Short Communication

Characterization of Sardinian Bentonite

A. Mannu[1,2•], G. Vlahopoulou[1,2*], V. Sireus[3], G. Mulas[1], G. L. Petretto[1]

[1]Department of Chemistry and Pharmacy, via Vienna 2, University of Sassari, Sassari, Italy

[2]Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29, Rostock, Germany

[3]Departament de Física, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain

Abstract

The employment of clays in industry and on laboratory scale is still of interest, despite their long history. The chemical-physical characteristics of such materials are strongly related to their geographical origin and the availability of proper characterization techniques is of great importance in order to gain as more information about their behavior when utilized as filling materials. In the present contribution, a physical characterization by meaning of Thermogravimetry and N_2 physisorption analyses of samples of bentonite collected from the deposit of S´Aliderru in the north of Sardinia (Italy) is reported.

Keywords: Bentonite; N_2 physisorption; BET; Thermogravimetry; Clay.

1. Introduction

Clay earths were employed in the last 50 years as clarification agents, including applications in vegetal and mineral oil decolouration and deodorization [1], as well as in the field of wine clarification [2]. With the terms "clay minerals" we usually label a large family of natural alumina-silicates with a wide range of structures and properties. In particular, the subfamily of the bentonites is characterized by a high concentration of montmorillonite (MMT), and is considered a member of the family of the smectites, originated from the decomposition of volcanic ashes. The chemical structure of bentonite is characterized by alternated layers with a tetrahedral symmetry separated by an octahedral intermediate layer (TOT) [3,4]. The tetrahedral layer contains silicium atoms bonded to four oxygen atoms which form six terms rings where every tetrahedron shares three oxygens. As consequence of this structural motif, the characteristic element of bentonite is the anion $Si_2O_5^{2-}$, which determines a negative overall charge. Between the

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* *Corresponding author:* gvchimica@gmail.com; albertomannu@gmail.com

octahedral layers, neutral magnesium or aluminum oxides are presented [5]. The overall negative charge usually observed in the bentonite is a result of the replacement of octahedral Al or Mg atoms by lower oxidation number atoms. Inorganic cations located in the interlayer spaces, such as Na^+ and Ca^{2+} balance this negative charge. The interlayer space surface usually shows a hydrophilic character due to the presence of H_2O clusters surrounding the inorganic cations. The structure of the interlayer spaces is also characterized by the presence of cavities or micro-pores [6]. Specific applications of bentonite are usually related to its characteristic composition. In the case of wine clarification, the negative charge of the layers is usually exploited for protein sequestering [7,8]. In the case of edible oils, filtration on a pad of activated bentonite allows to remove cations, wax and pigments. Additionally, waste cooking oils can be treated with bentonite for decolouring procedure [9]. Bentonite has also been employed for water treatment, as resulted efficient in adsorbing organic matter and in retaining Fe [10-12] or copper [13], or for retain pollutants in industrial wastewaters as the O-cresol [14]. Clays have been largely employed in foundries, cosmetic, enology, and catalysis industries main for its easy availability, and for the possibility to tune its swelling behaviour, adsorption and cation exchange capacity and surface area by modifying the kind of cation and the dimension of the pores [15]. These intrinsic characteristics of the clay materials are strongly related to the geographic area of origin [16]. Italy represents one of the bigger sources of rocks in the world, and produces about the 4% of the world available bentonite [17]. Within the several Italian deposits of clays, the ones located in Sardinia are the most important in terms of amount of production and for the quality of the bentonite extracted [18]. In the present contribution, a physical chemical characterization of a bentonite originated from the deposit of S´Aliderru, situated in the north of Sardinia (Italy), by meaning of BET and XRD analysis will be presented, including its thermal stability evaluation by thermogravimetric analysis.

2. Materials and Methods

Samples of bentonite originated from the deposit of s´Aliderru (SP 65, Porto Torres, Sassari, Italy) were considered for the present study.

2.1. *Thermogravimetric analysis*

Thermal stability of bentonite was evaluated using a thermogravimetric apparatus (TGA) coupled with a differential scanning calorimeter (DSC) (Labsys Setaram). The experiment was carried out on 20 mg of sample under an Ar flow of 120 mL min^{-1} between 25 °C and 800 °C with heating and cooling rates of 30 °C min^{-1}. A ceramic crucible was used for the analysis in order to avoid undesired reaction with the powders during the annealing.

2.2. N_2 *Physisorption*

N_2 sorption isotherms were collected with a Sorptomatic 1990 instrument (Fisons Instruments, Milan, Italy). For a standard measure, 200 mg of sample were collocated in a quartz tube and degassed under high vacuum (1×10^{-3} bar) at 250 °C for 24 h. The dead volume was evaluated through helium measurements.

3. Results and Discussion

It is known that the deposit of S´Aliderru contains a bentonite composed almost entirely by montmorillonite with small amounts of free silica and only traces of quartz (2%), which is 90% of respirable size. The above characteristics combined with the absence of arsenic, zinc and copper are the main reasons for considering bentonite of a great interest on industrial applications [19]. Recently, as part of a study on the recycling of waste cooking oils [20] we reported some IR and XRD studies of this bentonite, confirming the excellent quality of the material [9]. As the distribution of the superficial area, as well as the size and the volume of the pores are within the most important parameters in clay´s characterization, we employed N_2 physisorption technique for the measurement of the external surface area according to the Brunauer–Emmett–Teller (BET) equation [21]. In addition, Barrett, Joyner and Halenda (BJH) method was used to calculate the distribution of the porous [22]. In Fig. 1, the adsorption and desorption curves for samples of bentonite are reported and respectively indicated with blue and red colour.
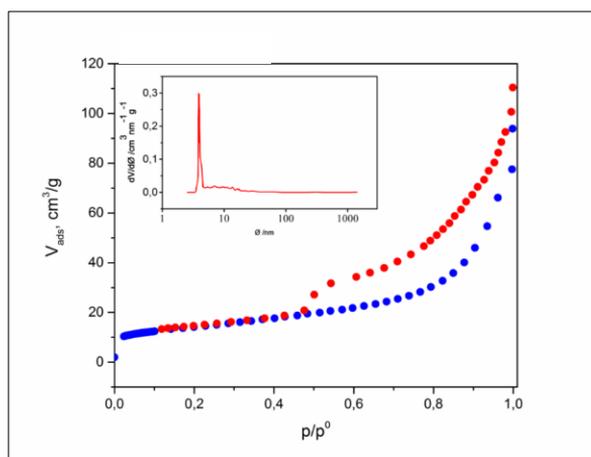

Fig. 1. N_2 physisorption isotherm for bentonite.

The experimental curve obtained was classified as a type IV adsorption isotherm (BDDT classification) [23-25], in agreement with the observations reported by Hayati-Ashtiani for a bentonite originated from the Isfahan Province of Iran [26]. The classification of the hysteresis is consistent with a type H3, referred to aggregates of

platelike particles forming slit-like pores [24]. The sample presents a value of superficial area of 49.09 m^2/g, a porous volume of 0.094 cm^3/g and maximum porous size of 3.949 nm at -196 °C. The distribution of the porous is monomodal as showed in Fig. 1 (inbox). The main constituent in the samples considered was the montmorillonite, which showed the absence of defects usually observed in the crude clays. In order to evaluate the thermal stability of the specific bentonite considered, the superficial area, as well as the porous size and volume were measured after three subsequent thermic treatments (from 25 °C to 120 °C, at 200 °C and 300 °C) as reported in Table 1.

Table 1. Structural parameters of bentonite samples at different temperatures.

Entry		Nitrogen absorption		
		S_{BET} ± 5 m^2/g	Porous volume ± 0.002 cm^3/g	Porous size ± 0.5 nm
1	25 °C	49	0.094	3.9
2	120 °C	46	0.089	3.9
3	200 °C	45	0.087	3.9
4	300 °C	44	0.086	3.9

BET and BJH analysis do not show any significant difference pointing to a high thermal stability of the material in the rage 25-300 °C. In order to evaluate the thermal stability of the bentonite, a thermogravimetric profile was registered through TGA analysis.
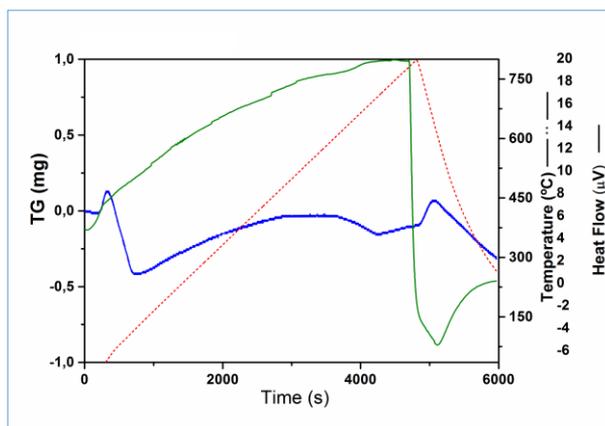

Fig. 2. TG-DSC plot of s´Aliderru bentonite. Blue colour indicates the TG profile, the red one the heating ramp and the green one the DSC profile.

The results reported in Fig. 2 (blue line), show two endothermic peaks corresponding to two distinct steps where a part of the mass of the sample is lost. The first step, between 60 °C and 120 °C, is associated to the physically adsorbed water, which is lost in an amount of 0.5 mg, corresponding to the 2.5% of the total initial mass. The second step, between   600 °C and 800 °C, is related to the condensation of the oxidryl structure,

expulsed in form of water [27]. Similar results were observed in the case of Brazilian [28] and Turkish bentonites [29]. The DSC profile (green line) does not show any significant thermal events.

4. Conclusion

Samples of bentonite from the deposit of S´Aliderru, sited in the north of Sardinia have been characterized by N_2 physisorption and by thermogravimetric analysis, including an evaluation of the thermal stability. BET and BJH data are in agreement with the typical structural characteristics of montmorillonite and clearly indicate a high purity of the material.

Acknowledgments

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