Photoreductive Defluorination of Hexafluorobenzene on Metal-doped ZnS Photocatalysts under Visible Light Irradiation

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Metal-(Cu, Ni, or Pb) doped ZnS photocatalysts have the ability to photoreductively defluorinate hexafluorobenzene under visible light irradiation; the defluorination mechanism on Pb-, or Cu-doped ZnS is different from that on Ni-doped ZnS. The role of Pb and Cu dopants in ZnS is not only to extend the photocatalytic response toward visible light but also to act as redox reaction sites in the photoreductive defluorination.

Perfluorinated organic compounds are well known to be thermally and chemically stable, because of their strong C–F bonds and the small size of the fluorine atom. Photochemical reactions have attracted much attention with respect to inducing defluorination or decomposition for such perfluorinated compounds under mild conditions.[1–3] Photoredox reactions on semiconductor photocatalysts can also lead to such defluorination reactions. In particular, zinc sulfide (ZnS) has an advantage in photoreductive defluorination because of its high conduction band (CB) levels.[4] Recently, Yin et al. have reported the photodefluorination of hexafluorobenzene (F6) using ZnS and CdS nanocrystallites, under UV and visible light irradiation, respectively.[5] Concurrently, one of us (A. K.) has developed Cu-doped ZnS (Cu-ZnS),[6] Ni-doped ZnS (Ni-ZnS),[7] and Pb, Cl-codoped ZnS (Pb,Cl-ZnS)[8] photocatalysts in order to extend the photocatalytic response of ZnS toward the visible region (Diffuse reflectance spectra are given in Electronic Supporting Information). The new absorption bands that appeared in the 350–540 nm region have been assigned to transitions from the metal impurity levels (Cu 3d, Ni 3d, and Pb 6s) formed in the bandgap to the CB of ZnS. Although the impurity levels of the three metal-doped ZnS are different, the CB levels are common and identical to that of nondoped ZnS. Therefore, the photoreductive defluorination of F6 is expected to occur upon photoexcitation with visible light.

In this letter, we report the photoreductive defluorination of F6 using Cu-ZnS, Ni-ZnS, and Pb,Cl-ZnS in triethylamine (a reducing reagent), dissolved in acetonitrile, under visible light irradiation. Products have been identified by gas chromatography-mass spectrometry (GC-MS). In order to clarify the hydrogen source for the pentafluorobenzene (F5) produced by the defluorination of F6, deuterated reagents such as triethyl-d_{15}-amine ($N(C_2D_5)_3$, 99.7 atom % D) and D_2O (>99.75 atom % D) were added to the solutions and reaction mixtures were analyzed by GC-MS.

Ni (0.1 atom %)-ZnS and Pb (1.4 atom %), Cl (2.5 atom %)-ZnS photocatalysts were prepared by the coprecipitation method and then heat-treated as reported previously.[7,8] Cu (4.3 atom %)-ZnS was also synthesized by the coprecipitation method.[6] The Cu-ZnS was used immediately after preparation without drying, because this condition was favorable to the photocatalytic performance. F6 (25 mmol dm^{-3}), triethylamine (1 mol dm^{-3}), and photocatalyst powders (1 g dm^{-3}) contained in acetonitrile (25 cm^3) were placed in a cylindrical quartz vessel and degassed with N_2 gas flow. Irradiation experiments were carried out using a 300-W xenon lamp equipped with an appropriate cut-off filter with stirring in a water bath (280 K).

Figure 1 shows the decrease in F6 and evolution of F5 obtained with the three metal-doped and nondoped ZnS photocatalysts under visible light irradiation. When the metal-doped ZnS was used, F5 was produced with decreasing F6 in all cases. The three F6 degradation reactions follow first-order rate kinetics, with nearly the same rate constant of 0.1 day^{-1}. On the contrary, in a nondoped ZnS sample, the decrease rate for F6 was much slower (indicated by crosses in Figure 1) and negligible evolution of F5 was observed. It is demonstrated that Ni, Cu, and Pb metals doped in ZnS are responsible for the defluorination reaction observed upon photoexcitation with visible light. Decrease in the photocatalytic activity for Cu-ZnS was brought about when dried Cu-ZnS powders were used. On the other hand, efficient degradation of F6 as well as formation of F5 were observed in a nondoped ZnS solution under UV irradiation; F6 was completely decomposed within 2 days, and ca. 50% of F6 was converted into F5.

In GC-MS analyses, F5, as well as a considerable amount of diethylamine, were observed from all of the metal-doped ZnS suspensions. Furthermore, a trace amount of acetaldehyde was detected from the head space gas above the solutions in the vessels for all samples. Diethylamine and acetaldehyde are produced in the oxidative dealkylation of triethylamine induced by hole oxidation at the surface of ZnS, as reported in the liter-

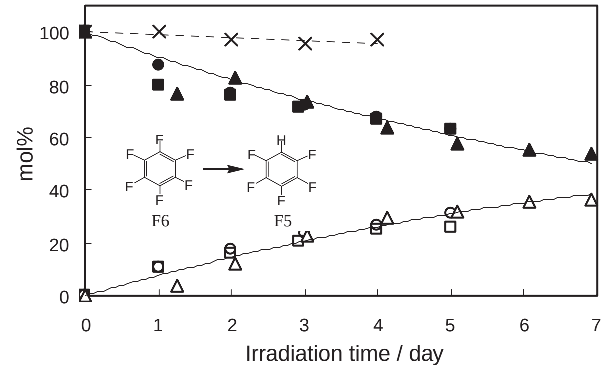

Figure 1. Degradation of F6 (filled symbols) and formation of F5 (open symbols) with Cu-ZnS (triangles), Pb,Cl-ZnS (circles), and Ni-ZnS (squares) under visible light irradiation (>400 nm, 1.6 W cm^{-2}) at 280 K. The solid decay curve is a simulated one, with a first-order rate constant of 0.1 day^{-1}. The cross plots indicate the decrease in F6 with nondoped ZnS.

ature.[5,9] In the mechanism, water contained in solution takes part in the dealkylation of triethylamine.

A trace amount of 1,2,4,5-tetrafluorobenzene (1,2,4,5-F4) was also detected. However, further defluorination of 1,2,4,5-F4 was not observed in our study. Yin et al. have reported that nanocrystalline ZnS has the ability to induce photoreductive defluorination of F5, F4, and trifluorobenzenes to afford several F4 isomers, trifluorobenzene, and difluorobenzene. This discrepancy may be caused by the difference in the CB levels between metal-doped ZnS and nanocrystalline ZnS. The CB edges of the three metal-doped ZnS would be located at the same level as that of the ZnS single crystal (ca. -2.4 V vs SCE in acetonitrile).[4] Therefore, F6 (F6/F6$^-$: -2.11 V vs SCE in DMF)[10] is easily reduced by CB electrons generated in the metal-doped ZnS, while F5 (F5/F5$^-$: -2.35 V vs SCE)[10] and 1,2,4,5-F4 (F4/F4$^-$: -2.40 V vs SCE)[10] may be reduced only to a slight extent. On the other hand, the CB level of nanocrystalline ZnS is located at a more negative potential than that of bulk ZnS because of the quantum size effect.[5]

There are two candidates for the hydrogen source of F5: one is triethylamine, and the other is water contained in acetonitrile. Here, we prepared the following complementary solutions and examined the molar ratios of C_6F_5H and C_6F_5D by use of GC-MS analysis: (a) a normal $N(C_2H_5)_3$ and a small amount of D_2O (0.46 mol dm^{-3}) contained in anhydrous acetonitrile ($H_2O < 30$ ppm), and (b) deuterated $N(C_2D_5)_3$ contained in HPLC grade acetonitrile ($H_2O < 500$ ppm). Molar ratios were obtained from peak areas observed at specific charges (m/z) of 168 and 169, corresponding to the molecular ions of C_6F_5H and C_6F_5D, respectively (Representative data for Pb,Cl-ZnS are given in Electronic Supporting Information).

Figure 2 shows molar ratios after a 1-day irradiation. The indicated ratios remained nearly unchanged during several days for all samples. In the case of nondoped ZnS (UV irradiation) and Ni-ZnS, the hydrogen of F5 came predominantly from triethylamine. Therefore, water contained in acetonitrile made a relatively small contribution to the defluorination of F6. On the contrary, for Pb,Cl-ZnS, a considerable amount of the hydrogen of F5 was derived from not only triethylamine but also water contained in acetonitrile. This result is supported by the fact that the ratio of C_6F_5H was diminished in anhydrous acetonitrile containing deuterated $N(C_2D_5)_3$ (solution (c)). Thus, a small amount of water in acetonitrile contributes greatly to the defluorination of F6 for Pb,Cl-ZnS, compared (b) to (c). This is not due to the presence of codoped Cl^- ion in Pb,Cl-ZnS powders, because Pb-doped ZnS (not including Cl^-) also gave a similar molar ratio in solution (a), although the defluorination rate was slower than that for Pb,Cl-codoped ZnS. The rate reduction may arise from enhancement of electron–hole recombination at defect sites, which would be formed by the doping of large Pb cations in the ZnS lattice. The codoped Cl^- anions may be useful for the relaxation of the distortion induced by the Pb doping, as reported previously.[8] For Cu-ZnS, the molar ratio of F5 in solution (b) shows a similar tendency to that of Pb,Cl-ZnS, while the result in solution (a) seemingly resemble that of Ni-ZnS or nondoped ZnS. However, the small C_6F_5D ratio in solution (a) is probably underestimated because a relatively large amount of normal H_2O from the wet Cu-ZnS powders can contribute to the production of C_6F_5H.

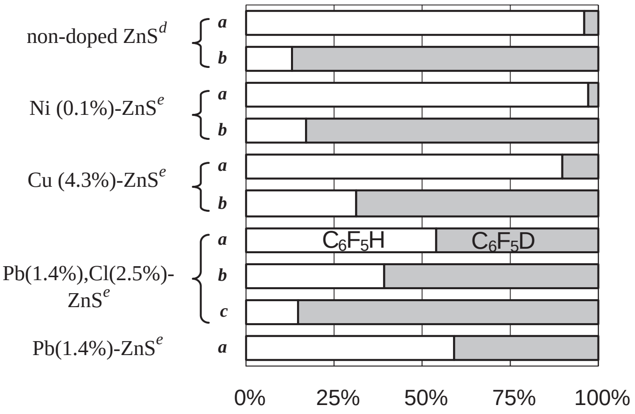

Figure 2. Molar ratios of C_6F_5H and C_6F_5D in nondoped and metal-doped ZnS suspensions after a 1-day irradiation (280 K). All indicated values were corrected by considering natural abundance of ^{13}C (1.1%) in C_6F_5H or C_6F_5D. Symbols: ^{a}normal $N(C_2H_5)_3$ (1 mol dm^{-3}) and D_2O (0.46 mol dm^{-3}) contained in 25 cm^3 of anhydrous acetonitrile ($H_2O < 30$ ppm); ^{b}deuterated $N(C_2D_5)_3$ (1 mol dm^{-3}) contained in 10 cm^3 of HPLC grade acetonitrile ($H_2O < 500$ ppm); ^{c}deuterated $N(C_2D_5)_3$ (1 mol dm^{-3}) contained in 10 cm^3 of anhydrous acetonitrile ($H_2O < 30$ ppm); ^{d}UV and visible light irradiation (>300 nm, 1.9 W cm^{-2}); ^{e}visible light irradiation (>400 nm, 1.6 W cm^{-2}).

In conclusion, the mechanism of photoreductive defluorination of F6 on Pb,Cl-ZnS and Cu-ZnS is different from that of nondoped ZnS. Pb and Cu cations on the surface of metal-doped ZnS should act as redox reaction sites, where electrons and holes generated upon visible light irradiation may be concentrated and react with F6, triethylamine and/or water. Thus, the role of Pb and Cu in ZnS is not only to extend the ZnS photocatalytic response toward visible light but also to act as the redox reaction sites in the photoreductive defluorination. On the other hand, the result for Ni-ZnS in Figure 2 is very similar to that of nondoped ZnS. This means that Ni cations on the surface of ZnS would not be the main redox reaction sites because of the very small amounts of Ni doping (0.1%). The defluorination reaction on Ni-ZnS would therefore occur on the pure ZnS surface, as in nondoped ZnS.

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