Supplementary File

Theoretical Study of Zirconium Isomorphous Substitution into Zeolite Frameworks

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1. Equations

1.1. Substitution Energies (E_{sub})

Because the distribution of substituted T sites in frameworks is determined by the thermodynamic stability of molecular sieve frameworks [1,2], the substitution energy (E_{sub}) is an appropriate criterion for evaluating the energetic priority for a specific T site substitution by a heteroatom. The following virtual reaction is carried out to represent the substitution process:

$$(O\text{-}Si\text{-}O)_n^{SOD} + nAl(OH)_3 + nH_2O \rightarrow (O\text{-}Al\text{-}OH)_n^{SOD} + nSi(OH)_4 \quad (1)$$

$$(O\text{-}Si\text{-}O)_n^{SOD} + nZr(OH)_4 \rightarrow (O\text{-}Zr\text{-}O)_n^{SOD} + nSi(OH)_4 \quad (2)$$

$$(O\text{-}P\text{-}O)_n^{AlPO/SAPO} + nZr(OH)_4 \rightarrow (O\text{-}Zr\text{-}OH)_n^{AlPO/SAPO} + nH_3PO_4 \quad (3)$$

Also, one can define the substitution energies (E_{sub}) as follows [3,4]:

$$E_{sub\text{-}nAl} = E_{(O\text{-}Al\text{-}OH)_n^{SOD}} + nE_{Si(OH)_4} - E_{(O\text{-}Si\text{-}O)_n^{SOD}} - nE_{Al(OH)_3} - nE_{H_2O} \quad (4)$$

$$E_{sub\text{-}nZr} = E_{(O\text{-}Zr\text{-}O)_n^{SOD}} + nE_{Si(OH)_4} - E_{(O\text{-}Si\text{-}O)_n^{SOD}} - nE_{Zr(OH)_4} \quad (5)$$

$$E_{sub\text{-}nZr} = E_{(O\text{-}Zr\text{-}OH)_n^{AlPO/SAPO}} + nE_{H_3PO_4} - E_{(O\text{-}P\text{-}O)_n^{AlPO/SAPO}} - nE_{Zr(OH)_4} \quad (6)$$

where $E_{sub\text{-}nAl/Zr}$ corresponds to the substitution energies of the optimized SOD, AlPO-34, and SAPO-34 framework substituted by Al or Zr atoms; $E_{(O\text{-}Si\text{-}O)_n^{SOD}}$ and $E_{(O\text{-}P\text{-}O)_n^{AlPO/SAPO}}$ are the energies of the SOD, AlPO-34, SAPO-34 frameworks, respectively; $E_{(O\text{-}Zr\text{-}O)_n^{SOD}}$ and $E_{(O\text{-}Zr\text{-}OH)_n^{AlPO/SAPO}}$ are the energies of the corresponding Zr-substituted SOD, AlPO-34, and SAPO-34 frameworks, respectively. $E_{Si(OH)_4/Zr(OH)_4/H_3PO_4}$ is the energy of the virtual complexes.

The average substitution energy ($E_{av\text{-}sub}$) is used in this work to compare the difficulty of substitutions with different Zr content in the framework

$$E_{av-sub} = E_{sub}/n \quad (7)$$

1.2. Deprotonation Energies (E_{DPE})

The deprotonation energy (E_{DPE}) is defined as follows [5]:

$$(O\text{-}Al\text{-}OH)^{SOD}/(O\text{-}Zr/Si\text{-}OH)^{AlPO/SAPO} \rightarrow (O\text{-}Al\text{-}O^-)^{SOD}/(O\text{-}Zr/Si\text{-}O^-)^{AlPO/SAPO} + H^+$$

$$E_{DPE} = E_{(O\text{-}Al\text{-}O^-)^{SOD}/(O\text{-}Zr/Si\text{-}O^-)^{AlPO/SAPO}} + E_{H^+} - E_{(O\text{-}Al\text{-}OH)^{SOD}/(O\text{-}Zr/Si\text{-}OH)^{AlPO/SAPO}} \quad (8)$$

where $E_{(O\text{-}Al\text{-}O^-)^{SOD}/(O\text{-}Zr/Si\text{-}O^-)^{AlPO/SAPO}}$, E_{H^+}, and $E_{(O\text{-}Al\text{-}OH)^{SOD}/(O\text{-}Zr/Si\text{-}OH)^{AlPO/SAPO}}$ are the respective energies of the framework anion after deprotonation, the gaseous proton, and the neutral protonated form of the molecular sieve.

1.3. Electrostatic Potential (ν)

ν is calculated as:

$$\nu = \frac{1}{4\pi\varepsilon}\sum_{i=1}^{4}\frac{q\times q_i}{r_i} = A\sum_{i=1}^{4}\frac{q\times q_i}{r_i} \quad (9)$$

where ε is the electrostatic constant, q and qi are the charges (|e|) of the Al atom and neighboring O atoms, and ri is the bond length (Å) of the four Al-O bonds. In this work, we mainly consider the relative value of ν, and thus the $\frac{1}{4\pi\varepsilon}$, q and r_i are contributed to A.

1.4. Structural Distortion (Θ and Ω)

The local structural perturbations of [TO_4] (T = Al, Zr) from a regular tetrahedron using the root mean square deviation parameter (Θ), which is defined as [6,7]:

$$\Theta = \sqrt{\frac{1}{6}\sum_{i=1}^{6}\left(\alpha_i - \bar{\alpha}\right)^2} \tag{10}$$

where α_i represents the i^{th} Θ(O-T-O) angle and $\bar{\alpha}$ is the average of the six Θ(O-T-O) angles. The Θ is not a direct measure of the distortion caused by the incorporation of heteroatoms into the framework positions of zeolites [8]. The changes in local [TO_4] geometries caused by the heteroatom substitution can be quantified using the parameter Ω, which is defined as [8]:

$$\Omega_{Si\to Al} = \left(\Theta_{Al} - \Theta_{Si}\right)/\Theta_{Si} \tag{11}$$

$$\Omega_{Si\to Zr} = \left(\Theta_{Zr} - \Theta_{Si}\right)/\Theta_{Si} \tag{12}$$

$$\Omega_{P\to Zr} = \left(\Theta_{Zr} - \Theta_{P}\right)/\Theta_{P} \tag{13}$$

where Θ_{Al}, Θ_{Zr}, Θ_{Si}, and Θ_P are the root mean square deviations from regular tetrahedron for the Al/Zr atom substitution in SOD, AlPO-34, and SAPO-34 frameworks.

2. Figures

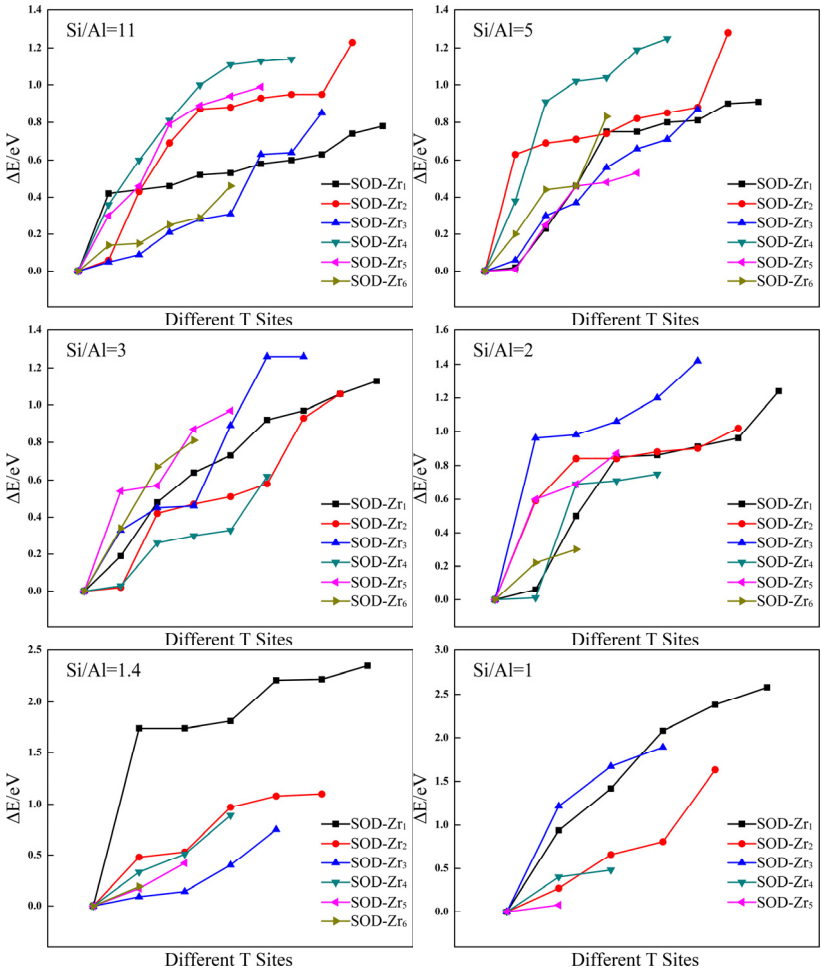


Figure S1. The relative energies (ΔE/eV) of different T site for Zr atom substitution in the SOD framework with Si/Al ratio from 11 to 1.

The location sites of Zr atom in the framework can refer to Figure 1 in the manuscript which shows location of Tn sites in the framework.

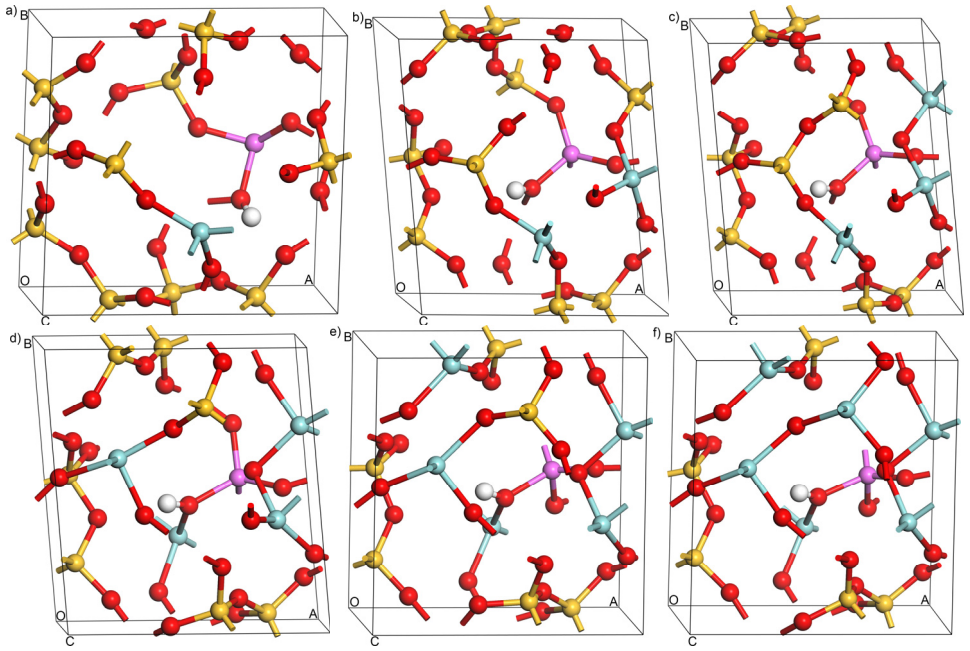
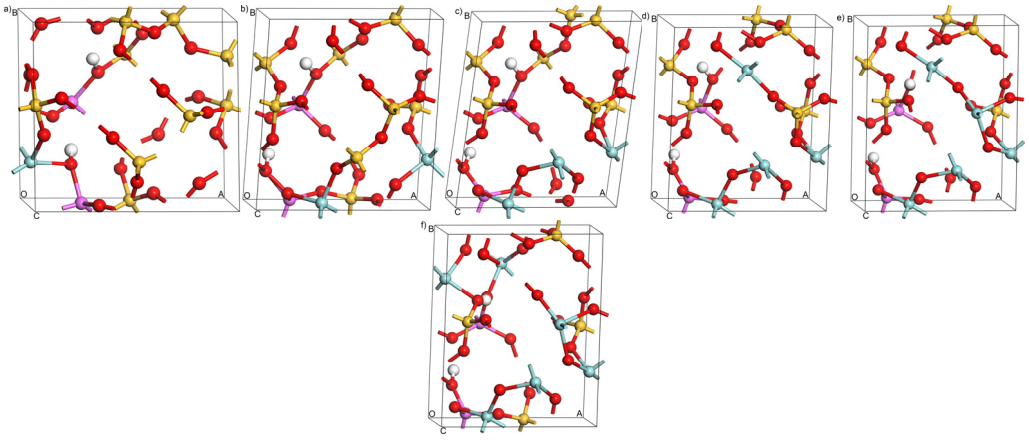
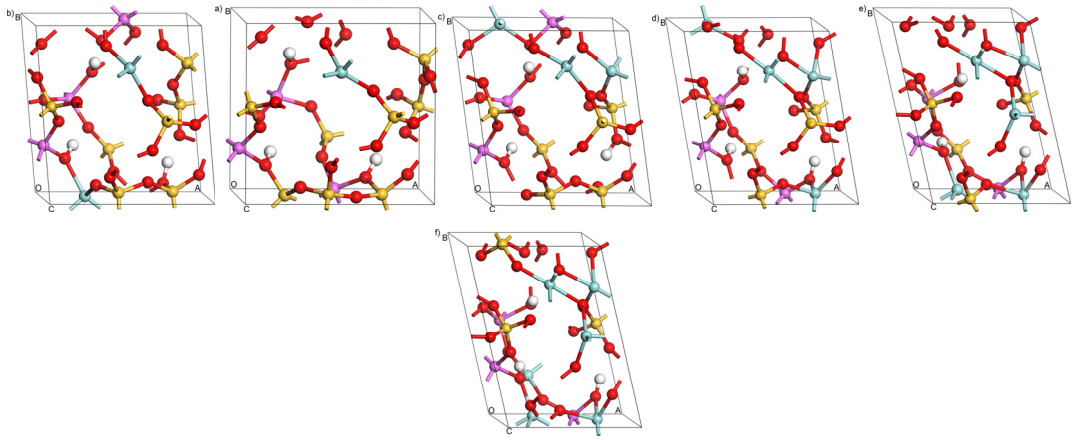


Figure S2. The most stable configurations of (**a**) one, (**b**) two, (**c**) three, (**d**) four, (**e**) five, and (**f**) six Zr atoms substitution on the basis of SOD framework with Si/Al = 11. Zirconium is blue-green.

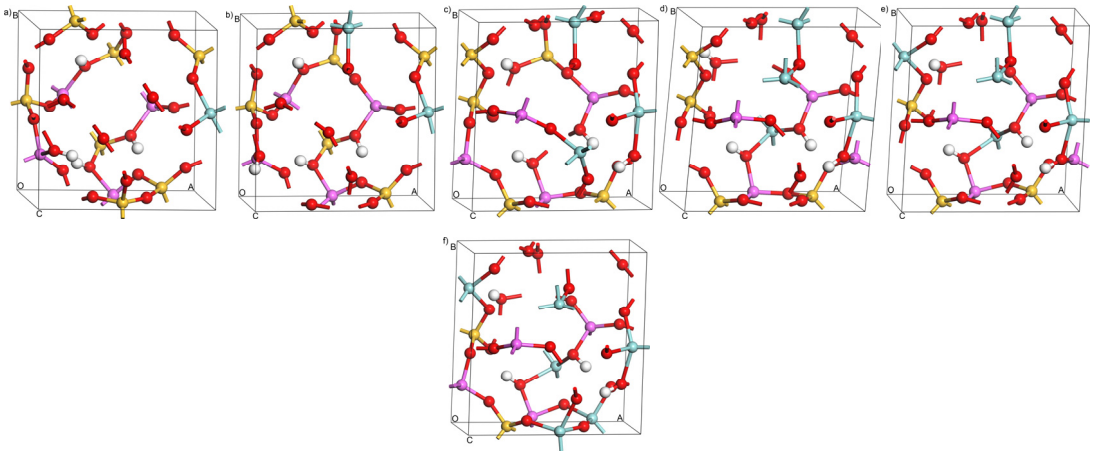
The location sites of Zr atom in the framework can refer to Figure 1 in the manuscript which shows the location of Tn sites in the framework.



Si/Al = 5



Si/Al = 3



Si/Al = 2

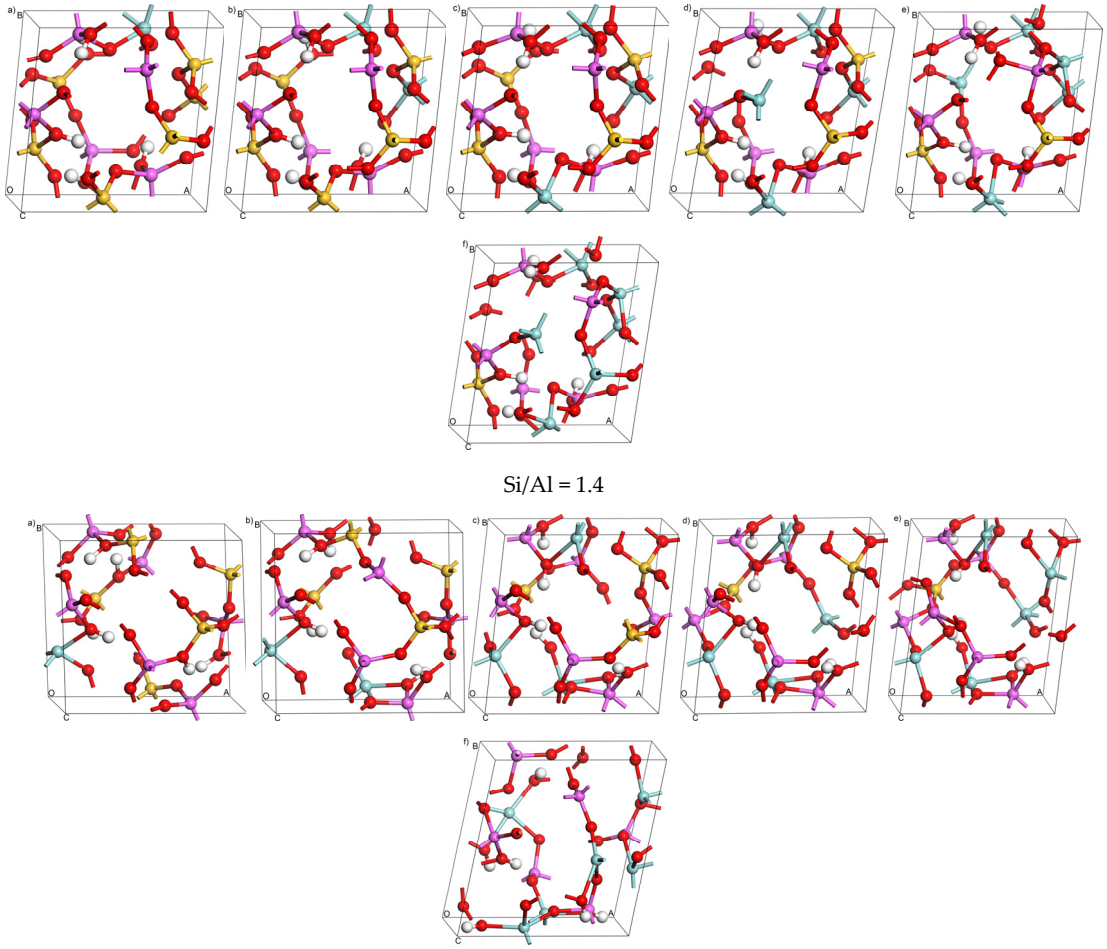


Figure S3. The most stable configurations of (**a**) one, (**b**) two, (**c**) three, (**d**) four, (**e**) five, and (**f**) six Zr atoms substitution on the basis of SOD framework with Si/Al = 5~1.

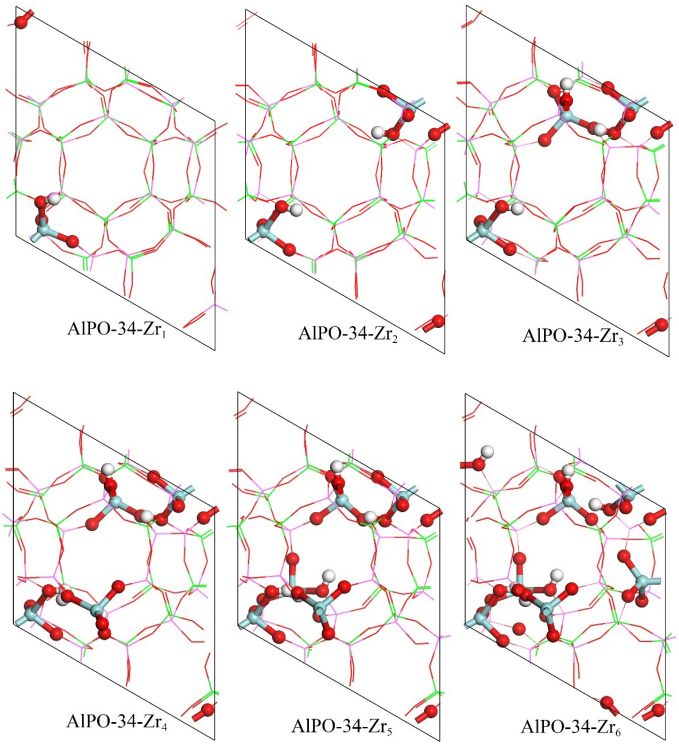


Figure S4. The most stable configurations of AlPO-34-Zr1-6.

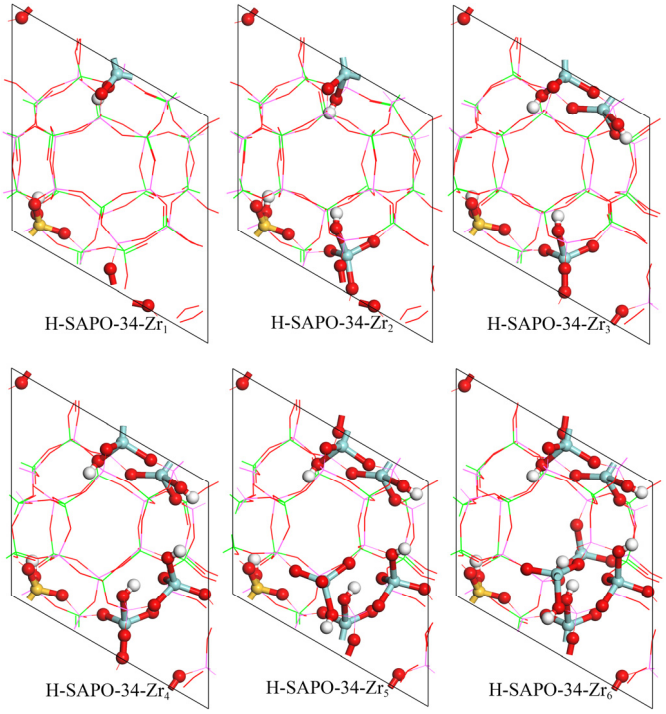


Figure S5. The most stable configurations of SAPO-34-$Zr_{1\sim6}$.

References

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