Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Robust CON-type zeolite nanocatalyst in methanol-to-olefins reaction: downsizing, recrystallisation and defect-healing treatments toward prolonged lifetime

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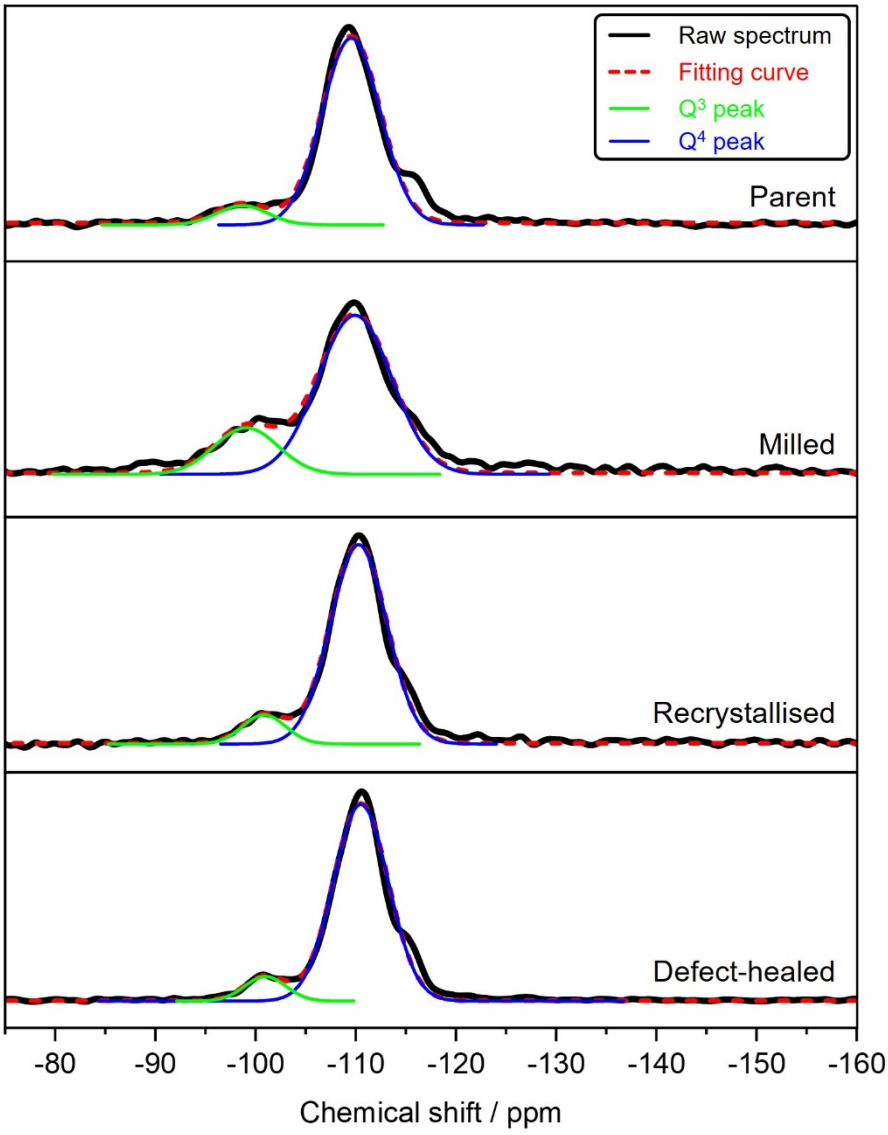

Figure S1. Peak deconvolutions for ^{29}Si DD MAS NMR spectra.

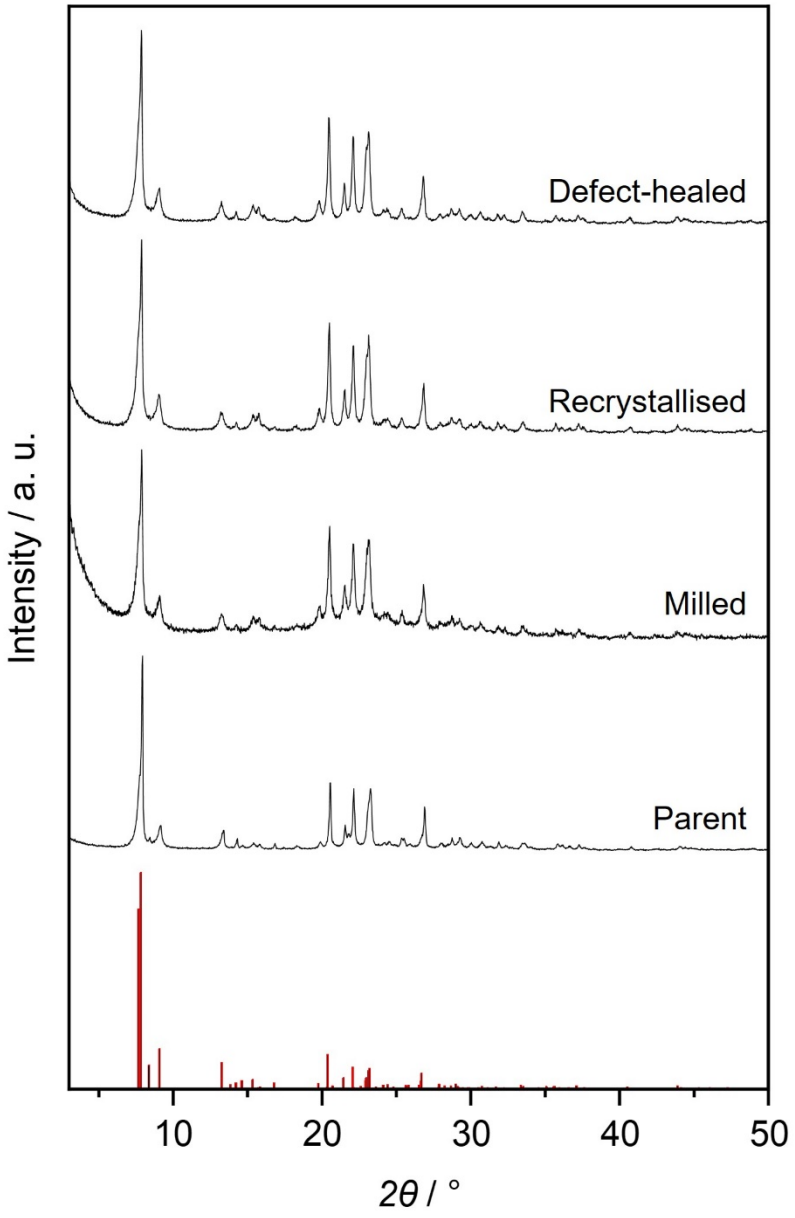

Figure S2. PXRD patterns of zeolite samples. Red bars represent pattern of CON-type zeolite.[1] In all PXRD patterns, the diffraction peak at $2\theta = 9.09^{\circ}$ can be observed. This indicates that these CON-type zeolite samples are the pure polymorph B, called as CIT-1. [2]

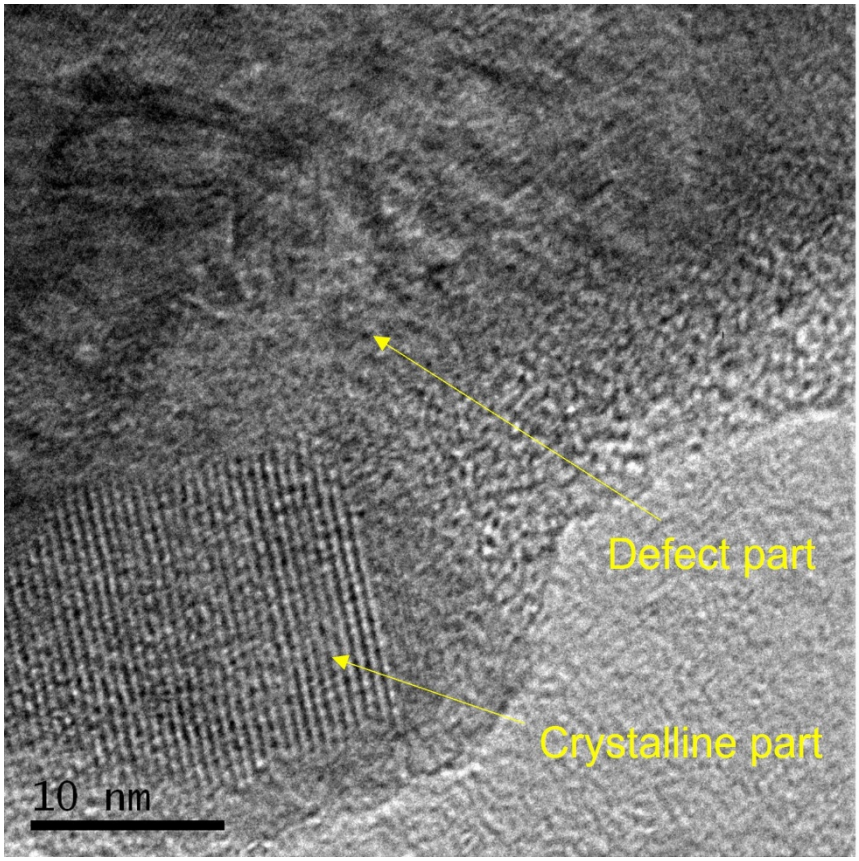

Figure S3. TEM image of the milled zeolite.

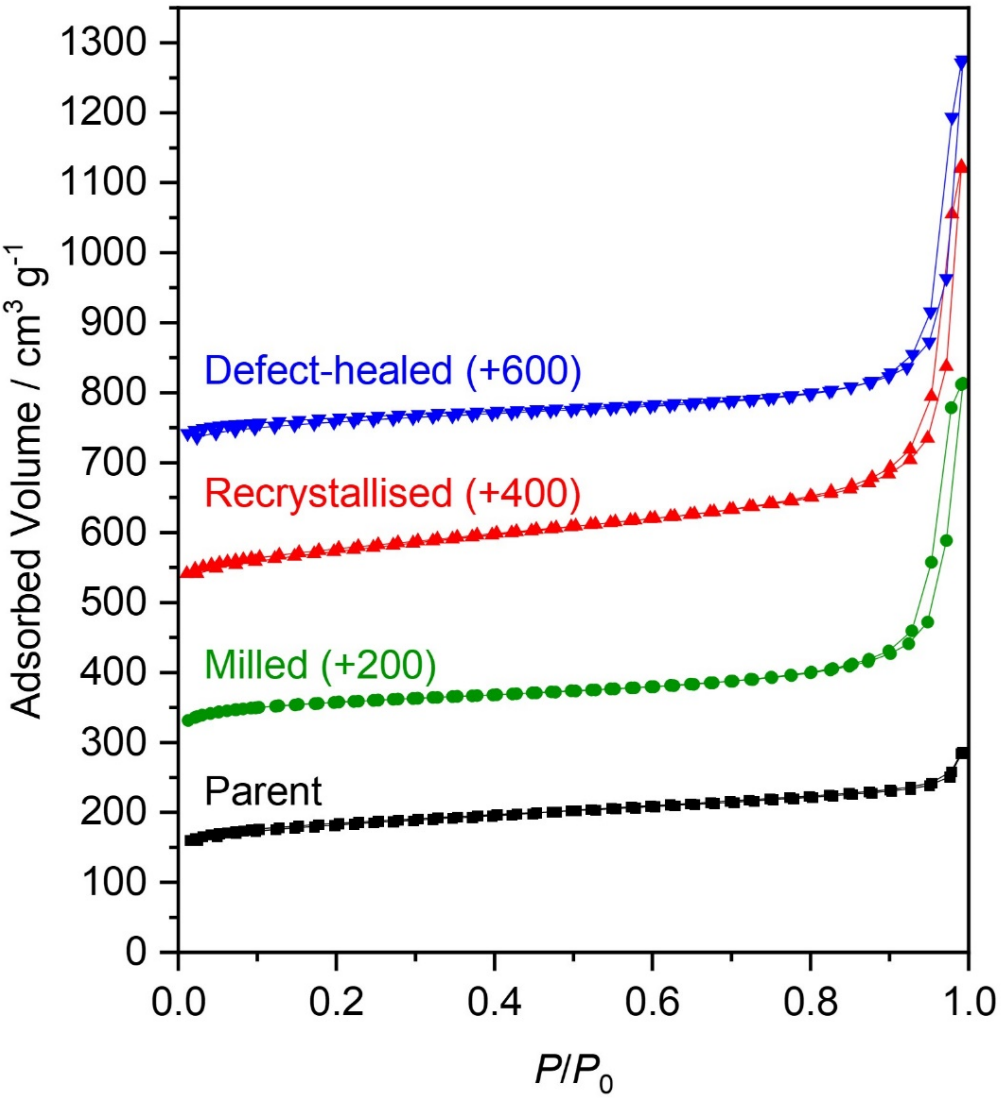

Figure S4. N_2 adsorption-desorption isotherms of zeolite samples.

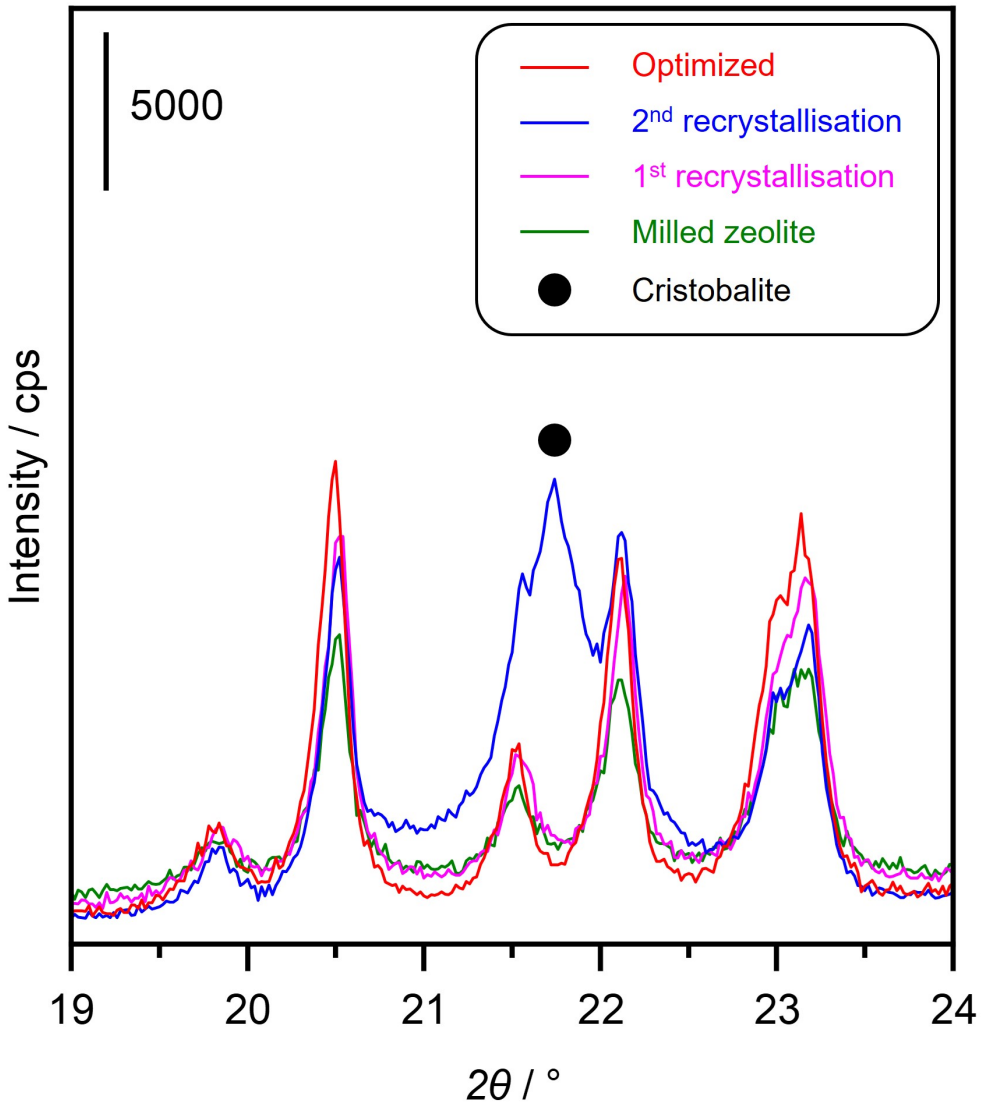

Figure S5. Enlarged view of PXRD patterns of zeolites samples in the range from 19° to 24°.

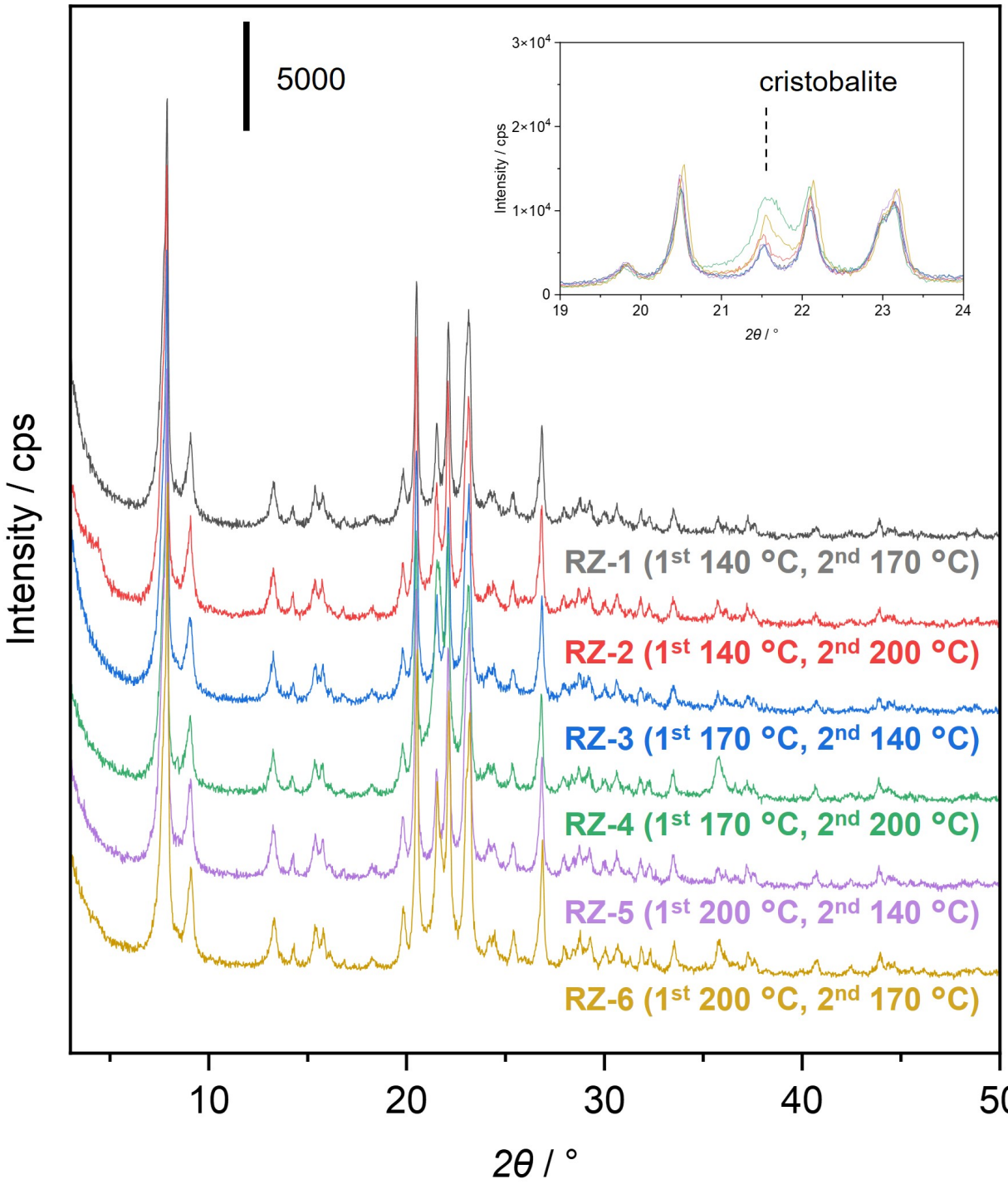

Figure S6. XRD patterns of recrystallised zeolites prepared at different temperatures. Inset shows an enlarged view ranging from 19 to 24°. In XRD pattern of RZ-2, small diffraction peak at 4.7° associated with layered silicate was observed as impurity. Furthermore, diffraction peaks at 21.6°, originating from cristobalite (shown in inset), were observed in RZ-2, RZ-4 and RZ-6.

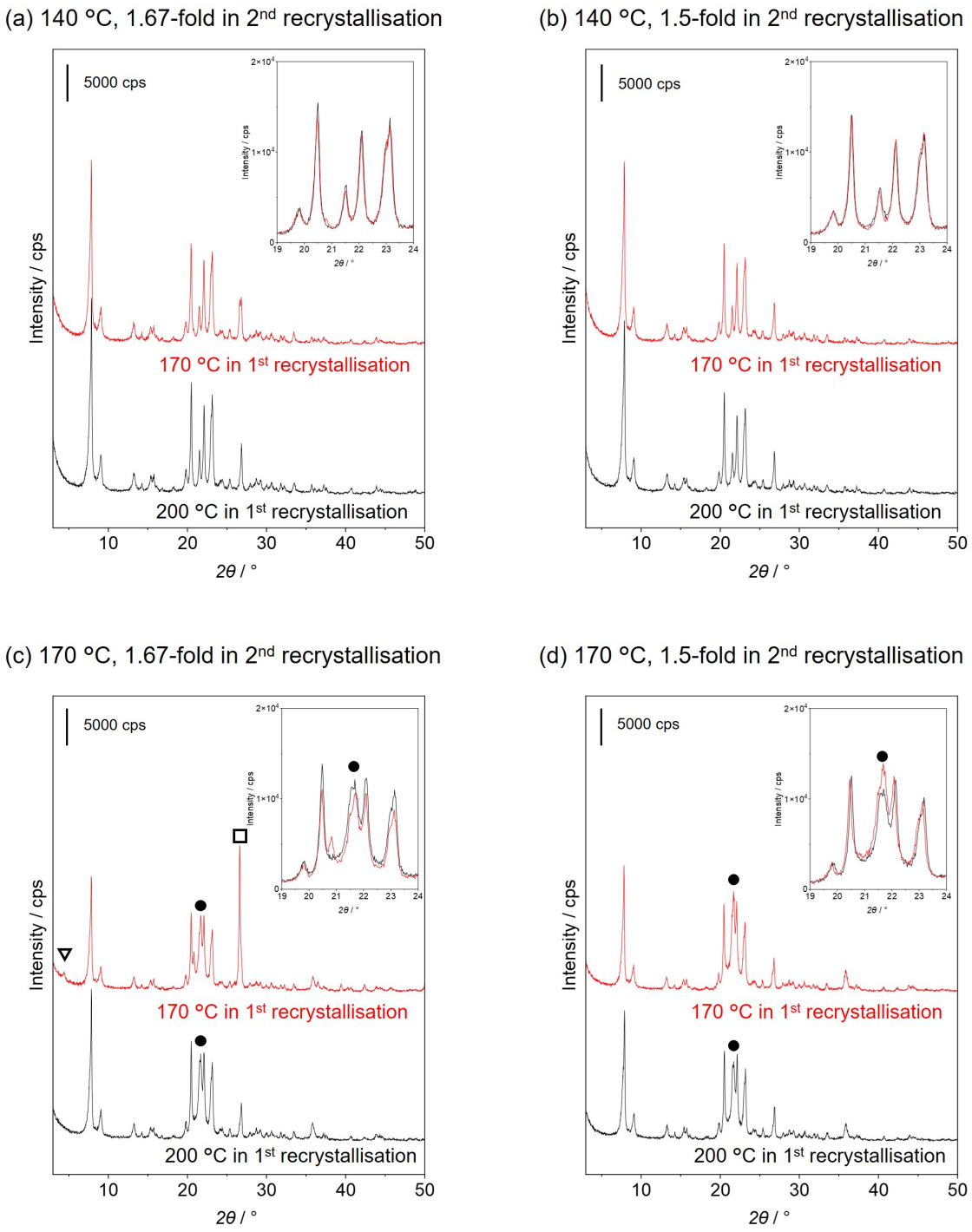

Figure S7. XRD patterns of zeolites obtained after second recrystallisation in highly concentrated mother liquors. □: Quartz, ●: Cristobalite, ▽: Layered silicate. Temperatures for second recrystallisation were set at (a-b) 140 or (c-d) 170 °C.

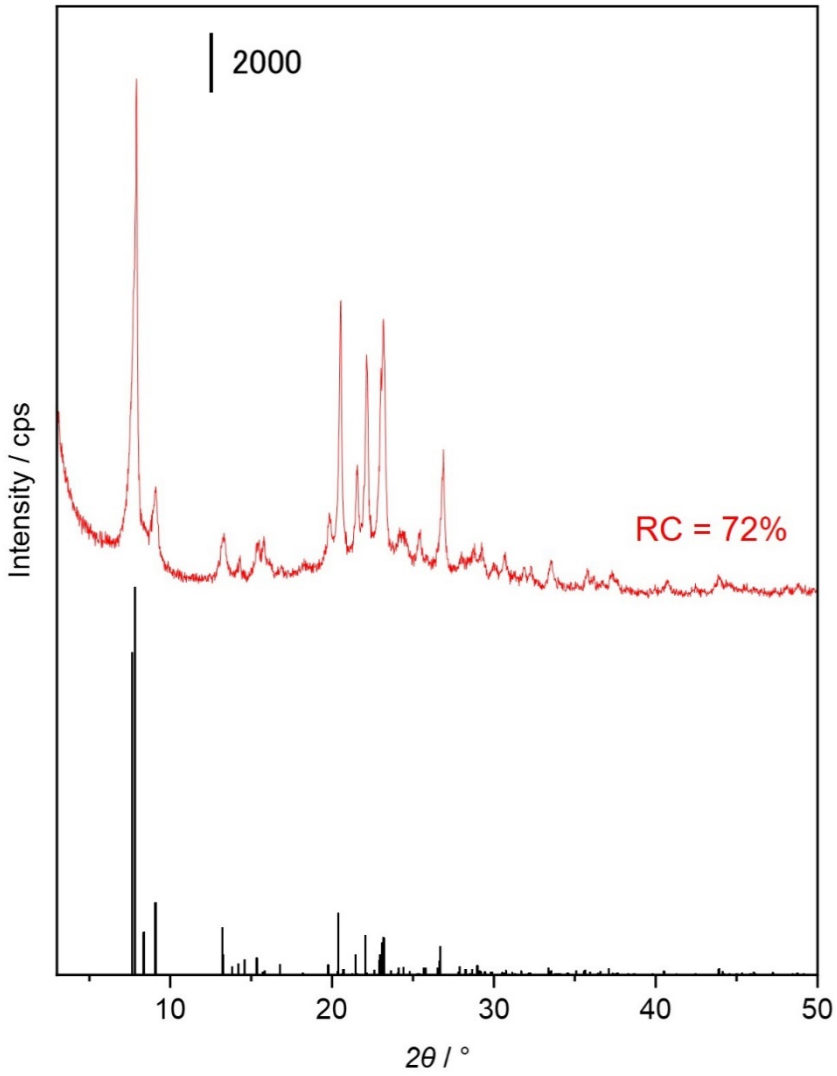

Figure S8. PXRD pattern of defect-healed zeolite prepared without two-step recrystallisation treatment.

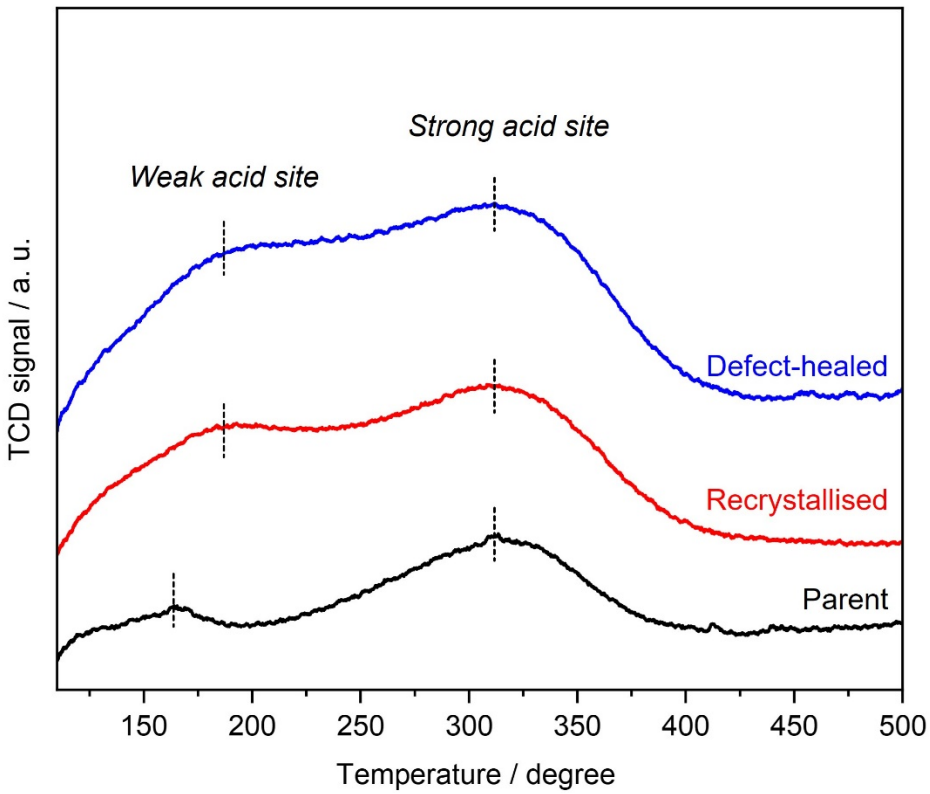

Figure S9. NH_3-TPD profiles for the parent, the recrystallised and the defect-healed zeolites. The amount of acid sites was determined by using the area of the *h*-peak in the profile. [3] All NH_3-TPD profiles showed two broad peaks, corresponding to NH_3 desorption from weak and strong acid sites. No peak shift of the desorption peak of the strong acid site (at 312 ºC) was observed, which indicates that three zeolite catalysts have similar acidic strength. The amount of the acid sites in the parent zeolite (0.049 mmol g^{-1}) was lower than those in the recrystallized (0.087 mmol g^{-1}) and in the defect-healed (0.095 mmol g^{-1}). The increases of acid sites in the recrystallized and the defect-healed zeolites were caused by desilication, confirmed by ICP-AES, through the two-step hydrothermal and NH_4F/TEAOH treatments.

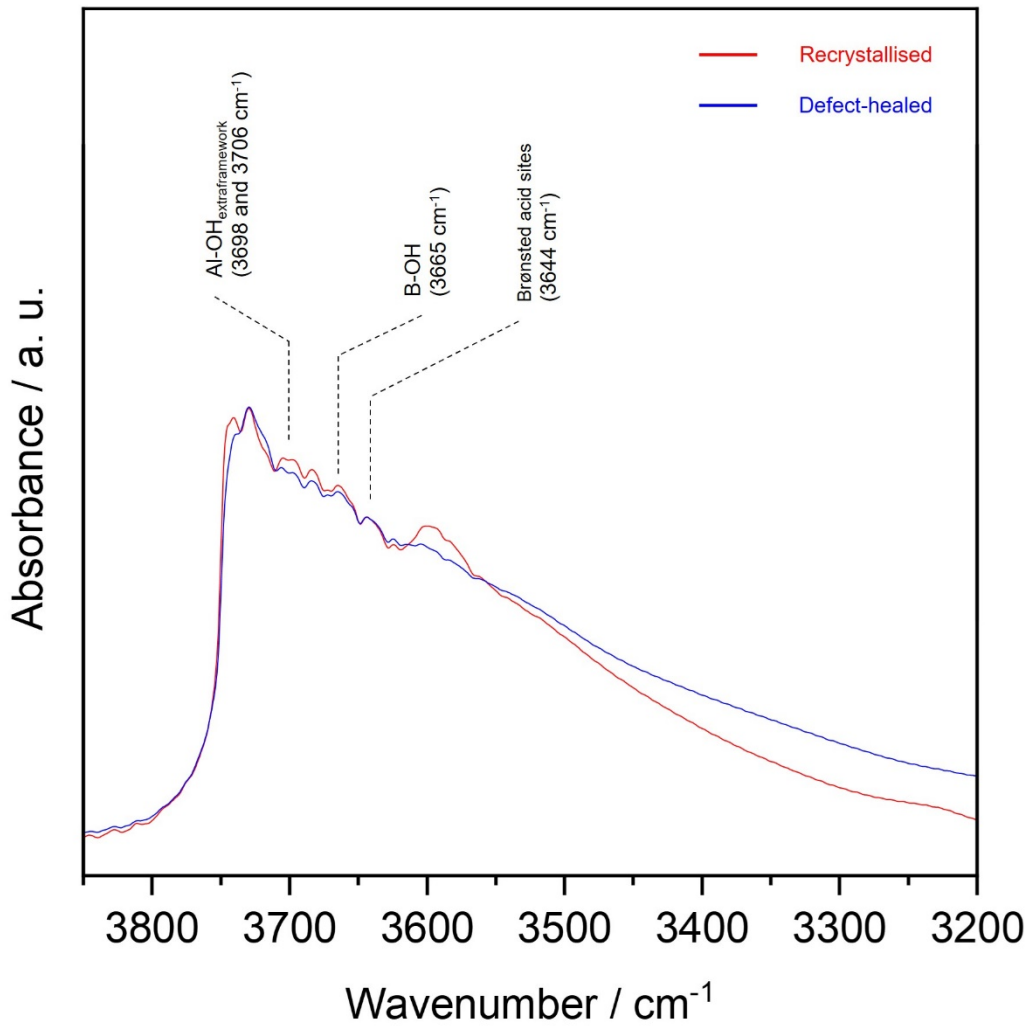

Figure S10. Peak assignment in region of 3710–3620 cm^{-1} in FT-IR spectra of recrystallised (red coloured) and defect-healed (blue coloured) zeolites. Both FT-IR spectra showed FT-IR bands at 3706, 3698, 3665, and 3644 cm^{-1}. Two peaks at 3706 and 3698 cm^{-1} originated from Al–OH in extra frameworks.[4] Other two peaks at 3665 and 3644 cm^{-1} were related to B–OH[5] and Brønsted acid sites,[6] respectively.

Table S1. Effects of temperatures for two-step hydrothermal treatment.

Sample ID	Recrystallisation Temperature [a] [°C]		Products [b]	Yield [wt%]	Relative Crystallinity [%]
	1st	2nd			
Milled zeolite	-	-	-	-	61
RZ-1	140	170	CON	65	54
RZ-2	140	200	CON + impurities	74	71
RZ-3	170	140	CON	80	83
RZ-4	170	200	CON + impurities	62	63
RZ-5	200	140	CON	75	89
RZ-6	200	170	CON + impurities	84	74

[a] performed for 20 h in first and second recrystallisations; and the fabricated supernatant was used. [b] analysed by PXRD.

Table S2. Optimisation of concentration of mother liquors and temperatures for two-step hydrothermal treatment.

1st Recrystallisation [a]		2nd Recrystallisation [b]		Products [c]	Yield [wt%]	Relative Crystallinity [%]
Temp. [°C]	Supernatant	Temp. [°C]	Supernatant			
170	1.25	140	1.67	CON	71	97 (Optimized)
200	1.25	140	1.5	CON	65	103
170	1.25	140	1.67	CON	65	85
200	1.25	140	1.5	CON	63	91
170	1.25	170	1.67	CON + impurities	60	65
200	1.25	170	1.5	CON + impurities	84	65
170	1.25	170	1.67	CON + impurities	59	68
200	1.25	170	1.5	CON + impurities	88	68

[a] performed for 16 h. [b] performed for 20 h. [c] analysed by PXRD.

References

[1] http://www.iza-structure.org/ (15/06/2021)

[2] R. F. Lobo, M. E. Davis, *J. Am, Chem. Soc.*, 1995, **177**, 3766-3779.

[3] M. Niwa, N. Katada, *Catal. Surv. Jpn.*, 1997, **1**, 215-226.

[4] P. Sazama, B. Wichterlova, J. Dedecek, Z. Tvaruzkova, Z. Musilova, L. Palumbo, S. Sklenak, O. Gonsiorova, *Microporous Mesoporous Mater.*, 2011, **143**, 87-96.

[5] S. Park, G. Sato, H. Onozuka, S. Tsutsuminai, M. Koike, K Kuroda, H. Gies, J. N. Kondo, T. Yokoi, *Catal. Sci. Technol.*, 2020, **10**, 4293-4304.

[6] M. S. Holm, S. Svelle, F. Joensen, P. Beato, C. H. Christensen, S. Bordiga, M. Bjørgen, *Appl. Catal. A*, 2009, **356**, 23-30.