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### Rhodium-catalyzed Electrochemical Hydrodefluorination: A Mild

### **Approach for the Degradation of Fluoroaromatic Pollutants**

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**ABSTRACT:** Many fluoroorganic compounds are toxic and persistent, and achieving their efficient degradation under mild conditions is currently a challenge. Herein, we developed a new electrochemical hydrodefluorination (HDF) system based on rhodium electrocatalyst for the degradation of fluoroaromatic (FA) pollutants. The HDF system realized the rapid degradation of 18 representative FAs to form nonfluorinated organics and  $F^-$  under mild conditions (room temperature and pressure, water medium, air atmosphere, without the use of hazardous reagents). This study may provide a new promising alternative for the practical treatment of waste water containing FA pollutants.

**Keywords:** Electrocatalytic Hydrodefluorination; Fluoroaromatic Pollutants; Rhodium; Ni foam; 4-Fluorophenol

#### 1. Introduction

Fluoroorganic compounds (FOCs) are becoming widespread environmental pollutants because of their wide and increasing applications [1-12]. Many of these compounds are particularly persistent in the environment [4-6]; they are strongly resistant to traditional biological degradation [7,8] and conventional chemical processes [9,10] because of the inertness of C–F bond. The compounds gradually accumulate in the environment, achieving concentrations that are hazardous to living organisms [11,12].

Hydrodefluorination (HDF) is one of the most facile approaches to dispose of FOC pollutants [4]. The process simply transforms the C–F bond of FOCs to C–H, which could then dramatically increase the compounds' biodegradability. Numerous efficient HDF methods have been developed for FOCs degradation. Among these approaches are the Lewis acid mediated [13,14], homogeneous [15-17] or heterogeneous [18,19] transition metal-catalyzed, and photo-reductive [20-22] HDF processes. Unfortunately, these HDF methods require harsh reaction conditions such as high temperature [15], high pressure [16], inert atmosphere [20-22], or using toxic organic solvents, such as the explosive hydrogen gas [18,19] and toxic organic solvents [13,14,17]. The persistent need for these conditions hinders wide practical application of the aforementioned HDF methods. Compared with the above-mentioned HDF methods, electrochemical HDF is intrinsically milder and more likely to be operated under mild condition. So far, only few electrochemical HDF cases have been reported and these HDF examples do not remove the use of high pressure [23] or toxic organic solvents [24]. Therefore, the development of HDF systems under mild conditions would be a significant achievement to address emerging environmental problems from the increasing use of FOCs and their persistence in the environment.

In this communication, we presented a mild and robust electrochemical HDF system for the degradation of fluroaromatic (FA) pollutants. To the best of our knowledge, this paper is the first to report an electrochemical HDF system that degrades FAs to form nonfluorinated organics and  $F^-$  under room temperature and pressure without resorting to the use of toxic organic solvents and inert gases.

#### 2. Material and methods

All FAs and their HDF products with purities of 98%–99%, as well as RhCl<sub>3</sub> hydrate (99.5%), were acquired from Aladdin Reagent Co., China. Ni foams (1.0 mm thickness), Cu foams (1.0 mm thickness), Ag mesh (open area 37%), and carbon felt (2.0 mm thickness) were obtained from Cells Electrochemistry Co., Ltd., China (www.hzcell.com). Rh-modified nickel (Rh/Ni) foam, silver (Rh/Ag) mesh, and copper (Rh/Cu) foam, were prepared by a metallic replacement reaction (exposing to a 30 mL aqueous solution containing 1 M NaCl and 1.5 mM RhCl<sub>3</sub> at pH 2 adjusted using HCl until the rose color of the RhCl<sub>3</sub> solution disappeared). Rh-modified carbon felt (Rh/Carbon felt) was prepared by electrodeposition (using constant current of 2 mA in the same RhCl<sub>3</sub> solution until the rose color disappeared). The abovementioned four Rh-modified materials

have same Rh loading of 0.77 mg/cm<sup>2</sup> (projected area), unless otherwise noted. The Rh/Ni foam exhibited the highest HDF activity among the four Rh-modified materials. Hence, its surface morphology and composition, as well as the Rh<sup>n+</sup>/Rh<sup>0</sup> ratio value of surface Rh were determined by SEM (Hitachi S-4700 II) equipped with EDS (Thermo NOANVANTAGE ESI) and XPS (KRATOS AXIS ULTRA DLD), respectively. As shown in Fig. 1, a uniform Rh film formed on the surface of Ni foam. It implies that the above-mentioned metallic replacement reaction is applicable to the preparation of Rh/Ni foam.

A conventional two compartment glass or PTFE H-cell separated by a Nafion-117 membrane was used for electrochemical HDF experiments. The cathode was fabricated from a piece of Rh/Ni foam, Rh/Ag mesh, Rh/Cu foam, or Rh/carbon felt (projected area:  $2 \times 3 \text{ cm}^2$ ), whereas the anode was fashioned from a graphite sheet ( $2 \times 3 \text{ cm}^2$ ). 30 mL phosphate buffer solutions (20 mM) served as both the catholyte and the anolyte. Unless otherwise noted, the catholyte was stirred with a stirring velocity of 350 rpm during electrolysis. The concentrations of reactants and their products were determined by an Agilent 7890A gas chromatograph (GC) and a Waters HPLC system, using standard calibration curves. The fluoride ion ( $F^-$ ) concentration was determined by a REX PHSJ-4F pH/mV meter combined with  $F^-$  selective electrode (REX PF-202-C).

The specific electric energy consumption (*SEEC*,  $kW \cdot h \cdot m^{-3}$  catholyte) of the HDF process was calculated from the following equation:

$$SEEC = \frac{I \times U \times t}{1000 \times V}$$

where *I* is the applied current (A), *U* is the average cell voltage (3 V), *t* is HDF time (h), *V* is the volume of the catholyte  $(3 \times 10^{-5} \text{ m}^3)$ .

Unless otherwise noted, all above-mentioned experiments were performed under air atmosphere, at 25  $^{\circ}$ C.

#### 3. Results and discussion

#### **3.1 Optimization of HDF conditions**

The electrocatalyst and its support, as well as the catholyte pH used usually determine the reaction efficiency of electrochemical hydrodechlorinations [25-28]. Thus, these parameters of the presented HDF system were optimized primarily with 4-fluorophenol (4-FP) as the target compound. We first examined the pH effects, of which the results are listed in Table 1 (entries 1–3). At pH values of approximately 11 and 7, the HDF efficiencies were discouraging over a Rh/Ni foam cathode (Rh as the electrocatalyst and Ni foam as the support), whereas the HDF efficiency was inspiring at a pH of approximately 3 (4-FP was completely converted, and near 100%  $F^-$  yield was achieved). We then examined the effects of the electrocatalyst and its cathode support. After screening different types of electrocatalysts (entries 3–7), such as Rh, Pt, Ir, Ru, and Pd, we determined that Pt exhibited the best performance as an HDF electrocatalyst besides Rh. Cathode

support screening revealed that Ni foam provided a much higher yield of  $F^-$  compared with Cu foam, Ag mesh, and carbon felt (entries 3, 8–10). The higher HDF performance of the Rh/Ni foam probably was due to its small Rh<sup>n+</sup>/Rh<sup>0</sup> ratio value of 0.66 [29]. Aside from the above-mentioned three parameters, we also found that the HDF system is immune to air and the glass of the cell (entries 11–13) and that 4-FP at two higher concentrations degraded rapidly with 100% conversion and high  $F^-$  yield (entries 14 and 15).

#### 3.2 Degradation pathway of 4-fluorophenol and rate-limiting step

With the optimal HDF conditions in hand (water of pH 2.7-3.2 as the catholyte, Rh/Ni foam as the cathode), we evaluated the degradation pathway of 4-FP. 4-FP was reduced linearly to cyclohexanone (CYC.one) and cyclohexanol (CYC.ol) as the main organic products (Fig. 2A) with a pseudo-first-order rate constant ( $k_{obs}$ ) of 0.00057 s<sup>-1</sup> (entry 3, Table 2). The concentration of CYC.one increased up to approximately 3 mM and then remained almost constant with prolonged degradation time. These results imply a shift in the formation pathway of CYC.ol during the degradation process of 4-FP. Direct reduction of 4-FP to CYC.ol was the main pathway during the earlier stage of degradation process, whereas the main pathway was the two-step consecutive reductions (from 4-FP to desorbed CYC.one and then to CYC.ol) during the later stage of degradation process [30]. Additionally, very low phenol (PhOH) concentrations were found with a maximum concentration of 0.4 mM in the degradation process (Fig. 2B). This result indicates PhOH also was a potentially intermediate product of the degradation process. To confirm these theories, we performed separate experiments using CYC.one or PhOH as the starting material under identical conditions (Fig. 2C and 2D). We then observed the quantitative reduction of PhOH to CYC.one ( $k_{obs} = 0.00070 \text{ s}^{-1}$ , entry 2 in Table 2) and of CYC.one to CYC.ol ( $k_{obs} = 0.00028 \text{ s}^{-1}$ , entry 1 in Table 2). The above-mentioned results suggest that the main degradation process of 4-FP followed the pathway of 4-FP $\rightarrow$  PhOH $\rightarrow$  CYC.one $\rightarrow$  CYC.ol, and the reductive activity of former three compounds decreased in the follow order: PhOH > 4-FP > CYC.one. The ecotoxicity of CYC.ol is much lower than those of PhOH and CYC.one [31]. Therefore, the optimized HDF system is a promising candidate for the disposal of wastewater containing 4-FP.

Moreover, the rate-limiting step in the degradation process of 4-FP was preliminarily elucidated (Table 2). Almost same  $k_{obs}$  were gained at the stirring velocities of 350 and 500 rpm (entries 4 and 5), meanwhile the  $k_{obs}$  was proportional to the Rh loading from 0.77 to 1.54 mg/cm<sup>2</sup> (entries 5 and 6). These results strongly suggest that the degradation process was kinetically limited by a surface reaction step rather than by a diffusion step of 4-FP from bulk catholyte to the cathode surface.

#### 3.3 Degradation mechanism

On the basis of the aforementioned reaction pathway and the well-reported electrochemical hydrodechlorination mechanism over Pt group metal-modified cathodes [32-34], we proposed the degradation mechanism of FAs in the presented HDF system as described by Eqs. (1)–(6) R-F + Rh  $\leftrightarrow$  (R-F)<sub>ads</sub>Rh (1)

$$\begin{array}{ll} 2(n+1) H^{+} + 2(n+1) e^{-} + Rh \leftrightarrow 2(n+1) H_{ads}Rh & (2) \\ (R-F)_{ads}Rh + 2 H_{ads}Rh \rightarrow (R-H)_{ads}Rh + HF + Rh & (3) \\ (R-H)_{ads}Rh \leftrightarrow R-H + Rh (slow) & (4) \\ (R-H)_{ads}Rh + 2n H_{ads}Rh \rightarrow (R'H_{(2n+1)})_{ads}Rh (fast) & (5) \\ (R'H_{(2n+1)})_{ads}Rh \leftrightarrow R'H_{(2n+1)} + Rh & (6) \end{array}$$

First, adsorbed FAs are formed on Rh [Eq. (1)] that competes with the generation of chemisorbed hydrogen [Eq. (2)]. Hydrogenolysis of FAs then proceeds as in catalytic hydrogenation [Eq. (3)] by the reaction of the adsorbed FAs with chemisorbed hydrogen, followed by the slow desorption and further rapid hydrogenation of the product [Eqs. (4) and (5)]. Finally, the hydrogenated products desorb from Rh [Eq. (6)]. This reaction mechanism is analogous to the HDF and hydrogenation mechanism of fluorobenzene (using H<sub>2</sub>) over Rh/Al<sub>2</sub>O<sub>3</sub> catalyst supposed by McNeill' group [30]. The main difference between these two mechanisms is the source of hydrogen which reacts with the adsorbed FAs. The hydrogen comes from the electroreduction of H<sup>+</sup> or H<sub>2</sub>O in the electrochemical mechanism, while it originates from the dissociative adsorption of H<sub>2</sub> in the catalytic mechanism. This is why the electrochemical HDF system can avoid the using of H<sub>2</sub>, which is hazardous when it is in use or in transit.

#### 3.4 Scope and practicability of HDF system

At last, we evaluated the scope and practicability of the optimized electrochemical HDF system. With sufficient passed charge, 100% conversion and  $F^-$  yield were achieved for all selected 18 representative FAs (Table 3). The apparent HDF rate of the 18 FAs under the optimized conditions decreased in the following order: fluoropyridine > fluorophenol  $\approx$  fluoroaniline  $\approx$  fluoroanisole  $\approx$  fluorotoluene  $\approx$  fluorotoluene > fluorobenzoic acid > fluorobenzoitrile. The *SEEC* of the electrochemical HDF system would be very low (0.078–0.936 kWh/m<sup>3</sup> waste water) if the waste water contained a low concentration of FA pollutants (120  $\mu$ M).

#### 4. Conclusions

In summary, an efficient electrochemical HDF system (water of pH = 2.7-3.2 as the catholyte, Rh/Ni foam as the cathode) was developed for the first time. This goal was achieved by optimizing the catholyte pH ( $2.7\sim11.1$ ), the electrocatalyst used (Rh, Pt, Ir, Ru, and Pd), and its cathode support (Ni foam, Cu foam, Ag mesh, and carbon felt). The HDF system realized the rapid degradation of 18 representative FAs under extremely mild conditions (room temperature and pressure, water medium, air atmosphere, without the use of hazardous reagents). The apparent HDF rate of the 18 FAs in the HDF system decreased in the following order: fluoropyridine > fluorophenol  $\approx$  fluoroaniline  $\approx$  fluoroanisole  $\approx$  fluorotoluene  $\approx$  fluorotoluene > fluorobenzoic acid > fluorobenzonitrile. In addition, the main degradation path of 4-FP in the HDF system was demonstrated as following: 4-FP  $\rightarrow$  PhOH  $\rightarrow$  CYC.one  $\rightarrow$  CYC.ol. Moreover, a reaction mechanism was proposed for the degradation process, in which the catalytic hydrogenation

between adsorbed FAs and chemisorbed hydrogen on rhodium is the key step. This study may provide a new promising alternative for the practical treatment of waste water containing FA pollutants. It should be point out that the electrochemical HDF system developed here is inefficient for the HDF of saturated FOCs, which are also an important class of pollutants.

#### **Conflict of interest**

There is no conflict of interest among authors for this paper.

#### Acknowledgement

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### **Figure caption**

Fig. 1 SEM and EDS of the Ni foam and Rh/Ni foam.

**Fig. 2** Concentration profiles of 4-fluorophenal (4-FP) and its products (PhOH, phenol; CYC.one, cyclohexanone; CYC.ol, cyclohexanol;  $F^-$ ) during electrochemical HDF and hydrogenation at 25°C. Catholyte: 30 mL of a 20 mM phosphate buffer aqueous solution of pH 2.7–3.2 containing 12 mM (mmol·L<sup>-1</sup>) reactants; cathode: Rh/Ni foam (2×3 cm<sup>2</sup>); applied current: 52 mA. (A) 12 mM 4-FP; (B) Partial enlarged drawing of (A); (C) 12 mM PhOH; (D) 12 mM CYC.one.







Fig. 2

### **Graphical abstract**



Entry	Cathodes	pH	Conv. (%)	Yield of $F^-$ (%)
1	Rh/Ni foam	10.8-11.1	5	3
2	Rh/Ni foam	6.8-7.2	6	4
3	Rh/Ni foam	2.7-3.2	100	98
4	Pt/Ni foam	2.7-3.2	58	56
5	Ir/Ni foam	2.7-3.2	17	13
6	Ru/Ni foam	2.7-3.2	10	4
7	Pd/Ni foam	2.7-3.2	4	2
8	Rh/Cu foam	2.7-3.2	7	4
9	Rh/Ag mesh	2.7-3.2	14	5
10	Rh/Carbon felt	2.7-3.2	4	3
11 <sup>[b]</sup>	Rh/Ni foam	2.7-3.2	54	51
12 <sup>[c]</sup>	Rh/Ni foam	2.7-3.2	52	50
13 <sup>[d]</sup>	Rh/Ni foam	2.7-3.2	54	51
14 <sup>[e]</sup>	Rh/Ni foam	2.7-3.2	100	98
15 <sup>[f]</sup>	Rh/Ni foam	2.7-3.2	100	103

Table 1 Optimization of the electrocatalytic HDF system with 4-fluorophenol (4-FP) as the target	get
compound. <sup>[a]</sup>	

[a] Unless otherwise noted, 30 mL of a 20 mM phosphate buffer aqueous solution containing 120  $\mu$ M ( $\mu$ mol·L<sup>-1</sup>) 4-FP served as the catholyte, the applied current for 90 min was 0.52 mA (i.e., 0.52 mA/90 min, charge passed was 8 F: 8 mol of electrons per mol 4-FP), area of the cathode used was 2×3 cm<sup>2</sup> and a glass cell was used. [b] 0.52 mA/22.5 min. [c] Air free (N<sub>2</sub>), 0.52 mA/22.5 min. [d] 0.52 mA/22.5 min, using a PTFE cell. [e] 1.2 mM 4-FP, 5.2 mA/90 min. [f] 12 mM 4-FP, 52 mA/90 min.

Entry	Reactants	Reaction conditions	$k_{obs}(s^{-1})$	$\mathbf{R}^2$
1	CYC.one	12 mM reactant, 52 mA/90 min	0.00028	0.98
2	PhOH	12 mM reactant, 52 mA/90 min	0.00070	0.84
3	4-FP	12 mM reactant, 52 mA/90 min	0.00057	0.92
4	4-FP	500 rpm, Rh loading:0.77 mg/cm <sup>2</sup> , 0.52 mA/90 min	0.0010	0.97
5	4-FP	350 rpm, Rh loading:0.77 mg/cm <sup>2</sup> , 0.52 mA/90 min	0.0012	0.93
6	4-FP	350 rpm, Rh loading:1.54 mg/cm <sup>2</sup> , 1.04 mA/90 min	0.0023	0.91

**Table 2** Pseudo-first-order rate constants ( $k_{obs}$ ) for the reduction of cyclohexanone (CYC.one), phenol (PhOH), and 4-fluorophenol (4-FP).<sup>[a]</sup>

[a] Unless otherwise noted, catholyte: 30 mL of a 20 mM phosphate buffer aqueous solution at pH = 2.7-3.2 containing 120  $\mu$ M reactants, stirring velocity: 350 rpm, cathode: Rh/Ni foam ( $2\times3$  cm<sup>2</sup>) with Rh loading of 0.77 mg/cm<sup>2</sup>, the applied current for 90 min was 0.52 mA (i.e., 0.52 mA/90 min).

				-		
Entry	HDF time	Reactants	Final product yield (%) <sup>[b]</sup>			
	(h)					
1	1.5	2-fluorophenol	PhOH (0)	CYC.one (40	))	CYC.ol (57)
2	1.5	3-fluorophenol	PhOH (0)	CYC.one (33	3)	CYC.ol (66)
3	1.5	4-fluorophenol	PhOH (0)	CYC.one (40	))	CYC.ol (57)
4	3	2,4-difluorophenol	PhOH (1)	CYC.one (39	<del>)</del> )	CYC.ol (60)
5	7.5	pentafluorophenol	PhOH (0)	CYC.one (42	2)	CYC.ol (56)
6	1.5	4-fluoroaniline	aniline (0)	CYC.one (78	3)	CYC.ol (22)
7	7.5	pentafluoroaniline	aniline (0)	CYC.one (77	7)	CYC.ol (22)
8	1.5	4-fluoroanisole	anisole (0)	CYC.one (4	)	methoxycyclohexane (94)
9	1.5	4-fluorotoluene	toluene (17)		methylcyclohexane (83)	
10	7.5	pentafluorotoluene	toluene (9)		methylcyclohexane (91)	
11	1.5	monofluorobenzene	benzene (26)		cyclohexane (73)	
12	9	hexafluorobenzene	benzene (12)		cyclohexane (87)	
13	4.5	4-fluorobenzoic acid	Cyclohexanecarbox		ylic acid (100)	
14	15	pentafluorobenzoic acid	Cyclohexanecarbox		ylic acid (100)	
15	1.5	2-fluoropyridine	pyridine (13)		piperidine (87)	
16	7.5	pentafluoropyridine	pyridine (0)		piperidine (100)	
17	6	4-fluorobenzonitrile	cyclohexanemethylamine (35)		cyclohexanemethanol (63)	
18	18	pentafluorobenzonitrile	cyclohexaner	methylamine	(33)	cyclohexanemethanol (65)

### Table 3 Scope and practicability of the electrochemical HDF system.<sup>[a]</sup>

[a] Catholyte: 30 mL of a 20 mM phosphate buffer aqueous solution at pH = 2.7-3.2 containing 120  $\mu$ M reactants, cathode: Rh/Ni foam ( $2\times3$  cm<sup>2</sup>), applied current: 0.52 mA. [b] PhOH, phenol; CYC.one, cyclohexanone; CYC.ol, cyclohexanol.

### Highlights

> We developed a new Rh-catalyzed electrochemical hydrodefluorination (HDF) system.

> Cathode material and solution pH were optimized with 4-fluorophenol as the substrate.

> The HDF system realized the rapid degradation of 18 fluoroaromatics (FAs).

> This study provides a new promising alternative for the treatment of FA pollutants.

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