

COMMUNICATION

A Theoretical Investigation of the Adsorption Activity of DNL-6 by DFT Method

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Abstract: DNL-6 as a novel zeolite successfully separates CO₂ from CH₄ with the highest selectivity. The adsorption activity and structure character of DNL-6 are investigated using cluster model by DFT calculation. The result shows that the higher Si/Al ratio and low Si/P content structure (Al₄SiP₃O₈H₁₆) is favorable in the DNL-6 zeolite. The equiprobability of substitution energies of isomers is same, while the strength of Bronsted acid of isomers is different. The adsorption energies of CO₂ in three models are more than those of CH₄. Furthermore, the adsorption activity of Al₄Si₂P₂O₈H₁₇ is the strongest. The theoretical results of adsorption capability of CO₂ and CH₄ in DNL-6 are consistent with the experimental study.

AMS subject classifications: 34D30, 37C20, 53A20

Key words: Adsorption energy, DNL-6 zeolite, DFT calculation.

The chemical recycle of CO₂ can reduce even eliminate the climate change caused by the human factors of excess combusting fossil fuel. There are an increasing number of researches on the CO₂ separated from nature or industry processing proceeds hydrogenated reduction to recycle the CO₂ and translate into the CH₃OH and it's derivate. Furthermore, the separation of CO₂ from CH₄ is one of the most important issues in natural-gas processing to prevent pipeline corrosion [1, 2]. Several zeolite-type materials as sorbents are used to capture the CO₂ from mixtures [1, 3-12]. New catalysts are being developed for selective CO₂ conversion to higher hydrocarbons C₂₊ and to methanol for chemicals and fuels. Liu et

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al. recently reported a new DNL-6 zeolite and applied it in CO₂ separation experiments to adsorb CO₂ from CH₄ and N₂ [2, 13-17]. They found that M-DNL-6 was a promising adsorbent for CO₂ separation from CH₄ and N₂ mixtures by comparing different Si content of DNL-6 zeolites. Despite the important role that zeolite DNL-6 plays in CO₂ separation, few studies have been investigated the catalytic properties of DNL-6, and none have report shown its theoretical properties. The adsorption of CO₂ and CH₄ on different Bronsted acid sites of the zeolite is unclear from experiments. The question still mains unclear about the nature of the strengths of acid sites in DNL-6. In this communication, we investigated the acidic properties of DNL-6 and adsorption for carbon dioxide and methane by DFT calculation.

DNL-6 is a new microporous silicoaluminophosphate zeolite with RHO framework which is first synthesized by Liu et al [13-16, 18]. The adsorption capacity of zeolite is due to its structure to a certain extent. However, the substitution of Al and P is not determinate during the synthesis processing in most cases. We built 8T clusters with 1-4 aluminum and 1-3 phosphorus substitutions. All Si atoms incorporated into the framework with Si (4Al) environment at a high amount close to the theoretical maximum value. In our work, a cluster model 8-ring cut from crystallographic structure of DNL-6 is considered for calculation (**Figure 1**). The dangling Si and Al atoms were terminated by H atoms. The Cartesian coordinates of peripheral H atoms were held frozen to retain the zeolite structure during the geometry optimization. The B3LYP functional was used and the basic set was carried out with 6-31g (d, p) for optimization [19].

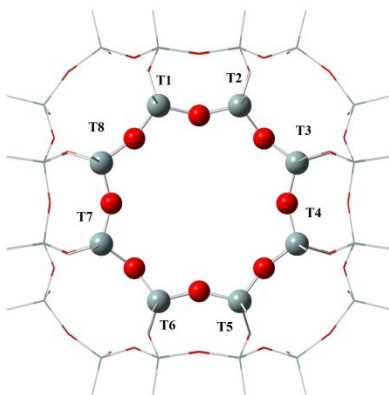


Figure 1: Structure of 8T cluster in 24T cluster model of DNL-6.

First of all, possible substitution structures are searched by theoretical investigation. The substitution energy was calculated as a function of Al and P substitution Si shown in **Table 1**. The substitution energy of $\text{Al}_4\text{Si}_4\text{O}_8\text{H}_{16}$ is found to be the highest, while that of $\text{Al}_4\text{Si}_1\text{P}_3\text{O}_8\text{H}_{16}$ is the lowest. In this case, the substitution energy increases as the Si/Al ratio decreasing and

decreases with the P/Si ratio increasing. As we know, the substitution energy refers to the stability of zeolite structure. The larger relative substitution energy is the more difficult substitution is. The structure with larger relative substitution energy is more changeable. The low Si content structure ($\text{Al}_4\text{Si}_{11}\text{P}_3\text{O}_8\text{H}_{16}$) is more favorable in the DNL-6 zeolite. Therefore, the structure of substitution is more preference with a higher Si/Al ratio, while it is more preference with the lower Si/P ratio. For Si and P coexistence zeolite, the structure of P substitution at T4, T6 and T8 sites ($\text{Al}_4\text{Si}_{11}\text{P}_3\text{O}_8\text{H}_{16}$) is the stablest. Another important finding to be considered, the substitution energies of the isomer have approximately equal value when Si is substituted by Al at T1 and T3, T1 and T4 sites, T1 and T5 sites, respectively. When Si is substituted by Al at T1 and T3 sites, the substitution energy is 94.31 kcal/mol. The result is similar to its isomers disubstituted at T1 and T4 sites, T1 and T5 sites, respectively. This phenomenon appears at the P disubstitution ($\text{Al}_4\text{Si}_2\text{P}_2\text{O}_8\text{H}_{16}$). The substitution energies of isomer for P substitutes Si are both 84.85 kcal/mol at T4 and T8 sites, T6 and T8 sites, respectively. The substitution energies of isomers are same at Si/P = 1 and Si/Al = 3 ratio.

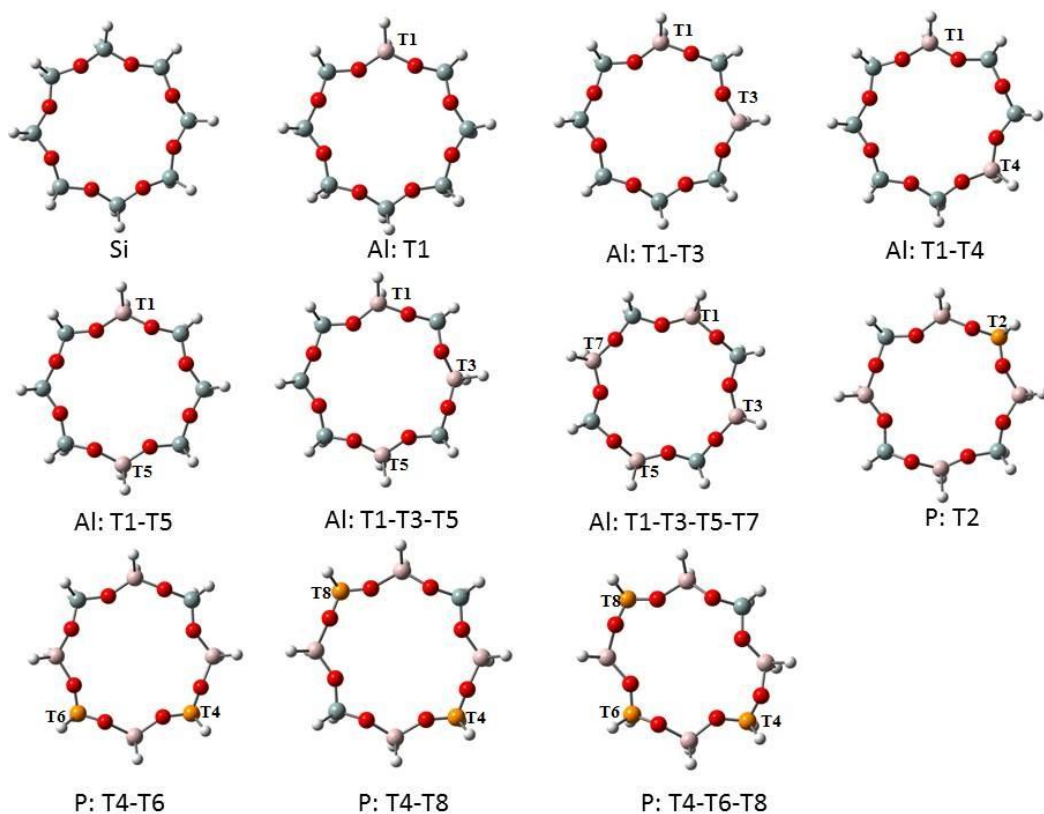


Figure 2: Structure of different substitution

The deprotonation energy is shown in **Table 2**. The deprotonation energy was calculated by $E_{\text{dep}} = E_{\text{Z-H}} - E_{\text{Z}}$, where E_{dep} , $E_{\text{Z-H}}$ and E_{Z} are denoted deprotonation energy, H-zeolite cluster energy and zeolite cluster energy, respectively. There, we can find that the deprotonation energy of single Bronsted acid site is a nonmonotonic trend with vary Si/Al and Si/P ratio. The value of deprotonation energy can reflect the strength of Bronsted acid. As can be seen in **Table 2**, **Al₄Si₄O₈H₁₇** is with the highest relative deprotonation energy value 74.74 kcal/mol, while the Si/Al ratio is 1:1. This structure is corresponding to the weakest acid site. When the Si/Al ratio is 5:3, the deprotonation energy is the lowest. Therefore, the strength of acid is strongest on **Al₃Si₅O₈H₁₇**. In addition, it is obvious that the deprotonation energies of P substitution structures are lower than those of the non-P substitution structures. With a Si/P ratio of 1, the deprotonation energies of the two isomers of **Al₄Si₂P₂O₈H₁₇** are a wide discrepancy. Comparing the deprotonation energy of **Al₄Si₂P₂O₈H₁₇-para (T4-T8)** model with that of **Al₄Si₂P₂O₈H₁₇-ortho (T6-T8)** model, the variation is close to 44kcal/mol. Consequently, the deprotonation behaviour of **Al₄Si₂P₂O₈H₁₇ (T4-T8)** is dramatically different from that of **Al₄Si₂P₂O₈H₁₇ (T6-T8)**. The isomer is equiprobability in the zeolite and the strength of Bronsted acid is different.

Table 1. Substitution energy (kcal/mol)

	SCF/	ZPE	G
Si₈O₈H₁₆	0	0	0
AlSi₇O₈H₁₆ (T1)	47.13	47.13	47.13
Al₂Si₆O₈H₁₆-ortho (T1-T3)	94.31	94.30	94.30
Al₂Si₆O₈H₁₆-ortho-2 (T1-T4)	94.30	94.30	94.30
Al₂Si₆O₈H₁₆-para (T1-T5)	94.31	94.30	94.30
Al₃Si₅O₈H₁₆ (T1-T3-T7)	141.40	141.40	141.40
Al₄Si₄O₈H₁₆ (T1-T3-T5-T7)	188.63	188.62	188.61
Al₄Si₃P₁O₈H₁₆ (T2)	136.69	136.68	136.68
Al₄Si₂P₂O₈H₁₆-ortho (T6-T8)	84.85	84.84	84.84
Al₄Si₂P₂O₈H₁₆-para (T4-T8)	84.85	84.85	84.84
Al₄Si₁P₃O₈H₁₆ (T4-T6-T8)	32.99	32.99	32.99

Table 3 shows the adsorption effect of CH₄ and CO₂ on different acid site of DNL-6. The adsorption energy was using $E_{\text{ads}} = E_{\text{Z-H}} + E_{\text{gas}} - E_{\text{Z-gas}}$, where $E_{\text{Z-H}}$, E_{gas} and $E_{\text{Z-gas}}$ are the energy of zeolite, adsorbed gas molecule and adsorbed gas with zeolite, respectively. Different Si concentrations (H-DNL-6, M-DNL-6 and L-DNL-6) were used as adsorbents for CO₂ and CH₄ in Liu's work [2]. In our calculation, the cluster models of **Al₄Si₃P₁O₈H₁₇**, **Al₄Si₂P₂O₈H₁₇** and **Al₄Si₁P₃O₈H₁₇** are corresponding to H-DNL-6, M-DNL-6 and L-DNL-6,

respectively. The uptakes of CH₄ on M-DNL-6 are similar to those on L-DNL-6 at two different pressures. It is found that the adsorption capability of CH₄ on M-DNL-6 is closely approximate to L-DNL-6. From **Table 3**, it is clearly evidenced that the CH₄ adsorption energy of **Al₄Si₂P₂O₈H₁₇ (T4-T8)** is 3.98 kcal/mol considered the same as the 3.83 kcal/mol of **Al₄Si₁P₃O₈H₁₇**. This suggests that adsorption performance of the two different Si/P ratio zeolite models is nearly on the same level. The result is consistent with the experimental phenomenon mentioned. As can be seen in **Table 3**, the adsorption energies of CO₂ are larger than those of CH₄ at two equilibrium pressures. The same adsorption behavior of a much higher selectivity for CO₂ on three different DNL-6 samples is observed in adsorption isotherms. The adsorption energy of CO₂ on **Al₄Si₂P₂O₈H₁₇ (T6-T8)** is higher than **Al₄Si₃P₁O₈H₁₇**. It indicates that **Al₄Si₂P₂O₈H₁₇ (T6-T8)** cluster model has a larger CO₂ adsorption capacity. For above three points, our results are good agreement with the experimental study. **Al₄Si₂P₂O₈H₁₇ (T4-T8)** and **Al₄Si₂P₂O₈H₁₇ (T6-T8)** can coexist in the same Si/P ratio because of the same substitution energy. The results for adsorption investigation confirmed the difference of the adsorption capability for **Al₄Si₂P₂O₈H₁₇** isomers. Furthermore, the adsorptions of CH₄ and CO₂ on cluster models are focused on the physical adsorption based on the magnitude of the adsorption energy. Our calculation serves as a guide for material stability and catalyst activity. The CO₂ and CH₄ adsorption on cluster models proved the adsorption capacity of DNL-6 zeolite in experiment. The M-DNL-6 zeolite has an outstanding selectivity for CO₂/CH₄ adsorption.

Table 2. Deprotonation energies of different Bronsted acid sites (*kcal/mol*)

	SCF	ZPE	G
AlSi₇O₈H₁₇ (T1)	24.85	25.10	25.10
Al₂Si₆O₈H₁₇-para (T1-T5)	50.26	50.20	50.20
Al₂Si₆O₈H₁₇-ortho(T1-T4)	48.01	50.20	50.20
Al₃Si₅O₈H₁₇ (T1-T3-T5)	0	0	0
Al₄Si₄O₈H₁₇ (T1-T3-T5-T7)	74.74	75.30	75.30
Al₄Si₃P₁O₈H₁₇ (T2)	12.55	18.53	6.28
Al₄Si₂P₂O₈H₁₇-para (T4-T8)	6.28	12.55	12.55
Al₄Si₂P₂O₈H₁₇-ortho(T6-T8)	50.20	50.20	50.20
Al₄Si₁P₃O₈H₁₇ (T4-T6-T8)	18.83	18.83	18.83

Table 3. Adsorption energy of CH₄ and CO₂ on different activity site of DNL-6 (kcal/mol).

Adsorped gas	CH ₄		CO ₂	
Zeolite model	AlSi ₂ P ₂ O ₈ H ₁₇ (T4-T8)	AlSiP ₃ O ₈ H ₁₇ (T4-T6-T8)	AlSi ₂ P ₂ O ₈ H ₁₇ (T6-T8)	AlSiP ₁ O ₈ H ₁₇ (T8)
Cal.	3.98	3.83	7.24	6.66
Uptake Exp.a	0.069	0.070	1.52	1.42
Uptake Exp.b	0.38	0.38	4.65	4.30

a. Equilibrium pressure 10 kpa b. Equilibrium pressure 101 kpa

*Uptake (mmol/g)

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