



Adsorption of phosphates and phosphoric acid in zeolite clinoptilolite: Electronic structure study



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ABSTRACT

Phosphate (H_2PO_4^- and HPO_4^{2-}) and phosphoric acid adsorption in zeolite clinoptilolite was examined by electronic structure methods. The interactions of the anionic species with Lewis basic sites of the zeolite framework prevail over the interaction with extraframework cations (Na^+ , Ca^{2+} , Mg^{2+}) and the strength of the hydrogen bonds is quantitatively assessed by the shift of the ν_{OH} vibrational frequencies. Brønsted acid sites compete with cations in the binding of H_2PO_4^- and H_3PO_4 . The B-channel of clinoptilolite, which is accessible via eight-member ring windows, provides more favorable coordination to phosphates and phosphoric acid in presence of cations. The dianions (HPO_4^{2-}) reside only in channel B, coordinated to a divalent cation (Ca^{2+} , Mg^{2+}) and forming one hydrogen bond with a framework oxygen atom, acting as Lewis basic site. The monoanion H_2PO_4^- finds best coordination in channel B by adsorption at a Na^+ cation and forming two hydrogen bonds. The negative charge of phosphate anions is efficiently delocalized over the framework oxygen atoms. The adsorbed phosphates and phosphoric acid acquire more polarized P–O bonds compared to the free molecules and anions. In the presence of a Brønsted acid site, phosphoric acid is coordinated to the zeolite framework by four hydrogen bonds, the additional hydrogen being provided by the acid site. Hydrogen bond formation is essential for stronger binding of phosphoric acid and phosphate anions and the presence of Brønsted acid sites together with Lewis basic sites would increase zeolite adsorption capacities.

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1. Introduction

Zeolite clinoptilolite is the most widely used adsorbent for water purification and waste removal from agricultural and industrial sources [1–5]. It is abundant in nature as a mineral with high purity, though some sources contain admixtures of iron oxides, mordenite and quartz [3,6]. Synthetic analogs with the same topology, e.g. LZ-219, CIT-3, have been produced for reliable testing [7,8]. The framework of aluminosilicate zeolites and zeolite-like microporous materials, e.g. aluminophosphates, is built by corner-sharing tetrahedra TO_4 , where the tetrahedral atom is Si and Al for aluminosilicates, or P, Al, Si for silicoaluminophosphates [8]. Each oxygen atom bridges adjacent tetrahedra and this implies a ratio $\text{O/T} = 2$. The tetrahedra join to form secondary building units typical for a particular framework topology and as the angles T–O–T may vary in a broad range, micropores, channels and cavities are

intrinsic property of zeolites [8,9]. Due to their unique opened framework architecture and the presence of regularly spaced cavities and channels, zeolites are able to host different species, and the diffusion inside the channel is restricted by the size of the windows to the micropore channels [9]. The presence of an aluminum atom at a tetrahedral site of a silicate framework, $\text{Al} \rightarrow \text{Si}$ substitution, assigns a formal negative charge, which is compensated by an extraframework cation, or a proton in the form of bridging hydroxyl group $-\text{Al}(\text{OH})-\text{Si}-$ (Brønsted acid site). In natural zeolites, such as clinoptilolite, alkali and alkaline-earth cations are the most common compensating extraframework cations (Na^+ , Ca^{2+} , Mg^{2+}) [3]. These cations are loosely bound to the framework and easily exchangeable. Most of the zeolite applications as adsorbents are related to cation exchange, but the adsorption and retention of anionic species was also reported and it is of utmost importance [10–13]. Phosphates leak from soils to surface waters and are a major concern for natural water quality [11]. They can be retained by zeolites or other adsorbents. The interaction of phosphates with zeolites however, is not limited to water purification [14]. The phosphate species or phosphoric acid

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introduced in zeolite frameworks may alter their catalytic properties in a versatile way [15]. Phosphatation can improve hydrothermal stability and enhance catalytic activity, e.g. in catalytic cracking [16], but phosphates act as a catalytic poison for the reaction of selective catalytic reduction of nitrogen oxides [17]. The Brønsted acid sites play a major role in the interactions with proton-acceptor adsorbates. Zeolite frameworks bear also basic properties via the bridging oxygen atoms, the strongest basic sites being related to the areas in proximity to Al → Si substitution. Phosphates as anions can be retained by the extraframework cations; H_2PO_4^- and HPO_4^{2-} and phosphoric acid are also able to interact with framework oxygen atoms via hydrogen-bond formation. Experimental studies established that phosphate anions in clinoptilolite were held predominantly as Na-phosphates, NaH_2PO_4 and NaHPO_4 , followed by hydrated free H_2PO_4^- , while the concentration of CaHPO_4 and MgHPO_4 was much lower [11]. Intramolecular bond between H_3PO_4 and framework oxygen (Al–O–Si) or a Brønsted acid site was suggested for ZSM-5 [15]. This type of interaction was found to be reversible, though subsequent thermal treatment results in partial loss of Brønsted acid sites via AlO–Si bond breaking and formation of AlOH groups. Computational studies confirmed hydrogen-bond formation between phosphoric acid and a Brønsted acid site in ZSM-5 and different adsorption sites were examined [18]. The adsorption of phosphate anions and the interaction of phosphates and phosphoric acid with the extraframework cations and the Lewis basic sites in zeolite frameworks have not been examined by electronic structure methods so far. Zeolite clinoptilolite has advantages as a model system for examining adsorbent-adsorbate interactions, because all of the extraframework cation sites are accessible through the two-dimensional channel system. The structure of ZSM-5 comprises two channel types of nearly identical size, while clinoptilolite has a two-dimensional channel system with three straight channels A, B and C, among which A is the widest channel accessible via 10-member ring (10 MR) with free aperture of 5.5×3.1 Å, followed by channel B, accessible by symmetric 8 MR with free aperture of 4.1×4.1 Å, as shown in Fig. 1a. Channel C, which intersects both A and B channels, is accessible via an asymmetric 8 MR with free aperture of 3.4×2.8 Å, Fig. 1b [8,19,20]. Clinoptilolite has a flexible framework and the cation site occupancies as well as the cell parameters and the free apertures of channels vary with temperature and composition to a larger extent than in other zeolites [21]. Considering the size and shape of the window openings, it can be expected that phosphate species would be able to find optimal coordination inside the clinoptilolite channels. The present study aims to distinguish the interaction of phosphoric acid, phosphates and polyphosphates

with the extraframework cations, the Brønsted acid sites and the Lewis basic sites in the channels of clinoptilolite by density functional theory (DFT). Two approaches were applied: (i) QM/MM in ONIOM [22], where a selected array of the structure is treated with high accuracy using a quantum mechanical method and the surrounding part of the structure (low-layer) is described by molecular mechanics, (ii) periodic model study with DFT using the PBE density functional. The use of finite models via the ONIOM approach is justified, because the clinoptilolite unit cell is of relatively big size. It includes 108 atoms without extraframework cations and adsorbates, so ONIOM has the advantage of lower computational costs and also avoids a strict repetition of the adsorption sites, as the population of adsorption centers does not follow the periodicity of the unit cell. With periodic boundary conditions the crystal structure and the long-range properties are assessed. In the present study, the binding energies of phosphates and phosphoric acid are calculated for the lowest energy positions of Mg^{2+} , Ca^{2+} and Na^+ cations in the channels of clinoptilolite with relevant Si,Al orderings. The role of the framework acid/base properties on the strength of the adsorption complexes is elucidated. IR frequencies and frequency shifts upon adsorption are estimated. The adsorption of polyphosphates is also considered, provided that the sizes of the polymeric species allow penetration and diffusion in the channels of clinoptilolite.

2. Structure and methods

The extraframework cation sites have been determined in early crystallographic studies of mineral samples and were summarized by Alberti [19] and Koyama et al. [20] for alkali and alkaline-earth cations. In Channel B there is one site, located in proximity to the T2–O–T2 bridges, denoted as B site, according to the notation of Godelitsas et al. [23], see Fig. 1a. The B-site is coordinated by the O1 and O10 framework oxygen atoms. In the large channel A, the site relevant for adsorption is the A1 site, also positioned close to the T2–O–T2 bridges and linked to O2 atoms from the side eight-member-rings. This site leaves free space in the channel for diffusion of adsorbates. Other sites in channel A were found at the channel center or close to it, and they were occupied mostly by small-size hydrated cations. Sites near the channel center, when available to extraframework cations in zeolites, cannot be expected to form a stable adsorption site [24]. All structural models employed in the present study bear no residual charge: the extraframework cations are balanced by the framework charge and the most stable Si, Al orderings as reported in previous studies were

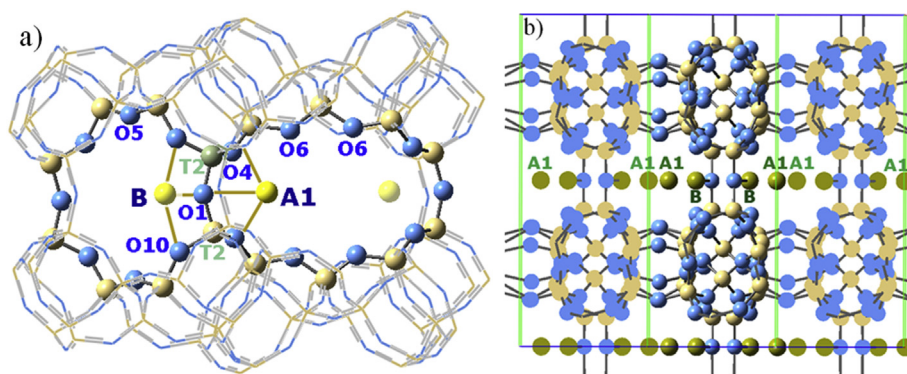


Fig. 1. The clinoptilolite structure, a) viewed along [001] with the main extraframework cation sites in channels A and B. b) viewed along [100] with the C channel and the extraframework cation sites. Oxygen atoms are blue, Si – light brown, extraframework cations are light green. The replicated cells are shown with matted colors. The notation of cation sites of ref. 23 is used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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