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Location and reactivity of extra-framework cation in the alkali exchanged LTL zeolites: A periodic density functional study

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ABSTRACT

Locations and reactivity of extra-framework alkali cations, Li^+, Na^+ and K^+, in LTL zeolite framework have been investigated by the periodic density functional theory (DFT). The relative stability of six different cation sites, A–F, was systematically studied for all AIs. The calculated results show that the energetically preferable sites for these alkali cations locate inside the cancrinite cage (B), at the center of the nonplanar 8-membered ring (MR) window (C), and at the edge of the nonplanar 8-MR window connected with the 12-MR windows (D). Among the three stable cation sites, only site D is able to directly interact with a CO molecule. The calculated adsorption energy and the C–O stretching frequency decrease when the cation size decreases. The adsorptions of CO on mono-, di-, and nona-cation systems (Si/Al = 35, 17, and 3, respectively) are not significantly different because of the large pore size of LTL zeolite and the small occupancy of the adsorbate. In addition, the photonic antenna prototype system representing by proflavine dye-zeolite L has been simulated to investigate the orientation of the adsorbed dye inside the channel of zeolite host. Proflavine dye interacts with K cation locating at the D site, the adsorbed dye is found to be slightly bent and aligned in parallel with the channel of LTL zeolite. This causes changes of photophysical properties of the adsorbed dye compared with its gas phase.

1. Introduction

Zeolite L or LTL has attracted much attention for its applications in catalysis [1–3] and photonic devices [4–7] because of its unique one-dimensional pore structure. The LTL zeolite frameworks consist of cancrinite cages that are linked by double 6-MRs (D6R) to form columns in the c-direction. These columns are connected to each other by sharing oxygen atoms resulting in a non-planar 8-MR, and forming a part of 12-MR windows [8], as shown in Fig. 1. The channel of LTL zeolite has a barrel-like shape with a large diameter from 7.1 to 12.6 Å [9,10]. Depending on its topology, LTL is an excellent choice for hosting dye molecules due to its ability to force the dyes to align in the channels without any aggregation. Moreover, the photochemical and photophysical properties of these encapsulated dyes are remarkably altered when compared to those observed in solution and other zeolite types [7,11–16].

Besides structural characteristics of zeolites, the chemical properties can also affect their performance. The proton (Brønsted acid) and extra-framework cations (Lewis acid) of LTL zeolite can influence the chemical and optical properties of adsorbing molecules [4]. In the case of an extra-framework cation, its position can be easily exchanged with other cations and the cationic dyes [11,17] and this exchange behavior can induce stronger electric fields compared to that corresponding to the presence of a proton. Because of this remarkable property, many studies have been focused on the cation-exchanged LTL zeolites [3,9,11,18–22].

Knowledge of the location and acidity of extra-framework cations is fundamental to understanding and rationally modifying the activity of zeolites. An experimental study has reported that LTL zeolite has six possible locations for cations: site A is inside double 6-MR, site B is inside the cancrinite cage, site C is at the center of nonplanar 8-MR, site D is at the connecting area between nonplanar 8-MR and 12-MR windows, site E is midway between two adjacent nonplanar 8-MRs, and site F is at the center of 12-MR windows [23,24]. Among various cations, alkaline (Al) ion is the common extra-framework cation in zeolite L used for hosting dye molecule in particular for photonic device application [11,13,20]. Fois et al. theoretically reported that fluorenone dye interacts with K ion in LTL zeolite by pointing its oxygen atom to

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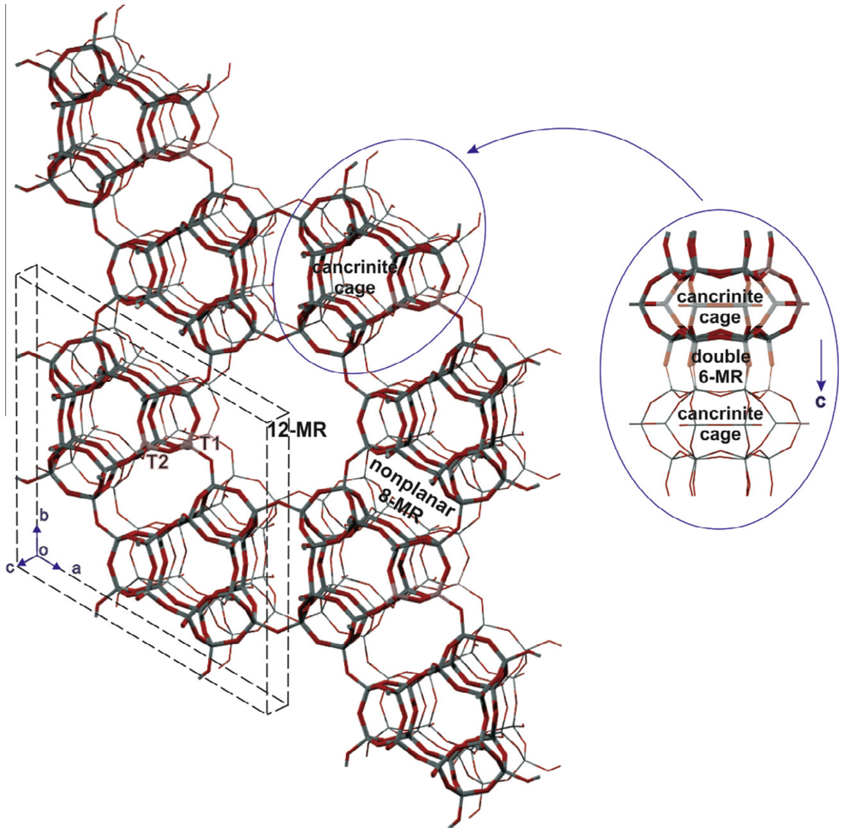

Fig. 1. Structure of LTL zeolite projected along the *c*-axis [left] and composite building units of LTL zeolite framework, cancrinite cage and double 6-membered ring (6-MR) [right]. Framework Si, Al and O atoms are depicted in gray, pink and red colors, respectively. Thick lines in the box represent atoms in a unit cell of LTL zeolite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

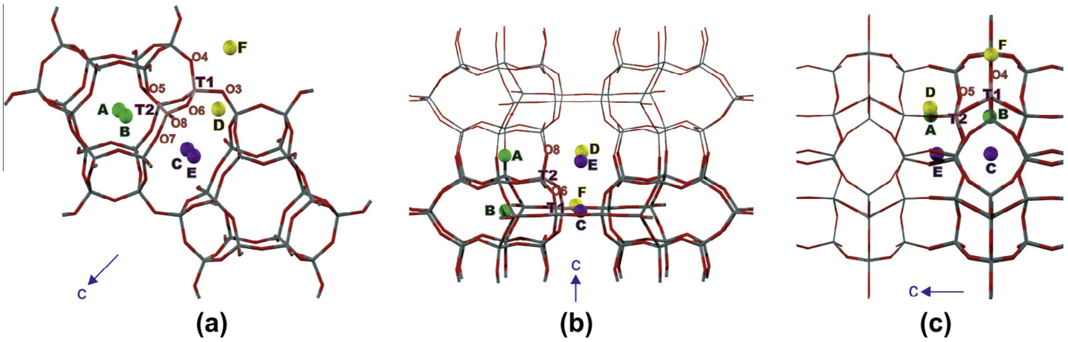

Fig. 2. The possible locations of extraframework alkali cation (Li, Na and K) in LTL zeolites (a) view along the c-direction, (b) perpendicular view of the c-direction and (c) side view of the c-direction. Green, purple and yellow balls represent the alkali cations located in the cancrinite cage, nonplanar 8-membered ring, and 12-membered ring window of the LTL zeolite framework, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

K (K^+---O = dye) [20]. The position of K ion in zeolite framework is therefore expected to affect the location, stability and orientation of the adsorbed dye. In experiment, it has been reported that potassium ions occupy different B, C and D sites of K-LTL and Ba, K-LTL zeolite for different Si/Al ratios [17,19]. Sites B and C were suggested as unexchangeable sites for the larger cations such as Rb^+ and Cs^+ [25]. However, in the case of gallosilicate K-LTL zeolite, site C was found to be accessible for larger cations [21] which is surprisingly contradictory to the case for normal K-LTL. Therefore, atomic level details of cationic locations on the zeolite and their activities after adsorption need to be explored.

Theoretical studies have been successfully performed to investigate the coordination structures of different extra-framework cation sites. A number of alkali-exchanged zeolites were studied such as ZSM-5 [26–28], FAU [29,30], FER [31] and CHA [32]. For LTL zeolite, we recently studied the locations and Brønsted acidity of isomorphously substituted [Al, B, Ga]-LTL zeolites by using periodic density functional theory (DFT) calculations [33]. In the case of Lewis acids, there are only a few theoretical studies dealing with alkali-exchanged LTL zeolites [13,20,34], and the local structures and chemical properties of extra-framework cation sites in these zeolite types have not been intensively reported.

Generally, the activity of an extra-framework cation is evaluated by its interaction with a weakly basic molecule. Carbon monoxide (CO) is frequently used as the weak base because it is highly sensitive to cations in zeolites. Recently, combined experimental