Title: Intrinsic kinetics of plasmon-enhanced reverse water gas shift on Au and Au-Mo interfacial sites supported on silica

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Graphical Abstract

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Abstract

Well characterized AuMo_x catalysts were synthesized by controlled surface reactions (CSR) and studied in reverse water gas shift (RWGS) reaction with and without visible light addition. The numbers of Au and Au-Mo interfacial sites on these catalysts were quantified using low temperature (173 K) CO adsorption with Fourier transform infrared spectroscopy (FT-IR) and electron microscopy. Due to the localized surface plasmon resonance (LSPR) effect, visible light irradiation of the catalyst caused a decrease in the apparent activation energy from 80.2 ± 3.9 kJ/mol to 55.5 ± 3.1 kJ/mol and 67.5 ± 1.3 kJ/mol to 38.7 ± 1.9 kJ/mol with visible light irradiation over Au/SiO_2 and $\text{Au}_1\text{Mo}_{0.1}/\text{SiO}_2$, respectively. The catalytic activity went through a maximum upon addition of Mo, with $\text{Au}_1\text{Mo}_{0.1}/\text{SiO}_2$ being the most active catalyst. The $\text{Au}_1\text{Mo}_{0.1}$ catalyst with LSPR was 30 times more active than the reference Au catalyst under dark conditions. Visible light irradiation increased the reaction rate 4.7-4.8 times at 573 K for all catalysts. The turnover rates (CO mole produced per mole of Au or AuMo_x site per min) on the Au and AuMo_x interfacial sites were measured to be 0.98 min^{-1} and 14 min^{-1} in the dark conditions and 4.4 min^{-1} and 63 min^{-1} under the light conditions at 573 K. The rate per AuMo_x interfacial site is 14 times greater than the rate per Au site under both dark and light conditions. These results indicate that the LSPR has the same enhancement effect on both Au and AuMo_x catalytic sites.

Introduction

In the last two decades, supported gold catalysts have begun to receive considerable attention since Haruta and co-workers discovered that dispersed gold nanoparticles are catalytically active in low-temperature CO oxidation reaction [1, 2]. Supported Au nanoparticles

also have catalytic activity for a wide variety of reactions including hydrogen dissociation [3], formic acid decomposition [4], water-gas shift reaction (WGS) [5], reverse water gas shift (RWGS) [6], and selective and total oxidation of hydrocarbons [7, 8]. The RWGS is the first step in the catalytic conversion of CO₂ into fuels or chemicals. The generated CO can then be used to produce methanol, dimethyl ether (DME), or liquid fuels using commercially available technologies like Fischer-Tropsch synthesis [9].

The activity of Au catalysts changes with the Au particle size[4, 10-12], the support used[11-13] and the addition of various promoters such as Mo [14], La [15] and Ag [16, 17]. Previous studies have reported that the active catalytic sites for Au could be under-coordinated Au atoms [4, 18], ionic Au atoms,[13, 19, 20] or interfacial sites between metal and metal-oxide support [3, 21-23]. For example, Nakamura and Fujitani investigated the reaction mechanism and active sites for CO oxidation over Au/TiO₂ catalysts, concluding that O₂ reacts with H₂O forming a hydroperoxide species at the interface between the Au nanoparticles and TiO₂ support [24]. Similarly, Rodriguez and co-workers demonstrated the importance of the interface between Au particles and TiO₂(110) in the WGS reaction, based on experiments and theoretical calculations [12]. They showed that dissociation of water and the formation of an OCOH intermediate decomposing into CO₂ and H₂ occurs at the interface [12].

Gold catalysts have been shown to be one of the most promising plasmonic photocatalytic materials due to their ability to absorb visible light through surface plasmon resonance (SPR) [25]. SPR is defined as a photon-driven coherent oscillation of the surface conduction electrons on metallic nanoparticles caused by a light-driven electromagnetic field [26-28]. This effect leads to plasmons that oscillate locally around the nanoparticles with a

frequency known as the localized surface plasmon resonance (LSPR) [26-28]. Several recent papers have demonstrated that surface plasmons can enhance chemical reaction rates on Au catalysts for CO oxidation [29, 30], WGS [31], RWGS [6], methyl orange decomposition [32], and water splitting [33-35]. It has been suggested that the interface between Au and metal oxide is responsible for the catalytic activity in many plasmon-enhanced reactions. Moskovits and co-workers showed that devices fabricated with multilayers of Au nanoparticles on a TiO₂ film produced over 1000-fold increase in photoconductance compared to TiO₂ film without Au nanoparticles under 600 nm light illumination [36]. Cronin and co-workers reported up to a 66-fold enhanced photocurrent with Au/TiO₂ catalyst for water splitting reaction under visible light irradiation [33]. They attributed the enhanced activity to the local fields generated by LSPR at the interface between Au and TiO₂ by using a finite-difference time-domain (FDTD) simulation estimating the electromagnetic response [33]. Other groups also reported similar results demonstrating the importance of the intense local fields generated at the interface between Au and TiO₂ [37, 38]. Both research groups observed the occurrence of electromagnetic field enhancement at the Au and TiO₂ interface with finite element method (FEM) electromagnetic simulation [37, 38]. Importantly, enhanced local electric fields were concluded to increase e⁻/h⁺ pair generation and improve catalytic activity [33, 39, 40]. In spite of the previous work suggesting a change in the local electric field at the interface with light irradiation, there are only limited experimental studies reporting on the types of catalytic sites that are active for plasmonic photocatalytic reactions using intrinsic reaction kinetics data on well-defined catalysts.

Recently, we demonstrated the rate per AuMo_x interfacial site is an order of magnitude higher than the rate per under-coordinated Au site in RWGS reaction under dark condition at 573 K [14]. We prepared a series of AuMo catalysts supported on silica by controlled surface

reactions (CSR) where we were able to quantify the concentration of under-coordinated Au and AuMo_x interfacial sites using CO adsorption at sub-ambient temperatures. Silica was used as a support for this study because: (1) it is inert in this reaction, (2) Mo/SiO₂ has no activity, and (3) SiO₂ does not exhibit plasmonic resonance with visible light irradiation. Our CSR preparation method allowed us to prepare Au-Mo catalysts where the Mo was preferentially deposited onto the Au sites as indicated by Raman spectroscopy, X-ray absorption near edge spectroscopy (XANES) and scanning transmission electron microscopy (STEM).

In this paper, we report on the intrinsic activity of Au and AuMo_x sites for the RWGS with and without visible light using well characterized silica supported AuMo_x catalysts prepared by the CSR method. The objective of this paper is to measure the plasmonic enhancement of Au and AuMo_x interfacial sites, allowing us to determine the extent of enhancement that occurs at the interfacial sites compared to the Au sites.

2. Experimental

2.1 Catalyst Preparation

The AuMo/SiO₂ catalysts were synthesized by a modified CSR method that is illustrated in Figure 1. The reference SiO₂ supported Au catalyst was prepared by a deposition-precipitation method. Dried silica (Cab-o-Sil EH-5) was dispersed in Milli-Q water and gold (III) chloride trihydrate (HAuCl₄·3H₂O, Sigma-Aldrich) solution was added into the suspension at room temperature. The pH of the mixture was adjusted to 9 by drop-wise addition of 2.5 M ammonium hydroxide (NH₄OH, Sigma-Aldrich). The mixture was aged for 6 h under stirring at room temperature, and the solid material was then filtered and washed with deionized water to remove

103 chloride ions. The sample was dried overnight at 383 K in air. The dried catalyst was reduced in
104 a flow-through cell at a temperature of 623 K (with a heating rate of 2 K min⁻¹) under hydrogen
105 flow (30 cm³(STP) min⁻¹) for 4 h. The reduced sample was then transferred to a glove box for the
106 Mo deposition. AuMo/SiO₂ catalysts were prepared by a modified CSR method as described in
107 detail elsewhere [14, 41]. Briefly, a solution of cycloheptatriene molybdenum tricarbonyl (Strem
108 Chemicals) in n-pentane (1 mg precursor/g solvent) was added to the 4 wt% Au/SiO₂ catalyst
109 inside the glove box. Then, the mixture was transferred to a vacuum oven where the sample was
110 dried overnight at 318 K to evaporate the residual n-pentane. The dried sample was stored inside
111 the glove box until use. Hereafter, AuMo/SiO₂ samples will be referred to as Au₁Mo_x, where x =
112 the nominal Mo/Au atomic ratio. Mo/SiO₂ samples were prepared by incipient wetness
113 impregnation method of dried silica (Cab-o-Sil EH-5) with an aqueous solution of ammonium
114 heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄ · 4H₂O, Sigma-Aldrich).

Figure 1. Schematic representation of the controlled surface reactions (CSR) method for a Mo-Au/SiO₂ catalyst. (a) Reference Au/SiO₂ catalyst is prepared by deposition-precipitation; (b) Mo precursor, Mo(CO)₃(cycHep), is added to reduced Au/SiO₂ catalyst by selective deposition of precursor on Au surface; (c) Removal of precursor ligands occurs on the surface of Mo deposited Au/SiO₂ catalyst during the RWGS reaction at 573K

Reactivity Measurements.

RWGS reaction studies were conducted with a Harrick scientific reactor (HVC-MRA-5) containing 3-5 mg of catalyst loaded in the heater cup of the Harrick reactor. The top 1-2 mm of the catalyst cup was loaded with the catalyst to ensure illumination of catalyst bed described elsewhere [6]. Catalysts were activated in a flowing RWGS gas mixture (H₂:CO₂ 2:1), and the flow rate for the reactant gases CO₂ and H₂ was controlled using Cole-Parmer mass flow controllers (FF-32907-59). Research grade CO₂ (CDR200) and ultra-high purity (UHP) H₂ (UHP

129 HY300) gas cylinders from Airgas were used. The temperature of the catalyst bed was controlled
130 by a PID temperature controller. The total pressure in the reactor was maintained at 8.1 bar using
131 a back-pressure regulator. The catalyst bed was photo-irradiated using a Dolan-Jenner broadband
132 visible light source (MI-150). The light was filtered through a high performance long-pass filter
133 (#62-981; Edmund optics) to give light wavelength of $\lambda > 400$ nm, as measured with a NIST-
134 traceable, ISO-17025 calibrated spectroradiometer (ILT950; International Light Technologies).
135 Products were analyzed by an online gas chromatograph with a barrier discharge ionization
136 detector (GC-BID) system equipped with an auto-sampling 6-port valve (Shimadzu). The BID
137 uses helium plasma to detect permanent gases such as CO₂, CO, H₂ with high sensitivity. The
138 GC-BID system was calibrated using Scott specialty gases (P/N 34507 and 34512). Control
139 experiments without catalyst determined there was no reactivity from the reactor. The stability of
140 the Au₁Mo_{0.1}/SiO₂ and reference Au/SiO₂ catalyst was investigated at 573 K under dark and light
141 conditions. Also, the temperature gradient was measured by filling the heater cup with sand, as
142 reported in our previous study [6]. The gradient was less than 5% of the set point temperature as
143 measured in Kelvin, and this gradient inside the reactor is sufficiently small that it does not
144 affect our measurement of apparent activation energy or apparent reaction orders [6]. The
145 specific reaction rate at 613 K with light was obtained under differential reaction conditions
146 where the CO₂ conversion was less than 3% which is below the thermodynamic limit of 11%.
147 The effects of heat and mass transport were estimated for our system using the dimensionless
148 criteria we have previously used for this same reaction [6]. Heat and mass transfer coefficients
149 and material properties were estimated using correlations available in the literature [42-44]. The
150 catalyst particle size of 150 μ m was estimated using sieves. All computed values are smaller than
151 the heat or mass transfer controlling regime criteria indicating that our data were collected in an

intrinsic kinetic regime. For example, the calculated intraparticle mass transfer number (or Weisz-Prater number) for the system was 3.8×10^{-6} which is below 0.3, suggesting the absence of intraparticle pore diffusion limitations [45, 46]. The CO₂ conversion rate was calculated based on the CO concentration in the product gas. The reaction rate was calculated after CO₂ conversion stabilized (less than 5% difference in conversion between data points). Typically it took approximately 2 hr for the CO₂ conversion rate to stabilize for each reaction condition. Once steady state was reached, approximately 4-5 data points over a 2 hr period were taken for the rate measurement. No products other than CO and H₂ were observed with our carbon balance closure being greater than 99%.

Fourier Transform Infrared Spectroscopy (FT-IR).

Catalyst samples were pressed into self-supporting pellets using a 1.2 cm die. Au/SiO₂ and AuMo/SiO₂ pellets were fixed in the sample holder of a transmission cell described elsewhere [14, 47]. The cell was sealed and the sample was activated in a flowing RWGS gas mixture (H₂:CO₂ 2:1) for 4 h at 573 K (2 K min⁻¹). After activation the sample was cooled under RWGS flow to room temperature and evacuated to 10⁻⁵ Torr. A background scan was then recorded. Fourier transform infrared (FTIR) (Nicolet 6700) spectra of adsorbed CO were obtained in transmission mode in the presence of 1% CO in He (Airgas). The spectra were collected at temperatures ranging from 148 to 383 K, and the cell was allowed to equilibrate for 5 min at each individual temperature. The temperature was measured by a type-K thermocouple and heating was controlled by a PID controller (Love Controls Series 16A) connected to a variable autotransformer. The sample holder was designed for collecting spectra at sub-ambient

temperatures using flowing liquid nitrogen, as described previously [47]. All data were collected by averaging 256 scans with a resolution of 4 cm^{-1} . Spectral deconvolution was performed using Origin 9.1 to determine the areal contribution from each peak. The final spectrum of CO adsorbed on each catalyst was represented by two superimposed Gaussian curves described elsewhere [14].

Inductively Coupled Plasma-Absorption Emission Spectroscopy (ICP-AES)

The Au and Mo loadings of catalysts were determined using a Perkin-Elmer Plasma 400 ICP Emission Spectrometer. Typically, 10-15mg of catalyst samples were digested with a mixture of 2 mL of nitric acid (Fischer, 65 %) and 6 mL of hydrochloric acid (Fischer, 37 %) in a Teflon beaker at 383 K. Au and Mo standards for the ICP analysis were prepared from Au and Mo ICP standards (Fluka, $1000 \pm 2\text{ mg L}^{-1}$). The post-digestion mixture was cooled to room temperature, diluted in water, filtered and analyzed with ICP emission spectrometer.

Ultraviolet-Visible Diffuse Reflectance Spectra (UV-Vis DRS)

The light absorption of the catalysts was characterized using diffuse reflectance ultra-violet visible spectroscopy. Thermo Scientific Evolution 300 UV-Vis spectrometer was used with Praying Mantis diffuse reflectance accessory to collect UV-Visible absorption data over the wavelength range 210-1080 nm.

3. Results and Discussion

3.1. Characterization of active sites

Raman spectroscopy and Energy-dispersive X-ray spectroscopy (EDS) were performed on the AuMo/SiO₂ and Mo/SiO₂ catalysts, as described elsewhere.[14] A peak at 975 cm⁻¹ in the Raman spectra was observed for the Mo/SiO₂ catalyst, and the intensity of this peak increased with Mo loading.[14] This peak corresponds to a dioxo (O=)₂Mo(-O-Si)₂ surface species on SiO₂. [48, 49] This feature was not present on SiO₂, Au/SiO₂ or the AuMo/SiO₂ catalysts, suggesting that Mo was selectively deposited on Au/SiO₂. In addition, we carried out EDS analysis which showed that most of the metal particles for the Au₁Mo_{0.1} catalyst are associated with Mo. We performed X-ray absorption near edge spectroscopy (XANES) to determine the extent of Mo oxidation in the Mo/SiO₂ and AuMo/SiO₂ samples.[14] The Mo moieties deposited on AuMo samples were in a high oxidation state (Mo⁺⁶), suggesting that structure of Au and Mo is not a bimetallic alloy but a metal-metal oxide combination.

Infrared spectra of CO chemisorbed on the pre-reduced reference Au/SiO₂ and AuMo_x/SiO₂ catalysts activated in flowing RWGS conditions at 573 K are shown in Figure 2. Au sites were saturated with 3 × 10⁻¹ torr of CO, and the spectra were collected at 173 K. In addition, 173 K is the lowest temperature where CO bands on SiO₂ support were not observed. The total area of the spectra is smaller for the AuMo_x/SiO₂ catalysts compared to the reference Au/SiO₂ catalyst. The CO adsorption spectra can be deconvoluted into two bands as observed in the previous studies: 1) under-coordinated Au⁰-CO with a band centered at 2111 cm⁻¹ and 2) under-coordinated Au^{δ+}-CO with a band centered at 2122 cm⁻¹ [50-55]. Although there can be a minor shift in bands depending on the CO coverage on the surfaces [56], we observed that after RWGS the Au/SiO₂ catalyst undergoes oxidation, with a decrease in the number of Au⁰ sites from 74 ± 5% to 22 ± 1% after H₂ activation, which is consistent with the work of Behm and co-workers [57, 58]. Thus, the CO FTIR spectra were collected after exposure to the RWGS conditions. Also, we

218 performed several deconvolutions of the spectra by changing the fit parameters, and the
 219 difference in the final values was less than 5%.

220
 221 **Figure 2.** IR spectra for CO adsorbed on Au/SiO₂ and AuMo_x/SiO₂ at 173 K and 3×10^{-1} Torr of
 222 CO. The intensities are normalized by the pellet density. Catalysts were activated in flowing
 223 RWGS conditions at 573 K.

224 Table 1 shows the Au and Mo loadings and amounts of Mo deposited and CO adsorbed
 225 of Mo/SiO₂, Au/SiO₂ and AuMo_x/SiO₂ catalysts. The actual Mo/Au molar ratio of Au₁Mo_{0.15}
 226 sample is approximately 0.1. Thus in the preparation of this catalyst not all of the Mo deposited
 227 onto the under-coordinated Au sites. The concentration of Au-Mo interfacial sites on this catalyst
 228 is also lower than the Au₁Mo_{0.1}/SiO₂ catalyst. As we have previously reported [14], the amount
 229 of adsorbed CO on undercoordinated Au sites was calculated from the FTIR and STEM data by:
 230 (1) obtaining the total FTIR area (per gm of catalyst) of CO adsorbed on under-coordinated Au⁰
 231 and Au^{δ+} sites for each catalyst, (2) calculating the number of under-coordinated Au sites (i.e.

adsorbed CO) by combining our estimates of the Au particle size from STEM with a correlation of the number of under-coordinated Au sites (i.e. perimeter and corner sites) and Au particle size reported elsewhere [11], and (3) calculating the number of under-coordinated Au sites for each catalyst by multiplying the site density of Au/SiO₂ by the normalized CO FT-IR area assuming a 1:1 CO to undercoordinated Au site stoichiometry. The average Au particle size used for these calculations was 2 nm which is within the error of our STEM microscope measurements, 1.7 ± 1.3 nm [14]. As seen in the Table 1, Mo deposition on Au/SiO₂ catalysts decreased the number of undercoordinated Au sites (S_{Au}) or CO uptake, indicating that the Au sites available for CO binding are covered by Mo. The CO uptake was smallest for the Au₁Mo_{0.1}/SiO₂ catalyst and increased with a higher nominal Mo loading (Au₁Mo_{0.15}/SiO₂ catalyst). The concentration of AuMo_x interfacial sites (S_{AuMo_x}) was estimated by subtracting the number of undercoordinated Au sites on each of the AuMo_x/SiO₂ catalysts from the number of undercoordinated Au sites on the Au/SiO₂ parent catalyst.

Table 1. Characterization of Au/SiO₂ and AuMo_x/SiO₂ catalysts

Sample	Au loading (%)	Nominal Mo/Au molar ratio	Actual Mo/Au molar ratio	Theoretical Mo deposited (μmol gcat ⁻¹)	Actual Mo deposited (μmol gcat ⁻¹) ^a	Normalized CO FTIR Area ^b	S_{Au} (μmol gcat ⁻¹) ^c	S_{AuMo_x} (μmol gcat ⁻¹)
Au	3.925	0	0	0	0	1	41.5 ± 3.1	0
Au ₁ Mo _{0.05}	3.925	0.05	0.049	10.2	10.1	0.83	34.3 ± 3.9	7.2
Au ₁ Mo _{0.1}	3.925	0.1	0.095	20.3	19.4	0.52	21.7 ± 3.1	19.8
Au ₁ Mo _{0.15}	3.925	0.15	0.104	30.5	21.2	0.78	32.2 ± 2.8	9.3

^a Ratio Mo/Au was determined by ICP ^b Combined integrated area of CO on Au⁰ and Au^{δ+} sites. ^c Calculated from the total number of perimeter and corner sites for a 2 nm average particle size catalyst, 41.5 μmol gcat⁻¹, multiplied by the normalized CO FTIR area

3.2. UV-Vis spectroscopy

251 The UV-Vis absorbance spectra for the catalysts were collected after RWGS activation at 573 K
252 over the wavelength range 210-1080 nm, as shown in Figure 3. The UV-Vis DRS spectrum of
253 supported Au catalysts shows a broad absorption band in the visible light range, ascribed to the
254 inter-band transition from the d-electron bands located below the Fermi level (E_F) to an empty sp
255 state above E_F of Au particles under the visible light irradiation [59-61]. The supported Au
256 catalyst exhibited a distinct peak at 515 nm from the surface plasmon absorption of Au
257 nanoparticles [62]. The absorbance spectra of its plasmonic resonance are dependent on the size
258 and shape of the plasmonic metal nanoparticles [63]. It has been reported that the absorption
259 peak from the surface plasmon absorption of the gold nanoparticles is located between 510 and
260 530 nm [62]. The 515 nm peak from gold nanoparticles becomes slightly smaller after Mo
261 deposition on Au catalysts, suggesting that the Mo deposits on the Au nanoparticle surface [62].
262 In addition, a small red-shift in the UV-Vis absorption spectra was observed with increased Mo
263 loading, which can be associated with a change in the dielectric constant. It has been reported
264 that the medium dielectric constant (ϵ_m) can affect the peak of plasmon absorption spectra [64],
265 and the change in the spectra was theoretically calculated in bimetallic systems such as Au-
266 Pd[65], Au-Ag[66] and Au-Cu[67] using Mie theory. The Mo/SiO₂ sample exhibited a peak
267 centered at 270 nm, while the SiO₂ support shows a broad spectrum of light absorption.

Figure 3. Diffuse reflectance UV-visible absorption spectra of SiO_2 , Mo/SiO_2 , Au/SiO_2 and $\text{AuMo}_x/\text{SiO}_2$ catalysts

3.4. Activity measurements and modeling

Table 2 shows the intrinsic reaction rates at 573 K and activation energies of Au/SiO_2 and $\text{Mo-deposited Au/SiO}_2$ catalysts under both light and dark conditions. The catalytic activities of the SiO_2 support and Mo/SiO_2 sample were below our detection limit (CO_2 conversion rate less than $2 \mu\text{mol g}^{-1} \text{min}^{-1}$) in RWGS reaction under dark and light conditions. Deposition of Mo onto the Au/SiO_2 catalyst increased the catalytic activities under both light and dark conditions. The catalytic activity increases with Mo loading up to 0.1 Mo-Au molar ratio, with the $\text{Au}_1\text{Mo}_{0.1}/\text{SiO}_2$ catalyst having almost six times higher activity than Au/SiO_2 . The addition of more Mo ($\text{Au}_1\text{Mo}_{0.15}/\text{SiO}_2$) decreased the reaction rate.

Visible light illumination enhances the RWGS catalytic activity for both Au/SiO₂ and Mo-deposited Au/SiO₂ catalysts by a factor of 4.7 to 4.8 times at 573 K. The light enhancement decreases with increasing reaction temperature as can be seen in Figure 4. This behavior is consistent with our previous study on RWGS on Au/TiO₂, where the light enhancement decreased with increasing temperature [6]. The light enhancement for all catalysts was similar at all temperature levels used in this study.

The apparent activation energy was determined by varying the temperature from 553 to 613 K with steps of 20 K. The apparent activation energies under dark conditions ranged from 67.5 kJ/mol for the Au₁Mo_{0.1}/SiO₂ catalyst to 80.2 kJ/mol for the Au/SiO₂ catalyst. Light illumination decreased the apparent activation for all the catalysts. The apparent activation energy for the RWGS reaction over Au/SiO₂ catalyst changed from 80.2 ± 3.9 kJ/mol to 55.5 ± 3.1 kJ/mol with visible light irradiation. Light illumination on the Au₁Mo_{0.1}/SiO₂ catalyst decreased the apparent activation energy from 67.5 ± 1.3 kJ/mol to 38.7 ± 1.9 kJ/mol. Mo deposition on supported Au catalysts and visible light illumination both changed the apparent activation energy. The change in apparent activation energy indicates that surface plasmons change the intrinsic reaction kinetics of the RWGS reaction.

We have previously studied the LSPR enhancement of RWGS reaction on Au/TiO₂ [6]. We observed that LSPR decreases the apparent activation energy, causes a shift in the CO₂ reaction order, and causes a rate enhancement. However, the rate enhancement for the Au/TiO₂ was 2.2 at 573 K, which is lower than the rate enhancement for the AuMo_x/SiO₂ catalysts. This difference is probably because the Au/TiO₂ catalyst had a larger particle size (3.5 nm) compared to the AuMo_x/SiO₂ (1.7 nm) catalysts. In our previous study we suggested that LSPR increases

the rate of RWGS by increasing the rate of either hydroxyl hydrogenation or carboxyl decomposition [6].

Table 2. Reaction rate for RWGS for Au/SiO₂ and AuMo_x/SiO₂ under dark and light conditions. RWGS experimental conditions: Total gas flow rate= 15 cm³(STP)/min , CO₂:H₂ molar ratio=1:2, P=117 psi.

Sample Name	CO ₂ Conversion Rate ^a / (μmol) g ⁻¹ min ⁻¹		Light Enhancement	E _{activation} ^b /kJ mol ⁻¹	
	Dark	Light		Dark	Light
Au/SiO ₂ ^c	41.0 ± 8.5	187.3 ± 24.2	4.8 ± 1.3	80.2 ± 3.9	55.5 ± 3.1
Au ₁ Mo _{0.05} /SiO ₂	139.5 ± 4.7	655.3 ± 12.3	4.7 ± 0.2	72.1 ± 0.9	42.3 ± 2.2
Au ₁ Mo _{0.1} /SiO ₂	261.5 ± 12.0	1238.5 ± 72.8	4.8 ± 0.4	67.5 ± 1.3	38.7 ± 1.9
Au ₁ Mo _{0.15} /SiO ₂	191.5 ± 26.1	909.5 ± 135.1	4.8 ± 1.0	68.2 ± 1.2	39.9 ± 1.5

^a Measured at the reaction temperature of 573 K ^b Measured at the reaction temperature range from 553 to 613 K ^c Activation energy of Au/SiO₂ measured at the reaction temperature range from 573 to 613 K due to the low rate at 553 K under dark condition below the detection limit of GC

Figure 4. RWGS rate enhancement as a function of temperature at 8.1 bar and a H₂:CO₂ ratio of 2:1.

The time-on-stream data for the Au₁Mo_{0.1}/SiO₂ catalyst at 573 K under dark and light conditions are shown in Figure 5. No change in catalyst activity was observed without light for up to 7 hrs. A gradual decrease in the activity of about 15 % after 8 hr was observed with light illumination. Air exposure of catalysts at room temperature after reaction recovers the activity. This slight loss in activity could be due to changes in the oxidation state of the Mo or migration of the Mo during the reaction. Further research is needed to clarify the exact cause of this deactivation. All data points in Table 2 were collected after the CO₂ conversion stabilized. Once steady state was reached approximately 4-5 data points over a 2 hr period were taken for the rate measurement.

Figure 5. RWGS activity as a function of time-on-stream at 573 K and 8.1 bar of H₂:CO₂ (2:1) for Au₁Mo_{0.1}/SiO₂.

The reaction rate of the two different active sites (under-coordinated Au and interfacial AuMo_x sites) was deconvoluted from the kinetic data using Equation 1.

$$R_{total} = R_{Au} + R_{AuMo_x} = S_{Au}r_{Au} + S_{AuMo_x}r_{AuMo_x} \quad (1)$$

The r_{Au} and r_{AuMo_x} refer to the turnover rate (the mole of CO production per mole of Au and AuMo_x site per min) for the under-coordinated Au and AuMo_x sites respectively. The R_{Au} and R_{AuMo_x} indicate the rate of CO production per mass of catalyst per min from under-coordinated Au sites and interfacial AuMo_x, respectively. The experimental rate and model predicted rates under both dark and light conditions are plotted in Figure 6. A parity plot comparing the measured experimental rate and model predicted rate is shown in Figure 7. The slope, as estimated by a least square method, of the parity plot in Figure 7 is 0.9923 ± 0.0766 . The model estimated the various turnover rates to be $r_{Au} = 0.98 \text{ min}^{-1}$ and $r_{AuMo_x} = 14 \text{ min}^{-1}$ under dark and $r_{Au} = 4.4 \text{ min}^{-1}$ and $r_{AuMo_x} = 63 \text{ min}^{-1}$ under visible light condition. The rate per AuMo_x site is approximately 14 times greater than the rate per Au site under both dark and light conditions. It has been reported in computational studies that visible light irradiation near the plasmon resonance frequency generates a local electric field which becomes more intense at the metal/TiO₂ interface [33, 37, 38]. It has been suggested that the enhanced electric fields compared with the field intensity of the photon flux are responsible for the increase in the activity [68-70]. Our experimental indicates the LSPR enhances the activity of all types of catalytic sites at similar rates.

347

348 **Figure 6.** RWGS at 573 K and 8.1 bar of H₂:CO₂ (2:1) for Au/SiO₂ and AuMo_x/SiO₂. Dashed
 349 lines indicate model predicted rates. The model predictions are $r_{Au} = 0.98 \text{ min}^{-1}$ and $r_{AuMo_x} = 14$
 350 min^{-1} under dark and $r_{Au} = 4.4 \text{ min}^{-1}$ and $r_{AuMo_x} = 63 \text{ min}^{-1}$ under light. The rate per AuMo_x site
 351 (r_{AuMo_x}) is approximately 14 times greater than that of Au site (r_{Au}) under both dark and light
 352 conditions.

Figure 7. Parity plot of model versus experimental rates for the RWGS reaction.

The formation of the AuMo_x interfacial sites increased the intrinsic activity of the catalyst; but did not influence the plasmonic enhancement. The catalyst containing the largest number of AuMo_x interfacial sites ($\text{Au}_1\text{Mo}_{0.1}/\text{SiO}_2$) exhibited the highest catalytic activity. This result could be extended to other catalytic systems that contain metal oxide promotion, including MoO_x , TiO_x , CeO_x , or ZnO_x , of a plasmonic active metal catalyst, where the interfacial metal-metal oxide sites are more active than the metal sites [6, 71, 72]. We expect that the metal-oxide Au sites have a higher activity than Au sites for a range of reactions including WGS, RWGS, and CO oxidation reactions [73-75],[24]. The result from this paper suggests that on these catalyst systems, changing the concentration of metal oxide promoters on a plasmonic metal will not influence the plasmonic enhancement on both metal and interface catalytic sites. The optimal amount of metal

oxide to enhance catalyst activity in both dark and light conditions can be found solely by optimizing the number of interfacial sites. The LSPR enhancement on the catalytic materials can be adjusted by tuning the size and shape of metal nanoparticles [76, 77]. Therefore, to design the most active LSPR catalyst, the first step should be to optimize the size and shape of metal nanoparticle to get the highest LSPR enhancement. Then the metal oxide should be added to this base catalyst in such a way to maximize the number of interfacial metal-metal-oxide sites.

Conclusions

We prepared well-defined Au catalysts containing different amounts of Mo by controlled surface reactions (CSR). The concentration of under-coordinated Au and AuMo_x interfacial sites on these catalysts was quantified using Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and scanning transmission electron microscopy (STEM). Visible light addition to the catalyst increased the catalyst activity for RWGS by 4.7-4.8 times by LSPR. We found that the intrinsic activity of the AuMo_x interfacial site is approximately 14 times greater than the rate per Au site under both dark and light conditions. The apparent activation energy for the RWGS reaction changed from 80.2 ± 3.9 kJ/mol to 55.5 ± 3.1 kJ/mol and 67.5 ± 1.3 kJ/mol to 38.7 ± 1.9 kJ/mol with visible light irradiation over Au/SiO₂ and Au₁Mo_{0.1}/SiO₂, respectively. These results suggest that to design the most active metal oxide promoted LSPR metal catalysts, the first step should be to optimize the size and shape of the metal nanoparticle and the second step should be to optimize the number of metal-oxide – metal interfacial sites.

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