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Flexibility of dehydrated zeolite-X pores quantified by quantum modeling

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This talk is abundantly illustrated with video animations produced from ab-initio simulations of ordered zeolite materials. In a preliminary effort to parameterize the zeolite structure types, we identify and illustrate comprehensively here the crystal-chemical degrees of flexibility of the porous framework of dehydrated zeolite-X structures. Single-crystal X-ray diffraction (XRD) structure refinements of essentially ordered crystals with experimental stoichiometry $Cd_{0.46}Al_{0.92}SiO_4$ and $Na_{0.92}AlSiO_4$ exist in the literature [1, 2], but no quantum optimization of a zeolite seems to have been performed so far. Ab-initio optimization with VASP of corresponding fully ordered models with compositions $CdAl_2Si_2O_8$ and $NaAlSiO_4$ in space group Fd-3 exposes both the correctness of these X-ray structures and the fact that they can be modeled nowadays by quantum methods. Agreement is within XRD experimental uncertainty for atomic coordinates and within 1% for cell data. We then extend the ab-initio simulations to hypothetical dehydrated zeolite-X structures with alkali [IA] and alkaline earth [IIA] metallic substitutions ([IA] = H, Li, Na, K, Rb, Cs; [IIA] = Be, Mg, Ca, Sr, Ba). Fully ordered model structures in space group Fd-3 with compositions $[IA]AlSiO_4$ (Z=96), $[IA]Na_{11}Al_{12}Si_{12}O_{48}$ (Z=8) and $[IIA]Al_2Si_2O_8$ (Z=48) were optimized with VASP. Due to different ionic or atomic radii, those substitutions deform the zeolite framework in steps, exposing its degrees of flexibility (see figure below). We derived second-degree least-squares expressions for each atomic coordinate of each atom, as well as for the a cell edge, as a function of the relevant radius. Local structure views with same scale in pixels/Å were then produced and assembled into 3D-animated movies, which will be presented at the session. For each of the three compositional series studied, as the unit cell volume increases with radius size, rotations of tetrahedra enable a lateral expansion of the double six ring (D6R) towards a more hexagonal configuration, while a tilt adjusts its height. Least-squares expressions were also derived to express the total free energy E of these zeolite formulations (per Bravais or primitive cell) as function of the a lattice parameter or the cell volume V. Plots of E vs. a with the period of the substituted [IA] or [IIA] element within each series as the third axis are discussed. Such plots may guide attempts to synthesize zeolitic materials with mixed binary [IA]-[IIA] chemical substitutions. Finally, based on the spatial descriptors obtained here for the various zeolite materials studied, we will discuss the progressive evolution of the catalytic activity of dehydrated zeolite-X compounds with alkali and alkali earth metallic substitutions. All ab-initio calculations were executed with VASP4.6. All VASP input, interpretation of VASP output, structure modeling, plots and animations were performed with Materials Toolkit.

[1] Kim, Y. et al. (1993). J. Phys. Chem. 97, 12663-12664.

[2] Kwon, J. H. et al. (1996). J. Phys. Chem. 100, 13720-13724.
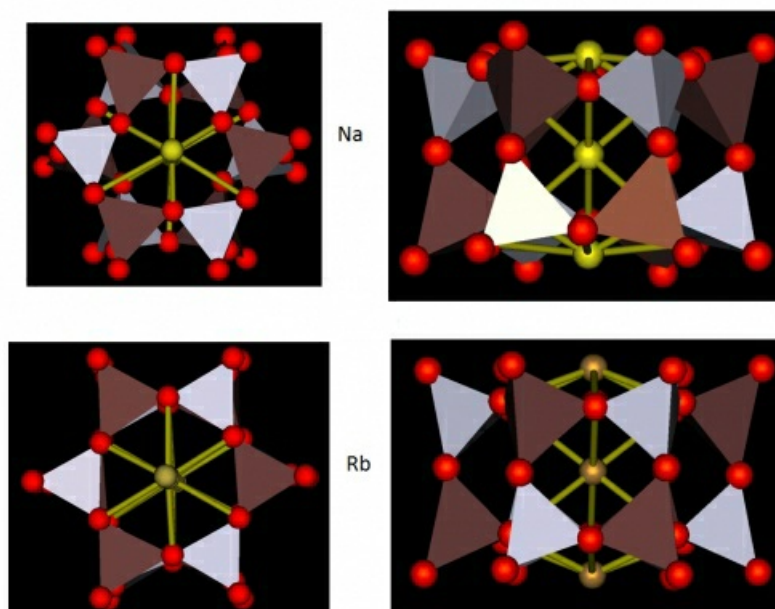
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