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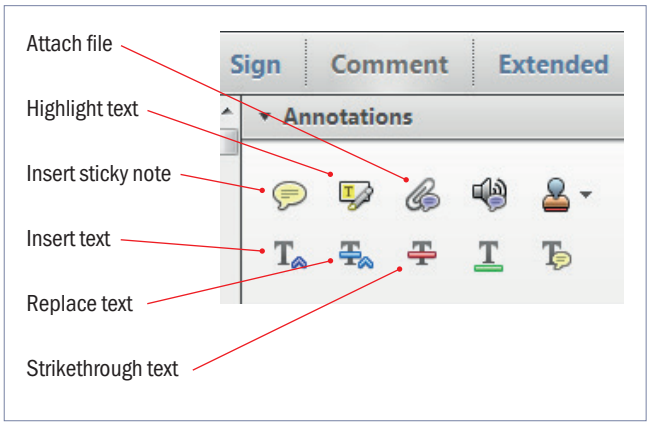

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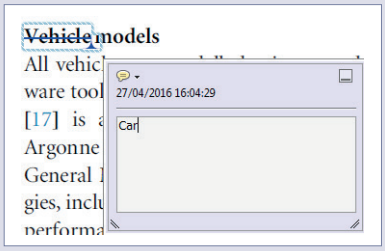

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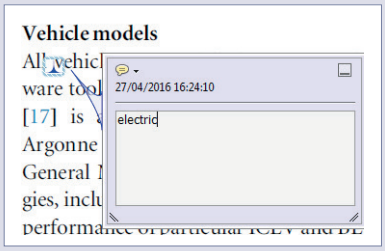

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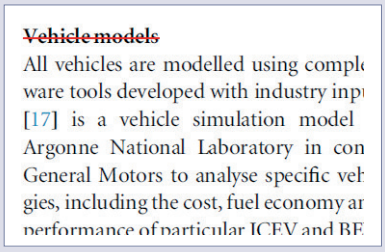

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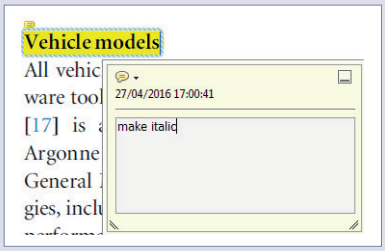

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Chemical states of surface oxygen during CO oxidation on Pt(1 1 0) surface revealed by ambient pressure XPS

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Abstract

The study of CO oxidation on Pt(1 1 0) surface is revisited using ambient pressure x-ray photoemission spectroscopy. When the surface temperature reaches the activation temperature for CO oxidation under elevated pressure conditions, both the α-phase of PtO_2 oxide and chemisorbed oxygen are formed simultaneously on the surface. Due to the exothermic nature of CO oxidation, the temperature of the Pt surface increases as CO oxidation takes place. As the CO/O_2 ratio increases, the production of CO_2 increases continuously and the surface temperature also increases. Interestingly, during the diffusion limited regions, the amount of surface oxide changes little while the chemisorbed oxygen is reduced.

Keywords: CO oxidation, ambient pressure XPS, Pt(1 1 0), surface oxide

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Introduction

Many important discoveries in surface science are made with the development of innovative surface science techniques [1]. As a good example, the visualization and manipulation of individual atoms on surface were made possible with the invention of the scanning probe microscope (SPM) [2]. The low energy electron microscope has made it possible to observe the change of surface structural morphology in real time [3]. However, many of these surface science techniques can only be operated under UHV conditions, which are suitable for the study of model systems. Consequently, a so-called bridging the pressure gap between UHV and elevated pressure conditions has become an important topic of study in the community of surface science [4].

Since early 2000, various *in situ* operando surface science techniques have been developed and started to deliver the information on surface properties that are close to realistic conditions in temperature and pressure. e.g. high-pressure SPM [5], ambient pressure x-ray photoemission spectroscopy (AP-XPS) [6], polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) [7], and high-pressure

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surface x-ray diffraction (HP-SXRD) [8, 9]. These *in situ* operando techniques have delivered numerous intriguing results and shown that the surface reaction under high-pressure conditions can be different from those under UHV conditions [5, 10–13].

Particularly, CO oxidation on Pd and Pt surfaces has received much attention for its interesting surface properties under high-pressure reactive conditions. In fact, CO oxidation on transition metals, one of the simplest catalytic reactions, has been exhaustively studied as an ideal model system in studying surface reaction mechanisms [14–16]. As a result, almost all of the essential information about the nature of CO oxidation on metal surfaces has been discovered under low pressure conditions. For instance, in the early 1990s, with the use of photoemission electron microscopy (PEEM), SPM, and mathematical modeling, the Ertl group clarified the details on how CO oxidation occurs on a Pt surface at an atomic level under relatively low pressure region, below 10^{-6} Torr [17–19]. Also, the oscillatory behavior of surface reaction kinetics and non-linear phases on Pt surface were well elucidated [20].

Then, in 2002, using high-pressure STM, the Frenken group reported the formation of surface oxides as Pt(1 1 0) surface was used for the CO oxidation process [5]. At the onset of the active CO oxidation reaction, roughening of the surface was observed, which was interpreted as catalytically active surface oxide. They proposed that the observed surface oxide could be more reactive than the Pt metal surface under elevated pressure conditions, supporting the presence of the Mars van Krevelen (M-K) mechanism [21]. The same group continued their investigation on Pd(1 0 0) surface and arrived at the analogous conclusion, i.e. the surface oxide is catalytically more active. Later, the same group used HP-SXRD and observed the formation of thin surface oxide during the highly reactive region and claimed the interaction between the surface oxide and surface steps was the origin of the oscillatory behavior in CO oxidation at elevated pressure conditions [8].

On the other hand, the Goodman group presented a different view on the CO oxidation reaction on identical Pd and Pt surfaces [12]. Utilizing PM-IRAS, the group categorized the CO oxidation process into three regimes depending on the surface condition. First is the CO inhibited surface with low CO oxidation reaction below the reaction temperature. Second is an oxide covered surface on which CO reactants diffuse through the surface oxide to form CO_2, the so-called diffusion limited high temperature regime [12]. The surface oxide is formed under the oxygen rich environment of the surface out of the diffusion limited steps during CO oxidation. Third is a short transient metallic state that exist between the CO inhibited surface and the oxide covered surface. The Goodman group claimed that this metallic surface was the most catalytically active state and pointed out the short lifetime of its existence, which made the states difficult to detect. According to Goodman and co-workers, the Langmuir–Hinshelwood (LH) mechanism [22] is still a valid explanation for the CO oxidation process on both Pt and Pd surfaces and the enhanced reaction regime of Pd and Pt surfaces, observed by the Frenken group, is the diffusion limited oxygen covered surface, which is less reactive than the transient metallic surface [12]. However, it is noteworthy that the evidence of surface oxide on the Pd surface under diffusion limited steps high temperature region is indirectly probed with PM-IRAS under the oxygen rich reaction condition, and no surface oxide is found in the case of the Pt(1 1 0) surface under the identical diffusion limited region [12]. Later, with AP-XPS, Butcher *et al* confirmed the formation of surface oxide under oxygen rich environment, yet the reactivity of surface oxide was found not to be significantly higher than that of surface chemisorbed oxygen [23].

In this report, using AP-XPS, we revisited CO oxidation reaction to observe the surface chemical properties on Pt(1 1 0) under various conditions. We carefully look at the surface chemical states during the diffusion limited high temperature regions at various pressure ratios of O and CO. At the onset of the CO oxidation reaction, both surface oxide and chemisorbed oxygen are clearly observed. Due to the exothermic nature of CO oxidation, the temperature of Pt surface increases as CO oxidation takes place. As the CO/O_2 ratio increases, the surface temperature continuously rises with higher CO_2 production. Interestingly, under the higher reaction conditions, we find that the amount of surface oxide changes little while the chemisorbed surface oxygen reduces, showing signs of the M-K mechanism during CO oxidation on Pt(1 1 0) surface.

Experiment

Experiments were carried out at the AP-XPS endstation of BL13 at KEK-Photon Factory, Japan and AP-XPS endstation of BL 9.3.2 of advanced light source (ALS) at Lawrence Berkeley National Laboratory, USA. The specifications of beamline and endstation can be found elsewhere [24, 25]. A well-ordered Pt (1 1 0) single crystal, provided by Princeton Scientific Corp., was prepared with the repeated cleaning cycles of annealing and Ar Ion sputtering process. The cleaning cycles were repeated until no surface contaminant was found.

The O_2 and CO gases were introduced to the high-pressure chamber though UHV leak valves. A pyrolytic boron nitride (PBN) button heater was employed to control the sample temperature and a K-type thermocouple was attached to the top surface of the Pt crystal. During the CO oxidation process, the partial pressure of the reactant and gas products were continuously monitored with a residual gas analyzer (RGA) installed at the second stage of the differential pumping system that is located between the reaction chamber and electron analyzer.

Photoelectron spectra of the O 1s, and Pt 4f core levels were measured with photon energies of 650 eV, and 250 eV, respectively. These photon energies correspond to the kinetic energy of ~150 eV that provided highly surface sensitive XPS measurements. The measured XP spectra were de-convoluted by using Gaussian and Doniach-Sunjic line shapes after subtracting the Shirley background.

Discussion and result

Before discussing the AP-XPS measurements, it is informative to examine the RGA profile, which was measured simultaneously with AP-XPS spectra. Figure 1(a) shows the intensity profiles of partial pressures of CO, O_2, and CO_2 during the reaction processes. The observed sample temperature is shown in figure 1(b). To begin with, the high-pressure reaction chamber was filled with 40 mTorr of CO gas pressure. Once the pressure of CO was stabilized, 200 mTorr of O_2 gas was introduced, i.e. $CO/O_2 = 0.2$. Then, the sample temperature was increased slowly. As soon as O_2 gas was introduced, a sudden increase of CO_2 production was found. With the CO-poisoning Pt surface, the production of CO_2 is most likely due to the reaction of O gas with the residual CO gas on the chamber wall. Also, there is a possibility that CO oxidation occurs at the surface domains boundaries of the Pt surface, where a precursor-mediated reaction can occur. Especially in the case of domains boundaries reaction, it has been shown that only low activation energy is required [26]. The amount of initial production of CO_2 did not increase further until the surface temperature reached the critical reaction temperature, shown in the region (I) of figures 1(a) and (b). When the temperature approached ~550 K, CO_2 production increased rapidly as CO gas pressure made a sudden drop, i.e. the onset of the exothermic reaction. At this point, the sample temperature rose rapidly, e.g. as high as 558 K, and then remains at 553 K, shown in region (II) of figure 1(b). During this onset of the CO oxidation reaction, no external control on sample temperature was made. It is well known that the increase of sample temperature is due to the exothermic nature of the CO oxidation process. The observed reaction temperature and its behavior agreed well with the reported value of activation temperatures for CO oxidation processes [12].

Next, to observe how the ratio of CO and O_2 gas pressure contributes on surface reaction, the pressure of CO gas was further increased to 60, 100, and 140 mTorr with oxygen pressure fixed at 200 mTorr, i.e. $CO/O_2 = 0.3$, 0.5, and 0.7, as shown in the region (III, IV, and V) of figure 1. At each step, the CO_2 production continuously increased while that of O gas phase decreased. Again, during each step, the sample temperature was not manually regulated. That is, the current setting for the button heater remained the same. Nonetheless, as the pressure ratio increased, the sample temperature constantly increased, revealing the enhanced exothermic process during the CO oxidation reaction under higher CO gas pressure. Fluctuation of the sample temperature is also observed when the additional CO gas is introduced, which possibly comes from the thermal exchange process between the external gases environment and the increasing sample temperature during the exothermic process. The observed sample temperatures at each stabilized state match well with the reported values [12]. Finally, at 569 K, the region (VI) of figure 1(b), the sample temperature was reduced manually. Intriguingly, the production of CO_2 does not drop immediately and remains constant until the sample temperature drops to 545 K. This delay is most likely due to the dissipation of a large heat load accumulated on the sample surface during the reaction. Overall, figure 1 clearly shows the presence of CO oxidation processes on the Pt(1 1 0) surface and the occurrence of an exothermic process during the reaction.

More information is obtained from the measurement of O 1s and Pt 4f core level spectra during the CO oxidation process. In figure 2, the intensity of the O1s is plotted in a color scale as a function of binding energy and time during the reaction. The scan rate of each spectrum was 59.0 s. Upon introducing CO and O_2 gases at room temperature, the region (I) of figure 2, a strong presence of surface CO peak is observed near ~532.6 eV, indicating that CO molecules adsorb on the surface. Also, the gas phase of oxygen is seen near ~538 eV. Under CO rich conditions, no chemisorbed oxygen is observed due to the presence of CO molecules on the surface. As the surface temperature reaches about 550 K, the region (II) of figure 2, a strong intensity of chemisorbed oxygen peak is found near ~530 eV with the small amount of surface oxide peak near ~531 eV. Also, the adsorbed CO molecules disappear immediately from the surface and the position of O_2 gas molecules component shifts to the lower binding energy side by almost ~0.5 eV. The shift of O_2 gas phase peak is due to the change of Pt surface work function as the surface experiences an exothermic process from the CO oxidation reaction. Namely, the gas molecules in front of sample surface experiences the changes of surface potential that came from the surface temperature variation. Furthermore, the replacement of adsorbed CO by oxygen species contributes to the work function change. At the onset of CO oxidation reaction, a weak trace of CO_2 gas phase can be observed at ~535 eV.

When the pressure of CO gas is further increased to 60 mTorr, the region (III) of figure 2, $CO/O_2 = 0.3$, the surface oxide can be clearly distinguished while the amount of CO_2 production increases. As the pressure of CO gas was further increased to 100 then 140 mTorr, the regions (IV, V) of figure 2, the intensity of CO_2 gas phase peak continuously increases while that of O_2 gas phase peak decreases, which is consistent with the result of RGA in figure 1. Similarly to the region (IV) of figure 1, the gas phase peak of CO_2 remains constant until the surface temperature drops to 545 K. Interestingly, at $T = 545$ K, the CO gas phase peak emerges immediately while the surface oxide peak disappears, indicating the close relation between surface oxide and CO gas. It is also noteworthy that the background intensities of spectra fluctuate each time that the CO pressure was modulated. This can be correlated to thermal fluctuation, which is also observed in figure 1.

To look into further details of surface chemical states during the reaction processes, the O 1s and Pt 4f AP-XPS spectra were deconvoluted. The results are shown in figure 3 and table 1. At room temperature under $P(O_2) = 200$ mTorr and $P(CO) = 40$ mTorr, both O 1s of CO and O_2 gas phases peaks are observed, i.e. 537.00 eV for CO gas and 537.9, 539.0 eV for the doublet of O_2 gas, shown in figure 3(a) (I). The CO molecules on on-top and bridge site of Pt surface can be also identified at 531.19, and 532.56 eV, respectively. In figure 3(b) (I), the Pt 4f shows two components, one attributed to the bulk at about 71 eV, and a second one at higher binding energy, 71.8 eV, corresponding to the chemical shift due to CO surface chemisorption. Under a CO rich environment,

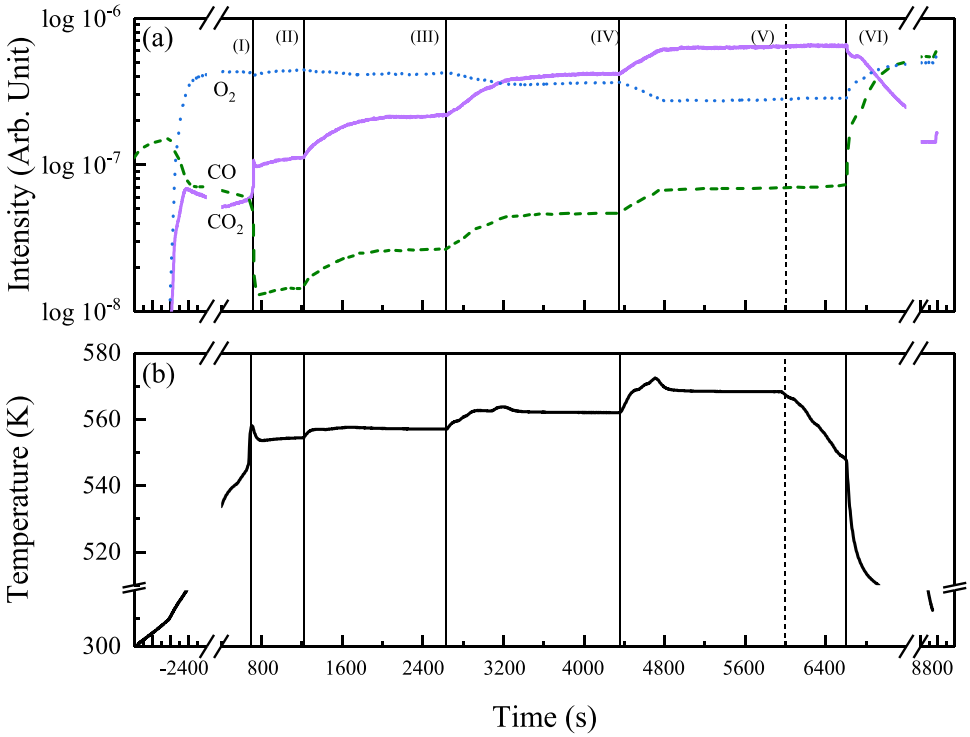

Figure 1. (a) Intensity plots of CO, O_2, and CO_2 partial pressures from RGA during CO oxidation reaction. Initially, 40 mTorr of CO and 200 mTorr of O_2 gases were introduced at room temperature, region (I). Once the sample temperature was adjusted to 553 K, the incoming pressure of CO gas was adjusted as 40 mTorr in region (II), 60 mTorr in region (III), 100 mTorr in region (IV), and 140 mTorr in region (V). During the region (II–V), no external control on sample temperature was made. In region (VI), the sample temperature was decreased slowly. (b) Plot of sample temperature during the CO oxidation condition in each region of figure (a).

both O 1s and Pt 4f spectra show no surface chemisorbed oxygen. When the surface temperature reached 553 K, i.e. the CO oxidation reaction temperature at $CO/O_2 = 0.2$, the gas phase peak of oxygen molecules in figure 3(a) (II) shifted to lower binding energy while the gas phase of CO_2 started to emerge at 535.30 eV. As mentioned before, the shift of gas phase component is related to the changes of surface work function during the reaction. In this case, the change of work function is due to the surface coverage from CO to oxygen. In addition, the spectra of figure 3(a) (II) revealed that, under reaction conditions, the adsorbed CO molecules are removed from the surface (disappearance of the peak components at 531.3 and 532.6 eV) as chemisorbed oxygen (529.8 eV) and surface oxide (531.1 eV) takes up the surface. The Pf 4f spectrum of figure 3(b) (II) exhibits both features of chemisorbed oxygen and surface oxide, 71.7 and 73.2 eV, respectively, yet the intensity of surface peak is small due to a low coverage as well as the low cross-section from relatively higher photon excitation energy. The binding energy position of surface oxide O 1s and Pt 4f in figure 3 (II) matches well with the reported value for α-phase PtO_2 [23]. As the CO pressure increases, the intensity of oxygen gas phase peaks from CO reduces, as shown in figure 3 (III, IV, and V). The O 1s from CO_2 shows the opposite behavior to CO. Also, the intensity of chemisorbed oxygen peak at Pt 4f follows similar behavior. As expected, the intensity of both CO and CO_2 gas phase peak shows a similar trend as those of CO and CO_2 gas partial pressure of RGA in figure 1.

One interesting point is that the amount of surface oxide of O 1s spectra remains almost constant at elevated CO pressure. That is, under enhanced reaction condition, the surface oxide remains on surface without much change while the amount of chemisorbed oxygen is reduced. In fact, from figure 3, it is clear that the chemisorbed surface oxygen is involved in the CO oxidation process. However, it is not possible to identify whether the surface oxide is participating in the reaction. When the sample temperature is reduced to 545 K, both O 1s and Pt 4f spectra of figure 3 (VI) displayed identical features as figure 3 (I), i.e. the surface is covered by CO molecules.

Comparing our AP-XPS results to previous reports, the roles of surface oxide and chemisorbed oxygen during the reaction becomes very interesting. First, the presence of an oxide peak is found even under relatively low oxygen pressure region, e.g. surface oxide at $CO/O_2 \sim 0.7$. However, in the case of PM-IRAS study of Goodman group, the surface oxide was not observed on Pt(1 1 0) surface under the identical condition [12]. They only mentioned that the surface was covered with oxygen during diffusion limited regions. As the PM-IRAS can only monitor CO species, i.e. PM-IRAS cannot detect oxygen species, the Goodman group could not observe the surface oxides if the Pt surface oxide and CO molecule did NOT interact directly. In the case of Pd(1 0 0), in which the CO strongly interact with Pd oxide, the presence of surface oxide was confirmed with PM-IRAS. This fact reveals that the surface oxide on Pt(1 1 0), the α-phase Pt oxide, does NOT interact with CO directly. Instead, the α-phase Pt surface

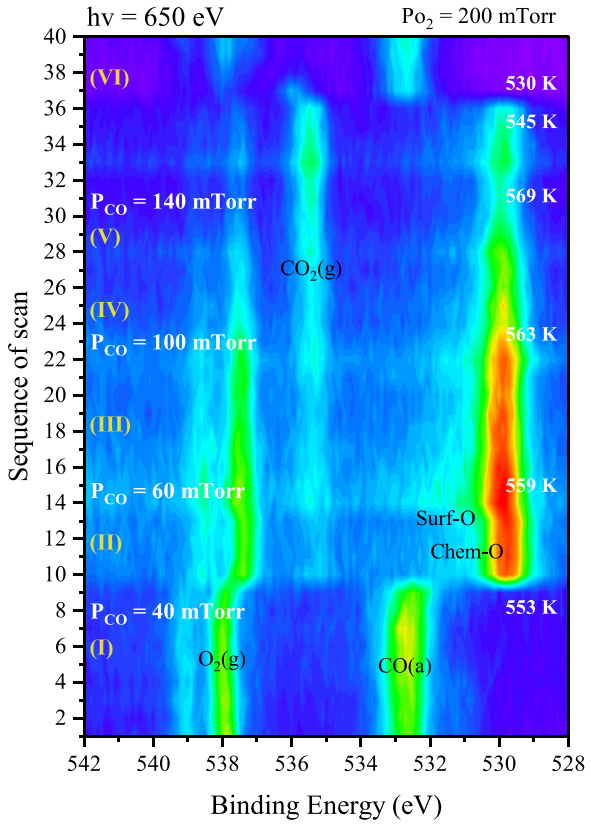

Figure 2. Sequence plots of O 1s photoemission spectra measured during CO oxidation reaction in pressure ratio (CO/O_2) ~ 0.2, 0.3, 0.5, and 0.7 and fixed 200 mTorr O_2. The regions shown on the left are identical to the regions of figure 1. In region (I), the surface adsorbed CO peak can be seen at ~532 eV while the gas phase of O_2 is observed at 538 eV. In region (II), surface oxide and chemisorbed oxygen peaks appear as the CO oxidation takes place. Also, the shift of gas phase of O_2 peak takes place due to the change of surface work function. As the incoming CO pressure increases, the intensity of gas phase of O_2 becomes enhanced while the intensities of surface oxide and chemisorbed oxygen peaks become reduced, region (III–V). In region (V), the surface oxide and chemisorbed oxygen peaks disappeared from the surface as the temperature of the sample was reduced.

oxide can possibly follow the M-K mechanism and contribute to the reaction in an indirect manner. According to the M-K mechanism, the lattice oxygen from the surface oxide participates in the reaction while the neighbor oxygen fills the vacant lattice oxygen site, maintaining the forms of surface oxide. That is, under diffusion limited regions, the α-phase Pt oxide facilitates the oxygen needed for the CO oxidation and maintains its presence on the surface, as suggested by the M-K mechanism. In order to test the presence of the oxygen dynamics suggested by M-K mechanism on Pt(1 1 0) surface, it is necessary to monitor the oxygen interaction dynamics between surface oxide and chemisorbed oxygen. However, the residence time of CO on the oxide is estimated 10^{-9} s, which requires an advanced time-resolved spectroscopy [26].

Next, in regard to the role of chemisorbed oxygen, there are two possibilities. One possibility is that the chemisorbed oxygen is being consumed as a direct participant of the

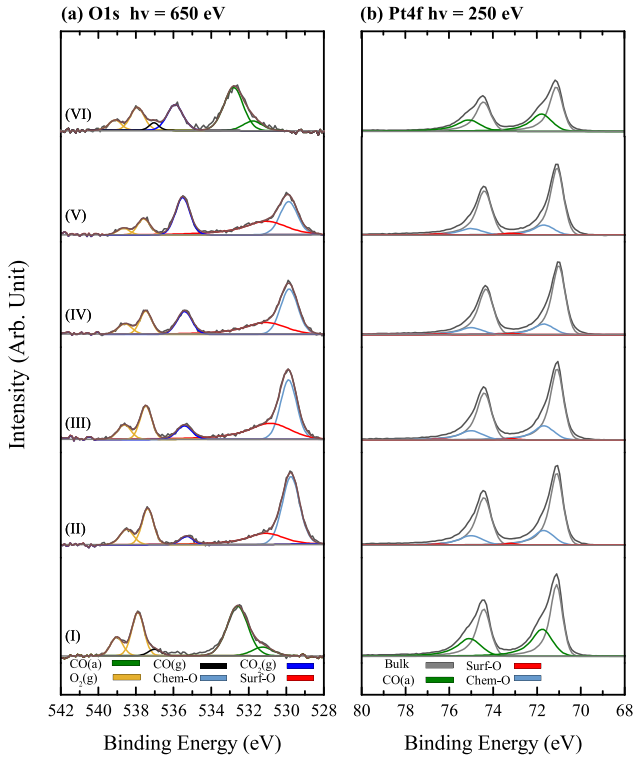

Figure 3. Fitting of the O 1s and Pt 4f photoemission spectra at each region of figure 2.

Table 1. Fitting parameters for O 1s and Pt 4f AP-XP spectra. Peak positions of O 1s and Pt 4f are referenced in [23]. AQ4

Unit: eV

Pt4f	B.E.			FWHM	DS(a,n)
Bulk 7/2	71.15	±	0.13	0.77–0.82	(0,2)
Bulk 5/2	$a + 1.1$			0.77–0.82	(0,2)
CO(a) 7/2	71.77	±	0.13	0.92–1.13	(0,2)
CO(a) 5/2	$a + 1.1$			1.05–1.34	(0,2)
Surf-O 7/2	73.22	±	0.13	0.79–0.84	(0.001,2)
Surf-O 5/2	$a + 1.1$			0.90–0.96	(0.001,2)
Chem-O 7/2	71.71	±	0.13	0.90–1.09	(0.001,2)
Chem-O 5/2	$a + 1.1$			1.03–1.24	(0.001,2)

O1s	B.E.			FWHM	DS(a,n)
O_2(g1)	537.63	±	0.23	0.71–0.82	—
O_2(g2)	1.10			0.77–0.87	—
CO(g)	537.02	±	0.23	0.56–0.84	—
CO(a1)	532.70	±	0.23	1.18–1.32	—
CO(a2)	531.53	±	0.23	1.18–1.32	—
CO_2(g)	535.52	±	0.23	0.84–0.99	—
Surf-O	531.05	±	0.23	2.26–2.58	(0.001,45)
Chem-O	529.83	±	0.23	1.03–1.1	—

CO oxidation process in either the M-K or LH mechanism, which is not clear at the moment. The other possibility is a simple thermal desorption process due to the increased surface temperature. However, considering that the reduced amount of chemisorbed oxygen is not as much as the CO_2

production increased at each region, it can be inferred that there is an additional CO oxidation reaction outside of the surface. Previously, Reuter *et al*, with the Monte Carlo simulation of thermal distribution near surface at the onset of CO oxidation, demonstrate that the surface temperature is increased due to the exothermic nature of CO oxidation under the diffusion limited step [27] and the CO oxidation can occur above the surface due to the exothermic process during these diffusion limited steps.

Conclusion

In this report, we carried out the *in situ* operando study of the CO oxidation on Pt(1 1 0) surface using AP-XPS. The presence of both the α-phase Pt surface oxide and chemisorbed oxygen are found at the onset of the reaction. It was suspected that the previous PM-IRAS measurement could not observe the surface oxide due to a lack of direct interaction of CO and surface oxide. Interestingly, during the diffusion limited regions, the amount of surface oxide remains almost unchanged while that of chemisorbed oxygen is significantly decreased with increasing reactivity. In order to further understand the complex nature of CO oxidation reaction, the advanced time resolved technique to AP-XPS will help to identify the oxygen interaction dynamics between surface oxide and chemisorbed oxygen, which can further disclose the nature of complex catalytic reactions.

AQ5 ## Acknowledgments

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