**Importance of metal-oxide interfaces in heterogeneous catalysis:
a combined DFT, microkinetic, and experimental study of water-gas shift
on Au/MgO**

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Abstract

The water-gas shift (WGS) reaction is central to a spectrum of industrially important catalytic processes, ranging from the manufacture of hydrogen to the processing of biomass-derived feedstocks. Recently, oxide-supported Au catalysts have attracted attention for low-temperature WGS reactions, but the role of the Au/oxide interface in promoting this chemistry remains under debate. In this contribution, we combine periodic Density Functional Theory (DFT) calculations, detailed microkinetic modeling, and rigorous kinetic measurements to elucidate the impact of this interface on the molecular-level features of WGS chemistry of a gold nanowire supported on a MgO(100) substrate. The results demonstrate that the barrier to activate water, which is prohibitively high (~ 2 eV) on a clean Au(111) surface, is decreased to essentially zero at the Au/MgO interface. From the DFT-calculated energetics, a dual-site microkinetic model of the Au/MgO interface is constructed. Rate and thermodynamic control analysis demonstrate both the high degree of kinetic control of COOH formation at the interface and a strong influence of competitive adsorption between CO and H. A procedure to refine the microkinetic predictions by iterative replacement of the energies of kinetically sensitive steps with a higher accuracy hybrid HSE06 prediction is introduced, and the determined effective activation barriers and reaction orders agree well with the results of detailed kinetic measurements on Au nanoparticles on MgO substrates. The results clearly show the critical role that the metal/oxide interface plays in WGS catalysis, and the approach introduced to predict kinetics at the metal/oxide interface should be applicable to a variety of catalytic processes on oxide-supported metal nanoparticles.

Keywords

Metal/oxide interface, Density Functional Theory, water-gas shift, gold, nanocatalysis, dual functional catalysts, kinetic modeling

1. Introduction

The water gas shift (WGS) reaction, wherein CO reacts with H₂O to form CO₂ and H₂, is central to a spectrum of industrial chemistries. It is, for example, directly involved in the manufacture of hydrogen, ammonia, methanol, hydrocarbons via Fischer-Tropsch synthesis, and many biomass-derived chemicals.¹ The most widely used commercial WGS catalysts include iron oxide, which promotes WGS at temperatures in the range of 350-450°C and is therefore termed a high temperature shift (HTS) catalyst, and copper-zinc oxide, which works in a much lower temperature range (190-250°C) and is dubbed a low temperature shift (LTS) catalyst.¹ Although these commercial catalysts already demonstrate adequate efficiencies, there is nonetheless continued interest in developing improved WGS catalysts for applications ranging from biomass reforming to fuel cell feed stream purification.² In addition to these practical motivations for elucidating fundamental WGS chemistry, the reaction is a model system for the study of catalysis at metal nanoparticle/oxide interfaces, a subject that has been fundamental to the field of heterogeneous catalysis for decades.³⁴ WGS is sufficiently mechanistically complex to exhibit rich catalytic phenomena that are not observed for the widely studied CO oxidation reaction.⁴⁻⁶ However, as we demonstrate below, it is nonetheless amenable to a synergistic combination of Density Functional Theory (DFT) modeling, microkinetic rate analysis, and rigorous kinetic measurements.

Among many candidates for next-generation low temperature WGS catalysts, oxide-supported Au catalysts have attracted significant attention.⁷ Extensive studies have been carried out to determine the WGS activity of many such systems, including Au/TiO₂,⁸⁻¹⁰ Au/CeO₂,¹¹⁻¹⁴ Au/Fe₂O₃,^{15,16} Au/ZrO₂,¹⁶⁻¹⁸ Au/ZnO,^{14,16} and Au/Al₂O₃.⁸ A general observation from these analyses is that the WGS activity strongly depends on the choice of support. Various explanations for this support effect, including either direct promotion of elementary reaction steps^{9,19,20} or indirect modification of the properties of the Au nanoparticles,^{21,22,23} have been proposed. A recent study by Shekhar *et al.*,⁹ for example, reported an enhancement of a factor of twenty in WGS activity between Al₂O₃ and TiO₂ supports, with the increase attributed to stronger binding of water/hydroxyl groups in the latter case. From a detailed analysis of the effect of particle size on the WGS activities, these authors also concluded that the low-coordinated perimeter and corner sites are the dominant active sites for WGS on Au/Al₂O₃ and Au/TiO₂.⁹

Although the above studies have produced valuable insights into the mechanisms and kinetics of WGS chemistry, it is nonetheless difficult to obtain direct experimental evidence

for the molecular-level role of the metal/oxide interface in promoting this chemistry. On the other hand, computational studies, based largely on density functional theory (DFT) methods, provide powerful tools to develop an atomistic understanding of these complex systems.²⁴⁻²⁸ Previous theoretical studies^{29 - 33} have explored several experimentally proposed WGS mechanisms, including redox and carboxyl pathways, as well as the nature of formate intermediates, on numerous late transition metal (111) surfaces without explicit consideration of the oxide support. Of particular interest for the present work, on Au(111), the activity of WGS is expected to be low due to a very high barrier (> 2 eV) for water dissociation.^{33,34} Meanwhile, DFT studies on dissociation of water dimers or trimers over TiO_2 ,³⁵ Al_2O_3 ,³⁶ and MgO ³⁷ surfaces showed significantly lower barriers (< 0.3 eV) for this step. Although pure oxides such as these are generally not active for WGS, the lower barriers hint that a plausible mechanism for WGS on oxide-supported Au nanoparticles might involve a combination of water dissociation on the oxide followed by promotion of the other elementary steps by the Au particles themselves. Even more intriguing is the possibility that the Au nanoparticles and support could act synergistically to yield catalytic properties that are much more than the sum of the contributions from the separate metal and oxide species.³⁸ This possibility is strongly suggested, for example, by the fact that the calculated water dissociation barriers on TiO_2 and Al_2O_3 are quite similar to each other,^{35,36} but the WGS activity on Au/TiO_2 is twenty times higher than it is on $\text{Au/Al}_2\text{O}_3$.⁹

To fully probe the synergistic possibilities discussed above, a model that explicitly treats both the gold particle and the oxide substrate must be employed. A natural treatment of such a system would involve metal clusters immobilized on oxide substrates, and many elegant treatments of this nature have been developed for a variety of model reactions,⁴⁻⁵ including WGS.³⁹⁻⁴² To maintain a reasonable computational expense, however, and to increase the likelihood that the ground state morphology of the cluster can be found, these models must generally be restricted to relatively small numbers of atoms. Smaller Au clusters, in turn, can be strongly influenced by finite and quantum size effects,^{43,44} and the ability to extrapolate from these models to larger nanoparticles is therefore limited. An alternative class of models focuses on quasi-one dimensional periodic Au nanowires on the oxide substrate (Au/MgO ,^{5,6} Au/TiO_2 ,⁴⁵⁻⁴⁸ Au/TiC ⁴⁹ and Au/CeO_2 ^{50,51}). Compared to the cluster models mentioned above, the nanowire models are generally believed to provide better representations of Au particles in the nanometer (or larger) size range.⁴⁶

In addition to the considerations associated with the development of structural models, discussed above, further challenges in the development of realistic descriptions of kinetics at

metal/oxide interfaces are related to both the mechanistic complexity of WGS and to the difficulty of obtaining electronic structure calculations of reasonable accuracy for mixed metal/oxide systems. Selected studies have partially addressed these issues by combining DFT calculations with microkinetic models of interfacial kinetics,^{40,41} but such studies have not, to our knowledge, either refined the analyses with higher accuracy calculations or proposed efficient strategies to ensure that the detailed kinetic predictions are consistent with experiments. The development of an approach that will accomplish these goals is, in turn, essential for producing theoretical kinetic analyses with truly predictive power.

In this contribution, we address the above challenges by developing a detailed model of WGS chemistry at the interface between a quasi-one dimensional Au nanowire and a MgO(100) support. We evaluate the thermochemistry and kinetics of multiple WGS mechanisms at the Au/MgO interface with two levels of DFT calculations, including standard PW91-GGA calculations and hybrid HSE06 calculations (see details in Section 3.1). The latter method is computationally costly, but it is generally more accurate for oxides and is known to correct for the overbinding of many GGA functionals on Au surfaces.^{52, 53} We further produce quantitative predictions of reaction rates, orders, effective barriers, and degrees of rate control with a dual-site microkinetic model. We introduce an efficient iterative method by which the predictions of standard DFT-GGA functionals are systematically refined with selected calculations of more accurate hybrid functionals, and we demonstrate that the results show reasonable agreement with kinetic measurements of WGS rates, reaction orders, and effective activation barriers on the same system. The combined theoretical and experimental analysis clearly shows that the Au/MgO(100) interface plays a central role in the WGS chemistry, with the formation of the carboxyl intermediate being the rate-limiting step.

2 Methods

2.1 Computational Models and Details

The MgO-supported Au catalyst is modeled with a quasi-one dimensional Au nanowire supported on an planar MgO(100) substrate. The MgO(100) surface is represented with a $p(5\times3)$ unit cell. The slab is four layers thick and is repeated in a supercell geometry with at least two nanometers of vacuum spacing between mirror images in the direction perpendicular to the slab surface. To represent the Au catalyst, a nanowire that is three layers thick and two or three atoms wide is adsorbed on one side of the MgO(100) slab, as shown

in Figure 1. The Au wire is periodic in the direction of the shorter cell vector (Figure 1a), and at least two types of interface and oxide sites can be identified. All the reactions are calculated at the Au(111) and MgO(100) interface, which is the right side of the wire of Figure 1b. The size of the unit cell is set according to the optimized MgO lattice constant, with the Mg-Mg distance equal to 3.00 Å, which is close to the experimentally reported value of 2.98 Å.⁵⁴ The optimized Au lattice constant (Au-Au distance = 2.95 Å) is slightly shorter than the MgO value, indicating a small tensile strain in the adsorbed Au wire. The most stable configuration of the Au wire, maintained in all future calculations, is found to involve Au atoms located directly above surface O atoms, consistent with a previous study.⁵

Figure 1.(a) Top view and (b) side view of the Au/MgO interface model. * and # indicate the two types of adsorption sites considered in the analysis (see text for details). Colors: Au-gold; Mg-green; O-red.

DFT calculations are performed with the planewave-based Vienna *Ab-initio* Simulation Package, VASP.^{55,56} We employ the generalized-gradient approximation in the form of the exchange-correlation functional PW91.⁵⁷ The total energies of all the PW91 optimized structures are further refined in a single point fashion at the hybrid level with HSE06 (see further discussion below).⁵⁸ The interaction between the atomic cores and electrons is described by the projector augmented wave (PAW) method.^{59,60} The Brillouin zone is sampled using a Monkhorst-Pack⁶¹ mesh of $2 \times 3 \times 1$ k points with a Gaussian smearing width of 0.05 eV, and the valence wave functions are expanded in a plane wave basis with a cutoff energy of 400 eV. All the slab atoms, together with the Au wire and adsorbates, are allowed to relax during geometry optimizations until the force on each atom is less than 0.02 eV/Å. Similar parameters are used for gas phase calculations, except that a smaller Gaussian smearing width, 0.005 eV, and a single k point, are employed. Transition states (TS) of the reactions are determined with the climbing image nudged elastic band (CINEB) method,⁶² with five images used to form a discrete approximation of the path between fixed end points. The TS structures obtained in this way are further refined until the forces on atomic centers

reach 0.02 eV/Å. Each optimized TS structure is checked with a normal mode analysis to ensure that only a single imaginary frequency exists. Bader charge analysis is performed with VASP TST Tools.⁶³⁻⁶⁵ Zero-point energy corrections are applied to all calculated initial states (IS), transition states (TS), and final states (FS). Frequencies determined with PW91 are employed for the HSE06 ZPE corrections.

The binding energy (BE) of an adsorbate is defined as $BE = E_{ad/sub} - E_{ad} - E_{sub}$, where $E_{ad/sub}$ is the total energy of the slab model with adsorbate, while E_{ad} and E_{sub} are the total energies of the adsorbate in the gas phase (ground state) and of the clean substrate, respectively. In the case of OH, COOH, and H, we use closed shell states, $H_2O - 1/2 H_2$, $CO + H_2O - 1/2 H_2$, and $1/2 H_2$, as the gas phase references. With the above definitions, negative values of the BE imply an exothermic adsorption process.

A mean field microkinetic model is developed based on the DFT-obtained thermodynamic and kinetic information of all elementary steps. The rate constants are calculated according to transition state theory:

$$k = Ae^{-\frac{E_a}{k_b T}} \quad (1)$$

where k is the rate constant for an elementary reaction step, A is the corresponding preexponential factor, E_a is the ZPE-corrected activation energy, and T is the reaction temperature. Due to the poor performance of the harmonic approximation for determination of entropy in low frequency vibrational modes, we assume no entropy change for all surface elementary steps. Thus, a standard A of 10^{13} s^{-1} is employed in our modeling, similar to a previous study.⁶⁶ The change of entropies for adsorption processes is calculated according to the relationship proposed by Campbell *et al.*:⁶⁷

$$S_{ad}^0(T) = 0.70S_{gas}^0(T) - 3.3R \quad (2)$$

where S_{ad}^0 and S_{gas}^0 are the entropy of a species in gas phase and adsorbed on surface, respectively, and R is the ideal gas constant. This approach introduces a small inconsistency (0.06 eV at 220°C in this study) between the sum of entropy changes for all elementary steps in the WGS network and the entropy change of the overall gas phase WGS reaction. This error is less than the expected uncertainty in the DFT model itself and of the linear relationship to obtain the S_{ad}^0 of the adsorption process (Eqn (2)). We employ a two-site model, where Au/MgO interface sites (top and bridge of perimeter Au sites and Au-Au-Mg or Au-Mg-Mg hollow sites) are depicted by a “*” in Figure 1a, and top sites of O atoms on MgO close to the interface are indicated by a “#” symbol. Species may either adsorb on * or #

sites separately, or they may simultaneously occupy a $*^{\#}$ dual site, as well as multiple $*$ and $\#$ sites. Note that only $*$ and $\#$ sites at the Au/MgO interface were included in the microkinetic modeling. The possibility that species adsorbed in one type of site might sterically interact with species on another site was accounted for by allowing simultaneous occupation of the two sites by a few of the adsorbates. For example, H_2O adsorbed on $*$ site, and one H atom points to a neighbor $\#$ site, blocking the $\#$ site and yielding an $H_2O*^{\#}$ species. Diffusion of adsorbates from the Au wire or the MgO to the interface was not explicitly included in the microkinetic model, except in the case of atomic hydrogen moving from the $\#$ to the $*$ site, as such steps are very unlikely to be rate-limiting.⁶⁸ Finally, as shown in Figure 1a, the ratio between the number of $*$ and $\#$ sites is 1:1. The site balances are as follows:

$$\theta_* = 1 - \theta_{CO*} - \theta_{H_2O*^{\#}} - \theta_{(H+OH)*^{\#}} - \theta_{COOH*} \quad (3)$$

$$\begin{aligned} & - \theta_{H*} - \theta_{(H+H)*^{\#}} - 2\theta_{(CO_2+H_2O+H)*^{\#}\#} - \theta_{(CO_2+H)*^{\#}} \\ \theta_{\#} = & 1 - \theta_{H_2O*^{\#}} - \theta_{(H+OH)*^{\#}} - \theta_{H\#} - \theta_{(H+H)*^{\#}} \\ & - 2\theta_{(CO_2+H_2O+H)*^{\#}\#} - \theta_{(CO_2+H)*^{\#}} \end{aligned} \quad (4)$$

Steady state coverages are determined numerically, with typical WGS conditions⁹ (0.068 atm CO, 0.219 atm H_2O , 0.085 atm CO_2 and 0.374 atm H_2) assumed. Apparent activation energies are evaluated in the temperature range 200 - 240 °C, and the reaction orders for all reactants and products are determined at 220 °C. In order to further interpret the kinetic data, the degrees of rate and thermodynamic control are evaluated according to Campbell's method:⁶⁹

$$X_{RC,i} = \left(\frac{\partial \ln r}{\partial \ln k_i} \right)_{k_{j \neq i}, K_i} \quad (5)$$

$$X_{TRC,i} = \left(\frac{\partial \ln r}{\partial (-G_n^0 / RT)} \right)_{G_{m \neq n}^0, G_i^{0TS}} \quad (6)$$

where r is the reaction rate, k_i is the rate constant of step i , and G_n^0 is the free energy of species n and R is the gas constant. The derivatives are calculated numerically with 1% changes to the corresponding k 's and G 's. Additional details are provided in the Results section.

2.2 Experimental

Catalyst synthesis: The Au/MgO catalyst is prepared using a two-step deposition precipitation urea method, slightly modified from the method used by Milone et al.⁷⁰ MgO is obtained from US Research Nanomaterials, Inc., in nanoparticle form (MgO, 99+%, 20 nm).

The as-received MgO is steamed in a flow of 66.5 sccm of ~22% H₂O in air at 450°C for 12h before use for catalyst preparation. The Au precursor (99.99% HAuCl₄·3H₂O from Alfa Aesar) is added to millipore water to give a 0.0024 M gold solution. Once the solution is heated to 85°C, the support MgO is added to the solution, and the mixture is kept at 85°C for 30 min. Urea is then added into the mixture, and the concentration of urea is 1.26 M. The final mixture is kept at 85°C for 15.5 h in the absence of light. After cooling, the mixture is centrifuged to separate the solids from solution, washed, and dried at room temperature under vacuum.

Kinetic measurements: For each of the kinetic experiments, about 400 mg of catalyst is loaded into the reactor. An automated, parallel tubular plug flow reactor system with four independent tubes is used and described elsewhere.⁹ The catalysts are reduced in a 25% H₂, 75% Ar mixture with a flow rate of 50 sccm at 150°C for 2 h (ramping rate 2°C/min), followed by annealing in Ar at a flow rate of 50 sccm at 400°C for 2 h. They are stabilized at the standard WGS conditions (6.8% CO, 21.9% H₂O, 8.5% CO₂, 37.4% H₂, and balance Ar under atmospheric pressure) with a flow rate of 75.4 sccm at 220°C. Measurement of the rate over a 60 hour time span showed a minimal deactivation that was linear at a rate of less than a 0.2% decline per hour (see Figure S7). Nevertheless, we allowed a stabilization period of 20 hours before measurement of the apparent orders with respect to both reactants and products, together with apparent activation energy. Note that XRD data (see supplementary material) indicate that the support remains MgO after stabilization, and all characterization data in the manuscript are reported after this stabilization period. To determine the apparent activation energy, the temperature is varied over a range from 205 to 235 °C, and the concentrations are kept constant at the standard conditions. The apparent reaction orders with respect to the reactants and products are measured by changing one gas concentration at a time. Concentrations of the reactants and products are varied over the ranges 4-21% CO, 11-34% H₂O, 5-25% CO₂, and 14-55% H₂, while the temperature remained at 220 °C.

Atomic Absorption (AA): Atomic Absorption spectroscopy is performed to determine the actual Au loading with a PerkinElmer AAnalyst 300 Atomic Absorption Spectrometer. Approximately 80 mg of the sample is used for digestion. 5 ml aqua-regia is added to the sample and sealed in a bottle. The mixture is placed in a hood and digested at room temperature for three days before measurement. During the digestion, the bottle is shaken regularly to ensure that the sample solid is well-mixed with the acid. Eventually, the solid disappears, and a clear solution is obtained. Finally, the solution is diluted by millipore water to around 60 ml.

Powder X-ray diffraction (XRD): Powder XRD patterns are collected in air on a RigakuSmartLab X-ray diffractometer. The patterns are collected from 2θ angles of 10 to 80 degrees in 0.01 degree steps. The collection time per step is 0.25 s.

High Angle Annular Dark Field Scanning TEM (HAADF-STEM): Au/MgO is characterized by an FEI Titan 300 kV S/TEM equipped with a Gatan Imaging Filter (GIF) and a Fischione Model 3000 annular dark field (ADF) detector. Z-contrast high angle ADF scanning TEM (HAADF-STEM) imaging is performed to clearly visualize distributions of Au nanoparticles on the lower Z supports (i.e., MgO) and to determine particle size distributions. ADF images are collected at the camera length of 195 mm. Image collection time and dwell time for ADF-STEM images are 25 seconds and 24 μ sec, respectively.

3. Results and Discussion

In general, there are three widely discussed mechanisms⁷¹ for the water-gas shift reaction: 1) carboxyl, 2) redox, and 3) formate pathways (the latter is often thought to be an inactive spectator species in the reaction network). All pathways are initialized by water dissociation, followed by divergent reactions with CO, including either direct oxidization by O (redox) or reaction with OH and H to form carboxyl and formate intermediates, respectively (Scheme 1). In the following, we analyze these pathways by first presenting the adsorption of the relevant reactants, products, and key intermediates on the Au/MgO model. Next, we report the barriers of the considered elementary steps. Subsequently, we describe the DFT-based microkinetic analysis of the WGS activities at the Au/MgO interface, and we introduce an efficient scheme whereby the kinetic predictions made by the GGA-PW91 kinetic analysis may be systematically refined with results from higher level HSE06 calculations. We close by comparing these predictions to the results of rigorous kinetic measurements.

Scheme 1 Schematic diagram of water-gas shift reaction mechanism

3.1 Adsorption of surface species

We begin by reporting adsorption geometries and energies on sites that are close to the

Au/MgO(100) interface, including Au perimeter sites (* in Figure 1) and oxygen sites on MgO close to the interface (# in Figure 1). Results for both standard GGA-PW91 calculations and more accurate hybrid HSE06 calculations are described, and comparisons to selected calculations on clean Au(111) and MgO(100) surfaces are made. Adsorption of H_2 and CO_2 are not discussed in detail since the results demonstrate that these species are only weakly physisorbed at the interface.

Figure 2. Optimized structures of (a) CO; (b) H_2O ; (c) OH; (d) COOH; (e-f) H at the Au/MgO interface. The H atom is not visible inside of the Au wire in the side view of (e). Colors: Au-gold; Mg-green; O-red; C-black; H-gray.

CO adsorption: CO binds preferentially to top or bridge sites of interface Au atoms (Figure 2a), consistent with previously reported results.⁵ The strongest binding site for CO predicted by PW91 is bridge, with a BE of -0.70 eV (Table 1). CO binding on top is weaker by 0.06 eV. The calculated binding energy at the interface is 0.30 eV stronger than on Au(111), and it is also stronger than on clean MgO(100) (BE = -0.14 eV). The latter result could be explained by the absence of the back donation to the CO $2\pi^*$ (LUMO) orbital from the substrate.⁷²

It is well known that standard DFT-GGA calculations tend to predict incorrect adsorption sites for CO on several different transition metal surfaces,⁷³ including Au,⁵² and these problems can be alleviated, in part, by employing more expensive, higher level methods such as hybrid functionals.⁵² The present results also show differences between GGA and hybrid functionals, with HSE06 predicting the most favorable binding of CO on a top site, with a binding energy of -0.55 eV, suggesting modestly weaker CO binding than is predicted by the GGA-PW91 calculations. These differences could be ascribed to the increased HOMO-LUMO gap of CO predicted with hybrid functionals, which weakens the back donation of the metal electrons to the $2\pi^*$ (LUMO) orbital of CO.⁷⁴

H₂O adsorption: Water binds preferentially though its oxygen atom to a Mg atom close to the interface (Figure 2b). The H₂O BE is -0.44 eV with the PW91 functional, which is stronger than what is determined on a Au(111) surface, where the binding energy is -0.10 eV. However, the binding at the interface is not substantially different from what is found on clean MgO(100), with a value of -0.42 eV for a water molecule adsorbed on the same $p(5\times 3)$ unit cell as our interface model. The weaker binding on Au(111) is believed to be related to the reduced electrostatic interaction with the metal substrate compared to the oxide.⁷⁵ The binding obtained with the hybrid HSE06 is 0.03 eV weaker than the PW91 result (Table 1).

OH adsorption: OH binds to the hollow sites of the interface, at either Au-Au-Mg (Figure 2c) or Au-Mg-Mg threefold sites. The BE at the Au-Au-Mg site is -0.20 eV, about 0.4 eV stronger than at the Au-Mg-Mg site (Table 1). The binding of OH is dramatically enhanced at the interface compared to the adsorption on both Au(111) and MgO(100). The BE of OH on Au(111) is 1.24 eV (endothermic with respect to the gaseous water and hydrogen reference states), and the binding on clean MgO(100) is even weaker, at 1.83 eV. At the Au-Au-Mg site, OH adsorbs at a considerable distance from any surface oxygen atoms (>320 pm) on Au/MgO, while the closest O-O distance is only 220 pm on clean MgO.

This configuration may, in turn, permit maximum electrostatic attraction between OH and Mg without significant electrostatic repulsion between OH and surface oxygen. Honkala et. al. observed similar behavior for Ag supported on MgO⁷⁶ and attributed the stronger binding to an increase in charge transfer to the adsorbate. The two explanations may be related although, in the present case, we see differences of only 0.1 electrons in the Bader charge of OH at the interface compared to OH on clean MgO(100). HSE06 predicts slightly weaker binding for both hollow sites by 0.07 and 0.11 eV (Table 1).

COOH adsorption: COOH tends to bind on a Au-Mg bridge site, forming C-Au and O-Mg bonds (Figure 2d). This carboxyl can bind either through C=O or COH oxygen to the Mg ion. The binding energy is 0.26 eV more favorable in the former than the latter mode. As with most of the other intermediates, the binding of COOH at the Au/MgO interface is stronger than on Au(111) and on MgO(100). HSE06 predicts slightly weaker binding at the interface compare to the values calculated from PW91 (Table 1).

H adsorption: The most stable site for H adsorption is the Au bridge site at the interface (Figure 2e), with an adsorption energy of -0.21 eV compared to gas phase H₂. Although it is not as stable, binding of H to the O atoms on the MgO surface close to the interface is also possible (Figure 2f), and this adsorption site is important for the mechanistic analysis presented below. Adsorbed H carries a -0.15 e charge on the Au bridge site and a +0.7 e charge on an oxide O ion. This amphoteric character of H leads to a “cooperative” adsorption⁷⁷ of two H on adjacent Mg and O sites of Au-free MgO(100) of +0.12 eV. As is the case with OH, binding of H at the Au/MgO interface is stronger than on Au(111) (binding of 0.02 eV, Table 1). HSE06 predicts similar binding to the PW91 result, with a value of -0.18 eV on the Au-Au interface bridge site.

Table 1: Calculated binding energies (eV) of CO, H₂O, H, OH and COOH on the Au/MgO(001) interface, clean Au(111), and clean MgO(100). The reference states are CO(g), H₂O(g), 1/2H₂(g), H₂O(g) – 1/2 H₂(g), and CO(g) + H₂O(g) – 1/2 H₂(g), respectively.

	Au / MgO			Au(111)		MgO(100)	
	Site	PW91	HSE06	site	PW91	site	PW91
CO	Au-top	-0.64	-0.55	bridge	-0.40	Mg-top	-0.14
	Au-bridge	-0.70	-0.36				
H ₂ O	O-top	-0.44	-0.41	top	-0.10	Mg-top	-0.42

OH	Au-Au-Mg	-0.20	-0.13	top	1.24	hollow	1.83
	Au-Mg-Mg	0.21	0.32				
COOH	Au-Mg(O)	-0.87	-0.71	top	-0.15	O-top	0.58
	Au-Mg(OH)	-0.61	-0.45				
H	Au-bridge	-0.21	-0.18	fcc	0.02	O-top	1.87
	O-top	0.29	0.29				

Summary of adsorption properties: All species are found to bind more strongly at the Au/MgO interface than on the clean Au(111) or MgO(100) surfaces. A simple qualitative explanation for these results is that the existence of the three phase boundary presents opportunities for simultaneous covalent bonds with Au atoms and electrostatic interactions with the oxide. The adsorbates can adjust their adsorption configurations at the interface to balance these two types of interactions, leading to stronger binding compared to the separated Au or oxide. Bader charge analysis also shows that Au atoms at the Au/MgO interface become slightly negatively charged, by $\sim 0.1 e$, suggesting that electronic perturbations might have some influence on the binding strength of the adsorbate.

Comparison of the PW91-GGA and HSE06 binding energies reveals weaker predicted adsorption with the hybrid functional for CO, COOH and OH. The prediction of a weakened adsorption energy for CO, in particular, has a significant effect on the performance of the microkinetic model (described below) and is believed to result, in part, from an improved description of well-known problems with CO electronic energy levels in GGA functionals.⁵² In contrast, only minor differences are seen for adsorbed water and atomic hydrogen.

3.2 Thermochemistry and kinetics of elementary reaction steps

We now turn to a description of the calculated thermochemical and activation energies of the elementary steps for the carboxyl, redox, and formate pathways. All pathways are initiated by the same water dissociation step discussed at the beginning of the section, and they then diverge according to the species that react with CO. Unless otherwise stated, we report the reaction energies and barriers determined with the less expensive PW91 functional, but we provide a summary of the difference between PW91 barriers and HSE06 barriers at the end of the section. For initial or final states with more than one species involved in the reaction, we refer all energetics to the infinitely separated state unless attractive interactions between

adsorbates, for example, a hydrogen bond, are observed. In the latter case, we refer the energies to coadsorbed structures (Figure 3) that are, in turn, more stable than the separated fragments.

Figure 3. Top and side views of optimized structures of selected coadsorbed systems. Colors: Au-gold; Mg-green; O-red; C-black; H-gray.

H₂O dissociation: As discussed above, cleavage of a water O-H bond is common to all WGS mechanisms, and at the Au/MgO interface, two broad classes of pathways are possible for this elementary step. The first involves movement of the H atom to the Au atoms at the interface and OH to near the Au-Au-Mg site described in Section 3.1. The GGA-computed barrier for this process is 0.99 eV. In the second, the OH moves to the same final state while the dissociated hydrogen atom moves to the adjacent oxygen on the MgO surface (Figure 4, panel R2). The process is essentially barrierless and the reaction is nearly thermoneutral (Table 2, R2). A strong hydrogen bond exists in the final, dissociated state (Figure 3a), with the dissociated hydrogen atom forming an OH-like group with the surface oxygen. The distance between this dissociated hydrogen atom and the product OH is only 1.57 Å, which is considerably less than the corresponding distance on a clean MgO surface (>3.00 Å). The product OH, in turn, is located close to the Au perimeter, with an O-Au distance of 2.52 Å

(we note that the OH group has moved away from the most stable Au-Au-Mg site due to the strong interaction with co-adsorbed $H^\#$). Compared to infinitely separated H and OH products, the co-adsorbed $(H+OH)^{*\#}$ pair, which simultaneously occupies adjunct $*$ and $\#$ site, is 0.53 eV more stable. In the following, therefore, we will consider the $(H+OH)^{*\#}$ pair as the reactant for subsequent WGS steps.

Figure 4. Top and side views of optimized structures of calculated transition states in the carboxyl mechanism. Rx is the x th elementary step listed in Table 2. Colors: Au-gold; Mg-

green; O-red; C-black; H-gray.

We note, in passing, that we observed in experiments the formation of surface OH groups under WGS reaction conditions after long periods of catalyst operation. To estimate the effect of such groups on the kinetics, we have evaluated the effect of an additional OH group on MgO, which is equivalent to the $H^\#$ species mentioned above, on the water dissociation barrier. The additional hydrogen has only a minor influence on the water dissociation barrier (<0.1 eV— see Supporting information section S1).

Promotional effect of the Au/MgO interface. As discussed above, the dissociation of water is an elementary step common to all water-gas shift mechanisms, and this step is strongly promoted at the Au/MgO interface, as shown in Figure 5. Clean Au(111) is incapable of dissociating water, with a barrier of over 1.79 eV. Dissociation of a single water molecule on clean MgO(001) also exhibits unfavorable kinetics, with a barrier of 1.19 eV (we note that Alvim *et al.*³⁷ have demonstrated that water dimers and trimers can be more readily dissociated on MgO(001), with barriers of less than 0.3 eV, suggesting more facile water activation in the liquid phase or at high water partial pressures). However, at the Au/MgO interface, water dissociation has essentially no barrier. As discussed in Section 3.2, there is a strong stabilization of dissociated water at the Au/MgO interface due to the H-OH interaction, which is consistent with a low barrier according to the Brønsted-Evans-Polanyi principle.⁷⁸

Figure 5. Comparison of water dissociation barrier over the Au/MgO interface, MgO(100), and Au(111).

Carboxyl mechanism. After activation of water, the next step in the carboxyl

mechanism is reaction of adsorbed CO with OH to form COOH. As stated above, we consider the H-OH pair as the reactant instead of isolated OH, because of the strong interaction between H and OH close to the interface. CO reacts with this H-OH pair from the OH side along the Au perimeter. At the transition state (Figure 4, panel R3), the H-O distance in the (H+OH)^{*#} pair further elongates to 1.85 Å. A new C-O bond simultaneously forms with a bond length of 1.67 Å. The barrier for this step is 0.78 eV, and the reaction is endothermic by 0.57 eV (Table 2, R3). As discussed further below, this step becomes rate-limiting for the WGS network at the Au/MgO interface.

The next step in the carboxyl mechanism is dehydrogenation of the carboxyl intermediate. Similar to the case with water dissociation, direct dissociation of COOH, with the dissociated hydrogen atom moving to the Au edge, has a relatively high barrier of 1.2 eV. However, a lower barrier (0.42 eV, Table 2, R10) is obtained when the dissociated hydrogen moves to the oxygen on the MgO surface, whose TS is shown in Figure 4, panel R10. Due to the existence of a hydrogen bond between the resulting surface hydrogen and the CO₂ product, the newly formed CO₂ still binds at the interface on the partially extracted Au atom (Figure 3b). This structure is 0.10 eV more stable compared to the case where CO₂ completely desorbs to the gas phase (Table 2, R11). We additionally note, as discussed further below, that the partial extraction of the Au atom blurs the distinction between edge and corner sites on Au nanowires, implying that both may be active sites for WGS.

The COOH dissociation step can be assisted by an additional, coadsorbed, intact water molecule, with water facilitating transfer of a hydrogen atom to its preferred site on the MgO surface. Note that a dissociated H and OH pair does not provide the same acceleration of hydrogen transfer, and indeed, a transition state calculation suggests that the separated pair converts to H₂O before assisting in COOH dissociation. The additional water molecule adsorbs in close proximity to the hydroxyl moiety in the COOH group. In the transition state, the O-H bond in COOH elongates slightly, to 1.00 Å, and this hydrogen atom moves towards the water molecule (Figure 4, panel R4). Simultaneously, one hydrogen atom from water begins to dissociate, with the corresponding O-H bond elongating to 1.33 Å and a bond of 1.14 Å forming between the dissociating hydrogen and the surface oxygen. In the final state, the newly formed CO₂ is stabilized at the interface due to the hydrogen bond with the adjacent water molecule (Figure 3c). There is also an additional hydrogen bond between water and the dissociated hydrogen atom. This coadsorbed complex is more stable, by 0.26 eV (Table 2, R5), than separated adsorbed H₂O, H on surface oxygen, and CO₂ in the gas phase, and the barrier to the reaction decreases to 0.28 eV (Table 2, R4). We note that

analogous water-assisted dehydrogenation mechanisms have also been observed by Grabow et al. for the WGS reaction over Pt(111)³¹ and for water dissociation over MgO(001).³⁷

After formation of CO₂, two hydrogen atoms remain adsorbed on surface oxygen on MgO. Previous calculations have suggested a relatively low H-H recombination barrier on Au(111),²⁹ motivating the consideration of a similar recombination pathway over the gold nanowire. For such recombination to occur, hydrogen must first diffuse from the oxide to the gold edge. This step is strongly exothermic, by 0.49 eV (Table 2, R6), due to the stronger binding of hydrogen on the Au-bridge site at the Au perimeter, and the calculated barrier is 0.42 eV. We note that, similar to the case with the COOH intermediate, described above, the diffusing hydrogen atom partially extracts a Au atom from the perimeter of the Au wire (Figure 4, panel R6). The additional flexibility of this lower coordinated Au atom can apparently offer more stabilization to the transition state of the diffusing hydrogen atom, again partially obscuring the distinction between edge and corner sites in MgO-supported Au nanostructures.

The final step is the recombination of two hydrogen atoms to form H₂. We have identified two possible pathways for this process with accessible barrier heights, including heterolytic and homolytic recombination, and corresponding transition states are shown in Figure 4 (panels R8 and R9, respectively). In the heterolytic pathway, one hydrogen atom comes from the Au perimeter site and the other from a nearby surface oxygen atom. The co-adsorbed (H+H)^{*#} (Figure 3d) is slightly more stable, by 0.14 eV (Table 2, R7), than the separated H atoms. Subsequent combination of these two H atoms is slightly endothermic (by 0.06 eV), and the barrier is 0.51 eV (Table 2, R8). In the homolytic pathway, both hydrogen atoms originate on Au perimeter sites. This pathway is endothermic by 0.42 eV, and the corresponding barrier, 0.75 eV (Table 2, R9), is higher than in the heterolytic case. The direct recombination from two H[#] is unfavorable, as transition state searches demonstrate that the H[#] atoms diffuse to the Au/MgO interface site (H*) before forming H-H bonds.

Other mechanisms: In the redox mechanism, a second dehydrogenation step is needed in order to form adsorbed oxygen from OH at the interface. Similar to the water dissociation case, the dissociated hydrogen can occupy either an oxygen site on the MgO surface or a Au perimeter site. In the case of isolated OH groups at the initial state, the direct dissociation barrier is 0.96 eV for hydrogen dissociation to surface MgO. In this case, coadsorption of water has only a small effect on the barrier (1.01 eV). However, an additional ~0.5 eV is required to separate co-adsorbed H-OH to form the isolated OH groups on the surface. Thus,

the effective barrier will be at least ~ 1.5 eV (we note that directly activating the O-H bond in the H-OH pair, without separation, is endothermic by 1.12 eV, implying that the barrier for this process will also be high). The barrier is even higher, > 2 eV, when the dissociated hydrogen moves to perimeter gold atoms. Formation of atomic oxygen via reaction of two adjacent OH groups is similarly unfavorable. This step is strongly endothermic, by 0.71 eV, with a 0.73 eV barrier, and the effective barrier will be much higher due to the need to break two hydrogen bonds (~ 0.5 eV each) to form the reactant OH groups. More details can be found in the Supporting Information, section S2.

Finally, we note that another previously proposed mechanism for formate formation occurs via initial formation of a CHO intermediate.³³ In this mechanism, CO reacts with a coadsorbed H to form CHO. Due to the strong hydrogen bond between H and OH after H₂O dissociation at the interface (discussed above), the corresponding reactants are CO and an H-OH pair (Supporting Information, Fig. S2e). We determined a high reaction barrier, at 1.40 eV, for this elementary step at interface, suggesting that it is not competitive (see Supporting Information section S2 for additional details).

Table 2: List of elementary steps of carboxyl mechanism with the corresponding reaction energies (ΔE , in eV) and activation energies (E_a , in eV). Barriers of adsorption, desorption and diffusion steps to form or break co-adsorption systems (R0, 1, 5, 7, 11) are assumed to be zero in the exothermic direction. * and # stands for two type of adsorption sites, which are Au perimeter site and O site on MgO adjacent to Au/MgO interface (Figure 1a), respectively.

		ΔE			E_a		
		PW91	HSE	$\Delta\Delta E$	PW91	HSE	ΔE_a
R0	$\text{CO} + * \leftrightarrow \text{CO}^*$	-0.70	-0.55	0.15			
R1	$\text{H}_2\text{O} + * + \# \leftrightarrow \text{H}_2\text{O}^{*\#}$	-0.44	-0.41	0.03			
R2	$\text{H}_2\text{O}^{*\#} \leftrightarrow (\text{H}+\text{OH})^{*\#}$	-0.01	-0.03	-0.02	0.00	0.00	0.00
R3	$\text{CO}^* + (\text{H}+\text{OH})^{*\#} \leftrightarrow \text{COOH}^* + \text{H}^\# + *$	0.57	0.56	-0.01	0.78	0.74	-0.04
R4	$\text{COOH}^* + \text{H}_2\text{O}^{*\#} + \# \leftrightarrow (\text{CO}_2 + \text{H}_2\text{O} + \text{H})^{* \# \#}$	0.06	0.24	0.18	0.28	0.30	0.02

R5	$(\text{CO}_2+\text{H}_2\text{O}+\text{H})^{*}\text{H}^{\#}\leftrightarrow\text{CO}_2+*+ \text{H}^{\#}+\text{H}_2\text{O}^{*}\text{H}^{\#}$	0.26	0.11	-0.15			
R6	$\text{H}^{\#}+*\leftrightarrow\text{H}^{*}+\text{H}^{\#}$	-0.49	-0.46	0.03	0.42	0.67	0.25
R7	$\text{H}^{\#}+\text{H}^{*}\leftrightarrow(\text{H}+\text{H})^{*}\text{H}^{\#}$	-0.14	-0.22	-0.08			
R8	$(\text{H}+\text{H})^{*}\text{H}^{\#}\leftrightarrow\text{H}_2+*+\text{H}^{\#}$	0.06	0.11	0.05	0.51	0.61	0.10
R9	$\text{H}^{*}+\text{H}^{*}\leftrightarrow\text{H}_2+*+*$	0.42	0.36	-0.06	0.75	0.80	0.05
R10	$\text{COOH}^{*}+\text{H}^{\#}\leftrightarrow(\text{CO}_2+\text{H})^{*}\text{H}^{\#}$	0.23	0.38	0.15	0.42	0.56	0.13
R11	$(\text{CO}_2+\text{H})^{*}\text{H}^{\#}\leftrightarrow\text{CO}_2+\text{H}^{\#}+*$	0.10	-0.03	-0.12			

Most favorable reaction pathway and rate determining steps

The highest barrier in the carboxyl mechanism is 0.78 eV, which corresponds to the formation of COOH. This barrier is at least 0.7 eV lower than the highest barriers in the redox and formate mechanisms, strongly suggesting that the carboxyl mechanism is the most active route for WGS at Au/MgO interface. Indeed, the preference for the carboxyl mechanism seems not to be unique for WGS on Au/MgO. A recent study by Aranifard *et al.*⁴⁰ reported similar observations on Pt/CeO₂. Their microkinetic modeling showed that the carboxyl mechanism is about 5-7 times more active than redox pathway at different reaction conditions, although in this case, vacancies on the highly reducible CeO₂ surface contribute significantly to the kinetics. Similar favoring of the carboxyl mechanism has also been observed on Au/CeO₂⁵¹ and on Pt(111).^{31,71,79}

Energetics calculated with the HSE06 functional: Given the above energetics, the carboxyl mechanism appears to be the most favorable at the Au/MgO interface. In Figure 6, we compare the energetics for this process using the standard PW91 functional with the corresponding energies determined using the more accurate, and costly, HSE06 hybrid functional. In general, a good correspondence in the trends is seen, with differences in most barriers being less than 0.2 eV. The most significant differences, as we discuss further below, are generally weaker binding predicted by HSE06 and a higher diffusion barrier for hydrogen from the oxide to the metal. While none of these differences affect the general trends in the mechanism, we will demonstrate below that HSE06 calculations are important for obtaining quantitatively reasonable estimates of apparent activation energy and reaction

orders. In addition, we will introduce an efficient method for combining the best features of both electronic structure approaches to optimize the accuracy and efficiency of the kinetic predictions.

Figure 6. Energy profile of carboxyl mechanism. Transition states are indicated in red text. The initial and final states correspond to reactants and products, respectively, in the gas phase.

Influence of corner sites: A previous study by Shekhar *et al.*⁹ suggested that both corner and perimeter sites are active sites for WGS on a Au catalyst supported by TiO₂. To evaluate the influence of such features in our model, we created a simple model of a corner site by adding three additional Au atoms to the Au/MgO interface. Determination of barriers for CO and OH combination ($E_a=0.46$ eV), hydrogen diffusion ($E_a=0.45$ eV), and hydrogen formation steps ($E_a=0.62$ eV) showed slightly lower barriers compared to the corresponding steps at perimeter sites. Although the differences are not large, the results suggest that corner sites are at least of similar activity to the edge sites. More interestingly, the coordinative flexibility of edge atoms, discussed above, suggests that the perimeter of gold nanoparticles may, in general, be somewhat flexible, leading to stabilization of transition states.⁸⁰

3.3 Catalyst characterization

Catalyst characterization: As discussed above, a two-step deposition precipitation with

a urea method is used to synthesize the Au/MgO catalyst. During the synthesis, the support MgO is found to hydrolyze to form $\text{Mg}(\text{OH})_2$. To decompose $\text{Mg}(\text{OH})_2$, the as-prepared catalyst is annealed at 400°C during a catalyst pretreatment step. As shown in XRD analysis (Figure 7), the support is completely converted to MgO after annealing at temperatures above 400°C.

Figure 7. XRD spectra of steam treated MgO support and Au/MgO annealed in Ar for 2 hours at different temperatures.

Figure 8. Typical HAADF-STEM images of 2.5 wt% Au/MgO used to determine the Au particle size distributions.

To check the particle size distribution of Au/MgO, HAADF-STEM analysis is performed on the used catalysts. Figure 8 shows typical HAADF-STEM images that are used to measure the Au particle size distribution for Au/MgO. The number average Au particle size for Au/MgO is 4.1 ± 0.4 nm after WGS reaction.

3.4 Experimental and DFT-based kinetic analysis

Experimental kinetic studies: The WGS kinetics are measured under 6.8% CO, 21.9% H₂O, 8.5% CO₂, and 37.4% H₂, with the balance Ar. The WGS reaction rate per total mole of Au is 0.9×10^{-3} mol H₂/(molAu·s) at 180°C, comparable to the rate on Au/Al₂O₃ (0.6×10^{-3} mol H₂/(molAu·s) at a similar particle size.⁹ Figure 9 shows the Arrhenius plot and the plot used in the determination of apparent reaction orders with respect to CO, CO₂, H₂ and H₂O. A relatively low apparent activation energy, 28 ± 3 kJ/mol, is observed for Au/MgO, similar to Au/Al₂O₃. The Au/MgO catalyst shows an apparent CO order of 0.86 ± 0.04 , a CO₂ order of -0.26 ± 0.05 , an H₂ order of -0.35 ± 0.03 , and an H₂O order of 0.74 ± 0.07 . The CO₂ order is somewhat more negative compared to other gold catalysts with different supports, such as Au/Al₂O₃ and Au/TiO₂. This is most likely due to a higher coverage of CO₂ or bicarbonate on alkaline supports.⁹

DFT dual-site microkinetic analysis: To further elucidate the kinetics associated with the metal/oxide interface, we construct a dual-site microkinetic model, as described in Section 2 and in Supporting Information Section S3. We begin by describing the results using energetic predictions from the efficient GGA-PW91 functional, and we demonstrate that, although broad energetic trends are well described by this functional, the predicted reaction orders and effective activation barriers by our dual-site mean field microkinetic model deviate significantly from our experimental results. We then show how the inclusion of selected calculations with the more costly hybrid HSE06 functional can systematically improve the predictions. As the carboxyl mechanism shows the most favorable barriers (section 3.2), we focus on this chemistry, and we include a total of twelve elementary steps in the model. For elementary steps with more than one species involved in the reactant or product states, we reference both the thermodynamics and the activation barriers to a state where each adsorbate binds on separate unit cells. However, in several cases, there is significant interaction, for example hydrogen bonding, between adsorbates that results in

more favorable coadsorption than the case with adsorbates separated from each other. In such cases, we further added the coadsorbed state as a minimum in our kinetic simulations, and we included a diffusion step to break the (H-bond) interaction (see reactions R5, R7 and R11).

Figure 9. Arrhenius plot (a) and apparent reaction order plot (b) for WGS on 2.5% Au/MgO.

Calculated apparent activation energies (E_a), reaction orders, and degrees of rate and thermodynamic control for the various elementary steps and intermediates are given in Tables 3-5. The GGA-PW91 results suggest an apparent activation energy of 0.87 eV, a negative CO order, -0.67, and a high coverage of adsorbed CO*, $\theta=0.87$ ML, at steady state. The second most abundant surface species is H* ($\theta=0.05$ ML), consistent with a slightly negative order (-0.06) for H₂. The water order is 0.98, and its coverage is approximately 0.02 ML. Rate control analysis⁶⁷ suggests that the COOH formation step (R3) is rate determining. Thermodynamic control analysis, on the other hand, implies that the rate is most sensitive to the binding of CO*, with a degree of thermodynamic control of -1.74, implying strong CO poisoning. These results differ substantially from our experimental values (section 3.4), which show a positive CO order (0.86) and a much lower effective activation barrier (0.29 eV).

As we discuss further below, the surprisingly negative CO reaction order predicted by the PW91 calculations, and the correspondingly high CO coverage, suggest that the PW91 calculations overbind CO at the Au/MgO interface. A simple strategy to address this problem is to systematically replace kinetically and thermodynamically sensitive parameters with results of higher accuracy calculations from the hybrid HSE06 functional. Due to the high computational cost of HSE06, however, an iterative strategy is more suitable to achieve

efficient convergence between the predicted kinetic data and the experimental results. The reaction orders, energies, and degrees of rate control from the PW91 analysis form the starting point of the method. Subsequently, the reaction barrier and energies of the rate determining step, as well as the binding energy of the species with the highest degree of thermodynamic control, are replaced by the corresponding HSE06 values (see Supporting Information, section S4, for details); these values correspond to formation of COOH* and the CO* binding energy, respectively. The kinetic parameters are then recalculated with the microkinetic model, and the process is repeated until no more PW91 values need to be replaced by HSE06 values, and the rate determining step and thermodynamic determining species do not change between the last two iterations. Although this procedure leads to introduction of small errors in the overall energy change of the WGS reaction, such errors should not affect our kinetic predictions since the reaction is simulated far from equilibrium.

Within two iterations, the kinetic simulation result is already very close to the values simulated with only HSE06 data (Table 3). The HSE06-only results, in turn, show a CO order of 0.75 with a much lower CO coverage ($\theta=0.24$ ML) than is predicted by PW91 (Table 3). In addition, the apparent activation energy drops to 0.09 eV, while the rate control analysis indicates the rate determining step remains COOH formation. Both the iterative strategy and the HSE06 analysis show good agreement with the experimentally determined trends (activation energies and reaction orders), although the absolute magnitude of the predicted rates is still not accurate (differs by several orders of magnitude), as suggested by the residual error of about 0.2 eV in the HSE-predicted effective barriers. With the iterative strategy, it is only necessary to calculate the HSE06 BE of CO*, H* and the barrier of the COOH formation step, while the full HSE06 analysis requires determination of binding energies of nine species and reaction barriers for 12 elementary steps. We emphasize that this approach does not require fitting to experimental data, and although the quantitative agreement with experiment is not perfect, it is considerably better than what would be predicted by a simple PW91-GGA analysis alone, and it could thus be useful for fast ab-initio screening of more general catalytic processes at metal/oxide interfaces.

A central result to emerge from the iterative microkinetic analysis, described above, is that a relatively small change in CO binding energy (0.15 eV weaker with HSE06 than with PW91) is associated with a very significant change in predicted kinetics. Note that the changes to other parameters, including binding energies of H on both * and # sites, as well as the barrier to form COOH, are even smaller (less than 0.06 eV). The CO order increases by about one, and the CO coverage drops from 0.87 ML (PW91) to 0.24 ML (HSE06). In order

to further understand this behavior, we perform an additional set of calculations wherein we simply vary the binding energy of CO and keep all other parameters constant. Such variations provide a rapid, although approximate, approach to estimate the impact of CO binding energy changes from either functional effects or other factors, such as nanoparticle size changes. As shown in the supporting information (Figure S5), weakening the CO binding energy systematically decreases the CO* coverage and increases the coverage of H* at interface. From this correspondence, we postulate that the significant decrease of the CO* coverage is caused primarily by the competitive adsorption of CO* and H* at interface sites. Note that we did not consider coverage depended CO binding energy⁷¹ since the predicted CO coverage with HSE06 or iterative method are very close to 1/3 ML, which is the coverage employed to calculate DFT binding energies. Due to the complexity of the system, it is not easy to verify this postulate analytically. However, we note that similar behavior can be observed for a much simpler system, Langmuir adsorption of A and B on a single site surface, where the BE's of A and B are relatively evenly balanced. In addition, the thermodynamic control analysis shows a trend consistent with these conclusions. X_{TRC,CO^*} has its most negative value in the strong CO binding limit, while X_{TRC,H^*} becomes most negative as the CO binding weakens, suggesting that the most abundant surface species of WGS shift could change from CO* to H* as the CO BE becomes weaker. Note that the net rate of reaction R9 is negative, resulting in net formation of H*, and leading to a negative degree of thermodynamic control for H*. The changing of this species is associated, in turn, with a maximum of the reaction rate. At that point, the multiplication of the CO* and (H+OH)*[#] coverages is a maximum, which is the optimal situation for WGS within our calculated series. We note that the modification of the CO BE does not influence the rate determining step, which is in all cases the formation of COOH.

The microkinetic model, as discussed above, predicts zero CO₂ order, while a slightly negative value is observed experimentally. To address this puzzle, several additional possibilities for CO₂ chemisorption and reaction on MgO surfaces have been analyzed. It is found that the formation of formate, which most likely interacts with co-adsorbed –H on the surface, can lead to a modestly negative CO₂ order; the influence of this spectator species is further discussed in the Supporting Information Section S5.

Finally, we briefly discuss the relationship between the apparent activation energy and the other energetic parameters. We begin by noting that simple treatments of model Langmuir–Hinshelwood mechanisms can show a relationship between apparent reaction orders and apparent activation energies,⁸¹ and we expect a similar relationship to hold in the

present case. Our microkinetic modeling demonstrates that CO^* and $(\text{H}+\text{OH})^{*\#}$ combination is the rate determining step, and this step is strongly irreversible. In this scenario, we will have following relationship between apparent activation energy and apparent reaction order:

$$E_a^{app} = E_{a(\text{CO}+\text{OH})} + n_{\text{CO}}\Delta H_{\text{CO}} + n_{\text{H}_2\text{O}}\Delta H_{\text{H}_2\text{O}} + \Delta H_{\text{H}_2\text{O dissociation}} + f(n_{\text{H}_2}, \Delta H_{\text{H}_2}) , \quad (5)$$

where we do not provide the complete expression for contributions from the H_2 term since these are quite complex in the dual-site model. Because ΔH_{CO} is negative, a more positive CO order will result in a smaller E_a , and this is precisely what is observed when varying the CO binding energies, as described above. In fact, the E_a calculated according to this simple formula agrees with the values predicted by microkinetic modeling to within about 0.2 eV if we neglect the $f(n_{\text{H}_2}, \Delta H_{\text{H}_2})$ term.

Table 3. Elementary steps of carboxyl mechanism and the corresponding reaction and activation energies (eV).

Method	E_a	n_{CO}	n_{CO_2}	n_{H_2}	$n_{\text{H}_2\text{O}}$
Full PW91	0.87	-0.67	0.00	-0.06	0.98
Iterative method	0.18	0.66	0.00	-0.24	0.73.
Full HSE06	0.09	0.75	0.00	-0.23	0.93
Experiment	0.29 ± 0.03	0.86 ± 0.04	-0.26 ± 0.05	-0.35 ± 0.03	0.74 ± 0.07

Table 4. Calculated degrees of rate control.

		PW91	HSE06
R3	$\text{CO}^* + (\text{H}+\text{OH})^{*\#} = \text{COOH}^* + \text{H}^\# + *$	1.022	1.120
R4	$\text{COOH}^* + \text{H}_2\text{O}^{*\#} + \# = (\text{CO}_2 + \text{H}_2\text{O} + \text{H})^{**\#\#}$	0.000	0.011
R5	$(\text{CO}_2 + \text{H}_2\text{O} + \text{H})^{**\#\#} = \text{CO}_2 + * + \text{H}^\# + \text{H}_2\text{O}^{*\#}$	0.000	0.033
R6	$\text{H}^\# + * = \text{H}^* + \#$	-0.023	-0.002

R7	$H^\# + H^* = (H+H)^{\#}$	0.000	0.000
R8	$(H+H)^{\#} = H_2 + * + ^\#$	0.018	0.049
R9	$H^* + H^* = H_2 + * + *$	-0.017	-0.226
R10	$COOH^* + ^\# = (CO_2+H)^{\#}$	0.000	0.015
R11	$(CO_2+H)^{\#} = * + CO_2 + H^\#$	0.000	0.000

Table 5. Calculated degrees of thermodynamic control.

	PW91	HSE06
CO*	-1.738	-0.443
H ₂ O* [#]	-0.021	-0.087
(H+OH)* [#]	-0.029	-0.208
COOH*	0.000	0.000
H [#]	0.000	0.000
H*	-0.109	-0.312
(H+H)* [#]	0.000	-0.004
(CO ₂ +H ₂ O+H)* ^{##}	0.000	0.000
(CO ₂ +H)* [#]	0.000	0.000

4. Conclusions

The mechanism of the water gas shift (WGS) reaction at the interface between a gold nanowire and an MgO(100) substrate is examined with a combination of Density Functional Theory calculations, microkinetic modeling, and kinetic experiments. The DFT calculations demonstrate that the highest barrier for WGS elementary steps decreases from ~2 eV on clean Au(111) to ~0.75 eV at the Au/MgO interface, clearly demonstrating the central role of the interface in promoting this chemistry. Among the multiple mechanisms considered, including redox, carboxyl and formate, the carboxyl mechanism is the most energetically favorable. Based on the determined DFT energetics, a dual-site microkinetic model is

developed. Kinetically significant steps are determined from the model, and the predicted reaction orders and effective activation barrier are shown to be highly sensitive to the treatment of CO at the Au/MgO interface. In all cases, COOH formation is determined to be the rate-limiting step at the interface. By iteratively replacing the energies of the kinetically significant steps and binding energies with higher accuracy calculations from HSE06 hybrid functionals, it is possible to efficiently improve the model predictions to achieve excellent agreement with experimentally measured kinetic parameters. We expect that the approach introduced in this contribution will be suitable for rapid and efficient analysis of mechanisms of other reactions that are strongly promoted at metal/oxide interfaces.

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Supporting Information

Descriptions of water dissociation with coadsorbed surface OH groups, less reactive additional reaction pathways, formation of HCOO, HCO₃ and its influence on microkinetic simulations, and additional details on the microkinetic simulations, iterative method, and treatment of surface entropies are included in the Supporting Information.

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