



Physicochemical characterization of a diatomaceous upon an acid treatment: a focus on surface properties by inverse gas chromatography



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ABSTRACT

Natural diatomite from Sig/Algeria was treated with 0.5, 1.0, 3.0 and 5.0 M nitric acid solutions for 2 h under reflux at 333 K in order to improve its performance as support of catalyst. The purified silica powders obtained from frustules can also be used to reinforce composites. The solids obtained were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, thermal analyses, and nitrogen adsorption–desorption at 77 K. Treatment of diatomite earth with nitric acid reduced mineral impurities, such as Fe₂O₃ and alkali metal oxides (CaO, MgO), eliminated carbonates and increased SiO₂ ratio from 88% to 98%. The SEM micrographs showed the original geometry of the pores to be preserved. The surface properties were also evaluated using inverse gas chromatography at infinite dilution (IGC-ID) and finite concentration (IGC-FC). The interest here was to establish whether the technique is sufficiently sensitive to detect variations in the surface properties of the diatomite due to this chemical treatment. The IGC analysis permitted to reach several surface energy components with organic probes. Between them, the distribution function of the adsorption energy sites obtained with the isopropanol probe revealed a silica structure after the 5 M nitric acid treatment.

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1. Introduction

Diatomaceous also known as diatomaceous earth, kieselguhr, tripolite, etc. is a siliceous sedimentary rock mainly made from the skeletons of aquatic plants or algae called diatoms [1]. Amorphous silica, a constituent of the diatom frustules, is the main component of diatomite, although variable quantities of impurities such as metal oxides, mineral clays, salts (mainly carbonates) and organic matter may also be present [2,3]. The diatom shell has properties such as a high porosity with a strong adsorption ability and an excellent thermal resistance related to physical structures and aggregates of fine particles perforated by regular pattern of very small holes. Hence, diatomite has been widely used as filter aid, pharmacy carrier and adsorbent [2–4].

The abundance and availability of these mineral reserves as a raw material source and their relatively low cost guarantee their continued utilization in the future. Recently the diatomite was examined as a perfect support material in preparation of solid catalysts [5]. The main features of a catalyst support according to Satterfield [6] are its chemical

nature which is defined by the acidic or basic character of the surface depending on physical or chemical treatments they have received and the presence of impurities in the catalyst quarry. Similar to the synthetic amorphous silica, the reactivity of diatomite is linked to the presence of reactive sites on its surface such as hydroxyl groups which are the main reactive sites. Apart from the hydroxyl groups, acid sites as iron or aluminum oxides are also considered as important sites on the surface of diatomite [7]. But the presence of impurities such as clay, carbonate calcium on the diatomaceous surface limits the use of this material.

There are several methods to modify the surface characteristics of clays minerals for various purposes. Acid treatment is usually employed for improving surface properties of diatomite. The aim of acid treatment is to eliminate impurities such as carbonate groups, which are inhibitors of photocatalytic reactions implementing hydroxyl ions. Indeed hydroxyl ions are trapped by carbonates and lead to radicals less reactive. On the other hand, carbonates can fill the natural pores of the diatomite. So an other interest of removing carbonates is to open these blocked pores and to increase the specific surface area of the diatomite, the performance of a catalyst being directly related to the specific surface area. Extensive studies were carried out in order to evaluate the effect of acid treatments on the porous texture or structure [8,9].

The present investigation sets out the influence of nitric acid treatment on a diatomaceous silica sample, with the aim of its valorization

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as a catalyst support. Different methods, such as X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy were used to characterize the variation of the diatomite properties before and after treatments with different concentrations of nitric acid. Inverse gas chromatography (IGC) was also carried out; it is now a well-established technique for the study of surface properties, extensively applied for characterization of various finely divided powders, mineral fillers, pigments, silicates [10,11], composite materials [12], organic materials such as plastics, textiles, food or pharmaceutical solids [13], etc. With this technique, the surface characterization of the solids is performed by injecting probes of known properties into a column containing the solid of interest. The retention time or the retention volume of these probes, measured near zero surface coverage, allows the determination of interactions, including London (i.e. apolar) and specific (i.e. polar) interactions, established between the probes and the solid and then the characterization of the solid surface. In a second time, if the solid surface is entirely covered with a probe monolayer, a distribution function of adsorption sites can be determined.

2. Theory on inverse gas chromatography

Depending on the amount of probe molecules injected into the chromatographic column, IGC may be performed at infinite dilution (IGC-ID) [14], but also at finite concentration conditions (IGC-FC) [15,16].

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

This technique consists in filling a column with the solid under test and in injecting very small amount of probe molecules (vapor) with known properties (length of the carbon atoms chain, polarity, ramification), at the limit of the detector sensitivity. Depending on the chemical nature of the probe and its geometry, the three following parameters can be determined:

- The dispersive component of the surface energy, obtained by injections of a n-alkanes series [17]. This parameter gives a measurement of the non-specific interactions that is to say London forces developed between the probes and the solid surface.
- The nanomorphological index, determined by injections of branched or cyclic alkanes. This index delivers information about the surface roughness of the solid at the scale of the injected probe [18,19].
- The specific interaction parameters, established by injections of polar probes, that give access to polar interactions, mainly the acid–base interactions [19].

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

In IGC-FC, a few microliters of a liquid probe are injected into the column containing the solid to be analyzed, in order to cover entirely with a molecule mono-layer the solid surface. A strong asymmetric chromatographic peak is obtained when ideal, nonlinear conditions are fulfilled.

IGC-FC permits the access to desorption isotherms of the probe molecule [15,21]. The simplest method, from the point of view of the analysis duration, is “the elution characteristic point method” (ECP) that allows the acquisition of part of the desorption isotherm from a unique chromatographic peak. According to this method, the first derivative of the isotherm is related to the retention time for each point of the rear diffuse profile of the chromatogram by the Conder's Eq. (1):

$$\left(\frac{\partial N}{\partial P}\right)_{L,t_r} = \frac{JD}{mRT}(t_r - t_0) \quad (1)$$

where N is the number of desorbed molecules, P the partial pressure of the probe at the output of the column, L the column length, t_r the retention time of a characteristic point on the rear diffuse profile of the chromatogram, t_0 the retention time of CH_4 , D the flow rate at the output of

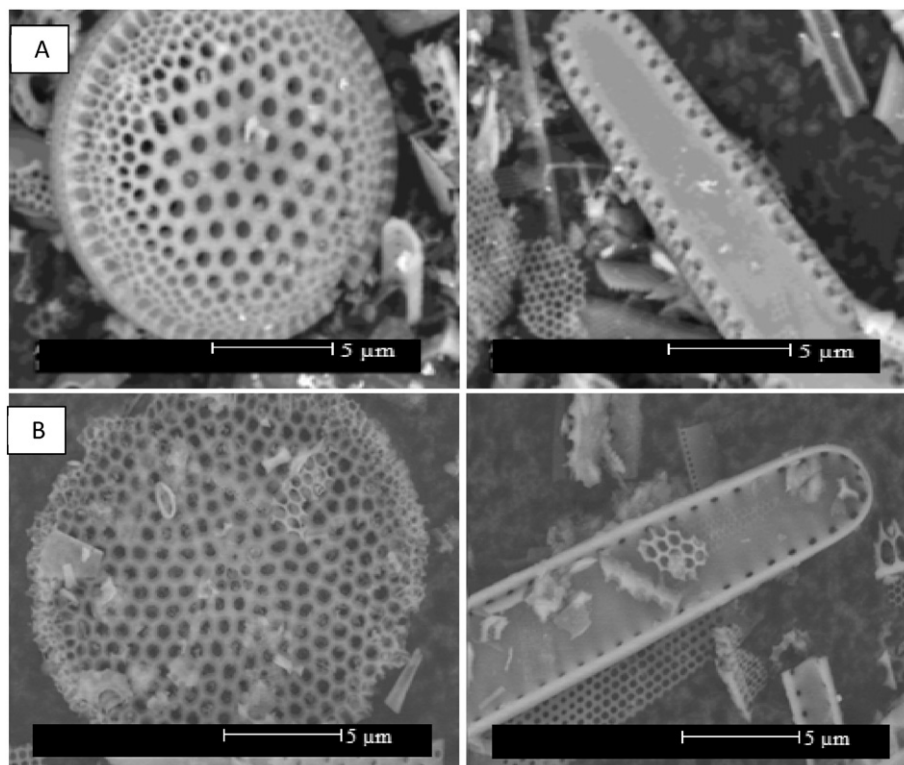


Fig. 1. SEM micrographies of (A) raw diatomite and (B) diatomite after 2 h with HNO_3 0.5 M.

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