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## Inverse gas chromatography (IGC) as a tool for an energetic characterisation of porous materials

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### ABSTRACT

The surface properties of controlled pore glass, silica gel and ordered mesoporous silica SBA-15 having different functional groups (hydroxyl, trimethylsilyl and aminopropyl) were investigated by inverse gas chromatography. The porous silicates were used as model system to study correlations between surface chemistry and surface energy by means of the IGC technique. The van Deemter equation was used for the determination of optimum carrier gas flow rate. The dispersive part of surface energy, the specific free energy of adsorption, acceptor–donor properties and heat of adsorption were determined from IGC experiments for an energetic characterisation of the porous materials. It is shown that different surface functional groups have an influence onto dispersive interactions with *n*-alkanes as well as onto the specific interactions with polar molecules.

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### 1. Introduction

Porous materials are of great interest for all applications where surfaces are involved. Catalysis, filtration, separation, energy storage and conversion, sensors are some examples of the field of application of porous materials. The characterisation of the surface properties of porous materials is of great importance for understanding their performance in almost all fields of application. This comprises the characterisation of the texture properties on the one hand and on the other hand the characterisation of the surface chemistry. The characterisation of texture properties is well established on the basis of the standard techniques of low temperature nitrogen sorption [1,2] and mercury intrusion porosimetry for macroporous materials (pore width > 50 nm) [3].

Unfortunately, surface area, pore size distribution and porosity give no information about surface chemistry or surface activity. The texture properties are simply geometric parameters. But, it is important to obtain information about the activity of the surface for a better understanding and further development of porous materials. Therefore, estimation of surface properties indicating the ability of the surface to participate in dispersive and specific (acid–base) interactions is necessary [4]. Dispersive and specific interactions can be quantified by inverse gas chromatography experiments due to the estimation of thermodynamic properties

(e.g. dispersive component of surface energy, heat of adsorption, free energy of adsorption and acid–base properties). IGC is a fast and versatile technique. Physicochemical properties are obtained on the basis of several chromatograms of different non-polar and polar gaseous probe molecules.

Recently, the IGC technique was applied successfully for the characterisation of the effect of surface modification of porous silicates. Correlations were observed between different surface groups and the dispersive part of surface energy [5]. Thielmann [6] and Grajek et al. [7,8] used IGC technique for the quantification of dispersive and specific interactions of surface modified ordered mesoporous MCM-41. Katsanos et al. optimised Pt–Rh supported on SiO<sub>2</sub> catalysts on the basis of reversed flow GC [9]. Reversed flow GC (RFGC) is time-resolved IGC technique [10]. In RFGC the direction of the carrier gas flow is changed for a short time, followed by a restoring of the flow in its original direction. The change in the direction of the gas flow results in a short enrichment of the solute quantity in the carrier gas and creates extra chromatographic peaks.

The aim of the present work was the investigation of specific interactions, heat of sorption and acid–base properties of porous silicates on the basis of IGC measurements. Different porous silicates were synthesised and characterised by means of IGC. Furthermore, the influence of different surface groups on specific interactions was investigated. Therefore, porous silicates were modified by reaction with hexamethyldisilazane (HMDS) and 3-aminopropyltriethoxysilane (APTS).

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## 2. Experimental

### 2.1. Materials

Commercial silica gel (ACROS Organics) with 8 nm mean pore diameter was used without further purification (sample name SG8).

Controlled pore glass (CPG) beads with 10 nm mean pore diameter were synthesized according to the following procedure. Glass beads with a composition of 70 wt.% SiO<sub>2</sub>, 23 wt.% B<sub>2</sub>O<sub>3</sub> and 7 wt.% Na<sub>2</sub>O were phase separated at 550 °C for 48 h, followed by a combined acid and alkaline leaching treatment. The resulting porous glass beads were washed with deionised water and dried at 80 °C for 24 h (sample name CPG10) [11].

Furthermore, ordered mesoporous silica SBA-15 was synthesized according to Fulvio et al. [12].

The surface of all kinds of porous silica was modified by different standard procedures. (I) Reaction of surface hydroxyl groups with HMDS in *n*-hexane as solvent under reflux [13]. HMDS treated samples are indicated by the suffix “H”. (II) Reaction of surface hydroxyl groups with 3-APTS in water under the formation of aminopropyl groups onto the surface of the porous silica [14]. Samples that were modified with 3-APTS are indicated by the suffix “NH”.

### 2.2. Apparatus and procedure

Inverse gas chromatographic experiments were carried out using SMS-iGC 2000 equipment with a flame ionisation detector. All samples were activated at 393 K for 24 h prior to measurement. The samples were packed into a glass column of 30 cm length and 0.2 cm inner diameter. Columns were filled with 50–100 mg material, packed under mechanical vibration using a tapping machine from Surface Measurement Systems and fixed with glass wool at the top and bottom of the sample. Then the sample was conditioned in situ for 2 h at 389 K with a helium carrier gas flow-rate of 30 ml/min to remove physisorbed water. Pulse experiments were performed at 366 K under infinite dilution in the Henry region ( $p/p_0 = 0.04$ ) to exclude interactions of probe molecules. Non-polar *n*-alkanes (hexane, heptane, octane and nonane) and ethyl acetate, chloroform, acetone and 1,4-dioxane as polar probe molecules were used to quantify non-polar and polar interactions. All injected solutes were of chromatographic quality and used without further purification. Dead times for the instrument were measured using methane. The van-Deemter-Equation [15] was utilized to obtain optimal experimental flow-rates (see Chapter 4.1). Therefore a flow rate variation (between 5 and 40 ml/min carrier gas flow) was done with ethyl acetate and nonane as adsorbate. The heat of adsorption was determined on the basis of the temperature variation of 4 different temperatures between 356 and 366 K.

The surface concentration of hydroxyl groups has been obtained on the basis of thermogravimetric analysis (TGA) according to de Boer and Vleeskens [16]. Elemental analysis was used for the quantification of the HMDS treatment. The amount of trimethylsilyl groups was calculated on the basis of the carbon content according to Berendsen et al. [17]. The aminosilylated samples were titrated using the chloride method to determine the concentration of amino groups [18].

## 3. Theoretical analysis and calculation

### 3.1. Determination of retention time and optimal flow rate

The fundamental quantity of an IGC experiment is the retention time ( $t_r$ ) of a probe molecule. This quantity has to be calculated very accurate and reproducible. Narrow symmetrical peaks are

the basis for the determination of the retention time from the peak maximum [19]. In gas chromatography the peak shape of a pulse of probe molecules is affected by two effects: adsorption/desorption and diffusion.

The adsorption process is independent of the surface coverage in the Henry region, in the infinite dilution range. This is reflected by a linear adsorption isotherm and a symmetrical Gaussian peak [20]. However, in some cases the resulting peaks are broad and/or skewed. On the one hand this can be a result of the influence of gas phase diffusion or on the other hand a result of a heterogeneous surface.

A theoretical treatment of peak broadening due to diffusion effects can be made on the basis of the van Deemter equation (Eq. (1)). Initially, this method was developed for analytical chromatography.

$$H = A + \frac{B}{u} + C \cdot u \quad (1)$$

where  $H$  is the theoretical plate height,  $A$ ,  $B$  and  $C$  are constants and  $u$  is the linear flow rate. Constant  $A$  represents the Eddy-diffusion and is related to the column packing. The constant  $B$  represents the longitudinal diffusion and  $C$  describes the mass transfer. The van Deemter approach takes these effects into account. The van Deemter equation can also be used for IGC experiments to predict optimum flow rates for the realisation of narrow peaks. A plot of the theoretical plate height  $H$  versus the linear flow rate shows a curve minimum representing the optimum linear flow rate.

The linear flow rate is calculated from the bed length  $L$  and the dead retention time  $t_0$  (Eq. (2)).

$$u = \frac{L}{t_0} \quad (2)$$

The theoretical plate can be calculated according to Eq. (3),

$$H = \frac{L}{8 \cdot \ln 2} \cdot \left( \frac{W_{1/2}}{t_R} \right)^2 \quad (3)$$

where  $W_{1/2}$  is the peak width at half height and  $t_R$  is the retention time.

The curve minimum can be obtained from the constants  $B$  and  $C$  (Eq. (4)).

$$u_{\min} = \sqrt{\frac{B}{C}} \quad (4)$$

### 3.2. Determination of dispersive and specific interactions

The theory and principles of IGC have been well developed and described in several publications [19,21,22]. In this article only crucial equations and assumptions are listed.

IGC experiments/chromatograms provide several information: (I) retention time of a probe molecule  $t_r$ , (II) dead retention time of methane  $t_0$ , (III) carrier gas flow rate  $F$  and (IV) inlet  $p_i$  and outlet pressure  $p_o$ . These data enable the calculation of the net retention volume  $V_N$  according to Eq. (5):

$$V_N = \frac{T}{273.15} (t_r - t_0) F J \quad (5)$$

where  $T$  is the column temperature and  $J$  is the James–Martin correction factor [23], which corrects the retention time for the pressure drop along the packing (Eq. (6))

$$J = \frac{3}{2} \left( \frac{p^2 - 1}{p^3 - 1} \right) \quad (6)$$

where  $p$  is the relative pressure

$$p = \frac{p_i}{p_o} \quad (7)$$

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