DFT Comparison of Intrinsic WGS Kinetics over Pd and Pt

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Abstract

We report density functional theory (DFT) results for five competing water-gas shift (WGS) pathways on identical Pd and Pt(111) surface models. We develop analytical kinetic models to compare intrinsic catalytic activity under conditions relevant to low-temperature WGS. The baseline model predicts that WGS proceeds preferentially through a carboxyl intermediate, that water dissociation is rate limiting, and that the intrinsic rate on Pt is greater than on Pd. Absolute rates are unphysically low because of unphysically high CO coverage. Systematically decreasing the CO binding energy in keeping with its known coverage dependence yields more realistic coverages and absolute rates, shifts the rate limiting step to carboxyl formation, and retains the same ordering of activity. Predicted rate orders and activation energies are not consistent with those observed for supported Pt and Pd catalysts, suggesting that even on nominally inert supports, the support plays an active role in WGS activity.

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Graphical Abstract

Keywords

Water Gas Shift, DFT, Kinetic Modeling, Pt, Pd

1 Introduction

The Water Gas Shift (WGS) reaction (equation 1) is widely used for H₂ production [1].

WGS is mildly exothermic ($\Delta H^\circ = -41 \frac{\text{kJ}}{\text{mol}}$), and thus lower temperatures favor higher conversions. Precious metal catalysts, including Pt and Pd, are of interest for their activity at low temperatures.

WGS activity over oxide-supported Pt and Pd has been widely studied [2–16]. Supports have a large influence on measured WGS rates. $\gamma\text{-Al}_2\text{O}_3$ is observed to have the smallest promoting effect, which suggests that the observed activity is representative of the metal alone [3–5, 7–9]. Over alumina-supported catalysts the WGS turnover rate (TOR), measured as the amount of product produced per total amount of exposed metal per unit time, is higher on Pt than on Pd. Consistent with having a higher TOR, supported Pt has a lower apparent activation barrier (68 kJ mol^{-1}) than Pd (82 kJ mol^{-1}). Table 1 summarizes reported WGS kinetic parameters for Pt and Pd supported on $\gamma\text{-Al}_2\text{O}_3$ obtained at representative and identical reaction conditions [2,4]. Hydrogen inhibits the WGS rate, and the $-1/2$ order dependence suggests that desorption is associative. The CO₂ order is small and the H₂O order positive. The CO order on Pt/ $\gamma\text{-Al}_2\text{O}_3$ is near zero, and, as expected for product inhibited reactions, is observed to be sensitive to whether WGS products

are included in the feed stream [3, 4, 13–15]. Infrared spectroscopy indicates that CO is near the saturation coverage on both metals [2, 4]. Also, O–C–O bond stretches around 1350-1600 cm^{-1} have been assigned to formates (HCOO) on the support [2–7, 11]. Because of these observations, early experimental reports proposed formates as intermediates in the WGS mechanism [2–7, 11].

Density functional theory (DFT) has been widely used to assess WGS mechanisms and as a basis for rate modeling on noble metals [15, 17–29]. Grabow *et al.* computed binding energies, reaction energies, activation barriers and rate constants for WGS on Pt(111) using the generalized gradient approximation developed by Perdew and Wang (GGA-PW91) and an ultrasoft pseudopotential (USPP) treatment of atomic cores, and then developed a kinetic model [15]. A coverage-dependent CO binding energy was introduced and kinetic parameters adjusted to recover observed Pt/ γ -Al₂O₃ rates. This kinetic model suggests that the surface is nearly CO-saturated, the decomposition of the carboxyl (COOH) intermediate is rate limiting, and that formate is a spectator rather than an intermediate.

Schumacher *et al.* compared the rate of the redox WGS pathway on a number of late transition metals based on DFT-computed binding energies on terraces and on steps combined with activation energy correlations. They found a higher activity for Pt than Pd on the terraces and a reversal on the steps for this particular pathway. Stamatakis and co-workers studied the structure sensitivity of WGS through DFT and kinetic Monte Carlo (kMC) simulations over the (111), (211), and (322) surfaces of Pt including a larger variation of pathways [26, 27]. They found similar kMC-computed rates on each surface and conclude that the reaction is structure insensitive, consistent with conclusions from experiments on supported particles [16, 30], and proceeds through a carboxyl intermediate, with carboxyl formation as the rate limiting step on all surfaces. Wang and co-workers used DFT and larger supercells that preserved the CO + H₂O stoichiometry to compute activation energies of some of the WGS steps over Pt(111) and Pd(111) using GGA-PW91 and

Table 1: Observed WGS Activation Energies (E_a) and Rate Orders on Pd/ γ -Al₂O₃ and Pt/ γ -Al₂O₃ [2, 4]

Metal	E_a ($\frac{\text{kJ}}{\text{mol}}$)	CO Order	H ₂ O Order	H ₂ Order	CO ₂ Order
Pt	68	0.06	1.00	−0.44	−0.09
Pd	82	0.38	0.44	−0.36	−0.06

the projector augmented wave (PAW) method for treatment of atomic cores [18,19]. While they did not report a kinetic model, they did conclude that water dissociation is rate limiting, that the reaction proceeds through a carboxyl intermediate, and that formate is a spectator species, all based on observations of nudged elastic band (NEB)-computed reaction barriers. Differences in DFT supercell models and core electron treatments between Grabow and Wang lead to differences in binding energies, reaction energies and activation barriers of $\lesssim 0.2$ eV [15,18,19]. Similar studies have been conducted for other noble metals, including the (111) surfaces of Co, Ni, Cu, Rh, Ag, Ir, Au [18–20,25], Cu(321) [21], Au and Cu nanoparticles [22,23,29], the (110) surfaces of Cu and Au [22,23], and noble metal alloys [24,28]. The main conclusions are that water dissociation is rate limiting, and that the preferred pathways favor carboxyl formation and not the decomposition of the hydroxyl (OH) species.

Because H_2O dissociation is important to WGS, this step has been compared on several metals. Phatak *et al.* used supercell models and the GGA to compare the binding energies of H_2O , OH, O, and H and determined the water and hydroxyl dissociation pathways on the Cu, Au, Ni, Pd and Pt(111) surfaces [31]. The computed H_2O and OH dissociation activation barriers on Pt are slightly smaller (0.1 eV) than on Pd. The lower water dissociation barrier on Pt may explain experimentally observed differences in observed WGS rates. Fajín and co-workers built upon the work of Phatak by establishing Brønsted-Evans-Polanyi (BEP) relations between the water dissociation barrier and reaction energy, oxygen binding energy, and hydroxyl-oxygen co-adsorption energies [32].

Previous DFT studies do not permit a direct and complete comparison between the intrinsic Pt and Pd WGS activities due to differences in the computational methods, molecular models, and pathways that are considered, and do not come to consistent conclusions about rate limiting steps. In this paper, we report an internally consistent, DFT-based kinetic comparison of these two, using supercell models similar in construction to those of Grabow [15]. We report binding energies, reaction energies, activation barriers, and rate constants for five potential competing WGS pathways, including a new pathway for the concerted formation of carboxyl from CO and water. We then develop and analyze an analytical kinetic model drawing on an analogy with circuit analysis [33, 34] to determine preferred pathways, rate limiting steps, and apparent activation barriers. We find that both metals are CO-covered at reaction conditions, both metals prefer a carboxyl pathway, and that the intrinsic reaction rate is greater on Pt than on Pd. We show that

these conclusions are robust to the inclusion of a coverage-dependent CO binding energy. However, the rate limiting step shifts from water dissociation to carboxyl formation as the CO binding energy diminishes. The calculated reaction rates and rate orders are not consistent with observed Pd/ γ -Al₂O₃ and Pt/ γ -Al₂O₃ reaction rates and rate orders, suggesting that even the γ -alumina support participates in the WGS reaction mechanism.

2 Computational Details

DFT calculations were performed with the Vienna *ab initio* Simulation Package (VASP) [35,36] using the projector augmented wave (PAW) method [37,38], and electron exchange and correlation were treated by the generalized gradient approximation developed by Perdew and Wang (GGA-PW91) [39,40]. Plane waves were included for the electronic wave functions up to a cutoff energy of 400 eV. Forces were converged to 0.03 eV/Å. Transition states were located by the Climbing-Image Nudged Elastic Band method (CINEB) [41–43], and were further confirmed by the existence of one imaginary frequency along the proper reaction coordinate. The initial and final states for transition state searches correspond to the most stable configurations of the reactants and products within the supercell.

The lattice constants calculated using the Birch-Murnaghan equation of state [44,45] are 3.954 Å for Pd and 3.985 Å for Pt and are in agreement with the experimental values of 3.859 Å for Pd and 3.912 Å for Pt [46]. The (111) surface was modeled with a 2×2 supercell, using a three-layer-thick slab separated from its periodic image by a 20 Å vacuum gap. The top metal layer was allowed to relax in all optimizations. The first Brillouin zone was sampled with a Γ -centered $8 \times 8 \times 1$ Monkhorst-Pack **k**-point mesh [47]. To prevent unfavorable adsorbate-adsorbate interactions, some transition state searches were carried out in a 3×3 unit cell, three Pd layers thick, with the top layer allowed to relax and 15 Å of vacuum. Here the first Brillouin zone was sampled with a Γ -centered $6 \times 6 \times 1$ Monkhorst-Pack **k**-point mesh. Binding energies and reaction energies differ by at most 0.15 eV with a 5-layer-thick, 4×4 supercell paired with a Γ -centered $4 \times 4 \times 1$ Monkhorst-Pack **k**-point mesh, and by less than 0.10 eV using a 600 eV cutoff.

Reaction rate constants (k) were calculated using harmonic Transition State Theory (TST) [48]:

$$k = \frac{k_B T}{h} \frac{q_{\text{TS}}}{q_{\text{React}}} \exp \left(-\frac{E_a}{k_B T} \right) \quad (2)$$

Here k_B is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, E_a is the zero-point-corrected energy difference between the transition state and the co-adsorbed reactants. For partition functions, q , for surface reactions we only consider vibrational degrees of freedom, and they are calculated in the harmonic model in equation 3, where ν is the vibrational frequency.

$$q = \frac{1}{\prod_{i=1}^{\text{Vibrations}} 1 - \exp \left(-\frac{h\nu_i}{k_B T} \right)} \quad (3)$$

For reactions where no transition state was found, the activation barrier was defined as $\max(0, E_{\text{Reaction}})$, and the prefactor was assumed to be 10^{13} s^{-1} .

For use in the kinetic model, we estimate reaction free energies ($G^\circ(T)$) according to

$$\Delta G^\circ(T) \approx \Delta E_{\text{DFT}} - T \Delta S^\circ(T) \quad (4)$$

where ΔE_{DFT} is the DFT computed energy, and ΔS° is the standard entropy change and assumed to be zero for all surface reactions. For the adsorption/desorption steps, we assumed two different treatments for the entropy change: complete loss/gain of translational entropy, and adsorbed species retaining 2/3 of the gas phase translational entropy [49, 50]. The gas-phase entropy was calculated using the Sackur-Tetrode equation [48]:

$$S = k_B \ln \left(\frac{\exp \left(\frac{5}{2} \right) k_B T}{P^\circ \Lambda^3} \right) \quad (5)$$

In equation 5, P° is the standard pressure of 1 bar, and Λ is the thermal wavelength, defined in equation 6, where m is the mass of the adsorbate molecule.

$$\Lambda = h \left(\frac{1}{2k_B T \pi m} \right)^{\frac{1}{2}} \quad (6)$$

Figure 1: Commonly proposed WGS Pathways. (*) represents a surface site.

3 DFT Results

3.1 Proposed Pathways

Figure 1 summarizes the steps in four commonly considered WGS mechanisms on metal surfaces, including the redox, carboxyl, carboxyl-hydroxyl, and dual-hydroxyl paths [15,20]. These pathways share a common set of adsorption and desorption steps (reactions 1, 2, 13, 14) and a water dissociation step (reaction 3), but differ in intermediates and how they are produced and consumed. The carboxyl pathway involves the formation of a *cis* carboxyl (COOH) intermediate from CO and hydroxyl (OH), which then isomerizes to the *trans* isomer. Carboxyl subsequently decomposes to CO_2 and adsorbed atomic hydrogen (reactions 4-6). The carboxyl intermediate could also decompose via reaction with an adsorbed hydroxyl in the carboxyl-hydroxyl pathway (reactions 7 and 8). In the redox pathway, hydroxyl dissociates to adsorbed atomic oxygen and hydrogen. The atomic oxygen then oxidizes the CO to CO_2 (reactions 9 and 10). The hydroxyl could also decompose via reaction with another hydroxyl to form the atomic oxygen in the dual hydroxyl pathway (reactions 11 and 12). In addition, we include a pathway in which COOH is formed from direct, concerted reaction of adsorbed CO and water (reaction 15).

3.2 Adsorption

We first calculated optimized structures and binding energies of all WGS intermediates by searching over all possible binding sites on the (111) surfaces. Figure 2 shows the most stable adsorption structures. The site preferences and geometries are similar on Pt and Pd. CO prefers a 3-fold hollow site on both metals within the GGA; higher level models show that the atop site is actually preferred

on Pt at low coverage [51]. Hydrogen has two isoenergetic binding sites on both Pd (FCC and HCP hollow sites, Figure 2E and 2F) and Pt (FCC and Atop sites, Figure 2E and 2F). Hydroxyl (OH) has two isoenergetic binding sites on Pd (bridge-bent and FCC-linear configurations, Figure 2G and 2H), but only one binding site on Pt (atop-bent configuration, Figure 2G). Formate (HCOO) binds as mono-coordinated (Figure 2J) and di-coordinated (Figure 2K) isomers on both metals. Carboxyl (COOH) has two stable isomers: *cis* (H-up, Figure 2L) and *trans* (H-down, Figure 2M).

Table 2 compares the binding energies of the WGS intermediates on both metals with respect to appropriate proportions of the gas-phase molecular species. Binding energies are quite similar on both metals. Species bound through the oxygen atom (O, OH, HCOO) generally bind more strongly on Pd, while species bound through the carbon atom (*cis* and *trans* COOH) prefer Pt over Pd. The exception to this rule is CO, which binds more strongly to Pd than Pt. Di-coordinated formate is preferred over the mono-coordinated isomer, while the *trans* isomer of carboxyl is more stable than the *cis* form.

Table 2: Binding energies (E_{Binding}) of intermediates in WGS for Pd and Pt(111). (*) represents a binding site.

Reaction	Pd(111)	Pt(111)
$\text{CO(g)} + * \rightleftharpoons \text{CO}\cdot$	-1.95	-1.87
$\text{H}_2\text{O} + * \rightleftharpoons \text{H}_2\text{O}\cdot$	-0.28	-0.26
$\frac{1}{2}\text{H}_2\text{(g)} + * \rightleftharpoons \text{H}\cdot$	-0.57	-0.55
$\text{H}_2\text{O(g)} + * \rightleftharpoons \text{O}\cdot + \text{H}_2\text{(g)}$	1.19	1.18
$\text{H}_2\text{O} + * \rightleftharpoons \text{OH}\cdot + \frac{1}{2}\text{H}_2\text{(g)}$	0.62	0.77
$\text{CO}_2\text{(g)} + * \rightleftharpoons \text{CO}_2\cdot$	-0.04	-0.02
$\text{CO(g)} + \text{H}_2\text{O(g)} + * \rightleftharpoons \text{HCOO}\cdot + \frac{1}{2}\text{H}_2\text{(g)}$	-0.04	0.03
$\text{CO(g)} + \text{H}_2\text{O(g)} + 2\cdot \rightleftharpoons \text{HCOO}\cdot\cdot + \frac{1}{2}\text{H}_2\text{(g)}$	-0.98	-0.93
$\text{CO(g)} + \text{H}_2\text{O(g)} + * \rightleftharpoons \text{cis} - \text{COOH} * + \frac{1}{2}\text{H}_2\text{(g)}$	-0.90	-1.16
$\text{CO(g)} + \text{H}_2\text{O(g)} + * \rightleftharpoons \text{trans} - \text{COOH} * + \frac{1}{2}\text{H}_2\text{(g)}$	-1.14	-1.31

Our calculated binding site preferences are the same as identified in previous DFT reports, while binding energies are more variable (Tables S2 and S3 in the Supplemental Information) [15, 18, 19, 26, 27, 31, 52–54]. When the same computational method (GGA-PW91, PAW, 400 eV cutoff) is compared, energy differences on the order of 0.02 eV arise due to differences in details of the supercells, slab layers, and coverages [18, 19]. Differences up to 0.5 eV are found between our results and those of Grabow *et al.*, likely due to different treatments of core electrons (PAW vs. USPP) and different plane wave cutoffs (400 eV vs. 340 eV) [15]. The results reported here are

Figure 2: Side and top views of computed WGS intermediates on Pd (gold) and Pt(111) (purple) surfaces, including (A) CO (FCC), (B) CO (HCP), (C) Water, (D) Oxygen, (E)-(F) Hydrogen, (G) Hydroxyl (OH, bent configuration), (H) Hydroxyl (OH, linear configuration), (I) CO₂, (J) Mono-Coordinated Formate (HCOO^{*}), (K) Di-Coordinated Formate (HCOO^{**}), (L) *cis*-Carboxyl (*cis*-COOH), (M) *trans*-Carboxyl (*trans*-COOH).

Table 3: Reaction Energies (E_{React}) and Activation Barriers (E_{Act}) WGS steps on Pd and Pt(111). Reaction energies are calculated at infinite separation. The activation barrier is calculated with respect to the the reactants in the same supercell.

Reaction	Pd(111)		Pt(111)	
	E_{React} (eV)	E_{Act} (eV)	E_{React} (eV)	E_{Act} (eV)
$\text{H}_2\text{O}\cdot + * \rightleftharpoons \text{OH}\cdot + \text{H}\cdot$	0.33	0.84	0.49	0.60
$\text{OH}\cdot + * \rightleftharpoons \text{O}\cdot + \text{H}\cdot$	0.00	0.88	-0.15	0.35
$2 \text{OH}\cdot \rightleftharpoons \text{H}_2\text{O}\cdot + \text{O}\cdot$	-0.33	0.00	-0.63	0.00
$\text{CO}\cdot + \text{O}\cdot \rightleftharpoons \text{CO}_2\cdot + *$	0.02	0.75	-0.04	0.57
$\text{CO}\cdot + \text{OH}\cdot \rightleftharpoons \text{cis} - \text{COOH} * + *$	0.43	0.87	-0.06	0.26
$\text{cis} - \text{COOH} * \rightleftharpoons \text{trans} - \text{COOH} *$	-0.24	0.26	-0.15	0.27
$\text{trans} - \text{COOH} * + * \rightleftharpoons \text{CO}_2\cdot + \text{H}\cdot$	-0.18	0.61	0.03	0.62
$\text{trans} - \text{COOH} * + \text{O}\cdot \rightleftharpoons \text{CO}_2\cdot + \text{OH}\cdot$	-0.18	0.03	0.18	0.00
$\text{trans} - \text{COOH} * + \text{OH}\cdot \rightleftharpoons \text{CO}_2\cdot + \text{H}_2\text{O}\cdot$	-0.50	0.00	-0.46	0.00
$\text{CO}\cdot + \text{H}_2\text{O}\cdot \rightleftharpoons \text{cis} - \text{COOH} * + \text{H}\cdot$	0.76	1.70	0.42	1.00

internally consistent, as appropriate to our goal of comparing rates between Pt and Pd.

3.3 Reaction Energies and Barriers

The WGS reaction energy (equation 1) computed within the approximations used here is $-68.4 \text{ kJ mol}^{-1}$, 28 kJ mol^{-1} more exothermic than the 0 K experimental enthalpy of $-40.4 \text{ kJ mol}^{-1}$. Within the ideal gas/rigid rotor/harmonic oscillator approximations and using PW91-derived parameters, the WGS free energy at 553 K is 54 kJ mol^{-1} and, due to fortuitous error cancellation, agrees well with the experimental value of 61 kJ mol^{-1} . We calculated the energies of all the surface reactions in Figure 1 with respect to the related adsorbates at infinite separation; results are shown and compared in Table 3. Reaction energies differ by at most 0.5 eV between Pt and Pd. The larger differences are related to reactions involving the carboxyl and hydroxyl intermediates. The decomposition of the carboxyl intermediate is more exothermic on Pd, while its formation is more exothermic on Pt. The opposite trends are seen with the hydroxyl intermediate, where the decomposition is more exothermic on Pt and the formation is more exothermic on Pd. These differences derive from the a greater carboxyl binding energy to Pt and hydroxyl binding energy on Pd, respectively.

We next determined reaction pathways and activation barriers for reactions 3-12 and 15 in Figure 1. Computed transition state geometries are shown in Figures S1-S4. Transition state geometries

are generally similar on Pt and Pd. The largest differences are in reactions involving the O–H bond. The O–H distances are more elongated at the transition state on Pt compared to Pd as a consequence of the different OH site preferences on the two metals noted above. Reaction paths are similar to previously reported results, with maximum differences of 0.10 Å between interatomic distances found here and previously reported. Table 3 compares the computed activation energies on the two metals. In general, barriers are lower on Pt than Pd. Assisted decompositions of hydroxyl and carboxyl (involving transfer of an H to another surface adsorbate) have lower barriers than the unassisted pathways. Computed activation barriers are within 0.5 eV of previously reported results (Tables S5 and S6) [15, 18, 19, 26, 27, 31, 32, 54–56]. To our knowledge, no literature results are available for reactions 15 on Pt and Pd or reactions 8 and 12 on Pd (Figure 1). The larger discrepancies might be caused by different treatment of atomic cores and energy cutoffs. Smaller differences, on the order of 0.1 eV, could arise from supercell differences.

Because water dissociation has been proposed to be rate limiting, we looked for a reaction pathway in which adsorbed H₂O reacts directly with adsorbed CO, reaction 15 in Figure 1. Results are shown in Figure 3. The energy required to bring the reactants from infinite separation to the co-adsorbed state is –0.1 eV on Pt and 0.1 eV for Pd. The reaction then proceeds by CO diffusion to an atop site and water rotation to form the C–O bond while breaking one of the O–H bonds. The barrier for this concerted process is larger than energy difference between the transition state for carboxyl formation and infinitely separated CO and water on either metal. This pathway is thus unlikely to be important on the purely metallic surfaces and we do not consider it further.

Figure 4 compares key features of reactions involving O–H (Figure 4A and 4C) and C–O bond breaking (Figure 4B and 4D). The top panels compare computed activation energies against computed reaction energies on the two metals. Activation energies increase roughly linearly with increasing reaction energies, consistent with general expectations noted for diatomic dissociations [57], but these correlations are not strong. H₂O dissociation is an exception to this rule, as noted previously [31], and the majority of the assisted formations are endothermic with no activation barrier. The bottom panels compare the activation energies with O–H or C–O distances corresponding to the bonds being cleaved in the respective transition states. Distances span a significant range for these superficially similar reactions. Correlations between these geometric descriptors and activation energies are not strong, although in general, barriers are greater for reactions in which

Figure 3: Comparison of concerted and two-step carboxyl formation from adsorbed CO and H₂O on (A) Pd(111) and (B) Pt(111).

distances are closer to their equilibrium values and lesser for more elongated bonds.

3.4 Free Energy Surfaces

We used the binding energies, reaction energies, and activation barriers presented above to construct free energy surfaces (Figure 5) at $P=1$ atm, $T=553$ K, $y_{\text{CO}}=6.8\%$, $y_{\text{CO}_2}=8.5\%$, $y_{\text{H}_2\text{O}}=21.9\%$, $y_{\text{H}_2}=37.4\%$, and balance inert, typical of laboratory WGS conditions [2,4]. The first three steps in all pathways involve CO adsorption and H₂O adsorption and dissociation, and the Pd free energy surface lies below the Pt surface due to stronger CO binding on the former. For the pathways that involve the carboxyl intermediate (Figure 5A and B, reactions 5-9 in Figure 1), most of the Pt free energy surface lies below the Pd free energy surface. For the pathways that involve the hydroxyl intermediate (Figure 5, reactions 10-13 in Figure 1), the Pd free energy surface lies below the Pt surface. In all cases, CO adsorption is the lowest free energy point, suggesting that both surfaces

Figure 4: DFT-computed activation barriers against reaction energies and transition state (TS) atom separations. (A) O–H scission activation energies vs. reaction energies. (B) C–O scission activation energies vs. reaction energies. (C) O–H separations vs. reaction energies. (D) C–O separations vs. reaction energies. Filled and empty symbols represent Pt(111) and Pd(111), respectively. Legend numbers reference reaction numbers in Figure 1.

are CO-covered under reaction conditions, as confirmed below by the kinetic models.

4 Kinetic Modeling

4.1 Development of Kinetic Models

We next developed rate models to compare reaction pathways and metals. Rate parameters were calculated according to equation 2 using activation barriers relative to the adsorbates at infinite separation from each other. Computed rate constants are in Table S4. To solve the overall kinetic equations, we applied an analysis developed by Vilekar *et al.* [33,34], in which the rate r_{total} of a

Figure 5: Free energy surfaces for the (A) Carboxyl pathway, (B) Carboxyl-Hydroxyl pathway, (C) Redox pathway, and (D) Dual OH pathway on Pd and Pt(111). Conditions for free energy calculations: $P=1$ atm, $T=553$ K, $y_{\text{CO}}=6.8\%$, $y_{\text{CO}_2}=8.5\%$, $y_{\text{H}_2\text{O}}=21.9\%$, $y_{\text{H}_2}=37.4\%$, balance inert. The zero of energy is defined as the clean surface with two water molecules and a CO molecule in the gas phase. The numbers in the figure refer to the species involved in the products for the reactions in Figure 1. $\Delta S_{\text{ads}} = -S_{\text{trans}}$.

reaction network is related to the resistance R_{Total} of the various pathways:

$$r(T, P_i) = \frac{1}{R_{\text{Total}}} (1 - z_{\text{OR}}) \quad (7)$$

Here the reversibility z_{OR} is the ratio of the mass action expression and the equilibrium constant K_{eq} :

$$z_{\text{OR}} = \frac{1}{K_{\text{eq}}(T)} \prod_{i=1}^n \left(\frac{P_i}{P_i^0} \right)^{\sigma_i} \quad (8)$$

where P_i and σ_i are the partial pressure and stoichiometric coefficient of species i , respectively. In analogy to an electrical circuit, for a linear reaction sequence containing N elementary reactions

and N intermediate species, including the vacant site, the resistance can be written as the sum of individual resistances:

$$R_{\text{Series}} = \sum_{j=1}^N R_j \quad (9)$$

A similar analogy applies to M parallel reaction pathways:

$$\frac{1}{R_{\text{Parallel}}} = \sum_{j=1}^M \frac{1}{R_j} \quad (10)$$

The resistance of an individual reaction is $R_j = 1/r_j$, where r_j is the overall rate under the assumption that reaction j is rate limiting and all other elementary steps in the reaction sequence and all pathways not involving reaction j are quasi-equilibrated [58]. As shown by Vilekar *et al.*, this analysis is exact for networks that are linear in all intermediates and reliable for networks that contain some non-linearities [33,34]. As demonstrated below, it has the advantage of ready analysis of rate-determining features in terms of the resistances. The same group has shown the approach to give results close to a full microkinetic solution when applied to a comparable WGS network on Cu(111) [59].

4.2 Kinetic Modeling Results

For comparison purposes, we first computed the rates of each serial pathway in Figure 1 on Pd(111) independently under the conditions of $P = 1$ atm, $T = 553$ K, $y_{\text{CO}}=6.8\%$, $y_{\text{CO}_2}=8.5\%$, $y_{\text{H}_2\text{O}}=21.9\%$, $y_{\text{H}_2}=37.4\%$, and balance inert that are typical WGS laboratory conditions [2,4]. We assumed that adsorption and desorption of molecular reactants (CO and H₂O) and products (CO₂ and H₂) were equilibrated and therefore could not be rate limiting. We first consider the carboxyl pathway, reactions 1–6 and 13–14 in Figure 1. Because the computed carboxyl isomerization barrier is small, we treat this reaction as essentially equilibrated. The r_j for water dissociation, carboxyl formation, and carboxyl decomposition along this pathway are shown in the left limit of Figure 6A. (The figure plots these results as a function of CO binding energy, as introduced and discussed in Section 4.3). For example, the r_j for water dissociation was calculated assuming the step to be rate determining and carboxyl formation and decomposition to be quasi-equilibrated. r_j for the other two steps were calculated similarly. The net rate along the carboxyl pathway is given

Figure 6: Individual reaction rates r_j and total reaction rate r as a function of CO binding energy considering (A) carboxyl, (B) carboxyl-hydroxyl, (C) redox, and (D) dual OH pathway on Pd. The black vertical line correspond to the low coverage CO binding energy. In panels (A) and (B) the water dissociation and total rates are nearly identical; in panel (C) the OH dissociation and total rates are nearly identical.

by equation 7 and the total resistance by equation 9 and shown as a solid black line in Figure 6A. Because the water dissociation rate is eight orders of magnitude less (and its resistance is eight orders of magnitude greater) than the other steps, it dominates the resistance and is thus rate limiting along this pathway. Similar analyses are applied to the carboxyl-hydroxyl, redox, and dual OH pathways in panels B–D. The carboxyl-hydroxyl path (panel B) has similar absolute rate to the carboxyl path (panel A), and like the latter is limited by water dissociation. The redox (panel C) and dual OH (panel D) pathways have absolute rates approximately 10 orders of magnitude less than the pathways involving carboxyl; the rate of each is limited primarily by the O–H dissociation step.

These four pathways are linked via several common intermediates and reaction steps. This integrated WGS reaction network is illustrated in Figure S5. Applying Eqs. 9 and 10 together and assuming CO, H₂O, and H₂ adsorption and desorption and COOH isomerization are equilibrated, the total resistance is

$$R_{\text{Total}} = R_3 + \frac{1}{\frac{1}{R_4 + \frac{1}{\frac{1}{R_6} + \frac{1}{R_7 + R_8}}} + \frac{1}{\frac{1}{R_9 + \frac{1}{R_{11} + R_{12}}} + R_{10}}} \quad (11)$$

Details of the derivation are given in the Supplementary Information. The total rate on Pd is shown in the left limit of Figure 7. The water dissociation resistance, R_3 , is seven orders of magnitude greater than the other terms and water dissociation is thus rate limiting in this case. The carboxyl pathway resistance (first term in denominator of Eq. 11) is fourteen orders of magnitude smaller than the resistance for the redox pathways (second term). WGS thus proceeds preferentially through the carboxyl pathway. We computed an apparent activation barrier of 441 $\frac{\text{kJ}}{\text{mol}}$ by numerical differentiation of the natural log of the overall WGS reaction rate ($\ln(r_{\text{WGS}})$) with respect to the inverse temperature ($1/T$) from 453 to 673 K. The result is close to what one would infer from the difference between the highest TS and the lowest point (adsorbed CO) on the carboxyl free energy surface. Rate orders were similarly determined by numerical differentiation of the natural log of the overall WGS reaction rate ($\ln(r_{\text{WGS}})$) with respect to the natural log of the partial pressure ($\ln(P_i)$). Computed rate orders are -2 , 1 , 0 , and 0 for CO, H₂O, H₂ and CO₂, respectively. The large and constant CO binding energy drives the CO coverage to nearly one monolayer (Figure S22 in the Supplemental Information), reducing the overall WGS reaction rate law to a power law rate expression that is first order in H₂O partial pressure and inversely proportional to the square of the CO partial pressure. These results are summarized in Table 4.

We applied the same analysis to the Pt(111) reaction network at the same reaction conditions described above. As in Figure 6, the four panels in Figure 8 analyze individual and total rates for each pathway separately. The carboxyl and carboxyl-hydroxyl routes have similar pathway rates while the redox and dual hydroxyl rates are five and twelve orders of magnitude less. As with the Pd analysis, the resistance of one step dominates in each case and dictates the overall rate. These rate-determining steps are water dissociation, water dissociation, hydroxyl dissociation and assisted hydroxyl dissociation for the carboxyl, carboxyl-hydroxyl, redox, and dual hydroxyl

Figure 7: Total WGS reaction rate (r_{WGS}) as a function of CO binding energy.

pathway, respectively. The overall WGS rate determined by Eq. 7 is shown in the left limit of Figure 7. The water dissociation resistance, R_3 , is six orders of magnitude greater than the other term, and again water dissociation is predicted to be rate determining. The carboxyl pathway resistance is nine orders of magnitude smaller than the redox resistance and thus dominates the production of WGS products. The apparent activation barrier is calculated to be 405 kJ mol^{-1} and rate orders are identical to those calculated for Pd, for the same reasons noted above.

Table 4 summarizes the kinetic results on Pd and Pt. Pd and Pt share preferred WGS pathways and rate orders, while the apparent activation barrier on Pt is 36 kJ mol^{-1} lower than on Pd and, as a consequence, the total modeled WGS rate (r_{WGS}) on Pt is four orders of magnitude higher than Pd. The lower barrier for water dissociation on Pt is the largest contributor to this difference. Absolute rates are on the order of 10^{-24} for Pd and 10^{-20} molecules per second per site for Pt and absolute barriers exceed 400 kJ mol^{-1} , far from physically reasonable values. The use of low coverage CO binding energies drives absolute coverages to nearly a full monolayer and greatly diminishes rates per total metal sites (Figure S22 in the Supplemental Information).

4.3 CO Binding Energy Dependence

CO coverages will be less than modeled above due to adsorbate-adsorbate interactions that decrease binding energy with increasing coverage [52,60]. Previous kinetic models of WGS on Pt and Cu(111)

Figure 8: Individual reaction rates r_j and total reaction rate r as a function of CO binding energy considering (A) carboxyl, (B) carboxyl-hydroxyl, (C) redox, and (D) dual OH pathway on Pt. The black vertical line correspond to the low-coverage CO binding energy. In panels (A) and (B) the water dissociation and total rates are nearly identical; in panel (C) and (D) the OH dissociation and total rates are nearly identical.

also predict CO to be the most abundant surface species and include a coverage-dependent CO binding energy that produces more realistic coverages [15, 20, 26]. Experiments reveal that under WGS conditions CO is near saturation coverage [2, 4], which is $\frac{3}{4}$ and $\frac{2}{3}$ ML on Pd(111) and Pt(111), respectively [61, 62].

To examine the direct consequences of diminished CO binding with increasing CO coverage, we manually decreased the absolute value of the CO binding energy while keeping the net WGS reaction energy constant. We achieved this by decreasing the reaction energy of steps involving adsorbed CO (carboxyl formation and CO oxidation (reactions 5 and 13 in Figure 1) by the same amount that the absolute value of the CO binding energy was decreased, while keeping all other

Table 4: Kinetic model comparisons. RDS identifies step in Figure 1 with largest resistance. Reaction conditions: $P=1$ atm, $T=553$ K, $y_{\text{CO}}=6.8\%$, $y_{\text{CO}_2}=8.5\%$, $y_{\text{H}_2\text{O}}=21.9\%$, $y_{\text{H}_2}=37.4\%$, balance inert. Experimental results from [2, 4].

	Pd(111)				Pt(111)			
	Kinetic Model			Exp't	Kinetic Model			Exp't
$\Delta H_{\text{ads}}^{\text{CO}}$ (eV)	-1.95	-0.66	-0.66		-1.87	-0.66	-0.66	
ΔS_{ads}	$-S_{\text{trans}}$	$-S_{\text{trans}}$	$-\frac{1}{3}S_{\text{trans}}$		$-S_{\text{trans}}$	$-S_{\text{trans}}$	$-\frac{1}{3}S_{\text{trans}}$	
r_{WGS} (s ⁻¹)	3.87×10^{-24}	1.93×10^{-10}	3.25×10^{-8}	2.7×10^{-3}	1.19×10^{-20}	3.81×10^{-8}	5.40×10^{-7}	1.6×10^{-2}
E_{a} (kJ mol ⁻¹)	441	190	217	82	404	154	190	68
RDS	3	4	4		3	4	4	
CO Order	-2.00	0.97	-0.91	0.38	-2.00	0.98	-0.92	0.06
H ₂ O Order	1.00	1.00	0.99	0.44	1.00	1.00	0.99	1.00
CO ₂ Order	0.00	0.00	-0.02	-0.06	0.00	0.00	0.00	-0.10
H ₂ Order	0.00	-1.50	-0.74	-0.36	0.00	-1.49	-0.56	-0.44

reaction energies and activation barriers constant. Figures 9 illustrates the changes in the free energy surfaces along each path that correspond to these changes in the CO binding energy. As the CO binding energy changes from -1.95 to -0.69 eV (black to blue lines), the steps preceding C–O bond formation are shifted upward to higher free energy while the subsequent steps are unchanged. The behavior on Pt (Supplementary Information) is very similar to that of Pd.

Figures 6 and 8 show the effect that these continuous changes to the CO binding energy have on the individual pathway and overall WGS reaction rates. As the absolute value of the CO binding energy decreases relative to the (assumed constant) hydrogen binding energy, hydrogen coverage increases and the CO coverage decreases. An increase in density of free sites results in several orders of magnitude increases in all the calculated rates. Because carboxyl formation and CO oxidation has a first-order dependence on both CO and OH coverage, their rates goes up less rapidly with the varying CO binding energy than does H₂O dissociation. As a result, along all pathways, the rate limiting step shifts from H₂O dissociation to carboxyl formation or CO oxidation as CO binding and coverage diminishes. The total WGS rate, calculated according to Eq. 7, is shown in Figure 7. As the absolute value of the CO binding decreases, the overall WGS rate increases by twenty orders of magnitude and the apparent activation barrier decreases to around 200 kJ mol^{-1} on both metals (Figure 10). The resistance of the carboxyl pathway is less than the resistance of the parallel redox pathway, so that the former still dominates the reaction. The contribution of carboxyl formation (R_4) to the overall resistance is fourteen orders of magnitude larger than the water dissociation resistance. In the lower absolute CO binding energy limit, carboxyl formation becomes overall rate

Figure 9: Free energy surfaces for the (A) Carboxyl pathway, (B) Carboxyl-Hydroxyl pathway, (C) Redox pathway, and (D) Dual OH pathway on Pd(111) as a function of the CO Binding Energy. Conditions for free energy calculations: $P=1$ atm, $T=553$ K, $y_{\text{CO}}=6.8\%$, $y_{\text{CO}_2}=8.5\%$, $y_{\text{H}_2\text{O}}=21.9\%$, $y_{\text{H}_2}=37.4\%$, balance inert. The zero of energy is defined as the clean surface with two water molecules and a CO molecule in the gas phase. The numbers in the figure refer to the species involved in the products for the reactions in Figure 1.

limiting. Finally the rate orders of CO and H₂ change to approximately 1 and -1.5 while the H₂O and CO₂ rate orders remain unchanged. Pt retains a lower apparent activation barrier and higher intrinsic reaction rate (r_{WGS}). Table 4 summarizes the results from the WGS kinetic model on Pt and Pd at CO absolute binding energy of -0.66 eV, corresponding to a 0 eV free energy of binding, and also includes a comparison to observed WGS on Pt and Pd supported on $\gamma\text{-Al}_2\text{O}_3$. In spite of the improvements, the shifted binding energy models overestimate apparent activation energies by a factor of more than two, underestimate observed rates by at least six orders of magnitude, and fail to capture observed CO or H₂O orders.

Figure 10: Apparent activation energy as a function of CO binding energy.

This simple coverage model captures the beneficial effect of lower CO coverage on the availability of surface sites. A more complete model would include coverage effects on the binding energies of all species as well as the influence of this coverage-dependence on reaction barriers [26,27], at the expensive of the insights we gain from the analytical analysis here. As we expect this coverage sensitivity to be nearly the same on Pd and Pt, we anticipate the relative effects on rate behavior to be comparable [63], and not to alter the insights gained from the analysis just discussed.

4.4 Adsorption Entropy Dependence

Campbell *et al.* have recently observed that at the conditions at which metal catalysts turn over, the lateral motion of adsorbates is better approximated as a two-dimensional (2D) gas than as species

vibrating within an adsorption site. In this mobile adsorbate limit, adsorbates lose $1/3$ of their gas-phase translational entropy ($-\frac{1}{3}S_{\text{trans}}$) upon adsorption and recover $\frac{1}{3}S_{\text{trans}}$ upon desorption [49,50]. This difference makes the modeled free energy of adsorption more negative and should increase the coverage of surface species at a given adsorption condition. To test the effect of this choice on the kinetic modeling results, we repeated the analysis using this revised entropy estimate for all adsorption and desorption steps.

Figure 9 compares the base case Pd free energy model (black line) to one in which the adsorption entropy is reduced (red line) at a CO binding energy of -1.95 eV. As anticipated, the free energies of all the intermediates and transition states are suppressed. The effect on H_2O adsorption and H_2 desorption are particularly dramatic, which reflects the scaling of the magnitude of the translational entropy with the inverse of the molecular mass. As described above, the base case gives a very high CO coverage and low WGS rate. Decreasing the entropy penalty only increases the coverage further and, when analyzed within the kinetic model, diminishes the rates even more.

More interesting is the weaker CO binding energy limit. Figure 9 compares the potential energy surfaces on Pd assuming a CO binding energy of -0.66 eV and either the full (blue line) or partial (green line) loss of S_{trans} . The decreased absolute value of the CO binding energy and entropy nearly compensate one another, so that the final free energy surface is similar to the base energy and entropy case. We compared kinetic results on these two models. Decreasing the adsorption entropy penalty shifts the surface from H-dominated ($\theta_{\text{H}} \approx 0.95$ ML) back to CO-dominated ($\theta_{\text{CO}} \approx 0.90$ ML, Figure S22 in the Supplemental Information). The rates (r_j , pathway, and overall WGS) are similar in both entropy models at the lower absolute CO binding energy, and the relative contributions of the various steps to the overall reaction resistances remain qualitatively the same. Results for the overall reaction are summarized in Table 4. Regardless of entropy choice, WGS proceeds through the carboxyl intermediate. The rate limiting step, determined by a comparison of the resistances, shifts from water dissociation to carboxyl formation as the CO binding energy diminishes. The difference in the CO and hydrogen coverage are responsible for the differences in the calculated rate orders for CO and H_2 between the two models.

5 Discussion

The computational results here allow us to make several observations. First, while intermediate reaction energies are similar on Pd and Pt, reaction barriers on Pt are consistently lower than on Pd. As a result, a baseline kinetic model and its modifications all predict a higher intrinsic WGS rate on Pt metal than on Pd, consistent with experimental observation. Second, the kinetic models consistently indicate that reaction on the metal proceeds through a carboxyl intermediate. The existence and identity of a single rate determining step is less clear. As CO binding is made progressively less exothermic, we find that the identity of the rate limiting step, determined by comparison of the resistances, shifts from water dissociation to carboxyl formation on both metals.

One point of comparison with the present model is provided by the work of Flaherty *et al.* [64] who report WGS kinetics measured above a Pt(111) single crystal at zero conversion, that is, with no H_2 or CO_2 in the feed, at temperatures between 525 and 675 K. We reran the Pt(111) kinetic model at comparable conditions ($P_{\text{CO}} = 25$ Torr, $P_{\text{H}_2\text{O}} = 15$ Torr, $P_{\text{H}_2} = P_{\text{CO}_2} = 0$ and $T = 625$ K) and obtained an absolute turnover rate ($\approx 4 \text{ s}^{-1}$) comparable to the Mullins result ($\approx 1 \text{ s}^{-1}$) in the weak CO binding limit of -0.66 eV and the mobile adsorbate entropy assumption. This absolute TOF is quite sensitive to the model parameters, but it is encouraging that agreement can be obtained in some reasonable range of the parameter space. More telling are the apparent activation energies and rate orders. Using the same model assumptions, we obtain an apparent activation energy of 167 kJ mol^{-1} , considerably above the experimental value of 96 kJ mol^{-1} . This difference could well reflect underlying uncertainties in the GGA energies and assumptions related to the CO coverage dependence. Flaherty *et al.* also report observed zero order dependence on both CO and H_2O pressures, which as they describe, implies a surface covered with carboxyl and rate-limiting carboxyl decomposition. Neither of these observations are qualitatively consistent with the calculations, which as shown in Supplemental Figure S22 always yield a surface dominated by either CO or H_2 . Further, we always find unit rate order in H_2O and non-zero order in CO, and always find the overall reaction to be rate limited either by H_2O dissociation or carboxyl formation. It is difficult to reconcile the computational results with these experiments. Further experiments on single crystals at representative WGS conditions would be helpful towards this end.

The more complete set of kinetic results on supported catalysts provide another point of compar-

ison. In no case do we recover absolute reaction rates that approach experiment on the supported catalysts, and computed apparent activation energies exceed experimental observation. As shown in Table 4, computed rate orders for CO_2 are always zero, consistent with experiment. Rate orders for H_2O are always near unity, consistent with that observed on supported Pt but significantly different from experimental observation on supported Pd. H_2 orders are quite sensitive to the model assumptions and encompass the fractional inhibiting contribution observed experimentally. The CO orders similarly depend sensitively on model assumptions. Overall the metal-only model only qualitatively captures the observed kinetics on the supported materials.

Grabow *et al.* were able to recover experimentally observed WGS rates, apparent activation energies, and rate orders measured on $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ measured under different conditions than those reported in Table 1. To achieve this agreement, reaction energies and activation barriers of a number of steps, including H_2O dissociation, were modified by at least 0.30 eV from their DFT-determined values [15]. Stamatakis *et al.* used a model similar to that reported here, with the addition of a coverage-dependent CO binding energy and Brønsted-Evans-Polanyi (BEP) relations for carboxyl formation activation, reaction energy and CO oxidation reaction energy (reactions 4 and 10 in Figure 1) Using kinetic Monte Carlo simulations, they inferred carboxyl formation to be rate limiting, similar to that observed under some conditions here, and calculated an apparent activation barrier of 127 kJ mol^{-1} , closer to the number calculated in the models here than to the 68 kJ mol^{-1} observed experimentally [26,27]. A kinetic model for WGS on Pd(111) has not to our knowledge been reported in the literature. We applied the approach here to the unmodified DFT results of Wang *et al.* [18,19]. Absolute rates are about five orders of magnitude lower and apparent activation barriers are about 90 kJ mol^{-1} higher than the stronger binding CO model in Table 4. This difference derives from a larger computed water dissociation barrier in their supercell models. In general, all the DFT models based on metal-only calculations do not recover experimentally observed behavior.

These discrepancies between computation and observation may indicate that inclusion of steps involving the support are necessary to recover observed kinetics even on an “inactive” support like $\gamma\text{-Al}_2\text{O}_3$. Water dissociation is rate limiting under many of the conditions modeled here, and an active role in water dissociation is a plausible role for the support. Several groups have used DFT to examine WGS reactions on supported metals and generally concluded that the water dissociation

barrier is diminished at the metal-support interface relative to the (111) metal surface [23,65–73]. Water dissociation is known to be facile at an alumina surface itself [74,75] and to strongly influence the adsorption of O and OH on supported Pd and Pt atoms [76].

6 Conclusions

The mechanism of WGS and its dependence on metal and support remain topics of considerable theoretical interest. A fully satisfactory microkinetic model should capture absolute rates and rate derivatives over operational ranges of experimental interest. Here we use a consistent set of DFT calculations to construct internally consistent WGS models on Pt and Pd, two metals of particular interest for low temperature WGS. The kinetic models satisfactorily recover the experimentally observed ordering of relative rates but fail to recover kinetic parameters observed on γ -Al₂O₃-supported materials, the least active of commonly studied supports. Even on these materials, the support itself likely has a role in the WGS mechanism.

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