

1 Supporting Information for

2 Mono-directional pressure induced
3 downsizing of zeolite crystals increases their
4 catalytic performances

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10 **1 Experimental Section**

11 **1.1 Pressure treatment**

12 NH₄-ZSM-5 crystals of Si/Al = 19 were provided by Sud Chemie (now Clariant AG). The zeo-
13 lite was used as such without any further modification unless mentioned. The zeolite crystals
14 were subjected to a mono-dimensional pressure in a manual hydraulic press where 100 mg
15 of zeolite was placed in a pressing cylinder having a diameter of 1.6 cm. Then, the pressure
16 was increased from zero to 10 tons (488 MPa) for 1 min and maintained for 10 min. Finally, the
17 pressure was released for 1 minute. As such, the pressure applied is equivalent to 4.87 MPa/mg
18 of zeolitic material.

19 For treatment under hydraulic isostatic pressure, we used a GEC Alsthom-ACB isostatic press
20 that applies pressure in the range of 0-10000 bars on a chamber possessing an internal diameter
21 of 5.1 cm using a mixture of 75% hydraulic oil and 25% white spirit. Prior to the pressurization,
22 we placed 0.5 g of the ZSM-5 into a vacuum bag which was then subjected to different values
23 of press (5, 7, and 9 tons) for 10 minutes. As such the pressure applied is equivalent to 0.048,
24 0.067, and 0.086 MPa/mg for the 5, 7, and 9 tons respectively.

25 **1.2 Characterization**

26 X-ray diffraction was analyzed using a PANalytical X'Pert PRO-MPD diffractometer with Cu
27 K α_1 radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned in the 2θ range of 5–50° with a step
28 size of 0.0167° . The size and morphology of ZSM-5 zeolite samples were investigated using a
29 scanning electron microscope (SEM, MIRA-LMH TESCAN) supplied with a field emission gun
30 operating at 30 kv. Textural properties of the samples were determined by N₂ physisorption at
31 77 K and CO₂ adsorption analysis was performed at 293 K using a Micromeritics ASAP 2020
32 volumetric adsorption analyzer. The samples were degassed under vacuum at 573 K for 15
33 hours before the measurement.

34 The coordination environment of Al and Si species in the H-form ZSM-5 was determined using
35 solid-state ²⁷Al and ²⁹Si magic-angle spinning (MAS) NMR. The spectra were recorded using a

36 4 mm zirconium rotor on a Bruker Avance-500 spectrometer using a spinning rate of 12 kHz,
37 a pulse length of 0.77 μs (15° flip angle), and a recycle time of 1 s.
38 The acidity of self-supported zeolite wafers under a pressure of 2 tons was determined using
39 a Nicolet Magna 550-FTIR spectrometer (4 cm^{-1} optical resolution) equipped with a DTGS
40 detector connected to a homemade in situ cell. Pyridine (Py) was chosen as a probe molecule to
41 measure the concentration of Brønsted and Lewis acid sites in ZSM-5. Before the adsorption of
42 pyridine each sample was activated under a 10^{-6} torr vacuum using the following program: the
43 temperature was increased from 303 to 423 K at a rate of 2 K min^{-1} , held at 423 K for 1 hour;
44 then increased to 773 K at a rate of 1.46 K min^{-1} and held at this value for another 4 hours.
45 As such the NH_4 -ZSM-5 is converted to its protonic form, H-ZSM-5. The probe molecule was
46 adsorbed at 373 K under saturation pressure of 1.2 torr, followed by temperature-programmed
47 desorption (TPD) up to 623 K with a 50 K interval. All spectra were normalized to a wafer
48 weight of 20 mg. The infrared analysis was performed twice to ensure the reproducibility of
49 the experiments.

50 **1.3 Catalytic tests**

51 The methanol to olefin (MTO) conversion was performed in a continuous-flow fixed-bed re-
52 actor holding catalyst-sieved pellets (20 mg wet catalyst, particle size between 250-500 μm)
53 mixed with inert silicon carbide catalyst-sieved (Zeolite/SiC = 1). Prior to the catalytic testing,
54 all samples were activated using the same program described for the infrared analysis under
55 airflow of 100 ml min^{-1} . The methanol feed was delivered by a liquid HPLC pump (Gilson
56 302) with a flow rate of 50 ml min^{-1} with an hourly weight space-velocity (WHSV) of 19.32
57 g/g.h. The catalytic conversion was at a temperature of 673 K under atmospheric pressure.
58 The reaction products were analyzed online with a Varian 3800 gas chromatograph equipped
59 with a silica capillary column (Chromopack CP-SIL 5 CB WCO).

60 1.4 Breakthrough curve analysis

61 Before analyzing the breakthrough curve, the parent NH_4 -ZSM-5 and mono-directional pressed
62 NH_4 -ZSM-5 were subjected to ion exchange in a 0.5 M sodium chloride solution to convert
63 them into the Na form. To do this, 1 g of each material was suspended in a 20 ml sodium
64 chloride solution and kept at 80 °C for three hours. This process was repeated three times, and
65 the crystals were subsequently washed until a neutral pH was achieved. Finally, they were col-
66 lected through centrifugation at 21000 rpm for 10 minutes. Breakthrough curve experiments
67 were performed using a 3P Instruments SHP eco and Cirrus-3 Quadrupole Mass Spectrometer.
68 Powder samples of zeolite adsorbent were pelletized by loading the powder between two core
69 dice in a 20 mm die sleeve with a base plate and plunger and increasing the applied pressure
70 to 1.5 tons. The pellets were gently crushed with an agate pestle and meshed from 60 to 35
71 (250–500 μm) before being loaded into the column, weighed, and covered with a thin layer of
72 glass wool. After each instance of loading the meshed sample into the column, the column was
73 tapped 100 times to remove inter-particle voids. The inner diameter of the column was 6 mm,
74 and the height of the adsorbent bed was 6 cm. The samples were pre-treated under He flow (20
75 mL/min) with heating from room temperature to 300 °C at 10 °C/min (measured by an inter-
76 nal temperature probe) and held at 300 °C for 6 h using a heating mantle. TG analysis of the
77 zeolite samples was performed to determine the weight loss of water during the pre-treatment
78 step. The final amounts of the Na-ZSM-5-Parent and Na-ZSM-5-10T loaded in the column af-
79 ter activation were 0.969 and 0.947 g, respectively. After pre-treatment, the samples were kept
80 under a flow of He (20 mL) at room temperature before commencing the breakthrough curve
81 experiments.

82 Breakthrough curve experiments were conducted using a binary mixture of CO_2 (analytical
83 component) and He (carrier gas) at 1 bar with a flow rate of 2 and 38 mL/min, respectively (to-
84 tal 40 mL/min), representing 5 and 95 vol% of the feed composition. Prior to the breakthrough
85 curve experiments, the mass spectrometer was calibrated by passing the binary feed mixture
86 through a bypass line to the mass spectrometer. Before contacting the binary feed mixture with
87 the adsorbent column, the sample was maintained under He flow. The adsorption feed mix-

88 ture was flowed through the adsorbent column after the temperature and spectrometer signals
 89 were stable, as determined using a bypass line. Breakthrough experiments were conducted
 90 at 20 °C by immersing the column in a water bath isothermally maintained by a chiller. The
 91 analysis time was 30 min to allow sufficient time for the bed to reach equilibrium after the
 92 breakthrough. Due to the significant difference in mass between the sample and the water
 93 bath, a negligible excursion of the temperature profile (<0.15 °C) of the column occurred dur-
 94 ing the breakthrough of CO₂ (Figure S8A). The pressure drop across the column loaded with
 95 the sample was determined by a pressure sensor located immediately before the column and
 96 the pressure controller located immediately after the column. For all experiments conducted,
 97 the pressure drop was <0.13 bar.

98 All breakthrough curve data was processed using the mixSorb Manager software. The differen-
 99 tial loading of CO₂ was calculated from the integrated areas, as depicted in Figure S8B.

$$n_{\text{adsorbed}} = \int V_{\text{in}}(t)c_{\text{in}}(t)dt - \int V_{\text{out}}(t)c_{\text{out}}(t)dt \quad (1)$$

100 The advanced computed flow rate changes was employed to account for changes in the flow
 101 rate using the He carrier gas as an internal standard.

$$V_{\text{out}}(t) = \frac{V_{\text{He}}(t)}{1 - \sum_{i=1}^n y_{\text{adsorptive},i}(t)} \quad (2)$$

102 Blank experiments under identical feed composition, temperature, flow rate, and pressure con-
 103 ditions were performed using granular quartz to determine the loading of molecules in the free
 104 space between the adsorbent particles and were directly subtracted from the loading values of
 105 the zeolite samples. Helium is considered as a non-adsorbing gas.

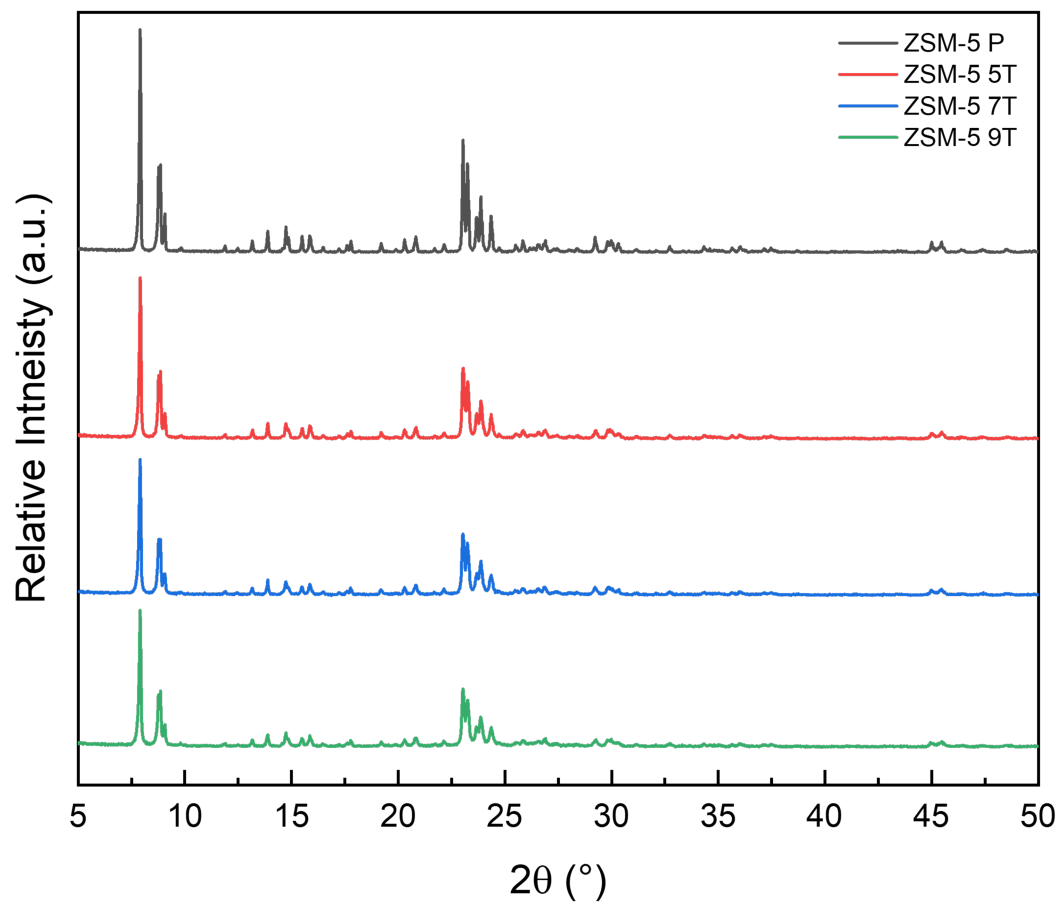


Figure S1: PXRD patterns of NH₄-ZSM-5 before and after hydraulic isostatic pressing.

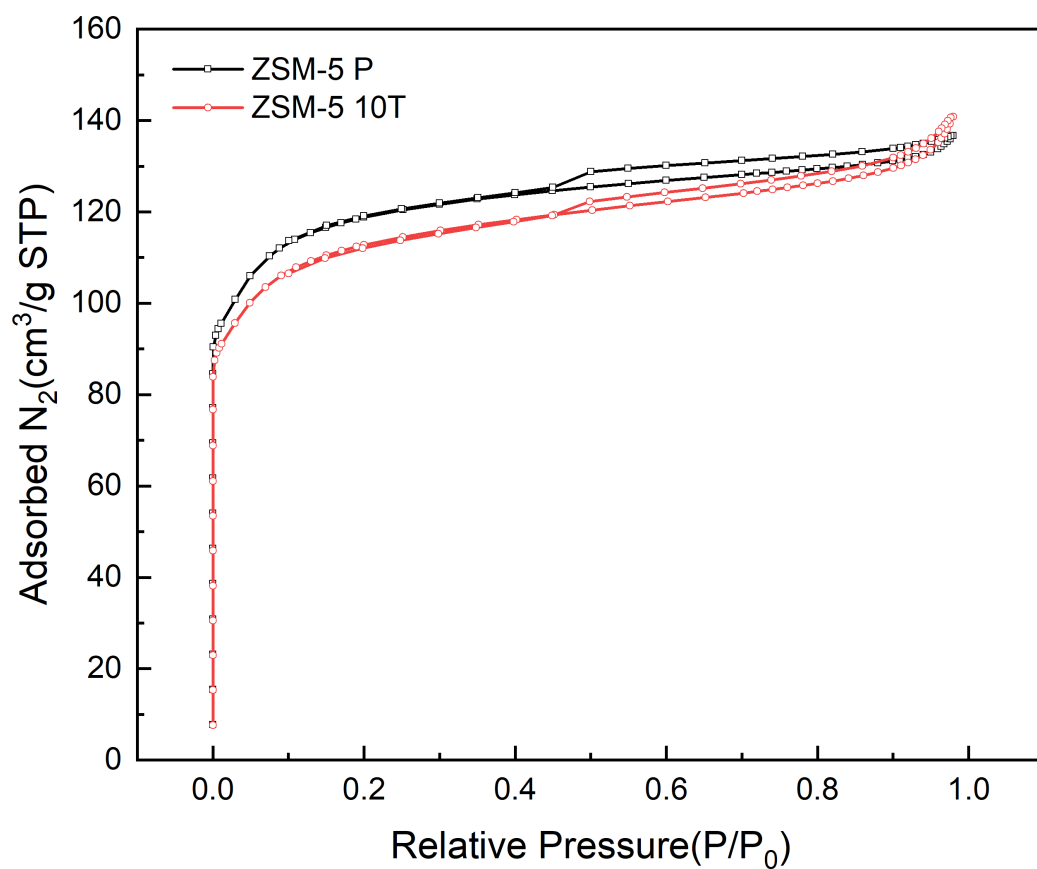


Figure S2: Nitrogen adsorption and desorption isotherms at 77 K for the parent H-ZSM-5 and its derivative after mono-directional hydraulic pressing.

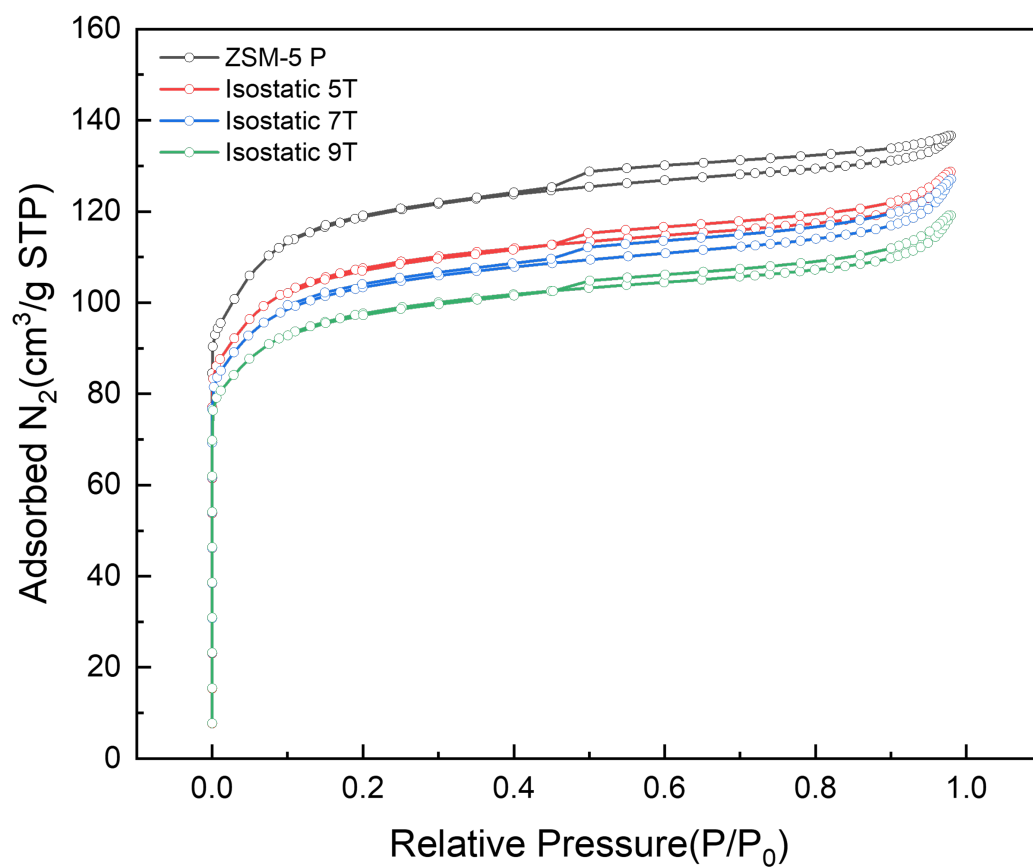


Figure S3: Nitrogen adsorption and desorption isotherms at 77 K for the parent H-ZSM-5 and isostatic hydraulic pressed derivatives.

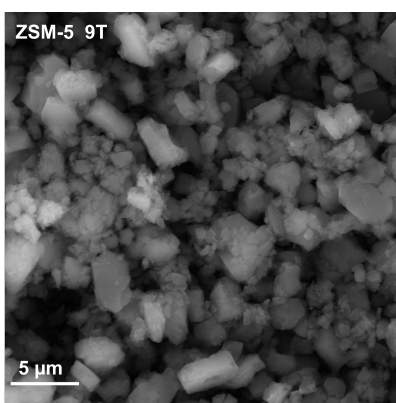
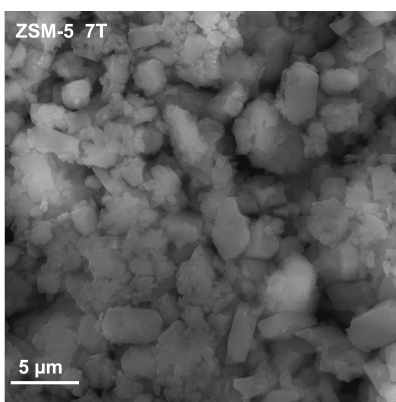
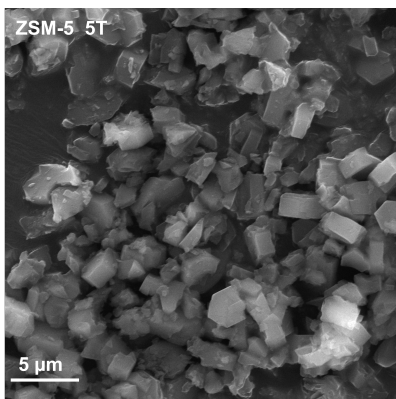


Figure S4: SEM images of the iso-directional hydraulic press treated NH_4 -ZSM-5 at 5, 7, and 9 tons.

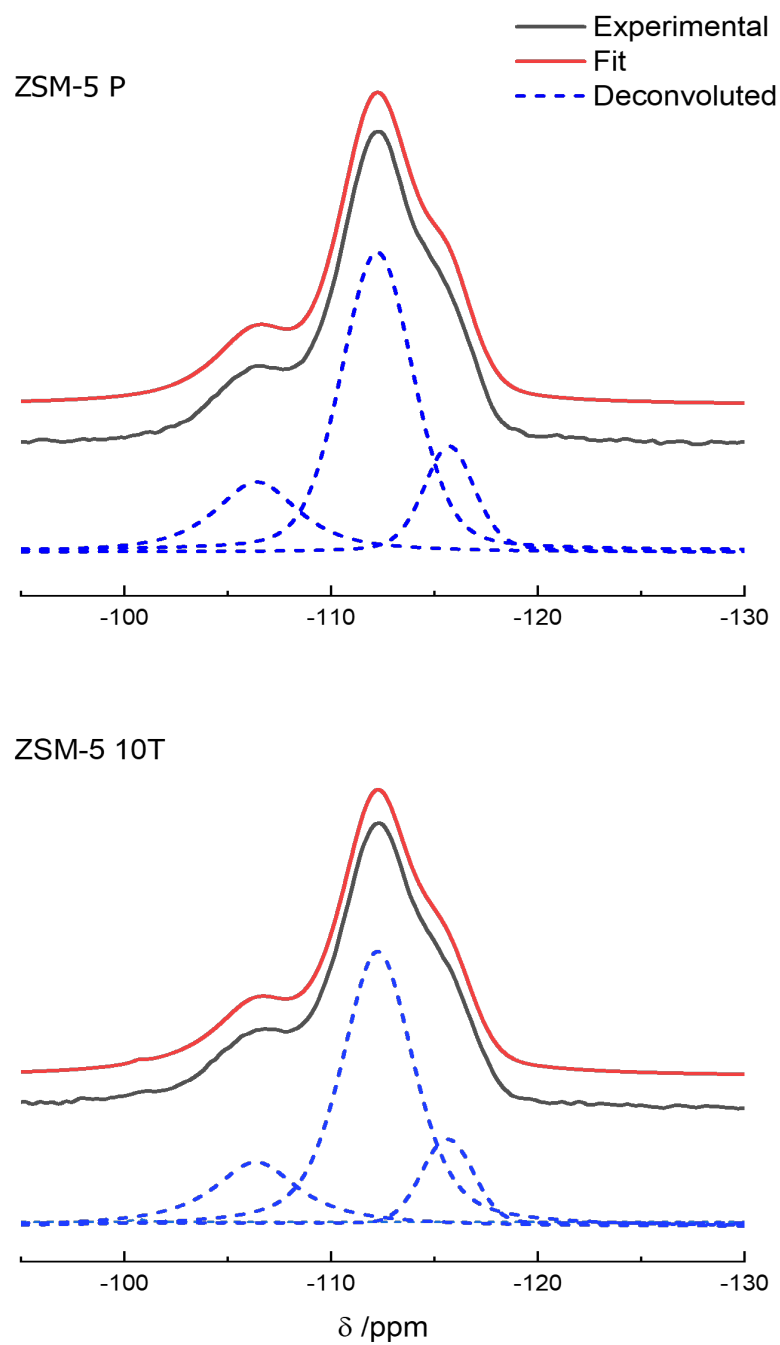


Figure S5: ^{29}Si MAS NMR spectra for NH_4 -ZSM-5 before and after mono-directional hydraulic pressing.

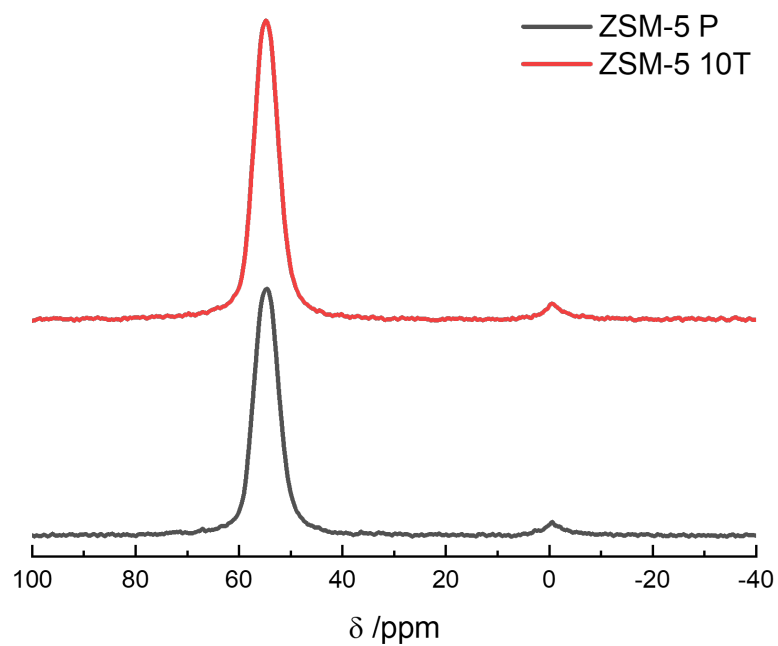


Figure S6: ^{27}Al MAS NMR spectra for NH_4 -ZSM-5 before and after mono-directional hydraulic pressing.

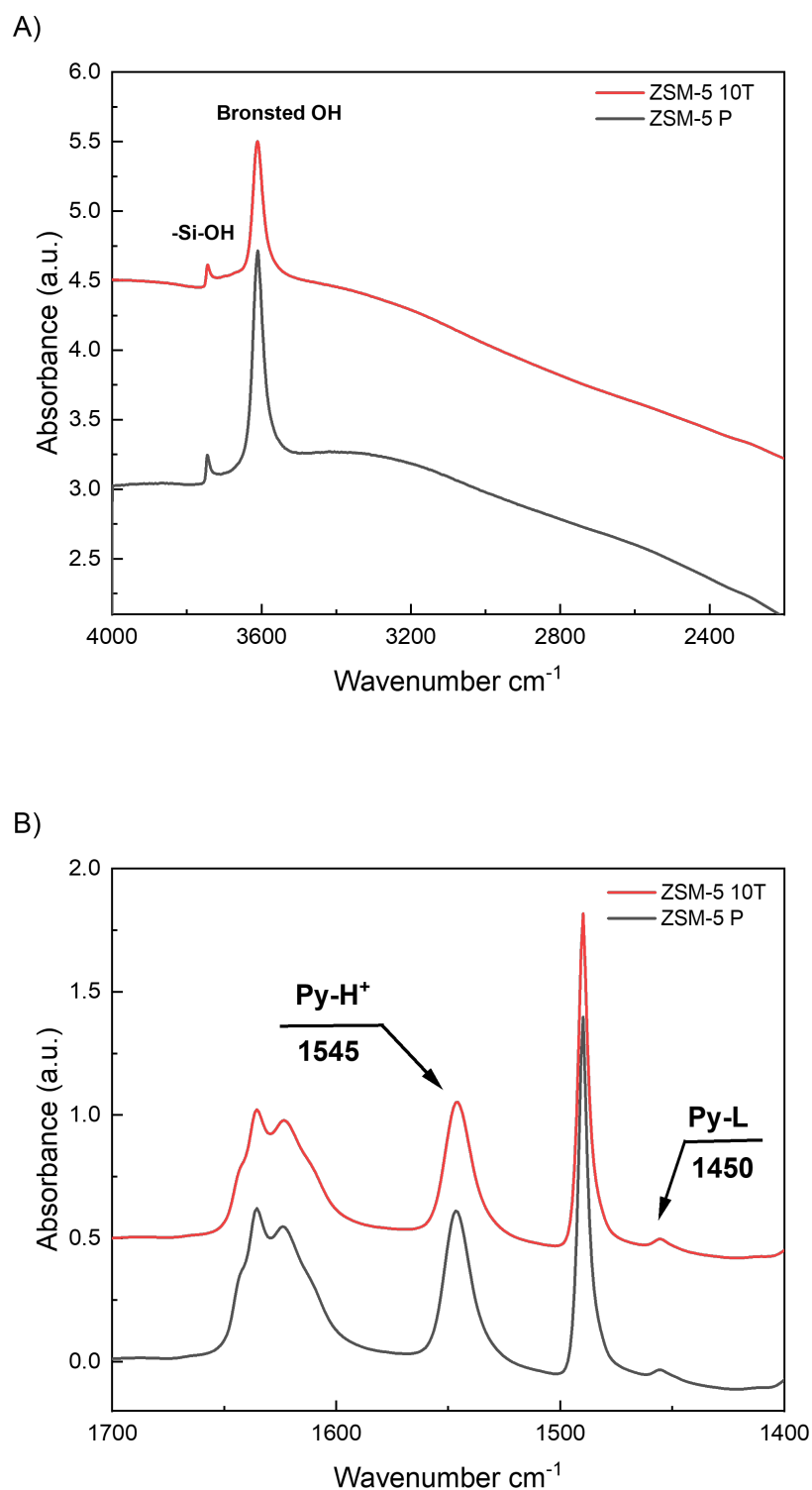


Figure S7: FTIR spectra of the parent H-ZSM-5 and its mono-directional pressed derivative in the A) OH region after activation, and B) after the adsorption and evacuation of pyridine at 423 k.

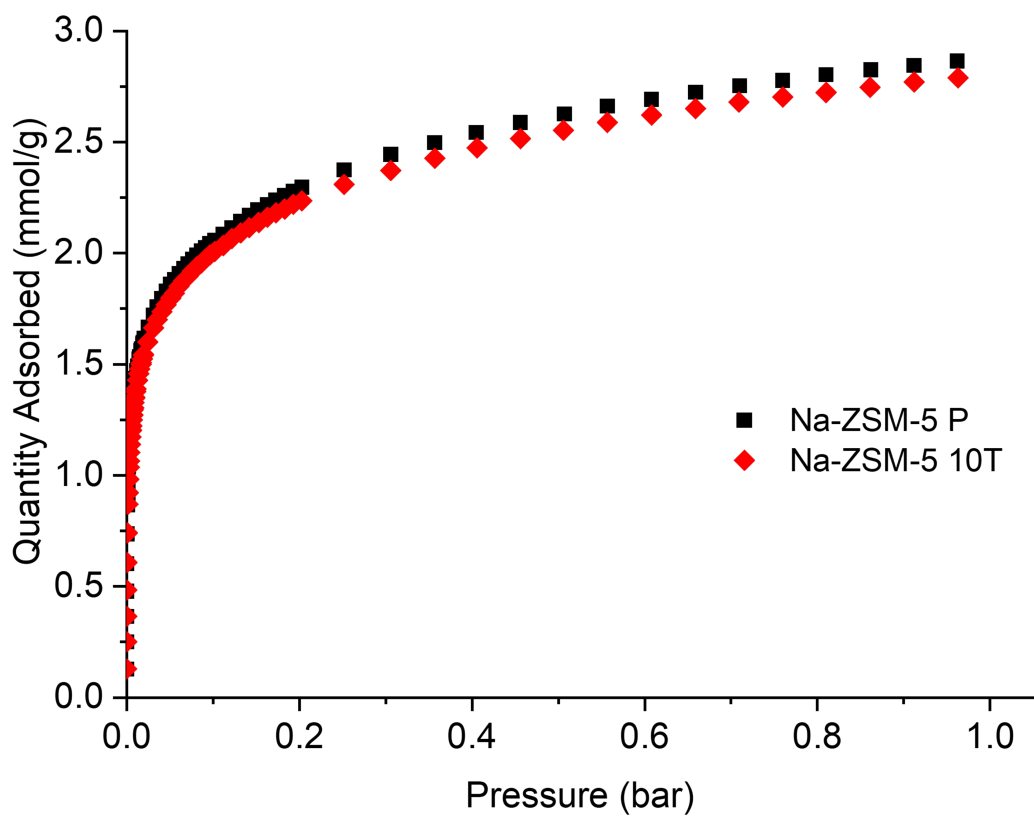


Figure S8: CO₂ adsorption isotherms recorded at 20 °C on the parent and mono-directional pressed Na-ZSM-5.

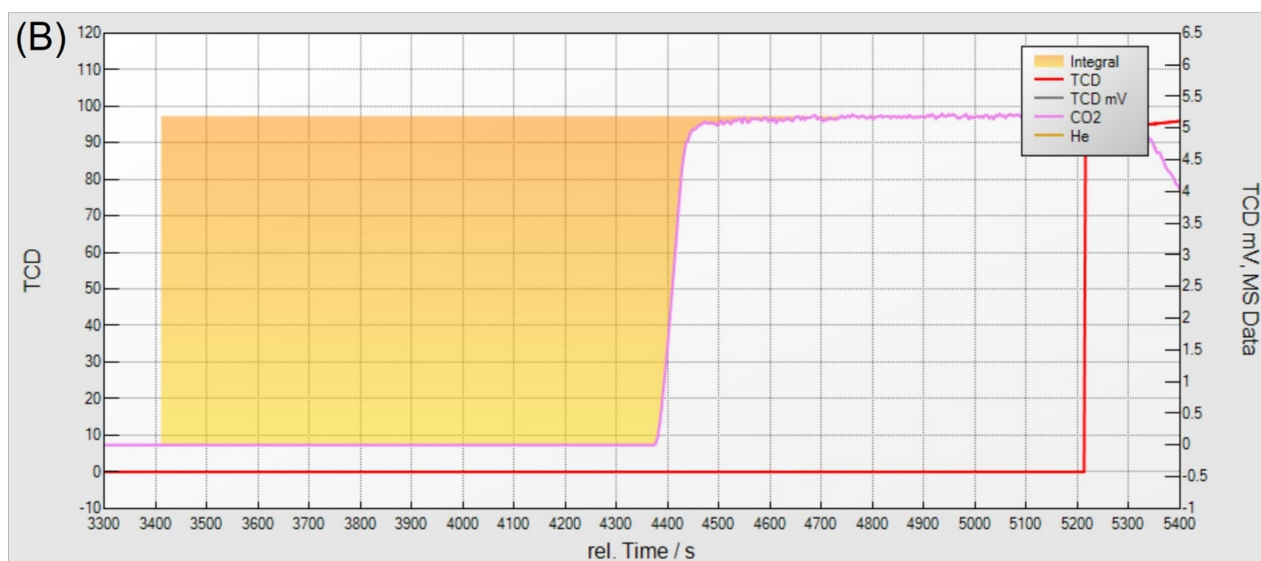
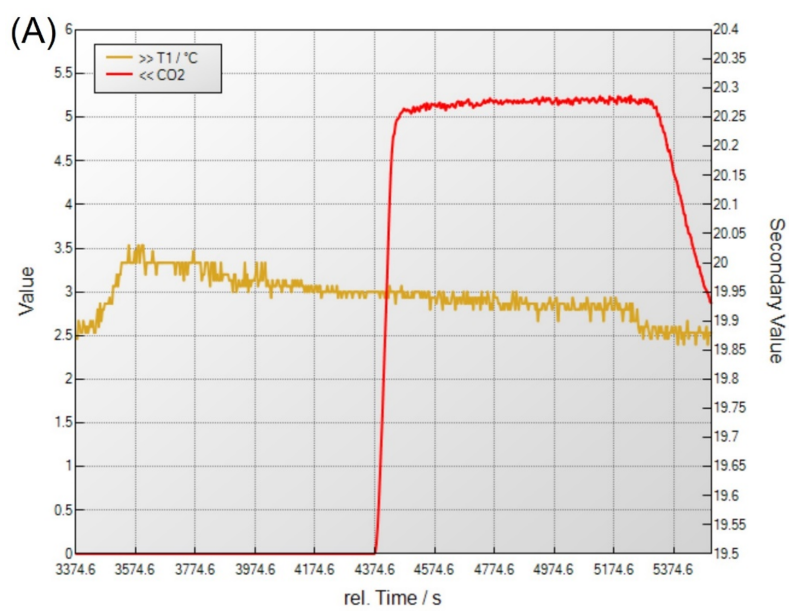


Figure S9: (A) Plot of the CO₂ outlet concentration (% , left) and temperature profile (°C, right) during the CO₂ breakthrough curve experiment on the parent Na-ZSM-5. (B) CO₂ breakthrough curve area (orange region) calculation using the mixSorb Manager software for calculating the adsorbed amount at saturation at 20 °C for the parent Na-ZSM-5. He and CO₂ concentrations (right y-axis) were determined by a calibrated mass spectrometer while the column outlet mixture is also measured by a TCD.

Table S1: Textural properties of H-ZSM-5 before and after isostatic pressuring.

Samples	S_{BET} [m ² g ⁻¹] ^[a]	V_{micro} [cm ³ g ⁻¹] ^[b]	V_{meso} [cm ³ g ⁻¹] ^[c]
ZSM-5 P	434	0.13	0.08
ZSM-5 Isostatic 5T	400	0.12	0.08
ZSM-5 Isostatic 7T	385	0.11	0.08
ZSM-5 Isostatic 9T	360	0.11	0.08

[a] Apparent surface area calculated using the Roquerol BET criteria. [b] Micropore volume and external surface area are calculated by the t-plot method. [c] Mesopore volume calculated by $V_{meso} = V_{total} - V_{micro}$, where V_{total} is the total pore volume calculated at $P/P_0 = 0.98$.