

Supplementary information

Experimental

Sample preparation

Nanocrystalline TiO₂ powder was prepared at 573 K using the HyCOM method.¹² Titanium(IV) tetra-n-butoxide was used as the starting material and the product was calcined at 823 K. This HyCOM-TiO₂ powder (148.5 mg) was suspended in 80 vol% aqueous solution of acetic acid containing palladium(II) acetate (as 1.5 mg Pd) in a test tube. The test tube was sealed with a rubber septum under Ar and then photoirradiated at a wavelength $\lambda > 300$ nm by a 400 W high-pressure mercury arc (Eiko-sha, Osaka, Japan) with magnetic stirring in a water bath continuously kept at 298 K. The Pd source was reduced by photogenerated electrons and the Pd metal was deposited on HyCOM-TiO₂ particles, resulting in the formation of Pd-loaded HyCOM-TiO₂ (Pd-TiO₂). Various metals other than Pd were also deposited on HyCOM-TiO₂ particles using the photodeposition method. The resultant powder was washed with acetone and distilled water and then dried at 310 K overnight under air.

Photocatalytic dechlorination of chlorobenzene

Photocatalytic dechlorination of chlorobenzene was carried out in 2-propanol suspension of metal-loaded TiO₂ powder in the presence of dissolved NaOH. Here 2-propanol acted as both reaction media and hole scavenger. A small amount of NaOH dissolved in 2-propanol previously dried with molecular sieves was used to remove chloride ions released from chlorobenzene as sodium chloride (NaCl) because of low solubility of NaCl in 2-propanol. One wt% metal-loaded TiO₂ powder (50 mg) was suspended in 2-propanol (5 cm³) containing NaOH (220 μ mol) in a test tube. After the mixture had been bubbled with argon and sealed with a rubber septum,

chlorobenzene (98 μmol) was injected into the mixture. The test tube was photoirradiated in the same way as photodeposition. During photoirradiation, the test tube was set in a water bath kept at 298 K to avoid thermal reaction. The amounts of H_2 and CO_2 in the gas phase were measured using a Shimadzu GC-8A gas chromatograph equipped with MS-5A (H_2) and Porapak QS (CO_2) columns, respectively. The amounts of benzene and chlorobenzene in the liquid phase were determined with a Shimadzu GC-14B gas chromatograph equipped with a DB-1 capillary column (30 m \times 0.25 mm). The amount of acetone in the liquid phase was determined with a Shimadzu GC-14A gas chromatograph equipped with a fused silica capillary column (HiCap-CBP20, 25 m \times 0.22 mm). Toluene was used as an internal standard sample and the amounts of benzene, chlorobenzene and acetone were determined using the ratios of the peak areas of benzene, chlorobenzene and acetone to the peak area of toluene. The reaction solution (1 cm^3) was added to a diethyl ether/water mixture (2:1 v/v, 3 cm^3). After the mixture had been stirred for 10 min, the ether phase was analyzed by the method previously described. The amount of chlorine ion was determined with a JASCO co-2060 Plus ion chromatograph.