Commun. Comput. Chem.
doi: 10.4208/cicc.2015.v3.n1.2

Vol.**3**, No.**1**, pp.11-17
April 2015

COMMUNICATION

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

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Received 15 March; Accepted (in revised version) 20 April 2015

Abstract: DNL-6 as a novel zeolite successfully separates CO_2 from CH_4 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 ($Al_4SiP_3O_8H_{16}$) 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 CO_2 in three models are more than those of CH_4. Furthermore, the adsorption activity of $Al_4Si_2P_2O_8H_{17}$ is the strongest. The theoretical results of adsorption capability of CO_2 and CH_4 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 CO_2 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 CO_2 separated from nature or industry processing proceeds hydrogenated reduction to recycle the CO_2 and translate into the CH_3OH and it's derivate. Furthermore, the separation of CO_2 from CH_4 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 CO_2 from mixtures [1, 3-12]. New catalysts are being developed for selective CO_2 conversion to higher hydrocarbons C_{2+} 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 CO_2 separation experiments to adsorb CO_2 from CH_4 and N_2 [2, 13-17]. They found that M-DNL-6 was a promising adsorbent for CO_2 separation from CH_4 and N_2 mixtures by comparing different Si content of DNL-6 zeolites. Despite the important role that zeolite DNL-6 plays in CO_2 separation, few studies have been investigated the catalytic properties of DNL-6, and none have report shown its theoretical properties. The adsorption of CO_2 and CH_4 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].

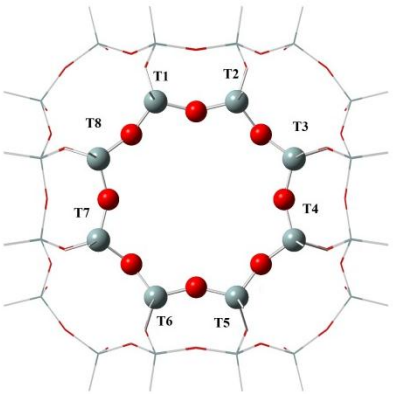

Figure 1: Structure of 8T cluster in 24T cluster model of DNL-6.

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 substation energy of $\mathbf{Al_4Si_4O_8H_{16}}$ is found to be the highest, while that of $\mathbf{Al_4Si_1P_3O_8H_{16}}$ is the lowest. In this case, the substation energy increases as the Si/Al ratio decreasing and