UNIVERSITÄT LEIPZIG
Faculty of Chemistry and Mineralogy

Adsorption of polar and nonpolar vapors on porous materials studied by Inverse Gas Chromatography (IGC)

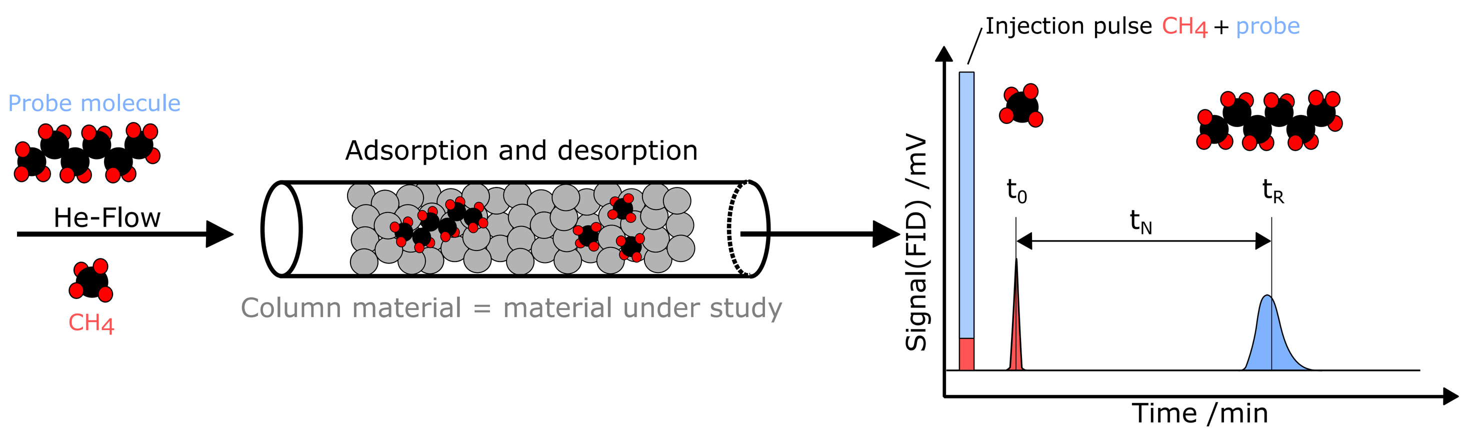
Frank Bauer, Ralf Meyer, Dirk Enke
Institute of Chemical Technology, Universität Leipzig, Germany

The ENKE Group – Porous Monoliths for all Purposes

Introduction

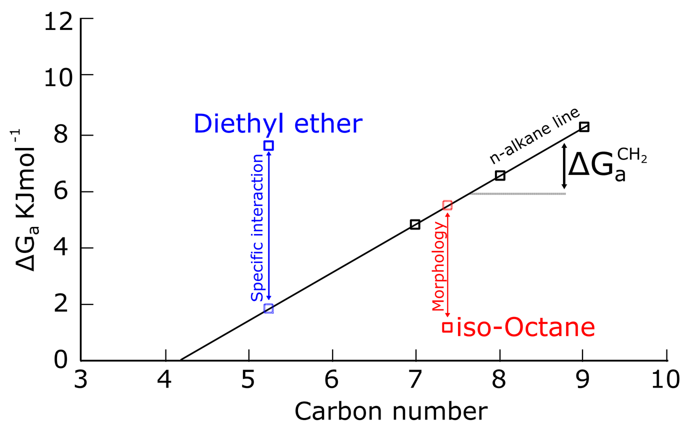
For elucidating catalytic processes and enhancing process efficiency, the characterization of porous catalysts is crucial. Therefore, a number of catalyst properties are investigated by various established analytical methods, e.g., porosity, specific surface area, redox properties. However, the characterization of the catalyst surface is often neglected, although all heterogeneously catalyzed reactions take place at the surface. While chemical surface characterization is possible by, e.g., Infrared and X-ray photoelectron spectroscopy, the energy-related characterization of surface sites is still challenging.
Inverse gas chromatography (IGC) is a gas phase method to investigate surface properties of particles, granulates or fibers. This method is able to determine a large number of physico-chemical properties, for example, surface energies, acid/base/polar functionality of surfaces, solubility parameters, diffusion kinetics, surface heterogeneity and phase transition temperatures [1]. In this study, we investigated porous glass beads prepared by a modified VYCOR process. These materials have well-defined surface properties, a large pore volume and a high diffusivity.
For potential catalytic and sensoric applications, porous silica materials were grafted with organofunctional silanes [2]. The aim of this work was to examine the influence of surface modification on the physico-chemical properties of porous silica materials.

Principle of IGC-ID

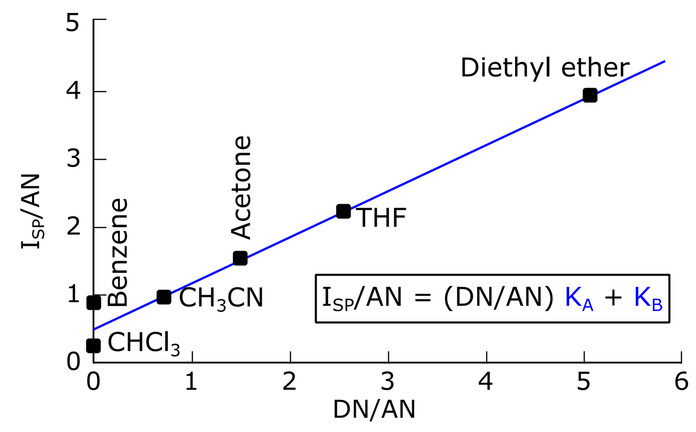


$$V_N = t_N \cdot \dot{V} \cdot T_M \cdot j$$

$$\gamma_s^d = \frac{1}{\gamma_{CH_2}} \left[\frac{(\Delta G_{ad}(CH_2))}{(2N_A A_{CH_2})}\right]^2$$



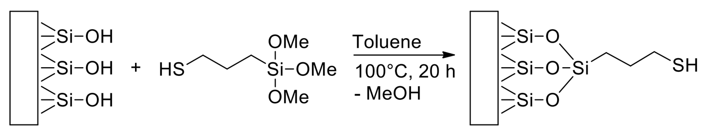
Polar probe molecules



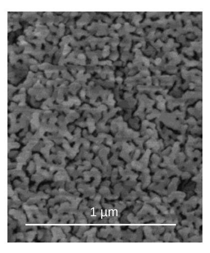
The material under study is filled in typical GC columns which are placed into a conventional gas chromatograph. The signals of injected probe molecules are detected by a flame ionisation detector. The chromatographic conditions are: oven temperatures 30°-120°C, helium carrier gas flow of 20 mL/min and infinite dilution conditions (IGC-ID). Based on the net retention volume of linear alkanes, the free adsorption enthalpy can be calculated and thereby the dispersive component of the surface energy as shown by DORRIS and GRAY [3]. Using polar probe molecules and the VAN OSS approach, the polar surface energy component can be determined [4]. Thus, the total surface energy of porous material can be obtained describing the wettability of the internal pore system. In addition, information about the surface morphology of microporous samples is given by branched alkanes. Moreover, polar probe molecules can result in the acidity/basicity parameter (K_A/K_B) according to the GUTMANN approach [5].

Column Material

- Controlled porous glass (CPG)
- Grafted with Mercaptosilane



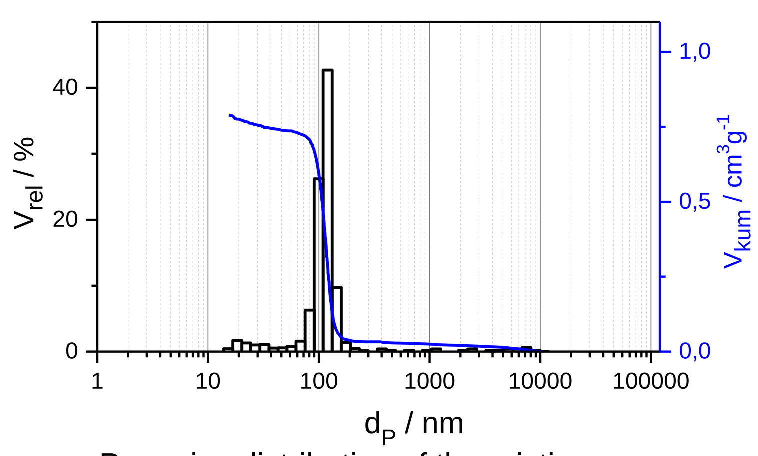
Schematic representation of the modification of porous glass



SEM picture of the porous glass structure

Material	BET-Surface*
Pristine glass	21 m²/g
Modified glass	15 m²/g

Material	Pore Volume**	Pore Diameter**
Pristine glass	0.8 cm³/g	112 nm

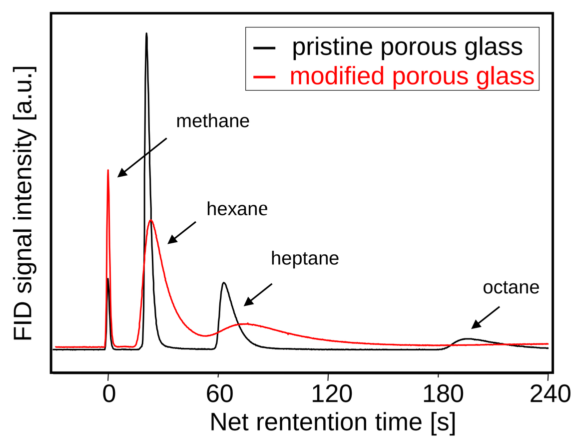


Pore size distribution of the pristine porous glass

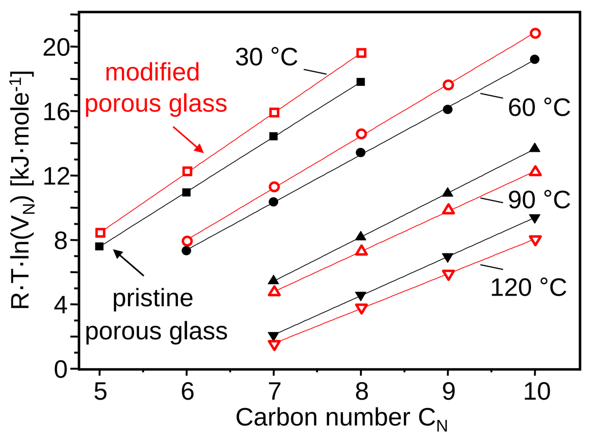
*) Data from N_2-Adsorption
**) Data from Mercury Intrusion

Results

Nonpolar probe molecules



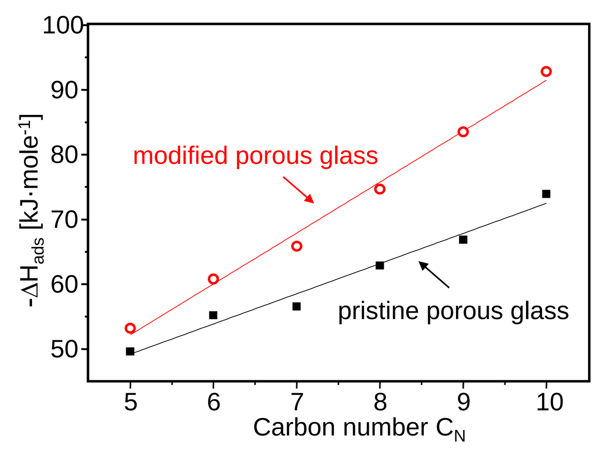
Chromatogram of nonpolar probe molecules



Free adsorption energy of nonpolar probe molecules on porous glass at different temperatures

Parameter	Influence on Adsorption
Carbon number ↑	$-\Delta G_{ads}$ increases
Temperature ↑	$-\Delta G_{ads}$ decreases

Effect of surface modification on free adsorption energy

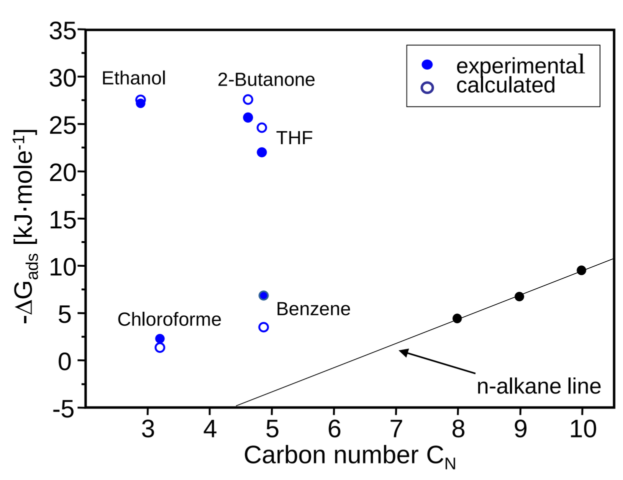


Heat of adsorption for nonpolar probe molecules on porous glass

Dispersive component of surface energy

Temperature	Pristine glass /mJm⁻²	Modif. glass/ mJm⁻²
30°C	63.7	75.4
60°C	50.1	59.3
90°C	39.1	38.9
120°C	38	29.9

Polar probe molecules



Free adsorption enthalpie of polar probe molecules for pristine porous glasses at 120°C

Van Oss approach of acidity/basicity

$$\Delta G^{sp} = \mathrm{N} \cdot \mathrm{a} \cdot 2 \cdot \left(\sqrt{\gamma_1^- \cdot \gamma_s^+} + \sqrt{\gamma_1^+ \cdot \gamma_s^-}\right)$$

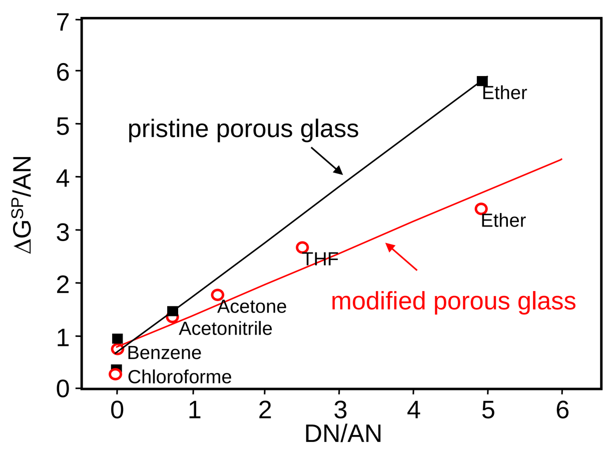
	$CPG_{pristine}$	$CPG_{modif.}$
γ_s^+ (acid)	182	66
γ_s^- (basic)	155	168
γ_s^+/γ_s^-	**1.2**	**0.4**

Reduction of silica acidity due to surface modification

$$\gamma_s^{sp} = 2 \cdot \sqrt{\gamma_s^+ \cdot \gamma_s^-}$$

	γ_S^{SP} /mJm⁻²
Pristine glass	335
Modified glass	210

Specific component of surface energy at 120 °C



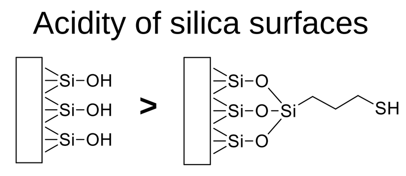
Determination of acidity/basicity according to Gutmann's approach

Gutmann's Acidity/Basicity

$$\Delta G^{sp} = K_A \cdot DN + K_B \cdot AN$$

	$CPG_{pristine}$	$CPG_{modif.}$
K_A	105.0	59.4
K_B	65.4	79.9
K_A/K_B	**1.6**	**0.7**

Acidity of silica surfaces



Conclusions

- IGC proved to be a versatile characterization method to investigate subtle changes in surface properties of porous siliceous materials after surface modification.
- IGC measurements at 120°C demonstrated that a modification of glass surfaces with mercaptosilane results in a reduction of the dispersive component of surface energy.
- Alkanes are stronger adsorbed on silane-modified porous glass.
- Compared to hydrophobic alkanes, polar probe molecules showed more intense interactions with the hydrophilic surface of porous glass.
- Due to grafting mercaptosilane, the acidity of silica surface can be significantly decreased as shown by the approaches of Van Oss and Gutmann.

[1] S. Mohammadi-Jam, K.E. Waters; Advances in Colloid and Interface Science, **212**(2014),21-44.
[2] F. Bauer, S. Czihal, M. Bertmer, U. Decker, S. Naumov, S. Wassersleben, D. Enke, Microporous Mesoporous Mater. **250** (2017), 221-231.
[3] G.M. Dorris, D.G. Gray; J. Colloid Interface Sci.,**77** (1980), 353-362.
[4] C.J. Van Oss, R.J. Good, M.K. Chaudhury, Langmuir, **4** (1988), 884-891.
[5] V. Gutmann; „The Donor-Acceptor Approach to Molecular Interactions", New York (1978).

contact: frank.bauer@uni-leipzig.de