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Periodic density functional investigation of Brønsted acidity in isomorphously substituted chabazite and AlPO-34 molecular sieves

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Abstract

The relative strength of Brønsted acid sites in isomorphously substituted chabazite (M–CHA; $Me = Al^{3+}$, Ga^{3+} , Ba^{3+} , Sc^{3+} and Fe^{3+}) and aluminophosphate-34 (MAIPO-34; $Me = Ti^{4+}$, Si^{4+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+}) have been investigated using periodic density functional theory. Adsorption energy of NH₃ and deprotonation energy are considered for measuring the acidity. It has been found that Al^{3+} –CHA and Mn^{2+} –AlPO-34 possess the strongest acidic character. Moreover, a correlation between deprotonation energy and adsorption energy of NH₃ has been observed. © 2004 Elsevier Inc. All rights reserved.

Keywords: Chabazite; AlPO-34; Acidity; Ammonia adsorption; Density functional theory; Deprotonation energy

1. Introduction

Zeolitic materials play an important role as catalytic materials in petroleum refining and petrochemical industry [1]. It is well accepted that Brønsted acid sites control mainly their catalytic activity. Using microporous catalysts, which are selective for light olefins, becomes of great interest for natural gas conversion to polyolefins [2]. Chabazite (CHA), one of the promising structures, has been extensively studied experimentally due to its small pores and theoretically, because of its small unit cell (36 ions) compared to the other zeolite structures e.g., ZSM-5 (288 ions/uc) [3]. On the other hand, aluminophosphate (AIPO) molecular sieves consist of discrete aluminum and phosphate ions [4]. Since their first synthesis in 1982 [5], these materials have given

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much attention owing to their catalytic and sorptive properties. Recently, metal-substituted aluminophosphates (M-AlPOs) have been effectively used as unique catalysts for many industrial and environmental applications viz., conversion of cyclohexane to adipic acid [6], methanol-to-olefins (MTO) process [7,8], selective oxidation of hydrocarbons [9], isomerization of alkenes [10], and De–NO_x [11]. In spite of the structural similarities between zeolites and AlPOs, the latter exhibits quite different properties like thermal stability and ability to accommodate higher concentrations of hetero-ions. This is mainly due to the nature of chemical bonding, which has more ionic character than that of zeolites.

Generally, isomorphous substitutions in either silicabased or phosphate-based molecular sieves are usually carried out to produce novel materials with unique acidic or redox properties. Microporous molecular sieves are extensively used as solid acid catalysts. Hence, tuning the acid site strength, by isomorphous substitution, remains a significant issue in heterogeneous catalysis. Temperature-programmed desorption (TPD) and microcalorimetry (MC) are widely used for acidity characterization. However, it was reported that the position of maximum peak's temperature (T_{max}) can differ by about 100 K, depending on the experimental conditions [12]. Furthermore, these techniques cannot directly determine the nature of different acid sites which have similar strength. For this problem, computational methods have become effective tools for providing detailed analyses at the atomic-scale level. Our study presents a systematic investigation of the relative Brønsted acid site strength in isomorphously substituted chabazite designated as M–CHA ($M = Al^{3+}$, Ga^{3+} , B^{3+} , Sc^{3+} and Fe³⁺) and aluminophosphate-34 designated as MeAl-PO-34 (M = Ti⁴⁺, Si⁴⁺, Cr²⁺, Mn²⁺, Fe²⁺, Co²⁺ and Ni²⁺) molecular sieves using the density functional theory (DFT) method with periodic boundary conditions. Ammonia (NH₃) is used as a basic probe molecule, and the relative acidity is determined from the calculated values of the adsorption energies. Deprotonation energies (DPE), another method for intrinsic acidity characterization, have been calculated as well. Results obtained from NH₃ adsorption are compared with those from the deprotonation energy method.

2. Structure models

Fig. 1 illustrates the AlPO-34 structure. The unit cell contains 36 ions with the chemical formula (Al₆P₆O₂₄). The 3D-channels are controlled by 8-membered rings, with small pore diameter of ~3.8 Å [3]. There are two ways to create Brønsted acid site in metal-substituted AlPOs (MAlPO-34): replacement of one phosphorus ion by one tetravalent ion e.g., Ti⁴⁺ or Si⁴⁺ as shown in Fig. 2a, or replacement of one aluminum ion by one divalent ion e.g., Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} or Ni²⁺ as shown in Fig. 2b. Likewise, the presence of a trivalent aluminum



Fig. 1. Super cell $(2 \times 2 \times 2)$ of AlPO-34 showing small pores controlled by 8-membered rings.

or another trivalent ion $(Ga^{3+}, B^{3+}, Sc^{3+}, Fe^{3+})$ in the silicalite framework of the CHA topology generates one Brønsted acid site as shown in Fig. 3.

3. Computational details

Geometry optimizations and energy calculations were carried out, for all periodic models before and after NH₃ adsorption, using the Dmol³ program package [13–16] at a generalized gradient approximation (GGA) level with HCTH/407 exchange and correlation functionals. It has been shown that the HCTH functional has a greater universality than the previous GGA functionals and performs well with respect to hydrogen-bonded systems [17–20]. A double numerical (with polarization) basis set (DNP) was used for all calculations. The DNP basis set is comparable to the 6-31G** set, however the numerical basis set is much more accurate than the Gaussian basis set of the same size (all core electrons were included). Moreover, this basis set is known to produce a small basis set super position error (BSSE) [21]. Partial atomic charges (q) were calculated according to the Mulliken population scheme. Spin-unrestricted calculations were performed for all structures, except for silicon and titanium substituted AlPO-34, as well as trivalent ions-doped CHA. The convergence, at a real space cutoff value of 5.5 Å, was achieved when the following conditions were fulfilled: energy 2×10^{-5} Ha; force 4×10^{-3} Ha/Å; displacement 0.005 Å. The adsorption energy of NH3 was calculated according to the following equation.

$$E_{\rm ads} = E_{\rm MZ-NH_4} - E_{\rm HZ} - E_{\rm NH}$$

where E_{ads} , E_{MZ-NH_4} , E_{HZ} , and E_{NH_3} refer to the calculated adsorption energy, total energy of the adsorption complex, acidic molecular sieve, and ammonia, respectively. We should mention here that we are interested in the relative adsorption energy values rather than absolute ones. The deprotonation energy (DPE) was calculated for the acidic structures of isomorphously substituted AlPO-34 according to the following equation

$$ZOH \rightarrow ZO^- + H^-$$

Brändle and Sauer [22] reported that the contribution to the adsorption energy of NH_3 from the deprotonation energy of zeolite framework is approximately three times greater than that from ion-pairing energy. Hence, the ion-pair binding energy was not expected to dominate the calculated adsorption energy values.

4. Results and discussion

Table 1 summarizes the structural parameters and heats of NH₃ adsorption of isomorphously substituted



Fig. 2. Creation of Brønsted acid sites in MeAIPO-34: P is replaced by either Si or Ti (a), Al is replaced by a divalent ion (b).



Fig. 3. Creation of Brønsted acid sites in silicalite of CHA topology: Si is replaced by a trivalent ion.

chabazite structures. The calculated adsorption energy for Al–CHA is –128.8 kJ/mol. No experimental values are available in the literature for making comparisons. However, a recent computational study predicted on adsorption energy of –114 kJ/mol [22]. Furthermore, the calculated value is in the range of the reported heats of ammonia adsorption of different zeolite structures: –150 ± 35 kJ/mol [23]. Table 2 shows that the calculated average bond distance of M–O_H is in good agreement with the available experimental results [24,25]. The adsorption energy decreases in the order Al–CHA > Sc– $CHA > Ga-CHA > Fe-CHA \gg B-CHA$. Accordingly, the Brønsted acid site strength decreases in the same order. A similar trend was also observed for other zeolite structures, e.g., H-MOR and H-ZSM-5 [26,27]. Thus, it seems that the relative Brønsted acid site strength has the same order irrespective of the zeolite structural topology. This reflects the covalent nature of bonding in these materials. Direct correlations between the Brønsted acid site strength and the acidic proton charge (qH) or geometrical parameters e.g., $\angle M$ –O–Si, O-H have not been observed. This is also noticed by a recent periodic Hartree-Fock (HF) study [28]. Nevertheless, a direct relation between adsorption energy values and the charge of oxygen in the bridging hydroxyl group (O-H) is observed. The more negative charge on oxygen the stronger the interaction with NH_4^+ , giving rise to higher adsorption energies. It can be suggested that the electronegativity of the dopants plays an important role for the oxygen charge as well as for the adsorption energy value. Indeed, this is clearly reflected by the strong Brønsted acidity of Sc-CHA compared to Fe-CHA and can be attributed to the lower electronegativity of scandium compared to iron (see Table 2). Likewise, boron, aluminum and gallium-doped CHA exhibited Brønsted acidity in the order B−CHA≪ Ga-CHA<Al-CHA. Thus, our findings give a direct correlation between the adsorption energy and the electronegativity of the dopants.

Unlike a computational study on cluster models of M-ZSM-5 [27], NH_4^+ formation upon NH_3 adsorption on all acidic structures has been observed in our study.

Table 1

Structural parameters and adsorption energies of NH3 for isomorphously substituted chabazite (M-CHA) structures

| Dopant | Geometrical parameters for M–CHA (bond lengths in Å, bond angles in degrees, and Mulliken charge q) | Adsorption energy (kJ/mol) |
|------------------|--|-------------------------------|
| Al^{3+} | Al–O, 1.892; Si–O, 1.701; O–H, 0.966; ∠Al–O–Si, 133.2; qO, −0.731; qH, 0.349 | -128.8 |
| Sc^{3+} | Sc–O, 2.181; Si–O, 1.686; O–H, 0.968; ∠Sc–O–Si, 125.7; qO, -0.780; qH, 0.358 | -122.3 |
| Ga ³⁺ | Ga–O, 2.020; Si–O, 1.694; O–H, 0.967; ∠Ga–O–Si, 130.2; qO, −0.719; qH, 0.356 | -121.9 |
| Fe ³⁺ | Fe–O, 2.072; Si–O, 1.685; O–H, 0.913; ∠Fe–O–Si, 126.1; qO, -0.778; qH, 0.340 | -112.8 |
| ${ m B}^{3+}$ | В–О, 2.406; Si–О, 1.630; О–Н, 0.959; ∠В–О–Si, 133.8; qО, −0.683; qН, 0.302 | -25.3 |

| Property | erty Dopants | | | | |
|---------------------|--------------|------|-----------|------|-----------|
| | В | Al | Ga | Sc | Fe |
| $R_{\rm M}$ (Å) | 0.23 | 0.54 | 0.62 | 0.75 | 0.65 |
| X _M | 2.04 | 1.61 | 1.81 | 1.36 | 1.83 |
| $(M-O_H)_{Av}$ (Å) | 1.64 | 1.76 | 1.86 | 1.99 | 1.89 |
| $(M-O_H)_{Exp}$ (Å) | _ | - | 1.83 [24] | _ | 1.89 [25] |

Structural and electronic features of the dopants in CHA: ionic radius, $R_{\rm M}$; Pauling electronegativity, $X_{\rm M}$; the calculated average value of M–O_H, $(M-O_{\rm H})_{\rm Av}$ and the corresponding available experimental value $(M-O_{\rm H})_{\rm Exp}$

This may be due to the advantage of the periodic model approach over the cluster model approach in considering the long range of interaction.

Table 3 presents the structural parameters for isomorphously substituted AlPO-34 structures before and after NH₃ adsorption, as well as the calculated adsorption energy and deprotonation energy values. From the data given in this table, we can see the following structural changes upon NH₃ adsorption. First, an increase of the O–H distance as a result of proton transfer to form NH₄⁺. Second, a decrease of the M–O_H bond distance and M–O_H–P, Al–O_H–M bond angles as compared to the acidic structures. This could be attributed to the removal of local distortion by the acidic proton.

It can also be seen from this table that MnAlPO-34 gives the highest adsorption energy value (-136.1 kJ/mol), while the lowest is observed for TiAlPO-34 (-87.4 kJ/mol). Furthermore, the adsorption energy of SiAlPO-34 (-111.8 kJ/mol) is lower than that for Al-CHA (-128.8 kJ/mol). This indicates a to the stronger

Brønsted acidity in Al-CHA compared to SiAPO-34. The same finding was observed earlier in a computational study by Sauer et al. [29]. Based on the calculated adsorption energy values, the relative strength of Brønsted acid sites follows the order MnAlPO-34 > CoAlPO-34 > FeAlPO-34 > NiAlPO-34 > SiAlPO-34 > CrAlPO-34 > TiAlPO-34. On the other hand, deprotonation energy results show the following order: MnAlPO-34 > CoAlPO-34 > NiAlPO-34 > FeAlPO-34 > SiAlPO-34 > CrAlPO-34 > TiAlPO-34. The acidity orders derived from both methods are nearly the same, except for (Ni, Fe) AlPO-34 structures, where the order is reversed. This may be due to the small difference in acidity between these two structures. Brändle and Sauer [22] studied the adsorption energy of NH₃ on different zeolite structures viz., MOR, Y, CHA, and ZSM-5. They found that the acidity sequence from NH₃ adsorption is different from the deprotonation energy results. They attributed that to the different ways of interaction between NH₄⁺ and the negative lattices of

Table 3

Structural parameters, and adsorption energies for the optimized structures of MAlPO-34 and NH_4 –MAlPO-34 as well as deprotonation energies for the acidic structures

| Dopants | Structural parameters (bond lengths in Å, bond angles in degrees | Adsorption energy (kJ/mol) | Deprotonation energy (kJ/mol) | |
|------------------|---|--|----------------------------------|--------|
| | MAIPO-34 | NH ₄ -MAlPO-34 | | |
| Si ⁴⁺ | Si–O, 1.764; Al–O, 1.842; O–H, 0.964; ∠Si–O–Al, 133.5 <i>q</i> Si, 1.790; <i>q</i> Al, 1.401; <i>q</i> O, −0.742; <i>q</i> H, 0.336 | Si–O, 1.651; Al–O, 1.737; O–H, 1.664; ∠Si–O–Al, 132.2 <i>q</i> Si, 1.808; <i>q</i> Al, 1.370; <i>q</i> O, −0.984 | -111.8 | 1358.9 |
| Ti ⁴⁺ | Ti–O, 2.006; Al–O, 1.815; O–H, 0.963; ∠Ti–O–Al, 127.2 <i>q</i> Ti, 1.635; <i>q</i> Al, 1.427; <i>q</i> O, −0.767; <i>q</i> H, 0.317 | Ti–O, 1.853; Al–O, 1.742; O–H, 1.627; ∠Ti–O–Al, 126.8 <i>q</i> Ti, 1.615; <i>q</i> Al, 1.410; <i>q</i> O, −0.983 | -87.4 | 1385.7 |
| Cr ²⁺ | Cr–O, 2.561; PO, 1.596; O–H, 0.973; \angle Cr–O–P, 138.1 <i>q</i> Cr, 0.978; <i>q</i> P, 1.666; <i>q</i> O, -0.599; <i>q</i> H, 0.345 | Cr–O, 2.298; P–O, 1.524; O–H, 1.542; ∠Cr–O–P, 135.9 <i>q</i> Cr, 0.986 <i>q</i> P, 1.691; <i>q</i> O, −0.840 | -94.6 | 1373.1 |
| Mn ²⁺ | Mn–O, 2.343; P–O, 1.622; O–H, 0.972; ∠Mn–O–P, 131.9 <i>q</i> Mn, 1.079; <i>q</i> P, 1.690; <i>q</i> O, −0.632; <i>q</i> H, 0.343 | Mn–O, 2.090; P–O, 1.529; O–H, 1.776; ∠Mn–O–P, 126.8 <i>q</i> Mn, 1.091; <i>q</i> P, 1.696; <i>q</i> O, −0.855 | -136.1 | 1335.9 |
| Fe ²⁺ | Fe–O, 2.376; P–O, 1.607; O–H, 0.975; ∠Fe–O–P, 135.7 <i>q</i> Fe, 1.331; <i>q</i> P, 1.660; <i>q</i> O, −0.641; <i>q</i> H, 0.347 | Fe–O, 2.062; P–O, 1.531; O–H, 1.717; ∠Fe–O–P, 128.1 <i>q</i> Fe, 1.380; <i>q</i> P, 1.666; <i>q</i> O, −0.901 | -124.3 | 1351.4 |
| Co ²⁺ | Co–O, 2.308; P–O, 1.607; O–H, 0.969; ∠Co–O–P, 140.8 <i>q</i> Co, 0.906; <i>q</i> P, 1.668; <i>q</i> O, −0.603; <i>q</i> H, 0.338 | Co–O, 2.009; P–O, 1.522; O–H, 1.719; Co–O–P, 136.9 <i>q</i> Co, 0.925; <i>q</i> P, 1.687; <i>q</i> O, -0.832 | -128.9 | 1345.8 |
| Ni ²⁺ | Ni–O, 2.331; P–O, 1.607; O–H, 0.968; ∠Ni–O–P, 128.9 <i>q</i> Ni, 0.973; <i>q</i> P, 1.653; <i>q</i> O, −0.602; <i>q</i> H, 0.329 | Ni–O, 2.024; P–O, 1.530; O–H, 1.608; ∠Ni–O–P, 121.6 <i>q</i> Ni, 1.000; <i>q</i> P, 1.677; <i>q</i> O, −0.851 | -118.4 | 1349.4 |

Table 2

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Table 4

| Property | Dopants | | | | | | |
|---------------------------------------|---------|------|------|-----------|------|-----------|-----------|
| | Si | Ti | Cr | Mn | Fe | Со | Ni |
| $R_{\rm M}$ (Å) | 0.26 | 0.42 | 0.73 | 0.66 | 0.63 | 0.56 | 0.49 |
| X_{M} | 1.90 | 1.54 | 1.66 | 1.55 | 1.83 | 1.88 | 1.91 |
| (M–O _H) _{Av} (Å |) 1.64 | 1.83 | 2.13 | 2.09 | 2.06 | 2.02 | 2.01 |
| (M–O _H) _{Exp} (Å | A) – | _ | _ | 2.02 [30] | _ | 1.94 [31] | 1.94 [32] |

Structural and electronic features of the dopants in AlPO-34: ionic radius, $R_{\rm M}$; Pauling electronegativity, $X_{\rm M}$; the calculated average value of M–O_H, $(M-O_{\rm H})_{\rm Av}$ and the corresponding available experimental value $(M-O_{\rm H})_{\rm Exp}$

different zeolite structures. In the current study, such an effect was not encountered since the acidic structures have the same structural topology as chabazite. Table 4 shows certain important properties for the dopants in AlPO-34 e.g., electronegativities, and ionic radii. As it can be seen from this table, there is a good agreement between the calculated average M-O_H values and the experimental results available from the literature [30-32], confirming the reliability of our calculation method. Unlike M-CHA structures, direct correlations between electronic features of the dopants or structural parameters e.g., qO (charge of the bridging oxygen in the hydroxyl group) and the relative strength of Brønsted acid sites could not be observed (Tables 3 and 4). This may be due to the ionic bonding nature of these structures and that many parameters may have contributions to the acidity at the same time.

Although, no systematic experimental study for all isomorphous substitutions considered here is available, the results from the NH₃ adsorption can be supported by deprotonation energies and the available experimental results for some structures. Tusar et al. [33] measured the relative Brønsted acid site strength using in situ IR measurements of pyridine and ammonia adsorption/desorption. They concluded that the strength of Brønsted acid sites in MAPO-31 decreases in the following order MnAlPO-31 > CoAlPO-31 > AlPO-31. Zahedi-Niaki et al. [34] investigated the acidic properties of TiAlPO-5, TiAlPO-36, SiAlPO-5 and SiAlPO-36 molecular sieves by FTIR and proton MAS NMR spectroscopy of chemisorbed pyridine. They found that the Brønsted acid site strength in titanium substituted structures is weaker than those in their silicon counterparts. Concerning catalysis, Lee et al. [6] drew the same conclusions. A recent periodic Hartree-Fock (HF) study of metal ions-doped AlPO-34 revealed the following acidity sequence Fe≫Si>Co, Mn≫Ni≫Cr, based on the stretching frequency of the acidic OH groups [35]. The disagreement compared with our results may be due to the absence of electron correlations in the HF method. It is interesting to note that the results of the relative acidity order are in good agreement with the available experimental data obtained by frequency shift measurements rather than from NH₃-TPD experiments e.g., [36]. This may be due to the disadvantages that were mentioned earlier for the latter technique.

5. Conclusions

The relative strength of Brønsted acid sites in isomorphously substituted CHA structures is evaluated using the periodic density functional theory. The acid site strength decreases in the following order Al- $CHA > Sc-CHA > Ga-CHA > Fe-CHA \gg B-CHA$. The ease of acid site strength prediction in silica-based molecular sieves is attributed to the covalent bonding nature of these structures, where electronegativity of the dopants plays a dominant role. In the case of metal substituted AlPO-34 molecular sieves, it is deduced from NH₃ adsorption that the Brønsted acid site strength follows the order MnAlPO-34 > CoAlPO-34 > FeAlPO-34 > NiAlPO-34 > SAPO-34 > CrAlPO-34 > TiAlPO-34, while the order concerning the deprotonation energy is MnAlPO-34 > CoAlPO-34 > NiAlPO-34 > FeAlPO-34 > SiAlPO-34 > CrAlPO-34 > TiAlPO-34. For the first time (for periodic models of MAIPO-34) a direct correlation between the deprotonation energy and the adsorption energy of NH₃ is observed. Finally, unlike M-CHA structures, the prediction of Brønsted acidic site strength in MAIPO-34 structures is difficult due to the ionic bonding and to the fact that many parameters contribute to the acidity at the same time.

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