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# 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 ($CO + H_2O \leftrightarrow CO_2 + H_2$). 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.

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## 1. Introduction

The design and development of catalytic materials stand 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 toward 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 was 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 ($CO + H_2O \leftrightarrow CO_2 + H_2$), 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-$ZnO/Al_2O_3$ catalysts are sensitive to oxygen exposure, water condensation, thermal deactivation, and 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, $Co_3O_4$, $Al_2O_3$, $Cr_2O_3$, $Fe_2O_3$, $Y_2O_3$, $La_2O_3$, $Nd_2O_3$, $SiO_2$, $TiO_2$, $ZrO_2$, $HfO_2$, $CeO_2$, $ThO_2$, $MoO_2$, $MoO_3$, mixed oxides, zeolites, C, $Mo_2C$, 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].

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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 (1 1 1) 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 bifunctional 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 $H_2O$, 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:

$$CO + * \leftrightarrow CO^* \quad (1)$$

$$H_2O + * \leftrightarrow H_2O^* \quad (2)$$

$$H_2O^* + * \leftrightarrow OH^* + H^* \quad (3)$$

$$CO^* + OH^* \leftrightarrow COOH^* + * \quad (4)$$

$$COOH^* + * \leftrightarrow CO_2 + H^* + * \quad (5)$$

$$2H^* \leftrightarrow H_2 + 2^* \quad (6)$$

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:

$$COOH^* + OH^* \leftrightarrow CO_2^* + H_2O^* \quad (7)$$

$$COOH^* + O^* \leftrightarrow CO_2^* + OH^* \quad (8)$$

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 was 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 $P_{CO}$ = 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, is 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 $\Delta H$ 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. $\Delta S$ is the entropy of reaction at 548 K. $\Delta S$ is determined by assuming that CO is immobile on the surface. Consequently, $\Delta S$ 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 the following:

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

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, $\theta_*$max, for surfaces on which CO is strongly adsorbed is determined by the CO coverage:

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

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 $2 \times 10^{12}$ $s^{-1}$, as determined for the reactions on the Pt(1 1 1) surface [45]. The activation energies

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