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Influence of carbonate species on elastic properties of NaX and NaKX zeolites

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ABSTRACT

The inter-relation between chemical and mechanical properties is demonstrated regarding Young's modulus variation of the NaX and NaKX (83% exchange Na/K) zeolites upon carbonate formation or CO_2 adsorption. The force field (FF) approach is based on the combination of known FFs for the zeolite atoms, alkali cations, CO_2, and carbonate atoms. Contrary variations of the Young's modulus are obtained in NaX upon CO_2 adsorption (increase far from CO_2 condensation conditions) or carbonate formation (decrease). Higher decreases of the Young's and bulk moduli are predicted for K-exchanged form that was not yet tested experimentally.

1. Introduction

The requirement of high mechanic resistance and thermal stability remains the important condition of successful application of aluminosilicate zeolites or aluminophosphates upon hard conditions of many industrial catalytic processes. However, these mechanic properties are less systematically studied till now that is partly a consequence of their complex and expensive measurements [1,2 and Refs. therein]. Another difficulty of experimental studies is the absence of the anisotropy in the modulus measured and the absence of the possibility to exactly assign respective variations of the modulus (Young's, bulk, shear) to any specific phenomenon in the oriented zeolite structure. The complexity of zeolite synthesis is due to the necessity of numerous high temperature steps, *i.e.*, burning of template molecules, dehydroxylation, *etc*., each of them could produce various defects. But the relative impact of each type of defect on the mechanic resistance and thermal stability is not yet classified or evaluated comparing to other possible reasons of modulus variations upon the reaction conditions. As the example we can consider the structural changes due to the impact of adsorbed species like pyridine [3], water [4–6], alcohols [2], carbon dioxide [7,8], halocarbons [9–11], *etc.* Such changes can be also a consequence of an adsorbate penetration into the framework [2]. However, some of the molecules (pyridine, water) stimulate redistribution of cations between the available cationic sites. Evidently, the possibility of recoding such changes depends on characteristic residence times. Exchange between the cationic positions with new methods like PFG NMR self-diffusion measurements shows rather small time-of-life of cations in different positions, *i.e.*, between 40 and 150 ms for Li [12], that is too fast to be recorded during the measurements of LiZSM-5 modulus. Could the cation drift with respective adsorbate redistribution be the reason of increased or decreased bulk, shear, or Young's modulus? In order to influence various zeolite moduli and to allow their measurement, the cation must possess much longer residence time at the new position.

In the relevant work [13] the drift of Na cations from SIII′ sites in NaX and from SII and SI′ sites in NaY was interpreted due to only CO_2 influence. Detailed consideration of the important work [13] is presented in the Discussion. The authors admitted that CO_2 is physisorbed in the NaY and NaX zeolites at 400 K according to the molecular dynamics (MD) calculation. This assumption is justified for NaY [14] but not for NaX [15,16]. The presence of symmetric CO_3^{-2} species has been quantitatively shown in the NaX zeolite up to 573 K [15,16]. To summarize, the arguments in [13] do not prove that NaIII cations diffuse together with CO_2 in NaX. In addition, one can ask the following question: can the carbonates cause a cation displacement? The Na^+ and CO_3^{-2} ionic species are linked by stronger Coulomb forces and could demonstrate the higher stability and the longer time-of-life as compared to the "Na^+–CO_2" complex. Then common drift of the cation and carbonate can be

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the reason of cation displacement from its crystallographic position and of a bad balance of the electrostatic forces between the cations and the framework. The latter can lead to a weakening of the whole system. This phenomenon can be accompanied by bulk (BM) and Young's (YM) moduli variations. Such YM change owing to the chemical reasons, *i.e.*, carbonate formation, has not yet been studied, while the YM drop due to physical processes, for example, upon carbon dioxide adsorption close to critical conditions for CO_2 condensation in pores, was recorded [7]. We believe that this YM change [7] can be discussed in the same terms as presented for the shortage of NaX crystals [17] using NLDFT method [18,19]. Some arguments about the similar origins of both results [7,17] are presented in the Part S1 of Supplementary Materials. The data in the publication [7] related to the YM variation upon carbon dioxide could serve as a landmark for the influence of carbonate formation. The carbonates can be both symmetric and asymmetric in NaX [15].

Asymmetric carbonate species are not an exclusive feature of the NaX zeolite. In NaCaY they are formed if Ca exchange is higher or equal than 46% [14]. In alkali MeETS-10 forms the band splitting of asymmetric carbonates is as large as in NaX ($350\ cm^{-1} = 1715\ cm^{-1} – 1365\ cm^{-1}$ [16]). The high catalytic activity of MeETS-10 with supported Pt in aromatization reaction of hexane is connected with the quantity of CO_2 desorbed [20]. The desorption at temperatures of 422 K (Me═Li) or 503 K (Me═Cs) can be caused by carbonate forms whose high and low frequency peaks of CO_3^{-2} vibration bands in the MeETS-10 are strongly split, *i.e.*, show the highest interval between the peaks of $312\ cm^{-1}$ for Li and 325/362 cm^{-1} for Cs [20]. According to the direct relation [21] between the band splitting (BS) and distortion of carbonate species

$$\delta = \sum_{i=1,3} (|| \mathrm{C—O}|_i — |\mathrm{C—O}|_{aver}|) \qquad (1)$$

where $|\mathrm{C—O}|_{aver} = (\Sigma_{i=1-3}|\mathrm{C—O}|_i)/3$, one could predict that these BS values correspond to asymmetric species with δ around 0.13–0.15 Å using the linear function fitted with any computational approach [21]. Two types of the bi-dentate species were successfully observed *via* IR spectroscopy in Rb- and Cs-forms but thermo-desorption showed two peaks of desorbed species for all the forms [20].

Some anomalies in the adsorption by cationic form zeolites upon CO_2 adsorption allow discussing the participation of the carbonate species. The CO_2 adsorption was observed at the K/Na exchange higher than 17% which should already exclude the CO_2 penetration due to blocking of the 8R windows by K cations of larger radii [22]. Earlier [23], we have demonstrated that K cation moves from its crystallographic position KII in 8R of the NaKA zeolite as a result of the interaction with carbonates. Such displacement effectively opens the 8R window and provides CO_2 passing as well as any gas component of appropriate kinetic diameter if an activation barrier of adsorption is small at the temperature of the study. In the experiments with binary mixtures both components should pass the window if the sieve effect is not involved owing to different sizes. The presence of carbonate species was approved in the NaKA system *via* IR technique [22] while a possible presence of both mono- and bi-coordinated carbonates in NaX was first experimentally shown in 1963 [15]. In accordance with our recent work [21] we would like to use the terms of symmetric and asymmetric carbonate species (instead of mono- and bi-coordinated ones) whose distortion is measured by the splitting of the symmetric and asymmetric bands of carbonate vibrations and whose equilibrium can be driven by external pressure of any gas [15]. Asymmetric carbonates were optimized in NaKA in accordance with experimental IR data (band shift or BS and intensity ratio) [23]. However, the NaKA model can be applied for comparative adsorption studies being constructed with pseudo unit cell locally violating the Loewenstein rule [23]. That is why the YM values cannot be properly calculated in NaKA to estimate its relaxation in the presence of asymmetric carbonates. If the cations are more effectively displaced from their positions upon the influence of asymmetric species than upon that of symmetric ones, then the YM calculation in the presence of symmetric carbonates will provide the lower boundary for possible influence of asymmetric species on the Young's modulus. To obtain the lower boundary, the influence of symmetric carbonates on the NaX cations could be tested and compared with that of the asymmetric ones in NaKA.

In the earlier work [23] we have shown using density functional theory (DFT) with periodic boundary conditions that K cations can be displaced by asymmetric carbonates from their crystallographic positions in NaKA zeolite. In this work we have undertaken such analysis to check the influence of symmetric carbonates at the level of empirical force fields (FFs). In the next parts we have described the computational details and the selected models. Then carbonate geometries and cationic displacements are compared as well as Young's moduli for selected models.

2. Computational details

The FAU structure was constructed first using the spatial subgroup *F23* and subsequently shifting the crystallographic origin from (0, 0, 0) to (1/8, 1/8, 1/8) [24,25]. Then it was allowed to relax without symmetry (P1 group). Hence, we have worked with the primitive cell of smaller volume as much as 4 times. Empirical core-shell FFs with GULP3.4 code [26] have been applied using periodic boundary conditions. The final FF is the combination of the Catlow [27–29] or Sierka–Sauer [30,31] FFs for the framework atoms, Bush FF for alkali cations [32], Maurin FF for CO_2 [33], and the Rohl–Wright–Gale for carbonates [34,35]. The latter contains three- and four-term potentials that control the O—C—O angular distortions and deviations of the carbonate anion from planarity, respectively. Bush FF delivers the parameters of Buckingham potential between alkali cations (Na, K cores) and the shell of the O framework atoms of the T–O–T′ type, where T or T′ = Si and/or Al [32]. Additionally, we made only necessary assumptions to unify the FFs. We accepted: (1) *A*, *ρ*, *C* parameters of Buckingham potentials $Ae^{-r/\rho}–C/r^6$, between three possible O types[1], *i.e.*, carbonate (or CO_2) oxygen shell, hydroxyl oxygen Al—O(H)—Si core, and framework oxygen T–O–T′ shell, are the same for all pairs with the parameters from Ref. [29,32]; (2) the alkali cations (core only) interact with all O shells (carbonate oxygen shell or framework oxygen T–O–T′ type shell) *via* the same potential as with hydroxyl oxygen Al—O(H)—Si core. This combined FF [27–29,32,34,35] was applied to the case of none, one, or two carbonate species adsorbed per unit cell (UC) of the NaX zeolite. Carbonate was modeled as a product of the reaction between water and CO_2 so that two protons were located at the framework that also provided a neutral UC. Calculated elastic moduli for NaX with CO_2 or with carbonates were compared to the experimental data [7] and discussed.

The NaKX zeolite model was constructed by 83% (5/6) exchange of the Na cations at the II, II′, and III positions by K ones while a part of NaI (in double 6R prisms) remains at their positions where they do not contact with carbonate (or CO_2) species. It is a usual practice due to a hard exchange of the NaI cations by the others. The final NaKX and NaX formulae correspond to $Na_4K_{20}Si_{24}Al_{24}O_{96} \times nH_2CO_3$ and $Na_{24}Si_{24}Al_{24}O_{96} \times nH_2CO_3$, respectively, $n = 0–2$.

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[1] In the case of Catlow FF: $A = 22764$ eV, $\rho = 0.149$ Å^{-1}, $C = 27.879$ eV×Å^6, if $0 < r < 12$ Å.