

Supplementary Information

Fabrication of hydrophobic zeolites using triethoxyfluorosilane and their application as supports for TiO₂ photocatalysts

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Materials: Proton-type Y zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5, 40$ and 200) was supplied by Union Syowa K.K.. Pure titanium dioxide powder (P-25) was supplied by Ishihara industry Inc.. Triethoxyfluorosilane (TEFS : $(\text{OC}_2\text{H}_5)_3\text{SiF}$) was purchased from Aldrich Inc. and 2-propanol, ammonium titanyl oxalate n -hydrate $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$ and tetraisopropyl orthotitanate (TPOT : $\text{Ti}(\text{OC}_3\text{H}_7)_4$) were purchased from Wako Pure Chemical Inc., Ltd. Solvents and all commercially available organic compounds for catalytic reactions were purified using standard procedures.

Sample Preparation: To prepare surface modified Y-zeolites, proton type Y-zeolites (2.0 g) were impregnated into triethoxyfluorosilane (TEFS) (0.45 g, 0.90 g, 1.80 g to the molar ratio of 10, 20, 40 mol %, respectively) solution diluted in 2-propanol (200 mL) and stirred at room temperature for 5 h. The suspension was then evaporated in vacuo, dried at 383 K over a night and calcined at 773 K for 5 h in air. The prepared samples were denoted as FSm-Y(n), where m and n describes the ratio of TEFS reagent (10, 20 and 40 mol %) and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (5, 40 and 200), respectively.

To prepare TiO_2 photocatalysts on FS-Y zeolites, the FS-Y zeolites (1.0 g) were suspended in aqueous solution (200 mL) of $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$ (0.458 g) and stirred at room temperature for 5 h. The suspension was then evaporated under vacuum, dried at 383 K over a night and calcined at 823 K for 5 h in air.

The elemental analysis was performed by inductively coupled plasma (ICP) analysis and X-ray photoelectron spectroscopy (XPS) analysis.

Characterization: BET surface area measurement was performed using an ASAP 2010 system (Shimadzu) at 77 K. The sample was degassed under vacuum at 473 K prior to data collection. Powder X-ray diffraction patterns were recorded using a Rigaku RINT2500 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). XPS was recorded with JOEL microprobe system using the Mg $K\alpha$ line. Binding energy was calibrated using the C1s photoelectronic peak at 285.0 eV. FT-IR measurement was performed using FT/IR-6100 (JASCO). The spectrometer settings were 24 scans, 4 cm^{-1} of resolution. The IR spectra were recorded in the spectral range of 4000 to 400 cm^{-1} with a TGS type detector under vacuum. Ti K-edge XAFS spectra were recorded in the fluorescence mode at 295 K at BL-9A facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Japan. A Si(111) double crystal was used to monochromatize the X-rays from the

2.5 GeV electron storage ring. EXAFS data were examined using an EXAFS analysis program, Rigaku EXAFS. The pre-edge peaks in the XANES regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region. Fourier transformation (FT) of k^3 -weighted normalized EXAFS data was performed over the range $3.5 < k/\text{\AA}^{-1} < 11$ to obtain the radial structure function.

Photocatalytic degradation: Powdered $\text{TiO}_2/\text{FS-Y}$ (50 mg) photocatalysts or P-25 were placed with 25 mL of diluted 2-propanol aqueous solution ($2.61 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) into a reaction vessel (50 cc) with a reflux condenser. The resulting mixtures were reacted at room temperature with magnetic stirring. The progress of the reaction was monitored by GC analysis at appropriate intervals. Analytical GC was performed using a Shimadzu GC-14B with flame ionization detector equipped with Porapak Q columns.

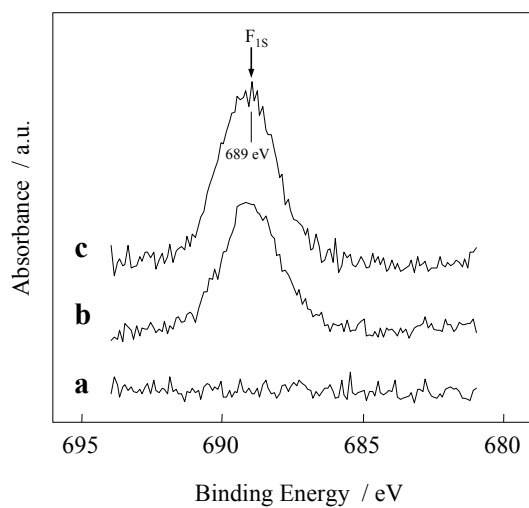


Figure S1 XPS spectra of F_{1s} in a) HY(200), b) FS1-Y(200) and c) FS4-Y(200).