Characterisation of porous materials by Inverse Gas Chromatography (IGC)

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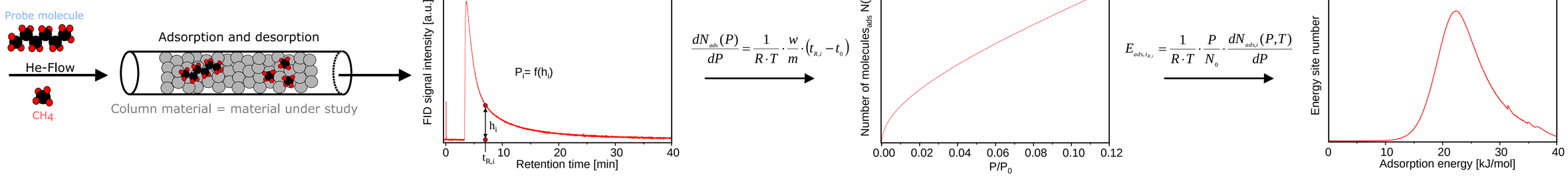
Introduction

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-FC

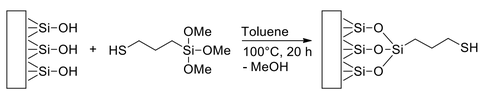


The material under study is filled in typical GC columns which are placed into a conventional gas chromatograph. The signals of injected probe molecules are detected by a flame ionisation detector. Chromatographic conditions are: oven temperatures 30°-120°C, helium carrier gas flow of 20 mL/min and finite concentration conditions (IGC-FC).

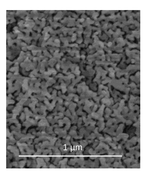
The analysis of the tailing of a chromatographic peak leads to the desorption isotherm of the injected probe molecule. The first derivative of the isotherm is directly related to the neat retention time and the partial pressure can be related to the height of the signal at a given point [3]. The lower part of the isotherms allows the evaluation of specific surface (BET) areas using the dimensions of the respective probe molecule. Moreover, IGC delivers the surface heterogeneity in the form of adsorption energy distribution of the various sites [4]. Using probe molecules of different morphology and functionality enables to study different aspects of the surface heterogeneity.

Column Material

- Controlled porous glass (CPG)
- Grafted with Mercaptosilane



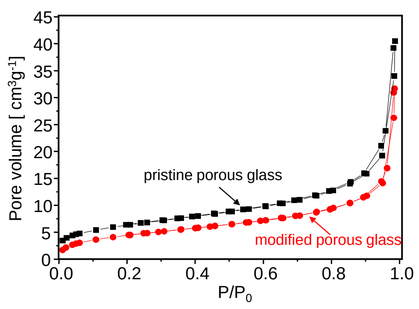
Schematic representation of the modification of porous glass



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

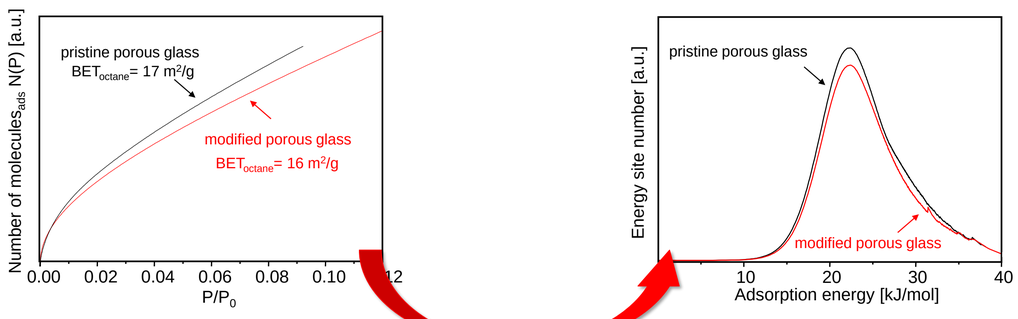


Nitrogen sorption of porous glass before and after modification

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

Results

Non-polar probe molecules

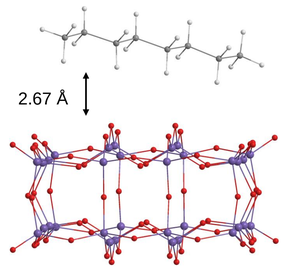


Desorption isotherms determined by IGC-FC for n-octane (30 °C)

Distribution functions of the adsorption energies of n-octane probe

The distribution functions of adsorption energies of n-octane are monomodal, indicating the insufficient character of hydrophobic n-octane as probe molecule for elucidating the surface of hydrophilic silica materials (even after modification by organosilanes).

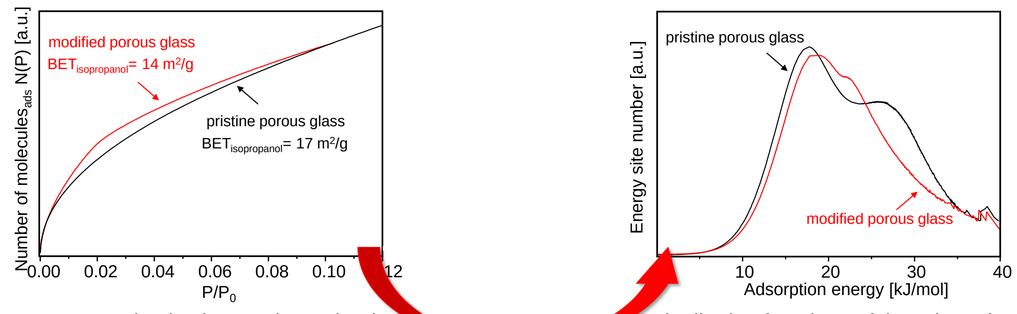
Distance of probe molecules to silica surface*



DFT calculations of n-octane adsorbed on a 32T silica slab model (ΔE_{ads}~ -5 kJ·mol^{-1})

* using B3LYP/6-31G(d,p) level of theory

Polar probe molecules

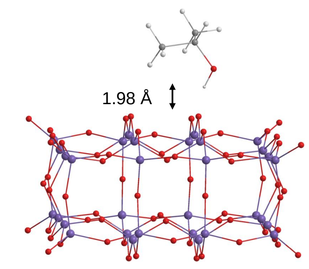


Desorption isotherms determined by IGC-FC for isopropanol (60 °C)

Distribution functions of the adsorption energies of isopropanol probe

The distribution functions of adsorption energies of isopropanol are bimodal, pointing to the character of the silica surface made of non- hydroxylated (low energy component) and hydroxylated domains (high energy component) which are reduced by silanization.

Distance of probe molecules to silica surface*



DFT calculations of isopropanol adsorbed on a 32T silica slab model (ΔE_{ads}~ -50 kJ·mol^{-1})

* using B3LYP/6-31G(d,p) level of theory

Conclusions

- IGC proved to be a versatile characterization method to investigate subtle changes in surface properties of porous siliceous materials after surface modification.
- Due to mercaptosilane grafting, the interaction of hydrophobic alkanes to the modified silica surface is increased and the surface acidity has been significantly decreased.
- IGC measurements of polar and nonpolar probe molecules at conditions of finite concentrations revealed realistic BET surface areas.
- Polar probe molecules such as isopropanol are better suited for estimating the heterogeneity of surface sites than nonpolar ones.
- Quantum chemical calculations on the adsorption of probe molecules onto silica clusters are useful to surface characterization by IGC.

[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] E. Cremer, H. Huber, Angew. Chem., Int. Ed. Engl. **73** (1961) 461-&..
[4] H. Balard, A. Saada, E. Papirer, B. Siffert, Langmuir **13** (1997) 1256-1259.

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