

Direct synthesis of nano-ferrierite along the 10-ring channels direction boost the catalytic behavior

Vicente J. Margarit, M. Rocío Díaz-Rey, M. Teresa Navarro, Cristina Martínez*, Avelino Corma*

Abstract: Ferrierite zeolites with nanosized crystals and external surface areas higher than $250 \text{ m}^2\cdot\text{g}^{-1}$ have been prepared at relatively low synthesis temperature (120°C) by means of the collaborative effect of two Organic Structure Directing Agents (OSDA). In this way, hierarchical porosity is achieved without the use of post-synthesis treatments that usually involve leaching of T atoms and solid loss. Adjusting the synthesis conditions it is possible to decrease the crystallite size in the directions of the 8- and 10-ring channels, [010] and [001] respectively, increasing the number of pores accessible and reducing their average pore length to 10-30 nm. The small crystal size of the nano-ferrierites results in an improved accessibility of reactants to the catalytic active centers and enhanced product diffusion, leading to higher conversion and selectivity with lower deactivation rates for the oligomerization of 1-pentene into longer-chain olefins.

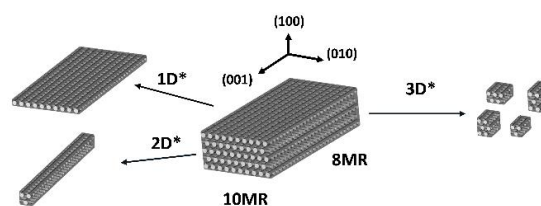
Zeolites are microporous silico-aluminates with crystalline structures presenting well defined channels and cavities of molecular dimensions,^[1] widely employed as adsorbents, ion exchangers and for gas separation or refining, petrochemical and environmental catalytic applications^[2] due to their molecular sieve and shape selectivity effects^[3]. Nevertheless, based on confinement effects, a new concept and methodology for the “Ab initio” synthesis of zeolites for preestablished catalytic reactions has been reported very recently^[4]. In processes dealing with bulky molecules, their microporous structure may impose diffusional problems and underuse of the overall micropore volume, directly affecting activity, selectivity and deactivation rate. Among the different approaches proposed to increase the accessibility to the zeolites active sites^[5], the generation of inter-crystalline mesoporosity by reducing the crystallite size from the micro- to the nanoscale^[5d, 6] has been thoroughly explored in the last years.

Ferrierite [FER] is a zeolite with a bidirectional microporous structure formed by interconnected medium (10-ring, $4.2 \times 5.4 \text{ \AA}$) and small (8-ring, $3.5 \times 4.8 \text{ \AA}$) pores. Along the 8-ring channels a cavity is formed, accessible only through 8-ring windows, and known as the FER cage^[7]. This zeolite, highly stable towards thermal, hydrothermal and chemical treatments, has been applied as catalyst in different processes, such as isomerization of n-butenes^[8] and others^[9].

Although highly selective, the topology and pore dimensions

of ferrierite limits the reaction to the active sites closer to the crystal surface and results in fast deactivation due to pore blocking with coke precursors. One possible solution would be to decrease the diffusional path lengths. Thus, a delaminated FER, ITQ-6, was obtained by delamination of a layered precursor (PREFER)^[10], following a procedure similar to the one used for preparing zeolite ITQ-2^[6]. When efficiently delaminated, ITQ-6 is highly active for the conversion of bulky reactants^[10b] due to its high external surface area. However, its reduced micropore volume results in decreased shape selectivity and confinement effects. Mesoporosity generation in ferrierite crystallites by post-synthesis desilication treatments has also been attempted^[11], but this procedure is less efficient than in other zeolites due to its high chemical stability^[11a, 12].

A different approach is the direct synthesis of nanocrystalline ferrierite with different morphologies (see **Scheme 1**), and nanocrystals (40-60 nm)^[13] or nanoneedles (10 x 100 nm)^[14] have been reported. Although these zeolites can be considered as nanosized, decreasing crystal size from 40 to 10-15 nm can have an enormous effect on initial activity, selectivity and catalyst life^[15]. Regarding the nanoneedles, as they grow along the direction of the 10-ring channels, the diffusion path lengths are not reduced in this case. Other groups describe the synthesis of ferrierite nanocrystal aggregates^[16] or the crystallization of FER nanosheet assemblies^[17], but none of the final solids combine high external surface areas with acceptable micropore volumes. Thus, the most interesting and challenging objective, i.e., to obtain very small nanocrystals (<15 nm) along the [001] direction of the 10-ring channels, maintaining a well-preserved microporous structure, has not yet been achieved, as far as we know.



*Pore length reduction in 1, 2 or 3 directions.

Scheme 1. Representation of crystal size reduction in (100) (1D), in (100) and (010) (2D) and (100), (010) and (001) (3D) to ferrierite layers, needles and nanocrystals, respectively.

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For that purpose, we propose in this work the cooperative use of piperidine and a modified surfactant for the synthesis of ferrierite nanozeolites under hydrothermal conditions (see **Table S1**). Varying the synthesis time (7-17 days) and temperature ($120\text{-}150^\circ\text{C}$) nanoferrierites were obtained with the smallest crystal size in the (001) and (010) directions reported

so far. Although the use of modified surfactants as single OSDAs has successfully led to the one pot synthesis of layered MWW^[18], MFI and MOR^[19], and nanosized BEA^[20] zeolites, this strategy involves high costs related to the OSDA preparation, which requires multiple steps and large excess of reagents. Thus, a cheaper option is to introduce a simpler modified surfactant in combination with the classical OSDA^[21], which is the approach followed in this work.

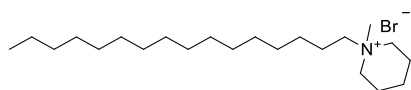


Figure 1. Modified Surfactant C₁₆MPip.

Piperidine (Pip) is known to direct the synthesis towards the crystallization of ferrierite^[22]. Moreover, we have added cetylmethylpiperidinium bromide, C₁₆MPip (see **Figure 1**) to the synthesis media, a surfactant easily obtained by alkylation of N-methylpiperidine with 1-bromohexadecane (see Supporting Information for more details). Piperidine is expected to initiate the crystallization of the FER structure, and in a similar way, the piperidine-derived head of the surfactant should fit into the microporous channel system, whereas the long carbon chain should limit crystal growth. Both OSDAs, piperidine and the modified surfactant, were stable within the zeolite structure under the synthesis conditions (see **Figure S1 and S2**).

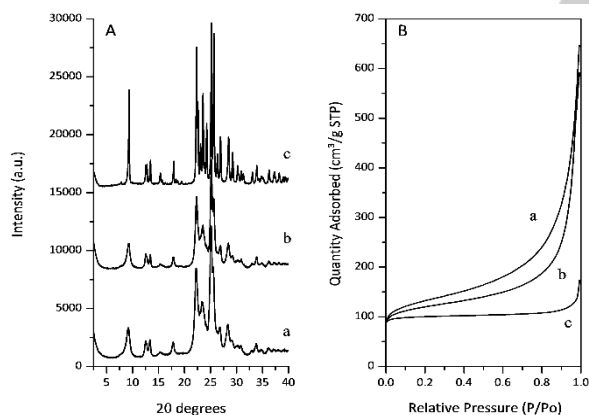


Figure 2. XRD patterns of as synthesized ferrierites (A) and nitrogen adsorption isotherms (B) of the acid ferrierites. N-FER(15) synthesized at 120°C (a), 150°C (b) and R-FER (c).

Ferrierite is crystallized in all cases as a single phase (see **Figures 2A, S3A and S4A**), and the structure is maintained after obtaining the acid form of the zeolite (see **Figure S3B and S4B**). When compared to a reference zeolite synthesized at 150°C using piperidine as a single OSDA (R-FER), the diffraction peaks of the nano-ferrierites are significantly broader and less intense, suggesting a notably smaller crystal size.

The shape of the nitrogen adsorption isotherms obtained for the N-FER and the conventional ferrierite evidence their different

textural properties (see **Figures 2B and S5**). R-FER showed a type I isotherm, typical of microporous materials. This zeolite, with a total pore volume of 0.27 cm³·g⁻¹ and a micropore volume of 0.149 cm³·g⁻¹, has a very low contribution of the external surface area (17 m²·g⁻¹) to the total BET value (320 m²·g⁻¹) (see **Table S2**). In the case of the N-FER zeolites, the isotherms have a type IV shape, typical of materials presenting mesoporosity. The external surface areas increase to 157 and 262 m²·g⁻¹ for the N-FER synthesized with Si/Al molar ratios of 15 at 150°C and 120°C, respectively. In both cases the total pore volume increases up to ≈0.9–1.0 cm³·g⁻¹ (see **Table S2**), while preserving most of the micropore volume (0.09–0.12 cm³·g⁻¹). Still, the argon isotherms in the low-pressure region show a small but increasing reduction of the volume adsorbed when decreasing crystal size (see **Figures S6**).

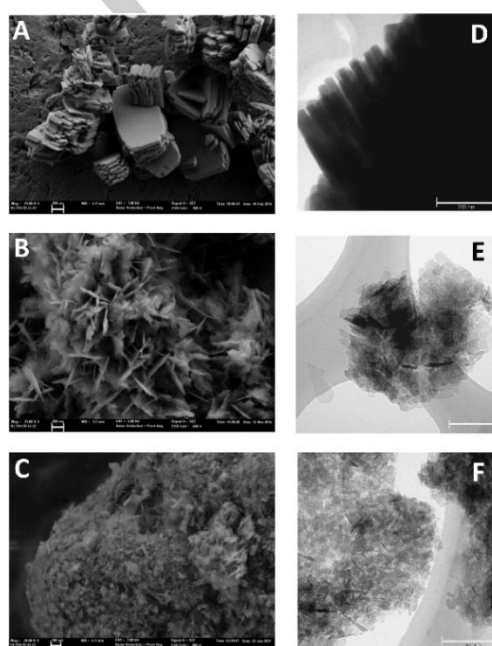


Figure 3. FESEM (A–C) and TEM (D–F) images corresponding to zeolites R-FER(15) (A,D), N-FER(15)-150 (B,E) and N-FER(15)-120 (C,F). Scale bar corresponds to 200 nm in all images.

The much smaller particle size of N-FER as compared to the reference ferrierite is confirmed by electron microscopy. The FESEM images (see **Figure 3A**) reveal the plate-like shape of the R-FER crystals with a preferential crystal growth in the *b-c* plane^[23]. In the case of the N-FER two different morphologies are observed (see **Figures 3B–C and Figures S7A–E**): nanocrystals, isotropic in shape, where the crystal size in the *b-c* plane is largely decreased as compared to the plate-like morphology, and layered leaf-shaped crystals (see also Scheme 1).

When lowering the synthesis temperature there is a clear crystal size reduction for both type of crystallites, and an increased proportion of the nanocrystals. This has been related to differences in activation energy for the stages of nucleation and crystal growth during the synthesis of the zeolite^[1, 24]. Thus,

sample N-FER(15)-120 mainly crystallizes as nanocrystals with sizes in the range of 10-20 nm (see HRTEM images in **Figure S8**). Structure-morphology relations can be clearly observed in **Figure 4**. In this HRTEM image three different crystals are clearly visualized, a small isotropic nanocrystal (A), facing the (001) direction, and two layer-shaped crystals, one exposing the (010) orientation (B), and the other showing the (100) orientation but tilted 45° over the (010) axis (C). Crystallite intergrowth or twinning, as those described for MFI^[25], have not been observed.

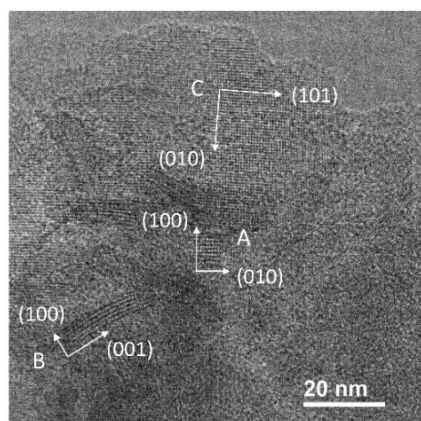


Figure 4. HRTEM image of N-FER(15)-150.

The Si/Al ratios of the calcined samples are 9 and 10 to 12 for the R-FER and the N-FER(15) zeolites, respectively (see **Table S2**). This aluminum exhibits a tetrahedral coordination in the as-made material (see the ²⁷Al-MAS-NMR spectra in **Figure S9**) and a good thermal stability, with 85% of the trivalent element remaining in framework positions in the final acid zeolites. It should be remarked that the smaller crystal size of the N-FER as compared to the R-FER does not result in a larger dealumination during the zeolite calcination process. This framework Al³⁺ confers the zeolite its Brønsted acidity (see **Figure S10**).

In microcrystalline ferrierites an important fraction of the Brønsted acid sites is not accessible to most of the reactants, as part of the protons may be pointing into the 8-ring channels or into the FER cages, being only accessible through 8-ring windows^[10b, 25-26]. Indeed, only 40% of the total sites in R-FER are accessible to pyridine (see **Figure S10** and **Table S3**), but more than 55% of the sites are accessible in the N-FER(15) samples.

The remarkable textural properties of the N-FER zeolites, combining well preserved micropore volumes ($\approx 0.09 \text{ cm}^3 \cdot \text{g}^{-1}$) and external surface areas above $260 \text{ m}^2 \cdot \text{g}^{-1}$, the increased exposure of 10-ring pore mouths and the reduced length of these 10-ring channels, should result in an improved catalytic behavior when used as acid catalysts. Thus, N-FER in their acid form have been used to catalyze the oligomerization of 1-pentene to liquid fuels under industrially relevant liquid phase conditions, at 200°C and 4.0 MPa and space velocity (WHSV) of 3 to 50 h⁻¹ in a down-flow fixed bed reactor (see Supporting Information for details). Oligomerization of light alkenes to liquid

fuels is a process of increasing applied interest^[2b, 27] as it enables the conversion of olefins in the C3 to C6 range present in orphan or low value industrial streams into clean liquid fuels such as gasoline, jet fuel or diesel^[28]. Ferrierites have been described as active for oligomerization of pentenes^[29] and 1-butene^[30], highly selective to dimers and trimers, respectively. However, selectivity to the most interesting diesel range oligomers is low and the catalysts rapidly deactivate due to pore blocking by deposition of heavier hydrocarbons inside the micropores. Still, the synthesis of the N-FER with very short 10-ring channels may offer ferrierite a new opportunity as olefin oligomerization catalyst.

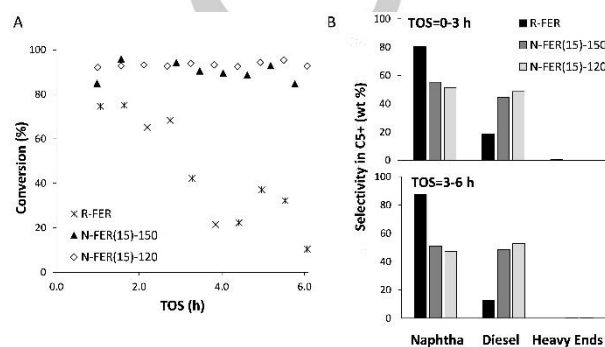


Figure 5. (A) 1-Pentene conversion vs. TOS and (B) selectivity within the C₅₊ liquid fraction for ferrierite zeolites at WHSV=8 h⁻¹, T=200°C, P = 4.0 MPa, 60% mol olefin in the feed.

When comparing the activity of the reference R-FER and the nano-ferrierite zeolites with Si/Al ratios of 15 synthesized at 150°C and 120°C at WHSV=8 h⁻¹ (see **Figure 5A**), the initial olefin conversion is increased from 80% to values above 90% obtained with the N-FER(15) zeolites. However, the most remarkable result is the improvement of catalyst life. Working at this very high WHSV to study the deactivation behavior at short times on stream, the N-FER zeolites maintain the initial activity for 6 hours, whereas the conventional ferrierite gives olefin conversions below 50% after 3 h of reaction. When comparing with the sample with less Al, N-FER(30), the latter is slightly less active than the N-FER(15) samples (see **Figure S11**), in good agreement with its lower Brønsted site density (see **Table S3**), but deactivation rate is comparable. It has to be remarked that working at WHSV=3.3 h⁻¹, still in the upper limit of that relevant for industrial operation, catalyst N-FER(15)-120 presents olefin conversion above 95% after 24 h bench scale experiment (see **Figure S12**).

Regarding product selectivity, **Figure 5B** shows that the smaller crystal size along the 10-ring channels of the nanocrystalline ferrierites favors the formation of oligomers in the diesel range (mainly C₁₅ trimers).

When increasing the operation severity to WHSV = 15, 25 and 50 h⁻¹, the differences among the nano-ferrierites become larger (see **Figure S13** and **Figure S14**) and initial activity and catalyst life are in direct correlation with the crystal size of the nano-zeolites (N-FER(15)-150 < N-FER(15)-125 < N-FER(15)-120). It is not until space velocity is increased to values as high as 50

h^{-1} that we see a clear activity loss with TOS for the N-FER(15) zeolites. Notice that R-FER presented an initial olefin conversion below 20%, and no pentene conversion after 3 hours on stream already at a space velocity of $25 h^{-1}$.

Summarizing, we have presented a simple procedure to synthesize nanosized ferrierites in the presence of two cooperative OSDAs, piperidine and C_{16} MPip, with good solid yields. The nano-ferrierites present crystallite dimensions in the *bc* plane as low as 10×10 nm, corresponding to 13 unit cells along the direction of the 10-ring channels, and Si/Al ratios in the range of 8 to 20. These N-FER, with external surface areas as high as $262 m^2 \cdot g^{-1}$, mesopore and total pore volumes of 0.43 and $1.00 cm^3 \cdot g^{-1}$, respectively, present increased accessibility to the Brønsted acid sites, higher activity and diesel selectivity, and longer catalyst life than a micro-sized reference for the liquid phase oligomerization of 1-pentene. The outstanding catalytic behavior observed is mainly due to the reduced crystallite size along the (001) direction, reducing the diffusional path length of the molecules along the 10-ring channels.

Experimental Section

Details on the synthesis of the ferrierite zeolites and of the ODSA C_{16} MPip can be found in the Supporting Information. Liquid phase oligomerization of 1-pentene was performed in a down-flow stainless-steel fixed-bed reactor at $200^\circ C$, 4.0 MPa, and WHSV in the range of 3 to $50 h^{-1}$. A detailed description is given in the Supporting Information.

Acknowledgements

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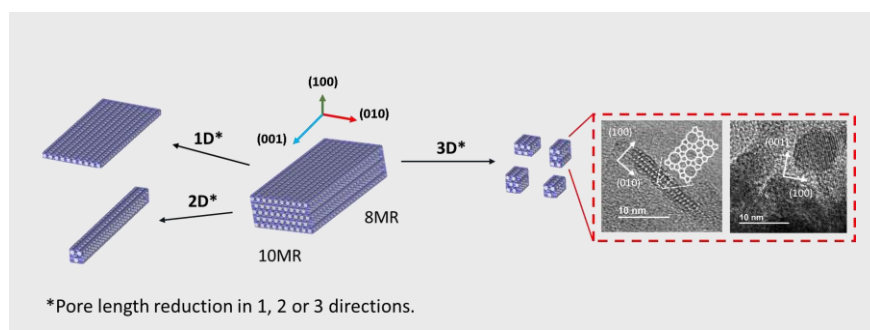
Keywords: Nano-zeolite, ferrierite [FER], modified surfactant as OSDA, 1-pentene oligomerization, catalyst lifetime.

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COMMUNICATION



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Nanocrystalline ferrierite with reduced crystal dimension along the 10-ring channels: efficient and stable catalysts for the oligomerization of 1-pentene to diesel due to decreased diffusional path lengths.