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# CATALYTIC OXIDATION OF FLUORINATED AROMATIC COMPOUNDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF μ-NITRIDODIMERIC IRON PHTHALOCYANINATE

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*It has been shown that μ-nitrido(bis) iron phthalocyaninate is an effective catalyst for the oxidation of fluoroaromatic compounds with hydrogen peroxide, including such difficult to oxidized substrates as hexafluorobenzene and pentafluoropyridine. The main fluoride containing product is inorganic fluoride. It has been found that this catalyst, when supported on a graphite, exhibits high stability and can be used after simple regeneration.*

## Introduction

The catalytic oxidation of halogen-containing aromatic compounds is a very urgent task by several reasons:

1. These compounds are poorly undergoing to biodegradation and are toxic for the micro-organisms used in wastewater treatment.
2. Halogen-containing compounds used in industry, such as trichlorophenol, can turn into extremely toxic dioxins under proper conditions, e.g., in alkaline medium.
3. There is a rapidly growth of fluoroaromatic compounds use worldwide. For example, production increased more the three times, from 10,000 tons per year in 1994 to 35,000 tons per year in 2000 [1].

The first paper showed that iron (III) phthalocyanates are effective catalysts for the oxidation of trichlorophenol was published in Science Magazine in 1995 [2]. Since the field has developed extensively [3, 4]. However, this approach was ineffective for fluoroaromatic compounds due to the significantly stronger C-F bond compared to C-Cl, and it was not until 2014 that the first patent for catalytic defluorination of fluoroaromatic compounds was granted. μ-nitridodimeric iron complexes with tetrapyrrole macroheterocycles have been proposed as catalysts [5]. This reaction was later investigated in more detail in terms of its mechanism [6]. It should be mentioned the synthetically difficult and expensive octa(*tret*-butyl)-(III,IV) ($(FePctBu_4)_2N$) was used in reaction as a catalyst [6].

Iron(III) phthalocyanate (PsFe) is commercially available, is inexpensive and is also more stable and easier to purify than its *tert*-butyl derivative. Its μ-nitridodimer complex can be obtained in one step, for example, by the method described in [7].

Due to above, the aim of this paper was to study the catalytic activity of μ-nitride dimer iron phthalocyanate complex ($(FePc)_2N$) and to create an active and stable heterogeneous catalyst based on it.

**Study**

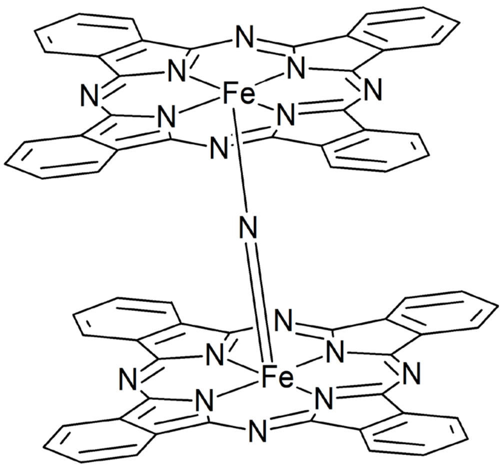

Fig. 1. Structural formula $(PcFe)_2N$

All reagents were obtained from Aldrich company and used without further purification. $(PcFe)_2N$ (Fig. 1) was obtained and purified according to the method described in [7]. $^{19}F$ PMR spectra were measured on a Brucker AMD 200 ($^{19}F$ operating frequency 235 MHz). Quantification of the reaction mixtures was carried out as follows: Hexafluoroisopropanol (solution in $CD_3CN$), (sealed capillary with $d$ = 3 mm and $L_{solution}$ = 54 mm) was used as external standard. The standard was placed in a PMR ampoule. The analyzed reaction mass was added in immediately before the measurement. The height of the liquid layer in the ampoule was 54 mm in all cases. The system was pre-calibrated using KF as standards for $D_2O$ and hexafluorobenzene for $CD_3CN$. The integrated intensities linearly depend on concentrations of organic and inorganic fluorine for both cases. To validate the results, fluoride ion concentrations were also determined spectrophotometrically after dilution of reaction masses by deionized water, using the method described in [8]. All catalytic experiments were conducted at 60 °C in glass or teflon reactors.

Preparation of heterogeneous catalyst. The inert carrying agent was the graphite HSAG 300 with a specific surface of 300 $m^2/g$ (Lidl, Switzerland). The inert carrying agent and a calculated amount of catalyst (final concentration 12 μM/g) and dichloromethane (200 ml per 2 g of carrying agent) were added to the round-bottomed flask. The obtained mixture was held in intensive mixing for 6 hours, the solvent was removed and the catalyst was dryed in vacuum at 60 °C. If reused, the catalyst was filtered, deionized with water and dried at 120 °C. A heterogeneous catalyst using $SiO_2$ as a carrying agent was obtained by the method described in the patent [5].

At the first phase of our work, we investigated the catalytic activity $(PcFe)_2N$ as a homogeneous catalyst in the oxidation reaction of fluoranyl. The reaction was performed in $CD_3CN$ in the presence of a fourfold excess hydrogen peroxide. Fig. 2 shows the $^{19}F$ PMR spectrum of fluoranyl. According to the data provided, only one singlet at -145 m.d., corresponding to four equivalent substrate fluorine atoms has been detected in the spectrum.

The oxidation reaction was initiated by adding a four-fold excess of hydrogen peroxide (30% solution in water) and a catalyst. Fig. 3 shows the $^{19}F$ PMR spectrum of reaction mass. A quantitative spectrum analysis showed the substrate had been converted to 70 per cent, with inorganic fluorine at 0.034 M.

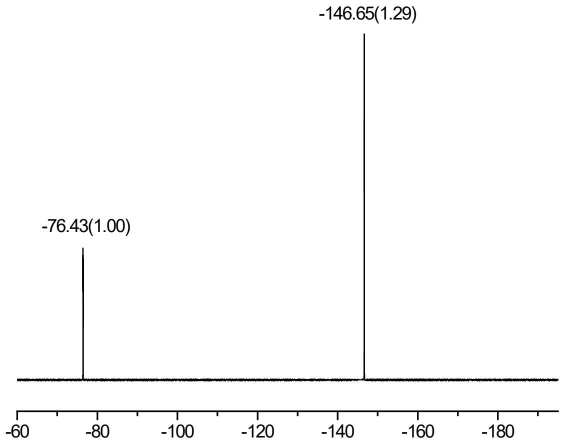

**Fig. 2.** $^{19}F$ PMR spectrum of fluoranyl. Test conditions: Fluoranyl is 0.1M in $CD_3CN$. External Standard for hexafluoridepropanol (-76.43 m.d.)

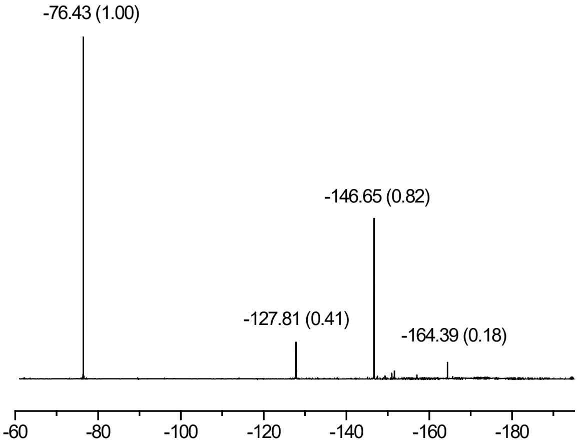

**Fig. 3.** $^{19}F$ PMR spectrum of reaction mass. Test conditions: Fluoranyl i (0.1M) in $CD_3CN$, 0.4 $MH_2O_2$, catalyst ($2 \cdot 10^{-4}$ M). 54% mineralization, based on the reaction substrate. $[F^-] = 0.038M$

Although the catalyst has been effective for homogeneous oxidation of fluoranyl, from a practical point of view this process is not promising for two reasons. Firstly, the catalyst cannot be regenerated and reused. And secondly, there is a side oxidation of the solvent under the process conditions [9]. According to the above, we studied the catalytic activity of $(PcFe)_2N$ deposited on silicon dioxide, which acted as both catalyst and trap for hydrogen fluoride in order to exclude its transfer to the gas phase, which would have made the quantitative analysis difficult. The reactions were carried out in deuterated water.

Fig. 4 shows the $^{19}F$ PMR spectrum of reaction mass before and after the oxidation reaction of pentafluorophenol.

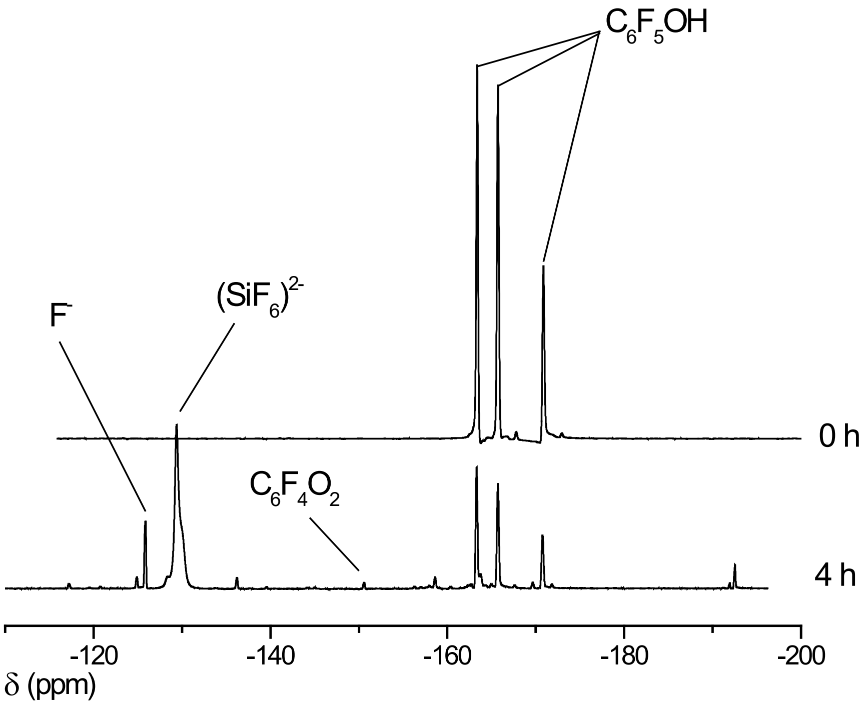

**Fig. 4.** $^{19}F$ PMR spectrum of reaction mass before and after the oxidation reaction. Test conditions: heterogeneous catalyst (10 μM/g, $SiO_2$) – 36 mg, $D_2O$ 2 ml, $C_6F_6OH$ 0.2M, $[H_2O_2] = 0.8M$, 60 ºC. Conversion 87% 93% mineralization per responsive substrate ($F^-$ and $SiF_6^{2-}$)

Hexafluorobenzene is one of the most difficult-to-oxidize compounds in organic chemistry. In addition, organofluorocarbons are often found in low concentrations in wastewater, so we have studied the applicability of $(PcFe)_2N$ as a catalyst for its oxidation in aqueous solution at low substrate concentrations. Fig. 5 shows the $^{19}F$ PMR spectrum of reaction mass produced after the oxidation of hexafluorobenzene.

As known, the one of the intractable problems encountered by researchers working in the field of metal-composite catalysis is the fact that many substrates, as well as reaction products, tend to coordinate on active catalyst centers. This way, they can act as catalytic poisons, blocking the reaction center of the catalyst. In this case $(PcFe)_2N$ contains two iron cations in the low-spin state with a formal oxidation state of +3.5 and a coordination number of 5, and therefore its reaction centers can be deactivated neither by the substrate nor by the reaction products. This hypothesis was confirmed experimentally by using pentafluoropyridine as a substrate (Fig. 6). In addition, sulphuric acid was used as a co-catalyst, as its addition has previously been shown to increase the catalytic activity and stability of this type of catalyst [10].

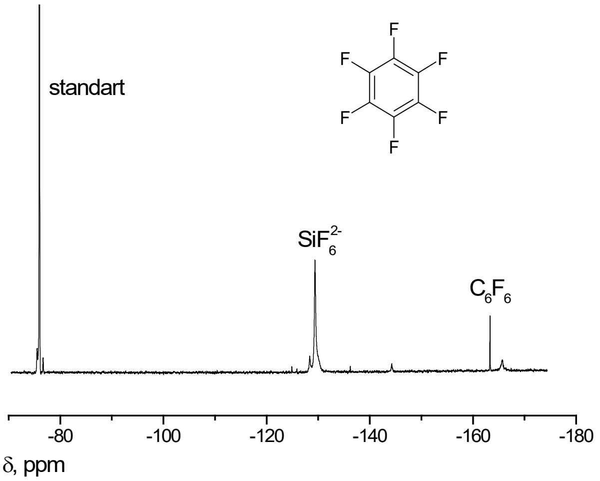

**Fig. 5.** $^{19}F$ PMR spectrum of reaction mass after oxidation reaction. Test conditions: $[C_6F_6] = 0.009M$ (2 ml saturated solution in $D_2O$). $[H_2SO_4] = 0.1M$, catalyst (10 μM/g, $SiO_2$) 30 mg, $[H_2O_2] = 0.4M$, 60 °C, 14 hours. Conversion 94%, mineralisation 82%

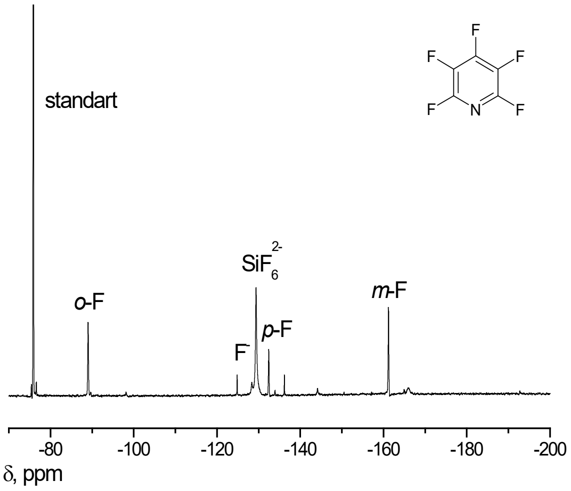

**Fig. 6.** $^{19}F$ PMR spectrum of reaction mass after oxidation reaction. Test conditions: $[C_6F_5N] = 0.05M$ (2 ml saturated solution in $D_2O$). $[H_2SO_4] = 0.1M$, catalyst (10 μM/g, $SiO_2$) 30 mg, $[H_2O_2] = 0.4M$, 60 °C, 14 hours. Conversion 46%, [inorganic F] = 0.055M

Thus, the synthetically available and inexpensive catalyst $(PcFe)_2N$ has been shown to be effective also in the oxidation of difficult to oxidize substrates such as hexafluorobenzene and the more inert pentafluoropyridine.

However, the use of a catalyst deposited on silicon oxide does not seem to be feasible from a practical point of view. Silicon dioxide is known to react with the resulting hydrogen fluoride, making it impossible to reuse. Therefore, we prepared a heterogeneous catalyst where graphite acts as a carrying agent. The catalyst withstands at least three cycles and can be easily regenerated (Fig. 7, Table 1), which was confirmed experimentally by the oxidation of pentafluorophenol. Of course, mechanical losses are inevitable when regenerating such small quantities of catalyst, so in Table 1 we also give the masses of catalyst used for the experiment. The reaction was carried out in a sealed teflon reactor with a volume of 5 ml.

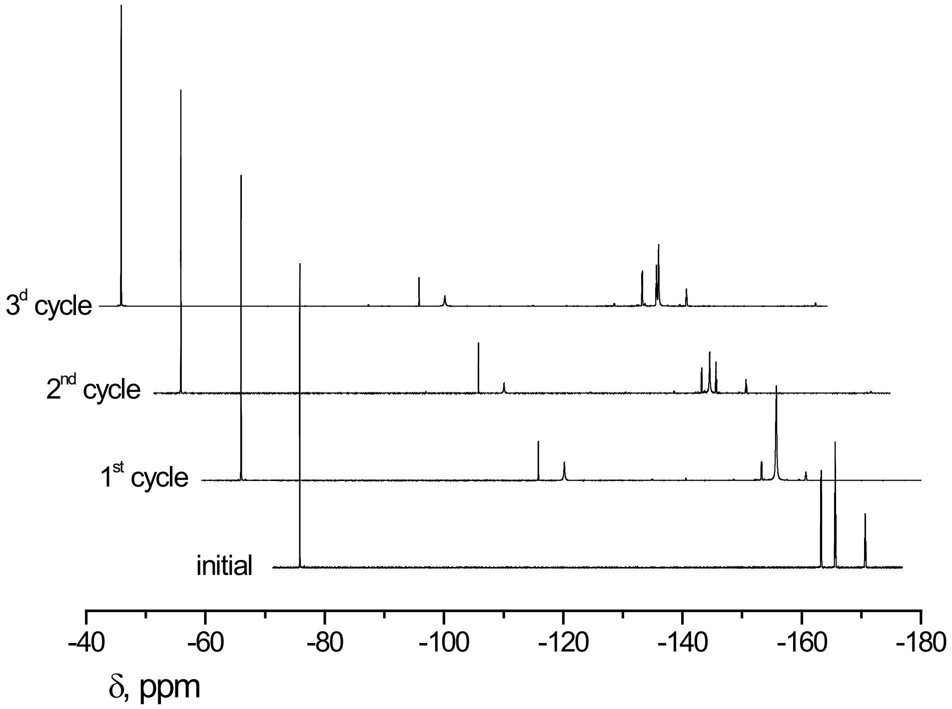

**Fig. 7.** $^{19}F$ PMR spectrum of reaction mass after oxidation reaction and reuse of catalyst. Test conditions: $[C_6F_5OH]$ 0.1M, $[H_2SO_4]$ 0.1 M, $[H_2O_2] = 0.8M$, [Catalyst 12 μM/g] = 20 mg, $D_2O$ 1 ml, 60 °C, 14 hours

**Table 1.** Results of the catalyst reuse experiment

| | Conversion, % | Concentration, mol/l | | | Mass catalyst, mg |
|---|---|---|---|---|---|
| | | $F^-$ | Difluoromaleic acid | HF | |
| Cycle 1 | 84 | 0.034 | 0.032 | 0.405 | 20 |
| Cycle 2 | 76 | 0.021 | 0.027 | 0.248 | 14 |
| Cycle 3 | 68 | 0.017 | 0.024 | 0.170 | 11 |

## Conclusions and recommendations

Synthetically easily available and inexpensive $(PcFe)_2N$ is an efficient catalyst in oxidation reactions of fluoroaromatic compounds, including such hard-to-oxidize compounds as hexafluorobenzene and pentafluoropyridine. This produces inorganic fluorine compounds as the main product of the reaction. Thus, the first reusable catalyst with high catalytic activity and good stability has been developed. The investigation of other halogen-containing compounds in the above reaction, such as the widely used chlorinated hydrocarbons of the aliphatic and aromatic series, could be the further development of the study.

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