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THE INVESTIGATION OF THE EFFECT OF GRAIN SIZE ON RAMAN AND ^{29}Si MAS NMR SPECTRA OF BENTONITES FROM TURKEY

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ABSTRACT

There is a great deal of interest in clays in various fields of science and industry. In the literature, it can be easily seen that vibrational spectroscopic particularly FT-IR and NMR methods have been widely employed for the scientific studies of clays. However, especially not much data is available for Raman spectrum since it is difficult to obtain a good and interpretable spectrum. Most of the time, particle size or grain size is not considered as an element which can affect the quality of the Raman and NMR spectra. In this paper, we prepared clay samples having different grain sizes obtained from Ünye region and we observed the effect on the Raman and ^{29}Si NMR spectral quality.

Keywords: Grain size, Raman spectrum, ^{29}Si MAS NMR, Spectral quality, Band shape

TÜRKİYE ORJİNLİ BENTONİTLERDE PARÇACIK BOYUTUNUN RAMAN VE ^{29}Si MAS NMR SPEKTRUMLARINA ETKİSİNİN İNCELENMESİ

ÖZET

Bilim ve endüstri alanında killere oldukça yoğun bir ilgi vardır. Literatürde; titreşim spektroskopisi ve özellikle FT-IR ve NMR spektroskopik yöntemlerinin, killer üzerine olan bilimsel çalışmalarda sıklıkla kullanıldığı görülmektedir. Buna karşın yorumlanabilir bir spektrum eldesinin güç oluşundan dolayı özellikle Raman spektrumlarına aynı sıklıkta rastlanılmamaktadır. Çoğu zaman, birçok çalışmada parçacık boyutu Raman ve NMR spektrumlarının kalitesine tesir eden bir unsur olarak ele alınmaz. Bu çalışmada Ünye yöresinden elde edilen killer için farklı parçacık boyutlarına sahip numuneler hazırlanmış, Raman ve ^{29}Si NMR spektrumları alınmış ve parçacık boyutunun spektrumlar üzerine tesiri incelenmiştir.

Anahtar Kelimeler: Parçacık boyutu, Raman spektrumu, ^{29}Si MAS NMR, Spektral kalite, Band şekli

1. INTRODUCTION

Bentonite mainly composed of montmorillonite belongs to the dioctahedral smectites group those of which are the most important mineralogical component in bentonite having a 2:1 layer clay mineral. It has an octahedral (O) sheet including Al $^{+3}$ and Mg $^{+2}$ ions placed between two Si tetrahedral (T) sheets [1-3]. Bentonites and smectites have found extensive possible applications in science and industry. For example, they were widely used in oil, petroleum, cosmetics, perfume and ceramics industry [4-6].

The particle size is an important parameter for bentonite samples in order to control various parameters such as charge state, diffusion behavior and adsorption [7-9]. In its different regions, Turkey has large bentonite reserves. In order to use these bentonites more efficiently, their structural and spectroscopic properties must be investigated. Spectral quality is strongly related to the experimental conditions. Most of the time randomly prepared samples in different grain size or powder quality were used in the spectral measurements. The aim of this study is to examine the grain size or particle size effect on spectral quality of the obtained Raman and ^{29}Si MAS NMR spectra. All related findings were also given in this study.

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2. MATERIALS AND METHODS

Natural bentonite samples were obtained from Ünye region of Turkey. The mineralogical components of the sample were reported elsewhere [10]. The samples were crushed, ground and sieved to pass through 20, 32, 45, 53, 63, 90, 120 µm sieves. Natural bentonite samples labeled as N1 (20 µm), N2 (32 µm), N3 (45 µm), N4 (53 µm), N5 (63 µm), N6 (90 µm) and N7 (120 µm). The Raman spectra of all the prepared samples were obtained between the region of 3700–154 cm^{-1} with a Bruker Senterra Dispersive Raman microscope spectrometer with 785 nm excitation from a 3B diode laser having a resolution of 3 cm^{-1}. Bruker Avance 300 spectrometer operating at 59.59 MHz for ^{29}Si was used to obtain the solid state ^{29}Si MAS NMR spectra. Finely powdered samples were packed into Zirconium oxide rotor with a 4 mm diameter and it was used to acquire the NMR spectra of ^{29}Si. Data collection was carried out under MAS technique and spectra gathered with 3000 scans. External reference TMS was for chemical shift assignment of ^{29}Si.

3. RESULTS AND DISCUSSION

Raman spectra of the samples were given in Figure 1. There is a scarcity in the Raman spectra of bentonites or montmorillonites in the literature. Therefore, the assignments of the Raman bands in this work were given in comparison only with the studies reported by Frost and Rintoul, Bishop and Murad [11-12].

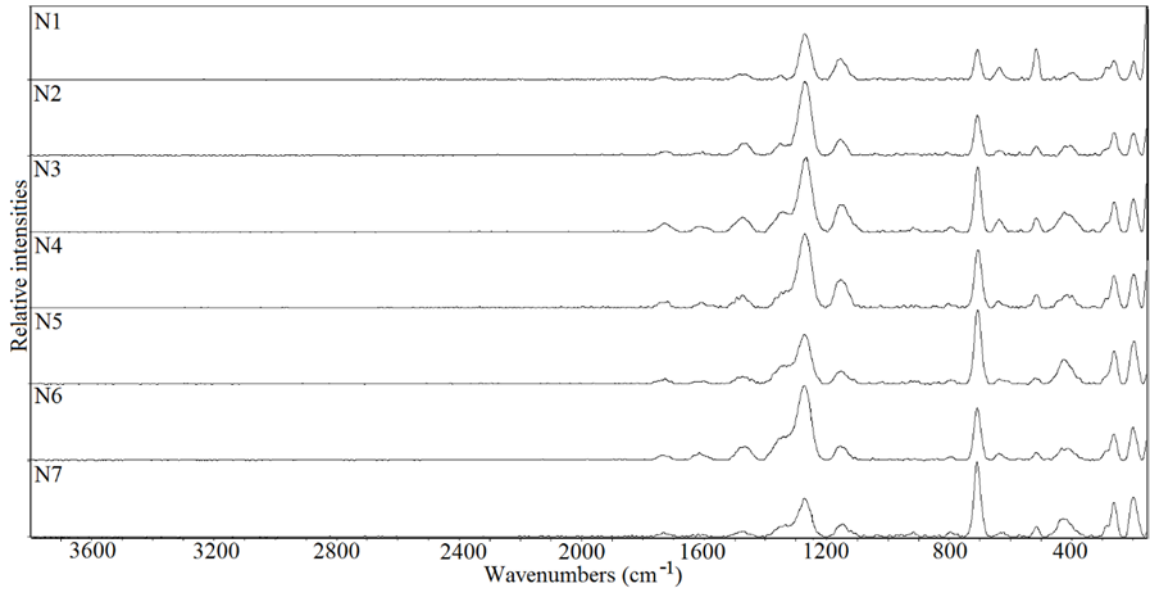

Figure 1. Raman spectra of bentonite samples having different grain sizes; N1 (20 µm), N2 (32 µm), N3 (45 µm), N4 (53 µm), N5 (63 µm), N6 (90 µm) and N7 (120 µm)

Several bands of the Raman spectrum are discussed here as following. Si-O stretching bands of various types of montmorillonites in Raman spectrum were reported in previous studies between 1090-1135 cm^{-1}. In present work it was found as 1151 cm^{-1} for N4 (53 µm) which is the band having the highest intensity. For the sample labelled with N7 (120 µm) the intensity dropped almost half of the N4 and the peak point of the band was shifted to 1145 cm^{-1}. The band appeared around 706 cm^{-1} having almost the same value for each sample (N1-N7) is due to $\upsilon_1(a_1)$ vibrational mode [12]. While the sample N1 (20 µm) shows the lowest intensity, N7 (120 µm) possesses the highest intensity for the mentioned vibrational mode. The band appeared around 423 cm^{-1} for N5 (63 µm) is due to $\upsilon_3(a_1)$ of SiO_4 [12]. The band shape seems much distorted for that vibration depending on the grain size of the prepared samples. The bands at 259 cm^{-1} and 283 cm^{-1} arising from the structural lattice vibrations [11] are located almost

at the same value for each sample and band shape and intensity again show grain size dependence. The bands in Raman spectra at 193-194 cm^{-1} (N1-N7) were due to A_{1g} (υ_1) of AlO_6 vibrational mode [12]. N5 shows highest intensity and N1 is the lowest one and band shape is not distorted for any sample. The detailed description of vibrational definitions can be found in previously reported works [13].

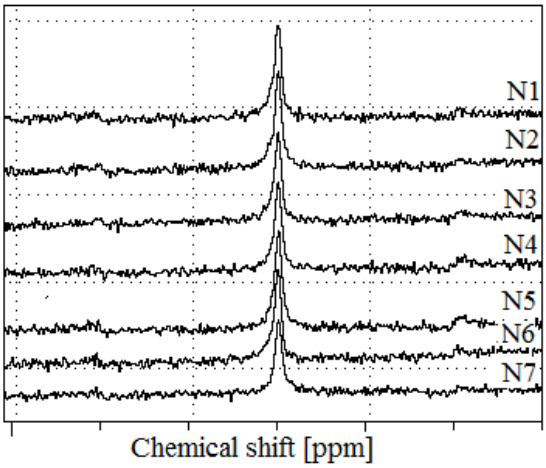

Figure 2. ^{29}Si MAS NMR spectra of the examined samples

^{29}Si MAS NMR spectra were seen in Figure 2.The intense band appeared in the Figure 2 is due to SiO_4 groups crosslinked in the tetrahedral sheets [14]. If the band shapes and the intensities of each sample is examined, it is seen that as long as the samples are tightly packed into the NMR spinner before the each spectral measurement, no noticeable differences are observed between the ^{29}Si NMR spectra of the studied samples, N1 (20 µm), N2 (32 µm), N3 (45 µm), N4 (53 µm), N5 (63 µm), N6 (90 µm) and N7 (120 µm).

4. CONCLUSION

In the present work, Raman and ^{29}Si MAS NMR spectra of natural bentonite samples were analyzed depending on the grain size. In conclusion, following results can be summarized:

i. Band shape and band intensity show a dependence on the grain size of bentonite samples.

ii. Before making a comment about the origin of the possible shifts of the peak values of the vibrational bands or more generally wavenumbers, one has to consider the preparation conditions of samples especially grain sizes of the samples. As can be seen in this work particle size may cause shifts in the vibrational bands appeared in Raman spectrum. This point must be taken into account for the further studies.

iii. Different vibrational modes reacted differently to the change in grain size considering the band shape and intensity. So it is not possible to say that as the grain size increases the band intensity or spectral quality increases or vice versa.

iv. Actually it is important where the laser is focused during the Raman measurements. Therefore, it is hard to make more general proposes.

v. As for the ^{29}Si NMR spectral results it can be concluded that each measurement was almost yielded with the same spectral quality for the examined samples.

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