Influence of different dry milling processes on the properties of an attapulgite clay, contribution of inverse gas chromatography

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ARTICLE INFO

ABSTRACT

The effect of dry milling processes on the surface properties of an attapulgite clay, also called palygorskite, was investigated by carrying out experiments with different types of grinding devices. Ground products were then characterized by size measurement, scanning electron microscopy, X-ray diffraction, adsorption–desorption of N_2 and inverse gas chromatography at infinite dilution (IGC-ID) as well as finite concentration conditions (IGC-FC). These analyses were performed to evaluate the changes in particle size distribution, morphology, crystallinity and surface properties of attapulgite powder, respectively. Among the tested dry grinding devices, grinding in an air jet mill (Alpine 50 AS) and a vibratory ball mill (Pulverisette 0) led to the most significant particle size reduction. SEM photomicrographs showed that a breakage of the fibrous structure took place during dry grinding. Moreover, long grinding in Pulverisette 0 resulted in the complete destruction of fibre morphology followed by agglomeration. XRD analysis showed that whatever the grinding process, the microstructure of the attapulgite was not affected. IGC confirmed that only grinding in Pulverisette 0 affected the surface properties notably. In this case, the most significant decreases were observed in the dispersive component of the surface energy (164 to 116 mJ/m^2) and in the specific surface area obtained with the octane probe (114.5 m^2/g to 62.6 m^2/g) by IGC-ID and IGC-FC, respectively. At the same time, a modification of the distribution functions of the adsorption energies (DFAE), giving information about surface heterogeneity, was noticed.

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1. Introduction

Grinding processes are widely used in mineral industry, particularly for the preparation of mineral fillers. The aim of these mechanical treatments is often to reduce particle size. However, depending on the ground material, grinding conditions and mechanical stresses, they often result not only in a reduction of particle size, but also in other unexpected changes that directly affect the physicochemical properties of the initial solid. Furthermore, grinding can induce an increase or decrease in the specific surface area depending on the grinding tools and parameters.

Grinding of phyllosilicate materials, like clays, was the subject of several studies, namely the grinding of montmorillonite [1,2], kaolinite [2–6], talc [6–10], chrysotile [11,12], and vermiculite [13,14]. In these papers, the influence of grinding on the morphology, microstructure, specific surface area or porous structure was investigated.

However, grinding can also modify the adsorption capacity of the phyllosilicate. Liu explored the effect of dry grinding on the capacity of attapulgite to adsorb a dye, methylene blue [15]. Liu also showed an improvement in the swelling properties of the superabsorbent

nanocomposites made of modified cellulose and ground attapulgite [16]. Suraj and Hongo studied the capacity of kaolinite [7] and vermiculite [17] respectively, to adsorb heavy metals in the course of grinding. In these studies, the authors were interested in the adsorption capacity of organic/inorganic components through end-used properties of the solid. Upstream from the end-used properties, it would be of a great interest to investigate the surface properties of the solid leading to the end-used property. There are only a few methods to measure the surface energies of powders, one of which is the inverse gas chromatography (IGC). IGC is a powerful method for the investigation of the modification of the solid surface properties upon grinding. In contrast to conventional gas chromatography, IGC studies the adsorption of a known adsorptive on an unknown adsorbent. The adsorbent (solid sample) is placed in the GC column while the adsorptive is a gas carrying probe molecules. Therefore, the probes, which are clearly identified molecules such as alkanes, acidic or basic molecules, are used to determine surface properties of the material packed into the column. In mineral field, Balard and Papirer showed the applicability of IGC to evaluate changes in the interactivity, morphology and heterogeneity of the solid surface after a grinding treatment [18–20]. In the present study, IGC was used to examine the modifications upon grinding of the surface properties of an Algerian attapulgite. This phyllosilicate material, also called palygorskite, is a rock extracted from mines or quarries. After a required

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grinding step, this material is used in powder form for a wide range of applications and fields: adsorption, catalysis, environmental, agro-food, pharmaceutical industries and production of ceramics [21,22]. In this work, we examined the influence of three types of grinding devices, a batch ball mill, a vibratory ball mill also called pulverisette zero, and an air jet mill. In the two first devices, the particles undergo impact and compression between two surfaces (the wall of the jar and a ball or between two balls). In the case of the third device, grinding occurs in an autogenous way, the impacts occur between the particles themselves. The air jet mill, widely used in the pharmaceutical industry, can produce sizes of ultra-fine particles; its advantage is that contamination with grinding media can be avoided. After the examination of the particle size, morphology and microstructure, the main objective of this work was to show that IGC is a characterisation technique suitable to emphasize the surface modifications under grinding.

2. Theory of inverse gas chromatography (IGC)

IGC is widely used to characterize a wide range of solid surfaces, for example attapulgite [23], aluminas [24], graphites [18], kieselguhr [25], polymers [26], pharmaceutical powders [27] and cotton [28]. This technique provides a lot of information about the analysed solid, especially concerning its surface properties (surface energy, thermodynamic properties, acid–base behaviour, etc.).

The term 'inverse' indicates that the material examined in the chromatographic column acts as the stationary phase. The probes with known properties, which are injected into the column, are chosen according to their ability to interact with the support, and thus they give information about the solid surface in the column.

Depending on the amount of injected probes, IGC can be classified as inverse gas chromatography at infinite dilution (IGC-ID) and inverse gas chromatography at finite concentration (IGC-FC).

The outcome of an IGC-ID test is the retention time of the injected probe, t_r. This value reflects the intensity of interactions between the solid surface and the probe.

Retention volume, V_n, which is used to determine the thermodynamic parameters, is related to retention time by Eq. (1):

$$V_n = D_c(t_r - t_0) \tag{1}$$

where t_r is the retention time of the probes, t_0 the retention time measured with a non-adsorbing probe (methane) and D_c is the corrected flow rate, which is related to D_m, the flow rate measured with an electronic flow meter, according to Eq. (2):

$$D_c = D_m \cdot j \cdot \left(\frac{T_c}{T_a}\right)\left(\frac{\eta_{T_a}}{\eta_{T_c}}\right) \tag{2}$$

where T_a and T_c are the ambient and oven temperatures, η_{T_a} and η_{T_c} are the viscosities of the carrier gas at the T_a and T_c temperatures, and j is the coefficient of James Martin for taking into account the compressibility of the carrier gas under the effect of the pressure drop ΔP as shown in Eq. (3):

$$j = \frac{3}{2} \frac{\left(1 + \frac{\Delta P}{P_{atm}}\right)^2 - 1}{\left(1 + \frac{\Delta P}{P_{atm}}\right)^3 - 1} . \tag{3}$$

2.1. Inverse gas chromatography at infinite dilution (IGC-ID)

2.1.1. The dispersive component of the surface energy, γ_s^d

This parameter traduces the potential of a solid to undergo London or dispersive interactions. It is calculated according to the Dorris and Gray approach [29], by injecting linear alkanes (pentane, hexane, heptane, etc.). The slope of the straight line obtained when plotting

RTLn(V_n) versus the number of carbon atoms of the alkane probes, $\Delta G_a^{CH_2}$, gives access to γ_s^d by applying Eq. (4):

$$\gamma_s^d = \frac{\left(\Delta G_a^{CH_2}\right)^2}{4N^2 a_{CH_2}^2 \gamma_{CH_2}} = \frac{\left(RTLn\frac{V_n(n+1)}{V_n(n)}\right)^2}{4N^2 a_{CH_2}^2 \gamma_{CH_2}} \tag{4}$$

where N is Avogadro's number, a_{CH_2} is the surface area of one adsorbed methylene group (0.06 nm²), γ_{CH_2} is the surface energy of a solid with only methylene groups, i.e., polyethylene $\left(\gamma_{CH_2} = 35.6 + 0.058(293 - T)\right)$ in mJ/m², with T being the oven temperature.

2.1.2. The nanomorphology index, $I_M(\chi_t)$

The solid surface is never entirely smooth at the molecular scale due to the existence of structural defects, which are emphasized by the size exclusion effects of some probes during the chromatographic process. Indeed, branched or cyclic alkanes can behave differently from linear alkanes when adsorbed on the surface of a rough solid. This effect of surface morphology can be quantified by comparing the adsorption behaviour of linear and non-linear (branched or cyclic) alkanes, using the nanomorphology index, $I_M(\chi_t)$ [30], defined in Eq. (5):

$$I_M(\chi_t) = e^{\frac{-\Delta G_a^M}{RT}} \tag{5}$$

where ΔG_a^M is the variation between the representative point of the branched or cyclic alkane and the reference n-alkane straight line, χ_t is the topology index proposed by Brendlé [31] and derived from Wiener's topology indices.

When $I_M(\chi_t)$ is equal to 1, the solid surface can be considered as flat at the molecular scale. Under these conditions, the bulky (branched or cyclic) and the linear alkanes have access to the same surface. So both probes have similar retention times and variations of free energy of adsorption (RT lnVn). ΔG_a^M is near zero.

When the surface roughness increases, $I_M(\chi_t)$ decreases and its value can reach 0.1 as in the case of talc [32]. The access to the rough parts of the surface is more limited for cyclic (or branched) alkane molecules than for linear ones due to steric hindrance. In the case of the cyclic (or branched) alkanes, the retention time and the variation of the free energy are weaker, and ΔG_a^M deviates from 0.

2.1.3. The specific component of the surface energy, I_{sp}

This parameter characterizes the polar surface and acid–base interactions; it represents the contribution of specific interactions, ΔG_a^{sp}, also denoted by I_{sp}, between polar probes and the solid surface [31]. It can be determined from the variation between the global free energy of the injected polar probe, ΔG_a, and the straight line of alkane probes ΔG_a^d (Fig. 1).

The principles, advantages and limitations of IGC-ID have been summarized in a review paper [31] and will not, therefore, be discussed here.

2.2. Inverse gas chromatography at finite concentration (IGC-FC)

In the case of IGC-FC, a few microlitres of the liquid probe are injected into a column containing the solid to be analysed, in order to provide an approximately mono-layered coverage on the surface of the solid. The results of this technique reflect the interaction of probe molecules with all the sites on the solid surface. The obtained chromatographic peak (Fig. 2) is highly asymmetric when ideal, nonlinear conditions are fulfilled. Due to the presence of very-high-energy adsorption sites, it is usually observed that a non-negligible part of the injected probe is not eluted despite of the fact that the signal returns to the initial baseline.