

Electronic Supplementary Information for

A high-pressure-induced dense CO overlayer on Pt(111) surface: A chemical analysis using *in-situ* near ambient pressure XPS

Ryo Toyoshima,^a Masaaki Yoshida,^a Yuji Monya,^a Kazuma Suzuki,^a Kenta Amemiya,^b Kazuhiko Mase,^b Bongjin Simon Mun,^c and Hiroshi Kondoh*^a

^a Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan

^b Institute of Materials Structure Science, High Energy Accelerator Research Organization, and The Graduate University for Advanced Studies, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

^c Department of Physics and Photon Science, and Ertl Center for Electrochemistry and Catalysis, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea

*To whom correspondence should be addressed.

E-mail: kondoh@chem.keio.ac.jp

Index	Page
1. O 1s x-ray photoelectron spectra at different CO pressures	S2
2. Reversibility of surface coverage for CO pressure	S3
3. Optimized geometric parameters of CO adlayers	S4
4. CO adsorption at hollow site	S5
5. References	S6

1. O 1s x-ray photoelectron spectra at different CO pressures

Since O 1s x-ray photoelectron spectroscopy (XPS) gives information on coverage and adsorption site for CO adsorbed on solid surfaces similarly to C 1s XPS, it has been extensively used in previous studies on CO adsorption. Fig. S1 shows O 1s XP spectra taken at different surface conditions using a photon energy of 630 eV.

After 20 L CO dose, two distinct peaks are clearly observed; the lower energy peak at 531.9 eV is assigned to bridge bonded CO (red curve), while the higher energy one at 532.9 eV to top bonded CO (blue curve). The peak positions are well consistent with the previous XPS studies.^{1,2} Here, the surface CO coverage is estimated to be 0.43 monolayer (ML) from Pt 4f_{7/2} level.

At a higher pressure condition (50 mTorr), we recognize two main peaks are largely enhanced in intensity. The estimated surface CO coverage from O 1s level is 0.71 ML, which is quite similar to the result deduced from Pt 4f_{7/2}. It is noted that we can see an additional peak at ~537 eV, which is attributed to the gas-phase CO over the Pt surface. The full widths at half maxima (FWHMs) for the O 1s peaks keep constant irrespective of CO pressure. This indicates that the O 1s level is less sensitive to adsorption state of CO than C 1s level, which may be explained by the adsorption configuration of CO: Since the CO molecules adsorb on the surface via the C atoms, the lateral shift of CO position less influences on the electronic state of the O atom. These O 1s XPS results support the interpretation for the C 1s and Pt 4f XPS results described in the text.

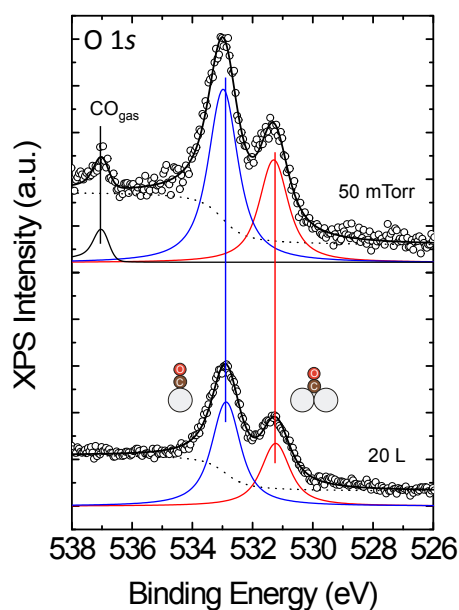


Fig. S1. O 1s XP spectra from Pt(111) taken after 20 L CO exposure (bottom) and under 50 mTorr CO (top). The spectra were deconvoluted to distinct components. These spectra were recorded at the same time with the Pt 4f and C 1s levels shown in Fig. 1.

2. Reversibility of surface coverage for CO pressure

Fig. S2(a) shows Pt 4f XP spectra taken at different CO gas pressures. All the spectra were recorded at 298 K with an incident photon energy of 150 eV. After 20 L exposure of CO, the Pt(111) surface is saturated by CO under UHV condition (A). The spectrum taken under 50 mTorr (B) drastically changes from that under the UHV condition. Then, the CO gas was evacuated to $P_{\text{background}} < 10^{-8}$ Torr (C).

To clarify the spectral change, the residuals are shown in Fig. S2(b). The clear enhancement of CO-induced components are observed in B–A. It indicates that the CO adsorbed on the Pt(111) surface changes to the high-density phase by increasing of CO pressure. After the high-pressure CO dose and subsequent evacuation, the difference spectrum (C–A) appears almost flat, indicating that the surface CO phase is almost the same as that formed after 20 L exposure. A small trace of CO-induced component shows the surface coverage becomes closer to the ideal coverage after the high-pressure dose. At the initial dose of 20 L, there would be domain boundaries and defects of the $c(4 \times 2)$ -2CO phase. While after the high-pressure dose and subsequent evacuation, such irregular structures become less resulting in a CO coverage closer to the ideal one (0.5 ML). These results indicate that the transition between the UHV phase and the high-density phase is essentially reversible with respect to CO gas pressure.

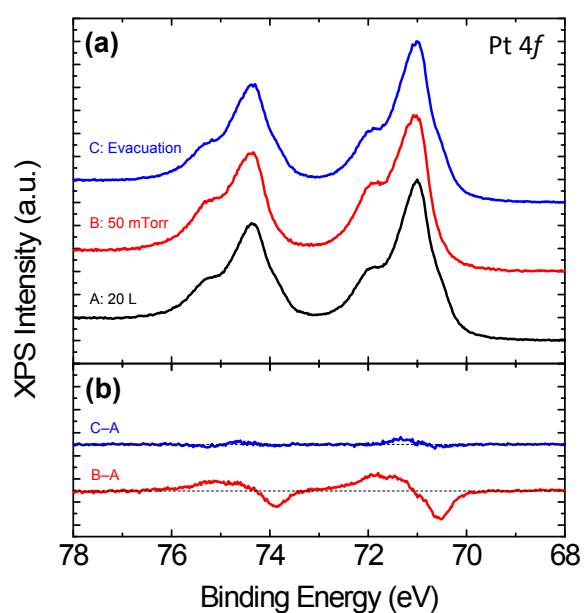


Fig. S2. Reversibility of surface CO phases with respect to the CO gas pressure. (a) Pt 4f XP spectra of a Pt(111) surface taken under an ultrahigh vacuum (UHV) condition after 20 L CO exposure (A), under 50 mTorr CO (B) and after CO evacuation (C). (b) Residuals of XP spectra after subtracting of the spectrum taken after 20 L CO exposure.

3. Optimized geometric parameters of CO adlayers

We employed density functional theory (DFT) calculations to gain a detailed understanding of experimental results. In this work, we modeled CO-induced $c(4 \times 2)$ -2CO and $(\sqrt{19} \times \sqrt{19})R23.4^\circ$ -13CO (hereafter $\sqrt{19}$ -13CO) structures. Optimized geometric parameters are summarized in Table S1.

The $c(4 \times 2)$ -2CO structure consists of CO molecules at bridge and top sites with a molecular ratio of one to one (Fig. 3a). In the present case, the top- and bridge-CO molecules in the $c(4 \times 2)$ unit cell have an upright configuration with the molecular axis perpendicular to the surface. On the other hand, a part of CO molecules in the $\sqrt{19}$ -13CO phase have tilted configurations. Since the average intermolecular distance is $\sim 9\%$ shorter than that of the $c(4 \times 2)$ -2CO phase, a part of CO molecules are tilted to reduce the CO-CO repulsion. For the top-CO molecules there are two types of CO configurations. The top-CO molecules at the corner of the unit cell have a perpendicular configuration, while the other top-CO molecules are tilted from the surface normal ($\sim 11^\circ$). For the bridge-CO molecules, the C atoms are located at quasi-regular positions of the bridge sites, while the O atoms exhibit slight lateral shifts in such that they are arranged into a hexagonal arrangement with almost the same O-O spacing, which results in a small tilting ($< 3^\circ$).

Table S1. Optimized geometric parameters of CO-overlayers on Pt(111). d_{A-B} is the bond length between atom A and atom B, whereas h_{A-B} is the difference in vertical height between atom A and atom B. α is a tilt angle of CO molecular axis from the surface normal. The CO molecules at top sites have two different types of adsorption geometry; upright (u) and tilted (t).

Structure	Site	$d_{\text{Pt-C}}$ (Å)	$d_{\text{C-O}}$ (Å)	$h_{\text{Pt-C}}$ (Å)	$h_{\text{Pt-O}}$ (Å)	α (°)
$c(4 \times 2)$ -2CO	Bridge	2.02	1.19	1.47	2.66	0.1
	Top	1.86	1.16	1.86	3.01	0.5
$\sqrt{19}$ -13CO	Bridge	2.03	1.18	1.49	2.67	~ 2.6
	Top (u)	1.85	1.16	1.85	3.01	0.0
	Top (t)	1.86	1.16	1.82	2.96	~ 11

4. CO adsorption at hollow site

So far a (4×4) -9CO structure has been proposed from a high pressure scanning tunneling microscopy (HP-STM) observation, which includes CO molecules located at hollow sites as shown in Fig. S3.³ To check the core-level-shift (CLS) for CO at the hollow site, we calculated the CLSs for an isolated CO at a hollow site of Pt(111) with the upright configuration.

The calculated results are summarized in Table S2. The CLS of surface Pt atoms bound to the hollow-CO is very small with respect to the bulk Pt. If the number of hollow-CO increases with increasing the CO pressure, the apparent intensity of the bulk component in Pt 4*f* XP spectra should be enhanced due to contribution from the surface Pt atoms bound to the hollow-CO. The CLS of C 1*s* for the hollow-CO exhibits a negative value, which is opposite to the CLSs for the top- and bridge-CO. However, our experimental results showed neither enhancement of the bulk component in Pt 4*f* nor appearance of the negatively shifted component in C 1*s* at any pressure.

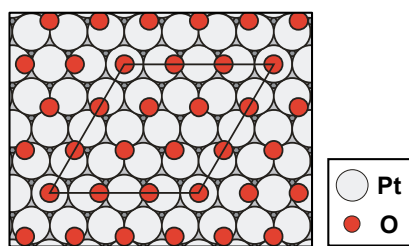


Fig. S3. Top view of the (4×4) -9CO structure model. Pt and O atoms are colored as gray and red, respectively. The black enclosure indicates the (4×4) unit cell of the structure.

Table S2. Calculated CLSs for the hollow-CO/Pt(111) system. The CLSs of Pt 4*f* and C 1*s* are obtained with respect to the binding energies of the bulk Pt and CO at a bridge site, respectively.

System	Level	Theoretical CLS (eV)
CO on hollow site	Pt 4 <i>f</i>	+0.05
	C 1 <i>s</i>	-0.19

5. References

1. Björneholm, A. Nilsson, H. Tillborg, P. Bennich, A. Sandell, B. Hernnäs, C. Puglia and N. Mårtensson, *Surf. Sci. Lett.*, 1994, **315**, L983.
2. M. Kinne, T. Fuhrmann, J. F. Zhu, C. M. Whelan, R. Denecke, and H.-P. Steinrück, *J. Chem. Phys.*, 2004, **120**, 7113.
3. J. A. Jensen, K. B. Rider, M. Salmeron and G. A. Somorjai, *Phys. Rev. Lett.*, 1998, **80**, 1228.