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PII: S0013-4686(18)30506-1

DOI: 10.1016/j.electacta.2018.03.018

Reference: EA 31384

To appear in: Electrochimica Acta

Received Date: 13 December 2017

Revised Date: 12 February 2018

Accepted Date: 3 March 2018

Please cite this article as: Y. Xu, T. Ge, H. Ma, X. Ding, X. Zhang, Q. Liu, Rh-Pd-alloy catalyzed electrochemical hydrodefluorination of 4-fluorophenol in aqueous solutions, *Electrochimica Acta* (2018), doi: 10.1016/j.electacta.2018.03.018.

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# **Rh-Pd-alloy catalyzed electrochemical hydrodefluorination of**

# 4-fluorophenol in aqueous solutions

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## ABSTRACT

Hydrodefluorination (HDF) is the key step in fluoroaromatic pollutant (FAP) degradation, making the search for efficient HDF catalysts and the determination of the corresponding mechanism a matter of great importance. In this study, we developed an efficient HDF catalyst (a Rh-Pd alloy) and investigated the underlying catalytic reaction mechanism, using 4-fluorophenol (4-FP) as a model FAP. Specifically, the rapid aqueous-phase HDF of 4-FP at pH 3 was achieved on a Rh-Pd alloy-modified Ni foam electrode, which was followed by ring hydrogenation (RH) of the HDF product (phenol) to afford cyclohexanone and cyclohexanol. Inductively coupled plasma optical emission spectrometer (ICP-OES) and thermodynamic analyses showed that, in addition to those supplied by the applied current, the electrons involved in the HDF of 4-FP and the RH of phenol were largely provided by the oxidative dissolution of the Ni foam support. Hydrogenation and cyclic voltammetry experiments indicated that the HDF of 4-FP probably follows an indirect mechanism (featuring adsorbed H atoms as the direct reductant) and that the strength of 4-FP adsorption onto the surface of the catalyst significantly influences its HDF activity.

**Key words:** Hydrodefluorination; Rh-Pd alloy; Oxidative dissolution of Ni; 4-Fluorophenol; Ring hydrogenation

#### 1. Introduction

Fluoroaromatics (FAs) are important fine chemical intermediates widely used to prepare pesticides [1], pharmaceuticals [2,3], liquid crystals [4], etc., as exemplified by the use of 2-fluorophenol, 3,5-difluroaniline, 2,6-difluorobenzonitrile, 4-fluorophenol, 2,3,5,6-tetrafluorobenzyl alcohol, and 2,3,5,6-tetrafluoro-4-methylbenzyl alcohol for commercial pesticide production [1]. From 2003 to 2011, 25 new pharmaceutical products containing FA intermediates or FA fragments were marketed globally, which accounted for 16.2% of all pharmaceutical products marketed during this period [2,3]. Additionally, 2,3-difluorophenol, 3,5-difluorophenol, and 3,4,5-trifluorophenol are key intermediates in the synthesis of popular colored liquid crystal materials [4]. Due to their excellent performance in the aforementioned fields, the production of FA intermediates has been steadily growing, with the global FA market expanding from 10,000 tons/year in 1994 to 35,000 tons/year in 2000 [5]. The output of FA, in China, has reached approximately 50,000 tons/year in 2014 [6]. Since 2015, five new projects have been established in China solely for the production of pentafluorophenols as intermediates for peptide and liquid crystal syntheses [7-11]. The small radius and high electronegativity of fluorine atoms account for the high energy of the C-F bond, which contributes to the high biological activity, high fat solubility, high metabolic stability, high chemical stability, and other characteristics of FAs [12]. On the one hand, these characteristics make FAs perfectly suited for the production of pesticides, pharmaceuticals, liquid crystals, etc.; however, these properties are also responsible for the environmental hazards posed by FAs [13,14]. As the global production of FAs and their derivatives is currently on the rise, the amount of fluoroaromatic pollutants (FAPs) entering the environment is expected to increase, which necessitates the development of efficient FAP degradation methods.

Analogous to dechlorination being the key step of chlorinated organic pollutant degradation [15-17], defluorination is the key step of FAP degradation. Due to the presence of fluorine atoms, FAPs cannot be completely degraded in natural aerobic environments and are mostly likely converted to more toxic end products [13]. Conversely, completely defluorinated products can be treated using conventional approaches or be recycled as raw materials. A variety of FAP defluorinated by

aerobic bacterial degradation. However, such microbial degradation results in the formation of numerous intermediates, some of which exhibit high toxicity [13]. FAPs can also be defluorinated in acetonitrile or water employing an iron phthalocyanine– $H_2O_2$  catalytic oxidation system, with the maximum realized extent of defluorination being 89% [18]. As another example, defluorination of 2-fluoroaniline can be achieved using a bioelectrochemically assisted microbial system, with the corresponding maximum defluorination extent exceeding 60% [20].

Compared to the aforementioned oxidative defluorination methods, reductive hydrodefluorination (HDF) exhibits the advantage of high reaction product controllability [21]. Unfortunately, FAPs cannot be efficiently hydrodefluorinated using conventional zero-valent metal [20] and Pd-catalyzed  $H_2$  gas [22] reduction methods, despite these approaches being efficient for the hydrodehalogenation of brominated and chlorinated aromatics. Recently, McNeill et al. have proposed an HDF system comprising a Rh/Al<sub>2</sub>O<sub>3</sub> catalyst and hydrogen (as the reducing agent), achieving efficient aqueous-phase HDF of various fluorobenzenes under ambient conditions [23]. Chiu et al. investigated the HDF of vinyl fluoride over Rh/Al<sub>2</sub>O<sub>3</sub> in liquid and gas phases, showing that HDF mainly occurred in the liquid phase, whereas double bond hydrogenation mainly occurred in the gas phase [24]. In addition, a BH<sub>4</sub>-promoted electrochemical HDF system has been developed by Huang et al., allowing the selective HDF of various FAs in organic solvents [25]. Inspired by these efforts, our research group has developed an electrochemical HDF system featuring Rh/Ni foam electrodes and used it to efficiently and completely hydrodefluorinate 18 representative FAs in water under ambient conditions without the use of hydrogen gas [26].

The high cost of Rh makes the improvement of its catalytic activity crucial for the application of Rh-catalyzed electrochemical HDF, hydrogen gas reductive HDF, and zero-valent metal reductive HDF techniques. In this work, we developed a Rh-Pd alloy as an efficient HDF catalyst utilizing catalyst loading, element proportion, and phase screening, employed 4-fluorophenol (4-FP) as a model FAP, and investigated the underlying reaction mechanism. Electrodeposition was utilized to fabricate Pd- and Rh-modified Ni foam electrodes with different noble metal loadings, Rh/Pd and Pd/Rh composites, and Rh-Pd alloy-modified Ni foam electrodes, and the HDF activities of these electrodes were subsequently compared in solution at optimized pH values. Moreover, we also compared the degradation pathways of 4-FP on Rh- and Rh-Pd alloy-modified Ni (Rh-Pd/Ni) foam electrodes. Finally, the mechanism of 4-FP degradation on the Rh-Pd/Ni foam electrode was investigated using ICP-OES analysis, thermodynamic analysis, hydrogenation with H<sub>2</sub> as a reducing agent, and cyclic voltammetry (CV). To the best of our knowledge, this paper is the first report of Rh-Pd alloy-catalyzed HDF and the associated reaction mechanism.

#### 2. Material and methods

#### 2.1. Chemicals

Ni foam (1.0 mm thickness) and carbon (C) paper (TGP-H-060 and AvCarb EP40T) were purchased from CEEE Co., China (<u>www.hzcell.com</u>). 4-Fluorophenol (4-FP) and its HDF and RH products (phenol, cyclohexanone, and cyclohexanol), with purities of 98 wt%–99 wt%, and PdCl<sub>2</sub> (99.5 wt%), RhCl<sub>3</sub> (99.5 wt%), NaF, H<sub>2</sub>SO<sub>4</sub>, NaOH, H<sub>3</sub>PO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, ethanol and acetone,—all with 97 wt%–99 wt% purity—were purchased from Aladdin Reagent Co., China. Rh/Al<sub>2</sub>O<sub>3</sub> with 5 wt% Rh loading was obtained from Sigma-Aldrich Corporation. Methanol and acetonitrile (HPLC grade) used for HPLC analysis were obtain from National Medicines Co., Ltd., China. Water with resistivity of 18 MΩ·cm obtained from a Millipore Milli-Q system was used to prepare all reaction solutions.

#### 2.2. Electrode modification

All modified nickel foams were prepared by similar electrodepositions (Table 1). Prior to electrodeposition, we degreased and cleaned the nickel foam supports in acetone under ultrasonic vibration for 20 min and then etched them in a diluted H<sub>2</sub>SO<sub>4</sub> (0.8 M) solution for 300 sec to remove surface native oxides. Electrodepositions (A constant current of 10 mA was passed through an aqueous solution (40 mL) containing 1 M NaCl and 0.75 mM RhCl<sub>3</sub> (or 0.75 mM RhCl<sub>3</sub> and 0.375 mM PdCl<sub>2</sub>) at pH 2 (adjusted using HCl) until the rose or orange-red color disappeared) were used to prepare Rh/C paper and Rh-Pd/C paper. All electrodepositions were carried out in air at 30 °C. We prepared a number of electrodes under exactly the same conditions to ensure reproducibility. After modification, we kept the electrodes in water for later use without drying.

#### 2.3. Apparatus

The surface morphology and elemental/crystal phase compositions of the modified nickel foams were determined by scanning electron microscopy (SEM, Hitachi S-4700 II) equipped with

energy dispersive spectrometry (EDS, Thermo NOANVANTAGE ESI) and X-ray diffraction (XRD, Thermo ARLSCINTAG X'TRA, 45 kV and 40 mA, Cu Kα).

A potentiostat (PAR 283), a potentiostat (PAR 273), and a DC-regulated power supply (HZC-061) were used to perform cycle voltammetry (CV), chronoamperometry (CA), chronopotentiometry (CP), and constant current electrolysis experiments, respectively. We used a three-electrode cell composed of a Pt (2 cm × 2 cm) counter electrode, a Ag/AgCl reference electrode, and a Ni, 0.5Pd/Ni, 1Rh/Ni, or 1Rh-0.5Pd/Ni disk (2 mm diameter) working electrode to carry out the CV experiments. The 0.5Pd/Ni, 1Rh/Ni, and 1Rh-0.5Pd/Ni disks were prepared by the same electrodeposition method as that used for the 0.5Pd/Ni, 1Rh/Ni, and 1Rh-0.5Pd/Ni foam, respectively. A two-compartment H-cell (glass) composed of a Nafion-117 membrane, a Ag/AgCl reference electrode, a graphite sheet (2 cm × 3 cm) counter electrode, and a Ni, 1Rh/Ni, or 1Rh-0.5Pd/Ni foam  $(2 \times 3 \text{ cm}^2)$  working electrode was used for the CA and CP experiments. The electrode potentials in the CV, CA, and CP experiments were reported versus the Ag/AgCl/(saturated KCl) reference. The constant current electrolysis experiments were performed using a conventional two-compartment H-cell (glass) separated by a Nafion-117 membrane to obtain the optimized HDF conditions. Ni or modified Ni foams (projected area:  $2 \text{ cm} \times 3 \text{ cm}$ ) or modified C paper (projected area:  $2 \text{ cm} \times 2.5 \text{ cm}$ ) were served as the cathode and graphite sheet (2  $cm \times 3$  cm) was served as the anode in the electrolysis experiments. 40 mL catholyte and 40 mL anolyte were used in the electrolysis experiments, and the catholyte was maintained under vigorous stirring during electrolysis. A 0.1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the anolyte in all CA, CP, and electrolysis experiments and all experiments were carried out at 30 °C.

A three-necked jacketed reactor (glass) equipped with a  $H_2$  supply was used for hydrogenation experiments. A piece of modified foam or carbon paper or a certain amount of catalyst (Rh/Al<sub>2</sub>O<sub>3</sub>) was placed into the mixed solution of 40 or 100 mL solvent and under a continuous flow of  $H_2$  at 10 mL min<sup>-1</sup>. The reaction solution was maintained under vigorous stirring for 45, 120, or 180 min at 30 °C.

#### 2.4. Analytical methods

The concentrations of 4-FP and its degradation products (PhOH, phenol; CYC.one, cyclohexanone; CYC.ol, cyclohexanol; F, fluoride ion) were determined by a Waters HPLC system, an Agilent 7890 A gas chromatograph (GC), and a Dionex ICS-2100 ion chromatograph

(IC), respectively. The Waters HPLC system mainly composed of a Waters 2996 photodiode array detector ( $\lambda$  210 nm), an injection valve fitted with a 20  $\mu$ L sample loop, and a symmetry column  $(250 \text{ mm length} \times 4.6 \text{ mm i.d.}, 5 \text{ µm particle size})$ . A mobile phase of water/methanol/ acetonitrile (6:3:1 v/v) containing 30 mM H<sub>3</sub>PO<sub>4</sub> at a flow rate of 60 mL  $\cdot$  hr<sup>-1</sup> was used to carry out isocratic elution. The GC was equipped with an Agilent 7683B auto-sampler coupled to a flame ionization detector. The analysis was performed on an HP-INNOWAX capillary column (30 m  $\times$  0.32 mm i.d.  $\times$  0.5 µm), and the column temperature program was raised from 50 °C to 250 °C at a rate of 15 °C·min<sup>-1</sup>. Nitrogen of high purity (99.999%) was used as the carrier gas at a flow rate of 6.5 mL·min<sup>-1</sup>. The temperature of the injector was set at 250 °C. The organic product samples for GC analysis were obtained through the following procedures: (1) extraction with CH<sub>2</sub>Cl<sub>2</sub> from the catholytes, (2) desiccation over anhydrous sodium sulfate, (3) filtration using a sand core funnel, and (4) appropriate dilution with CH<sub>2</sub>Cl<sub>2</sub>. The Dionex ICS-2100 IC was equipped with a Dionex IonPac AS11-HC column. After appropriate dilution with water, the catholytes of the HDF experiments were filtered with an injection filter head and then directly subjected to HPLC and IC. Ni concentration in solutions was determined with an Inductively coupled plasma optical emission spectrometer (ICP-OES, iCAP 7400, Thermo Scientific, USA). Three ICP-OES measurements were performed for individual solution samples under exactly the same conditions to ensure reproducibility.

The concentrations of 4-FP and its degradation products, and Ni were determined using standard calibration curves. The precision of the mass balance in the measurement was approximately 97–103% for HPLC and IC analysis, 95–115% for GC analysis, and 95–105% for ICP-OES analysis. The conversion of 4-FP was defined as the molar ratio of 4-FP eliminated to the initial amount of 4-FP. The yields of the organic product and F were defined as the molar ratio of product produced to the initial 4-FP charged. Unless otherwise noted, faradic efficiency (FE, %) in the degradation of 4-FP was determined using the following equation:

$$FE = \frac{(n_1 \Delta C_{PhOH} + n_2 \Delta C_{CYC.one} + n_3 \Delta C_{CYC.ol})FV}{I \times \Delta t}$$

where  $n_1, n_2$ , and  $n_3$  are the electron transfer numbers per molecule of PhOH ( $n_1 = 2$ ), CYC.one ( $n_2 = 6$ ), and CYC.ol ( $n_2 = 8$ ), respectively;  $\Delta C_{PhOH}$ ,  $\Delta C_{CYC.one}$ , and  $\Delta C_{CYC.ol}$  are the concentration differentials (mol·L<sup>-1</sup>) of PhOH, CYC.one, and CYC.ol during  $\Delta t$ , respectively; *F* is the Faraday

constant (96500  $\text{C} \cdot \text{mol}^{-1}$ ); *V* is the volume of the total catholyte (0.04 L); and *I* is the applied current (A).

#### 3. Results and discussion

#### 3.1 Electrode characterization

Due to the fact that the 1Rh-0.5Pd/Ni foam exhibited the best HDF performance among all modified Ni foams, its morphology and elemental/crystal phase compositions were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). As shown in the SEM images of Fig. 1, the surface of the above foam was covered with a film containing five major elements (13.12 wt% C, 7.54 wt% O, 48.59 wt% Ni, 20.63 wt% Rh, and 10.12 wt% Pd), as determined by EDS. Notably, the Rh/Pd ratio of the film was close to that of the solution used for electrodeposition, implying that these metals were uniformly electrodeposited over the Ni foam surface. Fig. 2 shows the XRD patterns of fresh Ni, 1Rh/Ni, 0.5Pd/Ni, and 1Rh-0.5Pd/Ni foams and that of used 1Rh-0.5Pd/Ni foam, with the pronounced Rh-Pd alloy (111) diffraction peak [27] observed for the 1Rh-0.5Pd/Ni foam (Fig. 2B), confirming the presence of a Rh-Pd alloy on the Ni foam surface and indicating that the Rh-Pd alloy is the main HDF reaction site. It should be pointed out that Rh-Pd alloys of different compositions are easily produced by co-electrodeposition from solutions containing Rh<sup>3+</sup> and Pd<sup>2+</sup> [28]. Moreover, based on the XRD half-peak widths of fresh 1Rh/Ni, 0.5Pd/Ni, and 1Rh-0.5Pd/Ni in the  $2\theta$  range of  $38-42^\circ$ , the noble metal crystal size was suggested to decrease in the order Pd > Rh-Pd > Rh, which means that the specific surface areas of the three films on Ni foam decreased in the same order. This conclusion was further confirmed by the results shown in Fig. 3A, which revealed that the double-layer charging current of three modified Ni electrodes at 0 V decreased in the order Rh/Ni > Rh-Pd/Ni > Pd/Ni. Furthermore, the similar heights and half-peak widths of the (111) diffraction peak observed for both fresh and used 1Rh-0.5Pd/Ni foams suggested that the Rh-Pd alloy film was relatively steadily held on the Ni foam during one HDF experiment.

#### 3.2 Optimization of HDF catalysts and other conditions

Based on our previous report [26], the efficiency of electrochemical HDF is determined by the nature of the corresponding catalysts. Herein, catalyst optimization was performed using 4-FP as the target compound, with the obtained results listed in Table 2 (entries 1–11). Screening of

different types of catalysts, such as Pd, Rh, Rh/Pd composites, Pd/Rh composites, and Rh-Pd alloys, revealed that the best HDF performance was observed for a Rh-Pd alloy. Notably,  $F^-$  was not detected in the catholyte when Ni and Pd/Ni foams were used as electrodes, implying that Rh was the HDF-active ingredient in the Rh-Pd alloy. With the optimized catalyst (1Rh-0.5Pd) in hand, we then examined the effects of catholyte pH (entries 12–16), showing that the HDF efficiency decreased with increasing pH, with the best performance observed at pH 3. In addition to the abovementioned two parameters, we also found that the HDF system was immune to air (entry 17), and that at a low concentration of 0.1 mM, 4-FP degraded rapidly with 100% conversion and 98%  $F^-$  yield (entry 18), which suggested that the Rh-Pd alloy catalyst is potentially suitable for the remediation of 4-FP-contaminated groundwater.

# 3.3 Degradation pathway of 4-FP and FE of 4-FP degradation

With the optimal HDF conditions (catalyst = 1Rh-0.5Pd, catholyte pH = 3), the degradation pathway of 4-FP were evaluated. As shown in Figs. 4A and B, concentration profiles of 4-FP and its degradation products observed on the 1Rh-0.5Pd/Ni foam electrode is quite different from that observed on the Rh/Ni foam electrode. The primary difference is the much higher concentration of intermediates (PhOH and CYC.one) in the catholyte observed for the 1Rh-0.5Pd/Ni foam electrode. As described elsewhere [29], the selectivity of CYC.one formation during the ring hydrogenation (RH) of PhOH depends on the strength of CYC.one adsorption on catalysts, with weaker adsorption strength resulting in higher selectivity. Therefore, we speculated that the strength of PhOH and CYC one adsorption on the 1Rh-0.5Pd/Ni foam was weaker than that on the Rh/Ni foam. This is probably the reason why the former catalyst resulted in a higher HDF performance. In addition, during HDF and RH over 1Rh-0.5Pd/Ni foam electrodes, the concentration of the CYC.ol generated was very low during the 30-min period when the concentrations of 4-FP and PhOH were high. Moreover, the rate of CYC.one concentration growth was dependent only on the concentration of PhOH and not on that of 4-FP. This indicated that the main degradation pathway of 4-FP can be expressed as 4-FP  $\rightarrow$  PhOH  $\rightarrow$  CYC.one  $\rightarrow$  CYC.ol, with competitive adsorption between 4-FP, PhOH, and CYC.one taking place on the 1Rh-0.5Pd/Ni foam electrode and the adsorption of CYC.one thereon being much weaker than that of 4-FP and PhOH.

FEs were calculated for PhOH, CYC.one, and CYC.ol as target products. The calculation

revealed that the FE of 4-FP degradation exceeded 100% at both electrodes (Figs. 4C and D). Since the maximum FE of an electrochemical reaction equals 100% according to Faraday's law, we assumed that the degradation of 4-FP was accompanied by oxidative dissolution of nickel or that a large number of hydrogen atoms were immobilized on Rh/Ni and 1Rh-0.5Pd/Ni foam electrodes during their fabrication via adsorption and/or absorption. Thus, the oxidation of nickel or hydrogen on electrodes can provide additional electrons, leading to FEs of greater than 100% during degradation.

#### 3.4 Catalytic reaction mechanism

#### 3.4.1 Rationalization of overly high FE values

Theoretically, hydrogen atoms can be absorbed/adsorbed by Ni [30], Rh [31], and Rh-Pd alloys [28] on 1Rh/Ni and 1Rh-0.5Pd/Ni foam electrodes during preparation, with the subsequent oxidation of these hydrogen atoms providing electrons for 4-FP degradation and leading to FE values above 100%. To verify this hypothesis, we performed CV, CA, and CP experiments. Figs. 3A and C show the CV curves of Ni, Rh/Ni, and Rh-Pd/Ni electrodes, with Fig. 3A clearly displaying the current responses corresponding to the reduction of  $H^+$  to  $H_{ads}$  and the oxidation of  $H_{ads}$  to  $H^+$  on the above electrodes in the range of 0 to -0.4 V. For the wide potential range of 0.4 to -0.8 V in Fig. 3C, the current responses for the reduction of H<sup>+</sup> to H<sub>abs</sub> and H<sub>ads</sub>, as well as the corresponding reverse reactions, were observed for all three electrodes, indicating that these electrodes could absorb and adsorb hydrogen atoms. Fig. 3B shows the CA curves of freshly prepared Rh/Ni and Rh-Pd/Ni electrodes, with their open-circuit potentials (OCPs) of ~0.3 and -0.05 V, respectively, implying that both electrodes exhibited no or low hydrogen storage capacities during preparation. Figs. 3A and C indicate that the OCPs of these electrodes lay between the hydrogen oxidation and reduction peak potentials (in the presence of oxidizable Hads or Habs on Rh/Ni and Rh-Pd/Ni), i.e., these OCPs were expected to be seen around -0.25 V. Fig. 3D presents the CP curves of Ni, Rh/Ni, and Rh-Pd/Ni electrodes, with the current plateau observed for Ni foam during the first 2 min (corresponding to the oxidation of hydrogen) indicating that a certain amount of hydrogen may have been stored in the above foam during pretreatment. Conversely, no such plateaus were observed for Rh/Ni and Rh-Pd/Ni during the first 30 min, which indicated the absence of hydrogen storage during fabrication [28]. Although a profound oxidation current appeared within 30 min in the CP curves of Rh/Ni and Rh-Pd/Ni, it was significantly smaller than

that observed for the Ni electrode, and was thus considered not to be related to the oxidation of hydrogen. Based on the aforementioned results and discussion, it was concluded that FEs of over 100% observed for 4-FP degradation were not caused by hydrogen storage.

As described in Section 3.3, oxidative dissolution (OD) of the nickel support during 4-FP degradation can also result in FEs exceeding 100%. To test this hypothesis, the 4-FP degradation efficiency and Ni<sup>2+</sup> concentration were measured with and without an applied cathodic current. Table 3 shows that high concentrations of Ni<sup>2+</sup> were observed in both cases when Rh/Ni and Rh-Pd/Ni foam electrodes were used, demonstrating that 4-FP degradation was accompanied by the OD of nickel in both materials. When the degradation FEs were recalculated considering the above process, the obtained values were less than 100% in both cases, confirming that the OD of nickel caused the FE to exceed 100%.

Additionally, it should be pointed out that the recalculated FE of Rh-Pd/Ni foam was significantly higher than that of the Rh/Ni foam. Taking into account the conclusion of Section 3.1 that the surface area of the catalytic Rh-Pd/Ni foam layer was smaller than that of the Rh/Ni foam layer, it was concluded that Rh-Pd led to a higher intrinsic catalytic activity for the degradation of 4-FP than that offered by Rh. To further support this conclusion, 4-FP degradation experiments were performed using Rh/C and Rh-Pd/C paper electrodes, with the obtained results (Table 3, entries 5 and 6) confirming the above hypothesis.

#### 3.4.2 Direct/indirect HDF mechanism

Based on the previous work of McNeill [5] and our group [26], the HDF of 4-FP on Rh-Pd/Ni foam is likely to follow an indirect mechanism:

$4\text{-FP} + \text{Rh-Pd} \leftrightarrow (4\text{-FP})_{\text{ads}}\text{Rh-Pd}$	(1)
$2 \text{ H}^+ + 2 \text{ e}^- + \text{Rh-Pd} \leftrightarrow 2 \text{ Rh-Pd-H}_{ads}$	(2)
$(4-FP)_{ads}Rh-Pd + 2 Rh-Pd-H_{ads} \rightarrow (PhOH)_{ads}Rh-Pd + HF$	(3)
$(PhOH)_{ads}Rh-Pd \rightarrow PhOH + Rh-Pd$	(4)

The first step of the above mechanism features the formation of adsorbed 4-FP [Eq. (1)] and adsorbed hydrogen [Eq. (2)] on Rh-Pd, with the subsequent HDF proceeding [Eq. (3)] by the hydrogenation of the adsorbed 4-FP with the adsorbed hydrogen, followed by desorption of PhOH [Eq. (4)], similarly to the case of catalytic hydrogenation. Additionally, it is also possible that the HDF of 4-FP proceed via a direct mechanism, as described by Eqs. (5) and (6) [25,32]:

$$(4-FP)_{ads}Rh-Pd + 2e^{-} \rightarrow [(R)_{ads}Rh-Pd]^{*}$$
(5)

#### $[(R)_{ads}Rh-Pd]^* + 2 H^+ \rightarrow (PhOH)_{ads}Rh-Pd + HF$

(6)

The above pathway features the successive formation of series of adsorbed intermediates [Eq. (5)] by electron transfer from the Rh-Pd/Ni electrode to 4-FP, which is followed by protonation of these intermediates [Eq. (6)] and product desorption [Eq. (4)].

The HDF mechanism was investigated by performing CV experiments on Ni, Pd/Ni, Rh/Ni, and Rh-Pd/Ni electrodes at different 4-FP concentrations. As indicated by Figs. 5A and B, 4-FP did not react on the nickel electrode, with its adsorption being negligible. Similarly, 4-FP was only weakly adsorbed on the Pd/Ni electrode, and almost no reaction occurred. These results were consistent with those listed in Table 2 (entries 1 and 2). Moreover, it is worth noting that the double-layer charging current of Pd/Ni was smaller than that of the Ni electrode in the range of 0.4-0 V, indicating the presence of a very compact Pd coating on the Ni surface [33]. CV curves of Rh-Ni and Rh-Pd/Ni (Figs. 5C and D, respectively) exhibited similar shapes and trends, i.e., the intensity of reduction and oxidation peaks between 0 and -0.4 V gradually decreased with increasing 4-FP concentration, with the same trend observed for the double layer charging current at 0 V. Thus, the obtained results indicated that 4-FP was strongly adsorbed on both electrodes [34]. Changes in the reduction and oxidation peak intensities and those in the double layer charging current were more significant for Rh/Ni, implying that 4-FP was more strongly adsorbed on Rh/Ni than on Rh-Pd/Ni. The above results, together with those depicted in Figs. 5A and B, indicated that 4-FP was mainly adsorbed by Rh in Rh/Ni and Rh-Pd/Ni, with Pd tuning the adsorption affinity of 4-FP to Rh and thus improving the HDF activity of these catalysts. In addition, the decrease in the reduction peak intensities observed for Rh/Ni and Rh-Pd/Ni was much less pronounced than that observed for the corresponding oxidation peak between 0 and -0.4 V after adding 1 mM 4-FP to a blank solution, which suggested that 4-FP was reduced on both electrodes. This conclusion was consistent with the phenomenon demonstrated in Fig. 3B, i.e., the stable potentials of both electrodes were within the range of -0.3 to -0.35 V during 4-FP degradation. In addition, since the redox peaks of Rh/Ni and Rh-Pd/Ni corresponded to the reversible oxidation-reduction between  $H_{ads}$  and  $H^+$  at 0 to -0.4 V, the aforementioned reduction of 4-FP was likely to follow the indirect mechanism (with H<sub>ads</sub> as the direct reducing agent).

To confirm the indirect mechanism of 4-FP reduction on Rh/Ni and Rh-Pd/Ni, we conducted HDF experiments using hydrogen as a reducing agent, additionally employing self-made Rh/C

and Rh-Pd/C papers and commercial Rh/Al<sub>2</sub>O<sub>3</sub> as catalysts to avoid possible direct HDF reactions caused by the OD of Ni. As a result (Table 4), significant HDF of 4-FP was observed when Rh/Ni and Rh-Pd/Ni foam were used as catalysts, with this reaction being accelerated by hydrogen. Conversely, almost no HDF was observed in the case of Rh/C paper, whereas this reaction was pronounced when Rh-Pd/C paper and Rh/Al<sub>2</sub>O<sub>3</sub> were used. Therefore, the HDF of 4-FP on Rh/Ni and Rh-Pd/Ni was believed to either fully or partially occur via the indirect mechanism. In addition, the Rh content of Rh/Al<sub>2</sub>O<sub>3</sub> was much lower than that of Rh/C paper, which indicated that the HDF activity of the Rh catalyst was greatly influenced by its support.

#### 3.4.3 Thermodynamic Analysis

Based on the above results and discussion, the HDF of 4-FP was suggested to comprise the following steps:

$N_{r}^{2} \leftrightarrow N_{r}^{2+} + 2 c^{-1}$	(7)
$NI \leftrightarrow NI + 2e$	(7)
$2 H^+ + 2 e^- \leftrightarrow H_2$	(8)
$Ni + H^+ + e^- \leftrightarrow Ni - H$	(9)
$Ni-H \leftrightarrow 2 Ni + H_2$	(10)
$Rh-Pd + H^+ + e^- \leftrightarrow Rh-Pd-H$	(11)
2 Rh-Pd-H ↔ 2 Rh-Pd + H <sub>2</sub>	(12)
$(4-FP)_{ads}Rh-Pd + 2 Rh-Pd-H \rightarrow Rh-Pd + PhOH + HF$	(13)
$(4-FP)_{ads}Rh-Pd + 2H^+ + 2e^- \rightarrow Rh-Pd + PhOH + HF$	(14)

Firstly, the possibility that the OD of nickel (Eq. (7)) provides electrons for indirect HDF (Eq. (13)) of 4-FP was analyzed. Based on the maximum nickel ion concentration (4.1 mM, Table 3), the equilibrium potential of nickel OD was determined as -0.717 V (vs. Ag/AgCl) using the Nernst equation (Eq. (15)).

$$E = E^{0} + \frac{RT}{nF} \ln \frac{[Ni^{2+}]}{[Ni]}$$
(15)  
$$E = E^{0} + \frac{RT}{nF} \ln \frac{[H^{+}]}{[H_{2}]}$$
(16)

Fig. 3A shows that the potential of  $H^+$  to  $H_{ads}$  reduction on Ni and Rh-Pd/Ni electrodes varied between -0.1 and -0.4 V, being more positive than the equilibrium potential of nickel OD. Thus, the reduction of  $H^+$  to  $H_{ads}$  (Eqs. (9) and (11)) was thermodynamically allowed. In addition, since the HDF reactions on Rh-Pd/Ni occurred via the indirect mechanism with  $H_{ads}$  acting as the reducing agent (Section 3.4.2), the electrons generated by nickel OD could be thermodynamically exploited in the indirect HDF of 4-FP.

Next, we analyzed whether the nickel OD provides electrons for the hydrogen evolution reaction (HER) (Eq. (8)) and characterized HER-active sites. The HER equilibrium potential at an  $H^+$  concentration of 1 mM (pH = 3) and a hydrogen pressure of  $\leq 1$  atm was calculated to exceed – 0.527 (vs. Ag/AgCl) (Eq. (16)). Since the equilibrium potential of the nickel OD is more negative than that of HER, the former reaction can provide electrons for the latter one in the studied system. The reaction represented by Eq. (11) was thought to take precedence over that represented by Eq. (9), since hydrogen atoms were more strongly adsorbed on Rh and Pd than on Ni [35], as supported by the results in Fig. 3A, which showed that the current of  $H^+$  to  $H_{ads}$  reduction on Rh-Pd/Ni significantly exceeded that on the Ni electrode. For the Ni electrode, Eq. (9) represents the rate-determining step of HER, whereas HER on Rh and Pd is controlled by reactions represented by both Eqs. (11) and (12), implying that the HER active sites mainly correspond to Rh-Pd. In addition, the partial pressure of hydrogen at the degradation potential of 4-FP (-0.30 to -0.35 V) was calculated as 0.008-0.02 atm (Eq. (16)), which indicated that HER on Rh/Ni and Rh-Pd/Ni electrodes should be slow. This result was consistent with the high FE efficiencies observed for entries 1-4 in Table 3. Unfortunately, the thermodynamic feasibility of direct HDF (Eq. (14)) could not be determined based on the available data.

#### 4. Conclusions

In this study, we developed an efficient HDF catalyst (Rh-Pd alloy) and established a preliminary mechanism of HDF over a Rh-Pd alloy-modified Ni foam electrode. The above alloy achieved more rapid HDF of 4-FP than the Rh catalyst, with the subsequent ring hydrogenation (RH) of the HDF product (phenol) affording cyclohexanone and cyclohexanol. The HDF of 4-FP over the Rh-Pd alloy probably follows an indirect hydrogenation mechanism (i.e., one featuring adsorbed H as the direct reductant), and the strength of 4-FP and HDF product adsorption onto the catalyst surface significantly affects the catalytic activity. In addition to those supplied by the applied current, most of the electrons for the HDF of 4-FP and RH of phenol are provided by the oxidative dissolution of Ni foam. The high HDF activity of the Rh-Pd alloy and its tendency to afford less toxic end products make this catalyst potentially suitable for the remediation of

4-FP-contaminated groundwater. In addition, it should be noted that the Rh-Pd alloy can be utilized not only as an electrochemical HDF catalyst, but also as a zero-valent metal reductive HDF catalyst, in analogy to the efficient use of the zero-valent reduction method for the remediation of chlorinated organics-contaminated groundwater [36].

# **Conflict of interest**

There is no conflict of interest among authors related to this paper.

#### Acknowledgement

This research was supported by NSFC (Grant No. 21106133, 21576238), the Natural Science Foundation of Zhejiang Province, China (Grant No. LY16B060012), the Hangzhou Science and Technology Development Foundation of China (Grant No. 20170533B07), and the Special Program on Science and Technology Development of Guangdong Province, China (Grant No. 2017A070702012).

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# **Table captions**

Table 1. Electrodeposition conditions used to fabricate modified nickel foams.

Table 2. Optimization of HDF catalysts and catholyte pH using 4-FP as the target compound.

Table 3. Degradation of 4-FP in the presence/absence of applied current under  $N_2$ .

**Table 4.** HDF of 1 mM 4-FP in 20 mM aqueous phosphate buffer with pH 3 performed at 30  $^{\circ}$ C using H<sub>2</sub>.

Entry <sup>a</sup>	Modified nickel foams	Concentration of Rh (mM)	Concentration of Pd (mM)
1	0.5Pd/Ni foam	0	0.5
2	1Pd/Ni foam	0	1
3	1.5Pd/Ni foam	0	1.5
4	0.5Rh/Ni foam	0.5	0
5	1Rh/Ni foam	1	0
6	1.5 Rh/Ni foam	1.5	0
7 <sup>b</sup>	1Rh/0.5Pd/Ni foam	1	0.5
8 <sup>b</sup>	0.5Pd/1Rh/Ni foam	1	0.5
9 <sup>c</sup>	0.5Rh-1Pd/Ni foam	0.5	1
$10^{\circ}$	1Rh-0.5Pd/Ni foam	1	0.5

Table 1.

<sup>a</sup> A constant current of 4 mA was passed through an aqueous solution (40 mL) containing 1 M NaCl and different concentrations of  $RhCl_3$  and/or  $PdCl_2$  at pH 2 (adjusted using HCl) until the rose, yellow, or orange-red color disappeared.

<sup>b</sup> Rh and Pd were separately deposited in different solutions.

<sup>c</sup> Rh and Pd were co-deposited in the same solution.

Entry <sup>a</sup>	Cathodes <sup>b</sup>	Concentration	pН	Atmosphere	I mA/t	Conv.	Yield of F <sup>-</sup> (%)
		of FP			min	(%)	
1	Ni foam	1.0 mM	3	N <sub>2</sub>	4/45	2	0
2	0.5Pd/Ni foam	1.0 mM	3	N <sub>2</sub>	4/45	4.5	0
3	1Pd/Ni foam	1.0 mM	3	$N_2$	4/45	2.5	0
4	1.5Pd/Ni foam	1.0 mM	3	$N_2$	4/45	4	0
5	0.5Rh/Ni foam	1.0 mM	3	$N_2$	4/45	31	30
6	1Rh/Ni foam	1.0 mM	3	$N_2$	4/45	46	45
7	1.5 Rh/Ni foam	1.0 mM	3	$N_2$	4/45	66	67
8	1Rh/0.5Pd/Ni foam	1.0 mM	3	$N_2$	4/45	55	53
9	0.5Pd/1Rh/Ni foam	1.0 mM	3	$N_2$	4/45	53	50
10	0.5Rh-1Pd/Ni foam	1.0 mM	3	$N_2$	4/45	76	75
11	1Rh-0.5Pd/Ni foam	1.0 mM	3	$N_2$	4/45	97	98
12	1Rh-0.5Pd/Ni foam	1.0 mM	3	$N_2$	4/30	88	85
13	1Rh-0.5Pd/Ni foam	1.0 mM	5	$N_2$	4/30	44	42
14	1Rh-0.5Pd/Ni foam	1.0 mM	7	$N_2$	4/30	5	1
15	1Rh-0.5Pd/Ni foam	1.0 mM	9	$N_2$	4/30	2	0
16	1Rh-0.5Pd/Ni foam	1.0 mM	11	$N_2$	4/30	1	0
17	1Rh-0.5Pd/Ni foam	1.0 mM	3	Air	4/45	99	98
18	1Rh-0.5Pd/Ni foam	0.1 mM	3	$N_2$	0.4/45	100	98

Table 2.

<sup>a</sup> Unless Specifically Noted Otherwise, 20 mM aqueous phosphate buffer (40 mL) containing 1.0 mM 4-FP served as the catholyte, a current of 4 mA was applied for 45 min (i.e., 4 mA/45 min, the passed charge equaled 2.8 F: 2.8 mol of electrons per mol 4-FP), and the electrode area equaled  $2 \times 3$  cm<sup>2</sup>.

<sup>b</sup> 0.5Pd corresponds to a Pd loading of 0.33 mmol  $dm^{-2}$  and 1Rh corresponds to a Rh loading of 0.67 mmol  $dm^{-2}$ . For detailed preparation conditions, refer to Table 1.

Entry <sup>a</sup>	Cathodes	Project area	I/mA	Conv.	Yield of F <sup>-</sup>	Concentration of	$FE^{b}$
		$/ \mathrm{cm}^2$	(t / Min)	(%)	(%)	$Ni^{2+}$	(%)
1	1.5 Rh/Ni foam	2×3	4 (45)	67	65	3.2 mM	51
2	1.5 Rh/Ni foam	2×3	0 (45)	48	47	4.1 mM	41
3	1Rh-0.5Pd/Ni	2×3	4 (45)	95	95	2.2 mM	92
	foam						
4	1Rh-0.5Pd/Ni	2×3	0 (45)	81	82	3.1 mM	91
	foam						
5 <sup>c</sup>	0.75 Rh/C paper	2×2.5	12 (120)	64	60		/
6 <sup>c</sup>	0.5Rh-0.25Pd/C	2×2.5	12 (120)	93	94		/
	paper						

Table 3.

<sup>a</sup> Catholyte: 40 mL of 20 mM aqueous phosphate buffer with pH 3 containing 1 mM 4-FP.

<sup>b</sup> Faradaic efficiency (FE, %) for the degradation of 4-FP was calculated as

$$FE = \frac{n_1 \times F \times V \times \Delta C_{4-FP}}{I \times \Delta t + n_2 \times F \times V \times \Delta C_{Ni^{2+}}},$$

where  $n_1$  and  $n_2$  are the electron transfer numbers for the degradation of 4-FP ( $n_1 \approx 7$ ) and the oxidative dissolution of Ni<sup>2+</sup> ( $n_2 = 2$ ), respectively;  $\Delta C_{4-\text{FP}}$  and  $\Delta C_{\text{Ni}}^{2+}$  are the concentration differentials (mol L<sup>-1</sup>) of 4-FP and Ni<sup>2+</sup> during time  $\Delta t$ , respectively; *F* is the Faraday constant (96500 C mol<sup>-1</sup>); *V* is the total volume of the catholyte (0.04 L); and *I* is the applied current.

<sup>c</sup> The model number of the C paper is TGP-H-060.

#### Table 4.

Entry	Volume of	Catalytic materials	Atmosphere	Reaction	Conv.	Yield of
	reaction solution			time	(%)	F <sup>-</sup> (%)
1	40 mL	$2 \times 3 \text{ cm}^2$ 1.5 Rh/Ni foam	$H_2$	45 min	85	83
2	40 mL	$2 \times 3 \text{ cm}^2 1.5 \text{ Rh/Ni}$ foam	$N_2$	45 min	48	47
3	40 mL	2×3 cm <sup>2</sup> 1Rh-0.5Pd/Ni foam	$H_2$	45 min	100	100
4	40 mL	2×3 cm <sup>2</sup> 1Rh-0.5Pd/Ni foam	$N_2$	45 min	81	80
5 <sup>a</sup>	40 mL	2×2.5 cm <sup>2</sup> 0.75 Rh/C paper	$H_2$	120 min	3	0
6 <sup>a</sup>	40 mL	2×2.5 cm <sup>2</sup> 0.5Rh-0.25Pd/C	$H_2$	120 min	7	3
		paper				
7 <sup>b</sup>	40 mL	2×2.5 cm <sup>2</sup> 0.5Rh-0.25Pd/C	$H_2$	120 min	13	12
		paper				
8	100 mL	$5 \text{ mg Rh}/\text{Al}_2\text{O}_3$	$H_2$	180 min	37	36

<sup>a</sup> The model number of the C paper is TGP-H-060.

<sup>b</sup> The model number of the C paper is AvCarb EP40T.

# **Figure captions**

Fig. 1. SEM images of Ni and 1Rh-0.5Pd/Ni foams, and an EDS spectrum of the latter foam.

**Fig. 2.** XRD patterns of (A) Ni, 1Rh/Ni, 0.5Pd/Ni, fresh 1Rh-0.5Pd/Ni, and used 1Rh-0.5Pd/Ni foams. (B) Magnified section of (A).

**Fig. 3.** ((A) and (C)) CV curves (third cycle) of Ni, 1Rh/Ni, and 1Rh-0.5Pd/Ni disks (diameter = 2 mm) recorded in 20 mM aqueous phosphate buffer with pH 3 (blank solution). (B) CA curves of fresh 1Rh/Ni and 1Rh-0.5Pd/Ni foams  $(2 \times 3 \text{ cm}^2)$  recorded in the blank solution containing 1 mM 4-FP. (D) CP curves of fresh Ni, 1Rh/Ni, and 1Rh-0.5Pd/Ni foams  $(2 \times 3 \text{ cm}^2)$  recorded in blank solution under N<sub>2</sub>.

**Fig. 4.** Faradic efficiency and concentration profiles of 4-FP and its degradation products (PhOH = phenol; CYC.one = cyclohexanone; CYC.ol = cyclohexanol) observed during HDF at an applied current of 4 mA, under ambient conditions. Catholyte = 40 mL of 20 mM aqueous phosphate buffer with pH 3 containing 1 mM 4-FP; electrode = ((A) and (C)) 1Rh/ Ni foam (projected area:  $2 \times 3 \text{ cm}^2$ ), ((B) and (D)) 1Rh-0.5Pd/Ni foam (projected area:  $2 \times 3 \text{ cm}^2$ ).

**Fig. 5.** CV curves of (A) Ni, (B) 0.5Pd/Ni, (C) 1Rh/Ni, and (D) 1Rh-0.5Pd/Ni disks (diameter = 2 mm) recorded in 20 mM aqueous phosphate buffer with pH 3 containing various concentrations of 4-FP at a scan rate of 50 mV s<sup>-1</sup> under N<sub>2</sub>.











Fig. 3.



Fig. 5.

> We developed an efficient Rh-Pd alloy catalyst for hydrodefluorination (HDF). > The HDF of 4-fluorophenol (4-FP) over the catalyst follows the indirect hydrogenation mechanism. > The catalyst could be used in electrochemical and zero-valent metals reductive HDF. > The catalyst is potentially viable to remediate the 4-FP-contaminated groundwater.