

New synthesis routes and catalytic applications of ferrierite crystals. Part 1: 1,8-Diaminooctane as a new OSDA

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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 diaminoctane (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 crystlas 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 characterized with XRD, TG/DTA, SEM, N₂ adsoprtion/desorption, FTIR and ²⁷Al-26 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 very few zeolite structures have found significant catalytic application in petrochemical
and refining industries. FAU (X and Y), MFI (ZSM-5 and Silicalite-1), MOR, BEA
(beta), MWW (MCM-22), AEL (SAPO-11) and CHA (SAPO-34) are examples of
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 by 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. Göğebakan 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 the range 10-25) and OSDA amount did not significantly influence the crystallization
rate. On the contrary, OSDA affected crystal morphology: individual or platelet
crystallites were obtained in presence of pyrrolidine or ethylenediamine, respectively.
Furthermore, the authors even found mordenite as competitive phase only when
pyrrolidine is used as OSDA.

Kamimura et al. [9] reported the synthesis of ferrierite in presence of pyridine as OSDA, obtaining well-defined plate-like crystals with a SiO₂/Al₂O₃ up to 324. In particular, the synthesis of pure siliceous ferrierite was successful in presence of sodium fluoride. Aluminium-free ferrierite was also obtained in presence of ethylediamine as OSDA and boric acid as templates [18].

On the contrary, Forbes et al. [19] reported that, using diethanolamine as OSDA, pure
phase ferrierite crystals may be obtained only in a narrow Si/Al ratio. In particular, the
authors found that by increasing the SiO₂/Al₂O₃ from 16 to about 25, a ferrierite/ZSM-5
mixed phase was obtained.

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

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

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

Pinar et al. assert that the choice of organic template molecules (OSDA) in FER-type 95 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.

In this paper, FER-type crystals were synthesized by using a long amine as 1,8diaminooctane as OSDA. This molecule is usually used for the synthesis of MEL, TON and ZSM-48 zeolites. In the case of MEL and TON zeolite, the success of the crystallization of the desired phase strongly depends on the stirring condition: static or high-speed agitation condition lead to the selective formation of high pure MEL or TON phase, respectively [25]. Crystallization with stirring is also required for the synthesis of
ZSM-48 [26].

To the best of our knowledge, there has been no report on the synthesis of ferrierite by using 1,8-diaminoctane as OSDA. In this work the crystallization of ferrierite in presence of 1,8-diaminioctane is carried out with the aim to assess the effect of this molecule on physico-chemical properties of obtained materials. Furthermore, in order to have new insights about the role of amine molecule length, FER-type zeolite with ethylenediammine 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 NH₃-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 (SiO₂, 40 wt% suspension in H₂O, Aldrich), sodium aluminate (NaAlO₂, 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 adopting136 the following synthesis gel molar composition [28]:

137
$$19.7 \text{ En} - 1.85 \text{ Na}_2\text{O} - 15.2 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 590 \text{ H}_2\text{O}$$

In a typical synthesis 0.3 g of NaOH and 1.3 g of sodium aluminate were dissolved in 64.1 g of distilled water. Then 8.2 g of ethylenediamine were added to dropwise and the solution was stirred for 30 min. Afterwards 15.8 g of colloidal silica were added dropwise to the solution, and the obtained gel was stirred (300 rpm) at room temperature for 1 h. Crystallization was carried out in 120 ml stainless-steel Teflon 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

148

 $x DAO - 1.85 Na_2O - 15.2 SiO_2 - 1 Al_2O_3 - 590 H_2O - y En$

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

In the synthesis of DAO-FER only DAO was used as SDA. For this latter synthesis, 0.3 g of NaOH and 1.3 g of sodium aluminate were dissolved in 21 g of distilled water. A secondary solution was prepared by dissolving 7.8 g of DAO into 42 g of distilled water, under vigorous stirring. Afterwards, the two solutions were blended and 15.8 g of colloidal silica were added dropwise and the obtained gel was stirred (300 rpm) at room temperature for 1 h. Crystallization was carried out in 120 ml stainless-steel Teflon 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 $5^{\circ} < 2\theta < 50^{\circ}$, 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).

The specific surface area and the micropores volume of the calcined samples were
obtained from BET and t-plot analysis of porosimetry data (ASAP 2020 Micromeritics)
under nitrogen adsorption at -196 °C, after a pre-treatment in vacuum at 200°C for 12 h.
The thermo-gravimetric analysis over the as-synthesised samples was performed on the
automatic TG/DTA instrument (Shimadzu) under 50 cc/min of air flow in the
temperature range 25-850°C (heating rate of 5 °C ·min⁻¹).

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

181 The ²⁷Al-NMR spectra were acquired at 130.3 MHz with radiofrequency power of 54 182 kHz, a pulse length of 4.6 μ s 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 NH₃-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 150°C and saturated with 10% v/v NH₃/He mixture with a flow rate of 20 STP mL·min⁻ 188 ¹ for 2 h. Ammonia physically adsorbed was removed by purging in helium at 150°C for 189 190 1 h until TCD baseline stabilization. Desorption measurement was carried out in the temperature range of 100-950°C (10 °C·min⁻¹) using a helium flow rate of 20 STP 191 192 $mL \cdot min^{-1}$.

193 Brønsted and Lewis acid sites concentration was measured via FT-IR analysis by using 194 D₃-acetonitrile as a probe molecule. Infrared spectra were recorded with a Bruker 195 Equinox 55 spectrometer. The adsorption of D₃-acetonitrile was performed at room 196 temperature with a pressure of 10 Torr, after that the samples were degassed under high vacuum condition (cell pressure: 10^{-6} Torr) at 300°C for 4 h, in order to purge adsorbed 197 198 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 °C (temperature step of 50°C), outgassing the sample for 30 minutes at any 201 temperature variation.

The amount of D_3 -acetontrile adsorbed on Brønsted and Lewis was determined by using a literature value for the molar absorption coefficient [30]. The number of Brønsted sites was calculated from the area of the bands observed at 2297 cm⁻¹ by adopting an extinction coefficient of 2.05 cm/ μ mol, whilst the number of Lewis acid sites was calculated from the area of the bands between 2310–2325 cm⁻¹ by adopting an extinction factor of 3.6 cm/ μ mol. Peaks analysis and deconvolution for both FT–IR and NH₃-TPD profiles were performed by using commercial software (PeakFit 4.12, 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 patters 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.

Because DAO was never reported as a template in FER zeolite synthesis, a deeper investigation by TG/DTA analysis of as-synthesised materials was performed. The thermo-analytic results of DAO-containing systems are reported in Figure 2, in terms of thermogravimetric (TG) and first derivate (dTG) profiles. Heat flow profiles (DTA) are
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 ethylendiammine, 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 ethylediamine 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 diaminooctane 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-diaminooctane 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.

Figure S.3 shows the ²⁷Al MAS NMR spectra of the H-form FER-type zeolites with En or DAO as OSDA. They are dominated by a signal centered at around 55 ppm, characteristic of tetra-coordinated aluminium species in zeolite framework. A broad signal at around 0 ppm revealing the presence of octahedral extra-framework aluminium (about 10%) for both the samples. The observed quadrupolar line broadening can be caused by distortions of the octahedral symmetry of AlO_6 sites.

It is well-known that the zeolite structure is generated by a network of SiO_4 and $AlO_4^$ tetrahedral linked together by a shared oxygen atom. Due to the presence of trivalent atoms (e.g. aluminium) in the tetrahedral units, the framework offers a negative charge which needs to be balanced with non-framework exchangeable cations that are 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, expecially. 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 diethanolammine, 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. Therefore, theoretically the $(OSDA^+ + Na^+)/AIO_2^-$ molar ration should be about one in 293 294 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: En_{3.9}Na_{0.2}Al_{3.8}Si_{32.2}O₇₂·2.8 H₂O

298 DAO-FER: DAO_{1.0} Na_{2.8}Al_{4.7}Si_{31.3}O₇₂·7.8 H₂O

299 Results clearly show that ethylenediamine is able to compensate the aluminium negative 300 charge of zeolite framework since En^+/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.

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

Figure 4 shows representative SEM micrographs reveailing that all samples exhibit the typical of ferrierite plat-like morphology with a well-developed {1 0 0}. However, the crystals differ in size and the level of agglomeration. The En-FER crystals (Figure 6A) have the following characteristics: length 2-3 μ m, length/width ratio around 2 and thickness 100 nm, while DAO as OSDA generates smaller crystals with size below 1 μ m 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 $T_M < 300 \,^{\circ}\text{C}$ 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 $300^{\circ}C < T_M < 500^{\circ}C$ are associated with ammonia molecules desorbed from strong acid sites (both Brønsted and Lewis acid sites). The peak with $T_M > 700$ °C can be 337 338 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.

Quantitative results of NH₃-TPD measurements reported in Table 2. DAO-FER sample exhibits a higher total acid sites concentration according to the higher aluminium content measured by atomic absorption technique. DAO-FER also shows a higher $T_{M,HT}$ 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 elucidate346 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 deuterated acetonitrile. Fore bare samples, two main bands observed at 3745 cm⁻¹ and 348 3600 cm⁻¹ are associated with terminal silanol Si-OH and Brønsted acid sites Al-OH-Si 349 groups, respectively [41, 42]. A shoulder at around 3645 cm⁻¹ is also present. Similar 350 351 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 band at 3645 cm⁻¹ can be associated to OH groups connected to the so called 'invisible' 357 358 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.

After adsorption of CD₃CN, two main bands at about 2296 cm⁻¹ and 2322 cm⁻¹ appear, revealing the presence of both Brønsted and Lewis acid sites, respectively, in boith cthe samples. Smaller bands at lower wave length associated with physisorbed acetonitrile are also presents [30]. The concentration of Brønsted and Lewis sites were obtained from the integral intensities of the IR bands of adsorbed CD₃CN at 2296 cm⁻¹ and 2322 cm⁻¹, respectively, by using the extinction factor coefficients reported in Section 2. Brønsted and Lewis site distribution of the investigated samples was calculated from the area of bands recorded at 25 °C; both the samples exhibits a significant amount
(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 D_3CN 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

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

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

The binding of both En and DAO with the 10 MR pore walls of zeolite are thermodynamically favoured (i.e. negative binding energies are calculated) suggesting that SDAs bind though hydrogen-bond formations with the lattice of zeolite. In particular, the strong interaction energy calculated for En-FER system may be attributed to the short hydrogen bond lengths, that are also almost linear and therefore stronger 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 the 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 in416 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^{-1} 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 measurements reveal that both DAO- and En-FER samples possess a high amount of 433 434 Lewis acid sites (about 40%) that are stronger for DAO-FER sample.

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

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530 TABLES CAPTIONS

- Table 1 Chemical composition, pore volume and surfaces characteristics of synthesised FER-type materials.
 Table 2 Acidic properties of investigated catalysts.
 Table 3 Calculated binding energies and lengths for the investigated SDA-FER systems from DFT simulation
- 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		$DAO/En=\infty$ (D).		
544	Figure 3	N_2 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	NH ₃ -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 CD ₃ CN molecules at 25°C (b).		
551		All the spectra are recorded at 10^{-6} torr.		
552	Figure 7	FT-IR spectra of D ₃ -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 (\bullet) and Lewis (\blacksquare)		
555		acid sites free of adsorbed D ₃ CN 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		

561and d. The dashed lines indicate all the H-bonds \leq 3 Å. The lengths of562the shorter and linear H-bonds bellow 2.5 Å are reported in Table X.563Atomic colour code: dark blue for Si; red for O; light blue for Al3⁺, black564for C, violet for N, grey for H and yellow for Na.

SAMPLE	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 [m ² /g]	329	287
V _{mic} ^c [cm ³ /g]	0.131	0.125

^a Atomic absorption

^b BET superficial area

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

	En-FER	DAO-FER
NH ₃ -uptake [µmol/g _{cat}]	1052	1418
$T_{M,LT}^{a}$ [•C]	245	231
$x_{LT}^{[b]}$	0.30	0.40
$T_{M,HT}^{c}$ [•C]	436	455
x_{HT}^{d}	0.70	0.60
Lewis acid sites ^e [%]	0.41	0.40
Strong Lewis acid sites ^f [%]	0.16	0.24

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

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

 $^{\rm c}$ Temperature of maximum desorption of NH_3 above 300°C

^d Fractional population of sites above 300°C

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

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

S man la	Binding energy (eV/mol)		Binding lengths (Å)			
Sample						
	8 MR	10 MR	8 MR	10 MR		
-			1.820	1.864		
En-FER	-24.01	-25.76	1.908	1.902		
			1.710	2.473		
				2x1.960; 2.042 ^a		
DAO-FER	N.a.N	-22.67	-	2.129; 1.498 ^b		
				2.441, 2.488 ^c		
^a NH ₃ ⁺ O(ZEO) H-bond;						
^b NH ₂ O(ZEO) H-bond						
C(CH)O(ZEO) H-bond						



Figure 1



Figure 2



Figure 3





Figure 5



Figure 6



