Supporting Information

Interconversion of the CDO Layered Precursor ZSM-55 between FER and CDO Frameworks by Controlled Deswelling and Reassembly

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Contents:

ZSM-55 properties and characterization methods

ZSM-55 structure, reference 32: Cmcm probable unit cell with a= 7.792 Å, b=21.976 Å, and c=13.968 Å; calcined (for ZSM-52, Al analogue): a= 7.4332 Å, b= 18.2857, and c=13.8034 Å.

ZSM-55 composition, reference 30, in wt %, Example 1: SiO_2, 78.0, B_20_3 0.60, Na_2O 0.20, Al_20_3 0.057; N 2.14, Ash 81.0. Molar Ratios: SiO_2/B_2O_3 - 140, SiO_2/Al_2O_3 - 2346.

Boron content was determined by ICP; The results – as-synthesized ZSM-55 0.2 %, detemplated by acid/methanol treatment – 0.012%.

X-ray powder diffraction (XRD) measurements were carried out using a Philips X'Pert diffractometer APD and was carried out using a Bruker AXS D8 Advance diffractometer with CuKα radiation (λ = 0.154 nm) in various appropriate ranges 1-50° 2θ with steps of 0.02°.

Nitrogen adsorption isotherms were determined by the standard method at -196 °C (liquid nitrogen temperature) using an ASAP 2025 (Micromeritics) static volumetric apparatus. Before adsorption the samples were outgassed at 350 °C using turbomolecular pump to remove adsorbed water.

SEM images were obtained using Tescan Vega3 LMU microscope with LaB6 emitter, 30 kV voltage. Samples were coated with gold before imaging.

QE-TPDA measures the amount of sorbate desorbed or adsorbed by a sample as a function of temperature which is changing cyclically. QE-TPDA measurements of hexane (Sigma-Aldrich, >99 %, used without further purification) were performed with the use of the thermodesorption apparatus equipped with a thermal conductivity detector (Micro Volume TCD, Valco). Prior to the QE-TPDA experiment a sample (ca. 6–10 mg) was activated by heating in He flow (10 °C min^{-1} to 500 °C). The initial adsorption was carried out at room temperature by replacing pure helium used as the carrier gas with helium containing a small admixture of a hydrocarbon (ca. 0.4 vol %). After adsorption was completed, the QE-TPDA experiment was performed by cyclic heating and cooling the sample (10 °C min^{-1} to 400 °C) in He/hydrocarbon flow (6.5 cm^3 min^{-1}). The desorption-adsorption cycles were separated by 1 h isothermal segments at room temperature. The micropore volume calculations were carried out by integration of the experimental desorption maxima and adjustment based on the calibration data. The density of hexane was assumed to be equal to that of the liquid (0.659 g cm^{-3}).

Figure 1S. ^{11}B NMR showing complete leaching of boron from ZSM-55 upon detemplation: the as-synthesized ZSM-55 (top); exchanged with ammonium nitrate and calcined (the CDO framework) (middle); detemplated with acid in methanol (H-ZSM-55) (bottom).

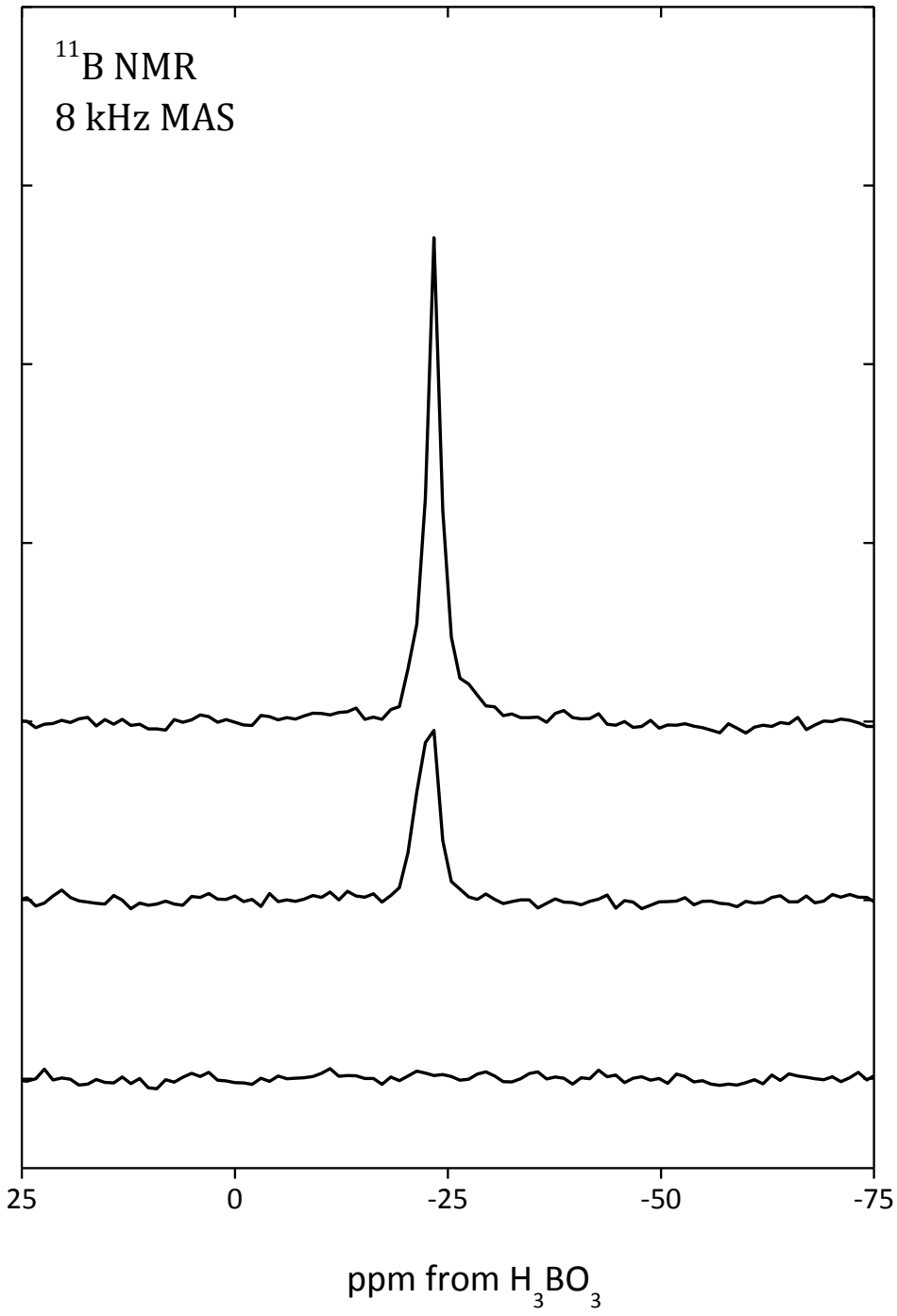


Figure 2S. X-ray powder diffraction patterns for as-synthesized (black line) and calcined (red line) deswollen surfactant – ZSM-55 with different cationic compounds: dedma – diethyldimethyl-ammonium, TEA – tetraethylammonium, and choline.

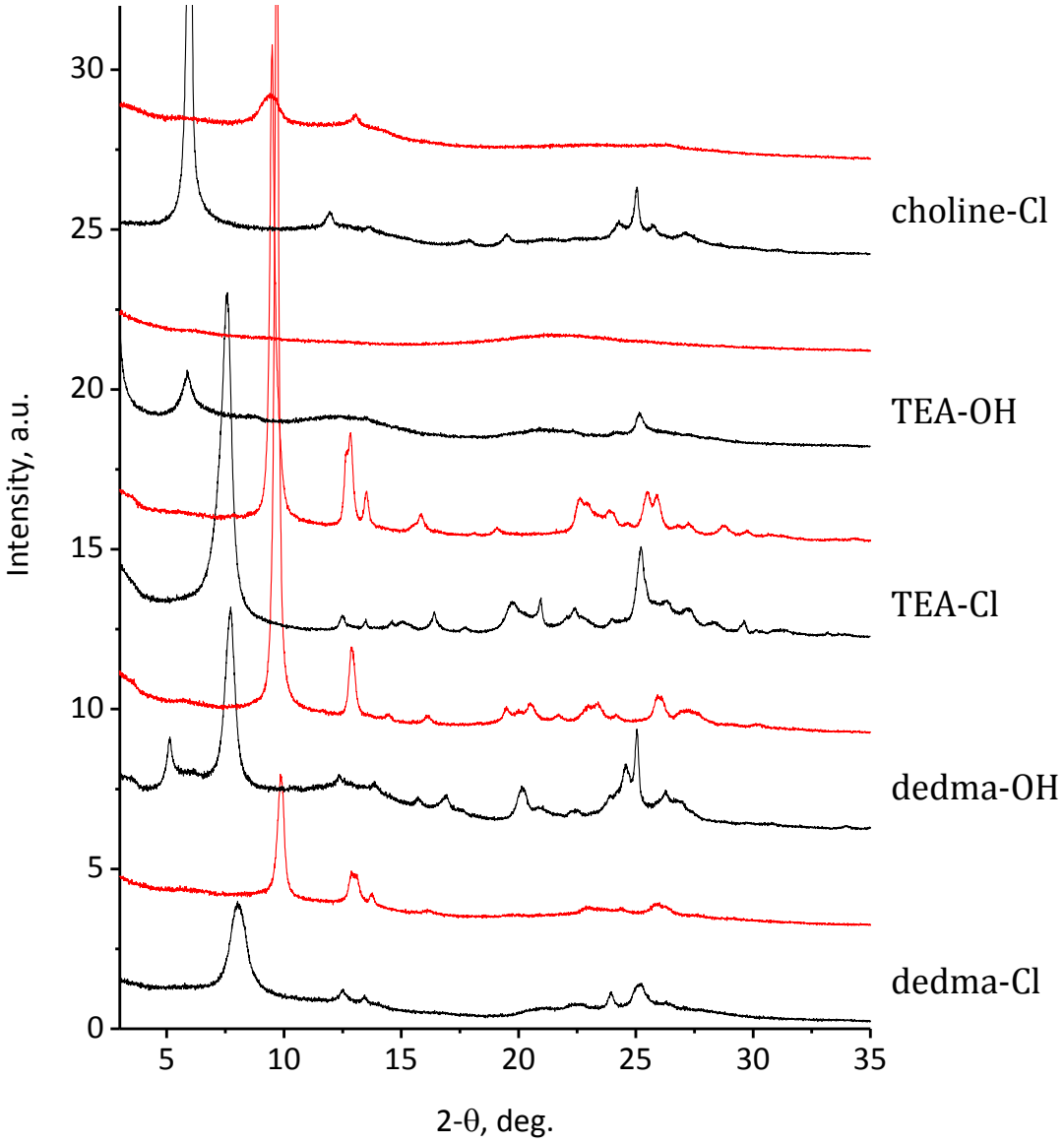


Figure 3S (enlarged copy of Fig. 2 in the article). X-ray powder diffraction patterns of ZSM-55 and the products of its transformation.

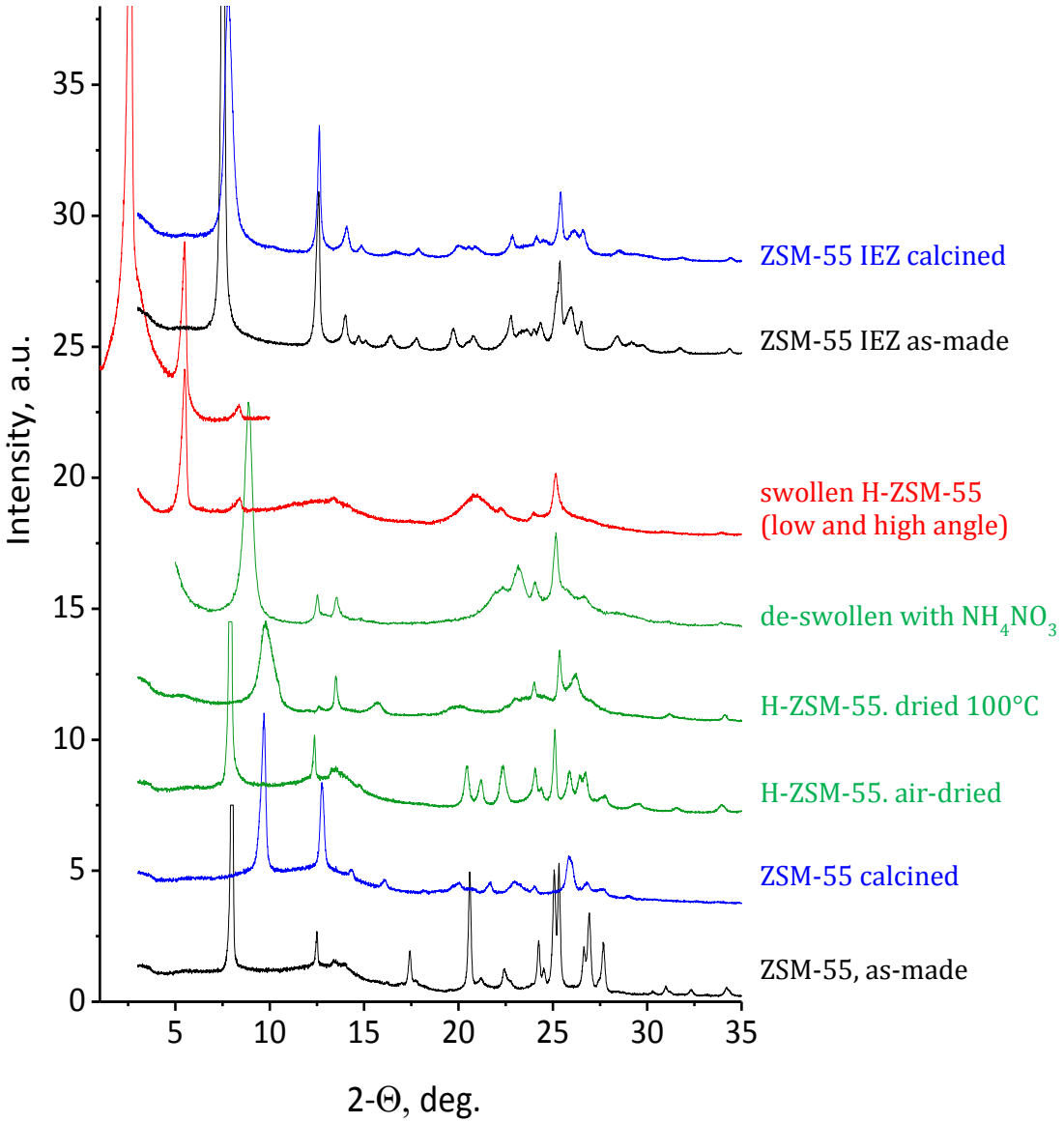


Figure 4S (enlarged copy of Fig. 3 in the article). X-ray powder diffraction patterns of ZSM-55 and derivatives calcined after swelling and de-swelling with dedma chloride and hydroxide in ethanol.

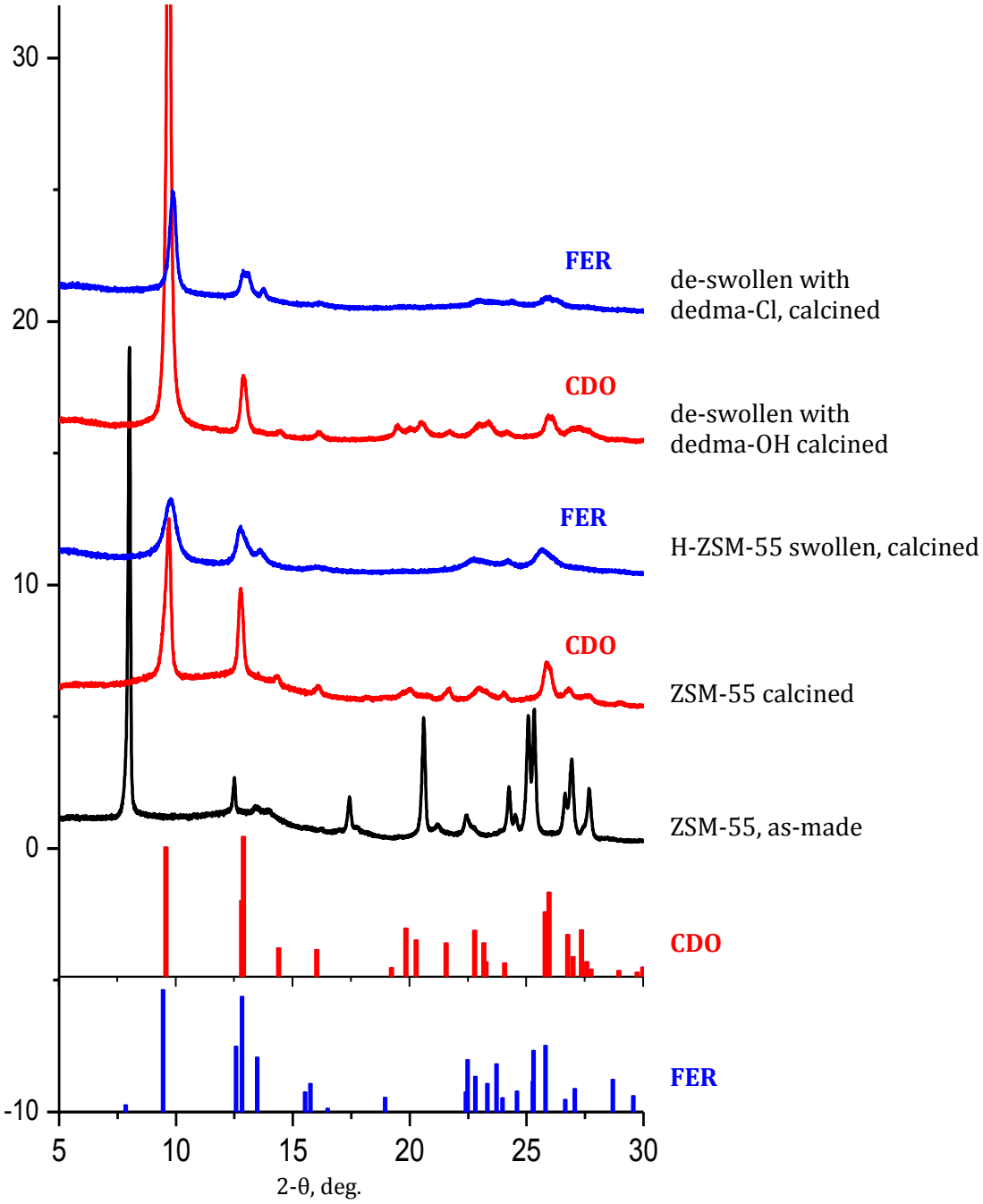
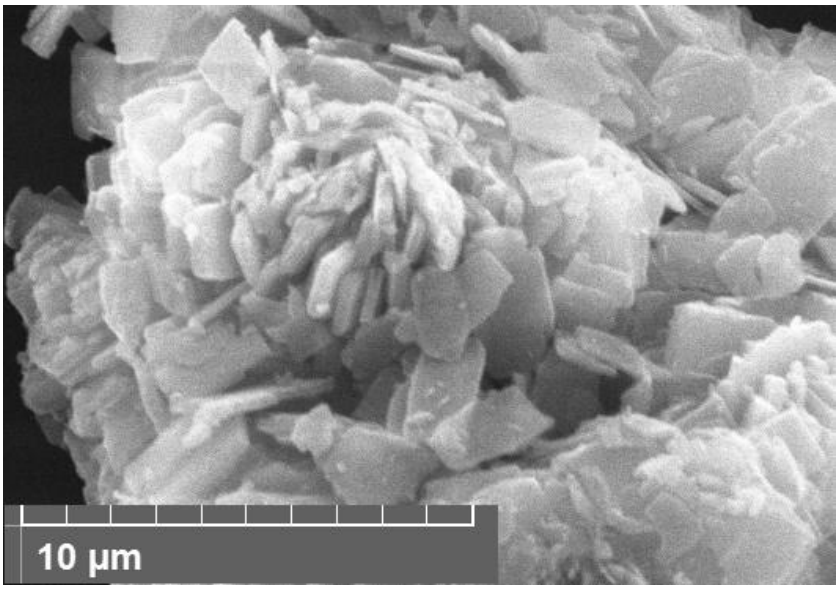
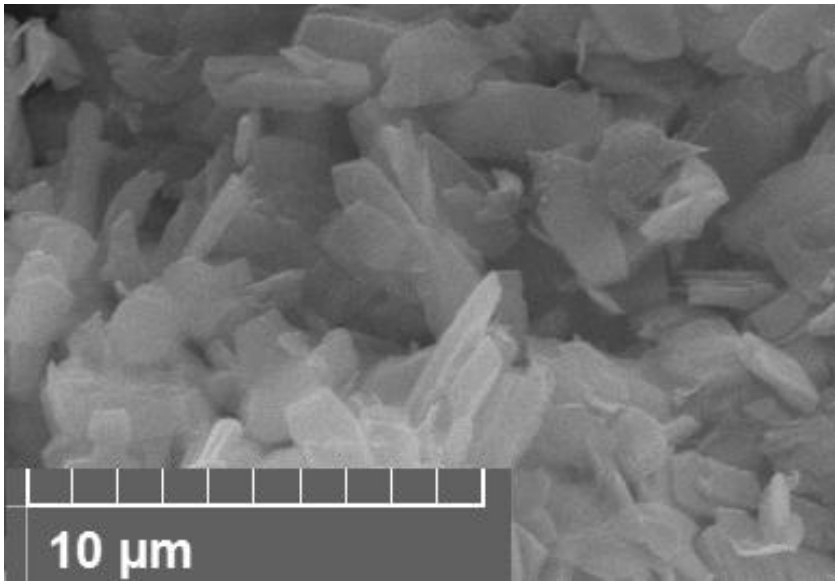


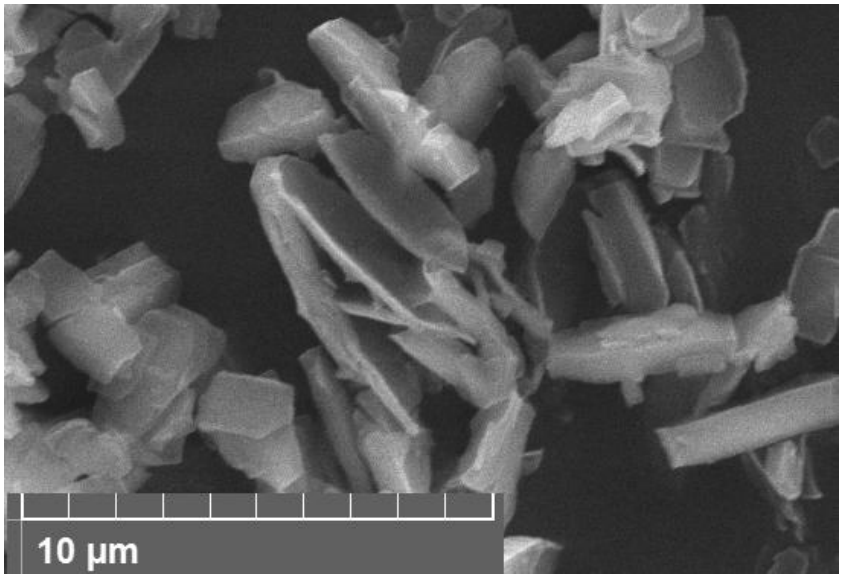
Figure 5S. SEM images of selected ZSM-55 samples before and after transformation.



As-synthesized
ZSM-55



Final CDO
after swelling,
+ dedma-OH in ethanol
+ calcined



Final FER
after swelling,
+ dedma-Cl in ethanol
+ calcined

Figure 6S. X-ray powder diffraction patterns for swollen H-ZSM-55 (bottom) detemplated with dedma-OH at different times proving that: (i) deswelling is very quick – under 1 hour, (ii) there is no indication of dissolution and recrystallization, i.e. the fer layers preserve integrity and only undergo interlayer changes.