

**Di- and trioxacyclohexane as structure directing molecules in the synthesis of
zeolites omega and ECR-1**

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Supplementary information

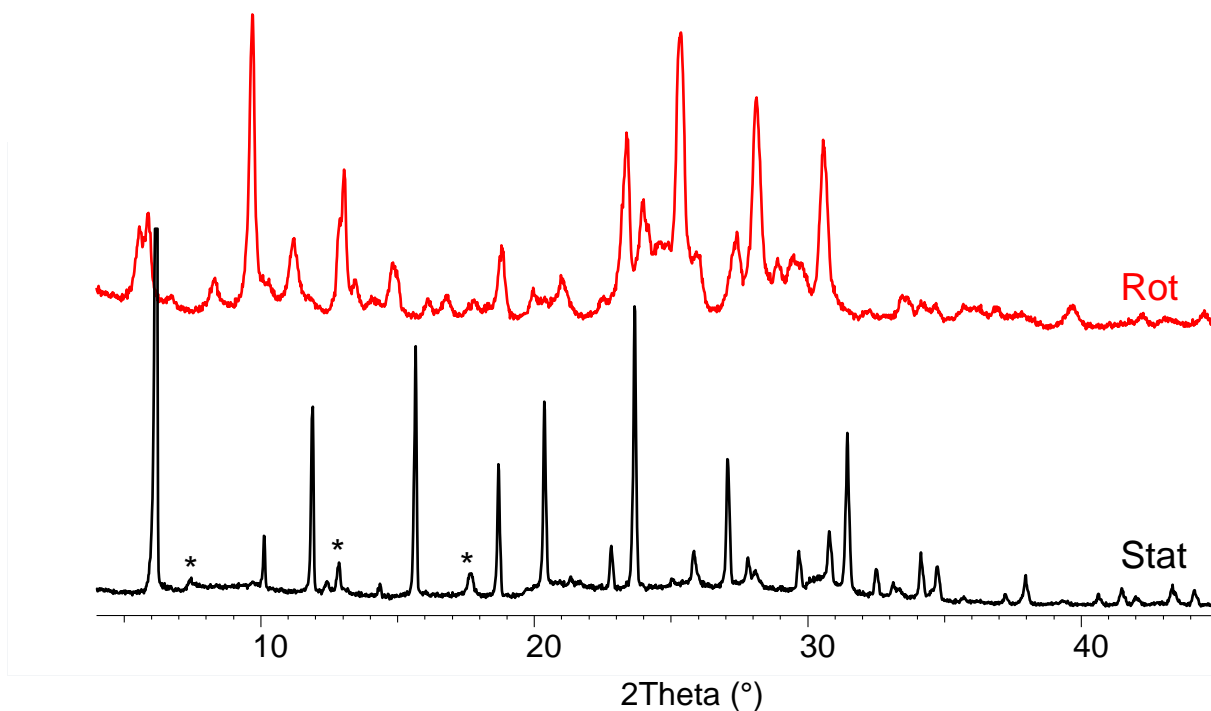


Fig. S1 XRD patterns of solids obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 2.2 \text{ Na}_2\text{O} - 0.5 \text{ trioxane} - 0.5 \text{ 15-crown-5} - 140 \text{ H}_2\text{O}$ at 115°C for 7 days under static (Stat) and dynamic (Rot) conditions. Asterisks indicate reflections characteristic of the **GME** topology.

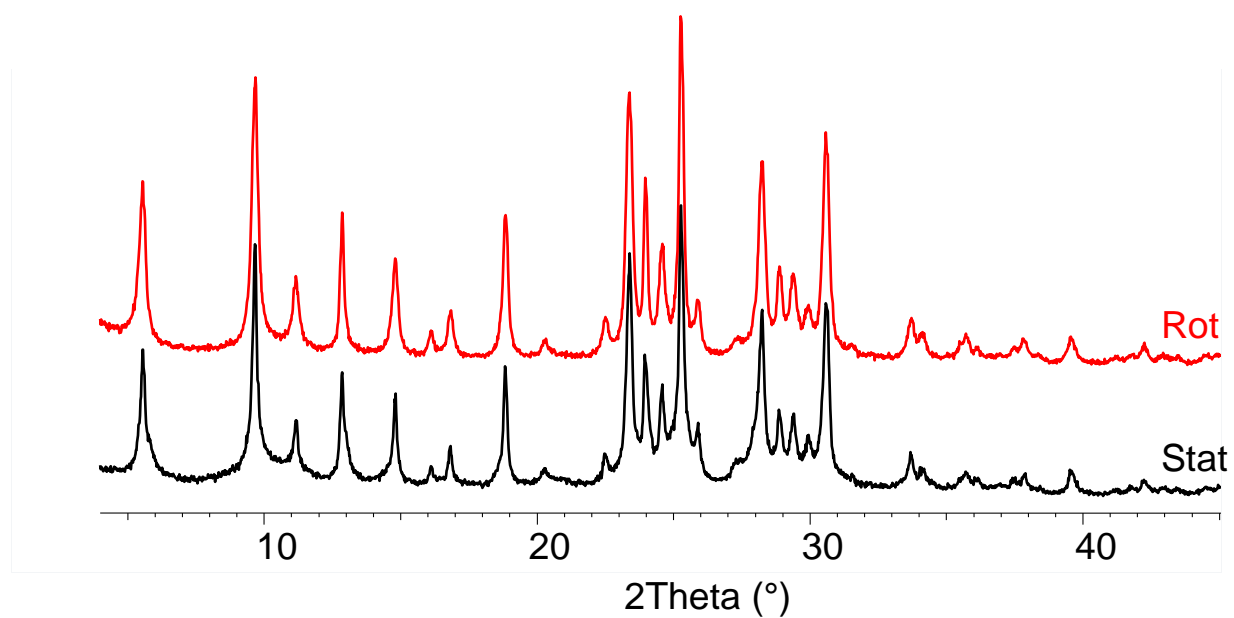


Fig. S2 XRD patterns of solids obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 2.2 \text{ Na}_2\text{O} - 7.5 \text{ trioxane} - 0.5 \text{ 15-crown-5} - 140 \text{ H}_2\text{O}$ at 115°C for 7 days under static (Stat) and dynamic (Rot) conditions.

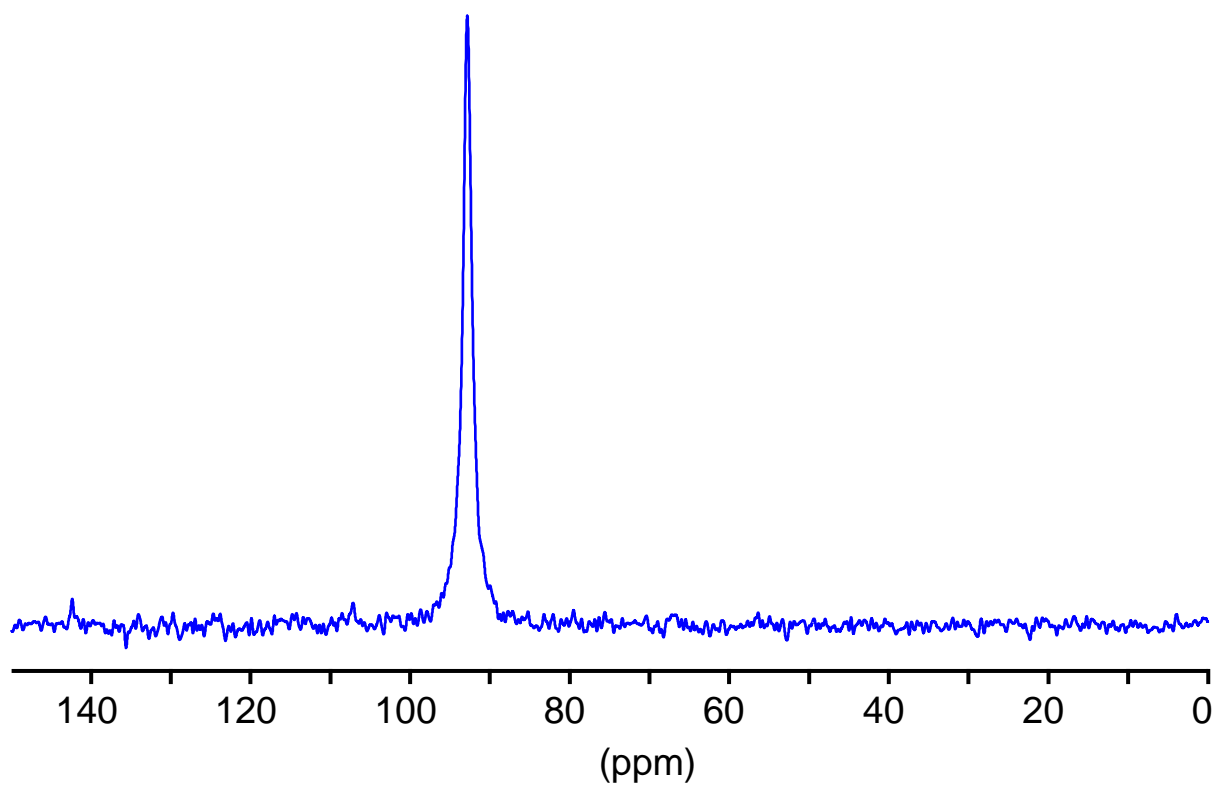


Fig. S3 ^1H - ^{13}C CP/MAS NMR spectrum of zeolite omega obtained using a mixture of 1,3,5-trioxane and 15-crown-5 in the synthesis gel.

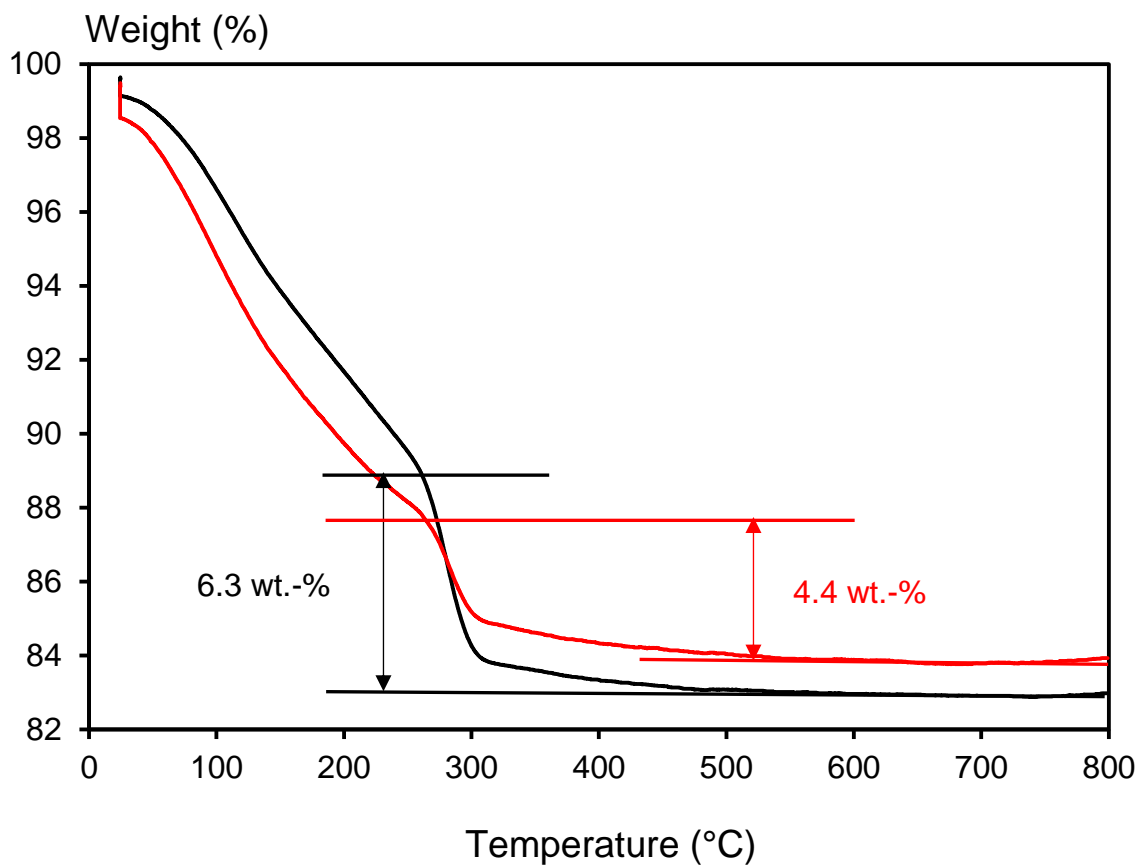


Fig. S4 Thermogravimetric analysis of zeolites omega (black) and ECR-1 (red) synthesized using 1,3,5-trioxane as structure directing molecule.

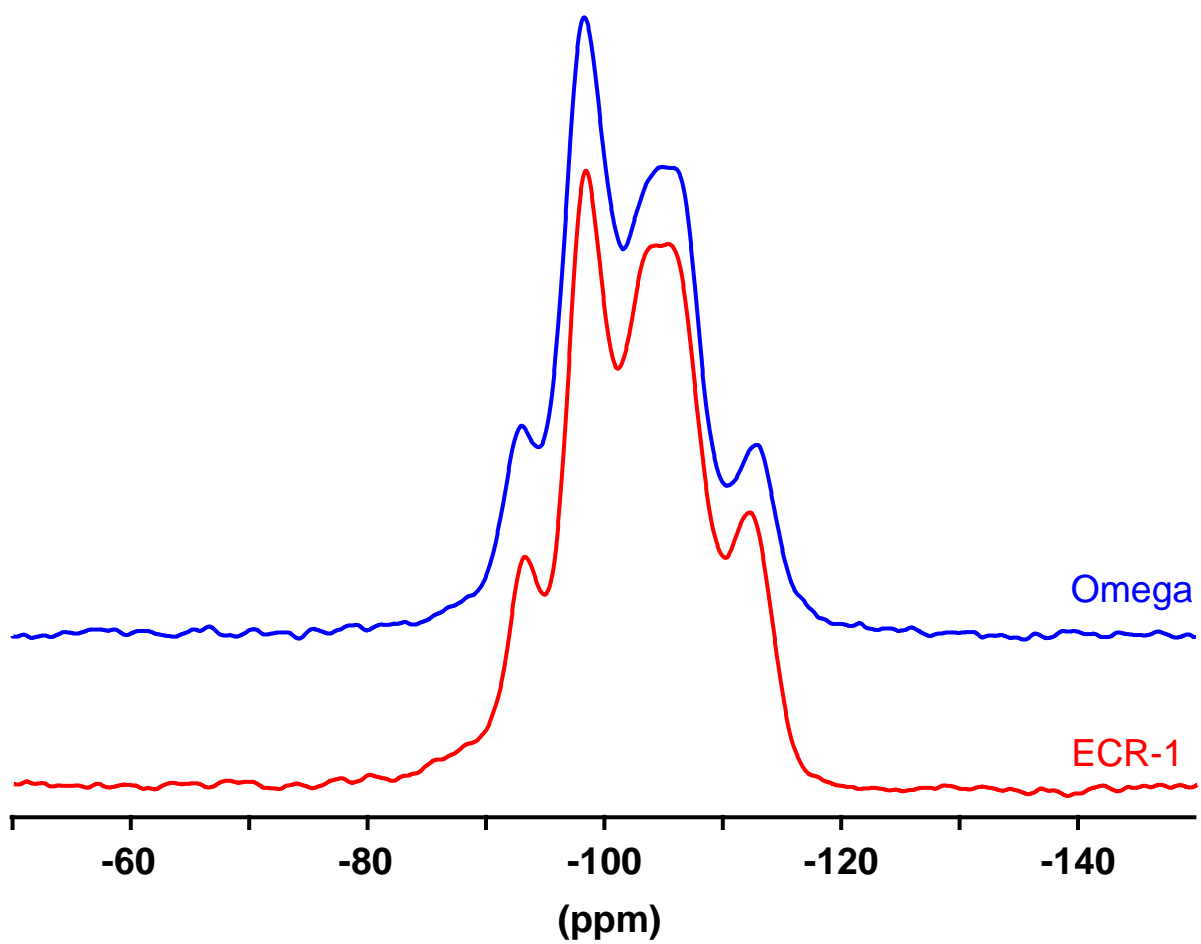


Fig. S5 ^{29}Si MAS NMR spectra of zeolites omega (blue) and ECR-1 (red) synthesized using 1,3,5-trioxane as structure directing molecule.

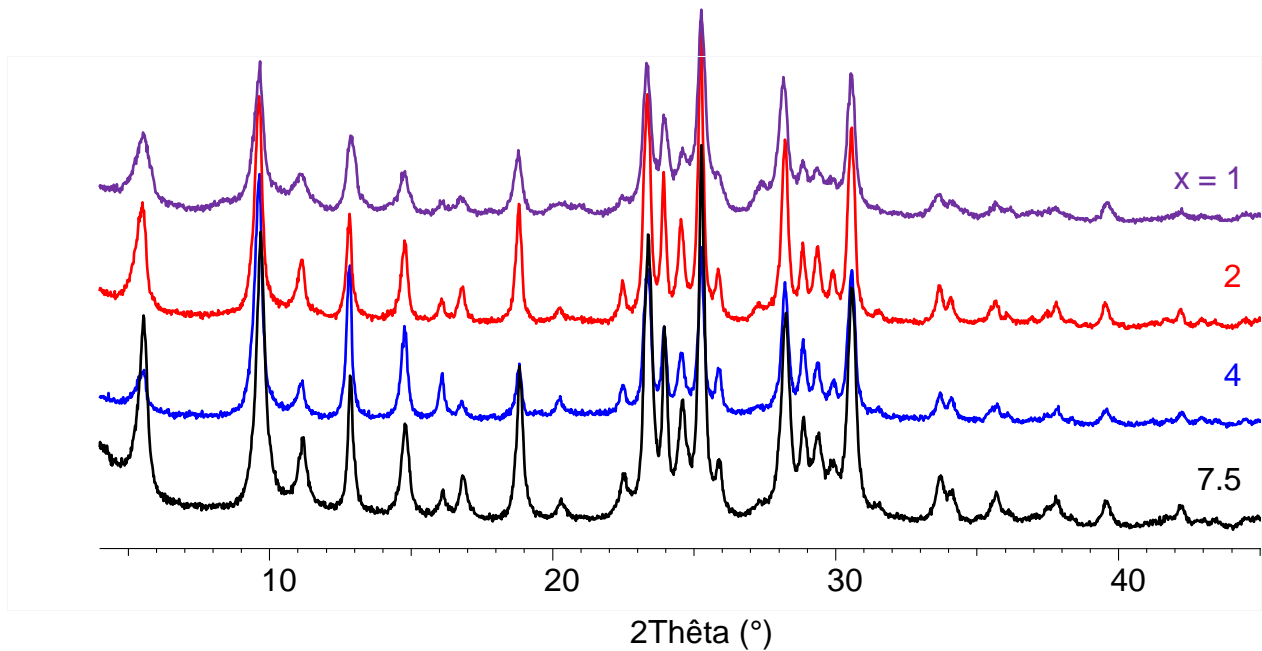


Fig. S6 XRD patterns of zeolites omega obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 2.2 \text{ Na}_2\text{O} - x \text{ trioxane} - 140 \text{ H}_2\text{O}$ at 115°C for 7 days under dynamic conditions. The amount of trioxane was varied from $x = 1$ to 7.5.

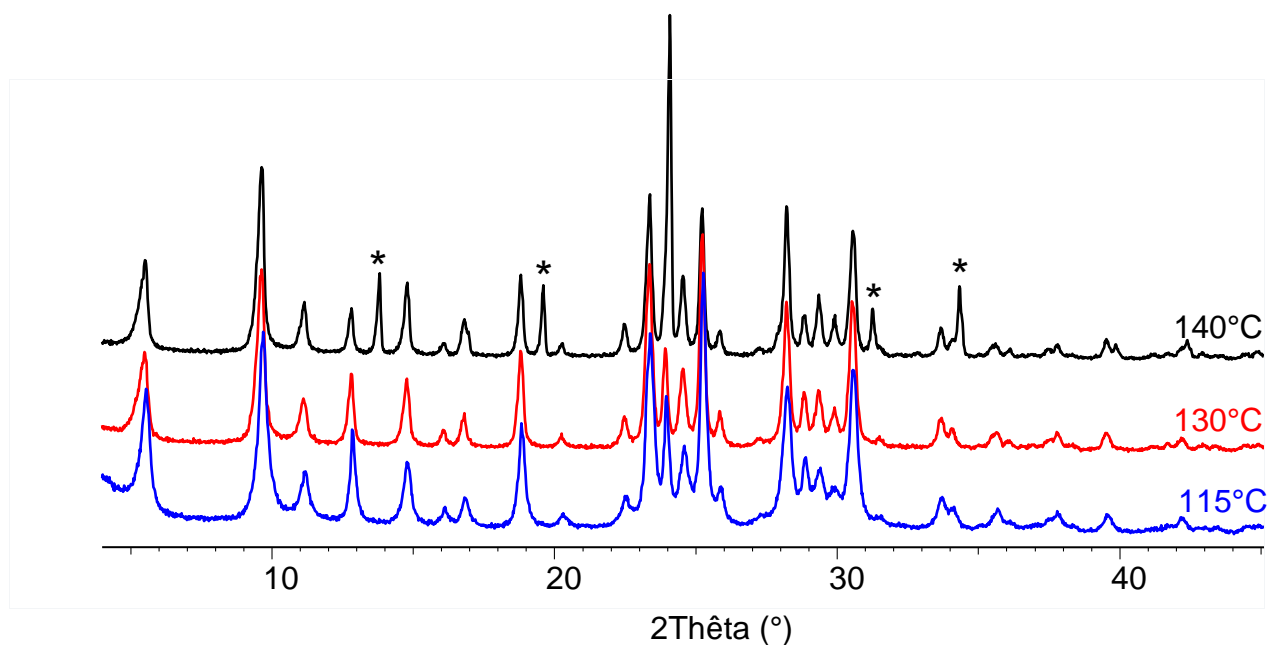


Fig. S7 XRD patterns of zeolite omega obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 2.2 \text{ Na}_2\text{O} - 7.5 \text{ trioxane} - 140 \text{ H}_2\text{O}$ for 7 days under dynamic conditions at different temperatures. Asterisks on the pattern obtained at 140°C indicate reflections of zeolite P.

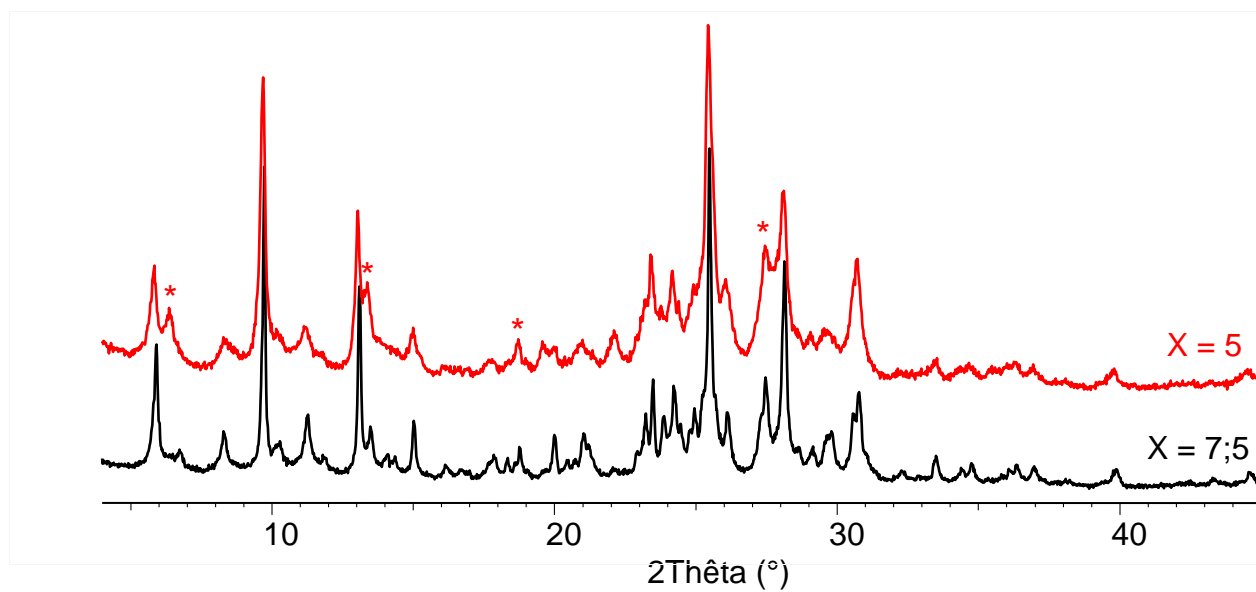


Fig. S8 XRD patterns of zeolites obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 2.2 \text{ Na}_2\text{O} - x \text{ trioxane} - 140 \text{ H}_2\text{O}$ ($x = 5$ and 7.5) for 7 days under dynamic conditions at 130°C . Asterisks indicate reflections of mordenite.

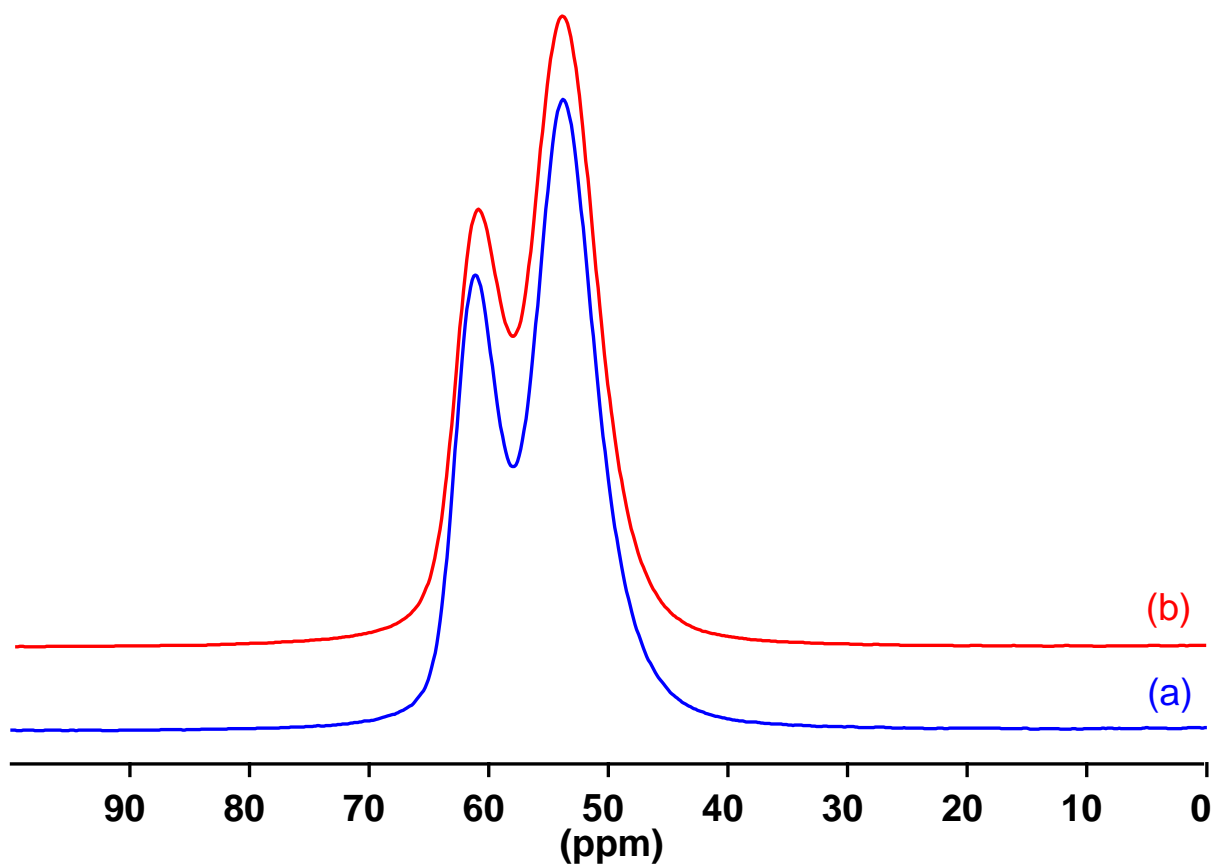


Fig. S9 ^{27}Al NMR spectra of zeolites obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 1.7 \text{ Na}_2\text{O} - 7.5 \text{ R} - 140 \text{ H}_2\text{O}$ for 7 days under dynamic conditions. R = 1,3,5-trioxane, T = 115°C (a); R = 1,4-dioxane, T = 130°C.

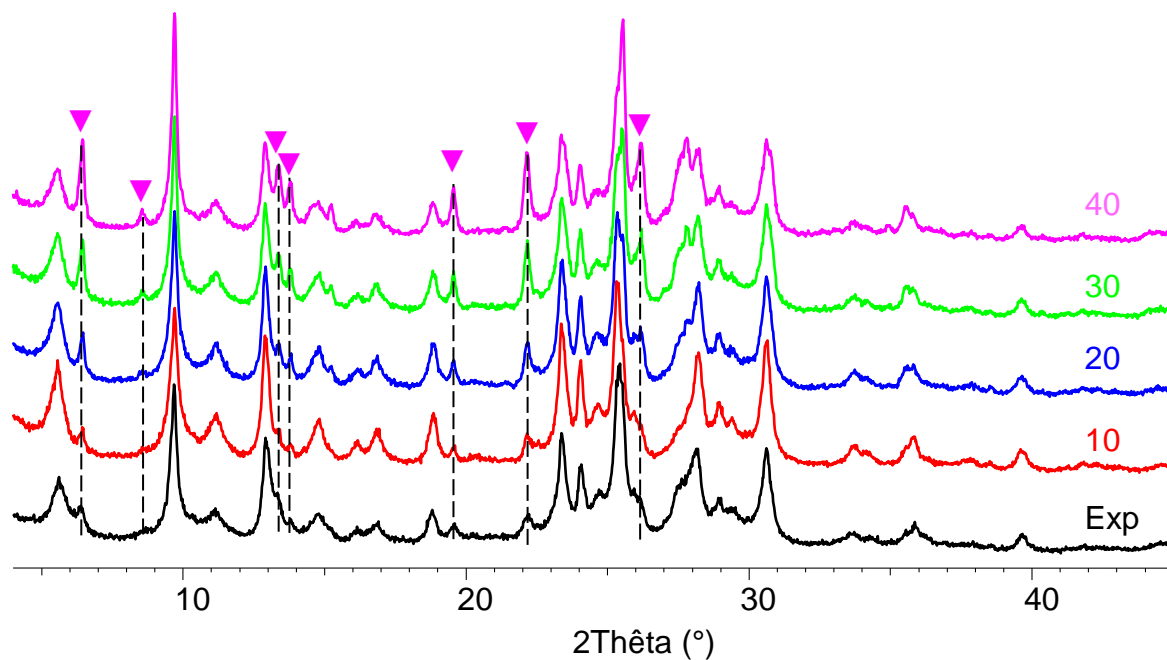


Fig. S10 XRD patterns of a zeolite obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 1.7 \text{ Na}_2\text{O} - 7.5 \text{ dioxane} - 140 \text{ H}_2\text{O}$ for 7 days under dynamic conditions at 130°C (Exp) and mixtures of **MAZ** and **MOR** with 10 (red), 20 (blue), 30 (green) and 40 (pink) wt.-% MAZ. The best fit is obtained with 10 wt.-% **MOR** in the mixture. Pink triangles and dashed lines point out the main reflections of **MOR** whose intensity increase with the percentage of mordenite in the mixture.

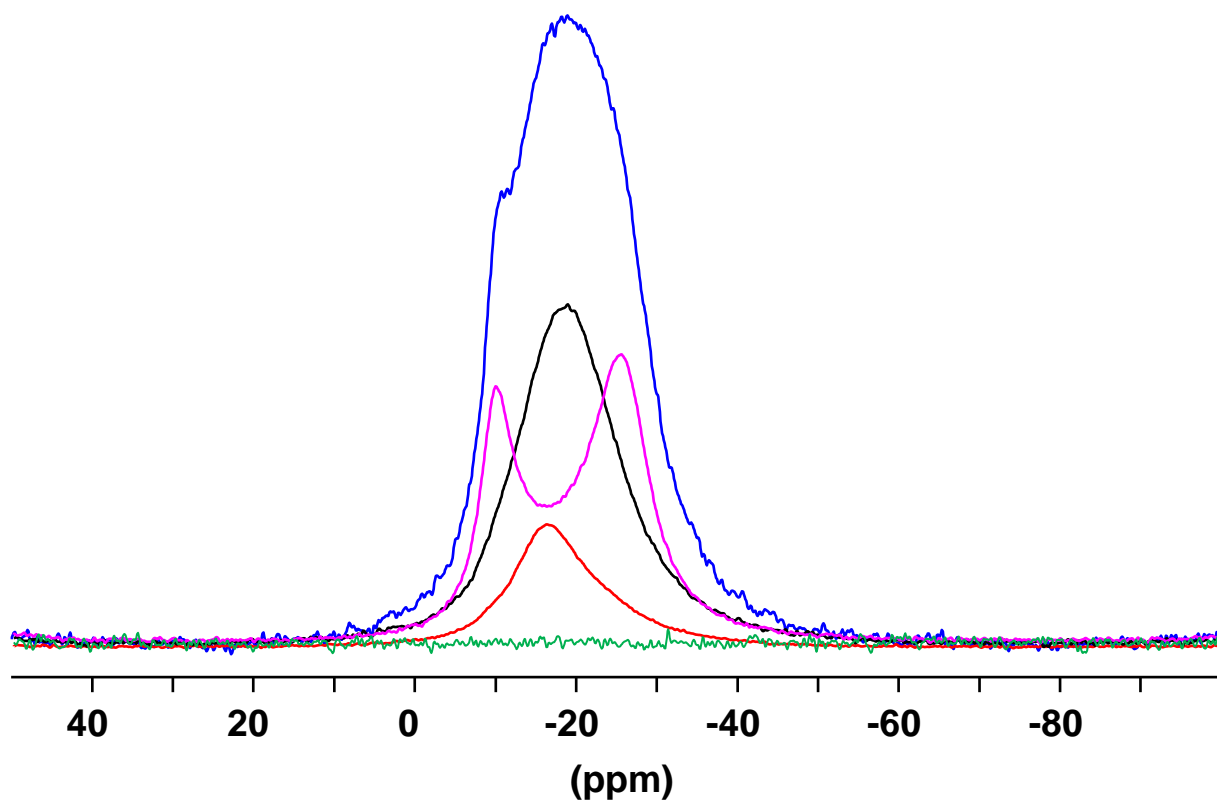
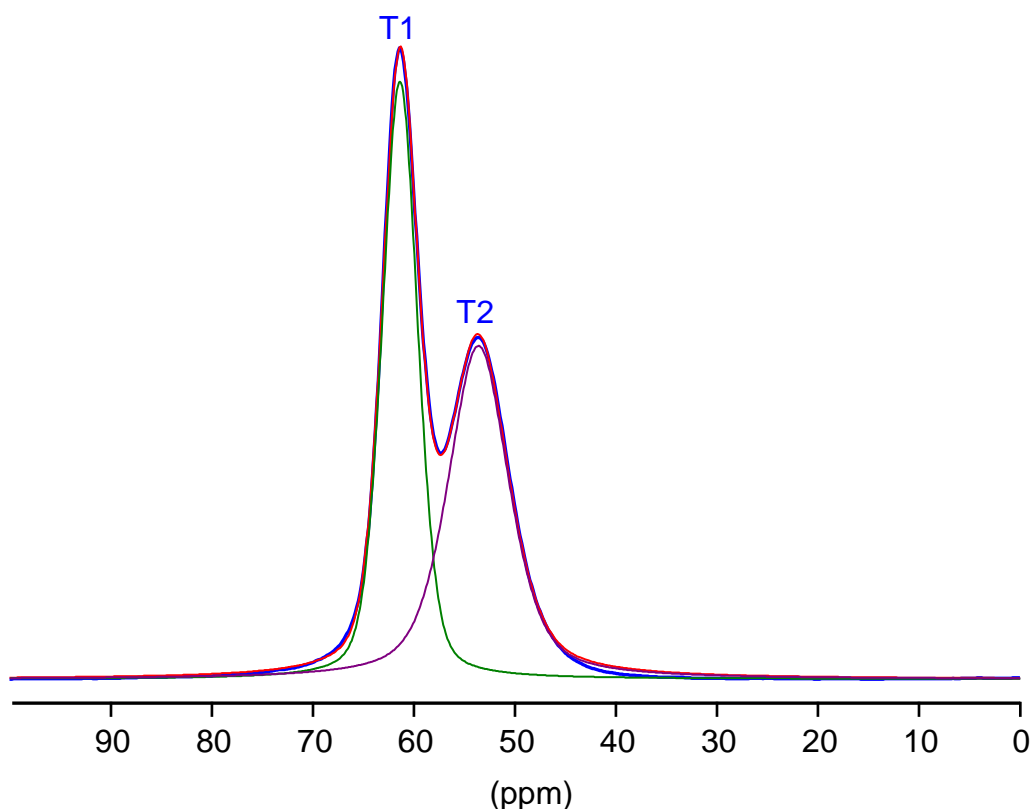


Fig. S11 ^{23}Na MAS NMR spectrum of a zeolite obtained from the crystallization of a gel with the composition $10 \text{ SiO}_2 - 1 \text{ Al}_2\text{O}_3 - 1.7 \text{ Na}_2\text{O} - 7.5 \text{ dioxane} - 140 \text{ H}_2\text{O}$ for 7 days under dynamic conditions at 130°C (blue) and decomposition of the signal using lines corresponding to zeolite omega (pink), ECR-1 (black) and mordenite (red).

Section S1

²⁷Al NMR intensities in MAZ+EON mixtures

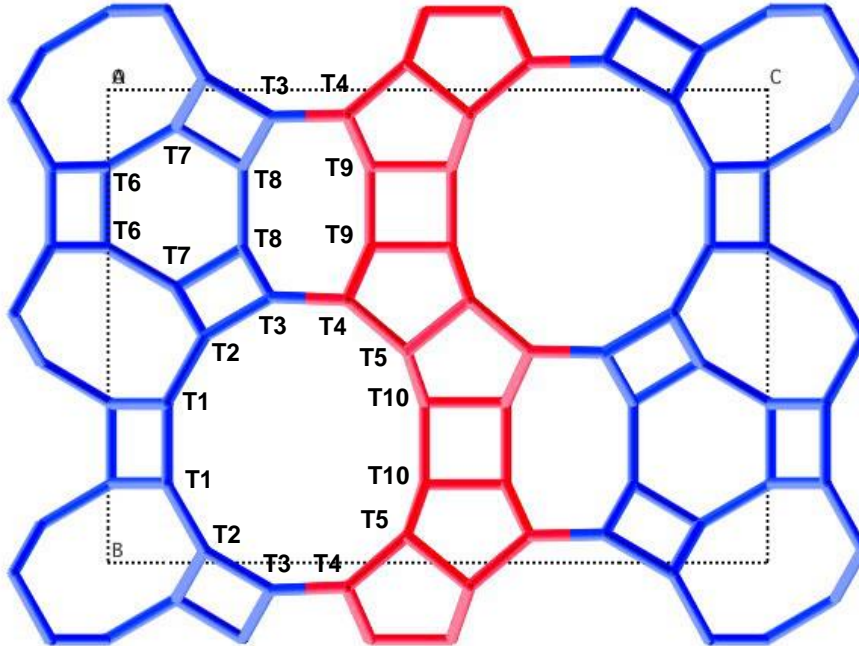
The unit cell of the MAZ structure contains 36 T atoms, 24 T1 and 12 T2. Theoretically, the corresponding ²⁷Al NMR spectrum should be composed of two lines with a relative intensity of 2:1. However, the ratio is always < 1 on experimental spectra, revealing a deficiency of Al in site T1. It is also known that the ratio strongly depends on the way the signal is deconvoluted. Deconvolution with symmetric lines shapers such as Lorentzian lines significantly underestimates the real value. An example shown below on a zeolite synthesized with trioxane gives T1:T2 = 0.95 (measured by déconvolution of the spectrum with a combination of Gaussian and Lorentzian lines (see main text)).



²⁷Al NMR spectrum of zeolite omega prepared with 1,3,5-trioxane and assignment of the lines to the 2 crystallographic non-equivalent T sites in the structure.

The structure of ECR-1 consists of a strict alternation of **MAZ** (blue) and **MOR** (red) sheets. The unit cell contains 60 T atoms with 10 crystallographic non-equivalent sites:

8T1, 8T2, 8T3, 8T4, 8T5, 4T6, 4T7, 4T8, 4T9 and 4T10. Sites T1, T2, T3, T6, T7 and T8 are located in the **MAZ** sheet whereas T4, T5, T9 and T10 are in the **MOR** sheet.



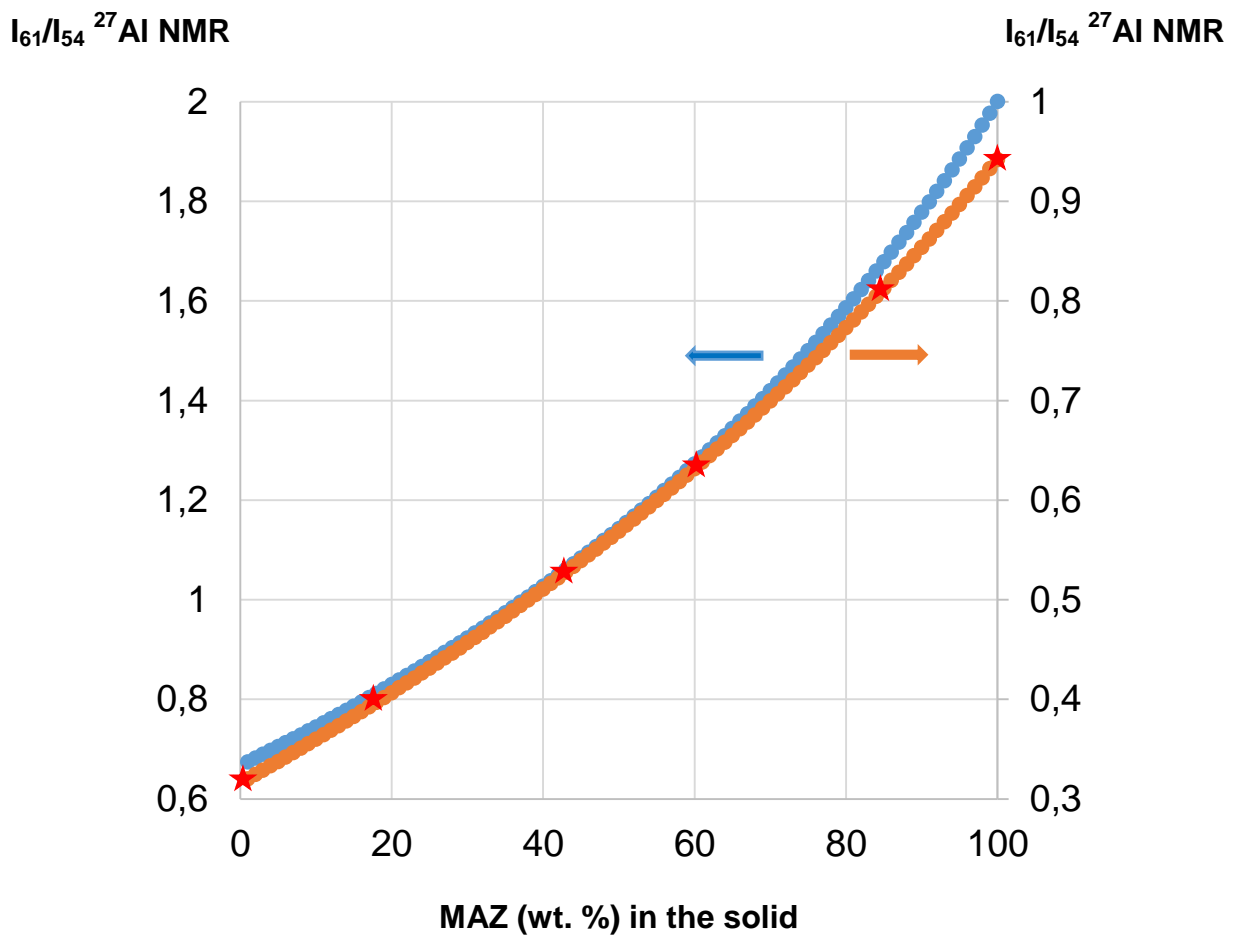
*Structure of zeolite EXCR-1 showing the alternation of **MAZ** (blue) and **MOR** (red) sheets with the 10 non-equivalent T sites of the framework.*

Moreover, T1, T2 and T3 correspond to T1 site in the **MAZ** structure whereas T6, T7 and T8 correspond to T2 site. Assuming that chemical shifts of Al atoms in MAZ sheets are the same as in zeolite omega and that all Al atoms of **MOR** sheets resonate at 54 ppm (which is observed experimentally on a pure mordenite), the I_{61}/I_{54} ratio can be estimated to $I_{61}/I_{54} = 24/36 = 0.66$. Of course, this estimation supposes that Al is randomly distributed in the framework, which is not always verified experimentally. However, experimental I_{61}/I_{54} values obtained on pure ECR-1 zeolites are in the range 0.30-0.32, indicating that the ratio is certainly underestimated, as previously observed for zeolite omega.

For a **MAZ/EON** mixture containing x wt.-% zeolite omega and (100-x) wt.-% zeolite ECR-1, the I_{61}/I_{54} ratio corresponds to:

$$I_{61}/I_{54} = (0.0266x + 4)/(6 - 0.0267x)$$

This corresponds to the blue curve in the figure below. However, this curve cannot be used as a calibration curve to estimate the composition of the different solids because measured values significantly differ from “theoretical” ones. Thus, the same relationship has been plotted using experimental measured values for the pure zeolites, i.e. 0.95 for zeolite omega and 0.32 for ECR-1 (orange line). It is interesting to see that the two curves almost superimpose over the whole range of compositions, confirming that the error made on the estimation of the I_{61}/I_{54} ratio is independent on the composition and depends only on the deconvolution method.



Evolution of the ratio between lines at 61 and 54 ppm in ^{27}Al NMR spectra (I_{61}/I_{54}) calculated assuming theoretical values (blue) and experimental ones measured by deconvolution of the spectra with Gaussian/Lorentzian lines (orange) .

Moreover, the graph also shows that real values are approx. twice the measured values, which was already the conclusion of Wouters et al. who deconvoluted spectra using line shapes deduced from 2D-3Q MAS spectra [1]. Experimental I_{61}/I_{54} values measured on spectra of solids prepared with various $\text{Na}_2\text{O}/\text{SiO}_2$ ratios (red stars) give the average compositions given in Table 1 of the main text.

- 1) B.H. Wouters, T. Chen, A.M. Goossens, J.A. Martens, P.J. Grobet, Determination of the $\text{Al}^{\text{T}1}/\text{Al}^{\text{T}2}$ Ratio in MAZ Zeolites Using Line Shapes of MQ MAS NMR, J. Phys. Chem. B 103 (1999) 8093-8096, <https://doi.org/10.1021/jp991722j>