



## An EPR study of clinoptilolite from Bigadiç in Turkey



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### ABSTRACT

Natural and synthetic zeolites have wide use industry and in many other applications as food additives, as molecular sieve to trap unwanted ingredients like heavy metallic ions and groups in fluids, as shielding materials against high energy radiations etc. Clinoptilolite is a type of zeolite composed of aluminasilicate forming tetrahedrons with micro cavities among them. The size and shape of cavities, impurities and the metal ions define their usage. Electron paramagnetic resonance (EPR) spectroscopy is a technique to determine paramagnetic species in host materials, and hence in the zeolites and clay type minerals. In this study natural clinoptilolite obtained from Bigadiç district in Western Anatolia, was studied using EPR spectroscopy in natural form and after some physical and chemical treatments, namely adsorbing CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> gases, [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ions and after exposing to gamma rays. The clinoptilolite including non-paramagnetic manganese ions as impurities in natural form reduced to paramagnetic Mn<sup>2+</sup> ions after CO<sub>2</sub> and H<sub>2</sub>S adsorption, and when SO<sub>2</sub> gas is adsorbed an unstable paramagnetic center was induced which changed with time when stored at room temperature. When Cu(H<sub>2</sub>O)<sub>6</sub> was adsorbed Cu<sup>2+</sup> ion complex was adsorbed in the cavity in slightly distorted octahedral structure. Gamma ray irradiation of clinoptilolite from Co-60 source produced anisotropic o<sub>2</sub><sup>3-</sup> radical ion.

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### 1. Introduction

Zeolites are minerals and are abundant in many resources all over the world and are easily available. They are composed of aluminasilicate forming tetrahedrons with micro cavities among them in the lattice available all over the world. Since they are inert, micro porous and have ion exchange capability, they become industrially important mainly as molecular sieve, ion exchangers, shields against high-energy radiation, etc. Therefore their structures, ion exchange and adsorption–desorption properties have been widely studied [1–5].

Clinoptilolite have the complex structure Al<sub>3</sub>(Al,Si)<sub>2</sub>·Si<sub>13</sub>O<sub>36</sub>·12H<sub>2</sub>O with ionic compensating 2 or 3 Na, K or Ca metals per molecule. The environment of a natural clinoptilolite reservoir defines its characteristics: seasonal and daily temperature differences, geographic location and soil composition cause slightly different and unique composition, e.g., trace amounts of impurities in the lattice, structural deformation etc. and therefore the clinoptilolite gains a unique property depending on the environment

[6,7]. Clinoptilolite is one of the most utilized and important natural zeolites in water purifying plants, in filter system of petrochemical or similar plants to trap some unwanted contaminating molecules, ions, heavy metals and low level radioactive elements [6,8,9]. At this point researchers are mainly interested in increasing the adsorbent and ion exchange properties of the clinoptilolite and similar structure under environmental, physical and chemical conditions. For example Kumar et al., [4], revealed that the adsorption capacity of the similar zeolite structures increase in the presence of N<sub>2</sub> and CO<sub>2</sub>. In another study it was shown that SO<sub>2</sub> adsorption capacity varied according to environmental acidic value of zeolites, and hence, of clinoptilolite [10]. In another study it was determined that ion exchange property of zeolites also varied with irradiation: the leaching capability under gamma irradiation caused a modest increase in desorption of exchangeable ions [11]. When zeolite was exposed to high-energy radiation some physical and chemical processes took place [12,13]. In all these processes, some structural and magnetic changes could be detected using EPR spectroscopic technique.

EPR spectroscopy provides valuable information about the local environment of the structures having unpaired electrons and therefore can be conveniently employed to detect paramagnetic species in chemical and even biological substances, minerals,

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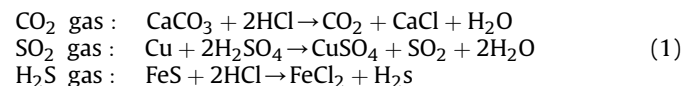
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stones and hence in zeolites in their natural forms after some physical and/or chemical treatments. Adsorption–desorption properties of zeolites can also be studied by EPR spectroscopy after inserting paramagnetic probes [14]. Khulbe et al., [15], revealed some ion exchange properties of clinoptilolite after treating with H<sub>2</sub>S, CO, and SO<sub>2</sub>.

In this work the paramagnetic species in natural clinoptilolite obtained from a mine in Bigadiç, Western Anatolia, after adsorbing CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> gases, after doping [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> ions and after irradiation with gamma rays, have been examined.

## 2. Materials and method

The natural and high quality clinoptilolite was obtained from the mine. The results of the chemical analysis of clinoptilolite were given in Table 1. The samples taken from the mine contains 88–95% clinoptilolite, 2–5% montmorillonite, 0–3% muskovit, 3–5% feldspat and 0–2% cristobalite. The samples were finely grinded, washed three times in distilled and deionized water and dried prior to use. Chemical reagents were purchased from Merck. The gases to adsorb zeolites were obtained in laboratory by means of related chemical reactions;



The moistures after reaction were removed by flowing the gaseous output through H<sub>2</sub>SO<sub>4</sub> bath and then from CaCl<sub>2</sub> column. Highly purified CO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>S gases were passed slowly through clinoptilolite column for about 3 h. The EPR spectra were taken at each half hour to observe whether any variation in paramagnetic centers occurs.

The Cu<sup>2+</sup> ion adsorption was made in 50 ml vials. The pH of the solution was adjusted by 0.1 M HCl and NaOH solutions and kept at the value of 5, and 0.5 × 10<sup>-4</sup> M CuCl<sub>2</sub> was added and kept for 48 h and then the samples were centrifuged at 100 rpm for 15 min. The samples were dried prior to spectral analyses.

The gamma-irradiation was made by a <sup>60</sup>Co gamma-ray source at Turkish Atomic Energy Agency (TAEK) up to dose of 10 kGy.

The X-band EPR spectra were recorded using a Varian E-109 Line Century Series spectrometer equipped with a Varian E-231 TE-102 rectangular cavity. The microwave frequency and power was kept 9.52 GHz and 2 mW respectively. Optimized sweep time was 8 min and the modulation amplitude was adjusted to 0.4 mT. Quartz sample tube was used to record spectra. The spectrometer frequency is corrected using the DPPH (diphenylpicrylhydrazyl) sample (g = 2.0036). All spectra were taken at room temperature and simulations were made using Bruker's WINEPR software.

Estimations of EPR spectra of this work were made qualitatively, just to determine the types and/or structures of the paramagnetic species.

**Table 1**  
Chemical composition (W%) of the Bigadiç clinoptilolite material.

Chemical composition	Bigadiç clinoptilolite
SiO <sub>2</sub>	72.12
Al <sub>2</sub> O <sub>3</sub>	10.48
CaO	2.49
MgO	1.2
Fe <sub>2</sub> O <sub>3</sub>	1.22
Na <sub>2</sub> O	0.55
K <sub>2</sub> O	2.20
SO <sub>3</sub>	0.006
Mn <sub>2</sub> O <sub>3</sub>	0.001
TiO <sub>2</sub>	0.07

## 3. Result and discussion

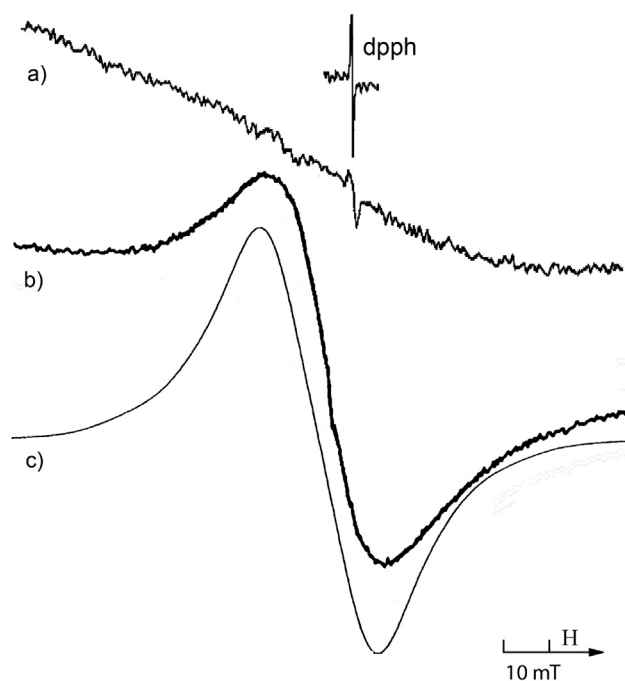
### 3.1. EPR spectrum of untreated clinoptilolite

The EPR spectra of the untreated clinoptilolite, except washing and drying, gave only a weak line at g = 2.002 which was attributed to carbonaceous radical existed during the natural formation process [16] and no other line was observed (Figs. 1a and 2a).

### 3.2. Gas adsorbed clinoptilolite

When CO<sub>2</sub> and H<sub>2</sub>S gases were adsorbed symmetric and broad envelope was observed in EPR spectra, Fig. 1b. The shape of spectra did not change, except intensities, with the amount of gas adsorbed. When same experiment was repeated with SO<sub>2</sub> gas the spectrum of Fig. 2b was observed where six separate lines were seen obviously. The spectrum was attributed to a complex of Mn<sup>2+</sup> ion. The point to be explained was the appearance of paramagnetic Mn<sup>2+</sup> spectra after gas adsorption while there was no such paramagnetic specie, even in trace amount, prior to adsorption. When overall width and the g values of EPR spectra of CO<sub>2</sub> and H<sub>2</sub>S adsorbed clinoptilolite were compared, it was concluded that both spectra aroused from paramagnetic Mn<sup>2+</sup> ion complex.

Table 1 gives the chemical composition of clinoptilolite of this work where weight percent of nonparamagnetic manganese(III) oxide (Mn<sub>2</sub>O<sub>3</sub>) is given as 0.001%, Table 1. It is also possible that non-paramagnetic permanganate ion (MnO<sub>4</sub>)<sup>-</sup> can also be trapped in the lattice in trace amount. Moreover, although there seems relatively high amount of Fe<sub>2</sub>O<sub>3</sub> impurity in the clinoptilolite, Table 1, no identifiable trace about paramagnetic Fe<sup>3+</sup> complex in the spectra of CO<sub>2</sub> and H<sub>2</sub>S adsorbed samples. In both adsorption processes non-paramagnetic Mn<sup>3+</sup> ion was reduced to paramagnetic Mn<sup>2+</sup> ion producing manganese centered complex structures [17]. EPR spectra of both samples on the other hand, brought to the same conclusion. The g and hyperfine values and



**Fig. 1.** The EPR Spectra of natural (a) CO<sub>2</sub> gas adsorption (b) and simulation (c) in Bigadiç clinoptilolite zeolite.

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