Local Silver Site Temperature Critically Reflected Partial and Complete Photooxidation of Ethanol Using Ag–TiO₂ as Revealed by Extended X-ray Absorption Fine Structure Debye– Waller Factor

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EXPERIMENTAL SECTION

The photooxidation tests of ethanol were performed in a closed circulation system. Ethanol (1.33 kPa) was introduced to the closed circulation system, and purified three times via freezeand-thaw cycle using liquid nitrogen (77.35 K). Then, O_2 (2.67 or 5.32 kPa) was introduced to the closed circulation system. The gas composition during the light irradiation was monitored using an online gas chromatograph equipped with a thermal conductivity detector (Shimadzu, Kyoto, Japan; Model GC-8AT). A part of reaction gas was sampled. The sampled gas was trapped using liquid nitrogen, and remained gas phase was injected to a packed column of Molecular Sieves 13X-S for the separation of O_2 , N_2 , CH_4 , and CO. Conversely, the sampled gas was trapped using liquid nitrogen, and the gas phase was evacuated for 3 sec to rotary and diffusion pumps. The trapped part was warmed to 290 K, and injected to a packed column of polyethene glycol-6000/Flusin P for the separation of CO_2 , CH_3 CHO, acetone, C_2H_5 OH, and H_2O .

The experimental setup for Ag K-edge EXAFS measurements for Ag (2.0 wt%)–TiO₂ under ethanol and O₂ irradiated by UV–visible light is depicted in Figure S1.



Figure S1. The experimental setup of Ag K-edge EXAFS measurements for Ag (2.0 wt %)–TiO₂ under C_2H_5OH and O_2 irradiated by UV–visible light.

RESULTS AND DISCUSSION

The angular wavenumber k^3 -weighted EXAFS χ -functions are summarized in Figure S2 for Ag (2.0 wt%)–TiO₂ samples and references. The difference of the pattern for Ag metal and AgI₂O is clear, and the changes of the amplitude for the oscillation for Ag metal were in accord with the peak intensity changes in its associated Fourier transform (Figure 6).



Figure S2. Time course changes of k^3 -weighted Ag K-edge EXAFS χ -function for Ag (2.0 wt %)–TiO₂ (a) fresh in air and (b) under C₂H₅OH (1.33 kPa) irradiated by UV–visible light (i), C₂H₅OH (1.33 kPa) and O₂ (2.67 kPa) by UV–visible light (ii), C₂H₅OH (1.33 kPa) and O₂ (2.67 kPa) by visible light ($\lambda > 390$ nm) (ii'), C₂H₅OH (1.33 kPa) and O₂ (2.67 kPa) by UV and IR light (245 nm < $\lambda < 386$ nm, $\lambda > 686$ nm)

(ii"), and C₂H₅OH (1.33 kPa) and O₂ (5.32 kPa) by UV–visible light (iii) followed by dark conditions (i, ii, ii', and iii), and (c) reference spectra for Ag metal foil and Ag₂O powder.