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Influence of the geological history, particle size and carbonate content on the surface properties of talc as determined by inverse gas chromatography at infinite dilution

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Abstract

Inverse gas chromatography at infinite dilution (IGC-ID) coupled with a controlled impregnation by polymer gives access to information about the surface of heterogeneous solids such as talcum powder. A limitation of IGC-ID is that it is mainly sensitive to the high-energy sites, in other words for the talc, to the lateral surfaces. Thus, a progressive impregnation of the surface of talc with a suitable polymer allows saturating the high-energy sites, making the chromatographic probes access less energetic free sites, specifically the basal surfaces. In this paper, impregnation has been made with polyethyleneglycol (PEG) 20000M and allows estimation of the ratio of basal to lateral surface of talc crystals which plays a very important role in many industrial applications for talc. We examine the influence of several parameters on the surface properties of different types of talc. These parameters are the particle morphology of talc (microcrystalline, lamellar or very lamellar structure), the carbonate content and the particle size.

Keywords: Inverse gas chromatography; Talc; Carbonate ratio; Surface properties

1. Introduction

Inverse gas chromatography at infinite dilution, i.e. IGC-ID, is a convenient method for the examination of the surface properties of a finely divided solid [1–3]. It consists in injecting clearly identified molecules, called probes, into a column made up of the solid under test. The injected probes interact with the surface of the solid as they are moved through the column by a carrier gas. The complexity of these interactions depends on the amount of probe injected. Two IGC techniques may be distinguished: infinite dilution or finite solute concentration. This study has been carried out at infinite dilution (IGC-ID) where very small amounts of probes are injected in such a way that the interactions between the probe molecules themselves can be considered to be negligible and only the interactions between an isolated probe and the surface of the solid exist. By

IGC-ID, one can access the apparent dispersive component of the free surface energy γ_s^d (injection of linear alkanes). However, IGC-ID gives only information on absolute thermodynamic parameters on perfectly homogeneous surface. On a heterogeneous surface, like talc, the sites of higher energy contribute mainly to the chromatography process. In the present work, we try to take advantage of this limitation by coupling the IGC-ID with a controlled modification of talc surface with PEG 20M. The idea is to progressively kill the more interactive sites by preferential adsorption so that the progressively increasing surface coverage ratio by PEG macromolecules forces probes to interact with the less and less energetic free sites.

Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) is a phyllosilicate with a lamellar structure. It consists of octahedral brucite sheets sandwiched between two tetrahedral silica sheets, to form talc layers superimposed indefinitely. The crystal is composed of two kinds of surfaces:

- Weakly energetic basal surfaces with basic and hydrophobic Si–O–Si groups.

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- More energetic lateral surfaces with acid and hydrophilic Si–OH groups and residual magnesium cations.

The structure of talc directs the choice of the macro-molecules used for the impregnation. It can be expected that a basic polymer such as polyethyleneglycol 20M (PEG 20M) will interact preferentially with the acid lateral surfaces. Then after saturating the acid sites with PEG, one can access the less energetic sites of the basal surfaces.

The industrial use of talc depends on the surface properties and on the ratio of basal to lateral surfaces. Different techniques allow access to this data such as immersion calorimetry [4], gas adsorption (nitrogen, argon, water vapor ...) [5,6] and the measurement of contact angles [7]. IGC-ID is an interesting supplement to these techniques because it gives a vision of the surface of the solid at the scale of the injected probe.

The aim of the study is to observe the variation of the surface properties of talc as a function of several parameters that play a very important role in many industrial applications, that says, the particle morphology of talc (microcrystalline, lamellar or very lamellar structure), the carbonate content and the particle size.

For this purpose, the change of γ_s^d has been studied according to the polymer coverage ratio. The dispersive component of the surface energy γ_s^d is obtained by analyzing the retention times of a series of linear alkanes injected as probes and gives a measurement of the dispersive London forces. Further theoretical details can be found elsewhere [8].

2. Materials and methods

2.1. Materials

The talcs used in this investigation were supplied by the Luzenac Company and their characteristics are given in Table 1. The mean particle size, d_{50} , is measured with a Micromeritics Sedigraph 5100. It is observed that for series M talcs, no correlation exist between the d_{50} and the specific surface area because their porosity. The BET specific

Table 2
Milling processes of the talc samples

Samples	Milling processes
T00	Pendular mill
M1	Pendular mill
M2	Pendular mill + hammer mill
M3	Pendular mill + air jet mill
M4	Pendular mill + hammer mill
M5	Pendular mill + hammer mill
L	Air jet mill
L3	Dry mill
L2	Dry mill
L1	Dry mill

surface, S_{BET} , is obtained by argon adsorption with a Micromeritics ASAP 2010. The milling processes of these talcs are given in Table 2. The PEG was obtained from Fluka, and was purified by dissolution in chloroform and precipitation in heptane.

2.2. Experimental IGC conditions

Two Hewlett Packard 6890 gas chromatographs each fitted with two flame ionisation detectors (FID) are used. The carrier gas is helium. The injector and detector are heated to 150 °C. All the columns were conditioned at 120 °C overnight and the analyses made at 100 °C. Net retention times are calculated by subtracting the retention time of a non retained molecule, methane, from the retention time of the probe.

2.3. Preparation of the samples: controlled impregnation of talc

A solution of polymer with a known concentration is prepared in dichloromethane. A given volume of this solution is diluted in a beaker with 5 ml of the same solvent. The mass of talc required to fill the column (around 2 g), is put in the same beaker and stirred with the polymer solution. The mixture is then put in a vacuum oven to evaporate the solvent and deposit the polymer on the surface of the talc.

Table 1
Characteristics of the talc samples provided by Luzenac Europe Company

Sample ^a	Geographical origin	Talc–chlorite (%)	Lamellarity	S_{BET} (m ² /g)	d_{50} (μm)
T00	France	92–7	Lamellar	3	10.6
M1	Spain	86.5–<0.5	Microcrystalline	8	11
M2	Spain (10% of carbonates)	86.5–<0.5	Microcrystalline	11.5	4.5
M3	Spain	86.5–<0.5	Microcrystalline	13	1.6
M4	Spain (4.5% of carbonates)	96–0	Microcrystalline	10	4.5
M5	Spain (1.5% of carbonates)	97–1.5	Microcrystalline	10	4.5
L	Italy	95–2	Very lamellar	14.5	1.2
L3	Italy	95–2	Very lamellar	20.5	0.8
L2	Italy	95–2	Very lamellar	9.5	2.75
L1	Italy	95–2	Very lamellar	7.5	3.85

The mean particle size, d_{50} , is measured with a Micromeritics Sedigraph 5100. The BET specific surfaces, S_{BET} , are obtained by argon adsorption.

^a L, lamellar; M, microcrystalline.

The chromatography column is afterwards filled with the impregnated talc.

The EG monomer unit coverage ratios expressed in MU/nm^2 were calculated using the following formula:

$$n_{\text{MU}} = \frac{6023\tau}{M_{\text{MU}}S}$$

where τ (%), coverage ratio expressed as a percentage; n_{MU} , PEG monomer unit number per nm^2 of talc; M_{MU} , molecular weight of the EG monomer; unit, 44 g/MU; S , specific area of powder in m^2/g .

3. Results

3.1. Preliminary study

As a first step, a reference talc denoted T00 was examined. The changes in the dispersive component of the surface energy (γ_s^d) with increasing PEG coverage ratios has been described and commented in a previous paper [9]. To summarize, four domains can be distinguished:

- A first plateau ($\gamma_s^d = 160\text{--}170 \text{ mJ}/\text{m}^2$) corresponding to the coverage of the slot like high energetic sites present on the lateral surfaces of the talc.
- A rapid decrease of γ_s^d attributed to the saturation of the wedge-like sites situated between the talc crystallites.
- A second plateau ($\gamma_s^d = 45 \text{ mJ}/\text{m}^2$) equal to that measured by contact angle measurements corresponding to the progressive coverage of the basal surfaces.
- A final plateau ($\gamma_s^d = 28 \text{ mJ}/\text{m}^2$) attributed to a thick layer of PEG.

This plot allows an assessment of the ratio of lateral to basal surfaces of the talc (estimated to 7.5/80 for the T00) [10].

3.2. Influence of the particle morphology

Talc samples of different geographical origins exhibit different morphologies. Changes due to the geological history of the talc are examined in this study on the basis of three different talcs coming from three different countries: France (T00), Italy (L) and Spain (M2). The first has a “normal” lamellar structure, the second a very pronounced lamellar structure and the third is a microcrystalline talc. The results obtained are presented in Fig. 1.

The main differences observed between the three talcs are the height of the first plateau at low polymer coverage ratios. The microcrystalline talc (M2) presents the highest γ_s^d on this plateau. It is difficult to interpret this result because these talcs have not only different lamellarities but also different chemical structures (different chlorite ratios for example). So, it's difficult to attribute the γ_s^d variations to only one parameter. It is possible that the microcrystalline talc has many structural defects into which the linear alkanes will insert giving high retention times. Thus these defects could be responsible for the high value of γ_s^d on the first plateau. The higher the lamellarity of the talc, the lower is the number of defects and therefore the lower is the value of γ_s^d at low polymer coverage ratios. The grinding processes are also different between the three talcs, T00 is obtained by pendular mill, L by air jet mill and M2 by pendular mill and hammer mill. So, an other observation is that the low γ_s^d value ($130\text{--}140 \text{ mJ}/\text{m}^2$) at the low polymer ratios is obtained with the talc (L) obtained by air jet mill.

Fig. 1. Influence of the particle morphology on the variation of the dispersive component of the surface energy, γ_s^d , of three impregnated talc samples with the PEG 20M coverage ratio.

Fig. 2. Influence of the particle size on the variation of the dispersive component of the surface energy, γ_s^d , of impregnated microcrystalline talc samples as a function of the PEG 20M coverage ratio for three samples of talc having different mean particle sizes.

3.3. Influence of the particle size for microcrystalline talcs

In order to study the influence of the particle size, a microcrystalline talc was ground to obtain three samples with different particle sizes: 1.6 μm (M3), 4.5 μm (M2), and 11 μm (M1). The results obtained are presented in Fig. 2. These three talcs are obtained with different grinding processes, M3 by pendular mill and air jet mill, M2 by pendular mill and hammer mill and M1 by pendular mill. With air jet mill, we observe a low γ_s^d value on the first plateau at the low polymer ratios, 160 mJ/m^2 for M3 compared to 190 mJ/m^2 for M2 and M1. At the polymer ratios higher to 1 MU/nm^2 , the change in γ_s^d with the coverage ratio is sensitive to the mean particle diameter. When the particle size decreases,

the decrease of the γ_s^d between 2 and 10 MU/nm^2 is shifted towards the low coverage ratio. Bigger particles need higher coverage ratios of PEG to cover the slot and wedge-like sites.

3.4. Influence of the particle size for lamellar talcs

The influence of the particle size was also studied on three lamellar talcs (Fig. 3), L1: 3.85 μm , L2: 2.75 μm and L3: 0.8 μm . These three talcs are obtained with air jet mill. They remain truly lamellar after fine grinding, we have the evidence by SEM pictures (Fig. 4). They all present a low γ_s^d value (130 mJ/m^2) on the first plateau. The air jet mill process seems to be responsible of this behavior, as we saw it on talcs L and M3, also obtained by air jet mill. If we compared the decrease of the γ_s^d , the talcs L1 and L2 present the

Fig. 3. Influence of the particle size on the variation of the dispersive component of the surface energy, γ_s^d , of impregnated lamellar talc samples as a function of the PEG 20M coverage ratio for three samples of talc having different particle mean diameters.

Fig. 4. SEM pictures of lamellar talcs (L1, L2 or L3).

Fig. 5. Influence of the carbonate content on the variation of the dispersive component of the surface energy (γ_s^d) of impregnated talc samples as a function of the PEG 20M coverage ratio.

same behavior as microcrystalline talcs. A shift of the curve towards the low coverage ratio is observed between 1 and 3 MU/nm² when the particle size decreases. This occurs in a smaller range of PEG coverage than for the microcrystalline talcs, which can be explained by:

- Firstly, noting that the range of particle size for the lamellar talcs is smaller: from 1 to 4 µm than that for the microcrystalline talcs from 1 to 11 µm.
- Secondly, the structural defects are fewer in lamellar talcs than in a microcrystalline talcs and because the grinding of more macroscopic crystal leads to the formation of few defaults.

3.5. Influence of the carbonate content

As impurities are always present in talc, another parameter examined is the carbonate content. Fig. 5 allows comparison of the evolution of the γ_s^d with the polymer coverage ratios for different samples with three different carbonate contents (M5: 1.5%, M4: 4.5%, and M2: 10%). These three talcs are obtained by the same grinding process: pendular mill and hammer mill. A difference can be seen in the higher part of the first plateau and in the slope of the first decrease. At the present stage of our study, it is difficult to give a final clear-cut interpretation of these results, and to say if the carbonate content has or has not a real influence on the γ_s^d .

4. Conclusion

In conclusion, coupling IGC-ID and controlled surface modification through polymer adsorption is a powerful

method for obtaining information on the surface heterogeneity of finely divided solids. This paper shows that the surface properties of talc are influenced by particle size and grinding process rather than the geological origin. All the talcs obtained by air jet mill have the same behavior at the low polymer ratios. It also seems that the carbonate content has no real influence on these properties but further investigations are necessary to complete the results and clarify the interpretations.

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