Zeolites Characterization by Inverse Gas Chromatography: Precise, Easy & Significant

1. Samples (powder, fibers, flakes) are filed into column
2. Many probes are injected (n-alkanes, branched, polar, ...)
3. IGC-ID (infinite dilution): very low amount, symmetrical peak
   - Surface energy (\(\gamma_s\)), nanoroughness, acid-base, \(\Delta G\), \(\Delta H\), \(\Delta S\)
4. IGC-FC (finite concentration): high amount, asymmetrical peak
   - Desorption isotherm, specific surface area, adsorption energy distribution function

Proprietary software, efficient operation and data acquisition (Adscientis)
Standard GC, 2 channels

**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 required, while the use of standard GCs allows great flexibility plus 2 channels.
The BEA type zeolite has higher surface energy \(\gamma_s\) 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.

**Dispersive Surface Energy (\(\gamma_d\))**
The method of determination of the dispersive component of the surface energy (\(\gamma_d\)) has been pioneered by DORRIS and GRAY1. Linear alkanes are injected, here n-pentane, n-hexane, n-heptane. \(\gamma_d\) is independent of specific surface area, volume, flow rate etc., but **ONLY if dilution is infinite**.

**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 \(V_d(M)\) and \(V_d(C)\) 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 (\(\gamma_d\)); and considers shape and Van der Waals volume.
This can be expressed as ratio of the retention volumes or derived from the free adsorption energy with similar results.
- \(V_d(M)\) retention volume of branched alkane
- \(V_d(C)\) retention volume of linear alkane

**Specific Interactions (ISP)**
The specific interaction parameter (ISP) is determined in relation to the reference n-alkane straight line. It is expressed as the difference between a polar probe \(\Delta G_p\) and the reference alkane molecule with non-polar, dispersive adsorption \(\Delta G_d\).

\[ ISP = \Delta G_p - \Delta G_d \]

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

**References**
G.M. DORRIS, D.G. GRAY; J. Colloid Interface Sci. 77 (1980), 353-362
E. BRENDEL, E. PAPIER; J. Colloid Interface Sci. 194 (1) 207-216 (1997)
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C. SAINT FLOUR, E. PAPIER; J. Colloid Interface Sci. 91 (1) 69-75 (1983).

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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

**Two Zeolites are compared: BEA and Silicalite-1.**
BEA: \(S_{BET} = 626\) m²/g, \(V_{pore} = 0.23\) cm³/g, both are powder of microporous Zeolite: \(S_{BET} = 394\) m²/g, \(V_{pore} = 0.18\) cm³/g
IGC conditions: 10 mg, short column 1.5 mm ID, measurement: 150°C, 20 ml/min, 3x injections

Silicalite-1 shows a very strong size exclusion effect for isoctane and cyclohexane, smaller, but significant effect for BEA.

**Stronger polar interaction by BEA (higher ISP) than Silicalite-1**
Quantitative and clear differentiation of adsorption behaviour and polar interactions is based on 8 probes.

**Zeolites characterization by IGC-ID (infinite dilution)**

**Inverse Gas Chromatography: Precise, Easy & Significant**

**Triangles**
Proprietary software, efficient operation and data acquisition (Adscientis)
Standard GC, 2 channels

**Surface energy**
\(\Delta G = \frac{1}{2} \gamma \left( \frac{N_s}{V_s} \right) \)

**ISP = \Delta G_p - \Delta G_d**

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

**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; the ISP value can be related to acid and base constants Ka and Kb.

ISP = DN*Ka + AN*Kb

ISP/AN = (DN/AN)*Ka + Kb

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

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