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Influence of relative humidity on the properties of examined materials by means of inverse gas chromatography☆

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ABSTRACT

Inverse gas chromatography (IGC) at infinite dilution was applied to evaluate the surface properties of sorbents and the effect of different carrier gas humidity. They were stored in different environmental humidity – 29%, 40%, and 80%. The dispersive components of the surface free energy of the zeolites and perlite were determined by Schulz-Lavielle method, whereas their tendency to undergo specific interactions was estimated basing on the electron donor–acceptor approach presented by Flour and Papirer. Surface parameters were used to monitor the changes of the properties caused by the humidity of the storage environment as well as of RH of carrier gas. The increase of humidity of storage environment caused a decrease of sorbents surface activity and increase the ability to specific interaction.

1. Introduction

Inverse gas chromatography (IGC) is used for physicochemical characterization of various materials as well as description of interactions between components in various systems. The examined material plays a role of stationary phase. Its properties influence the retention of carefully selected test solutes. Retention data are further converted into the parameters describing the required property of the examined substance [1,2]. Reversed-flow GC (or time-resolved GC) introduced by Katsanos and Karaiskakis [3] is version of IGC technique, which allows to determine e.g. adsorption energies [4], energy distribution functions [5].

Condition of IGC experiment will be crucial for a group of materials containing "natural" amount of water influencing their stability and activity. IGC examination with the use of standard, i.e. dry carrier gas will cause progressive loss of the water and, finally, the "demolition" of the examined substance. Therefore, the justified use of the wet carrier gas and the influence of the carrier gas humidity on the estimated parameters will be discussed in this paper. Comte et al. [6] found that carrier gas relative humidity (RH) significantly influence surface properties of low specific surface area glass beads. Decrease of the retention of the test solutes with RH increase was also reported by Garcia-Herruzo et al. [7]. Sunkersett et al. [8] found that γ_s^D values do not vary significantly with the increase of relative humidity.

Results of the examination of the surface properties for series of zeolites and perlite by the use of inverse gas chromatography will be reported. The influence of varying relative humidity of the environment during the IGC experiment will be presented and discussed.

2. Materials

The following types of solids were examined:

(a) Natural zeolites: zeolite thick, zeolite fine, zeolite ZCO, zeolite Micro20, zeolite Micro50.
(b) Perlite: Perlite EXP 50.

All materials were delivered by Certech Niedomice (Poland).

Each of studied sorbents was stored at three different environmental humidity – about 29%, 40%, and 80%. Measurement stations to store studied zeolites and perlite in an atmosphere of reduced and elevated humidity consisted of two exsiccators in which hygrostatic solutions were placed. Saturated solution of sodium chloride (RH = 80%) and saturated solution of sodium hydroxide (RH = 29%) were used as hygrostatic solutions.

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For solid surface characterization by IGC method polar and nonpolar test compounds were applied. The nonpolar probes were: pentane (p.a., POCH S.A.), hexane (99%, Chempur), heptane (99%, Sigma–Aldrich), octane (99%, Fluka) and nonane (99%, Acros Organics). The polar probes were: chloroform (p.a. POCH), ethanol (99%, POCH), ethyl acetate (POCH S.A., HPLC grade) and 1,4-dioxane (99%, Fluka) which are characterized by their donor, *DN*, and acceptor, AN^*, numbers.

3. Experimental

The experiment was divided into 3 parts:

(1) All the investigated materials were stored at two different environmental humidity (29% and 80%), then the materials were placed in a chromatographic columns and were tested using a dry carrier gas.
(2) All the investigated materials were stored at atmospheric humidity (40%), then the materials were placed in a chromatographic columns and each column were first tested using a dry carrier gas and next using the carrier gas with a moisture content of 40%.
(3) All the investigated materials were stored at three different environmental humidity (29%, 40%, 80%), then the materials were placed in a chromatographic column and were tested using in the measurement carrier gas with the same moisture content as that in which the material was stored.

3.1. Inverse gas chromatography

IGC measurements were carried out by using iGC SMS gas chromatograph (Surface Measurements Systems Ltd., London, UK) equipped with flame-ionization detector. This chromatograph gives possibility to study properties at different relative humidity. Chromatographic columns were from glass, silanized inside, I.D. 4 mm, length 30 cm. Carrier gas was helium at a flow rate of 25 ml/min. The measurements were carried out at 35 °C, the temperature of injector and detector was 150 °C. Vapors of test solutes were injected in an amount ensuring the achievement of the infinite dilution region.

3.2. Fourier transform infrared spectroscopy (FTIR)

In order to obtain more information concerning the surface functional groups of investigated solids FTIR spectra were collected. Brucker Vertex 70 spectrophotometer was applied. The KBr discs of different samples were prepared (2 mg of the sample per 250 mg of KBr). The spectra were recorded in the frequency range 400–4000 cm^{-1}.

3.3. BET determination

Specific surface areas of the studied materials was measured by low-temperature adsorption of nitrogen. The isotherms of nitrogen adsorption/desorption were measured at 77 K using Accelerated Surface Area and Porosimetry Analyzer ASAP 2020 (Micromeritics Instruments Co). Studied samples were degassed at elevated temperature in a vacuum chamber prior to measurements.

Moreover, the volume and size of pores of materials were examined.

3.4. Determination of humidity

Balance-dryer made by RADWAG was used to determine the humidity content in the studied materials. Fillers were first heated to the 120 °C. After 3 min the temperature was increased to 160 °C and the sample was dried until it was completely dry, i.e. to constant weight. The humidity content was determined as the difference between the sample weight before and after drying.

4. Calculations

In the present study IGC at infinite dilution was used to characterize the chemical surface of zeolites and perlite. The influence of changes of the environment relative humidity on the IGC experiment was also tested.

The net retention volume (V_N) was calculated from the following equation [9–11]:

$$V_N = j \cdot F \cdot (t_R - t_M) \quad (1)$$

where t_R – the retention time of the test compounds (min), t_M– the retention time of the methane (min), j – the correction factor for gas compressibility, F – the gas flow-rate at the column temperature (ml/min).

4.1. Determination of the dispersive surface free energy

γ_s^D parameter was calculated according to Schultz and Lavielle method based on the Eq. (2) [10–12]:

$$R \cdot T \cdot \ln\ V_N = 2 \cdot N \cdot a \cdot \sqrt{\gamma_S^D \cdot \gamma_L^D} + C \quad (2)$$

where R – the gas constant, 8.314 [J/mol K]; T – temperature of measurement [K]; V_N – net retention volume [m^3]; N – the number of Avogadro, 6.023×10^{23} [1/mol]; a – cross sectional area of the adsorbate [m^2]; γ_S^D – the dispersive component of surface free energy [mJ/m^2]; γ_L^D – the dispersive component of the surface tension of the probe molecule in liquid state [mJ/m^2]; C – constant.

This is the straight line equation $y = ax + b$ in which:

$$R \cdot T \cdot \ln V_N = y \quad a \cdot \sqrt{\gamma_L^D} = x \quad 2 \cdot N \cdot \sqrt{\gamma_S^D} = a \quad C = b$$

γ_S^D is determined from the slope.

4.2. Acid–base characteristics of materials surface

Retention data for polar and non-polar test compounds are necessary to quantify acidic and basic properties of the examined surface.

K_A and K_D parameters, expressing the acidity and basicity of the surface layer of the examined material, are related to the energy of specific interactions ΔG_{sp} (3) between the examined surface and the test compounds [12–14]:

$$\Delta G_{sp} = K_D \cdot AN^* + K_A \cdot DN \quad (3)$$

where K_A, K_D – parameters describing the ability of the tested material surface to act, respectively, as the electron donor and acceptor; *DN* – the donor number of the polar test compound; AN^* – modified acceptor number, expressed by the equation:

$$AN^* = 0.288(AN - AN^d) \quad [kJ/mol]$$

where AN^d– part of the forces of dispersion in the value of the acceptors number, which may be calculated from the measurement of surface tension; constant 0.288 expressed warm interaction between the acid–base $SbCl_5$ and Et_3PO and displacement spectra for the above system with respect to the transfer Et_3PO in hexane.

K_A and K_D parameters were obtained by dividing Eq. (3) by AN^*:

$$\frac{\Delta G_{sp}}{AN^*} = \frac{DN}{AN^*} \cdot K_A + K_D \quad (4)$$

and K_A was determined from the slope.