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# 1 **Imprinting isolated single iron atoms onto mesoporous silica by templating** 2 **with metallosurfactants**

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## 19 **Abstract**

### 20 *Hypothesis*

21  
22 One of the main drawbacks of metal-supported materials, traditionally prepared by the  
23 impregnation of metal salts onto pre-synthesized porous supports, is the formation of large  
24 and unevenly dispersed particles. Generally, the larger are the particles, the lower is the  
25 number of catalytic sites. Maximum atom exposure can be reached within single-atom  
26 materials, which appear therefore as the next generation of porous catalysts.

### 27 *Experiments*

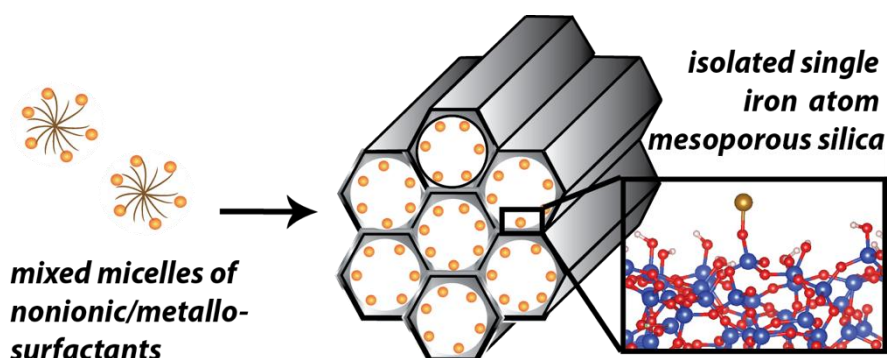
28 Herein, we designed single iron atom-supported silica materials through sol-gel hydrothermal  
29 treatment using mixtures of a non-ionic surfactant (Pluronic P123) and a metallosurfactant  
30 (cetyltrimethylammoniumtrichloromonobromoferrate, CTAF) as porogens. The ratio between  
31 the Pluronic P123 and the CTAF enables to control the silica structural and textural  
32 properties. More importantly, CTAF acts as an iron source, which amount could be simply  
33 tuned by varying the non-ionic/metallo surfactants molar ratio.

34

## 35 Findings

36 The fine distribution of iron atoms onto the silica mesopores results from the iron distribution  
37 within the mixed micelles, which serve as templates for the polymerization of the silica  
38 matrix. Several characterization methods were used to determine the structural and textural  
39 properties of the silica material (XRD, N<sub>2</sub> sorption isotherms and TEM) and the homogeneous  
40 distribution and lack of clustering of iron atoms in the resulting materials (elemental analysis,  
41 magnetic measurements, pair distribution function (PDF), MAS-NMR and TEM mapping).  
42 The oxidation and spin state of single-iron atoms determined from their magnetic properties  
43 were confirmed by DFT calculations. This strategy might find straightforward applications in  
44 preparing versatile single atom catalysts, with improved efficiency compared to nanosized  
45 ones.

## 46 Graphical abstract



## 48 Keywords:

49 Single iron atom catalysts, mesoporous silica, metallosurfactants, Density Functional Theory,  
50 spin state, pair distribution function.

## 51 1. Introduction

52 Increasing the number of active sites of a material in order to enhance its catalytic  
53 activity is a continuous challenge [1–3]. This is commonly addressed by increasing the  
54 active surface area of catalytic particles and thus by decreasing their size. The most  
55 promising catalysts with the lowest size limit and thus, the highest atom efficiency are  
56 considered isolated single atom catalysts (SACs) [4–10]. Several studies already  
57 demonstrated the efficiency of SACs compared to nanosized catalysts. For instance, in  
58 the water gas shift reaction [11] catalyzed by Ir<sub>1</sub>/FeO<sub>x</sub>, single atoms promoted more

59 than 70% of the catalytic activity, while subnano clusters and nanoparticles accounted  
60 for less than 30%. Pt-based SAC also proved to have high activity for the CO oxidation  
61 reaction [12,13]. This was correlated with the existence of vacant 5d orbitals of Pt ions,  
62 which reduce both the CO adsorption energy and the reaction activation barriers  
63 [13,14]. Also Au-based SAC dispersed on FeO<sub>x</sub> nanocrystallites showed higher  
64 stability and sintering resistance compared to conventional Au nanostructures [15,16].  
65 Liu *et al.* [17] succeeded to synthesize Pd/TiO<sub>2</sub> SACs, having nine times higher activity  
66 for C=C bond hydrogenation reaction than commercial Pd catalysts.

67 The main advancement of the SAC strategy was to reach similar or better catalytic  
68 activity with non-precious metal catalysts compared to expensive noble metals [18–  
69 22]. Thus, Pt catalysts could be replaced by Co[18] or Fe[19]-based SACs in the  
70 oxygen reduction reaction (ORR). The latter actually outperformed all ORR's reported  
71 catalysts to date, including commercial Pt/C.

72 Despite the progress in this topic, one important challenge remaining is the preparation  
73 of SACs, with a tuned porosity and a controlled metal loading, while preventing  
74 agglomeration and migration of isolated atoms [17,23]. In 2002, Tilley *et al.* [24]  
75 proposed a new strategy for the preparation of single-site iron (III) centers, through  
76 grafting reactions of iron complex with pre-synthesized SBA-15, and proved their high  
77 selectivities as catalysts for oxidation of alkanes, alkenes, and arenes. More recently,  
78 Hock *et al.* [25] compared the catalytic performance for selective propane  
79 dehydrogenation of isolated Fe(II) synthesized via grafting on silica, iron oxide  
80 particles, and metallic nanoparticles. Herein, we show for the first time that micelles of  
81 ferrosurfactants can act as both porogen of the silica framework and as fine imprinters  
82 of iron atoms at the surface of mesopores, leading thus to the formation of mesoporous  
83 silica-supported isolated single iron atom catalysts (Fe/SiO<sub>2</sub> SACs) via direct one-step  
84 method. The interest in such catalysts comes from their wide applications as  
85 bifunctional metal-acidic catalysts for biomass upgrading [26], syngas production [27],  
86 Fisher-Tropsch synthesis [28–30], Friedel-Craft alkylation [31], or oxidation reactions  
87 [24,32–34].

88 Common synthesis methods of Fe@SiO<sub>2</sub> involve either the salt impregnation of a pre-  
89 synthesized silica support with an iron salt solution [35] or the co-precipitation method  
90 [36]. However, those routes suffer from the formation of large nanoparticles aggregates

91 and the interference of metal precursors during the polycondensation of the silica  
92 framework. Campelo *et al.* [37] compared different synthesis methods and showed that  
93 the co-precipitation of silica and metal precursors directed by hydrothermal sol-gel  
94 synthesis gives a better dispersion of metal species on the silica surface than the salt  
95 impregnation of a pre-synthesized silica support. However, the metal precursors  
96 interfere with the polycondensation of the silica framework, resulting in undesirable  
97 altered structural morphology [38]. Improvement of nanoparticles distribution in a  
98 mesoporous silica matrix could be reached by using self-assembled surfactant phases,  
99 such as micelles or liquid crystals [39–41]. Among them, our group reported  
100 ferrosurfactants which are able to form either micelles [42], vesicles [43] or to stabilize  
101 solid lipid nanoparticles. The latter, dispersed in a micellar solution of a non-ionic  
102 surfactant, P123, could lead to highly dispersed iron oxide nanoparticles within a  
103 mesoporous-macroporous silica matrix. The ferrosurfactant acted as the only source of  
104 iron and thus triggered the formation of nanoparticles within the macropores [44].  
105 More recently, Yang *et al.* [20] also proposed a non-ionic surfactant (F127<sup>®</sup>)-assisted  
106 method for single iron atoms catalyst synthesis enabling the dispersion of iron species  
107 and therefore exhibiting a higher catalytic activity for ORR application.

108 Motivated by these pioneering works, the present study aims to elaborate mesoporous  
109 silica materials with supported isolated single iron atoms, Fe@silica SACs, through a  
110 sol-gel self-assembling mechanism from mixed micelles of non-ionic and metallo-  
111 surfactants. The non-ionic surfactant template (here the Pluronic P123<sup>®</sup>) was chosen to  
112 control the structural and textural properties of the silica framework (high surface-  
113 active area, pore volume, pore size) as it was demonstrated by XRD and N<sub>2</sub> sorption  
114 isotherms. More important, the metallosurfactant allows controlling the iron loading  
115 and the homogeneous distribution of iron atoms and lack of clustering as it was  
116 demonstrated by elemental analysis, STEM mapping, Pair Distribution Function (PDF)  
117 analysis, MAS-NMR and magnetic measurements.

## 118 **2. Materials and methods**

### 119 **2.1. Chemicals**

120 Tetramethylorthosilicate (TMOS), Pluronic<sup>®</sup> P123, and hexadecyltrimethylammonium  
121 bromide (CTAB) were purchased from Sigma-Aldrich. Iron(III) chloride (FeCl<sub>3</sub>) was

122 purchased from Alfa Aesar. All reagents were used without further purification.  
123 Cetyltrimethylammoniumtrichloromonobromoferrate (CTAF,  $C_{16}H_{33}N(CH_3)_3^{3+}$ ,  
124  $FeCl_3Br^-$ ) was synthesized as previously reported [42–44].

## 125 **2.2. Preparation of silica materials**

126 Silica materials were prepared by sol-gel process, through the cooperative templating  
127 mechanism, from micellar solutions of P123 ( $M_w = 5800 \text{ g}\cdot\text{mol}^{-1}$ ) and CTAF ( $M_w = 465.55$   
128  $\text{g}\cdot\text{mol}^{-1}$ ), and TMOS ( $M_w = 152.22 \text{ g}\cdot\text{mol}^{-1}$ ) as inorganic precursor. The micellar solutions  
129 were prepared by adding 200 mg of P123 and an appropriate amount of CTAF (18, 36, 90,  
130 181 mg) in 10 mL of 1M HCl, to reach the CTAF/P123 molar ratio  $r$  of 1, 2, 5 and 10,  
131 respectively. In a typical procedure, 310 mg of TMOS were added to those micellar solutions  
132 to obtain a P123/TMOS molar ratio of 0.017. The mixture was stirred at room temperature for  
133 30 min before being transferred into a Teflon bottle and placed in a stainless-steel autoclave at  
134 373 K for 48 h. The resulting hybrid product was then filtered through a paper filter on a  
135 funnel and dried in air for 24 h. The surfactant can be removed by Soxhlet extraction with  
136 ethanol to lead to pristine silica ( $P@SiO_2(r)$ ) or by calcination, to remove the organic part and  
137 to lead to ferrisilicates ( $Fe@SiO_2(r)$ ). The programming of the calcination procedure was set  
138 as follows: (step 1) increasing temperature from room temperature (RT) to 373 K ( $2K\cdot\text{min}^{-1}$ )  
139 and held for 1 h; (step 2) heating ramp from 373 K to 623 K ( $2K\cdot\text{min}^{-1}$ ) and held for 1 h; and  
140 (step 3) heating ramp from 623 K to 823 K ( $2K\cdot\text{min}^{-1}$ ) and held for 3 h. The yield of the sol-  
141 gel process was 80% while the one of the iron loading in ferrisilicates was evaluated to 25%,  
142 except for  $Fe@SiO_2(10)$ , only 7%.

## 143 **2.3. Characterization methods**

### 144 **2.3.1. Nitrogen sorption measurements**

145 The textural properties of the synthesized materials after calcination were determined  
146 from the nitrogen adsorption/desorption isotherms obtained at 77 K ( $p/p_0$  increasing  
147 from  $10^{-7}$  to 0.99 and decreasing from 0.99 to 0.10) using an automatic Micromeritics  
148 ASAP 2020 instrument. The specific surface area was determined using two methods,  
149 the BET method[45,46] and the NLDFT method [47]. The total pore volume was  
150 determined from the nitrogen adsorption at a relative pressure of 0.97, while the meso-  
151 pore volume  $V_{\text{meso}}$  was calculated by the difference between the total pore volume and  
152 the micro-pore volume calculated using the NLDFT method. The pores size

153 distributions in the mesopore range were determined by the Barret–Joyner–Halenda  
154 (BJH) method with the Kruk–Jaroniec–Sayari (KJS) correction to the desorption  
155 branch of the nitrogen isotherms [48,49]. Pore diameters corresponding to peaks in the  
156 latter PSDs were labelled  $D_{\text{BJH}}$ .

### 157 **2.3.2. X-ray diffraction**

158 The measurements were performed using a Panalytical X'Pert Pro diffractometer equipped  
159 with a Cu tube, a Ge (111) incident-beam monochromator ( $\lambda=1.5406\text{\AA}$ ) and an X'Celerator  
160 detector. Small-angle X-ray scattering (SAXS) measurements were collected using 0.02 rad  
161 Soller slits,  $1/16^\circ$  fixed divergence and anti-scatter slits. The X'Celerator detector was used as  
162 “scanning line detector (1D)” with  $0.518^\circ$  active length. Data collection was carried out in the  
163 scattering angle range  $0.8\text{--}12^\circ$  with a  $0.0167^\circ$  step over 60 min.

### 164 **2.3.3. Elemental analysis**

165 Si and Fe chemical analysis were performed using an Inductively Coupled Plasma Atomic  
166 Emission Spectroscopy (ICP-AES).

### 167 **2.3.4. Transmission electron microscopy and element mapping**

168 Transmission electron microscopy (TEM) analyses were performed using a JEOL 2100 F  
169 electron microscope operating at 200 kV and equipped with a probe Cs corrector. The  
170 “HAADF-STEM” images were acquired in scanning TEM (STEM) using a high angle  
171 annular dark field detector (HAADF). The elemental maps were acquired by Energy  
172 Dispersive X-Ray (EDX) Spectroscopy in STEM mode using a JEOL Silicon Drift Detector  
173 (DrySD60GV: sensor size  $60\text{ mm}^2$ ) with a solid angle of approximately 0.5 sr.

### 174 **2.3.5. Total scattering X-ray measurements and PDF analysis**

175 The total scattering X-ray measurements were performed at the High energy Beamline for  
176 Buried-interface Structures and Materials Processing ID31 of the European Synchrotron  
177 Radiation Facility (ESRF). The data-sets were collected using a large area, high energy  
178 single-photon counting detector, Pilatus3 2M CdTe and a high energy monochromatic beam  
179 ( $68.5\text{ keV}$ ,  $\lambda=0.18099\text{\AA}$ ). Sample powder was loaded into a 1 mm diameter Kapton capillary  
180 tube. The raw two-dimensional data-sets were azimuthally integrated and converted to one-  
181 dimensional intensity versus  $2\theta$  using PyFAI software package [50]. The total scattering

182 measurements have been carried out under the same experimental conditions for all the  
183 studied samples (Fe@SiO<sub>2</sub>(1), Fe@SiO<sub>2</sub>(2), Fe@SiO<sub>2</sub>(5) and Fe@SiO<sub>2</sub>(10)). The collected  
184 data were then corrected for experimental effects (absorption, multiple scattering,  
185 polarization, Compton scattering and Laue diffuse scattering) and the scattering signal from  
186 the air and the experimental set up was measured independently under the exact same  
187 conditions as the samples and subtracted as a background in the data reduction procedure. The  
188 data were truncated at a finite maximum value of  $Q_{\max} = 18 \text{ \AA}^{-1}$  beyond which the signal-to-  
189 noise ratio became unfavorable. All the differential experimental atomic pair distribution  
190 functions (d-PDF) were obtained by using the PDFgetX3 program [51] and following a  
191 procedure previously reported [52,53].

### 192 **2.3.6. Solid-state nuclear magnetic resonance**

193 Solid-state NMR spectra were acquired on an AVANCE III Bruker spectrometer operating at  
194 14 T (<sup>1</sup>H NMR at 600 MHz). A Bruker 4 mm MAS probe was used for the experiment with  
195 MAS frequencies of 12.5 kHz. For <sup>29</sup>Si experiments, the (rf)-field strength applied for the 90°  
196 pulse was set to 50 kHz for a duration of 5 μs. During acquisition, SPINAL-64 <sup>1</sup>H  
197 heteronuclear decoupling was applied at an rf-field strength of 80 kHz, with a pulse length of  
198 5.8 μs [54]. Optimized saturation recovery experiments were used for T<sub>1</sub> relaxation  
199 measurements with a list of 13 recovery delays. For <sup>29</sup>Si experiments a recovery delay of 300s  
200 was used for accumulating 256 scans. Regarding the evolution of <sup>29</sup>Si spinning sidebands, a  
201 recovery delay of 0.5s was used for accumulating 512 scans. A recovery delay of 3s was used  
202 for all <sup>1</sup>H experiments. The <sup>1</sup>H and <sup>29</sup>Si chemical shifts were reported relative to  
203 tetramethylsilane. The DMfit program was used for spectral deconvolution [55]. Mathematica  
204 11.2 software was used to fit the saturation-recovery T<sub>1</sub> relaxation curves and to perform the  
205 corresponding statistical analysis. Before NMR measurements, filled NMR rotors have been  
206 extensively dried for 72 h, at 323 K, with a turbo-molecular vacuum pump at pressure below  
207 10<sup>-4</sup> mbar.

### 208 **2.3.7. Magnetic measurements**

209 Magnetic measurements were performed with a SQUID-VSM magnetometer (from Quantum  
210 Design) used in the dc-mode. Samples were introduced in a gelatin capsule placed in a plastic  
211 straw. Both temperature (from 2K to 400 K) and field (up to 7 T) dependences of  
212 magnetization were investigated.



### 213 **2.3.8. Density functional theory calculations**

214 Periodic spin polarized density functional theory (DFT) calculations were performed using the  
215 VASP package [56] by means of the projector augmented wave (PAW) method [57]. The  
216 GGA+U [58–60] method was used for the exchange and correlation potential, in order to take  
217 into account the strong electron-electron interaction due to the iron localized d shell. The  
218 values of the parameters U and J were set to 3 eV and 0.9 eV, respectively [61]. Dispersion  
219 effects were considered by means of the DFT-D2 correction by Grimme *et al.* [62], as  
220 implemented in VASP [63].

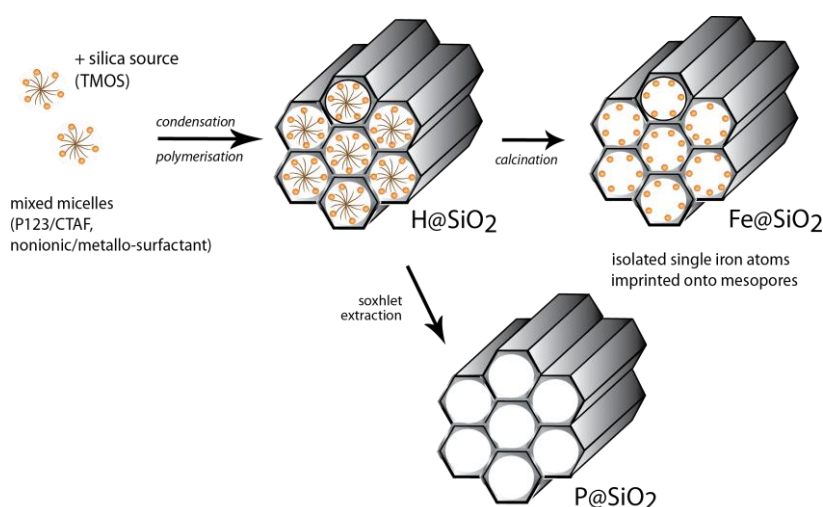
221 The interaction between a single iron atom and amorphous silica-surfaces was investigated by  
222 considering three different silanol densities: 7.2, 4.6 and 3.3 OH/nm<sup>2</sup> [64,65]. The fully  
223 hydroxylated surface (SiO<sub>2</sub>-7.2) was represented by a supercell containing 402 atoms, and for  
224 SiO<sub>2</sub>-4.6 and SiO<sub>2</sub>-3.3, 384 and 375 atoms, respectively. In all the cases, the periodically  
225 repeated slabs were separated by more than 20 Å of vacuum in the z direction. A plane-wave  
226 basis set with a kinetic energy cutoff of 450 eV was used to ensure the convergence of our  
227 calculations. Due to the large size of the supercell, only the  $\Gamma$  point was used to sample the  
228 Brillouin zone. The total energy converged within 10<sup>-6</sup> eV. For the atomic relaxation, the  
229 single iron atom and the atoms of the first layer of the silica-surface were relaxed by  
230 nullifying the forces on the atoms with a precision of 0.03 eV/Å and the other layers were  
231 kept fixed.

## 232 **3. Results and discussion**

### 233 **3.1. Synthesis of silica materials**

234 Silica materials were prepared through the self-assembling mechanism (Scheme 1) by adding  
235 a silica precursor (tetramethoxysilane, TMOS) to a mixed micellar solution of a non-ionic  
236 surfactant, the Pluronic P123, and a metallosurfactant, CTAF, at various molar ratio, r (of 1, 2,  
237 5, 10 where  $r = n_{\text{CTAF}}/n_{\text{P123}}$ ). All syntheses were performed at pH 1 to prevent precipitation of  
238 iron hydroxides. Therefore, the expected silica materials would be positively charged  
239 (SiOH<sub>2</sub><sup>+</sup>) and would need a cationic porogen to drive the silica-surfactant interaction through  
240 the anionic counterion (SiOH<sub>2</sub><sup>+</sup>/FeCl<sub>3</sub>Br<sup>-</sup>/CTA<sup>+</sup>) and to favor the imprinting of iron centers  
241 into the matrix.

242 The hydrothermal reaction conditions are similar to the one generally used for the synthesis of  
 243 SBA-15 (hydrothermal treatment under acidic catalysis, for 48 h at 373 K) [66,67]. Indeed,  
 244 under these reaction conditions and in the absence of CTAF, the pristine material exhibits  
 245 hexagonally ordered mesopores of around 8 nm diameter and a surface area ( $A_{\text{BET}}$ ) and pore  
 246 volume of  $846 \text{ m}^2 \cdot \text{g}^{-1}$  and of  $0.984 \text{ cm}^3 \cdot \text{g}^{-1}$ , respectively, as it was determined from XRD and  
 247  $\text{N}_2$  adsorption measurements (Figure SII). These values are in agreement with a typical SBA-  
 248 15 silica material.[67] By adding CTAF, mixed micelles are formed. This affects both the  
 249 meso-structure and the textural properties of the resulting materials, as reported in Table 1.



250

251 **Scheme 1.** Schematic representation of the sol-gel synthesis of silica materials through the  
 252 self-assembling mechanism based on mixed micelles of metallocsurfactant CTAF and pluronic  
 253 P123.

### 254 3.2. Structural and textural characterization of Fe@SiO<sub>2</sub>(r) materials

255 From the XRD data (Figure 1A), it can be first seen that the mesopore ordering of the  
 256 materials decreases with the increase in CTAF content. At low r values (r= 1 and 2), the  
 257 materials exhibit three reflection peaks located respectively at 9.4, 5.5 and 4.7 nm for  
 258 Fe@SiO<sub>2</sub>(1) and at 8.2, 4.9, and 4.4 nm for Fe@SiO<sub>2</sub>(2). Their relative positions are 1,  $\sqrt{3}$   
 259 and 2, which can be attributed to the (100), (110) and (200) reflections of a hexagonal  
 260 structure. According to Bragg's law, the unit cell dimension ( $a_0$ ) can be calculated and was  
 261 found to be equal to 10.9 nm for Fe@SiO<sub>2</sub>(1) and 9.5 nm for Fe@SiO<sub>2</sub>(2). This decrease of  
 262 the cell unit could be due to the silica wall thickness and/or pore diameter. The hexagonal  
 263 ordering of the pores was further confirmed by transmission electron microscopy (TEM)  
 264 micrographs showing honeycomb like arrangements (*i.e.* Fe@SiO<sub>2</sub>(1) in Figure 2). In  
 265 addition to those hexagonally organized mesopores of about 8 nm in diameter and 3 nm in

266 wall thickness, the micrographs also show the coexistence of larger, unorganized pores, of  
 267 about 12 nm in diameter.

268 At higher  $r$  values ( $r= 5$  and  $10$ ), the materials exhibit a broad peak located at 7.8 nm for  
 269  $\text{Fe@SiO}_2(5)$  and at 6.6 nm for  $\text{Fe@SiO}_2(10)$ . This indicates the formation of a wormhole-like  
 270 structures. The loss of ordering might be due to the increase of the total surfactant  
 271  $n_{\text{P123+CTAF}}/n_{\text{TMOS}}$  molar ratio ( $R$ ) with the increase of  $r$  values. As a matter of fact, in order to  
 272 control the iron/silica ratio, only the P123/TMOS molar ratio was maintained constant,  
 273 without adjusting  $R$  ( $n_{\text{P123+CTAF}}/n_{\text{TMOS}}$ ) as a function of  $r$  ( $n_{\text{CTAF}}/n_{\text{P123}}$ ). Yet, it is communally  
 274 accepted that the parameter  $R$  is essential in getting well-defined architectures and it strongly  
 275 depends on the nature of the surfactant. For instance, hexagonally ordered materials could be  
 276 obtained with solely P123 at  $R=0.017$  and with solely CTAF at  $R=0.17$ . Another important  
 277 parameter influencing the morphology and the pore size of the resulting material is the size  
 278 and nature of the micelles used as template. The iron ions from CTAF might induce the  
 279 complexation of ethylene oxide units of P123 and thus the shrinkage of the mixed micelles  
 280 and the reduction of the silica/surfactant interaction. Obviously, when increasing the CTAF  
 281 content, the repetition distance decreases, indicating a decrease of the pore size and/or of the  
 282 silica wall thickness.

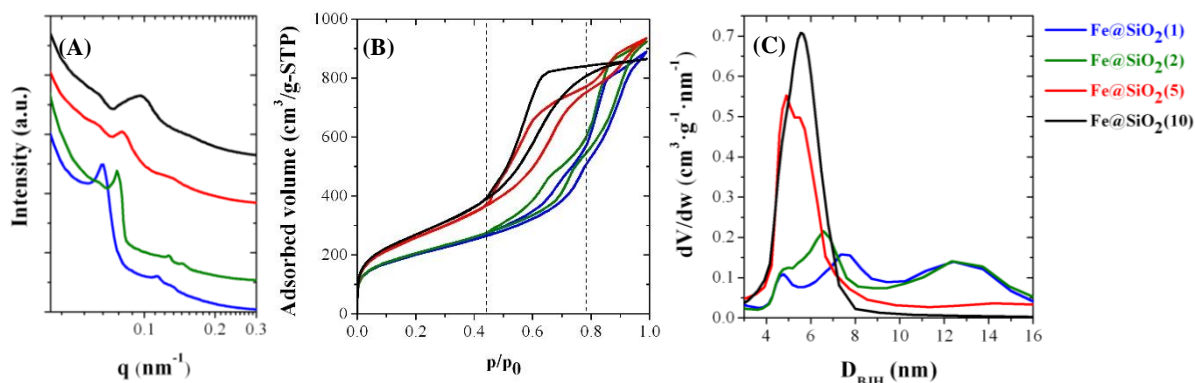
283

284 **Table 1.** Textural properties of  $\text{Fe@SiO}_2(r)$  materials ( $r = 1, 2, 5, 10$ ) and pristine material,  
 285 obtained in the absence of CTAF: interlayer distance/unit cell dimension for hexagonal  
 286 networks  $d_{\text{Bragg}}/a_0$ , pore diameter  $D_{\text{BJH}}$ , wall thickness  $\varepsilon$ , surface area  $A_{\text{BET}}$  and  $S_{\text{NLDFT}}$ ,  
 287 mesopores volume  $V_{0.97}$ , and silanols density  $\rho_{\text{Si-OH}}$ .

	$d_{\text{Bragg}}/a_0$ (nm)	$D_{\text{BJH}}$ (nm)	$\varepsilon$ (nm)	$A_{\text{BET}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$S_{\text{NLDFT}}$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$V_{0.97}$ ( $\text{cm}^3 \cdot \text{g}^{-1}$ )	$\rho_{\text{Si-OH}}$ ( $\text{OH}/\text{nm}^2$ )
$\text{Fe@SiO}_2(1)$	9.4/10.9	4.8/7.3 /12.4	3.6	731	809	1.34	9.6
$\text{Fe@SiO}_2(2)$	8.2/9.5	5.0/6.6 /12.3	2.9	750	819	1.41	5.5
$\text{Fe@SiO}_2(5)$	7.8/-	4.9	2.9	957	974	1.43	3.8
$\text{Fe@SiO}_2(10)$	6.6/-	5.5	1.1	993	1013	1.34	4.0
$\text{P@SiO}_2$	10/11.6	8	2	846	942	0.984	2.6

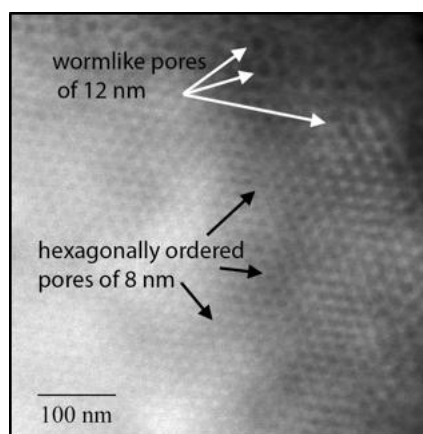
288

289 Further insights in the pore size distribution (PSD) were obtained from nitrogen  
290 adsorption/desorption isotherms. Except Fe@SiO<sub>2</sub>(10), which exhibits a type IV  
291 isotherm with one hysteresis loop, characteristic of unimodal mesoporous materials, all  
292 materials rather exhibit a type II isotherms with two main steps desorption branch  
293 indicating the coexistence of mesopores of different sizes (Figure 1B). On all  
294 isotherms, it can be observed that the value of the relative pressure, at which the first  
295 capillary condensation occurs is almost the same, between 0.4 and 0.5. Since the  $p/p_0$   
296 position of the inflection point is related to the pore diameter, according to Kelvin's  
297 equation, this observation suggests that all materials have mesopores of about 5 nm in  
298 diameter. As a matter of fact, Fe@SiO<sub>2</sub>(10) has a unimodal distribution of mesopores  
299 centered on 5 nm, as shown by the pore diameter distribution obtained by applying the  
300 BJH method to the nitrogen desorption isotherms ( $D_{\text{BJH}}$ , Figure 1C). The second  
301 inflection point appears for the other materials at a  $p/p_0$  value comprised between 0.7  
302 and 0.8, suggesting larger pores. For Fe@SiO<sub>2</sub>(1) and Fe@SiO<sub>2</sub>(2), three N<sub>2</sub>  
303 desorption steps can be identified at the following  $p/p_0$  intervals: between 0.50 and  
304 0.75, between 0.75 and 0.80, and between 0.80 and 0.99, which indicate the existence  
305 of mesopores within three ranges of pore diameters. For the Fe@SiO<sub>2</sub>(5) material, one  
306 can observe two zones N<sub>2</sub> desorption steps, at  $p/p_0$  between 0.50 and 0.80,  
307 corresponding to the porosity peak around 5 nm, and at  $p/p_0$  between 0.80 and 0.99,  
308 corresponding to larger pores ( $8 < D_{\text{BJH}} < 16$  nm), where  $dV \cdot dD_{\text{BJH}}^{-1}$  is around 0.05  
309  $\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{nm}^{-1}$ . The Fe@SiO<sub>2</sub>(10) sample shows one N<sub>2</sub> adsorption zone ( $0.50 < p/p_0 <$   
310  $0.80$ ) corresponding to the 5 nm pore diameter peak, with no adsorption for  $p/p_0$  above  
311 0.80. The pore sizes of all materials are wider than the one obtained by using only  
312 CTAF as template, without adding the non-ionic P123 surfactant (of 2.4 nm).[42] So is  
313 the wall thickness,  $\epsilon$ , as it was calculated by the subtraction of the pore size ( $D_{\text{BJH}}$ )  
314 from the interlayer distance ( $d_{\text{Bragg}}$ ) for the wormlike materials and from the cell unit  
315 for the hexagonal ordered ones. The surface areas are similar for the hexagonally  
316 ordered materials Fe@SiO<sub>2</sub>(1) and Fe@SiO<sub>2</sub>(2) on the one hand, and for the wormlike  
317 materials Fe@SiO<sub>2</sub>(5) and Fe@SiO<sub>2</sub>(10) on the other hand. All materials have high  
318 surface areas,  $A_{\text{BET}}$  and  $S_{\text{NLDFT}}$ , and total pore volumes  $V_{0.97}$  (Table 1). A sharp  
319 increase, of almost  $200 \text{ m}^2 \cdot \text{g}^{-1}$ , can be noticed between the two series of materials.  
320 Therefore, Fe@SiO<sub>2</sub>(5) and Fe@SiO<sub>2</sub>(10) might be considered more attractive for  
321 catalytic applications, such as in hydrodeoxygenation reactions for example.



322

323 **Figure 1.** Textural properties of Fe@SiO<sub>2</sub>(r) materials (r = n<sub>CTAF</sub>/n<sub>P123</sub> = 1, 2, 5, 10):  
 324 (A) XRD patterns, (B) N<sub>2</sub> adsorption-desorption isotherms, and (C) pore size  
 325 distribution.



326

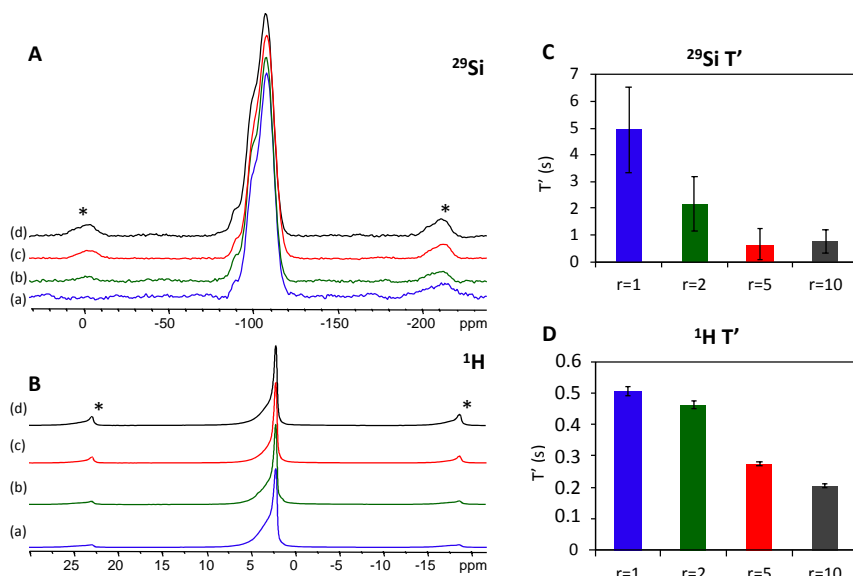
327 **Figure 2.** Transmission electron micrograph of Fe@SiO<sub>2</sub>(1).

### 328 3.3. Chemical characterization of Fe@SiO<sub>2</sub>(r) materials

329 The attenuated total reflectance infrared ATR-IR spectra of Fe@SiO<sub>2</sub>(r) materials confirms  
 330 the formation of the silica framework during the sol-gel process and the removal of the  
 331 organic part of the surfactant after calcination. Characteristic peaks of the stretching and  
 332 bending vibrations of Si-O-Si, Si-O and Si-OH bonds are present in the 900-1100 cm<sup>-1</sup> region,  
 333 while no peaks of CH<sub>2</sub> moieties appear between 2800 and 2900 cm<sup>-1</sup> (Figure SI2 left). The  
 334 ATR spectra also show the presence of OH groups at 1633 cm<sup>-1</sup> and at 3200-3700 cm<sup>-1</sup> that  
 335 were assigned to silanol groups and physisorbed water, respectively. Quantitative assessment  
 336 of silanol densities on the surface of those materials was obtained from BET and TGA  
 337 analysis (Table 1 and SI3 for the calculation method).

338 All materials exhibit silanols density values higher than for the similarly synthesized SBA-15-  
 339 like silica, with no CTAF (around 2.50 OH/nm<sup>2</sup>). This may be due to the existence of iron

340 atoms that hinder silica crosslinking during the polymerization, which may indicate the  
 341 formation of Si-O(H)...Fe bonds instead of Si-O-Si bonds.



342

343 **Figure 3.** Evolution of  $^{29}\text{Si}$  (A) and  $^1\text{H}$  (B) MAS NMR spectra for increasing r values  
 344 of  $\text{Fe@SiO}_2(r)$  materials: (a) r=1; (b) r=2; (c) r=5 and (d) r=10. Spinning sidebands are  
 345 marked by \* and  $\nu^{\text{MAS}} = 12.5\text{kHz}$ . Histograms showing the evolution of  $^{29}\text{Si}$  (C) and  $^1\text{H}$   
 346 (D) characteristic  $T_1$  spin-lattice relaxation times for increasing r-values in  $\text{Fe@SiO}_2(r)$   
 347 materials. Saturation recovery curves have been fitted to “stretched exponential”  
 348 functions with  $\beta=0.5$  for  $^{29}\text{Si}$  and  $\beta=0.74$  for  $^1\text{H}$ . Error bars reflect the 95% confidence  
 349 interval of the fits.

350 The condensation degree of silica in  $\text{Fe@SiO}_2(r)$  materials could be assessed from  $^{29}\text{Si}$  solid-  
 351 state NMR. Relative proportions of  $\text{Q}_2$  ( $\text{SiO}_2(\text{OH})_2$  silanols),  $\text{Q}_3$  ( $\text{SiO}_3(\text{OH})$  silanols), and  $\text{Q}_4$   
 352 ( $\text{SiO}_4$  bonds) units were determined after deconvolution of the peaks at -91, -100 and -110  
 353 ppm, respectively and all materials exhibit the same condensation degree  $\text{Q}_2:\text{Q}_3:\text{Q}_4$  of 4:24:72  
 354 (+/-2%). Nevertheless, despite the absence of additional  $^{29}\text{Si}$  signals, evidence is found for the  
 355 presence of paramagnetic Fe. Indeed, the very high magnetic moment of unpaired electrons,  
 356 located at paramagnetic centers, affects the NMR properties of coupled spins in different ways  
 357 [68]. Nuclei that are chemically bound, or in the first coordination shell of paramagnetic iron  
 358 cannot be observed due to extreme paramagnetic broadening. However, above this cutoff  
 359 radius, nuclear spins become observable despite considerable paramagnetic broadening [69].  
 360 Under Magic Angle Spinning (MAS) sample rotation, this broadening gives rise to intense  
 361 sideband patterns in the MAS NMR spectra, which are separated from the isotropic signal by  
 362 multiples of the rotation frequency [70]. Since the gradual signal loss and broadening occur  
 363 simultaneously, the boundary between observable and non-observable spins is somewhat

364 diffuse ( $\sim 3.3\text{\AA}$ ) [71,72], nevertheless it is possible to distinguish between short range effects,  
365 inducing signal loss, and medium range effects up to the nanometer scale, inducing line  
366 broadening and spin lattice  $R_1$  relaxation. Because of the low Fe concentration in the materials  
367 studied here, no short-range effects like the decrease in signal intensity or selective loss of  
368 pore surface ( $Q_2/Q_3$ ) sites with Fe loading could be established. Indeed, even for  
369 Fe@SiO<sub>2</sub>(10), the Fe content remains below 2 wt.% (Table 2). Nevertheless, medium-range  
370 effects such as an increase of sideband pattern intensity is indeed observed for <sup>29</sup>Si and <sup>1</sup>H  
371 NMR spectra when the CTAF/P123 ratio increases (Figure 3 A,B). This qualitative result is a  
372 consequence of the presence of paramagnetic species and indicates an increase of the average  
373 spatial proximity between paramagnetic iron spins and the diamagnetic neighbors, at the  
374 subnanometric scale as determined by the pair distribution function analysis (PDF).

375 Additionally, the study of spin lattice  $R_1$  relaxation also shows the existence of medium-range  
376 paramagnetic effects. Indeed, the <sup>29</sup>Si and <sup>1</sup>H characteristic  $T_1$  relaxation times are low  
377 compared to standard SBA-15 type material and therefore semi-quantitative information is  
378 best obtained by fitting the peak areas ( $M$ ) obtained from saturation recovery experiments to a  
379 modified “stretched exponential” equation of characteristic time  $T'$  with  $\beta < 1$ .

$$\frac{M}{M_\infty} = a \left( 1 - e^{-\left(\frac{t}{T'}\right)^\beta} \right)$$

380 " $M_\infty$ " being the peak area for the longest delay spectrum and " $a$ " a constant equal to 1 if  $M_\infty$   
381 corresponds to the fully relaxed signal [73,74].

382 While spin diffusion commonly induces relaxation of all spins at a same rate ( $\beta=1$ ), our data is  
383 best fitted for  $\beta$  fixed at 0.5 (Figure SI3) which is typical for relaxation dominated through  
384 space dipolar coupling with unpaired electronic spins ( $\chi^2$  is two times lower than for  $\beta=1$ ).  
385 This result is consistent with a homogeneous iron distribution on the nanometer scale. <sup>1</sup>H  $T_1$   
386 relaxation also shows non-exponential behavior and relaxation curves are best fitted with a  
387 higher value of  $\beta = 0.74$ . Despite the fact that NMR samples have been extensively dried to  
388 remove <sup>1</sup>H from adsorbed water molecules, <sup>1</sup>H spin diffusion relaxation is still active and this  
389 value of  $\beta$  is typical when mixed relaxation mechanisms act on the spins [75]. As seen on  
390 Figure 3 (C,D) characteristic  $T'$  relaxation times decrease when CTAF/P123 ratio increases.  
391 This trend suggests an increase in the number of paramagnetic iron sites within the materials.

### 392 **3.4. Characterization of single atom Fe@SiO<sub>2</sub>(r) materials**

393 A first quantitative assessment of the iron loading, obtained from both ICP-AES elementary  
394 analysis, is found to be about 0.56, 0.98, 2.31, and 2.64 wt.% for Fe@SiO<sub>2</sub>(1), Fe@SiO<sub>2</sub>(2),  
395 Fe@SiO<sub>2</sub>(5), and Fe@SiO<sub>2</sub>(10), respectively, as compared to Si (see Table 2 for the iron  
396 loading values compared to SiO<sub>2</sub>). Those results were further confirmed by the elemental  
397 mapping obtained by scanning transmission electron microscopy (STEM). The Fe content in  
398 these materials, as compared to the Si one, is found to be about 0.8, 1.1, 2.5, and 2.7 wt.% for  
399 Fe@SiO<sub>2</sub>(1), Fe@SiO<sub>2</sub>(2), Fe@SiO<sub>2</sub>(5), and Fe@SiO<sub>2</sub>(10), respectively. Moreover, as it can  
400 be seen in Figure 4B,C and SI4, the micrographs show a homogeneous dispersion of iron  
401 atoms within the silica matrix, without formation of any agglomerates.

402 UV-Vis diffuse reflectance spectra (Figure SI2 right) allowed us to determine the coordination  
403 of iron in the materials. The absorption band at 235 nm, which can be assigned to the charge  
404 transfer of  $p\pi-d\pi$  transition between oxygen and iron in the ferrisilicate material, suggests  
405 tetrahedral iron atoms, insulated from each other. In addition, the absence of any absorbance  
406 band above 350 nm in the spectrum reveals the absence of octahedral iron ions, and  
407 consequently the absence of iron oxide nanoparticles in the Fe@SiO<sub>2</sub> materials [76].

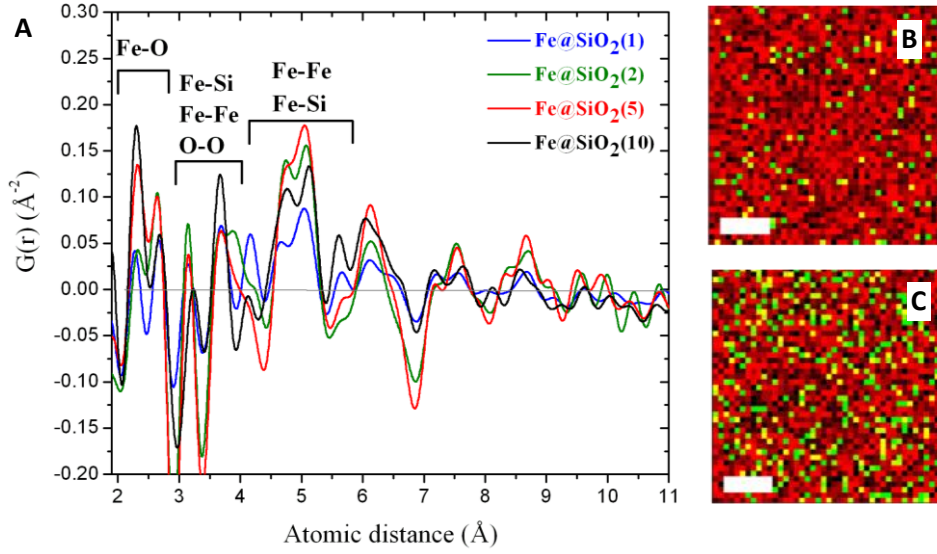
408 The absence of nanoparticles was also confirmed by the analysis of the experimental pair  
409 distribution function derived from the corresponding total scattering measurements of the  
410 materials (Figure 4A). From the PDF diagrams, one can clearly observe well-defined features  
411 up to about 7 Å. The rapid damping of PDF oscillations beyond this distance indicates that  
412 only isolated subnanometer iron clusters might be formed and are uniformly distributed  
413 throughout the samples, with no aggregation. Larger nanoparticles would have resulted a  
414 spatial extent of atomic correlations in the PDF diagram.

415 It is obvious that the intensities of the PDF peaks corresponding to the contributions of the Fe  
416 atoms increase as the molar ratio  $r$  (nCTAF/nP123) increases. The first two PDF peaks located  
417 in the  $r$  range of 2.0-2.6 Å are characteristic of Fe-O distances, while the PDF peaks located in  
418 the range of 3-6 Å can be assigned to the interactions of the iron atoms with the silica pore  
419 walls or to Fe-Fe correlations.

420 Finally, it is noteworthy that the presence of the double peak between 2.0 and 2.6 Å indicates  
421 two related Fe environments. Further insights on the Fe oxidation, spin states and on Fe-Fe  
422 interactions were gathered from magnetic measurements.

423





424

425 **Figure 4.** Comparison of experimental atomic pair distribution functions (PDFs) in  
 426 real space,  $G(r)$ , for  $\text{Fe@SiO}_2(r)$  materials and allocation of the main interatomic  
 427 distances in the range 2 – 7 Å (A). Relative elemental maps of Fe and Si obtained by  
 428 EDX in the scanning TEM mode for (B)  $\text{Fe@SiO}_2(1)$ , (C)  $\text{Fe@SiO}_2(10)$  (iron in green  
 429 and silica in red). The scale bare corresponds to 10 nm.

430 The magnetization field dependences of the  $\text{Fe@SiO}_2(r)$  measured at 10K after a first cooling  
 431 at  $15\text{K}\cdot\text{min}^{-1}$  are plotted in Figure 5. These measurements have been subtracted from the  
 432 diamagnetic contribution of sample holder and pristine  $\text{P@SiO}_2(r)$  silica, as described in SI,  
 433 and have been scaled with respect to Fe content using the ICP-AES elementary analysis  
 434 results. They can be fitted by a sum of two Brillouin functions as follow:

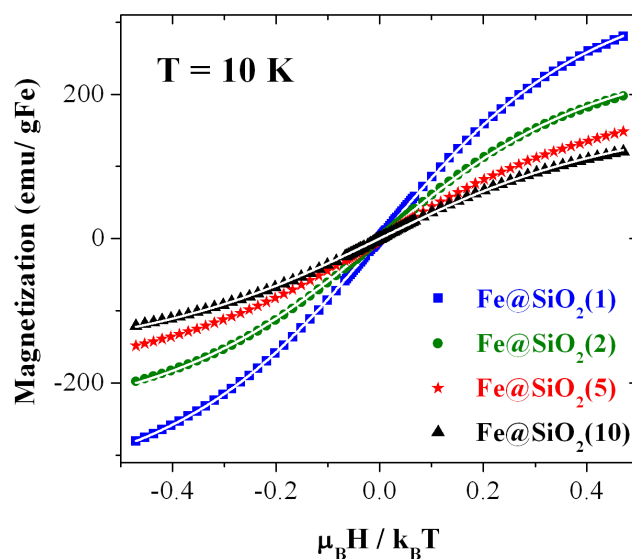
$$M(H, T) = xM_s^{5/2}B_{5/2}(H, T) + (1 - x)M_s^{1/2}B_{1/2}(H, T)$$

435 where  $x$  is the only fitted parameter giving the proportion of the high spin  $S=5/2$ ,  $M_s^{5/2}$  and  
 436  $M_s^{1/2}$  are the saturation magnetization of  $\text{Fe}^{3+}$  in the high spin and low spin states, respectively  
 437 ( $M_s^{5/2} = 500 \text{ emu/gFe}$  and  $M_s^{1/2} = 100 \text{ emu/gFe}$ ), and  $B_s(H, T)$  are the corresponding  
 438 Brillouin functions ( $S=5/2, 1/2$ ).

$$B_s(\alpha) = \frac{2S + 1}{2S} \coth \frac{(2S + 1)\alpha}{2S} - \frac{1}{2S} \coth \frac{\alpha}{2S}$$

where  $\alpha = \frac{\mu_B H}{k_B T}$ .

439 The fit with the aforementioned  $M(H, T)$  equation has been performed for samples exhibiting  
 440 a Curie temperature dependence under 79.6 kA/m above 10K (see Figure SI5).



441

442 **Figure 5.** Field dependence behavior of the magnetization measured at 10K and  
 443 corrected from the diamagnetic signal for Fe@SiO<sub>2</sub>(r) (r = 1, 2, 5, 10) samples. It is  
 444 plotted as a function of the dimensionless parameter  $\mu_B H / k_B T$  where  $\mu_B$  is the Bohr  
 445 magneton and  $k_B$  the Boltzmann constant. The straight lines are fits by the sum of the  
 446 two Brillouin functions corresponding to  $S = 5/2$  and  $1/2$ .

447 Despite only one parameter is fitted, a very good agreement is obtained between the simple  
 448 model and the measurements. The fit is not changing while taking into account an additional  
 449 contribution of Fe<sup>2+</sup> (S=2), confirming thus the presence of solely Fe<sup>3+</sup> ions. No ferromagnetic  
 450 contribution is detectable at this scale. The high spin fractions deduced from the fits are  
 451 reported in Table 2. They are in good agreement with those deduced from the Curie constant  
 452 (see Figure SI5). No fit with the Brillouin equation has been performed for the Fe@SiO<sub>2</sub>(5)  
 453 sample since the temperature dependence of the magnetization deviates from the Curie law  
 454 below 15 K (see figure SI6). This deviation is attributed to spin crossover towards low spin  
 455 with decreasing temperature, which occurs below 10 K for other samples (Figure SI7).  
 456 Nevertheless, the high spin fraction reported in Table 2 is stable with temperature above 10 K  
 457 (or 15 K for Fe@SiO<sub>2</sub>(5)) and is then a relevant parameter characterizing the Fe sites in the  
 458 silica pores. It decreases as the Fe content increases, concomitantly with the decrease of the  
 459 pore size. Thus, beyond the sharing of Fe spin state according to Si sites or pore sizes, the  
 460 consistent quantitative analysis in terms of Curie law or Brillouin function without interaction  
 461 between Fe spins (no Curie-Weiss temperature) supports the assumption of isolated Fe atomic  
 462 centers that are well dispersed within the materials.

463

464 **Table 2.** Fe content (wt.%) with respect to the total samples mass used to scale the  
 465 magnetization. Fraction of Fe<sup>3+</sup> spins in the high spin state (5/2) deduced from the  
 466 temperature dependence of magnetization (Curie law) or field dependence of magnetization  
 467 measured at 10 K.

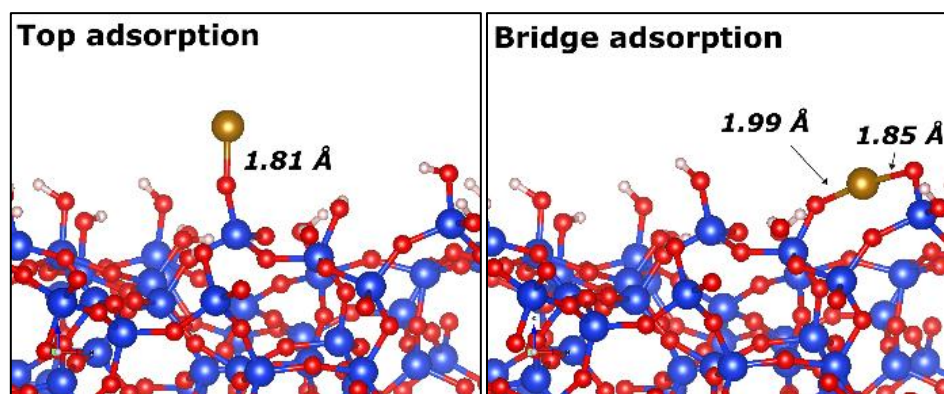
	Fe loading (wt.%)	$\chi_{5/2}^{Curie}$	$\chi_{5/2}^{Brillouin}$
Fe@SiO <sub>2</sub> (1)	0.23	0.72	0.71
Fe@SiO <sub>2</sub> (2)	0.41	0.49	0.47
Fe@SiO <sub>2</sub> (5)	0.97	0.31*	-
Fe@SiO <sub>2</sub> (10)	1.08	0.25	0.24

468 \*No fit with Brillouin functions has been performed for Fe@SiO<sub>2</sub>(5) as it deviates from the Curie law below  
 469 15K. For this sample, the fit with the Curie law has been performed in the 15-30 K.

470

### 471 3.5. DFT calculations

472 Several structural configurations of the Fe/SiO<sub>2</sub> system were calculated in order to determine  
 473 the most favorable adsorption position (top vs bridge, Figure 6) as well as the spin state,  
 474 without or under geometrical constraints (2% contraction of the silica surface along the x and  
 475 y directions), as in mesopores. The calculations were firstly started from reasonable  
 476 estimations at various adsorption positions (top, bridge) on surfaces with various silanol  
 477 densities (SiO<sub>2</sub>-7.2, SiO<sub>2</sub>-4.6 and SiO<sub>2</sub>-3.3) [64,65]. For each configuration, two sets of  
 478 calculations were performed for the Low-Spin (LS) and High-Spin (HS) states of iron.



479

480 **Figure 6.** Panels showing the single iron atom adsorbed on amorphous silica surface with a  
 481 silanol density of 4.6 OH/nm<sup>2</sup> at top (left) and bridge (right) positions, respectively. For the  
 482 top adsorption, the equilibrium distance between the iron atom and the substrate is found to be  
 483 1.81 Å in HS and 1.78 Å in LS (left). For the bridge adsorption, in the HS state, the  
 484 equilibrium iron-surface distances were found to be 1.99 and 1.85 Å for both oxygen atoms,  
 485 whereas in the LS state, these distances became 1.85 and 1.81 Å, respectively (right).

486 The Fe atom was adsorbed on the silica surface through its oxygen atoms by removing the  
 487 corresponding hydrogen atoms. Figure 6 shows the single iron atom adsorbed on the typical

488 silica surface with a silanol coverage equal to 4.6 OH per nm<sup>2</sup> at top (left panel) and bridge  
489 (right panel) positions. For the top positions, the HS state magnetic moment of iron is 4.97  $\mu\text{B}$   
490 ( $S = 5/2$ ) while the one of the LS state is 1.00  $\mu\text{B}$  ( $S = 1/2$ ), which correspond to Fe<sup>3+</sup>.  
491 However, the HS and LS state magnetic moments of the iron in the bridge positions are found  
492 to be 4.00  $\mu\text{B}$  ( $S = 2$ ) and 0.00  $\mu\text{B}$  ( $S = 0$ ), respectively, which are the HS and LS states of  
493 Fe<sup>2+</sup>. It is noteworthy that, for the various silica surfaces, the calculations show that the  
494 adsorption of the iron atom at top positions has always the lowest total energy. Thus, the Fe<sup>3+</sup>  
495 oxidation state is the most favorable whatever the silanols density, in agreement with  
496 experimental findings where no Fe<sup>2+</sup> contribution is observed. Nevertheless, the calculations  
497 show that, in the absence of geometrical constraints, the adsorption of the single iron atom on  
498 various amorphous silica-surface stabilizes the HS state. This result is in contrast with  
499 magnetic results where a contribution of low spins had to be considered. Such low spin state  
500 is however not surprising in presence of porous materials where strains are expected.

501 Therefore, additional DFT calculations were performed starting from optimized top positions  
502 at high and low spin, while taking into account geometrical constraints. The contraction of the  
503 geometries along the x and y directions has been set to mimic the fact that the silica surface is  
504 not perfectly planar but slightly curved which is modeled in our simulations by a pressure.  
505 The choice of a contraction value of 2% has been done as a follow: the calculations with an  
506 applied pressure smaller than 2% does not show a significant effect on the studied properties.  
507 Also, pressures exceeding 2% are probably unrealistic and could give rise to unphysical  
508 phenomena. For high silanols densities (7.2 and 4.6 OH/nm<sup>2</sup>), our calculations (Table SI3)  
509 confirm the coexistence of LS and HS Fe<sup>3+</sup> species determined from magnetic measurements  
510 (Table 2). For low silanols densities (3.3 OH/nm<sup>2</sup>), the LS and HS calculations converged to  
511 the same magnetic state (LS with a magnetic moment of 1  $\mu\text{B}$ ). This result is in line with the  
512 experimental trend observed in Table 2 showing that the relative amount of LS Fe<sup>3+</sup> increase  
513 when decreasing the silanol density. In conclusion, DFT calculations confirmed the  
514 experimental results obtained from magnetic measurements, indicating a mixture of HS and  
515 LS Fe<sup>3+</sup> species.

#### 516 **4. Conclusion**

517 In this study, we demonstrated that single iron atoms-supported materials (Fe/SiO<sub>2</sub>) can be  
518 prepared by hydrothermal synthesis using mixed non-ionic/metallosurfactants as templates.  
519 The non-ionic Pluronic P123 surfactant allows controlling the structural and textural

520 properties of the silica framework while the ferrosurfactant acts as a metal donor, in addition  
521 to its role of porogen. The iron loading in the final materials depends on the molar ratio of  
522 surfactants and can be accurately tuned, up to 1wt% (0.15 Fe atoms/nm<sup>2</sup>). Pair distribution  
523 function analysis, STEM mapping and magnetic measurements demonstrated the absence of  
524 any particle or cluster. Experimental data showed that the Fe species are Fe<sup>3+</sup>, in agreement  
525 with the DFT calculations. Those materials proved a good distribution of iron atoms on the  
526 silica surface, with increased number of active sites, which might find straightforward  
527 applications in catalysis [2–7].

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## 540 **Author Contributions**

541 The manuscript was written through contributions of all authors.

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## 544 **Abbreviations**

545 CTAF cetyltrimethylammoniumtrichloromonobromoferrate, DFT Density Functional Theory,  
546 STEM scanning transmission electron microscopy.

## 547 **Supplementary data**

548 1. Structural properties of pristine SBA-15-like material, obtained in the absence of CTAF; 2.  
549 Spectroscopic measurements (ATR and UV-Vis); 3. Thermogravimetric analysis; 4. NMR; 5.  
550 Elemental cartography; 6. Magnetic measurements (substraction of the diamagnetic signal and  
551 low temperature spin crossover) and 7. DFT calculations.

552

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