Inverse gas chromatographic studies on porous glass

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Porous glass is a well suitable system for the exploration of new characterization techniques due to adjustable texture properties and the possibility to "tailor-made" the surface chemistry. In this study porous glass beads were utilized as model system for the evaluation of inverse gas chromatography (IGC). Mesoporous glass beads with 10 and 20 nm pore size and macroporous glass beads with 50 nm pore size were synthesized and modified by thermal treatment and chemical reaction with hexamethyldisilazane (HMDS), ethyl-, propyl-, butyl- and octyldimethyl-chlorosilane. The correlations between the textural properties and the dispersive surface energy were investigated by means of the IGC technique. Furthermore dependences between surface chemistry and surface energy were pointed out on the basis of IGC measurements.

Keywords: inverse gas chromatography, porous glass, surface energy, surface hydrophobisation.

1. Introduction

Mechanical and chemical stability, a variety of shapes, adjustable porosity and optical transparency are noticeable properties of porous glasses. Porous glasses possess an increased scientific interest and a wide range of application because of this diversity of positive characteristics. The adjustment of textural and geometric properties is important for all application needs. Furthermore, the generation of a defined surface chemistry is of particular importance. It is possible to realize a pore range between 1 and 500 nm by varying the manufacturing process of porous glasses [1]. The different types of shape are beads, pellets, tubes, rings, *etc*., in adjustable sizes. The surface chemistry can be controlled and "tailor-made" by the reactive hydroxyl group on the surface.

Thus, porous glass provides an ideal model system for evaluating innovative techniques of the characterization of porous materials. In this study, the inverse gas

chromatography (IGC) is examined on the basis of porous glass as model system. The IGC represents a technique to quantify surface modifications and their influence on the properties of (modified) porous glass due to its sensitivity to the surface chemistry. IGC is a dynamic sorption technique that determines thermodynamic parameters of solids. These parameters are useful for a better understanding of surface phenomena. The principle of the IGC technique is to conduct gaseous probe molecules (mobile phase) with known properties over the surface of the stationary phase. This stationary phase represents the material of scientific interest and is placed into a column. The retention time of the mobile phase is influenced by the surface of the solid, hence enabling the calculation of physicochemical properties, *e.g.*, surface energy, heat of adsorption. Recently THIELMANN used the surface energy for the characterization of various porous materials [2].

The surface energy consists of a specific and dispersive term:

$$\gamma_S = \gamma_D^{SP} + \gamma_S^D \tag{1}$$

The specific term γ_D^{SP} is caused by polar interaction, like hydrogen bonds, dipole moments, *etc*. The dispersive term γ_S^D is caused by non-polar interactions based on the London forces. Thus, for the determination of the dispersive part of surface energy only non-polar adsorbates/probe molecules can be utilized. In IGC experiments conventionally a series of *n*-alkanes (hexane, heptane, octane, nonane and decane) are utilized. As mentioned, the retention time of the probe molecules represents the basic information of an IGC experiment. The retention volume can be calculated from the retention time at peak maximum by the following equation [3]:

$$V_N = \frac{T}{273.15}(t_R - t_0)F\frac{J}{m} \tag{2}$$

where T is the column temperature, t_R is the retention time and t_0 is the "dead-time" of a non-interacting probe molecule like methane or hydrogen. F is the flow rate of carrier gas and J is the James–Martin correction factor, which improve the retention time for the pressure drop in the column and m is the sample mass [4]. The relation between the free energy of sorption and the retention volume is given by:

$$\Delta G = RT \ln(V_N) + K \tag{3}$$

where R is the gas constant and K is a constant. Furthermore ΔG can also be related to the work of adhesion W_A between the probe molecule and the solid [5]:

$$\Delta G = N_A a_m W_A \tag{4}$$

with a_m as cross-sectional area of the probe molecule and N_A as Avogadro constant. The work of adhesion can also be split up into a dispersive and a specific term:

$$W_A = W_A^D + W_A^{SP} \tag{5}$$

FOWKES defined the dispersive part of the work of adhesion as a function of the dispersive surface energy γ_S^D and the surface tension of a liquid probe molecule γ_L^D (given literature value) according to the following equation [6]:

$$W_A^D = 2\sqrt{\gamma_S^D \gamma_L^D} \tag{6}$$

with γ_S^D as dispersive surface energy and the surface tension of the liquid probe molecule γ_L^D (given literature value). For non-polar probe molecules it is $W_A = W_A^D$. Combining Eqs. (3) and (4) then leads to a linear relationship of Eq. (7) given by SCHULTZ *et al.* [7]:

$$RT\ln(V_N) = 2N_A\sqrt{\gamma_S^D}\, a_m\sqrt{\gamma_L^D} + \text{constant} \tag{7}$$

For a series of *n*-alkanes the dispersive part of surface energy can now be obtained by linear regression and the slop $m = 2N_A\sqrt{\gamma_S^D}$ of this equation (Fig. 1). The regression line is characteristic of a series of *n*-alkanes and a solid. It is called the "alkane line".
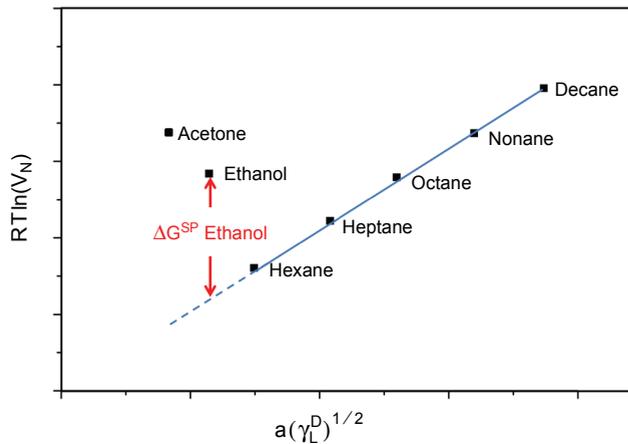

Fig. 1. Determination of dispersive part of surface energy and specific free energy.

The specific free energy can be calculated by the utilization of polar probe molecules like ethanol and aceton. The difference between the alkali line and the $RT\ln(V_N)$ value of a polar adsorbate is defined as specific free energy (Fig. 1).

2. Experiment

2.1. Materials

Meso- and macroporous glass beads were synthesized from initial glass beads with a composition of 70 wt% SiO_2, 23 wt% B_2O_3 and 7 wt% Na_2O. The glass beads have a diameter from 0.1 to 0.2 mm. A heat treatment of sodium borosilicate glass

beads at temperatures between 500 and 780 °C leads to porous glasses with controlled micro-, meso- and macroporosity. The glass separates into an interconnected structure of soluble sodium-rich borate phase and an almost pure SiO_2 phase due to spinodal decomposition within this temperature range. The thermal treatment is followed by a combined acid and alkaline leaching. The resulting glass beads were washed with deionized water and dried at 80 °C after each leaching step. Figure 2 shows the preparation procedure of the porous glass beads utilized in this study in detail.
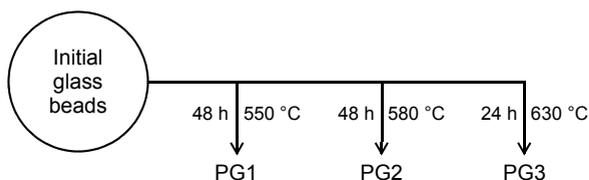
Fig. 2. Preparation procedure of the porous glass beads.

The surface of the porous glass beads was modified by different procedures with the aim to generate a diversity of the surface properties. In the following the procedures are described in detail:

i) The porous glass beads PG1 are thermally treated in a temperature range between 300–500 °C for 24 hours (the temperature of the thermal treatment is added to the sample name, *e.g.*, PG1_300). At these temperatures adjacent hydroxyl groups condense and siloxane species are formed. By the temperature dependence of the condensation, different concentrations of surface hydroxyl groups are generated, associated with a variety in the surface properties.

ii) PG3 is modified by reaction of hexamethyldisilazane (HMDS) with surface hydroxyl groups in *n*-hexane under reflux. Afterwards, the glass beads were washed with *n*-hexane and dried at 80 °C for 24 hours. Trimethylsilyl (TMS) groups were formed on the surface by this reaction. The degree of silylation was controlled by the reaction time (0–24 hours). Figure 3 summarizes the HMDS modification procedures and sample names. In addition, a combined modification of PG1 was performed by pretreatment at several temperatures (300, 400, 500 °C) for 24 hours followed by a chemical reaction with HMDS (0.5 ml HMDS/g sample, 48 hours) afterwards. In this case the sample name is composed of the temperature of pretreatment and "HMDS" for the HMDS modification.
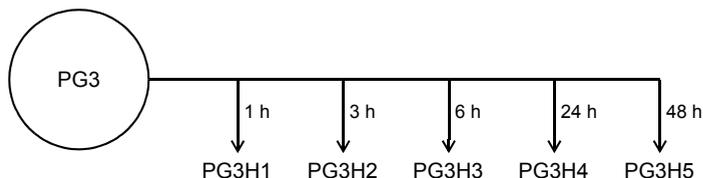
Fig. 3. HMDS modification procedure of mesoporous PG1.

iii) Furthermore, the surface of PG1 was modified with methyl-, ethyl-, propyl-, butyl- and octyldimethylchlorosilanes in dry toluene by incipient wetness impregnation at 90 °C for 24 hours. Alkyldimethylsilanes (organosilanes) with different alkyl chain length according to the reactant are formed on the surface. The resulting silica beads were washed with dry toluene and absolute ethanol and dried at 90 °C for 24 hours under vacuum (50 mbar). The alkyl chain length of the organosilanes is added to the sample name (*e.g.*, PG1C3 for a PG1 sample modified with propyldimethylchlorosilane).

2.2. Apparatus and procedure

The determination of the surface energy was conducted with IGC equipment by Surface Measurement Systems. The samples were activated prior to measurement at 120 °C for 24 hours. Samples were placed into a column with 2 mm diameter and 30 cm length and fixed with glass wool at the top and bottom of the sample. To realize a close-packing of spheres, each sample was packed under mechanical vibration. The samples were activated in the IGC equipment again at 116 °C with a helium flow-rate of 30 ml/min for 6 hours to remove physisorbed water. The *n*-alkanes hexane, heptanes, octane, nonane and decane were used as adsorptive for the determination of dispersive interactions. Acetone was used for the quantification of specific interactions. The experiments were carried out at 93 °C with a helium carrier gas flow of 10 ml/min and under infinite dilution of the adsorptive to prevent adsorptive–adsorptive interactions. For all experiments the concentration of the adsorptive was 4% in the helium flow.

Furthermore, the surface composition and texture properties of all samples were characterized by other techniques. Elemental analyses (EA) were performed in a CHNS 932 instrument to quantify the chemical modification by reaction with the alkylsilanes. The hydroxyl group density was determined by thermogravimetric analyses (TGA) with SDT 2960 Simultaneous DTA-TGA equipment by TA Instruments. The textural properties of the porous glass were measured by nitrogen sorption and mercury intrusion measurements by using Sorptomatic 1990 equipment and a Pascal 440 porosimeter by ThermoFinnigan.

3. Results and discussion

3.1. Texture properties

Surface area, pore diameter and pore volume are important standard parameters used for the characterization of porous glass. Porous glass beads with pore diameter of 11 nm, 21 nm and 53 nm were synthesized as a starting point for further modifications. The texture characteristics of the samples are summarized in Tab. 1.

The thermal treatment of PG1 shows no significant influence on the textural properties of the porous glass within the given temperature range. At higher

T a b l e 1. Texture properties of the synthesized samples.

Sample	Mean pore diameter [nm]	Specific surface area [m^2/g]	Pore volume [cm^3/g]
PG1	11[a]	112[a]	0.48[a]
PG1_300	11[a]	115[a]	0.48[a]
PG1_400	11[a]	109[a]	0.46[a]
PG1_500	11[a]	112[a]	0.47[a]
PG1HMDS	11[a]	73[a]	0.38[a]
PG1_300HMDS	11[a]	72[a]	0.41[a]
PG1_400HMDS	11[a]	70[a]	0.41[a]
PG1_500HMDS	11[a]	79[a]	0.43[a]
PG2	21[b]	79[b]	0.42[b]
PG3	53[b]	39[b]	0.47[b]
PG3H1	49[b]	39[b]	0.47[b]
PG3H2	49[b]	37[b]	0.45[b]
PG3H3	49[b]	38[b]	0.51[b]
PG3H4	50[b]	38[b]	0.52[b]
PG3H5	49[b]	40[b]	0.46[b]

[a] Textural characterisation by nitrogen adsorption.
[b] Textural characterisation by mercury intrusion.

temperatures the porous network collapses and the glass beads lose their porosity [8]. Also on the basis of the HMDS modification of PG3 no significant changes in the texture properties were observed. This is in contrast to the HMDS modified PG1 series. The thermally pretreated and afterwards HMDS modified PG1 show a significant decrease in specific surface area and pore volume in comparison with the solely thermally treated samples. On the one hand, this can be explained by the coverage of surface roughness, like cracks and flaws, due to the TMS groups and on the other hand, by larger TMS groups in comparison with the hydroxyl species. Within the series of the combined modified samples an increasing temperature of thermal pretreatment leads to an increase in the specific pore volume due to the reduction of reactive hydroxyl groups for the HMDS modification. So the amount of "large" TMS groups on the surface decreases by increasing temperature of thermal pretreatment.

3.2. Surface chemistry

The surface chemistry of porous glass is dominated by hydroxyl groups. The modification by: *i*) thermal treatment, *ii*) reaction with HMDS and *iii*) reaction with methyl-, ethyl-, propyl-, butyl- and octyldimethylchlorosilanes leads to a reduction of the density of hydroxyl groups on the surface. For this purpose thermogravimetric

analyses were performed to quantify the hydroxyl group density of thermally treated samples according to DE BOER and VLEESKENS [9]:

$$N_{\mathrm{OH}} = \frac{2 \times 100 \times W}{3 \times O_S} \tag{8}$$

where N_{OH} is the amount of hydroxyl groups per nm^2, W is the weight loss in a temperature range between 180–1000 °C in percentage and O_S is the specific surface area. The results for the hydroxyl group densities are consistent with the theory. By increasing the temperature the hydroxyl group density decreases (Tab. 2).

T a b l e 2. Hydroxyl group densities of thermally treated PG1 glass beads.

Sample	Weight loss [%]	OH-group density per nm^2
PG1	1.32	7.8
PG1_300	1.23	7.1
PG1_400	0.75	4.6
PG1_500	0.67	4.0

On the basis of the results of the elemental analysis the concentration of TMS and alkyldimethylsilane groups are calculated according to Eq. (9) by HEMETSBERGER and BERENDSEN [10, 11]:

$$\left[\mathrm{Alkyldimethylsilane} \right] = \frac{C_\% \times 10^6}{(100 \times n \times 12 - C_\% M) O_S} \tag{9}$$

where $C_\%$ is the carbon content, n is the number of carbon atoms of alkylsilane, O_S is the surface area of the initial porous glass beads and M is the molecular mass of the bonded organosilane.

The surface concentration of TMS groups obtained for the variation of reaction time of the macroporous glass beads PG3 is in the range of 2.35 and 5.02 μmol/m^2. A correlation between the reaction period and the amount of generated TMS was observed for the HMDS modified PG3 samples. It was shown that a reaction period of 24 hours realized the best conversion rates. For the initial mesoporous glass beads PG1 and the thermally pretreated samples a reaction time of 48 hours was utilized. Different concentrations of TMS groups were observed although the reaction time was constant. An increasing temperature of pretreatment is associated with a decrease in TMS concentration. The reduction of reactive hydroxyl groups by thermal pretreatment is responsible for the decrease of generated TMS groups. Furthermore, the variation of the alkyl chain lengths was investigated on the basis of PG1. A decreasing amount of bonded organosilane was observed for increasing alkyl chain length of the alkyldimethylchorosilane. Due to the enlargement of the molecules by increasing

T a b l e 3. Alkylsilane densities of chemically modified PG1 and PG3 samples.

Sample	Carbon content [%]	Alkylsilane density [μmol/m^2]	Number of alkylsilane groups per nm^2	Number of methyl groups per nm^2
PG3H1	0.33	2.4	1.4	4.2
PG3H2	0.35	2.6	1.6	4.8
PG3H3	0.46	3.3	2.0	6.0
PG3H4	0.69	5.0	3.0	9.0
PG3H5	0.68	4.8	2.9	8.7
PG1C1	1.47	3.2	2.0	5.9
PG1C2	1.80	3.0	1.8	7.2
PG1C3	1.91	2.5	1.5	7.6
PG1C4	2.16	2.4	1.4	8.6
PG1C8	3.38	2.3	1.4	13.7
PG1HMDS	1.44	3.6	2.2	6.6
PG1_300HMDS	1.28	3.2	1.9	5.7
PG1_400HMDS	1.19	3.1	1.8	5.4
PG1_500HMDS	0.99	2.5	1.5	4.5

alkyl chain length, the steric hindrance increases and fewer molecules can react at the same reaction time. This is reflected by the results of the elemental analyses (Table 3). However the difference in the conversion rates is slightly. So the alkylsilane densities are comparable. The results of elemental analysis and the calculated alkylsilane densities are shown in Tab. 3.

3.3. Surface energy

The inverse gas chromatography was utilized to determine the dispersive part of surface energy and the specific free energy of different porous glass samples. The dispersive parts of surface energy and the texture properties of the initial meso- and macroporous glass beads are summarized in Tab. 4. A dependence between the specific surface area and the dispersive surface energy was observed. With increasing surface area the surface energy decreases. Furthermore, a dependence was determined between the mean pore diameter and the dispersive surface energy. Dispersive surface energy increases with an increasing mean pore diameter. But, if more porous silicates are involved, it is obvious that no correlation exists between

T a b l e 4. Dispersive surface energy of meso- and macroporous glass beads.

Sample	Mean pore diameter [nm]	Specific surface area [m^2/g]	Dispersive surface energy [mJ/m^2]
PG1	11	112	40.63
PG2	21	79	45.45
PG3	53	39	50.76

these structural parameters and the dispersive surface energy [12]. The differences are caused by the manufacturing process. Larger pores require higher temperatures. Thereby boron deposits in the marginal area of the SiO_2 network. Due to the temperature dependence increases the amount of deposited boron with increasing pore diameter/decreasing surface area. As consequence the dispersive surface energy increases with the increase of boron [13].

On the basis of the HMDS modified PG3 series a correlation was observed between the concentration of TMS groups and the dispersive surface energy. The dispersive part of surface energy increases with an increasing amount of bonded TMS groups. The increase in the dispersive part of surface energy results from the modified surface. The surface becomes more hydrophobic with increasing TMS concentration. Figure 4**a** illustrates this correlation. Furthermore, a correlation between the dispersive surface and the number of methyl groups is determined. With increasing number of methyl groups the surface becomes more non-polar and the dispersive surface energy increases (Fig. 4**b**).
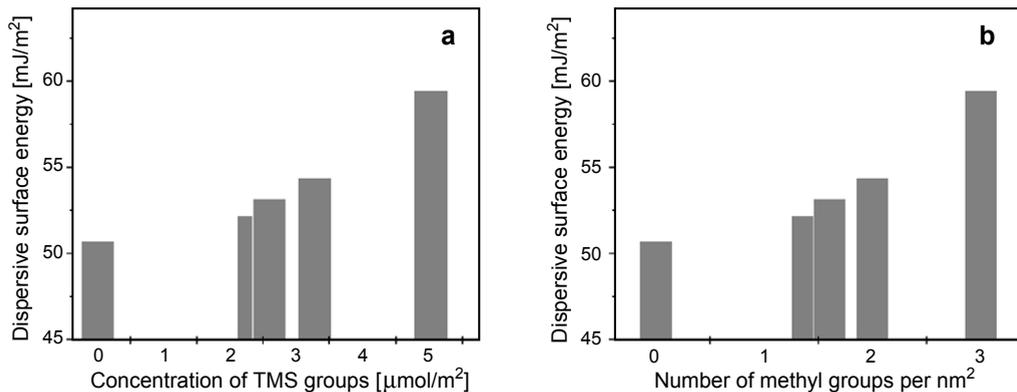

Fig. 4. Correlation between the dispersive surface energy and (**a**) concentration of TMS groups, (**b**) number of methyl groups per nm^2 of HMDS modified mesoporous glass beads PG1.

PG1 glass was modified with alkyldimethylchlorosilanes of different alkyl chain length to study the effect of the number of methyl groups. The realization of identical/ similar organosilane densities was the aim of this modification. Whereby, the modified glass beads only differ in the length of the alkyl chain/number of methyl groups. A plot of the dispersive surface energy versus the concentration of bonded alkylsilane approved the previous mentioned correlation between the concentration of alkylsilane groups and the surface energy. Figure 5**a** illustrates the correlation for the alkyl chain length variation of porous glasses. In contrast, by plotting the dispersive surface energy versus the number of alkyl groups no dependence was determined (Fig. 5**b**). This can be attributed to the fact that the probe molecules can only interact with the tail of the organosilane due to steric hindrance. The tail consists in each case of just one methyl group, so changes on the basis of alkyl chain length variation are
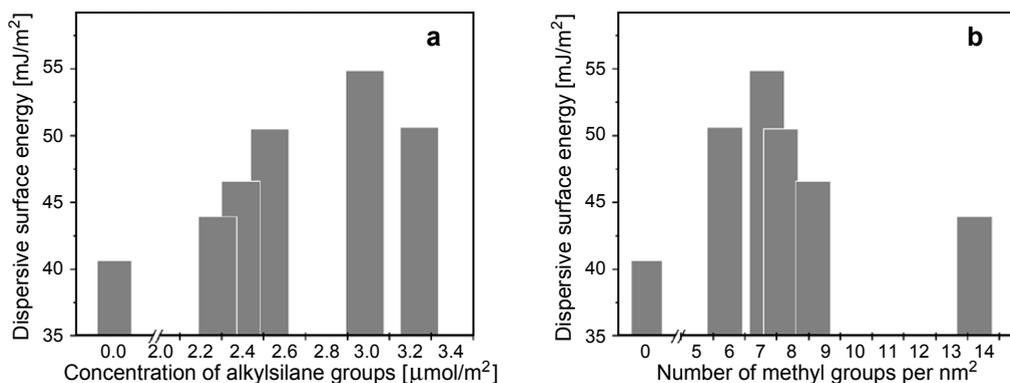
Fig. 5. Correlation between the dispersive surface energy and (**a**) concentration of alkylsilane, (**b**) number of methyl groups per nm^2 of mesoporous glass beads PG1 modified by different alkylsilanes.

not possible at this organosilane loading. Another possibility is that the concentration of hydroxyl groups is crucial for the dispersive surface energy.

On the basis of the alkyl chain variation also the influence of the surface chemistry on the specific free energy was examined. It was found that the initial porous glass possesses the highest specific interaction term (ΔG^{SP}) due to the high number of polar hydroxyl groups. The conversion of reactive hydroxyl groups into organosilanes leads to a drop in the specific free energy. Table 5 summarizes the determined specific free energies of modified PG1.

T a b l e 5. Specific free energy of modified porous glass.

Sample	Number of hydroxyl groups per nm^2	Number of alkylsilane groups per nm^2	Specific interaction term [kJ/m^2]
PG1	7.8	–	20.00
PG1C1	5.8	2.0	9.11
PG1C4	6.4	1.4	8.90

Within the series of thermally treated PG1 just a slight increase in the dispersive surface energy was observed (dark grey bars in Fig. 6). Although non-polar siloxane species are generated on the surface by thermal treatment due to the condensation of hydroxyl groups, the expected increase in the dispersive surface energy was not observed. The thermal treatment leads to a migration of boron within the glass and a formation of boron on the surface, which reduces the dispersive interactions. The effect of the opposite processes of reduction of hydroxyl groups and the formation of boron species on the surface of porous glass depends on the temperature and increases with increasing temperature. This causes the minor differences between the dispersive surface energies of the thermally treated samples (Fig. 6). The HMDS
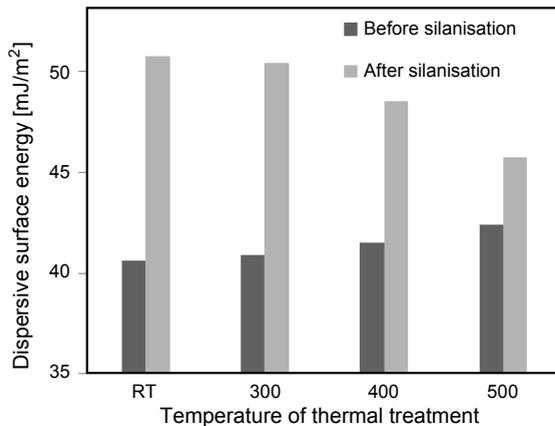
Fig. 6. Comparison of the dispersive surface energy of chemically and thermally treated mesoporous PG1 glass beads.

treatment of thermally pretreated sample leads in each case to an increase in the dispersive surface energy due to the reduced polarity of the porous glass caused by the TMS groups (light grey bars in Fig. 6). The differences between the exclusively thermally treated and afterwards HMDS modified sample decrease with the increasing temperature of pretreatment. This is caused by the already mentioned reduction of reactive sites, associated with a decreasing concentration of TMS groups, due to the thermal pretreatment.

4. Conclusions

Porous glass with different texture properties and different surface chemistry was utilized as an optimal model system for the evaluation of the IGC technique. The surface of the porous glass beads was modified by various procedures and characterized by IGC measurements. Due to a thermal treatment, no significant changes in the surface energy were observed. In this study, a dependence of the dispersive surface energy and the specific free energy on the surface chemistry of porous glass was demonstrated. Caused by the reduction of hydroxyl groups by the modification with trimethylsilyl groups the surface of the porous glass becomes more hydrophobic and the dispersive surface energy increases. A correlation was observed between the concentration of TMS groups and the dispersive surface energy. With increasing TMS group concentration the dispersive surface energy increases. In addition, for the HMDS modified samples, a correlation between the amount of methyl groups and the dispersive surface energy exists. This correlation was investigated by the variation of the alkyl chain length. By increasing alkyl chain length associated with an increasing amount of methyl groups no increase in the dispersive surface energy was determined. However, a correlation between the concentration of organosilane

groups and the dispersive surface energy was validated. The opposite behavior was observed for the specific free energy. With increasing concentration of hydrophobic organsilane groups the specific free energy decreases. IGC has been shown to be a useful technique to characterize the surface modification of porous glass.

References

[1] ENKE D., JANOWSKI F., SCHWIEGER W., *Porous glasses in the 21st century – A short review*, Microporous and Mesoporous Materials **60**(1–3), 2003, pp. 19–30.

[2] THIELMANN F., *Introduction into the characterisation of porous materials by inverse gas chromatography*, Journal of Chromatography A **1037**(1–2), 2004, pp. 115–123.

[3] KISELEV A.V., YASHIN Y.J., *Gas-Adsorption Chromatography*, Plenum Press, New York, 1965.

[4] ADOLPHS J., *Surface energies of hardenned cement paste depending on relative humidity*, Materials and Structures **38**(4), 2005, pp. 443–448.

[5] DORRIS G.M., GRAY D.G., *Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibers*, Journal of Colloid and Interface Science **77**(2), 1980, pp. 353–362.

[6] FOWKES F.M., *Attractive forces at interfaces*, Industrial and Engineering Chemistry **56**(12), 1964, pp. 40–52.

[7] SCHULTZ J., LAVIELLE L., MARTIN C., *The role of the interface in carbon fibre-epoxy composites*, The Journal of Adhesion **23**(1), 1987, pp. 45–60.

[8] JANOWSKI F., HEYER W., *Poröse Gläser – Herstellung, Eigenschaften und Anwendungen*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1982.

[9] DE BOER J.H., VLEESKENS J.M., Proceedings of the Koninklijke Nederlandse Akademie van Wetenschappen, Series B **60**, 1957, p. 45.

[10] BERENDSEN G.E., DE GALAN L., *Preparation and chromatographic properties of some chemically bonded phases for reversed-phase liquid chromatography*, Journal of Liquid Chromatography **1**(5), 1978, pp. 561–586.

[11] HEMETSBERGER H., KELLERMANN M., RICKEN H., *Behaviour of chemically bonded alkylmethyldichlorosilanes to silica gel in reversed-phase high-performance liquid chromatography*, Chromatographia **10**(12), 1977, pp. 726–730.

[12] RÜCKRIEM M., INAYAT A., ENKE D., GLÄSER R., EINICKE W.-D., ROCKMANN R., *Inverse gas chromatography for determining the dispersive surface energy of porous silica*, Colloids and Surfaces A **357**(1–3), 2010, pp. 21–26.

[13] BILIŃSKI B., WÓJCIK W., DAWIDOWICZ A.L., *Investigation of the surface free energy components of thermally treated controlled porosity glasses by inverse gas chromatography*, Applied Surface Science **47**(1), 1991, pp. 99–108.