



Catalytic microreactor with electrodeposited hierarchically nanostructured nickel coatings for gas-phase fluorination reactions

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ABSTRACT

The fabrication of a catalytic microreactor for the reaction of undiluted carbonyl difluoride and elemental fluorine to synthesize trifluoromethyl hypofluorite, CF_3OF , on CsF catalyst supported on F_2 -passivated nanostructured Ni coating was studied. The nanostructured Ni support for catalyst immobilization was electrodeposited by a two-step procedure, consisting of a low current density step followed by a brief high current density one, for a hierarchical differentiation of structural features. An aqueous solution of NiCl_2 with diethanolamine, as crystal modifier, and sodium lauryl sulphate, as anti-pitting agent, was used as electrolyte. Constant-pH Ni electrocrystallization was performed on H_2SO_4 -etched Cu substrates in a range of pH from 1 to 4 via a $\text{HCl}/\text{H}_3\text{BO}_3$ based buffer. Passivation was carried out under up to 300 mbar of undiluted F_2 . XRD, XPS, SEM, AFM, and static contact angle measurements were performed. Ni coatings obtained from pH 3 electrolytes were selected for microreactor fabrication on the basis of characterization data, due to the reproducibility and homogeneity of the structured Ni layers. The catalytic microreactor allowed the quantitative production of CF_3OF from pure reactants, on demand, and removing any criticality relative to thermal and safety control of the synthesis. The CF_3O -group selective transfer ability of the synthesized hypofluorite has raised interest in pharmaceutical and agrochemical industries in recent years.

1. Introduction

The use of microfabricated reaction devices represents a growing phenomenon within the framework of hazardous reactants handling. This kind of apparatuses, also called microreactors, introduces many fundamental and practical advantages in chemical synthesis, such as safety, high throughput, and, given optimal process conditions, high selectivity [1]. In fact, the reduced volume of microreactors ensures more efficient heat transfer due to higher surface-to-volume ratios compared to conventional chemical reactors [2]. Moreover, the compact nature of microreactors reduces the exposure to toxic or hazardous chemical species and guarantees safety in the event of thermal runaway [3,4]. As a consequence, the application of microreactors to direct fluorination reactions results particularly attractive because of the reduced volumes of reactants processed at any given time, the

attainability of an effective tuning of heat transfer and chemical selectivity, as well as the opportunity for a convenient and straightforward scale-up via numbering-up [5–10]. Fluorine chemistry, as a whole, and the study of fluorinated materials, in particular, represent ever-expanding research fields stretching out towards several different industrial contexts [11,12]. Fluorinated compounds find application, among others, as intermediates in the synthesis of industrial monomers [13–17], pharmaceuticals [18–20], and agrochemicals [21–25]. Direct fluorination is however seldom practiced on an industrial scale due to known problematics associated with the use of strong oxidants, and elemental fluorine in particular [26].

Oxides-based passivation layers are adequate in most cases as corrosion-resistant coatings, but fall short when reactive fluorinated species are involved [27]. Since fluorine is more oxidant than oxygen itself, even oxygen-passivated metal components have the tendency to

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undergo abrupt corrosion-related breakdown in the presence of reactive fluorinated species [26]. A passivation layer made of metal fluorides, rather than metal oxides or hydroxides, is required on the inner surface of reactors used for fluorination reactions in order to prevent corrosion. In stainless steel reactors, a passivation film is obtained by direct fluorination of the vessel, followed by an appropriate thermal treatment [28–30]. In Al- or Cu-based reactors, a protective layer of Ni is usually deposited on the inner surface and then passivated via mild direct fluorination [29–31]. The typical Ni-based coatings are prepared by chemical and electrochemical deposition methods coupled with colloid-based strategies, including the use of additives, surfactants, and templates [32,33]. The design of a microreactor chamber can be improved by structuring the catalyst support surface, providing important advantages such as increased surface area thanks to micro- and nanostructured morphologies, sensible wettability control, and availability of grafting sites suitable for the immobilization of catalytic species [34–37].

This work reports on the fabrication of a working catalytic microreactor for the synthesis of trifluoromethyl hypofluorite, CF_3OF , via direct fluorination of carbonyl difluoride. Trifluoromethyl hypofluorite is an interesting trifluoromethoxylating agent as CF_3O represents a highly valuable functional group in pharmaceutical and agrochemical applications owing to its peculiar physicochemical properties and high metabolic stability [18–25,38]. Moreover, CF_3OF can be directly synthesized from CO and F_2 immediately before use, circumventing handling/manipulation hazards along with the special conditions required for storage [39]. Indeed, as shown in the present work, a catalytic microreactor meets the safety and throughput requirements of industry processes, potentially leading to the introduction of CF_3OF as a readily available trifluoromethoxy transfer agent. *o*-trifluorinated anisoles are, for example, useful as intermediates for dyes and agrochemicals and they are industrially prepared on the large scale from other aromatic substrates, such as phenol or α,α,α -trichloroanisole, by treatment with HF [40–45]. Substituted α,α,α -trifluoroanisols can be directly synthesized also by reaction between CF_3OF and appropriate aromatics in good to medium yields [38]. Insights obtained from this research were applied to the fabrication of a hierarchically nanostructured nickel coatings acting as protective layers as well as catalyst support in the catalytic microreactors. In particular, the effect of electrolyte pH on morphology and wetting properties was investigated. The resulting coatings were exposed to elemental fluorine in order to obtain a fluorine-resistant passivation layer suitable for application in direct catalytic fluorination reactions. Bare and passivated nanostructured nickel coatings were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction spectroscopy (XRD). The wettability of the coatings was also evaluated by measurements of static water contact angle.

2. Experimental

2.1. Materials

Ni thin films for the preliminary optimization of electrodeposition and passivation conditions were deposited on a 30×20 mm area on commercial pure Cu plates (size: $60 \times 30 \times 0.6$ mm). Nickel(II) chloride hexahydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, boric acid, H_3BO_3 , hydrochloric acid, HCl, diethanolamine (DEA), $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, sodium lauryl sulphate, $\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4\text{Na}$, and sulfuric acid, H_2SO_4 , were used to prepare the solutions for electrodeposition. All the chemicals were of reagent-grade purity (supplied by Sigma Aldrich) and were used without further purification; doubly distilled water passed through a Milli-Q apparatus was used to prepare the solutions.

2.2. Electrodeposition of hierarchically nanostructured nickel coatings

Before the electrodeposition, Cu plates were pre-treated by etching in a 20 wt.% H_2SO_4 solution for 10 min at room temperature. Ni thin films were electrodeposited on Cu substrates from 1.0 M NiCl_2 solutions at different pH: 1.0, 2.0, 3.0, and 4.0. In each deposition, the electrolytic solution was augmented by addition of H_3BO_3 0.5 M as pH buffer agent, while the desired pH was achieved by addition of an appropriate amount of HCl. pH values of 1, 2, 3, and 4, were considered. DEA (0.5 M), as crystal modifier, and sodium lauryl sulphate (1 g/L), as anti-pitting additive, were also dissolved into the solution. The electrodeposition was performed under galvanostatic conditions in two separate steps. A first treatment at 20 mA cm^{-2} for 10 min produced the primer layer, while a successive treatment at 50 mA cm^{-2} for 1 min. The total charge was 15 C cm^{-2} for a final average thickness of about $5 \mu\text{m}$. A constant deposition temperature of 60°C was maintained throughout. A Ti mesh was used as counter electrode. After electrodeposition, the samples were rinsed with distilled water and dried under N_2 flux. Stirring of the electrolytic solution was deemed unnecessary, and thus switched off after reaching uniform thermal conditions prior to deposition, as it was found to be detrimental to the homogeneity of the final coatings.

2.3. Passivation towards fluorine resistance

Each nanostructured Ni coated sample was initially loaded into a previously-passivated stainless steel reactor connected to a vacuum line, and was exposed to a set amount of gaseous F_2 for a specific amount of time. The passivation procedure included four steps at increasingly aggressive conditions: 60 mbar of F_2 for 30 min (step 1); 150 mbar for 15 min (step 2); 200 mbar for 10 min (step 3); 300 mbar for 5 min (step 4). Vacuum conditions (under 8 mbar) were re-established in the reactor between each step.

2.4. Characterization

The morphology of the nickel coatings on copper plates was observed with the aid of a ZEISS EVO50 EP Scanning Electron Microscope. The samples were analysed without performing surface etching or conductive layer coating. The SEM parameters were as follows: working distance of 20.0 mm, beam current of 100 pA, acceleration voltage of 20.00 kV, magnifications of 1, 5 and 10 kx.

Atomic force microscopy (AFM) was performed using a Bruker Caliber scanning probe microscope. Scans of $5 \times 5 \mu\text{m}$ and $10 \times 10 \mu\text{m}$ were acquired for each sample in tapping mode, using Sb n-doped silicon tips. Surface roughness was evaluated by flattening the images (first order) using WSxM software.

XPS spectra were obtained by using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al $K\alpha$ radiation (1486.6 eV). A spot size of $200 \times 750 \mu\text{m}$ and a pass energy of 25 eV were used. 1 s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. Fits were performed using pure Gaussian peaks, Shirley's baseline, and without any constraints. For each sample, a survey analysis in the whole range of the X-ray spectrum and high-resolution analyses in the typical zone of C-1s, Ni-2p, O-1s, and F-1s, were performed.

X-ray diffraction (XRD) patterns were obtained with thin film configuration on a Philips PW 1830 X-ray Diffractometer equipped with a Philips PW 3020 Goniometer with Cu $K\alpha$ radiation ($\lambda = 1.54058 \text{ \AA}$) at a scan rate of $0.02^\circ \text{ s}^{-1}$.

Static contact angle (SCA) values with water were measured by sessile drop method in order to evaluate the hydrophilic/hydrophobic properties of the coatings immediately after rinsing and drying. SCA measurements were performed with a Dataphysics OCA contact angle instrument and elaborated with SCA20 software. The averaged contact angle for each coating was calculated as the average over five values

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