

Reaction of CO₂ on stepped Cu(997) surface revealed by ambient-pressure X-ray photoelectron spectroscopy

Today, society presents a strong demand towards developing novel catalysts that will solve energy and environmental problems. In catalysis research, the importance of *Operando* spectroscopy has recently begun to be realized. Gaps in pressure and temperature exist between ideal surface science studies (ultrahigh vacuum (UHV) and low/moderate temperature) and real catalytic conditions (above atmospheric pressure and high temperature). Such differences in pressure and temperature may result in distinct reactivity under ambient conditions compared with the case of UHV conditions, reflecting thermodynamic and kinetic effects. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) [1] is a powerful *Operando* spectroscopy that allows us to investigate electronic and chemical states of the adsorbate and substrate under gas atmosphere.

The activation of CO₂ is an important topic in the efficient use of CO₂ as a chemical feedstock. Methanol synthesis from CO₂ and H₂ on Cu/ZnO catalysts has been widely studied and is already developed industrially. CO₂ is chemically inert, and thus the interaction of the molecule with metallic Cu surfaces plays an essential role in molecular activation. The previous studies in UHV revealed that stepped Cu surfaces are active in the dissociation of CO₂ [2,3]. However, the reaction mechanism of CO₂ at defect sites such as steps and kinks on the Cu surface, which are abundant on real catalysts, is not yet fully understood. In this study [4], therefore, we investigated the reaction process of CO₂ on the stepped Cu(997) surface at a CO₂ pressure of 0.8 mbar and a temperature of 340 K by AP-XPS.

We developed a new AP-XPS system (Fig. 1) at the soft X-ray undulator beamline BL07LSU [5]. AP-XPS measurements were carried out using a differentially pumped electron analyzer (SPECS,

PHOIBOS 150 NAP) with an ambient-pressure gas cell. A one-dimensional delay-line detector (DLD) is adopted as the detector in the electron analyzer. The ambient-pressure gas cell is equipped with an Si₃N₄ window for X-ray transmission and a small aperture (300 μm in diameter), which is the entrance to the differentially pumped electron analyzer. The whole gas cell is mounted on a manipulator of the load-lock chamber, and is docked to the front of the electron analyzer. In the ambient-pressure gas cell, a sample is placed close (~300 μm) to the entrance aperture in order to minimize the scattering of photoelectrons by gas-phase molecules. The high performance of our AP-XPS instrument was confirmed by successful measurements of the Au 4*f* core level of polycrystalline Au foil in the presence of 20 mbar N₂ gas.

Figures 2(a) and 2(b) show a series of O 1*s* and C 1*s* AP-XPS spectra of Cu(997) at 340 K under a CO₂ pressure of 0.8 mbar as a function of elapsed time. Gas-phase CO₂ peaks in O 1*s* and C 1*s* spectra were observed at 536.6–536.4 eV and at 292.8–292.6 eV, respectively. A peak of the adsorbate was observed at 531.3 eV in the O 1*s* XPS (*t* = 376 s), whereas three peaks were observed in the C 1*s* XPS (*t* = 507 s): at 288.4 eV with a broader shoulder peak at higher binding energy (289.0 eV), and at 284.4 eV. The intensities of XPS peaks at 531.3, 289.0, and 288.4 eV were saturated at *t* ~ 2000 s, and then a new peak at 529.5 eV appeared in O 1*s* XPS spectra. Temporal evolutions of each O 1*s* and C 1*s* XPS peak are shown in Fig. 3.

The XPS peaks at 531.3, 289.0, and 288.4 eV are assigned to carbonate (CO₃) species, on the basis of the binding energies and the atomic O/C ratio of 3.1 ± 0.1 estimated from the area intensities of O 1*s* and C 1*s* XPS peaks. Two different C 1*s* peak positions of CO₃ may originate from different adsorption sites of CO₃ on Cu(997), such as steps. The O 1*s* XPS peak at 529.5 eV, which appeared after the saturation of CO₃, is attributed to atomic oxygen. The C 1*s* XPS peak at 284.4 eV is assigned to neutral carbon species (C₀) such as graphitic carbons and hydrocarbons.

Next we discuss the reaction mechanism of CO₂ on the Cu(997) surface under near-ambient conditions. Previous experimental studies in UHV revealed the dissociation of CO₂ on the stepped Cu surfaces [2,3]. The CO₂ dissociation should also proceed on the Cu(997) surface under near-ambient conditions to form atomic oxygen and CO. The formed CO is readily desorbed from the Cu surface at 340 K [3],

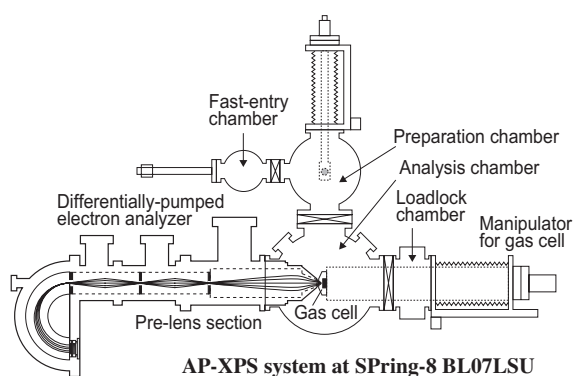
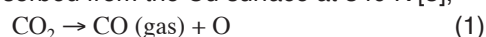


Fig. 1. Schematic of the AP-XPS system.

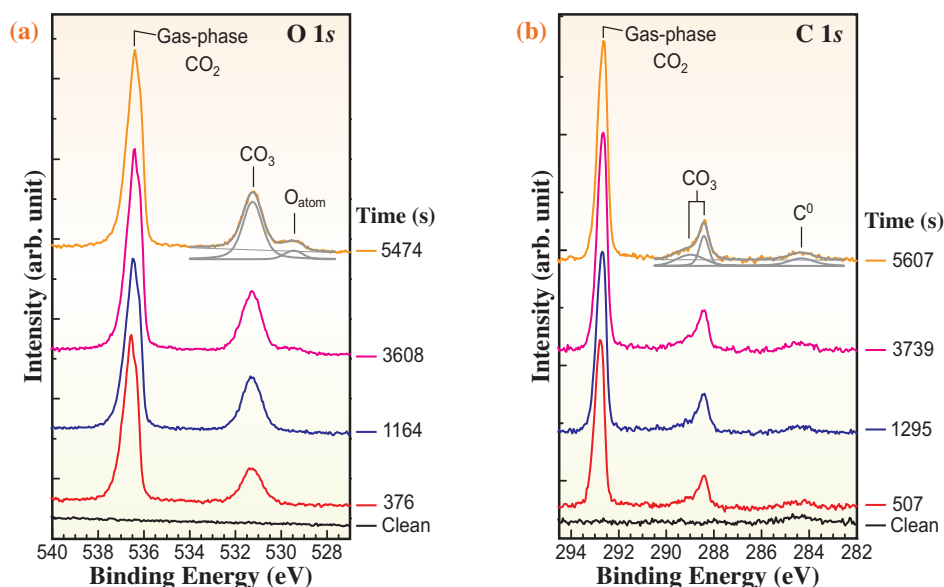


Fig. 2. A series of (a) O 1s and (b) C 1s AP-XPS spectra of Cu(997) at 340 K under CO₂ pressure of 0.8 mbar as a function of elapsed time. Only selected spectra from the whole series are shown in the figure. The photon energy was 630 eV. The CO₂ gas was introduced to the gas cell at $t = 0$ s. The fitting results for the spectra at $t = 5474$ s (O 1s) and $t = 5607$ s (C 1s) are also shown in the figures.

Then, the produced atomic oxygen reacts with CO₂ to form CO₃,



The produced CO₃ is stable on the Cu surface at 340 K, as seen in Fig. 2.

It should be noted that the estimated saturation coverage of CO₃ is rather small (0.05 molecules per surface Cu atom). This indicates that the formed CO₃ species stay at some specific sites, and probably

block further CO₃ formation. After the saturation of CO₃ coverage, the atomic O gradually appears on the surface. It may be because minor reaction sites for the CO₂ dissociation remain on the surface while most of the active sites are covered by CO₃.

The present study clearly shows the formation of CO₃ on the stepped Cu(997) surface, and suggests that CO₃ is a candidate for a reaction intermediate in the CO₂ chemistry on Cu surfaces.

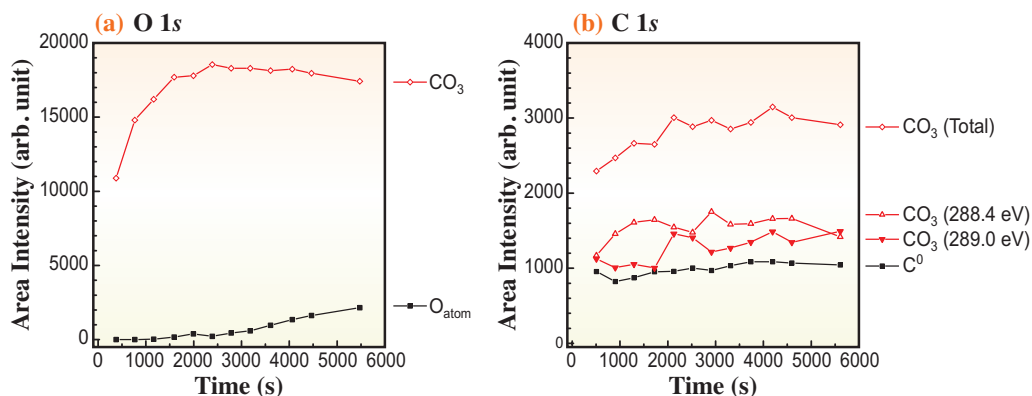


Fig. 3. Area intensities of each component in (a) O 1s and (b) C 1s spectra in Figs. 2(a) and 2(b) as a function of elapsed time ($p(\text{CO}_2) = 0.8$ mbar, $T = 340$ K).

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References

- [1] M. Salmeron, R. Schlögl: Surf. Sci. Rep. **63** (2008) 169.
- [2] S.S. Fu, G.A. Somorjai: Surf. Sci. **262** (1992) 68.
- [3] I.A. Bönicke *et al.*: Surf. Sci. **307-309** (1994) 177.
- [4] T. Koitaya, S. Yamamoto, Y. Shiozawa, K. Takeuchi, R.-Y. Liu, K. Mukai, S. Yoshimoto, K. Akikubo, I. Matsuda, J. Yoshinobu: Topics in Catalysis **59** (2016) 526.
- [5] S. Yamamoto *et al.*: J. Synchrotron Rad. **21** (2014) 352.