

THE INVESTIGATION OF THE ADSORPTION OF PROPYLAMINE, DIPROPYLAMINE AND TRIPROPYLAMINE ON SEPIOLITE SPECIMENS BY INFRARED SPECTROSCOPY

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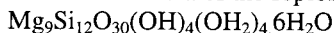
ABSTRACT

Propylamine, dipropylamine and tripropylamine were adsorbed on sepiolite specimens under reflux, at their normal boiling points. The infrared spectra of the original and the amine adsorbed specimens were recorded before and after heat treatments between 50-400°C. The examination of the spectra revealed that the adsorption of amines took place by the replacement of the zeolitic water in the pores of the sepiolite by the amines.

1. INTRODUCTION

The sepiolite known as the Eskişehir stone or Lüle stone in our country is a clay mineral that has a fibrous structure. The building stones of clay minerals are tetrahedrons generally containing Si⁴⁺ ions in the centers and octahedrons generally containing Al³⁺ and Mg²⁺ ions in the centers. The tetrahedrons which are bonded to each other through oxygen bridges at the corners, form the tetrahedron sheets or chains called "silica" and the octahedrons form the octahedron sheets or chains called "alumina" or "magnesia". The clay minerals of fibrous structure which are called "sepiolite" and "attapulgit" are formed by the bonding of silica chains and magnesia chains through oxygen bridges. All of the clay minerals which have sheeted and fibrous structures are either aluminium silicates or magnesium silicates¹. The chemical composition of clay minerals varies depending on the natural environment because of the isomorphic ion exchanges.

By combining the results of chemical analysis and X-ray diffraction^{2,3} the ideal chemical formula of the sepiolite mineral was determined to be



The four OH groups in the crystal are on the corners of octahedrons in the magnesia chain which is left unbonded through oxygen bridges to the tetrahedrons in the silica chains. Similarly, the four H₂O molecules called "bonded water" are bonded in couples to the magnesium ions at both ends of the chain through hydrogen bonds. On the other hand, the six H₂O molecules called "zeolitic water" seen in the formula is in the pores which originate from the empty spaces between the fibres. The replacement of Mg²⁺ ions by even a small amount of Al³⁺, Fe³⁺ and Fe²⁺ by isomorphic ion exchange, changes most of its properties principally its white color. The behavior of the hydroxyl groups⁴, the bonded water and the zeolitic water⁵ is investigated by different techniques including principally the Infrared Spectroscopy (IR). On the other hand, the surface properties⁷, catalytic activity⁸ and the transformation of sepiolite to clay minerals which have sheeted structures^{9,10} is investigated and its utilization areas are determined^{11,12}. Various touristic objects are produced depending on the size of sepiolite balls taken from the mineral beds in the region of Eskişehir. During this production about 30% of the mineral is left behind in the form of fragments or powders. In order to evaluate these residues it is necessary to investigate in detail the physical and chemical properties of the sepiolite mineral. For this reason, the porous structure^{13,14}, the surface acidity¹⁵ and effectiveness in cigarette filters of the Eskişehir stone were determined¹⁶. It is clear that the Eskişehir stone whose specific surface area is 370m²g⁻¹, total specific pore volume is 0.80 cm³g⁻¹, specific micro-, meso-, and macropore volumes are 0.16 cm³g⁻¹, 0.28 cm³g⁻¹ and 0.37 cm³g⁻¹ respectively, is a good adsorbent¹³. Therefore, it is necessary to investigate the adsorptive properties of this material in more detail.

It is thought that the sepiolite might be used as a catalyst or catalyst bed in organic reactions, hence, the adsorption of amines which are important organic compounds, on sepiolite was considered. The aim of this study was to investigate on one hand, the adsorption of propylamine (PA), dipropylamine (DPA) and tripropylamine (TPA) on the Eskişehir sepiolite and the variation of the adsorption by temperature, and on the other hand, to investigate the differences in the adsorption of primary, secondary, and tertiary amines by the IR spectroscopy. The considered bases whose subsequent formulas are C₃H₅NH₂, (C₃H₅)₂NH and (C₃H₅)₃N act both as Brönsted and Lewis bases.

EXPERIMENTAL

The chemical analysis results and the differential thermal analysis and the X-ray diffraction curves of the Eskişehir sepiolite chosen as the adsorbent were already given in our previous paper¹⁷.

The normal boiling points of the weak bases (PA), (DPA) and (TPA) chosen as the adsorbed material and supplied by Merck were determined as 49°C, 110°C, 157°C respectively.

Sepiolite was supplied in the form of fragments by the Lülestone workshops in Eskişehir. It was first dried and then ground such that particles could pass through a 325 mesh sieve. PA, DPA and TPA were subsequently adsorbed on different specimens taken from the ground sepiolite. The adsorption was realized by heating the amines up to their boiling points and keeping them in contact with the sepiolite in a soxlet under reflux, for 40 hours. The excess of amines that were left on the sepiolite specimens were eliminated by applying a drying process under vacuum at 30°C for 8 hours.

2mg specimens were taken from each of the original and the amine adsorbed specimens. Each specimen was mixed with 140 mg of KBr and pressed. Thus four different types of IR discs were prepared. The IR spectra of those discs which were prepared by the original and PA, DPA, and TPA adsorbed specimens were first recorded at room temperature. Each of the same type of discs were respectively kept at 50,100,150,200,250,300,350, and 400°C for 40 hours, cooled to room temperature in a dessicator and then their IR spectra were recorded i.e. Nine IR spectra for each type of disc, thus a total of thirty-six IR spectra were recorded, using a SHIMADZU IR-435 IR-Spectrometer.

RESULT AND DISCUSSION

By considering the studies realized by IR spectroscopy for the adsorption of different amines on alumina and silica-alumina catalysts¹⁸⁻²², the IR spectra recorded in this study were evaluated as follows.

The Original Sepiolite (OS): The IR spectra of the OS before and after heat treatment and cooling to room temperature, are given in Fig. 1. A sharp stretching band at 3675 cm⁻¹ of the OH groups which are bonded to the crystal, a stretching band at 3560 cm⁻¹ of the bonded water, a stretching band at 2415 cm⁻¹ of the zeolic water and a deformation band between 1630-1660 cm⁻¹ of the bonded and zeolitic water are observed as has been marked on the spectra.

Although the stretching band at 3675 cm⁻¹ of the hydroxyl groups which are bonded to the crystal, gets smaller by increasing temperature, it does not disappear completely. This shows that these groups did not leave the crystal completely even at 400°C. It was determined by previous differential thermal analysis (DTA) studies that the hydroxyl groups bonded to the crystal were eliminated by dehydroxylation only at 800°C¹⁷. After the dehydroxylation the crystal structure is destroyed

completely and solid phases of very low porosity called enstatite and α -cristobalite are formed.

The adsorption bands at 3560 cm^{-1} and 1660 cm^{-1} seen in the spectra get smaller as the thermal treatment temperature increases. This observation leads to the conclusion that although the bonded water is eliminated considerably it did not disappear completely at 400°C . It was determined by previous DTA studies that this water was completely eliminated before the temperature reached 800°C and the "sepiolite anhydride" was formed¹⁷.

The fact that the adsorption bands at 3415 cm^{-1} and 1630 cm^{-1} seen in the spectra get smaller and smaller by increasing thermal treatment temperature and disappear completely at 350°C shows that the zeolitic water is completely eliminated from the pores at this temperature.

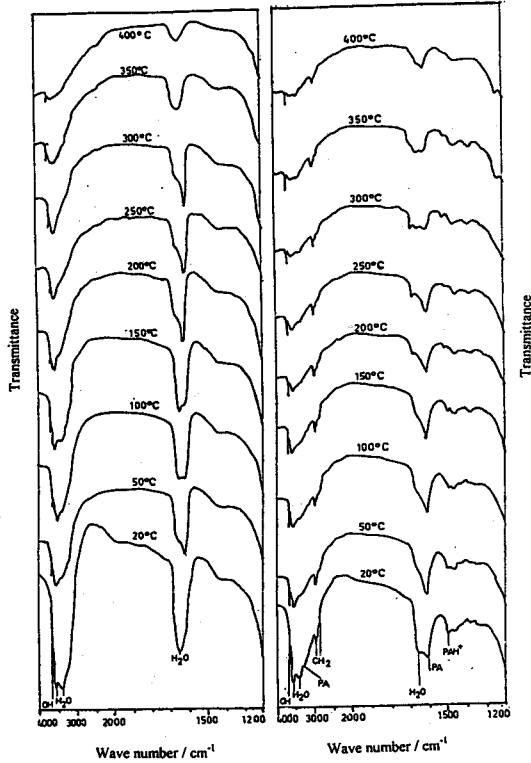


Fig. 1

Fig.1. The IR spectra of the original sepiolite

Fig. 2

Fig.2. The IR spectra of the propylamine adsorbed sepiolite specimens

Propylamine adsorbed sepiolite (PAS): The IR spectra of the PAS kept at room temperature and of the PAS which underwent heat treatments and cooled to room temperature are given in Fig.2. In these spectra besides the adsorption bands belonging to the OS, C-H absorption bands at 2980 cm^{-1} and 2880 cm^{-1} , N-H absorption bands at 3240 cm^{-1} and 1610 cm^{-1} are observed showing that the PA was adsorbed on sepiolite. The band at 3250 cm^{-1} is a result of the stretching vibration of the N-H bond and the band at 1610 cm^{-1} is a result of the bending vibration which causes the deformation of the same band. This bending band and the O-H bending band of the zeolitic water overlap to a great extent.

While the bands of the zeolitic water get smaller by increasing temperature the bands of N-H bonds become more apparent showing that the PA is adsorbed by replacing some of the zeolitic water.

The PA which is a weak base takes a proton and forms a cation represented as PAH^+ . The absorption band at 1495 cm^{-1} is a result of bending vibrations of the NH_3^+ group in this cation. The disappearance of this band at 400°C is related to the nonformation of PAH^+ because of the absence of zeolitic water in the pores at this temperature. Hence; it appears that the PA molecules take protons from the water in the pores.

Diproylamine adsorbed sepiolite (DAS): The IR spectra of the DAS kept at room temperature and of the DAS which underwent heat treatments and cooled to room temperature are given in Fig. 3. The fact that there is a great similarity between the spectra of Fig. 2 and Fig.3 except negligible displacements of the absorption peaks shows that the adsorption of the DPA on sepiolite is similar to that of the PA. The bending wave number of the NH_2^+ group in the cation represented as DPAH^+ which is formed by the DPA taking a proton from the zeolitic water, is the same as the bending wave number of the NH_3^+ group in the PAH^+ and is 1495 cm^{-1} .

Tripropylamine adsorbed sepiolite (TAS): The IR spectra of the TAS kept at room temperature and of the TAS which underwent heat treatments and cooled to room temperature are given in Fig. 4. Although the bands except for negligible displacements are similar to those of the PAS and DAS, the wave number of the NH^+ group in the cation represented as TPAH^+ which is formed by the TPA taking a proton from the zeolitic water, is greater than the same wave numbers of the NH_3^+ and NH_2^+ , and is 1545 cm^{-1} . The band of TPAH^+ cation, which is more apparent than the bands of PAH^+ and DPAH^+ cations and which moves to 1560 cm^{-1} by increasing heat treatment temperatures, disappears completely at 400°C .

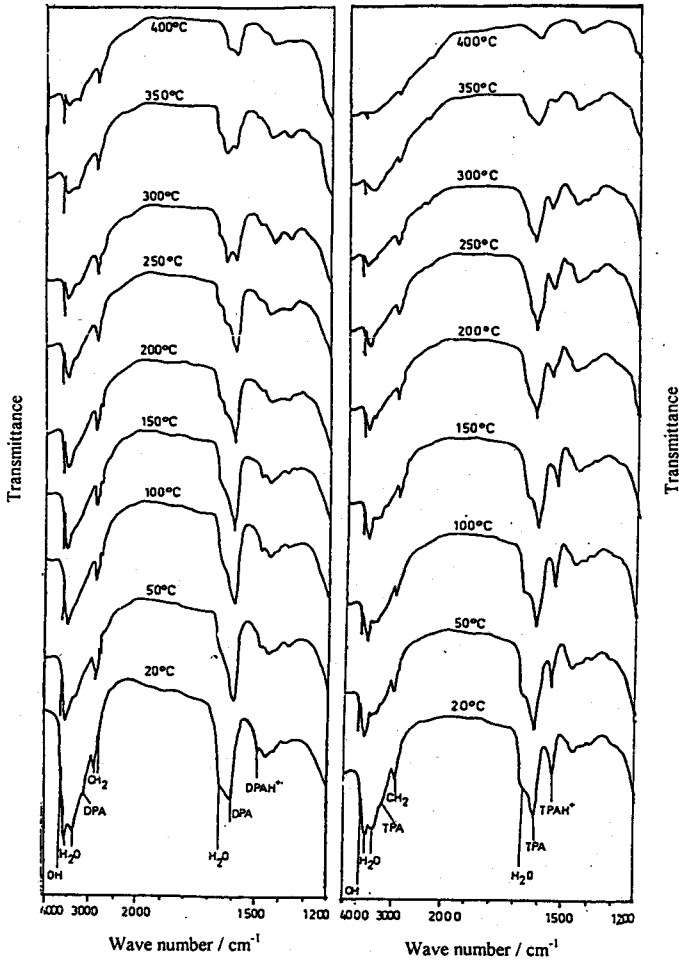


Fig. 3

Fig.3. The IR spectra of the dipropylamine adsorbed sepiolite specimens

Fig. 4

Fig.4. The IR spectra of the tripropylamine adsorbed sepiolite specimens

CONCLUSION

It was determined that there was a slight difference between the IR spectra of the Eskişehir sepiolite and the sepiolite taken from certain regions of Spain, Madagascar and France⁴. It was concluded that this situation originated from the chemical composition differences which occurred as a result of isomorphic ion exchanges.

It was observed that by increasing temperature the zeolitic water was eliminated gradually and disappeared completely at 350°C. In a previous study realized by the standard BET procedure, the specific surface area which was 370 m² g⁻¹ at 100°C decreased to 200 m² g⁻¹ at 300°C¹⁴. This situation was related to the fact that the sepiolite pores which were in the shape of rectangular segmented canals transformed into parallelogram segmented canals and some of the mouths of those canals got so narrow that the nitrogen molecules could not penetrate. The decrease of the specific surface area which is expected to increase as the zeolitic water is eliminated is due to the contraction of the sepiolite crystal caused by the geometric shape transformation. Since the zeolitic water can be taken in and given out reversibly the geometric shape transformation is also reversible.

It was observed that, although the bonded water and the hydroxyl groups were gradually eliminated by increasing temperature they were not completely eliminated at 350°C. It was determined by previous studies that, at temperatures which those groups disappeared completely, the crystal structure was destroyed considerably and collapsed at higher temperatures.

The presence of the stretching and bending bands related to PA, DPA and TPA shows that the propylamines were adsorbed on sepiolite. The adsorption of propylamines caused the bending bands of the hydroxyl groups of the original sepiolite to become more perceptible. This situation shows that the adsorbed amines interact with the hydroxyl groups bonded to the crystal structure.

There is a small difference between the variation of the IR absorption bands of the OS as a function of temperature and the variation of the IR absorption bands of the PASs as a function of temperature. This behavior is related to the interaction of the amines with Si⁴⁺ and Mg²⁺ ions besides the hydroxyl groups, bonded water and zeolitic water in the crystal.

REFERENCES

- [1] Grim, R.E. Clay Mineralogy, 2nd ed., McGraw-Hill, New York, 1968,p51,113.
- [2] Nagy,B.; Bradley, W.F.Amer. Mineralogist, 1955,40,885.
- [3] Brauner, K.; Preisinger, K. Mineral. Petrog. Mitt., 1956.6.120.
- [4] Ahlriches, J.L.; Serna, C.; Serratos, J.M. Clays and Clay Minerals, 1975,23,119.
- [5] Prost, R.Spectrochimica Acta, 1975,31A,1497.
- [6] Hayashi, H.; Otsuka, R.;Naoya, I. Amer. Mineralogist, 1969,53,1613.
- [7] Dandy, A.J.;Nadiye-Tabbiruke, M.S. Clays and Clay Minerals, 1982,30,347.
- [8] Corma, A.; Perez-Pariente, J.Clay Minerals, 1987,22,423.

- [9] Golden, E.C; Dixon, J.B.; Shadfan, H.;Kippenberger, L.A. Clays and Clay Minerals, 1985,33,44.
- [10] Komarneni, S.Clays and Clay Minerals, 1989,37,469.
- [11] Chambers, G.P.C. Silicates Industrials, 1959,181.
- [12] Robertson, R.H.S. Chem. Ind., 1957, 1942.
- [13] Sarıkaya, Y.; Ceylan, H.Doğa TU Kim. D.C., 1989,13,174
- [14] Sarıkaya, Y.Commucations, Fac. Sci. Uni Ank., 1981, 27,45.
- [15] Ceylan, H.; Sarıkaya, Y.Doğa TU Kim.D.C., 1989,13,130.
- [16] Sarıkaya, Y.; Yücel, A.; Eğilmez, Ö.; Makul, G.; Almaç, R.; Harman, İ.; Bozdoğan,İ. Doğa Bilim Dergisi, 1985,B9,277.
- [17] Sarıkaya, Y.;Ceylan,H.;Bozdoğan, İ.;Akınç, M.Doğa-Tr.J.of Chemistry., 1993,17,267
- [18] Rao, C.N.R. Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963,p 245
- [19] Parry, E.P.J. Catal., 1963,2,371.
- [20] Basila, M.R.; Kantner, T.R.; Rhee, K.H.J.. Phys. Chem., 1964, 68,3197.
- [21] Morimoto, T.; Imai, J.; Nagao, M.J.Phys. Chem., 1974,78,704.
- [22] Shuali, U.; Bram, L.; Steinberg, M.;Yariv,S. Thermochemica Acta, 1989, 148,445.