

Supporting information

S1. COOP technique

The crystal orbital overlap population is calculated using the specialized code LOBSTER downloaded from the website www.cohp.de. The code uses standard vasp output files, which are recorded when a successful relaxation of the structure is finished. No special parameters are necessary in the INCAR file.

S2. Visualization of contacts of Zn^{+} to the framework

The compensation of the Si/Al substitution in four irreducible T-sites of the ferrierite structure (T1-T4) by attaching the extraframework Zn^{+} cation to the AlO_4 tetrahedra in the framework produces the configurations displayed in Figure S1.

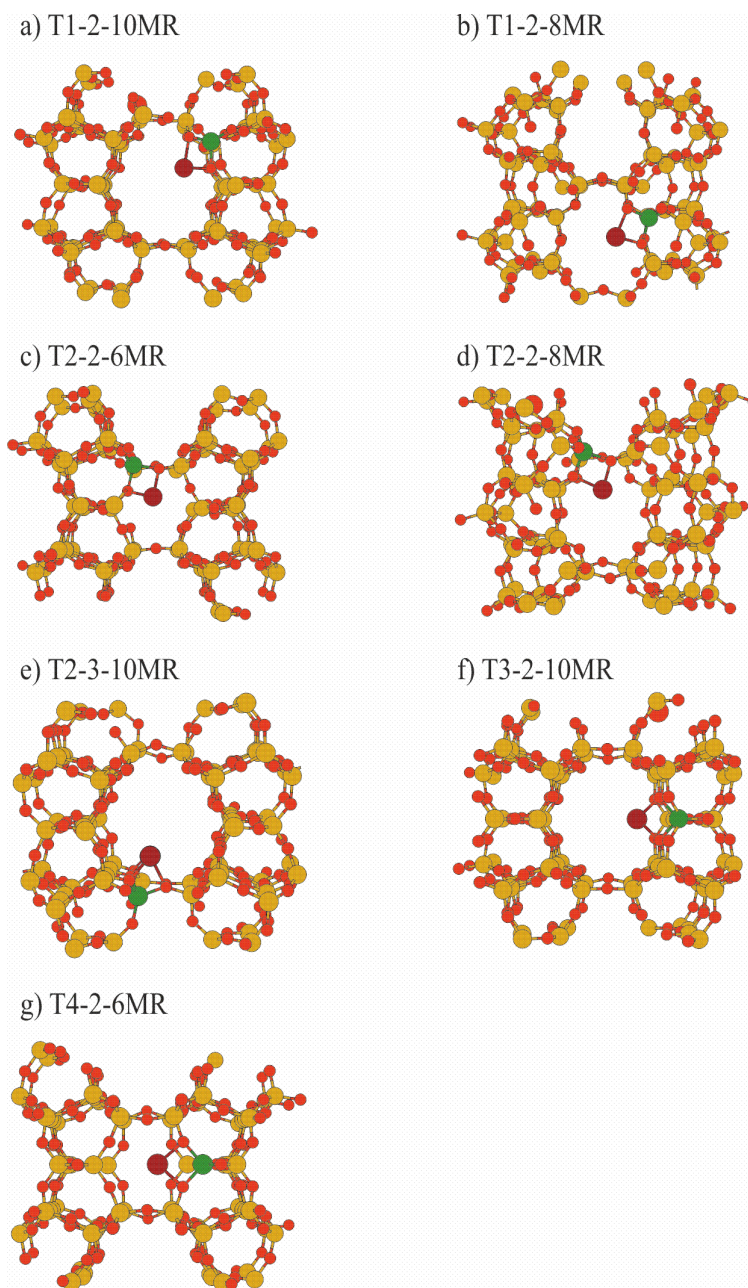


Figure S1. The configurations formed when the extraframework Zn^+ cation compensates the Si/Al substitution in the framework. Figures S1a, c, e-g are topviews along the c vector, Figures S1b and d are sideviews along the b vector. The nomenclature of the configurations is explained in the text. Yellow/red/green/brown balls are Si/O/Al/Zn atoms.

Details of the contact between the Zn^+ cation and the framework are shown in Figure S2 on the example of the relatively stable configuration T3-2-10MR (Figure S2a) and the less stable configuration T2-3-10MR (Figure S2b). The contact is formed between the Zn^+ cation and O atoms of the tetrahedral AlO_4 unit (encircled). In the stable configuration (Figure S2a) two oxygen atoms are oriented towards the channel (atoms A), and two oxygen atoms towards the zeolite framework (atoms B). This is the most common orientation of the tetrahedral unit in zeolites. Because the attraction of the Zn^+ cation to the AlO_4 unit is much weaker than the attraction of the stronger Zn^{2+} cation, only two Zn-O contacts are formed. This is in contrast to the Zn^{2+} cation, which typically forms four Zn-O contacts. The T2 site is located between the 10MR and the 6MR (Figures 2 and S2b). The orientation of the tetrahedral AlO_4 unit is such that three O atoms are directed towards the 10MR (Figure S2b, atoms A) and only one O atom points away from the 10MR (atom B). When the Zn^+ cation approaches the AlO_4 unit from the 10MR it can form three almost equivalent Zn-O contacts (Figure S2b). The energy of this configuration is disadvantaged by ~ 111 kJ/mol (Table 1). For the same T2 site, however, the Zn^+ cation can form another configuration, as well. When the cation is replaced from the 10MR to the 6MR into the position indicated by dotted circle (Figure S2b), the two strong Zn-O contacts are created and the T2-2-6MR configuration is formed. Because the configuration T2-2-6MR is much more stable than the configuration T2-3-10MR (Table 1) it is unlikely that a long-lived T2-3-10MR configuration can exist.

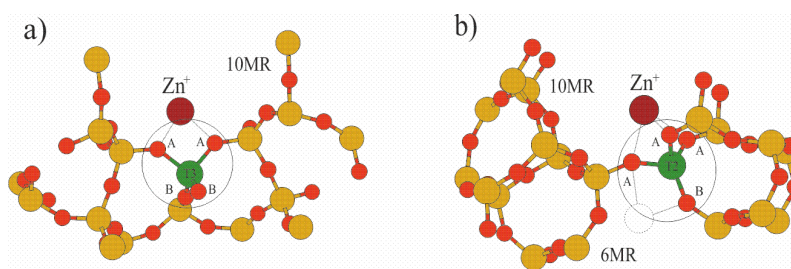


Figure S2. Two types of contacts between Zn^+ and the framework. The connection to two framework O atoms (a), and to three O atoms (b). The dashed circle in Figure S2b indicates another possible location of the Zn^+ cation.