Available online at www.sciencedirect.com

ScienceDirect

Microporous and Mesoporous Materials 114 (2008) 27–63

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Review

Extraframework cation distributions in X and Y faujasite zeolites: A review

T. Frising *, P. Leflaive

Institut Français du Pétrole – IFP Lyon, Catalysis and Separation Division, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

Received 1 October 2007; received in revised form 11 December 2007; accepted 18 December 2007
Available online 28 December 2007

Abstract

The catalysis and sorption properties of faujasites depend largely on the extraframework species present, notably the cations. Following the extensive and most valuable works of Smith in 1971 and Mortier in 1982, this review paper gathers all cation distributions in X and Y type faujasite zeolites known to the authors and available in the literature by mid-2007. The cation distribution in sodium exchanged samples is analysed first. Thereafter the alkaline cation, alkaline earth cation and transition metal cation exchanged samples are dealt with. A short commentary is given at the end of each section to highlight general trends and/or contradictions between different authors if they exist.

Keywords: Zeolite X; Zeolite Y; Cation distribution; Crystal structure; Ion exchange; Na–X; Na–Y; Alkaline; Alkaline earth; Transition elements; Rare earth

Contents

---

* Corresponding author. Fax: +33 4 78 02 20 66.
E-mail address: tom.frising@ifp.fr (T. Frising).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.12.024

1. Introduction

Faujasite zeolites exchanged with different cations (Na^+, K^+, Ba^{2+}, Cu^{2+}, Ni^{2+}, Li^+, Rb^+, Sr^{2+}, Cs^+, ...) have been extensively studied over the last forty years, amongst others due to their use in separation and catalysis engineering in the petrochemical industries. Faujasite zeolites are commonly separated into two classes: X having an Si/Al ratio between 1 and 1.5 and Y having an Si/Al ratio above 1.5. More recently LSX (Low Silica X) having an Si/Al ratio of 1.0 has been encountered in the literature.

The distributions of the different cations in the zeolitic structures is one of the key aspects to the understanding of the adsorption mechanisms and selectivities. Many experimental and, more recently, simulation methods have been put to use to try to localise the cations in different situations: dehydrated and hydrated zeolites and zeolites saturated with organic molecules, e.g. benzene, toluene, xylene.

The aim of the present review is to gather and confront all the different results that have been published in the literature over the years, results that have been obtained by different experimental methods, on different zeolites that have been treated differently before and/or during the experiments. Since the most valuable compilation works of Smith [1] in 1971 and especially Mortier [2] in 1982, no complete review has been published to our knowledge. However, since then, a lot of work has been done. This is the reason why, like Smith's but unlike Mortier's, the following work will only focus on extra framework cation distributions in faujasite-type zeolites. Whenever possible, the unit cell chemical composition and the experimental conditions (dehydration temperature and pressure if applicable, experimental method and temperature, nature and quantity of sorbed molecules) will be given. It has indeed been shown that the distribution of the cations in two identical zeolite samples that have been treated differently can be very different. Many different experimental methods have been used in the past to characterise the structure of zeolitic materials: single crystal and powder X-ray diffraction (XRD) [3–5], double-rotation (DOR) and magic angle spinning (MAS) nuclear magnetic resonance (NMR) [6–8], powder and pulsed neutron diffraction [9] and less often diffuse reflectance spectroscopy, infrared spectroscopy and EXAFS. These analytical techniques are not further described in the present work, but the interested reader can consult the referenced works and reviews.

For the convenience of the reader, the review has been divided into separate parts, one for each ion-exchanged form of faujasite (Na–Y, Na–X, K–Y, Ba–X, etc.). This allows the interested reader to consult only the section they are concerned with rather than having to read the whole document. The number of cations found per site is given in the tables below. Table 1 and Fig. 1 give a short reminder of the location of the different crystallographic sites. The authors have tried to give the most generally accepted definitions of these sites, but slight variations can be possible in some papers. Sodium exchanged samples are dealt with first (Tables 2–4), followed by alkaline cations (Tables