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Scaling the Acidic Properties of Microporous Molecular Sieves: A Combined Density Functional and Molecular Dynamics Study

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Introduction

The characterization of different acid sites in zeolites and zeolite-type materials is a significant issue in heterogeneous catalysis. Some experimental techniques are devoted to this purpose like temperature-programmed desorption and microcalorimetry. However, these techniques can not give many details about the nature of the acid sites that may exist in the material under investigation. Recently, computational methods have become important tools for obtaining detailed analysis at the atomic level. In this study, the Brønsted acidity of zeolites e.g., CHA, Zeolite-type materials e.g., AlPO-34, AlPO-5, and their metal substituted forms are investigated using density functional and molecular dynamics methods. Heats of NH_3 adsorption, deprotonation energies, and temperatures of NH_3 desorption are considered as a measure of the relative acidity.

Computational details

Geometry optimizations and energy calculations were carried out, for all periodic models before and after NH_3 adsorption, using Dmol^3 program package [1] at generalized gradient approximation (GGA) level. Molecular dynamics simulations are carried out for 2500 steps using a novel program "colors" developed in our laboratory [2].

Results and discussion

Figure 1 shows the unit cell of chabazite, where one silicon is replaced by trivalent aluminum and proton. The acidity decreases in the following order Al-CHA> Sc, Ga-CHA> Fe-HA>> B-CHA. Strong correlation between the adsorption energy of NH_3 and deprotonation energy is observed. Moreover, the electronegativity of the dopants plays a dominant role for predicting the acidity of isomorphously substituted aluminosilicate molecular sieves. On the other hand, in AlPO-34 the acidity sequence follows the order MnAlPO-34> CoAlPO034> SiAlPO-34> TiAlPO-34. Further, the predection of BrØnsted acid site strength is complex. The heat of NH_3 adsorption on AlPO-34 (–128.8 kJ/mol) is higher than on AlPO-5 (–86.3 kJ/mol).

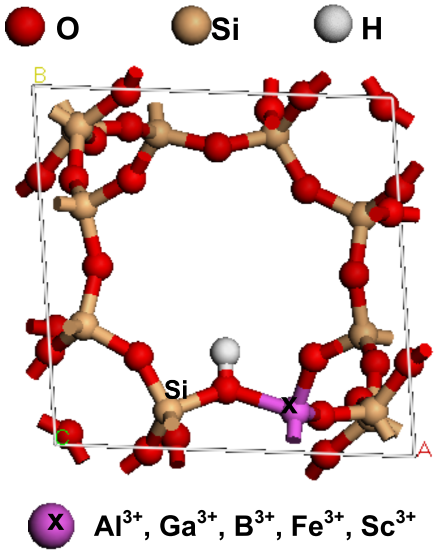

Fig. 1: Isomorphous substitution in CHA unit cell.

References

[1] Software from Accelrys Inc., www.accelrys.com
[2] Elanany, M. et al. J. Phys. Chem. B 2003, 107, 1518.