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1 Interfacial Charge Transfer and Substrate-Dependent 2 Oxidation States Drive SMSI Enhancements in Cobalt 3 Oxide Films

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15 ABSTRACT:

16 We investigated the mechanisms underlying strong metal–support interactions (SMSI) in CO
17 oxidation using model systems where noble metal crystals support reducible, monolayer-thick CoO_x
18 films. The effect of the Co oxidation state, film thickness, and substrate identity were studied in
19 varying reaction conditions using ambient pressure X-ray photoelectron spectroscopy (APXPS). At

low O₂ pressures, the same oxide phase forms on both Pt(111) and Au(111) surfaces. But when heated at higher O₂ pressures, the oxide phase depends on the substrate. We found that CoO_x/Pt is more active for the CO oxidation reaction than CoO_x/Au, even when both surfaces stabilize the same oxide phase.

DFT calculations on these and related noble-metal-supported CoO_x films reveal an SMSI-induced reactivity enhancement that strongly depends on the oxide film thickness and which is mediated by charge transfer between the metal and oxide. Charge transfer is also found to correlate with the reaction energy and activation barrier for CO oxidation. This effect was found to be greatest for oxide films on Pt, decreasing on other noble metal supports in the order Pt>Pd>Au>Ag, in agreement with the experiments. The role of charge transfer in the activation barriers and reaction energies provides insight into the nature of SMSI-induced catalytic activity, and suggests that the noble metal work function can serve as an indicator for the strength of SMSI effects.

KEYWORDS: Charge Transfer, Strong Metal-Support Interaction, CO Oxidation, Cobalt Oxide, Noble Metals, Ambient Pressure XPS, Density Functional Theory

Introduction

The oxidation of CO to form CO₂ is a key reaction in CO exhaust gas mitigation, and is used extensively as a probe for catalytic processes due to its relative simplicity. Pt-based catalysts are often used for the reaction, but the high cost of Pt and other noble metal catalysts has driven recent efforts to decrease the amount of noble metal used.¹⁻³ Decreasing nanoparticle size or using single-site (i.e.

1 single-atom) catalysts with synergistic support materials often yields increased activity at mild
2 temperatures.⁴⁻⁶ These approaches also reduce the amount of noble metal required for reactions. For
3 example, mesoporous oxides loaded with Pt-nanoparticles exhibit enhanced activity, and Pt/FeO_x
4 single-site catalysts are active for CO oxidation at nearly room temperature.⁷⁻⁸ Supported
5 nanoparticles and single-site catalysts can also benefit from synergistic strong metal-support
6 interactions (SMSIs), where the oxide support rearranges to cover the metal nanoparticle, particularly
7 when there is a high fraction of noble metal-oxide interface contact area.^{4,6,8-11} In such cases,
8 interactions between reducible oxides and noble metals produce activity enhancements driven by
9 factors such as the sample oxidation state, oxide-noble metal charge transfer, spillover of intermediate
10 species between metal and oxide, and by encapsulation of the noble metal by the reducible oxide
11 support.^{6,9} Indeed, noble metal nanoparticle encapsulation is considered the most salient aspect of
12 SMSIs.^{4-6,11-13} Oxide films that encapsulate metals differ from bulk oxides in both structure and
13 reactivity due to their low dimensionality and intimate contact with the metal substrate. By studying
14 well-defined model systems that facilitate simultaneous characterization using ambient pressure X-
15 ray photoelectron spectroscopy (APXPS) and density functional theory (DFT) simulations, this work
16 seeks to disentangle these influences and provide insight into the role of specific catalyst phases and
17 metal-oxide charge transfer on reactivity.

18 Cobalt oxides (CoO_x) are active for CO oxidation, but when loaded with Pt nanoparticles they show
19 dramatic activity enhancement compared with other Pt-loaded oxides, suggesting a strong synergistic
20 interaction between the Pt and CoO_x.⁷ The activity of CoO_x also depends on the oxidation state (Co^{α+},
21 α = 0 to 3).¹⁴⁻¹⁸ The highest, Co³⁺, appears in Co₃O₄, which is active for CO₂ formation at room
22 temperature (RT). However, Co₃O₄ catalysts deactivate over time,¹⁹ particularly when water is present

1 in the reactant gas mixture.^{20,21} Co²⁺ appears in CoO, but is less active than the 3+ sites in Co₃O₄.^{22,23}
2 Along these lines we recently reported that CoO becomes active at RT in model monolayer
3 CoO/Pt(111) catalysts when oxygen vacancies are present.²⁴ The Co₂O₃ and CoO₂ phases have been
4 less extensively characterized.^{25,26} CoO₂ forms in bulk layered structures (e.g. PdCoO₂ and
5 PtCoO₂),^{18,26,27} which possess unique correlated electron heterostructures and high electrical
6 conductivity.²⁸ Recently, it was shown that CoO₂ is formed also on Au(111) and Pt(111) surfaces.
7 However, on Au(111) it was found coexisting with CoO.^{23,29} In CoO₂ the Co valency has been reported
8 as 3+ due to charge transfer between the oxide and the noble metal, rather than the 4+ which might
9 be expected for CoO₂.³⁰ While the impact of cooperative reactant adsorption and activation on the
10 support is well-explored for such systems in the literature, the impact of charge transfer on the
11 activity is less well-understood. Hence, we explore substrate-dependent reactivity of CoO_x films using
12 APXPS and DFT to understand the relationship between charge transfer and CO oxidation activity.

13 Charge transfer between reducible oxides and noble metals can play a critical role in catalyst
14 behavior. On TiO₂, it was reported that electron transfer from Ti atoms to electronegative metal
15 adsorbates enabled the metals' adsorption stability.³¹ Au nanoparticles deposited on TiO₂ were also
16 found to enhance the activity for CO oxidation beyond that for pure TiO₂ surfaces.³² Meanwhile, the
17 extent of charge transfer between TiO₂ and metal adsorbates was altered by introducing oxygen
18 vacancies.^{31,33} These results suggest that charge transfer between a catalyst and its support plays an
19 important role in SMSI effects. In fact, numerous noble metal–oxide systems have also been shown
20 to exhibit enhanced CO oxidation activity including Pt/FeO_x,³⁴ Pt/Co₃O₄,³⁵ CoO/PtCo,^{36,37} Pt/NiO,
21 Pt/CeO₂, Pt/MnO₂, Pt/Fe₂O₃,⁷ CoO_x/Pd,¹¹ Co₃O₄/Ir,³⁸ and Au/CoO_x.³⁹ Thus, understanding the

influence of the encapsulating oxide phase and metal-oxide charge transfer stands to provide insights into catalyst reactivity.

In this study we use thin oxide films deposited on the (111) surfaces of Pt and Au single crystals, instead of the usual geometry where oxides support noble metal clusters, to better model the encapsulation of noble metals by reducible oxides. CoO₂ formed readily in submonolayer Co films on Pt(111), and these films were reduced to Co²⁺ and to Co⁰ by CO at mild temperatures ≤ 120 °C. On Au(111) however, Co films formed Co²⁺:Co³⁺ mixtures when oxidized, which were not easily reduced by CO. This behavior is maintained under CO:O₂ mixtures at elevated temperatures, where Co⁰ appears in the films on Pt(111), but again not on Au(111). The importance of film structure and film/substrate charge transfer are uncovered using DFT calculations of cobalt oxide films supported on Pt, Au, and other noble metal substrates. We found that oxide films in direct contact with noble metal substrates exhibit a correlation between charge transfer, reaction energy, and activity. This correlation is much more pronounced for 1 ML films than for thicknesses of 2 ML or more. Interestingly, this activity–charge transfer correlation was found to be most pronounced for CoO_x films on Pt, and to decrease for Au, Pd, and Ag substrates, following the decrease in the work function of the noble metals.

Experimental Results

XPS characterization of the Co/Pt(111) oxidation states

Characteristic Co 2p XPS peak shapes for the three oxidation states of Co are shown in Fig. 1. Co⁰ is characterized by a sharp main peak near 777.9 eV (Fig. 1a).¹⁷ In CoO, Co²⁺ is characterized by a broader peak around 780.2 eV and a broad satellite structure around 786.6 eV (Fig. 1b). CoO also has

a larger spin-orbit splitting between the Co $2p_{3/2}$ and $2p_{1/2}$ components compared with the metallic state.¹⁷ Fig. 1c shows Co³⁺ with a main peak at 778.6 eV and a small satellite peak at 788.8 eV.^{18,30} Finally, the characteristic spectrum of a Co²⁺:Co³⁺ mixture is shown in Fig. 1d. Conditions leading to the formation of each of these states will be discussed in the next section.

We note that increasing the oxidation state of an atom typically shifts core electron states to higher BE. Hence, one would expect the Co³⁺ intensity maximum to appear at higher BE than in Co²⁺. In CoO however, core electrons in Co²⁺ couple to unpaired valence electrons to produce a broad structure whose maximum is shifted to higher BE.¹⁷ In some cases, notably in high-spin Co²⁺ species, this significantly shifts the intensity maximum.^{40,41} The same effect is not present in Co³⁺, and its intensity maximum appears at lower BE. Caution should therefore be exercised when interpreting BE shifts due to oxidation because final state relaxation and chemical and coordination environments can generate negative BE shifts.⁴²⁻⁴⁶

Oxidation of CoO_x films on Pt(111) and Au(111)

Fig. 2 shows the evolution of the Co 2p XPS region during oxidation of a 0.4 MLE film on Pt(111), as the Co oxidizes from Co⁰ to Co²⁺ in the presence of 10⁻⁷ Torr O₂ at room temperature (RT). The formation of Co²⁺ is indicated by the increasing intensity of the peak at 780.2 eV and the broad satellite structure around 786 eV. At higher O₂ pressure and temperature, Fig. 3a shows the formation of Co³⁺. In 10⁻⁵ Torr O₂, exposures from 5000 Langmuir (L) to 15000 L of O₂ cause a shift of the Co 2p peak to higher BE due to formation of Co³⁺ (Fig. 3a, lower spectra). At higher O₂ pressure and temperature, the spectra show a larger contribution of the main Co³⁺ peak and a small satellite structure at 788.8 eV (also in Fig. 1c). Interestingly, the peak position continuously shifts from that of Co⁰ to that of Co³⁺

with only a small contribution from Co^{2+} , which would manifest a broader overlapping peak if present. This suggests that at or above 10^{-5} Torr O_2 , Co does not form a complete Co^{2+} film on Pt prior to the formation of Co^{3+} . Previous investigations have shown that Co^{3+} appears in the trilayer (M-O-Co-O, M = noble metal) structure characteristic of the CoO_2 phase.^{18,29} These results suggest that Co may transition here directly from the $2+$ state into the $3+$ state in this form. We note that Co^{3+} also appears in CoOOH , but the hydroxide decomposes to cobalt oxide well below the 280°C used in Fig. 3a.^{23,47,48} Hence, the Co^{3+} here is attributed to CoO_2 rather than CoOOH . Interestingly, for 3 MLE of Co^0 on Pt(111), Co instead oxidizes into a $\text{Co}^{2+}:\text{Co}^{3+}$ mixture (Fig. 1d).

For comparison, on Au(111) we deposited a 0.7 MLE Co^0 film (Fig. 3b). Because Co^0 forms bilayer islands on Au(111),²⁹ the deposited film should cover ~ 0.35 ML of the substrate, close to the coverage of the 0.4 MLE films on Pt(111). When heated in O_2 , the Co^0 films on Au(111) oxidize to form $\text{Co}^{2+}:\text{Co}^{3+}$ mixtures as shown in the top spectrum of Fig. 3b (fitting for this spectrum is shown in Fig. S1a). This is in contrast to 0.4 MLE Co films on Pt(111), which formed only Co^{3+} in the same conditions (Fig. 3a, top spectrum). This is in agreement with previous studies of submonolayer CoO_x on Au(111) under similar conditions, which revealed multiple oxide structures with mixtures of Co^{2+} and Co^{3+} states.²⁹ CO oxidation activity is influenced by these different oxide phases and by their interactions with the Au(111) and Pt(111) substrates, as we discuss next.

Influence of the noble metal support on catalytic activity for CoO_x in the CO oxidation reaction

Because the activity of supported oxide films for CO oxidation can be impacted by charge transfer between oxide and support, we now explore the impact of the noble metal support on the CO

oxidation activity of CoO_x films.^{6,9} Figure 4a shows Co 2p spectra of a 0.4 MLE Co^{3+} film on Pt(111) during its reduction by CO. The Co^{3+} was formed by heating the film to 280 °C in 40 mTorr O_2 . At RT in UHV, the film is stable in the Co^{3+} state (Fig. 4a, spectrum 1). Exposure to 40 mTorr CO at RT reduced the Co^{3+} to a $\text{Co}^{2+}:\text{Co}^{3+}$ mixture (spectra 2,3), with a small amount of Co^0 appearing in these conditions. Keeping the sample in 40 mTorr CO and heating to 120 °C further reduced the film, as evidenced by the increased intensity of the Co^0 peak (spectrum 6). Fig. 4c shows the spectral composition of Co oxidation states for 0.4 MLE Co on Pt(111) as a function of reduction condition, determined by extracting the Co^0 , Co^{2+} , and Co^{3+} components from the fits shown in Fig. 4a.

The Co 2p spectra of 0.7 MLE CoO_x on Au(111) under similar reaction conditions are shown in Fig. 4b. As the temperature increased, the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio increased as shown by the increasing intensity of the satellite at 786.6 eV, most noticeably above 220° C, until the film contained mostly Co^{2+} . However, even at 280 °C the $\text{CoO}_x/\text{Au}(111)$ was not reduced to Co^0 by reaction with CO, in contrast with the 0.4 MLE oxide film on Pt(111), which reduced from Co^{3+} to Co^{2+} and to Co^0 at 120 °C (Fig. 4a). Fig. 4d shows the spectral composition of Co oxidation states for 0.7 MLE Co on Au(111) as a function of reduction condition, determined by extracting the Co^0 , Co^{2+} , and Co^{3+} components via fitting the Co 2p region (a sample fit is provided in Fig. S1). The lower temperature reduction of the $\text{CoO}_x/\text{Pt}(111)$ under these conditions highlights the importance of the substrate (Pt vs. Au) to the activity of CoO_x for CO oxidation.

To explore whether film thickness affects the reducibility of CoO_x , we performed a similar experiment with a 2 MLE film covering the Au(111). The bottom curve in Fig. 5 shows the Co 2p spectrum produced by heating the metallic Co film to 280 °C in 40 mTorr O_2 . As in the previous experiments, this produced a $\text{Co}^{2+}:\text{Co}^{3+}$ mixture similar to that shown in Fig. 3b. Like the case of 0.7

MLE $\text{CoO}_x/\text{Au}(111)$, this film also was not reduced to Co^0 by exposure to 40 mTorr CO at any temperature investigated here. Further, we note that in recent work we demonstrated that 0.5 MLE $\text{CoO}_x/\text{Au}(111)$ also did not reduce to Co^0 , even when heated to 100 °C in CO pressures higher than those used here.⁴⁹ Once again this contrasts with the films on $\text{Pt}(111)$, which is reduced to Co^0 even at mild temperatures of just 120 °C.

The reduction of submonolayer CoO_x/Pt to Co^{2+} and to Co^0 at mild temperatures contrasts starkly with the stability of submonolayer CoO_x/Au studied both here at 0.7 MLE and in our previous work at 0.5 MLE.⁴⁹ Furthermore, while it is known that Co^{3+} can be reduced by CO at RT^{19,23}, the finding that CoO_x/Pt reduces to Co^0 at mild conditions has implications for the functional catalyst state under realistic reaction conditions, potentially altering the relevant reaction energy pathways, and thus directly impacting the activity.

Oxidation state of CoO_x in $\text{CO}:\text{O}_2$ gas mixtures

To determine the oxidation state of CoO_x films under reaction conditions on $\text{Pt}(111)$ and $\text{Au}(111)$, we exposed the films to $\text{CO}:\text{O}_2$ mixtures of 35 mTorr CO + 5 mTorr O_2 at 220 °C. This temperature was chosen because the Co^{3+} component of the films is reduced by CO at that temperature on both surfaces as shown in Fig. 4a,b and Fig. 5. Thus both systems should be active for CO oxidation to form CO_2 at that temperature. Meanwhile, the CO-rich reaction mixture provides a strong reducing condition to best probe the reducibility of both films on both surfaces.

During the reaction with a 0.4 MLE film on $\text{Pt}(111)$, XPS shows that the film contains both Co^0 and Co^{2+} (Fig. 6, top spectrum). Because Co^0 is readily oxidized at partial pressures of 5 mTorr O_2 , the presence of Co^0 suggests that some of the oxide is being reduced to Co^0 during the reaction. Otherwise

Co⁰ in the film should be oxidized at this O₂ pressure and temperature. While we did not measure 0.7 MLE CoO_x/Au(111) under the same conditions, the lower spectrum in Fig. 6 shows the Co 2p region for a 2 MLE CoO_x film on Au(111) under 35 mTorr CO + 5 mTorr O₂ at 220 °C. In contrast to the case for 0.4 MLE CoO_x/Pt(111), the 2 MLE CoO_x films on Au(111) contain Co²⁺, and little or no Co⁰ during the reaction. The stability of the Co²⁺ phase on Au(111) in the reaction mixture agrees with the stability of the Co²⁺ phase also observed on Au(111) in pure CO (Fig. 4b and Fig.5).

We showed already that 0.4 MLE Co films on Pt(111) readily oxidize to Co³⁺ when heated in O₂ (Fig. 3a). In CO gas, the Co³⁺ and Co²⁺ species on Pt(111) reduce at mild temperatures (Figs. 4a, S1b), indicating that both phases are active for CO oxidation. The presence of Co⁰ during the reaction suggests high CO₂ formation activity under reaction conditions. Meanwhile, CoO_x films on Au(111) could be reduced to Co²⁺, but not to Co⁰ by CO at any condition explored here at coverages of 0.7 – 2 MLE (Figs. 4b,5) or in our previous work⁴⁹ at 0.5 MLE coverage. Hence, the Co²⁺ phase is less active on Au(111) than on Pt(111).

Theoretical Models: Influence of substrate composition and oxide film thickness on charge transfer, reaction barriers, and activity

The reactivity of CO with lattice oxygen in CoO_x to form CO₂ can be impacted by the film's oxidation state, its structure, and charge transfer between the oxide film and noble metal support. Previous studies have investigated the impact of CoO_x island edge sites in CO oxidation⁵⁰⁻⁵² and their structural transformation upon reduction under reaction conditions.⁵⁰ Here, we explore the impact of oxidation state and charge transfer between the oxide and support.

1 To better understand the conditions leading to high activity for CoO_x on Pt, we first evaluated the
2 reaction pathway for CO reacting with lattice oxygen in $\text{CoO}_2/\text{Pt}(111)$ (Fig. 7). This was the most
3 active of the CoO_x films studied experimentally, and contains three atomic layers in the order of O-
4 Co-O. This is simulated as an epitaxial overlayer on $\text{Pt}(111)$, with the lower O layer situated atop
5 substrate Pt atoms (Fig. 7a inset). CO gas reacts with the outermost O layer by physisorbing on surface
6 oxygen with a 1.23 eV free energy barrier to form physisorbed CO_2 (Fig. 7a). The reaction is
7 exothermic, and the weakly bound CO_2 product can readily desorb from the surface. The adsorbed
8 CO_2^* could also form CO_3^{2-} (carbonate) by reacting with another surface O through a 0.16 eV barrier
9 (Fig. 7b steps 2-3). However, this reaction is still endergonic relative to CO_2 gas, making the CO_3^{2-}
10 group thermodynamically unstable under reaction conditions. Hence, the formation of CO_2 gas is
11 favored.

12 Compared to the single monolayer CoO_2 film, CoO on $\text{Pt}(111)$ has a higher CO oxidation barrier
13 (Figs. 7a, 8a), but the barrier shows a clear trend with respect to oxide thickness: 1 ML thick CoO is
14 the most reactive with a 1.44 eV barrier for CO gas reacting with surface O (Fig. 8a). Meanwhile, 2
15 ML and thicker films have higher barriers. The reaction proceeds through a transition state where
16 CO adsorbs between a surface O atom and a Co site (Fig. 8b inset), and the net reaction energy for
17 CO_2 gas formation on CoO is -1.66 eV (Fig. 8a,b). This is less exergonic than on CoO_2 (-1.80 eV, Fig.
18 7a). Hence, while CoO is less active for CO_2 formation than CoO_2 , its CO_2 formation barrier varies
19 with film thickness, rendering 1 ML films more active than thicker CoO films. Finally, the free energy
20 change for CO_2 gas to form CO_3^{2-} on CoO is 1.18 eV, with an energy barrier of 1.48 eV (Fig. 8a, steps
21 3-5), making it more endergonic than the same reaction on CoO_2 .

1 Interestingly, CO oxidation reactivity for CoO decreases (i.e. the energy barrier increases) non-
2 linearly with film thickness. Raising the thickness from 1 ML to 2 ML increases the barrier for CO
3 gas to react with surface O from 1.44 eV to 1.69 eV (Fig. 8a,b). But further increasing to 3 ML or
4 above only shifts the barrier to 1.75 eV and not any higher (Fig. 8b). Additionally, increasing the film
5 thickness beyond 1 ML leads to less negative reaction energies (Fig. 8b). Hence, the reaction energy
6 and reactivity vary non-monotonically with film thickness, and 1 ML CoO films on Pt are the most
7 reactive (Fig. 8a).

8 While the reaction barrier for CO₂ formation increased with CoO thickness, the opposite trend
9 appeared for CO₃²⁻ (carbonate) formation from CO₂ gas. The energy barrier decreased from 1.48 eV
10 at 1 ML to 1.26 eV at 2 ML, and decreased little for thicknesses beyond 2 ML (Fig. 8). Here, the free
11 energy barrier is the difference between CO₂ gas (third step in Fig. 8a) and the transition state to form
12 CO₃²⁻ (the fourth step in Fig. 8a). One possible origin of these trends could be the different
13 coordination environment of the Co atoms. Each Co in 1 ML CoO resides in an octahedral site and is
14 bound to three Pt atoms. Meanwhile, the Co atoms in 2 ML films and above are in tetrahedral sites
15 and are coordinated to 4 O atoms.

16 Another potential origin of this thickness-reactivity relationship is the electronic interaction
17 between the outermost CoO layer and the substrate. To examine this interaction, we calculated the
18 reaction energy for CO gas reacting with surface O to form CO₂ and leave an O vacancy. Following
19 the Brønsted-Evans-Polanyi relationship between reaction energy and activation barrier, the reaction
20 energy is taken as a signature for reactivity, with more negative reaction energies indicating a lower
21 activation barrier.⁵³ The reaction energy was explored for 1 ML and 2 ML films on substrates that
22 have various work functions (Pt, Pd, Au, and Ag). For 1 ML CoO films, the resulting reactivity varied

1 in the order $R_{Pt} > R_{Pd} > R_{Au} > R_{Ag}$ (R_i = CoO reactivity on substrate i) (Fig. 9a). The difference in
2 reactivity for CoO/Pt compared to CoO/Au agrees with the experimental results, which showed that
3 submonolayer CoO_x films on Pt were reduced to CoO and to Co⁰ at temperatures ≤ 120 °C, while films
4 on Au only reduced to CoO and did not reduce to Co⁰ under any condition explored.

5 For 1 ML films, the relationship between reactivity and substrate composition correlated well with
6 the total Bader charge transferred from the outermost Co-O layer to the noble metal (Fig. 9a, blue
7 dots). Charge transfer from the oxide to the metal substrate led to increasingly reactive films, as shown
8 in Fig. 9a. In contrast, reactivity and charge transfer for 2 ML CoO films both varied only weakly
9 with the substrate (Fig. 9a, green points). From a structural perspective, the charge transfer polarizes
10 and weakens Co-O bonds on the surface, leading to progressively more reactive films with increasing
11 charge transfer.⁵⁴ The polarization of Co-O bonds is reflected in the spacing between the outermost
12 Co and O layers in the surface-normal direction, which correlates well with the reactivity of the film
13 (Fig. 9b). Hence, charge transfer between the outermost CoO layer and the substrate, and the resulting
14 surface Co-O bond polarization, produce differences in the reactivity of CoO films. Finally, the work
15 function for Ag, Au, Pd, and Pt surfaces correlates well with charge transfer between the oxide and
16 its support (Fig. 9c). This suggests that the noble metal work function can play a role in the choice of
17 materials during catalyst design when noble metals are in contact with reducible oxides.

18 Interestingly, previous work showed that PdCo nanoparticles have the highest CO oxidation
19 activity when the amount of Co was sufficient to form a monolayer thick oxide at the nanoparticle
20 surface.¹¹ Additionally, numerous noble metal-oxide systems have been highlighted for enhanced CO
21 oxidation activity.^{7,11,34-39} Our findings indicate that monolayer oxide films in contact with noble
22 metals having high work functions may be optimal systems for CO oxidation at mild temperatures.

Taken together with known structural considerations⁵⁰⁻⁵², these findings provide a detailed picture of the impact of the substrate on CO oxidation for such thin oxide films.

Finally, we note that an experimental exploration of the relationship between film thickness and reactivity for CoO/Pt(111) would further support the DFT results. It would be expected that reactivity decreases with increasing film thickness (Fig. 8) until the activity no longer depends on the substrate. However, experimental verification is complicated because CoO_x films on Pt(111) exhibit Stranski-Krastanov growth. In this growth mode, the film forms a nearly complete first layer before the second layer begins to nucleate. However, growth becomes increasingly uneven as the Co coverage increases, leading to films where 1 ML, 2 ML, and 3 ML regions are co-exposed, thus complicating the necessary experiments and interpretation. Nevertheless, this is an important future direction.

Conclusions

Through a combined experimental and computational approach, we demonstrate the dependence of CO oxidation activity on substrate-dependent oxide phases and charge transfer in SMSI systems.

Using APXPS, we demonstrated the formation of Co³⁺ with little or no Co²⁺ remaining in submonolayer Co films on Pt(111) when exposed to pure O₂ gas above 10⁻⁵ Torr. Under pure CO at RT, the Co³⁺ reduced to Co²⁺ and then to Co⁰ at mild temperatures (~100 °C). This high activity behavior on Pt(111) contrasts with that on Au(111), where Co³⁺ is only reduced to Co²⁺ at elevated temperatures, and reduction to Co⁰ does not occur, even by heating to higher temperatures in pure CO. We note that CO also adsorbs readily on the Pt(111) surface, potentially providing a source of surface-bound CO which may contribute to the oxide reduction in submonolayer films in the APXPS experiments. Nevertheless, since Co³⁺ films on Pt reduce to Co²⁺:Co⁰ mixtures even under reaction conditions, such films present a potential pathway to efficient CO oxidation catalysts.

Using DFT calculations, we found that increased charge transfer between the oxide surface and the substrate is correlated with decreased activation barrier and decreased reaction energy for the CO oxidation reaction on CoO films. In agreement with the experiment, this effect was more pronounced for films on Pt than for films on Au. This effect was also found to be more pronounced for films on Pt than for those on Ag, or Pd. Furthermore, the reaction energies varied with charge transfer much more in 1 ML CoO films than in 2 ML films. This led to lower reaction energy for 1 ML CoO_x/Pt than for any other film investigated here. In all cases, increasing charge transfer leads to increased Co-O bond polarization, which correlates with differences in reactivity.

In the traditional model of the SMSI, a thin layer of reducible oxide substrate material encapsulates noble metal particles under reducing conditions.^{12,13} Our experimental and theoretical results provide insight into the nature of such strong metal-support interactions, indicating that substrate-dependent oxidation states and charge transfer between the encapsulating oxide layers and noble metals enhance the catalyst reactivity. The charge transfer from Co to the substrate weakens and polarizes the Co-O bond, which decreases the reaction barrier for CO oxidation. This indicates that the noble metal work function can serve as a predictive metric for the ease of lattice oxygen activation in monolayer thick oxides for oxidation reactions in SMSI systems.

Methods

APXPS measurements of CoO_x films on Pt(111) and Au(111) were performed at beamline 23-ID-2 (IOS) of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory, and at beamline 9.3.2 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Beamline 23-ID-2 at NSLS II provides a photon flux up to 10¹³ photons/s with a beam spot of 20 μm

1 $\times 80 \mu\text{m}$, while beamline 9.3.2 of the ALS provides approximately three orders of magnitude lower
2 flux, with a spot diameter of approximately 1.0 mm. To compensate for the lower flux in the latter
3 case, the pass energy was increased to decrease the necessary acquisition time. The Pt(111) surfaces
4 were cleaned by cycles of Ar^+ ion sputtering (1.5 kV, 15 min.) and annealing (700 °C, 5 min.), followed
5 by another annealing cycle in 5×10^{-8} Torr O_2 , and flash annealing to 800 °C. The Au(111) samples
6 were cleaned by cycles of Ar^+ ion sputtering (1.5 kV, 15 min.) and annealing (550 °C, 5 min.). The
7 absence of contaminants on each surface was confirmed within the detection limit by XPS.

8 Co films were formed using electron-beam evaporation from 99.99+% pure Co rods (Goodfellow)
9 using e-beam evaporation. Evaporation rates and film coverages were calibrated by quartz crystal
10 microbalance and XPS. Because both one- and two-atomic-layer thick Co islands can form on the
11 same Au(111) surface²⁹, we refer to the amount of Co on each surface in terms of monolayer
12 equivalents (MLE). One MLE is the amount of Co that would form one monolayer (ML) if the entire
13 film were Co^0 of one-atomic-layer thickness.

14 The films were then oxidized by exposure to O_2 gas at various temperatures and pressures, as
15 specified in the text. For all measurements involving CO, carbonyl traps were used to ensure purity
16 of the gas. The Co 2p spectra were obtained using 1000 eV or 900 eV X-ray photons, as specified in
17 the corresponding figure captions. Binding energies (BEs) in the spectra are referenced to the Fermi
18 edge in each experiment, and procedures used for peak fitting in this work are described in the
19 supporting information.

20 Density functional theory (DFT) calculations were performed using the Vienna Ab-initio
21 Simulation Package (VASP), version 5.4.1.⁵⁵⁻⁵⁷ The exchange correlation energy was calculated using
22 the Perdew-Burke-Ernzerhof (PBE) functional.⁵⁸ The core electrons were described using the

projector-augmented wave (PAW) method.⁵⁹ The one electron wavefunctions were expanded using a set of plane waves with kinetic energy up to 500 eV. To correct for the self-interaction error of Co 3d electrons, a Hubbard-like onsite repulsion term (DFT+ U) was included in the DFT calculations using Dudarev's approach, with an effective U value of 3.5 eV.^{60,61} Transition states were searched with the nudged elastic band (NEB), climbing image (CI) NEB, Dimer, and quasi-Newton algorithms.⁶²⁻⁶⁴ The electronic structure in each self-consistent field (SCF) cycle was considered converged when the difference in total energy of consecutive steps fell below 10^{-6} eV. Atomic positions were considered converged when the Hellman-Feymann forces on unconstrained atoms fell below 0.02 eV/Å. Free energies of CO and CO₂ gas were approximated using their translational and rotational partition functions.⁶⁵ Additional information on the structural models can be found in the SI.

FIGURES

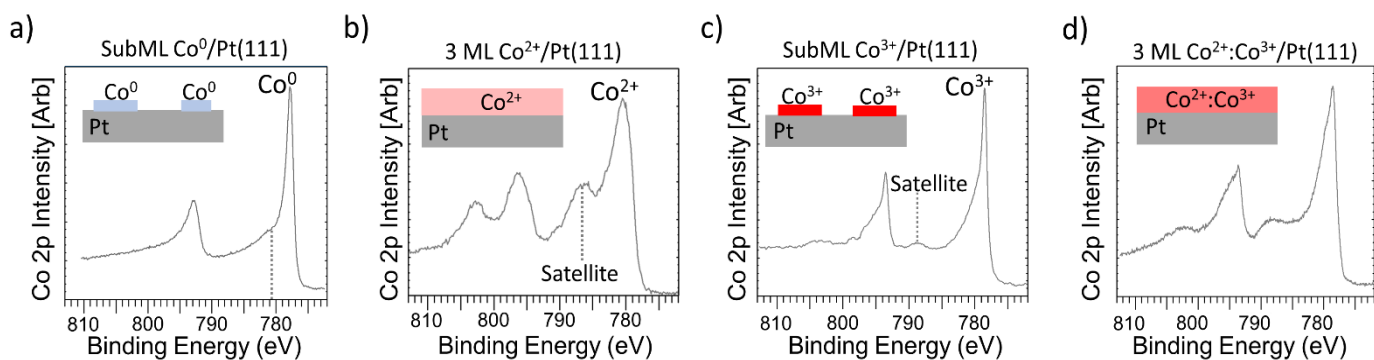


Figure 1. Co 2p XPS region for Co films on Pt(111). a) Submonolayer Co as deposited at room temperature on Pt(111), containing mostly Co⁰, with a small CoO (Co²⁺) component. b) 3 ML CoO (Co²⁺) on Pt(111). c) Submonolayer Co³⁺/Pt(111). d) 3 ML Co²⁺:Co³⁺ mixture on Pt(111), formed by heating 3 ML Co⁰ to 280 °C in 40 mTorr O₂. Incident photon energy = 1000 eV

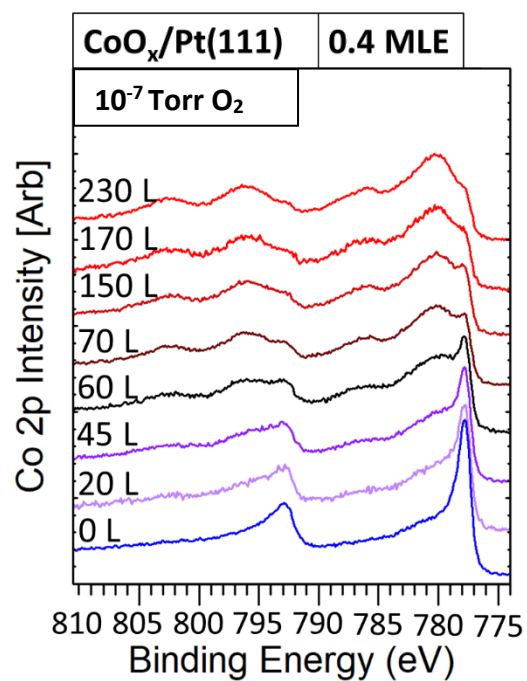


Figure 2. Co 2p XPS region for submonolayer CoO_x on Pt(111). At room temperature the as-deposited film contains mostly Co^0 (bottom spectrum), with only a small amount of CoO (Co^{2+}). Exposed to O_2 at 1×10^{-7} Torr, the submonolayer film oxidizes to CoO with increasing exposure (20 L – 230 L). Incident

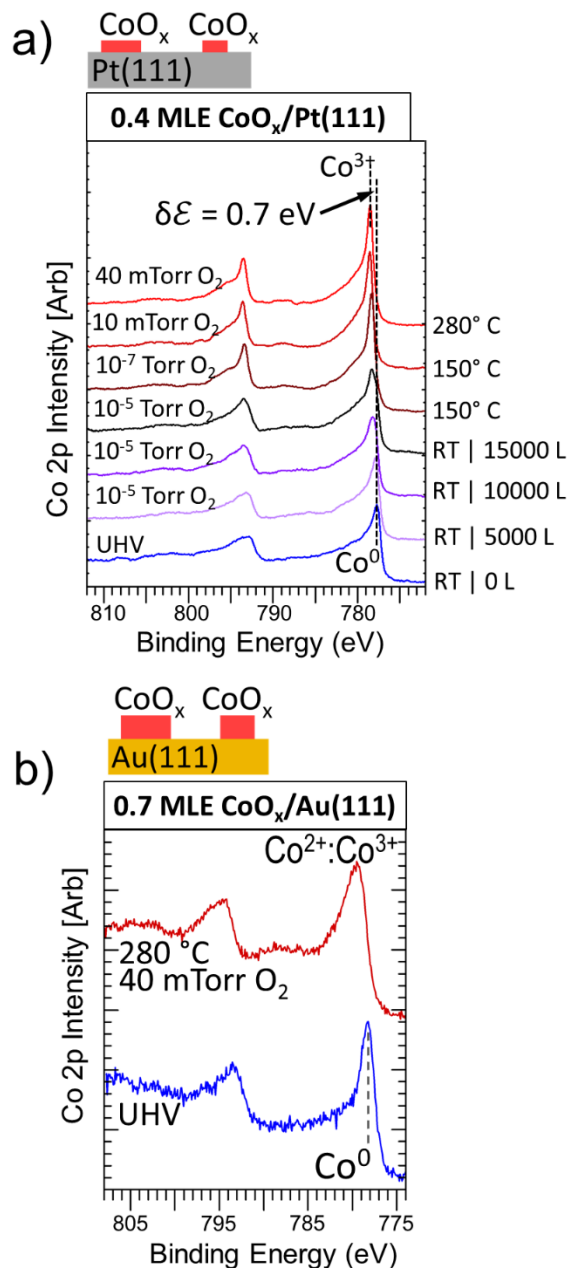
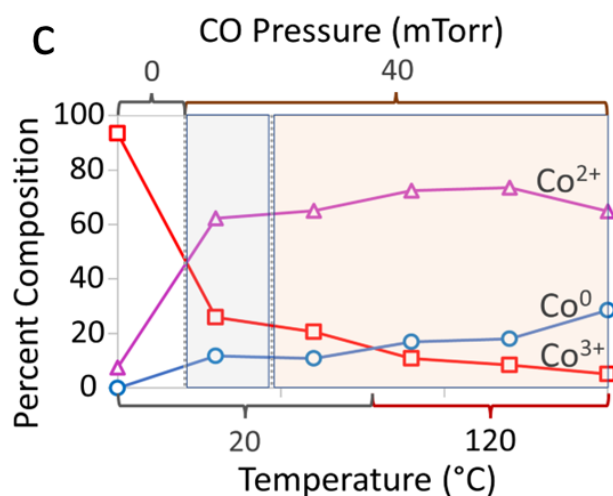
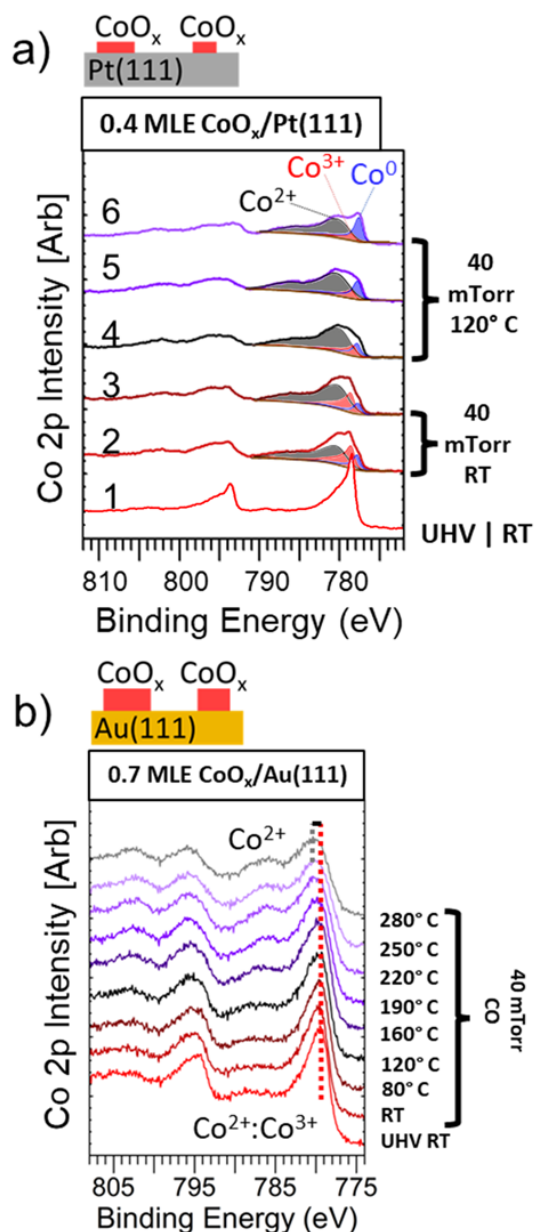
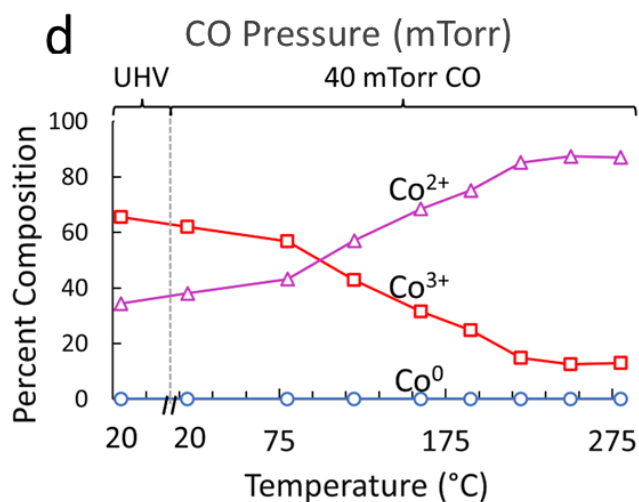


Figure 3. a) Co 2p XPS from 0.4 MLE Co/Pt(111) exposed to various O₂ pressures, and temperatures. The initial Co film is mainly Co⁰ (bottom). Increased O₂ exposure, pressure, and temperature (from UHV to 40 mTorr, and RT to 280 °C) convert Co⁰ to Co³⁺ (top), as indicated by the 0.7 eV BE shift and the small satellite near 788.8 eV. b) An initially clean 0.7 MLE Co/Au(111) film (blue, bottom) exposed to 40 mTorr O₂, and heated to 280 °C (red, top). The film formed a Co²⁺:Co³⁺ mixture while the same conditions converted 0.4 MLE Co⁰ to Co³⁺ on Pt(111). Incident photon energy: 1000 eV and



*300 seconds/point (1.2×10^7 Langmuir)



*2000 seconds/point (8×10^7 Langmuir)

Figure 4. a) Co 2p XPS from 0.4 MLE CoO₂/Pt(111): (1) In UHV at RT. (2,3) During exposure to 40 mTorr CO, which reduced the oxide from Co³⁺ to a Co²⁺:Co³⁺ mixture at RT. (4,5,6) Heating to 120 °C in 40 mTorr CO, which reduced the oxide further, first to Co²⁺, and then to Co⁰. b) Co 2p XPS from 0.7 MLE CoO_x/Au(111): Exposure to 40 mTorr CO reduced the Co²⁺:Co³⁺ mixture to Co²⁺ only at elevated temperature, and the oxide did not reduce significantly to Co⁰ even at 280 °C in 40 mTorr CO. Incident photon energy: 1000 eV and 900 eV for a) and b), respectively. c) Relative concentration of oxidation states for 0.4 MLE CoO_x/Pt(111) as a function of condition corresponding to (a). d) Relative concentration of oxidation states for 0.7 MLE CoO_x/Au(111) as a

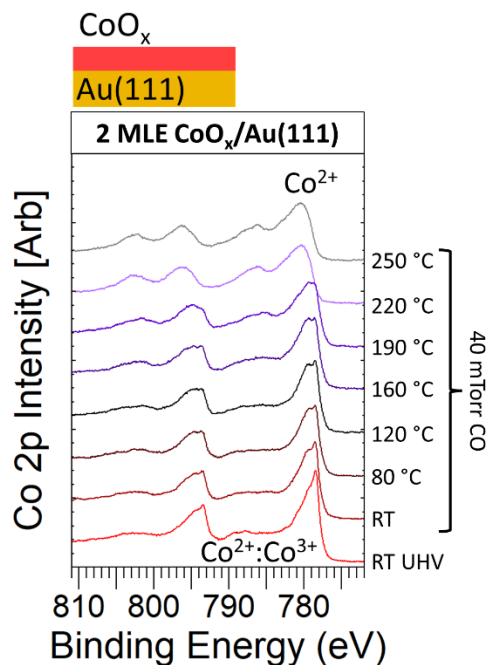


Figure 5. Co 2p XPS region from 2 MLE $\text{Co}^{2+}:\text{Co}^{3+}$ mixtures on Au(111): Exposure to 40 mTorr CO did not significantly reduce the oxide to Co^{2+} until a temperature of 200 °C or higher was reached. Under no condition explored here does the oxide reduce to metallic Co. Incident photon

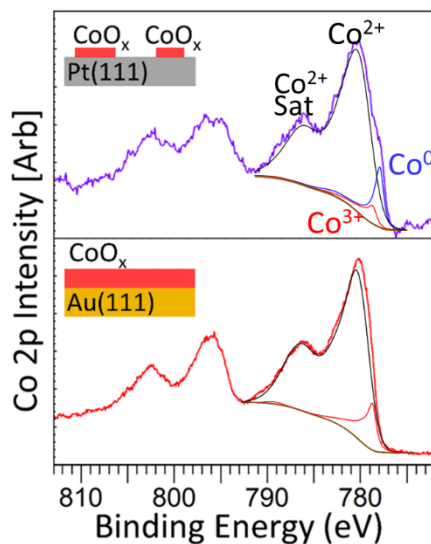


Figure 6. Co 2p XPS region from a 0.4 MLE CoO_x film on Pt(111) (top) and 2 MLE on Au(111) (bottom) under reaction conditions of 35 mTorr CO + 5 mTorr O_2 and 220° C. Incident photon energy: 1000 eV.

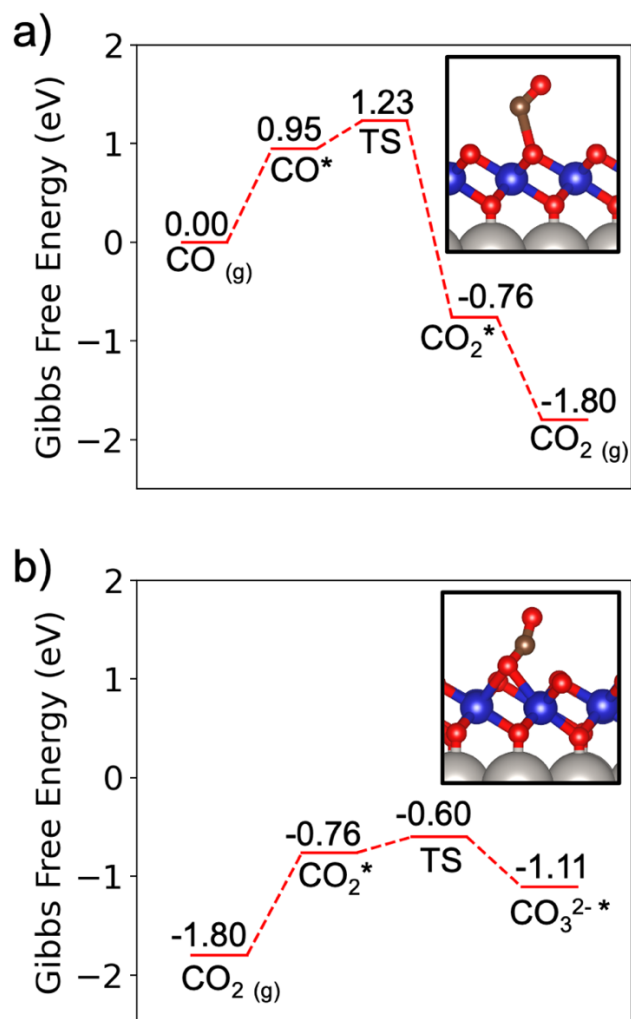


Figure 7. Free energy pathways of CO and CO₂ gas reacting with the lattice oxygen of 1 ML CoO₂/Pt(111). (a) By overcoming a 1.23 eV free energy barrier to the transition state (TS), CO reacts with O on the surface (O_{surf}) of the CoO₂ overlayer to form CO₂ gas, leaving behind an

O vacancy (O_{vac}). (b) A physisorbed CO_2^* is formed in the $\text{CO}-O_{\text{surf}}$ reaction and reacts with another O_{surf} to form CO_3^{2-} by overcoming a 0.16 eV barrier. The exergonic decomposition of CO_3^{2-} can proceed over a 0.51 eV barrier, rendering the CO_3^{2-} group thermodynamically unstable. The geometries of the transition states for the formation of CO_2 and CO_3^{2-} are shown in the insets of (a) and (b), respectively. The Gibbs free energies were evaluated for $T = 100^\circ\text{C}$, $P_{\text{CO}} = 100$ mTorr, and $P_{\text{CO}_2} = 0.1$ mTorr. (Atom color codes: blue = Co, red = O, grey = Pt, brown = C.)

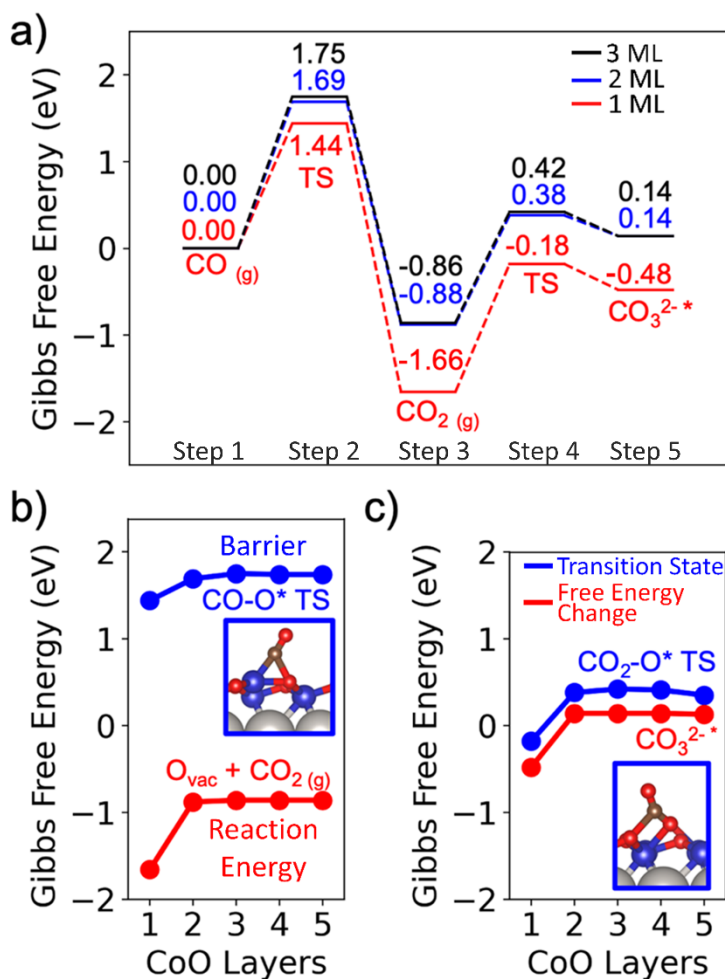


Figure 8. Dependence of reactivity on CoO film thickness, in overlayers on Pt(111). (a) The free energy pathway of CO reacting with 1 to 3 ML CoO/Pt(111) to form CO_2 gas and then for CO_2 gas to form CO_3^{2-} . (b) Free energy barrier (blue) to reach the transition state, and free energy change (red) to form CO_2 . (c) The transition state free energy (blue) between CO_2 and

CO_3^{2-} ; and net free energy change from CO gas (through CO_2 and O^*) to form CO_3^{2-} (red). The results highlight the unique reactivity of the CoO monolayer. Representative geometries of the transition states for the formation of CO_2 and CO_3^{2-} are shown in the insets of (b) and (c), respectively. Gibbs free energies are evaluated at $T = 100\text{ }^\circ\text{C}$, $P_{\text{CO}} = 100\text{ mTorr}$, and $P_{\text{CO}_2} = 0.1\text{ mTorr}$. (Atom color codes: blue = Co, red = O, grey = Pt, brown = C.)

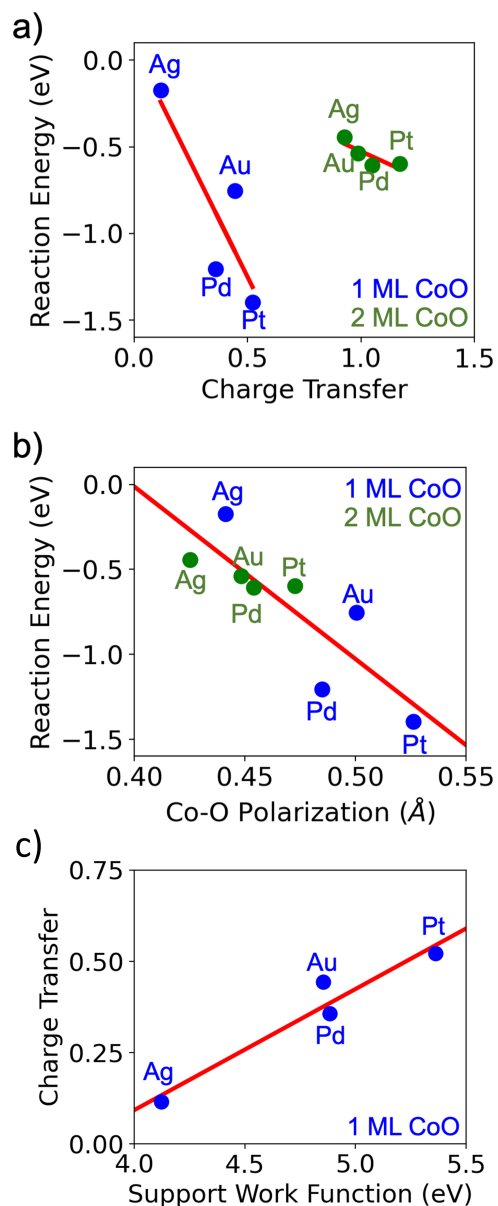


Figure 9. DFT calculations showing the influence of the noble metal substrate on the reactivity of supported CoO films in the CO oxidation reaction for different oxide film thicknesses. (a) Reaction energy to form CO₂ vs. Bader charge transfer between outermost CoO layer and noble metal substrate. (b) Reaction energy vs. Co-O bond polarization due to charge transfer between the outermost CoO layer and substrate. The lines in (a) and (b) are drawn as guides to the eye. (c) Relationship between the noble metal work function and charge transfer. The work function was evaluated for the bare support surface with its lattice spacing strained to 3.15 Å, and a trendline is drawn in red as a guide.

ASSOCIATED CONTENT

Supporting Information.

The following is available free of charge.

Fitting procedures for XPS data, additional fits and associated temperature dependent trends, and additional details on structural models used in the DFT calculations are contained in the Supporting Information (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. H.K., H.C., M.vS., C.M., I.W., A.H., and S.N. performed the experiments. H.K and M.S. performed data analysis. The DFT calculations were performed by G.Y., assisted by H.N., and supervised by PS. All authors have given approval to the final version of the manuscript.

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