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A reactivity index study to rationalize the effect of dopants on Brönsted and Lewis acidity occurring in MeAlPOs

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Abstract

The influence of both bivalent and trivalent metal substituents from a range of metal cation (Co, Mn, Mg, Fe and Cr) on the acidic property (both Brönsted and Lewis) of metal substituted aluminum phosphate MeAlPOs is monitored. The influence of the environment of the acid site is studied both by localized cluster and periodic calculations to propose that the acidity of AlPOs can be predictable with accuracy so that AlPO material with desired acidity can be designed. A semi-quantitative reactivity scale within the domain of hard soft acid–base (HSAB) principle is proposed in terms of the metal substitutions using density functional theory (DFT). It is observed that for the bivalent metal cations Lewis acidity linearly increases with ionic size, where as the Brönsted acidity is solely dependent on the nearest oxygen environment. Intramolecular and intermolecular interactions show that once active site of the interacting species is identified, the influence of the environment can be prescribed. Mg(II)-doped AlPO-34 shows highest Brönsted acidity and whereas Cr(III)-doped species shows lowest acidity. Fe(II)/Fe(III)-doped AlPO-34 shows highest Lewis acidity, whereas Mn(III), Mg (II) shows lowest acidity.

Keywords: Dopants; Brönsted acidity; Lewis acidity; MeAlPOs; Reactivity index; DFT

1. Introduction

Aluiminophospahates (AlPOs) are crystalline microporous molecular sieves. They are made up from alternating AlO_4 and PO_4 tetrahedra, connected through corner sharing of oxygen atoms. These tetrahedral moieties then form a three-dimensional network containing channels and pores. AlPOs are structurally analogous to the type of aluminosilicate zeolites, where the Si^{4+} can be substituted by P^{4+} to have an alternate arrangement of Al and P. AlPOs, though a structural analog of zeolite the show a better flexibility than zeolites towards chemical substitution [1], to which they have been shown to support acid and/or redox activity in the microporous materials [2–4]. AlPOs show Brönsted acidity when acid protons neutralize the charge resulted from a substitution by a lower valent metal ion in the framework. Transition metal substituted AlPOs (MeAlPOs) have shown a marked tendency to Lewis acidity as well associated with the metal dopants [5]. The metal-doped AlPOs have widespread application in the field of heterogeneous catalysis especially in oxidation of hydrocarbons [6]. The acid strength and catalytic activity, however depends on the type of metal dopants employed. There are many experimental studies, which have investigated the correlation between acidity and the local structure of the active site, and nature of metal dopant in the AlPOs [7–9]. MeAlPOs doped with transition metals due to their flexible oxidation state can play a prominent role in selective oxidation of hydrocarbons [10]. In a recent study of Saadoune et al. [11,12] have done a study on structural and electronic properties of dopant ions in AlPOs. They have shown that the acid strength of AlPOs is dependent on a complex combination of structural and electronic features of the dopant ions and does not have any considerable contribution from the local environment of the dopant cations both for bivalent and trivalent state in the framework. This is as well a little contradictory from their earlier views [13], where they proposed that larger the difference in ionic radius between the host ion and the dopant, the more site ordered phases become energetically stable. They have used Hartree–Fock label theory, which is inferior to the quality we were using in terms of predicting the geometry; which is important to interpret the effect of neighboring atoms in the real architecture,

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as well they were unable to propose an activity order for these dopants. We therefore wish to probe into these facts of the activity of the cations and the influence of local architecture of the framework on their said activity and look into the fact that whether the acidity in AlPO is really unaccounted for, which the other group has demanded. This is very important in terms of catalytic reactions, where the experimentalists wanted to use materials with varying acid strength for typical reactions. This will open an area of material designing.

The hard soft acid–base (HSAB) principles classify the interaction between acids and bases in terms of global softness. Pearson proposed the global HSAB principle [14]. The global hardness was defined as the second derivative of energy with respect to the number of electrons at constant temperature and external potential, which includes the nuclear field. The global softness is the inverse of this. Pearson also suggested a principle of maximum hardness (PMH) [15], which states that, for a constant external potential, the system with the maximum global hardness is most stable. In recent days, DFT has gained widespread use in quantum chemistry. Some DFT-based local properties, e.g. Fukui functions and local softness [16], have already been used for reliable predictions in various types of electrophilic and nucleophilic reactions [17–20]. Moreover, Gazquez and Mendez [21], proposed that when two molecules A and B of equal softness interact, thereby implicitly assuming one of the species as nucleophile and the other as an electrophile, then a novel bond would likely form between an atom A and an atom B whose Fukui function values are close to each other. In our study [20] we proposed a reactivity index scale for heteroatomic interaction with zeolite framework. The scale holds well for unisite interaction or in other way with one active site preset in the molecule, the scale does not hold good for systems with two or more active sites. So far there are many theoretical studies with the influence of zeolite structure and composition on acid strength [22,23]. There is a scant literature using reactivity descriptors [24]. A recent paper of Deka et al. [25] has dealt the issue with only monovalent cations.

With this background we performed first ab intio periodic calculation to monitor the role of the framework on the activity of dopants in MeAlPOs. We have performed a systematic study with metal dopants at their different oxidation state: Co^{2+}, Co^{3+}; Mn^{2+}, Mn^{3+}; Mg^{2+}; Fe^{2+}, Fe^{3+} and Cr^{2+}, Cr^{3+}. The trend observed through periodic calculation is validated by localized cluster calculation using localized reactivity index parameters to look into the localized interaction of these dopants with varying charge. Finally a semi-quantitative scale is proposed for the first time in terms of the activity of the dopants both in terms of Brönsted and Lewis acidity.

2. Theory

In density functional theory, hardness (η) is defined as [26]:

$$\eta = \frac{1}{2}\left(\frac{\delta^2 E}{\delta N^2}\right) v(r) = \frac{1}{2}\left(\frac{\delta\mu}{\delta N}\right)_v \tag{1}$$

where E is the total energy, N is the number of electrons of the chemical species and the chemical potential.

The global softness, S, is defined as the inverse of the global hardness, η.

$$S = \frac{1}{2\eta} = \left(\frac{\delta N}{\delta\mu}\right)_v \tag{2}$$

Using the finite difference approximation, S can be approximated as

$$S = \frac{1}{\mathrm{IE} - \mathrm{EA}} \tag{3}$$

where IE and EA are the first ionization energy and electron affinity of the molecule, respectively.

The Fukui function $f(r)$ is defined by [16]

$$f(r) = \left[\frac{\delta\mu}{\delta v(r)}\right]_N = \left[\frac{\delta\rho(r)}{\delta N}\right]_v \tag{4}$$

The function 'f' is thus a local quantity, which has different values at different points in the species, N is the total number of electrons, μ the chemical potential and v the potential acting on an electron due to all nuclei present. Since $\rho(r)$ as a function of N has slope discontinuities, Eq. (1) provides the following three reaction indices [16]:

$$f^-(r) = \left[\frac{\delta\rho(r)}{\delta N}\right]_v^- \quad \text{(governing electrophilic attack)},$$

$$f^+(r) = \left[\frac{\delta\rho(r)}{\delta N}\right]_v^+ \quad \text{(governing nucleophilic attack)},$$

$$f^0(r) = \tfrac{1}{2}[f^+(r) + f^-(r)] \quad \text{(for radial attack)}$$

In a finite difference approximation, the condensed Fukui function [26] of an atom, say x, in a molecule with N electrons are defined as:

$$\begin{aligned} f_x^+ &= [q_x(N+1) - q_x(N)] \quad \text{(for nucleophilic attack)},\\ f_x^- &= [q_x(N) - q_x(N-1)] \quad \text{(for electrophilic attack)},\\ f_x^0 &= \tfrac{1}{2}[q_x(N+1) - q_x(N-1)] \quad \text{(for radical attack)} \end{aligned} \tag{5}$$

where q_x is the electronic population of atom x in a molecule.

The local softness $s(r)$ can be defined as

$$s(r) = \left(\frac{\delta\rho(r)}{\delta\mu}\right)_v \tag{6}$$

Eq. (3) can also be written as

$$s(r) = \left[\frac{\delta\rho(r)}{\delta N}\right] v \left[\frac{\delta N}{\delta\mu}\right]_v = f(r)S \tag{7}$$

Thus, local softness contains the same information as the Fukui function $f(r)$ plus additional information about the total molecular softness, which is related to the global reactivity