Determination of CO, H₂O and H₂ coverage by XANES and EXAFS on Pt and Au during water gas shift reaction

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The turn-over-rate (TOR) for the water gas shift (WGS) reaction at 200 °C, 7% CO, 9% CO₂, 22% H₂O, 37% H₂ and balance Ar, of 1.4 nm Au/Al₂O₃ is approximately 20 times higher than that of 1.6 nm Pt/Al₂O₃. *Operando* EXAFS experiments at both the Au and Pt L₃ edges reveal that under reaction conditions, the catalysts are fully metallic. In the absence of adsorbates, the metal–metal bond distances of Pt and Au catalysts are 0.07 Å and 0.13 Å smaller than those of bulk Pt and Au foils, respectively. Adsorption of H₂ or CO on the Pt catalysts leads to significantly longer Pt–Pt bond distances; while there is little change in Au–Au bond distance with adsorbates. Adsorption of CO, H₂ and H₂O leads to changes in the XANES spectra that can be used to determine the surface coverage of each adsorbate under reaction conditions. During WGS, the coverage of CO, H₂O, and H₂ are obtained by the linear combination fitting of the difference XANES, or ΔXANES, spectra. Pt catalysts adsorb CO, H₂, and H₂O more strongly than the Au, in agreement with the lower CO reaction order and higher reaction temperatures.

1. Introduction

The water gas shift (WGS) reaction (eqn (1)), is an industrially important reaction for H₂ production and CO removal.^{1,2} It is mildly exothermic (ΔH = −40.6 kJ mol^{−1}), thus it is thermodynamically favored at lower temperatures. However, due to kinetic limitations, the reaction is typically conducted at temperatures between 200 and 450 °C. In commercial operation, WGS is, typically, a two-stage process with a high-temperature stage (320–450 °C) employing iron oxide-based catalysts and a low-temperature stage (180–250 °C) employing copper-based catalysts.

However, such two-stage process designs are not viable for small-scale applications. It was predicted that until 2030, approximately 10% of the world annual energy consumption will originate from the WGS reaction.¹ Thus, the development of new, higher activity low-temperature WGS catalysts is of scientific and practical interest.

Although commercial Cu/ZnO/Al₂O₃ WGS catalysts operate at low temperature, they suffer from poor stability under constant start-up–shutdown conditions and display poor sulfur tolerance.^{3,4} In the past decade, Pt and Au-based WGS catalysts have received intense attention as alternatives to Cu.^{5–14} The former are not pyrophoric and require no

exceptional pretreatment protocol. In general, Au catalysts operate at a lower temperature than Pt. Moreover, kinetic studies have shown different reaction orders on Au than on Pt. The reasons for the high rate per mole of Pt and Au compared to other metals and the differences in their kinetics are not fully understood.

In X-ray Absorption Near Edge Spectroscopy (XANES), the Pt and Au L₃ edges correspond to the 2p → 5d electronic transition, and therefore, the intensity and position of the XANES spectra are directly related to the 5d electronic structures. Most often XANES is used to determine the metal oxidation state, fraction of metallic and oxidized metal, formation of alloys, *etc.* At the L₃ edge, however, XANES is also affected by the surface coverage of adsorbates.^{15–19} For example, the amount of H₂ adsorbed on Pt¹⁸ has been quantified by looking at differences in XANES spectra and insights into the type of active sites for H₂ adsorption have been proposed.^{15–17} So far, no studies have reported analysis of the difference XANES spectra for identification of the surface coverage of adsorbates during the WGS reaction in order to elucidate the factors that govern turn-over-rates (TOR) and reaction orders.

In the present study, *operando* EXAFS and XANES have been used to identify the active sites on Pt nanoparticles supported on SiO₂ and Al₂O₃ and Au/Al₂O₃ WGS catalysts. Adsorption of CO, H₂, and H₂O induce changes in the shape and position of the Pt and Au L₃ XANES spectra. The XANES difference, or ΔXANES, method is used to identify adsorbates and quantify their individual coverage and under steady-state WGS reaction conditions (CO + H₂O + H₂). The CO surface coverage determined by FTIR agree well with those obtained by the ΔXANES analysis. The different reaction

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orders between Pt and Au are explained by the difference in CO surface coverage. In addition it is suggested that weak adsorption of CO leads to exposed sites on Au at low temperature, resulting in catalytic activity at lower temperature than that on Pt. Finally, the differences in adsorption properties of Pt and Au suggest potential opportunities for the development of new, low-temperature WGS catalysts.

2. Experimental

2.1 Catalyst preparation

4.3% Pt/SiO₂: 50 g of Davisil silica (Sigma-Aldrich, 280 m² g⁻¹, 1.1 cc/g) was slurried in 250 mL of deionized (DI) H₂O with about 2 mL of concentrated NH₄OH. The pH was approximately 10. 5.0 g of Pt(NH₃)₄(NO₃)₂ (PtTA) was dissolved in 250 mL of DI H₂O and 2 mL of concentrated NH₄OH was added. The PtTA solution was rapidly added to the stirring silica. After 15 min, the silica was settled and the solution was decanted. The Pt/silica was slurried in 200 mL of cold DI H₂O for 15 min and the solution was decanted. Following a second wash and decanting of the solution, the wet solid was filtered and washed on the filter with 200 mL of DI H₂O. The catalyst was dried overnight at 100 °C and calcined at 225 °C in flowing air for 5 h. The elemental composition was determined to be 4.3 wt% Pt by ICP analysis. By means of the double isotherm method, volumetric hydrogen and CO chemisorption indicated a dispersion of 0.95 H/Pt and 0.55 CO/Pt.

2.6% Pt/Al₂O₃: The solution of 2.3 g of Pt(NH₃)₄(NO₃)₂ (PtTA) in 23 mL of DI H₂O was added to 45 g of γ -alumina (200 m² g⁻¹, 0.5 cc/g). The catalyst was dried overnight at 110 °C and calcined in flowing air at 450 °C for 5 h. The elemental composition was determined to be 2.6 wt% Pt by ICP analysis. The H₂ and CO volumetric chemisorption values were 1.0 H/Pt and 0.85 CO/Pt.

0.7% Au/Al₂O₃: The 0.71% Au/alumina catalyst (BC17) was provided by the World Gold Council.

2.2 XAS reactor description

2.2.1 Operando XAS reactor. The temperature of the *operando*, fixed-bed plug flow reactor was controlled in an Al heating block. A type K thermocouple was mounted inside the reactor at the top of the catalyst bed to measure the reaction temperature. The design details of the reactor and its validation as a true plug flow reactor can be found elsewhere.²⁰ The flow rates of gases (CO, H₂, Ar) to the catalyst bed were controlled using mass flow controllers. The concentration of water was controlled by saturation of the reaction gas at different temperatures, thereby varying the partial pressure. The lines from the water saturator to the reactor were heat traced to prevent water condensation. The exit water vapor was condensed in an ice bath prior to injection of the products to the on-line gas chromatograph (GC).

Approximately, 10 mg of the Pt/Al₂O₃ catalyst was placed on a 3 mm plug of SiO₂ powder (Davisil 644, 280 m² g⁻¹) supported on Pyrex wool in a quartz tube reactor (O.D.: 0.25", I.D.: 0.123"), to achieve a level catalyst bed and clear visual distinction between the Pyrex wool, silica and catalyst. The catalyst bed height was approximately 6 mm.

Approximately 55 mg (*ca.* 6 mm) of the Au/Al₂O₃ catalyst was loaded into a thin walled, borosilicate NMR tube (O.D.: 0.256", I.D.: 0.224", Wilmad-Labglass part #: 6.5-PP-9). The catalyst was sandwiched between layers of silica and the Pyrex wool in the same manner as the Pt/Al₂O₃ catalyst.

The catalysts were pre-reduced at 200 °C and 280 °C for Au and Pt, respectively. The concentrations of the individual reactants for the WGS reaction were 6.8% CO in Ar, 20% H₂ in Ar, or 12.3% H₂O in Ar. The total gas flow rate over the Pt/Al₂O₃ catalyst in each experiment was constant at 10 mL min⁻¹, yielding a flow-rate-to-catalyst mass ratio of 0.91 mL min⁻¹ mg cat⁻¹. The total gas flow rate over the Au/Al₂O₃ catalyst in each experiment was 15 mL min⁻¹ giving a flow rate to catalyst mass ratio of 0.27 mL min⁻¹ mg cat⁻¹. The kinetic rates for WGS were determined by on-line gas chromatography at 120 and 200 °C for Au and 200 and 280 °C for Pt WGS, and agree with those determined in a laboratory reactor, which used larger amounts of catalyst.

2.3 XAFS measurements

X-Ray absorption measurements were conducted on the insertion device beamline of the Materials Research Collaborative Access Team (MRCAT, 10-ID) at the Advanced Photon Source (APS), Argonne National Laboratory. Ionization chambers were optimized for the maximum current with linear response (*ca.* 10¹⁰ photons detected per sec.) using a mixture of N₂ and He in the incident X-ray detector and a mixture of *ca.* 20% Ar in N₂ in the transmission X-ray detector. A third detector in the series collected a reference spectrum (Au or Pt foil) simultaneously with each measurement for energy calibration. The catalyst supports were spray-dried microspheres of about 100–200 mesh, which allowed the samples to be loosely packed without bed plugging. The reactor composition, diameter and wall thickness was chosen to give a total absorbance (μx) at the Pt L₃ (11.56 keV) edge or Au L₃ (11.92 keV) edge between 1–2 and edge steps ($\Delta\mu x$) between about 0.3–0.5. Three spectra were obtained in quick scan mode in about 4 min and were averaged for data analysis. For both reactors, the EXAFS and XANES spectra of the catalysts with adsorption of CO, H₂, H₂O or WGS gas mixture were obtained at room temperature, 120 °C, 200 °C and for Pt 280 °C. The gases were purified to remove traces of oxidants (air) by passing through a Matheson PUR-Gas Triple Purifier Cartridge.

2.4 XAFS data analysis

Phase shift and backscattering amplitudes were obtained from the Au and Pt foils for Au–Au and Pt–Pt scattering, respectively. Standard procedures based on WINXAS 3.1 software were used to fit the XAS data. The EXAFS coordination parameters were obtained by a least square fit in *q*- and *r*-space of the isolated nearest neighbor, *k*²-weighted Fourier transform data. The quality of the fits were equally good with both *k*¹ and *k*³ weightings. The EXAFS data and fits were obtained for reduced catalysts at 200 °C for Au and 280 °C for Pt and room temperature. A linear temperature dependence of the Debye–Waller factor (DWF) was assumed in order to calculate the values at intermediate temperatures.²¹

2.5 Difference (A) XANES spectra

The normalized, energy calibrated Pt L_3 and Au L_3 edge XANES spectra were obtained by standard methods. The XANES spectra were fit with a linear combination of the catalyst in He (no adsorbates) and with individual gases. For CO and H₂ the reference XANES spectra correspond to the coverage at room temperature, while for H₂O the reference XANES spectra correspond to the relative coverage at room temperature on Au, but 280 °C on Pt, *i.e.*, the temperature for the WGS reaction.

The Δ XANES spectra were obtained by subtracting the XANES spectrum of the supported catalyst in He from that with different reaction gases at various temperatures. For single gases (CO, H₂, and H₂O), the difference XANES spectra at elevated temperatures were fit using the room temperature Δ XANES as references. This gives a relative fraction of the adsorbed gas at that temperature compared to the amount adsorbed at the reference temperature. For mixed gas compositions, the Δ XANES spectra were fit as a linear combination of the Δ XANES spectra for each single adsorbate.

2.6 Laboratory testing of the WGS reaction

The catalytic activities of the Pt/Al₂O₃, Pt/SiO₂, and Au/Al₂O₃ catalysts were determined using a plug-flow, laboratory reactor, which has been described elsewhere.²² For each experiment, 250 to 300 mg of the catalyst was pre-treated *in situ* by drying at 100 °C in a flowing inert atmosphere, followed by heating to 200 °C for Au and 300 °C for Pt at 50 mL min⁻¹ in 25% H₂/75% Ar with a ramping rate of 5 °C min⁻¹. In this fashion, the Pt/Al₂O₃, Pt/SiO₂, and Au/Al₂O₃ catalysts were reduced for two hours. After reduction, the catalysts were exposed to a standard WGS composition of 6.8% CO, 8.5% CO₂, 21.9% H₂O, 37.4% H₂ and balance Ar. For all kinetic experiments, the total pressure was kept constant at ambient pressure with a total inlet flow rate of 75.4 mL min⁻¹. The Pt/Al₂O₃, Pt/SiO₂, and Au/Al₂O₃ catalysts were stabilized at 300 °C, 260 °C, and 200 °C respectively, under the standard gas composition for 15 to 20 h. Water in the reaction gas was condensed in an ice bath and the dry exit stream from the reactor was periodically injected into an Agilent 6890 GC. The dry inlet gases were analyzed before each injection to determine the response factors of the detectors and ensure precise measurements. The GC is equipped with a thermal conductivity detector and a Carboxen 1000 column operating with helium as a carrier gas.

After the stabilization process, the reactor temperature was adjusted to lower the CO conversion below 10% and maintain differential conditions during kinetic measurements. The rate of CO consumption was used to calculate the WGS rate under differential conditions. Reaction orders for the reactant and product gases were determined by varying each gas concentration independently. The four concentrations were varied over the ranges 4–21% CO, 5–25% CO₂, 11–34% H₂O, and 14–55% H₂. To determine the apparent activation energy, the temperature was varied over a range of 30 °C with the catalysts exposed to the standard gas concentrations.

2.7 Diffuse reflectance FTIR

Infrared spectra were obtained with a Nicolet Magna 550 FTIR augmented with a Thermo Spectra Tech Collector II diffuse reflectance (DR) mode attachment and equipped with a high-temperature, high-pressure environmental chamber. All DR spectra were collected *in situ* at a total flow rate of 50 mL min⁻¹ with approximately 10 mg of finely ground sample catalyst. The samples were each exposed to 2 different gas compositions: 6.8% CO and WGS reaction mixture of 6.8% CO, 37.3% CO, 4% H₂O and 8.6% CO₂. The carrier gas, Ar, was fed through a Matheson PUR-Gas Triple Purifier Cartridge to remove trace O₂, hydrocarbons and moisture. DR spectra were collected at 3 different temperatures always in order of decreasing temperature: 200, 120 °C and RT for Au/Al₂O₃ and 280, 120 °C and RT for the Pt samples. The maximum temperatures of 200 °C and 280 °C were chosen to correlate with the temperature used to collect laboratory kinetic data for Au and the two Pt samples, respectively. At each temperature, ten minutes were allowed for equilibration. Before each catalyst was exposed to the adsorbates it underwent surface cleaning by oxidation with 10% O₂ for 10 min at 200 °C and 300 °C for the Au and Pt samples, respectively, followed by reduction in 25% H₂ for 30 min. Background spectra (256 scans) were collected in Ar at each adsorption temperature as the catalyst was cooled to RT from the reduction temperature. Then the catalyst was heated to the highest adsorption temperature, the adsorbing gases were introduced and a DR spectrum was collected with respect to the Ar background. The catalyst was cooled to the next adsorption temperature without changing the gas-phase conditions and a new spectrum was collected. Background spectra for WGS reaction mixture were obtained while flowing Ar through a bubble saturator with H₂O at RT. Collecting backgrounds with H₂O allows for subtraction of gas phase H₂O bands. Spectra were averaged over 32 scans with 4 cm⁻¹ resolution.

Peak fitting and data analysis were completed in CasaXPS v. 2.3.14 slightly modified for IR data compatibility. As adsorbed hydrogen is not visible in IR, and as adsorbed H₂O is not distinguishable from gas phase H₂O, IR characterization was limited to adsorbed CO. CO has been extensively used as a catalyst probe molecule, including during *in situ* WGS.^{5,23} Bands found in the 2100–1700 cm⁻¹ region represent CO bonded on Pt in atop, bridged and threefold sites; CO chemisorbed to Au⁰ is generally found around 2100 cm⁻¹ regardless of the support.^{23–32} The spectra were background subtracted using a straight-line background from 2144 cm⁻¹ (the valley between the P and R branches of the gas phase CO bands) to approximately 1700 cm⁻¹. As the gas phase CO bands overlap chemisorbed CO, a model peak for the P branch of gas phase CO was created from a spectrum of metal-free Al₂O₃ support under WGS conditions. The model peak was highly constrained in shape (FWHM) and position allowing for fits of the very small peaks (linearly adsorbed CO on Au), which would otherwise be obscured by the significantly larger gas phase CO spectrum. For clarity, the CO gas peak was subtracted from the catalyst spectra. All fits assumed Gaussian peaks in positions known for CO adsorbed on Pt

or Au. The fits were optimized *via* a Levenberg–Marquardt algorithm in the CasaXPS software.

2.8 Transmission electron microscopy

The Pt catalyst samples were dispersed in ethanol and sonicated for 10 min, dispersed on 200 mesh carbon-coated copper grids, and dried for 15 min at room temperature. The Z-contrast imaging was done by using an electron microscope (JEM-2010F FasTEMm FEI) manufactured by JEOL, USA operated at 200 kV and an extracting voltage of 4500 V. Since most of the particles were circular in shape, an electronic grid was placed around the nanoparticle image in order to determine the diameter. The particle size distribution was obtained by measuring the diameter of approximately 1000 particles.

3. Results

3.1 Catalyst characterization

It was previously reported that adsorption of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ on SiO_2 at strongly basic pH followed by calcination at 225 °C gives 1–2 nm metallic particles with Pt loadings up to 2%.³³ For the higher loading of this Pt/ SiO_2 catalyst, similarly small sizes were obtained. Impregnation of PtTA on Al_2O_3 followed by calcination at 450 °C also gives small metallic nanoparticles upon reduction. Generally, Al_2O_3 -supported catalysts are less prone to sintering than those supported on SiO_2 . Assuming a H-to-surface Pt atomic ratio of 1, the dispersions estimated from hydrogen chemisorption experiments of both catalysts are near 1.0, *i.e.*, every atom is at the surface of the particles.

Dark-field STEM images are shown in Fig. 1(a) and (b) for Pt/ Al_2O_3 and Pt/ SiO_2 , respectively. For Pt/ SiO_2 , the particle size distribution (not shown) indicates an average size of 1.7 nm with about 5% of the particles larger than 2.5 nm. Similarly, the average particle size on Pt/ Al_2O_3 was 1.5 nm with less than 5% of particles larger than 2 nm.

Additional information on the Pt particle sizes was determined by EXAFS spectroscopy at room temperature after the catalysts were reduced in 4% H_2/He at 300 °C for 30 min. The isolated first-shell EXAFS spectra were obtained by a Fourier transform of the k^2 -weighted data from 2.75 to 12.2 Å^{−1}, followed by an inverse Fourier transform from 1.6 to 3.2 Å. The fit parameters were determined by fitting both the real and imaginary parts of the Fourier transform of the isolated k^2 -weighted EXAFS spectra and are summarized in Table 1. Assuming spherical nanoparticles,^{34,35} the average sizes, determined based on previous correlations of the coordination number, $N_{\text{Pt-Pt}}$, with dispersion,³⁶ give estimates of 1.5 nm for both Pt catalysts, in agreement with STEM and hydrogen chemisorption size estimates.

For these small Pt nanoparticles without adsorbates, there is a contraction in the Pt bond distances (2.69 and 2.68 Å for Pt/ Al_2O_3 and Pt/ SiO_2 , respectively) compared to Pt foil (2.77 Å). This shortened bond distance, however, increases upon adsorption of 4% H_2 (2.69 to 2.73 Å on Pt/ Al_2O_3 and 2.68 to 2.75 Å on Pt/ SiO_2). Similarly, there is a slightly larger increase in Pt bond distance for 7% CO (2.75 Å for Pt/ Al_2O_3 and Pt/ SiO_2).

Fig. 1 STEM dark-field image of (a) 4.3% Pt/ SiO_2 and (b) 2.6% Pt/ Al_2O_3 . Scale bar = 0.02 μm.

The 1% Au/ Al_2O_3 catalyst was a commercial sample provided by the World Gold Council. Au is well known to adsorb little H_2 or CO, ruling out the possibility of using chemisorption to estimate the dispersion and particle size. The Au particle size distribution by TEM was unsuccessful due to the poor contrast between the Au nanoparticles and alumina support. Therefore, the particle size was determined by EXAFS spectroscopy. As shown in Table 1, an estimate from $N_{\text{Au-Au}}$ also gives an average size of about 1.5 nm. In addition, the contraction of the Au bond distance to 2.77 Å is consistent with particles of this size.³⁶ Although there is a small increase of about 0.02 and 0.03 Å, upon adsorption of H_2 and CO, respectively, the change is much smaller than that on Pt and the Au–Au bond distance is still significantly shorter than in Au foil, *e.g.*, 2.88 Å.

3.2 WGS reaction kinetics

Results of the kinetic measurements are summarized in Table 2. An activation energy of approximately 10 kJ mol^{−1} was observed for the Au/ Al_2O_3 catalyst. Although this result is considerably lower than that for the Pt WGS catalysts, *e.g.*, 70–80 kJ mol^{−1}, it is typical of previously reported activation energies for Au/ Al_2O_3 .^{37–39} The rate for Au WGS catalysts has

Table 1 EXAFS fit parameters for the reduced supported Pt and Au catalysts under different treatment conditions at room temperature

Catalysts	Scatter	Gas	N_{M-M} ($\pm 10\%$)	$R/\text{\AA}$ (± 0.02 $\text{\AA}$)	DWF/ $\text{\AA}^2$ ($\times 10^3$)	E_0/eV	Size/nm
Pt/ Al_2O_3	Pt–Pt	He	5.8	2.69	1.5	–5.1	1.6
		H ₂	6.0	2.73	1.5	–6.1	
		CO	6.2	2.75	1.5	–5.3	
Pt/ SiO_2	Pt–Pt	He	5.7	2.69	1.5	–3.3	1.6
		H ₂	6.1	2.75	1.5	–4.9	
		CO	6.2	2.75	1.5	–5.3	
Au/ Al_2O_3	Au–Au	He	5.7	2.77	1.5	–2.6	1.4
		H ₂	5.5	2.77	1.5	–3.8	
		CO	5.6	2.78	1.5	–4.5	

been shown to depend strongly on the particle size.^{40,41} Consequently, it is difficult to make a direct comparison between our measured rates and those of others. Here we report the turn-over-rate (TOR) of Au/ Al_2O_3 and those on Pt/ Al_2O_3 and Pt/ SiO_2 with very similar size (and that of a commercial Cu catalysts with much larger size). The TOR is calculated as the moles of CO reacted per mole of surface metal (Pt, Au, or Cu) per second. At 200 °C the Au/ Al_2O_3 has a TOR, which is about 20 times that of Pt/ Al_2O_3 and has a similar TOR to that of a commercial Cu/ZnO/ Al_2O_3 catalyst. In addition, Pt/ SiO_2 has a TOR, which is about six times higher than Pt/ Al_2O_3 , which indicates the well-known support effect for the WGS reaction.

The reaction orders, activation energies, and rates are similar to what is reported in the literature.^{7,42–44} Small variations are based on factors such as the concentration of feed gases, temperature, or composition of catalysts. For example, in the study by Grenoble *et al.*,⁴³ the CO and H₂O reaction orders were –0.21 and 0.75 for platinum and 0.74 and 0.13 for Au/ Al_2O_3 . However, in that study, hydrogen inhibition of the reaction was not taken into account.

The H₂O and CO₂ reaction orders are very similar for the catalysts reported here. These catalysts, however, do display a variation in the H₂ reaction order, especially for the commercial Cu catalyst. The largest difference between Au and Pt is the CO reaction order. In general, Au catalysts have a CO reaction order near unity, while those for Pt are closer to zero.

3.3 XANES spectra of adsorbates on Pt WGS catalysts

Typically, the L_3 XANES spectra are used to determine the oxidation state, or fraction of metallic and oxidized Pt. Smaller changes in L_3 edge XANES spectra, however, also occur with chemisorption of gases, *e.g.*, H₂ and CO.^{15,16,45} Thus, such changes induced by reactant and product chemisorption can be used to determine adsorbate identity.

In addition, the change in Pt L_3 XANES intensity was shown to be linearly dependent on the amount of adsorbed H₂.¹⁸ Thus, the coverage of gases under WGS reaction conditions can also be determined.

3.3.1 CO adsorption. Adsorption of CO on Pt leads to significant changes in the position, intensity and shape of the Pt L_3 XANES spectrum. Fig. 2(a) shows a comparison of the L_3 edge XANES of 4.3% Pt/ SiO_2 in He at 280 °C, and in 6.8% CO from room temperature to 280 °C. Upon adsorption there is a shift in the edge position to higher energy. In addition, there is an increase in intensity up to about 20 eV above the edge. With increasing temperature up to 280 °C, there is only a small decrease in intensity, suggesting little CO desorbs at high temperature.

If one subtracts the XANES in He from that with adsorbed CO, the difference (or ΔXANES) shows how the shape and intensity of the edge changes with adsorption of CO. Fig. 2(b) shows the ΔXANES spectra of CO adsorption at room temperature, 120 °C, 200 °C, and 280 °C for Pt/ SiO_2 . A very similar series of ΔXANES (not shown) are observed for Pt/ Al_2O_3 . It can be seen that the shape of the ΔXANES is very similar for all temperatures and the spectra differ primarily in intensity. As the temperature increases, the magnitude of the ΔXANES decreases, corresponding to less adsorbed CO. Using the ΔXANES spectrum at RT as the reference, the relative fraction of CO at each temperature can be determined. The results of the ΔXANES fits are given in Table 3. Similar results for single adsorbates are obtained from the usual linear combination fit using the XANES spectra with He and RT CO. Since CO saturates the surface of Pt nanoparticles at RT, the relative coverage also corresponds to the fractional surface coverage. Upon heating to 280 °C, the surface CO coverage is about 70% of that at RT. Very similar CO coverages are obtained on Pt/ Al_2O_3 .

Table 2 Summary of catalytic performances of the supported Pt and Au catalysts and a commercial CuZn catalyst

Catalyst	$T^a/\text{°C}$	$E_a/\text{kJ mol}^{-1}$	Apparent reaction order				Dispersion	TOR ^e /s ^{–1} ($\times 10^{-3}$)
			CO	H ₂ O	H ₂	CO ₂		
Au/ Al_2O_3	180	6	0.79	0.66	–0.24	–0.09	0.91 ^b	21
Au/ Al_2O_3 repeat	180	8	0.78	0.67	–0.25	–0.08	0.67 ^b	26
Pt/ Al_2O_3	240	80	0.11	0.63	–0.44	–0.01	0.77 ^c	1.2
Pt/ SiO_2	190	71	0.08	0.60	–0.15	–0.03	0.48 ^c	7.7
Cu–ZnO/ Al_2O_3 ^d	190	79	0.80	0.80	–0.90	–0.90	0.06	20

^a Temperature at which the reaction orders were determined. ^b Dispersion measured from EXAFS. ^c Dispersion measured by CO chemisorption.

^d CO chemisorption after N₂O oxidation.⁶⁶ ^e Rates calculated at 200 °C, 7% CO, 22% H₂O, 8.5% CO₂, 37% H₂.

Fig. 2 (a) Pt L_3 XANES spectra from 11.54 to 11.59 keV for 4.3% Pt/SiO₂ with adsorbed 6.8% CO (Red: RT; Blue: 120 °C; Green: 280 °C and Pink: He at 280 °C), (b) Pt L_3 Δ XANES spectra of 4.3% Pt/SiO₂ with adsorbed 6.8% CO; (Red: RT; Blue: 120 °C; Pink: 200 °C; Green: 280 °C).

3.3.2 H₂ adsorption. Like CO, adsorption of H₂ leads to a shift in the edge position, increase in the Pt L_3 XANES intensity and a change in shape.^{15–17,45–49} Fig. 3(a) shows a comparison of the Pt L_3 XANES spectra of 4.3% Pt/SiO₂ in He at 280 °C, in 20% H₂ at room temperature, 120 °C, and 280 °C. Fig. 3(b) shows the corresponding Δ XANES spectra for Pt/SiO₂. Similar changes occur on Pt/Al₂O₃ with H₂ adsorption (not shown). As with CO, as the temperature increases, the magnitude of the Δ XANES spectra decreases. Using the Δ XANES spectrum at RT as the reference,¹⁵ the fraction of H₂ at each temperature can be calculated.¹⁵ The fitting results from the Δ XANES spectra are given in Table 3. At 280 °C, the relative coverage decreases to about 27% on Pt/SiO₂ and to 18% on Pt/Al₂O₃. Since at room temperature each surface Pt has one adsorbed H atom, the fractional fits at high temperature correspond to the H₂ surface coverage. Compared to CO, H₂ desorbs more easily, which is in agreement with the lower heat of adsorption.

3.3.3 H₂O adsorption. Compared to CO and H₂, adsorption of H₂O gives smaller changes in the Pt L_3 XANES. Fig. 4(a) compares the XANES spectra of Pt/SiO₂ in He at

200 °C and with adsorbed H₂O at two H₂O vapor pressures (also at 200 °C). Since H₂O condenses and adsorbs on the supports, H₂O adsorption was conducted at elevated temperature. In addition to smaller changes in intensity, there is a slight shift to lower energy upon H₂O adsorption. Fig. 4(b) shows the L_3 Δ XANES of H₂O adsorption at different H₂O vapor pressures for Pt/SiO₂. Consistent with the higher H₂O vapor, there is an increase in the Δ XANES intensity. Since Pt L_3 XANES intensity and position are dependent on the d orbital occupancy, these changes indicate that H₂O is chemically bonded, *i.e.* transfer of some electron density between Pt and H₂O, at this temperature. Since it was not possible to quantify the amount of chemisorbed H₂O on the Pt nanoparticles separately from that physisorbed on the support, the relative coverage (given in parenthesis in Table 3) at 280 °C (relative to that at 280 °C in the absence of other WGS adsorbates) was determined for comparison with H₂O coverage under WGS reaction (discussed below).

3.4 XANES spectra of adsorbates on 1.5 nm Au WGS catalysts

Consistent with the lower adsorption capacity of Au compared to Pt, the changes in XANES spectra with adsorbed gases are much smaller.^{50,51} Because of these small changes, careful calibration of the reference foil and energy correction of the data files are required to avoid small artifacts in the Δ XANES spectra.

3.4.1 CO adsorption. Fig. 5(a) shows the Au L_3 edge XANES spectra of Au/Al₂O₃ in He at 120 °C, in 6.8% CO at room temperature, in 6.8% CO followed by He purge at room temperature, and in 6.8% CO at 120 °C. Compared to adsorption on metallic Pt nanoparticles, the changes due to CO adsorption are very small and there is no shift in the edge position.⁵⁰ Fig. 5(b) shows the Δ XANES spectra on Au/Al₂O₃ at room temperature in 6.8% CO, room temperature with He purge (0% gas phase CO), and at 120 °C in 6.8% CO. In the Δ XANES it is evident that the changes in the XANES shape occur above the edge, *i.e.*, at higher than 11.92 keV. With increasing temperature, there is less adsorbed CO as expected. In addition, removal of gas-phase CO by purging with He also leads to a decrease in adsorbed CO indicating that even at room temperature, some CO is weakly bound.

The fits of relative CO coverage (compared to that at RT) from the Δ XANES adsorption are given in Table 4. Very similar fits were obtained by using a linear combination of Au with out adsorbate (He only) and that with adsorbate at RT. At RT, approximately 40% of the adsorbed CO desorbs with a He purge, and at 120 °C, the relative CO coverage (in flowing CO) is about 35% of that at RT. At 200 °C (spectra not shown), there is about 5% adsorbed CO on these Au nanoparticles.

3.4.2 H₂ and H₂O adsorption. The Au L_3 XANES spectra of Au/Al₂O₃ in He at 120 °C, in 20% H₂ at room temperature, and in 20% H₂ at 120 °C are given in Fig. 6(a). Similar to the adsorption of CO, the changes in the XANES spectra upon H₂ adsorption are very small, and there is no shift of the edge

Table 3 Temperature-dependent EXAFS and XANES fit parameters for Pt WGS catalysts with adsorbed gases

4.3% Pt/SiO ₂								
<i>T</i> /°C	Gas	Relative XANES coverage			EXAFS			
		CO	H ₂	H ₂ O	<i>N</i> _{Pt–Pt} (±10%)	<i>R</i> /Å (±0.02 Å)	DWF/Å ² (× 10 ³)	<i>E</i> ₀ /eV
RT	H ₂	—	1.0	—	6.1	2.75	1.5	−4.9
120	H ₂	—	0.74	—	5.9	2.73	2.7	−5.7
200	H ₂	—	0.53	—	5.9	2.71	3.9	−6.0
280	H ₂	—	0.27	—	5.8	2.70	5.0	−6.6
RT	CO	1.0	—	—	6.2	2.75	1.5	−5.3
120	CO	0.92	—	—	6.5	2.75	2.7	−5.0
200	CO	0.80	—	—	6.5	2.74	3.9	−5.0
280	CO	0.70	—	—	6.4	2.73	5.0	−5.2
280	H ₂ O	—	—	(1.0)	5.9	2.68	5.0	−6.8
280	WGS	0.70	—	(0.07)	6.6	2.74	5.0	−4.7
280	He	—	—	—	5.7	2.68	5.0	−6.9
2.6% Pt/Al ₂ O ₃								
<i>T</i> /°C	Gas	Relative XANES coverage			EXAFS			
		CO	H ₂	H ₂ O	<i>N</i> _{M–M} (± 10%)	<i>R</i> /Å (± 0.02 Å)	DWF/Å ² (× 10 ³)	<i>E</i> ₀ /eV
RT	H ₂	—	1.0	—	6.0	2.73	1.5	−6.1
120	H ₂	—	0.73	—	6.1	2.72	2.7	−6.4
200	H ₂	—	0.47	—	6.2	2.71	3.9	−6.6
280	H ₂	—	0.18	—	5.9	2.70	5.0	−7.1
RT	CO	1.0	—	—	6.2	2.75	1.5	−5.3
120	CO	0.91	—	—	6.4	2.74	2.7	−5.3
200	CO	0.80	—	—	6.4	2.73	3.9	−5.2
280	CO	0.70	—	—	6.4	2.72	5.0	−5.4
280	H ₂ O	—	—	(1.0)	6.5	2.69	5.0	−6.4
280	WGS	0.68	—	(0.12)	6.4	2.73	5.0	−5.4
280	He	—	—	—	5.9	2.69	5.0	−7.2

position.⁵¹ The Δ XANES spectra for adsorbed H₂ at room temperature and at 120 °C are shown in Fig. 6(b). The changes in the XANES spectra also occur above the edge. The fits of the relative coverages (compared to that at RT) are given in Table 4. Similar to the adsorption of CO, H₂ binds weakly to Au with a relative coverage of about 50% at 120 °C and 15% at 200 °C.

Adsorption of H₂O at RT and 120 °C on Au/Al₂O₃ also gives small changes in the XANES spectra [Fig. 7(a)]. The Δ XANES spectra are shown in Fig. 7(b) and the relative coverages are given in Table 4. The relative surface coverage decreases rapidly with increasing temperature, and little is adsorbed at 200 °C. Although the changes in Au XANES with adsorbates are much smaller and indicate weaker adsorption energies than on metallic Pt, the XANES shows that under WGS reaction temperatures, CO, H₂ and H₂O all chemisorb on the Au nanoparticle surface. In addition, despite the very low adsorbate coverage on Au at 200 °C, the WGS TOR is significantly higher than that on Pt, *e.g.*, Table 2.

3.5 FTIR of adsorbed CO

Since the infrared spectra of adsorbed CO are very similar for Pt/Al₂O₃ and Pt/SiO₂,²³ only the results for Pt/SiO₂ are presented here. Fig. 8 shows the diffuse reflectance IR spectra over a range from 2145 to 1700 cm^{−1} for 6.8% CO on 4.3% Pt/SiO₂ at different temperatures. At RT, the data shows three clear peaks, a sharp shoulder at 2088 cm^{−1}, a strong peak at

2070 cm^{−1} with an asymmetric tail and a broad low intensity peak at 1763 cm^{−1}. The largest peak at 2070 cm^{−1} is designated linear-bonded CO, while the asymmetric tail likely represents a distribution of sites that bond CO in a bridged-bonded conformation. While bridged CO is generally expected between 1900–1800 cm^{−1}, Sheppard and Nguyen propose that bridged-bonded CO species occur in the region from about 2000–1800 cm^{−1}.⁵² The low-frequency peak is assigned as three-fold bonded CO.^{23–25,30–32,53} The sharp shoulder is still under debate in the literature and is thought to be due to CO adsorbed in small islands or arrays,³¹ or CO adsorbed on Pt^{δ+}.^{29,30}

As temperature increases to 280 °C, the sharp shoulder shifts to 2078 cm^{−1}, the linear peak shifts to 2060 cm^{−1}, the bridged species becomes more prominent and the three-fold bonded CO peak shifts to 1762 cm^{−1}. It is well known that these shifts are due to a decrease in CO surface coverage leading to less dipole–dipole coupling and a shift to lower frequency.^{28,30} Under WGS conditions at 280 °C, Fig. 8b, there is a small decrease in the linear-bonded CO and a small shifts in the sharp shoulder, and intensity of the three-fold CO peak. The CO coverage measured by FTIR does not change significantly with changing CO or under WGS (CO + H₂O + H₂) reaction mixture.

Fig. 9(a) shows the DRIFTS spectra of CO on Au/Al₂O₃ from 2145 to 1950 cm^{−1} at different temperatures, with the CO gas-phase peak subtracted from the catalyst spectra. Since the peak intensities of CO on Au/Al₂O₃ are a factor of 10 smaller than those on Pt/SiO₂, the gas-phase CO bands obscure the

Fig. 3 (a) Pt L₃ XANES spectra from 11.54 to 11.59 keV for 4.3% Pt/SiO₂ with adsorbed 20% H₂ (Red: RT; Blue: 120 °C; Green: 280 °C and Pink: He at 280 °C) (b) Pt L₃ ΔXANES spectra of 4.3% Pt/SiO₂ with adsorbed 20% H₂; (Red: RT; Blue: 120 °C; Pink: 200 °C; Green: He at 280 °C).

peaks of CO adsorbed on the Au nanoparticles. The subtraction process was only used in presentation of the data, not the true data analysis. The difference spectra, however, allow for better determination of the peak shape, position and intensity. The linear CO adsorption peak is located at 2097 cm⁻¹ is similar to previous studies on metallic Au^{26,27,54} and the position does not change with temperature.

Fig. 9(b) shows the DRIFTS of adsorbed CO on Au under WGS reaction conditions. At both 200 and 120 °C the peak has red-shifted to 2094 cm⁻¹, while at RT the peak has blue-shifted to 2100 cm⁻¹. The blue-shift may result from competitive adsorption of H₂O on the metal as discussed below. At 200 °C the peak areas with 6.8% CO only and during WGS reaction are similarly small each showing a coverage of about 5% that for CO only at RT, while at 120 °C the relative coverage changes to 50% and 40% for CO only and under WGS reaction conditions, respectively. For the WGS gas mixture at RT, the relative coverage is also roughly 40%, a significant decrease from the higher CO-only coverage. The relative coverages determined by IR spectroscopy are very similar to those determined by XANES and ΔXANES fits in Table 4.

Fig. 4 (a) Pt L₃ XANES spectra from 11.54 to 11.59 keV for 4.3% Pt/SiO₂ with adsorbed H₂O at 200 °C (Red: H₂O saturator at 95 °C; Blue: H₂O saturator at 60 °C; Green: He at 200 °C), (b) Pt L₃ ΔXANES with adsorbed H₂O at 200 °C (Red: H₂O saturator at 95 °C; Blue: H₂O saturator at 60 °C).

4. Discussion

4.1 Structure of the Pt and Au WGS catalysts

It has been previously reported that the electronic structures of the atoms in metal nanoparticles differ from the bulk due to the rehybridization of the spd orbitals.⁵⁵ The rehybridization results in an increase in the local electron density between metal atoms, which in turn leads to a higher bond order and subsequently a contraction of the metal-metal bond distances.^{15,36,51,55,56} In the present study, EXAFS experiments reveal that the reduced 1.6 nm supported Pt catalysts have a Pt-Pt bond distance of 2.69 Å (0.08 Å shorter than bulk), and the 1.4 nm supported Au catalyst has a Au-Au bond distance of 2.75 Å (0.13 Å shorter than bulk). This contraction, however, occurs only in the absence of adsorbates. Upon H₂ or CO adsorption, the bond distance increases, as shown in Tables 1 and 3.

From fitting the XANES (or ΔXANES) with adsorbed hydrogen at different temperatures (RT, 120, 200 and 280 °C), the surface coverage was determined (Table 3). Over this temperature range, the EXAFS indicates there is little change in *N*_{Pt-Pt}, or particle size. While the size does not change, the

Fig. 5 (a) Au L_3 XANES spectra from 11.89 to 11.94 keV on 0.7% Au/ Al_2O_3 with adsorbed 6.8% CO (Red: He at 120 °C; Green: CO at RT; Pink: CO at RT followed by He purge; Blue: CO at 120 °C), (b) Au L_3 Δ XANES from 11.89 to 11.94 keV on 0.7% Au/ Al_2O_3 with adsorbed 6.8% CO (Red: CO at RT; Blue: CO at room RT by He purge; Green: CO at 120 °C).

Pt bond distance increases with decreasing temperature. Fig. 10 shows that the Pt–Pt bond distance is linearly correlated with the hydrogen coverage. In addition, extrapolation to zero coverage gives an adsorbate-free bond distance of 2.69 Å, which is the measured bond distance in He at RT and 280 °C

Fig. 6 (a) Au L_3 XANES spectra from 11.89 to 11.94 keV of 0.7% Au/ Al_2O_3 with adsorbed 20% H_2 (Red: He at 120 °C; Blue: H_2 at RT; Green: H_2 at 120 °C), (b) Au L_3 Δ XANES with adsorbed 20% H_2 (Red: RT; Blue: 120 °C).

(Table 1). It is thought that when H_2 is adsorbed on Pt nanoparticles, the Pt–Pt valence electron density is shared by the Pt–H bond making the Pt–Pt bonds weaker and the bond distance longer.^{15,51,56}

In Table 3, it can be seen that the Pt–Pt bond distance also increases upon adsorption of CO. Because CO has a higher heat of adsorption, the surface coverage is higher than that of

Table 4 Temperature-dependent EXAFS and XANES fit parameters for the Au/ Al_2O_3 catalyst with adsorbed WGS gases

$T/^\circ\text{C}$	Gas	XANES relative coverage			EXAFS			
		CO	H_2	H_2O	$N_{\text{Au-Au}} (\pm 10\%)$	$R/\text{\AA} (\pm 0.02 \text{\AA})$	$\text{DWF}/\text{\AA}^2 (\times 10^3)$	E_0/eV
RT	H_2	—	1.0	—	5.4	2.77	1.5	−3.8
120	H_2	—	0.55	—	5.5	2.75	3.0	−4.9
200	H_2	—	0.15	—	5.4	2.75	4.5	−4.1
RT	CO	1.0	—	—	5.2	2.77	1.5	−4.5
RT	CO + He purge	0.60	—	—	5.3	2.77	1.5	−4.0
120	CO	0.35	—	—	5.5	2.76	3.0	−4.5
200	CO	0.05	—	—	5.6	2.75	4.5	−4.0
RT	H_2O	—	—	1.0	5.6	2.78	1.5	−4.1
120	H_2O	—	—	0.40	5.7	2.75	3.0	−4.8
200	H_2O	—	—	0.10	5.8	2.74	4.5	−4.9
RT	WGS	0.65	—	0.35	5.6	2.77	1.5	−4.6
120	WGS	0.45	—	0.15	5.7	2.76	3.0	−4.6
200	WGS	0.10	—	—	5.9	2.75	4.5	−4.4

Fig. 7 (a) Au L_3 XANES from 11.89 to 11.94 keV of 0.7% Au/Al₂O₃ with adsorbed 4% H₂O (Red: He at 120 °C; Blue: H₂O at RT; Green: H₂O at 120 °C), (b) Au L_3 Δ XANES with adsorbed 4% H₂O (Red: RT; Blue: 120 °C).

H₂ at the same temperature. At the same surface coverage, however, the contraction in the Pt–Pt bond distance is similar for CO and H₂. For example, at 70% surface coverage (120 °C for H₂ and 280 °C for CO) on Pt/SiO₂, the Pt–Pt bond distance is 2.73 Å for both adsorbates. At 280 °C and under WGS reaction conditions, the Pt–Pt bond distance is larger than that in He, but is shorter than that of Pt foil. Thus, the Pt–Pt bond distance in small Pt nanoparticles is dependent on the fractional coverage of adsorbates, at least for CO and H₂.

On Au nanoparticles the surface coverage of adsorbates is low. Thus, there is little change in the metallic bond distance in the presence or absence of adsorbates. The metallic bond distance is similar in He, H₂, CO and under WGS reaction and is significantly shorter than that of Au foil.

The EXAFS of both Pt and Au indicate that the active phase is metallic, and for each adsorbate or under WGS reaction condition, there is no indication of oxidized metal as has been suggested for Au on CeO₂.^{11,13}

4.2 The effect of adsorbates on the L_3 XANES spectra

Pt and Au L_3 XANES correspond to the dipole allowed $2p \rightarrow 5d$ electronic transition, and is most often used to

Fig. 8 (a) DRIFTS spectra of 4.3% Pt/SiO₂ with 6.8% CO at 280 °C (blue), 120 °C (green), and RT (red), (b) FTIR spectra of at 280 °C (Blue: 6.8% CO and Red: WGS).

determine the oxidation state of the metal. As shown in this and other studies,^{15–18,45–51} the intensity and position of the L_3 XANES spectra are affected by the surface coverage of adsorbates. Although one can determine the metal oxidation states from the K-edge XANES, similar changes in the XANES shape and intensity induced by adsorbates are not observed.⁵⁷

For Pt, the changes in XANES position and intensity are sufficiently different to be used to identify the type of adsorbates. As shown in Fig. 11, the Δ XANES spectrum of H₂O adsorption at 280 °C for Pt/SiO₂ has a shape distinct from that generated by CO and H₂ adsorption. In an effort to understand these differences in shape, we have performed calculations using the CASTEP code to simulate the XANES spectra.⁵⁸ Briefly, the CASTEP simulation calculates the XANES (or EELS) spectra from matrix elements defined by an initial core state using a one-atom all electron calculation and a final state based upon an “on-the-fly” pseudopotential calculation. A 1×1 unit cell was utilized in order to reduce computational effort. Calculations were performed without the inclusion of a core hole due to the electron shielding of platinum. The calculated spectra are all shifted in energy by a constant value (11 564 eV) so that the calculated edge onset is consistent with experimental

Fig. 9 (a) DRIFTS spectra of 0.7% Au/Al₂O₃ with 6.8% CO at 200 °C (blue), 120 °C (green), and RT (red), (b) FTIR spectra of 1.0% Au/Al₂O₃ under WGS reaction conditions at 200 °C (blue), 120 °C (green), and RT (red).

Fig. 10 Dependence of Pt–Pt bond distance on H₂ coverage; the surface coverage was determined for 20% flowing H₂ at RT, 120, 200 and 280 °C.

results. Gaussian broadening of 3.0 eV is applied to mimic the instrument broadening. We approximate the surface coverage by assuming one monolayer of CO in the 3-fold hollow sites of

Fig. 11 Pt L₃ ΔXANES spectra from 11.54 to 11.59 keV of 4.3% Pt/SiO₂ with different adsorbates at 280 °C (Red: CO; Blue: H₂; Green: H₂O).

Pt(111) (this is the favored site using the PW-91 functional due to the well known over-coordination problem of GGA functionals⁵⁹). Since molecular water does not adsorb strongly on metal surfaces and has a calculated adsorption energy of 0.30 eV,⁶⁰ we model the effect of water adsorption as one monolayer of OH at atop sites on the Pt(111). In both cases, we have chosen coverages that are substantially higher than the experimentally determined values. However, our models, although not quantitative, will allow us to assess the effects of water and CO adsorption from a qualitative standpoint allowing for identification of trends.

Fig. 12(a) shows the simulated Pt L edge XANES (the calculations do not include spin-orbit coupling so we cannot differentiate between the L₂ and L₃ edges) for a platinum atom at the surface of Pt(111) as well as Pt with a monolayer of adsorbed CO and OH. The absorption spectrum shifts by 0.6 eV to lower energies with adsorbed OH and by 1.3 eV to higher energy with adsorbed CO. Fig. 12(b) shows the simulated ΔXANES spectra for CO and OH. It is clear that the simulated spectra replicate many of the features of experimental spectra, showing the positive peak for OH and the negative peak for CO associated with the edge shift. Recent work from Schweitzer *et al.*⁶¹ suggests that the position of the edge is directly related to the density of states at the Fermi level (and not due to the charge transfer effects). Fig. 13 shows the partial d-electron density of states for surface atoms of Pt with and without OH, CO adsorbates. Upon adsorption of OH and CO, two effects are observed. First, the d-electron density is significantly depleted in the presence of an adsorbate. Second, the center of the d-band is shifted away from the Fermi level in the presence of the adsorbate. The d-band center shifts from −2.64 eV for Pt(111) to −4.17 eV for CO/Pt(111) and to −3.39 eV for OH/Pt(111). However, important differences exist as well. While the d-electron density is strongly depleted near the Fermi edge when CO is adsorbed, there is still significant density near the edge when OH is adsorbed. This implies that d-orbitals of different symmetry are involved in the bonding of CO *versus* OH to the Pt(111) surface.⁶²

Fig. 12 (a) Simulated Pt L_3 XANES spectra (Black: Pt(111); Red: Pt(111) with one monolayer of adsorbed CO; Blue: Pt(111) with one monolayer of adsorbed OH), (b) simulated Pt L_3 Δ XANES spectra on Pt(111) (Red: one monolayer of adsorbed CO; Blue: one monolayer of adsorbed OH).

Fig. 13 Calculated partial density of states (Black: Pt(111) without adsorbate; Red: Pt(111) with one monolayer of adsorbed CO; Blue: Pt(111) with one monolayer of adsorbed OH).

In addition, in Fig. 12(a) there is a sharp increase in the XANES intensity above the edge when either CO or OH is

adsorbed. We hypothesize that the increase in intensity is related to the presence of empty (presumably antibonding) states above the Fermi level that are created from hybridization of d-states of the metal with adsorbate states. As proposed by Hoffmann,⁶³ both bonding and antibonding states will be created due to orbital overlap between filled states of the metal and both filled and empty states of the adsorbate. These hybrid states are now allowed transitions since they possess some d -symmetry.

4.3 Changes in the XANES spectra during WGS reaction

The Pt L_3 XANES spectra at 280 °C under WGS reaction and CO only are given in Fig. 14(a). The similarity of these indicates that the major surface species under WGS reaction is CO at about the same coverage as CO only. By subtracting the XANES spectrum under CO from that under WGS conditions, a small residual XANES feature is obtained and is shown in Fig. 14(b). Although this peak is very small, it has the same shape as the Δ XANES of H_2O . Using the Δ XANES of H_2O at 280 °C as the reference, the fit indicates that there is approximately 10% as much adsorbed H_2O under WGS as for H_2O only. The absolute coverage is unknown since it was not possible to quantitatively determine the amount of adsorbed H_2O on the Pt nanoparticles at 280 °C. Much of the reduced surface coverage is due to the high CO coverage, which is about 70%, essentially the same as for CO alone.

While the Δ XANES on Pt are sufficiently different to identify the adsorbed species in a mixture, the changes on Au are much smaller, and the position and shape are more similar. As a result, identification of the adsorbed species is less reliable. Fig. 15 shows the Δ XANES for adsorbed CO, H_2 and H_2O at RT on Au/ Al_2O_3 . While there are subtle differences in shape between CO and H_2 or H_2O , the Δ XANES spectra of H_2 and H_2O are identical. Fig. 16 compares the Δ XANES of the WGS gases and that of CO only at RT. The small difference indicates a second contribution. A fit of the WGS Δ XANES indicates that there is about 65% relative CO coverage and 35% relative H_2O (or H_2) coverage, Table 4. The relative CO and H_2O coverages decrease at 120 °C and there is only a trace amount of adsorbed CO at 200 °C. Small amounts of H_2O (or H_2) are likely present at 200 °C, but are too small to detect. Despite the low surface coverage of reactants on Au, this catalyst has a significantly higher TOR than Pt.

4.4 Comparison of the amount of adsorbed CO by Δ XANES and FTIR

FTIR can be used to quantify CO coverage on supported catalysts where the integrated absorption coefficient (IAC) has been determined. However, the application of IACs is not without difficulties. Hollins and Pritchard²⁸ have summarized some of the corrections that are required in order to be quantitative. For example, there is a transfer of peak intensity from low frequency to higher frequency, a blue-shift due to increased dipole coupling as coverage increases, and an overall intensity loss at high surface coverages.⁶⁴ As a result, significant errors in estimates of the amount of adsorbed CO can occur at high coverage. For our samples, the intensity loss at high

Fig. 14 (a) Pt L_3 XANES spectra from 11.54 to 11.59 keV of 4.3% Pt/SiO₂ at 280 °C (Red: under WGS (6.8% CO + 4% H₂O + 20% H₂) and Blue: 6.8% CO), (b) Pt L_3 ΔXANES spectra (Red: WGS (6.8% CO + 4% H₂O + 20% H₂) – 6.8% CO only; and Blue: 4% H₂O).

Fig. 15 Au L_3 ΔXANES from 11.89 to 11.94 keV of 0.7% Au/Al₂O₃ at RT (Red: 6.8% CO; Blue: 20% H₂; and Green: 4% H₂O).

coverage is especially significant on Pt/Al₂O₃, but occurs to a lesser extent on Pt/SiO₂. While this makes quantification difficult, these effects allow for some qualitative conclusions. For example, the dipole shift to higher wavenumber at lower

Fig. 16 Au L_3 ΔXANES from 11.89 to 11.94 keV of 0.7% Au/Al₂O₃ at RT (Red: 7% CO + 20% H₂ + 4% H₂O; and Blue: 7% CO).

adsorption temperature in Fig. 8 is an indication of an increase in CO coverage, despite the slight decrease in integrated area that is observed by us and others in the literature.⁵⁰

On the Au sample, coverage-dependent effects are not observed due to the low coverage at every temperature and integrated areas can be used for quantification of the relative surface coverages. Using FTIR CO coverage under 6.8% CO as a reference, we compute the Au CO coverages at different temperature and gas mixtures to be very similar to those determined by XANES (or ΔXANES). At 200 °C, on Au there is agreement by IR, XANES and chemisorption that the CO coverage is low. Also, at lower temperatures there is competitive adsorption of CO with H₂O, *i.e.*, the CO coverage is lower with the WGS gas mixture than for CO only. The competitive adsorption of CO with H₂O at low temperature is very different on Au *versus* Pt.

Although the amounts of adsorbed CO are similar by IR and XANES, DRIFTS affords the additional advantage of distinguishing between different CO adsorption conformations, and hence different CO adsorption sites. The advantage of the ΔXANES analysis is that one can identify and quantify IR inactive adsorbates (such as H₂), or highly IR absorbing molecules (such as H₂O). Furthermore, the changes in the XANES imply bond formation at the catalytic site.

4.5 Implications for WGS catalysts

4.5.1 Identification of the active site in Pt and Au WGS catalysts. Although the WGS reaction conditions are strongly reducing, *i.e.*, CO and H₂, the active site for the WGS reaction has been suggested to be ionic Au.^{11,13} While there is no evidence for Au oxide or ionic Au in the EXAFS of this catalyst, the increase in XANES intensity with adsorbates might reflect oxidation of a small number of metallic Au atoms under reaction conditions. Comparison of the ΔXANES for the catalyst oxidized in air and with adsorbed H₂O at RT is shown in Fig. 17 and indicates that the shape and position of oxidized Au and with adsorbed H₂O are substantially different. In addition, as shown in Table 4, the amount of adsorbed H₂O decreases with increasing temperature

Fig. 17 Au L_3 Δ XANES from 11.89 to 11.94 keV of 0.7% Au/ Al_2O_3 at RT (Red: 4% H_2O ; Blue: air at RT).

and is nearly completely desorbed at 200 °C. By contrast, the oxygen coverage on ionic Au does not change with temperature except at temperatures greater than about 350 °C.⁶⁵ Thus, the shape of the XANES spectra and differences in chemical properties indicate that the changes in the Au XANES are due to adsorbate-metal bond formation, rather than oxidation of the metal nanoparticle surface under WGS conditions.¹⁴

Fig. 18 shows a similar comparison of the Δ XANES of oxidized Pt and with adsorbed H_2O . The oxidized Pt Δ XANES was obtained by air oxidation of a 9 nm Pt nanoparticle supported on SBA-15 at RT. Oxidation leads to surface PtO , *i.e.*, Pt^{2+} , with a metallic core. Similar to the effect of H_2O on Au, the change in the Δ XANES intensity for H_2O on Pt increases with increasing partial pressure and decreases with increasing temperature. By contrast the amount of oxidized Pt does not reversibly change with O_2 partial pressure and cannot be desorbed in He until temperatures greater than about 500 °C.³³

The conclusion from both EXAFS and XANES under *operando* conditions, *i.e.*, high reaction rate, is that metallic Au and Pt are the active sites for WGS in these catalysts.

Fig. 18 Pt L_3 Δ XANES from 11.54 to 11.59 keV of 4.3% Pt/ SiO_2 (Red: 4% H_2O at 280 °C; Blue: air at RT on 9 nm Pt/SBA-15).

4.5.2 The influence of adsorption on the observed WGS kinetics. The results from this study also indicate possible reasons why Au has a higher apparent TOR at low reaction temperature, higher CO reaction order and, generally, operates at a lower temperature than Pt. Under WGS reaction conditions, the CO coverage on Pt is high, about 70% at 280 °C. Increasing the partial pressure of CO has a minimal effect on increasing the surface coverage and rate. Thus, the reaction order is near zero. Similarly, as one lowers the reaction temperature on Pt, the CO surface coverage increases to near saturation at room temperature. At low reaction temperatures, therefore, there are few sites to adsorb H_2O . In order to create exposed sites for H_2O adsorption, higher reaction temperatures are required. Finally, since the CO surface coverage is high, especially at low temperature, increasing the CO partial pressure would most likely lead to a decrease in rate by complete saturation of the Pt surface. It is suggested that strong CO adsorption and high surface coverage leads to few exposed catalytic sites and contributes to inhibition of the TOR at low temperature, low reaction order and higher reaction temperatures on Pt.

On Au, the heat of CO adsorption is much lower, leading to significantly lower surface coverage, more exposed catalytic sites and a CO reaction order close to 1. Since the Au surface is not saturated, catalytic activity is possible at lower temperatures than for Pt. In addition, increasing CO partial pressure would increase the surface coverage and reaction rate. At higher pressure, it may even be possible to conduct the WGS reaction at a lower temperature than was done here (1 atm and 200 °C).

There is a continual need to develop WGS catalysts with higher rates per unit volume and which operate at lower temperature where thermodynamics favors H_2 production and lower levels of CO. The results from this study suggest that adsorption is an important factor in determination of the apparent TOR, reaction order of CO and temperature of the reaction. It is expected that improved catalysts will be those having lower heats of CO adsorption than Pt. To be active, the next generation of catalysts will have partial CO coverages at low, or even room temperature.

5. Conclusions

Low-temperature Pt and Au WGS catalysts have been investigated by EXAFS and XANES spectroscopy in order to identify the structure of the active site, and origin of high activity. Using a plug-flow, kinetic-EXAFS reactor, the EXAFS, XANES and kinetic measurements were simultaneously measured. The EXAFS of both Pt and Au indicate the active phase is fully reduced, metallic nanoparticles. At the L_3 edge, the surface-adsorbed species alter the position and shape of the XANES spectra. For Pt, subtraction of the adsorption edge free of adsorbate from that with adsorbate gives a Δ XANES spectrum, which has a unique shape for each adsorbate. Thus, the Pt Δ XANES can be fit to identify the type and coverage of adsorbed species under reaction conditions. During WGS reaction at 280 °C, the CO surface coverage on Pt is approximately 70% similar to that of CO only. While the primary surface species is CO, a small amount of adsorbed H_2O is also observed.

On Au, the changes in the XANES spectra are much smaller, consistent with low coverage of reactants and products. At low temperatures, CO and H₂O are adsorbed, but under reaction temperatures near 200 °C, there is little adsorbed CO, H₂ or H₂O. Nevertheless, the Au TOR is significantly higher than that for Pt. The high TOR of Au is suggested to result from the weak adsorption of CO and the availability of free catalytic sites, even at low temperature, while on Pt, high CO surface coverage leaves few exposed active sites resulting in low rates. The implication is that enthalpy of CO adsorption is an important factor in development of low-temperature WGS activity.

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