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Deblocking effect of carbonates and hydrogen carbonates in the alkali form zeolites with narrow pores

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ABSTRACT

The alkali forms of MeRHO zeolite (Me = Li, Na, K, Cs) are studied theoretically at the DFT/PBE level using projector augmented wave method (PAW) and periodic boundary conditions (PBC). The equilibrium positions of the Me cations have been optimized at the D8R prisms where they control molecular transport in the pores of MeRHO. The effect of the displacement of alkali cations has been estimated due to coordination of both carbonate or hydrogen carbonate anions that can also induce RHO framework transformations. Admitting the CO_3^{-2} and HCO_3^- formations *via* the reactions between H_2O and CO_2, the energy of respective reactions was evaluated at various Si/Al moduli and analyzed regarding possible influence on the gas adsorption.

1. Introduction

Growing interest to the alkali exchanged form zeolites with narrow pores and 8R windows, which control molecular passing, can be explained by a possibility to develop a superior adsorbent for gas mixture separation [1–11]. For example, high CO_2/N_2 separation coefficients have been predicted in KCHA [1] and have been evaluated from individual isotherms of CO_2 and N_2 in NaKA [2]. Later, other KFI, ZK-5 [10,12] and RHO [4–5] zeotypes with the narrow pores have been involved into consideration of the effects which are important for adsorption: (a) the 8R flexibility in RHO [4,5] and (b) the cationic positions in CHA [1,3,6,13], KFI, ZK-5 [10,12], or RHO [4]. While the separation of CO_2 mixtures remains one of the central directions for future zeolite applications, where both the (a, b) effects are important, we would like to pay attention to the aspect of the formation of the carbonates whose influence has not been yet accurately estimated and whose relevance can be questioned. Their easy formation in alkali forms upon CO_2 adsorption has been discovered many years ago *via* IR spectroscopy [14–17]. Often, the carbonate presence is ignored owing to a relatively small concentration. However, such a small fraction of the carbonate species can be important for adsorption properties if the carbonates change appreciably the positions of bulky cations like K and Cs which block the diffusion through 8R rings. Similar N_2 blockage by even smaller Na cations in NaHRHO at low temperature has been recently discussed [4]. The dramatic increase of CO_2 adsorption was observed for the cationic content of NaKA zeolite (K/Na exchange > 17%) when the gas uptake should be negligible [2]. In such a situation the calculation of separation factors from individual isotherms becomes unreliable (because the carbonates modify the zeolite) and requires the analysis of the mixtures which is generally more complex.

The question under what conditions the carbonates may be formed, i.e., Si/Al ratio, water concentration, framework type etc., is thus useful practical topic which we need be concerned with. Its solution could determine the conditions and zeolites for which the gas separation from CO_2 requires an application of IR tools for parallel control over the carbonate presence. The formation of the carbonates in the zeotypes with a low Si/Al ratio like Linde type A (LTA) model (LiA [18], NaA [2,18–20], NaKA [2,20]), X (LiX [14], NaX [14,17], NaHX [17], KX [8,14], RbX [14,15,17], CsX [17], NaCaX [17], MgX [15,21], BaX [7], CoX, ZnX [21]), with higher Si/Al ratio like Y (nano-NaY [8], KY [9], CsNaY [9], NaCaY [16], MgY [21], CaY [17,19,21], BaY [8,21], NiY [22], MnY, CoY, ZnY [21]), LiRHO [4], and LiZK-5, NaZK-5 [12][1] is well documented. However, less evidences are accumulated for CHA, and KFI zeotypes with high Si/Al ratio. We can separate this long list into two parts which possess (LTA or A, RHO, CHA, KFI, and ZK-5 forms) or not (X and Y types) the 8R windows for which the deblocking effect had been registered [2,12]. As the deblocking effect we would like to name the capability of any species (of carbonates and hydrogen carbonates as proposed

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[1] The formation of hydrogen carbonates had been also found in other cationic ZK-5 forms but no illustrations are available there with the exception of Li and Na [12].

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by us [24] or possibly of CO_2 molecules [3,25]) to drift together with the cations and thus to vary the effective diameter of the 8R windows which can be blocked by the cation. The gas diffusion in the FAU types (cationic forms of X and Y frameworks) is limited by the larger 12R windows and no information is available about possible blockage of these rings by the large alkali cations. The difference between the cubic RHO (Fig. 1a and b) and LTA (Fig. 1c) types is in the D8R and 8R connections between the α-cages, respectively.

Our first attempt [24] to visualize the Na and K cation displacement upon the carbonate influence has been shown in the NaKA zeolite with Si/Al = 1 with DFT methods and periodic boundary conditions (PBC). The clear deviation of the K cation from its crystallographic site in the 8R plane was observed owing to the K coordination to the carbonate. However, the NaKA example has been selected for such illustration of K mobility from experimental point of view, i.e., owing to high CO_2/N_2 separation coefficients for this zeolite [2]. From computational point of view the LTA model (two α-cages in Fig. 1c) is sufficiently large for our computational facilities as a consequence of its Fm3c space group and Si/Al alternation [26]. These spatial features lead to a conventional cell which contains eight α-cages and around 800 atoms in total that requires huge computer resources consumption. In order to decrease the dimension of the model the smaller pseudo-cell of two α-cages (like in Fig. 1c) has been used [24] in which the Loewenstein rule was violated, i.e., at the positions far from 8R window with K cation. We have shown that the zeolite models, which are constructed with a violation of the Loewenstein rule, are less stable in thermodynamic sense [27] but can be acceptable for a comparative study. Such solution can be easily illustrated for another less complex system. The highest Si/Al ratio of 2.5, 3.9, and 4.7 is possibly related to the Y, RHO, and ZK-5 types, respectively, where carbonate's presence is confirmed using IR spectroscopy [4,8,9,22,25] or to Si/Al = 3.125 in NaCHA where TGA method had been used to confirm their formation [23]. Hence, the carbonate behavior at higher Si/Al moduli than that of LTA (Si/Al = 1) [24] is of interest. The CHA and RHO forms had been obtained within wide Si/Al range from 1.04 to 50.4 [6] and from 3.36 [28] to 14 [29], respectively. The reasons for this RHO choice are: 1) the presence of the cations in the 8R window which control molecular transport in the pores like the same in LTA [2] and CHA [1,3] types; 2) the smaller unit cell (UC) which can be directly calculated with DFT methods and PBC; 3) the presence of the carbonates at least in LiRHO [4]; 4) the higher Si/Al ratio as compared to the Si/Al = 1 in our previous work [24]. The illustration of cation displacement upon the carbonate influence for properly selected RHO models within variable Si/Al range is hence the first goal of this work.

The second goal is understanding of the difference between the carbonate and the hydrogen carbonate ion (also named often as the bi-carbonate) formation because usually one of them is revealed in IR spectra with next transformation to another form [14–17]. The

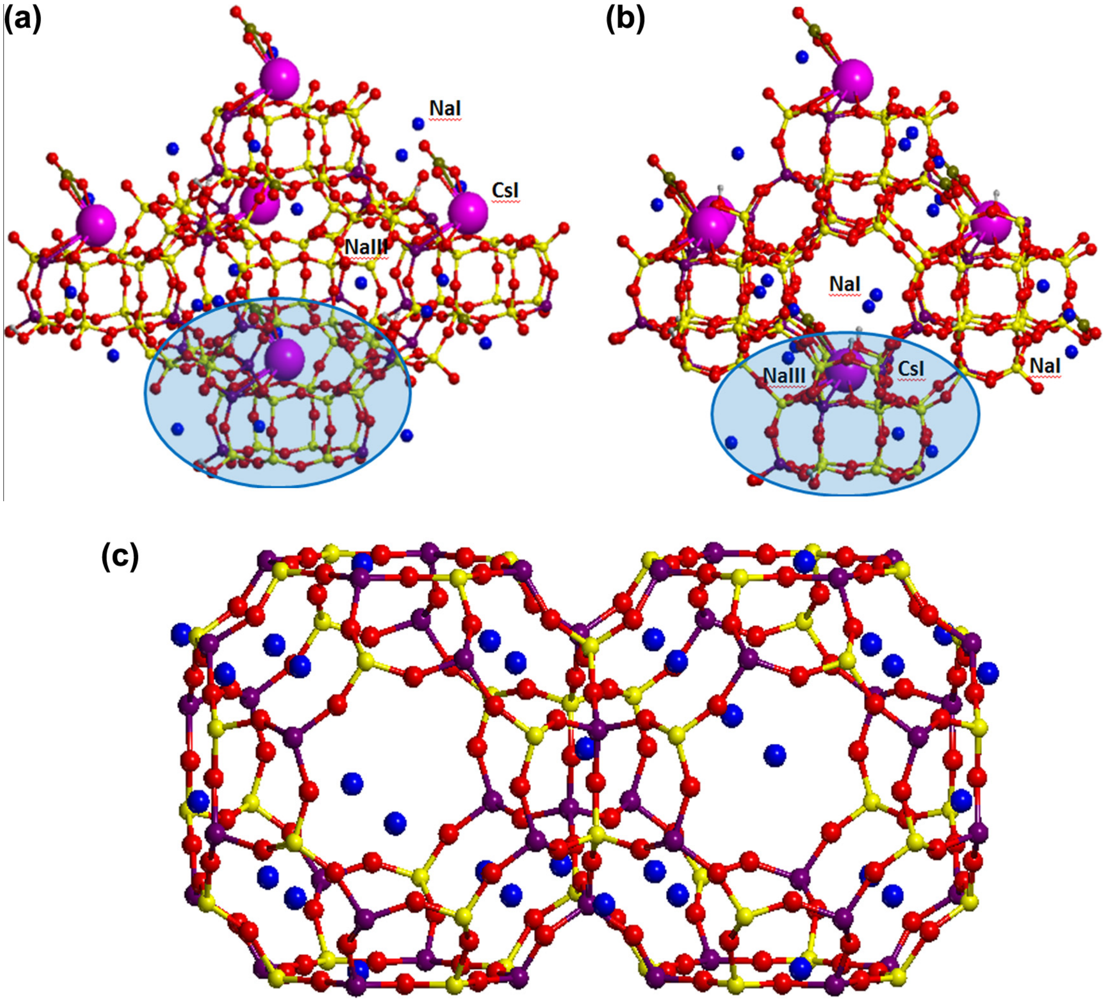

Fig. 1. The Na5Cs1RHO zeolite structure with adsorbed carbonate and protons (a, b) together with NaA fragment (c). The positions of NaI, NaIII, and CsI cations are shown (a, b). The atomic colors are given in magenta light, blue, red, yellow, magenta, and grey for Cs, Na, O, Si, Al, and H, respectively. The ellipses show the D8R fragment which is used below for illustration in Fig. 2 of the site occupancy by the cations in the RHO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)