A DFT-based study for optimizing dehydrated clinoptilolite models and their cation distributions for environmental remediation: Part I

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ABSTRACT

Since its advent, density functional theory (DFT) has been perceived as a black box, and with the increasing complexity of electronic structure codes, researchers often default to preset values for their input variables without investigating how this can lead to calculations that are far from accurate. In this work, we attempt to identify a reliable set of input parameters within the CP2K code to study the cationic distribution in the natural mineral, clinoptilolite, for ultimately investigating the adsorption of emerging contaminants at the surface level of these structures. Initially, hundreds of dehydrated clinoptilolite models for two samples were generated to study the aluminum distribution and its effect on the extra-framework cations such as Na^{+} and Ca^{2+}. Nine different functionals were tested in the framework of dispersion correction; it turns out that the B97-D3 functional is the best overall functional for this system partly due to its ability to minimize the self-interaction error. Additionally, it is observed that while Na^{+} exhibits a preference for the presence of Al at T2 and T3 sites and avoids it at T1 sites, Ca^{2+} tends to favor being present at the 8-membered ring (8MR) of channel B. In this case, Ca^{2+} does not avoid the presence of Al at T1, T2, or T3 sites. Analyzing the Na-dominated clinoptilolite was computationally demanding. However, a clinoptilolite that is dominated with Ca^{2+} or a combination of Na^{+} and Ca^{2+} cations was a challenging task due to a noticeable bad behavior of the self-consistent field (SCF) loop, possibly stemming from the incomplete basis sets or specific cationic sites. To this end, basis sets optimizations were performed, and different possible cation sites were investigated, which led to better and faster SCF convergence for Ca^{2+} being the predominant cation along with Na^{+}.