Supplementary Information

Tracking the evolution of embryonic zeolites into hierarchical ZSM-5

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Material synthesis

Firstly, а solution of aluminium isopropoxide (AIP, 98 wt%; Aldrich). tetrapropylammonium hydroxide (TPAOH, 40 wt%; Aldrich) and deionized water was prepared in a round bottom flask and stirred at room temperature until complete dissolution of AIP. Then, it was cooled down in an ice bath and the proper amount of tetraethyl orthosilicate (TEOS, 98 wt%; Aldrich) was added dropwise. The molar composition of the initial mixture is as follows: Al₂O₃: 60 SiO₂: 11 TPAOH: 1500 H₂O. A total of six different synthesis batches were so prepared. The alcohols produced as byproduct of TEOS and AIP hydrolysis for 40 h were eliminated by rotary evaporation at 50 °C under 75 mbar vacuum. Thereafter, one of the so resulting clear solutions was dried by evaporation at 50 °C under 42 mbar vacuum and then oven dried overnight at 110 °C to recover the solid sample designated as PZM-1.

The rest of the samples were placed in a silicone bath and subjected to a precrystallization treatment (heating at 90 °C, under reflux and 300 rpm stirring for 20 h) in order to promote the formation of protozeolitic entities. Thereafter, a second sample was recovered from the gel (still a clear solution) following a similar procedure to that above described, being designated as PZM-2.

The remaining batches were subjected to a silanization treatment with 5 mol% of organosilane (N-(2-N-benzylaminoethyl)-3-aminopropyltrimethoxysilane, 90%, Gelest) referred to the initial silica content of the gel. The resulting mixtures were stirred under reflux at 90 °C for 6 h. Subsequently, sample PZM-3 was recovered from the gel using the same procedure as above detailed.

The last three batches continued with the synthesis process, being crystallized in a teflon-lined autoclave reactor at 170 °C, for 1, 3 and 7 days, respectively. The former sample was designated as PZM-4 and the latter as h-ZSM-5 (1) and h-ZSM-5 (2) according to their XRD patterns. After the hydrothermal treatment, the synthesis mixture became a white solid, underneath a transparent supernatant phase, denoting the

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presence of relatively large particles. The solid material was recovered by centrifugation (11000 rpm), followed by washing with deionized water, which was repeated three times, being finally dried overnight at 110 °C.

All samples were subjected to a calcination treatment to remove the different organic species: TPA⁺ and organosilane (silanization agent, SIA). To that end, and in order to minimize the possible damage to the zeolitic entities present in the samples, calcination was performed using a two-step process in a tubular muffle¹. Thereby, a first heating up to 400 °C (1.8 °C/min) was performed under nitrogen flow for 4 h, followed by a second heating up to 550 °C (1.8 °C/min) for 5 h in air. This procedure is aimed to avoid the generation of hot spots during the exothermic combustion of organics that could destroy zeolite embryos.

Two additional samples were also prepared analogously to PZM-1 sample for comparison purposes only. PZM-1 (0.1) sample was prepared with a molar composition of the initial mixture of Al_2O_3 : 60 SiO₂: 1.1 TPAOH: 1500 H₂O. PZM-1 (0) sample was prepared by changing TPAOH with NaOH, with a molar composition of the initial synthesis gel as follows: Al_2O_3 : 60 SiO₂: 11 NaOH: 1500 H₂O. Both reference samples were recovered and calcined following the same procedure as for the PZM-1 sample.

Materials characterization

Wide-angle X-ray diffraction patterns of the calcined samples were collected with a Empyrean PANalytical diffractometer using Cu ($K_{\alpha} = 1.54$ Å) covering a 2 Θ range of 5° to 50°. Pair distribution function X-ray diffractograms (PDF-XRD) of calcined samples were measured in a Bruker D8 Advance A25 instrument with Ag (K_{α} =0.56 Å) radiation provided with 8 mm diameter of polyamide tube. XRD patterns were collected during 16 h over a 2 Θ range 4-150° (VCT/VSS with Variable Counting Time and Variable Scan Size), employing an Ag Göebel mirror optics and LYNXEYE XE linear detector.

Fourier transform infrared (FTIR) spectra were attained in a Varian Excalibur 3100 infinity series equipment to analyse the fingerprint region of a KBr-sample wafer. Spectra were measured in transmission mode and recorded with 64 scans and 4 cm⁻¹ resolution within the range of 400 – 4000 cm⁻¹. The concentration of Brønsted and Lewis acid sites (BAS and LAS, respectively) was determined by using pyridine as a probe molecule and monitored by FTIR in a house-made system. Self-supported wafers (8-12 mg/cm²) were prepared and activated under vacuum (10⁻³ – 10⁻⁴ mbar) at 450 °C for 4 h prior to the measurements. Thereafter, pyridine was introduced into the system at 150 °C, which was kept closed for 20 min. Thermal desorption was performed under vacuum from 150 °C to 450 °C, applying a 20 min period at each selected temperature. Spectra were recorded using a Nicolet iS50 instrument with a resolution of 4 cm⁻¹ and 128 scans. The following integrated molar extinction coefficients were used for the BAS and LAS quantification: $\mathcal{E}_{BAS} = 1.67$ cm µmol⁻¹ for the absorption band located at 1545 cm⁻¹ (PyH+) and $\mathcal{E}_{LAS} = 2.22$ cm µmol⁻¹ for the absorption band centred at 1455 cm⁻¹ (PyL)².

Solid-state²⁹Si MAS NMR measurements of the as-synthesized samples were performed at 79.41 MHz in a Bruker Avance III/HD 400 MHz spectrometer, fitted with a 9.4 T magnetic field at spinning frequency of 10 kHz, in one pulse with spinal 64 1H decoupling, 60 s pulse delay and kaolin as external reference (chemical shift at -91.26 ppm). Solidstate ²⁷Al MAS NMR spectra of the calcined samples were measured at a magnetic field of 11.75 T on a Bruker Avance III/HD 500WB spectrometer using a double-bearing MAS probe (DVT BL4) at a resonance frequency of 130.3 MHz. The spectra were recorded by applying single π /12-pulses (0.6 µs) with a recycle delay of 1 s (between 2400 and 9600 scans) at three different spinning rates (10 kHz, 13 kHz, and 14 kHz). The calcined samples were saturated in water vapour overnight before the measurement. The spectra were referenced to external 1 M aqueous solution of Al(NO₃)₃. The deconvolution of the experimental spectra was performed by using the solid lineshape analysis module implemented in the TopSpinTM 3.2 NMR software package from Bruker BioSpin GmbH.

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The Si/AI molar ratio of the calcined samples were determined by ICP-OES using Perking Elmer Optima 7300AD equipment. The relative proportion of OSDA and SIA agents were estimated from carbon, hydrogen and nitrogen weight content of the assynthesized samples measured using a CHN Elementar Vario EL III instrument. Likewise, thermogravimetric analyses were performed with an SDT 2960 instrument. Assynthesized samples were loaded into an alumina crucible and heated up to 700 °C with a rate of 5 °C/min under a 100 ml/min air flow.

Argon physisorption measurements were carried out on a Micromeritics 3Flex instrument. The materials were degasified under vacuum at 300 °C for 5 h before the analysis. TEM micrographs were collected using a high-resolution Field Emission TEM/STEM (200 kV) microscope (Talos F200X FEI-ThermoFischer Scientific), equipped with a CCD chamber 4k x 4k and a chemical analysis system via EDS, Super-X (Bruker).

Catalytic tests of low-density polyethylene cracking

Low-density polyethylene (LDPE) catalytic cracking reactions were carried out in a stainless-steel semi-batch reactor equipped with a helical stirrer. Tests were performed loading into the reactor a mixture of 10 g of LDPE (Repsol, Mw = 416,000; Alcudia grade) and 0.4 g of the catalyst sample, being heated up to 400 °C (atmospheric pressure), keeping constant this temperature for 2 h. A pre-heated (300 °C) nitrogen flow of 30 cm³ min⁻¹ was passed through the reactor sweeping the vapours formed in the LDPE cracking. Liquid products were condensed in an ice-trap whereas gaseous components were collected in a gas-bag. The residue remaining inside the reactor consisted of partially degraded LDPE, being quantified to close the mass balance. Conversion and product selectivity were calculated taking into account the products leaving the reactor with the nitrogen stream. Liquid and gaseous fractions were analysed in a Varian CP-3800 gas chromatograph, equipped with a 100 m length x 0.25 mm i.d. Chromopack CP SIL PIONA capillary column and FID detector.

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References

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Line #	Assignment	PZM-1	PZM-2	PZM-3	PZM-4	h-ZSM-5 (1)	h-ZSM-5 (2)
1	Tetrahedral	53.8 / 1145	53.6 / 904	53.5 / 1052	52.9 / 540	53.8 / 1067	53.9 / 1394
	(T-Al)	350 / 880	350 / 895	350 / 830	350 / 840	250 / 720	250 / 600
2	Tetrahedral	47.9 / 257	47.6 / 303	48.2 / 474	48.6 / 405	48.0 / 231	49.1 / 168
	(T-Al)	200 / 1440	200 / 1590	200 / 1670	200 / 1450	200 / 1600	200 / 1660
3	Distorted	36.4 / 514	33.0 / 510	33.0 / 443	35.0 / 307	32.6 / 248	33.0 / 211
	tetrahedral (DT-AI)	1200 / 4400	1200 / 4400	1200 / 4400	1200 / 4400	1200 / 4400	1200 / 4400
4	Octahedral	-10.6 / 895	-11.1 / 814	-10.5 / 882	-6.6 / 1045	-10.8 / 531	-11.7 / 476
	(FO-Al)	1800 / 2600	1800 / 2660	1800 / 2600	3300 / 2700	1800 / 2700	1800 / 2800
5	Octahedral. Al ³⁺	-0.2 / 103	-0.3 / 90	-0.3 / 88	-0.4 / 16	-0.4 / 47	-0.3 / 63
	(EFO-Al)	260 / 0	260 / 0	260 / 0	260 / 0	260 / 0	260 / 0
6	Tetrahedral.	-51.2 / 117	-51.2 / 89	-51.2 / 102	-53.6 / 65	-52.2 /108	-52.5 /187
	ssb (-1). CT+ST	1500 / 0	1500 / 0	1500 / 0	1500 / 0	1400 /0	1400 /0
7	Tetrahedral.	163.0 / 116	162.9 / 87	162.4 / 91	161.6 / 68	162.1 / 114	161.5 / 198
	ssb (+1). CT+ST	1500 / 0	1500 / 0	1500 / 0	1500 / 0	1400 / 0	1400 / 0
8	Tetrahedral.	-158.0 / 76	-158.0 / 69	-158.0 / 73	-158.0 / 31	-159.1 / 80	-159.8 / 136
	ssb (-2). ST	1400 / 0	1400 / 0	1400 / 0	1400 / 0	1300 / 0	1300 / 0
9	Tetrahedral.	56.8 / 76	56.8 / 69	56.8 / 73	56.8 / 31	56.1 / 80	56.1 / 136
	cb. ST	1400 / 0	1400 / 0	1400 / 0	1400 / 0	1300 / 0	1300 / 0

Table S1. Parameters used for the simulation of the ²⁷AI MAS NMR spectra of the studied samples.

• Entries: position (ppm) / integral (arbitrary units) LB (Lorentzian) / GB (Gaussian)

• $I_{T-AI} = I_1 + I_2 + I_6 + I_7 - 2I_8$

• ssb: side spinning band

• cb: centre band



Figure S1. FTIR spectra of the as-synthesized samples.



Figure S2. Argon isotherms at -186 °C and NL-DFT pore size distribution comparison of PZM-1, PZM-1 (0) and PZM-1 (0.1) calcined samples.



Figure S3. Electron diffraction pattern of the non-globular phase of PZM-4 sample.



Figure S4. Evolution of the C_{LAS}/C_{BAS} ratio along the h-ZSM-5 synthesis process (pyridine evacuation temperature: 150 °C).



Figure S5. LDPE catalytic cracking over the PZM samples: product selectivity per atom carbon number.