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A computational study on heteroatom distribution in zeotype materials

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ABSTRACT

SSZ-13 and SAPO-34 are a zeolite and a SAPO, respectively, both having the CHA topology. We present computational studies of the relative stabilities of a pair of acid sites in these materials as a function of their separation. The most stable configurations are found when the acid sites are next nearest neighbors, viz. separated by only one other T-atom. Replacing the acidic protons with a distributed charge leads to the most stable geometry involving a maximum distance between the two sites, in accordance with Dempsey's rule. Unsurprisingly, we find a negative correlation between calculated stability and calculated Brønsted acid strength. The results afford novel interpretation of earlier spectroscopic studies.

1. Introduction

Crystalline Nanoporous Framework Materials (CNFMs) have attracted great attention both from academic and industrial materials science over the past half-century. It is the molecular dimension of the pores within these materials, combined with the possibility to functionalize their huge internal surface that continues to hold both fascination for academics and promise for industrialists. When these properties are properly married, CNFMs such as zeolites and microporous aluminophosphates (AlPOs) have found utilization in areas as diverse as water softening, environmental cleanup, catalytic cracking and the production of value added products such as olefins and gasoline from fossil feedstocks [1].

The crystal structure and average composition to CNFMs have been characterized with improved resolution and sophistication since the pioneering work of Barrer and Breck in the 1950's and are now described in great detail. Properties that do not follow the crystalline regularity are, however, less well characterized. This applies both to the active site in these materials and even more to structural defects. The active sites are typically a consequence of heteroatoms in the lattice. Most common are aluminum that replaces silicon in zeolites and silicon replacing phosphorus in SAPO materials, but many other substitutions are known. In low concentrations, these active sites are best described as substitutional defects.

The substitution of aluminum for a tetrahedral silicon in a zeolite, and of silicon for a tetrahedral phosphorous in a SAPO, introduces a negative charge in the framework, and charge compensation with a proton creates a catalytically active Brønsted acid site. SAPO-34 and the zeolite SSZ-13 share the same CHA-topology, but show some different properties due to the difference in their elemental compositions. SAPO-34 and SSZ-13 both have the highly symmetric chabazite topology with only one symmetrically independent tetrahedral site (T-site) and four unique oxygen sites (Fig. 1). The protons introduced to ensure charge neutrality after silicon (SAPO-34) or aluminum (SSZ-13) inclusion may coordinate to one of the four different oxygens. The preferred position of the proton at isolated acid sites has been the subject of both experimental [2–6] and computational [7–11] studies.

Based upon electrostatic arguments it is assumed that the aluminum ions (or silicon ions in SAPOs) will be located with largest possible distance from each other. This is also known as Dempsey's rule [12]. According to this rule, the heteroatoms will consequently occur as isolated substitution defects when the Si/Al ratio exceeds a topology-dependent ratio (6.87 in the case of CHA [13]). This assumption has been challenged in the past. Schröder and Sauer [14], using molecular mechanics calculations with shell-model potentials, studied the distribution of aluminum atoms in a high-silica faujasite framework. They calculated relative energies for a system with two aluminum atoms per primitive unit cell (48 T-atoms) as a function of Al–Al separation distances. Their results indicate that Dempsey's rule is violated through the formation of next-nearest neighbor heteroatom pairs (NNNP)–Al–O–Si–O–Al

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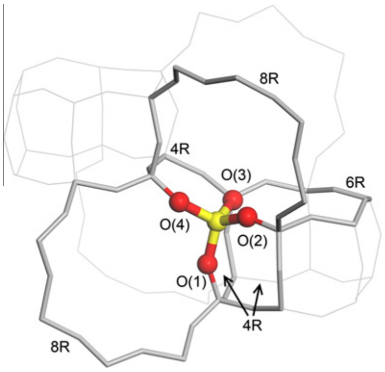

Fig. 1. SAPO-34 structure with four crystallographically different oxygen atoms. The positions are defined as follows: O(1): 2,4-member ring (MR) and 1 8-MR, O(2):1,4-MR, 6-MR and 8-MR, O(3): 2,4-MR and 1,8-MR, and O(4): 1,4-MR and 2,8-MR. The labeling scheme is taken from Ito et al. [31].

linkages. They found similar results by comparing relative energies of the structures containing Al–O–Si–O–A1 linkages and the structures with the largest possible separation of A1 atoms for chabazite, erionite, gmelinite, offretite, and zeolite L. Recently, Deroche et al. [15] found similar linkages (Si–O–Al–O–Si) for the SAPO material STA-7. Interestingly, the energetic preference for such pairs vanish upon removing the acidic protons and distributing their charges over all T-atoms; a condition which may mimic the situation in a catalyst when the pores become filled with species that may act as a delocalized positive charge. In the case of a freshly synthesized catalyst, template molecules and water would carry the delocalized charge, while in a deactivated catalyst, coke would be the charge-carrier. The charge distribution may therefore vary during the catalytic cycle of activation, deactivation and regeneration.

Shantz et al. [16] studied the aluminum distribution in ZSM-12 using different NMR techniques and found that distribution of Al sites is not random but controlled by electrostatic forces arising from the presence of template molecules during synthesis. They suggested that calcining zeolite materials in the presence of water leads to migration of the Al sites. Their conclusion is very similar to that of Sabater et al. [17], who studied the matter in ZSM-18 computationally. Barthomeuf et al. [18] studied silicon island formation during the synthesis of SAPO material and they observed that silicon dispersity depends on the packing value of the template used during synthesis; that is the number of template molecules which can be accommodated by a single cavity. Smaller templates, like morpholine, provide higher amounts of positive charge to balance the negative charge caused by silicon incorporation in the network, thus higher silicon dispersion is obtained. Gómez-Hortigüela et al. [19] suggested that differences in silicon incorporation is not derived by different packing values of the template, instead invoking the variation in the number of water molecules which locate in the cavities in the structure to fill the space left over by the template. Further, they suggested that more water molecules in the cavities lead to a greater dispersion of silicon atoms in the structure. Haouas et al. [20]used ^{29}Si MAS, ^{1}H MAS, and ^{29}SiCPMAS NMR spectroscopy to investigate as-synthesized and calcined SSZ-13. While their results indicate adherence to Dempsey's rule in the as-synthesized zeolite (in agreement with the abovementioned studies [16,17]), the picture changes when water and template molecules are removed from the pores by calcination. In the latter case, the experimental observations indicate the presence of NNNP sites. Dedecek et al. [21], employing ^{27}Al NMR and DFT/MM calculations, found Al–O–Si–O–Al moieties in ZSM-5.This has two implications: The aluminum atoms are mobile at calcination conditions (several hours at ≈750 K in air), and there is a thermodynamic driving force to formation of NNNP when the framework charge is neutralized by localized protons.

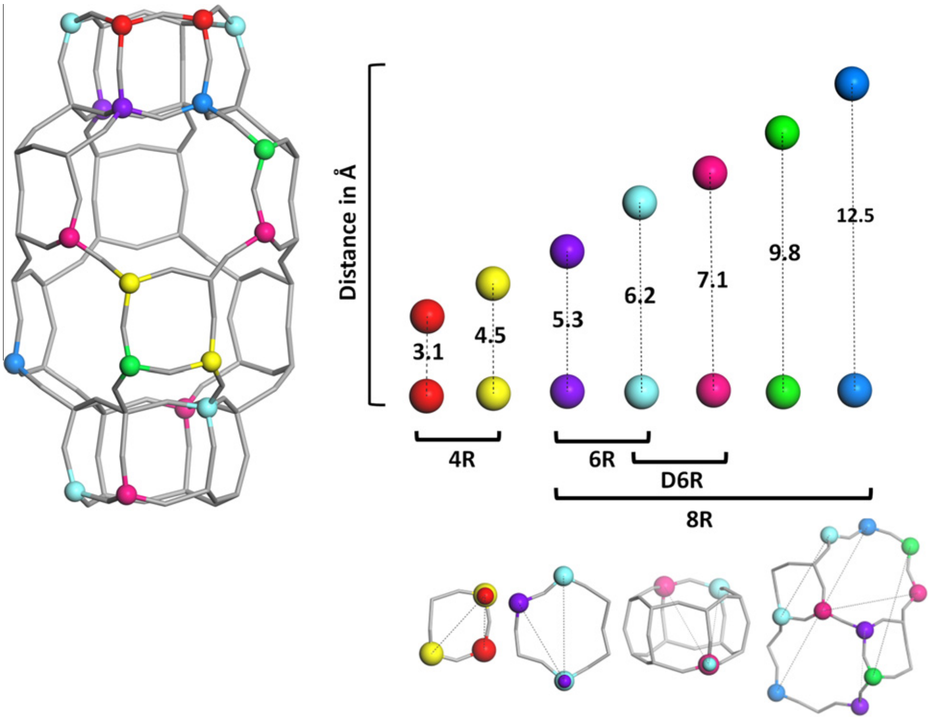

Fig. 2. Schematic drawing of the chabazite framework. The grey part of the structure is SiO_2 and colored balls are aluminum atoms (Each color code shows one pair of aluminum). Only one pair of aluminum atoms was included in each calculation. Note that the pair separated by 3.1 Å are nearest neighbors, representing a violation of Löwenstein's rule. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)