

CHARACTERIZATION OF IRON-EXCHANGED FORMS OF A MODIFIED CLINOPTILOLITE: A SOLID-STATE MULTI-NUCLEAR NMR STUDY

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Introduction

The position of iron atoms in a natural zeolite has been studied and discussed by different authors [1-3]. The controversy of this discussion has been focused around the presence of iron atoms in the zeolite structure, which replace isomorphically silicon or aluminum atoms. Recently we studied a natural clinoptilolite with iron located at the three discussed positions [4]. In this work the natural clinoptilolite was treated with orthophosphoric acid at pH 1.2 to extract almost all the iron content. After that the phosphorus sample was modified with FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ solution buffered with H_2SO_4 at pH 1.2 to reintroduce iron in the zeolite. The electron paramagnetic resonance (EPR) showed the presence of iron in tetrahedral and octahedral coordination in these samples. In the present work we tried to focus on the environment of iron species in the natural clinoptilolite structure before and after these chemical modifications, using multinuclear MAS/NMR technique.

Experimental

The natural clinoptilolite (NZ) was obtained from the Tasajera deposit, Cuba, following a sample purification method reported elsewhere [5]. The sample consisted of about 78% of clinoptilolite-heulandite, 4% of mordenite, and 17% of quartz, feldspar, montmorillonite and iron oxide.

The sample was modified using phosphoric acid and the obtained sample was named OPAZ [4]. This was also modified using FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ solutions: Fe^{2+} -OPAZ and Fe^{3+} -OPAZ samples [4]. In the present study we investigated two new samples: a modification of NZ with a HCl solution at pH 1.2 (NZH), and a modification of NZ with FeSO_4 buffered with H_2SO_4 at pH 1.2 (FZ), obtained under the same experimental conditions used for the other samples.

²⁷Al, ²⁹Si and ³¹P MAS/NMR measurements of the hydrated samples were performed at room temperature using an ASX-300 Bruker spectrometer. Al, Si and P spectra were recorded at 78.20, 58.62 and 121.49 MHz respectively.

Results and Discussion

The ²⁷Al MAS/NMR study showed that the clinoptilolite present in the NZ sample has all Al atoms in a tetrahedral coordination (Al_{tet}), corresponding to the line located at 55 ppm. In the OPAZ sample, a second line characteristic of Al in octahedral coordination (Al_{oct}), was observed at -7.0 ppm. This Al_{oct} is

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