Controlling the aluminum distribution in the zeolite ferrierite via the organic structure directing agent

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KEYWORDS: ferrierite, FER, SDA location, Rietveld refinement, pyrrolidine, TMA, control of acid site distribution

ASSOCIATED CONTENT

X-ray crystallographic information files (CIF) for the FER–PYRR– TMA and FER–PYRR structures, thermogravimetric analysis and ^{19}F MAS NMR spectroscopy results and scanning electron microscopy images. This material is available free of charge via the Internet at http://pubs.acs.org.

Characterization of the ferrierite samples:
Several steps are observed in the thermogravimetric analysis corresponding to the sample FER–PYRR (Figure 1S). The first one, up to 200 °C, corresponds to the desorption of water. It is followed by two additional steps at higher temperatures (at *ca*. 500 °C and at 550–750 °C) that correspond to the loss of *pyrr* species., Unfortunately, the complexity of the system, does not allow them to be assigned to two different kinds of pyrrolidine species (e.g. protonated and non-protonated, or in two different locations within the zeolitic framework). Several steps are also observed in the thermogravimetric analysis of samples FER–PYRR–TMA, but again they cannot be assigned individually to the desorption of *pyrr* and TMA. They probably correspond to the progressive decomposition of both as the sample is being heated up.

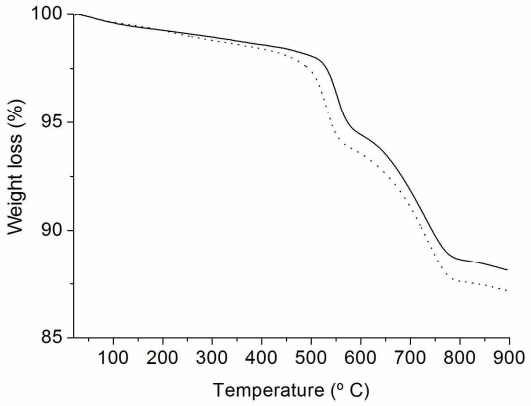

Figure 1S. Thermogravimetric analysis of the as-made ferrierite samples obtained after 10 days of hydrothermal treatment. FER–PYRR–TMA (solid line) and FER–PYRR (dotted line).

Two different signals can be observed in the ^{19}F MAS NMR spectra at –89 and –123 ppm. The first one is within the typical range for fluoride ions occluded within zeolitic cavities, but does not correspond to fluoride anions located in the [5^4] cage of ferrierite, for which a signal should appear at *ca*. –58 ppm.[1,2] The signal at –123 ppm appears at a chemical shift more negative than that usually found for fluoride anions occluded in zeolitic cavities, and might correspond to SiF_6^- anions[3-7]. Judging from the very low signal/noise ratio in the spectrum, there would only be traces of these hexacoordinated Si species, which have been detected in other zeolites synthesized in fluoride medium, such us levyne[8] and beta[9].

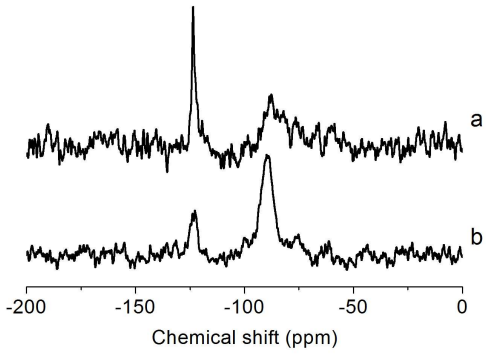

Figure 2S. ^{19}F MAS NMR spectra of samples FER–PYRR–TMA (a) and FER–PYRR (b).

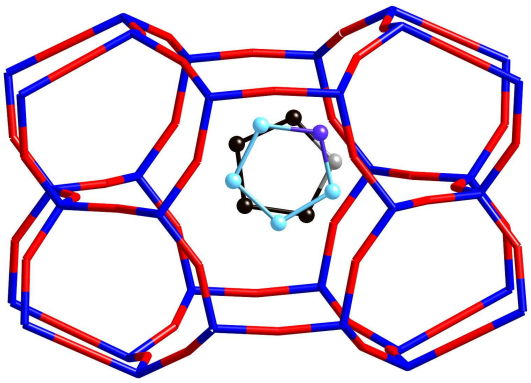

Figure 3S. Ferrierite ([$5^8 6^6 8^2$]) cavity comparing the position of pyrrolidine for sample FER–PYRR–TMA (blue) and FER–PYRR (black).

Table 1S. Organic content and chemical analysis of samples FER–PYRR–TMA and FER–PYRR.

		Chem. Analysis (wt. %)				TGA		ICP–AES	
Synthesis	Sample	C	H	N	C/N[a]	Organic[b] (wt.%)	Water[c] (wt%)	Si/Al[d]	Al /uc
FER-PYRR	FER-PYRR–7	7.63	1.75	2.03	4.4	11.5	0.9	15.0	2.3
	FER-PYRR–10	7.35	1.74	2.00	4.3	11.0	0.8	15.2	2.2
FER-PYRR-TMA	FER-PYRR–TMA–7	7.81	1.85	2.03	4.5	11.8	0.7	15.4	2.2
	FER-PYRR–TMA–10	7.58	1.86	1.97	4.5	11.7	0.6	15.9	2.1

[a]: atomic ratio.

[b]: weight loss in the temperature range 200 °C-900 °C in the thermogravimetric analysis.

[c]: weight loss at T < 200 °C in the thermogravimetric analysis.

[d]: atomic ratio.

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