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Flexibility in zeolites: origin, limits, and evaluation

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Abstract:

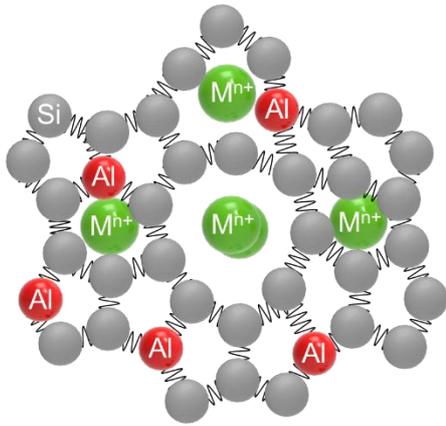
Numerous evidences in the literature suggest that zeolitic materials exhibit significant intrinsic flexibility as a consequence of the spring-like behavior of Si–O and Al–O bonds and the distortion ability of Si–O–Si and Al–O–Si angles. Understanding the origin of flexibility and how it may be tuned to afford high adsorption selectivity in zeolites is a big challenge. Zeolite flexibility may be triggered by changes in temperature, pressure, or chemical composition of the framework and extra-framework compounds, as well as by the presence of guest molecules. Therefore, zeolite flexibility can be classified into three categories: (i) temperature and pressure-induced flexibility; (ii) guest-induced flexibility; and (iii) compositionally-induced flexibility. An outlook on zeolite flexibility and the challenges met during the precise experimental evaluations of zeolites will be discussed. Overcoming these challenges will provide an important tool to design novel selective adsorbents.

Keywords: zeolites, flexibility, sorption

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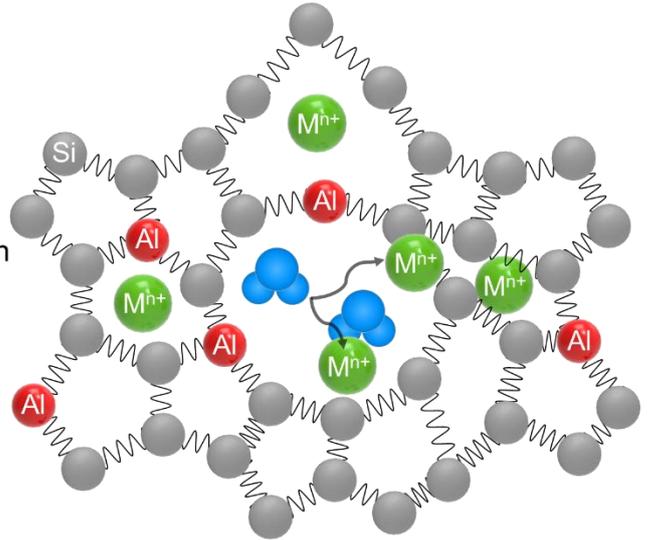
Zeolites

Rigidity?



Origin and limitation
Evaluation

Flexibility?



1. Introduction

Zeolites are microporous materials playing a key role in industrial applications as catalysts, gas adsorbents and ion exchangers in many processes intimately related to environmental and economic challenges.¹⁻³ Different approaches have been applied to control the selectivity of zeolite adsorbents and simultaneously control the adsorption and release of guest molecules.⁴⁻⁷ One of the key contributors to the selectivity towards adsorbed gas molecules was recently regarded to result from the zeolite framework's flexibility.⁸ **Yet, there is not a generally established definition in the literature of the term "flexibility of zeolites".** This flexibility may be defined as a reversible framework deformation (expansion/contraction) or a dynamic of the zeolite structure including the movement of extra-framework cations, an intrinsic property of zeolitic frameworks due to the spring-like behavior of Si-O and Al-O bonds and the distortion of Si-O-Al and Si-O-Si angles as a response to an external trigger such as gas adsorption/desorption or a change in temperature or pressure.^{5,9-11} This spring-like behavior was used in the development of flexible force field parameters for the modeling of porous materials (zeolites) using Monte Carlo calculations or molecular dynamics simulations for many years.¹²⁻²⁰ These models allow to simulate the dynamics-related parameters in zeolites such as diffusion coefficients.²¹⁻²⁵ Moreover, theoretical calculations of minimal and maximal possible framework densities showed that zeolitic frameworks exhibit a *flexibility window* in their all silica forms and almost all of them show some degree of flexibility in their aluminosilicate forms.²⁶⁻²⁸ As a result of these framework density calculations, 25 zeolitic frameworks were highlighted as potentially flexible structures: ACO, AST, ASV, DFO, EAB, EMT, ERI, FAU, KFI, LEV, LTA, LTL, MER, MOZ, MTN, OFF, PAU, RHO, SAS, SOD, SSF, TSC, UFI, UOS, and UOZ.^{29,30}

The term *flexibility window* and its related parameters are merely theoretical and they have been used to predict the synthesis of millions of hypothetical zeolitic frameworks.^{29,31} However, a cohesive experimental factor describing zeolite flexibility is still not established and different aspects of zeolite flexibility are not fully explored yet. In this contribution, the different aspects of zeolite flexibility are summarized in three categories: (i) temperature and pressure-induced flexibility; (ii) guest-induced flexibility; and (iii) compositionally-induced flexibility.

1.1. temperature and pressure-induced flexibility

Zeolite flexibility can be observed as a response to temperature and pressure changes. Temperature-induced flexibility usually manifests as alteration of the lattice parameters of the zeolite framework (e.g. RHO, SOD, MFI, etc.) or by migration of extra-framework cations within the zeolite structure (e.g. RHO, CHA, etc.).^{3,10,32} Zeolites undergo alterations in their lattice parameters when subjected to pressure.^{11,33-35} These alterations are reversible until they reach a maximum pressure,

commonly referred to as the 'threshold pressure' in the literature. These physical triggers can occur in gas adsorption, gas storage, and sensing applications.

1.1.1. Temperature-induced flexibility

The change in the zeolite's lattice parameters in response to temperature variation was the first to be highlighted in the literature.^{36–40} The most prominent example is the work reported for RHO zeolite in 1984.³⁶ The structural flexibility of RHO zeolites can be observed due to changes in temperature, however, the effect of temperature can also be linked to guest molecule (dehydration) and extra-framework cation behavior. RHO zeolite has shown a unit cell deformation and, subsequently, a change in its symmetry from acentric (*I-43m*) to centric (*Im-3m*) when heated from 30 to 800 °C and these results were supported by both theoretical and experimental data (a variation of around 8 % in RHO's unit cell volume - see Fig. 1).^{37,41–43}

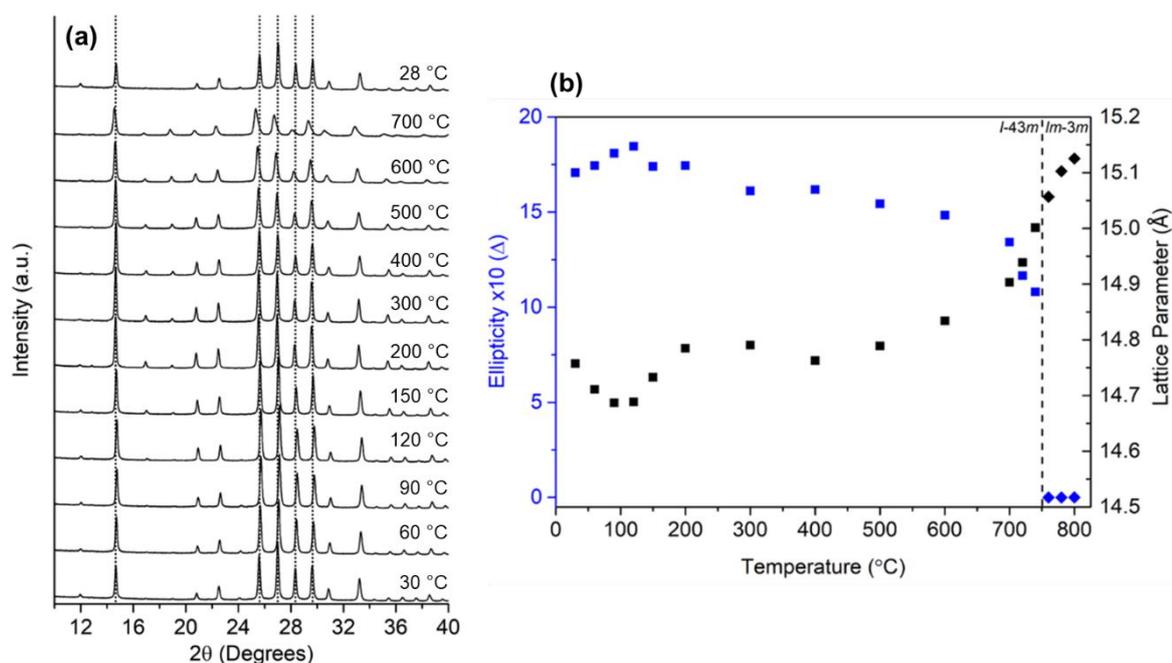


Fig. 1. (a) In-situ variable-temperature XRD scans of nanosized RHO zeolite from 30 to 700 °C and back to 28 °C, (b) plot of the ellipticity of eight-membered ring opening (in blue) and the lattice parameter (black). The dashed line delineates the adoption of either the acentric (squares) or centric (diamonds) space groups (reprinted with permission from 43, copyright 2022 American Chemical Society).

Recently, our group observed such changes in the zeolite RHO's lattice parameter by in-situ variable-temperature XRD measurements and the expansion of the lattice parameter was also visualized by in-situ TEM imaging (Fig. 2) which was identified due to the temperature-induced oscillations of the extra-framework Cs^+ around their average position.³² Another example is the encapsulation of Ar and Kr atoms (kinetic diameters of 3.3 and 3.6 Å, respectively) inside the sodalite framework with a pore

diameter of 2.4 Å.⁴⁴ Admission of these gasses was only possible because of sodalite's framework flexibility at elevated temperatures as it was shown by molecular dynamics simulations.⁴⁵ Similar behavior about flexibility of zeolites at higher temperatures was observed for other zeolite topologies, e.g. MFI, MEL and CHA.^{38,43,46}

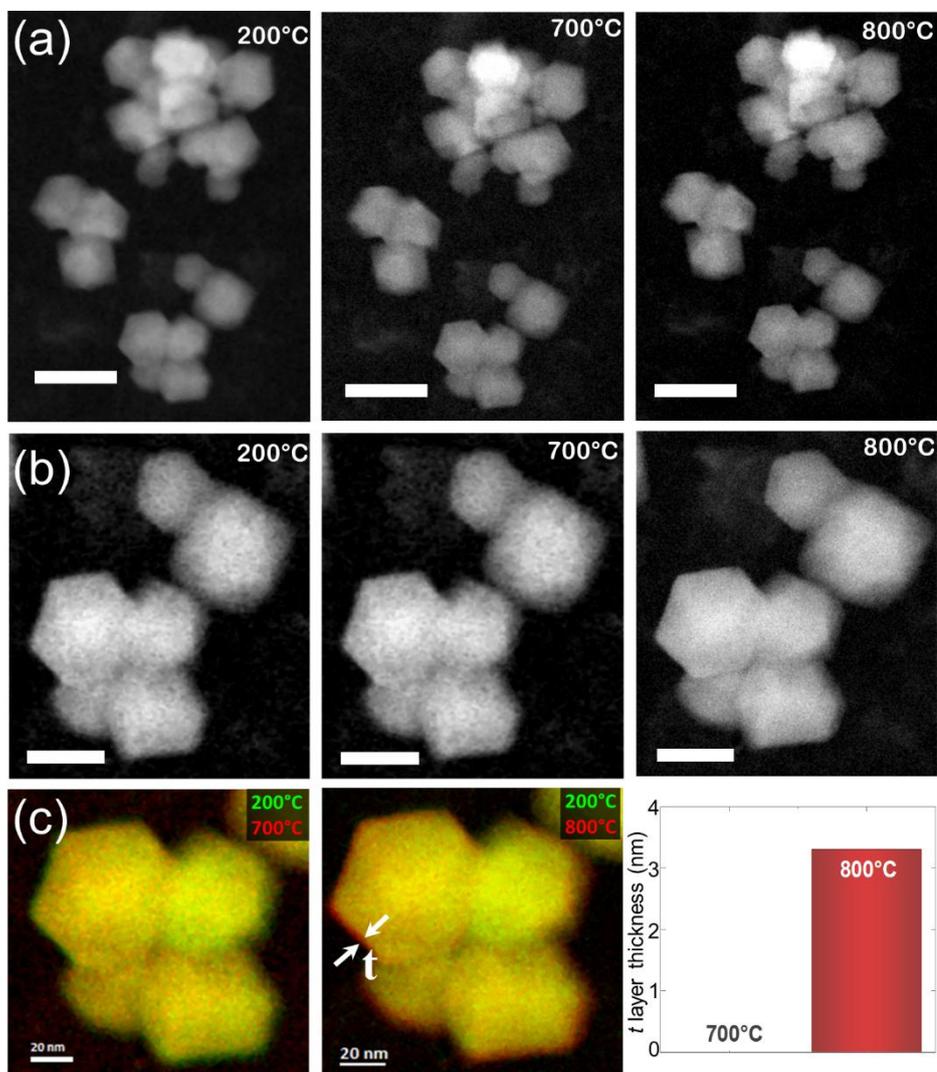


Fig. 2. (a, b) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis of the nanosized RHO submitted to thermal treatment between 200 and 800 °C at different magnifications. Scale bars of 50 and 20 nm for the first and second rows, respectively. (c) Superimposed micrographs acquired at different temperatures show the volume expansion of the region highlighted by red color and denoted by t (adopted with permission from 32, copyright 2023 American Chemical Society).

An expansion of the lattice parameter is not always happening when the temperature increases. In some zeolitic frameworks a contraction of lattice parameters is observed upon the increase of temperature which is called negative thermal expansion.⁴⁷⁻⁵¹ This phenomenon is only observed in some metal oxides, metal cyanides, polymers, and zeolites. In zeolites which show negative thermal expansion

(e.g. CHA, LTA, FAU) upon increasing the temperature, the whole tetrahedra SiO_4 units rotate inside the zeolite structure reducing the unit cell volume.^{19,47,52–54}

The temperature-induced zeolite flexibility is not limited to contractions or expansions of the zeolite lattice; changes within the structure, such as cation movements, are also triggered by temperature variations.^{39,40,55,56} For example, when cadmium-exchanged zeolite RHO (Cd-RHO) is heated up to 300 °C, the pore blocking Cd^{2+} cations relocate from the double eight-ring to the six-ring site, which are 5.7 Å apart.³⁹ This phenomenon was also reported for Ba^{2+} and Sr^{2+} cations, which migrate from the single to the double eight-rings of RHO.⁴⁰ However, for Cd-RHO it was later found that the migration of the cation was associated with the removal of water upon increasing the temperature.⁵⁷ Another well-known example for cationic movements triggered by temperature is the potassium exchanged CHA zeolite (K-CHA).¹⁰ Depending on the temperature, it is possible for the pores of K-CHA to permit access of certain guest molecules due to their interactions with the K^+ cations; the movement of the K^+ cations is described as a temporary and reversible displacement. Upon decreasing the temperature the K^+ cations go back to their original position in the middle of CHA main pores (eight-membered rings), blocking the access of guest molecules.¹⁰ This behavior is very important for gas storage applications and was observed for different zeolitic frameworks.^{55,56,58} Fig. 3 illustrates the effects of temperature and pressure-induced flexibility on zeolites.

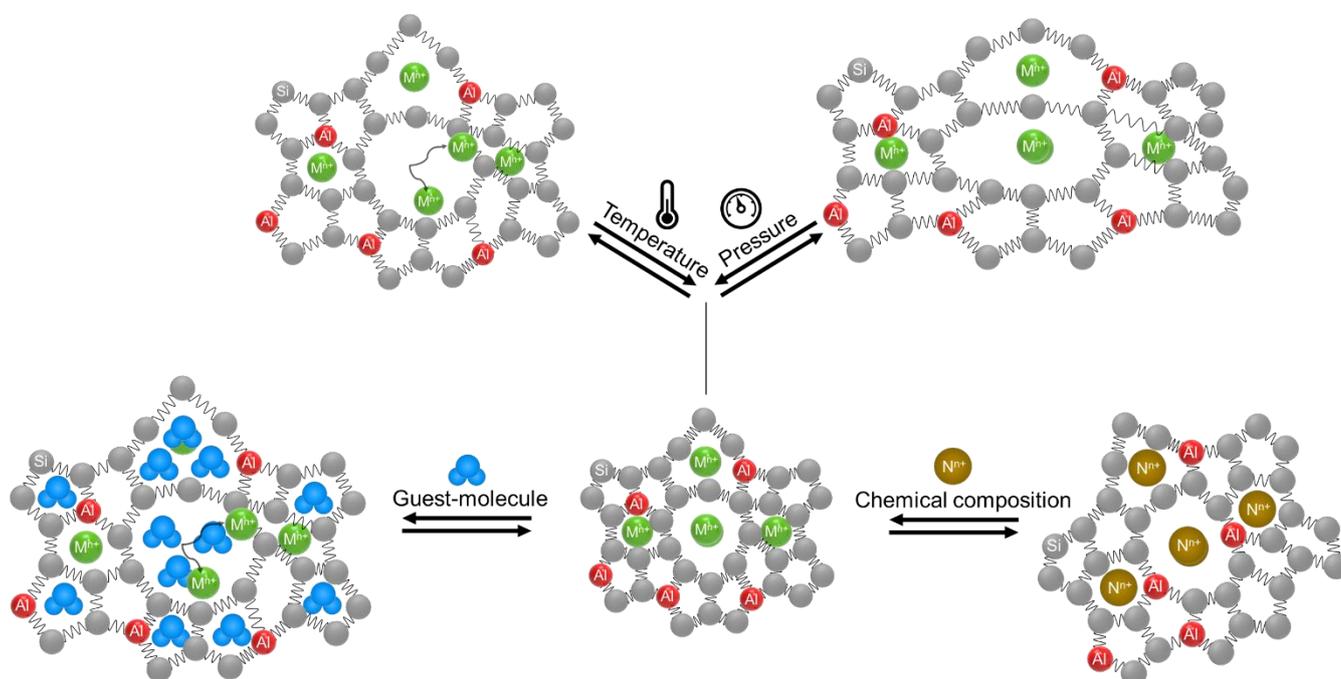


Fig. 3. Schematic illustration of temperature and pressure-induced, guest-induced, and compositionally-induced flexibility in zeolites (M^{n+} and N^{n+} are two arbitrary cations assuming smaller cationic diameter for M^{n+} compared to N^{n+}).

1.1.2. Pressure-induced flexibility

Zeolites undergo alterations in their lattice parameters when subjected to pressure. These alterations are reversible until they reach a maximum pressure, commonly referred to as the 'threshold pressure' in the literature. Beyond that threshold pressure, an irreversible change in the zeolite topology occurs reaching amorphization at high pressures.^{11,33–35,59} The threshold pressure limit is a distinct quality of zeolite frameworks.^{11,33,59} The pressure-induced flexibility observed in zeolites is mainly associated with movements of the rigid tetrahedra around the shared O atoms that behave like hinges within the framework.⁶⁰ The channel content, i.e. adsorbed gasses (H₂O, CO₂, etc.) or extra-framework cations, govern the compressibility of the cavities, leading to different degrees of unit cell volume changes.⁶⁰ For instance, sodium-exchanged LTA (Na-LTA) and natural yugawaralite zeolites can exhibit 18.4% and 15% reversible volume changes, respectively, under non-intrusive medium at a pressure of up to 10 GPa.⁶¹ All zeolites related to the ANA framework family with initial space groups of *Ia-3d*, *I4₁/a*, *Ia-3d*, and *I2/a* for analcime⁶², leucite⁶³, pollucite⁶⁴, and wairakite⁶⁵, respectively change and converge their symmetry to triclinic (*P-1*) under pressures as low as 1.08 GPa followed by a reduction of their average Si–O–T (T = Al or Si) angle from 150 to 123°.^{33,66–68} Similar behavior was observed for NAT type zeolite with a reduction of its Si–O–T angle from 133 to 119° under 8.5 GPa.^{69–71} CHA and MFI zeolites also show 10% and 16% volume variations under pressures of up to 8 GPa, respectively.^{11,33} KFI (ZK-5 type zeolite), RHO and SOD frameworks change their space group symmetry from *Im-3m* to *I4/mmm*, *I-43m*, and *I-43m* respectively, under pressure (Fig. 3).^{26,42,59,72–76}

Both temperature and pressure variations change the energy level of the zeolite structure thermodynamically (ΔG , Gibbs free energy), hence, there is always an energy barrier to see aforementioned structural flexibilities. Temperature changes vary the entropic term of Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). While, pressure changes are directly correlated to the Gibbs free energy and unit cell volume as well ($\Delta G = V\Delta P$). As a result, these structural flexibilities categorized as temperature and pressure-induced flexibility are all of a thermodynamic nature and the necessary energy barriers for these structural changes can be estimated via thermodynamic simulations. More works are needed to determine these energies.

1.2. Guest-induced flexibility

Zeolite flexibility can also be observed as a response to guest molecules adsorption or desorption. This can manifest as changes to the zeolite lattice parameters (framework dynamics) or by relocation of extra-framework cations within zeolite pores (extra-framework dynamics).^{9,77,78} Guest-induced flexibility is highly interesting for gas separation and storage applications.

1.2.1. Framework dynamics

The first attempts to describe guest-induced flexibility in zeolites were done using molecular dynamics simulations.^{79–82} Rigid zeolitic force fields were dynamically modified using transition state theory to include lattice flexibility, and the results obtained by these models were in a good agreement with experimental data.^{79–81,83,84} It was shown that framework flexibility in silicalite-1 (MFI type framework) is responsible of the adsorption of large molecules such as isobutane and heptane with inflection behavior at high loadings,⁸⁰ while enhanced self-diffusivity at low loadings of short alkanes (i.e. methane and *n*-butane) was observed.⁸¹ Framework flexibility is also crucial for aromatics adsorption on MFI zeolite, especially at high pressures.^{84,85} While the use of rigid zeolitic models lead to the underestimation of the aromatics adsorption in MFI zeolite by a factor of two,^{84,85} the use of flexible models to simulate diffusion coefficients of various alkanes in silicalite-1 zeolite resulted in a convergence of experimental and theoretical values.⁸⁶ Recently by using in-situ Integrated differential phase contrast scanning transmission electron microscopy (iDPC-STEM) while adsorbing benzene molecules on MFI zeolite, Xiong *et al.* showed that MFI structure goes through severe deformations giving another proof of guest-induced flexibility in zeolites (see Fig. 4).⁸⁷

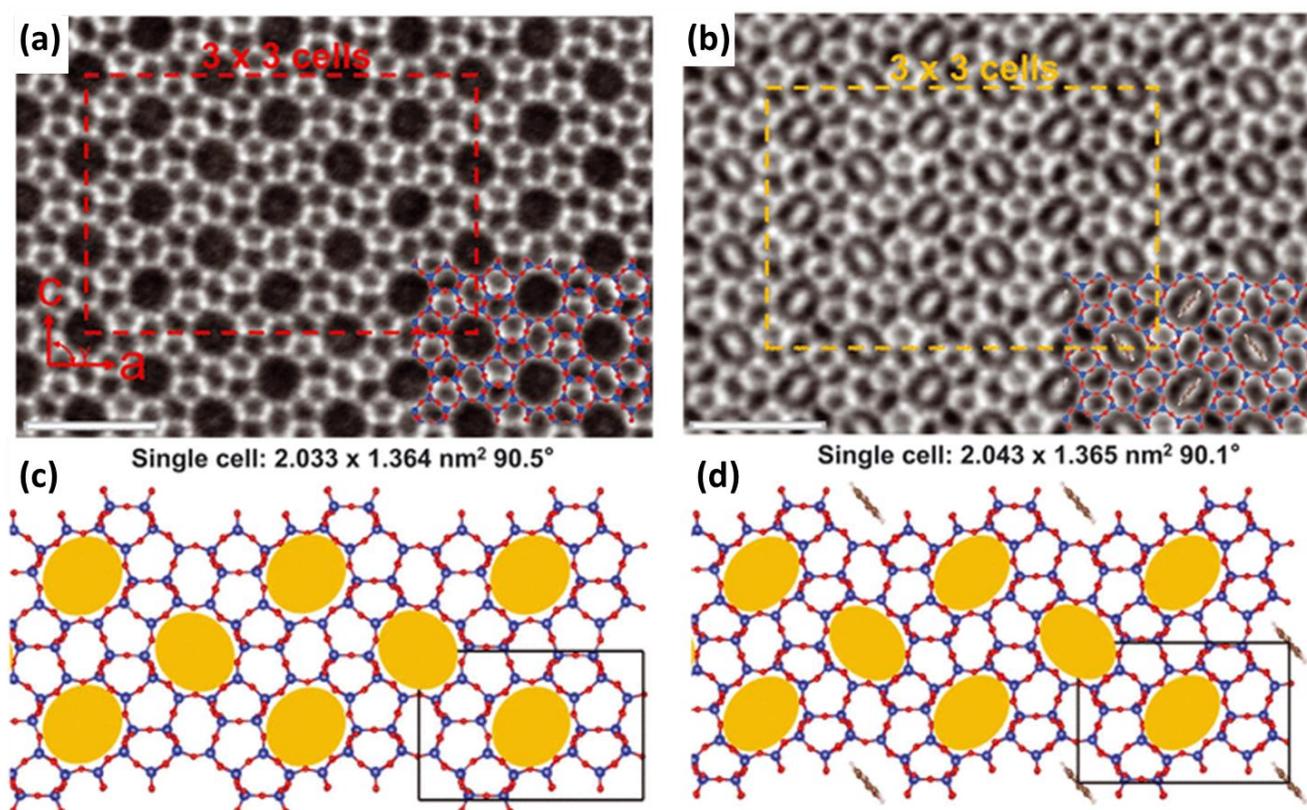


Fig. 4. Integrated differential phase contrast scanning transmission electron microscopy (iDPC-STEM) images of MFI straight channels (a) before and (b) after benzene adsorption. MFI structure

flexibility is also schematically highlighted (c) before and (d) after benzene adsorption. Scale bar, 500 pm (reprinted with permission from ⁸⁷, copyright 2022 The American Association for the Advancement of Science).

For the diffusion of small gas molecules such as methane through AFI and LTL pores, the diffusion coefficients were calculated and measured at high loadings.⁷⁹ Calculations of methane adsorption in LTA zeolites showed that using flexible zeolitic models largely influences the diffusion coefficients and it is dependent on the type of extra-framework cations, the loading of methane in the structure, and the force field parameter used for simulations.⁸⁸ Small-pore ITQ-55 zeolite with minimal pore aperture diameter of 2.4 Å showed expansion of this minimal aperture to 3.1 Å, while allowed for ethylene to be adsorbed. This framework flexibility was used for separation of ethylene from ethane with a selectivity enhanced by a factor of ~100.⁸⁹ Fig. 3 illustrates the guest-induced flexibility in zeolites.

Water adsorption on Na-LTA zeolite showed a phase transition with a small contraction followed by an expansion of the LTA framework, suggesting a hydration-driven flexibility transition, with a two phase region separating hydrated zeolite A from its dehydrated form.⁹⁰ Moreover, it was also observed that preferential water adsorption sites are within the beta cages of zeolite A.^{91,92} Thus, it was suggested that the diffusion of water molecules can only be simulated when flexible models are employed.⁹¹ Furthermore, the S-shaped water adsorption isotherms observed in LTA zeolite resemble those found in another significant category of porous materials: metal-organic frameworks (MOFs), known for their remarkable flexibility.^{93,94} This type of S-shaped adsorption behavior in MOFs is linked to pore expansion induced by adsorbates, which is comparable to the outcomes observed in various zeolites like LTA.^{90,95} These results suggest that zeolites, to varying degrees, may exhibit similar flexibility behavior to MOFs in the presence of guest molecules.

Na⁺ form of zeolite PAU, up to 5% unit cell shrinkage was observed upon dehydration.⁹⁶ Water adsorption in silicalite-1 showed a transition from monoclinic to orthorhombic and this behavior was successfully modeled using flexible framework parameters during molecular dynamics simulations.⁹⁷ Similar behavior was recorded for both water and CO₂ adsorption on Na⁺ and Rb⁺ forms of gismondine (Na-GIS and Rb-GIS) where the ellipticity of the empty pores is reduced significantly by CO₂ and water adsorption to a circular pore shape with up to 14% expansion of the unit cell volume.⁹⁸ Ni-exchanged zeolite Y (FAU framework type) undergoes a series of structural rearrangements during dehydration from 20 to 400 °C. The Ni²⁺ cations start migrating towards tightly confined sites when water molecules desorb, thus a unit cell contraction happens with a strong deformation of the hexagonal prism of the FAU framework.⁹⁹ Similar behavior was also observed for Na-Y sample.¹⁰⁰ Dehydration of zeolites Na-MER, K-MER, and Cs-MER also results in 10, 8, and 7% shrinkage of their unit cell volumes, respectively.¹⁰¹ All

these studies suggested a zeolite framework flexibility in the presence of guest molecules. The most important flexibility observed was the 8% variation of the unit cell volume of RHO zeolite by dehydration, a completely reversible process after adsorption of H₂O or CO₂ molecules (Fig. 5).^{9,43,102–106}

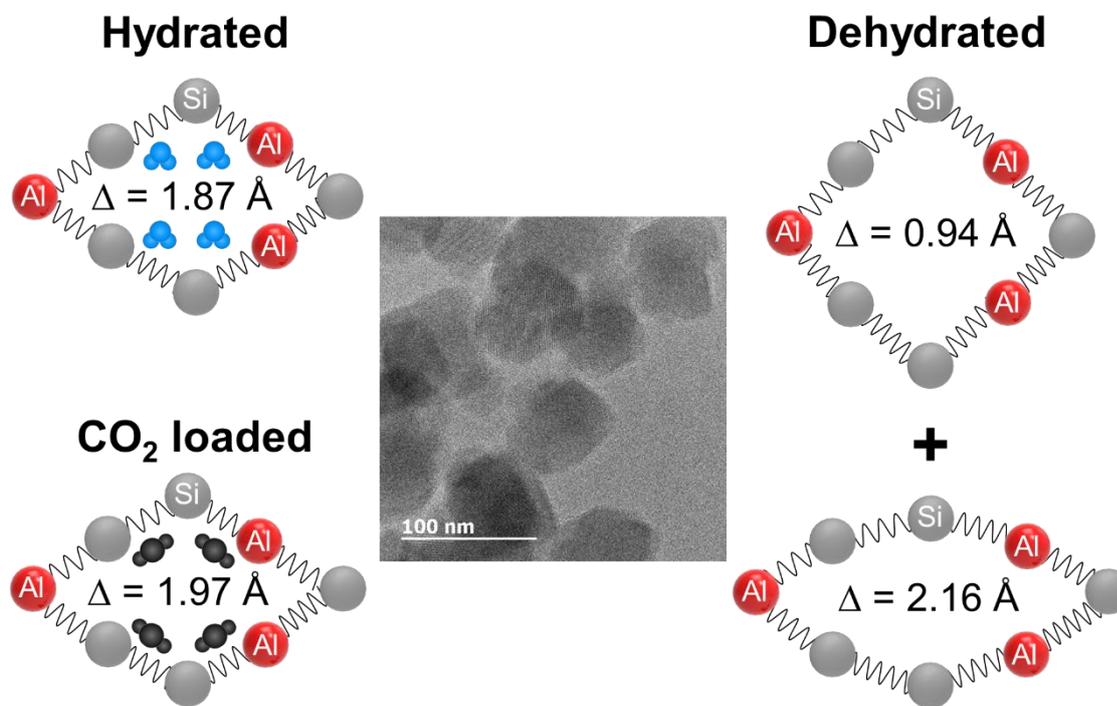


Fig. 5. Schematic illustration of reversible ellipticity of RHO nanosized zeolites upon dehydration and CO₂ adsorption (adopted with permission from 9, copyright 2020 American Chemical Society).

1.2.2. Extra-framework dynamics

Similar to the cation relocations within the zeolite framework triggered by temperature (*vide supra*), it has been shown in the literature that sorption of guest molecules can also trigger such cation movements.^{9,77,107} The migration of Fe³⁺ cations inside the FAU cages after dehydration was confirmed by electron spin resonance spectroscopy.¹⁰⁸ Similarly, the migration of La³⁺ cations from the supercages of FAU to small sodalite cages was observed during dehydration.¹⁰⁹ In Li⁺ and Mg²⁺ forms of ZK-5 zeolite (KFI framework type), the migration of these cations from the center of the hexagonal prisms of their structure to the α -cages was observed after CO₂ adsorption.¹¹⁰ These cation relocations are known as “cation gating” (also known as “trapdoor behavior”), they were proposed simultaneously by P. Wright and P. Webley and co-workers in 2012.^{77,111} It was shown that the gating movement of cations is responsible for opening or closing the pore access depending on the nature of guest molecules.^{77,111,112} In Na-RHO, a migration of the Na⁺ cations was described and CO₂ molecules could pass through the pores between the α -cages while Na⁺ cations migrate from the single eight-membered rings (see Fig. 6a).¹¹¹ In K-CHA; however, K⁺ cations reject or admit the guest molecules based on their attraction and repulsion towards

them and the movement of K^+ cations are completely reversible from and to the single eight-membered rings (see Fig. 6b).⁶ Based on DFT calculations, door-keeper cations have to pay an energy penalty to move away from the center of the pore aperture (thus allows gas admission) in typical trapdoor zeolites such as Cs-CHA, Na-RHO, etc.^{78,104,113} The difficulty of this pore opening process is reflected by the energy barrier associated with the cation movement path from its most stable position (where it blocks the entrance of the pore aperture) to the second most stable position inside the zeolite (where the pore aperture is open).¹¹³ The energy difference between these two configurations can qualitatively feature the actual energy barrier. The presence of polarizable gas molecules that possess some sort of dipole or quadrupole interactions with the door-keeper cations such as CO_2 and CO can substantially lower the energy difference, whereas those non-polar molecules such as N_2 , CH_4 , and H_2 can hardly change the energy difference.¹¹³ Hence, the polarizable guest molecules (e.g. CO_2) induce the door-keeper cations to move out from the center of the pores of the zeolite and selectively admit CO_2 to the CHA or RHO structure while rejecting nonpolar molecules such as N_2 and CH_4 .^{3,10,77,112–115} Similar behavior was observed also for other zeolitic types such as MER and PAU frameworks.^{96,101} Another interpretation of the “cation gating” phenomenon, namely “swinging door” mechanism focuses on the thermal motions of door-keeper cations rather than their movement.¹¹⁶ Based on this interpretation, the amplitude of the thermal motion of the door-keeper cations is always large and thus CO_2 is able to squeeze in while the gate is swinging because of the stronger attraction to the framework (quadrupole interactions of CO_2 and the cations), while nonpolar guests such as methane cannot.¹¹⁶ The consequence of the “cation gating” phenomenon, regardless of which interpretation (“trapdoor behavior” or “swinging door” mechanism) used, is superior selectivity for separation of CO_2 from CH_4 or N_2 (CO_2/CH_4 up to 583 and CO_2/N_2 up to 688 for K-CHA with $Si/Al = 1.9$).¹¹⁷ In summary, a large opportunity is available to design materials for gas separation applications already suggested by many works.^{3,10,77,112–115,118} Fig. 6 shows a schematic illustration of the trapdoor behavior in Cs-CHA proposed by Shang et al.⁷⁷

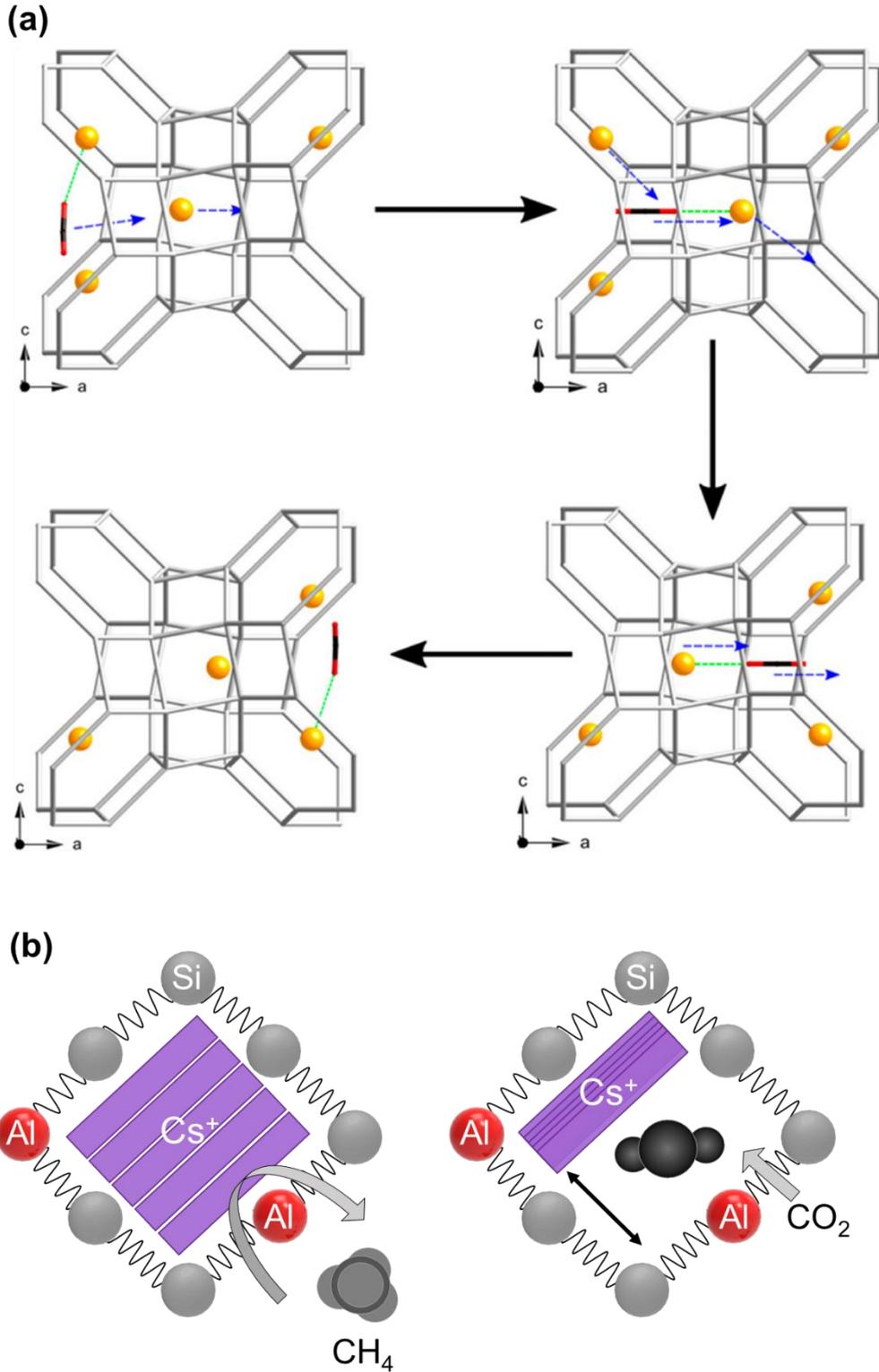


Fig. 6. Schematic illustration of cation gating (a) permanent relocation of Na^+ cations, this is a cooperative mechanism by which CO_2 molecules could pass through a window site between α -cages in zeolite Na-Rho proposed by Lozinska et al. (reprinted with permission from ¹¹¹, copyright 2012 American Chemical Society). (b) reversible Cs^+ relocations namely trapdoor behavior in Cs-CHA proposed by Shang et al.⁷⁷ (adopted with permission from ⁷⁷, copyright 2012 American Chemical Society).

1.3. Compositionally-induced flexibility

Compositional changes in zeolites were also shown to play an important role in framework flexibility. Substitution of Si atoms with Al (framework composition) and the type and content of extra-framework cations inside the zeolite structure (extra-framework composition) can also induce significant changes in the zeolite lattice parameters. The ability to engineer the pore diameter and pore shape of zeolites is another important aspect of zeolite flexibility especially for gas separation applications. A schematic illustration of compositionally-induced flexibility in zeolites is presented in Fig. 3.

1.3.1. Framework composition

Based on computational studies, it was found that the flexibility of LTA zeolite depends also heavily on the Al content.¹¹⁹ Higher Al amounts result in longer Al–O bond lengths and more flexibility of the Si–O–Al bridging angles which creates a more open and more flexible framework.¹¹⁹ In our group, we recently showed for a series of RHO zeolites with different Si/Al ratios and lattice parameters, that changes to the Al distribution within the nanosized RHO samples, represented by the shift in the ²⁹Si NMR barycenter, could be correlated with the CO₂ adsorption capacity.¹²⁰ Changing the Si/Al ratio of RHO from 1.5 to 1.7, resulted an increase of the CO₂ capacity from 1.37 to 2.01 mmol g⁻¹.¹²⁰ This is due to changes in the framework charge distribution, which play a fundamental role in controlling the CO₂ adsorption capacity and should not be overlooked as the cation distribution will always be guided by the negative charge distribution within the framework.¹²⁰

1.3.2. Extra-framework composition

Another important factor affecting zeolites flexibility is the type and content of the extra-framework cations. The calcium-exchanged RHO zeolite is an example: the partial exchange of deuteron cations with calcium cations resulted in 21% decrease in the zeolite's unit cell volume.¹²¹ Depending on the cationic composition, RHO zeolites have shown significantly different unit cell volumes, pore diameters, and pore shapes (see Fig. 7).^{73,102,122} For example, the proton form of RHO (H-RHO) shows a circular pore with a size of 3.9 Å, while a lithium form shows an elliptical pore with a size of 1.9 Å (Fig. 7a) while Si/Al ratio of these RHO samples are the same.⁵

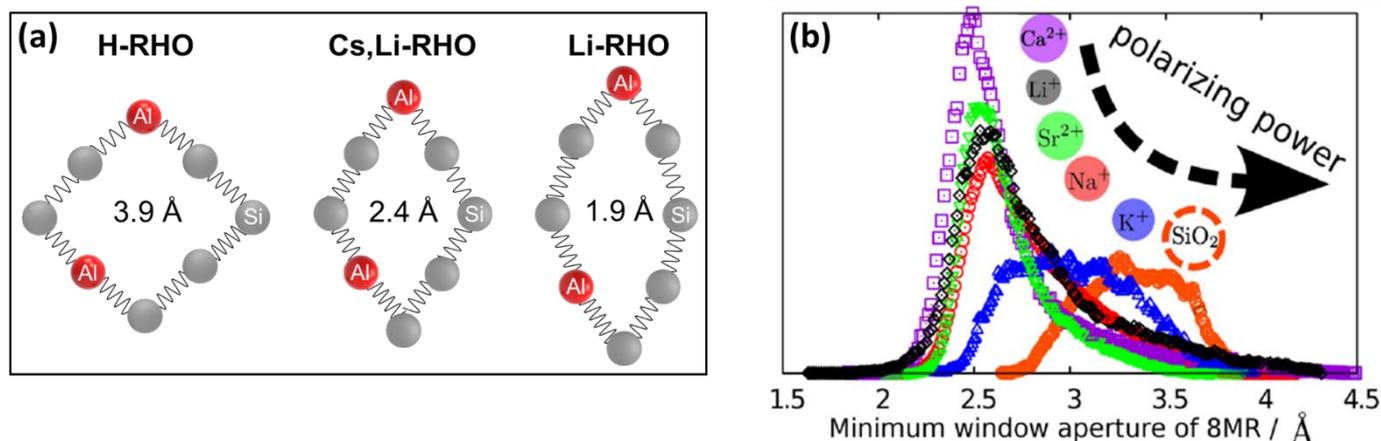


Fig. 7. Ellipticity of zeolite RHO containing different cations (a) based on experiments and (b) based on simulations (adopted with permission from 5 and ¹²³, copyright 2015 and 2016 American Chemical Society).

Similarly to RHO, different alkali-metal (Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+)^{124,125} and alkaline earth metal (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+})¹²⁶ forms of zeolites PST-3 and PST-4 (NAT framework) show significantly different pore shapes and sizes with unit cell volumes ranging from $\sim 2120 \text{ \AA}^3$ (for Li-form of natural NAT) to $\sim 2680 \text{ \AA}^3$ (for Cs-PST-4). Using different alkali-metal cations, it is possible to tune the pore opening of different GIS samples with unit cell volumes of 877, 853, and 851 \AA^3 for Na-GIS, K-GIS, and Rb-GIS, respectively.⁹⁸ Similarly, the unit cell volume of different alkali-metal forms of MER zeolite can be tuned to 1809, 1823, and 1881 \AA^3 for Na-MER, K-MER, and Cs-MER, respectively.¹⁰¹ These changes are due to the tetrahedral tilts and changes in T–O–T bonds and angles (T = Si or Al). The extent of these changes is influenced by the polarizing power of the extra-framework cations and their interaction with the negative charge of the framework due to the presence of Al (Fig. 7b).^{5,123}

2. Evaluation of framework's flexibility of zeolites

A major effort was done by Sartbaeva and co-workers to identify and explain flexibility in zeolites.¹²⁷ They have analyzed the geometry of the structural polyhedra in 14 pure silica zeolites structures determining a *flexibility window* explained by the Coulombic inflation: a repulsion between close oxygen atoms that appeared to play a role in stabilizing the open frameworks of zeolites when dehydrated.^{127,128} The *flexibility index* is defined as the ratio of the maximum over the minimum feasible framework densities for a particular framework type ($\rho_{\text{max}}/\rho_{\text{min}}$).^{128,129} It has been tabulated for most of the known zeolite framework types but remains a limited descriptor of actual framework flexibility because most framework types can be folded along multiple paths starting from the maximum symmetry point, which occurs very often at the minimum framework density.¹²⁹ Furthermore, real zeolite materials tend to occupy the low-density end of the *flexibility window*, so flexibility behavior at higher densities may not play a key role in determining flexibility.¹²⁹ In addition, to compare the flexibility of different zeolitic

frameworks with each other (both pure silica and aluminosilicates), and perhaps to other porous materials like Metal Organic Frameworks (MOF), a quantitative parameter is missing in the literature. To illustrate that, Fig. 8 shows the maximum changes in the unit cell volume observed for the most flexible structures found in the literature. Based on Fig. 8, the changes in the unit cell volume upon different flexibility triggers can be as significant as 20%, which once more proves the importance of understanding flexibility as a way to design smart materials for selective separation or catalysis in porous materials. However, standard protocols are missing in the literature to be able to quantify flexibility in zeolites and compare them with other porous materials. Perhaps, performing in-situ powder X-ray diffraction (XRD) measurements at different temperatures would be sufficient to explore the temperature-induced flexibility of different zeolites. XRD patterns of dehydrated forms of different zeolites with variable compositions (mainly their Si/Al ratios and extra-framework cationic contents) could be used to study compositionally-induced flexibility. However, to study the guest-induced flexibility, the immediate challenge is whether the *probe molecule* is a non-polarizable molecule such as N₂ or Ar or a polarizable one such as CO₂. If a non-polarizable probe molecule is selected, some parts of guest-induced flexibility related to cation gating effect will be hindered. On the other hand, the selection of polarizable probe molecules may interfere with compositionally-induced flexibility due to the dynamics of cations inside the zeolite structure. Additional work is required to establish a protocol for the experimental evaluation of zeolite flexibility. This is of great importance as it will substantially help in designing smart materials for selective gas separation or catalytic applications.

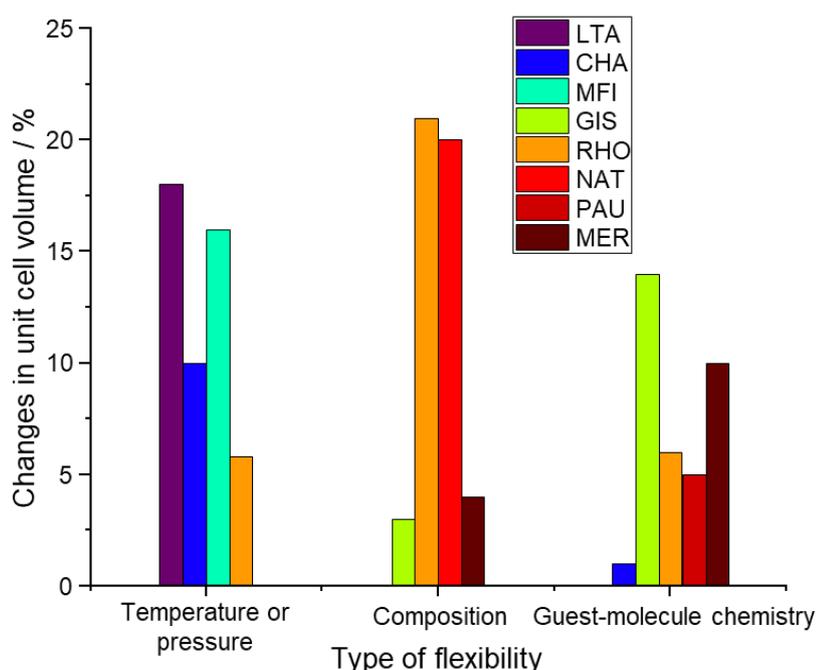


Fig. 8. Maximum changes in the unit cell volume of the most flexible zeolite structures presented in literature.^{5,33,37,41-43,46,61,96,98,101,122,125,126}

2.1. Challenges in characterization of flexibility

To establish rigid protocols for evaluation of zeolite flexibility using different in-situ spectroscopic techniques can be considered as a solution to probe zeolites' atomic order. Temperature-induced flexibility can be assessed using in-situ XRD measurements at different temperatures (ex. from 25 to 800 °C) followed by lattice parameter evaluations by Le Bail and Rietveld refinement. Similar procedures have been reported for RHO zeolite.⁴³ Pressure-induced flexibility can be measured by in-situ XRD when applying a non-intrusive pressure (ex. up to 15 GPa); this also has been reported for several zeolites including LTA, ANA, etc.^{33,61–63,65}

The biggest challenge is to quantify guest-induced flexibility. The guest-induced flexibility can manifest both in the form of changes in zeolites' lattice parameters or by a dynamic movement of extra-framework cations within the zeolites structure. Both these phenomena often happen simultaneously and they are intertwined. As a result, their quantification is not a trivial task. To tackle this issue, the use of in-situ spectroscopic techniques can be considered. In-situ XRD measurements can be considered while different gas molecules are adsorbed on the zeolite samples. Conterosito and co-workers reported on CO₂ and Xe adsorption in FAU zeolite followed by in-situ XRD thus enabling estimation of the lattice parameters and location of extra-framework cations during adsorption and desorption processes.¹³⁰ The in-situ XRD under adsorption of gasses can be coupled with DFT calculations and machine learning approaches in order to provide information concerning the necessary energies for extra-framework cations relocations. Additionally, in-situ solid-state NMR while adsorbing guest molecules can be of importance to clarify the atomic order that contributes to the guest-induced flexibility.¹³¹ Recently, Ilkaeva and co-workers developed a method to follow CO₂ adsorption using in-situ solid-state NMR which shed light on different CO₂ chemisorbed species on SBA-15.¹³² In-situ FTIR while adsorbing guest molecules also illustrates the atomic orders especially those of the silanol sites.^{131,133} As a result, combining all these in-situ techniques (i.e. XRD, NMR, and FTIR), while adsorbing guest molecules, can help to solve the intertwined dynamics between the zeolite framework and extra-framework cations.

For the compositionally-induced flexibility due to the framework's T-site composition, we propose to consider lattice parameters of all silica zeolite of any particular framework as the reference in the future. Thus, the flexibility can be compared to all silica zeolite when Al is replacing the Si and the Si/Al ratio varies. The use of NMR spectroscopy may give insights on the distortion of the framework due to the inclusion of Al tetrahedra by monitoring changes in the quadrupolar coupling constants of ²⁷Al and ¹⁷O nuclei but also the chemical shifts of ²⁹Si nuclei. For the compositionally-induced flexibility due to the extra-framework cations compositions, the zeolites proton form (H-form) can be considered as a

reference and different cationic forms can be compared to the proton form of zeolites at a constant Si/Al ratio. The framework distortions can be examined by conducting Rietveld refinement of the XRD patterns and by monitoring the framework's vibrational bands through Raman spectroscopy. This terminology was used to estimate the changes in unit cell volume of several zeolites (GIS, RHO, NAT, and MER) presented in Fig. 8. Significantly more detailed works are needed to explore zeolite flexibility; however, understanding flexibility in zeolites can open a new avenue for zeolites utilizations.

2.2. Emerging applications related to the flexibility of zeolites

The concept of inducing and controlling flexibility in zeolites can be utilized in different applications. The most prominent one is the bulk separation and purification of small gas molecules such as gas drying (H₂O removal), CO₂ separation from N₂ in flue gas, CO₂ separation from CH₄ in landfill gas separation or bio-methane upgrading, CO₂ separation in dilute streams for direct air capture, etc. The main advantage for using flexible zeolites for gas separation is the ability of fine-tuning the zeolite pore aperture (size and shape) due to compositionally-induced flexibility by using various extra-framework cations. This has been illustrated for zeolite RHO.⁵ In addition, thanks to guest-induced flexibility (extra-framework dynamics – cation gating phenomenon), superior selectivity was observed towards any non-neutral gas molecules such as H₂O (polar) and CO₂ (polarizable molecule – quadrupole moments).^{3,77,78} These separations are important since enormous efforts have been dedicated to develop materials for carbon capture and storage since rising concentration of CO₂ is contributing to the current anthropogenic global climate change.

In addition, gas storage of CH₄, CO₂, O₂, H₂, etc. is of significant importance. Storage of these small gas molecules are extremely hard and can be achieved only under very high-pressures and low-temperatures. Thanks to guest-induced flexibility (extra-framework dynamics), it is possible to selectively admit and store specific gas species at pressures and temperatures near ambient conditions. One example is on the storage of CH₄ and H₂ in CHA zeolite as reported by Li *et al.*¹⁰ The additional advantage of using flexible zeolite for gas storage is controlled release of the guest molecules at ambient conditions (ex. CH₄) which is much safer compared to the traditional gas storage inside high-pressure vessels (usually between 50 – 200 bars); the encapsulation and release of CH₄ gas molecules inside K-CHA zeolite was reported as well by Li *et al.*¹⁰ Another example of controlled guest molecule release is in biological applications where FAU zeolites was used to deliver O₂ as well as other necessary drugs to cancer cells.^{134,135}

Finally, flexible zeolites are also suitable candidates for sensing applications as it was reported before.^{136–138} Wales *et al.* demonstrated that zeolites hold great promise for various sensing applications, as discussed in their work.¹³⁹ In this prospective review, we have highlighted zeolites such as FAU, MFI, MOR, and others, showcasing their remarkable flexibility.¹³⁹ This underscores the idea that understanding

various aspects of zeolite flexibility can also contribute to sensing applications. Another important class of porous materials used as gas adsorbents or sensors, which exhibit structural flexibility, are MOFs.^{140–143} However, zeolites offer advantages in terms of greater chemical and thermal stability (some zeolites can withstand temperatures up to 1200°C compared to 500°C for MOF-related zeolitic imidazolates¹³⁹), environmentally-friendly synthesis methods, and ease of integration into smaller devices such as sensors. This perspective is further supported by the work of Wales et al., who reviewed zeolitic and MOF-based sensors for automotive applications and found that approximately 62% of these sensors were zeolite-based, while 38% were MOF-based.¹³⁹

Zeolites can no longer be considered exclusively as rigid materials. Based on calculations, all zeolitic frameworks can theoretically show different degrees of flexibility.^{26–28} Flexibility in zeolites can be defined as a reversible framework deformation (expansion/contraction) or a dynamic of extra-framework cations, an intrinsic property of zeolitic frameworks due to the spring-like behavior of Si–O and Al–O bonds and the distortion of Si–O–Al and Si–O–Si angles as a response to an external trigger such as gas adsorption/desorption or a change in temperature or pressure. Based on these different triggers, we categorized zeolite flexibility into three categories: 1. temperature and pressure-induced flexibility, 2. guest-induced flexibility, and 3. compositionally-induced flexibility. Evaluation of zeolite flexibility is another challenge which can be solved by combining in-situ spectroscopic techniques (XRD, FTIR, NMR), gas adsorption measurements, high resolution microscopy, DFT calculations, and machine learning techniques. Understanding and quantifying zeolite flexibility can open a new avenue of applications such as gas separation, gas storage, drug delivery, sensing applications, etc.

3. Conclusions and outlook

In this perspective article, the origin of zeolite flexibility is revealed based on understanding of spring-like features of Si–O and Al–O bonds and the distortion of Si–O–Al and Si–O–Si angles as a response to an external trigger. Different aspects of zeolites' flexibility were presented including the main triggers of zeolite flexibility identified as temperature and pressure, guest-molecule, and composition variations. By tuning the temperature and zeolite composition, one can tune the size and shape of zeolite pores. Guest molecule chemistry can also be used to design smart zeolites to capture/separate targeted molecules. The zeolite flexibility can be either at the unit cell level (changes in the lattice parameters) or at the atomic level (relocation of extra-framework cations within the zeolite). Further works are necessary to develop experimental methods to quantify, normalize and compare the flexibility of different zeolite frameworks and perhaps for other porous materials. By gaining a deep understanding of zeolite flexibility, we can manipulate and control zeolites adsorption and separation properties. Moreover, this newfound ability opens up exciting possibilities for diverse applications, such as drug delivery and sensing. In drug delivery,

the flexible nature of zeolites can be exploited to design innovative carriers that respond to specific stimuli, releasing therapeutic agents precisely when and where needed. Similarly, in sensing applications, zeolite flexibility can be leveraged to create advanced sensor materials with improved sensitivity and selectivity. These sensors can detect and quantify various substances, ranging from gases and liquids to biomolecules, enabling their application in environmental monitoring, healthcare, and other industries. Overall, the growing understanding of zeolite flexibility opens up a vast array of emerging applications in diverse fields.

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