Characterization of Porous Solids by Inverse Gas Chromatography: Precise, Easy & Significant

E. Brendlé[1], R. Dümpelmann[2], M. Rückriem[3], J. Adolphs[3]

[1] Adscientis S.A., Wittelsheim, France
[2] Inolytix AG, Sisseln, Switzerland
[3] POROTEC GmbH, Hofheim, Germany

Outline

- Introduction and Motivation
- Results: 2 Case Studies for porous Silica
  - -> Microporous Silica (Zeolites)
  - -> Mesoporous Silica (Silica Gel and Porous Glass)
- Conclusion

Introduction and Motivation

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- Application of porous silicates
  - „tailor-made“ properties
  - Adjustable texture properties
  - Diversity of geometric shapes
  - Modifiability of functional surface groups

- Deficit of characterization techniques of surface chemistry and interactions
  - Potential of the Inverse Gas Chromatography, sensitive regarding differences of the material

- Evaluation of the technique of Inverse Gas Chromatography on the basis of porous silicates as model systems

Introduction and Motivation

- Retention time depends on the surface chemistry of the stationary phase and represents the basic information of an IGC experiment

- Due to the variation of probe molecules, concentrations and column temperatures a wide range of physico-chemical properties can be determined

  - Dispersive Part of Surface Energy
  - Surface Morphology (IM)
  - Specific Interactions
  - Acid – Base Parameters
  - Adsorption Energy Distribution
  - Desorption Isotherm
  - Specific Surface Area

Infinite Dilution

Finite Concentration

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Zeolites characterization by IGC-ID (infinite dilution)

BEA: S_{BET} = 626 m^2/g, V_{pore} = 0.23 cm^3/g
Silicalite-1: S_{BET} = 394 m^2/g, V_{pore} = 0.18 cm^3/g

Dispersive Surface Energy (γs^d)

- Linear alkanes are injected (and analyzed according Dorris and Gray)

Surface energy	$\Delta G_a(CH_2)$ [kJ/mol]	r^2	γ_s^d [mJ/m²]
BEA	5.90 ± 0.01	1.0000	**237.5 ± 9.5**
Silicalite-1	5.30 ± 0.02	1.0000	**192.0 ± 8.4**

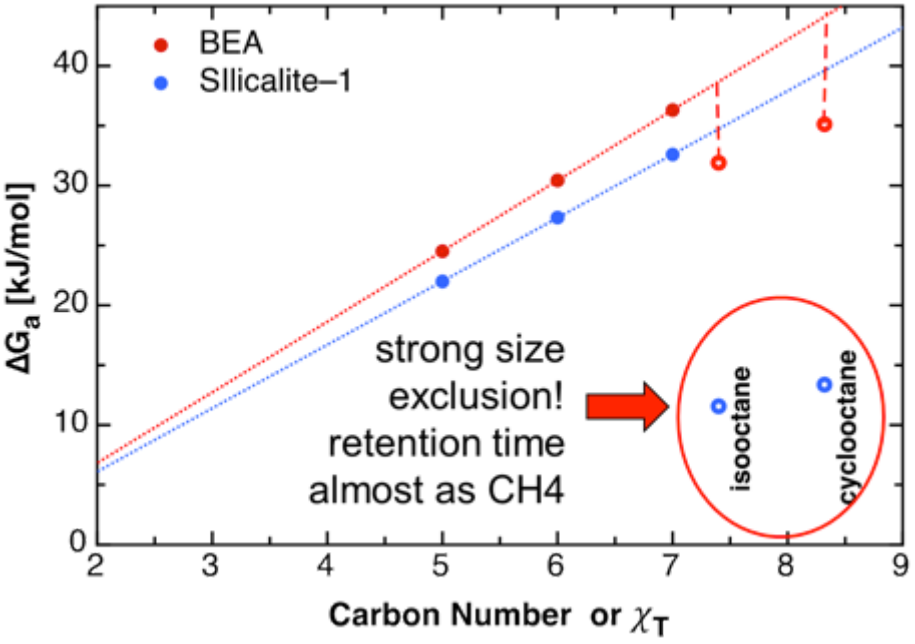
BEA has significantly higher γs^d with 237 mJ/m² than Silicalite-1 with 192 mJ/m²

Surface Morphology (IM), nanoroughness, size exclusion

- Morphology index (IM) is the ratio of the retention volume of a branched alkane and the retention volume of a n-alkane

$$IM = V_G(M)/V_G(C)$$

IM values	IM isooctane	IM cyclooctane
BEA	0.15 ± 0.01	0.08 ± 0.01
Silicalite-1	< 0.01	< 0.01

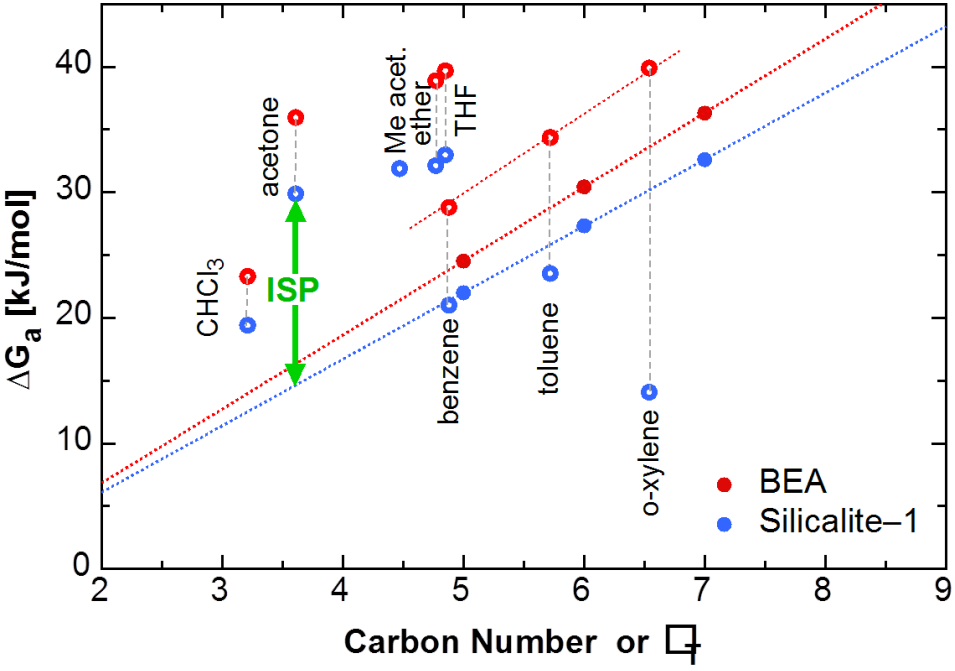


Silicalite-1 shows a very strong size exclusion effect for i-octane and cyclooctane smaller but still significant for BEA.

Specific Interaction Parameter (ISP)

$$ISP = \Delta G_a^{sp} = \Delta G_a - \Delta G_a^{d}$$

ISP [kJ/mol]	BEA	Silicalite-1
Acetone	19.6 ± 0.7	15.2 ± 1.1
THF	16.0 ± 0.6	11.8 ± 0.7
Ether	15.7 ± 0.5	11.3 ± 0.6
Chloroforme	9.3 ± 0.5	6.9 ± 0.7
Me-Acetate	> 24	12.7 ± 1.0
Benzene	5.0 ± 0.7	-0.4 ± 1.0
Toluene	5.6 ± 0.8	-2.3 ± 0.9
o-xylene	6.3 ± 0.8	-16.1 ± 5.3



Stronger polar interaction by BEA (higher ISP) than Silicalite-1

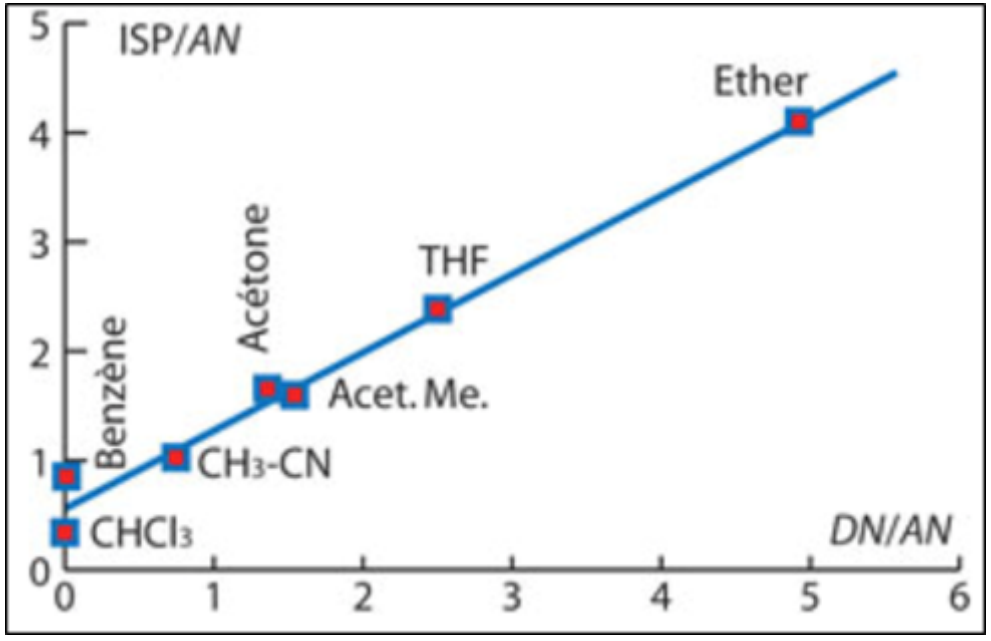
Quantitative and clear differentiation of adsorption behavior and polar interactions

Acid-Base Constants (K_a, K_b)

By injecting probes of known electron acceptor (AN) and donor numbers (DN), according to the semi-empirical acid/base scale of GUTMANN, the ISP value can be related to acid and base constants Ka and Kb.

$$ISP = DN \cdot Ka + AN \cdot Kb$$

$$ISP/AN = (DN/AN) \cdot Ka + Kb$$

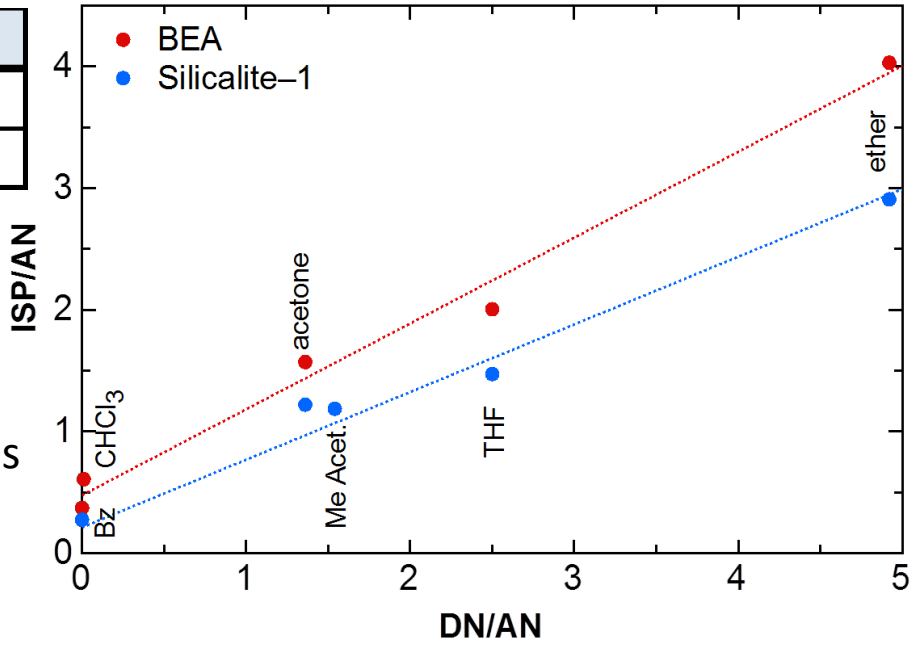


Acid-Base Constants (K_a, K_b)

Acid-Base constants	Ka	Kb
BEA	70.6	47.7
Silicalite-1	55.6	21.2

for better readability: Ka*100, Kb*100

BEA zeolite shows stronger interaction potential with electron donor (Ka= 70.6) and acceptor (Kb= 47.7) molecules than Silicalite-1.



The two zeolites can be clearly differentiated by their electron donor and acceptor potential based on the retention times of known molecules

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Characterization of Mesoporous Silica by IGC-ID (infinite dilution)

Dispersive Surface Energy (γ^{d}_{s})

Sample	Dispersive surface energy [mJ/m^2]	Mean pore diameter[a)] [nm]	Specific surface area[a)] [m^2/g]
CPG10	40,80	11,3	112
CPG20	45,45	21,4	79
CPG50	50,67	53,2[b)]	34

Excursus: Preparation of nanoporous glass beads

initial glass beads

T

500 - 720 °C

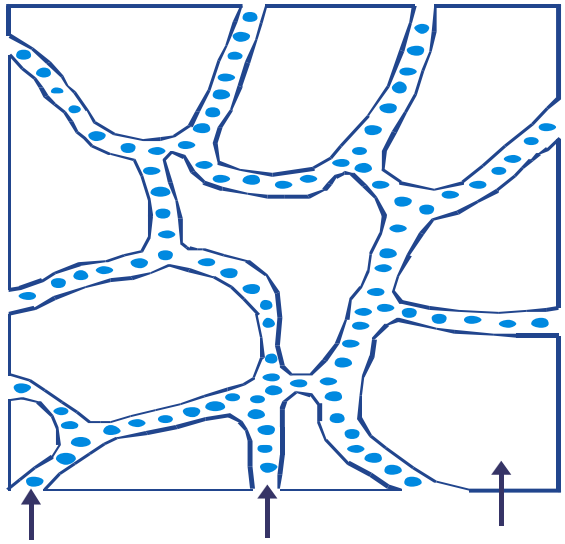
phase separation

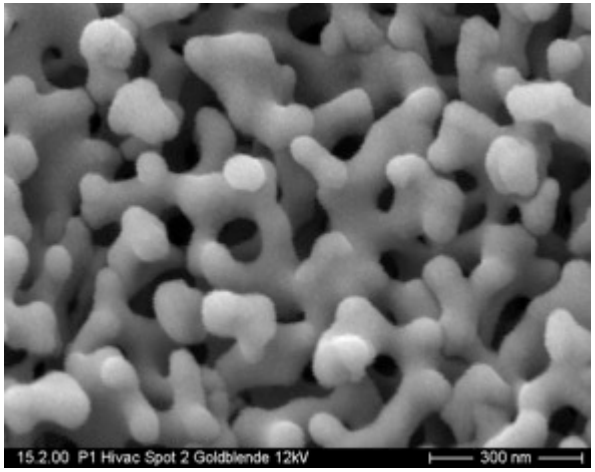
Extraction

acid, base

porous glass beads

d_P = 1- 70 nm





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CPG10	40,80	11,3	112
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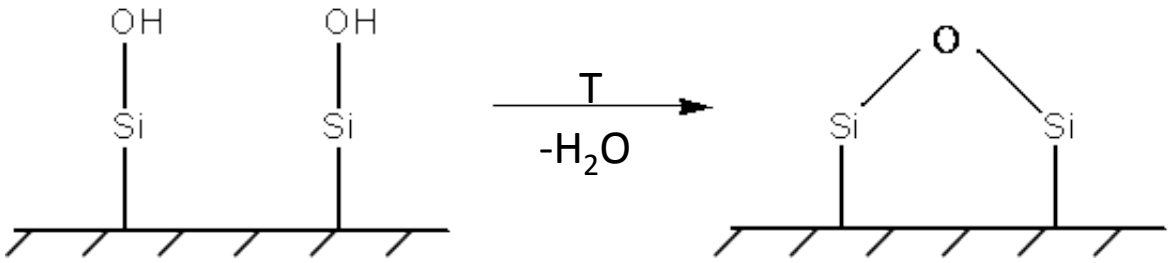
- Effect of the surface chemistry
- Detected by IGC due to the determination of dispersive surface energy

• Surface chemistry of porous silicates was changed by different post-synthetic modification procedures

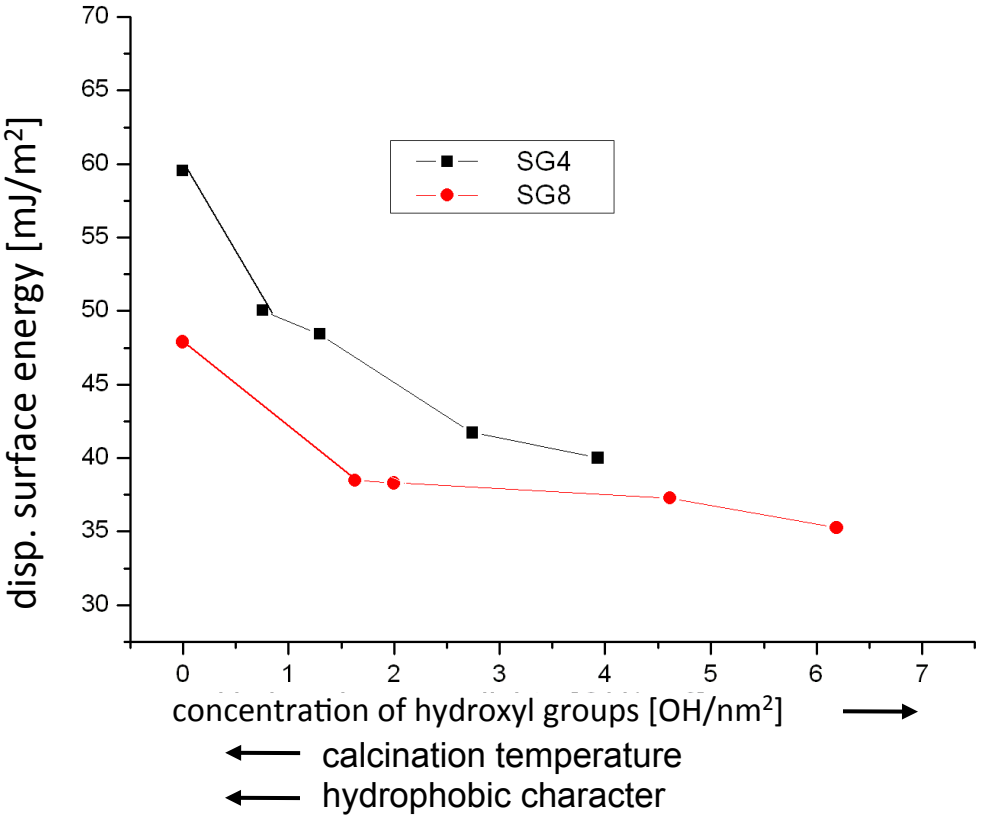
(i) Calcination between 300 - 900°C



Variation in the surface chemistry is realised by different concentrations of hydroxyl groups.
(c_{OH} is essential for the hydrophilic/hydrophobic properties of silica*)

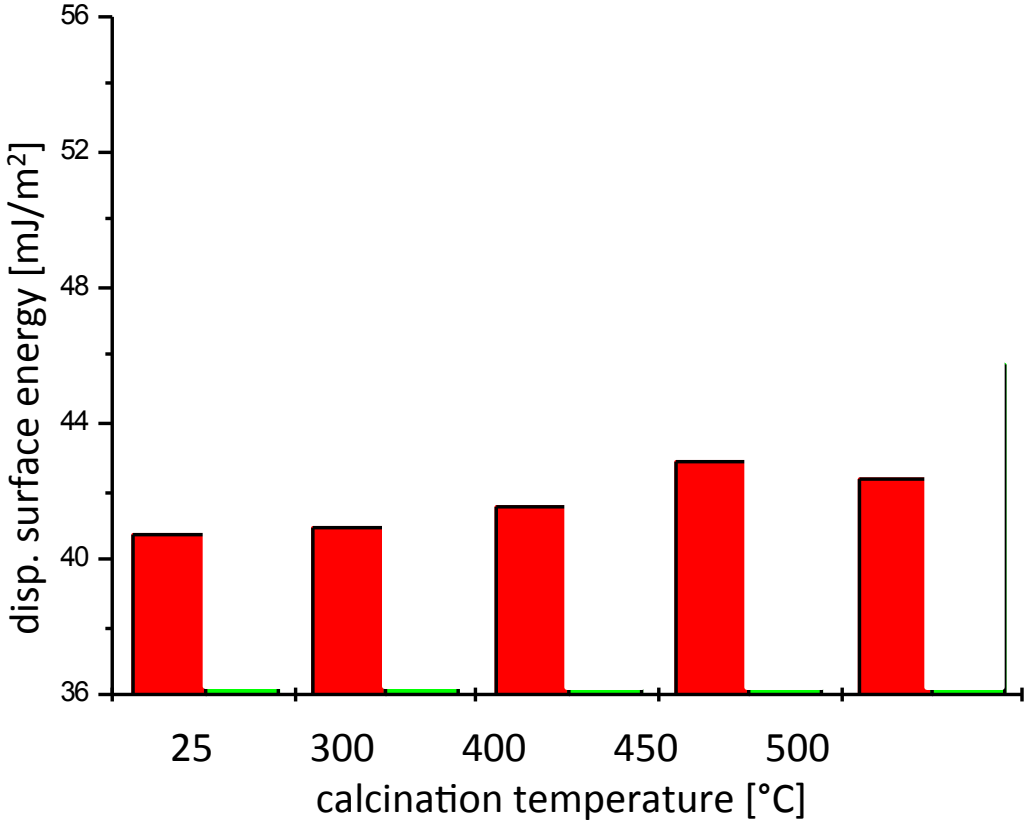
***L.T. Zhuravlev, Colloids and Surface A Phys. Eng. Aspects 173 (2000) 1 - 38.**

Mesoporous Silica



Increase of the dispersive part of surface energy with decreasing concentration of hydroxyl groups

Mesoporous Silica

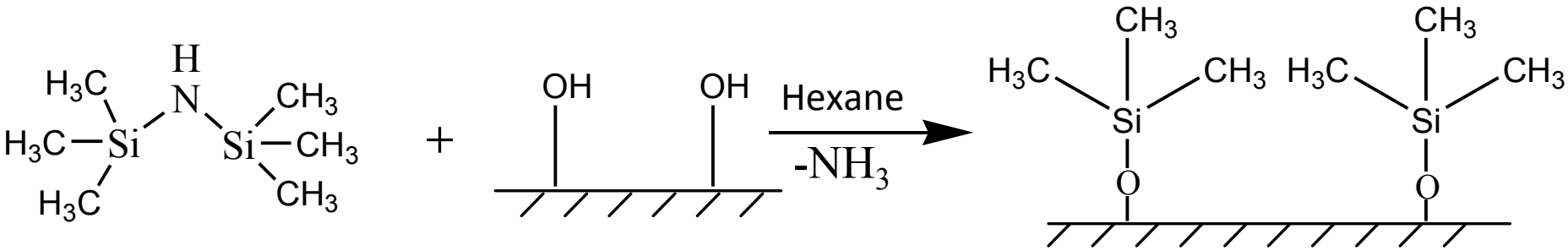


Porous glass beads exhibit a residual content of boron, that migrates to the surface during thermal treatment*

***F. Janowski, D. Enke in: Handbook of Porous Solids, Volume 3, Wiley-VCH, Weinheim, 2002.**

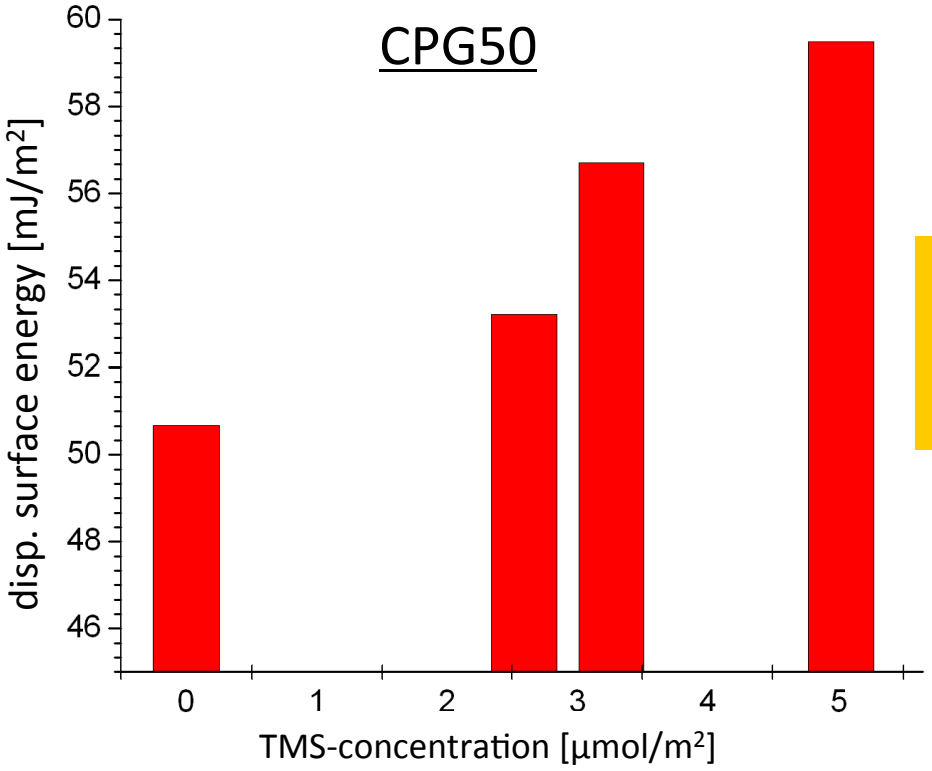
• Surface chemistry of the porous silica systems was changed by different post-synthetic modification procedures

(ii) Treatment with hexamethyldisilazane (HMDS)



➡ Generation of hydrophobic trimethylsilyl (TMS) groups onto the surface of the silicates

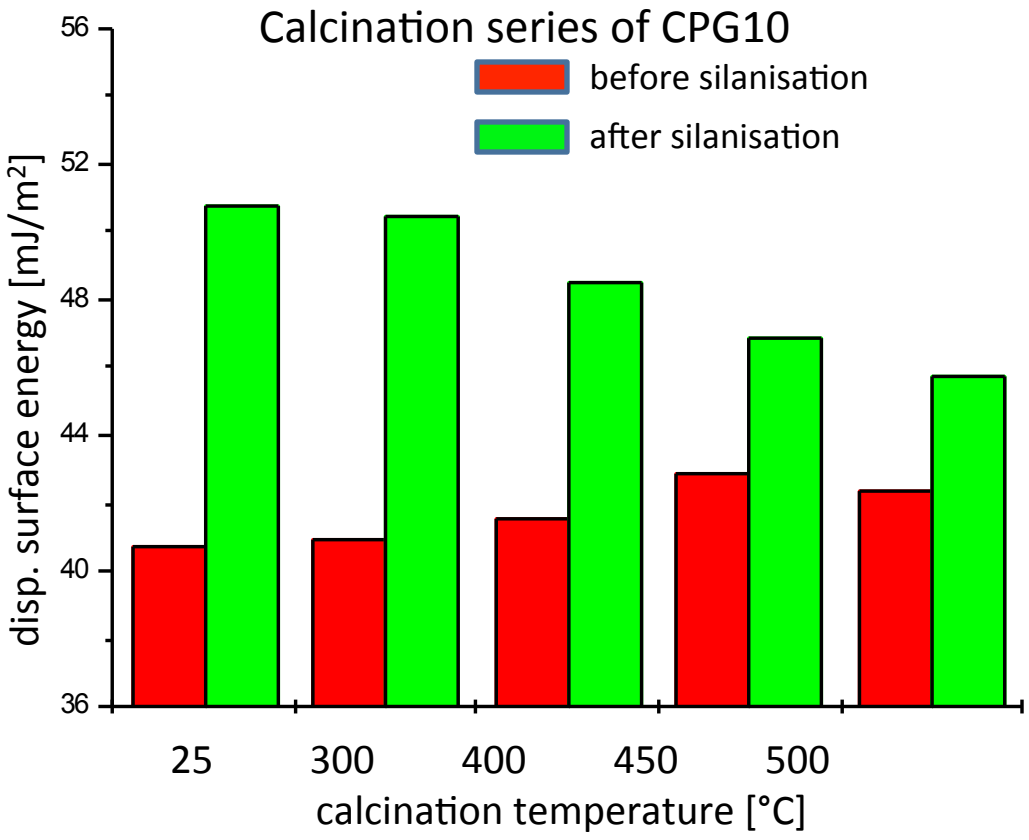
• Due to the variation of the reaction time of HMDS treatment (1-24h) of CPG50 different concentrations of TMS-groups are realised and quantified by elemental analysis and IGC measurements



Correlation between the amount of TMS-groups and the dispersive part of surface energy was observed*

*D. Enke, M. Rückriem, D. Stoltenberg, A. Böhme in Characterisation of Porous Solids VIII, ed. S. Kaskel, P. Llewellyn, F. Rodriguez-Reinoso, N.A. Seaton, RSC Publishing, Cambridge, 2009, 408-415.

Mesoporous Silica



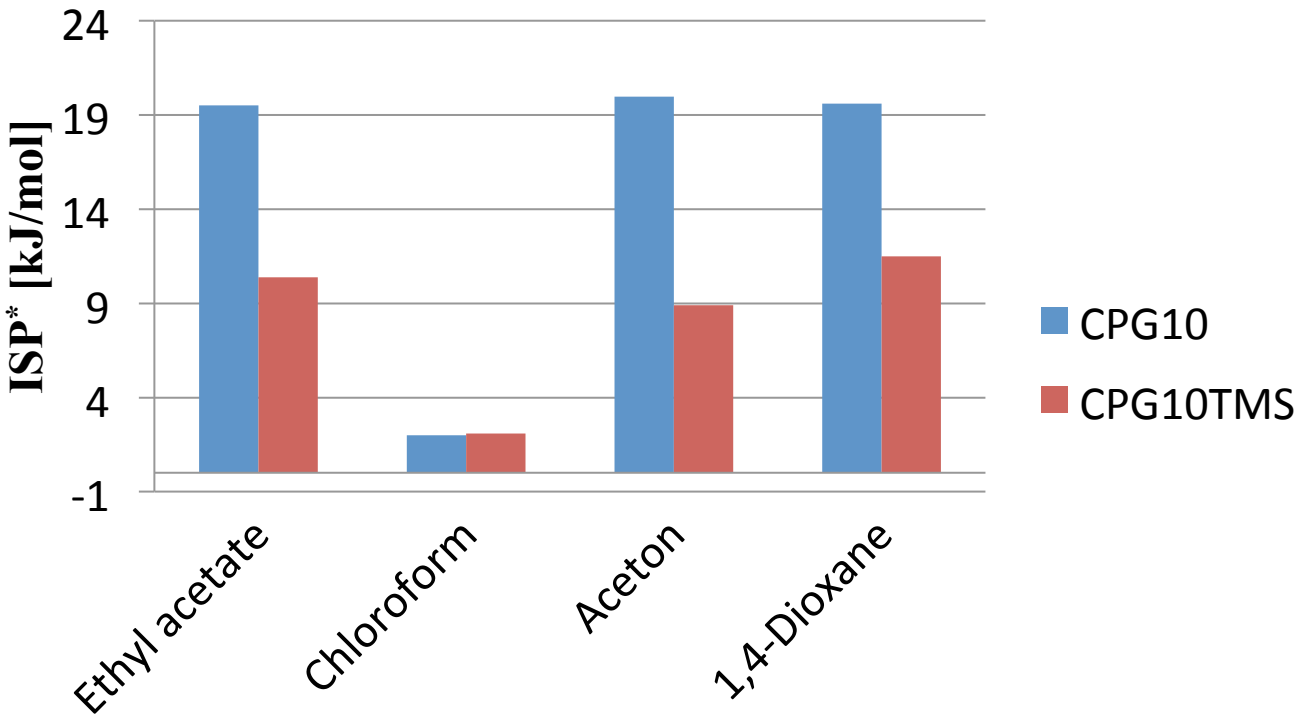
(i) All silica samples were treated according to the same standard procedure with HMDS

(ii) An increase of the surface energy by this modification of the surface was determined

(iii) TMS-groups generate a higher polarisability and an increasing hydrophic character of the silica surface*

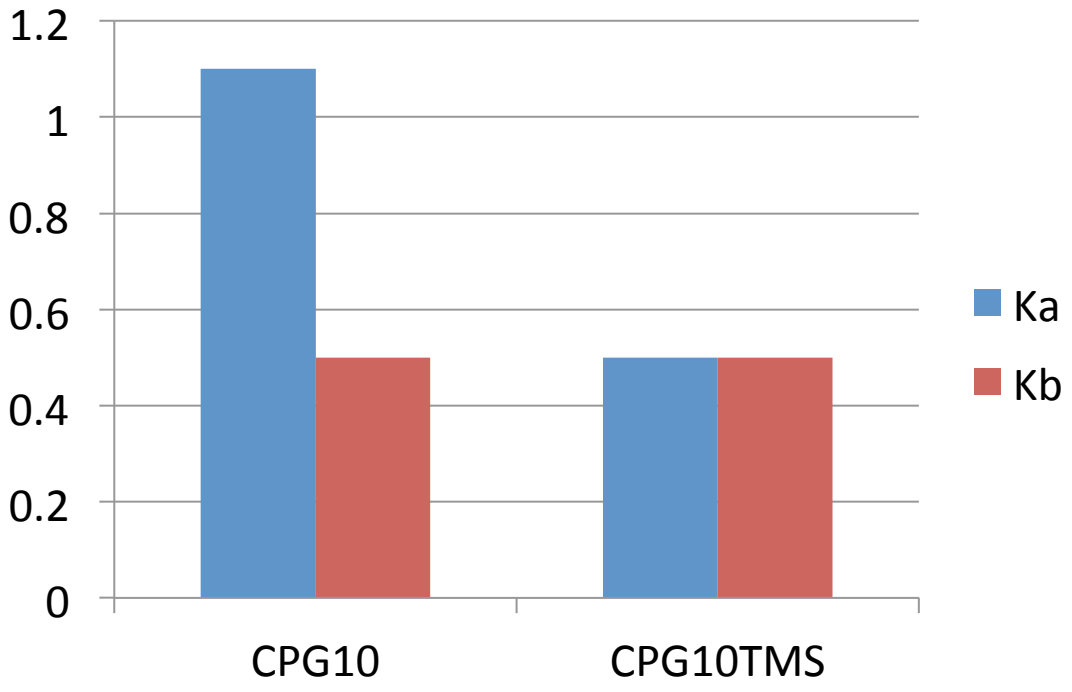
***D. Enke, M. Rückriem, A. Schreiber, J. Adolphs, Applied Surface Science 256 (2010) 5482-5485.**

Specific Interactions (ISP)



The surface modification has a strong impact onto the specific interactions. Generation of non-polar TMS groups causes a significant decrease of specific interaction parameter.

Acid-Base Constants



The surface modification with TMS groups has a significant impact on the potential of porous glass to interact with electron donating molecules (decreasing K_a value)

Conclusion

• The effect surface chemistry was investigated for porous silica by means of IGC technique

•The sensitivity for differences in the surface chemistry was shown

• The potential of IGC measurements to chracterize to effect of surface modification was demonstrated on the basis of the dispersive part of surface energy, the specific interaction parameter, acid-base properties.

Thank you for your attention!