

Trinity University

Digital Commons @ Trinity

Chemistry Faculty Research

Chemistry Department

6-2016

Controlling Activity and Selectivity Using Water in the Au-Catalysed Preferential Oxidation of CO in H₂

Johnny Saavedra

Trinity University, jsaaved1@trinity.edu

Todd N. Whittaker

Trinity University, twhattak@trinity.edu

Z. Chen

Christopher J. Pursell

Trinity University, cpursell@trinity.edu

R. M. Rioux

See next page for additional authors

Follow this and additional works at: https://digitalcommons.trinity.edu/chem_faculty

 Part of the [Chemistry Commons](#)

Repository Citation

Saavedra, J., Whittaker, T., Chen, Z., Pursell, C. J., Rioux, R. M., & Chandler, B. D. (2016). Controlling activity and selectivity using water in the Au-catalysed preferential oxidation of CO in H₂. *Nature Chemistry*, 8(6), 584-589. <https://doi.org/10.1038/nchem.2494>

This Article is brought to you for free and open access by the Chemistry Department at Digital Commons @ Trinity. It has been accepted for inclusion in Chemistry Faculty Research by an authorized administrator of Digital Commons @ Trinity. For more information, please contact jcostanz@trinity.edu.

Authors

Johnny Saavedra, Todd N. Whittaker, Z. Chen, Christopher J. Pursell, R. M. Rioux, and Bert D. Chandler

Controlling activity and selectivity using water in the Au-catalysed preferential oxidation of CO in H₂

Johnny Saavedra^{1,2}, Todd Whittaker¹, Zhifeng Chen³, Christopher J. Pursell¹, Robert M. Rioux^{3,4} and Bert D. Chandler^{1*}

Industrial hydrogen production through methane steam reforming exceeds 50 million tons annually and accounts for 2–5% of global energy consumption. The hydrogen product, even after processing by the water–gas shift, still typically contains ~1% CO, which must be removed for many applications. Methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) is an effective solution to this problem, but consumes 5–15% of the generated hydrogen. The preferential oxidation (PROX) of CO with O₂ in hydrogen represents a more-efficient solution. Supported gold nanoparticles, with their high CO-oxidation activity and notoriously low hydrogenation activity, have long been examined as PROX catalysts, but have shown disappointingly low activity and selectivity. Here we show that, under the proper conditions, a commercial Au/Al₂O₃ catalyst can remove CO to below 10 ppm and still maintain an O₂-to-CO₂ selectivity of 80–90%. The key to maximizing the catalyst activity and selectivity is to carefully control the feed-flow rate and maintain one to two monolayers of water (a key CO-oxidation co-catalyst) on the catalyst surface.

The global chemical industry produces over 50 million tons of hydrogen for several important processes, including ammonia and methanol synthesis, petroleum refining and hydrogenation reactions^{1,2}. Hydrogen is produced predominately through a combination of methane steam reforming and water–gas shift reactions; the resulting reformat typically contains about 1% CO in H₂. Many end uses, particularly ammonia synthesis catalysts and fuel cells, are highly sensitive to CO. It must therefore be removed; however, economically removing the last bit of CO has proved challenging. Pressure-swing adsorption requires large capital investments and low flow rates, which reduce throughput and limit H₂ recovery to 70–90%². Methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) uses ~5% of the produced H₂, but actual H₂ losses can be up to 10–15% because of the unselective methanation of CO₂ ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) present in the reformat².

The scale of hydrogen production and the potential for preparing hydrogen of fuel-cell grade make hydrogen purification an enormously impactful process. State-of-the-art Pt–Ru catalysts for the fuel-cell anode require CO levels below 50 ppm; economic hydrogen production with lower CO levels may allow for simpler monometallic anode materials³. Ammonia production for fertilizer accounts for 2–3% of the total global energy consumption⁴, so the use of methanation to purify the hydrogen stream represents an enormous global energy loss. The US National Renewable Energy Laboratory estimates 11.9 kg of CO₂ equivalents are produced for every kilogram of H₂ produced⁵. Consequently, to prevent the (estimated) loss of 1.2 million tons of H₂ used in methanation would eliminate the release of 15 million tons of CO₂ equivalents annually. This is equivalent to saving 35 million barrels of oil per year, or removing more than three million cars from the road⁶.

A more-attractive option for hydrogen purification, which could drastically reduce this hydrogen and energy loss, is the preferential oxidation of CO with O₂ (the PROX reaction). A typical benchmark goal for this reaction, which arises primarily from the requirements for a proton-exchange membrane fuel cell, is to reduce the CO

concentration at the reactor outlet (hereafter referred to as the ‘CO slip’) to 50 ppm with O₂ selectivity to CO₂ $\geq 50\%$ ^{7–9}. We refer to this as the 50/50 goal. Supported Au nanoparticles are well-known to be highly active CO-oxidation catalysts^{10–12} and notoriously poor hydrogenation catalysts¹³. They should be excellent PROX catalysts, but 20 years of research has produced very few catalysts capable of achieving the 50/50 goal (Fig. 1a)^{7,14}. Numerous studies have searched for better catalysts, examining particle-size effects^{12,15}, metal–oxide-support effects^{16,17}, mixed metal oxides^{15,18} and ordered mesoporous materials¹⁹. Bimetallic catalysts²⁰, the inclusion of polyoxometallates in liquid-phase media²¹, Au–ceria nanocomposites²² and embedded Au@CeO₂ catalysts²³ have also been examined, with limited success.

A general lack of consensus on the CO-oxidation mechanism has hampered catalyst development. Surface hydroxyl groups on the support are clearly necessary for the most-active catalysts^{24–26}, and we showed¹¹, following work by the Haruta^{27,28}, Davis^{26,29}, Fujitani³⁰ and Iglesia³¹ groups, that water greatly enhances reaction rates. Several groups also suggested that oxygen vacancies on the support play in important mechanistic role^{32–34}. More-specific mechanistic PROX investigations by Widmann *et al.* showed that H₂ promotes CO oxidation over Au and the same activated oxygen species is involved in both H₂ and CO oxidation³⁵. There is a fairly clear consensus that, for low-temperature CO oxidation, the metal–support interface plays a critical role in the catalysis^{11,30,35–38}.

We recently proposed a new mechanism for CO oxidation over Au/TiO₂ catalysts, in which water functions as a co-catalyst¹¹; the study reported herein applies our newly found mechanistic understanding to CO PROX. Preliminary tests showed that Au/Al₂O₃ catalysts have the same basic CO-oxidation reaction kinetics, and therefore probably operate via the same mechanism (Supplementary Section 3.1) as Au/TiO₂. The Au/Al₂O₃ catalysts were more selective for PROX in our initial testing, so we focused additional studies on this system. Although the promotional effects of water in PROX have been reported^{7,39}, there is no

¹Department of Chemistry, Trinity University, San Antonio, Texas 78212-7200, USA. ²Pacific Northwest National Laboratory, Richland, Washington 99352, USA. ³Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802-4400, USA. ⁴Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802-4400, USA. *e-mail: bert.chandler@trinity.edu

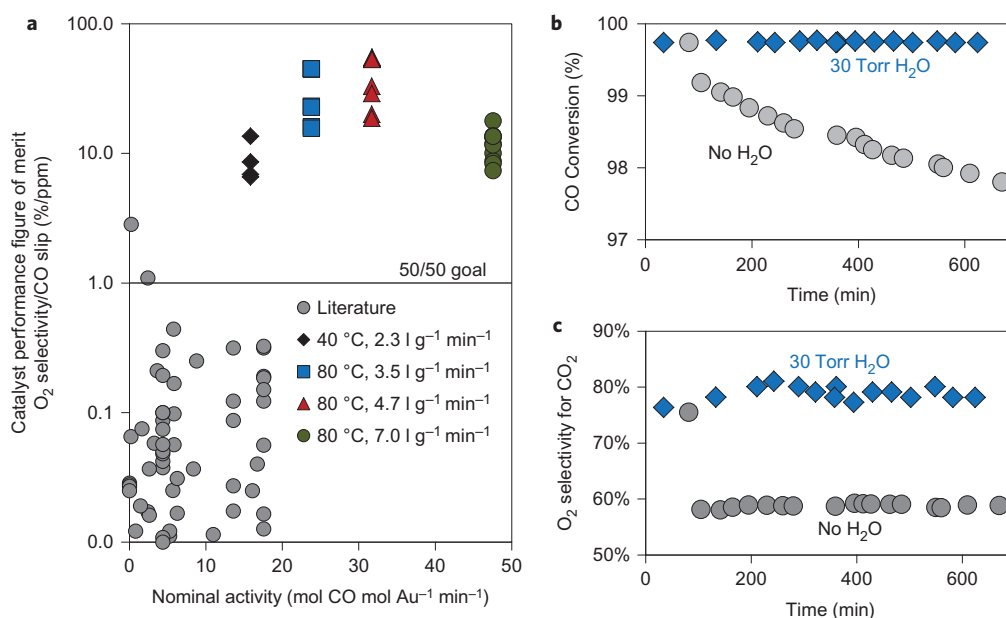


Figure 1 | PROX performance and deactivation of Au/Al₂O₃ with water in the feed (1% CO, 1.4% O₂, 60% H₂, balance He). **a**, Performance (described by the figure of merit in equation (1)) comparison between Au/Al₂O₃ operated at 40 °C and 80 °C (various SVs, 1–20 Torr H₂O (see Fig. 2)) and literature reports (Supplementary Table 8). When the feed-water content and SV are properly controlled, this Au/Al₂O₃ catalyst far surpasses the literature reports of CO PROX performance, and easily achieves the literature benchmarks. **b,c**, CO conversion (**b**) and O₂ selectivity (**c**) during ten hour experiments with Au/Al₂O₃ at 80 °C. When water is removed, the selectivity immediately drops; CO oxidation activity also drops, but more slowly. Thus, maintaining sufficient water on the catalyst prevents deactivation over ten hours, and is critical for optimum catalyst performance. CO-conversion measurements are typically $\pm 0.02\%$; O₂-selectivity measurements are typically $\pm 5\%$.

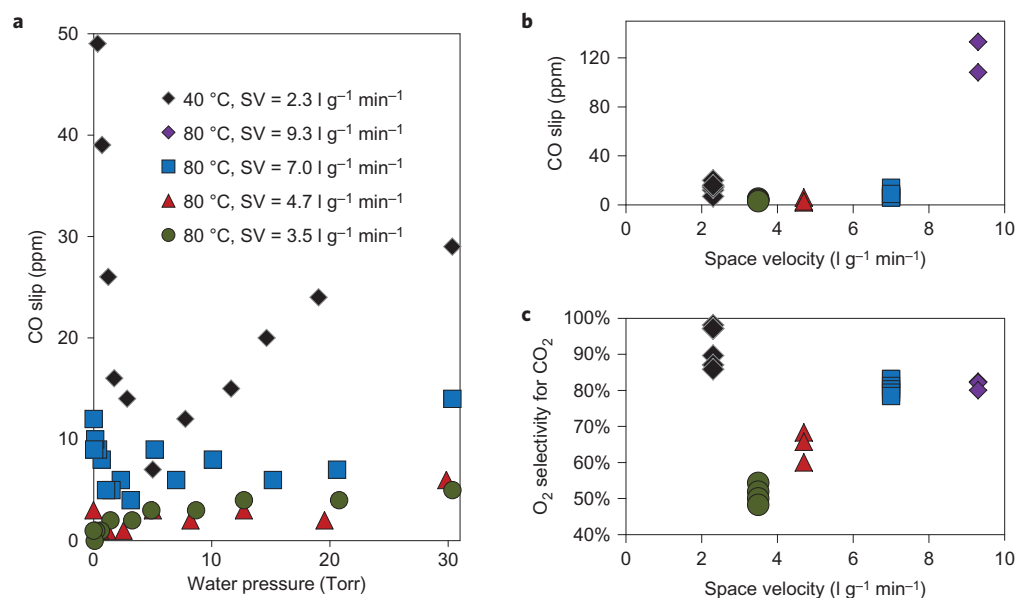


Figure 2 | High conversion PROX reactivity over Au/Al₂O₃. **a**, CO slip versus $P_{\text{H}_2\text{O}}$ at several SV values; CO slip is equivalent to the concentration of CO in the reactor outlet. At 40 °C, activity (low CO slip) and selectivity ($\sim 90\%$) are maximized at ~ 5 Torr added water; CO-oxidation activity increased at 80 °C, but the reaction was less sensitive to added water. **b**, CO slip versus SV for the data in **a**. **c**, O₂ selectivity versus SV for the data in **a**. The data demonstrate that controlling SV can tune the catalyst performance. When the SV is low, very low CO slips (~ 5 ppm) are achieved, but at the expense of O₂ selectivity. Similarly, if the SV becomes too high, there is insufficient time for the CO to react fully and the CO slip increases. This indicates that the two reactions are essentially sequential: a majority of the CO reacts first, and then the remaining O₂ begins to react with the available H₂. There appears to be a maximum O₂ selectivity of about 80% at 80 °C, which suggests there is insufficient added water.

systematic study that seeks to control the activity and selectivity by adjusting the feed-water content. Herein we show that carefully controlling the feed-water content and space velocity (SV) leads to significant improvements in catalyst performance—far surpassing the

50/50 goal. We also show that the catalyst functions best when the surface coverage of water on the support is about one monolayer and interpret the activity and selectivity gains in terms of our most-recent mechanistic proposal.

Results and discussion

Influence of water on catalyst performance. We studied a commercial Au/Al₂O₃ catalyst, controlling the water content in a model reformate gas stream (Supplementary Section 2.1-3). As catalysts are tested under a wide variety of conditions in various labs, we defined a figure of merit (FOM, Supplementary Section 3.2) to compare efficiently the key aspects of catalyst performance:

$$\text{FOM} = \frac{\text{O}_2 \text{ selectivity (\%)}}{\text{CO slip (ppm)}} \quad (1)$$

For reference, a FOM value of one describes a catalyst and reaction conditions that meet the 50/50 goal.

Figure 1a plots several FOM values against the nominal activity for some of our experimental conditions. Approximately 60 literature reports are included (details in Supplementary Section 3.3); most of the data were collected at 80 °C, the operating temperature of many fuel-cell systems³. The literature results vary greatly, so the nominal activities are normalized to the total amount of Au, with no adjustments made for Au particle size. We are aware of only two reports that achieve the 50/50 goal, both of which use low SVs and nominally dry feeds^{7,14}. By controlling the amount of water added to the reaction (*vide infra*) and using higher SVs, we far surpassed the 50/50 goal, and did so at SVs 1–2 orders of magnitude larger than those in the literature (Fig. 1a and Supplementary Table 8).

Catalyst deactivation is similarly important in PROX, and water may prevent the deposition of carbonates, which poison CO oxidation^{8,40,41}. Long-term activity and selectivity plots are shown in Fig. 1b,c, respectively. When water is added to the feed, there is no deactivation over the course of ten hours, and O₂ selectivity remains both constant and high (~80%). When water is removed, O₂ selectivity immediately drops and the CO-oxidation activity begins to degrade over time. These experiments, which employed an unoptimized catalyst, show that huge improvements in PROX performance are possible when the feed-water content is controlled carefully. Furthermore, the potential hydrogen production per unit time is increased by 1–2 orders of magnitude over previous reports, with negligible catalyst deactivation over ten hours.

SV effect. Figure 2 shows CO slip and O₂ selectivity data for the experiments in Fig. 1a. The experimental protocol (Supplementary Section 2.2-3) was critical to achieve a high activity and selectivity, so catalysts were always equilibrated with 30 Torr water before initiating the reaction. The water pressure (*P*_{H₂O}) was then systematically lowered, which allowed the CO conversion to stabilize at each *P*_{H₂O} (generally over 30 minutes). To achieve a high activity and selectivity it is critical to control the SV, which is simply the flow rate normalized to the amount of catalyst. When both *P*_{H₂O} and SV are controlled properly (Fig. 2b,c), the reaction can operate at very high conversions (99.9%, <10 ppm CO slip) and still maintain a high O₂ selectivity (>80%); if the SV drops too low, O₂ selectivity suffers (Fig. 2c).

A SV study at 20 °C (Fig. 3) demonstrated that CO conversion increases as the SV decreases, whereas O₂ selectivity is essentially the same up to 99% CO conversion. Similarly, when CO conversions are high (CO slip ~10 ppm), a decrease in the SV only serves to decrease the O₂ selectivity (Fig. 2b,c; 80 °C). These data indicate that the PROX reaction is largely sequential, with CO reacting before H₂. This conclusion differs somewhat from the most-popular literature mechanisms, which either require H₂ activation to generate the active oxidant⁴² or utilize support O atoms³⁵.

The trends in PROX activity and selectivity, both for our data and much of the PROX literature, can be readily understood in the context of our recently proposed CO-oxidation mechanism for Au/TiO₂ (ref. 11). The key elements of this mechanism are:

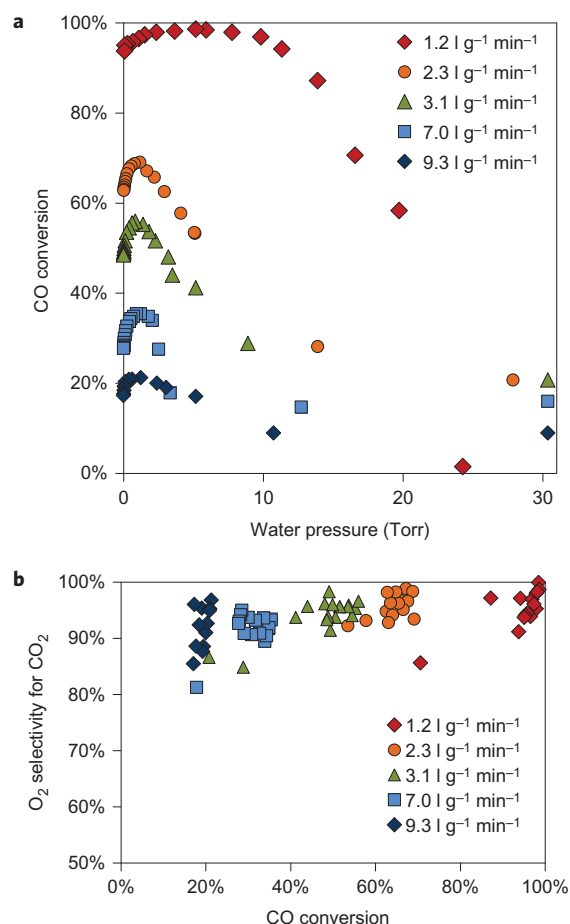


Figure 3 | Effect of SV on CO PROX catalysis over Au/Al₂O₃.

a, CO conversion as a function of water content at several different values for the SV. **b**, O₂ selectivity for CO₂ as a function of CO conversion at 20 °C. These data show that CO conversion increases as the SV decreases, whereas O₂ selectivity is essentially the same up to a 99% CO conversion. Although there is a small amount of nascent H₂ oxidation at all conversions, the reaction is largely sequential—CO is oxidized first, and then the catalyst begins to oxidize H₂. CO conversion measurements are typically ±0.02%; O₂-selectivity measurements are typically ±5%.

(1) the facile generation of reactive Au–OOH from O₂ and a proton from water adsorbed at the metal–support interface, (2) a very low reaction barrier between Au–OOH and Au–CO and (3) the rate-limiting decomposition of Au–COOH (ref. 11). The CO-oxidation kinetics and H/D kinetic isotope effect for Au/Al₂O₃ are essentially identical to those of Au/TiO₂, which indicates the same mechanism is probably at work (Supplementary Section 3.1). Our results are largely consistent with the extensive PROX mechanistic work from Behm's group^{8,35} and Piccolo and co-workers⁴²; however, there are two important distinctions from their previous interpretations. First, H₂ activation is not required for the CO-oxidation activity because the active Au–OOH species is derived from O₂ and water. Second, our mechanism does not require the participation of support O, which makes it consistent with isotope-labelling studies in the absence of H₂ (refs 29,31).

Influence of temperature and water coverage. To explore further the roles of water and temperature in PROX, we operated the catalyst under a similar conversion at several temperatures. For each temperature, this necessitated adjusting the SV to achieve a roughly 75% CO conversion at 30 Torr added water. The feed-water content was then decreased systematically. To visualize the trends (Fig. 4a),

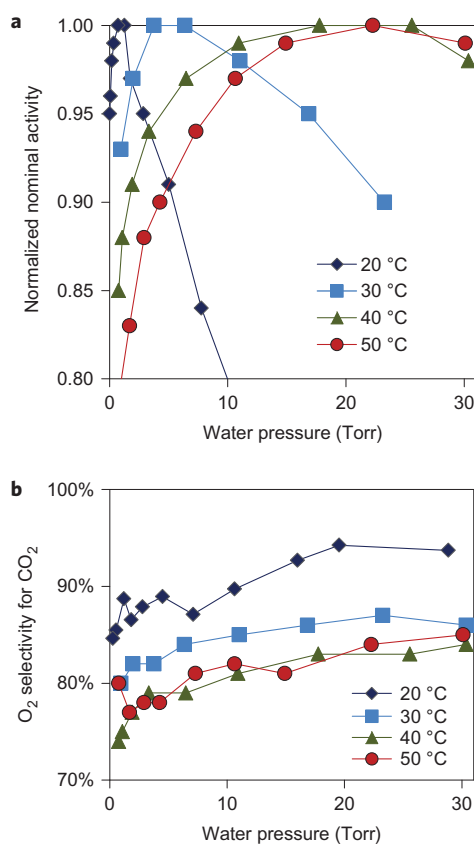


Figure 4 | Effect of water and temperature on CO PROX catalysis over Au/Al₂O₃. **a,b**, Normalized nominal activity (**a**) and O₂ selectivity for CO₂ (**b**) as functions of $P_{\text{H}_2\text{O}}$ and temperature. As the reaction temperature increases, the water pressure required to reach the maximum activity shifts to a higher $P_{\text{H}_2\text{O}}$ and broadens substantially. This suggests that a certain water coverage on the support yields the highest activity. Additionally, the selectivity for CO₂ decreases somewhat as the reaction temperature increases. This is consistent with the mechanistic role of water as a co-catalyst in CO oxidation. Activity measurements are typically $\pm 0.02\%$; O₂-selectivity measurements are $\pm 5\%$.

the nominal activity was normalized to the maximum CO conversion at that temperature; associated O₂ selectivity plots are given in Fig. 4b. At 20 °C, Fig. 4a shows a maximum activity at ~ 2 Torr added water; this value is somewhat lower than the maximum found for CO oxidation in the absence of H₂ (~ 4 – 5 Torr (Supplementary Section 3.4)). This is readily explained by the O₂-selectivity data, which show that O₂ selectivity drops at low $P_{\text{H}_2\text{O}}$. There are two sources of water

in the system—water intentionally added to the inlet feed stream and water produced *in situ* from H₂ oxidation. As Table 1 shows, under the conditions that yield the maximum activity at 20 °C, the water produced *in situ* is important because it accounts for about half of the total water in the system. This explains why so many catalyst reports in the literature show a relatively low activity and O₂ selectivity using dry feeds—in the absence of sufficient surface water, the system oxidizes H₂ to generate the water co-catalyst necessary to oxidize CO. As the amount of water on the support is governed by adsorption–desorption equilibrium and the gas flow constantly removes water from the catalyst surface, the catalyst must constantly oxidize H₂ to maintain a somewhat consistent water coverage on the support. Thus, with insufficient water in the feed, neither high activity nor selectivity is attainable.

The $P_{\text{H}_2\text{O}}$ range that yields the highest activity increases dramatically as the temperature increases, that is, the peak in Fig. 4a broadens with temperature. This is entirely consistent with the important mechanistic role of water adsorbed on the support because, as the water-adsorption isotherms in Fig. 5a show, as the temperature increases, increasing $P_{\text{H}_2\text{O}}$ causes a small change in the amount of adsorbed water. To illustrate this, we used the activity and selectivity data from Fig. 4 to estimate the total amount of water in the system (water intentionally added plus water formed by H₂ oxidation) at the activity maximum. This estimate was used along with the adsorption isotherms to estimate the water coverage ($\theta_{\text{H}_2\text{O}}$) at the activity maximum (Table 1). At each temperature, the maximum activity occurs at about the same $\theta_{\text{H}_2\text{O}}$ (6–9 molecules nm⁻²), which corresponds to roughly one monolayer of water on the support⁴³. This range is illustrated by the box outline in Fig. 5a. This optimum water coverage is compellingly consistent, and is similar to the maximum value found for CO oxidation over Au/TiO₂ (~ 13 molecules nm⁻²) (ref. 11).

As Figs 3a and 4a show, if $\theta_{\text{H}_2\text{O}}$ increases above the apparent maximum of approximately one monolayer, then catalytic activity drops. Water binds more strongly to itself than it does to Au (ref. 44); indeed, Au surfaces are considered hydrophobic and require cryogenic experiments to observe water adsorption⁴⁵. This suggests the drop in activity is caused by water that is adsorbed on the support at the metal–support interface physically blocking CO from adsorbing on the Au particles. To test this, we measured CO-adsorption isotherms in the presence of water (Fig. 5b) using infrared spectroscopy⁴⁶. Even in the $P_{\text{H}_2\text{O}}$ regime in which the activity increases to the maximum value, CO adsorption decreases by 50% relative to the amount adsorbed in the absence of water. Nominal activities for CO oxidation are largely insensitive to CO pressure in this kinetic regime (Supplementary Section 3.1), so physical blocking has little impact on CO-oxidation activity until a very large fraction of the Au sites is blocked.

Beyond the influence on catalytic activity, Figs 1c and 4b clearly show that the addition of water also improves O₂ selectivity. This,

Table 1 | Estimated water content and coverage at maximum PROX activity.

Temperature	20 °C	30 °C	40 °C	50 °C
SV (l g _{cat} ⁻¹ min ⁻¹)	2.3	3.5	4.7	9.3
$P_{\text{H}_2\text{O}}$ at maximum activity*	1.5 Torr	6.1 Torr	17.8 Torr	22.3 Torr
CO conversion	68%	70%	82%	68%
O ₂ conversion	28%	30%	35%	30%
O ₂ selectivity for CO ₂	87%	84%	84%	83%
Total O ₂ converted	3,910 ppm	4,170 ppm	4,940 ppm	4,100 ppm
O ₂ lost to H ₂ oxidation	508 ppm	667 ppm	840 ppm	696 ppm
H ₂ O produced <i>in situ</i>	0.8 Torr	1.0 Torr	1.3 Torr	1.0 Torr
Estimated total $P_{\text{H}_2\text{O}}$	2.3 Torr	7.1 Torr	19 Torr	23 Torr
Adsorbed H ₂ O†	2.4 mmol g ⁻¹	3.1 mmol g ⁻¹	3.5 mmol g ⁻¹	2.7 mmol g ⁻¹
$\theta_{\text{H}_2\text{O}}$ (molecules nm ⁻²)‡	6.1	7.6	8.9	7.1

*From Fig. 4a. Feed: 10,000 ppm (1%) CO, 14,000 ppm (1.4%) O₂, variable water, 60% H₂, balance He. †Estimated from the total $P_{\text{H}_2\text{O}}$ and water-adsorption isotherms (Fig. 5a). ‡Based on the N₂ BET (Brunauer, Emmett and Teller) surface area.

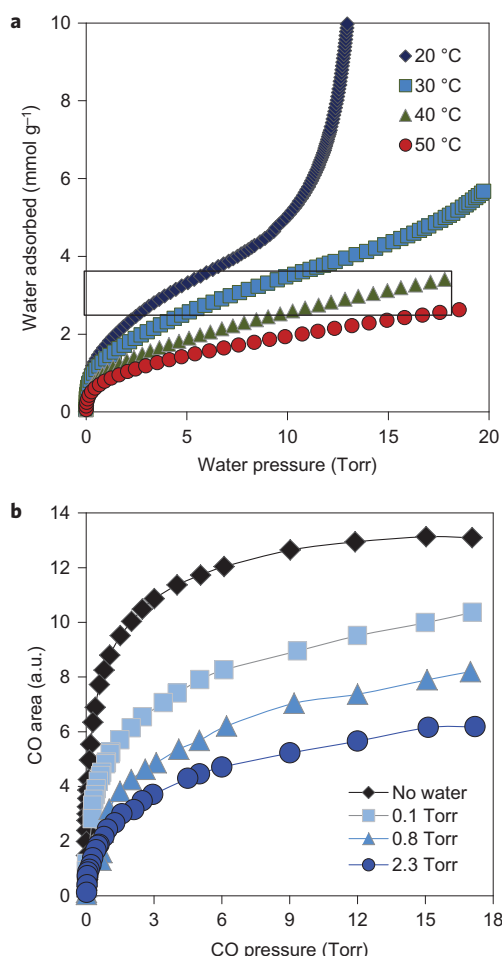


Figure 5 | Gas-adsorption data. **a**, Volumetric water-adsorption isotherms (20–50 °C) on the Au/Al₂O₃ catalyst. As the temperature increases, the amount of water adsorbed on the catalyst at a given pressure decreases substantially. The box indicates the range of $\theta_{\text{H}_2\text{O}}$ that corresponds to the activity maxima in Fig. 4a and Table 1. A relatively narrow range of water coverage enables the highest CO-oxidation activity, regardless of the reaction temperature. **b**, CO-adsorption isotherms (20 °C) determined by infrared spectroscopy in the presence and absence of water. At pressures as low as 2.3 Torr, at which total CO oxidation activity is maximized, roughly half of the CO-adsorption sites are blocked by water. This is presumably because of the physical blocking of the adsorption sites at the metal-support interface by water adsorbed on the support. Errors in adsorption-isotherm measurements are typically $\pm 5\%$. a.u., arbitrary units.

too, can be understood in the context of our recently proposed reaction mechanism for CO oxidation¹¹. The $P_{\text{H}_2\text{O}}$ and SV studies indicate that the reaction is largely sequential, such that most of the CO is consumed before H₂ is oxidized. This suggests catalyst selectivity is largely determined by the competition between adsorbed CO and H₂ for the Au–OOH intermediate. Spectroscopic evidence for peroxo and superoxo species stabilized on the support have been reported for Au/CeO₂ catalysts⁴⁷. CO binds to Au much more strongly than does H₂, so the CO coverage is expected to be high relative to the H₂ coverage, even under excess H₂. When the reaction is pushed to a very high CO conversion (Fig. 2), towards the bottom of the catalyst bed there are sufficient Au sites available for H₂ to react. Thus, the SV, conversion and water coverage control the fraction of Au sites available to catalyse H₂ oxidation.

There may also be kinetic influences on the high selectivity. Our previous density functional theory study found a very low reaction barrier (0.1 eV) for Au–CO reacting with Au–OOH (ref. 11). Hydrogen chemisorption on Au is an activated process⁴⁸, which

suggests that at a low temperature this may be slow relative to CO activation. The general trend of decreasing O₂ selectivity as temperature increases (Fig. 4b) is also consistent with a H₂ adsorption/reaction with Au–OOH having a larger activation barrier.

At all the temperatures studied, PROX selectivity generally increased with $P_{\text{H}_2\text{O}}$ (Fig. 4b). Behm's group showed that CO and H₂ compete for a common reactive oxygen intermediate³⁵, which indicates that water has a larger effect in blocking H₂-adsorption sites than it does in blocking CO sites (Fig. 4b). As water is adsorbed on the support, this is consistent with the conclusion that H₂-adsorption/activation sites are located at the metal-support interface^{35,36,42}. This provides an interesting positive feedback loop—when water coverage is low, H₂ oxidation begins to produce water, which accelerates CO oxidation. This interpretation is largely consistent with the bulk of the PROX mechanistic literature, and explains why previous studies have not successfully achieved the 50/50 goal.

Our results show that an unoptimized catalyst can be a commercially viable H₂-purification catalyst provided the SV, $\theta_{\text{H}_2\text{O}}$ and reaction temperature are controlled carefully. Understanding the fundamental steps in the reaction mechanism essentially turns this from a catalyst optimization problem to one of reaction engineering. Controlling SV and $\theta_{\text{H}_2\text{O}}$ essentially allows us to tune the number of available active sites, which allows adjustments for differing feeds. This is a substantial advantage, and potentially allows us to uncover additional active sites as a catalyst begins to deactivate over time (for example, because of sulfur poisoning). For wet feeds, this may be accomplished simply by cooling to a temperature at which the water vapour pressure is close to the $P_{\text{H}_2\text{O}}$ required for the maximum catalytic activity.

This is not to say that the catalyst cannot or should not be optimized; rather, the mechanistic understanding provides similarly clear directions as to how the catalyst can be improved or tuned for specific conditions. Balancing the water-binding properties of the support with the feed-water content is likely to be important. Supports that bind water more tightly will be desirable for relatively dry feeds—this should reduce the need to add water to the system; conversely, supports that bind water weakly will probably be better for wet feeds. Selectivity improvements should arise from tuning the CO- and H₂-binding properties of Au, as Bond *et al.* suggested¹³. Any electronic effects (for example, support effects, particle-size effects or promoters) that increase the CO-adsorption energy relative to the H₂-adsorption energy should provide for a greater differentiation between the two reactants and a higher selectivity.

Methods

Further details are available in the Supplementary Information. Catalysis experiments were performed in a single-pass plug-flow microreactor. The reaction zone consisted of finely ground fresh catalyst (5–100 mg) diluted in SiC (1,200 mg). Gas flows were controlled with electronic mass-flow controllers. The gas-feed (1% CO, 1.4% O₂, 60% H₂, balance He 140 ml min^{−1}; SV = 1.4–28 l g^{−1} min^{−1}) and reactor-effluent compositions were determined using a Siemens Ultramat 23 infrared gas analyser. Moisture (0.1–30 Torr) was added to the feed with a water saturator immersed in a cooling bath. The reaction temperature (20–80 °C) was maintained with a water bath and recirculating water pump. The catalyst was first stabilized in the wettest reactive atmosphere until steady-state conditions were reached. The feed-water pressure was then decreased by decreasing the saturator-bath temperature.

CO-adsorption infrared experiments were performed as described previously⁴⁹. Approximately 25 mg of the sample were pressed into a 30 × 30 mesh Ti wire cloth (Unique Wire Weaving Co.) and mounted into a custom-built copper cell and vacuum chamber with a gas-phase optical-path length of 1.2 cm. The sample was first dried under vacuum at room temperature and a background spectrum was recorded. CO (20 Torr) was added to the cell and allowed to equilibrate for 5–10 minutes. Once at equilibrium, an infrared spectrum was collected. The CO pressure was then decreased incrementally and infrared spectra were collected at each equilibrated CO pressure. The cell was then evacuated, 0.1 Torr water was added to the chamber and allowed to equilibrate. CO was then added incrementally to the chamber and infrared spectra were collected at each CO pressure. This general procedure was repeated for higher water pressures.

Water-adsorption isotherms were measured at four different temperatures (20, 30, 40 and 50 °C) using a Micromeritics 3Flex volumetric adsorption apparatus.

Details of the sample pretreatment are given in Supplementary Section 2.7. The sample temperature was maintained using a Neslab recirculating bath coupled to a Cryofab Dewar. The water-source temperature was maintained at 43 ± 0.1 °C and the instrument manifold was maintained at 45 ± 0.02 °C. During the measurements, small doses of water (0.05 mmol g^{-1}) were equilibrated with the sample to develop high-resolution adsorption and desorption isotherms.

Received 1 May 2015; accepted 8 March 2016;
published online 18 April 2016

References

- Neef, H. J. International overview of hydrogen and fuel cell research. *Energy* **34**, 327–333 (2009).
- Liu, K., Song, C. & Subramani, V. *Hydrogen and Syngas Production and Purification Technologies* (John Wiley & Sons, Inc., 2010).
- Ghenciu, A. F. in *Fuel Cells Compendium* (eds Brandon, N. & Thompson, D.) Ch. 5, 91–106 (Elsevier, 2005).
- European Commission *Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers* (European Commission, 2007).
- Spath, P. L. & Mann, M. K. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming* (Department of Energy, National Renewable Energy Laboratory, 2001).
- Greenhouse Gas Emissions Calculations and References (US Environment Protection Agency, 2015); www.epa.gov/energy/ghg-equivalencies-calculator-calculations-and-references
- Landon, P. *et al.* Selective oxidation of CO in the presence of H₂, H₂O and CO₂ utilising Au/α-Fe₂O₃ catalysts for use in fuel cells. *J. Mater. Chem.* **16**, 199–208 (2006).
- Schumacher, B., Denkwitz, Y., Plzak, V., Kinne, M. & Behm, R. J. Kinetics, mechanism, and the influence of H₂ on the CO oxidation reaction on a Au/TiO₂ catalyst. *J. Catal.* **224**, 449–462 (2004).
- Lakshmanan, P., Park, J. & Park, E. Recent advances in preferential oxidation of CO in H₂ over gold catalysts. *Catal. Surv. Asia* **18**, 75–88 (2014).
- Green, I. X., Tang, W., Neurock, M. & Yates, J. T. Jr. Spectroscopic observation of dual catalytic sites during oxidation of CO on a Au/TiO₂ catalyst. *Science* **333**, 736–739 (2011).
- Saavedra, J., Doan, H. A., Pursell, C. J., Grabow, L. C. & Chandler, B. D. The critical role of water at the gold–titania interface in catalytic CO oxidation. *Science* **345**, 1599–1602 (2014).
- Valden, M., Lai, X. & Goodman, D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science* **281**, 1647–1650 (1998).
- Bond, G. C., Louis, C. & Thompson, D. T. *Catalysis by Gold* Vol. 6 (Imperial College Press, 2006).
- Avgiropoulos, G. *et al.* A comparative study of Pt/γ-Al₂O₃, Au/α-Fe₂O₃ and CuO–CeO₂ catalysts for the selective oxidation of carbon monoxide in excess hydrogen. *Catal. Today* **75**, 157–167 (2002).
- Grisel, R. J. H. & Nieuwenhuys, B. E. Selective oxidation of CO, over supported Au catalysts. *J. Catal.* **199**, 48–59 (2001).
- Ivanova, S., Pitchon, V., Petit, C. & Caps, V. Support effects in the gold-catalyzed preferential oxidation of CO. *ChemCatChem* **2**, 556–563 (2010).
- Widmann, D., Liu, Y., Schueth, F. & Behm, R. J. Support effects in the Au-catalyzed CO oxidation—correlation between activity, oxygen storage capacity, and support reducibility. *J. Catal.* **276**, 292–305 (2010).
- Tompos, A. *et al.* Role of modifiers in multi-component MgO-supported Au catalysts designed for preferential CO oxidation. *J. Catal.* **266**, 207–217 (2009).
- Liu, Y. *et al.* Three-dimensionally ordered macroporous Au/CeO₂–Co₃O₄ catalysts with mesoporous walls for enhanced CO preferential oxidation in H₂-rich gases. *J. Catal.* **296**, 65–76 (2012).
- Li, X. *et al.* Activation and deactivation of Au–Cu/SBA-15 catalyst for preferential oxidation of CO in H₂-rich gas. *ACS Catal.* **2**, 360–369 (2012).
- Kim, W. B., Voith, T., Rodriguez-Rivera, G. J., Evans, S. T. & Dumesic, J. A. Preferential oxidation of CO in H₂ by aqueous polyoxometalates over metal catalysts. *Angew. Chem. Int. Ed.* **44**, 778–782 (2005).
- Carrettin, S., Concepcion, P., Corma, A., Lopez Nieto, J. M. & Puentes, V. F. Gold catalysts: nanocrystalline CeO₂ increases the activity of Au for CO oxidation by two orders of magnitude. *Angew. Chem. Int. Ed.* **43**, 2538–2540 (2004).
- Cargnello, M. *et al.* Active and stable embedded Au@CeO₂ catalysts for preferential oxidation of CO. *Chem. Mater.* **22**, 4335–4345 (2010).
- Singh, J. A., Overbury, S. H., Dudney, N. J., Li, M. & Veith, G. M. Gold nanoparticles supported on carbon nitride: influence of surface hydroxyls on low temperature carbon monoxide oxidation. *ACS Catal.* **2**, 1138–1146 (2012).
- Ketchie, W. C., Murayama, M. & Davis, R. J. Promotional effect of hydroxyl on the aqueous phase oxidation of carbon monoxide and glycerol over supported Au catalysts. *Top. Catal.* **44**, 307–317 (2007).
- Ide, M. S. & Davis, R. J. The important role of hydroxyl on oxidation catalysis by gold nanoparticles. *Acc. Chem. Res.* **47**, 825–833 (2014).
- Date, M. & Haruta, M. Moisture effect on CO oxidation over Au/TiO₂ catalyst. *J. Catal.* **201**, 221–224 (2001).
- Date, M., Okumura, M., Tsubota, S. & Haruta, M. Vital role of moisture in the catalytic activity of supported gold nanoparticles. *Angew. Chem. Int. Ed.* **43**, 2129–2132 (2004).
- Calla, J. T. & Davis, R. J. Oxygen-exchange reactions during CO oxidation over titania- and alumina-supported Au nanoparticles. *J. Catal.* **241**, 407–416 (2006).
- Fujitani, T. & Nakamura, I. Mechanism and active sites of the oxidation of CO over Au/TiO₂. *Angew. Chem. Int. Ed.* **50**, 10144–10147 (2011).
- Ojeda, M., Zhan, B.-Z. & Iglesia, E. Mechanistic interpretation of CO oxidation turnover rates on supported Au clusters. *J. Catal.* **285**, 92–102 (2012).
- Widmann, D. & Behm, R. J. Activation of molecular oxygen and the nature of the active oxygen species for CO oxidation on oxide supported Au catalysts. *Acc. Chem. Res.* **47**, 740–749 (2014).
- Kung, M. C., Davis, R. J. & Kung, H. H. Understanding Au-catalyzed low-temperature CO oxidation. *J. Phys. Chem. C* **111**, 11767–11775 (2007).
- Haruta, M. Spiers Memorial Lecture. Role of perimeter interfaces in catalysis by gold nanoparticles. *Faraday Discuss.* **152**, 11–32 (2011).
- Widmann, D., Hocking, E. & Behm, R. J. On the origin of the selectivity in the preferential CO oxidation on Au/TiO₂—nature of the active oxygen species for H₂ oxidation. *J. Catal.* **317**, 272–276 (2014).
- Fujitani, T., Nakamura, I., Akita, T., Okumura, M. & Haruta, M. Hydrogen dissociation by gold clusters. *Angew. Chem. Int. Ed.* **48**, 9515–9518 (2009).
- Cargnello, M. *et al.* Control of metal nanocrystal size reveals metal–support interface role for ceria catalysts. *Science* **341**, 771–773 (2013).
- Kotobuki, M., Leppelt, R., Hansgen, D. A., Widmann, D. & Behm, R. J. Reactive oxygen on a Au/TiO₂ supported catalyst. *J. Catal.* **264**, 67–76 (2009).
- Schubert, M. M., Venugopal, A., Kahlisch, M. J., Plzak, V. & Behm, R. J. Influence of H₂O and CO₂ on the selective CO oxidation in H₂-rich gases over Au/α-Fe₂O₃. *J. Catal.* **222**, 32–40 (2004).
- Saavedra, J., Powell, C., Panthi, B., Pursell, C. J. & Chandler, B. D. CO oxidation over Au/TiO₂ catalyst: pretreatment effects, catalyst deactivation, and carbonates production. *J. Catal.* **307**, 37–47 (2013).
- Denkwitz, Y. *et al.* Stability and deactivation of unconditioned Au/TiO₂ catalysts during CO oxidation in a near-stoichiometric and O₂-rich reaction atmosphere. *J. Catal.* **251**, 363–373 (2007).
- Quinet, E. *et al.* On the mechanism of hydrogen-promoted gold-catalyzed CO oxidation. *J. Catal.* **268**, 384–389 (2009).
- Carrasco, J., Hodgson, A. & Michaelides, A. A molecular perspective of water at metal interfaces. *Nature Mater.* **11**, 667–674 (2012).
- Gong, J. Structure and surface chemistry of gold-based model catalysts. *Chem. Rev.* **112**, 2987–3054 (2011).
- Ikemiya, N. & Gewirth, A. A. Initial stages of water adsorption on Au surfaces. *J. Am. Chem. Soc.* **119**, 9919–9920 (1997).
- Pursell, C. J., Hartshorn, H., Ward, T., Chandler, B. D. & Bocuzzi, F. Application of the Temkin model to the adsorption of CO on gold. *J. Phys. Chem. C* **115**, 23880–23892 (2011).
- Guzman, J., Carrettin, S. & Corma, A. Spectroscopic evidence for the supply of reactive oxygen during CO oxidation catalyzed by gold supported on nanocrystalline CeO₂. *J. Am. Chem. Soc.* **127**, 3286–3287 (2005).
- Bus, E., Miller, J. T. & van Bokhoven, J. A. Hydrogen chemisorption on Al₂O₃-supported gold catalysts. *J. Phys. Chem. B* **109**, 14581–14587 (2005).
- Hartshorn, H., Pursell, C. J. & Chandler, B. D. Adsorption of CO on supported gold nanoparticle catalysts: a comparative study. *J. Phys. Chem. C* **113**, 10718–10725 (2009).

Acknowledgements

The authors kindly thank J. Kevin (Micromeritics Instrument Corporation) and S.M.K. Shahri (Pennsylvania State University) for assistance with the measurement of the water-adsorption isotherms. The authors gratefully acknowledge the US National Science Foundation (Grant No CBET-1160217 and No. CHE-1012395) for financial support of this work. Z.C. and R.M.R. acknowledge the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Catalysis Sciences Program under grant No. DE-FG02-12ER16364 for partial funding of this research.

Author contributions

J.S., B.D.C. and C.J.P. designed the catalysis experiments; J.S. performed the catalysis experiments and analysed the data; B.D.C. and C.J.P. designed the infrared spectroscopy experiments; T.W. performed the infrared spectroscopy experiments and analysed the data; B.D.C. and R.M.R. designed the gas-adsorption experiments and analysed the data; Z.C. and R.M.R. designed and performed the X-ray photoemission spectroscopy and X-ray diffraction experiments (see the Supplementary Information) and analysed the data; J.S., B.D.C., R.M.R. and C.J.P. co-wrote the paper.

Additional information

Supplementary information is available in the [online version of the paper](http://www.nature.com/naturechemistry). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to B.D.C.

Competing financial interests

The authors declare no competing financial interests.