

Supporting Information

Adsorption of nickel ions on the γ -alumina surface:
Competitive effect of protons and its impact on
concentration profiles

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Contents

		Pages
S1	TEM images of the alumina extrudates	S-3
S2	Characteristics of the reactor chosen for the impregnation experiments	S-4
S3	Further details on the laser and spectrometers used for the LIBS technique, as well as the sample preparation technique	S-7
REFERENCES		S-12

S1: TEM images of the alumina extrudates.

The structure of the γ -alumina extrudates used in this work were analyzed by TEM imaging, prior to impregnation. For the analysis, an extrudate is placed in an oven at 80 °C overnight and embedded in Araldite resin (EMbed 812, Electron Microscopy Sciences, Hatfield, PA, U.S.A.). The extrudate is then trimmed to obtain a trapezoidal surface and cut in 70 nm thick slices using an ultramicrotome (Reichert, Wien, Austria). Slices with homogeneous color (homogeneous thickness) are withdrawn to a lacey carbon grid. Finally, images are taken with a TEM microscope (JEM-2100F, JEOL Tokyo, Japan) operating at 200 kV, in bright field mode, using a charge-coupled device (or CCD) camera (UltraScan, Gatan, Pleasanton, CA, U.S.A.).

The TEM images are presented in **Figure S1**. They show an organized structure of the alumina platelets, proving a homogenous pore size distribution and that the solids are purely mesoporous.

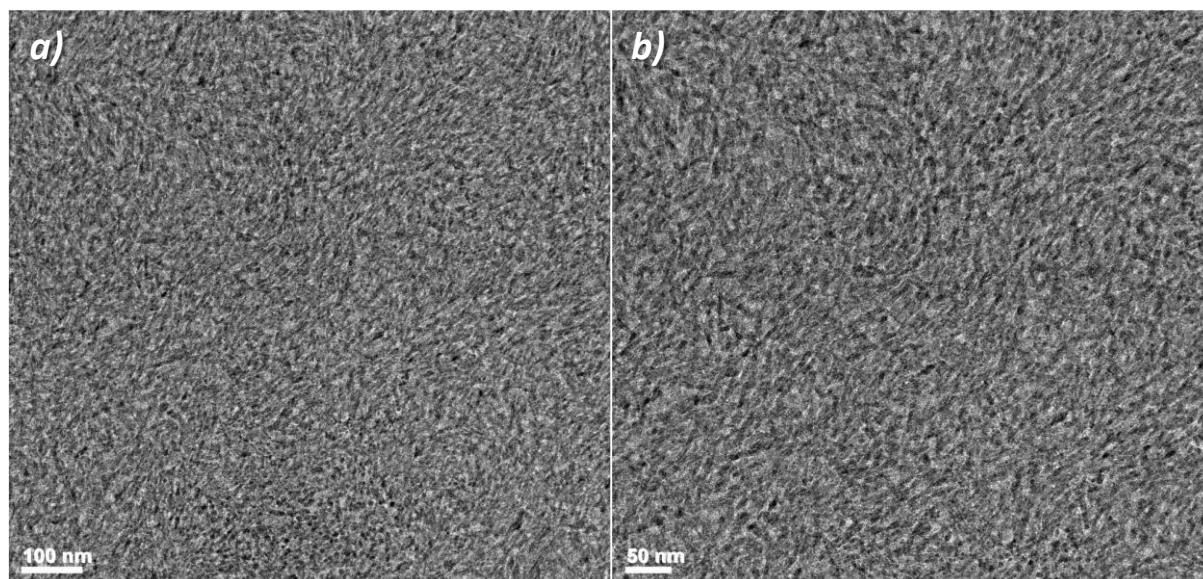


Figure S1. TEM images at different magnifications of the γ -alumina extrudates.

S2: Characteristics of the reactor chosen for the impregnation experiments.

A hydrodynamic study has been conducted to determine the characteristics of the reactor when there is no adsorption (e.g., the residence time and the liquid volume). For this, an inlet step signal of an inert electrolyte (sodium chloride) at a very low concentration (0.015 M) is introduced in the reactor at the usual flowrate of 1 mL. min⁻¹. The response signal of the system is determined at the outlet by measuring the conductivity using an InLab 731-ISM probe from Mettler Toledo (with an external diameter of 12 mm) placed in cell (7) (refer to **Figure 1**). This is called the breakthrough. When the outlet conductivity reaches the conductivity of the inlet solution (which is measured beforehand), the system is purged from the electrolyte by switching the inlet flow to a step function of water. When the outlet conductivity reaches that of water, the experiment is stopped. The residence time and liquid volume can be determined from either the breakthrough or purge signals, using theoretical calculations of the first moment. For further detail on this technique, the reader is referred to the study of *Robin et al. (2020)*¹.

This study has been conducted on the system in three cases:

1. With the reactor in bypass mode, to measure the residence time and liquid volume in the tubing and the cells (7) and (8) at the reactor outlet (refer to **Figure 1**).
2. With the reactor only containing the inert glass beads.
3. With the reactor containing the glass beads and γ -alumina solids previously impregnated with nickel till saturation, to determine the liquid volume and residence time in the actual impregnation system when no adsorption takes place.

The theoretical calculations using the purge curve for the case 3) are shown in **Figure S2**. They are compared with the output conductivity signal from one impregnation experiment at initial proton and nickel concentrations of 10⁻⁵ M and 0.05 M, respectively.

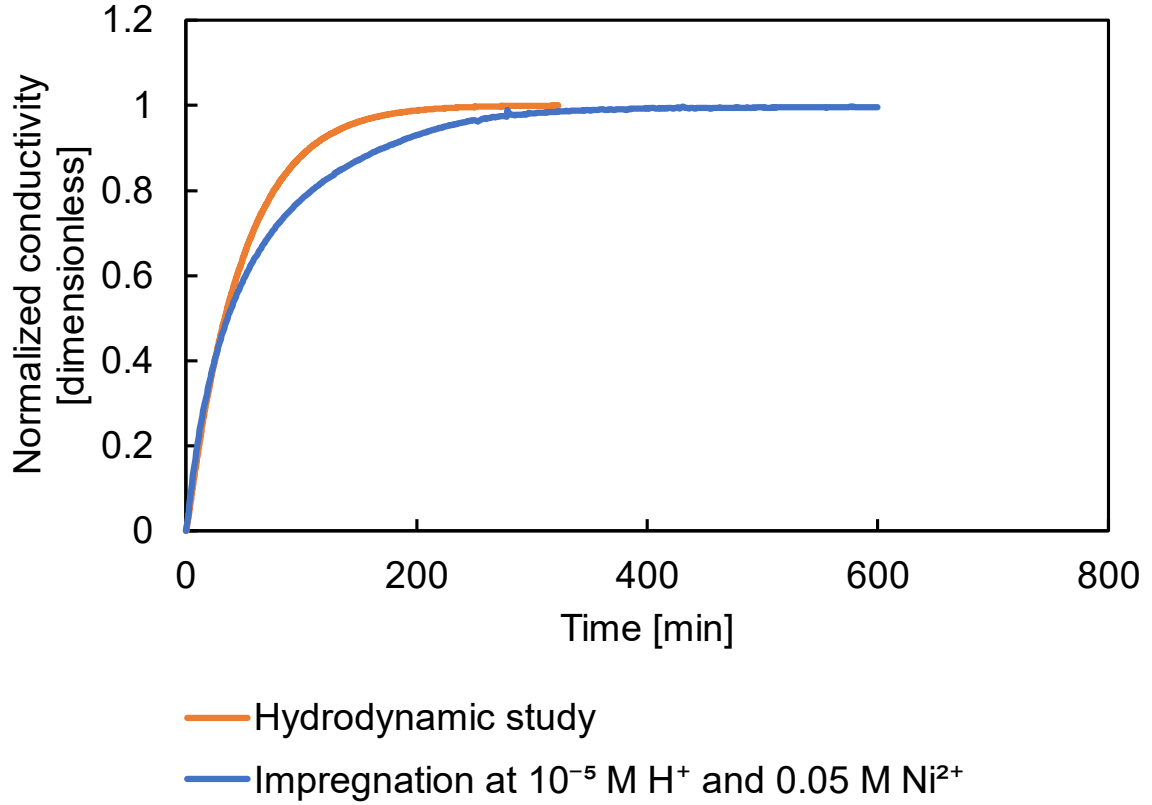


Figure S2. Comparison of the output conductivity signals obtained during 1) the hydrodynamic study of the system with the reactor containing inert glass beads and saturated alumina solids and 2) an impregnation experiment at initial proton and nickel concentrations of 10^{-5} M and 0.05 M, respectively.

In statistics, a moment is a theoretical value that can be used to characterize signals. The moment of order n (or μ_n) of an outlet signal (which is the conductivity or EC in this case) in response to a step inlet function is calculated as:

$$\mu_n = \int_0^{\infty} t^{n-1} \left(1 - \frac{EC(t)}{EC_0} \right) dt \quad (\text{S1})$$

where μ_n is expressed in min; $EC(t)$ is the conductivity at the outlet measured at the time t (in $\mu\text{S}\cdot\text{cm}^{-1}$); and EC_0 is the inlet conductivity at $t = 0$ min². The first moment μ_1 (i.e., the moment of order $n = 1$) is used to characterize the time response of the variables measured at the outlet liquid phase and corresponds to the residence time in the system. Applying **eq. S1** yields a residence time of 47 min for the reactor filled with the solids in the case of no adsorption, which corresponds to a liquid volume of 47 mL. This experimental liquid volume is very close to the theoretical liquid volume of the reactor measured experimentally (by weighing the reactor before and after filling it with water), which proves that the reactor is perfectly stirred.

Notice how the evolution of the output conductivity during the hydrodynamic test is faster than the one during impregnation since in the latter case adsorption occurs, which increases the residence time.

S3: Further details on the laser and spectrometers used for the LIBS technique, as well as the sample preparation technique.

More details on the characteristics of the laser and the two spectrometers used for the LIBS analysis are provided in **Tables S1** and **S2**, respectively.

Table S1. Laser characteristics.

Wavelength (nm)	Frequency (Hz)	Pulse duration (ns)	Laser energy (mJ)	Step size between laser shots (or resolution) (mm)	Total number of shots (–)
1064	100	8	2	0.02	14400

Table S2. Characteristics of the two spectrometers.

	First Czerny-Turner spectrometer	Second Czerny-Turner spectrometer
Spectral range (nm)	223 – 311	309 – 373
Spectral resolution (nm)	0.21	0.14
Delay during acquisition (ns)	800	700
Gate width during acquisition (ns)	2000	5000
Gain (–)	1000	1500

Regarding the sample preparation for the LIBS analysis, impregnated solids are removed from the reactor once the desired residence time is achieved. The external surface is carefully dried with a cloth and the solids are cut near the extrudate center using a sharp scalpel to form a surface as smooth as possible (an earlier study conducted by *Catita et al. (2020)* shows the nickel distribution profiles to be constant at different extrudate lengths near the center)³. This step takes about 10 min since several extrudates are dried at the same time and they are all cut

before starting the LIBS analysis for repeatability. The prepared samples are analyzed one at a time; each sample is placed on the moving plate of the LIBS equipment (which takes around 3 min) and the cut surface is exposed to the laser. The plate moves in the x and y directions in a serpentine motion as shown in **Figure S3** so the laser can scan the whole surface. The spatial resolution between every laser pulse is 0.02 mm. It takes 2.4 min for the laser to cover the whole solid surface.

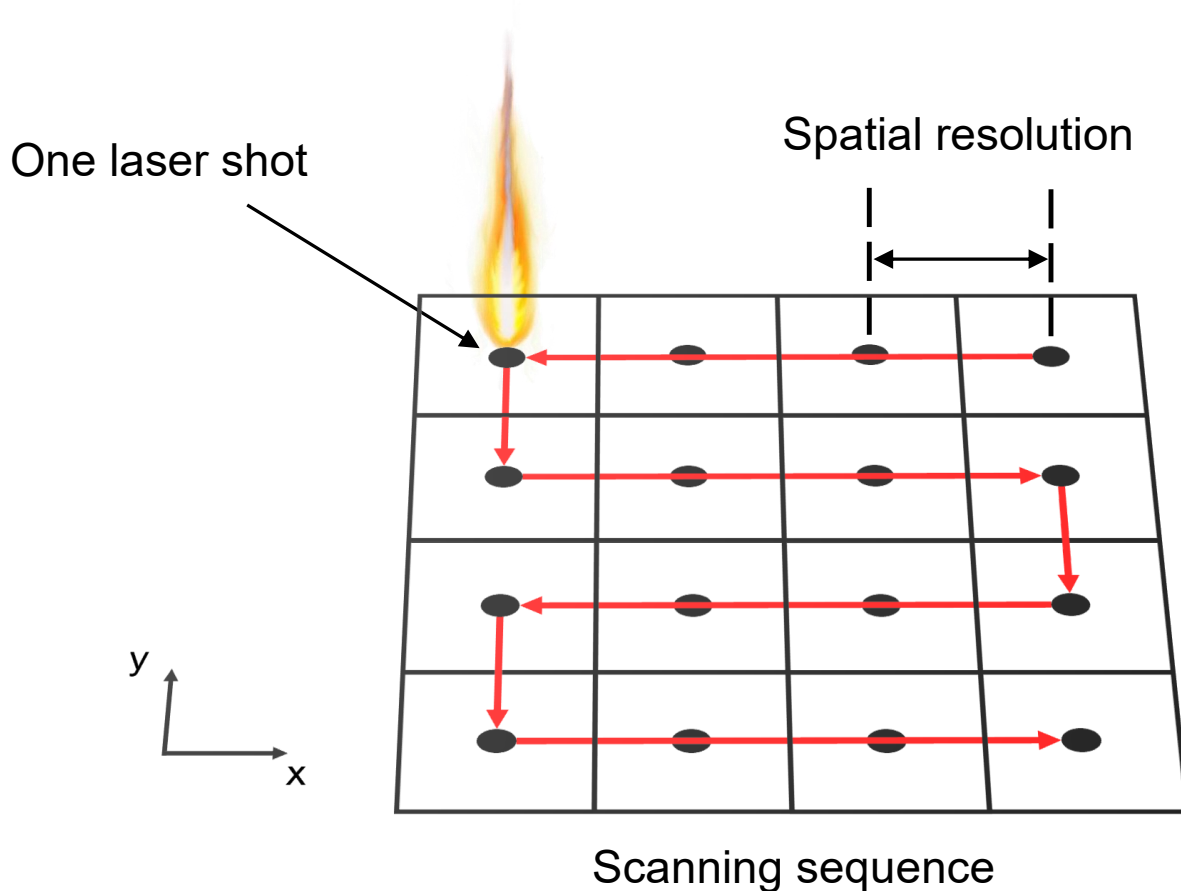


Figure S3. Schematic representation of the pulse sequence of the laser on the solid surface during LIBS analysis.

The effect of the sample preparation time has also been investigated. Extrudates impregnated at 0.05 M of nickel and 0.01 M of protons for 80 min are removed from the reactor and their external surfaces are dried. In this test, however, the extrudates are separated into three lots. The first lot is cut and analyzed by LIBS directly after drying (this lot is referred to as 0 min), while waiting times of 15 and 30 min are allowed before cutting the second and third lots, which are referred to as 15 min and 30 min, respectively. After the respective waiting times, the extrudates from each lot are cut and analyzed by LIBS. The 2D images and nickel distribution profiles obtained from the LIBS analysis of extrudates from the three lots are compared in **Figure S4** below.

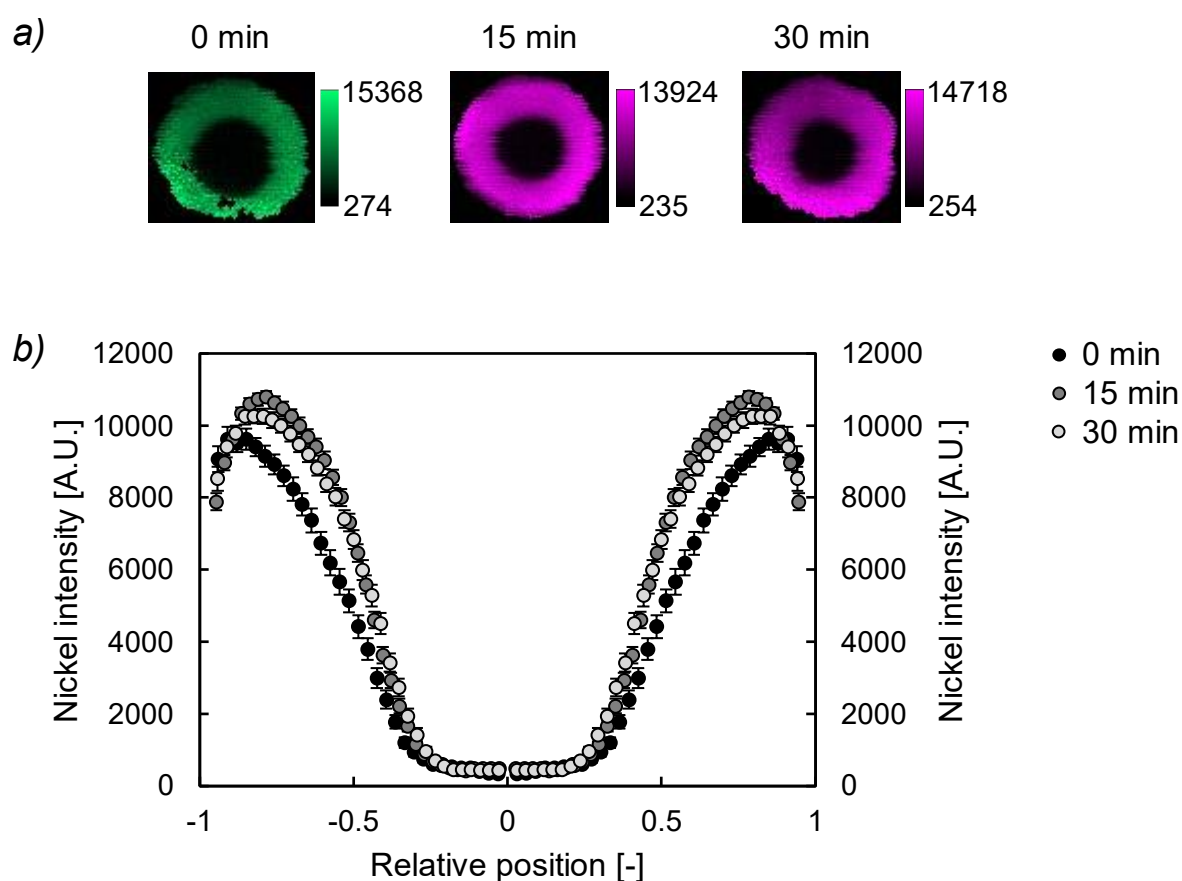


Figure S4. a) 2D images obtained from the LIBS analysis of impregnated alumina extrudates with waiting times of 0, 15, and 30 min before cutting the samples and

analyzing them, along with their b) nickel distribution profiles (based on the intensity). The extrudates were impregnated at 0.05 M nickel and 0.01 M protons for 80 min. The legend corresponds to the waiting times before cutting the extrudates for analysis.

Some differences exist between the three profiles. When waiting times are allowed before cutting the samples, the nickel species can travel a little further inside the extrudates modifying the nickel distribution. Based on these findings, it is decided to dry and cut the extrudates directly after removing them from the reactor, and then conduct the LIBS analysis when the whole batch of extrudates to be analyzed has been prepared. In this case, the difference is much smaller between samples removed, dried, and cut at approximately the same time but analyzed at different times, as is shown in **Figure S5**.

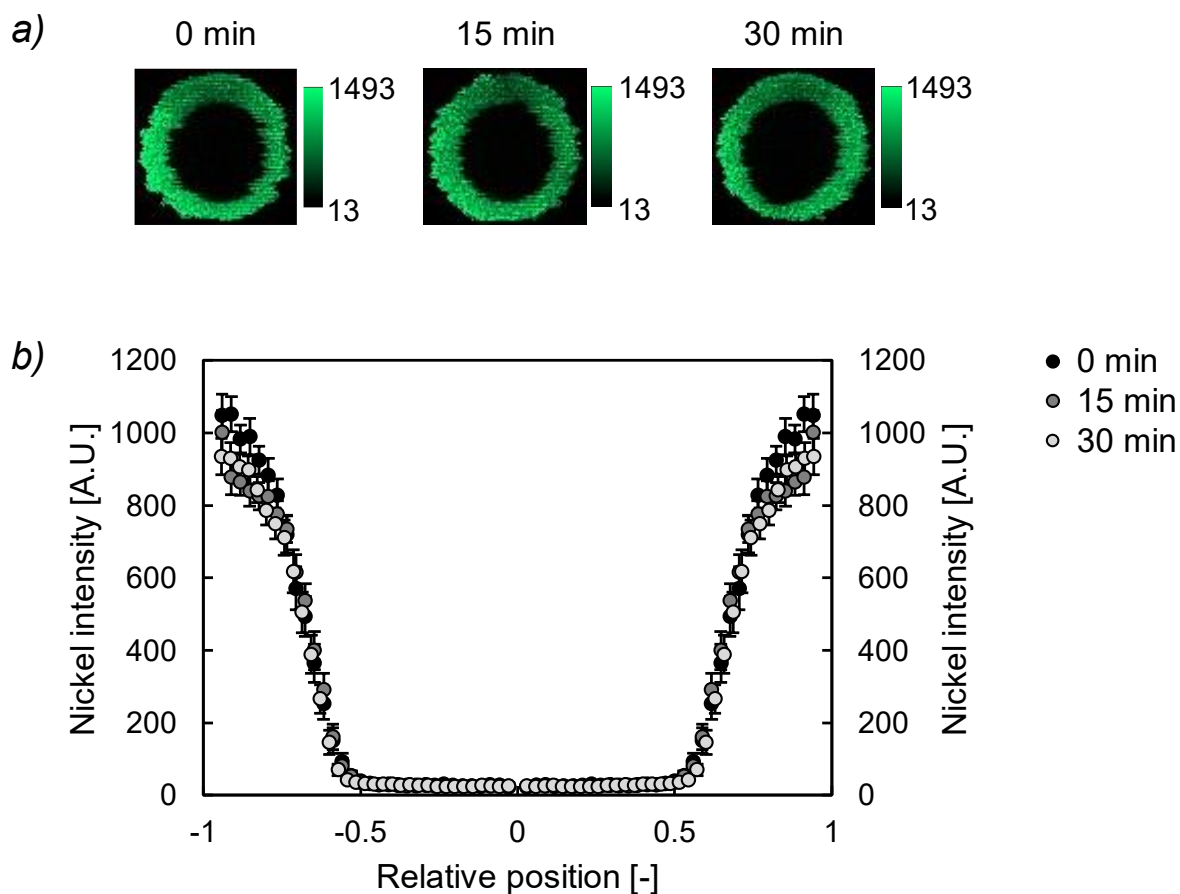


Figure S5. a) 2D images obtained from the LIBS analysis of impregnated alumina extrudates with waiting times of 0, 15, and 30 min after cutting the samples and before analysis, along with their b) nickel distribution profiles (based on the intensity). The extrudates were impregnated at 0.5 M nickel and 10^{-5} M protons for 10 min. The legend corresponds to the waiting times before the LIBS analysis.

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