Electronic Supplementary Information

Hierarchical high-silica zeolites as superior base catalysts

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Table S1. Properties, suppliers and coding of parent zeolite samples.

Code	Commercial name	Supplier	Si/Al[a] (-)	Cation	S_{BET}[b] ($m^2 g^{-1}$)	S_{meso}[c] ($m^2 g^{-1}$)	V_{pore}[d] ($cm^3 g^{-1}$)	V_{micro}[c] ($cm^3 g^{-1}$)
X1.4	13X	Acros	1.4	Na^+	421	32	0.24	0.20
Y2.6	CBV300	Zeolyst	2.6	NH_4^+	543	28	0.30	0.27
USY15	CBV720	Zeolyst	17	H^+	759	148	0.54	0.32
USY30	CBV760	Zeolyst	34	H^+	776	174	0.55	0.31
USY385	HSZ-390HUA	Tosoh	385	H^+	697	141	0.58	0.29
Z1000	HSZ-980HOA	Tosoh	1040	H^+	328	60	0.19	0.14

[a] Molar Si/Al ratio determined by ICP-OES, [b] BET method, [c] *t*-plot method, [d] $p/p_0 = 0.99$.

Table S2. Kinetic diameter and reaction times for aldehydes reacted with malononitrile in the reactant size study.

Substrate	d_{kin} (nm)	$t_{reaction}$ (min)
butanal	0.31	15
heptanal	0.31	15
2-methylbutanal	0.35	15
cyclohexylcarbaldehyde	0.40	60
benzaldehyde	0.39	120
2,2-dimethylpropanal	0.40	480
1-naphthaldehyde	0.47	480
9-carboxyphenantrene	0.57	480

Table S3. Reaction conditions for solvent-free condensation reactions.

Reactants[a]	Internal standard[b]	m_{cat} (g)	T (°C)	$t_{reaction}$ (h)
BA (8 mmol) + ECA (8 mmol)	TOL (8 mmol)	0.1	120	4
BA (8 mmol) + EAA (8 mmol)	TOL (8 mmol)	0.1	140	4
BA (8 mmol) + DEM (8 mmol)	TOL (8 mmol)	0.1	140	4
BA (10 mmol) + HA (2 mmol)	DEC (6 mmol)	0.1	125	24
BA (5 mmol) + NE (10 mmol)	XYL (8 mmol)	0.5	125	8

[a] BA = benzaldehyde, ECA = ethyl cyanoacetate, EAA = ethyl acetoacetate, DEM = diethyl malonate, HA = heptanal, NE = nitroethane; [b] TOL = toluene, DEC = *n*-decane, XYL = *p*-xylene.

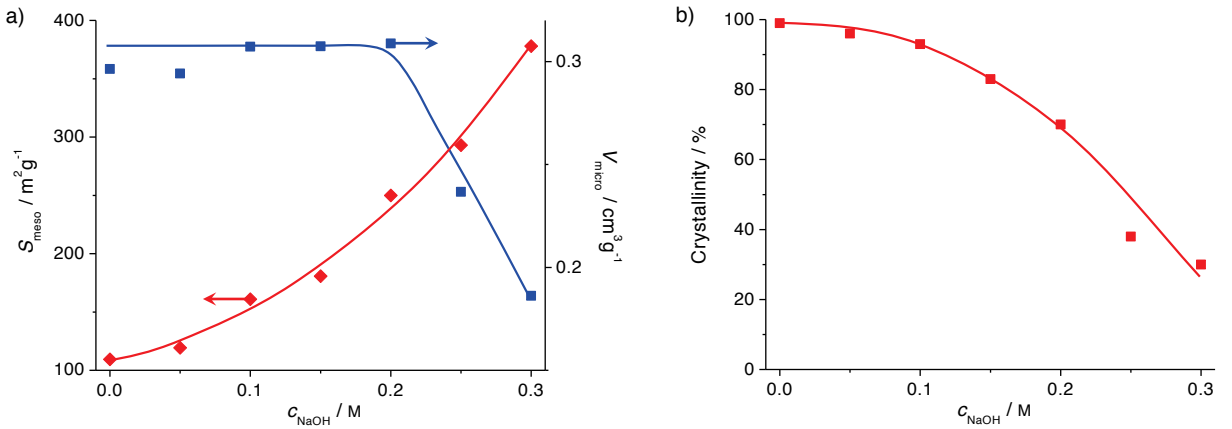

Fig. S1 a) External surface (S_{meso}), micropore volume (V_{micro}) and b) crystallinity of base-leached USY385 zeolites mapped against the applied NaOH concentration. While the external surface increases with the alkalinity of the base-leaching solution, the crystalline structure of the zeolite remains preserved up to a NaOH concentration of 0.2 M. Representative N_2 isotherms and XRD diffractograms are given in Fig. S5.

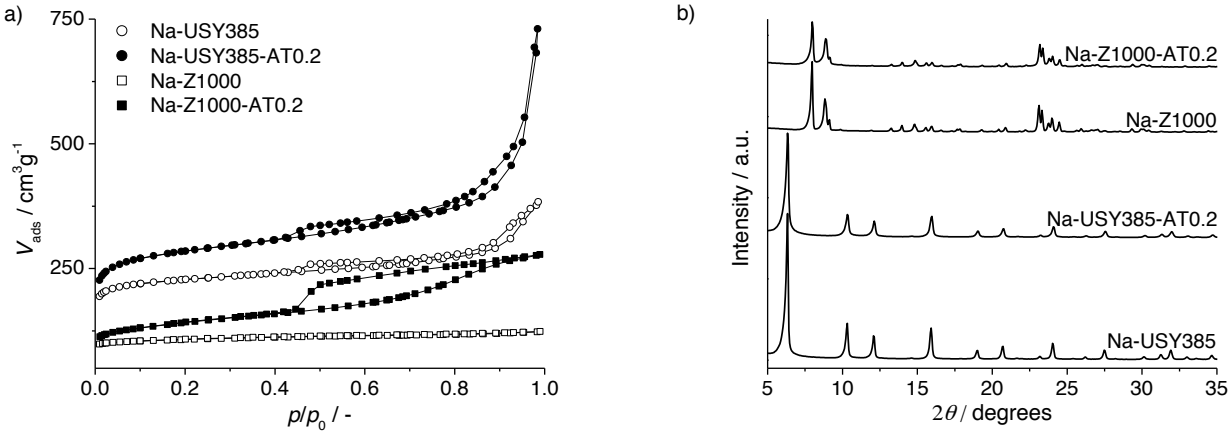

Fig. S2 Representative a) nitrogen isotherms and b) X-ray diffraction patterns of parent and alkaline-treated USY385 and Z1000 zeolites. The increased uptake in the range of $p/p_0 > 0.4$ in the nitrogen isotherms highlights the formation of mesoporosity in the alkaline-treated samples. The XRD diffractograms evidence that the crystalline character of the zeolites is preserved upon mesopore generation.

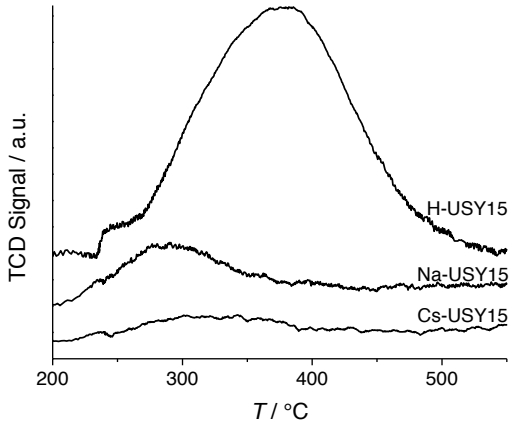

Fig. S3 NH_3-TPD profiles for USY15 zeolites exchanged with various cations. While the H-USY15 zeolite shows a high uptake at elevated temperature due to strong acidity, the Na-USY15 only shows a minor desorption around 300°C, which can be attributed to weak acidity generated by extra-framework aluminium. In contrast, Cs-USY15 evidences almost no desorption of NH_3, indicating that the acidity was practically null due to the larger alkali metal cations incorporated. Temperature-programmed desorption of NH_3 was carried out in a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector. The zeolite (0.1 g) was pretreated at 550°C in He flow (30 cm^3 min^{-1}) for 3 h. Afterwards, 10 vol.% of NH_3 in He (30 cm^3 min^{-1}) was adsorbed three times at 200°C for 30 min, followed by He purging at the same temperature for 60 min. NH_3-TPD was monitored with a thermal conductivity detector (TCD) in the range of 200–700°C (heating rate: 10°C min^{-1}).

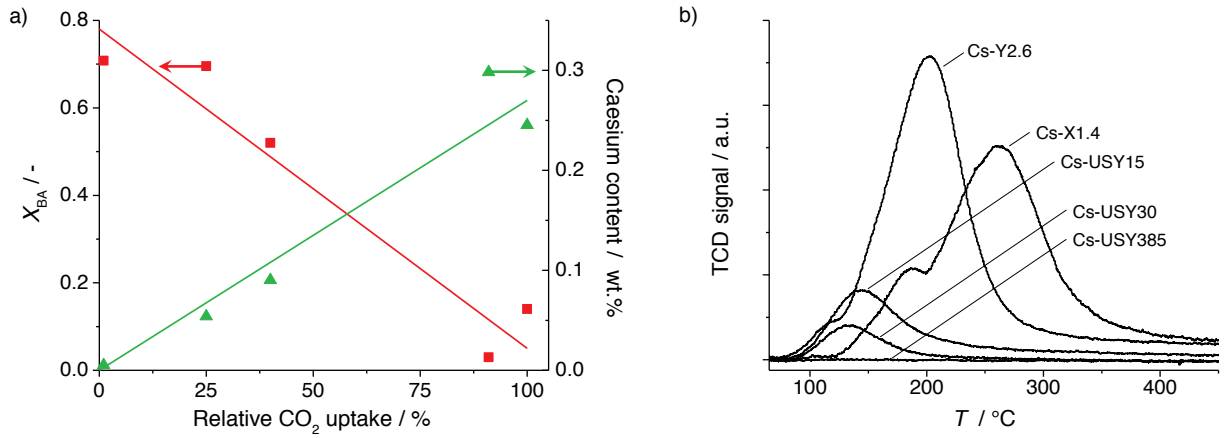

Fig. S4 a) Caesium content (▲) and conversion of benzaldehyde (X_{BA}) in the Knoevenagel condensation with malononitrile (■) *versus* the normalised CO_2 uptake assessed by temperature-programmed desorption of CO_2 on Cs-exchanged FAU-type zeolites. While a linear correlation with positive slope between caesium content and catalytic performance would be expected, the observed negative slope indicates the inability of the method to detect the active sites. Instead, the CO_2-based descriptor appears to probe directly the caesium content, as evidenced by the clear correlation for this descriptor. b) Temperature-programmed desorption of CO_2 over Cs-exchanged faujasite zeolites. Desorption of CO_2 was monitored with a thermal conductivity detector (TCD) in the range of 50–700°C (heating rate: 10°C min^{-1}). Temperature-programmed desorption of CO_2 was carried out in a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector. The zeolite (0.1 g) was pretreated at 550°C in He flow (30 cm^3 min^{-1}) for 3 h. Afterwards, 2 vol.% of CO_2 in N_2 (30 cm^3 min^{-1}) was adsorbed at 50°C for 90 min, followed by He purging at the same temperature for 60 min. The relative CO_2 uptake was obtained by integration of the TCD signal from 65°C to 450°C after baseline correction, followed by normalisation to the highest obtained area.

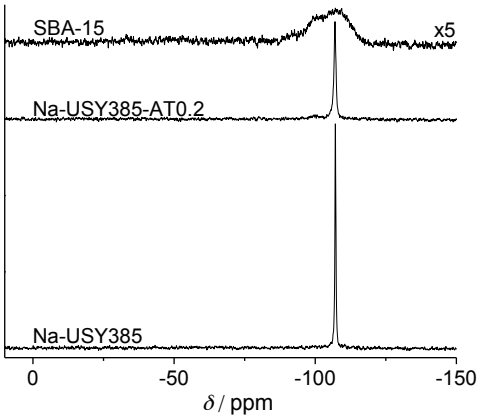

Fig. S5 ^{29}Si MAS NMR spectra of siliceous USY zeolites and SBA-15, highlighting the sharply defined coordination of high-silica zeolites compared to mesoporous silica. Spectra were recorded at a spinning speed of 10 kHz on a Bruker Avance 700 NMR spectrometer equipped with 4 mm ZrO_2 rotors at 139.1 MHz using 1024 accumulations, 90° pulses with a pulse length of 12.5 µs, a recycle delay of 10 s, and octakis(trimethylsiloxy)silsesquioxane (Q8M8) as reference.

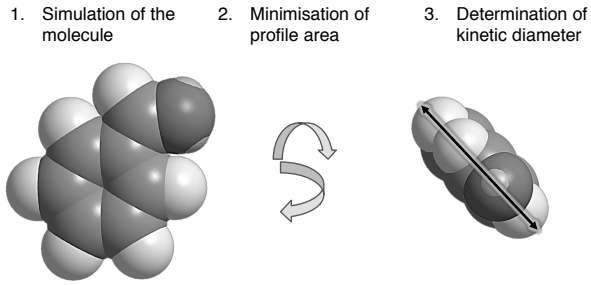

Fig. S6 Schematic procedure for the determination of the kinetic diameter equivalent. First, the molecule is simulated assuming van-der-Waals radii for each atom and its geometry is optimised (MM2 energy minimisation). Then, the molecule is rotated until the minimum profile area is found. Finally, the maximal diameter of the minimised profile area is measured as kinetic diameter.

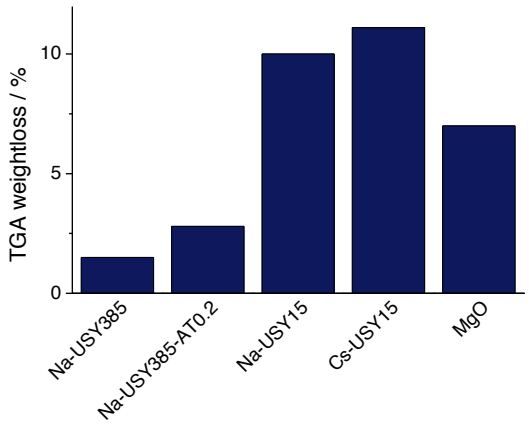

Fig. S7 Weight loss upon thermogravimetric analysis (TGA) of catalysts after their use in the aldol condensation of propanal. Experiments were carried out with a Mettler Toledo TGA/DSC 1 analyser. In a typical measurement, 20 mg of the coked catalyst was heated from 25 to 900ºC in flowing air (60 cm^3 min^{-1}) at a rate of 10 ºC min^{-1}.