

Electronic Supporting Information

Balancing Ge de-intercalation and Si re-insertion rates stabilizes hydrolytically labile germanosilicate zeolites

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Experimental methods

Preparation of organic structure-directing agents

1-Butyl-3-methylimidazolium hydroxide (OSDA1), 1,5-bis(tetramethylimidazolium)pentane hydroxide (OSDA2), 1,2-dimethyl-3-(3-methylbenzyl)imidazolium hydroxide (OSDA3) were used as OSDAs for the synthesis of UWY¹, IWV^{2,3} and *CTH⁴ zeolites, respectively. All organic structure-directing agents were transformed to hydroxide forms from commercially available bromide forms by ion exchange with Ambersep® 900(OH) anion-exchange resin. Propane-1,3-bis(trimethylphosphonium) dihydroxide (OSDA4) used for the synthesis of ITR zeolite was prepared according to the procedure described in Ref.⁵.

Synthesis of germanosilicate zeolites

UWY. The synthesis of UWY-1.6 zeolite with Si/Ge = 1.6 determined by ICP-MS was performed according to Ref.¹ Cab-O-Sil M5, amorphous germanium oxide GeO₂, HF acid (40%), distilled water, OSDA1 were used to prepare the reaction mixture with the following molar composition: 0.6 SiO₂ : 0.4 GeO₂ : 0.5 OSDA1 : 0.5 HF : 10 H₂O. The resulting gel was autoclaved at 175 °C for 14 days under static conditions. The obtained solid was separated by filtration, washed with distilled water, and dried overnight at 95 °C. The occluded OSDA2 was removed from as-synthesized zeolite by the thermal treatment at 550 °C for 6 h. The heating rate was 1 °C min⁻¹.

The OSDA-free UWY-1.6 was used as seeds for the synthesis of UWY-1.9 and UWY-2.6 with Si/Ge = 1.9 and 2.6 determined by ICP-MS, respectively. The hydrothermal crystallization of the reaction mixtures with the molar compositions of (1-x) SiO₂ : x GeO₂ : 0.5 OSDA1 : 0.5 HF : 10 H₂O (x = 0.33 and 0.25 for UWY-1.9 and UWY-2.6, respectively) were performed similarly to that described for the UWY-1.6 sample, while replacing 20 wt. % of silica source with UWY-1.6 seeds. The samples were recovered and OSDA1 was removed by calcination as described *vide supra*.

IWV. Germanosilicate IWV zeolite was synthesized following the procedure described in Ref. ^{2,3}. Tetraethyl orthosilicate, amorphous germanium oxide GeO₂, distilled water, OSDA2 were used to prepare the reaction mixture with the following molar composition: 0.75 SiO₂ : 0.25 GeO₂ : 0.19 OSDA2 : 15 H₂O. The resulting gel was autoclaved at 175 °C for 14 days under static conditions. The obtained solid was separated by filtration, washed with distilled water, and dried overnight at 95 °C. The occluded OSDA2 was removed from as-synthesized zeolite by the thermal treatment at 550 °C for 6 h at the heating rate of 1 °C min⁻¹. The thus prepared OSDA-free IWV sample was used as seeds to promote the crystallization of IWV-4.3 and IWV-5.2 with Si/Ge = 4.3 and 5.2 determined by ICP-MS, respectively. The hydrothermal crystallization of the reaction mixtures with the molar compositions of (1-x) SiO₂ : x GeO₂ : 0.19 OSDA2 : 15 H₂O (x = 0.5 and 0.33 for IWV-4.3 and IWV-5.2, respectively) was performed similarly to that described for the IWV sample, while replacing 20 wt. % of silica source with IWV seeds. The samples were recovered and OSDA2 was removed by calcination as described *vide supra*.

***CTH.** CTH-4 zeolite with Si/Ge = 4 determined by ICP-MS was prepared according to Ref. ⁴ using tetraethyl orthosilicate, amorphous germanium oxide GeO₂, distilled water, HF acid (40%), OSDA3. The reaction gel had the following molar composition: 0.8 SiO₂: 0.2 GeO₂: 0.5 OSDA: 0.5 HF: 10 H₂O. Crystallisation was carried out at 175 °C for 30 days under static conditions. After recovery of the solid product via filtration, its washing with deionised water and drying at 60 °C overnight, as-synthesized CTH-4 was calcined at 580 °C for 6 h in the air flow.

ITR. ITR-2.6 zeolite with Si/Ge = 2.6 determined by ICP-MS was synthesized based on the protocol described in Ref. ⁵ in the absence of fluoride ions. Tetraethyl orthosilicate, amorphous germanium oxide GeO₂, distilled water, OSDA4 were used to prepare the reaction mixture with the following molar composition: 0.67 SiO₂: 0.33 GeO₂: 0.075 OSDA: 8.5 H₂O. The resulting gel was autoclaved at 175 °C for 10 days under agitation at 60 rpm. The obtained solid was separated by filtration, washed with distilled water, and dried overnight at 95 °C. The occluded OSDA4 was removed from

as-synthesized zeolite by the thermal treatment at 550 °C for 6 h at the heating rate of 1 °C min⁻¹.

Powder X-ray diffraction (PXRD) patterns were collected using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in Bragg-Brentano geometry on a Bruker AXS D8 Advance diffractometer equipped with a LYNXEYE XE-T detector. To minimize the impact of the preferential orientation of individual zeolite crystals, the samples were gently ground to reduce their size and carefully packed into the holder, which was spun horizontally during measurement to enhance particle statistics. PXRD patterns were measured in continuous scanning mode in a range of 3 – 40° 2 θ with a step size of 0.02 ° 2 θ and 2 s counting time per step. To determine the relative crystallinity degree and lattice parameters of the parent and stabilized zeolites, a full-profile Le Bail refinement was done on the resulting PXRD patterns using Jana2020[©] software ⁶. The zeolite structure models were sourced from the International Zeolite Association Database. The XRD reflections for the zeolite phases were adjusted using pseudo-Voigt functions. The crystallinity of the stabilized samples was evaluated as the ratio of the diffraction intensity of the crystalline component to the total diffraction intensity and presented relative to the crystallinity of the parent zeolite, which was set at 100%. The diffraction intensity for the crystalline component was determined by subtracting the data above the baseline corresponding to the amorphous phase. The baseline curve is described by (10-30) terms of Legendre Polynomials.

SEM images were collected on a FEI Quanta 200F scanning electron microscope equipped with a wavelength-dispersive X-ray detector. The samples were placed on the conducting carbon tape without any metal coating prior to measurement.

Argon sorption isotherms were collected on a Micromeritics 3Flex volumetric Surface Area Analyzer at – 196 °C. Before the measurements, the zeolite samples were degassed in a Micromeritics Smart Vac Prep instrument under vacuum at 250 °C for 8 h. The pore size distributions, as well as external surface and micropore were calculated using the adsorption branch of the Argon isotherms by applying the NL-DFT (Non-Local Density Functional Theory) model assuming cylindrical pore geometry.

The chemical composition of the zeolites and mother liquor was determined by ICP-MS analysis (Agilent 7900 ICP-MS). For the analysis of solid samples, 50 mg of the sample were mixed with 1.8 mL of HNO₃ (67-69%, ANALPURE®), 5.4 mL of HCl (34-37%, ANALPURE®), 1.8 mL of HF (47-51%, ANALPURE®), then transferred to a closed Teflon vessel (60 mL, type DAP60), placed in the microwave (Speedwave® XPERT, Berghof) and heated at 210 °C (5 °C min⁻¹) for 25 min. After cooling, the surplus HF was neutralized by adding 12 mL of H₃BO₃, followed by further treatment in the microwave at 190 °C for 10 min. Finally, the cooled-down solutions obtained were diluted for analysis.

²⁹Si and ¹⁹F MAS NMR spectra were recorded on a Bruker Avance III HD spectrometer at room temperature with a ²⁹Si Larmor frequency of 99.4 and 470.9 MHz for ²⁹Si and ¹⁹F, respectively. The samples were packed in 2.5 mm ZrO₂ MAS rotors, rotating at an MAS speed of 20 kHz. Given a small amount of material filling the rotors, as well as a low natural abundance of ²⁹Si and its intrinsic long relaxation, a conventional single-pulse acquisition was found to be impractical for signal averaging. Instead, a multiple echo acquisition was employed, with a pulse sequence $90_x^0 - [180_y^0 - acq -]_n$, allowing accumulation as many as n = 256 echo signals per scan. The acquisition window *acq* was set to 2.5 ms, which was wide enough to accommodate a whole echo down to the noise level. The number of scans was 720, and the delay between scans was 1 min; hence the total experiment time was 12 h per sample. The acquired echoes were summed up and processed into a real spectrum using an NMR data processing program *ssNake*⁷. The resultant spectra were decomposed into five Gaussian components with fixed centers, but variable widths and areas (for more robustness, the signal FWHM values were restricted to be less than 10 ppm during decomposition).

¹H→²⁹Si CP/MAS NMR spectra were collected with a 5 s relaxation delay, 5852 scans and contact time of 10 ms.

The ¹⁹F signals (free induction decays) were acquired following a single 90°-pulse, with 1280 signal repetitions at 30-sec intervals. Prior to the measurement, fluoride was incorporated into the as-made zeolites following a previously reported method⁸. For

that, 0.2 g of NH_4F was mixed with 1 g of zeolite, ground in the mortar, and then heated at 150 °C for 24 h. After cooling, the solid was washed with water and dried overnight at 110 °C.

The strength of acid sites in UWY-2.6 and UWY-2.6/SBZ/Al samples was assessed after adsorption of pyridine (Py) by Fourier-transform infrared spectroscopy (FTIR) on Nicolet iS50 FTIR spectrometer with MCT/B detector. The zeolites were pressed into self-supporting wafers with a density of 8–12 mg cm^{-2} and activated in situ at 450 °C for 4 h. Pyridine adsorption was carried out at 150 °C for 20 minutes at 600–800 Pa partial pressure, followed by desorption for 20 min at 150, 250, 350 or 450 °C. Before adsorption, pyridine was degassed by freezing and thawing cycles. All spectra were recorded with a resolution of 4 cm^{-1} by collecting 128 scans for a single spectrum at room temperature. Spectra were calculated at a wafer density of 10 mg cm^{-2} . The strength of acid sites was estimated using the relative intensities of the respective absorption bands after pyridine desorption at 450 °C (reflecting the number of strong acid sites) and 150 °C (reflecting the total number of acid sites): 1545 cm^{-1} for Brønsted acid centers and 1455 cm^{-1} for Lewis acid centers.

The catalytic experiments were performed in the liquid phase under atmospheric pressure at 130 °C in a multiexperiment workstation Star-Fish (Radleys Discovery Technologies). Before use, the catalyst (50 mg) was activated at 450 °C for 90 min at a rate of 10 °C min^{-1} . Typically, p-xylene (5 mL), internal standard (dodecane, 0.25 g), and the catalyst (50 mg) were added to a three-neck flask. Benzoyl chloride (5 mmol) was added to the flask when the required temperature was reached.

The samples of the reaction mixture were taken periodically and analyzed using a gas chromatograph (Agilent 7890B) equipped with a HP-5 column (30 m \times 0.32 mm \times 0.25 μm) and FID detector.

Conversion (X), yield (Y) and selectivity (S) were calculated according to the following equations:

$$(1) X = [(n(\text{reactant})_0 - n(\text{reactant})_t) / n(\text{reactant})_0] * 100 \quad [\%]$$

$$(2) Y = [n(\text{product})_t / n(\text{reactant})_0] * 100 \quad [\%]$$

$$(3) S = [Y/X] * 100 \quad [\%]$$

$n(\text{reactant})$ values in Eq. 1 and 2 were determined based on the internal standard calibration method, using commercially available p-xylene ($\geq 99\%$, Sigma Aldrich), benzoyl chloride ($\geq 99\%$, Sigma Aldrich), dodecane ($\geq 99\%$, Sigma Aldrich). The amounts of commercially unavailable product, $n(\text{product})$, were estimated using the concept of effective carbon number.⁹

The reaction products were identified by gas chromatography-mass spectrometry analysis on a Thermo Scientific Trace 1310 system equipped with a TG-5MS column (30 m x 0.25 mm x 0.25 μm) and by standard electron impact ionization.

Additional Figures

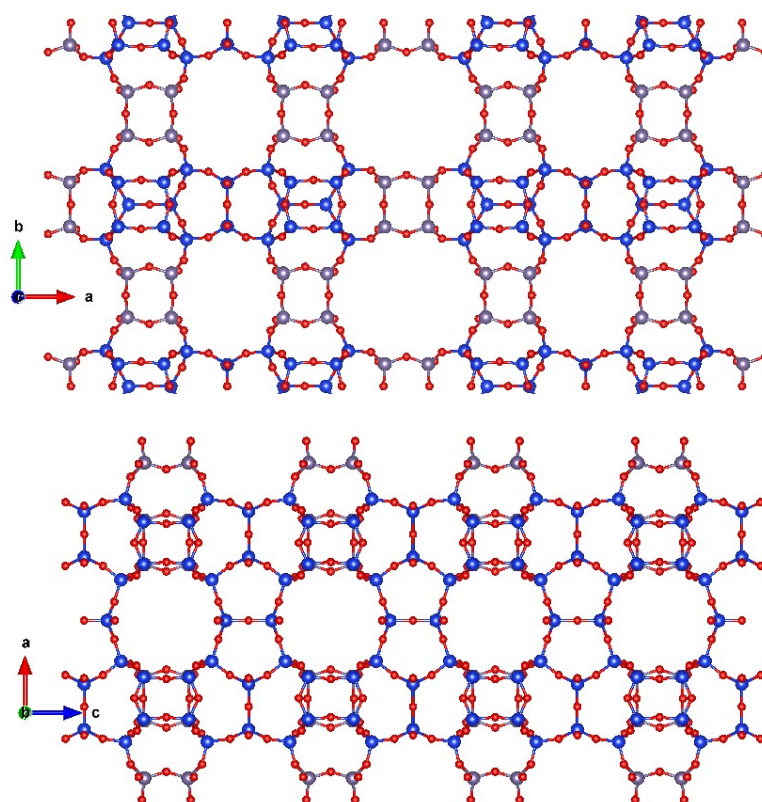


Figure S1 Crystal structure of UWY zeolite. The T atoms of the *D4R* units are shown in purple, while the other T atoms are shown in blue. Oxygen atoms are coloured red. The UWY topology has *D4R* units propagated along *a* and *b* directions.

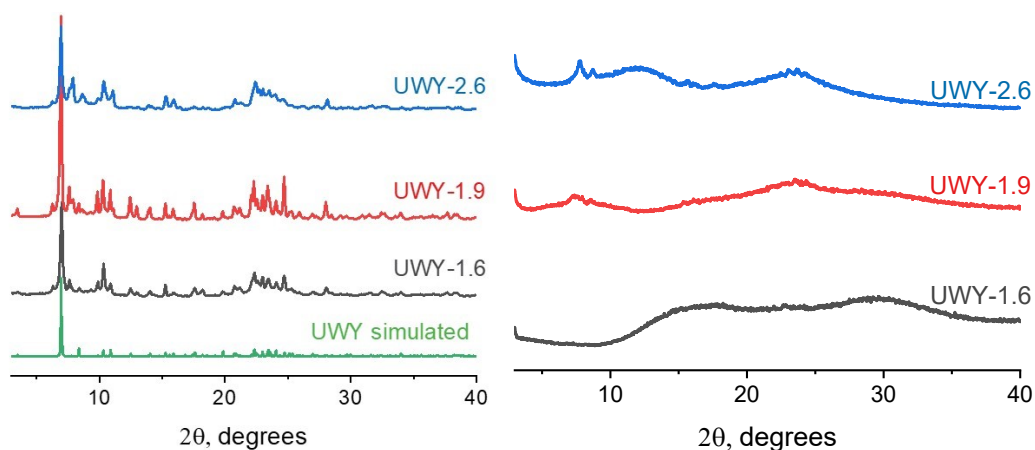


Figure S2 XRD patterns of OSDA-free UWY-1.6, UWY-1.9, and UWY-2.6: as-prepared (left) and treated with water at RT for 24 h (right).

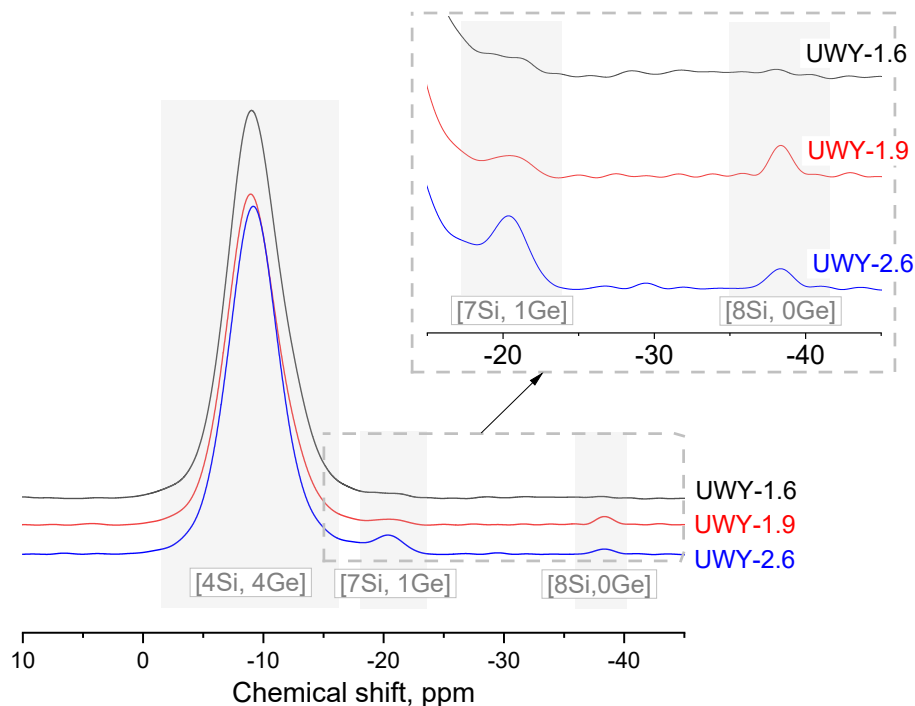


Figure S3 ^{19}F MAS NMR spectra of UWY materials with different chemical compositions. The observed signals correspond to the $D4R$ units with different chemical compositions, i.e., $[\text{nSi}, (8-\text{n})\text{Ge}]$. Prior to the measurement, the as-prepared UWY samples were treated with NH_4F to ensure occupancy of all $D4R$ units with fluoride ions.

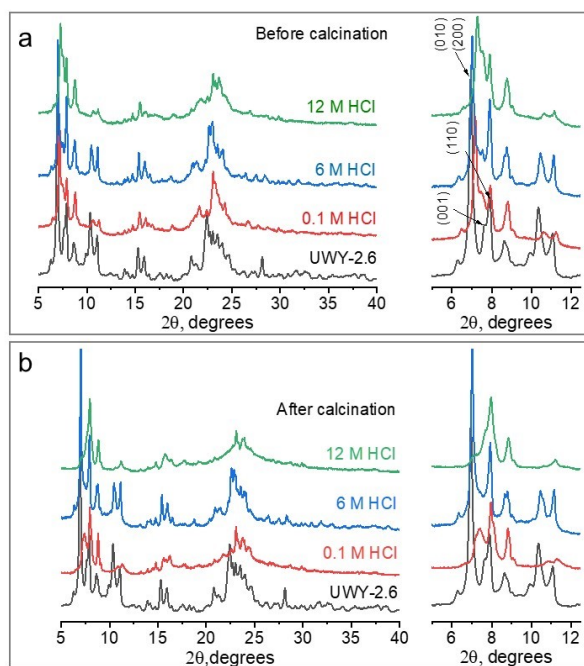


Figure S4. XRD patterns of OSDA-free UWY-2.6 samples treated with 0.1 – 12 M HCl at RT for 16 h (a) and subsequently calcined at 350 °C for 2 h (b). In each figure, the zoomed low-angle region is shown on the right.

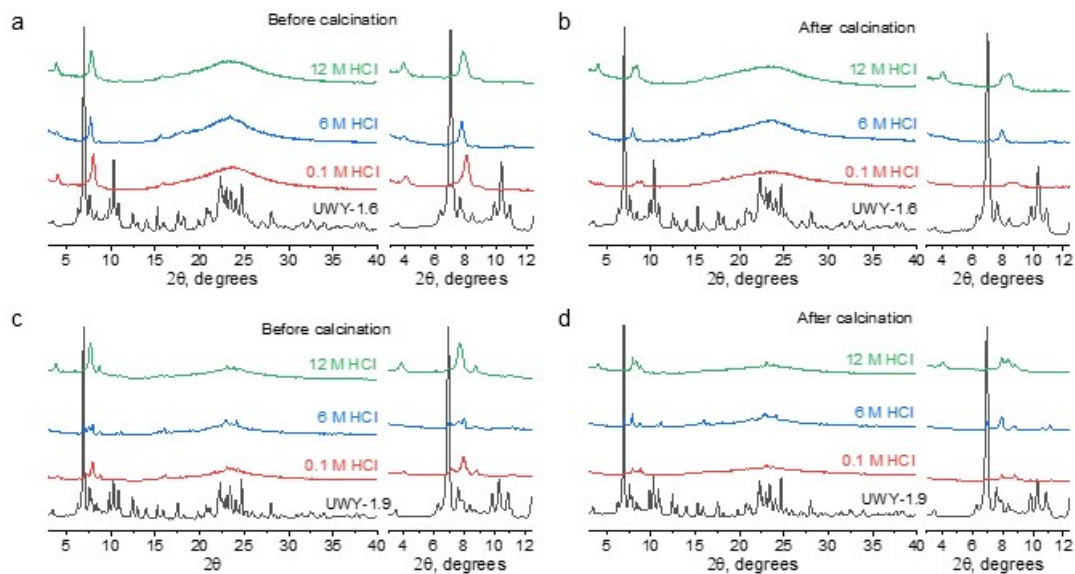


Figure S5 XRD patterns of OSDA-free UWY-1.6 (a-b) and UWY-1.9 (c-d) after the treatment with 0.1M (red), 6M (blue), or 12M (green) HCl at RT for 16 h and subsequently calcined at 350 °C for 2 h. In each figure, the zoomed low-angle region is shown on the right.

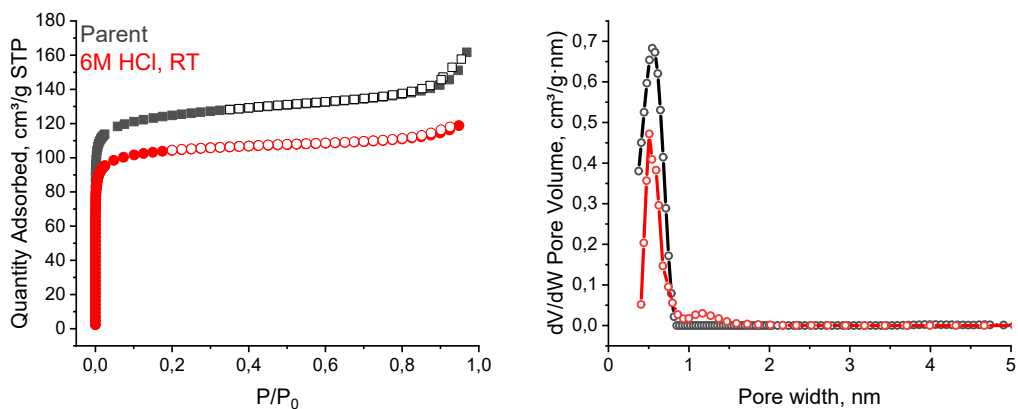
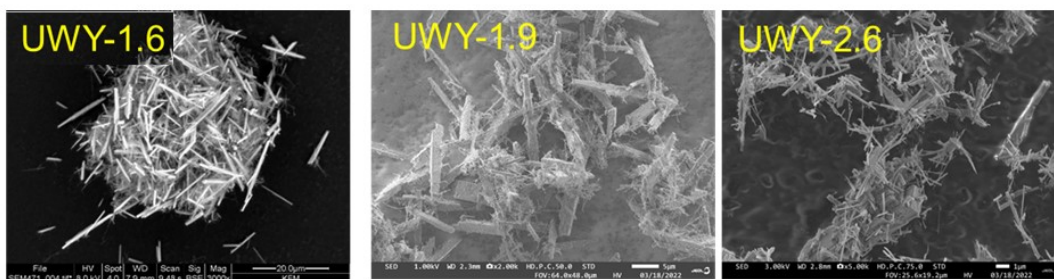
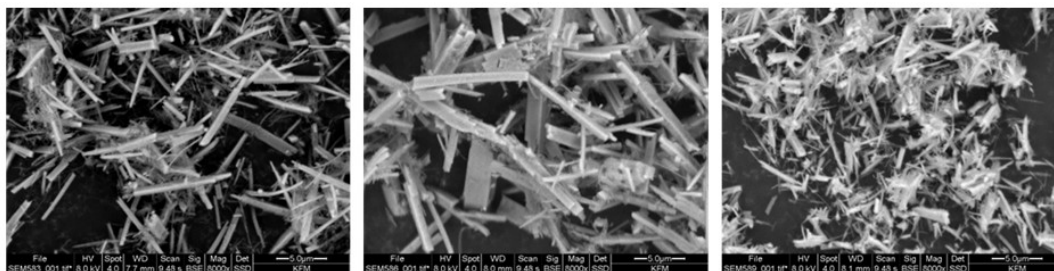


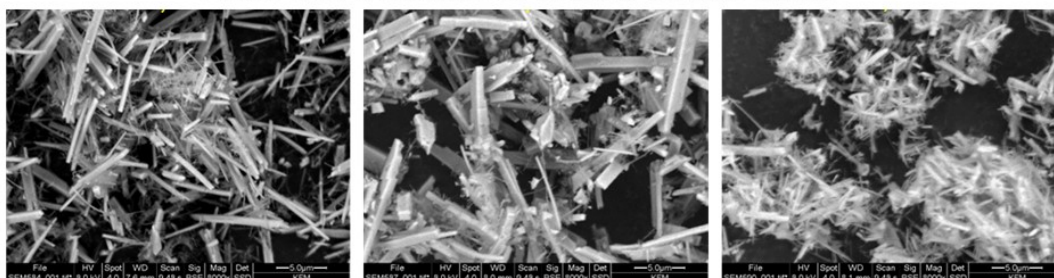
Figure S6 Ar adsorption/desorption isotherms (left) and respective pore size distributions (right) of the OSDA-free UWY-2.6 sample before (black) and after the treatment with 6M HCl at RT for 16 h and subsequently calcined at 350 °C for 2 h (red).



After the treatment with 0.1 M HCl at RT



After the treatment with 6 M HCl at RT



After the treatment with 12 M HCl at RT

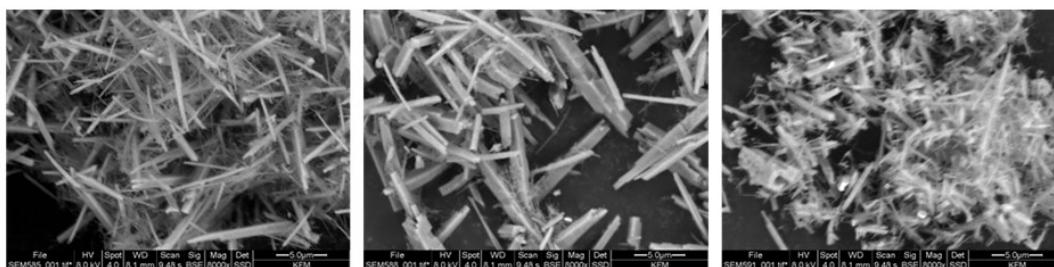


Figure S7 SEM images of OSDA-free UWY-1.6, UWY-1.9 and UWY-2.6 before and after the treatment with 0.1 – 12M HCl at RT for 16 h and subsequently calcined at 350 °C for 2 h.

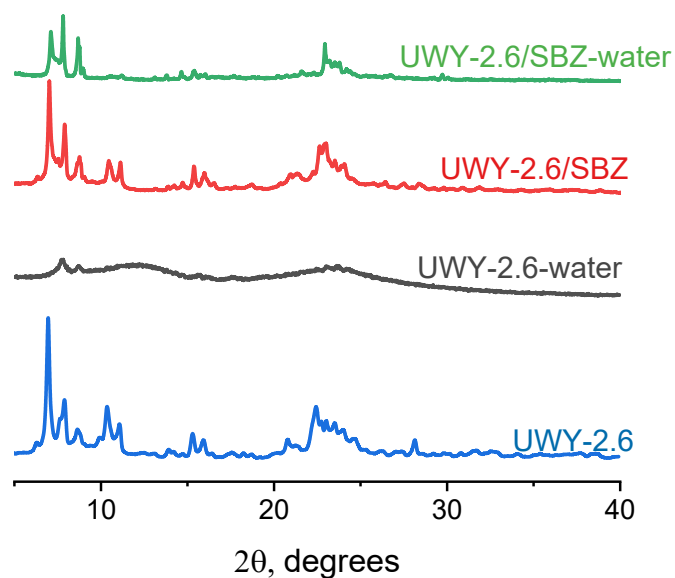


Figure S8. XRD pattern of UWY-2.6 zeolite (blue), UWY-2.6 stabilized in 6M HCl at RT for 20 h (UWY-2.6/SBZ, red), and respective samples treated with water at RT for 24 h (black and green).

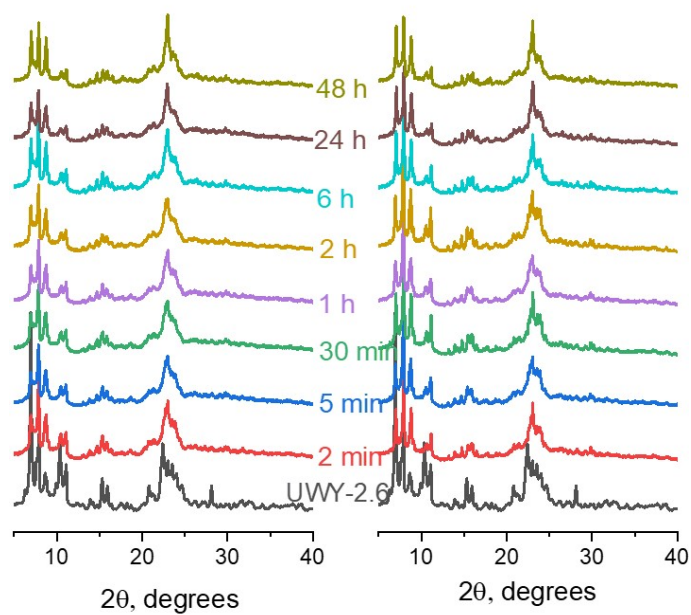


Figure S9 XRD patterns of OSDA-free UWY-2.6 samples treated with 6M HCl at RT for 2 min – 48 h (left) and subsequently calcined at 350 °C for 2 h (right).

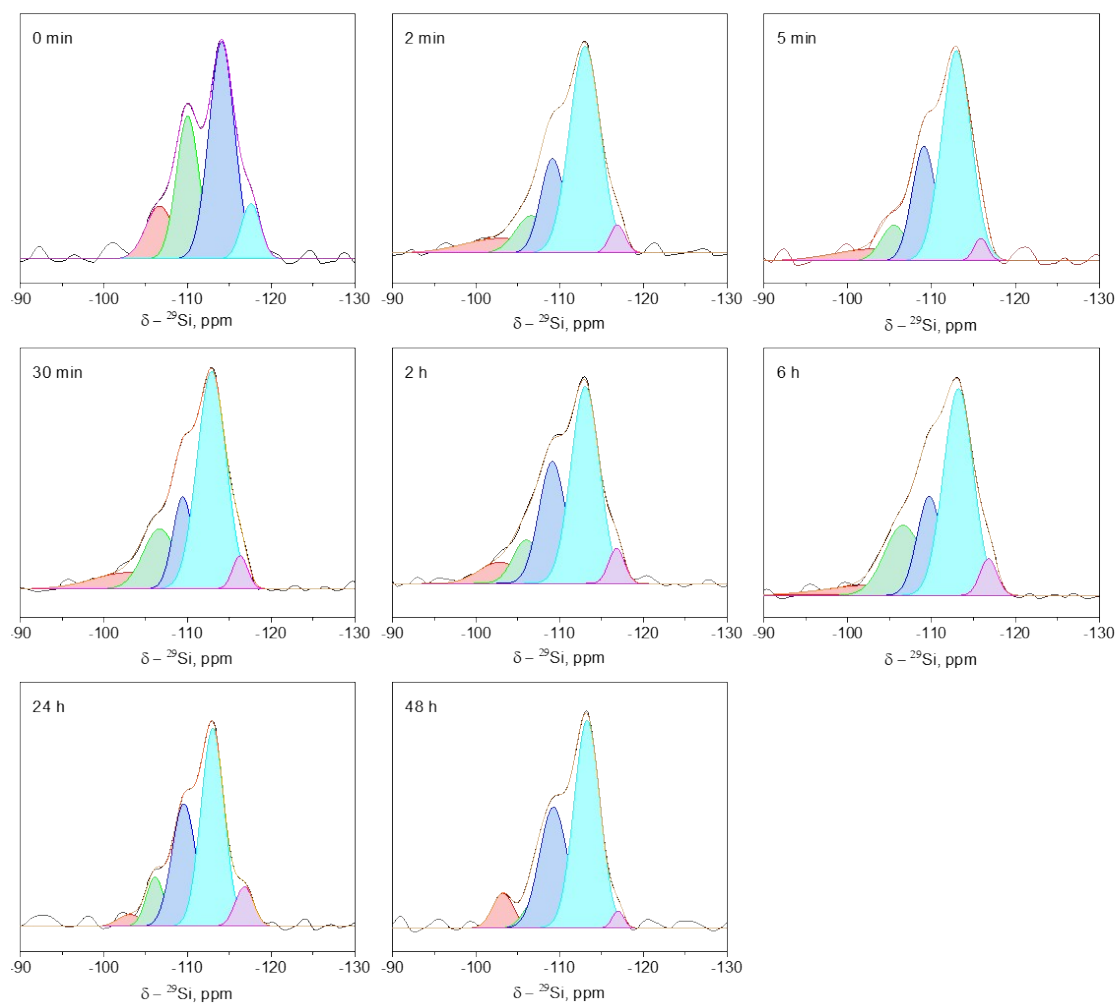


Figure S10. ^{29}Si MAS NMR spectra of the starting OSDA-free UWY-2.6 zeolite (0 min) and of OSDA-free UWY-2.6 samples treated with 6M HCl at RT for different times (2 min, 5 min, 30 min, 2 h 6 h, 24 h, and 48 h) and subsequently calcined at 350 °C for 2 h.

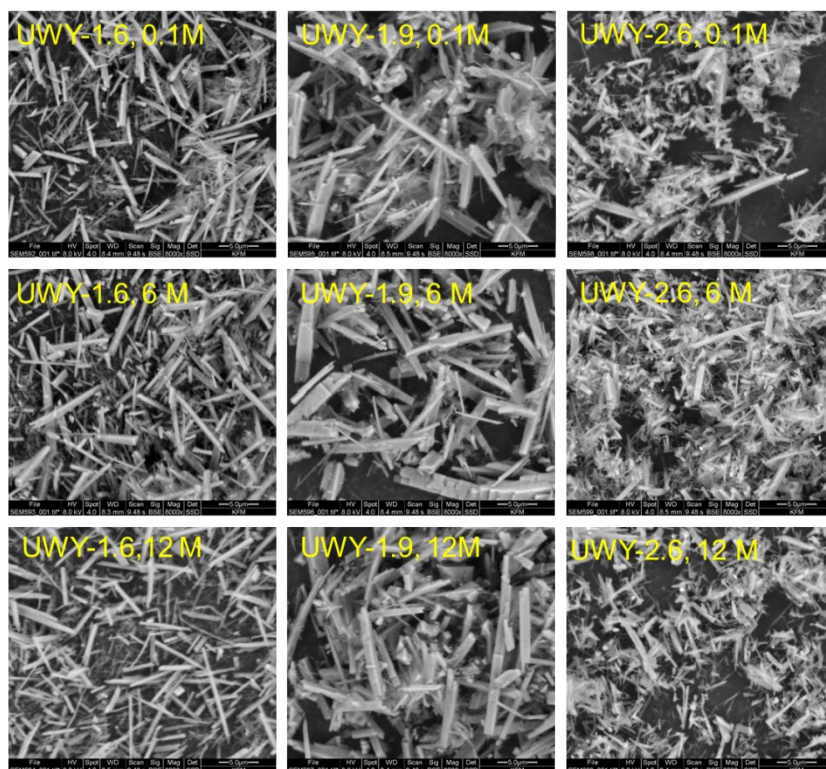


Figure S11. SEM images of OSDA-free UWY-1.6, UWY-1.9 and UWY-2.6 before and after the treatment with 0.1 – 12M HCl at 100 ° C for 16 h and subsequently calcined at 350 °C for 2 h

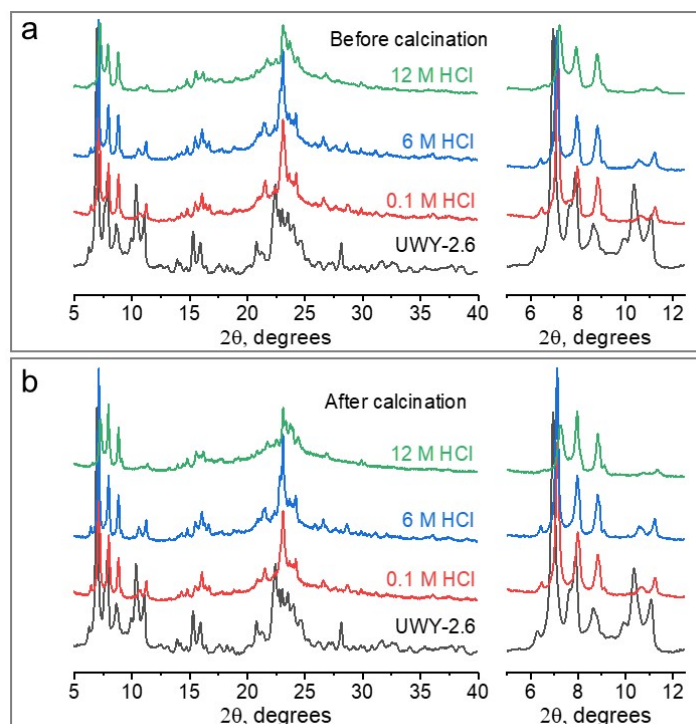


Figure S12. XRD patterns of OSDA-free UWY-2.6 samples treated with 0.1 – 12M HCl at 100 °C for 16 h (a) and subsequently calcined at 350 °C for 2 h (b). In each figure, the zoomed low-angle region is shown on the right.

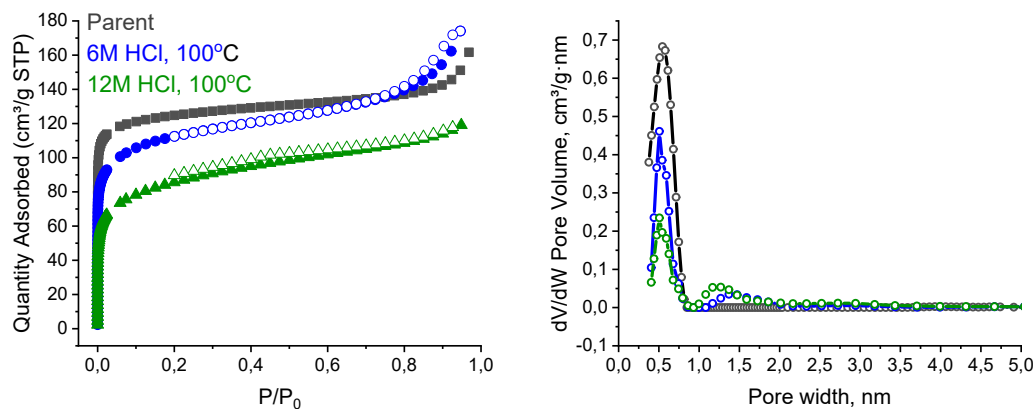


Figure S13. Ar adsorption/desorption isotherms (left) and respective pore size distributions (right) of the OSDA-free UWY-2.6 sample before (black) and after the treatment with 6M or 12M HCl at 100 °C for 16 h and subsequently calcined at 350 °C for 2 h (blue and green).

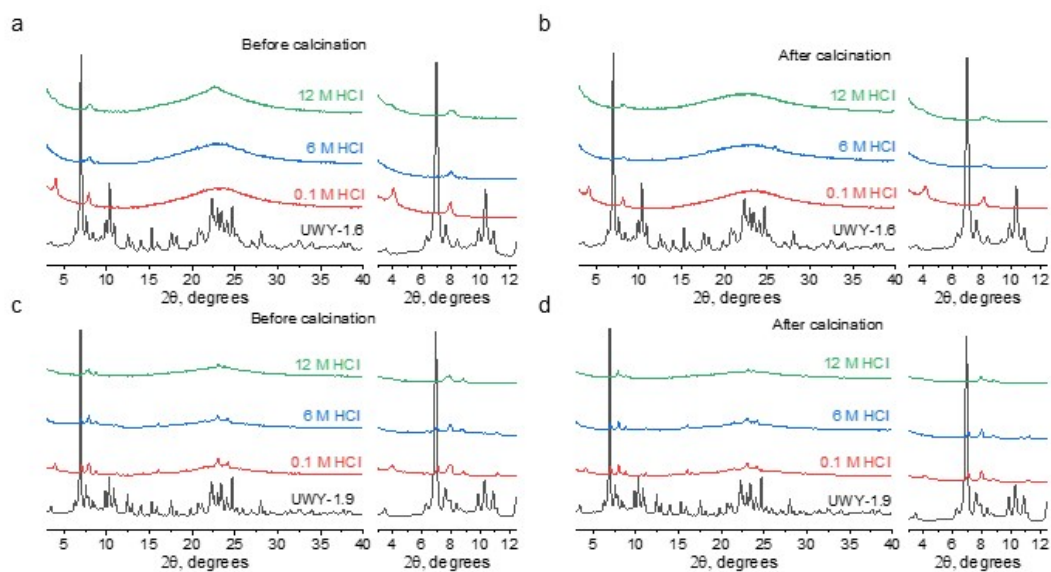


Figure S14. XRD patterns of OSDA-free UWY-1.6 (a-b) and UWY-1.9 (c-d) after the treatment with 0.1M (red), 6M (blue), or 12M (green) HCl at 100 °C for 16 h and subsequently calcined at 350 °C for 2 h. In each figure, the zoomed low-angle region is shown on the right.

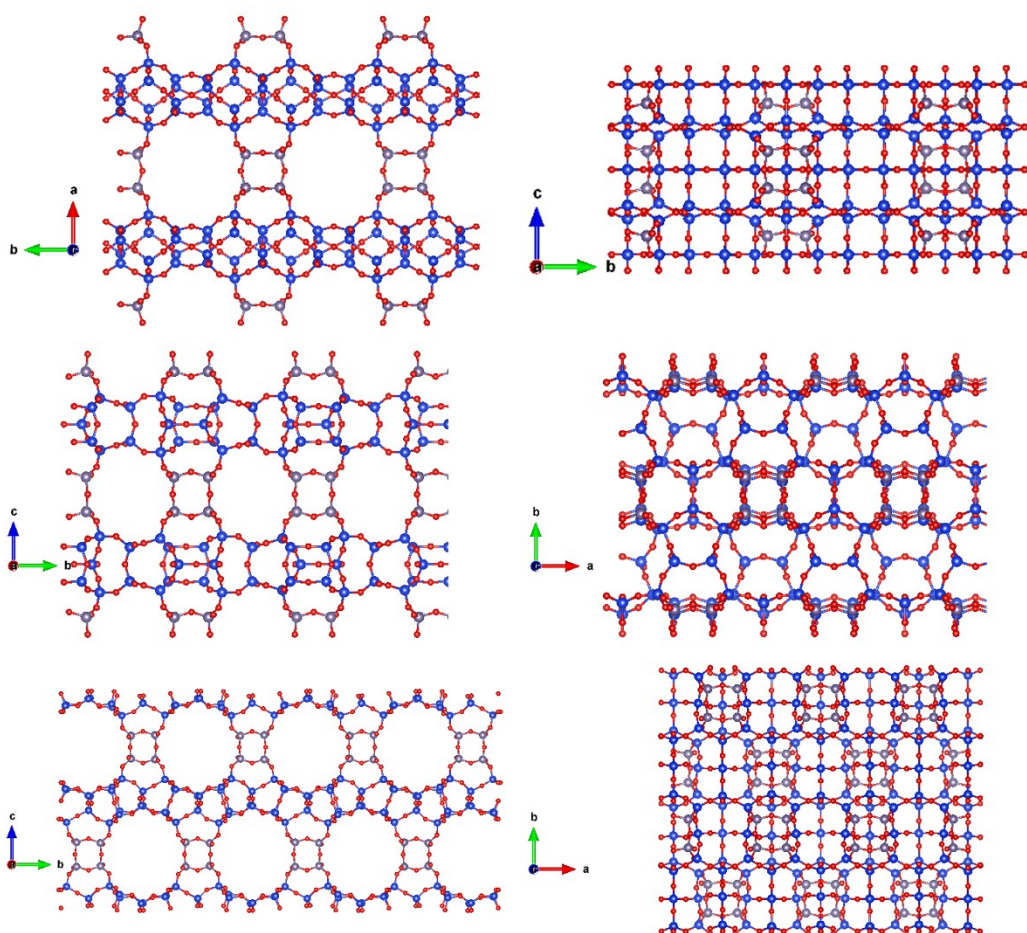


Figure S15. Crystal structures of IWV with intersecting 12x12-ring pore system (top), ITR with intersecting 10x10x9-ring pore system (middle) and *CTH with intersecting 14x10-ring pore system (bottom). Ge atoms are shown in grey; Si atoms are shown in blue; O atoms are shown in red. All zeolites are characterized by “planar” location of *D4R* units.

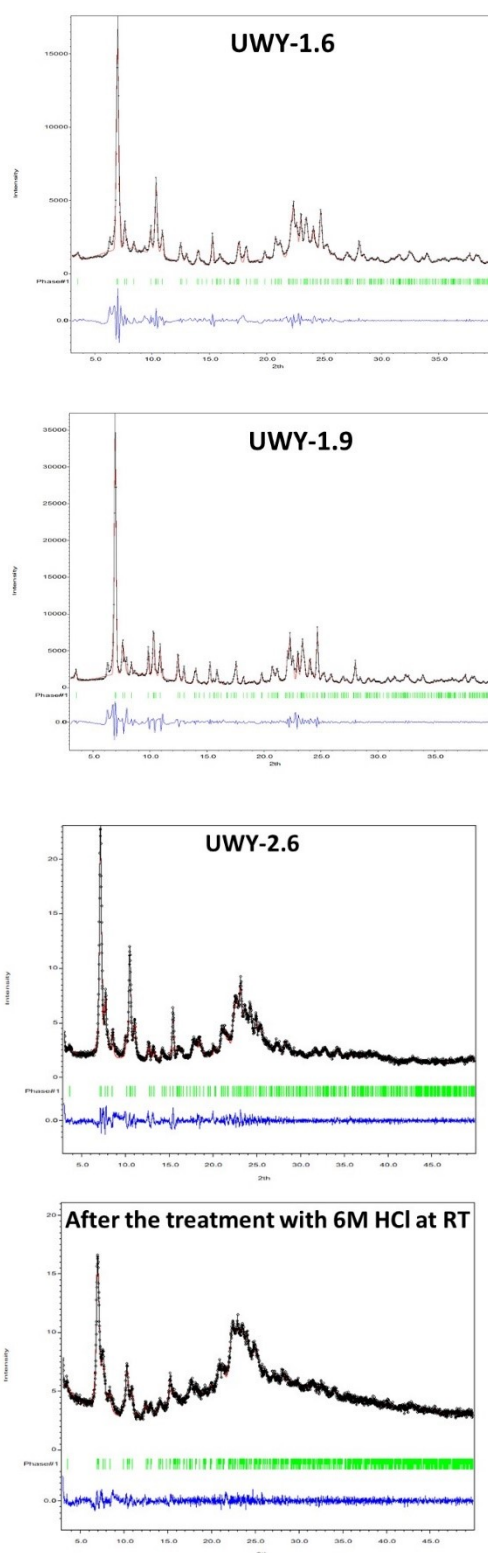


Figure S16. Le Bail fit of PXRD patterns of UWY-1.6, UWY-1.9, UWY-2.6 and UWY-2.6 zeolite after stabilization in 6M HCl at RT for 16 h based on published unit cells: experimental (black circles), calculated after the Le Bail refinement (red line), Bragg positions (green bars), and difference curve (blue line).

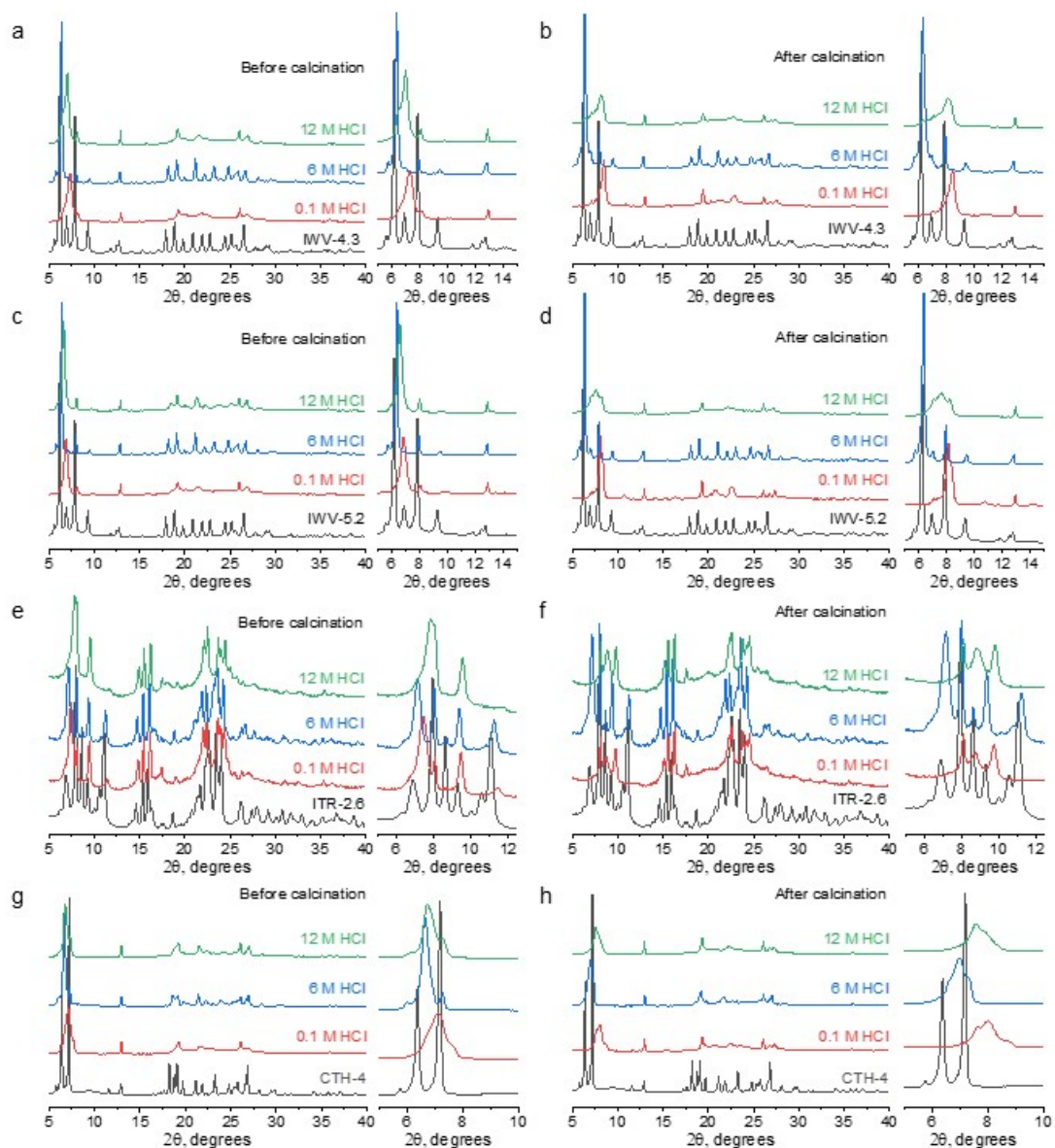


Figure S17. XRD patterns of OSDA-free IWW-4.3 (a-b), IWW-5.2 (c-d), ITR-2.6 (e-f), and CTH-4 (g-h) after the treatment with 0.1M (red), 6M (blue), or 12M (green) HCl at RT for 16 h and subsequently calcined at 350 °C for 2 h. In each figure, the zoomed low-angle region is shown on the right.

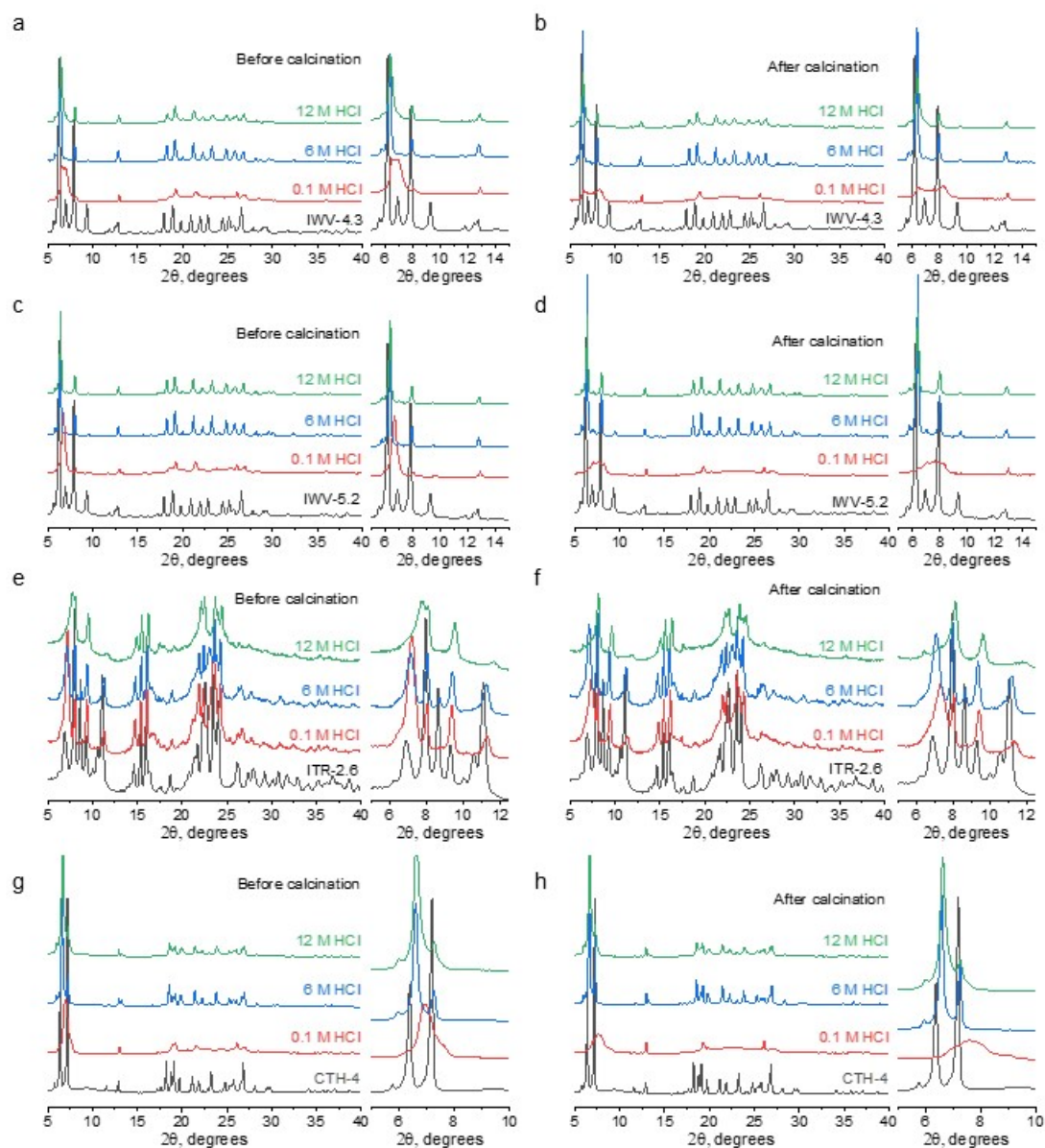


Figure S18. XRD patterns of OSDA-free IWV-4.3 (a-b), IWV-5.2 (c-d), ITR-2.6 (e-f), and CTH-4 (g-h) after the treatment with 0.1M (red), 6M (blue), or 12M (green) HCl at $100\text{ }^{\circ}\text{C}$ for 16 h and subsequently calcined at $350\text{ }^{\circ}\text{C}$ for 2 h. In each figure, the zoomed low-angle region is shown on the right.

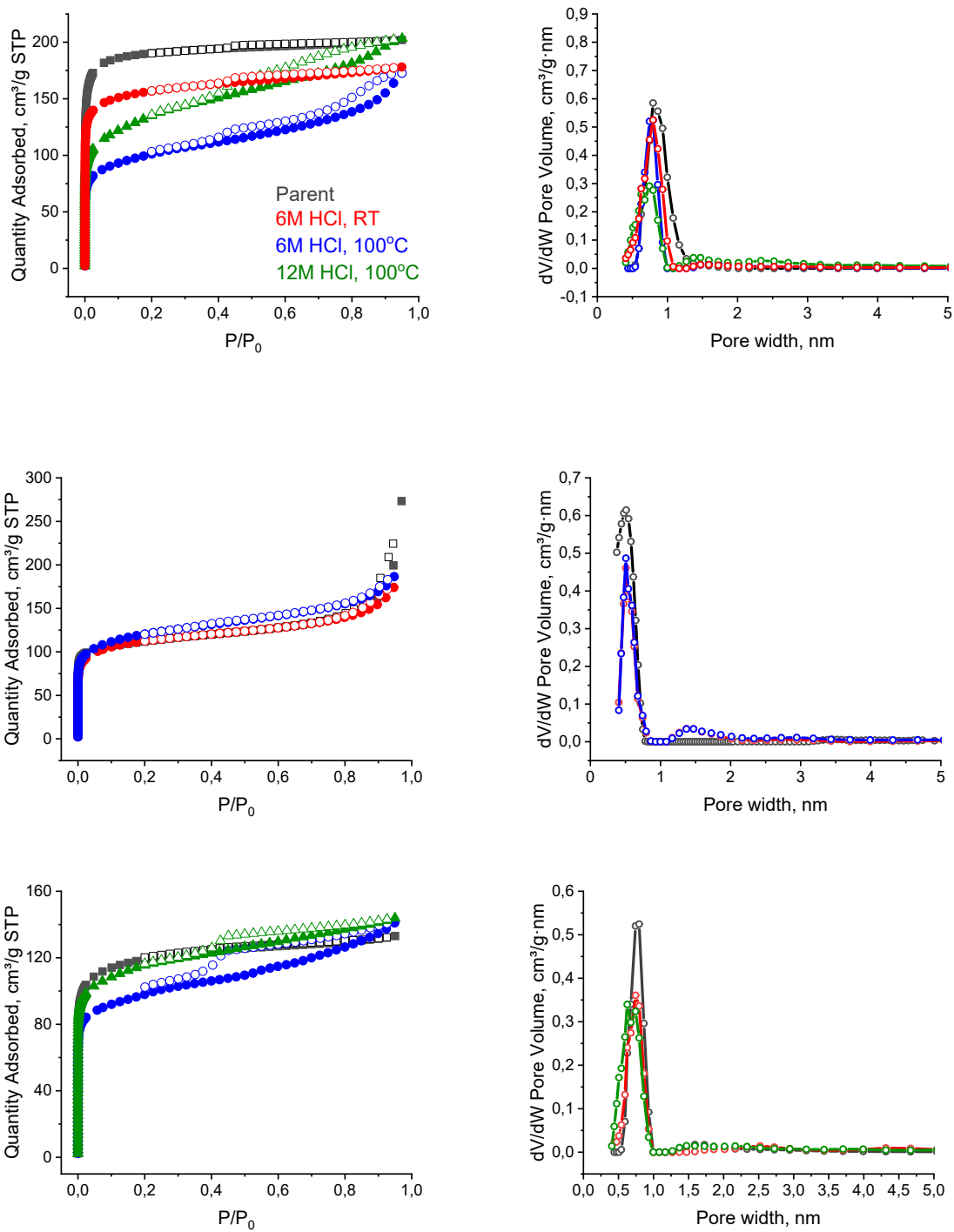


Figure S19. Ar adsorption/desorption isotherms (left) and respective pore size distributions (right) of the IYW-4.3 (up), ITR-2.6 (middle), and CTH-4 (bottom) samples before (black) and after the treatment with 6M HCl at RT for 16 h and subsequently calcined at 350 °C for 2 h (red), 6M HCl at 100 ° C for 16 h and subsequently calcined at 350 °C for 2 h (blue) or 12M HCl at 100 ° C for 16 h and subsequently calcined at 350 °C for 2 h (green).

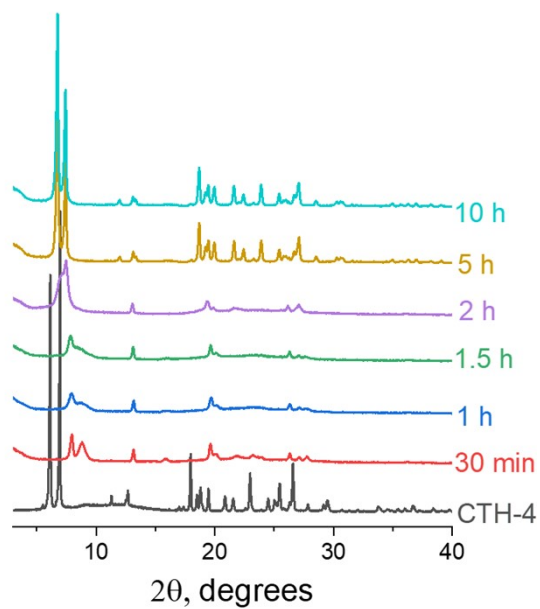


Figure S20. XRD patterns of CTH-4 zeolites treated with 6M HCl at 100 °C for 30 min – 10 h and subsequently calcined at 350 °C for 2 h.

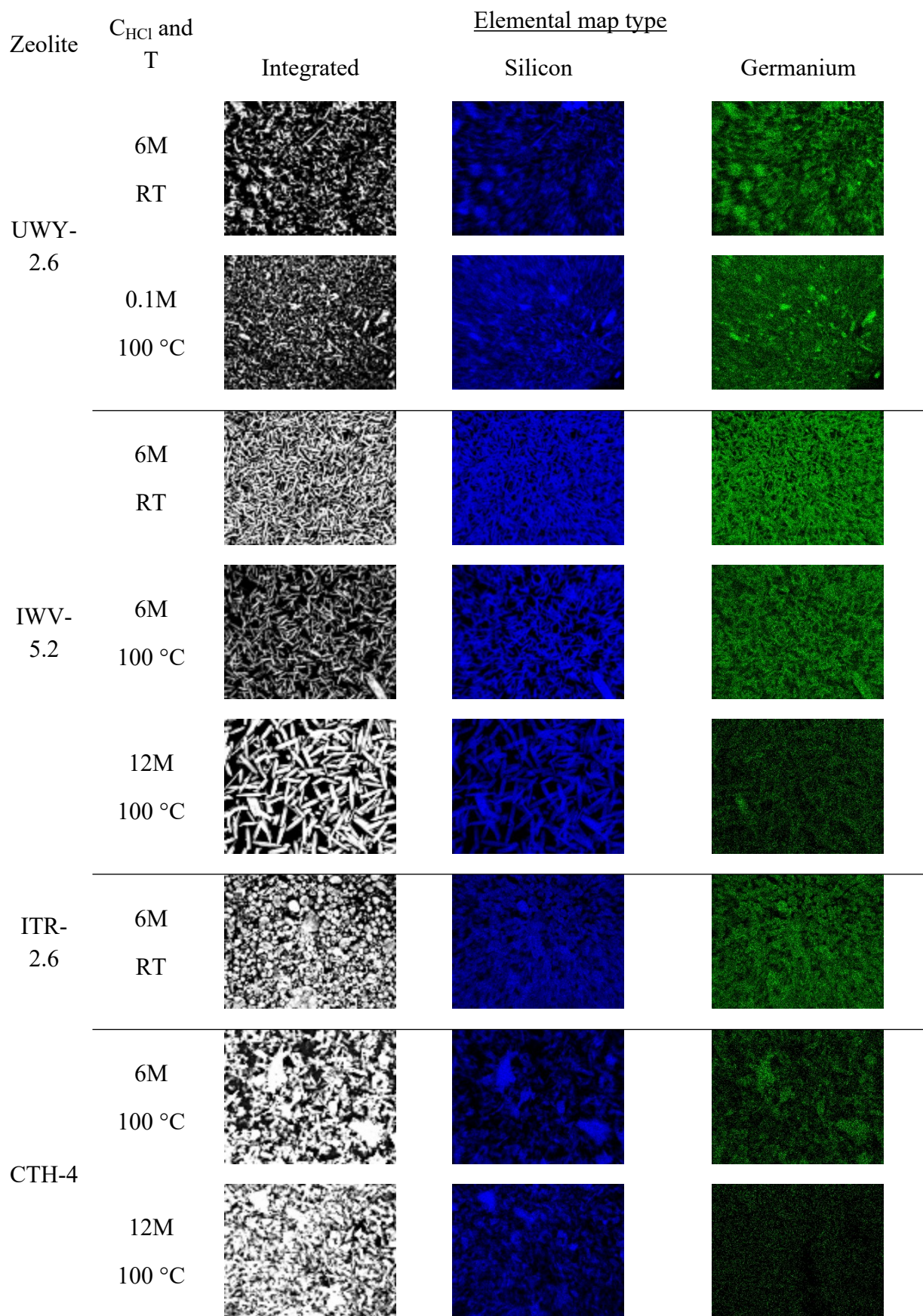


Figure S21. EDS maps (integrated image – black, Si – blue, Ge – green) for UWY-2.6, IYW-5.2, ITR-2.6, CTH-4 before and after stabilization under different conditions.

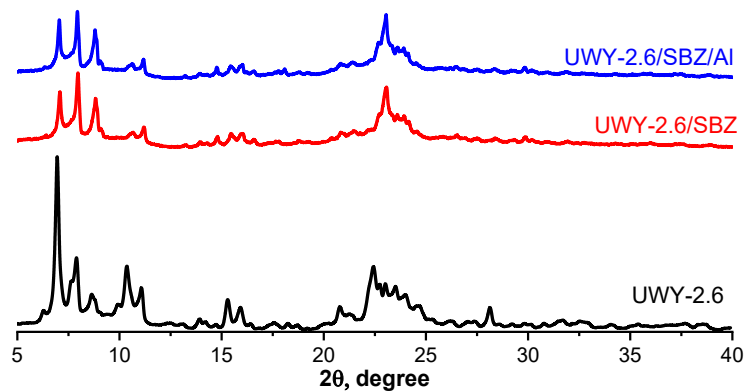


Figure S22. XRD patterns of UWY-2.6, UWY-2.6/SBZ and UWY-2.6/SBZ/Al zeolites.

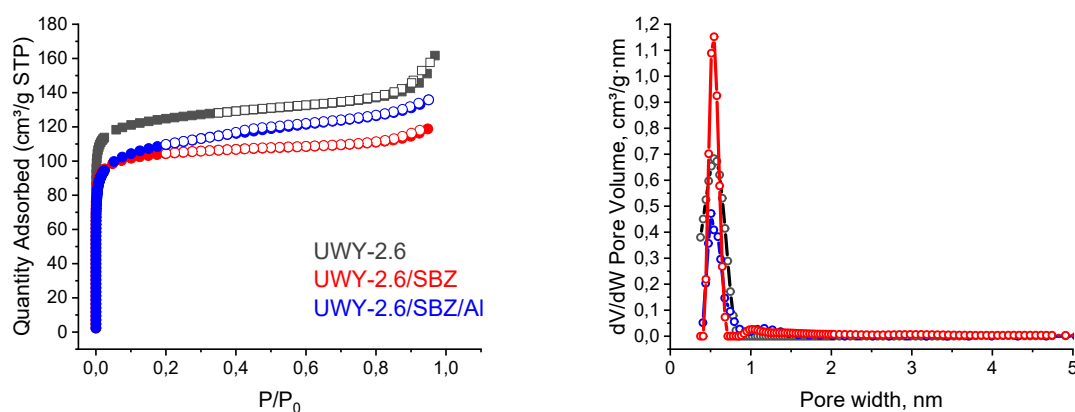


Figure S23. Ar adsorption/desorption isotherms (left) and respective pore size distributions (right) of UWY-2.6 (black) UWY-2.6/SBZ (red) and UWY-2.6/SBZ/Al (blue)

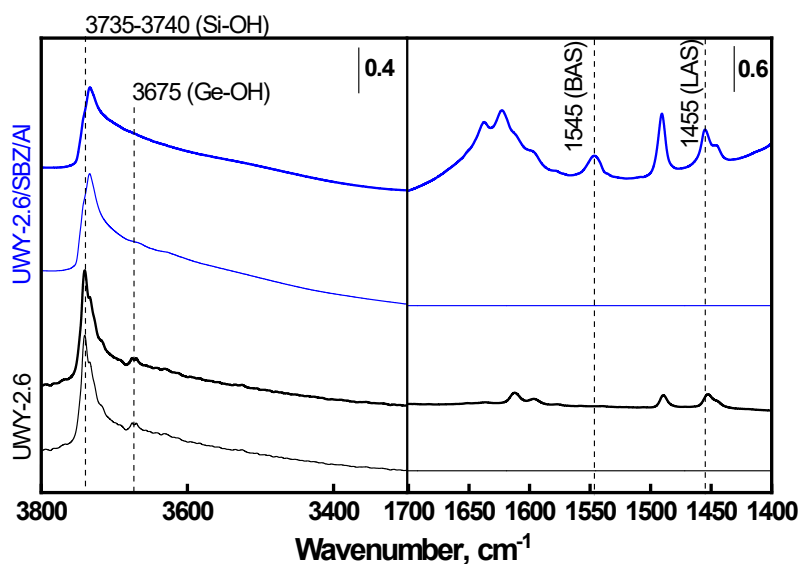


Figure S24. FTIR spectra of UWY-2.6 and UWY-2.6/SBZ/Al in the hydroxyl-group (left) and pyridine-ring vibration region (right) before (thin lines) and after (thick lines) pyridine adsorption.

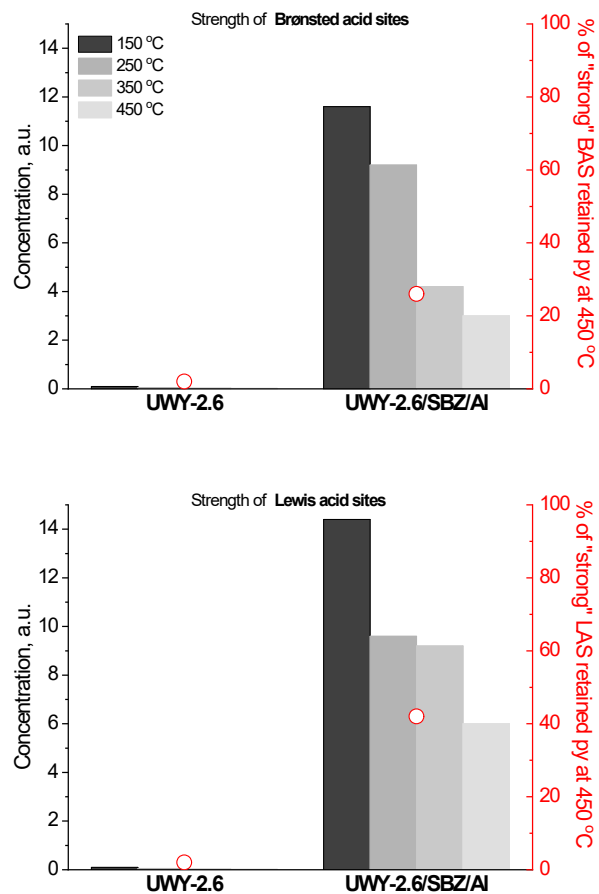


Figure S25. Absolute total concentrations (bars) and relative concentrations of strong acid centers (circles) for Bronsted acid sites (BAS) and Lewis acid sites (LAS), determined by thermodesorption of adsorbed pyridine monitored by FTIR spectroscopy.

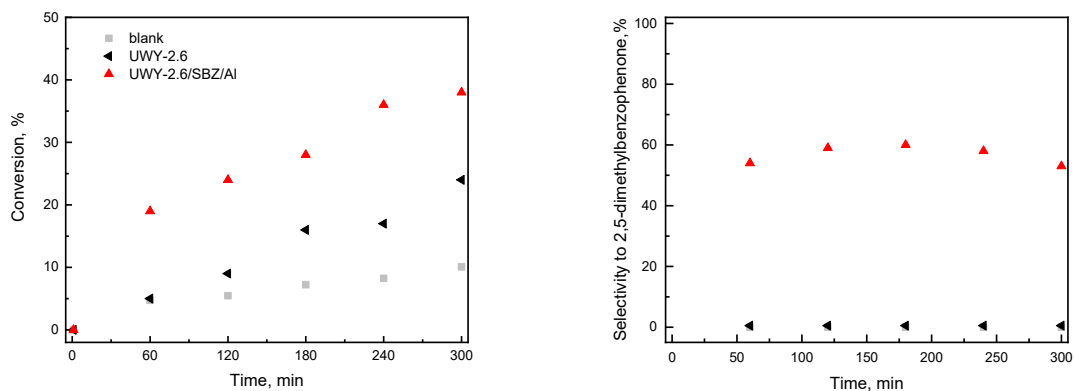
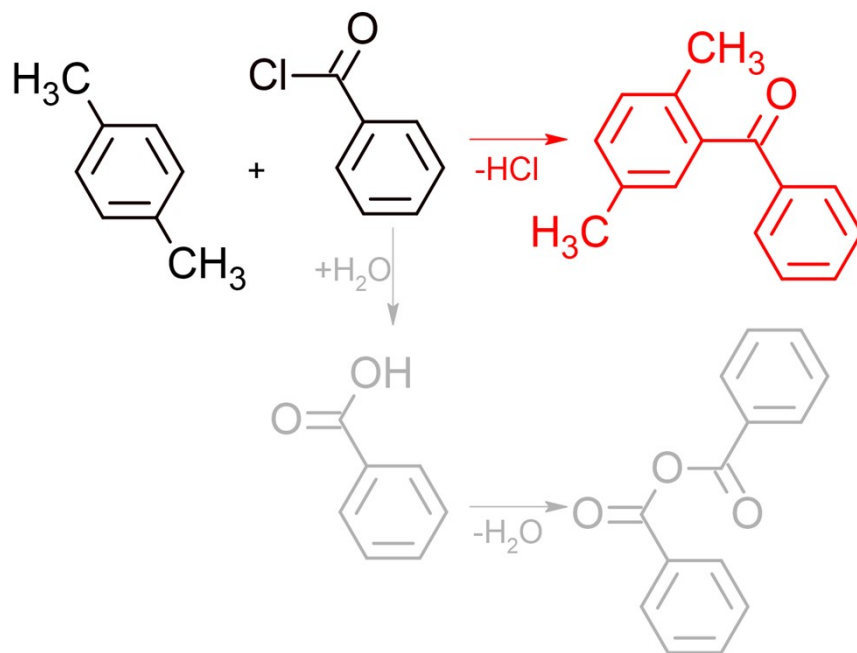


Figure S26. Zeolite-catalyzed benzoylation of p-xylene: targeted path shown in red and side-reaction of benzoyl chloride hydration/dehydration is shown in grey (top). Conversion of reactant (left) and selectivity to the targeted product over UWY-2.6 and UWY-2.6/SBZ/Al. Reaction conditions: 50 mg of zeolite catalyst, 5 mL of p-xylene as both solvent and reactant, 5 mmol of benzoyl chloride, 0.25 g of dodecane as internal standard, 130 °C, batch reactor.

Additional Tables

Table S1. Unit cell parameters derived from structureless Le Bail fitting of UWY zeolites

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
UWY-1.6	25.21(33)	12.702(54)	11.604(34)	90	90	90
UWY-1.9	25.169(48)	12.716(20)	11.590(04)	90	90	90
UWY-2.6	24.853(92)	12.681(49)	11.562(40)	90	90	90
UWY-2.6/SBZ	24.489(99)	12.602(90)	11.590(98)	90	90	90

Table S2. Chemical compositions and textural characteristics of germanosilicate zeolites before and after stabilization.

Samples	Treatment conditions			Characteristics			
	[HCl], M	Temperature, °C	Si/Ge	Crystallinity, %	S_{ext} , m^2g^{-1}	V_{micro} , cm^3g^{-1}	V_{meso} , cm^3g^{-1}
UWY-2.6		-	2.6	100	58	0.13	0.07
	6	RT	6.1	98	41 (48*)	0.12 (0.12*)	0.03 (0.05*)
	0.1		18.5	96	94	0.12	0.07
	6	100	26.8	99	105	0.11	0.11
	12		>150	85	122	0.06	0.09
IWV-4.3		-	4.3	100	60	0.22	0.04
	6	RT	10.7	100	89	0.16	0.06
	6	100	38.1	97	89	0.09	0.13
	12		>500	97	224	0.07	0.19
ITR-2.6		-	2.6	100	94	0.10	0.10
	6	RT	5.3	89	107	0.09	0.12
		100	17.8	85	130	0.10	0.15
CTH-4		-	4.0	100	78	0.12	0.05
	6	100	27.9	100	111	0.09	0.09
	12		>150	100	110	0.10	0.08

*-after incorporation of Al

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