Highly active surfaces for CO oxidation on Rh, Pd, and Pt

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Abstract

Studies show that the rate of CO oxidation on Pt-group metals at temperatures between 450 and 600 K and pressures between 1 and 300 Torr increases markedly with an increase in the O_2/CO ratio above 0.5. The catalytic surfaces, formed at discrete O_2/CO ratios >0.5, exhibit rates 2–3 orders of magnitude greater than those rates observed for stoichiometric reaction conditions and similar reactant pressures or previously in ultrahigh vacuum studies at any reactant conditions and extrapolate to the collision limit of CO in the absence of mass transfer limitations. The O_2/CO ratios required to achieve these so-called "hyperactive" states (where the reaction probabilities of CO are thought to approach unity) for Rh, Pd, and Pt relate directly to the adsorption energies of oxygen, the heats of formation of the bulk oxides, and the metal particle sizes. Auger spectroscopy and X-ray photoemission spectroscopy reveal that the hyperactive surfaces consist of approximate 1 ML of surface oxygen. *In situ* polarization modulation reflectance absorption infrared spectroscopy measurements coupled with no detectable adsorbed CO. In contrast, under stoichiometric O_2/CO conditions and similar temperatures and pressures, Rh, Pd, and Pt are essentially saturated with chemisorbed CO and exhibit far less activity for CO oxidation.
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The oxidation of CO, although one of the simplest catalytic reactions known, is very important for practical and fundamental reasons [1–10]. For example, the importance of removing toxic CO from industrial and automotive exhausts [11] and traces of CO from H_2 feed gas for fuel cells [12,13] have stimulated numerous basic and practical investigations over a variety of catalysts. The simplicity of CO oxidation makes it an ideal model reaction for surface science investigations [3–7,9,10,14–28]. These studies, in turn, have led to an indepth understanding of the elementary surface processes involved in this reaction. As such the reaction is known to proceed via the Langmuir–Hinshelwood (L–H) mechanism between chemisorbed CO molecules and dissociatively chemisorbed O atoms. For Rh, Pd, Ir and Pt, at or near stoichiometric reaction conditions, the reaction mechanism at pressures near one atmosphere is similar to that found at ultrahigh vacuum (UHV) condi-

tions [4]. In contrast, for Ru the reaction mechanism is dramatically different for CO oxidation at UHV conditions and at atmospheric conditions [14,25]. In UHV, Ru is less active than the Pt-group metals for CO oxidation [28], while near atmospheric conditions, Ru is more active [25], i.e. the rate observed at near atmospheric pressure is 2–3 orders higher than that measured in UHV. The significantly higher activity near one atmosphere at stoichiometric reaction conditions has been explained as due to reaction between a weakly-bound CO and the oxygen of an oxygen-covered surface (~1 ML) [29]. In contrast under UHV reaction conditions, the surface is covered with both strongly-bound, chemisorbed CO and oxygen [3,30,31].

In recent years, a variety of surface oxides had been reported to evolve on late transition metals upon increasing the pressure of oxygen from UHV to pressures approaching one atmosphere [32–40]. These surface oxides exhibit chemisorptive and catalytic properties that are quite different from the corresponding bare metal surfaces. In this letter we demonstrate that the catalytic activity for CO

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oxidation at temperatures between 450 and 600 K and pressures between 1 and 300 Torr on oxygen-covered surfaces of the Pt-group metals is enhanced by 2–3 orders of magnitude compared to the oxygen-deficient surface, analogous to previous results for Ru [4,14,25]. Ongoing work suggests that the reaction probabilities of CO in the limit of mass transfer limitations under the reaction conditions leading to this high activity may approach unity.[1] Here after in the text, this highly reactive state is defined as the hyperactive state.

The experiments were carried out in several surface analytical chambers. The UHV systems are coupled to a micro-reactor for *in situ* vibrational spectroscopic and kinetic studies, and are equipped with polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), Auger electron spectroscopy (AES), X-ray spectroscopy (XPS), and low energy electron diffraction (LEED). The preparation of the model catalysts and the experimental methodologies used in these studies are described elsewhere [14,15,25]. Briefly, the high purity (>99.99%) Pd, Rh and Pt wires were first cleaned and mounted into the reaction cell, then further cleaned in 10 Torr 1:1 $CO:O_2$ mixture at 650 K for 10 min following an anneal at 1200 K. The single crystal samples were cleaned by Ar^+-sputtering followed by an anneal at 1200 K. After confirmation of the cleanness and order of the surfaces by AES and LEED, the samples were transferred into an elevated-pressure batch reactor (~0.5 L). A $CO:O_2$ gas mixture with the desired $CO:O_2$ ratio and at a specified pressure was introduced into the reaction cell at room temperature. The sample was then ramped to 525 K to initiate the kinetic measurements. For CO oxidation, $CO + 1/2\ O_2 \rightarrow CO_2$, the maximum total pressure decrease is equal to 1/2 the initial CO partial pressure for O_2-rich conditions or to the initial O_2 partial pressure for O_2-deficient conditions. Accordingly, the reaction rate can be measured by monitoring the decrease in the total pressure.

Fig. 1a shows a typical experiment where the total pressure change is monitored as a function of reaction time on Pd(110) at 525 K. For a $CO:O_2$ mixture with an O_2/CO ratio of 5 (higher than the stoichiometric ratio of 0.5) and a total pressure of 80 Torr, the O_2/CO ratio increases continuously with reaction time as shown in Fig. 1a. The total pressure change in Fig. 1a is not linear but accelerates as the reaction proceeds. This behavior is consistent with previous results at a similar total pressure and a fixed initial
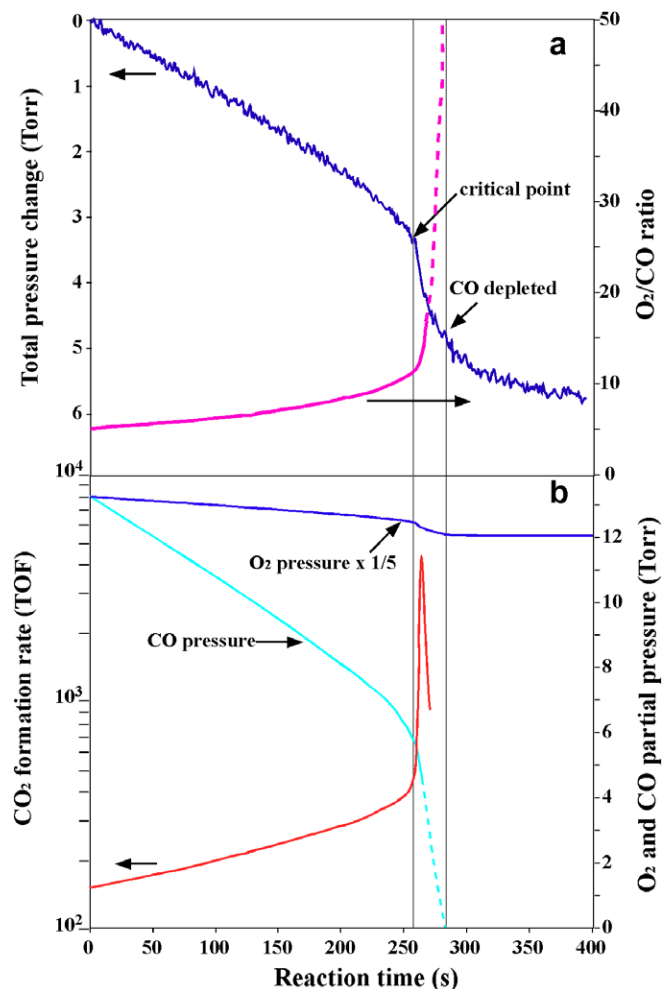
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[1] The steady state CO_2 formation rate measured for a Pd(110) single crystal disc with a diameter of 10 mm and thickness of 1 mm is ~1400 per site per second at 525 K, which is confined by mass transfer limit. To reduce the mass transfer limit effect, a small Pd sample with a diameter of 0.35 mm was embedded in a catalytically inactive metal disc. With this sample a rate of 40,000 per site per second was obtained at 525 K in 0.5 Torr CO and 9.5 Torr O_2. At this reaction condition, the flux of CO to the surface is ~96,000 molecules per site per second, which means a reaction probability of 0.42. In ongoing experiments we are investigating micro- and nano-meter supported metal particles.

Fig. 1. A typical experiment to measure CO oxidation rate by monitoring the total pressure change. (a) Total pressure decrease and change in the O_2/CO ratio as a function of reaction time. (b) CO_2 formation rate and the change in the partial pressures of O_2 and CO as function of reaction time. The reaction was carried out over a Pd(110) surface at 525 K with an initial O_2/CO ratio of 5 and a total pressure of 80 Torr.

CO partial pressure that show the CO_2 formation rate increases with increasing O_2 partial pressure [15]. These data also agree with results obtained under UHV conditions that show a higher rate on oxygen-rich surfaces and an apparent shift in the reaction mechanism [3,41–43]. A significant feature in Fig. 1a is the dramatic pressure drop that occurs at the point where the supply of CO is nearly exhausted. Immediate termination of the reaction at this rapid pressure drop point shows that the CO is completely consumed, i.e. the total pressure decrease is 6.6 Torr, 1/2 of the initial CO pressure of 13.2 Torr. Moreover, the molar amount of CO_2 formed, found by liquid nitrogen condensation, is equal to the initial molar quantity of CO. The CO_2 formation rate per metal atom site per second or turnover frequency (TOF), computed from the pressure change as a function of reaction time, is displayed in Fig. 1b, together with the partial pressure changes of CO and O_2. It is evident that the reaction rate increases with an increase in the O_2/CO ratio. The rate at the point of the rapid

pressure drop is ∼3000 site^{-1} s^{-1}, two orders of magnitude higher than the rate measured at stoichiometric reaction conditions and similar pressures [4]. Subsequent studies using a larger volume reactor (∼100 L) indicate that this unusually high rate is a steady-state value albeit limited by mass transfer, as indicated by the thin dotted line in Fig. 2a. Using a smaller size sample, a CO_2 formation rate of 40,000 site^{-1} s^{-1} was obtained at 525 K in 0.5 Torr CO and 9.5 Torr O_2 as shown by the thick dashed lines in Fig. 2a. These preliminary results, extrapolated to a reactive catalyst with a size comparable to the reactant mean free path, suggest that the CO reaction probability under these reaction conditions is near unity. Further studies to investigate the specific activity in the absence of mass transfer are underway using ultra-small samples and high space velocities [44].

The unusually high rate or TOF of 3000 CO_2 molecules per site per second observed at high O_2/CO ratios with a total pressure of ∼80 Torr suggests that the oxygen-covered surface is far more active than is a CO-covered surface in a stoichiometric mixture of O_2/CO at elevated pressures. The nature of the surface was monitored by *in situ* PM-IRAS measurements which showed an intense v_{CO} feature related to CO bound to metallic Pd prior to the sharp pressure drop, whereas spectra acquired subsequent to the dramatic pressure drop showed no adsorbed CO [44]. Current experiments are underway to ascertain whether the absence of adsorbed CO is due simply to the fact that under these conditions the reaction is mass transfer limited in CO or whether CO is weakly bound to the highly active surface. In any case, after quenching to room temperature, XPS

data showed that subsequent to the depletion of CO, ∼1 ML oxygen was present on the surface. Furthermore, only a very thin oxygen-covered surface (<2 ML) was formed in pure oxygen at the same oxygen partial pressure, i.e. 66 Torr, when reacted for 1 min. Note that the region of rapid pressure drop lasts for less than 1 min in a 0.5 L reactor. We note that CO oxidation rates with reaction probabilities near unity have been observed in a number of studies see, for example, [4,17,45] on Pt-group metals under oxygen-rich compared with stoichiometric conditions, however such rates reflecting these high reaction probabilities have not previously been observed at the temperatures and pressures of the present study. The significantly higher CO oxidation rate observed for an oxygen-covered surface compared to an oxygen-deficient surface for Pd is similar to the results observed for Ru where the CO oxidation rate on a 1 ML oxygen-covered surface is 2–3 orders higher than that on a chemisorbed CO-dominant surface [25,46]. The lower rate on an oxygen-deficient Pd surface, under conditions close to stoichiometry, is due to the high surface coverage of strongly chemisorbed CO, i.e. the rate is limited by the adsorption/dissociation of O_2 on the surface essentially saturated by CO. In fact, it has been reported that O_2 dissociative adsorption is blocked on a CO-saturated surface [8,47,48]. In contrast, in a high O_2/CO ratio reactant mixture at elevated pressures, the surface is predominately covered with chemisorbed atomic oxygen [49] which reacts with neighboring weakly adsorbed CO to form CO_2 [29]. Indeed this chemisorbed surface oxygen on Pd(110) can react with CO at room temperature [44].
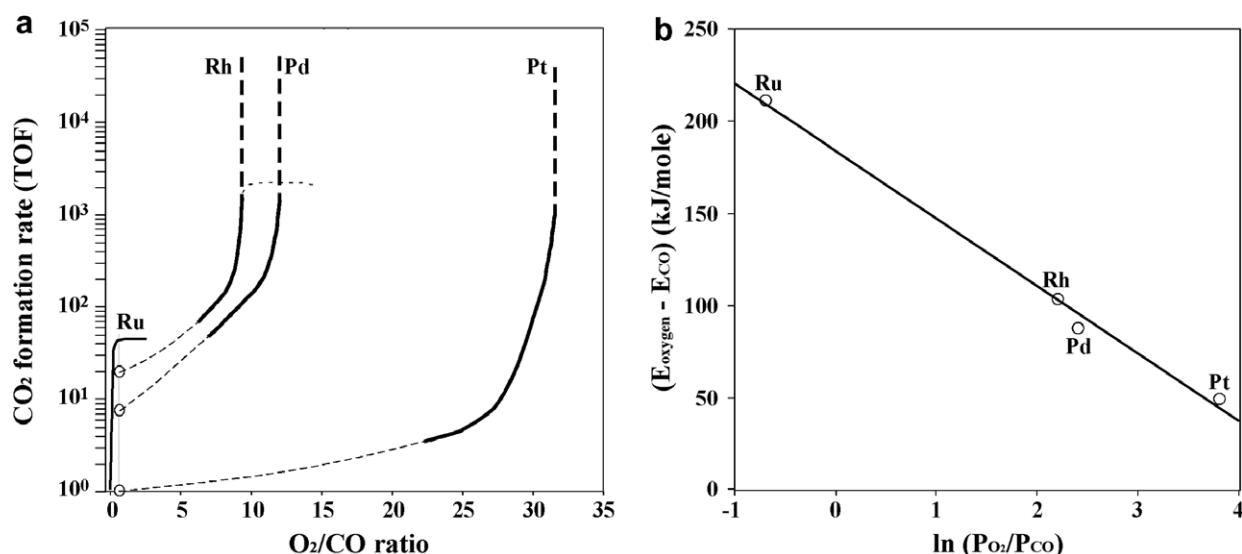

Fig. 2. (a) CO_2 formation rates on various metal catalysts as a function of O_2/CO ratio. The data for Rh, Pd and Pt were obtained under an initial total pressure of 80 Torr with a O_2/CO ratio of 5, and reaction temperatures of 525, 525 and 550 K for Rh, Pd and Pt, respectively. Data for Ru are from Ref. [25]. Rates indicated by the small circles were measured at stoichiometric reaction conditions (O_2/CO = 0.5). A steady-state value of ∼1400 site^{-1} s^{-1} (flat top solid line) was obtained using a larger reactor volume (∼100 L) for a single crystal with a size of 10 mm (thin dotted line). However, a rate of 40,000 site^{-1} s^{-1} was obtained using a significantly smaller sample which minimizes the mass transfer limit. Accordingly a dashed line is used to indicate that the rate may increase to the flux limit of the impinging reactant molecules. (b) Plot of $(E_O - E_{CO})$ for Ru, Rh, Pd, and Pt vs. $\ln(P_{O_2}/P_{CO})$ required to achieve the hyperactive state on that metal at a given temperature. The point for Ru was deduced from Ref. [25] where the steady-state rate of CO_2 formation was obtained at ∼8 Torr O_2 and 16 Torr CO at 500 K.

The time required to achieve the hyperactive state increases with a decrease in the initial O_2/CO ratio; however, the critical O_2/CO ratio required to achieve the hyperactive state is essentially fixed for a given O_2 pressure. This implies that the oxygen chemical potential for a particular O_2/CO ratio [40] is the key parameter for formation of the hyperactive catalytic state for a given metal surface and reaction temperature. Similar experiments were carried out for Rh and Pt. CO_2 formation rates on Rh (525 K), Pd (525 K), and Pt (550 K) surfaces as a function of O_2/CO ratio, are summarized in Fig. 2a along with previous results for Ru(0 0 0 1) [25]. The onset for the highest catalytic rate on Ru occurs at a O_2/CO ratio lower than stoichiometry, while the hyperactive state on Rh, Pd and Pt occurs at O_2/CO ratios of approximately 9, 11 and 28, respectively. As discussed above, the catalytic hyperactive state corresponds to an oxygen-covered surface, therefore the adsorption energy of oxygen and the stability of the corresponding metal oxide should play a key role in determining the oxygen chemical potential for achieving the hyperactive state [40]. In addition, the adsorption energies of CO should be important since the active surface changes from predominantly CO to predominantly chemisorbed oxygen. O_2 dissociative adsorption energies of 334, 234, 230 and 188 kJ/mole-oxygen atoms are reported for the close-packed Ru [50], Rh [51], Pd [52], and Pt [53] surfaces, respectively. Whereas, the adsorption energies for CO on these surfaces are very close, 122, 130, 142 and 138 kJ/mole, respectively, for the close-packed Ru, Rh, Pd and Pt surfaces [54–56]. The order of the O_2/CO ratios required for Pt, Pd, Rh, and Ru to achieve the hyperactive state in Fig. 2a was found to relate directly to the oxygen adsorption energies and also to the standard heats of formation for RuO_2, Rh_2O_3, PdO and PtO of −153, −119, −116 and −71 kJ/mole (the values were calculated on a per mole per oxygen atom), respectively [57]. The relatively large oxygen adsorption energy and oxide formation energy for Ru lead to formation of a highly active, oxygen-covered surface at a O_2/CO ratio lower than stoichiometry [14,25]. In contrast, the relatively low adsorption energy of oxygen on Pt precludes formation of the hyperactive reaction state at 525 K even at O_2/CO ratios as high as 50. Experiments carried out at 550 K on Pt, on the other hand, show a rapid rate increase at an O_2/CO ratio of 28. In general a higher O_2/CO ratio is required to form the hyperactive oxygen-covered surface as the surface temperature is lowered [40], and vice versa as shown in Fig. 3a. Regarding the fact that the active surface transforms from a CO-covered to an O-covered surface at relative high O_2/CO ratios, the surface free energy difference in these two, $(G(O) - G(CO))$, for a given metal surface should be the key factor. These values can be approximated by the heats of adsorption of oxygen and CO on a given metal surface, i.e. $(E_O - E_{CO})$. As described by Campbell [40], such a transformation will also be affected by the presence of the oxidizing and reducing agent, e.g. $\ln(P_{O_2}/P_{CO})$. Indeed, a linear relationship was observed in a plot of the adsorption energy differences $(E_O - E_{CO})$ for various metals vs. the logarithm of the O_2/CO pressure ratios required to achieve the hyperactive state, $\ln(P_{O_2}/P_{CO})$, for various Pt-group metal, as shown in Fig. 2b. This linear relationship demonstrates that a comparable sum of $\ln(P_{O_2}/P_{CO})$ and $(E_O - E_{CO})$ is required for shifting to the hyperactive state at a given temperature.

Nanoparticles generally exhibit remarkably different catalytic properties compared to the corresponding infinite surface since small particles are easier to oxidize than large particles [58,59]. This suggests that formation of a hyperactive oxygen-covered surface should occur at a lower oxygen chemical potential for smaller particles than for larger particles. Indeed, the order of the O_2/CO ratios required to achieve the hyperactive state correlates very well with particle size, as shown in Fig. 3b. For a reaction temperature of 450 K, smaller Pd particles on Al_2O_3 acquire the hyperactive state at a O_2/CO ratio of ∼6, 7.5 and 12 for
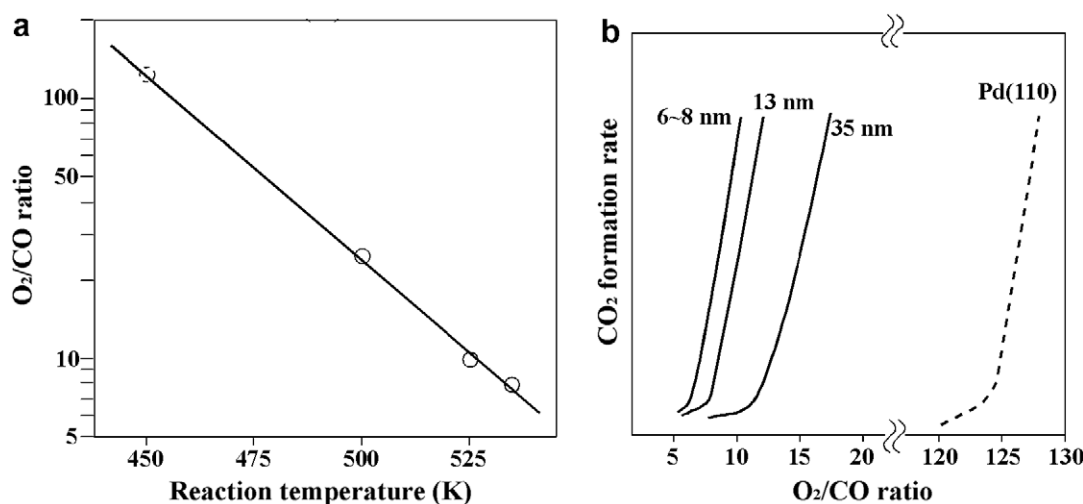

Fig. 3. (a) A correlation of reaction temperature and the critical O_2/CO ratio required to achieve the hyperactive state for a Pd(1 1 0) single crystal. These data were used to estimate the CO oxidation data for the Pd(1 1 0) single crystal at 450 K. (b) CO_2 formation rates on Al_2O_3 supported Pd nanoparticles of various sizes (mean diameter shown) and a Pd single crystal surface at 450 K as a function of O_2/CO ratio.

particle sizes of 6–8, 13 and 35 nm, respectively, compared to a O_2/CO ratio of 125 required for a Pd single crystal surface. Results of this study will be published in detail elsewhere [60]. It should be noted in this context that relatively small metal particles may form the bulk oxide at relatively low oxygen chemical potentials or temperatures resulting in deactivation [61,62]. This trend may explain why metals that form less stable oxides, like Au, are inactive toward activation of oxygen in the bulk yet are extraordinarily active as supported nanostructures [9,10,24,26,63,64].

In summary, this study has shown that oxygen-covered surfaces of Rh, Pd, and Pt, formed at O_2/CO ratios in excess of stoichiometry, exhibit extraordinary catalytic activity for CO oxidation at elevated pressures, e.g. total pressure of 1–300 Torr. A rate of ~ 3000 CO_2 molecules per site per second was obtained at 525 K and a total pressure of 80 Torr, a rate significantly higher than for a CO-covered surface at stoichiometry ($O_2/CO = 0.5$) and a similar total pressure. This behavior of Rh, Pd, and Pt is analogous to Ru, where the rate of reaction at comparable pressures increases by approximately three orders of magnitude for the oxygen-covered surface, i.e. Ru(0001)–(1×1)–O (1 ML), compared to an oxygen-efficient Ru surface. The oxygen chemical potential required to achieve the highly active state was found to closely related to the intrinsic properties of the metal, the particle size and the reaction temperature, i.e. the most easily oxidized metal, smaller particles, or higher reaction temperatures need a lower oxygen chemical potential to promote the highly active state.

Acknowledgements

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