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1 **New synthesis routes and catalytic applications of ferrierite crystals.**

2 **Part 1: 1,8-diaminooctane as a new OSDA**

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19 **ABSTRACT**

20 *Ferrierite zeolite crystals were successfully prepared by a long amine as 1,8-*
21 *diaminooctane (DAO) as organic structure directing agent. By comparison, shorter*
22 *amine, i.e. ethylenediamine (EN), was also used as OSDA. Results shows that the*
23 *presence of DAO reduces the crystallization time and allows to obtain single FER-type*
24 *crystals with smaller size and higher acidity, being these significant parameters to take*
25 *into account when zeolites are applied in catalysis. The obtained samples were*
26 *characterized with XRD, TG/DTA, SEM, N₂ adsorption/desorption, FTIR and ²⁷Al-*
27 *NMR. In particular, TGA clearly shows that DAO may be accommodate in zeolite*
28 *framework and theoretical modeling suggests a preferential location in the 10-MR ring*
29 *channels.*

30

31 **Keywords:** Ferrierite, zeolite synthesis, 1,8-diaminooctane, Brønsted-Lewis acidity,
32 FT-IR, DFT calculation,

33 **1. INTRODUCTION**

34 **The possibility of preparing zeolites with tailored physicochemical properties by both in**
35 **situ and post-synthesis treatments is of considerable importance for the industrial**
36 **perspective, particularly in the area of heterogeneous catalysis where zeolites are widely**
37 **used [1-6]. In fact, the suitability of zeolite for specific applications, such as catalysis,**
38 **strongly depend on several factor such as zeolite structure (i.e. size, shape and**
39 **orientation of the channels), its chemical composition, acidity and crystal morphology.**
40 **At moment, more than 240 zeolite framework types are known and most of them are not**
41 **currently applied in industrial processes due to both costs and performances aspects, and**

42 very few zeolite structures have found significant catalytic application in petrochemical
43 and refining industries. FAU (X and Y), MFI (ZSM-5 and Silicalite-1), MOR, BEA
44 (beta), MWW (MCM-22), AEL (SAPO-11) and CHA (SAPO-34) are examples of
45 zeolite structures currently used in industrial catalysis.

46 Ferrierite (FER) is another zeolite structure that has or may have some importance for
47 industrial applications. FER framework consists of an intersecting 2-dimensional
48 system of 10- (5.4 x 4.2 Å) and 8- (4.8 x 3.5 Å) member ring channels and can be
49 synthesised with Si/Al ratios ranging from 5 to infinity [8, 9]. The particular channel
50 configuration of FER framework is appropriate for processing small molecules. For
51 instance, FER-type zeolite is mainly applied as catalyst in the skeletal isomerization of
52 n-butene for the production of iso-butene and as additive to ZSM-5 catalyst in the
53 dewaxing by selective cracking process for the production of lubricant [10]. Recently,
54 FER-type crystals have also ranked as a highly performing catalyst for dimethyl ether
55 (DME) production via both methanol dehydration reaction and one-pot CO or CO₂
56 hydrogenation, if compared with other zeolite structures such as MFI, BEA, MOR,
57 CHA, MTW and TON [11-14]; the superiority of ferrierite over the traditional catalyst
58 for DME synthesis, i.e. γ -Al₂O₃, was also reported [15].

59 Ferrierite can be synthesized combining both Na⁺ and K⁺ cations [16]. However, it is
60 usually obtained from sodium and OSDA containing systems which give more
61 flexibility in the control of the physicochemical properties of the ultimate product.
62 Amines are often used as OSDA in the synthesis of FER-type materials. Gögebakan et
63 al. [17] reported a study on crystallization field and rate in presence of pyrrolidine or
64 ethylenediamine in the synthesis temperature range 150-225 °C, founding a strong
65 dependence of crystallization rate from temperature, whereas both SiO₂/Al₂O₃ ratio (in

66 the range 10-25) and OSDA amount did not significantly influence the crystallization
67 rate. On the contrary, OSDA affected crystal morphology: individual or platelet
68 crystallites were obtained in presence of pyrrolidine or ethylenediamine, respectively.
69 Furthermore, the authors even found mordenite as competitive phase only when
70 pyrrolidine is used as OSDA.

71 Kamimura et al. [9] reported the synthesis of ferrierite in presence of pyridine as
72 OSDA, obtaining well-defined plate-like crystals with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ up to 324. In
73 particular, the synthesis of pure siliceous ferrierite was successful in presence of sodium
74 fluoride. Aluminium-free ferrierite was also obtained in presence of ethylenediamine as
75 OSDA and boric acid as templates [18].

76 On the contrary, Forbes et al. [19] reported that, using diethanolamine as OSDA, pure
77 phase ferrierite crystals may be obtained only in a narrow Si/Al ratio. In particular, the
78 authors found that by increasing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 16 to about 25, a ferrierite/ZSM-5
79 mixed phase was obtained.

80 OSDA type as well as synthesis environment also affects the morphology and the size
81 of the final crystals. In this concern, Rakozý et al. [20, 21] report the synthesis of all-
82 silica large FER-type crystals by using unbranched monoalkyl C3-C5 amines in mixture
83 with pyridine, showing the possibility to tune the shape and size of obtained crystals. In
84 particular, by increasing the number of carbon atoms of the amine, the crystal shape
85 changed from hexagonal to rectangular flat prismatic morphology.

86 Lee et al. [22] successfully synthesised ferrierite zeolite nanoneedles about 10 nm in
87 diameter and 100 nm in length. The success of the synthesis strongly depends on both
88 Si/Al ratio and ion types. In particular, the authors obtained high pure ferrierite by

89 adopting a Si/Al=20 in presence of Na⁺, while mixed or amorphous phases were
90 obtained for lower or higher aluminium content and using other ion types (e.g. Li⁺, K⁺,
91 Rb⁺, Cs⁺).

92 The effect of organic solvent such as triethylamine, tetra- or diethylene glycole,
93 dimethylsulfoxide, lutidine and mineral oil on the shape and size of final crystals from
94 non-aqueous syntheses was also deeply investigated [23].

95 Pinar et al. assert that the choice of organic template molecules (OSDA) in FER-type
96 materials is of paramount importance for aluminium distribution and incorporation [23],
97 affecting acid sites distribution, location, and accessibility [24]. The authors synthesised
98 ferrierite crystals with a Si/Al ratio of about 15 starting from a sodium-free gels in
99 fluoride media by using some specific combinations of tetramethylammonium (TMA),
100 pyrrolidine and benzylmethylpyrrolidinium (bmp), founding that the acid sites
101 distribution between the ferrierite cage accessible to through 8-MR window and the 10-
102 MR pores depend on the OSDA mixture composition. In particular, the accessibility to
103 Brønsted sites is higher when TMA/bmp or TMA/pyrrolidine mixture are used
104 respected to alone pyrrolidine with a direct effect on catalysis. Therefore, the already
105 published studies highlighted the possibility to obtain tailored ferrierite crystals by
106 choosing proper SDAs and synthesis conditions, with an effective control of both acid
107 properties and crystal morphology.

108 In this paper, FER-type crystals were synthesized by using a long amine as 1,8-
109 diaminoctane as OSDA. This molecule is usually used for the synthesis of MEL, TON
110 and ZSM-48 zeolites. In the case of MEL and TON zeolite, the success of the
111 crystallization of the desired phase strongly depends on the stirring condition: static or
112 high-speed agitation condition lead to the selective formation of high pure MEL or TON

113 phase, respectively [25]. Crystallization with stirring is also required for the synthesis of
114 ZSM-48 [26].

115 To the best of our knowledge, there has been no report on the synthesis of ferrierite by
116 using 1,8-diaminooctane as OSDA. In this work the crystallization of ferrierite in
117 presence of 1,8-diaminooctane is carried out with the aim to assess the effect of this
118 molecule on physico-chemical properties of obtained materials. Furthermore, in order to
119 have new insights about the role of amine molecule length, FER-type zeolite with
120 ethylenediamine as OSDA was also prepared for comparison.

121 TG/DTA analysis allowed to assess the interaction between the OSDA and zeolite
122 framework whilst DFT calculations gave information about molecules location.
123 Brønsted/Lewis acid sites distribution and concentration of synthesised materials have
124 been investigated with NH_3 -TPD and FT-IR of several adsorbed probe molecules while
125 morphology and crystallinity has been analysed by scanning electron microscopy and
126 powder XRD, respectively. Finally, DFT calculations allowed validate the experimental
127 evidences.

128

129 **2. EXPERIMENTAL**

130 *2.1 Samples preparation*

131 The following chemicals were used in all the synthesis: colloidal silica Ludox AS-40
132 (SiO_2 , 40 wt% suspension in H_2O , Aldrich), sodium aluminate (NaAlO_2 , Aldrich),
133 sodium hydroxide (pellets, Aldrich), ethylenediamine (Fluka), 1,8-diaminooctane
134 (Aldrich), and distilled water.

135 Synthesis of FER sample by using ethylenediamine (En-FER) was prepared by adopting
136 the following synthesis gel molar composition [28]:



138 In a typical synthesis 0.3 g of NaOH and 1.3 g of sodium aluminate were dissolved in
139 64.1 g of distilled water. Then 8.2 g of ethylenediamine were added to dropwise and the
140 solution was stirred for 30 min. Afterwards 15.8 g of colloidal silica were added
141 dropwise to the solution, and the obtained gel was stirred (300 rpm) at room
142 temperature for 1 h. Crystallization was carried out in 120 ml stainless-steel Teflon
143 coated autoclave up to 12 days at 180 °C in a tumbling oven (rotation speed: 15 rpm).

144 The potential role of 1,8-diaminooctane as OSDA was investigated by gradually
145 replacing En with DAO, starting from the En-FER (i.e. DAO free) synthesis gel. FER-
146 type crystals were obtained from synthesis gel with different DAO/En molar ratio: 0.25,
147 0.5, 1, 2 and ∞ (i.e. En free), by using the following molar gel composition



149 with $5 < x < 10$ and $0 < y < 19.7$.

150 In the synthesis of DAO-FER only DAO was used as SDA. For this latter synthesis, 0.3
151 g of NaOH and 1.3 g of sodium aluminate were dissolved in 21 g of distilled water. A
152 secondary solution was prepared by dissolving 7.8 g of DAO into 42 g of distilled
153 water, under vigorous stirring. Afterwards, the two solutions were blended and 15.8 g of
154 colloidal silica were added dropwise and the obtained gel was stirred (300 rpm) at room
155 temperature for 1 h. Crystallization was carried out in 120 ml stainless-steel Teflon
156 coated autoclave up to 12 days at 180 °C in a tumbling oven (rotation speed: 15 rpm).

157 After crystallization, the solid was separated by vacuum filtration and washed several
158 times with distilled water until the pH of filtered solution was close to the neutral value.
159 The obtained white solid was then dried for 15 hours in a static oven kept at 80 °C. In
160 order to remove template from zeolite, air-flow calcination was carried out at 550 °C
161 with an holding time of 8 hours and a heating rate of 2 °C/min. Afterwards, H-form
162 solid was obtained by ion-exchange with a NH₄Cl 1 M solution at 80 °C followed by a
163 secondary air-flow calcination at 550 °C with an holding time of 8 hours and a heating
164 rate of 2 °C/min [29].

165 2.2 Physicochemical characterization

166 X-Ray powder diffraction (APD 2000 Pro) (region 5° < 2θ < 50°, step 0.02°/ s) was
167 used to verify both purity and crystallinity of obtained phase; the morphology of the
168 crystalline phase was observed on a scanning electron microscope (SEM, FEI model
169 Inspect) and a transmission electron microscopy (TEM, Philips CM12). The sodium,
170 aluminum and silicon content in the calcined catalysts was measured by atomic
171 absorption spectroscopy (GBC 932 AA).

172 The specific surface area and the micropores volume of the calcined samples were
173 obtained from BET and t-plot analysis of porosimetry data (ASAP 2020 Micromeritics)
174 under nitrogen adsorption at -196 °C, after a pre-treatment in vacuum at 200°C for 12 h.

175 The thermo-gravimetric analysis over the as-synthesised samples was performed on the
176 automatic TG/DTA instrument (Shimadzu) under 50 cc/min of air flow in the
177 temperature range 25-850°C (heating rate of 5 °C·min⁻¹).

178 Solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-
179 NMR) was used to characterize the local ²⁷Al environment in the zeolite samples. All
180 data were recorded on a Bruker Advance 500 MHz spectrometer using a 4.0 mm rotors.

181 The ^{27}Al -NMR spectra were acquired at 130.3 MHz with radiofrequency power of 54
182 kHz, a pulse length of 4.6 μs with a corresponding angle theta of $\pi/4$. Rotors were spun
183 at 14 kHz, and the recycle delay used for both nuclei was 1 second.

184 Surface acidity of H-form sample was measured by NH_3 -TPD analysis (TPDRO1100,
185 ThermoFisher) according to the following procedure. Dried sample (100 mg, pellet
186 mesh 90-150 μm) was loaded in a linear quartz micro-reactor and pre-treated at 300°C
187 in helium flow for 1 h to remove adsorbed water. The sample was cooled down to
188 150°C and saturated with 10% v/v NH_3/He mixture with a flow rate of 20 STP $\text{mL}\cdot\text{min}^{-1}$
189 for 2 h. Ammonia physically adsorbed was removed by purging in helium at 150°C for
190 1 h until TCD baseline stabilization. Desorption measurement was carried out in the
191 temperature range of 100-950°C (10 $^\circ\text{C}\cdot\text{min}^{-1}$) using a helium flow rate of 20 STP
192 $\text{mL}\cdot\text{min}^{-1}$.

193 Brønsted and Lewis acid sites concentration was measured via FT-IR analysis by using
194 D_3 -acetonitrile as a probe molecule. Infrared spectra were recorded with a Bruker
195 Equinox 55 spectrometer. The adsorption of D_3 -acetonitrile was performed at room
196 temperature with a pressure of 10 Torr, after that the samples were degassed under high
197 vacuum condition (cell pressure: 10^{-6} Torr) at 300°C for 4 h, in order to purge adsorbed
198 water. Physisorbed acetonitrile was removed by further degassing until the vacuum
199 condition was recovered. The FT-IR spectra were recorded in the temperature range 25-
200 300 $^\circ\text{C}$ (temperature step of 50°C), outgassing the sample for 30 minutes at any
201 temperature variation.

202 The amount of D_3 -acetonitrile adsorbed on Brønsted and Lewis was determined by
203 using a literature value for the molar absorption coefficient [30]. The number of
204 Brønsted sites was calculated from the area of the bands observed at 2297 cm^{-1} by

205 adopting an extinction coefficient of 2.05 cm/ μ mol, whilst the number of Lewis acid
206 sites was calculated from the area of the bands between 2310–2325 cm^{-1} by adopting an
207 extinction factor of 3.6 cm/ μ mol. Peaks analysis and deconvolution for both FT–IR and
208 NH_3 -TPD profiles were performed by using commercial software (PeakFit 4.12,
209 Seasolve–USA).

210

211 **3. RESULTS AND DISCUSSION**

212 *3.1 Structural properties of FER-type zeolites synthesized with different OSDA*

213 X-ray patterns as a function of crystallization time of En-FER and DAO-FER are
214 reported in Figure 1. Crystal growth kinetics of En-FER is relatively slow (see Figure 1-
215 A) as traces of FER phase are observed after 3 days and after 6 days the crystalline
216 phase is dominant. A crystallization time of 10 days can be considered as optimal to
217 obtain high crystalline En-FER since, for longer time (12 days), traces of kaetite phase
218 appear. Figure 1-B reports the XRD patterns as a function of crystallization time for
219 DAO-FER sample. Results show that En replacing with DAO speeds the crystallization.
220 In fact, after 3 days FER-phase is almost completely crystallized whilst only traces of
221 crystalline product are observed for En-FER after the same synthesis period. That
222 evidence suggests that in presence of DAO, the induction period is shortened, even
223 reducing the crystal size as discussed later.

224 Because DAO was never reported as a template in FER zeolite synthesis, a deeper
225 investigation by TG/DTA analysis of as-synthesised materials was performed. The
226 thermo-analytic results of DAO-containing systems are reported in Figure 2, in terms of

227 thermogravimetric (TG) and first derivate (dTG) profiles. Heat flow profiles (DTA) are
228 reported in Figure S.1 (Supporting Information).

229 From the analysis of the dTG profiles, it can be deducted that **1,8-diaminooctane** might
230 plays the role of template for FER structure. In fact, dTG profile of DAO-free sample
231 (En-FER, Figure 2A) shows the presence of four main peaks [28]. The endothermic
232 peak (see Figure S.1A) at ca. 73 °C is attributed to water release and the corresponding
233 weight loss for En-FER was of ca. 2 wt%. In addition, En-FER sample contains about
234 11 wt% of ethylenediamine, released in the temperature range 250-700 °C. The
235 associated exothermic phenomena (see DTA profile reported in Figure S.1A) are related
236 to the organic combustion. It is evident from Figure 1A, that at least four different dTG
237 peaks can be associated to **ethylenediamine** decomposition (249°C, 302 °C, 420 °C and
238 605 °C), indicating the presence of different interactions between OSDA and zeolite
239 framework. As the DAO/En ratio increases from 0 to 0.5 or 1 an effect of a shift toward
240 low temperatures is observed for these dTG peaks. If the peak of En-FER at 420° C is
241 considered, it clearly appears that it decreases down to 366 °C and 352 °C (Figures 2B-
242 C) when the DAO/En ratio is increased to 0.5 or 1, respectively. Also, dTG profile
243 reported in Figure 2C shows that the interaction between **ethylenediamine** and zeolite
244 framework characterised by the lowest temperature decomposition (around 249°C for
245 En-FER) tends to disappear when DAO progressively replaces En as OSDA. It is
246 worthy to clarify that this effect it is not attributable to lower amount of En in synthesis
247 gel because the TG/dTG profile of a DAO-free FER synthesised with the same
248 **ethylenediamine** content of the sample with DAO/En=2 (i.e. En/Al₂=5) shows the same
249 peaks of the En-FER (En/Al₂=19.7), as reported in Figure S.2 of Supporting
250 information. This result suggests that the amount of ethylenediamine in the synthesis gel

251 slightly affects its incorporation and the changing of dTG profiles that are, on the
252 contrary, mainly affected by the presence of DAO in the synthesis gel and then in the
253 zeolite structure. The effect of the only DAO in the FER synthesis is shown in Figure
254 2.D, where the main exothermic peak at 348 °C can be unequivocally attributed to 1,8-
255 diaminoctane combustion. The weight loss due to organic molecules decomposition,
256 measured in the temperature range 250-650 °C decreases from ca. 11 wt% to ca. 7 wt%
257 when the DAO/En ratio increases from 0 to ∞ respectively. On the contrary, the weight
258 loss between 25 and 200 °C, attributed to physically adsorbed water, increase from 2
259 wt% to 5 wt % by increasing the DAO/En ratio from 0 to ∞, respectively, suggesting
260 that the presence of 1,8-diaminoctane also promotes the water incorporation. Even
261 though the role and the location of DAO molecules is not fully elucidated yet, we
262 anticipate that DAO molecules are located inside the 10 MR of FER structure since the
263 8 MR channel is too small to accommodate them.

264 Figure S.3 shows the ²⁷Al MAS NMR spectra of the H-form FER-type zeolites with En
265 or DAO as OSDA. They are dominated by a signal centered at around 55 ppm,
266 characteristic of tetra-coordinated aluminium species in zeolite framework. A broad
267 signal at around 0 ppm revealing the presence of octahedral extra-framework aluminium
268 (about 10%) for both the samples. The observed quadrupolar line broadening can be
269 caused by distortions of the octahedral symmetry of AlO₆ sites.

270 It is well-known that the zeolite structure is generated by a network of SiO₄ and AlO₄⁻
271 tetrahedral linked together by a shared oxygen atom. Due to the presence of trivalent
272 atoms (e.g. aluminium) in the tetrahedral units, the framework offers a negative charge
273 which needs to be balanced with non-framework exchangeable cations that are
274 generally elements of the group IA and group IIA as sodium, potassium, magnesium

275 and calcium. In this work, sodium is used to synthesise FER-type materials, and this is
276 the cation that balances negative charges associated with aluminium atoms.
277 Furthermore, the high quantity of tetrahedral aluminium species detected by NMR
278 analysis, suggests that the Na/Al ratio should be theoretically around one. The chemical
279 analysis reported in Table 1 shows that Na/Al is 0.06 for En-FER and 0.6 for DAO-
280 FER. These results disagree with the previous theoretical assumption, suggesting that
281 sodium cations do not balance an important amount of aluminium species in tetrahedral
282 position, especially. Vuono et al. [31] reported a Na/Al ratio value below to unity
283 (around 0.6) for MCM-49 materials synthesised in the presence of hexamethylenimine
284 despite aluminium was mainly tetra-coordinated as in our case. Forbes et al. [32, 33]
285 report that during the synthesis of ZSM-5/Theta-1 materials in the presence of
286 diethanolamine, the organic molecules were considered to have both a pore-filling
287 role and charge compensatory role. Furthermore, Rollmann et al. [34] assert that
288 protonated amine (e.g. ethylamine, pyrrolidine, hexamethylenimine) play the role as
289 counter ion of negative charge associated to tetrahedral aluminium atoms located into
290 zeolite framework, also for FER-type materials. Therefore, because in this work,
291 aluminium atoms are mainly present in tetrahedral coordination, protonated organic
292 molecules can be reasonably present to compensate negative charge of zeolite lattice.
293 Therefore, theoretically the $(\text{OSDA}^+ + \text{Na}^+)/\text{AlO}_2^-$ molar ration should be about one in
294 order to have the balance of aluminium negative charge. In this regard, it is possible to
295 calculate the unit cell molar composition for En-FER and DAO-FER, respectively, as it
296 follows:

297 En-FER: $\text{En}_{3.9}\text{Na}_{0.2}\text{Al}_{3.8}\text{Si}_{32.2}\text{O}_{72} \cdot 2.8 \text{H}_2\text{O}$

298 DAO-FER: $\text{DAO}_{1.0} \text{Na}_{2.8}\text{Al}_{4.7}\text{Si}_{31.3}\text{O}_{72} \cdot 7.8 \text{H}_2\text{O}$

299 Results clearly show that ethylenediamine is able to compensate the aluminium negative
300 charge of zeolite framework since $\text{En}^+/\text{AlO}_2^-$ molar ration is near one and a negligible
301 sodium amount is incorporated. On the contrary, 1,8-diaminooctane is not able to
302 compensate all of the aluminium negative charge and a higher amount of sodium is
303 incorporated. Moreover, in order to respect the electro-neutrality of the framework, one
304 DAO molecule should be able to compensate two aluminium negative charge. This
305 condition may be obtained if both the amino groups of DAO molecules are protonated
306 and able to compensate two different aluminium negative charge. This statement is also
307 confirmed by DFT theoretical study later reported.

308 The results of N_2 adsorption analysis are summarized in Table 1. En-FER sample shows
309 a slightly higher micropore volume than DAO-FER sample. This difference may be
310 related to the sodium content.

311 Figure 3 shows the adsorption/desorption isotherms of synthesised samples in protonic
312 form. Both En-FER and DAO-FER sample exhibit a type I adsorption isotherms typical
313 of microporous materials [28] but some differences may be highlighted. In fact, for En-
314 FER sample an uptake increase is observed at $P/P^\circ > 0.9$, that is less evident for DAO-
315 FER sample. This isotherm shape of En-FER may indicate the presence of external
316 mesopores due to agglomeration of crystals, as also revealed by SEM.

317 Figure 4 shows representative SEM micrographs revealing that all samples exhibit the
318 typical of ferrierite plat-like morphology with a well-developed $\{1\ 0\ 0\}$. However, the
319 crystals differ in size and the level of agglomeration. The En-FER crystals (Figure 6A)
320 have the following characteristics: length 2-3 μm , length/width ratio around 2 and
321 thickness 100 nm, while DAO as OSDA generates smaller crystals with size below 1
322 μm and lower length/width ratio (around 1.3). As showed by XRD analysis, a higher

323 crystallization rate is observed for DAO-FER sample, that may cause the formation of
324 smaller crystals. Moreover, a significant agglomeration is observed for En-FER sample,
325 while single crystal is obtained in presence of DAO.

326 3.2 Zeolite acidity

327 The NH₃-TPD profiles are reported in Figure 5 for all the synthesised samples
328 displaying three main peaks characterised by different ammonia maximum desorption
329 temperatures peaks (T_M) as an indicator of different acid sites family (the higher is T_M ,
330 the stronger is the acid sites).

331 As suggested by Niwa and Katada [35, 36], the interpretation of peaks with $T_M < 300$ °C
332 may be quite misleading since the desorption effect may also be related to physically
333 adsorbed ammonia interacting via a hydrogen bond with the NH₄⁺ ions adsorbed onto
334 acid sites. In this condition, having comparable desorption energy, the presence of weak
335 acid sites, may be partially hidden by physisorbed ammonia. On the contrary, the peaks
336 with $300^\circ\text{C} < T_M < 500$ °C are associated with ammonia molecules desorbed from strong
337 acid sites (both Brønsted and Lewis acid sites). The peak with $T_M > 700$ °C can be
338 associated to dehydroxylation phenomena [37, 38] since it is detected either in NH₃-
339 TPD experiments or in the corresponding “blank” TPD experiments performed over the
340 same catalyst and under the same experimental conditions, without NH₃ feed.

341 Quantitative results of NH₃-TPD measurements reported in Table 2. DAO-FER sample
342 exhibits a higher total acid sites concentration according to the higher aluminium
343 content measured by atomic absorption technique. DAO-FER also shows a higher $T_{M,HT}$
344 indicating a major strength of acid sites. Such aspect may be related to aluminium

345 distribution and location and further investigations should be done in order to elucidate
346 the role of OSDA on the aluminium siting [39, 40].

347 Figure 6 depicts the FT-IR spectra of H-ferrierite samples before and after adsorption of
348 deuterated acetonitrile. For bare samples, two main bands observed at 3745 cm^{-1} and
349 3600 cm^{-1} are associated with terminal silanol Si-OH and Brønsted acid sites Al-OH-Si
350 groups, respectively [41, 42]. A shoulder at around 3645 cm^{-1} is also present. Similar
351 result was reported already [28, 43], but the peak is not well-identified. Peixoto et al.
352 [44] suppose that the observed shoulder can be associated to a silanol group anchored
353 on extra-framework aluminium species (e.g., octahedral aluminium) as reported also by
354 Rachwalik et al. [45] even though in the investigated samples, NMR analysis suggests
355 that octahedral aluminium species are nearly absent. It is known from the literature that
356 aluminium in highly distorted coordination might become NMR silent and the observed
357 band at 3645 cm^{-1} can be associated to OH groups connected to the so called ‘invisible’
358 aluminium species [46, 47] that can play a role of Lewis acid sites [48, 49]. The
359 presence of these species could explain the non-stoichiometric Na/Al ratio discussed
360 above.

361 After adsorption of CD_3CN , two main bands at about 2296 cm^{-1} and 2322 cm^{-1} appear,
362 revealing the presence of both Brønsted and Lewis acid sites, respectively, in both the
363 samples. Smaller bands at lower wave length associated with physisorbed acetonitrile
364 are also present [30]. The concentration of Brønsted and Lewis sites were obtained
365 from the integral intensities of the IR bands of adsorbed CD_3CN at 2296 cm^{-1} and 2322
366 cm^{-1} , respectively, by using the extinction factor coefficients reported in Section 2.
367 Brønsted and Lewis site distribution of the investigated samples was calculated from the

368 area of bands recorded at 25 °C; both the samples exhibits a significant amount
369 (asround 40 %) of Lewis acid sites.

370 In order to estimate the strength of Brønsted and Lewis acid sites TPD measurements
371 were carried out in the range 25-400 °C. Figure 7 shows both the FT-IR profiles and
372 the fraction of Brønsted and Lewis acid sites free of adsorbed D₃CN molecules as a
373 function of desorption temperature.

374 The set of data show that Lewis acid sites are stronger than Brønsted ones for all the
375 samples. The desorption of Brønsted sites becomes significant above 150°C while the
376 Lewis sites are still occupied above 300°C. In particular, the desorption of acetonitrile
377 molecules starts at 50 °C and no occupied sites are present above 250 °C for both the
378 samples, indicating a similar strength distribution. On the contrary, the desorption of
379 probe molecules from Lewis acid sites starts above 25 °C and 150 °C for En-FER and
380 DAO-FER, respectively. This result indicates that En-FER possesses weaker Lewis acid
381 sites than DAO-FER. By considering as strong Lewis acid sites fraction, the value of
382 Lewis acid sites still occupied by CD₃CN molecules at 300 °C, it is possible to calculate
383 the fraction of strong Lewis sites reported in Table 2 (last column). DAO-FER
384 possesses a higher amount of strong Lewis acid sites than En-FER, indicating that the
385 synthesis system affects both typology and strength of acid sites.

386 ***3.3 DTF calculations***

387 As previously discussed, 1,8-diaminooctane was never reported as a template for FER-
388 type structure, to the best of our knowledge. Our data unambiguously show that DAO is
389 incorporated in FER channels and fulfil the function of OSDA and charge balancing
390 cation, similarly to the other nitrogen-SDA. This aspect was also addressed from a

391 theoretical point of view, by performing a DFT simulation for the investigated systems.
392 In this regard, zeolite is considered as an infinite crystal and dispersion corrections are
393 used in order to take into account confinement effects. Both binding energies and length
394 of H(SDA)---O(FER) hydrogen bonds are reported in Table 3 and the optimized
395 structures are displayed in Figure 8.

396 The binding of both En and DAO with the 10 MR pore walls of zeolite are
397 thermodynamically favoured (i.e. negative binding energies are calculated) suggesting
398 that SDAs bind through hydrogen-bond formations with the lattice of zeolite. In
399 particular, the strong interaction energy calculated for En-FER system may be attributed
400 to the short hydrogen bond lengths, that are also almost linear and therefore stronger
401 than the other systems.

402 Similarly, DAO is stabilized in FER cavity via several short and linear N-H---O(ZEO)
403 H-bonds, which explains, also in this case, the computed strong interaction energy with
404 pore walls of FER zeolite. Furthermore, the computed dispersion energies for all the
405 systems is about 0.3% to the total energy, indicating that there is not a particular
406 stabilization of SDA molecules due to the attractive dispersion interactions or
407 confinement effect. Concerning DAO-FER system, DFT calculations suggest that DAO
408 molecules may be located in 10 MR channels of FER zeolite and that the formation of
409 H-bond is the driving force for the stabilization of the molecules within the voids of
410 zeolite. These results are in agreement with the chemical analysis. In fact, in the case of
411 En, SDA molecules are protonated and they are able to compensate the negative charge
412 of aluminium located in both 8 MR and 10 MR channels, and therefore, a low amount
413 of sodium is required. On the contrary, if the accommodation of protonated SDA
414 molecules within 8 MR channels is difficult, as in the case of DAO, more sodium is

415 required for compensating negative charge inside 8 MR channels. This conclusion is in
416 agreement with previous studies on ferrierite [50, 51].

417

418 **4. CONCLUSIONS**

419 In this work, for the first time, FER-type crystals were successfully synthesised by
420 using 1,8-diaminooctane (DAO) as organic structure directing agent (DAO-FER
421 sample). The obtained results in terms of crystals morphology and acidity were
422 discussed by taking FER zeolite prepared with ethylenediamine as reference (En-FER
423 sample). XRD analysis suggests that the presence of DAO reduces the induction time
424 respect to ethylenediamine, leading to the formation of smaller crystals with a lower
425 agglomeration. TG/DTA clearly indicates the presence of DAO inside the cavity of
426 zeolite, whilst chemical analysis suggest that protonated DAO is able to balance AlO_2^-
427 charge of the framework along 10 MR channels, while sodium shall be incorporated
428 along the 8 MR. On the contrary, a negligible amount of sodium is requested in the case
429 of ethylenediamine. In fact, DFT simulations show that DAO may be incorporated
430 along the 10 MR only, whilst ethylenediamine is able to balance the charges of Al
431 centres along both 8 and 10 MR channels. Furthermore, a higher amount of aluminium
432 is incorporated when DAO is used as OSDA leading to a higher total acidity. FT-IR
433 measurements reveal that both DAO- and En-FER samples possess a high amount of
434 Lewis acid sites (about 40%) that are stronger for DAO-FER sample.

435 The obtained results show the possibility to control the physicochemical properties of
436 zeolite crystals by selecting the type of structure directing agent leading to tailored
437 materials for specific applications, e.g. heterogeneous catalysis.

438

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442

443 **REFERENCES**

444 [1] A. Corma, *J. Catal.* 216 (2003) 298 – 312.

445 [2] B. M. Weckhuysen, J. Yu, *Chem. Soc. Rev.* 44 (2015) 7022

446 [3] F. Di Renzo, *Catal. Today* 41 (1998) 37-40.

447 [4] J. N. Armor, *Catal. Today* 163 (2011) 3-9

448 [5] S. Mintova, J.-P. Gilson, V. Valtchev, *Nanoscale* 5 (2013) 6693-6703.

449 [6] J. Pérez-Ramírez, C. H. Christensen, K. Egeblad, C. H. Christensen, J. C.
450 Groen, *Chem. Soc. Rev.* 37 (2008) 2530-2542.

451 [7] V. Valtchev, G. Majano, S. Mintova, J. Pérez-Ramírez, *Chem. Soc. Rev.* 42
452 (2013) 263-290.

453 [8] W.-Q. Xu, Y.-G. Yin, S. L. Suib, J. C. Edwards, C.-L. O'Young, *J. Phys. Chem.*
454 *99* (1995) 9443-9451.

455 [9] Y. Kamimura, C. Kowenje, K. Yamanaka, K. Itabashi, A. Endo, T. Okubo,
456 *Microp. Mesop. Mater.* 181 (2013) 154-159.

457 [10] S. F. Abdo, S. T. Wilson, in: J. Cêjka, R. Morris, P. Nachtigall (Eds.), *Zeolites*
458 *in catalysis: properties and applications*, The Royal Society of Chemistry,
459 London, UK, 2017, RSC Catalysis Series 28, pp. 310-350.

- 460 [11] E. Catizzone, A. Aloise, M. Migliori, G. Giordano, *Microp. Mesop. Mater.* 243
461 (2017) 102-111.
- 462 [12] E. Catizzone, G. Bonura, M. Migliori, F. Frusteri, G. Giordano, *Molecules*, 23
463 (2018) 31-58.
- 464 [13] G. Bonura, M. Migliori, L. Frusteri, C. Cannilla, E. Catizzone, G. Giordano, F.
465 Frusteri, *J. CO₂ Util.* 24 (2018) 398-406.
- 466 [14] P.S.S. Prasad, J.W. Bae, S. Kang, Y. Lee, K. Jun, *Fuel Process. Technol.* 89
467 (2008) 1281 – 1286.
- 468 [15] E. Catizzone, M. Milgiori, A. Purita, G. Giordano, *J. Energ. Chem.* 30 (2019)
469 162-169
- 470 [16] Y. Suzuki, T. Wakihara, K. Itabashi, M. Ogura, T. Okubo, *Top. Catal.* 52 (2009)
471 67-74
- 472 [17] Z. Gogebakan, H. Yucel, A. Culfaz, *Ind. Eng. Chem. Res.* 46 (2007) 2006-2012
- 473 [18] H. Gies, R.P. Gunawardane, *Zeolites* 7 (1987) 442-445.
- 474 [19] N.R. Forbes, L.V.C. Rees, *Zeolites* 15 (1995) 444-451
- 475 [20] R.A. Rakoczy, M. Breuninger, M. Hunger, Y. Traa, J. Weitkamp, *Chem. Eng.*
476 *Technol.* 25 (2002) 273-275.
- 477 [21] R. A. Rakoczy, Y. Traa, P. Kortunov, S. Vasenkov, J. Kärger, J. Weitkamp,
478 *Microp. Mesop. Mater.* 104 (2007) 179-184.
- 479 [22] Y. Lee, M. B. Park, P. S. Kim, A. Vicente, C. Fernandez, I.-S. Nam, S. B. Hong,
480 *ACS Catal.* 3 (2013) 617-621.

- 481 [23] A. Kuperman, S. Nadimi, S. Oliver, G. A. Ozin, J. M. Garcés, M. M. Olken,
482 Nature 365 (1993) 239-242.
- 483 [24] A.B. Pinar, L. Gómex-Hortiguela, L.B. McCusker, J. Pérez-Pariente, Chem.
484 Mater. 25 (2013) 3654-3661.
- 485 [25] A.B. Pinar, C. Márquez-Álvarez, M. Grande-Casas, J. Pérez-Pariente, J. Catal.
486 263 (2009) 258-265.
- 487 [26] M. Derewinski, M. Machowska, Stud. Surf. Sci. Catal. 154 (2004) 349-354.
- 488 [27] G. Giordano, N. Dewale, Z. Gabelica, J. B. Nagy, E. G. Derouane, Appl. Catal.
489 71 (1991) 79-87.
- 490 [28] X. Chen, T. Todorova, A. Vimont, V. Ruaux, Z. Qin, J.-P. Gilson, V. Valtchev,
491 Microp. Mesop. Mater. 200 (2014) 334-342.
- 492 [29] P. Lanzafame, G. Papanikolaou, S. Perathoner, G. Centi, M. Migliori, E.
493 Catizzone, G. Giordano, Appl. Catal. A: Gen. 580 (2019) 186-196.
- 494 [30] B. Wichterlová, Z. Tvarůková, Z. Sobalík, P Sarv, Micropor. Mesopor. Mat. 24
495 (1998) 223 – 233.
- 496 [31] D. Vuono, L. Pasqua, F. Testa, R. Aiello, A. Fonseca, T.I. Korányi, J. B.Nagy,
497 Micropor. Mesopor. Mat. 97 (2006) 78 – 87.
- 498 [32] N.R. Forbes, L.V.C. Rees, Zeolites 15 (1995) 444-451.
- 499 [33] N.R. Forbes, L.V.C. Rees, Zeolites 15 (1995) 452-459.
- 500 [34] L.D. Rollmann, J.L. Schlenker, S.L. Lawton, C.L. Kennedy, G.J. Kennedy, D.J.
501 Doren, J. Phys. Chem. B 103 (1999) 7175-7183.
- 502 [35] M. Niwa, N. Katada, Chem. Rec. 13 (2013) 432 – 455.
- 503 [36] N. Katada, M. Niwa, Catal. Surv. Asia 8 (2004) 161 – 170.

- 504 [37] C.V. Hidalgo, H. Itoh, T. Hattori, M. Niwa, Y. Murakami, *J. Catal.* 85 (1984)
505 362-369.
- 506 [38] C. Costa, I.P. Dzikh, J.M. Lopes, F. Lemos, F.R. Ribeiro, *J. Mol. Catal. A:*
507 *Chem.* 154 (2000) 193-201.
- 508 [39] N. Wang, M. Zhang, Y. Yu, *Microp. Mesop. Mater.* 169 (2013) 47-53
- 509 [40] D. Zhou, Y. Bao, M. Yang, N. He, G. Yang, *J. Mol. Catal. A: Chem.*, 244
510 (2006) 11-19.
- 511 [41] Y.P. Khitev, Y.G. Kolyagin, I.I. Ivanova, O.A. Ponomareva, F. Thibault-
512 Starzyk, J.-P. Gilson, C. Fernandez, F. Fajula, *Microp. Mesop. Mater.* 146 (2011)
513 201-207.
- 514 [42] J. Datka, M. Kawalek, K. Góra-Marek, *Appl. Catal. A: Gen.* 243 (2003) 293-
515 299.
- 516 [43] P. Cañozares, A. Carrero, P. Sánchez, *Appl. Catal. A: Gen.* 190 (2000) 93-105
- 517 [44] D.P.B. Peixoto, S.M. Cabral de Menezes, M.I. Pais da Silva, *Mater. Lett.* 57
518 (2003) 3933-3942.
- 519 [45] R. Rachwalik, Z. Olejniczak, J. Jiao, J. Huang, M. Hunger, B. Sulikowski, *J.*
520 *Catal.* 252 (2007) 161-170.
- 521 [46] A. Bonilla, D. Baudouin, J. Pérez-Remírez, *J. Catal.* 265 (2009) 170-180.
- 522 [47] C.P. Grey, A.J. Vega, *J. Am. Chem. Soc.* 117 (1995) 8232-8242.
- 523 [48] D. Verboekend, K.C. Groen, J. Pérez-Remírez, *Adv. Funct. Mater.* 20 (2010)
524 1441-1450.
- 525 [49] F. Deng, Y. Yue, C. Ye, *Solid State Nucl. Magn. Reson.* 10 (1998) 151-160.
- 526 [50] L. Domokos, L. Lefferts, K. Seshan, J.A. Lercher, *J. Mol. Catal. A: Chem.*, 162
527 (2000) 147-157.

528 [51] P. Sarv, B. Wichterlová, J. Čejka, J. Phys. Chem. B, 102 (1998) 1372-1378.

529

530 **TABLES CAPTIONS**

531 **Table 1** Chemical composition, pore volume and surfaces characteristics of
532 synthesised FER-type materials.

533 **Table 2** Acidic properties of investigated catalysts.

534 **Table 3** Calculated binding energies and lengths for the investigated SDA-FER
535 systems from DFT simulation

536

537

538 **FIGURES CAPTIONS**

- 539 **Figure 1** XRD pattern of FER samples synthesized with ethylenediamine and 1,8-
540 diaminooctane (DAO). (*) indicates the presence of Kaetite phase.
- 541 **Figure 2** TGA (continuous line) and dTG (dashed line) data of FER samples
542 synthesised with DAO/En=0 (A), DAO/En=0.5 (B), DAO/En=2 (C) and
543 DAO/En= ∞ (D).
- 544 **Figure 3** N₂ adsorption (closed circle) and desorption (open circle) isotherms at 77
545 of En-FER and DAO-FER samples.
- 546 **Figure 4** SEM micrographs of FER-type materials synthesised with
547 ethylenediammine and 1,8-diaminooctane.
- 548 **Figure 5** NH₃-TPD profiles of En-FER and DAO-FER samples.
- 549 **Figure 6** FT-IR spectra of of En-FER and DAO-FER samples after evacuation at
550 300 °C for 4h (a) and after adoption of CD₃CN molecules at 25°C (b).
551 All the spectra are recorded at 10⁻⁶ torr.
- 552 **Figure 7** FT-IR spectra of D₃-acetonitrile adsorbed on En-FER (A), and DAO-
553 FER (B) evacuated at 25 °C (a), 50 °C (b), 100 °C (c), 150 °C (d), 200
554 °C (e), 250 °C (f) and 300 °C (g). Fraction of Brønsted (●) and Lewis (■)
555 acid sites free of adsorbed D₃CN molecules as a function of desorption
556 temperature for En-FER (A') and DAO-FER(B').
- 557 **Figure 8** DFT optimized crystal structures of FER with SDA molecules. SDA in
558 10 MR and in 8 MR are shown in the top and down panels, respectively,
559 in Figs. a, b, c. Optimized unit cells structures of every FER-SDA are
560 displaced at the left-side and 2x2x2 cells - at the right side in Figs. a, b, c

561 and d. The dashed lines indicate all the H-bonds $\leq 3 \text{ \AA}$. The lengths of
562 the shorter and linear H-bonds below 2.5 \AA are reported in Table X.
563 Atomic colour code: dark blue for Si; red for O; light blue for Al^{3+} , black
564 for C, violet for N, grey for H and yellow for Na.
565

<i>SAMPLE</i>	En-FER	DAO-FER
Na/Al_{bulk}^a [mol/mol]	0.06	0.60
Si/Al_{bulk}^a [mol/mol]	8.4	6.6
S_{BET}^b [m²/g]	329	287
V_{mic}^c [cm³/g]	0.131	0.125

^a Atomic absorption

^b BET superficial area

^c Micropore volume calculated by *t*-plot method

Table 1

	En-FER	DAO-FER
<i>NH₃-uptake</i>		
<i>[μmol/g_{cat}]</i>	<i>1052</i>	<i>1418</i>
<i>T_{M,LT}^a</i>		
<i>[°C]</i>	<i>245</i>	<i>231</i>
<i>x_{LT}^[b]</i>	<i>0.30</i>	<i>0.40</i>
<i>T_{M,HT}^c</i>		
<i>[°C]</i>	<i>436</i>	<i>455</i>
<i>x_{HT}^d</i>	<i>0.70</i>	<i>0.60</i>
<i>Lewis acid sites^e</i>		
<i>[%]</i>	<i>0.41</i>	<i>0.40</i>
<i>Strong Lewis acid sites^f</i>		
<i>[%]</i>	<i>0.16</i>	<i>0.24</i>

^a Temperature of maximum desorption of NH₃ between 100 and 300°C

^b Fractional population of sites between 100 and 300°C

^c Temperature of maximum desorption of NH₃ above 300°C

^d Fractional population of sites above 300°C

^e Estimated by FT-IR analysis of adsorbed D₃-acetonitrile at 25°C

^f Estimated by FT-IR analysis of adsorbed D₃-acetonitrile at 300°C

Table 2

<i>Sample</i>	<i>Binding energy</i> (eV/mol)		<i>Binding lengths</i> (Å)	
	8 MR	10 MR	8 MR	10 MR
En-FER	-24.01	-25.76	1.820	1.864
			1.908	1.902
			1.710	2.473
DAO-FER	N.a.N	-22.67	-	2x1.960; 2.042 ^a 2.129; 1.498 ^b 2.441, 2.488 ^c

^a NH₃⁺---O(ZEO) H-bond;
^b NH₂---O(ZEO) H-bond
^c C(CH)---O(ZEO) H-bond

Table 3

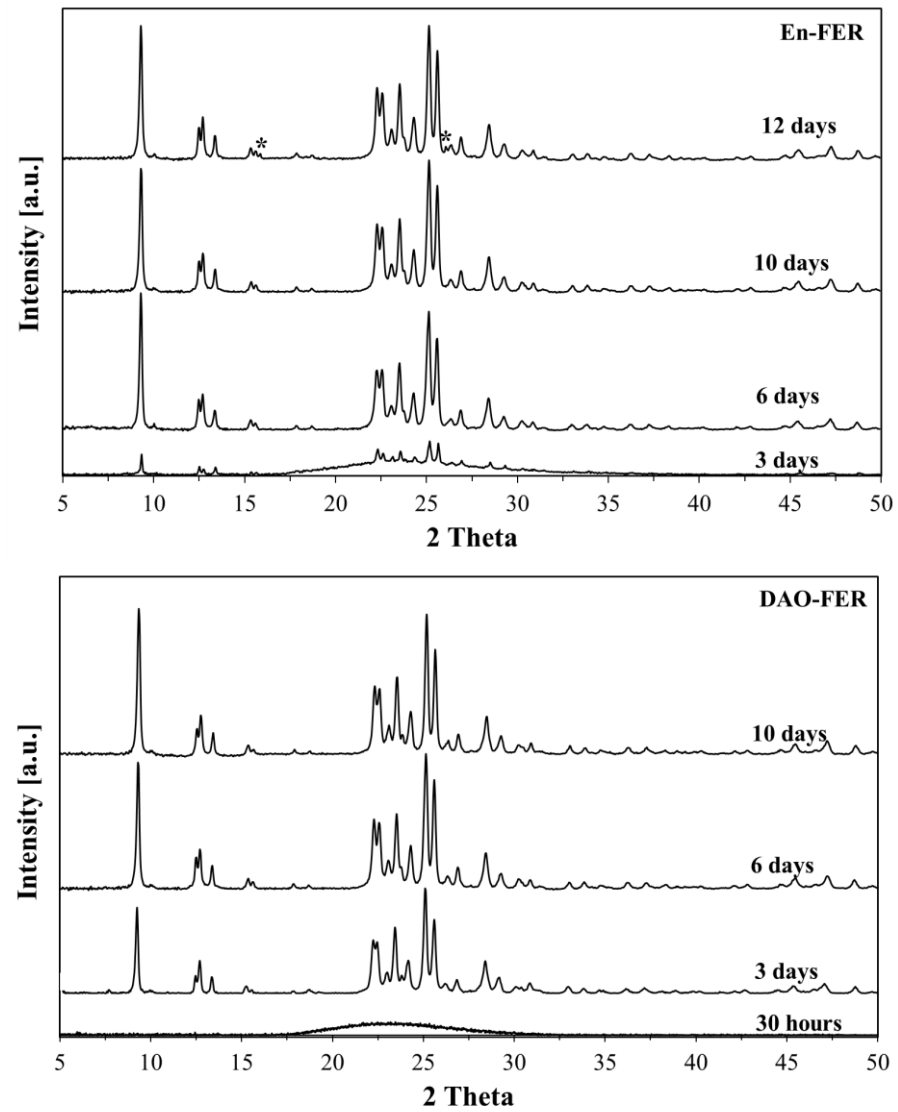


Figure 1

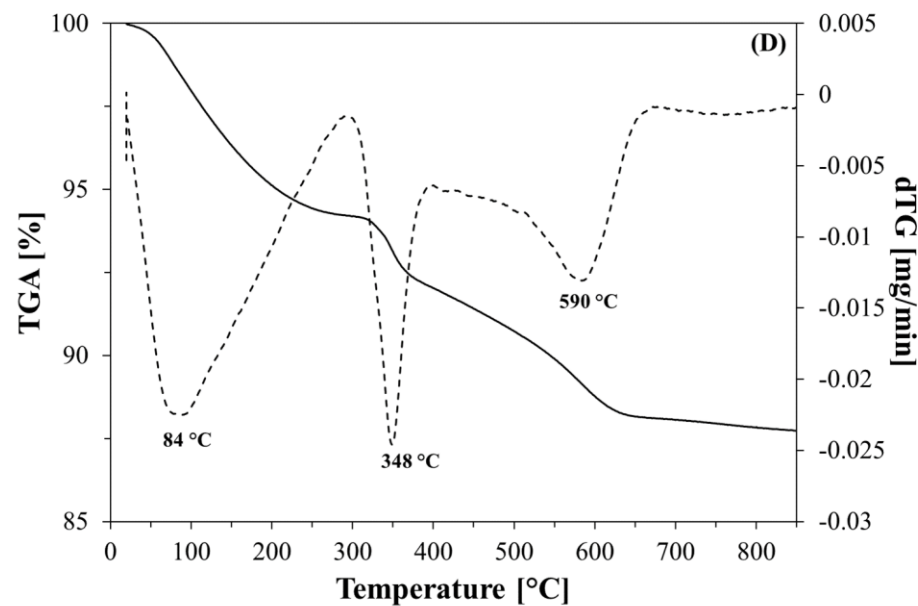
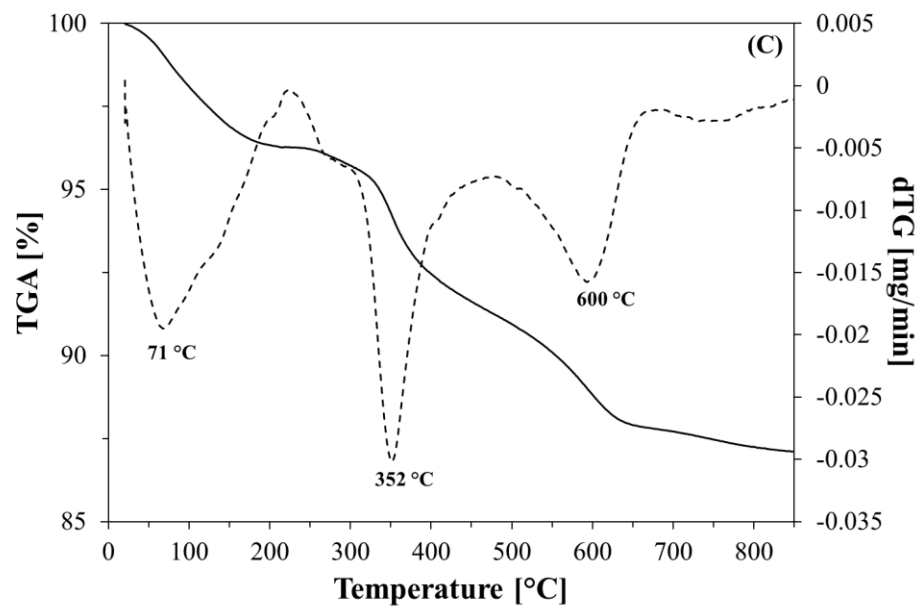
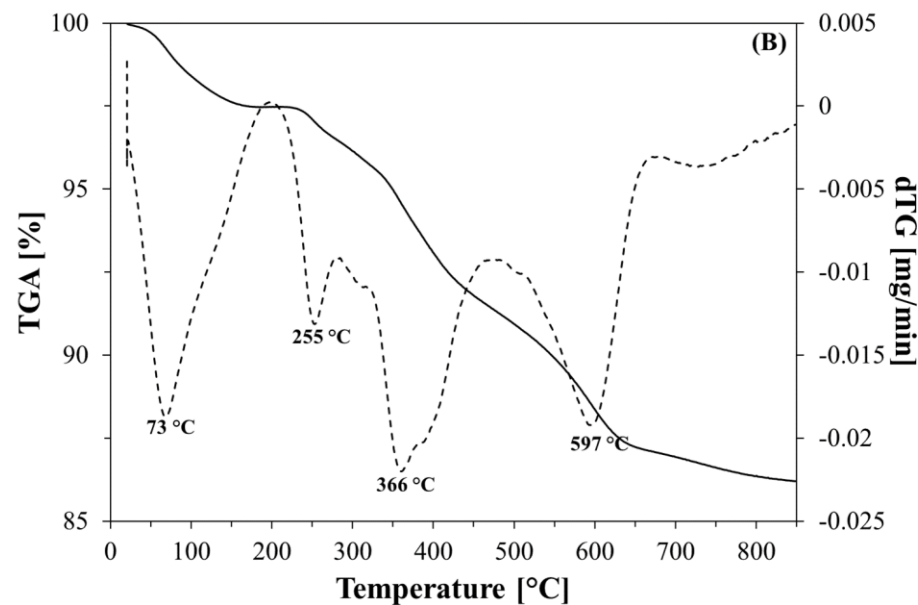
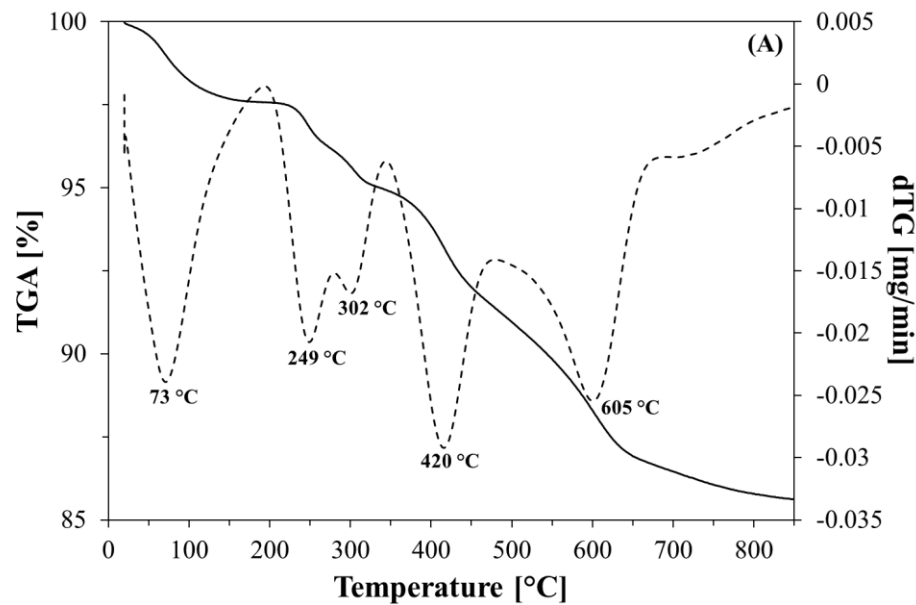


Figure 2

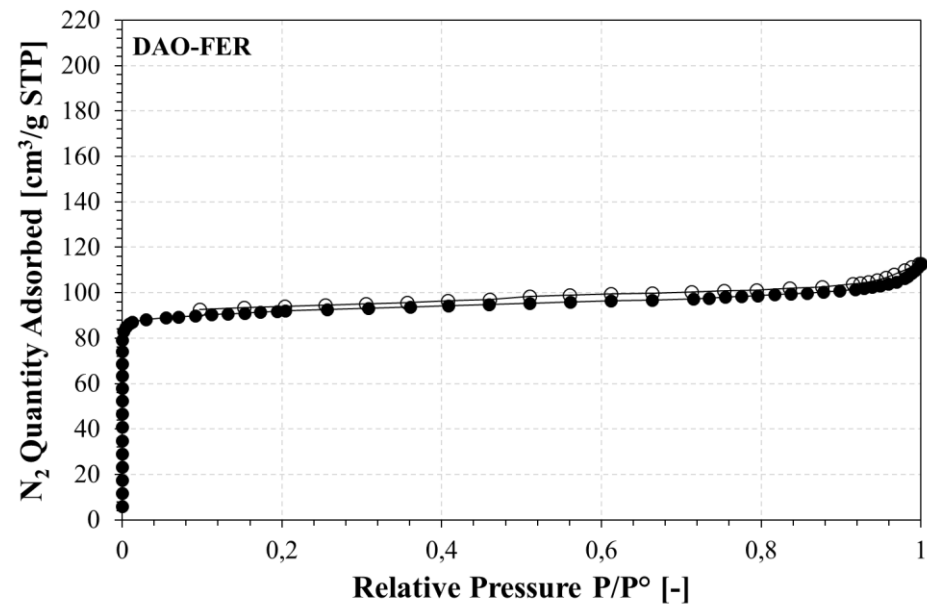
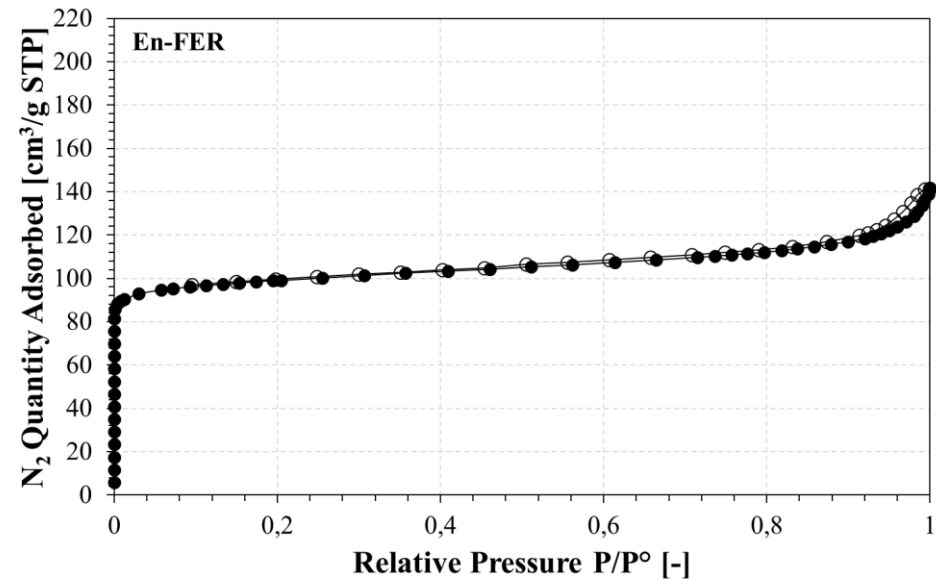


Figure 3

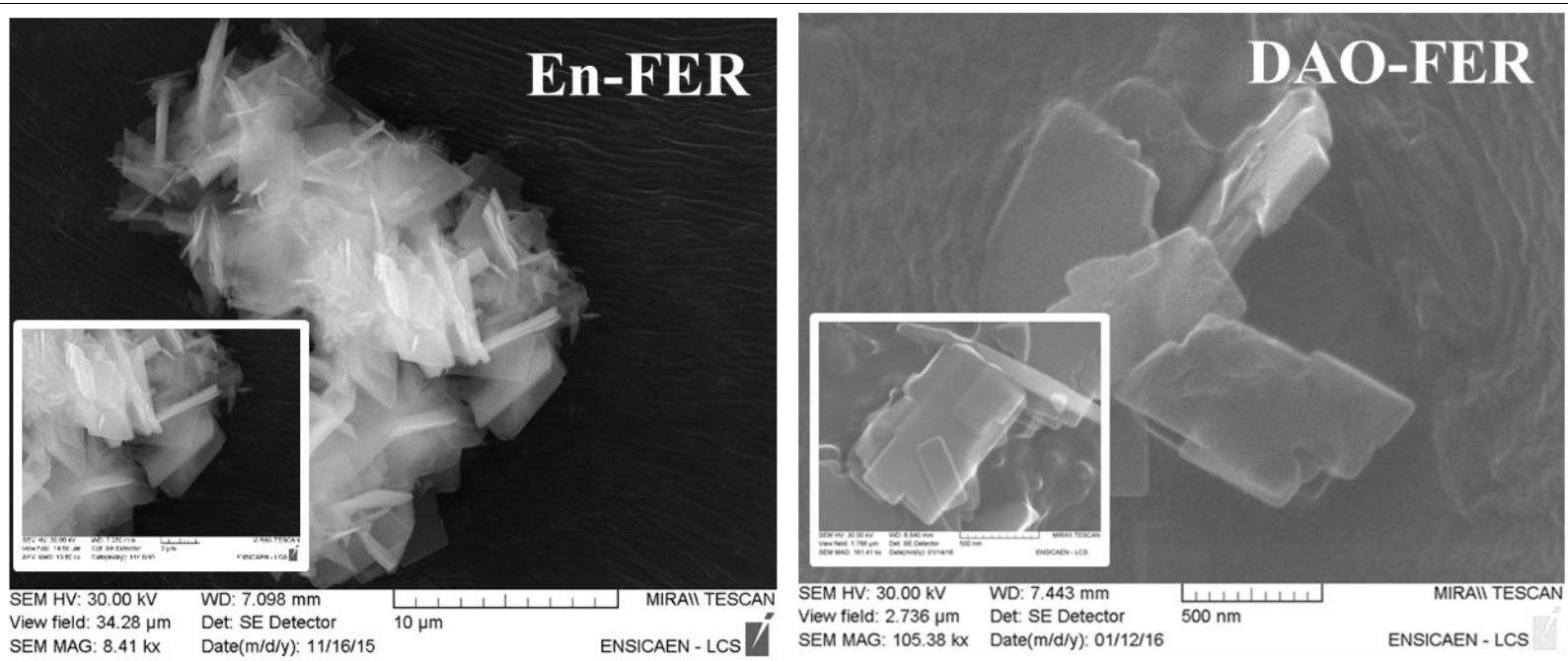


Figure 4

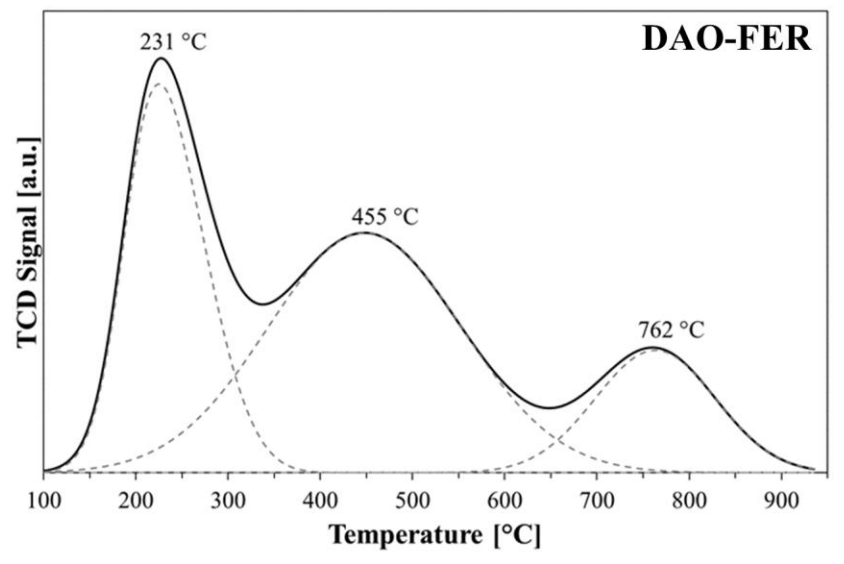
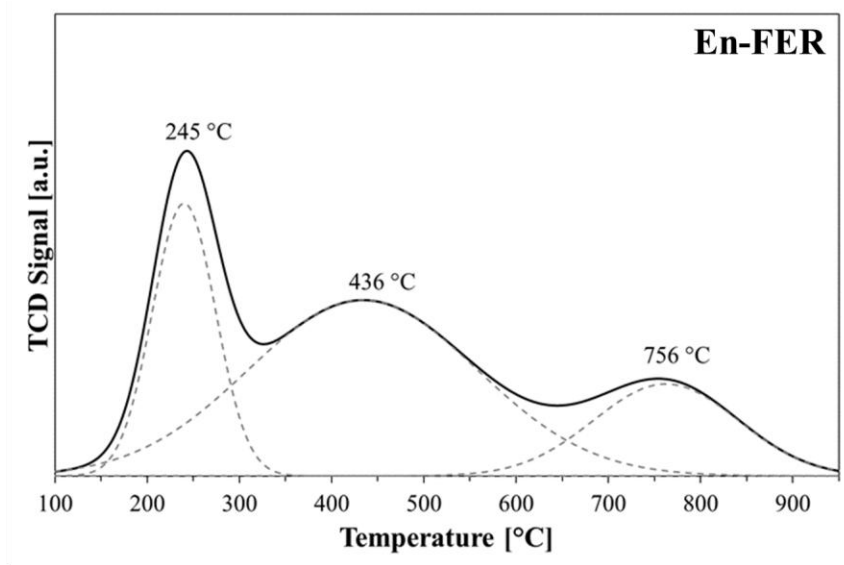


Figure 5

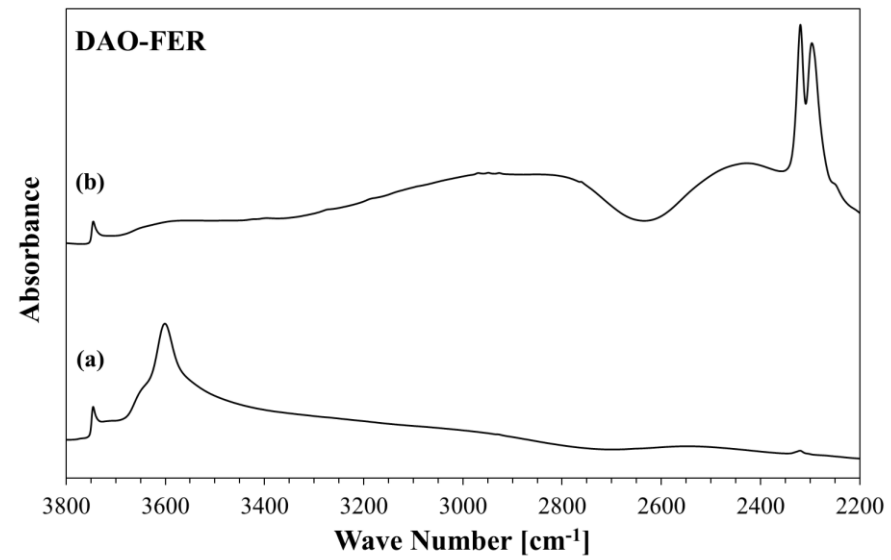
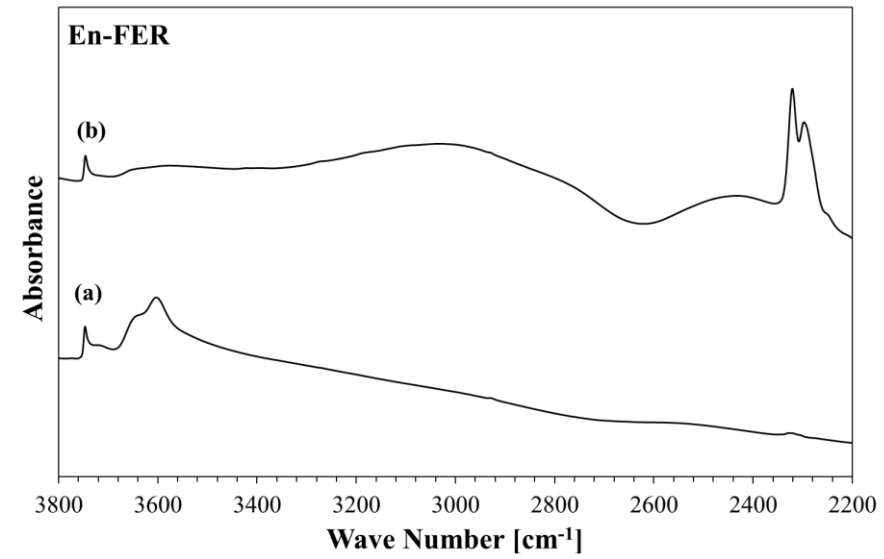


Figure 6

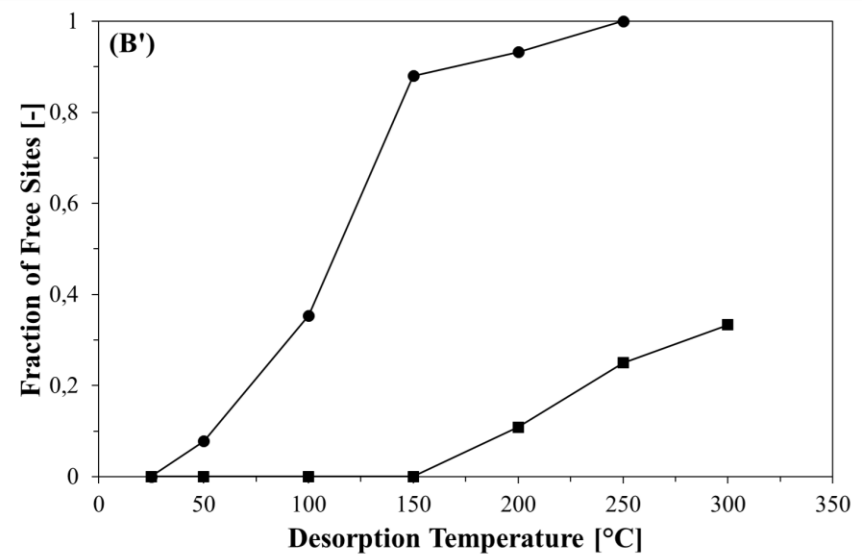
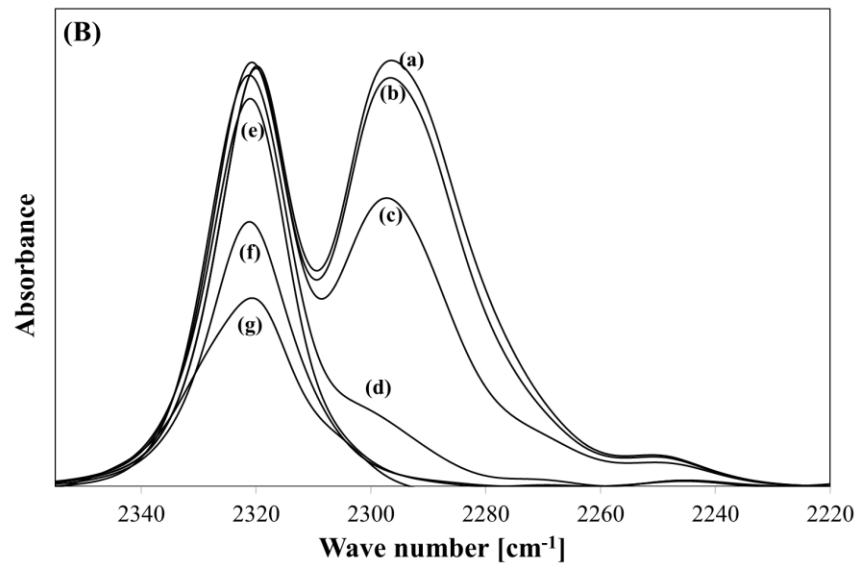
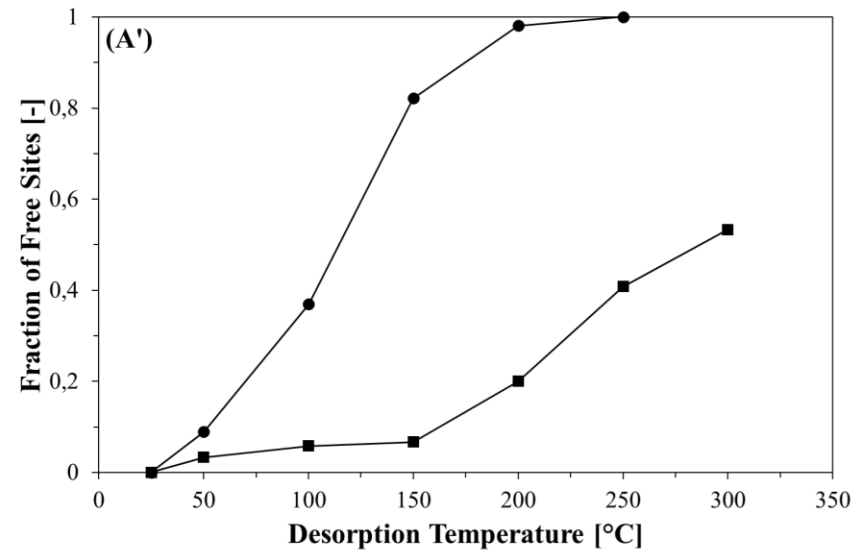
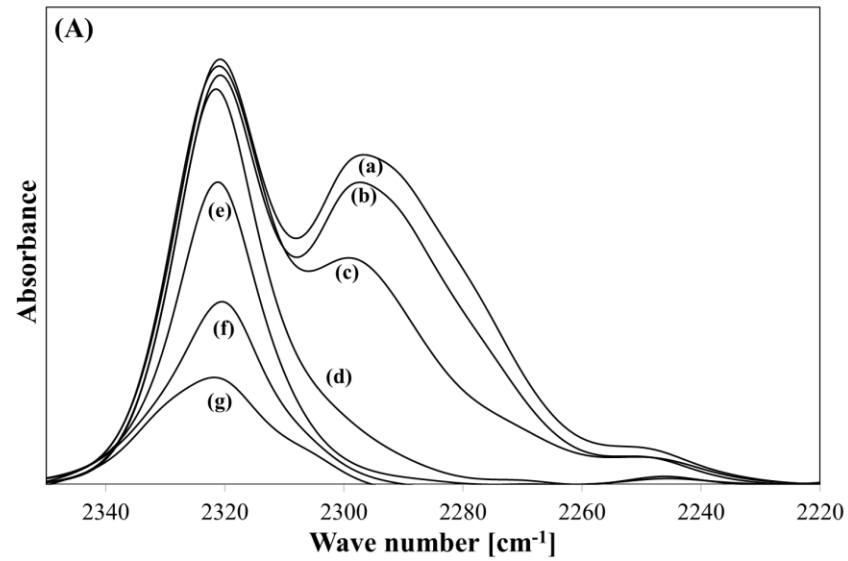


Figure 7

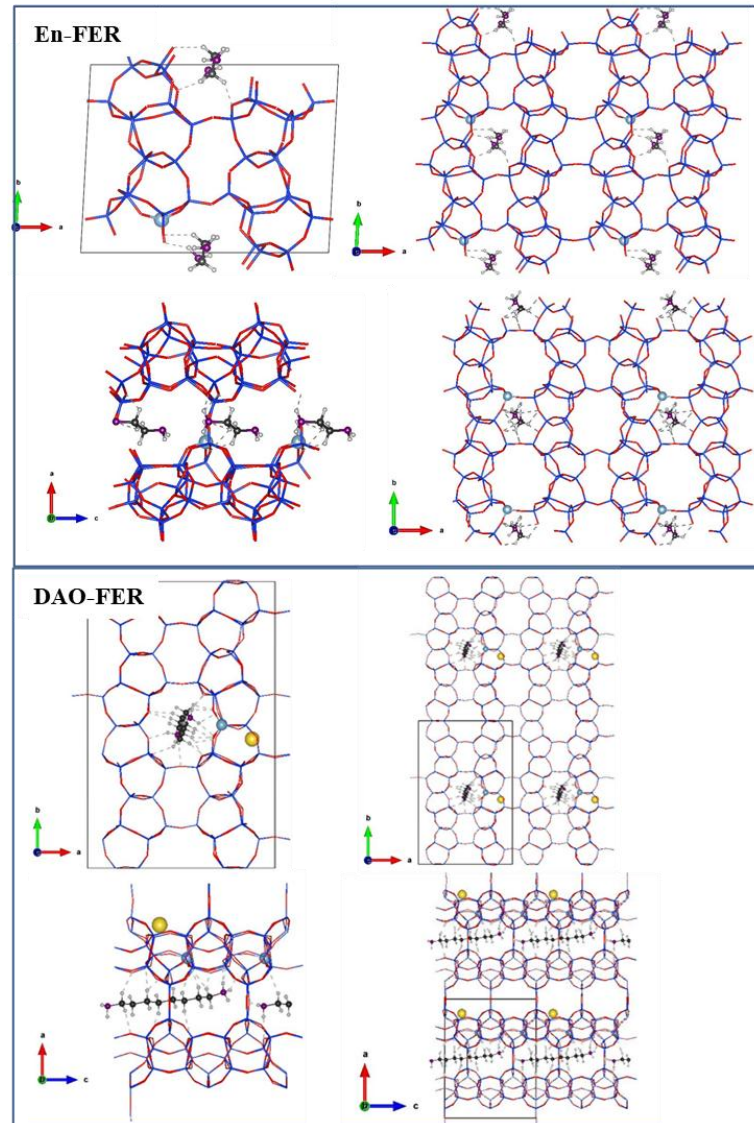


Figure 8