

UNDERSTANDING CO ADSORPTION IN FAUJASITE ZEOLITE

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Abstract - This study explained CO adsorption in extra-framework Li⁺ cation of faujasite (FAU) zeolite with Si/Al = 2.69 using density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and dispersion correlation method. Li⁺ cation locations were investigated by CO probe molecule via hydrogen bonds. The adsorption energies of CO show that the energies do not depend only on Li⁺ site but also on Al concentration and their positions. The vibrational frequency of CO was calculated by using ω/r correlation method and the calculations were compared with the experiment results to bring a clearer understanding of the mechanisms of CO adsorption in faujasite zeolite as well as the others zeolites.

Key words - Li⁺ cation; FAU zeolite; CO adsorption; extra framework zeolite; Density Functional Theory.

1. Introduction

Carbon monoxide is produced from incompletely oxidation of carbon-containing compounds such as coal, fossil fuel and so on, this concentration in the air has been increasing and causing big problem to human health because of interaction with hemoglobin in blood and environment, especially global warming due to CO + O₃ → CO₂ + O. In order to cut off the atmospheric level of CO and reach minimizing cost, many strategies are being investigated and considered: adsorption in metal oxide [2,4], adsorption in porous solid materials, such as zeolite [3,8], metal organic framework [14]. Porous materials have shown a various structure that are amenable for adsorption and storage a lot of gases, CO₂, CO, N₂, H₂... Whereas, there is still lacking method to understand CO adsorption in zeolite. Therefore, looking for mechanisms of CO adsorptions and their properties in zeolite are challenge and attraction works.

Zeolites are microporous crystalline structures that contain aluminum, silicon, oxygen and some extra-framework cations (Na⁺, K⁺, Li⁺...) in their framework. In among if them Li⁺ cation have used frequently because of small size thus site-specificity and only effect from local framework but not effect from all zeolite framework [9]. These materials show promising application for gases adsorption, including CO because they are low cost, porous structure and high thermal stability. Up to date, there are approximately 200 distinguishing structural zeolites that are formally recognized by International Zeolite Association [12] and the number of zeolite is increasing every year. One of zeolites which are suitable framework for CO adsorption is faujasite (FAU) [1,13]. This structure consists of sodalite cages connected through hexagonal prisms or double six-ring (D6R). The 12-membered ring pores has a relative diameter approximately 7.4 Å. The structure with six different positions of cation in faujasite is shown in Figure 1.

In this study, we have explored Li⁺ cation position in

vicinity of AlO₄⁻ tetrahedral, the geometries of CO adsorption at these Li⁺ sites, and energies of CO adsorption on extra framework Li-FAU were studied using DFT method. These results bring us mechanism to understand CO adsorption in zeolite.

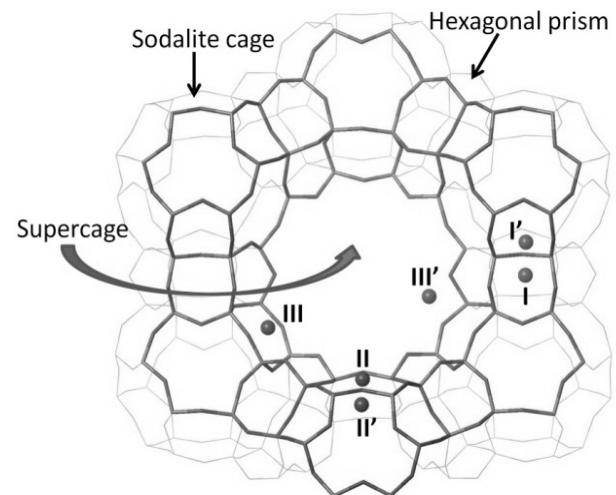


Figure 1. The structure of faujasite (FAU) and extra framework cation (purple colour) sites are labeled following Roman numerals [5]

2. Computational Methods

Li-FAU and CO adsorption complexes geometries were performed within the periodic DFT model employing the Vienna Ab initio Simulation Package (VASP) program [6], PBE exchange-correlation functional [11] and dispersion correlation [5]. The plane wave basis set with a kinetic energy cutoff of 400 eV was used. Brillouin-zone sampling was restricted to the G point. The FAU zeolite was represented by a reduced unit cell with the composition Si₃₅Al₁₃Li₁₃O₉₆ (Si/Al=2.69:1) and cell parameters $\alpha=\beta=\gamma=60$ degree and $a=b=c=17.37$ Å [7, 13].

All CO adsorption energies were performed by DFT method with PBE functional. The adsorption energies were calculated following [8]:

$$E_{ad} = E_{CO-Li-FAU} - (E_{CO} + E_{Li-FAU}) + \Delta ZPE$$

Where E_{CO-Li-FAU}, E_{CO} and E_{Li-FAU} are the total energies for the adsorption complex, isolated CO molecule, and isolated Lithium FAU, respectively. ΔZPE is zero-point energy correlation which is calculated within and the harmonic approximation using 6 degrees of freedom of CO.

CO frequency adsorbed on Li⁺ cations in FAU zeolite have reliably applied using the ω/r correlation method [8]. According to this method, CO stretching frequency, ν_{CO}, is expressed as a function of bond length of CO, r_{CO}, following:

$$\nu_{CO}[CCSD(T)] = a * r_{CO}[DFT] + b + \Delta v$$

Where $\Delta v = v - \omega$ is anharmonicity, a and b were calculated from CCSD(T) and DFT method on some sets of cluster model. In this work, a= -6508.18, b= 9623.4 and Δv = -31.6. Equation becomes:

$$v_{CO}[\text{CCSD(T)}] = -6508.18 * r_{CO}[\text{DFT}] + 9623.4 - 31.6$$

3. Results and discussion

3.1. Li^+ cations location in FAU

Table 1. Li^+ distribution in FAU zeolite

Distribution type	I	I'	II	III'
D1	3	2	8	0
D2	4	0	8	1



Figure 2. Three type of site II in FAU zeolite, II_2Alasy (a); II_2Alas (b) and II_1Al (c). Silicon, oxygen, aluminum, lithium atom are colored in grey, red, black and purple colour, respectively.

Table 2. Optimized geometries parameters of CO adsorption on different Li^+ cation sites

Li^+ Site	R(O _f -Li ⁺) (Å)	R(CO) (Å)	R(Li ⁺ -C) (Å)
II_2Alsy	1.948 2.058 2.190	1.13862	2.31467
II_2Alasy	1.939 1.991 2.186	1.13892	2.33301
II_1Al	1.982 2.137 2.498	1.13858	2.30666
III'	1.897 1.930	1.13589	2.24755

Al³⁺ substituted Si⁴⁺ in FAU zeolite with the ratio Si/Al = 2.69, Li⁺ were introduced in the vicinity of Al sites to balance charge of zeolite structure. In this calculated unit cell, FAU zeolite structure contains 35 silicon atoms, 13 aluminum atoms, 13 lithium atoms and 96 oxygen atoms. We have found that there are two types of Li⁺ cations distribution according to the position (Figure 1), shown in Table 1. In both of these types, the Li⁺ cations distributed almost in site II because this site is in supercage which is large pore size. Li⁺ cations can coordinate with either two (site III') or three oxygen atoms (site I, I', II) in framework FAU zeolite. The distances of Li⁺ cations with framework oxygen atoms (R(O_f-Li)) in different site are shown in Table 2. The distances are similar in range from 1.8 Å to 2.4 Å. In order to investigate Al effect to Li⁺ location and CO adsorption complexes, the Al concentration and position are reported in site II. There are three types of site II, shown in Figure 2, with different Al content, in which, one Al in six membered ring (denote II_1Al), two Al in six membered ring with asymmetry (denote II_2Alasy) and two Al in six membered ring with symmetry (denote II_2Alas) coordination.

3.2. O interaction with Li⁺/FAU zeolite

Carbon monoxide is one of the most molecules which

probe alkali metal cation exchange in zeolite because CO is high sensitivity to metal cation location in framework zeolite. Therefore, CO has been widely used in adsorption and FTIR studies [7].

Table 3. CO adsorption energies and vibration frequencies on different sites of FAU zeolite

Li^+ Site	E _{ad} (kJ/mol)	vCO(cm ⁻¹)
II_2Alsy	-28.16	2181
II_2Alasy	-25.98	2179
II_1Al	-28.98	2182
III'	-44.49	2199
Experiment[3]	-27.50	2183

The CO adsorptions on Li-FAU depend on the ratio of Si/Al, Li⁺ cations site which coordinate with framework oxygen atoms, and charge from framework. CO can interact with Li⁺ cation via Li⁺...CO complex (C-end) or Li⁺...OC complex (O-end) by electrostatic interaction but it was reported that C-end was more stable than O-end because of negative charge on C atom of CO causing by Li⁺ cation and zeolite framework[10]. In this work, all CO adsorption complexes with C-end were investigated. However, CO cannot interact with Li⁺ cations in site I and I' because they located in small cage in which inaccessible for CO molecular. Thus, CO adsorption complexes are considered in supercage on site II and III'. All optimized parameters and geometries of interaction between CO and extra framework cations were shown in Table 3 and Figure 3. We can see that the distances of Li⁺...CO are almost the same about 2.2-2.3 Å (R(Li⁺-C)) and CO distances are also similar (1.138 Å). By calculation of adsorption energies (Table 3 (E_{ad})), it is clear that CO adsorbed on site III' with -44.49 kJ/mol is 11kJ/mol higher than in site II. This is due to Li⁺ cation coordinate with two oxygen atom of framework (Figure 3-d) or loose binding with framework, thus causing more binding with CO via electrostatic interaction. Considering CO interacts with Li⁺ in SII, it is interesting to note that the same adsorption site (on site II) is exhibited different adsorption energies with different amount of Al, one Al in six-membered ring (Figure 3c) and two Al in six-membered ring but different position either asymmetry or symmetry (Figure 3a, 3b respectively). It reveals that the CO adsorption on site II with one Al are more stable than those with two Al in six-membered ring. And the Al with asymmetry position show better CO adsorption than those symmetry positions (Table 3). These results are in good agreement with experimental data. It can be concluded that the more coordination of Li⁺ with framework, the smaller charge on Li⁺, therefore, the interaction with CO becomes weaker.

3.3. CO frequency

The application of scaling method for assessment stretching frequencies of CO adsorption on alkali metal cations in zeolite has been exhibited exactly [10]. According to vibrational frequency equation as mention in method, it requires optimization of CO bond length at DFT level but we get excellent results at CCSD(T) level. So, this method reduces significant computer time and computing expenses.

The stretching frequencies of CO adsorption on different Li^+ cation sites in FAU are presented in Table 3. All the frequencies are blue shift comparing to frequency of free CO, 2143 cm^{-1} . This is caused by CO polarization effect, therefore, it can be used to characterize alkali metal exchange zeolite in particular site. It is consistent with adsorption energies, CO adsorbed on sites II are in excellent agreement with experiment data (number in Table 3 in Ref. [3]), deviating about $1\text{-}4 \text{ cm}^{-1}$ comparing to experiment. On the contrary, frequency of CO in site III' is 16 cm^{-1} higher than experimental value because it is strong interaction with Li^+ cation which coordinate with two oxygen atoms. Thus, the C-O bond length increase and consequently, increasing significantly stretching frequency comparing to Li^+ cations which coordinate with 3 framework oxygen atoms. However, Li^+ cations distribution in site III' are minor (Table 1). The CO adsorption is abundance in site II. So that is why there is only one peak of CO vibrational frequency in experimental data.

4. Conclusion

The Li^+ cations in FAU have been elucidated. Optimized geometries and adsorption of carbon monoxide on Li-FAU zeolite has been investigated by means of density functional theory using PBE and dispersion correlation. This method is good tool to explain gas adsorption in zeolite. Computed results represent that Li^+ strongly prefers on sites II with one Al than two Al in the supercage. The CO adsorption energies and frequencies are in good agreement with experiment. The results explained clearly that CO preferably adsorbed on site II in Li^+ FAU zeolite. The CO adsorptions were affected not only position of Li^+ cation but also the number of framework oxygen atoms coordination with Li^+ cation; the concentration of aluminum, and their geometries.

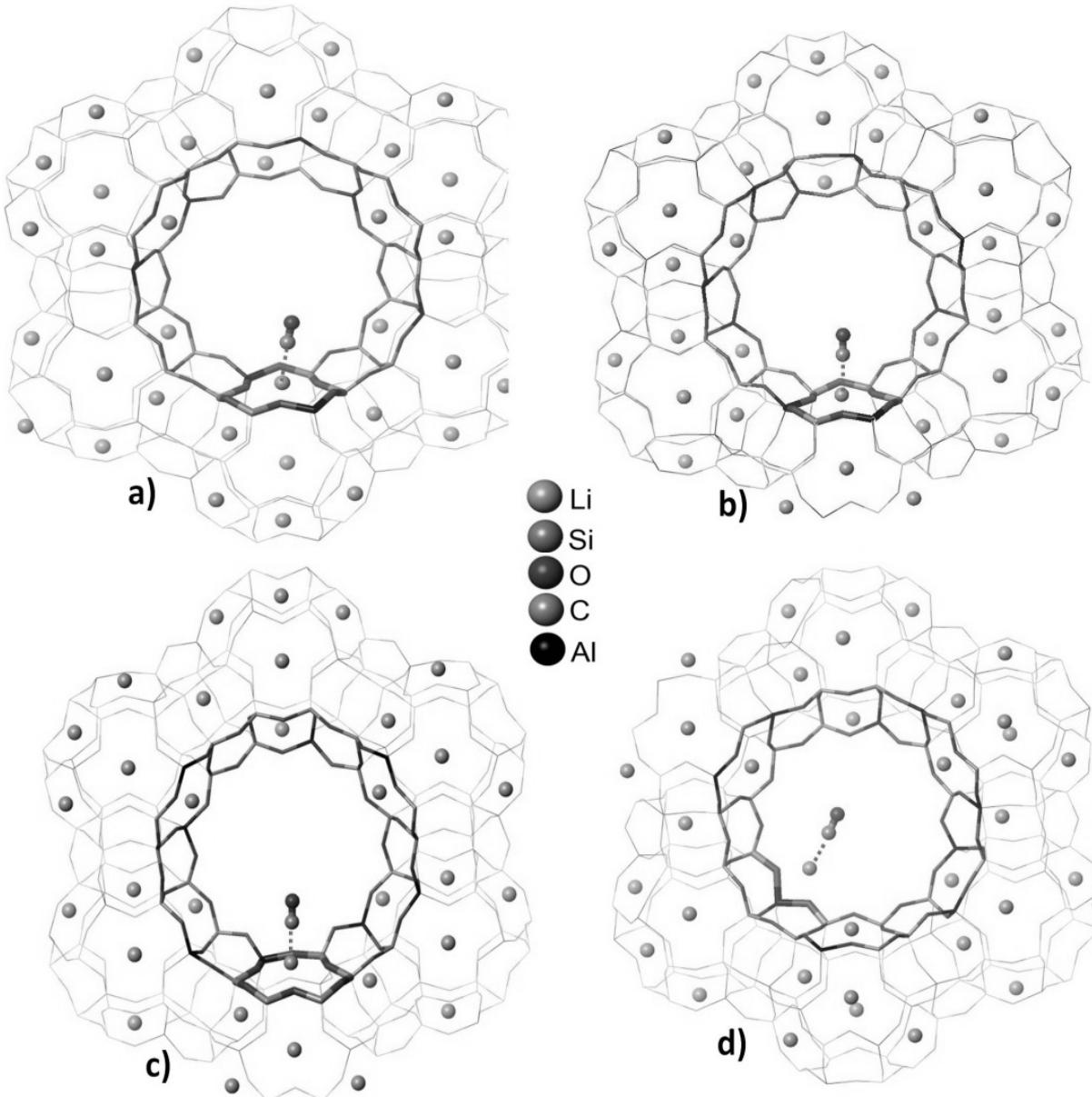


Figure 3. CO adsorption complexes on site II_2Alsy (a); site II_2Alas (b); site II_1Al (c) and site III' (d)

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(The Board of Editors received the paper on 12/01/2014, its review was completed on 11/08/2014)