



## An insight into the surface properties of calcined kaolinitic clays: The grinding effect



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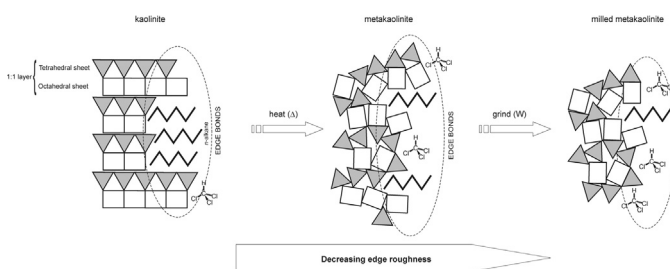
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### HIGHLIGHTS

- Surface Lewis basic properties increase from kaoline to metakaolinitic materials.
- The extensive grinding of metakaolinitic materials affords a decrease of the  $\gamma_s^d$ .
- Lewis basic properties of the metakaolines surface also increase with grinding.
- Grinding results are largely explained by changes in the surface nanoroughness.
- Shown results may have interest in the composites area/cation-exchange properties.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The present work aimed characterizing in a systematic way the surface of metakaolinitic materials produced by calcination of a kaolinitic clay at different temperatures and to study the effect of grinding on the surface properties of metakaolinitic materials. Using X-ray photoelectron spectroscopy, it was found for all materials a Si/Al atomic ratio close to 1, confirming the presence of the 1:1 clay structure. By inverse gas chromatography, an increase of the Lewis basic properties of the surfaces of metakaolinitic materials in comparison to the original clay was found, which was due to the condensation of hydroxyl groups in the structure of the clay. The grinding of the metakaolinitic materials afforded a decrease of the dispersive component of the surface energy ( $\gamma_s^d$ ) as well as an increase of the specific interaction with sterically hindered molecules, caused by the diminishing of the materials surface nanoroughness. The Lewis basic properties of the materials surface also increased with grinding. Noticeably, for all studied materials a good inverse relation could be found between the  $\gamma_s^d$  and the specific interaction of trichloromethane (but not with dichloromethane), showing the importance of surface nanoroughness on the adsorption process of bulky molecules.

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### 1. Introduction

Calcined kaolin or metakaolin is an artificial material used in advanced ceramics [1,2], as filler in papermaking, [3,4], as a pozzolanic material in mortars [5,6], concrete [7,8] and cement-wood composites [9], as extender in plastics [10] and natural rubber

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[11], as opacifier in oral medicine prosthesis [12], in processing of oil shale [13] and food wastes [7], in paints [14], and as a fundamental component for the production of some types of inorganic polymeric materials – geopolymers [2,15]. Metakaolin contains high content of Si and Al and is obtained by heating (calcining) kaolin raw material, a georesource mainly composed by kaolinite,  $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ . The calcination process at temperatures ranging from  $\approx 450^\circ\text{C}$  to  $\approx 750^\circ\text{C}$  promotes the removal of the structural water (dehydroxylation) in kaolinite and its transformation into metakaolinite that is an amorphous (disordered) aluminosilicate. Calcination at higher temperature ( $>950^\circ\text{C}$ ) results in the formation of crystalline phases, such as silicon-spinel or mullite.

The physico-chemical surface properties of calcined clays have high importance considering their influence in the context of the production of composites with polymeric matrices (e.g., composites with cellulose for papermaking, when calcined materials are used as fillers), or in cation exchange processes or pozzolanic reactions.

Inverse gas chromatography (IGC) is a suitable technique to assess the surface properties of fibrous materials (e.g., glass fibres and cellulosic fibres) and powders such as clays and calcined clays since it gives a wide range of physico-chemical surface parameters not accessed by other techniques. On this point, contact angle measurements are not so adequate for the analysis of powders due to the associated problems of heterogeneity, roughness, porosity, and surface energy gradients. Another useful technique to study the materials surface is the X-ray photoelectron spectroscopy (XPS) that can provide information of the chemical composition and structure of the surface up to about 10 nm depth.

Several studies have been reported on the use of IGC to evaluate the surface properties on clayey materials, such as kaolinites [16–22], illites [16,17,22], smectites [23,24], and palygorskites (attapulgites) [25,26]. In particular, the dispersive component of the surface energy and the surface morphology of kaolinites (and illites) were evaluated by IGC using *n*-alkanes and branched alkanes as probes [16]. For the same type of materials, the effect of pre-conditioning temperature on the heats of adsorption of several organic probes was also considered [22]. Regarding calcined kaolinitic clays, Burry and Keller [18] analysed the effect of the pre-conditioning temperature on the dispersive component of the surface energy (at  $100^\circ\text{C}$ ) of two calcined clays (one experimental and another commercial) and compared with kaolin samples. Ansari and Price [27] analysed two commercial grades of calcined kaolin for their dispersive properties and specific interactions with a few probes, in order to produce composites with polyethylene. These two pioneer studies were restricted to a small number of calcined clays and the specific acid-base interactions were not in depth analysed. On the other hand, the use of XPS on calcined kaolinitic materials has also been reported (e.g. [28]).

In the present study, one kaolinitic raw material as starting material, five experimental metakaolins and one commercial metakaolin were thoroughly analysed by IGC and XPS in order to evaluate the surface properties of these materials. Several methods for the IGC data analysis were employed, in order to obtain a wide range of parameters of the surface properties of the calcined kaolinitic materials. Particular emphasis was given to the grinding effect on the surface properties of calcined kaolinitic clays.

## 2. Materials and methods

### 2.1. Materials

A kaolinitic raw material (kaolinitic mud) collected from an industrial sand wash plant was the starting material used in this

study. The kaolinitic raw material was calcined in an oxidizing atmosphere, on a 2.5 m scale prototype rotary kiln with fast firing cycles (1:00 h to 1:30 h), in order to obtain experimental metakaolinitized samples. Three experimental calcined kaolinitic clays (referenced as “MK”) were obtained after calcination of the kaolinitic raw material at  $750^\circ\text{C}$ ,  $840^\circ\text{C}$  and  $940^\circ\text{C}$ . After the calcination, the materials were subjected to a disaggregation stage in an alumina ball mill (Gabbrielli Fast Mill) during 5 min. Two experimental metakaolinitized samples were also subjected to an additional grinding (milling) stage (referenced as “M”), which was accomplished in a vibratory agate disc mill (Retsch RS1) during 20 min at 700 rpm. The experimental metakaolinitized samples were compared with the commercial Optipozz (Burgess, USA) highly-reactive metakaolin, which served as reference to the parameters evaluated in this study. Overall, six samples of metakaolins (MK-750, MK-840, MK-940, MK-750-M, MK-940-M, MK-USA) and the sample of the initial kaolinitic raw material (referenced as “K”) were considered for analyses.

### 2.2. Methods

The materials were analysed for their mineralogical composition, particle size and specific surface area. The mineralogical analysis was performed by powder X-ray diffraction (XRD) in a Philips X’Pert PRO MPD diffractometer. The crystalline phases were identified by comparison with the standards from the International Centre for Diffraction Data. Particle size analysis was carried out by sedimentation and absorption of X-rays in a Micromeritics Sedi-graph 5100 apparatus. The determination was performed in the 0.1–63  $\mu\text{m}$  size range. Specific surface area was determined by  $\text{N}_2$  adsorption in a Micromeritics Gemini 2.0 instrument, using the BET method. Samples were pre-treated at  $200^\circ\text{C}$  under a nitrogen flow before measurements were made.

### 2.3. Inverse gas chromatography and X-ray photoelectron spectroscopy

The clayey materials were analysed by inverse gas chromatography and X-ray photoelectron spectroscopy, in order to assess their surface properties and surface chemical composition.

The material for IGC analysis was previously compacted through axial compression of 6–7 g of powder at  $\approx 120\text{ MPa}$ . The pressed disc was then crumbled in a porcelain mortar and finally sieved between 710 and 500  $\mu\text{m}$  to obtain “coarse” granulates, before being packed in the IGC column. Using this procedure it was possible to obtain enough gas flow rate in the IGC column. IGC analysis was done using a DANI GC 1000 digital pressure control gas chromatograph equipped with a hydrogen flame ionization detector. Stainless-steel columns, 0.5 m long and 0.4 cm inner diameter were washed with acetone and dried before packing. Approximately 5 g of each sample was packed into the gas chromatograph column. The columns were shaped in a smooth “U” to fit the detector/injector geometry of the instrument. The packed columns were conditioned overnight at  $110^\circ\text{C}$ , under a helium flow, before any measurements were made. Experiments were carried out at a column temperature of  $110^\circ\text{C}$  with the injector and detector kept at  $180^\circ\text{C}$  and  $200^\circ\text{C}$ , respectively. Helium was used as carrier gas with flow rates typically between 25 and 40 mL/min. Small quantities of probe vapor ( $<1\ \mu\text{l}$ ) were injected into the carrier gas, allowing work under infinite dilution conditions. The probes used for the IGC data collection were *n*-pentane (C5), *n*-hexane (C6), *n*-heptane (C7), *n*-octane (C8), trichloromethane (TCM), dichloromethane (DCM), 1-pentene, 1-hexene, and cyclohexane (CyHex). All probes were of chromatographic grade and were used as received (Sigma–Aldrich). Methane was used as the reference probe. The retention times ( $t_r$ ) were the average of three

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