

# The acidic properties of H-MeAlPO-5 (Me = Si, Ti, or Zr): A periodic density functional study

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## Abstract

The relative strength for Brønsted acid sites of isomorphously substituted H-MeAlPO-5 molecular sieves (Me = Si, Ti, or Zr) is investigated using density functional theory employing periodic models. The results are consistent with the experimental observation and show that H-ZrAlPO-5 has the weakest Brønsted acid sites. Furthermore, the Brønsted acidity of H-MeAlPO-5 (Me = Si or Ti) is compared with that of H-MeAlPO-34 (Me = Si or Ti) [M. Elanany, K. Koyama, M. Kubo, P. Selvam, A. Miyamoto, *Micropor. Mesopor. Mater.* 71 (2004) 51].  
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## 1. Introduction

Microporous crystalline aluminophosphate (AlPO) molecular sieves have attracted much attention in recent years due to their catalytic and sorptive properties [1–5]. It is known that AlPOs consist of discrete aluminium and phosphate ions where trivalent aluminium and pentavalent phosphorous are in tetrahedral environment in the dehydrated materials [6]. In the area of catalysis, the acidity of AlPOs plays an important role and the incorporation of various elements in their framework by the way of isomorphous substitution leads to the synthesis of new materials with novel acidic or redox properties. Numerous elements have been reported to replace trivalent aluminium and/or pentavalent phosphorous in the framework [2,7]. Among the various AlPOs, an extensively studied structure, AlPO-5, which has a one-dimensional channel controlled by 12-membered rings (12-MRs) along the *c* direction [8], presents interesting analogues (Fig. 1). The titanium analogue of AlPO-5, viz. H-TiAlPO-5, has been used as an efficient catalyst for the conversion of cyclohexene to adipic acid by hydrogen peroxide [3]. The silicon containing AlPO-5, viz. H-SiAlPO-5, has potential applications

in environmental catalysis [9]. Furthermore, Zr-AlPO-5 has been synthesized and characterized aiming to increase the catalyst life for the skeletal isomerization of linear butanes and the isomerization of toluidines [10].

Measuring the acid site strength of microporous molecular sieves is very significant because it gives a direct hint to the selection of an efficient catalyst. For example, the very strong Brønsted acidity of mordenite, which contains uni-directional 12-MR channels as AlPO-5, is crucial for its applications in cracking and isomerization of hydrocarbons [11]. The estimation of the acidity of aluminosilicate molecular sieves is usually carried out using temperature programmed desorption (TPD) technique [12–15]. Nonetheless, measuring the acidity of doped AlPOs is not an easy task as in the case of zeolites. It is due to one or more of the following reasons: (i) doped AlPOs have weaker Brønsted acidity compared to their aluminosilicate counterparts; (ii) the flexibility of AlPO frameworks to accommodate hetero atoms by replacing Al, P, or both; (iii) the ionic nature of bonding in AlPO structures [6]. A promising way to measure the relative strength of acid site is then to use highly accurate quantum mechanical *ab initio* methods as density functional theory (DFT). In this study, a systematic investigation of the acidic properties of H-MeAlPO-5 (Me = Si, Ti, or Zr) structures is carried out and a comparison with the acidic properties of H-MeAlPO-34 (Me = Si or Ti) [16] is shown.

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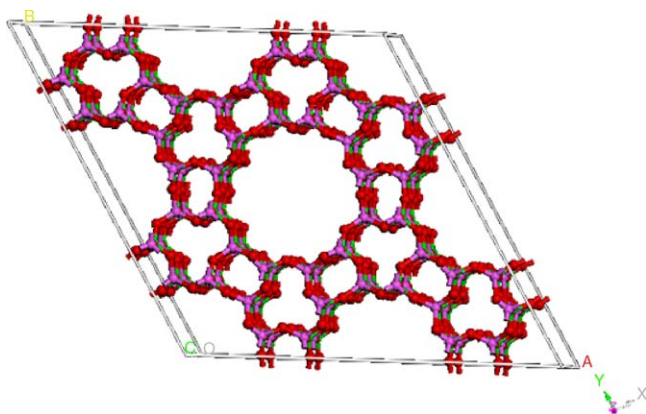


Fig. 1. Supercell of AlPO-5 showing one-dimensional channel along *c* direction controlled by 12-membered rings.

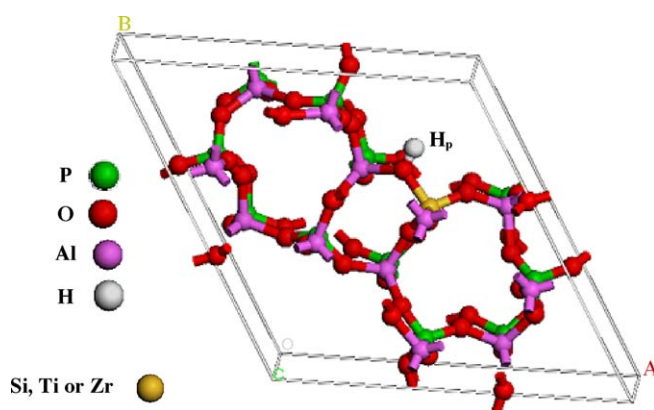


Fig. 2. Structures of H-MeAlPO-5 (Me = Si, Ti, or Zr), where a tetravalent ion and a proton replace one phosphorous ion.

## 2. Structural models and computational details

The whole unit cell of AlPO-5 containing 72 ions is considered for geometry optimization and energy calculations by applying periodic boundary conditions to achieve higher accuracy and reliability than with the conventional cluster model approach. To create a Brønsted acid site in AlPO-5 structure, one tetravalent ion such as Si<sup>4+</sup>, Ti<sup>4+</sup>, or Zr<sup>4+</sup> has to replace one of the phosphorous ions in the framework, and the compensating proton is attached to the neighboring oxygen, as shown in Fig. 2. In the AlPO-5 unit cell, there are 24 equivalent tetrahedral sites

(T) equally occupied by P and Al. Furthermore, there are four types of oxygen ions: O<sub>1</sub> and O<sub>3</sub> connect Al and P to form the 12-MRs, O<sub>2</sub> connects the 12-MR sheets along the *c* direction, and O<sub>4</sub> links the 12-MRs into the 4-MRs and 6-MRs sheets, which are perpendicular to the *c* direction [17]. In the acidic structure models, the proton was attached to O<sub>3</sub>. This makes the acid site accessible for the direct interaction with guest molecules in the main channel of H-MeAlPO-5.

Initially NH<sub>3</sub> was placed at a distance of about 2 Å before starting the geometry optimizations. Geometry optimizations and energy calculations were carried out at generalized gradient approximation (GGA) level with HCTH/407 exchange and correlation functionals [18] using the Dmol<sup>3</sup> program [19,20]. Double numerical with polarization basis set (DNP) was used for all calculations. For models containing Zr, relativistic correction was considered. In a similar way to the computational and calculation methodologies used previously in the case of H-MeAlPO-34 structures [16], the adsorption and deprotonation energies are considered for acidity characterization. For example, the adsorption energy of NH<sub>3</sub> was calculated according to the following equation:

$$E_{\text{ads}} = E_{\text{HAlPO-NH}_3} - E_{\text{HAlPO}} - E_{\text{NH}_3}$$

where  $E_{\text{ads}}$ ,  $E_{\text{HAlPO-NH}_3}$ ,  $E_{\text{HAlPO}}$ , and  $E_{\text{NH}_3}$  refer to the calculated adsorption energy, total energy of the adsorption complex, energy of the acidic molecular sieve, and the energy of ammonia, respectively.

## 3. Results and discussion

Table 1 summarizes the structural parameters for the optimized H-MeAlPO-5 (Me = Si, Ti, or Zr) structures as well as the NH<sub>3</sub> adsorption and deprotonation energies. It can be seen from this table that O–H<sub>p</sub> bond lengths for H-SiAlPO-5, H-TiAlPO-5, and H-ZrAlPO-5 are very similar, i.e. 0.962, 0.960, and 0.960 Å, respectively. Therefore, the O–H<sub>p</sub> bond distance cannot be used to rationalize the acidic properties of these catalysts. It is interesting to note here that after NH<sub>3</sub> adsorption, the proton transfers to form NH<sub>4</sub><sup>+</sup> in case of H-SiAlPO-5 and H-TiAlPO-5, while in the case of H-ZrAlPO-5, no proton transfer has been observed. The N–H<sub>p</sub> distance is 1.610 Å versus 1.077 and 1.109 Å for H-SiAlPO-5 and H-TiAlPO-5, respectively. At this low loading ratio of NH<sub>3</sub> (1:1), ammonia adsorbs

Table 1  
NH<sub>3</sub> adsorption energies, deprotonation energies, and geometrical parameters of H-(Si, Ti, or Zr)AlPO-5 before and after NH<sub>3</sub> adsorption as well as the Mulliken charge (*q*) of the bridging oxygen

| Models                    | Structural parameters  | Adsorption energy (kJ/mol) | Deprotonation energy (kJ/mol) |
|---------------------------|--|----------------------------|-------------------------------|
| H-SiAlPO-5                | O–H <sub>p</sub> , 0.962; Si–O, 1.768; Al–O, 1.846; <Al–O–Si, 132.9; <i>q</i> <sub>O</sub> , –0.749 <i>e</i> | –                          | 1437.4                        |
| NH <sub>4</sub> -SiAlPO-5 | O–H <sub>p</sub> , 1.607; N–H <sub>p</sub> , 1.077; Si–O, 1.669; Al–O, 1.748; <Al–O–Si, 125.8                | –86.3                      | –                             |
| H-TiAlPO-5                | O–H <sub>p</sub> , 0.960; Ti–O, 2.012; Al–O, 1.819; <Al–O–Ti, 119.4; <i>q</i> <sub>O</sub> , –0.765 <i>e</i> | –                          | 1460.3                        |
| NH <sub>4</sub> -TiAlPO-5 | O–H <sub>p</sub> , 1.482; N–H <sub>p</sub> , 1.109; Ti–O, 1.879; Al–O, 1.753; <Al–O–Ti, 118.2                | –67.9                      | –                             |
| H-ZrAlPO-5                | O–H <sub>p</sub> , 0.960; Zr–O, 2.161; Al–O, 1.817; <Al–O–Zr, 116.8; <i>q</i> <sub>O</sub> , –0.833 <i>e</i> | –                          | 1466.6                        |
| NH <sub>4</sub> -ZrAlPO-5 | O–H <sub>p</sub> , 1.035; N–H <sub>p</sub> , 1.610; Zr–O, 2.104; Al–O, 1.786; <Al–O–Zr, 117.2                | –                          | –                             |

The interatomic distances are given in Å, and bond angles in °.

preferably to the Zr ion in the framework. This indicates the weak Brønsted acidity of H-ZrAlPO-5. It should be mentioned here that although results from NH<sub>3</sub> adsorption show the weaker acidity of H-ZrAlPO-5 compared to H-SiAlPO-5 or H-TiAlPO-5, it does not indicate how weak the acid site of H-ZrAlPO-5 is. The calculated adsorption energy of NH<sub>3</sub> on H-SiAlPO-5, -86.3 kJ/mol, is higher than that on H-TiAlPO-5, -67.9 kJ/mol, indicating the stronger acidity of the H-SiAlPO-5 structure. The data in Table 1 show that the calculated deprotonation energies increase in the following order: H-SiAlPO-5 < H-TiAlPO-5 < H-ZrAlPO-5. Hence, the strength of Brønsted acid sites in these structures follows the order: H-SiAlPO-5 > H-TiAlPO-5 > H-ZrAlPO-5. In a consistent way to the above results, the negative charge of the bridging oxygen of the acidic structures calculated from Mulliken population (Table 1) is increasing in the order -0.749e for H-SiAlPO-5 < -0.765e for H-TiAlPO-5 < -0.833e for H-ZrAlPO-5. It indicates the weak Brønsted acid site of H-ZrAlPO-5 where the proton is bounded strongly to the bridging oxygen. The weaker acid site of H-ZrAlPO-5 compared to that of H-SiAlPO-5 was observed experimentally using FT-IR spectroscopy of adsorbed ammonia [10].

Recently, Nur and Hamdan [21] have claimed a correlation between acidity and Me-O-P bond angle, i.e. the larger bond angle the stronger acidity. However, Elanany et al. [16] and Saadoune et al. [22] could not draw such correlation when Al was substituted by divalent metal ions.

In this study, a strong correlation between Brønsted acid site strength and Me-O-Al bond angle is presented for the first time. Table 1 shows that bond angles of H-MeAlPO-5 catalysts increase in the following order:  $\angle\text{Zr-O-Al} = 116.8^\circ < \angle\text{Ti-O-Al} = 119.4^\circ < \angle\text{Si-O-Al} = 132.9^\circ$ . The increase in bond angles and bond lengths Si-O = 1.768 Å, Ti-O = 2.012 Å, and Zr-O = 2.161 Å is attributed to the decrease in ionic radii, Zr = 0.59 Å; Ti = 0.42 Å; Si = 0.26 Å [23], of the tetravalent dopants. It is also noteworthy to mention that a similar trend is observed in the earlier study of H-MeAlPO-34 (Me = Si or Ti), where  $\angle\text{Ti-O-Al} = 127.2^\circ < \angle\text{Si-O-Al} = 133.5^\circ$  [16]. It clearly shows that such correlation between the bond angle  $\angle\text{Me-O-Al}$  and acid site strength is valid for all doped AlPO molecular sieves. The important question here is why rationalizing the acidity of doped AlPOs is easier when P is substituted by tetravalent ions rather than when Al is substituted by divalent ions? To answer, we should recall the ionic nature of bonding in AlPOs [6], which indicates the more ionic Al-O bond versus the P-O bond. Therefore, substituting P in the framework is expected not to be the same as substituting Al.

The large differences in the calculated deprotonation energies and bond angles for H-SiAlPO-5 on one hand, and H-TiAlPO-5 or H-ZrAlPO-5 on the other hand, can be attributed to the relative large differences in the chemical properties of Si, e.g. electronic configuration, ionic radius, and electronegativity, when compared to Ti or Zr. This in turn explains the closer results obtained for H-TiAlPO-5 and H-ZrAlPO-5 compared to those for H-SiAlPO-5. By comparing the acidic properties of H-MeAlPO-5 with H-MeAlPO-34 counterparts in Ref. [16], it can be seen that the adsorption energies of NH<sub>3</sub> on H-SiAlPO-5, -86.3 kJ/mol, and H-TiAlPO-5, -67.9 kJ/mol, are signifi-

cantly lower than those of H-SiAlPO-34, -111.8 kJ/mol, and H-TiAlPO-34, -87.4 kJ/mol [16]. Consistently, the deprotonation energies of H-SiAlPO-5, 1437.4 kJ/mol and H-TiAlPO-5, 1460.3 kJ/mol are also significantly higher than those of H-SiAlPO-34, 1358.9 kJ/mol and H-TiAlPO-34, 1385.7 kJ/mol [16]. These results clearly indicate the weaker Brønsted acidity of H-MeAlPO-5 as compared to their H-MeAlPO-34 counterparts. Experimental evidences for the stronger acidity of SAPO-34 compared to SAPO-5 has been presented by Campelo et al. [24] and more recently by Zhu et al. [25] using ammonia TPD. Thus, the results for acidic properties using computational DFT presented here are in good agreement with the experimental findings.

#### 4. Conclusions

The present study demonstrates that the catalyst H-ZrAlPO-5 possesses very weak Brønsted acid sites, however, the silicon and titanium analogues, viz. H-MeAlPO-5 (Me = Si or Ti), have relatively stronger Brønsted acid sites. The present investigation also reveals that H-MeAlPO-5 (Me = Si or Ti) have weaker Brønsted acid sites than H-MeAlPO-34. Furthermore, a correlation between Brønsted acidity and Me-O-Al (Me = Si, Ti, or Zr) bond angle is established for the first time.

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