



## Review

## General aspects of zeolite acidity characterization



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## ABSTRACT

This paper describes the most used techniques in the determination of the acid property in zeolite materials. Two families of techniques, namely spectrometric (IR, NMR) and adsorption–desorption methods (calorimetry, TPD) are considered. Typical experimental conditions, schematics of equipment setup, and rules for molecular probe selection are shown. Selected experiments that make use of these methods are briefly discussed, and their most relevant results are presented. This review shows some of the possibilities that can be used to “measure” acidity in zeolites. It is also shown that the interpretation of such results could be deceiving in certain situations, especially because acidity and catalytic performance are not synonyms and acidity is inherently a relative term.

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## 1. Introduction

Zeolites are crystalline silicoaluminates with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions. As the pores preferentially adsorb molecules that fit snugly and exclude molecules that are too large, they act as sieves on a molecular scale [1]. Zeolites are also recognized by their ion exchange ability originating from the presence of exchangeable extra-framework cations that compensate the negative charges in the lattice. These characteristics put zeolite materials in the hotspot of separation and heterogeneous catalysis processes.

Catalytic cracking of hydrocarbons is a clear example where zeolites have had large impact on both economy and catalysis science. Zeolite application made it possible to increase the catalyst activity and allowed a further exploitation of the FCC unit. At the same time, the cracking reactions became much more selective in favor of desired products such as gasoline [2]. As much as  $200 \times 10^5$  tons of Y zeolite are intended every year for use in catalytic cracking [1]. The question about why zeolites are special in the catalytic upgrading of hydrocarbons in comparison to other crystalline oxide materials, can be answered on basis of zeolite's

unique properties: uniform microporosity, ensuring high catalyst selectivity; ion exchange ability, allowing to perform several types of ion exchange reactions; internal acidity, related to zeolite catalytic activity for hydrocarbon transformation, and thermal stability, to resist the severe reaction conditions [2]. This document is about zeolite acidity, an important property closely related to the ability to crack and isomerize hydrocarbon structures [3]. It is important to keep in mind that it is the combination of these properties, and not acidity alone, what grants zeolites with such catalytic features.

Zeolite acidity comprises two distinct facets: the acid amount, i.e., the number (mole) of acidic sites sensed in a portion (kg) of material, and the acid strength, i.e., the energy (kJ) involved during the interaction between such acid sites and the basic molecule used to sense them. It can be seen that the acid amount as well as the acid strength depend strongly on the characteristics of the basic molecule used in the determination. In systems such as aqueous solutions of weak acids, the acid amount and the acid strength are inherently referred to water, which not only acts as a solvent, but as a base. If the solvent is changed, for example to acetone, it is expected that the energetics and extents of dissociation be also affected. This shows that acidity is a relative concept at all levels, and acid solids are not the exception.

The acid sites that can be found on the zeolite structure and in solids, in general, are Brønsted (protonic) or Lewis (non-protonic) in nature. It can be realized that the holistic description of acidity requires the characterization of several factors, so that in general several techniques must be used. In the attempt of measuring solid acidity, the experiments have to convey information on an ample

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variety of properties: chemical nature of the acid sites (Brønsted or Lewis), site abundance, acid strength distribution, and accessibility to acid sites because of textural features.

Some of the research goals in catalysis science are to find reliable experimental methods for characterizing these properties in different catalysts, and to understand the observed changes when either the catalyst structure or its composition are varied. Understanding how acidity can be tuned by adequate synthesis procedures or how it evolves after zeolite exposure to particular conditions is crucial in the design of new catalysts, in the improvement of existing ones, and in the prediction of catalyst performance under actual reaction conditions [4].

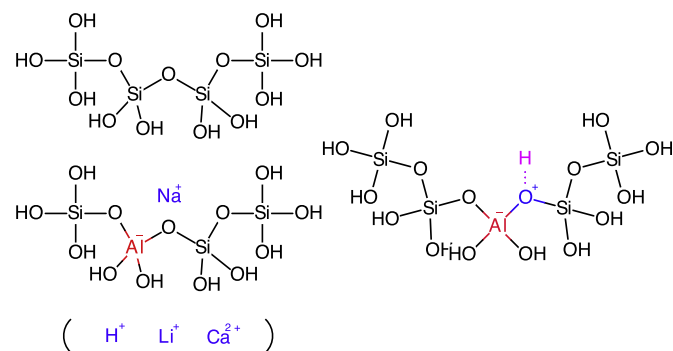
The objective of this document is to stand out important features of the most used techniques towards the determination of zeolite acidity. The principles over which these methods rely are briefly presented; their advantages and limitations are also discussed. The text is roughly divided in 3 sections: Origins of zeolite acidity, determination of zeolite acidity by spectroscopic techniques (IR and NMR), and zeolite acidity by adsorption–desorption methods (microcalorimetry, TPD, catalytic reactions).

### 1.1. Origins of zeolite acidity

Thomas [5] was the first to propose that zeolite acidity originated from aluminum tetrahedral bonding in the silicoaluminate structure. Aluminum and silicon atoms (the T-atoms) of the zeolite lattice are chemically bound together by the sharing of oxygen atoms on the corners. The angle formed by T–O–T (inter-tetrahedrons) varies in a broad interval ( $130^\circ$ – $180^\circ$ ) [1], giving rise to the elevated number of known zeolite structures [6,7]. The introduction of trivalent aluminum atoms in the tetrahedral framework bring negative charges that get balanced by extra-framework cations (Fig. 1) such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$  [8]. Protons acting as compensating cations near aluminum centers behave as Brønsted acid sites (BASs) under certain conditions.

Milliken et al. [9] conceived a different structure for the acid site, with tricoordinated silicon atoms located on small structure defects acting as electron-acceptor sites, i.e., as Lewis centers. Other Lewis sites can be created by local charge imbalances originating from defect sites, thermal dehydroxylation or collapse, presence of active metals and surface defects, etc. Lewis sites are important in catalytic reactions that involve redox steps.

Eischens and Mapes [10] tested these possibilities with experiments of ammonia adsorption and *in situ* IR spectroscopy. They found that Lewis and BASs both exist in zeolite catalysts when the solids are deeply dried, but in the presence of small amounts of water, the IR bands corresponding to  $\text{NH}_4^+$  increase at the expense



**Fig. 1.** Top left: Fragment of the tetrahedral silica lattice. Bottom left: The isomorphic insertion of aluminum in the lattice gives rise to negative charges compensated by extra-framework cations. Right: Structure of the BAS.

of ammonia's. The existence of BASs was inferred by the formation of  $\text{NH}_4^+$ , since ammonia adsorption on Lewis centers does not entail probe protonation. Parry later confirmed these results with experiments of pyridine adsorption [11]. Hall and Leftin [12] found that alkanium ions form during hydrocarbon cracking on silicoaluminate catalysts, and demonstrated that only BASs can produce such intermediaries. Kazansky et al. showed that protons in BASs are bound to the structure by strongly polarized covalent bonds rather than by ionic interactions [13]. Today, it is recognized that Lewis and BASs can be found in the zeolite, and the structure of the acid site ( $\text{SiOHAl}$ ) has been confirmed by several experimental techniques.

## 2. Experimental methods to determine zeolite acidity

### 2.1. Zeolite composition

The content of framework aluminum informs about the highest possible abundance of BASs. However, aluminum and acid amounts barely match because zeolites tend to release aluminum very easily as a result of thermal or chemical treatments. This is a characteristic of Y zeolite, one of the most important commercial zeolites. Additionally, the ion exchange is an equilibrium process that cannot be taken to the 100%, and BASs use to dehydroxylate at high temperature [14]. Released framework aluminum accumulates inside zeolite porosity to produce what is known as extra-framework aluminum; this acts as a neutralizing agent since it can experience ion exchange with BASs [14] and may cause blockage at pores' entrance, reducing further the acid amount. It can be seen that aluminum content is just a rough estimate of zeolite potential.

Dissolving the zeolite powder in concentrated HF, and then determining the composition of the solution by atomic emission–absorption spectroscopy usually gives acceptable results. The use of inductively coupled plasma (ICP) has recently gained in popularity since this is much more sensitive than the traditional atomic spectroscopy. Semi-quantitative analysis can also be performed directly on solid powders by X-ray fluorescence (XRF) and energy-dispersive X-ray spectroscopies (EDX). The information attainable from these procedures, however, is very limited because they give no insights upon aluminum distribution, i.e. on how much aluminum is in the framework or in the cavities.

Powder X-ray diffraction can be used for the identification of crystal phases, their purity, unit cell parameters, and the indirect determination of some compositional features. Si–O bonds are slightly shorter than Al–O, meaning that the unit cell size of the zeolite increases with framework aluminum contents. X-ray diffraction is capable of measuring these variations related to framework composition. The ASTM D3942-03 (2008) method describes how to calculate unit cell sizes in Y zeolite from powder X-ray diffraction experiments. The correlation between unit cell size and framework aluminum content follows a linear trend [15]

$$\frac{FAI}{u.c.} = m((u.c.s.) - X). \quad (1)$$

Here, *u.c.* and *u.c.s.* are unit cell and unit cell size, respectively. The number of framework aluminum atoms per unit cell ( $FAI/u.c.$ ) can be calculated provided *m* and *X* are known. Different authors report slight differences in these, as can be seen in Table 1 for the parameters of FAU [16–21].

Jorik [22] reported a modification to Eq. (1), with the purpose of including the effect of sodium ions on the structural parameters of the zeolite. The combination of results from X-ray diffraction and total composition can be used to calculate the amount of framework aluminum per gram of zeolite. Even so, this is just an estimate

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