

Ambient Pressure Soft X-ray Photoelectron Spectroscopy Study on Chemical Reactivity of TiO₂ Surfaces towards CO and O₂

Kenichi Ozawa^{1,*}, Kensuke Tobishima², Kazuhisa Isegawa³, Tetsuya Miyazawa⁴, Hiroshi Kondoh³, Hiroo Kato² and Kazuhiko Mase^{4,5}

¹Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan

²Hirosaki University, Hirosaki, Aomori 036-8561, Japan

³Keio University, Kohoku, Yokohama 223-8522, Japan

⁴SOKENDAI, Tsukuba, Ibaraki 305-0801, Japan

⁵High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan

1 INTRODUCTION

Photocatalytic activity of TiO₂ is superior to any other semiconductor materials. This leads to TiO₂ as a photocatalyst that is used in many commercially available photocatalytic products. It has been recognized that the photocatalytic activity depends on not only the crystal structure of TiO₂ but also the orientation of the crystal surface. For example, the (101) surface of anatase TiO₂ is more active than the (001) surface in various photocatalytic reactions like photooxidation to generate OH radicals [1], which initiate decomposition of chemical species on the surface. Regarding the rutile TiO₂ (r-TiO₂) surfaces, an activity order of (001) > (100) > (110) has been found for photooxidation of methanol and hydroxylation of terephthalic acid [2]. Contrastingly, r-TiO₂(011) exhibits the highest activity for methyl orange decomposition, followed by (110), (001) and (100) surfaces [3]. A face-dependent redox potential [1], a face-specific electron-trapping probability [4], anisotropic diffusion of the charge carriers in the bulk [3], etc. have been proposed to explain the surface-dependence of the photocatalytic activity. In the present study, we have verified another possible origin of the face-dependence, i.e., the surface chemical activity. The chemical activity of the r-TiO₂ surfaces is comparatively assessed in a CO atmosphere by ambient pressure X-ray photoelectron spectroscopy (AP-XPS). It is found that r-TiO₂(110) is the most active surface, while the least active one is r-TiO₂(011). r-TiO₂(100) and (001) are in-between them.

2 EXPERIMENTAL

Commercially available r-TiO₂ single crystals with (110), (011), (100) and (001) orientation were used. The crystal surfaces were cleaned in the ultrahigh vacuum by cycles of Ar⁺ sputtering and annealing in O₂ atmosphere. APXPS measurements were carried out at BL-13B [5]. C 1s, O 1s and Ti 2p core-level spectra were acquired in the environment of CO, O₂ and CO + O₂ mixture gases. All the experiments were carried out at room temperature.

3 RESULTS and DISCUSSION

Chemical species on the r-TiO₂ surfaces under the CO atmosphere (13 Pa) are identified from the C 1s spectra (a left panel in Fig. 1) as molecularly adsorbed CO (285–286 eV) and carboxylate (which also includes

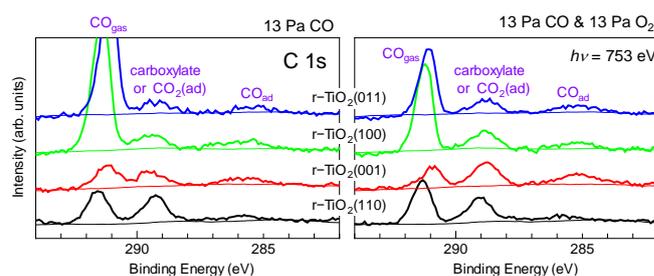


Figure 1 C 1s spectra of the r-TiO₂ surfaces under the CO (13 Pa) and CO + O₂ (26 Pa) atmosphere. The photon energy used was 753 eV. An intense peak at 291–292 eV is gaseous CO.

adsorbed CO₂) (~289 eV). The carboxylate should be formed between adsorbed CO and lattice O of the r-TiO₂ surface. Involvement of the O atoms that are formed as a result of CO dissociation is safely denied because atomic C is absent on the surface. The fact that the amount of the carboxylate is larger than that of adsorbed CO irrespective of the surface orientation suggests that the activation barrier for CO oxidation must not be high. Judging from the peak intensities, the order of the chemical reactivity for CO adsorption (and, thus, CO oxidation) is (110) > (001) ≈ (100) > (011). This order is unchanged when O₂ coexists with CO, though the activity is enhanced on the (001), (110) and (011) surfaces. The activity order towards CO adsorption and oxidation is the same as that for acetic acid adsorption. This indicates that the stability of the adsorbed carboxylate should determine the activity of the r-TiO₂ surfaces.

The experimental results obtained in the present study will help to assess the contribution of the surface chemical activity to the face-dependent photocatalytic activity once the photocatalytic activity is determined under the same ambient condition. This will be the next step in our research.

References

- [1] J. Pan *et al.*, *Angew. Chem. Int. Ed.* **50**, 2133 (2011).
- [2] A.Y. Ahmed *et al.*, *J. Phys. Chem. Lett.* **2**, 2461 (2011).
- [3] T. Luttrell *et al.*, *Sci. Rep.* **4**, 4043 (2014).
- [4] T. Tachikawa *et al.*, *J. Am. Chem. Soc.* **113**, 7197 (2011).
- [5] H. Kondoh *et al.*, *Catal. Today* **260**, 14 (2016).

* ozawa.k.ab@m.titech.ac.jp