Water Activation and Carbon Monoxide Coverage Effects on Maximum Rates for Low Temperature Water-Gas Shift Catalysis

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Abstract

Linear scaling relations and Brønsted-Evans-Polanyi (BEP) relations help to elucidate trends in activation energies and adsorption energies on different metal surfaces. In this paper, Density Functional Theory (DFT) calculations available in the literature are utilized to analyze these trends and their effect on the reactivity of transition metals for the low temperature water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$). The importance of O-CO bond formation in water-gas shift is shown for metals not limited by water dissociation. In addition, the CO binding energy is shown to be an important parameter, as CO can crowd out the free sites which participate in adsorption steps, water dissociation, and carboxyl decomposition. From these results, we propose a catalyst design strategy to combine metals that adsorb O weakly, such as Au clusters or Pt nanoparticles, with supports that exhibit strong enough interactions with oxygen to be capable of easily dissociating water.

Keywords: water-gas shift, microkinetic modeling, scaling relations, transition metals, support effect, catalyst design, volcano plots

1. Introduction

The design and development of catalytic materials stands to benefit tremendously from the improved understanding of adsorbate interactions that density functional theory (DFT) provides. Understanding how rate constants for a particular reaction step vary on different surfaces offers the potential to identify trends in catalytic activity. As a step towards predicting rate constants on new materials, DFT-based methods have been introduced for creating linear scaling relations and Brønsted-Evans-Polanyi (BEP) relations [1–6]. These relations help to elucidate trends in activation energies and adsorption energies on different metal surfaces. By creating models with input from these types of calculations, one can gain a fundamental understanding of the underlying chemistry in different catalytic processes. The overall goal is to use the information from the model to yield a more systematic and efficient approach to catalyst design.

In this paper, we address the low temperature water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$), which is important in the industrial production of hydrogen from carbon based sources. The water-gas shift (WGS) reaction is exothermic and reversible, so higher equilibrium conversions are achievable at lower temperature. Consequently, WGS is often performed in high and low temperature shift stages when complete conversion of CO is desired. Copper based catalysts are a good low cost choice for the low temperature WGS reaction, but they also suffer from several drawbacks. Cu-ZnO/Al₂O₃ catalysts are sensitive to oxygen exposure, water condensation, thermal deactivation, sulfur and chlorine poisoning, and require a careful reduction process [7,8].

To overcome these shortcomings, recent interest in hydrogen production involving WGS has led to research on a plethora of different catalyst formulations.

Catalysts tested under WGS conditions have included various metals (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au) on a multitude of supports (MgO, ZnO, Co₃O₄, Al₂O₃, Cr₂O₃, Fe₂O₃, Y₂O₃, La₂O₃, Nd₂O₃, SiO₂, TiO₂, ZrO₂, HfO₂, CeO₂, ThO₂, MoO₂, MoO₃, mixed oxides, zeolites, C, Mo₂C, etc.) [9–26]. Furthermore, supports with different surface crystal planes (e.g. [111], [110], [100], amorphous) [17,27,28] have been evaluated along with a large number of different promoters [11,29]. Using an Edisonian guess-and-test method on all of the aforementioned combinations would be time consuming and expensive. Clearly, it would be preferable to guide our catalyst design by understanding the trends which determine the relative magnitudes of the important reaction steps for WGS on these various surfaces [30,31].

Inspired by several works in the literature (predominantly by Schumacher et al. [32] and Falsig et al. [33]), we have created a model which incorporates scaling relationships obtained from calculations involving the carboxyl intermediate (O=C–O–H or “COOH”) for water-gas shift on close-packed (111) ideal metal surfaces. Instead of creating a full microkinetic model utilizing scaling relationships [34,35], we have made a model based on the idea of a maximum possible Sabatier rate [33,36], the rate at which the surface coverages are ideal for each reaction step. The water-gas shift reaction is often described to have a bi-functional mechanism which involves CO activation on a metal and water dissociation on the support or metal/support interface [7,14,37–42]. Consequently, it is instructive to separate those functions within the model and only evaluate the Sabatier rate which would exist at ideal surface coverages. As has been reported [14,43], a calculation of the full microkinetic model for reaction on the metal surface, while meaningful, may not provide useful information about the actual supported

systems. This is because the coverage of H₂O, OH, or O adsorbates cannot be determined from calculations on metal surfaces if the support or metal-support interface is responsible for dissociating water.

Using the results of the model, we seek to understand what makes a good water-gas shift catalyst by analyzing the inherent trends in activation energies and carbon monoxide coverages. Furthermore, analysis of the reaction rates for individual steps provides the necessary foundation to identify how supported catalysts may differ from close-packed surfaces due to the presence of multiple types of sites or adsorbate-adsorbate interactions. The carboxyl intermediate was considered to be the main intermediate in previous works which were based on microkinetic models on Cu- and Pt-based catalysts. For Cu, it was determined that the main reaction proceeded through carboxyl decomposition with an OH species [44], while for Pt, the main reaction was determined to proceed through carboxyl decomposition with a free site [45]. The calculations used to create our model are derived from the DFT values reported by Huang et al. [46]

2. Methods

The carboxyl mechanism described in Huang et al. [46] has the following mechanistic steps on a metallic surface:

where * represents a free surface site and X* represents molecule X adsorbed on a site. Additional steps for COOH decomposition are considered in the works by Mavrikakis et al., such as:

The steps involving COOH decomposition with an OH or O adsorbate have lower activation energies on Pt and Cu than do steps involving decomposition with a free site [44,45]. However, in the literature, the relative contribution of these reaction steps to the overall rate was found to be dependent on the surface coverage of OH and O on the Pt, and in order to simplify the analysis presented, the additional reaction steps were not considered due to the lack of information about the transition state energies on the surfaces evaluated and to the generally low coverages calculated for OH* and O* in microkinetic models on precious metal surfaces.

In a full microkinetic model, it is necessary to evaluate the equilibrium constants for several steps because they will be important in setting the relative coverages of various intermediates. However, our goal is only to evaluate the maximum possible rate for this mechanism, so we do not need to know all of the equilibrium constants. In this analysis, we have assumed that CO is a reactant at a set concentration of $P_{\text{CO}} = 0.068$ atm. In order to calculate the Sabatier rate, the forward rate of reaction and the ideal surface coverages under the assumed conditions are the only necessary inputs. For the forward reaction, the pressure of the products, hydrogen and carbon dioxide, are approximated as

zero, and the pressure of water is allowed to vary in the analysis. Based on the following mathematical analysis, which is also detailed in the supporting information, the only equilibrium constant which is explicitly calculated is that for CO adsorption on the metal. This approximation will allow us to concentrate on the effect of CO as we separate the water steps from the overall mechanism.

We explicitly take the equilibrium constant of CO into account because it will be important in setting the coverage of CO and the coverage of free sites, both of which will influence the maximum possible rates for the different mechanistic steps. The equilibrium constant for CO adsorption is defined as K_{CO} :

$$K_{CO} = e^{\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right)} = e^{\left(\frac{\Delta S}{R} - \frac{BE_{CO}}{RT}\right)} \quad (9)$$

where ΔH is the enthalpy of reaction and is equal to the CO binding energy (BE_{CO}). The binding energies are represented as negative values in line with exothermic adsorption processes. ΔS is the entropy of reaction at 548 K. ΔS is determined by assuming that CO is immobile on the surface. Consequently, ΔS of reaction for step 1 is equal to a constant at 548 K derived from the Sackur-Tetrode equation [47]:

$$\Delta S = -R \ln \left(\left(\frac{2\pi M k_B T}{h^2} \right)^{1.5} \frac{k_B T}{P} \right) - 2.5R \quad (10)$$

where M is the mass of the molecule, h is the Planck constant, and k_B is the Boltzmann constant.

Using Langmuir-Hinshelwood-type expressions, the maximum CO coverage, $\theta_{CO \max}$, will occur when the site balance is $1 = * + CO^*$. Based on the equations in the supporting information, $K_{CO} P_{CO} (*) = CO^*$ leads to:

$$\theta_{CO \max} = \frac{K_{CO} P_{CO}}{1 + K_{CO} P_{CO}} \quad (11)$$

where P_{CO} is the assumed partial pressure of CO. Note that we have assumed here that CO and empty sites must be present on the surface of the noble metal in order for the reaction to proceed. Similarly, the maximum fraction of free sites, $\theta_{* \text{max}}$, for surfaces on which CO is strongly adsorbed is determined by the CO coverage:

$$\theta_{* \text{max}} = \frac{1}{1 + K_{\text{CO}} P_{\text{CO}}} \quad (12)$$

Figure 1: Maximum fraction of free sites (θ_{*}) as determined from the CO binding energy, $K_{\text{CO}} = e^{\left(\frac{\Delta S}{R} - \frac{\text{BE}_{\text{CO}}}{RT}\right)}$, with $P_{\text{CO}} = 0.068$ atm and temperature = 548 K.

With the knowledge of the maximum CO and free site coverages, it is possible to calculate a maximum rate for steps 3-6 once the activation energies and pre-exponential factors for those steps have been determined. As mentioned above, to calculate the maximum rate, only the forward rate of reaction is considered [33].

For reaction steps 3-5 we set the pre-exponential factors equal to constant values of 10^{13} , 10^{13} , and $2 \times 10^{12} \text{ s}^{-1}$, as determined for the reactions on the Pt(111) surface [45]. The activation energies are approximated by using the curves shown in Figure 2. The individual values are from the DFT work of Huang et al., in which a 5 layer metal slab with a (4x4) unit cell was used in VASP with GGA-PW91 [46]. Note that the type of

approximation used for the activation energies is similar to that shown in the work of Schumacher et al., where the binding energy of oxygen was used to determine the activation energy for ($\text{CO}^* + \text{O}^*$) and for water dissociation [32]. The pre-exponential factor for step 6, hydrogen desorption, is estimated as 10^{13} s^{-1} , and in agreement with Schumacher et al., the activation energy is observed to scale better with the CO binding energy than that for O.

Figure 2: Activation energies versus binding energy determined for Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au (111) surfaces [46]. $\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$ (squares); $\text{CO}^* + \text{OH}^* \rightarrow$

COOH* + * (circles); COOH* + * $\rightarrow$ CO₂ + H* + * (triangles); 2H* $\rightarrow$ H₂ + 2* (diamonds).

With maximum values for the surface coverages, and values approximated for rate constants, we can calculate a maximum value for the rate of the non-adsorption steps using equations of the following form:

$$r_3 = \max \{k_{3f}\theta_*\theta_{H_2O}\} = k_{3f} \theta_* \max/4 \quad (13)$$

$$r_4 = \max \{k_{4f}\theta_{CO}\theta_{OH}\} = k_{4f} \theta_{CO} \max/4 \quad (14)$$

$$r_5 = \max \{k_{5f}\theta_{COOH}\theta_*\} = k_{5f} \theta_* \max/4 \quad (15)$$

$$r_6 = \max \{k_{6f}\theta_H \frac{\theta_H}{2}\} = k_{6f}/2 \quad (16)$$

Note that the ideal surface coverage for each reaction is different and provides an upper-bound for each reaction step. The surface intermediates considered for equations 13-16 respectively are as follows: (*, CO*, H₂O*), (*, CO*, OH*), (*, CO*, COOH*), (*, CO*, H*). Consequently, the analysis is different from a typical microkinetic model where the coverage of each intermediate is necessary to calculate a rate for all of the reaction steps simultaneously.

In order to derive equations 13-16, the constraint was applied that CO must be present on the surface of the metal which limits the maximum value for the fraction of empty sites. For equation 13, the maximum rate was taken as $r_3 = k_{3f} \theta_* \max/4$. This is based on the Langmuir-Hinshelwood (LH) expression for reaction 3, which gives $r_3 = k \frac{y}{(1+x+y)^2}$, where $x = K_{CO}P_{CO}$ and $y = K_{H_2O}P_{H_2O}$. After calculating y at which $d(r_3)/dy = 0$ and checking that $d^2(r_3)/dy^2 < 0$, the maximum value for the LH expression occurs when $y = 1+x$ so that $r_3 = k \frac{1+x}{4(1+x)^2} = k \frac{1}{4(1+x)} = k\theta_* \max/4$; note that we are implicitly assuming that the water pressure will adjust to fulfill the maximum rate condition.

Similar math applies to equation 15 where $y = f(P_{CO}, P_{H_2O})$. For equation 14, the LH expression gives $r_4 = k \frac{x * z}{(1+x+z)^2}$ where $z = f(P_{CO}, P_{H_2O})$. The maximum rate occurs when $z = 1+x$ so that $r_4 = k \frac{x(1+x)}{4(1+x)^2} = k \frac{x}{4(1+x)} = k\theta_{CO}max/4$. For equation 16, it has been assumed that the coverage of θ_H is ideal to give the maximum rate possible for that individual reaction rate so that $\theta_H \approx 1$.

The Sabatier rate for a group of elementary steps is then determined by the lowest of the rates within that group, as in the work by Falsig et al. [33], and in this case the stoichiometric number for each of the steps is 1. Four different cases are considered here.

$$r_S = r_3 \quad (17)$$

$$r_S = \min\{r_3, r_4, r_5, r_6\} \quad (18)$$

$$r_S = \min\{r_4, r_5\} \quad (19)$$

$$r_S = r_4 \quad (20)$$

Contour maps of equations 17-20 are shown in Figures 4-6. The points corresponding to the (111) surfaces of Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au, as determined from the calculations of Huang et al. [46], are marked on each graph. Two additional points have been added to each graph. The “Pt : *~33% ML” data point is meant to represent the effect that adsorbate-adsorbate interactions might have on the model. For example, in the Grabow et al. microkinetic model on Pt, a coverage dependent CO binding energy was used which yielded $BE_{CO} = -1.1$ eV at 2/3 monolayer coverage [45]. Furthermore, other modeling works in literature also use coverage dependent binding energies that reduce the CO binding energy by approximately 1 eV for Pt and are based on empirical and theoretical values [43,48,49]. At 548K and $P_{CO} = 0.068$ atm, a $BE_{CO} = -1.09$ eV yielded a maximum empty site

fraction equal to 33% ML as seen in Figure 1. Therefore, the label Pt: *~33% ML represents the mathematically defined maximum empty site fraction given the BE CO, temperature, and CO concentration.

The “Au : 12 atoms” data point represents the BE CO and BE O of a gold nanoparticle as calculated by Falsig et al. with the BE O and BE CO values adjusted so that the difference between the values for Au (111) and “Au : 12 atoms” is the same as that calculated from the reference [33]. A figure representing CO and H₂O interacting with a Au cluster supported on MgO is shown in Figure 3. The figure was adapted from the DFT study by Zhao et al. [42] which describes the importance of the Au/MgO interface in dissociating water.

Figure 3: Depiction of the WGS mechanism on a Au₁₂ cluster supported on MgO. Adapted from the work of Zhao et al. [42] Colors: Mg – green; Lattice O – red; O – blue; C – black; H – grey.

3. Results

The ability of water to dissociate on metal surfaces is important in determining the rate on unsupported catalysts because all proposed water-gas shift mechanisms necessitate the breaking of the O-H bond in water. A contour plot of equation 17 is

shown in Figure 4. The O binding energy determines the activation energy of water dissociation, as shown in Figure 2, and the CO binding energy determines the fraction of free sites, as shown in Figure 1.

Figure 4: Log of the Sabatier rate for water dissociation from Equation 17 at $P_{CO} = 0.068$ atm and 548 K. $H_2O^* + * \rightarrow OH^* + H^*$

For CO binding energies weaker than -1 eV, the number of free sites is large enough such that only the oxygen binding energy has an effect on the maximum rate possible for water dissociation. However, for metals which have strong CO binding energies, the fraction of free sites is below 10^{-5} . The lack of free sites has a significant effect on the maximum possible rate for water dissociation because that step requires a free site as written ($H_2O^* + * \rightarrow OH^* + H^*$). As shown in Figure 4, allowing for adsorbate-adsorbate interactions enhances the model rate for water dissociation on Pt by over 6 orders of magnitude. The difference in magnitude is due to the change in the number of free sites in the equation $r_3 = k_{3f} \frac{1}{4(1+K_{CO}P_{CO})} = k_{3f} \theta_{*,max}/4$. As shown in Figure 1, stronger binding energies of CO result in larger values for K_{CO} and fewer free sites.

The Sabatier rate for the full carboxyl mechanism is shown in Figure 5. Note that the rate of hydrogen desorption does not have an effect on this particular graph and $\min [r_3, r_4, r_5, r_6] = \min [r_3, r_4, r_5]$. The rate for r_6 only varies with respect to the activation energy for reaction 6 and the temperature. Thus, r_6 does not influence the results in this case because the rate coefficient is sufficiently large and, unlike the other reaction steps, its rate is not dependent on the CO coverage, nor is it dependent on the number of empty sites. The results show that Cu is near the top of the volcano curve, and the other metal surfaces have over two orders of magnitude lower rates under the conditions considered. Although we have only considered the Sabatier rate in this model, the results are qualitatively very similar to those from Schumacher et al., where a full microkinetic model was employed [32]. In those results, Cu is observed to be near the pinnacle of the graph, followed by Co(111) and Au nanoparticles, and the rest of the close-packed metal surfaces have relative rates near zero. Co stands out, for its strong O binding energy, which contributes to its ability to dissociate water, as seen in Figure 2 and Figure 4. On the other hand, Au nanoparticles cannot dissociate water well, but benefit from a weak CO binding energy [18].

Figure 5: Log of the Sabatier rate for steps 3-6 of the carboxyl mechanism from Equation 18 at $P_{\text{CO}} = 0.068$ atm and 548 K.

A close examination of the similarities between Figure 4 and Figure 5 reveals that the rate of water dissociation is responsible for setting the Sabatier rate for Ni, Rh, Pd, Ag, Ir, Pt and Au in Figure 5. In other words, $\min [r_3, r_4, r_5, r_6] = r_3$ because water dissociation is limiting the Sabatier rate on those metals. Evidence in the literature suggests that the water-gas shift reaction on supported metal catalysts is bi-functional in nature. Furthermore, many researchers have proposed that the metal activates CO while the support is responsible for activating the water [7,37–42]. Several researchers have also argued in favor of metal and support interface sites being the active site for the reaction, but the reason for the enhanced activity is generally proposed to be related to improved water dissociation associated with the support [50,51]. Consequently, we would like to know what the rate might look like if the metal surfaces are not responsible for water dissociation. To accomplish this, the same Sabatier rate analysis is performed on the water-gas shift mechanism, but we assume that water dissociation, r_3 , is not rate limiting. This assumption is equivalent to grouping reactions 2 and 3 together to yield the overall equilibrated reaction $\text{H}_2\text{O} + * + * \leftrightarrow \text{OH}^* + \text{H}^*$.

Graphs of these Sabatier rates are shown in Figure 6 and Figure 7 for the carboxyl formation and dissociation steps. Those steps are typically assumed to involve the metal due to its ability to bond CO and H species. The hydrogen desorption step 6 is not included in Figure 6 for simplicity, but it does not have a significant effect on the overall trend. The activation energy necessary for making the O-CO bond is approximated by using the scaling relationship shown in Figure 2 for carboxyl formation ($\text{CO}^* + \text{OH}^* \rightarrow$

COOH* + *). Hence, the O binding energy impacts the rate of formation of the main intermediate through the activation energy, but the CO binding energy influences that rate because it controls the maximum coverage of CO. Additionally, the CO binding energy affects the rate of COOH decomposition through the fraction of free sites available. Comparing Figure 6 to the Sabatier rate for the full mechanism in Figure 5 shows that the rates for Co, Ni, and Cu are approximately the same. On the other hand, maximum achievable rates for the other metals are enhanced by 2 to 9 orders of magnitude.

Figure 6: Log of the Sabatier rate for carboxyl formation and carboxyl dissociation, steps 4-5, from Equation 19 at $P_{CO} = 0.068$ atm and 548 K. $CO^* + OH^* \rightarrow COOH^* + * \rightarrow CO_2 + H^* + *$

Figure 7: Log of the Sabatier rate for O-CO bond formation in carboxyl formation, step 4, from Equation 20 at $P_{\text{CO}} = 0.068$ atm and 548 K. $\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$

When the CO binding energy is strong in the case of Pt or Pd, the rate in Figure 6 is controlled by the fraction of free sites available. That is again why the rate is observed to increase over 6 orders of magnitude when the adsorbate-adsorbate interactions are taken into account for Pt. The rate for Pt is controlled by COOH decomposition with a free site for Figure 6. In Figure 7, the rate is not controlled by the fraction of free sites so there is no difference in rate at 548K as the BE CO varies from -2eV to -1eV. However, as the O binding energy becomes stronger, the rate is observed to decrease due to the activation energy required to form the O-CO bond. For metals such as Cu, Ag, and Au, the rates in Figure 6 and Figure 7 are controlled by their ability to form the O-CO bond. However, the maximum rate achievable on those surfaces is influenced by the CO binding energy because the maximum CO coverage is lower on those metals.

4. Discussion

As the O binding energy becomes weaker, a clear correlation is observed from the DFT calculations that the activation energy for O-CO bond formation decreases [46].

The same trend is observed for the reaction $\text{CO}^* + \text{OH}^* \rightarrow \text{COOH}^* + *$ as for the reaction $\text{CO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *$ [46]. Based on this finding, several of the trends observed in this model for water-gas shift should be applicable to CO oxidation as well. As discussed by Huang et al., this result indicates that metals with weak O binding energies, such as Pd, Pt, Ag, and Au, might make better water-gas shift catalysts when placed on supports which perform the water dissociation function [46]. The activation energies are certainly important in determining the trends in catalyst activity, but an evaluation of key surface coverages also yields important information that supports their conclusions.

Here, the Sabatier rate reported is significantly larger for Au, Ag, Pt, and Pd when water activation is not included as a potentially rate limiting step. Figure S1 and Figure S2 in the supporting information show graphs of the rate determining steps for equations 18 and 19 respectively. In Figure S1, the rates for Cu and Co are at the edge of the region which is controlled by carboxyl formation. Weaker BE O causes a shift to regions which are controlled by water dissociation or carboxyl dissociation. Therefore, the Sabatier rates are controlled by water dissociation or carboxyl dissociation. Therefore, the Sabatier rates predicted for Co, Ni, and Cu are the same whether water dissociation is included or not. However, this does not necessarily mean that enhancing the rate of water activation could not influence the rate on those catalysts. The Sabatier rates calculated assume ideal surface coverages of CO, H₂O, and OH, when possible. The OH coverage will be determined by the rate of reaction for water dissociation and the relevant equilibrium constants on those surfaces. Consequently, if surface coverages are not ideal under reaction conditions, then a support may influence the rate by changing them. At least in the case of Cu, the OH coverage is not expected to be ideal, as the activation energy

expected for water dissociation is still near 1 eV, the heat of reaction for water dissociation is mildly exothermic / endothermic, and the water binding energy is weak (above -0.3 eV) [52].

The results of Figures 4-6 indicate that Pt and Pd should be among the worst materials for water-gas shift catalysts due to the lack of free sites available. The result occurs because the rate for Pt is controlled by COOH decomposition with a free site for Figure 6. While the activation energies for COOH formation and decomposition were determined by the oxygen binding energy, the fraction of free sites is determined by the temperature, CO concentration, and BE CO. Therefore, adsorbate-adsorbate interactions which could influence the BE CO will impact the rate for equations involving water dissociation or carboxyl dissociation with a free site. These results are in agreement with the work of Grabow et al., on CO oxidation [34], where it was observed that the use of adsorbate-adsorbate interactions can influence the rate predicted for strongly adsorbing catalysts.

As seen in Figure 7, the results suggest that Pt should be the best metal surface at forming the O-CO bond. The Pt (111) surface is expected to yield better results than Au or Ag (111) because the latter surfaces do not bond CO strongly enough to have sufficient CO surface coverages. Based on Figure 7, the largest Sabatier rate predicted for O-CO bond formation is that for coordinatively unsaturated gold atoms in gold nanoparticles, Au : 12 atoms. The Au₁₂ nanoparticles are predicted to have Sabatier rates at least 3 orders of magnitude larger than the Au (111) surface. This is because the maximum steady state CO surface coverages, as determined from the equilibrium constants, are predicted to be 10⁰, 10⁻⁶, and 10⁻⁸ monolayers on Au₁₂, Au (111), and Ag

(111) respectively. An improved comparison of the Sabatier rates for the ideal close-packed surface and nanoparticles would be possible by creating the volcano plots based on other stepped surfaces or nanoparticles. The scaling relationships have been shown to apply to the stepped surfaces and generally yield the same linear relationship between adsorption energies with a different intercept value [6,33,53].

Other factors not included in the model may also influence the difference in rate predicted for Au nanoparticles versus the close-packed metal surfaces. For example, we have not included a scenario in the model where CO adsorption might be rate limiting at weak CO binding energies. Small values for the sticking coefficients of CO on the Ag or Au (111) surfaces could limit the CO adsorption rate for those materials. In addition, the Sabatier rate calculated assumes the OH coverage is ideal on the Ag and Au (111) surfaces, but the weak O binding energies for those materials suggests that the OH coverage will be far from ideal under typical reaction conditions, resulting in OH and CO being less likely to interact [13]. A low O or OH coverage on the metal would further support the hypotheses that the support and metal-support interface sites are critical for enhancing the water-gas shift rate. In the event that metal-support interface sites are important, the support may also influence the character of the metal sites and the bonding energy of adsorbates with the metal [16,37,50,51].

The general trend of the activation energy for water dissociation on the metal surfaces indicates that materials which bond strongly with oxygen will be best at dissociating water (see Figure 2). Thus, the highest maximum rates observed in Figure 4 exist for strong BE O and weak BE CO. However, we have only taken the BE CO into account in determining the availability of free sites. Following the Sabatier principle and

the trends observed for CO adsorption, as the adsorption strength of H₂O and OH increases on the catalyst, the rate for water dissociation should plateau and then decrease due to a lack of free sites.

Experiments of the WGS activity have confirmed different rankings for the TORs of various metal nanoparticles when they are placed on supports with different functionalities and Cu tends to have the highest TOR on inert supports while Pt has a higher TOR on active supports [14]. Because water dissociation is more difficult on metals with weak O binding energies, those metals stand to benefit from being supported on materials which easily dissociate water. In the case of metals dissociating water, Figure 4 suggests that those materials should bind strongly with O to yield high rates. Consequently, materials which are pyrophoric or react strongly with oxygen may be good supports for such metals as Pd, Ag, Pt, and Au. Indeed, one of the catalysts with the highest rates per mole of Pt reported for water-gas shift to date is Pt supported on Mo₂C, a pyrophoric support [23,24,38,39]. Furthermore, experimental data has shown that Au nanoparticles on Mo₂C have comparable rates to Pt [38]. If higher rate catalysts are to be developed for Pd, Ag, Pt, and Au, it will be important to understand how the support contributes to the rate, and what trends exist for water dissociation on different materials such as metal oxides or carbides. For water dissociation on metal oxides, the coordination environment and the electronegativity of the metal cation have been suggested as important parameters [54].

The trends observed in the models have several implications for the water-gas shift mechanism of different catalysts. First, a higher OH coverage may be expected for metals which have stronger O binding energies because they can more easily dissociate

water. A higher OH coverage would then make it more likely that a carboxyl intermediate would dissociate with the aid of another OH adsorbate [44]. The opposite situation (weak O binding energy) is expected to produce a mechanism where carboxyl dissociates with a free site, as was observed in the case of two microkinetic models based on DFT values of Pt (111) [45,55]. Furthermore, a low OH coverage could lead to carboxyl formation becoming rate limiting [43].

For the full carboxyl mechanism on close-packed metal surfaces, the scaling relationships provide general insight into how the different catalytic surfaces are expected to behave. We observe that the trends in DFT activation energies are fundamentally related to the Sabatier principle. As O binds more strongly to the metal surfaces, the products of water dissociation are bound more strongly to the metals. The activation energy decreases corresponding to the decrease in the enthalpy of reaction through the Brønsted-Evans-Polanyi relationship. However, as the BE O becomes more negative, the oxygen becomes too strongly bound and will not react with CO to form an intermediate species.

An analysis of the overall reaction mechanism leads to the same conclusions as those from Clay et al. on Pt and Pd, where it was found that COOH formation was rate limiting at low CO coverage and that water dissociation was rate limiting at high CO coverage [43]. Not coincidentally, Cu falls at the intersection of the two lines representing the activation energies for water dissociation and carboxyl formation in Figure 2. However, we find that the activation energies of the reaction steps are not the only important factor in determining the rates. The coverage of CO is also important, and the effect of temperature is used to demonstrate the relative changes in the reaction rates

with surface coverage on this model. Limited work has been done to evaluate the effect of surface coverage on scaling relationships, but some evidence suggests that the presence of adsorbates can significantly influence the slope and intercept of scaling relationships [6,56]. Impacts of surface coverage on the binding energy of CO or on the activation energy of individual reaction steps would alter the shape and contour of the volcano plots, further complicating the analysis.

At higher temperatures, the coverages of CO on both Cu and Pt will decrease, which should be expected to increase the relative rate of Pt to that of Cu. In a paper on water-gas shift on the Pt (111) single crystal, it is observed that Pt has a TOF which is similar to that for Cu (111) at high temperature (612 K) [57]. Contour maps of the Sabatier rate for the full carboxyl mechanism at 473 K and 623 K are shown in Figure 8. We note that the Sabatier rates of Cu and Pt are expected to be very similar at 612 K and at higher temperatures when the CO coverage of Pt does not block free sites.

Figure 8: Log of the Sabatier rate determined for steps 3-6 of the carboxyl mechanism from Equation 19 at $P_{\text{CO}} = 0.068$ atm and (Top) Temperature = 473 K and (Bottom) Temperature = 623 K.

The effect of temperature on the calculated Sabatier rates is caused by the changes to the maximum possible values for θ_* and θ_{CO} , and an interesting trend emerges from an analysis of those changes. As water-gas shift temperatures increase, Pt and other metals which bond CO strongly (Co, Ni, Rh, Pd, and Ir) are expected to have increasing relative rates compared to Au, Ag, and Cu as the coverage of CO on all of the surfaces decreases. In contrast, metals like Cu which bond CO weakly are expected to have higher relative rates at lower temperatures where metals like Pt are covered by CO. Accordingly, the coverage of CO on the metals and their ability to form O-CO bonds as determined from their oxygen binding energies are the important parameters which are observed to control the Sabatier rates for the water-gas shift reaction.

5. Conclusions

The use of scaling relationships from DFT to calculate the maximum possible rates for individual reaction steps is a simple method which is capable of identifying trends in catalytic systems in order to examine what variables will influence the rates of

microkinetic models. For the water-gas shift reaction, the BE of CO on the metal surface is found to be an important parameter in determining the activity of the metal surfaces. CO can crowd out the free sites which participate in adsorption steps, water dissociation, and carboxyl decomposition, but, when appropriate, the use of coverage dependent binding energies in microkinetic models can prevent overcrowding of the surface. The correlation of the binding energy of O on the metal surface with the activation energy of O-CO bond formation and water dissociation in water-gas shift [32,46] dictates that stronger O binding energies encourage water dissociation but can cause OH or O to bond too strongly to interact with CO. The results are discussed in regards to implications for bi-functional water-gas shift catalysts. To achieve maximum turnover frequencies, a proposed catalyst design strategy is to combine metals that adsorb O weakly, such as Au clusters or Pt nanoparticles, with supports that exhibit strong interactions with oxygen and are capable of easily dissociating water. This design strategy can benefit from a greater understanding of the metal and support interface in order to better model the interactions between CO and H₂O derived intermediate species at that location.

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Supplementary Material

Details on the derivation of equations 13-16, Figure S1, and Figure S2 are included in the Supporting Information.

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Graphical Abstract