Electric fields in zeolites: fundamental features and environmental implications‡

Christopher J. Rhodes*

Fresh-lands Environmental Actions, Caversham, Berkshire RG45 5BE, UK

Received 16 March 2015; Revised 7 May 2015; Accepted 11 May 2015

A critical review of zeolites and their use in practical applications is presented. Specifically-considered are their role as media for selective light-induced oxidations using molecular O₂, and the relationship between this phenomenon and the surface electric fields that exist in zeolites. Methods for the determination of the strength of zeolite surface fields are discussed using sorbed molecules such as CO (with IR detection), spin-probes, di-tert-butyl nitroxide, and NO (measured using EPR spectroscopy). Relationship between the surface fields and molecular reorientation energetics for free radicals sorbed in zeolites, obtained using muonium as a spin-label, is explored. Finally, results obtained from exposing the naturally occurring zeolite, clinoptilolite, to high energy electrons as a means for activating materials toward selective removal of radioactive caesium and strontium cations from wastewaters of nuclear power plants are presented.

© 2015 Institute of Chemistry, Slovak Academy of Sciences

Keywords: zeolites, muon, photooxidation, surface electric field, radioactive waste, EPR

Introduction

Zeolites are solid materials with numerous and various applications in industry and environmental pollution control (Armbruster, 2001; Barrer, 1978; Čejka et al., 2010; Mumpton, 1999; Rhodes, 2005, 2007, 2010a, 2010b; Sherman, 1999). They can be used both to remove environmental contamination and, in preemptive strategies, to prevent the egress of pollutants into the environment, a priori (Rhodes & Dintinger, 2012; Yeritsyan et al., 2013). A zeolite has a microporous aluminosilicate framework with an overall negative electric charge, along with a sufficient number of cations to neutralise this framework charge. The overall stoichiometry of zeolites can be expressed by the general formula \( M_{x/n} [Al_xSi_yO_{2(x+y)}] \cdot pH_2O \), where \( M \) represents the cations that are present in a particular type of zeolite (e.g., Na, K, Li, Ca, Mg, Ba, Sr), \( n \) is the cation-charge, \( p \) represents the water molecules contained in the zeolite, \( y/x = 1–6 \), and \( p/x = 1–4 \) (Yeritsyan et al., 2013). Since the cations are present, but loosely, in the zeolite structure, they can be exchanged by other types of cations, generally from the aqueous media; thus, zeolites are excellent ion-exchange agents and find applications in water softening (e.g., removal of Ca\(^{2+}\) and Mg\(^{2+}\) cations and their replacement with Na\(^{+}\) cations) for the decontamination of liquid nuclear waste of radioactive cations (mainly Sr\(^{2+}\) and Cs\(^{+}\)) and in the removal of heavy-metal cations (e.g., Pb\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\)) from wastewater. In their H\(^{+}\)-exchanged forms, zeolites provide solid acid catalysts, and are used on the hundred thousand tonne per annum scale for cracking petroleum distillates into fuels, in the petrochemical industry, and to manufacture raw chemical feedstocks for various processes (Mumpton, 1999). Zeolites contain pores (conventionally termed “micropores”, but which are really “nanopores”) with diameters typically of less than 13 Å (1.3 nm), and so simple organic molecules are readily sorbed into them. Thus,

*Corresponding author, e-mail: cjrhodes@fresh-lands.com
‡Presented at the XXV. International Conference on Coordination and Bioinorganic Chemistry, Smolenice, Slovakia, 31 May–5 June 2015.
the pores can serve as microreactors (Rhodes, 2008) within which a range of “green” chemical reactions can be performed, e.g. oxidations, with a gentler impact on the environment than standard solution phase reactions since, for example, the use of organic solvents is minimised or avoided. A zeolite grain is typically of micron dimensions, with an internal surface area of hundreds of m$^2$ g$^{-1}$ and an external surface area which is an order of magnitude smaller (Rhodes, 2010a). There are strong surface electrostatic fields in zeolites stemming mainly from the presence of poorly solvated cations, which can promote chemical transformations, such as photooxidation reactions.

The first zeolite was discovered in 1756 by Cronstedt (1756) who observed that when heating some unusual stones in a blow-pipe flame, effervescence of hot water and steam occurred, as if the stones were themselves boiling. Accordingly, he called them “zeolites” which from the Greek (zein, “to boil”; lithos, “a stone”) means “boiling stones” (Čejka et al., 2010). The underlying cause of this effect is that zeolites can absorb a considerable proportion of their own volume of water, and other liquids, which are driven out by heating. Along with their cation-exchange properties, such a high micropore volume yield an abundance of applications for zeolites. Due to the fact that naturally occurring zeolites (of which 50 are known) often contain impurities, which are principally other minerals (including other types of zeolite), they are not suitable for applications in which a consistent composition is required. There are 150 synthetic zeolites available which can be designed to catalyse specific and selective transformations such as the MTG process. Zeolites were used to reduce environmental radioactivity caused by both the Chernobyl (Rhodes, 2007; Rhodes & Dintinger, 2012) and Fukushima (Rhodes & Dintinger, 2012) nuclear disasters.

**Photooxidation in zeolite pores**

Due to the low cost and availability of molecular oxygen, it may seem to be an ideal oxidising agent, but in fact, it is typically lacking in selectivity and tends to produce unwanted by-products which require separation, which add costs to both the energy and fiscal budgets. Oxidation reactions in the gas phase or liquid phase are often mediated by free radicals, which encourage over-oxidation and the formation of secondary products of coupling and disproportionation reactions. Reactions with O$_2$ also tend to be relatively exothermic, and an indiscriminate attack on initial hydrocarbon chains but also on their primary oxidation products can occur. The latter is a consequence of the products being more readily attacked by free radicals than the hydrocarbon starting materials, which favours poly-substitution or secondary oxidation products on a simple kinetic basis. This effect becomes more acute as the reaction proceeds and its products accumulate, and in many practical situations only a small percentage conversion of starting materials to products is achieved (Fossey et al., 1995). When such photochemical oxidations of hydrocarbons are carried out in zeolites, a far higher selectivity is achieved, as it is described in two reviews (Blatter et al., 1998; Blatter & Frei, 1993). The zeolite-contained molecules can be compared with “matrix isolated” systems used to make spectroscopic measurements on reactive species (Rhodes, 2014). The trapped molecules cannot diffuse widely through the medium, and so their reactions with other species are limited. The aluminosilicate framework acts as a fairly poor “solvent” of the cations, which accordingly contribute to intense surface electrostatic fields and can stabilise the highly polar charge-transfer (C-T) complexes ($\text{h}^+$/O$_2^-$) formed by a collision between a hydrocarbon molecule (h) and O$_2$ combined with light absorption by the contact pair. Thus, oxidation reactions can be driven using visible light, which limits the excess energy in the primary photo-products and minimises the decomposition of compounds containing weak bonds, e.g. O—O in peroxides and hydroperoxides. The problem of more extensive oxidation of primary products (e.g. benzaldehyde to benzoic acid) is also avoided. It can be noted that visible light is preferred to UV light, from the viewpoint of both cost and less draconian health and safety regulations. The following examples illustrate the efficacy of the approach in general.

Frei et al. (1996) reported that 2,3-dimethylbut-2-ene can be oxidised in zeolite NaY (Si/Al = 2.4), BaY, NaL, and BaL, which were the hosts used for most of their subsequent experiments too. Zeolite Y has the faujasite structure (Fig. 1, characterised later in the text), with a network of spherical 13 Å diameter supercages linked by 7.4 Å diameter “windows”, while zeolite L contains 7 Å diameter channels. When 2,3-dimethylbut-2-ene was exposed to 750 nm radia-

![Fig. 1. Structure of faujasite with central supercage surrounded by sodalite cages, along with cation sites. (Credit. Prof. N. J. Turro).](image-url)