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

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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 \(\gamma_d\) than Silicalite-1, 237 vs. 192 mJ/m\(^2\), 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, symmetrical peak
4. IGC-FC (finite concentration): high amount, asymmetrical peak

- Desorption isotherm, specific surface area, adsorption energy distribution function

Zeolites characterization by IGC-ID (infinite dilution)

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 GRAY\(^1\). Linear alkanes are injected, here n-pentane, n-hexane, n-heptane. \(\gamma_d\) is independent of specific surface area, volume, flow etc., but only if dilution is "infinite".

Important: \(\gamma_d\) is only the dispersive, non-polar surface energy.
- \(N\), Avogadro’s number
- \(V_{CH2}\), the surface energy of a solid entirely constituted by CH2 groups (Poly ethylene) \(V_{CH2} = 36.5 - 0.056 \times 10^{-20} \times T \times [^\circC]\)
- \(N_{CH2}\), the area of an adsorbed CH2 group (6 Å)
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Surface Morphology (IM), i.e. nanoroughness, size exclusion

The morphology index (IM) is given by the ratio of the retention volume of a branched molecule \(V_d(M)\) and \(V_d(CH2)\) 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
- \(V_d(CH2)\) retention volume of linear alkane

Specific Interactions (ISP)

The specific interaction parameter (ISP) is determined in relation to the reference n-alkane straight line\(^1\), i.e. it is the difference of the free energies of adsorption of a polar probe (\(\Delta G_a\)) and a reference alkane molecule with dispersive adsorption (\(\Delta G_d\)).

\[ ISP = \Delta G_{a}^{m} = \Delta G_{a} - \Delta G_{d} \]

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 known probes of electron acceptor (AN) and donor numbers (DN), according to the semi-empirical acid/base scale of GUTMANN\(^2\), 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

Example

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

References

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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.

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Table: Acid/Basic Constants Ka, Kb

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Ka</th>
<th>Kb</th>
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<tr>
<td>BEA</td>
<td>70.6</td>
<td>47.7</td>
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<tr>
<td>Silicalite-1</td>
<td>55.6</td>
<td>21.2</td>
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Table: Inverse Gas Chromatograph: Precise, Easy & Significant