Title: Measurement of intrinsic catalytic activity of Pt monometallic and Pt-MoO_x interfacial sites over visible light enhanced PtMoO_x/SiO₂ catalyst in reverse water gas shift reaction

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Graphical abstract

Abstract

Supported Pt-Mo catalysts were prepared with different Mo contents by a controlled surface reaction (CSR) method and studied for the reverse water gas shift (RWGS) reaction under dark and visible light irradiation conditions. Characterization results from Raman spectroscopy, scanning transmission electron microscopy (STEM), CO chemisorption, and inductively coupled plasma-absorption emission spectroscopy (ICP-AES) indicate that selective Mo deposition onto Pt was achieved at low Mo loading (Mo/Pt ratio < 0.3). Mo deposition changed the apparent activation energy and CO₂ and CO reaction orders. Visible light irradiation changed the apparent activation energy and reaction orders of CO₂, CO, and H₂, ascribed to **direct photoexcitation**. The intrinsic activity of a Pt site is 0.4 and 4.1 min⁻¹ under dark and light conditions at 473 K, respectively, whereas the intrinsic activity of a Pt-MoO_x site is increased to 22.7 and 160 min⁻¹ under dark and light conditions at 473 K, respectively.

1. Introduction

The catalytic activity of a wide variety of reactions on Pt group metals, including C-O bond hydrogenolysis in oxygenates,[1] glycerol reforming,[2-4] and electrocatalytic reactions[5, 6], can be improved by incorporation of an oxophilic metal such as Mo or Re to the Pt. For example, Ribeiro and co-workers observed up to an order of magnitude increase in the TOF for

the water gas shift (WGS) reaction over Pt catalysts promoted with Mo. They ascribed the increase in the turnover frequency (TOF) to a decrease in the CO binding energy after Mo deposition.[7] It has also been shown that Mo addition to Pt/SiO₂ and Pt/C catalysts increased the TOF by a factor of 15 and 4,000 for the WGS reaction, respectively.[8] In addition, an approximately 7 times higher TOF was observed over PtMo catalysts compared to Pt monometallic catalysts for hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran to 1,6-hexanediol.[9] Two different preparation methods were used to prepare PtMo catalysts: a controlled surface reaction (CSR) method and incipient wetness impregnation.[8, 9] The CSR method was more effective at forming uniform PtMo particles than the incipient wetness impregnation method and produced a catalyst with a higher activity at similar Mo to Pt nominal loadings.[8, 9]

Recent studies have suggested the importance of metal-metal oxide interfacial sites for reactions such as CO oxidation,[10-13] WGS[14, 15] and reverse water gas shift (RWGS).[16] It has been proposed that the active sites for these reactions are at the interface of the metal and metal oxide. While these interfacial sites appear to be common in the field of heterogeneous catalysis, the identification and characterization of the interfacial sites are difficult. We have recently measured the concentration of interfacial Au-MoO_x sites using a combination of low temperature CO Fourier transform infrared spectroscopy (FT-IR) and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDS).[17, 18] The interfacial Au-MoO_x sites were an order of magnitude more active than the Au sites for the RWGS reaction.[17, 18] The RWGS reaction is the first step in the desired conversion of carbon dioxide into fuels and chemicals. It would also be useful to quantify the activity of interfacial sites on other types

of catalytic materials besides Au. The objective of this paper is to measure the intrinsic activity of Pt and Pt-MoO_x sites for the RWGS reaction with and without visible light illumination.

A second objective of this paper is to measure how the intrinsic activity of the Pt and Pt-MoO_x sites changes with visible light illumination. Visible light can be used to enhance catalytic activity, and this approach has been proposed as an option for conversion of solar-to-chemical energy.[19-22] Conventional semiconductor-based photocatalysts have two major inherent drawbacks: 1) high electron-hole (e^-/h^+) pair recombination rate, and 2) limited utilization of solar spectrum.[23] However, plasmonic catalysts can use visible light, which alleviates these drawbacks. Certain metal nanoparticles are able to absorb visible light through a phenomenon called surface plasmon resonance (SPR).[24] It has been previously shown that visible light illumination can increase the catalytic activity in reactions such as reverse water gas shift (RWGS)[17, 25], propylene epoxidation,[26] methyl orange decomposition,[27] and water splitting[22, 28, 29]. Most of the studies using visible light have been performed with gold (Au) and silver (Ag) nanoparticles on supports via SPR effect.[28, 30, 31] Platinum (Pt) has received less attention as a photocatalyst utilizing visible light.[32-35] The LSPR frequency for small Pt nanoparticles (<30 nm diameter) is in the UV region, suggesting that in our study the light enhancement was possibly due to a photo excitation effect.[33, 34] Visible light absorption of the Pt nanoparticles (~5 nm diameter) has been reported to enhance catalytic activity in oxidation reactions, ascribed to interband excitation of Pt atoms.[35-38] Visible light illumination of Pt enhanced the activity of rhodamine B degradation with Pt/TiO₂,[39] organic pollutant decomposition over Pt/Bi₂O₃,[40] and oxidation reactions over Pt/TiO₂. [41] According to these studies, the visible light enhancement of Pt nanoparticles was due to LSPR.[39, 40]

2. Experimental

2.1. Catalyst Preparation

A SiO₂-supported Pt catalyst was prepared by incipient wetness impregnation of Davisil-Grade 646 (Sigma-Aldrich) with an aqueous solution of chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) (Sigma-Aldrich). SiO₂ was chosen as a support because it minimizes Pt metal-support interactions and allows the study of the effect of Pt-MoO_x interfacial sites. The impregnated catalyst was dried at 383 K for 3 h, and then reduced under flowing H₂ at 533 K for 4 h. Subsequently, the Pt/SiO₂ catalyst was passivated at room temperature with 1% O₂ in He for 1 h. PtMo/SiO₂ bimetallic catalysts were prepared by a controlled surface reaction (CSR) method, as described elsewhere.[8] The Pt/SiO₂ catalyst was re-reduced in a Schlenk tube at a temperature of 533 K under hydrogen flow. The sealed Schlenk tube was then transferred to an inert atmosphere glove box, and the reduced reference catalyst was added into a precursor solution made with cycloheptatriene molybdenum tricarbonyl (C₇H₈Mo(CO)₃) (Strem Chemicals) in *n*-pentane (Sigma-Aldrich). The mixture was stirred inside the glove box until the orange solution became clear, indicating that the precursor was adsorbed on the catalyst. Then, *n*-pentane was evaporated in a Schlenk line. For higher molybdenum loading, the preparation of the catalysts was achieved by applying multiple cycles, where the nominal Pt:Mo atomic ratio was increased by 0.15 in each cycle. The catalyst was reduced with H₂ at 673 K between each cycle and reduced at 773 K and passivated with 1% O₂ in Ar after the final cycle. Mo/SiO₂ samples were prepared by incipient wetness impregnation method of dried silica with an aqueous solution of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma-Aldrich).

2.2 Catalysts Characterization

2.2.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

The Pt and Mo loadings of catalysts were determined using a Perkin-Elmer Plasma 400 ICP Emission Spectrometer. Typically, 10-15 mg of catalyst was 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 until the sample dissolved. The post-digestion mixture was cooled to room temperature, diluted in water, and filtered before ICP analysis. Pt and Mo standards for the ICP analysis were prepared from Pt and Mo ICP standards (Fluka, $1000 \pm 2 \text{ mg L}^{-1}$).

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

The light absorption of the catalysts was characterized using diffuse reflectance ultraviolet visible spectroscopy. A Thermo Scientific Evolution 300 UV-Vis spectrometer was used with a Praying Mantis diffuse reflectance accessory to collect UV-Visible absorption data over the wavelength range 220-1070 nm.

2.2.3 CO Chemisorption

The CO chemisorption studies were carried out using a Micromeritics ASAP 2020C system. The catalysts were reduced under H_2 flow at 473 K, and CO adsorption was performed at 308 K after reduction. The adsorption stoichiometry between CO and surface Pt sites was assumed to be 1:1.

2.2.4 Scanning Transmission Electron Microscopy/Energy-dispersive X-ray Spectroscopy (STEM/EDS)

A FEI Titan STEM with Cs probe aberration corrector operated at 200 kV with spatial resolution < 0.1 nm was used for scanning transmission electron microscopy (STEM) studies. A high-angle annular dark-field (HAADF) mode, with HAADF detector angle ranging from 54 to 270 mrad, probe convergence angle of 24.5 mrad, and probe current of ~ 25 pA was used to record the images. Sample preparation procedure was carried out as described elsewhere.[9, 42]

2.2.5 Raman spectroscopy

Raman spectroscopy experiments were carried out using a high-performance Renishaw InVia Raman Spectrometer with a 325 nm (excitation) laser. The laser is a Kimmon IK3201R-F with an output of 20 mW and an approximate power of 4 mW at the sample. All measurements used a 2400, 1 mm⁻¹ grating with an efficiency of approximately 30% at 325 nm. *In situ* Raman studies used an OFR near-UV objective with 15 $\times$ magnification and a working distance of 8.5 mm. Scattered light was filtered into a UV enhanced (lumogen coated) deep depleted array detector (Renishaw). The laser line was calibrated with a Ne calibration lamp. In addition to calibrating the laser, the Raman spectrograph was calibrated to a diamond standard at 1332 cm⁻¹. Raman measurements were taken over a range of 100-1500 cm⁻¹ and a dispersion of 1.36565 cm⁻¹ pixel⁻¹. *In situ* measurements were taken using a fully open aperture and an exposure time of 100 s, with eight accumulations. Approximately 10 mg of sample was used for each *in situ* experiment. Experiments were performed in a high-temperature cell (Linkam CCR1000) designed for temperatures up to 1273 K using a quartz window with water-cooled O-rings. The temperature was controlled by a Linkam T95-HT system. Gas flows during *in situ* experiments were controlled by mass flow controllers (Bronkhorst EL-Flow) with a maximum flow rate of 8 cm³ (STP) min⁻¹ for hydrogen, helium, and oxygen/carbon dioxide. The mass flow controllers were

connected to a digital readout system (Bronkhorst series E-7000) capable of mixing gases with variable flow rates. Catalysts were first activated for 2 h at 573 K (10 K min^{-1}), under RWGS flow ($\text{H}_2\text{:CO}_2$ 2:1 $15\text{ cm}^3\text{ (STP) min}^{-1}$). The cell was then flushed with He for 10 min, and the sample was oxidized at 573 K under a flow of $16\text{ cm}^3\text{ min}^{-1}$ He (Airgas, UHP) and $4\text{ cm}^3\text{ (STP) min}^{-1}$ O_2 (Airgas, Research grade). The sample was oxidized for 2 h prior to obtaining a Raman spectrum. Samples were kept at 573 K for spectral acquisition.

2.3 Reactivity Measurement

RWGS reaction kinetics studies were conducted with a reaction chamber from Harrick scientific (HVC-MRA-5) containing 3-7 mg of catalyst loaded in the heater cup of the reactor. Only about the top 1-2 mm of the catalyst cup was loaded with the catalyst to ensure illumination of catalyst bed, as described in our previous study.[25] Prior to reaction kinetics studies, the catalysts were *in situ* reduced under flowing H_2 ($15\text{ cm}^3\text{ (STP) min}^{-1}$) with a heating rate of 2 K min^{-1} and maintained for 4 h at 573 K. The flow rates for CO_2 , H_2 , CO and He were controlled using Cole-Parmer mass flow controllers (FF-32907-59). Research grade CO_2 (CDR200), Ultra high purity (UHP) H_2 , 1% CO balance with He, and He gas cylinders from Airgas were used. The temperature of the catalyst bed was controlled by a PID temperature controller. The total pressure in the reactor was maintained at 7.1 bar using a back-pressure regulator. The catalyst bed was photo-irradiated using a Dolan-Jenner broadband visible light source (MI-150). The light was filtered through a high performance longpass filter (#62-981; Edmund optics) to give light wavelength of $\lambda > 400\text{ nm}$, where the light intensity measured with NIST-traceable, ISO-17025 calibrated spectroradiometer (ILT950; International Light Technologies) as shown in the Supplementary Information (Figure S1) .

After reaction, the composition of the product gases was analyzed by an online gas chromatograph with a barrier discharge ionization detector (GC-BID) system equipped with an auto-sampling 6-port valve (Shimadzu). The BID uses helium plasma to detect permanent gases such as CO₂, CO, and H₂ with high sensitivity. Control experiments without catalyst determined there was no reactivity from the reactor. Also, the temperature gradient in the reactor was measured by filling the heater cup with sand as reported in our previous study.[25] The gradient was less than 5% of the set point temperature as measured in Kelvin, and this gradient inside the reactor does not affect our measurement of apparent activation energy or apparent reaction orders.[25]

3. Results and Discussion

3.1 Catalyst Characterizations

Table 1 shows the characterization results for the Pt and PtMo_x/SiO₂ catalysts. The Pt and Mo loadings were characterized by ICP and EDS of Pt/SiO₂ and PtMo_x/SiO₂ catalysts. The Mo/Pt molar ratio from ICP of Pt₁Mo_{0.15}, Pt₁Mo_{0.3}, and Pt₁Mo_{0.45} catalysts are 0.11, 0.24, and 0.40, respectively. Assuming that the Mo preferentially deposits on the Pt surface, the Mo/Pt surface ratio is 0.45, 0.65, and 0.75 for the Pt₁Mo_{0.15}, Pt₁Mo_{0.3}, and Pt₁Mo_{0.45} catalysts, respectively. The Mo/Pt molar estimated by EDS is lower than the measurement from ICP, with the discrepancy increasing as the Mo loading increases. The CO uptake decreases with increasing Mo loading of the Pt and PtMo_x/SiO₂ catalysts. The CO uptake of a reference Pt/SiO₂ catalyst was 51.3 μmol g⁻¹. The CO uptake decreased to 45.4 μmol g⁻¹ after a control experiment where CSR was performed without Mo precursor on the same Pt/SiO₂ catalyst. The CO uptake decreased with an increase in Mo loading. The dispersion of the Pt/SiO₂ catalyst was calculated

from the CO uptake to be 20%. The decrease in the CO uptake and the Mo/Pt EDS molar ratio versus the nominal Mo/Pt molar ratio is shown in Figure 1 (d). The oxidation state of Mo is a mixture of MoO₂, MoO₃ and metallic Mo.[8]

Table 1. Characterization of Pt/SiO₂ and PtMo_x/SiO₂ catalysts

Sample	Pt wt% (ICP)	Mo wt% (ICP)	Mo/Pt molar ratio (Theo.)	Mo/Pt molar ratio (ICP)	Mo/Pt molar ratio (EDS)	Surface Mo/Pt molar ratio ^a (EDS)	CO uptake (μmol g ⁻¹)
Pt/SiO ₂	5.0	0	-	-	-	-	51.3
Pt ₁ Mo _{0.15} /SiO ₂	4.7	0.26	0.15	0.11	0.09	0.45	20.7
Pt ₁ Mo _{0.3} /SiO ₂	4.4	0.52	0.3	0.24	0.13	0.65	15.2
Pt ₁ Mo _{0.45} /SiO ₂	4.3	0.85	0.45	0.40	0.15	0.75	8.5

^a Calculated by dividing Mo/Pt molar ratio (EDS) by dispersion of the reference Pt catalyst.

Figure 1. EDS determined surface elemental compositions of (a) Pt₁Mo_{0.15}/SiO₂ catalyst, (b) Pt₁Mo_{0.3}/SiO₂ catalyst, (c) Pt₁Mo_{0.45}/SiO₂ catalyst, and (d) comparison between nominal and actual Mo/Pt molar ratio determined by EDS

Representative transmission electron micrographs of PtMo_x/SiO₂ and their corresponding nanoparticle size distributions are shown in Figures 2. No statistically significant change in particle size was observed with increasing Mo loading in the catalysts. The mean particle diameters of Pt₁Mo_{0.15}, Pt₁Mo_{0.3}, and Pt₁Mo_{0.45} catalysts are 3.6 ± 2.3 , 4.0 ± 2.9 , and 3.9 ± 2.6 nm, respectively, as shown in Figures 2 (d)-(f).

Figure 2. STEM image of (a) $\text{Pt}_1\text{Mo}_{0.15}/\text{SiO}_2$, (b) $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$, and (c) $\text{Pt}_1\text{Mo}_{0.45}/\text{SiO}_2$ and particles size distribution of (d) $\text{Pt}_1\text{Mo}_{0.15}/\text{SiO}_2$, (e) $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$, and (f) $\text{Pt}_1\text{Mo}_{0.45}/\text{SiO}_2$.

Figure 3 shows *in situ* Raman spectra (325 nm) of SiO_2 , Mo/SiO_2 , Pt/SiO_2 and $\text{PtMo}_x/\text{SiO}_2$ catalysts. Under oxidizing conditions, the signal at 973 cm^{-1} appears in $\text{MoO}_x/\text{SiO}_2$ samples and the intensity of this feature becomes stronger with increasing concentration of Mo. The signal at 973 cm^{-1} derives from the $\text{Mo}=\text{O}$ stretch commonly seen with dispersed MoO_3 on SiO_2 at sub-monolayer coverage.[43, 44] As shown in the Raman spectra of $\text{PtMo}_x/\text{SiO}_2$ catalysts, the feature at 973 cm^{-1} is absent in $\text{Pt}_1\text{Mo}_{0.15}/\text{SiO}_2$ and $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$, suggesting the selective deposition of Mo on Pt sites. However, the feature can be observed in $\text{Pt}_1\text{Mo}_{0.45}/\text{SiO}_2$, indicating that some of the Mo deposited on the SiO_2 . This result is in agreement with the trends observed from the EDS and CO chemisorption.

Figure 3. *In situ* Raman spectra (325 nm) of SiO₂ and SiO₂ supported Mo, Pt, and PtMo at 573 K under oxidizing conditions. The vertical line denotes the Raman shift corresponding to the symmetric stretch of a Mo(=O)₂ from a dioxo (O=)₂Mo(–O–Si)₂.

Figure 4 shows UV-Vis diffuse reflectance spectra (DRS) of SiO₂, Mo/SiO₂, Pt/SiO₂ and PtMo_x/SiO₂ catalysts collected over the wavelength range of 270-1050 nm. UV-Vis DRS spectra of 0.5 and 5 wt% Mo/SiO₂ catalysts exhibited a broad peak around 300 nm, in agreement with a previous study showing the UV-Vis spectra over mesoporous Mo/SiO₂.^[45] Compared to Mo/SiO₂ catalysts showing a negligible absorption in the visible light range, supported Pt catalysts exhibit a broad absorption band, ascribed to the inter-band transition of 5 d electrons on the Pt particles.^[36, 38, 46] The different visible light absorption spectra of Mo/SiO₂ and supported Pt catalysts correspond to the visible light enhancement in the catalytic activity, which will be discussed below.

Figure 4. UV-Vis diffuse reflectance spectra (DRS) of SiO_2 , Pt/SiO_2 , Mo/SiO_2 and PtMo/SiO_2 .

3.2 Activity measurements

The RWGS activity of the catalysts under dark and visible light illumination is summarized in Table 2 in terms of both CO_2 conversion rate and TOF (on a CO chemisorption basis) at 473 K. The SiO_2 support exhibited no activity under dark and light conditions. The 0.5 wt% Mo/SiO_2 catalyst (corresponding Mo loading of $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$ catalyst) had a RWGS rate of $5.5 \mu\text{mol g}^{-1} \text{min}^{-1}$ under dark conditions and showed no rate enhancement under light irradiation. This result suggests that Mo and SiO_2 do not have photoexcitation by visible light, which is consistent with our previous study.[17] The supported Pt catalysts and Mo-deposited Pt

catalysts were active in RWGS reaction under both dark and light conditions. As shown in Table 2, the CO₂ conversion rate increases as Mo loading increases up to 0.3 Mo:Pt additions under dark condition. Visible light irradiation showed a 6 to 10 times increase in CO₂ conversion rate compared to that in the dark at 473 K. The CO₂ conversion rate of Pt₁Mo_{0.3}/SiO₂ with visible light was 77-fold larger than that of Pt reference catalyst under dark condition. The CO₂ conversion rate decreases above 0.3 Mo:Pt loading, and this behavior can be explained by a decrease in the number of active sites by excessive loading of Mo. However, the highest TOF was observed with the Pt₁Mo_{0.45}/SiO₂ catalyst. The TOF of Pt₁Mo_{0.45}/SiO₂ with light illumination is 350 times greater than that of Pt reference catalyst under dark condition.

The apparent activation energy and reaction order with respect to CO, CO₂ and H₂ were measured for the RWGS reaction. The apparent activation energy, as shown in Table 2, was determined by measuring the reaction rates at temperatures from 448 to 523 K. The apparent activation energy for the RWGS reaction over Pt/SiO₂ catalyst decreased from 67.9 kJ/mol under dark condition to 42.3 kJ/mol with visible light irradiation. These values of apparent activation energies are similar to those reported in the literature.[47] The apparent activation energy for dark conditions decreased with Mo addition (a Pt-Mo molar ratio equal to 0.3) from 67.9 kJ/mol to 60.0 kJ/mol. Similarly, the activation energy under light irradiation decreased from 42.3 kJ/mol to 32.5 kJ/mol for the Pt₁Mo_{0.3}/SiO₂ catalysts. The decrease in apparent activation energy in the presence of visible light is consistent with several previous studies.[25, 48-51] For example, Singh and co-workers reported that light illumination reduces the apparent activation energy by 20 kJ/mol for the RWGS reaction over a nanocrystalline In₂O_{3-x}(OH)_y catalyst.[48] It was suggested that the decreased activation energy for photocatalytic reactions with light irradiation corresponds to a change in adsorption or desorption steps of the reactants or

products.[48, 52] This behavior would be in agreement with the increase in CO reaction order with light illumination as reported in Section 3.3.

Table 2. Reaction rate and activation energy for RWGS for Pt/SiO₂ and PtMo_x/SiO₂ by CSR method under dark and light conditions. RWGS experimental conditions: Total gas flow rate= 15 cm³ (STP) min⁻¹, CO₂:H₂ molar ratio=1:2, P=7.1 bar.

Sample Name	CO ₂ Conversion Rate ^a / (μ mol) g ⁻¹ min ⁻¹		TOF ^a / min ⁻¹		E _{activation} ^b /kJ mol ⁻¹	
	Dark	Light	Dark	Light	Dark	Light
Pt/SiO ₂	21 $\pm$ 3	209 $\pm$ 68	0.4 $\pm$ 0.1	4.1 $\pm$ 1.3	67.9 $\pm$ 0.4	42.3 $\pm$ 0.6
Pt ₁ Mo _{0.15} /SiO ₂	172 $\pm$ 1	1380 $\pm$ 240	8.3 $\pm$ 0.1	66.8 $\pm$ 11.5	62.1 $\pm$ 0.2	33.4 $\pm$ 0.7
Pt ₁ Mo _{0.3} /SiO ₂	237 $\pm$ 10	1640 $\pm$ 340	15.6 $\pm$ 0.7	108 $\pm$ 22	60.0 $\pm$ 0.3	32.5 $\pm$ 0.4
Pt ₁ Mo _{0.45} /SiO ₂	195 $\pm$ 13	1200 $\pm$ 140	22.9 $\pm$ 1.5	141 $\pm$ 16	60.3 $\pm$ 1.3	35.5 $\pm$ 1.5

^a Measured at the reaction temperature of 473 K ^b Collected at the reaction temperature range from 448 to 523 K

The extent of light enhancement for the Pt/SiO₂ and PtMo_x/SiO₂ catalysts, as measured by the rate under light illumination divided by the rate under dark conditions as a function of temperatures is shown in Figure 5. The light enhancement of all catalysts decreased with increasing reaction temperature, which is consistent with our previous study on RWGS over supported Au catalysts.[17, 25] The light enhancement also decreased with increasing Mo loading. In contrast, the light enhancement of Au and AuMoO_x catalysts was similar at the temperature range of 553 to 613 K.[17]

Figure 5. RWGS rate enhancement as a function of temperature at 7.1 bar and a H₂:CO₂ ratio of 2:1 at the reaction temperature range from 448 to 523 K

3.3 Reaction order studies

The dependence of the reaction rate on the partial pressure (*i.e.* reaction order) for H₂, CO₂, and CO was determined by varying each gas concentration individually. As shown in Figure 6 and Table 3, visible light illumination decreases the reaction order of H₂; however, Mo deposition did not change the H₂ reaction. The CO₂ reaction order increases with Mo loading and visible light irradiation, as shown in Figure 7 and Table 3. The CO₂ reaction order under dark condition increased from 0.47 ± 0.04 to 0.61 ± 0.03 from the pure Pt catalyst to the Pt₁Mo_{0.3}/SiO₂ catalyst. Visible light illumination further increased the CO₂ reaction order of Pt₁Mo_{0.3}/SiO₂ to 1.00 ± 0.03 . The CO reaction order also changed with Mo deposition and visible light irradiation. The CO reaction order of the Pt reference catalyst was -0.73 ± 0.08 , but

the reaction order became -0.43 ± 0.03 for the 0.3 Mo:Pt catalyst. This CO reaction order was further increased to -0.16 ± 0.01 with visible light illumination over the $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$ catalyst.

The changes in the reaction orders of H_2 , CO_2 , and CO suggest that Mo loading and visible light change the reaction energetics and the binding energy of adsorbed intermediates. The negative CO reaction orders suggest that CO poisoning occurs for our reaction conditions. The CO reaction order increased from -0.73 ± 0.08 to -0.16 ± 0.01 with 0.3 Mo:Pt addition and visible light illumination. This behavior indicates that CO poisoning was alleviated with the Mo deposition and light illumination. The change in CO binding energy after Mo deposition onto Pt surfaces has been reported in previous experiments and theoretical studies under dark condition.[4, 53, 54] Hammer and co-workers demonstrated that the CO adsorption bond strength was reduced by about 0.5 eV on a Pt_2Mo (111) model surface compared to a Pt (111) reference surface, using DFT calculations.[54] There are two possible mechanisms for how visible light transfers energy to the process. One option is that hot holes are produced that interact with species involved in the rate limiting step.[55, 56] Another option is that the bond between Pt and CO is weakened by direct photoexcitation as reported by Christopher and co-workers.[55] The second mechanism is consistent with a decrease in CO reaction order change with visible light illumination. It should be noted that visible light irradiation further changed the reaction orders of H_2 , CO_2 , and CO. We observed an increase in the reaction order of H_2 and CO_2 with visible light illumination over Au/TiO_2 catalyst, suggesting that visible light increases the rate of either the hydroxyl hydrogenation or carboxyl decomposition step in RWGS reaction.[25]

Figure 6. Reaction rate for reverse water gas shift reaction as a function of H_2 partial pressure over over (a) Pt/SiO_2 , (b) $\text{Pt}_1\text{Mo}_{0.15}/\text{SiO}_2$, (c) $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$, and (d) $\text{Pt}_1\text{Mo}_{0.45}/\text{SiO}_2$ catalysts. RWGS experimental conditions: Total gas flow rate = $15 \text{ cm}^3 (\text{STP}) \text{ min}^{-1}$, $P = 7.1 \text{ bar}$, $P_{\text{CO}_2} = 3.6 \text{ bar}$, $P_{\text{CO}} = 0 \text{ bar}$, and $T = 473 \text{ K}$

Figure 7. Reaction rate for reverse water gas shift reaction as a function of CO_2 partial pressure over (a) Pt/SiO₂, (b) Pt₁Mo_{0.15}/SiO₂, (c) Pt₁Mo_{0.3}/SiO₂, and (d) Pt₁Mo_{0.45}/SiO₂ catalysts. RWGS experimental conditions: Total gas flow rate= 15 cm³ (STP) min⁻¹, P=7.1 bar, P_{H₂} = 3.6 bar, P_{CO} = 0 bar, and T= 473 K

Figure 8. Reaction rate for reverse water gas shift reaction as a function of CO partial pressure over (a) Pt/SiO_2 , (b) $\text{Pt}_1\text{Mo}_{0.15}/\text{SiO}_2$, (c) $\text{Pt}_1\text{Mo}_{0.3}/\text{SiO}_2$, and (d) $\text{Pt}_1\text{Mo}_{0.45}/\text{SiO}_2$ catalysts. RWGS experimental conditions: Total gas flow rate = $15 \text{ cm}^3 (\text{STP}) \text{ min}^{-1}$, $P = 7.1 \text{ bar}$, $P_{\text{CO}_2} = 2.6 \text{ bar}$, $P_{\text{H}_2} = 2.6 \text{ bar}$, and $T = 473 \text{ K}$

Table 3. The reaction order of CO, CO₂ and H₂ partial pressures for RWGS for Pt/SiO₂ and PtMo_x/SiO₂ under dark and light conditions. RWGS experimental conditions: Total gas flow rate= 15 cm³ (STP) min⁻¹, CO₂:H₂ molar ratio=1:2, P=7.1 bar, T= 473 K

Sample	Reaction Orders					
	CO ₂		H ₂		CO	
	Dark	Light	Dark	Light	Dark	Light
Pt	0.47 ± 0.04	0.91 ± 0.05	0.25 ± 0.01	0.18 ± 0.02	-0.73 ± 0.08	-0.29 ± 0.01
Pt ₁ Mo _{0.15}	0.57 ± 0.04	0.92 ± 0.07	0.25 ± 0.02	0.17 ± 0.02	-0.64 ± 0.03	-0.23 ± 0.01
Pt ₁ Mo _{0.3}	0.61 ± 0.03	1.00 ± 0.03	0.25 ± 0.02	0.19 ± 0.02	-0.43 ± 0.03	-0.16 ± 0.01
Pt ₁ Mo _{0.45}	0.58 ± 0.04	0.91 ± 0.04	0.26 ± 0.01	0.17 ± 0.01	-0.68 ± 0.09	-0.27 ± 0.03

3.4 Modeling and TOF estimation of Pt and Pt-MoO_x interfacial sites

The measured catalytic activity of the catalysts was described in terms of two different active sites (Pt and interfacial Pt-MoO_x sites) using Equation 1.

$$\begin{aligned}
 R_{total} &= R_{Pt} + R_{Pt-MoO_x} = S_{Pt}r_{Pt} + S_{Pt-MoO_x}r_{Pt-MoO_x} \\
 &= (1 - x_{interfacial\ sites})S_{Pt}r_{Pt} + x_{interfacial\ sites}S_{Pt}r_{Pt-MoO_x} \quad (1)
 \end{aligned}$$

We have assumed that the deposition of Mo onto Pt sites with a 1:1 stoichiometry. The R_{Pt} and R_{Pt-MoO_x} are the mole of CO production per mass of catalyst per min from Pt sites and interfacial Pt-MoO_x, respectively. The S_{Pt} is the number of Pt surface sites (mole of Pt site per mass), which is the CO uptake determined by chemisorption shown in Table 1. The S_{Pt-MoO_x} is the number of Pt-MoO_x sites (mole of Pt-MoO_x site per mass) where the Pt is next to Mo sites. The r_{Pt} and r_{Pt-MoO_x} refer to the turnover rate (the mole of CO production per mole of Pt and Pt-MoO_x site per min) for the Pt and interfacial Pt-MoO_x sites, respectively. $x_{interfacial\ sites}$ is the

fraction of the Pt sites that are interfacial sites. The value used here is the surface Mo/Pt molar ratio as measured by EDS reported in Table 1. Similar results for the $x_{interfacial\ sites}$ of these catalysts can be determined by using the method of Sener *et al.*[8] The experimental rate and model predicted rates under both dark and light conditions are plotted in Figure 9. A parity plot comparing the measured experimental rate and model predicted rate is shown in Figure 10. The slope of the parity plot estimate by a least square method is 0.99 ± 0.06 . The r_{Pt} is the measured TOF of Pt/SiO₂ catalyst, which is 0.4 and 4.1 min⁻¹ under dark and light conditions, respectively. The r_{Pt-MoO_x} is the model predicted TOF of Pt sites interacting with Mo, which is 22.7 and 160 min⁻¹ under dark and light conditions, respectively. The TOF of Pt-MoO_x interfacial site is 57 and 39 times greater than that of Pt site under dark and light conditions, respectively. It has been proposed that the intense local electric fields generated at the interface by visible light irradiation are responsible for the enhanced activity.[28, 57] In our previous study on RWGS over Au and Au-MoO_x catalysts, we also observed that the TOF of Au-MoO_x is approximately 14 times greater than that of Au site under both dark and light conditions, suggesting the **visible light irradiation** enhances the activity of Au and Au-MoO_x interfacial sites at similar proportions.[17] Unlike the similar **visible light** enhancement on the activity of the Au and Au-MoO_x interfacial site observed in the previous study, the **photoexcitation** increases the activity of Pt sites more than that of Pt-MoO_x interfacial sites.

Figure 9. Reaction rate for reverse water gas shift reaction at 473 K and 7.1 bar of H₂:CO₂ (2:1) for Pt/SiO₂ and PtMo_x/SiO₂. Dots and dashed lines indicate experimental and model predicted rates, respectively.

Figure 10. Parity plot of model predicted versus experimental rates for the RWGS reaction.

The formation of Pt-MoO_x interfacial sites and visible light irradiation promoted the catalytic activity for the RWGS reaction over the supported Pt catalysts as demonstrated in our previous work with Au-MoO_x. Our approach to catalyst design can be extended to the preparation of other bimetallic catalysts, such as Pt-Ce, Au-Ti, and Au-Ce. We believe that incorporation of a metal **activated by visible light** with a second metal will exhibit enhanced activity for reactions where interfacial sites serve as active sites. Evaluation of the inherent activity of two distinct active sites (*i.e.* monometallic and interfacial sites) would be a significant contribution to the field of heterogeneous catalysis and the design of active catalysts.

4. Conclusions

We investigated the effects of molybdenum and visible light on the catalytic activity for the reverse water-gas shift (RWGS) reaction over supported Pt catalysts. We prepared Pt catalysts with different amounts of Mo using controlled surface reactions (CSR) to prepare catalysts with well-defined Pt-MoO_x interfacial sites. Characterization results from Raman spectroscopy, scanning transmission electron microscopy (STEM), CO chemisorption, and inductively coupled plasma-absorption emission spectroscopy (ICP-AES) indicate that selective deposition of Mo onto Pt was achieved with low Mo loading (Mo/Pt ratio < 0.3). We estimated the activity of Pt-MoO_x interfacial sites using a combination of CO chemisorption, scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy (STEM/EDS), and catalytic activity measurements. Visible light irradiation showed a 6 to 10 times increase in CO₂ conversion rate compared to that in the dark at 473 K. The CO₂ conversion rate of Pt₁Mo_{0.3}/SiO₂ with the visible light was 77 fold higher than the Pt reference catalyst under dark condition at 473 K. The Pt₁Mo_{0.45}/SiO₂ catalyst with light illumination was 350 times more active than the Pt reference catalyst under dark condition. The addition of Mo to Pt/SiO₂ at a Mo/Pt ratio of 0.3 decreased the apparent activation energy from 67.9 ± 0.4 kJ/mol to 60.0 ± 0.3 kJ/mol. Visible light irradiation of the catalyst leading photoexcitation resulted in a decrease in the apparent activation energy from 67.9 ± 0.4 to 42.3 ± 0.6 kJ/mol and 60.0 ± 0.3 to 32.5 ± 0.4 kJ/mol over Pt/SiO₂ and Pt₁Mo_{0.3}/SiO₂, respectively. The reaction order of CO₂ and CO increased from 0.47 ± 0.04 to 0.61 ± 0.03 and from -0.73 ± 0.08 to -0.43 ± 0.03 over Pt/SiO₂ and Pt₁Mo_{0.3}/SiO₂, respectively. The reaction orders of CO₂, CO, and H₂ was further changed from 0.61 ± 0.03 to 1.00 ± 0.03 , from -0.43 ± 0.03 to -0.16 ± 0.01 , and from 0.25 ± 0.02 to 0.19 ± 0.02 over Pt₁Mo_{0.3}/SiO₂, respectively. The change in the apparent activation energy and reaction orders

suggests that both Mo deposition and visible light change the intrinsic reaction kinetics. We measured the intrinsic activity of both a Pt and PtMoO_x sites over these four catalyst samples. The intrinsic activity of a Pt site is 0.4 and 4.1 min⁻¹ under dark and light conditions at 473 K, respectively. The intrinsic activity of a Pt-MoO_x site is 22.7 and 160 min⁻¹ under dark and light conditions at 473 K, respectively. We showed that the formation of Pt-MoO_x interfacial sites and visible light irradiation promoted the catalytic activity for the RWGS reaction over the supported Pt catalysts.

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