



Porosity in ion-exchanged and acid activated clays evaluated using n-nonane pre-adsorption



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ARTICLE INFO

Article history:

Received 30 November 2015

Received in revised form

9 June 2016

Accepted 16 June 2016

Available online 17 June 2016

Keywords:

Clays

n-Nonane pre-adsorption

Microporosity

Mesoporosity

ABSTRACT

The applicability of the n-nonane pre-adsorption method for characterising the porosity in clays is presented. Na-SD, a Na⁺-exchanged purified bentonite, and materials obtained by Al³⁺-exchange and acid treatments of Na-SD and SAZ-1 were used. Nitrogen adsorption isotherms, at −196 °C, were determined before and after n-nonane pre-adsorption on each of the samples. In all materials, n-nonane remained adsorbed in ultramicropores after outgassing at 25 °C. Outgassing at higher temperatures (50, 75 and 200 °C) removed nonane and ultramicropores became available for nitrogen adsorption. All treatments on Na-SD led to increase in micropore volume. Larger ultramicropore and supermicropore volumes were obtained for Na-SD acid activated with HCl at 95 °C than for treatments at 25 °C with HCl or following Al³⁺-exchange (Al-SD), and increased with increasing acid concentration to 3 M. Activation with 4 M HCl led to the largest pore volume with contribution from mesopores. However, the specific external surface area was the same as that obtained for Na-SD, Al-SD and for most of the other acid activated samples. Treatments at 95 °C with 1 M and 6 M HCl promoted increase in specific external surface area. The micropore volumes and specific external surface area for SAZ-1 treated with 1 M HCl at 95 °C were larger than those of Al-SAZ-1, but lower than those obtained for corresponding materials derived from Na-SD. The n-nonane pre-adsorption method enabled micropore volumes and specific external surface areas to be obtained for all samples.

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1. Introduction

The n-nonane pre-adsorption method was introduced in 1969 by Gregg and Langford for the evaluation of the microporosity present in certain carbon blacks [1]. The reasons for choosing n-nonane were, on the one hand, the long chain molecules are

strongly adsorbed in narrow pores and remain there upon outgassing at room temperature and, on the other hand, the narrow linear molecules are able to enter into narrow micropores. The original experimental procedure demonstrated the suitability of choosing n-nonane and consisted of determining the nitrogen adsorption isotherm when the micropores had been filled with n-nonane and then after they had been progressively emptied by outgassing at elevated temperatures, until they were completely empty [1,2].

n-Nonane pre-adsorption has subsequently been evaluated for a variety of other materials and it has been shown that it can be applied to other types of carbon materials, including activated carbons [3–5], carbon nanotubes [6] carbon aerogels [7,8], ordered mesoporous carbon and silicon carbide [9] and also other microporous materials, including titanium dioxide [10], γ-MnO₂ [11], ammonium phosphomolybdate, phosphotungstate and

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silicomolybdate [12], silicalite-I [13], silica-pillared layered manganese oxide [14], ordered mesoporous silicas [15] and silica spheres [16]. The results from this variety of materials have confirmed the value of using n-nonane pre-adsorption for the evaluation of microporosity and to obtain additional insight into the pore structures. To the best of our knowledge, there is not any previous article regarding application of n-nonane pre-adsorption to clays or materials derived from them.

Clay porosity, especially when expanding clays are dominant, is readily modified using acid activation and ion-exchange. The alterations depend on the specific treatment conditions and on the nature of the starting clays, as our previous works illustrate [17,18]. Complex porosity can result and, if micropores of different sizes are present together with external surface area, evaluation of the microporosity is not straightforward from nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ alone. Pre-adsorption of n-nonane can be an effective way of isolating the micropores [2,19,20].

Hence, in this work it is intended to show that n-nonane pre-adsorption method can be applied to clays and to obtain, using this method, a quantitative description of microporosity and specific external surface area of acid treated and ion-exchanged clays. The materials used in this study are a new set of materials resulting from acid treatment of Na-SD with HCl solutions, and also some materials from previous work [18] namely Na-SD, Al-SD, Al-SAz-1 and one sample of acid activated SAz-1.

2. Materials and methods

2.1. Materials preparation

The starting raw bentonite (SD) was collected at Serra de Dentro, Porto Santo Island (Madeira Archipelago, Portugal) as in our previous works [17,18]. The major impurities were removed by low speed centrifugation (6 min, at 600 rpm), to obtain the $<2\text{ }\mu\text{m}$ size fraction. Carbonates were removed by addition of sodium acetate-acetic acid buffer until the clay suspension reached pH 6.8. Removal of organic matter was accomplished using hydrogen peroxide in acidic medium, at $90\text{ }^{\circ}\text{C}$. Sodium dithionite-sodium citrate buffered at pH = 8.3 was used to eliminate free oxides of iron, aluminium, titanium and manganese. Then, the product was converted into the Na-exchanged form using 1 M aqueous sodium chloride solution. Excess Cl^- was removed by dialysis and the powdered clay, labelled Na-SD, was obtained after drying the gel collected following centrifugation at 4500 rpm for 30 min.

SAz-1 (Cheto, Arizona, USA) is a higher charge montmorillonite obtained from The Clay Mineral Society Source Clay repository (Purdue University); it was suspended in deionized water and the $<2\text{ }\mu\text{m}$ size fraction was collected by centrifugation. It was modified using two different approaches: (a) Acid activation by shaking with 1 M HCl at $95\text{ }^{\circ}\text{C}$ for 30 min, leading to the sample SAz195 and (b) ion exchange by shaking the original SAz-1 with $0.3\text{ M Al}(\text{NO}_3)_3$, for 30 min at room temperature. This was repeated, three times, before rigorous washing to provide Al-SAz-1. Al-SD was obtained from Na-SD using the same procedure.

Acid activated samples were prepared by mixing 10 g of Na-SD with 300 cm^3 aliquots of aqueous HCl at $25\text{ }^{\circ}\text{C}$ for 120 min or $95\text{ }^{\circ}\text{C}$ for 30 min. The samples were then mixed with a large quantity of cold water to effectively terminate the leaching process, centrifuged and washed successively until a stable pH was achieved, and finally they were air-dried for 24 h. Samples are labelled according to the acid concentration and temperature of activation. For example, SD495 is the material obtained when a 10 g sample of Na-SD was treated with 4 M HCl at $95\text{ }^{\circ}\text{C}$.

2.2. Nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ and n-nonane pre-adsorption

Nitrogen adsorption isotherms were determined, at $-196\text{ }^{\circ}\text{C}$, on a Quadrasorb SI from Quantachrome Instruments, using helium (for dead space calibration) and nitrogen of 99.999% purity supplied, respectively, by Linde and Air Liquid. Pre-adsorption of n-nonane was carried out in a custom made apparatus in pyrex and with J. Young greaseless teflon taps. Nonane ($>99\%$ purity, Sigma-Aldrich) was pretreated with 3 Å molecular sieves and then outgassed by three solidification-melting cycles. In all cases, high vacuum was attained using vacuum systems equipped with turbomolecular pumps.

Prior to the adsorption measurements, all initial samples were outgassed for 5 h at $200\text{ }^{\circ}\text{C}$, achieved using a heating rate of $1\text{ }^{\circ}\text{C min}^{-1}$. After determining the nitrogen isotherm, the sample cell was transferred to the custom made apparatus, and the sample was outgassed for 1 h. Subsequently, n-nonane pre-adsorption was carried out as follows. The sample was left in contact with n-nonane vapour for 1 h at room temperature and then the sample cell was immersed in liquid nitrogen for 30 min. Afterwards, the sample was outgassed at $-196\text{ }^{\circ}\text{C}$ for 30 min, then it was allowed to warm up to $25\text{ }^{\circ}\text{C}$ and outgassed for a further 5 h. It was then transferred to the analysis station to determine the nitrogen isotherm. Afterwards, each sample was then outgassed at increasingly higher temperatures and nitrogen adsorption isotherms were successively determined after each stage of outgassing. Outgassing procedures were 5 h at 50 and $75\text{ }^{\circ}\text{C}$, achieved using $1\text{ }^{\circ}\text{C min}^{-1}$, while for $200\text{ }^{\circ}\text{C}$ the temperature programme was $2\text{ }^{\circ}\text{C min}^{-1}$ up to $100\text{ }^{\circ}\text{C}$, then to $150\text{ }^{\circ}\text{C}$ and finally to $200\text{ }^{\circ}\text{C}$, staying 1 h at each temperature.

In all cases, the sample cell was filled with nitrogen (99.999% purity) before transferring it to and from the Quadrasorb analysis station, where the sample was again outgassed for a further 1 h before determining the nitrogen adsorption isotherm. In order to eliminate differences in amounts adsorbed due to the changes in mass of n-nonane, the amounts of nitrogen adsorbed are all expressed per g of the corresponding initial sample outgassed at $200\text{ }^{\circ}\text{C}$, prior to n-nonane pre-adsorption.

3. Results and discussion

3.1. Nitrogen isotherms and analysis by the Brunauer-Emmett-Teller (BET) method

Nitrogen adsorption-desorption isotherms, at $-196\text{ }^{\circ}\text{C}$, determined on Na-SD and acid treated Na-SD, before n-nonane pre-adsorption, are presented in Fig. 1. The isotherms were analysed by the BET method as recommended, to avoid any subjectivity in evaluating the BET monolayer capacity, following the main criteria [20], and the results are presented in Table 1. It is evident that the materials exhibit similar types of isotherm and hysteresis loop common to clays, indicating platy particles [20] even after the acid treatments up to high acid concentration. However, it is clear that the amounts adsorbed by acid treated materials are superior to those by Na-SD, indicating increase of specific surface area and/or porosity as confirmed by the BET specific surface areas, considering 0.162 nm^2 for the nitrogen cross-sectional area, presented in Table 1 for the initial samples. Nitrogen isotherms of Al-SD, Al-SAz-1 and SAz195 were previously reported [18] and results of the analysis by the BET method are included in Table 1 for Al-SD and in Table 2 for Al-SAz-1 and SAz195. It can be seen that similar features were found with the Al^{3+} -exchanged clay and SAz-1 treated with 1 M HCl (SAz195).

The specific surface areas of Na-SD and acid treated Na-SD are smaller than those from previous work [17], which, at least partially, probably reflects variations due to sampling location or

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