The state of iron in natural zeolites: A Mössbauer study

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The state of iron in natural zeolites is an important feature for the practical applications of these materials. A Mössbauer study, complemented with other methods, of iron-containing zeolitic rocks from several countries (Mexico, Cuba, Czechoslovakia, and the USSR) was developed. It has been determined that iron is located as high spin Fe^{3+} in framework tetrahedral sites, in extraframework octahedral sites as free $Fe(H_2O)_6^{3+}$, and as high spin Fe^{2+} in octahedral coordination in extraframework sites or in another aluminosilicate associated with the zeolite. Iron is also located in magnetite contained in the zeolite rocks.

Keywords: Iron; natural zeolite; Mössbauer spectroscopy; tetrahedral site; octahedral site; magnetite

INTRODUCTION

Mössbauer spectroscopy is a powerful tool in the elucidation of the state of iron in solid materials. In zeolites, this method has been applied during the last 2 decades in the study of the ion exchange of ferrous and ferric ions in several zeolites[1–7] and in adsorption studies.[8–13] Other authors have applied the method for the study of iron clusters in zeolites[14–16] and for the elucidation of the state of iron included in the framework of ferrisilicate, FAPO-5, etc.[17–21] Moreover, iron in aluminosilicates has been thoroughly investigated by Mössbauer spectroscopy,[22–25] but studies about the state of iron in natural zeolites are not often found.[26]

Natural zeolites are raw material for several processes,[27–29] and the knowledge of the state of iron is of real importance in applications where brightness is relevant or for use in agriculture or for zeolite synthesis.

The present paper attempts a closer approach to the state of iron in natural zeolite rocks. Well-characterized samples of zeolite rocks from several countries (Mexico, Cuba, Czechoslovakia, and the USSR) containing different zeolite phases (clinoptilolite, mordenite, and erionite) were studied by Mössbauer spectroscopy combined with other methods to provide information about the location and chemical state of iron.

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EXPERIMENTAL

Natural zeolite rocks were obtained from deposits of Aguas Prietas, Sonora, Mexico (label AD); Castillas, Havana, Cuba (HC); Tasajeras, Villa Clara, Cuba (CMT); Camaguey, Cuba (C1, C2, C4, C5, C6, C7); Palmarito, Santiago de Cuba, Cuba (MP); Nizny Hrabobec, Czechoslovakia (CZ); and Dzerbi, Georgia, USSR (GR). The corresponding elemental chemical analyses are reported in *Table 1* and phase analysis in *Table 2*.[30,31] Characterization methods are described elsewhere.[32]

Samples C1, C2, C4, C5, C6, C7, MP, CMT, and HC were refluxed five times during 4 h with 3 M solution of NaCl, KCl, and NH_4Cl (liquid/solid ratio = 2). The presence of iron in the solution after each exchange was tested by atomic absorption with a Pye Unican SP-1900 spectrophotometer.

Sample HC was thermally treated for 10 h at 400,

Table 1 Elemental composition of natural zeolites in oxide weight percent

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	H_2O
C1	62.3	13.1	1.7	2.8	1.2	0.9	1.4	15.1
C2	64.3	12.9	3.6	5.0	1.3	1.5	1.3	10.5
C4	65.3	10.2	2.1	2.7	0.5	1.7	1.2	14.0
C5	66.2	11.4	3.8	4.2	0.7	1.3	1.0	12.8
C6	67.5	11.0	1.9	4.9	0.5	1.9	0.7	11.9
C7	64.2	13.1	3.0	4.2	1.4	1.5	0.7	11.5
MP	66.9	11.6	2.7	4.4	0.8	1.8	0.8	12.1
CMT	66.6	12.5	2.0	2.7	0.7	1.7	0.8	12.9
HC	66.8	13.1	1.3	3.2	1.2	0.6	1.9	12.1
AD	59.6	14.2	2.3	2.2	1.5	2.4	3.3	13.8
CZ	69.8	14.2	1.2	3.0	1.5	2.4	3.3	13.9
GR	62.4	12.0	2.9	4.1	1.8	2.0	1.2	14.1