

Zeolites and zeolite-based materials in analytical chemistry

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Zeolites are inorganic materials with large surface areas and well-defined internal structures of uniform cages, cavities or channels. This review analyzes recent literature giving particular attention to applying zeolite and zeolite-based materials in developing approaches to electrochemical and optical sensing, and techniques for separation or preconcentration. We highlight the analytical potential of these materials and suggest avenues for further research.

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1. Introduction

The term “zeolite” was initially used to designate a family of natural minerals that presented as particular properties the exchange of cations and the reversible desorption of water. This latter property gave origin to the generic name of zeolite, which is derived from two Greek words: *zeo*, that boils, and *lithos*, stone [1]. Today, the term includes a great number of natural and synthetic minerals with common structural characteristics. The natural ones are formed in a variety of geological sites and from precursors, such as volcanic ash, clay, biogenic silica and different forms of quartz [2]. Among more than 40 natural and 200 synthetic zeolites, the most common are mordenite, clinoptilolite, chabaxite, erionite and phillipsite.

Zeolites are hydrated aluminosilicates belonging to the family of the tectosilicates, where the SiO_4 tetrahedra form three-dimensional supercages [3]. In their structure (Fig. 1), some Si atoms are substituted by Al atoms, resulting in a negatively charged structure that originates from the difference between the $(\text{AlO}_4)^{5-}$ and $(\text{SiO}_4)^{4-}$ tetrahedra [4]. These negative sites are balanced by counterions, usually alkaline and alkaline-earth cations, which can be substituted by

other cations, thus, providing zeolites with the property of ion exchange.

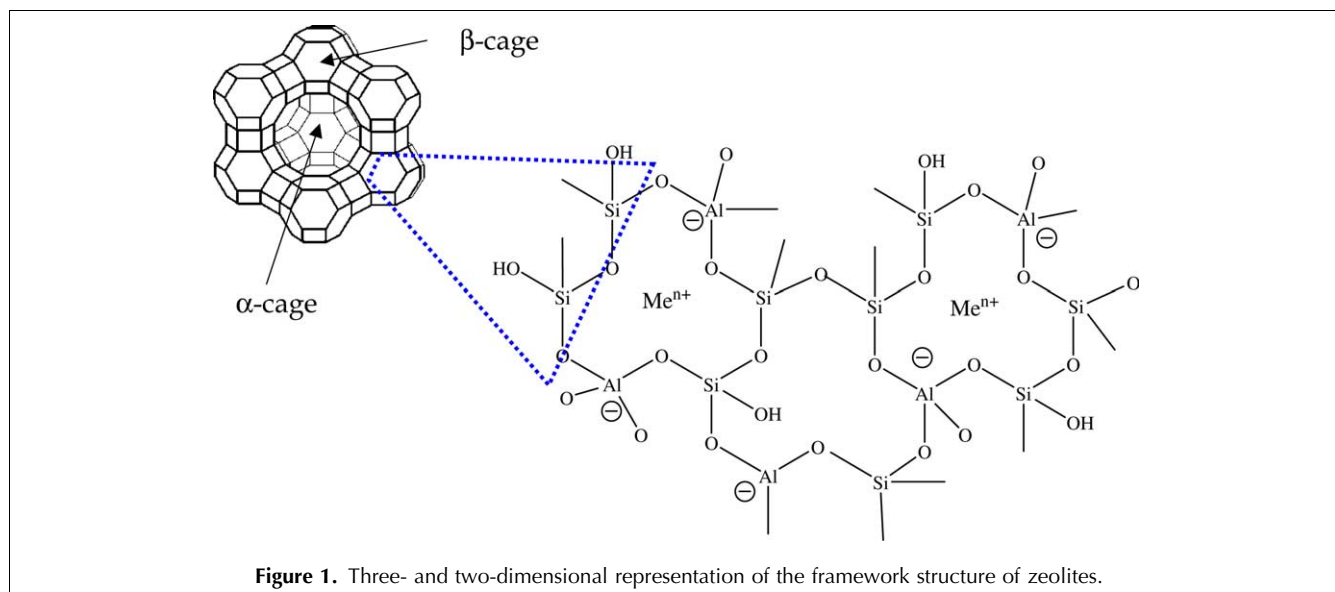
The crystalline skeleton may be formed by a three-dimensional combination of tetrahedra TO_4 ($\text{T} = \text{Si}, \text{Al}, \text{B}, \text{Ga}, \text{Ge}, \text{Fe}, \text{P}$ and Co) bonded by oxygen atoms (Fig. 1). The $\text{T}-\text{O}-\text{Si}$ links result in rings of great variety that are responsible for zeolites' cage and channel framework and also for their capacity for molecular discrimination, in both size and shape, as well as their molecular sieve character [5].

Over the years, a whole theory for ion exchange with zeolites has been developed [6]. Due to their rigid three-dimensional network, they exhibit this property without significant structural changes and are free of shrink-swell behavior. However, the process depends on so many characteristics of the zeolite, the solution and the ions present, that the behavior of zeolites does not exactly follow the normal rules of ion exchange [6,7].

The use of natural zeolites for environmental remediation (organic compounds and heavy-metal ions) is well established. Also, natural zeolites have been found to be helpful in the control of malodors (e.g., hydrogen sulfide and ammonia) emanating from confined livestock-rearing areas, kennels, pet shops, zoos and pet-litter trays. Their high surface area, and therefore their high adsorption capacity, as well as their ion-exchange properties make them very useful in these fields [8–12].

Another important inherent property of aluminosilicate zeolites is their catalytic action due to their strongly acidic nature. The terminal hydroxyl groups (Fig. 1) in the $\text{Si}-\text{OH}\cdots\text{T}$ framework are considered Brönsted-acid sites and the interaction of hydroxyl oxygen with a T atom produces Lewis-acid sites. Their technological importance in the petroleum industry

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arises precisely from their use as acid catalysts. According to Corma [13], who has recently reviewed the state of the art and future challenges of zeolites as catalysts, zeolites can be considered as catalytic micro-reactors.

Since many biological processes are related to properties exhibited by zeolites, these materials have also been studied and used in the medical field recently. Their biological activity has been tested in anticancer therapy and for the treatment of diarrhea [14,15].

It is evident from the literature that zeolites (both natural and synthetic) are versatile materials in their application, yet the situation is not exactly the same as far as analytical applications are concerned. Within the last decade, numerous studies have been devoted to understanding the physico-chemical properties of zeolites. Some of the principal advantages of zeolites are their low cost of extraction, their availability in great volumes, and their excellent stability in chemical and thermal processes. They can also be submitted to diverse treatments in order to give them desired physical and chemical properties. Those same properties that make zeolites an important material in petrochemistry, environmental science, agriculture and many other fields could be exploited in analytical chemistry; however, this is not the case. The aim of this review is to fill this gap and to revise some of the more important analytical applications of zeolites in recent years in the hope that analytical chemists (other than those dedicated to electroanalysis) will realize the great analytical potential these materials.

2. Sensors

2.1. Zeolite-modified electrodes (ZMEs)

Since the 1990s, the combination of some of the attractive properties of zeolites with electrochemical

methods of analysis has opened a new area of research in the field of chemically modified electrodes (CMEs). In 1999, Walcarius [16] excellently reviewed this topic and readers are advised to consult his paper which discusses close to 10 years of investigation into ZMEs. We will therefore analyze only some of the works that characterize the research done in this field since the 1990s.

ZMEs exploit the ion-exchange capacity and the molecular (size, shape and charge) selectivity of zeolites, so they have advantages over other CMEs. Any electrochemical scheme that relies on ion exchange or analyte preconcentration or size/shape/charge selectivity or catalyst-assisted reactivity, or any combination of these features, can be designed for use in ZMEs.

The hydrophilic character of zeolites makes them materials well suited to the co-immobilization of enzymes and mediators in the preparation of biosensors. For example, a modified type Y zeolite (MY) can be used as matrix to incorporate horseradish peroxidase (POD) and methylene green (MGH) onto a glassy carbon electrode to fabricate a biosensor for hydrogen peroxide [17]. The high selectivity is the result of the combined use of MGH as electron-transfer mediator, which minimizes interference from other electroactive species, and the selectivity of the MY membrane coating, which reduces interference from anionic species. The good reproducibility (2.1%) is attributed to the uniform pore and cage structure of the zeolite matrix.

Metal ion-doped zeolites allow exploitation of the ion-exchange capacity of zeolites for the development of electrochemical sensors. For example, carbon paste electrodes modified with copper-doped zeolites are likely candidates for sensing non-electroactive cations in flow-injection formats [18]. The detection mechanism is shown in Fig. 2: when a solution containing analyte ions (for example, K^+) contacts the electrode surface, an

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