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1 Direct multi-elemental imaging of freshly impregnated catalyst by 2 Laser-Induced Breakdown Spectroscopy

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8
9 *KEYWORDS LIBS imaging, Alumina, catalyst, impregnation, additive*

10

11 **ABSTRACT**

12 The preparation step of a catalyst is of primary importance as it may govern its performance. We report
13 here the first direct multi-elemental imaging of an alumina-supported catalyst during the maturation
14 process. Alumina extrudate support was impregnated with a nickel nitrate solution in the presence of
15 citric acid as an organic additive. Wet extrudates were sampled, cut in half and imaged by Laser-Induced
16 Breakdown Spectroscopy (LIBS) for varying maturation times. Results were validated by comparison with
17 more conventional techniques such as Raman and Magnetic Resonance Imaging. This communication
18 demonstrates the speed of acquisition, low detection limits and multi-elemental capabilities of LIBS to
19 provide valuable information to understand the phenomena occurring during catalyst impregnation. The

20 proposed approach allows one to shorten drastically the analysis time (by a factor of 30) and emphasizes
21 LIBS imaging potential as a unique characterization technique able to simultaneously monitor the distri-
22 bution of the metallic precursor, organic additive and support impurities.

23

24 **INTRODUCTION**

25 The preparation step of a heterogeneous catalyst is of paramount importance to control how the active
26 phase is dispersed on the support surface and distributed within the support [1]. These latter properties
27 may directly influence the catalyst performance and thus catalytic processes efficiency. Most of the in-
28 dustrial catalysts are prepared through incipient wetness impregnation. Active phase precursors are dis-
29 solved in a solution, sometimes with an additive. Dry support is then put in contact with a volume of this
30 solution equal to the support porous volume. After impregnation, the catalyst is left to mature for a
31 sufficient-time to allow the precursors to diffuse into the core. Matured catalyst is then dried, sometimes
32 calcined, and activated before use. Studying the maturation step of the catalyst is of utmost importance
33 for two reasons. First, in order to understand and rationalize the phenomena arising at this step, to adjust
34 solution and support characteristics (kind of precursor and solvent, concentration of precursors, pres-
35 ence of additives, specific surface area and porous volume of the support, etc.) to finally obtain the de-
36 sired dispersion and distribution of the active phase. Second, the maturation step governs the efficiency
37 of the industrial catalyst production line. On that purpose, several characterization techniques have been
38 employed such as Raman imaging [2,3], Magnetic Resonance Imaging (MRI) [3–10] or UV-visible spec-
39 troscopy [2,3,11]. All these techniques have shown serious limitations when applied to maturation pro-
40 cess investigation. MRI is an indirect method, with difficulties of image interpretation for multi-elemental
41 impregnation solutions. Besides, MRI and Raman require quite long acquisition times, which makes

42 these techniques not suitable for the study of fast kinetics phenomena, for example the redistribution
43 of species within the support. Other methods such as selective scratching of the catalyst beads [12],
44 optical microscopy [13–15] or X-ray energy dispersive spectrometry [16] require sample drying or calci-
45 nation before measuring elemental distribution, which may induce several transformations, such as de-
46 composition of the active precursors, formation of new surface species and redistribution effects. Differ-
47 ent models for dry or wet impregnation of catalysts have been proposed [10,12–18] in order to simulate
48 the final active phase distribution. Some of them take into account competitive impregnation [15,17].
49 The availability of direct, fast, and multi-elemental spatially resolved characterization techniques is of
50 primary importance for validation and improvement of such models.

51 Recently, laser-induced breakdown spectroscopy (LIBS) has emerged as a promising characterization
52 technique providing fast and multi-elemental imaging with high sensitivity and relevant spatial resolu-
53 tion to characterize the precursors and additive distribution at the catalyst's bead scale [19,20]. Besides,
54 this technique offers the possibility to operate under ambient conditions. LIBS imaging has been already
55 successfully applied to characterize elemental distribution on calcined [21] or dried [22] catalyst surface.
56 This communication reports the very first application of LIBS imaging on a maturing supported catalyst.
57 A nickel based catalyst supported on γ -alumina in the presence of an organic additive (here citric acid)
58 was chosen as a model system to exemplify this methodology. LIBS images were validated by comparison
59 with MRI and Raman imaging. This work aims to emphasize LIBS potential as a unique characterization
60 technique to simultaneously monitor the transport of the metallic precursor and organic additive at the
61 very initial times of the maturation stage, which can give new insights to optimize the preparation step
62 of heterogeneous catalysts.

63 **MATERIALS AND METHODS**

64 **Impregnation solution and support**

65 A solution of nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 98.5% purity) in deionized water was pre-
66 pared to obtain a concentration of $[\text{Ni}] = 0.05 \text{ mol/L}$ for nickel. Citric acid (CA) (Sigma-Aldrich, 99.5% pu-
67 rity) was added to this solution to obtain two impregnation solutions of $[\text{CA}] = 0.06 \text{ mol/L}$ and $[\text{CA}] = 0.2$
68 mol/L for citric acid. A single mesoporous $\gamma\text{-Al}_2\text{O}_3$ trilobed extrudate of 1.2–1.3 mm diameter and 6 mm
69 length, $0.6 \text{ cm}^3/\text{g}$ porous volume and $250 \text{ m}^2/\text{g}$ specific surface area was immersed during 30 s in 20 ml
70 of the impregnation solution. The extrudate was removed from the solution, wiped with absorbent pa-
71 per, and left to mature for a given maturation time T_M . The extrudate was cut in half, perpendicularly to
72 the direction of extrusion with a scalpel, and one of the half-extrudate was set aside to be imaged by
73 LIBS. The procedure was repeated for different extrudates, different maturation times ranging from 30 s
74 to 23 h and for both impregnation solutions. Such procedure mimics the incipient wetness impregnation
75 procedure while being easier to perform and more reproducible for single extrudates preparation.

76 **LIBS imaging**

77 The half extrudate was positioned on the LIBS sample holder with modeling paste so that the fresh cut
78 surface was horizontal and upwards. The LIBS instrument used in this study has already been described
79 in detail in a previous article [23]. A nanosecond Nd:YAG laser source was employed, operating at a 100
80 Hz repetition rate and emitting in the fundamental wavelength (1064 nm). The laser beam was focused
81 vertically into the sample surface by a 15× magnification objective. The laser energy was set at 1.5 mJ
82 leading to a typical crater size of less than 15 μm . Extrudates were scanned with the help of a motorized
83 *xyz* stage. A 15 μm step size was used by adjusting the motor speed according to the fixed laser repeti-
84 tion rate. Images of a single extrudate were 142×120 pixels wide and were acquired in 170 s. Homemade
85 software developed in the LabVIEW environment controlled the whole system and allowed automated

86 sequences in order to scan the region of interest. The plasma radiation was collected by two lens-fiber
87 systems, positioned with an angle of 35° relative to the sample surface. The outputs of the fibers were
88 connected to two independent Czerny-Turner spectrometers, a Shamrock 500 (Andor Technology) and a
89 Shamrock 303 (Andor Technology). Each of these spectrometers was equipped with an intensified CCD
90 camera (iStar, ICCD, Andor Technology). The spectral acquisition was performed by the synchronization
91 between the Q-switch of laser and the ICCD cameras. All experiments were carried out in ambient at-
92 mosphere with an argon gas flowing the plasma region (1.6 L/min) to both improve the signal to noise
93 ratio and prevent any surface contamination by ablated material deposition from previous laser shots.
94 Selected emission lines of each element of interest are summarized in supplementary Table 1. On each
95 pixel of an extrudate image, the net intensity of a given emission line was obtained by subtracting the
96 emission background on a spectral window, far from any emission line, from the intensity on a spectral
97 window centered around this emission line.

98 **MRI**

99 A wiped extrudate was placed vertically in a 1.7 mm diameter capillary tube further inserted in a 5 mm
100 NMR tube. MRI experiments were performed in a Bruker Avance 400 MHz (¹H) spectrometer equipped
101 with a 5 mm imaging probe (Micro5) and *xyz* gradient amplifiers (300 × 300 × 300 G/cm) at 60 A current,
102 which allowed selecting the voxels of interest. Experiments were carried out at a temperature of 17 °C.
103 Axial-oriented images were obtained using a spin-echo sequence, which consists of a $\pi/2$ pulse of 22.5
104 μ s length followed by a π pulse. A field of view of 2.5 × 2.5 × 8 mm and 64 × 64 × 8 acquisition points was
105 chosen, resulting in a voxel size of 39 μ m × 39 μ m × 1000 μ m. A slice thickness of 1 mm was defined. For
106 each MRI experiment, 8 images were obtained, each one corresponding to a certain position along the
107 *z* axis of the pellet. Only the images corresponding to the central *z* axis slice will be shown. The transport
108 of nickel and citrate ions was monitored simultaneously using the ¹H MRI method reported earlier [3,4].

109 As a result of the repetition time (T_R) and echo time (T_E) chosen (500 ms and 2.5 ms, respectively),
110 protons near nickel ions are observed thanks to a T_2 contrast (long T_E comparing to the T_2 of protons
111 close to Ni), while protons near citric acid were observed thanks to a T_1 contrast (small T_R comparing to
112 T_1 of protons close to the organic additive). Using such parameters, low or even null pixel intensity cor-
113 responds to high Ni local concentration, whereas high pixel intensities are attributed to a higher citric
114 acid local concentration in respect to Ni local concentration. The shorter image acquisition time for all
115 volumes was 17 min. Relaxation times were measured using Rapid Acquisition with Relaxation Enhance-
116 ment with variable repetition time T_R sequence (RARE) [24]. Proton T_1 and T_2 of pure water inside γ -
117 Al_2O_3 support was 370 ms and 4 ms, respectively. In the presence of nickel ions, these values were de-
118 creased to approximately 15 ms and 2 ms, respectively, at the lowest Ni concentration used. On the
119 contrary, T_1 value is increased to 470 ms in the presence of citric acid at the lowest CA concentration
120 used, while the T_2 value remained almost the same (4 ms). Paravision 5.1 software was used for 1H MRI
121 images acquisition.

122 Raman

123 A half wiped extrudate was positioned with the fresh cut surface upwards in a Renishaw inVia Reflex
124 Raman microscope. Excitation line of 532 nm wavelength and 3.5 mW power was provided by a Nd:YAG
125 laser fitted with EasyConfocal Renishaw device. The scattered light was dispersed with a 2400 lines/mm
126 grating leading to a spectral resolution around 0.9 cm^{-1} . Raman images were acquired in the Streamline
127 mode [25] with 60 s exposure and $16.2\text{ }\mu\text{m} \times 16.2\text{ }\mu\text{m}$ pixel size. The shorter acquisition time of a spectral
128 image lasted 9 h. The band at 1417 cm^{-1} , ascribed to the stretching vibrations of carboxylate group (COO^-
129) [26], allowed citrate distribution imaging from the intensity at 1417 cm^{-1} .

130 RESULTS

131 **Nickel and carbon imaging**

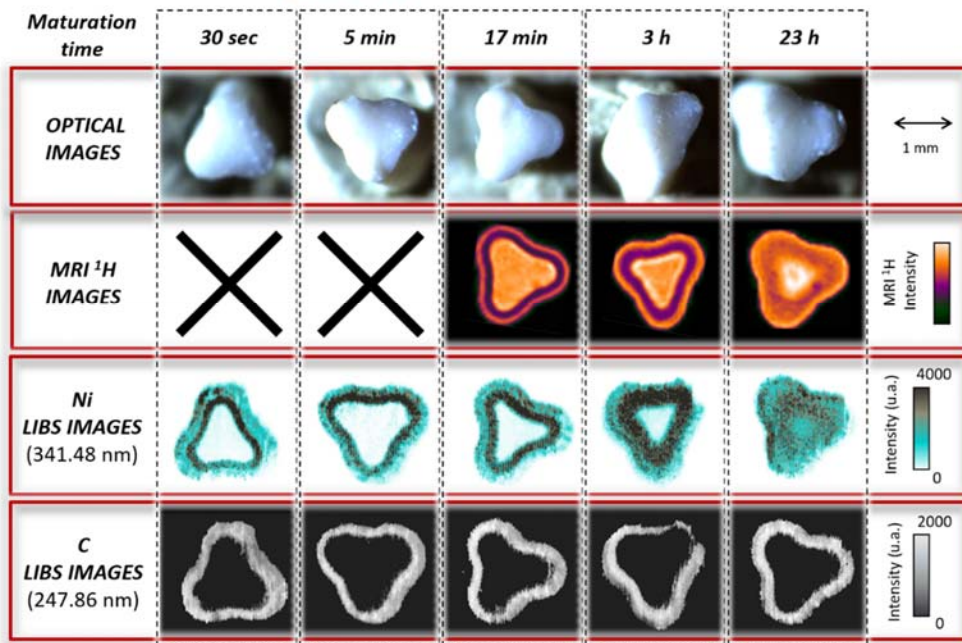
132 LIBS intensities images for nickel (Ni) and carbon (C) together with ^1H MRI images and citrate Raman
133 images are reported in Figure 1. Similar behaviour is observed for both impregnation solutions. Carbon
134 is distributed in a corona around the extrudate surface whatever the maturation times, whereas nickel
135 distribution is evolving over maturation time. One can clearly notice the thicker C corona for the more
136 CA concentrated solution. LIBS C elemental distribution is coherent with Raman imaging of citrate and
137 LIBS Ni distribution is in accordance with MRI. During transient regime, one can clearly notice an over-
138 concentration of Ni, just in the internal face of the C layer, and a significant concentration of Ni, overlap-
139 ping the C layer. Such information could not be extracted from Raman and MRI images. As LIBS mapping
140 is fast (measurement in less than 3 minutes), shorter maturation times were also accessible. In addition,
141 since LIBS measures only the first microns thick upper the sample surface, it is reasonable to assume
142 that the samples are (at least partially) dried at the time the extrudate is cut, before analysis. The ob-
143 served C and Ni distributions indicate a competitive adsorption mechanism between the active phase
144 precursor and the additive, resulting in a preferential adsorption of citrate ions on the γ -alumina surface
145 in relation to Ni ions. Consequently, egg-shell profiles of C are obtained, while almost uniform Ni profiles
146 are found at long maturation times.

147

148

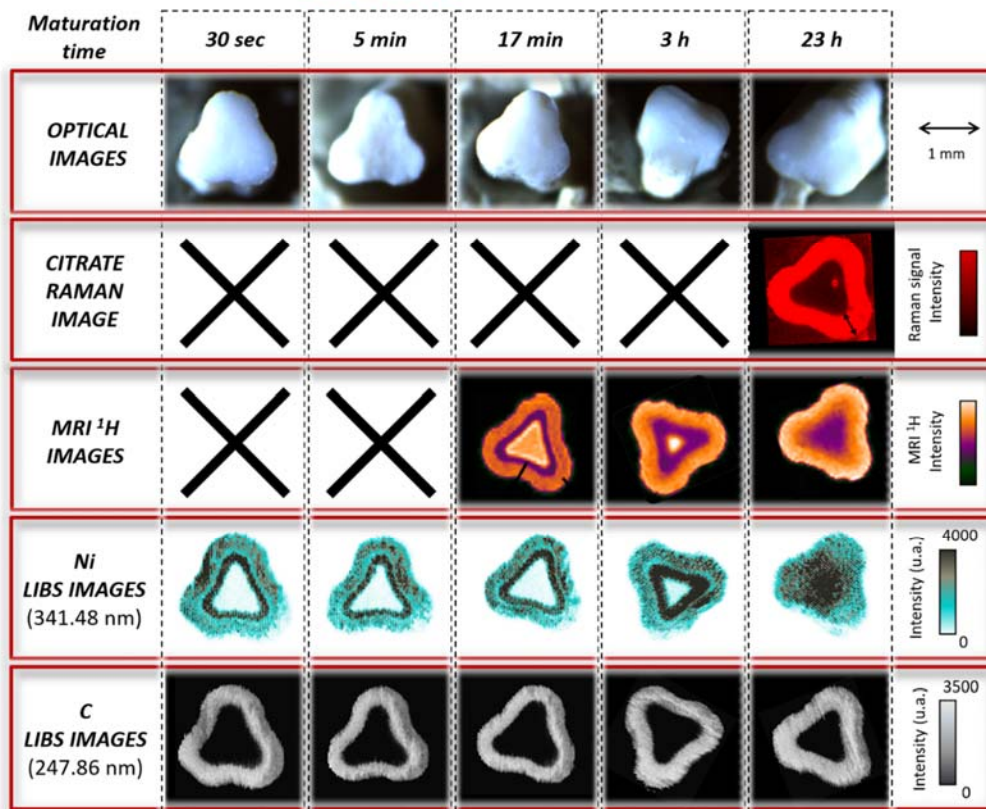
149

Solution 1 - [CA]=0.06 mol/L



150

Solution 2 - [CA]=0.2 mol/L

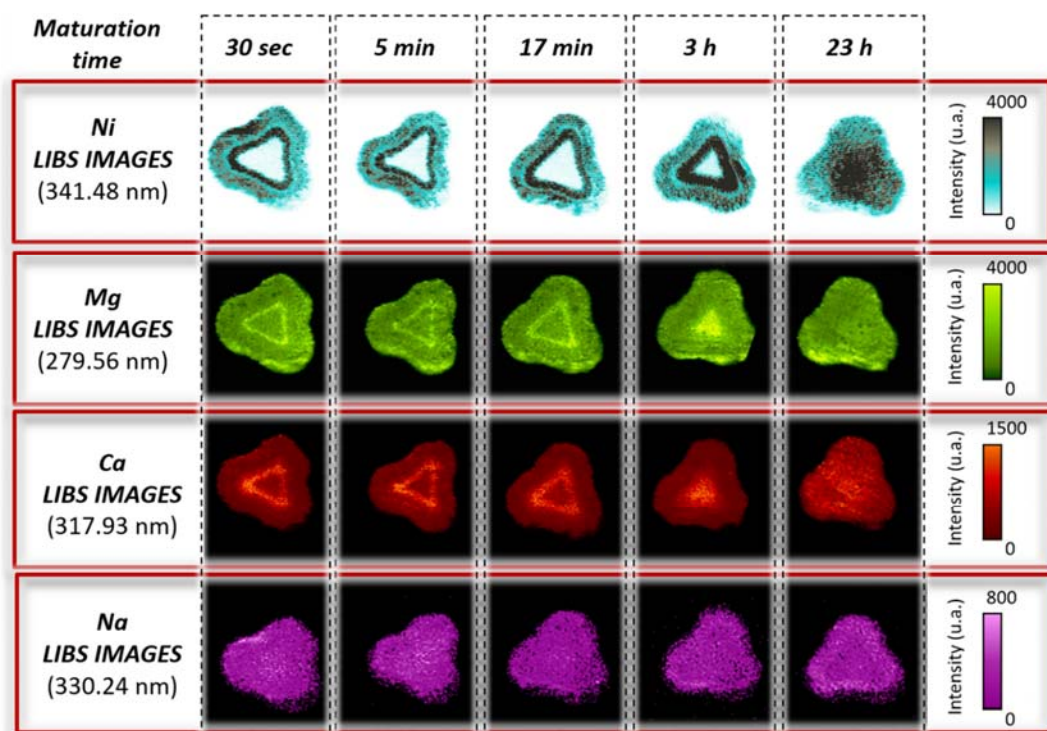


151

152 Figure 1. Ni and C LIBS intensities images, ^1H MRI and Raman citrate images for varying maturation times
153 T_M and impregnation solutions.

154 Support impurities imaging

155 Figure 2 shows LIBS imaging of support impurities that are displaced during the catalyst maturation.
156 We show for the very first time Mg, Ca and Na distribution evolving during the maturation process. These
157 elements are present in the alumina support and each one has a specific behavior during the impregna-
158 tion process. As Na seems to remain well distributed regardless the maturation time, Mg and Ca appear
159 to be pushed in the front of the Ni layer. This observation suggests a different strength of interaction
160 with alumina surface (Ca and Mg are less tightly bound to alumina surface than Na) or a different nature
161 (Mg and Ca are on hydroxydes forms which are dissolved by the acid solution whereas Na is not).



162

163 Figure 2. Ni, Mg, Ca, and Na LIBS intensities images for varying maturation times T_M for $[\text{CA}]=0.2$ mol/L.

164 **DISCUSSION**

165 These results show that LIBS imaging technique is particularly suitable to characterize the maturation
166 step of catalysts. LIBS elemental mapping provides a fast and direct analysis of the distribution of the
167 active phase and additive along alumina surface. It is important to notice that both active phase precursor
168 and additive are detected simultaneously with LIBS, allowing a unique and direct characterization of
169 the transport of the metallic precursor and organic additive. Short acquisition times provided by LIBS
170 technique allow the characterization of extrudates in the earliest times of the maturation process (30 s).
171 Until now, such acquisition times were not accessible as the first map could not be obtained before 17
172 minutes with MRI technique and several hours of acquisition are required to obtain Raman mappings in
173 streamline mode. At the longest maturation times, LIBS imaging is entirely in accordance with MRI and
174 Raman analysis, while revealing relevant new information with regards to the less concentrated species.
175 The multi-elemental capabilities of LIBS combined with its high sensitivity allows one to image the trace
176 impurities that are displaced during the catalyst maturation, involving very low concentrations down to
177 the ppm scale.

178 **CONCLUSION**

179 This work shows the high potential of LIBS imaging technique to image catalysts at different times of
180 the maturation step. Performed at ambient conditions, LIBS enables imaging wet samples without oper-
181 ating issues. Its multi-elemental capabilities allowed us to monitor simultaneously the active phase pre-
182 cursor (Ni) and the organic additive (C) that in the past required the use of different analytical ap-
183 proaches. Its sensitivity revealed the displacement (Mg and Ca) or the strong anchoring (Na) of the sup-
184 port impurities during maturation. Its speed of acquisition (image of an extrudate in less than 3 minutes)
185 enabled studying the early times of the maturation process never accessible until now with conventional

186 techniques. Such capabilities are expected to be of primary importance for the understanding of phe-
187 nomena during catalyst preparation and the development of quantitative impregnation models.

188 **ASSOCIATED CONTENT**

189 LIBS optical emission lines used in this study are available as supporting information.

190 **AUTHOR INFORMATION**

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193 **Author Contributions**

194 L.J.: Investigation, Formal analysis, Validation, Visualization, Writing - Review & Editing

195 L.C.: Methodology, Investigation, Writing - Review & Editing

196 O.D.: Methodology, Writing - Review & Editing

197 C.-P.L.: Conceptualization, Writing - Review & Editing, Supervision

198 L.S.: Conceptualization, Writing - Original Draft

199 V.M.-R.: Conceptualization, Methodology, Writing - Review & Editing

200 **ABBREVIATIONS**

201 CA, citric acid, LIBS, laser-induced breakdown spectroscopy, MRI, nuclear magnetic resonance imaging,

202 NMR, nuclear magnetic resonance.

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- 289
- 290

291

292

Supplementary Table 1

Element of interest	Selected emission line (nm)
Ni	341.48
C	247.86
Mg	279.56
Ca	317.93
Na	330.24

293