Computational Techniques for Studying the Structure/Acidity Relationship in Zeolites and Zeolite-type Materials

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The acidic properties of different aluminosilicate and aluminophosphate molecular sieves are investigated using periodic density function and molecular dynamics methods. In acidic mordenite, Brønsted acid sites in the side pockets are weaker than those in the main channels. Isomorphous substitution in chabazite produces acidic sites of strength which increases in the order B-CHA< Fe-CHA< Ga-CHA< Sc-CHA< Al-CHA while TiAlPO-5 has much weaker Brønsted acidity than SAPO-5. Moreover, simulation of NH₃ desorption in H-mordenite has been applied as a new method of characterization in heterogeneous catalysis. Key words: Mordenite, SAPO-5, acidity, NH₃ adsorption, computational techniques, isomorphous substitution.

1. INTRODUCTION

Zeolitic materials have been extensively studied because of their applications in various fields as sieves, catalysts, catalyst-supports ſ1, 2]. Detailed characterization for the nature of acidic sites in these materials remains a significant issue in order to understand their structure/activity relationship. Recently, computational methods have become an important tool for the characterization of different zeolites and zeolites-type materials at the atomic-scale level [3,4]. H-mordenite is known by its pronounced acidity among other zeolite structures viz., H-ZSM-5, H-CHA, and H-FER [3,5]. Hence, exploring different acidic sites using computational methods gives detailed insight view for such important materials. On the other hand, aluminophosphate molecular sieves and their metal substituted structures (MAPOs) attracted much attention recently as new catalytic materials for many industrial applications environmental and [6-8]. Aluminophosphates (AIPOs) consist of tetrahedral units of AlO₄ and PO₄ corner-sharing oxygen atoms. Despite their structural similarities to zeolites AlPOs exhibit different chemical behaviors for examples, their thermal stability and their ability to accommodate higher concentration of framework hetero-atoms. This is due to the nature of chemical bonding which has more ionic character than that in zeolitic structures [9]. Various mesoporous structures of phosphate-based molecular sieves are available now [10]. Isomorphous substitution is defined as the replacement of an element in the crystalline framework by another element with similar cation radius and coordination requirements. In crystalline molecular sieves, the isomorphous substitution is very important because it may produce novel materials of special acidic and/or redox properties. Furthermore, the synthesis of multi-element incorporated in the framework has been acclaimed [10]. Therefore it is interesting to measure and compare the acidic sites produced from the isomorphous substitution. Ammonia is a common basic probe molecule for the acidic sites in different molecular sieves because of its accessibility to all acidic sites located in the pores, channels or windows of diameter ≥ 4 Å.

In this study we explored different adsorption positions for NH₃ (viz., main channel, side pocket, and double four membered rings D4-MR) in acidic mordenite and measured the relative strength of different acidic sites from the calculated adsorption energy values. In order to know more details about the nature of acidic sites in crystalline molecular sieves generally and in H-mordenite specifically for the first time, we tried to simulate the desorption of NH3 on a Brønsted acid site in the main channel of H-MOR using a novel accelerated quantum chemical molecular dynamics program. For manipulating molecular sieves (MS) in heterogeneous catalysis, we studied the acidic properties of aluminosilicate-based MS viz., M-CHA (M = Al, Ga, B, Fe, Sc) and aluminophosphate-based MS viz., M-AlPO-5 (M = Si, Ti).

2. MODELS AND COMPUTATIONAL DETAILS 2.1 Models

Mordenite has straight one-dimensional channel running along c direction which is controlled by 12 membered-rings (6.7x 7.0 Å) and secondary channels in b direction (8-membered rings) with 2.8 Å diameter. These secondary channels are called side pockets [11]. The unit cell has 144 atoms with orthorhombic symmetry as shown in figure 1. In order to create Brønsted acid site one silicon atom was replaced by one aluminum and proton. The proton is attached to the bridging oxygen close to aluminum atom in the framework. There are four distinct tetrahedral sites for placing Al in the framework. Sauer et. al. [3] found that T_4 is the most stable site for Al, while Yuan et. al. [12] have found T₃ is more stable than T₄. We checked the energy for the optimized structures of Al at T₃ and T₄. Our results indicated that $T_3 \mbox{ is more stable than } T_4 \mbox{ by }$ small energy difference (4.7 kJ/mol). The adsorption energy values are used to measure the relative acidic sites strength. We studied the adsorption of NH_3 in three different positions viz., main channel, side-pocket, and double four-membered rings. Moreover, for the first time, using molecular dynamics we could predict the temperature of NH_3 desorption at Brønsted acid site in the main channel, as a new method for measuring the relative acidity of different sites. In this method molecular dynamics is used to simulate the real temperature programmed desorption (TPD) experiment.



Fig. 1 Optimized structure for H-MOR and the studied positions for NH₃ adsorption marked by x.

AlPO-5 of AFI topology has also one-dimentional main channel along c direction controlled by 12-MRs as shown in figure 2. The unit cell has the formula $(Al_{12}P_{12}O_{48})$ with hexagonal symmetry. All Al atoms are in equivalent sites. Aluminophosphate molecular sieves consist of AlO₄⁻ and PO₄⁺ tetrahedra which are corner-sharing oxygen atoms [11]. Creation of Brønsted acid site is taking place by either $P \rightarrow M^{IV}(Si) + H$ or + H. The former мп Al ----**}** called silicoaluminophosphate (SAPO-5) and the later called metal substituted aluminophosphate (MAPO-5). We introduced acidic site by the first way. Also the Brønsted acidic site in TiAPO-5 is compared with that in SAPO-5.



Fig.2 Super cell of H-AFI extended along x and y axes.

Chabazite (CHA) is known by its catalytic activity for the methanol conversion to olefins [13]. The unit cell contains 36 atoms with 3-dimentional channels controlled by 8-memberd rings. The Brønsted acid arises when $Si \rightarrow Al + H$ is taking place. The relative acidic site strength produced by the isomorphous substitution of Al by other M^{III} like (Fe, Ga, Sc, and B) is investigated for the first time employing periodic boundary conditions.



Fig. 3 The optimized structure for acidic chabazite.

2.2 Computational details

Geometry optimization and energy calculations have been carried out using Dmol³ program package [14] at generalized gradient approximation (GGA) level with HCTH exchange and correlation functional [15]. Double numerical with polarization basis set (DNP) was used. This basis set is comparable to $6-31G^{**}$ set, however the numerical basis set is much more accurate than the Gaussian basis set of the same size and that all core electrons were included. Moreover, this basis set is known to produce small basis set super position error (BSSE) [16]. The convergence is taking place when the following conditions are fulfilled: energy $2x10^{-5}$ Ha; force $4x10^{-3}$ Ha/Å; displacement 0.005Å. The adsorption energy is calculated according to the following equation

$\mathbf{E}_{ads} = \mathbf{E}_{HZ-NH3} - \mathbf{E}_{HZ} - \mathbf{E}_{NH3}$

Where E_{ads} is the calculated adsorption energy, E_{HZ-NH3} the total energy for the adsorption complex, E_{HZ} is the total energy for the acidic zeolites or zeolites-type structure, and E_{NH3} is the total energy for ammonia. Molecular dynamics simulation was carried out using a novel program "Colors" [17, 18] for 2500 steps. To simulate NH₃ desorption the temperature was increasing during the simulation by the rate of 4K/10 steps.

3. RESULTS AND DISCUSSION

Table I shows some geometrical parameters for the optimized acidic structures of various molecular sieves. For H-mordenite, we checked three different positions for NH₃ adsorption: main channel, side pocket, and double 4-memberd rings. In the main channel and D4-MRs aluminum atom occupies T_4 site while in the side pocket occupies T_3 site. The adsorption energy of NH₃ in the main channel -147.9 kJ/mol is very close to the experimental value determined by Katada et al. [5]. The higher adsorption energy in the main channel than in the side pocket (-111.0 kJ/mol) indicates that the

Brønsted acid in the main channel is stronger than that in the side pocket. This result agrees with a previous FTIR study using CO and pyridine as probe molecules [18]. They assigned two components for acidic OH groups one at 3612 cm⁻¹ in the main channel, and the other at 3585 cm⁻¹ in the side pocket. The low adsorption energy in D4-MR (-80.4 kJ/mol) compared to that in main channel reveals that NH₃ adsorbs preferably in the main channel than to be in the D4-MR. So we expect that ammonia will adsorb properly in main channels and side pockets.

Table I: Some geometrical parameters and adsorption energies in various molecular sieves. (Bond lengths in Å, bond angels in degrees and adsorption energies in kJ/mol)

Acidic	Geometrical parameters	Adsorption
structure		energy
MOR		
-Main channel	Si-O,1.686; Al-O,1.897;	-147.9
	∠Al-O-Si,133.2; O-H 0.982	
-Side pocket	Si-O,1.686; Al-O,1.898;	-111.0
	∠Al-O-Si,136.8; O-H 0.894	
-Double 4-MR	Si-O,1.573; Al-O,1.741;	-80.4
	∠Al-O-Si,159.4	
AFI		
SAPO-5	Si-0.1.768: Al-0.1.846:	-86.4
	Si-O-Al.123.9: O-H.0.977	
TiAPO-5	Ti-0.1.966:Al-0.1.798	-33.8
	Ti-O-Al,119.9; O-H,0.976	
СНА		
	ALO 1 802: 5: 0 1 701.	129.0
AI-CIIA	AI-0,1.892, SI-0,1.701,	-120.0
Co CHA	Z AI-O-SI,133.2	100.0
SC-CHA	Sc-0, 2.181; SI-0, 1.686;	-122.3
C. CIL	∠ Sc-O-Si, 125.7	101.0
Ga-CHA	Ga-O, 2.020; Si-O, 1.694;	-121.9
Fe-CHA	∠ Ga-O-Si, 130.2	110.0
	Fe-O, 2.072; Si-O, 1.685;	-112.8
D CITA	∠ Fe-O-Si, 126.1	
B-CHA	B-O, 2.406; Si-O, 1.630;	-25.3
	∠ B-O-Si, 133.8	

Adsorption of ammonia in aluminophosphate molecular sieves indicates clearly that these molecular sieves possess weaker Brønsted acid sites than their aluminum silicate counterparts, H-CHA and SAPO-34 have been compared in an earlier study [20] and the same trend was found. Furthermore, the bridging Ti(OH)Al species shows Brønsted acidity weaker than that of SAPO-5. The relative adsorption energies calculated agree with the reported experimental results [21]. Recently, TAPO-5 used as a bifunctional catalyst, cyclohexane conversion to adipic acid, in a way that its Brønsted acidity is effective for methanol dehydration besides its ability to release nascent oxygen from H_2O_2 [22].

Table I also shows that in chabazite, Brønsted acidic sites of different strength can be produced upon the isomorphous substitution. The acidic site strength depends clearly on the nature of the element incorporated in the framework. The acidic site strength is found to increase in the order B-CHA< Fe-CHA</p>
Ga-CHA< Sc-CHA< Al-CHA. This result agrees well</p>



Fig. 4 Molecular dynamics simulation of NH3 desorption in H-mordenite: snapshot at the beginning (a), and by the end of the simulation (b). Bond distance analysis during the simulation (c).

with the previous experimental and theoretical findings [12]. However, our method of using periodic boundary conditions is more accurate than simple cluster model calculations. The disadvantages of cluster model approach have been addressed elsewhere [3, 22]. Figure 4 shows snapshots taken from the dynamics simulation of ammonia desorption in H-mordenite. At the beginning of the simulation Fig. 4(a) there is an electrostatic interaction between NH4⁺ and oxygen atoms around Al site. The ammonium ion is stabilized by three hydrogen bonds [24]. However, by the end of the simulation Fig. 4(b) NH₃ diffuses away from the acidic site leaving the proton attached to the framework. Figure 4(c) displays the bond distance analysis during the dynamics simulation of NH3 desorption in H-mordenite. As can be seen, at 1260 step (~ 540.8 K) ammonia desorption is taking place from the Brønsted acid site in main channel. Although the calculated desorption temperature is lower than the reported experimental value from temperature programmed desorption technique (TPD)[5] we should bear in mind that the temperature of the peak maximum can vary by 100K depending on the experimental conditions [25]. Further work is in progress using this new method to determine the nature of different acidic sites and their relative strength in microporous molecular sieves.

4. CONCLUSIONS

Using density function, with high level of theory, and molecular dynamics methods to investigate the acidic properties of various microporous molecular sieves, our main results can be summarized as follows:

- In H-mordenite, acidic sites in main channel are stronger than those in side pockets.

- SAPO-5 has stronger bronsted acid sites than TAPO5.

- isomorphous substitution in H-CHA produces acidic sites of strength increases in the order

B-CHA< Fe-CHA< Ga-CHA< Sc-CHA< Al-CHA - Molecular dynamics can be used as a new tool to determine the nature of acidic sites in molecular sieves.

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