EFFICIENT DECOMPOSITION OF PERFLUOROALKYLSULFONATES USING IRON IN SUBCRITICAL WATER

Hori H[1], Nagaoka Y[1], Yamamoto A[1], Sano T[1], Kutsuna S[1], Osaka I[2], Arakawa R[2]

[1]National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba 305-8569, Japan; [2]Department of Applied Chemistry, Faculty of Engineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

Abstract

Perfluoroalkylsulfonates such as perfluorooctanesulfonate (PFOS) and related chemicals have recently received a great deal of attention because they are recognized as ubiquitous environmental contaminants. They have been widely used as products or raw materials for surface treatment agents, paper coatings, fire-fighting foams and so forth. After these chemicals were shown to persist and bioaccumulate in the environment, international legal measures for PFOS are discussed. However, they are still necessities in electronics industry as surface treatment agents in photolithography processes. Therefore, the development of techniques to decompose them (as waste, especially in wastewater) to environmentally harmless species under mild conditions is desired. The method should involve cleavage of the C–F bonds to form F- ions, because F- ions readily combine with Ca^{2+} to form harmless CaF_2.

Here we show the decomposition of PFOS and other perfluoroalkylsulfonates bearing shorter-chain (C_2–C_6) perfluoroalkyl groups in subcritical water. Addition of zerovalent metals to the reaction system enhanced the decomposition. When iron was added to the reaction system, these stable compounds were most efficiently decomposed to form F^- ions. We applied this method to the decomposition of PFOS contained in an antireflective coating agent used in photolithography processes in semiconductor manufacturing.

Introduction

Perfluoroalkylsulfonates and perfluorocarboxylic acids, especially perfluorooctanesulfonate ($C_8F_{17}SO_3^-$, PFOS) and perfluorooctanoic acid ($C_7F_{15}COOH$, PFOA), have recently received a great deal of attention because they are recognized as ubiquitous environmental contaminants.[1,2] These compounds have been widely used in industry as products or raw materials for surface treatment agents in photolithography, processing aids in polymer synthesis, paper coatings, waxes, fire-fighting foams, and polishes because of their specific characteristics such as a high surface-active effect, high thermal and chemical stability, and high light transparency.   Their high stability consequently results in environmental persistence. The largest fluorochemical manufacturer has ceased most PFOS production in the year 2000 and nowadays international legal measures for PFOS are discussed. However, it is still a necessity in the semiconductor industry as surface treatment agents (photoacid generator, antireflective coating agent, etc.) in photolithography processes.[3] Therefore, the development of techniques to decompose these compounds at stationary sources is strongly desired. The method should involve cleavage of the C–F bonds to form F^- ions, because F^- ions have a well-established waste-treatment process, based on a reaction with Ca^{2+} to form environmentally harmless CaF_2.

We have reported previously that perfluorocarboxylic acids such as PFOA in water were efficiently decomposed by use of a heteropolyacid photocatalyst[4] or persulfate (photochemical oxidant).[5,6] We report herein the reductive decomposition of PFOS and other perfluoroalkylsulfonates in subcritical water.[7] Reactions in sub- or supercritical water have been recognized recently as an innovative and environmentally benign reaction technique. We show that when iron powder was added to the reaction system, these stable fluorinated compounds were efficiently decomposed to form F^- ions. We also applied this method to the decomposition of PFOS contained in an antireflective coating agent used in photolithography processes in semiconductor manufacturing.

Materials and Methods

All perfluoroalkylsulfonates used were obtained in the form of potassium salts. Fine metal powders—aluminum

(> 99.99% purity, < 75 μm particle size), copper (99.9%, < 75 μm), iron (> 99.9%, < 53 μm), and zinc (99.99%, < 75 μm)—were purchased from Kojundo Chemical Laboratory, Co. (Saitama, Japan) and were used as received. Argon (99.99%) gas for the reaction was purchased from Tomoe Shokai Co. (Tokyo, Japan). Standard gas mixtures—H_2 (0.987%)/N_2 and CHF_3 (1.05%)/He— were obtained from Nippon Sanso Co. (Tokyo, Japan) and Takachiho Trading Co. (Tokyo, Japan), respectively.

A stainless steel high-pressure reactor (34.3 mL volume) equipped with a thermocouple and a stainless steel screw cap was used. In a typical run, an argon-saturated aqueous solution (10 mL) of PFOS (typically 3.72 μmol; 372 μM) and metal powder (9.60 mmol) were introduced into the reactor under an argon atmosphere, and the reactor was sealed. Then the reactor temperature was raised to the desired temperature and the temperature was held constant for the specified time (e.g., 6 h). After the specified time passed, the reactor was quickly cooled to room temperature using ice water. The reactor was opened under an argon atmosphere, and the reaction mixture was centrifuged to separate the solution phase and the solid phase (metal powder), and then subjected to measurements.

The F^- ion concentrations in reaction solutions were measured by ion-chromatography. Quantification of PFOS and other fluorinated substrates was carried out by HPLC with conductometric detection, where the mobile phase was a mixture of methanol and aqueous NaH_2PO_4 (20 mM, adjusted to pH 3.0 with H_3PO_4) at several mixing ratios (45–65% methanol). Electrospray ionization (ESI) mass spectrometry was employed to identify qualitatively the products and intermediates in the solution phase. A gas chromatography/mass spectrometry (GC/MS) system was used to identify the products in the gas phase. The analyses were conducted in full-scan mode (m/z 1.2 – 200) to survey the products. Changes in the solid phase (metal) due to reactions were determined by X-ray photoelectron spectrometry (XPS) with Al-Kα radiation and X-ray diffractometry (XRD) with Cu-Kα radiation. For the XRD measurements, the sample powder was mounted on a glass holder and was covered with polypropylene film to avoid oxidation during measurement.

Results and Discussion

PFOS Decomposition in Subcritical Water
The results of PFOS decomposition in subcritical water are summarized in Table 1, where the reactions were carried out at 350 ℃ for 6 h. In the absence of metal (entry 1), most (90.3%) of the initial PFOS remained in the reaction solution, accompanying formation of a very small amount of F^- with a yield [(moles of F^- formed)/(moles of fluorine content in initial PFOS $\times$ 100] of 0.16%, reflecting the high thermal and chemical stability of PFOS. Addition of aluminum did not enhance the decomposition at all (entry 2). Alternatively, addition of other metals clearly enhanced the decomposition, with an increasing order of Cu < Zn << Fe (entries 3–5). The highest enhancement of the PFOS decomposition was achieved by iron. After the treatment in subcritical water with iron for 6 h, no PFOS was detected in the reaction solution while the F^- yield reached 51.4% (entry 5).

Effect of Iron
Because the addition of iron powder led to the most efficient PFOS decomposition among the metals tested, we investigated the PFOS decomposition with iron in detail by changing the reaction conditions. The reaction-time dependence of the amounts of remaining PFOS and formation of F^- in the reaction solution is shown in Figure 1, where the reaction temperature was kept constant at 350 ℃. Surprisingly, the amount of PFOS in the solution phase decreased from 3.72 μmol (original added amount) to 2.13 μmol after addition of iron. Here, 42.7% of the initial PFOS was removed from the solution even before heating, suggesting that PFOS strongly adsorbed on the iron surface. After heating, the amount of PFOS in the reaction solution effectively decreased with increasing reaction time, while F^- in the reaction solution increased. After 6 h, PFOS was not detected in the reaction solution; this accompanied the formation of 32.5 μmol of F^- (yield: 51.4%) in the reaction solution. The amount of F^- in the reaction solution further increased as the reaction time increased. After 15 h, the amount of F^- in the reaction solution reached 38.6 μmol, corresponding to a yield of 61.0 %. The continuity of F^- formation after 6 h (at which point all of the PFOS had been removed from the reaction solution) suggested that PFOS remained on the iron surface and F^- was gradually released from the surface to the solution phase.

To elucidate the presence of the fluorine-containing species on the iron surface, we measured XPS spectra for the region corresponding to the binding energy of the F (1s) core electrons. When a mixture of the aqueous solution of PFOS and iron powder was allowed to stand at room temperature for 6 h under an argon atmosphere, the recovered iron powder showed a dominant peak around

Table 1. Decomposition of PFOS in subcritical water with and without metal additives[a]

Entry	Metal additive	Remaining PFOS (μmol) [ratio (%)]	F$^-$ (μmol) [yield (%)] [b]
1	none	3.36 [90.3]	0.10 [0.16]
2	Al	3.48 [93.6]	0.03 [0.05]
3	Cu	3.15 [84.7]	4.29 [6.78]
4	Zn	0.86 [23.1]	11.7 [18.5]
5	Fe	<0.02[c] [<0.54]	32.5 [51.4]

[a] An aqueous solution (10 mL) of PFOS(3.72 μmol) and metal powder (9.60 mmol) was introduced into the reactor under an argon atmosphere and the reactor was heated at 350 ℃ for 6 h. [b] F$^-$ yield = [(moles of F$^-$ formed)/(moles of fluorine content in initial PFOS, i.e., moles of initial PFOS × 17)] ×100. [c] Below the detection limit of HPLC.

689 eV in the XPS spectrum, which can be assigned to fluorine bonded to carbon. Alternatively, the recovered iron powder after the reaction in subcritical water at 350 ℃ for 6 h showed another large peak around 684 eV, which can be assigned to negatively charged monovalent fluorine, F$^-$. Although PFOS was not detected in the reaction solution after the treatment in subcritical water at 350 ℃ for 6 h, the XPS spectrum of the recovered iron powder indicated that the species containing fluorine-carbon bonds still remained on the iron surface. After a prolonged treatment (15 h) in subcritical water, the spectrum of the recovered iron showed the only peak of F$^-$; there was no peak corresponding to the species for fluorine-carbon bonds. Therefore, complete mineralization of PFOS was achieved on the surface during this period.

We measured the ESI mass spectra to elucidate the species in the reaction solutions. Raising the reaction temperature decreased the intensity of the PFOS peak (m/z = 499). While decreasing the intensity of the PFOS peak (corresponding to the decrease in the PFOS concentration in the solution phase), there was no peak with increasing intensity when raising the reaction temperature. Furthermore, when the measurements were conducted in positive ion mode, no significant peak was observed. These facts indicate that the decomposition of PFOS to F$^-$ occurred on the iron surface, with no release of the reaction intermediates from the surface to the solution phase.

Gas-Phase Product
After the treatment of PFOS in subcritical water with iron at 350 ℃ for 6 h, followed by cooling to room temperature, the resulting pressure inside the reactor was 0.47 MPa at 31
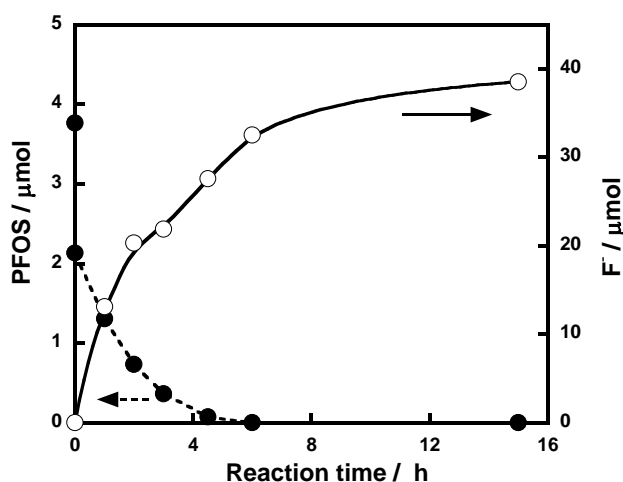

Figure 1. Reaction-time dependence of the amounts of PFOS and F$^-$ in the reaction solution. Iron powder (9.60 mmol) was added to an aqueous solution (10 mL) of PFOS (3.72 μmol), and the mixture was heated at 350 ℃ for 1–15 h. Two dots for PFOS at time 0 correspond to the values obtained before (higher value) and after (lower value) addition of the iron, respectively.

ºC. The higher-than-normal pressure suggested the presence of a gas product. In fact, the GC measurement showed that H_2 comprised 66.2% of the total gas after the reaction, corresponding to 2.99 mmol of H_2. The formation of a large amount of H_2 indicates that the iron reacted not only with PFOS but also with subcritical water (eq 1):

$$3Fe \quad + \quad 4H_2O \quad \rightarrow \quad Fe_3O_4 \quad + \quad 4H_2 \qquad (1)$$

Consistently, the XRD pattern of the recovered iron powder from the reaction mixture showed peaks assigned to Fe_3O_4. Furthermore, the GC/MS measurement indicated that the gas phase after the reaction contained a small amount of CHF_3 (46.5 ppmv, 0.21 μmol) with a yield [i.e., (moles of CHF_3)/(moles of carbon content in initial PFOS) $\times$ 100] of 0.7 %. We have previously reported that trifluoroacetic acid in water was photocatalytically decomposed to F^- by use of a heteropolyacid under an oxygen atmosphere, where a trace amount of CHF_3 was detected instead of the catalytic amount of F^- when the reaction was carried out under an argon atmosphere.[8] Thus, decomposition of perfluorinated compounds under anaerobic conditions is likely to produce a trace amount of CHF_3. Although CHF_3 is not toxic and the detected amount in the present case was much smaller, by a factor of 6.4×10^{-3}, than the amount of F^- in the reaction solution, attention should be given to the formation of species like this that are greenhouse gases. Other fluorine-containing gaseous species, such as CF_4 and C_2F_6, were not detected.

Application to Other Perfluoroalkylsulfonates and an Antireflective Coating Agent
We applied our method to shorter-chain perfluoroalkylsulfonates. In the absence of iron, almost no decomposition of C_2–C_6 perfluoroalkylsulfonates was observed in subcritical water at 350 ºC for 6 h; the remaining ratios of the substrates were 95.2–100%, and a very small amount of F^- formed with yields of <0.001–3.40%. The addition of iron greatly lowered the concentrations of these substrates in the solution phase, resulting in the remaining ratios of 3.61– 4.67% and formation of F^- with yields of 36.1– 62.3%. For PFOS decomposition in the antireflective coating agent solutions, the concentrations of PFOS in the two initial solutions were 55.9 mg L^{-1} (112 μM) and 118.8 mg L^{-1} (238 μM). After treatment in subcritical water at 350 ºC with iron for 6 h, the PFOS concentrations in both reaction solutions were below the HPLC detection limit (1.12 mg L^{-1}). This decomposition of PFOS accompanied formation of F^- with yields of 46.7% and 42.0% based on the fluorine content in the initial PFOS, for the samples of initial concentrations of PFOS of 55.9 mg L^{-1} and 118.8 mg L^{-1}, respectively. Therefore, most of (>98% and >99%) the initial PFOS was effectively removed from the reaction solutions.

References
1. Giesy, J. P. and Kannan, K. *Environ. Sci. Technol*. 2002; 36: 146A–152A.
2. Schultz, M. M., Barofsky, D. F. and Field, J. A.. *Environ. Eng. Sci*. 2003; 20, 487–501.
3. UK Department for Environment, Food and Rural Affairs Perfluorooctane sulfonate. Risk reduction strategy and analysis of advantages and drawbacks. Stage 4 final report. 2004; pp. 41–44.
4. Hori, H., Hayakawa, E., Einaga, H., Kutsuna, S., Koike, K., Ibusuki, T., Kitagawa, H. and Arakawa, R. *Environ. Sci. Technol*. 2004; 38: 6118–6124.
5. Hori, H., Yamamoto, A., Hayakawa, E., Taniyasu, S., Yamashita, N., Kutsuna, S., Kitagawa, H. and Arakawa, R. *Environ. Sci. Technol*. 2005; 39: 2383–2388.
6. Hori, H.; Yamamoto, A.; Kutsuna, S. *Environ. Sci. Technol*. 2005; 39: 7692–7697.
7. Hori, H., Nagaoka, Y., Yamamoto, A., Sano, T., Yamashita, N., Taniyasu, S., Kutsuna, S., Osaka, I. and Arakawa, R. *Environ. Sci. Technol*. 2006; 40: 1049–1054.
8. Hori, H.; Takano, Y.; Koike, K.; Takeuchi, K.; Einaga, H. *Environ. Sci. Technol*. 2003; 37: 418–422.