

ESR study of sepiolite

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Sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) is fibrous clay mineral consisting of micro "tunnel" structure. It adsorbs various gaseous or liquid molecules in the tunnels, especially hydrophilic molecules like CO_2 , NO , NO_2 and H_2O .

The ESR signals induced by gamma-rays in as-received sepiolite (a-sepiolite) and HCl treated sepiolite (t-sepiolite) showed the difference.

The signal of SO_3^- was found only in the a-sepiolite.

The ESR measurements at 77-200 K suggest that a new ESR center induced in sepiolite was in the vacancy of the matrix, and that the signal was split by two hydrogen nuclei.

The signal of NO_2 adsorbed on the a-sepiolite showed the two components of thermal stability. Probably, the NO_2 adsorbed on the carbonates desorbed faster, and the adsorbed on the sepiolite desorbed slower.

Sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) is fibrous clay mineral consisting of micro tunnel structure. The cross section of the tunnel is about 3.7×9.3 angstrom. It adsorbs various gaseous or liquid molecules in the tunnels, especially hydrophilic molecules like CO_2 , NO , NO_2 and H_2O . It has been studied well and widely used as adsorbent, for example, dehydrates, deodorant, molecular sieves, material of porous ceramics, enzyme carriers, and so on. However, there are no reports of sepiolite studied by Electron Spin Resonance (ESR).

We studied the lattice defect, condition of the surface, change of surface due to HCl treatment and adsorption of NO_2 on surface of sepiolite at various temperature.

The ESR signal induced by gamma rays in HCl treated sepiolite (t-sepiolite) was different from the signal of as-received sepiolite (a-sepiolite) at room temperature. The signal was found only in the a-sepiolite. The g-factors of the signal were very similar to those of the SO_3^- center in aragonite. Probably, the SO_3^- center was in the dolomite or aragonite contained in the sepiolite.

Paramagnetic signals in sepiolite at 77 K induced by gamma-rays were detected by ESR measurements, and three signals were separated by power dependence and isochronal annealing experiments. Presumably, the unpaired electron was at the $\text{O}(\cdot)$ radical, which was made by the removing of hydrogen nucleus of OH radical. The signals were considered due to the super hyperfine structure of the unpaired electron at $\text{O}(\cdot)$ radical nearby two hydrogen nuclei of next OH radicals in the lattice of sepiolite.

The signal in t-sepiolite was more stable than those in a-sepiolite. Therefore, treatment with HCl may change the process of the thermal annealing.

The ESR signal of NO_2 adsorbed on the sepiolite was detected. The hyperfine coupling constants of the NO_2 on sepiolite were smaller than those of other matrices like zeolite. The result suggested that the wave function of unpaired electron of NO_2 was spreading over the matrix.

Paramagnetic NO_2 signal adsorbed on the a-sepiolite showed the two components of thermal stability. On the other hand, the signal of NO_2 adsorbed on the t-sepiolite showed only one component. Probably, the NO_2 adsorbed on the carbonates desorbed faster, and the adsorbed on the sepiolite desorbed slower.