) hexafluoroacetylacetonate, *ACS Appl. Mater. Interfaces*, 6 (2014) 14702-14711.
- [22] C.S. Fadley, Basic concepts of x-ray photoelectron spectroscopy, in: C.R. Brundel, A.D. Baker (Eds.) *Electron Spectroscopy: Theory, Techniques and Applications*, Academic Press, New York, 1978, pp. 1-156.
- [23] I. Horcas, R. Fernandez, J.M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A.M. Baro, WSXM: A software for scanning probe microscopy and a tool for nanotechnology, *Rev. Sci. Instrum.*, 78 (2007) 013705.
- [24] C. Kittel, *Introduction to Solid State Physics*, 8th ed., John Wiley & Sons, Hoboken, NJ, 2005.
- [25] N.V. Gelfond, N.B. Morozova, E.S. Filatov, S.A. Gromilov, I.K. Igumenov, Structure of rhenium coatings obtained by CVD, *J. Struct. Chem.*, 50 (2009) 1126-1133.
- [26] Y. Isobe, M. Tanaka, S. Yamanaka, M. Miyake, Chemical Vapor-Deposition of Rhenium on Graphite, *J. Less-Common Met.*, 152 (1989) 177-184.

- [27] K.T. Kim, J.J. Wang, G. Welsch, Chemical Vapor-Deposition (CVD) of Rhenium, *Mater. Lett.*, 12 (1991) 43-46.
- [28] Y.G. Tong, S.X. Bai, H. Zhang, Y.C. Ye, Rhenium coating prepared on carbon substrate by chemical vapor deposition, *Appl. Surf. Sci.*, 261 (2012) 390-395.
- [29] J.F. Moulder, J. Chastain, R.C. King, Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data, Physical Electronics, Eden Prairie, MN, 1995.
- [30] M. Alnot, J.J. Ehrhardt, A Study of Oxygen-Rhenium Interactions in Various Pressure and Temperature Conditions, *J. Chim. Phys. Phys.- Chim. Biol.*, 79 (1982) 735-739.
- [31] R. Ducros, J. Fusy, Core Level Binding-Energy Shifts of Rhenium Surface Atoms for a Clean and Oxygenated Surface, *J. Electron. Spectrosc. Relat. Phenom.*, 42 (1987) 305-312.
- [32] A.S.Y. Chan, W.H. Chen, H. Wang, J.E. Rowe, T.E. Madey, Methanol reactions over oxygen-modified re surfaces: Influence of surface structure and oxidation, *J. Phys. Chem. B*, 108 (2004) 14643-14651.
- [33] C. Morant, L. Galan, J.M. Sanz, X-Ray Photoelectron Spectroscopic Study of the Oxidation of Polycrystalline Rhenium by Exposure to O-2 and Low-Energy O-2(+) Ions, *Anal. Chim. Acta*, 297 (1994) 179-186.
- [34] R. Ducros, M. Alnot, J.J. Ehrhardt, M. Housley, G. Piquard, A. Cassuto, A Study of the Adsorption of Several Oxygen-Containing Molecules (O-2, CO, NO, H2O) on Re(0001) by XPS, Ups and Temperature Programmed Desorption, *Surf. Sci.*, 94 (1980) 154-168.
- [35] R. Ducros, B. Tardy, J.C. Bertolini, Carbon-Monoxide Adsorption on Re(0001) between 120-K and 600-K Studied by Vibrational Electron-Energy Loss Spectroscopy, *Surf. Sci.*, 128 (1983) L219-L223.
- [36] M. Asscher, C.T. Kao, G.A. Somorjai, High-Resolution Electron-Energy Loss Spectroscopic Study of Co2 Adsorbed on Re(0001), *J. Phys. Chem.*, 92 (1988) 2711-2714.
- [37] K. Hahn, M. Mavrikakis, Atomic and Molecular Adsorption on Re(0001), *Top. Catal.*, 57 (2014) 54-68.
- [38] H. Steininger, S. Lehwald, H. Ibach, On the Adsorption of CO on Pt(111), *Surf. Sci.*, 123 (1982) 264-282.
- [39] J.L. Gland, B.A. Sexton, G.B. Fisher, Oxygen Interactions with the Pt(111) Surface, *Surf. Sci.*, 95 (1980) 587-602.
- [40] H. Steininger, S. Lehwald, H. Ibach, Adsorption of Oxygen on Pt(111), *Surf. Sci.*, 123 (1982) 1-17.
- [41] M.R. Columbia, A.M. Crabtree, P.A. Thiel, Effect of CO on Pt-Catalyzed Decomposition of Formic-Acid in Ultrahigh-Vacuum, *J. Electroanal. Chem.*, 345 (1993) 93-105.

- [42] M.Y. Smirnov, N.R. Gall, A.R. Cholach, V.V. Gorodetskii, A.Y. Tontegode, E.V. Rutkov, D.Y. Zemlyanov, HREELS Study and Catalytic Significance of Low-Temperature Interaction of Isolated Carbon-Atoms with Hydrogen on Pt(111), *Catal. Lett.*, 8 (1991) 101-106.
- [43] R. Ducros, M. Housley, G. Piquard, Influence of Structural Defects, Steps and Kinks, on Oxygen-Adsorption on Rhenium Single-Crystals, *Phys. Status Solidi A*, 56 (1979) 187-193.
- [44] C.A. Menning, H.H. Hwu, J.G.G. Chen, Experimental and theoretical investigation of the stability of Pt-3d-Pt(111) bimetallic surfaces under oxygen environment, *J. Phys. Chem. B*, 110 (2006) 15471-15477.
- [45] P. Weigand, P. Novacek, G. Vanhusen, T. Neidhart, P. Varga, Surface-Analysis of Pt₃Ni₁-X Single-Crystals, *Surf. Sci.*, 269 (1992) 1129-1134.
- [46] C.T. Campbell, G. Ertl, H. Kuipers, J. Segner, A Molecular-Beam Study of the Adsorption and Desorption of Oxygen from a Pt(111) Surface, *Surf. Sci.*, 107 (1981) 220-236.
- [47] G.J. Dooley, T.W. Haas, Some Properties of Rhenium (0001) Surface, *Surf. Sci.*, 19 (1970) 1-&.
- [48] B. Weber, A. Cassuto, States of Adsorption, Rate of Adsorption, Desorption of Oxygen on Rhenium and Atomization and Oxidation Mechanisms at High-Temperature and Low-Pressure, *Surf. Sci.*, 36 (1973) 81-108.
- [49] Y.G. Ma, P.B. Balbuena, Pt surface segregation in bimetallic Pt₃M alloys: A density functional theory study, *Surf. Sci.*, 602 (2008) 107-113.
- [50] G.F. Wang, M.A. Van Hove, P.N. Ross, M.I. Baskes, Monte Carlo simulations of segregation in Pt-Re catalyst nanoparticles, *J. Chem. Phys.*, 121 (2004) 5410-5422.
- [51] B. Hammer, J.K. Nørskov, Theory of adsorption and surface reactions, in: R.M. Lambert, G. Pacchioni (Eds.) *Chemisorption and Reactivity on Supported Clusters and Thin Films: Towards an Understanding of Microscopic Processes in Catalysis*, 1997, pp. 285-351.