Zeolites Characterization 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
[2] POROTEC GmbH, Hofheim, Germany

Adscientis – Smart Inverse Chromatography

inolytix

POROTEC – VERTRIEB VON WISSENSCHAFTLICHEN GERÄTEN GMBH

Summary

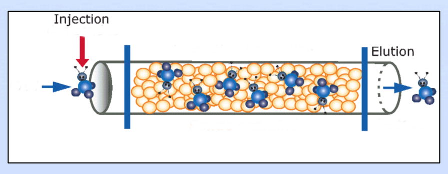
Characterization of solids, e.g. Zeolites, by Inverse Gas Chromatography (IGC) delivers precise and unique values about surface energy, size exclusion and acid/base properties.

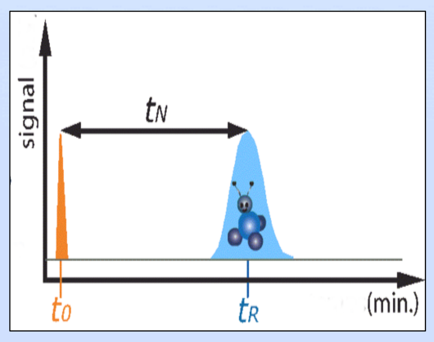
Proven software, as our own development, experience and proven operation conditions are requirements, while the use of standard GCs allows great flexibility plus 2 channels.

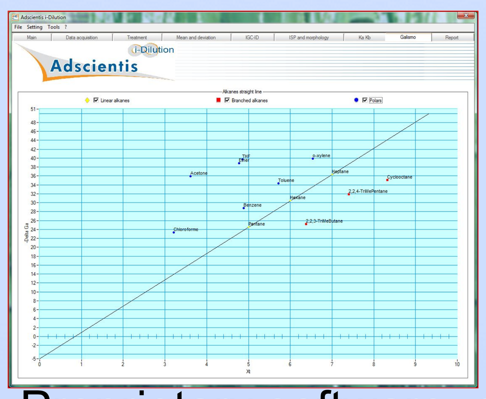
The BEA type zeolite has higher surface energy γ_s^d than Silicalite-1, 237 vs. 192 mJ/m², whereas Silicalite-1 shows a very strong size exclusion effect. BEA is more polar and has stronger electron donor (acid) and acceptor (base) properties.

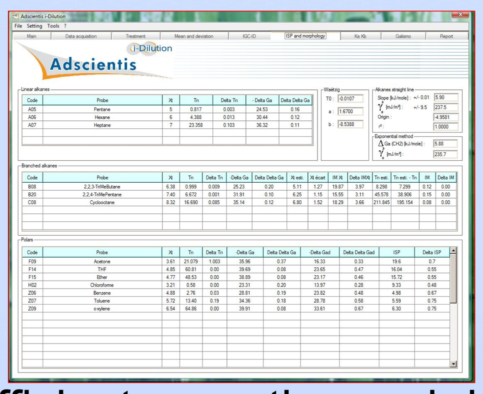
Principles of Inverse Gas Chromatography (IGC)

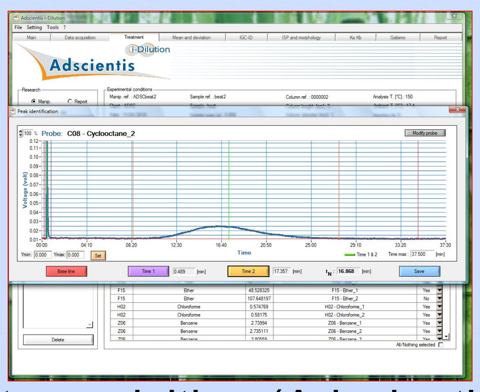
1. Samples (powder, fibers, flakes) are filled into column
2. Many probes are injected (n-alkanes, branched, polar, ...)
3. **IGC-ID (infinite dilution)**: very low amount, symetrical peak
   - ✓ Surface energy (γ_s^d), nanoroughness, acid-base, ΔG_a, ΔH_a, ΔS_a
4. **IGC-FC (finite concentration)**: high amount, asymetric peak
   - ✓ Desorption isotherm, specific surface area, adsorption energy distribution function











Proprietary software, efficient operation and data aquisition (Adscientis)

Standard GC, 2 channels

Zeolites characterization by IGC-ID (infinite dilution)

Dispersive Surface Energy (γ_s^d)

The method of determination of the dispersive component of the surface energy (γ_s^d) has been pioneered by DORRIS and GRAY[1]. **Linear alkanes are injected, here n-pentane, n-hexane, n-heptane.** γ_s^d is independent of specific surface area, volume, flow rate etc., but ONLY if dilution is "infinite".

IMPORTANT: γ_s^d is only the dispersive, non-polar surface energy.

$$\gamma_s^d = \frac{1}{\gamma_{CH_2}}\left(\frac{\Delta G_a(CH_2)}{2N a_{CH_2}}\right)^2$$

- N, Avogadro's number
- γ_{CH2} the surface energy of a solid entirely constituted by CH2 groups (Poly ethylene) γ_{CH2} = 36,5 – 0,056.(T-20) [T in °C]
- a_{CH2}, the area of an adsorbed CH_2 group (6 Å²)

Two Zeolites are compared: BEA and Silicalite-1

BEA: S_{BET} = 626 m²/g, V_{pores}= 0.23 cm³/g , both are powder of microcystals

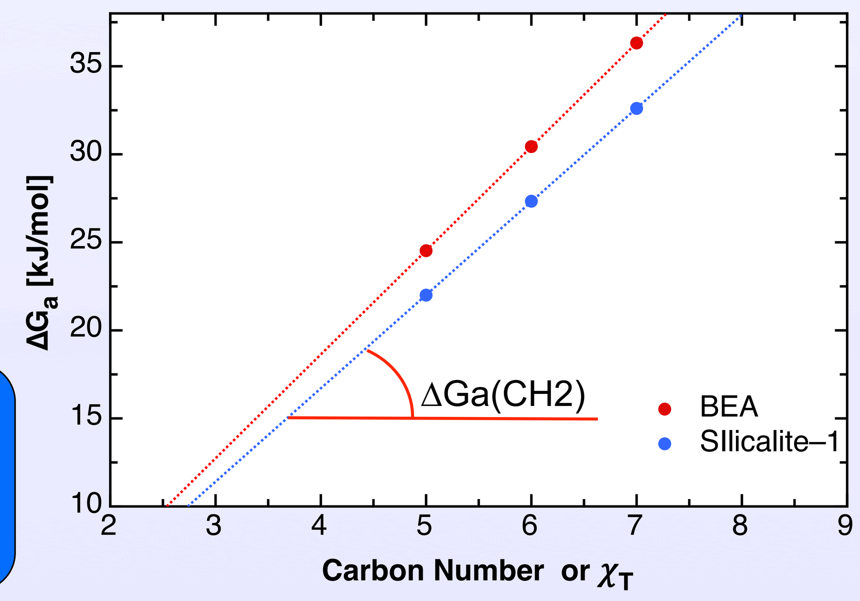
Silicalite: S_{BET} = 394 m²/g, V_{pores}= 0.18 cm³/g

iGC conditions: 10 mg, short column 1.5 mm ID, measurement: 150°C, 20 mL/min, 3x injections

Surface energy	ΔGa(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 γ_s^d with 237 mJ/m² than Silicalite-1 with 192 mJ/m².

Low error due to long-term experience.



Surface Morphology (IM), i.e. nanoroughness, size exclusion

The morphology index (IM) is given by the ratio of the retention volume of a branched alkane molecule $V_G(M)$ and $V_G(C)$ the retention volume of an n-alkane having the same accessibility to the solid's surface. It is based on the topology index concept of molecules (χ_T) and considers shape and Van der Waals volume[2].

This can be expressed as ratio of the retention volumes or derived from the free adsorption energy with similar results.

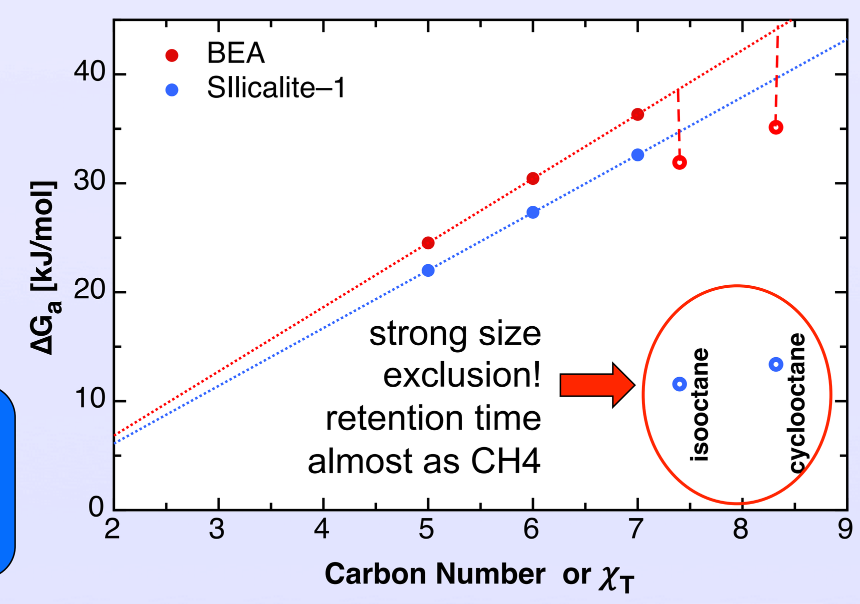
- $V_G(M)$ retention volume of branched alkane
- $V_G(C)$ retention volume of linear alkane

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

Isooctane and cyclooctane have much shorter retention times than n-alkanes. This quantifies a size exclusion effect in a very useful way.

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 cyclohexane, smaller, but significant effect for BEA.



Specific Interactions (ISP)

The specific interaction parameter (ISP) is determined in relation to the reference n-alkane straight line[3]. It is expressed as the difference between a polar probe (ΔG_a) and the reference alkane molecule with non-polar, dispersive adsorption (ΔG_a^d)[4].

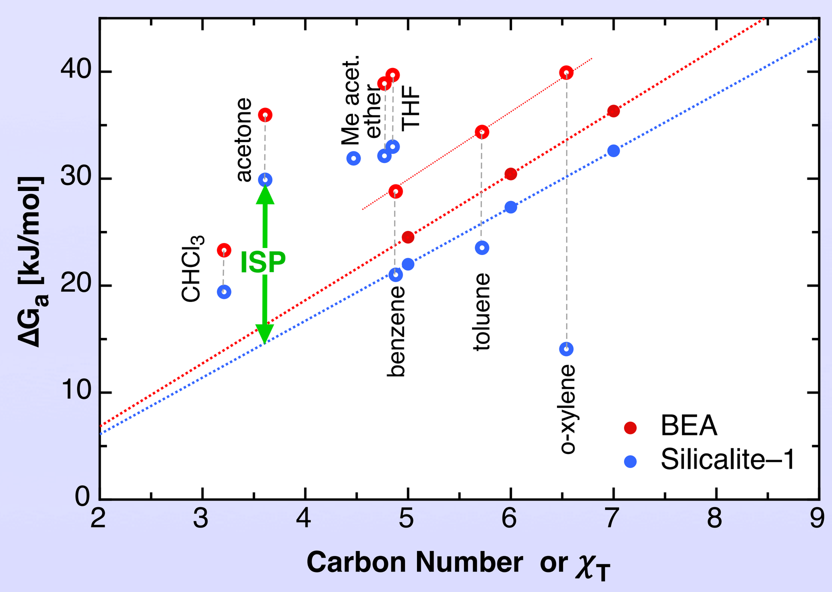
$$ISP = \Delta G_a^{sp} = \Delta G_a - \Delta G_a^d$$

By proper choices of injected probes (acid/base characteristics), the solid's surface acid/base properties can also be assessed.

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

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

Quantitative and clear differentiation of adsorption behaviour and polar interactions is based on 8 probes.



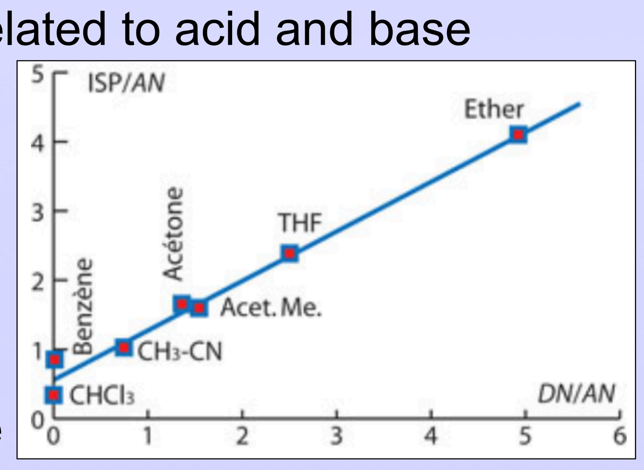
Determination of the acid and base constants (Ka, Kb)

By injecting probes of known electron acceptor (AN) and donor numbers (DN), according to the semi-empirical acid/base scale of GUTMANN[5], the ISP value can be related to acid and base constants Ka and Kb.

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

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

Example

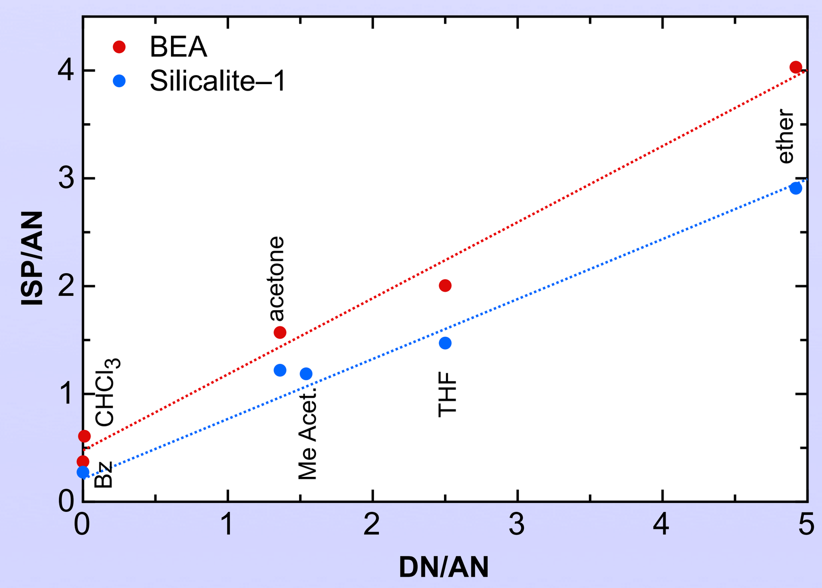


BEA zeolite shows stronger interaction potential with higher electron donor (Ka= 70.6) and acceptor (Kb= 47.7) values than Silicalite-1.

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

for better readability: Ka*100, Kb*100

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



References

G.M. DORRIS, D.G. GRAY; J. Colloid Interface Sci. 77 (1980), 353-362
E. BRENDLE, E. PAPIRER ; J. Colloid Interface Sci. 194 (1) 207-216 (1997)
E. BRENDLE, E. PAPIRER ; J. Colloid Interface Sci. 194 (1) 217-224 (1997)
C. SAINT FLOUR, E. PAPIRER ; J. Colloid Interface Sci. 91 (1) 69-75 (1983).
V. GUTMANN, "The Donor-Acceptor Approach to Molecular Interactions", Plenum Press, New York (1978)

Acknowledgement

Jean Daou from the team Materials with Controlled Porosity from the Institute of Material Science of Mulhouse, UMR CNRS 7361, University of Haute Alsace, Mulhouse, France, for providing the zeolites samples.

Contact: jean.daou@uha.fr