



Decomposition of environmental pollutants, Decomposition of PFAS

Development of the Hydrodefluorination reaction of perfluoroalkyl substances

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Abstract

The perfluoroalkyl substances are organofluorine compounds having several continuous CF_2 units. The perfluoroalkyl substances are recently recognized as environmental pollutants due to their high thermal and chemical stability. For example, we can frequently find newspaper issues about perfluorooctanoic acid (PFOS) and perfluorooctane sulfonic acid (PFOA). In this work, we developed hydrodefluorination reactions of perfluoroalkyl substances. In the presence of a nickel catalyst, the treatment of perfluoroalkyl arenes with hydrosilanes resulted in the conversion of all C-F bonds into C-H bonds. Our detailed mechanistic studies revealed that fluoroalkene is a key intermediate, and nickel catalyst plays multiple roles in the catalytic cycle.

Background & Results

In recent years, environmental pollution caused by perfluoroalkyl substances (PFAS) has become increasingly serious. When PFAS are released into the environment, they do not decompose and become long-lasting environmental pollutants. Practical methods for the decomposition of perfluoroalkyl substances are still under development.

Our research group has focused on hydrodefluorination reactions. This reaction replaces C-F bonds in organofluorine compounds with C-H bonds, thus converting perfluoroalkyl compounds into harmless hydrocarbons. While there have been numerous reports of defluorination reactions for the trifluoromethyl group (CF_3), there have been few precedents for defluorination of longer perfluoroalkyl chains.

Using a nickel catalyst and potassium phosphate (base), we conducted a reaction of 1-(pentafluoroethyl)naphthalene and hydrosilane. This reaction proceeded at a relatively low temperature of 60 °C, yielding 1-ethylnaphthalene with an 86% yield. In this reaction, the combination of a carbene ligand called ICy with $\text{Ni}(\text{cod})_2$ (cod = 1,5-cyclooctadiene) as a nickel source is essential. When we investigated the reactions of longer 1-heptafluoropropyl and 1-nonafluorobutyl naphthalenes, though higher temperature conditions were required, in both cases, small amounts of the corresponding alkanes were observed. By quantifying the co-produced fluorosilane, roughly half of the fluorine was found to be removed.

A detailed analysis of the reaction mechanism of 1-pentafluoroethyl naphthalene revealed that the reaction progresses through five steps: (1) benzylic hydrodefluorination, (2) HF elimination by the base, (3) hydrodefluorination of the fluoroalkene, (4) hydrosilylation of vinyl naphthalene, and (5) protonation of benzylsilane. The nickel was found to catalyze all of these processes except for the final protonation step.

Significance of the research and Future perspective

Our reaction enables the conversion of perfluoroalkyl substances into hydrocarbons. Generally, hydrocarbon is easy to combust. In addition, the environmental effect of hydrocarbon is negligible due to biological metabolism, which leads to a shorter lifetime than that of perfluoroalkyl substances. Currently, our reaction is applicable only to a specific perfluoroalkyl arenes. Further investigation to

expand the substrate scope and to use a cheaper reductant than hydrosilane is underway to establish an effective disposal method for perfluoroalkyl substances.

Figure 1. Research Background

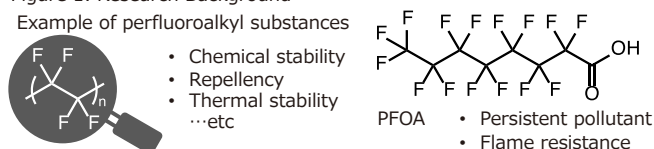
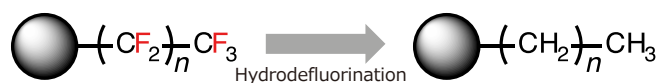
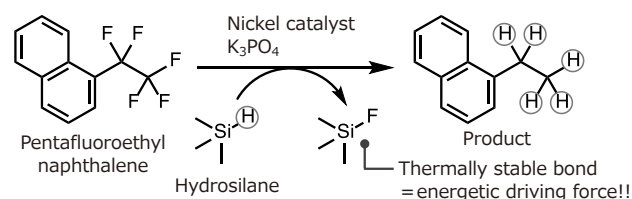
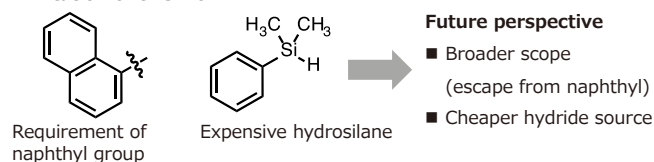


Figure 2. This work: Hydrodefluorination reaction



Perfluoroalkyl substances	Hydrocarbon
■ Thermal & chemical stability	■ Burnable waste
■ Persistent pollutant	■ Short environmental lifetime
■ Bioaccumulation	■ Biological degradation

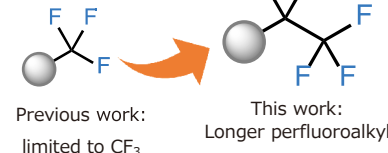
Limitation of this work



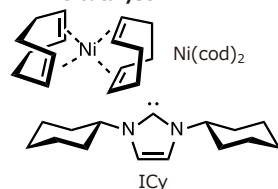
Future perspective

- Broader scope (escape from naphthyl)
- Cheaper hydride source

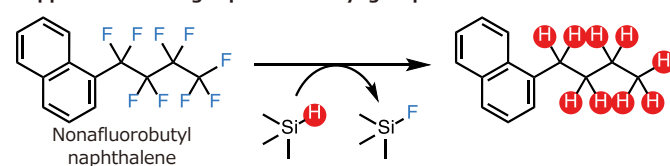
■ Feature of this work



■ The catalyst



■ Application to longer perfluoroalkyl group



Patent

Treatise

URL

Keyword

Doi, Ryohei; Yasuda, Masashi; Kajita, Naoki et al. Nickel-catalyzed exhaustive hydrodefluorination of perfluoroalkyl arenes. *Journal of the American Chemical Society*. 2023, 145 (20), 11449–11456. doi: 10.1021/jacs.3c03471

<http://www.chem.eng.osaka-u.ac.jp/~ogoshi-lab/en/index.html>

fluorine chemistry, nickel, PFAS