Mechanistic interpretation of CO oxidation turnover rates on supported Au clusters

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Abstract

Kinetic and isotopic data are used to interpret the mechanistic role of gaseous H$_2$O molecules and of non-reducible (Al$_2$O$_3$) and reducible (TiO$_2$, Fe$_2$O$_3$) supports on CO oxidation turnovers catalyzed by small Au clusters (<5 nm). H$_2$O acts as a co-catalyst essential for O$_2$ activation and for catalyst stability in CO oxidation at near-ambient temperatures, but also inhibits rates via competitive adsorption at higher H$_2$O pressures. The effects of CO, O$_2$, and H$_2$O pressures on CO oxidation turnover rates, the absence of $^{16}$O$^2$/$^{18}$O$_2$ and $^{16}$O$_2$/H$_2$O exchange, and the small H$_2$O/D$_2$O kinetic isotope effects are consistent with quasi-equilibrated molecular adsorption of CO, O$_2$, and H$_2$O on Au clusters with the kinetic relevance of H$_2$O-mediated O$_2$ activation via the formation of hydroperoxy intermediates ("OOH"), which account for the remarkable reactivity and H$_2$O effects on Au clusters. These elementary steps proceed on Au clusters without detectable requirements for support interface sites, which are no longer required when H$_2$O is present and mediates O$_2$ activation steps. Rate enhancements by H$_2$O were also observed for CO oxidation on Pt clusters (1.3 nm), which is also limited by O$_2$ activation steps, suggesting H$_2$O-aided O$_2$ activation and "OOH" species in oxidations involving kinetically-relevant O$_2$ activation. These intermediates have also been proposed to account for the ability of O$_2$/H$_2$O mixtures to act as reactants in alkene epoxidation on Au-based catalysts.

1. Introduction

The catalytic oxidation of CO has been extensively used to probe mechanisms and site requirements in heterogeneous catalysis and to remove CO from combustion effluent and H$_2$-containing streams [1-3]. Au-based materials catalyze CO oxidation at sub-ambient temperatures when present as small Au clusters (<5 nm) dispersed on oxide supports (TiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, etc.) [4-8]. The high reactivity of small Au clusters in CO oxidation catalysis has been variously attributed to the following: (i) low-coordination Au surface atoms, isolated Au atoms, or cationic Au species; (ii) electron transfer from the support to Au clusters; or (iii) supports that become active when placed in atomic contact with Au clusters [1]. The importance and relative contributions of these effects are controversial, and the specific evidence for each proposal remains equivocal and often contradictory.

Large differences in measured rates (>10-fold), in the observed effects of reactant and H$_2$O concentrations on such rates (kinetic order ranges of 0.02-1.01 and 0.07-0.46 for CO and O$_2$, respectively), and in deactivation rates have been reported on Au catalysts with similar cluster size, Au content, support material, and synthetic provenance [1,9]. The absence of consensus about these catalyst properties reflects, at least in part, the presence of adventitious H$_2$O at levels difficult to detect but consequential for catalysis. Previous studies have concluded that H$_2$O promotes [5,10,11], inhibits [12], or does not affect [13] CO oxidation catalysis. The most extensive studies [10,14] included Au clusters deposited on different supports (TiO$_2$, Al$_2$O$_3$, and SiO$_2$) and concluded that H$_2$O impurities in CO/O$_2$ reactants strongly increase CO oxidation rates, even at trace concentrations (0.1–1 ppm), which are undetectable by conventional analytical methods, and to very different extents on the various supports [14]. These H$_2$O effects have been attributed to the promotion of O$_2$ adsorption and/or dissociation, decomposition of unreactive carbonate deposits, and assistance in reducing inactive Au cations to Au$^0$ by CO [7,11,14-17], but their respective contributions remain the subject of persistent speculation and active debate. Recent reports also show that increasing concentrations of hydroxyl groups favor CO oxidation rates, either in alkaline aqueous phase using Au/TiO$_2$ and Au/C catalysts [18] or in the gas phase with Au/SiO$_2$ catalysts doped with NaOH [19].

Every plausible sequence of CO oxidation elementary steps and active sites has already been proposed, based on direct or indirect evidence, without even a modicum of consensus and with the implication of structures ranging from cationic or metallic Au species in some cases, but not others, in chemical or physical synergy

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with reducible or non-reducible supports, and with H2O acting as a promoter, participant, inhibitor, or spectator species [1,5,16,20–23]. The only complete sequence of plausible elementary steps supported by the comparison with rigorous rate data, in our assessment, involves parallel competitive and non-competitive adsorption of CO and O2 and their reactions in kinetically-relevant steps [24–26]; this mechanistic proposal did not consider what is currently accepted as a critical and perhaps even essential role of H2O in mediating CO oxidation catalysis at near-ambient temperature.

We provide here kinetic and isotopic evidence for a sequence of elementary steps for CO oxidation on stable Au catalysts with added H2O, present as a co-catalyst essential for stable turnover rates. These steps are mediated by hydridorropy species (‘OHOH), which may form on Au surfaces[27], and which account for the co-catalytic effect of H2O on CO oxidation rates and on catalyst stability and for the ability of these materials to catalyze propane epoxidation with H2O/O2 mixtures[28]. These kinetic data were obtained under conditions of strict kinetic control and without detectable deactivation in the presence of H2O as an essential component; the data and their mechanistic interpretation aim to resolve long-standing controversies that reflect, at least in part, the instability and mechanistic promiscuity imposed by uncontrolled and undetected concentrations of adventitious H2O in catalytic solids and reactant streams.

2. Experimental methods

2.1. Catalyst preparation and characterization

Al2O3-supported Au clusters (denoted here as Au/Al2O3) were prepared by the deposition–precipitation (DP) methods[5,20]. Tetraphenylaromatic acid hydrate (0.24 g, HAuCl4·2H2O, 99.999%, Aldrich) was dissolved in doubly-deionized H2O (80 cm3) at 353 K. γ-Al2O3 (5 g, Alcoa) was treated in flowing dry air (1.67 cm3 s⁻¹ g⁻¹, UHP grade, Praxair) at 923 K for 5 h, and then dispersed in doubly-distilled deionized H2O (120 cm3) at 353 K. Au was deposited onto γ-Al2O3 surface at 353 K and a pH of 7 (adjusted with 0.5 M NaOH, >98%, Fluka) by stirring for 1 h. The resulting solids were rinsed and washed with doubly-deionized deionized H2O (323 K) and dried at ambient temperature for 24 h. Samples were stored away from light without further treatment. The Au content was measured by inductively-coupled plasma emission spectroscopy (0.61% wt.; Galbraith Laboratories, Inc.). The mean diameter of these Au clusters (3.5 ± 1.2 nm) was determined by high-resolution transmission electron microscopy (TEM) and reported elsewhere[29]. Mean Au diameters (dAu) were calculated using dAu = n_i d^i_i / n_d, where d_i is the diameter measured from TEM images, and n_i is the number of Au clusters of diameter d_i. The pore size distribution was measured by N2 adsorption–desorption at 77 K using a Micromeritics ASAP 2000 apparatus. Pore size distributions were obtained from these adsorption data using the Barrett–Joyner–Halenda (BJH) equation [30].

Three different portions of the Au/Al2O3 solids were treated in O2/He (25 vol.% 30 cm3 g⁻¹ s⁻¹) by increasing the temperature from ambient to 873, 950, or 1023 K at 0.17 K s⁻¹ and holding at each temperature for 2 h. These samples are denoted as treated catalysts, Au/Al2O3-X, where X represents the treatment temperature (X = 873, 950, or 1023), and the Au/Al2O3 solid dried at ambient temperature is named as untreated Au/Al2O3.

Two reference Au catalysts (1.56% wt. Au/TiO2 and 4.44% wt. Au/FeO3, prepared by deposition–precipitation and co-precipitation, respectively) were provided by the World Gold Council (WGC). These two samples were used to examine the effects of support on CO oxidation rates and on the kinetic dependence of measured rates on reactant pressure in the presence and in the absence of co-fed H2O; these materials were also used to evaluate CO oxidation pathways operating with Au clusters deposited on reducible and non-reducible metal oxide supports. The mean Au cluster size (dAu) derived from TEM images are 3.3 ± 0.7 and 3.6 ± 0.7 nm for Au/TiO2 and Au/FeO3, respectively.

A Pt/Al2O3 catalyst (2.03% wt., Pt clusters of 1.1 nm) was also used in reactions of CO–O2 and CO/O2/H2O mixtures to probe any effects of H2O on CO oxidation rates on Pt clusters. The synthesis and characterization protocols used for this Pt catalyst have been reported elsewhere[31].

2.2. Steady-state CO oxidation rate measurements

CO oxidation rates were measured in a tubular packed-bed reactor with plug-flow hydrodynamics. Typically, catalysts (25–30 mg, 0.250–0.425 mm pellet size) were diluted with quartz granules (~1 g; washed with 1 M HNO3 at 298 K for 2 h and then treated in ambient air at 1023 K for 5 h). Samples were treated in flowing pure H2 (28 cm3 s⁻¹ g⁻¹, 99.999%, Praxair) at 373 K (heating rate of 0.167 K s⁻¹) for 0.5 h and in H2/O2 (28 cm3 s⁻¹ g⁻¹, 1 vol.% H2/O2) at 373 K for 0.5 h, using a previously reported procedure that forms stable Au metal clusters[32]. The catalyst was brought to the reaction temperature (282–303 K) in flowing He (99.999%, Praxair). Gas reactants (10 vol.% CO in He, 25 vol.% O2 in He, UHP grade, <10 ppm H2O, Praxair) were metered by electronic controllers, and H2O (doubly-distilled and deionized) was introduced into heated transfer lines using a syringe pump (Cole Parmer 74900 Series). Helium was used as balance. CO2, O2, and He streams were further purified with moisture traps (Matheson Tri-Gas). Reactants and products concentrations were measured by gas chromatography (Agilent 6890 GC) using a Porapak Q packed column (80–100 mesh, 1.82 m x 3.18 mm) connected to a thermal conductivity detector (TCD). All transfer lines were heated to 400–415 K to prevent H2O condensation. No reaction products were detected in the effluent when reactors contained only quartz diluent or Al2O3 supports. CO conversions were kept well below 10% in most experiments (and below 15% in cases) by changing residence times while keeping CO, O2, and H2O concentrations at constant values. These low conversions ensure the differential nature of measured rates and avoid their rigorous but more cumbersome interpretation in terms of integral equations.

Propene epoxidation rates using O2/H2O mixtures were measured on Au/TiO2, while HCOOH dehydrogenation and water–gas shift reactions were performed with all Au/Al2O3 samples. Gas reactants (C3H6, 25 vol.% O2 in He, 10 vol.% CO in He, UHP grade, Praxair) were metered by electronic controllers, and liquids HCOOH or H2O (doubly-distilled deionized) were introduced using a syringe pump. Reactants and products concentrations were measured with a mass spectrometer (Inficon Transpector) and a gas chromatograph (Hewlett-Packard 5890) equipped with a Porapak Q packed column (80–100 mesh, 1.82 m x 3.18 mm) connected to a thermal conductivity detector and a HP-1 capillary column (50 m x 0.32 mm x 1.05 μm) connected to a flame ionization detector (FID).

2.3. Isotopic exchange rates and kinetic isotope effects

Isotopic 16O2/18O2 and 16O2/H2/18O exchange rates were measured on Au/Al2O3 using a glass recirculating flow reactor[33]. Samples were treated as described above, and the recirculating and reactor volumes (550 cm3 total) were evacuated with mechanical and diffusion pumps before introducing reactants as vapors (16O2, 99.999%, Praxair; 18O2, 99%, Isotec; H2, 99 at% 18O, Sigma–Aldrich). Chemical and isotopic compositions were measured by direct sampling into a gas chromatograph (Hewlett-Packard
oxidation in the absence of H$_2$O [16,34]. In contrast, other studies implicate, without specific experimental evidence, a role of H$_2$O in elementary steps required for O$_2$ activation, possibly via the formation of activated oxygen species that react rapidly with CO to form intermediates that ultimately decompose to CO$_2$ [14,35].

The possible involvement of H$_2$O in the kinetically-relevant steps in CO oxidation catalytic sequences is examined next by comparing CO oxidation turnover rates measured with the untreated Au/Al$_2$O$_3$ (0.61% wt., 288 K, 5 kPa CO, 2 kPa O$_2$) measured on Au/Al$_2$O$_3$ using H$_2$O or D$_2$O (0.5 kPa) as additives. As we show later (Section 3.4), the small measured H$_2$O/D$_2$O isotope effects indicate that O–H(D) bonds are not cleaved in kinetically-relevant steps in the CO oxidation catalytic sequence.

Previous studies have proposed that H$_2$O inhibition effects (>0.5 kPa) reflect competitive adsorption by H$_2$O-derived intermediates [10,36]. It is also possible that H$_2$O condensation within catalyst mesopores imposes diffusional corrupions of chemical reaction rates by decreasing intrapellet CO or O$_2$ concentrations and thus the kinetic driving force for CO oxidation at active sites. We find, however, that CO oxidation turnover rates did not depend on pellet size (0.125–0.250 and 0.250–0.425 mm diameter; Fig. 2); thus, even if condensation occurred, the presence of H$_2$O within alumina pores did not impose transport barriers, which would have caused smaller rates on the larger pellets. Moreover, the pore size distribution of the Al$_2$O$_3$ used in this study did not lead to detectable pore filling below ~1.5 kPa H$_2$O at reaction temperatures (Supplementary Content). We conclude that the H$_2$O inhibition observed above ~0.5 kPa (Fig. 2) reflects competitive adsorption of H$_2$O-derived adsorbed species with reactive intermediates derived from CO or O$_2$ on Au clusters and arise from chemical origins instead of any transport corruptions.

Thermal treatments of Au/Al$_2$O$_3$ in 25 vol.% O$_2$/He at temperatures up to 1023 K did not lead to detectable changes in Au cluster size (transmission electron microscopy, TEM; Supplementary Content) or in CO oxidation rates in the presence of H$_2$O (288 K, 5 kPa CO, 2 kPa O$_2$, 0.5 kPa H$_2$O; Table 1), indicating that Au clusters on Al$_2$O$_3$ resist sintering even at these high temperatures and that the deactivation of Au-based catalysts reported during CO oxidation in the absence of H$_2$O at near-ambient temperatures cannot reflect cluster growth. These data also show that CO oxidation occurs on the Au clusters visible in transmission electron micrographs. In contrast, the rates of HCOOH dehydrogenation (353 K, 2 kPa HCOOH) and water–gas shift (523 K, 5 kPa CO, 2 kPa H$_2$O) decreased markedly with increasing treatment temperature, apparently as a result of the disappearance of smaller Au structures
undetectable at the resolution of these transmission electron micrographs (Table 1) [29].

### 3.2 Kinetic dependence of CO oxidation rates on reactants pressure and temperature

The stable CO oxidation turnover rates observed in the presence of H₂O allowed accurate and reproducible kinetic measurements over a wide range of CO, O₂, and H₂O pressures. Next, we report the kinetic effects of CO and O₂ pressures on CO oxidation turnover rates on Au/Al₂O₃ (0.5 kPa H₂O; Fig. 3). CO oxidation turnover rates increased with increasing CO (0.80–8.25 kPa) and O₂ (0.25–7.15 kPa) pressures, with empirical fractional orders of 0.24 ± 0.02 and 0.60 ± 0.02, respectively. Au/Al₂O₃ treated at 200°C He at various higher temperatures (873–1023 K) gave similar kinetic effects of CO and O₂ pressures on CO oxidation turnover rates (5 kPa CO, 2 kPa O₂, 0.5 kPa H₂O) on Au/Al₂O₃ (1.2–5.6 nm Au clusters) in the presence of H₂O (40 ppm) or H₂ (0.25–75 kPa) at 303–453 K [14,34,39]. However, in the absence of H₂O, other authors found lower CO oxidation activation energies (12 ± 1 kJ mol⁻¹, 295–373 K) with Au/Al₂O₃ (1.2 nm Au) [34]. Moreover, erratic and large differences in activation energies, ranging from 8 to 75 kJ mol⁻¹, have been reported in the literature for nominally anhydrous CO/O₂ reactions on Au clusters deposited on reducible and non-reducible supports (TiO₂, Fe₂O₃, CeO₂, SiO₂, etc.).

#### Table 1

Influence of Au/Al₂O₃ treatment temperature (O₂/He, 2 h) on Au clusters size obtained by TEM and on rates for CO oxidation, HCOOH dehydrogenation, and water-gas shift reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment temp. (K)</th>
<th>Mean Au size (nm)</th>
<th>Rate (mol h⁻¹ g-at Au⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al₂O₃</td>
<td>–</td>
<td>3.5 ± 1.2</td>
<td>2589</td>
</tr>
<tr>
<td>Au/Al₂O₃-873</td>
<td>873</td>
<td>4.0 ± 1.0</td>
<td>2827</td>
</tr>
<tr>
<td>Au/Al₂O₃-950</td>
<td>950</td>
<td>4.0 ± 1.1</td>
<td>2535</td>
</tr>
<tr>
<td>Au/Al₂O₃-1023</td>
<td>1023</td>
<td>4.3 ± 1.2</td>
<td>2610</td>
</tr>
</tbody>
</table>

*a 288 K, 5 kPa CO, 2 kPa O₂, 0.5 kPa H₂O.
*b 353 K, 2 kPa HCOOH.
*c 523 K, 5 kPa CO, 2 kPa O₂.

CO oxidation turnover rates (5 kPa CO, 2 kPa O₂, 0.5 kPa H₂O) on Au/Al₂O₃ catalysts increased with temperature (282–303 K) in a manner consistent with an apparent activation energy of 36 ± 3 kJ mol⁻¹ (Fig. 4); these values lie within the range reported by other authors (22–40 kJ mol⁻¹) on Au/Al₂O₃ (1.2–5.6 nm Au clusters) in the presence of H₂O (40 ppm) or H₂ (0.25–75 kPa) at 303–453 K [14,34,39]. However, in the absence of H₂O, other authors found lower CO oxidation activation energies (12 ± 1 kJ mol⁻¹, 295–373 K) with Au/Al₂O₃ (1.2 nm Au) [34]. Moreover, erratic and large differences in activation energies, ranging from 8 to 75 kJ mol⁻¹, have been reported in the literature for nominally anhydrous CO/O₂ reactions on Au clusters deposited on reducible and non-reducible supports (TiO₂, Fe₂O₃, CeO₂, SiO₂, etc.).

#### 3.3 CO–O₂ reaction pathways on Au/Al₂O₃ in the presence of H₂O

Scheme 1 depicts a sequence of elementary steps for low-temperature CO oxidation reaction consistent with the kinetic data discussed in Section 3.2. Steps 1, 2, and 3 represent quasi-equilibrated non-dissociative adsorption steps for all species in the reactant stream (CO, O₂, and H₂O). O₂ adsorption is assumed to be molecular and reversible. Irreversible O₂ adsorption (whether molecular or dissociative) would lead to CO oxidation rates proportional to O₂ pressures, in contradiction with our kinetic data and with most previous reports [1]. Reversible O₂ adsorption and subsequent reactions with the CO species present as most abundant reaction intermediates (MARI) would also lead to first-order O₂ kinetics,
1. CO + * → CO* \( K_1 \)
2. O₂ + * → O₂* \( K_2 \)
3. H₂O + * → H₂O* \( K_3 \)
4. O₂* + H₂O* → *OOH + *OH \( K_4 \)
5. *OOH + CO* → *OH + CO₂ + * \( k_5 \)
6. *OH + *OH → H₂O* + O* \( k_6 \)
7. CO* + O* → CO₂ + 2* \( k_7 \)

**Scheme 1.** CO oxidation pathways on Au(Al₂O₃) at low temperatures in the presence of co-fed H₂O (‘‘ denotes a vacant active site and ‘‘X’’ the various adsorbed species).

suggested that alternate steps must be involved in the activation of O₂ species. Step 4 represents the formation of hydroperoxyl species (‘‘OOH‘’) via proton transfer from water to O₂, in a step assumed to be fast and quasi-equilibrated based on the small measured H₂O/O₂/O₂ kinetic isotope effects (Section 3.4). In this sequence, O–O bond activation is assisted by H₂O, in a step that avoids the difficult dissociation of O₂ on Au surfaces; this step forms ‘‘OOH species that then react with CO to form CO₂ (step 5). Catalytic turnovers are completed via the recombination of ‘‘OH species (step 6) to re-form the H₂O molecule used to activate O₂ (which therefore acts as a co-catalyst instead of a stoichiometric reactant) and an O* atom; the latter is ultimately removed via the reaction with CO to form another CO₂ molecule (step 7), a step that exhibits a low activation barrier (24 kJ mol⁻¹) according to previous theoretical estimates on Au(111) and Au(221) model surfaces [40]. OOH recombination to HOOH (‘‘OH + ‘‘OH → HOOH + *) is not considered as a plausible alternate path to the proposed H₂O + O* reaction (\( E_a = 17–25 \text{ kJ mol}^{-1} \)) based on DFT estimates on Au(111) showing a much higher activation energy barrier (157 kJ mol⁻¹) [43].

The assumption of pseudo-steady-state [44] for all adsorbed species and of quasi-equilibrium for steps 1–4 in Scheme 1 leads to the following CO oxidation rate equation, the full algebraic derivation of which is included in Appendix A:

\[
\begin{align*}
\dot{r} &= \frac{\alpha (P_{CO} P_{O_2} P_{H_2O}^{3/2})(P_{CO}^{1/2} + \beta + \gamma + \delta)}{[1 + K_1 P_{CO} + K_2 P_{O_2} + K_3 P_{H_2O} + (\beta + \gamma)(P_{CO}^{1/2} P_{O_2}^{1/3} + \delta P_{CO} P_{O_2} P_{H_2O})^{1/3}]^{3/2}} \times \text{CO}^* + \text{O}_2^* + \text{H}_2\text{O}^* + \text{*OOH} + \text{*OH}
\end{align*}
\]

**Eq. (1)**

Each term in the denominator of this equation represents the concentration of the indicated adsorbed intermediate relative to the concentration of vacant sites on Au cluster surfaces. In Eq. (1), \( K_1, K_2, \) and \( K_3 \) are the equilibrium constants for molecular CO, O₂, and H₂O adsorption, respectively, and \( \alpha, \beta, \gamma, \) and \( \delta \) are given by the combinations of rate and equilibrium constants for elementary steps

\[
\begin{align*}
\alpha &= 3/2(K_1 K_2 K_3 K_4)^{2/3}(2K_6)^{1/3} \\
\beta &= (K_1 K_3 K_4)^{2/3}(2K_6)^{1/3}(K_1)^{-1/3} \\
\gamma &= K_1^{-1/3}(K_1 K_3 K_4)^{2/3}(K_3)^{1/3} (2)^{-2/3} (K_1)^{-1/3} \\
\delta &= (K_1 K_2 K_3 K_4)^{1/3}(2K_6)^{1/3}
\end{align*}
\]

**Eq. (2)–(5)**

The values of the kinetic parameters \( \beta, \gamma, \) and \( \delta \) derived from the nonlinear regression analysis of measured CO oxidation rates make the terms in the denominator of Eq. (1) containing these constants (relative surface coverage of O*, ‘‘OH, and ‘‘OOH) to be much smaller than the others (vacant sites, CO*, O₂*, and H₂O*; Supplementary Content) at the conditions of our experiments. Therefore, Eq. (1) becomes

\[
\begin{align*}
r &= \frac{\alpha (P_{CO} P_{O_2} P_{H_2O}^{3/2})}{[1 + K_1 P_{CO} + K_2 P_{O_2} + K_3 P_{H_2O}]^{3/2}} \\
\end{align*}
\]

**Eq. (6)**

when assuming that ‘‘OOH, ‘‘OH, and O* are minority surface species present in much lower concentrations than vacant sites (*), CO*, O₂*, and H₂O*.

The parity plot in Fig. 5 shows that Eq. (6) accurately describes the measured effects of reactants pressures (0.80–8.25 kPa CO; 0.25–7.15 kPa O₂; 0.03–1.15 kPa H₂O) on CO oxidation turnover rates on Au/Al₂O₃. We did not find other assumptions about most abundant surface species or about quasi-equilibrated steps consistent with these measured rates. Alternate CO/O₂/H₂O reaction pathways were also considered (Supplementary Content), but rigorous kinetic and isotopic (shown later) analyses demonstrated that none of them was able to successfully predict measured rate data. The kinetic parameters derived from the nonlinear regression analysis of measured CO oxidation rates with Au/Al₂O₃ are shown in Table 2. The H₂O adsorption equilibrium constant (3.1 ± 0.6 kPa⁻¹) is larger than for CO and O₂ (0.18 ± 0.05 and 0.06 ± 0.02 kPa⁻¹, respectively; CO is indeed expected to bind more strongly than O₂, based on first-principle density functional theory (DFT) with generalized gradient approximation (GGA) calculations on Au₈–Au₃₀(100) and Au₈–Au₃₀ model systems, which gave CO adsorption energies (90–100 kJ mol⁻¹) much greater than for O₂ (5–70 kJ mol⁻¹) [41,45–47]. The measured H₂O adsorption constant (\( K_1 \)) is, however, somewhat larger than the expected from

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**Table 2**

<table>
<thead>
<tr>
<th>Kinetic parameter</th>
<th>Au/Al₂O₃</th>
<th>Au/TiO₂</th>
<th>Au/Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) (kPa⁻¹)</td>
<td>11.0 ± 3.4</td>
<td>12.3 ± 3.4</td>
<td>13.3 ± 0.4</td>
</tr>
<tr>
<td>( K_1 ) (kPa⁻¹)</td>
<td>0.18 ± 0.05</td>
<td>0.24 ± 0.09</td>
<td>0.18 ± 0.07</td>
</tr>
<tr>
<td>( K_2 ) (kPa⁻¹)</td>
<td>0.06 ± 0.02</td>
<td>0.05 ± 0.02</td>
<td>0.16 ± 0.06</td>
</tr>
<tr>
<td>( K_3 ) (kPa⁻¹)</td>
<td>3.1 ± 0.6</td>
<td>3.4 ± 0.9</td>
<td>1.1 ± 0.5</td>
</tr>
</tbody>
</table>

\( \alpha = 3/2(K_1 K_2 K_3 K_4)^{2/3}(2K_6)^{1/3} \).
H$_2$O/D$_2$O isotope effects and isotopic exchange measurements

H$_2$O/D$_2$O isotope effects were used to probe the potential involvement of H$_2$O and of O–H bond activation in kinetically-relevant steps in the context of the CO oxidation catalytic sequence depicted in Scheme 1. CO oxidation turnover rates (288 K, 5 kPa CO; 2 kPa O$_2$) were measured on untreated Au/Al$_2$O$_3$ by adding H$_2$O or D$_2$O (0.5 kPa) to CO/O$_2$ reactant streams (Fig. 6). The small measured H$_2$O/D$_2$O isotope effects ($r_{H_2O}/r_{D_2O} = 1.21; \text{Fig. 6}$) are consistent with previous studies that report H$_2$O/D$_2$O isotope effects near unity on Au/Al$_2$O$_3$ (295 K, 1 kPa CO, 0.5 kPa O$_2$, 1.5 kPa H$_2$O(D$_2$O)) [16]. These data lead us to conclude that O–H (or O–D) bonds are not cleaved in kinetically-relevant steps, which would have shown large normal isotope effects at these low temperatures (288 K). These small normal H$_2$O/D$_2$O isotope effects reflect their probable thermodynamic origins stemming from quasi-equilibrated H$_2$O dissociation steps that occur before kinetically-relevant steps in CO oxidation catalytic sequences.

Next, we probe O$_2$ chemisorption steps on Au/Al$_2$O$_3$ by measuring the rate of formation of $^{16}$O$^{18}$O isotopologues from equimolecular $^{16}$O$_2$/$^{18}$O$_2$ mixtures (5 kPa) at 300 K in the absence of CO and H$_2$O. Quasi-equilibrated dissociation would form binomial isotopologue distributions (50% $^{16}$O$^{18}$O), while molecular adsorption steps would not form mixed $^{16}$O$^{18}$O isotopes. The rate of $^{16}$O$^{18}$O formation (300 K, 5 kPa $^{16}$O$_2$, 5 kPa $^{18}$O$_2$) was $\sim$50 times smaller than CO oxidation rates (288 K, 5 kPa CO, 2 kPa O$_2$, 0.5 kPa H$_2$O) even at higher temperatures and O$_2$ pressures than those used in CO oxidation catalysis (Fig. 7a); these findings are consistent with previous studies that reported no detectable $^{16}$O$^{18}$O formation during $^{16}$O$_2$/$^{18}$O$_2$ isotopic exchange at similar pressures on Au/TiO$_2$ (353 K) and Au/Fe$_2$O$_3$ (298 K) [13,49] and show that O$_2$ adsorbs molecularly (O$_2 + \rightarrow$ 2O$_2$) on Au clusters.

The rate of isotopic exchange between $^{16}$O$_2$ (5 kPa) and H$_2^{18}$O (0.5 kPa) was also measured on Au/Al$_2$O$_3$ at 300 K in the absence of CO. The formation of $^{16}$O$^{18}$O, $^{18}$O$_2$, or H$_2^{16}$O molecules was not detected (Fig. 7b). The absence of isotopic exchange between O$_2$ and H$_2$O reflects the non-dissociative nature of O$_2$ adsorption on Au, as also inferred from the absence of $^{16}$O$^{18}$O$_2$ exchange. We note that steps 2–4 in the catalytic sequence do not lead to the cleavage of O–O bonds, which instead occurs in latter steps via reactions with CO$^+$ in CO oxidation and with propene in propene epoxidation on Au catalysts [28]; as a result, the equilibrated nature of these O$_2$ adsorption and reaction steps cannot cause isotopic oxygen exchange.

3.5. Support effects on CO oxidation rates with Au-based catalysts

The identity of the support has been often implicated as an essential second function in the reactivity of Au clusters in CO oxidation [1,5,6,24,50], either via its participation in O$_2$ activation or because of its ability to stabilize small Au clusters. Reducible oxides (e.g., TiO$_2$, Fe$_2$O$_3$) have been reported to catalyze CO oxidation at higher rates than refractory oxides (e.g., Al$_2$O$_3$, SiO$_2$), a finding attributed to the requirement for O$_2$ activation on periphery sites located at Au-support interfaces [6,51]. The data used to reach these conclusions were obtained under nominally anhydrous conditions, but possibly in the presence of catalytically-consequential levels of H$_2$O, derived, at least in part, from H$_2$O adsorbed on supports and at concentrations that decrease with time as H$_2$O is depleted by desorption from these supports. These processes may have led, in turn, to the decrease in rates with time often interpreted as catalyst deactivation during CO oxidation on Au-based catalysts.

Fig. 8 and Table 3 compare turnover rates on Au clusters of similar size dispersed on reducible (TiO$_2$ and Fe$_2$O$_3$, 3.3 ± 0.7 and 3.6 ± 0.7 nm Au clusters, respectively) and non-reducible (Al$_2$O$_3$, TiO$_2$, and Fe$_2$O$_3$, 0.61% wt.; untreated).

![Fig. 6. H$_2$O/D$_2$O isotope effects on CO oxidation turnover rates measured with Au/Al$_2$O$_3$ (0.61% wt., 288 K; 5 kPa CO; 2 kPa O$_2$; 0.5 kPa H$_2$O (●) or D$_2$O (●)).](image)
3.5 ± 1.2 nm Au clusters) oxides for CO/O2 and CO/O2/H2O reactants. As in the case of Au/Al2O3 catalysts, the addition of H2O as a co-catalyst was essential for stable turnover rates on Au/TiO2 and Au/Fe2O3. H2O (0.5 kPa) increased CO oxidation rates on all catalysts, but to different extents, possibly because of the presence of support-dependent H2O concentrations even for nominally anhydrous CO–O2 reactants. Turnover rates with anhydrous CO–O2 reactants (based on TEM mean cluster sizes) on Au/TiO2 were significantly higher than on Au/Al2O3 (2.70 and 2.55 mol s⁻¹ g-at Au⁻¹, respectively) and somewhat smaller rates on Au/Fe2O3 (0.59 mol s⁻¹ g-at Au⁻¹). The latter values appear to reflect the encapsulation of some TEM-visible Au clusters within Fe2O3 as a consequence of the co-precipitation methods used, which in contrast with the deposition–precipitation method used for TiO2 and Al2O3 supports do not ensure the presence of Au clusters at accessible support surfaces.

We conclude from these data that supports influence CO oxidation turnover rates with anhydrous reactants, perhaps because they can contribute adsorbed H2O as co-catalyst or as periphery sites that become essential for O2 activation only under anhydrous conditions. These support effects and specifically the reducible nature of the support become much less consequential when H2O mediates the required O2 activation steps. The observed H2O effects on CO oxidation rates with Au/TiO2 and Au/Fe2O3 also suggest that the mechanistic pathways in Scheme 1 are also involved in CO oxidation reactions on reducible supports, as long as H2O is present as a co-catalyst. These elementary steps occur on Au cluster surfaces without any significant requirement for a second function provided by either interfacial or support sites. This is also consistent with previous reports [14] showing similar CO oxidation activation energies on Au/TiO2 and Au/Al2O3 (22 and 25 kJ mol⁻¹, respectively), which suggests a common reaction mechanism over these two catalysts.

The effects of CO and O2 pressure on CO oxidation turnover rates on Au/TiO2 and Au/Fe2O3 (Fig. 9; 288 K, 0.5 kPa H2O) were

---

Table 3

<table>
<thead>
<tr>
<th>Added H2O (kPa)</th>
<th>CO oxidation turnover rate (mol s⁻¹ g-at Au⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Au/Al2O3: 0.08, 0.54, 0.07</td>
</tr>
<tr>
<td>0.5</td>
<td>Au/TiO2: 2.55</td>
</tr>
<tr>
<td>0.5</td>
<td>Au/Fe2O3: 2.70, 2.55</td>
</tr>
</tbody>
</table>

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Fig. 8. H2O effect on CO oxidation turnover rates (288 K, 5 kPa CO, 2 kPa O2) measured with Au/TiO2 (a) and Au/Fe2O3 (b). Symbols: (○) 0.5 kPa H2O; (▲) 0 kPa H2O.

Fig. 9. Kinetic dependence of CO oxidation turnover rates on CO (●, 1–5 kPa CO, 2 kPa O2, 0.5 kPa H2O) and O2 (■, 0.5–6 kPa O2, 5 kPa CO, 0.5 kPa H2O) pressures measured at 288 K with Au/TiO2 (a) and Au/Fe2O3 (b).
similar to those measured on Au/Al2O3 (Fig. 3). Turnover rates increased with CO pressure (1–6 kPa, 0.29 ± 0.04, and 0.19 ± 0.02 orders on Au/TiO2 and Au/Fe2O3, respectively) and O2 pressure (0.5–6 kPa, 0.68 ± 0.01, and 0.49 ± 0.02 orders on Au/TiO2 and Au/Fe2O3, respectively). The sequence of elementary steps in Scheme 1 therefore appears to be generally applicable to CO oxidation reactions with CO/O2–H2O reactants on Au clusters dispersed on all three supports. The rate equation derived from the steps in Scheme 1 (Eq. (6)) accurately described all rate data as a function of CO, O2, and H2O pressures on Au/TiO2 and Au/Fe2O3. Fig. 10 shows the respective parity plots of measured and predicted turnover rates, and Table 1 lists the regressed kinetic parameters. As found on Au/Al2O3, H2O adsorption equilibrium constants are larger than for CO and O2 on Au/TiO2 and Au/Fe2O3 (Table 2). The values of K1, K2, and K3 are similar on all supports, consistent with the similar size of Au clusters and their exclusive involvement in mediating the elementary steps in Scheme 1.

### 3.6. Evidence for the presence and reactivity of hydroperoxy (‘OOH) species on Au

The elementary steps for CO–O2 reactions in the presence of H2O (Scheme 1) and the assumptions made about their reversibility lead to a rate equation (Eq. (6)) consistent with measured rates on Au clusters dispersed on both reducible (TiO2, Fe2O3) and non-reducible (Al2O3) supports. These steps and assumptions are also consistent with H2O/D2O isotope effects on CO oxidation rates and with the absence of isotopic exchange in H2O/D2O and H2O/16O2 mixtures. O2 activation involves reactions of O2 and H2O to form hydroperoxy species (‘OOH) with intact O–O bonds, but weaker relative to those in O2 molecules. These ‘OOH intermediates also account for the reactivity of small Au clusters in the formation of H2O2 from H2O–O2 mixtures [52,53], which proceeds via ‘OOH intermediates, as shown from theoretical estimates [27], electronic and spin resonance spectra [54], and inelastic neutron scattering [55]. ‘OOH species also account for propylene epoxidation with H2O/O2 mixtures on Au-based catalysts [56,57]. These ‘OOH species have been also proposed to account for the promotion of CO oxidation by H2O, without specific direct evidence [35,39,58]. The formation of H2O2 has been detected by UV–visible spectroscopy during CO oxidation on Au/TiO2 and Au/C in aqueous alkaline media [18].

The formation of ‘OOH species from O2/H2O mixtures is also evident from the formation of propylene oxide from propene at near-ambient temperatures on Au/TiO2 ([350 K], 4 kPa C3H6, 4 kPa O2) with Au/TiO2 (1.505 wt. Au, WGC). Table adapted from reference [28]. These epoxidation reactions provide independent evidence for the formation of ‘OOH species from O2–H2O reactants and for their involvement in O2 activation during CO oxidation reactions. These O2 activation pathways occur on Au clusters surfaces without detectable involvement of the support and remove the need for support-mediated O2 activation at the periphery of Au clusters as a requirement for CO oxidation catalysis. Theoretical calculations on Au18 and Au30 clusters indicate that coadsorbed H2O and O2 form O2–H2O complexes via partial proton sharing or transfer with low activation barriers (17–25 kJ mol⁻¹) to form ‘OOH species [41,42]. ‘OOH species may be responsible for the well-established promotional effect of H2 in CO/O2 reaction on Au catalysts [1,34,39,60,61], as proposed previously for model Ru–Pt core shell nanoparticles from first-principles calculations consistent with atomic H+ addition to O2 to form ‘OOH as the relevant pathway in the preferential oxidation of CO in H2-rich streams [62].

### 3.7. H2O effects on CO oxidation turnovers catalyzed by supported Pt clusters

A catalytic effect of H2O was also observed during CO oxidation on Pt clusters, the origins of which have not, to our knowledge, been examined in the extensive previous literature dealing with Pt-catalyzed CO oxidation catalysis [63,64]. Fig. 11a shows CO oxidation turnover rates on Pt/Al2O3 at 423 K (2.03% wt., 1.3 nm Pt clusters) with and without added H2O. CO oxidation rates decreased from 0.28 to 0.08 mol s⁻¹ g⁻¹ Pt⁻¹ in ~1 ks when H2O (0.5 kPa) was removed from the reactant mixture (1 kPa CO, 10 kPa O2). Initial CO oxidation rates were fully recovered upon reintroduction of H2O (0.5 kPa, Fig. 11a). The parallel formation of CO2 via water–gas shift occurs at negligible rates (< 10⁻³ mol s⁻¹ g⁻¹ Pt⁻¹, Pt clusters of 0.9–1.7 nm) at these temperatures (423 K, 3 kPa CO, 10 kPa H2O) [63,65]. The data in Fig. 11a suggest that H2O also provides a more facile route for O2 activation during CO oxidation on CO-covered Pt clusters. A recent study combining theory and experiment [31] showed that anhydrostatic CO oxidation on Pt occurs via CO–assisted O2 dissociation steps on surfaces nearly saturated by chemisorbed CO intermediates, which hinder O2 adsorption and subsequent activation. The presence of H2O may act to decrease local CO coverage and weaken inhibition effects by CO [64], but may also provide ‘OOH species as alternate O2 activation routes with lower activation barriers and concomitantly higher CO oxidation turnover rates than the CO-assisted O2 activation steps that limit CO oxidation with anhydrostatic CO/O2 mixtures. Indeed, apparent activation energies decrease from 84 ± 6 kJ mol⁻¹ (403–473 K, 1 kPa CO, 10 kPa O2) [31] to 68 ± 8 kJ mol⁻¹ (373–423 K, 1 kPa CO, 10 kPa O2, 0.5 kPa H2O, Fig. 11b) when H2O was present in CO/O2 reactants.

#### Table 4

<table>
<thead>
<tr>
<th>H2O pressure (kPa)</th>
<th>Metal-time yield (mol h⁻¹ g⁻¹ at Au⁻¹)</th>
<th>Selectivity (% carbon based)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Propene oxide</td>
</tr>
<tr>
<td>1</td>
<td>0.35</td>
<td>85.2</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>75.0</td>
</tr>
<tr>
<td>6</td>
<td>0.52</td>
<td>39.7</td>
</tr>
<tr>
<td>12</td>
<td>0.57</td>
<td>24.1</td>
</tr>
</tbody>
</table>

Fig. 10. Parity plot for measured (288 K; 1–6 kPa CO; 0.5–6 kPa O2; 0.12–0.53 kPa H2O) and calculated (from Eq. (6)) CO oxidation turnover rates with Au/TiO2 (a) and Au/Fe2O3 (A).
H2O addition molecules that mediate required O2 activation steps. In consequence for CO oxidation catalysis in the presence of the port sites; hence, the reducible nature of the support becomes much more facile on Au-based catalysts. The experimental evidence reported here for H2O effects on CO oxidation catalysis, and specifically its reducible nature, becomes much less important in the presence of H2O. Consequently, the adsorption of O2 and H2O and the subsequent formation of the oxidant species (hydroperoxy intermediates) is more facile on Au-based catalysts.

3.8. Role of H2O in CO oxidation pathways catalyzed by supported noble metal (Au, Pt) clusters

The experimental evidence reported here for H2O effects on CO oxidation turnover rates resolves long-standing conflicts among measured rates on Au catalysts with similar cluster size, Au contents, supports, and synthetic provenance. The presence of H2O as a co-catalyst in CO/O2 reactants, even at trace concentrations, affects significantly catalyst stability and measured CO oxidation rates. H2O addition is essential for stable turnover rates, and its presence leads to a sequence of elementary steps that are mediated by hydroperoxy species (‘OOH), which account for the co-catalytic effect of H2O on CO oxidation rates and on catalyst stability, as well as for the ability of Au clusters to catalyze propene epoxidation reactions with O2/H2O mixtures [28,59]. The elementary steps that form the hydroperoxy species from O2 and H2O occur exclusively on Au cluster surfaces without any significant involvement of support sites; hence, the reducible nature of the support become much less consequential for CO oxidation catalysis in the presence of the H2O molecules that mediate required O2 activation steps. In contrast, supports influence CO oxidation turnover rates with nominally anhydrous reactants, perhaps because they contribute either adsorbed H2O that acts as co-catalyst in CO oxidation or periphery sites that become essential for O2 activation, but which are required only in the absence of H2O.

The observed H2O effects in CO oxidation are not exclusive of reactions catalyzed by Au clusters. We find that H2O also influences significantly measured CO oxidation rates with Pt clusters. This strongly suggests that CO oxidation with H2O as a co-catalyst occurs on supported noble metal clusters via common elementary steps involving the formation of hydroperoxy species that are responsible for the higher measured CO oxidation rates compared to those with anhydrous CO/O2 mixtures.

4. Conclusions

Moisture levels in “anhydrous” CO/O2 streams well below the detection limits of typical speciation techniques are consequential for CO oxidation catalysis; this has led to our suggestion that the presence of H2O is essential both for practical CO oxidation rates, for their reproducible measurements, and for fundamental studies of the mechanism and site requirements of these reactions. H2O is an efficient co-catalyst necessary for O2 activation steps and for catalyst stability in CO/O2 reactions at near-ambient temperatures with Au clusters (<5 nm) deposited on reducible (TiO2, Fe2O3) and non-reducible (Al2O3) supports. Rigorous kinetic and isotopic data measured on stable Au catalysts have led us to propose a mechanistic picture of CO oxidation in the presence of H2O that involves H2O-mediated O2 activation steps that form hydroperoxy species (‘OOH), which precisely account for the remarkable co-catalytic effect of H2O on measured CO oxidation rates. These steps occur exclusively on the Au clusters; hence, the influence of support identity on CO oxidation catalysis, and specifically its reducible nature, becomes much less important in the presence of H2O. These H2O effects in CO/O2 reactions are also found with Pt catalysts, which suggest that common elementary steps during CO/O2/H2O reaction occur on supported noble metal clusters (Au, Pt). The formation of hydroperoxy species explains the significantly higher CO oxidation rates compared to those measured with anhydrous CO/O2 mixtures.

Acknowledgments

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Appendix A

The rate of CO oxidation via the sequence of elementary steps shown in Scheme 1 is given by

\[ r_{CO} = r_5 + r_7 \] (A1)

By applying the pseudo-steady-state approximation (PSSA) to O\(^{-}\) and OH\(^{\cdot}\) species, we find that \( r_6 = r_7 \) and \( r_5/2 = r_6 \), respectively. Consequently, Eq. (A1) becomes

\[ r_{CO} = \frac{3}{2} \frac{3}{2} \frac{3}{2} k_3 [CO]\] (A2)

where [L] is the number of active sites.

The quasi-equilibrium assumption for steps 1–4 gives

\[ [CO^\cdot]\] = \( K_1 P_{CO}[\cdot]\] (A3)

\[ [O_2^\cdot]\] = \( K_2 P_{O_2}[\cdot]\] (A4)

\[ [H_2O^\cdot]\] = \( K_4 [O_2^\cdot][H_2O^\cdot]\] (A5)

\[ [\cdot]OH\] = \( K_{4} [O_2^\cdot][H_2O^\cdot]\] (A6)

The PSSA to OH\(^{\cdot}\) gives

\[ [\cdot]OH\] = \( \frac{2 k_4 [OH]^2}{kk_{[CO]}} \] (A7)

Combining Eqs. (A3)–(A7)

\[ [\cdot]OH\] = \( \frac{(K_2 K_4 K_5 K_6)}{2 k_5} (P_{CO} P_{O_2} P_{H_2O})^{1/3}\] [\( ] (A8)

Substituting Eq. (A8) in Eq. (A6)

\[ [\cdot]OH\] = \( \frac{(K_2 K_4 K_5 K_6)}{2 k_5} (P_{CO} P_{O_2} P_{H_2O})^{1/3}\] [\( ] (A9)

Hence, the rate of CO oxidation (Eq. (A2)) becomes

\[ \frac{r_{CO}}{3} \frac{3}{2} \frac{3}{2} \frac{3}{2} k_3 \] (A10)

where

\[ \alpha = \frac{3}{2} (K_1 K_2 K_3 K_5) (2 k_6)^{1/3} \] (A11)

[\[ [\cdot]OH\] and [\[ [\cdot]OH\] can be written as follows:

\[ [\cdot]OH\] = \( \beta (P_{CO} P_{O_2} P_{H_2O})^{1/3}\] (A12)

and

\[ [\cdot]OH\] = \( \delta (P_{CO} P_{O_2} P_{H_2O})^{1/3}\] (A13)

where

\[ \beta = \frac{(K_2 K_3 K_4 K_5)}{2 k_5} (K_1 K_3)^{1/3}\] (A14)

and

\[ \delta = \frac{(K_1 K_2 K_3 K_4 K_5)}{2 k_5}\] (A15)

A site balance gives

\[ [L] = \[* + [CO^\cdot] + [O_2^\cdot] + [H_2O^\cdot] + [\cdot]OH\] + [\( ] \] (A16)

Since \( r_5 = r_7 \),

\[ [O^\cdot] = \frac{k_5 [OH]^2}{k_{[CO]}} = \frac{(K_2 K_4 K_5 K_6)}{K_1 (2)^{1/3} k_7} (P_{CO} P_{H_2O})^{1/3}\] (A17)

where

\[ \gamma = \frac{(K_2 K_4 K_5 K_6)}{K_1 (2)^{1/3} k_7}\] (A18)

The site balance can also be expressed as the following:

\[ [L] = \[* + K_1 P_{CO} [\cdot] + K_2 P_{O_2} [\cdot] + K_3 P_{H_2O} [\cdot] + \beta (P_{CO} P_{O_2} P_{H_2O})^{2/3}\] (A19)

Therefore,

\[ [L] = \frac{1 + K_1 P_{CO} + K_2 P_{O_2} + K_3 P_{H_2O} + \beta (P_{CO} P_{O_2} P_{H_2O})^{1/3} + \gamma (P_{CO} P_{O_2} P_{H_2O})^{2/3}}{P_{CO}^{1/3}}\] (A20)

Substituting Eq. (A20) in Eq. (A10)

\[ r_{CO} = \frac{\alpha (P_{CO} P_{O_2} P_{H_2O})^{2/3}}{(1 + K_1 P_{CO} + K_2 P_{O_2} + K_3 P_{H_2O} + \beta (P_{CO} P_{O_2} P_{H_2O})^{1/3} + \gamma (P_{CO} P_{O_2} P_{H_2O})^{2/3})^{3/2}}\] (A21)

Appendix B. Supplementary data

Discussion on the CO oxidation kinetics corruptions imposed by H\(_2\)O condensation and concomitant mass transfer limitations inside the \( \gamma - Al_2O_3 \) pores; TEM images and Au cluster size distribution for the untreated and thermally-treated Au/Al\(_2O_3\) samples; kinetic parameters obtained from nonlinear fitting to Eq. (1) of rate data measured with Au/Al\(_2O_3\); kinetic dependence of CO oxidation turnover rates on CO pressure and \( \gamma - Al_2O_3 \) pressure measured with the thermally treated Au/Al\(_2O_3\) catalysts; and examples of alternate CO oxidation pathways, the derived kinetic expressions and the corresponding parity plots for the kinetic data measured with Au/Al\(_2O_3\) (288 K; 0.80–8.25 kPa CO; 0.25–7.15 kPa O\(_2\); 0.03–1.15 kPa H\(_2\)O). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2011.09.015.

References