Dynamic physisorption of 15+ molecular probes for apolar and polar interactions, substance specific BET, heterogeneity and diffusion coefficients using Inverse Gas Chromatography (IGC)

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SUMMARY

A novel IGC setup allows a very flexible injection of 15+ molecular probes at either infinite dilution (IGC-ID) or a saturation of the surface by a finite concentration (IGC-FC) and subsequent desorption analysis.

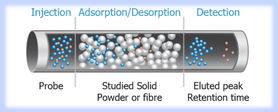
Using IGC-ID, the apolar and polar interactions of fresh, used, artificially aged and recycled catalysts were determined.

By IGC-FC the adsorption behaviour of zeolites by methanol was measured including adsorption energy distribution. Diffusion coefficients in alumina beads could easily be quantified by Zero Length Column (ZLC) using the IGC setup.

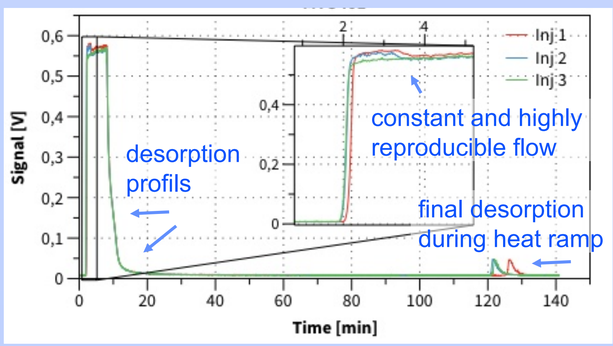
PRINCIPLES

Samples (powder, fibres, flakes) are filled into column. Any kind of volatile substance can be used as a „probe“ to study the surface properties. A standard set consists of 15+ probes of n-alkanes, branched and cyclic alkanes and different polar probes[1, 2, 3].

- **IGC-ID (infinite dilution)**: very low amount, symmetrical peaks
  - Surface energy (γ_s^d), nanoroughness (RIM, IM), overall polarity (∑ISP), acid-base (K_a, K_b) , ΔG_a, ΔH_a, ΔS_a
- **IGC-FC (finite concentration)**: saturation of the surface at a given p/p0 usually between 0.2-0.3, see figure right
  - The injection of any probe at constant flow is a unique feature.
  - Desorption isotherm, irreversible adsorption, specific surface area (BET), adsorption energy distribution function (AEDF)
  - Basis for diffusion coefficient determination (ZLC), see below



Instrumental setup of IGC Neuronic, Adscientis



GC detector signal at constant flow (2-8 min) and desorption (8-140 min) for 3 injections

CHALLENGES

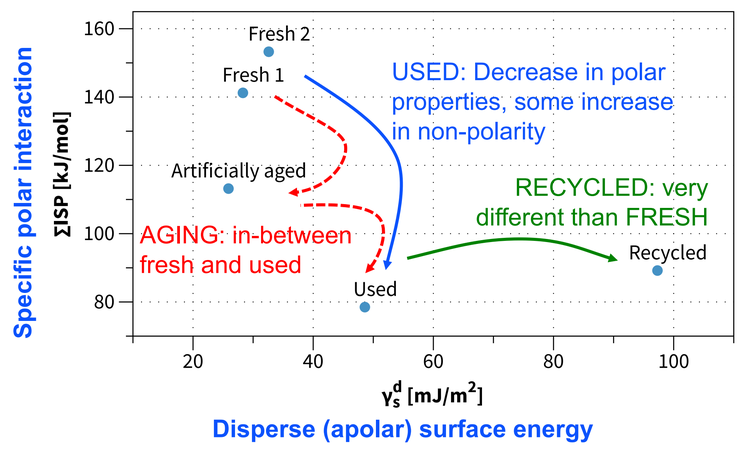
Fresh, recycled, used and artificially aged catalysts behave differently and not as expected.

What are the differences in surface properties of fresh, recycled, used and artificially aged catalysts?

Are the assumptions about recycling and artificially aging correct?

EXPERIMENTS and RESULTS

IGC at infinite dilution (ID) using 15 different non-polar and polar gas probes as n-alkanes, chloroform and diethylether revealed quantitatively the specific polar interactions (∑ISP) and the non-polar, disperse surface energy γ_s^d .



CONCLUSIONS

USED catalyst shows a great loss in polarity. Artificially AGED catalyst is between the properties of FRESH and USED with a lower apolar value than both.

RECYCLED catalyst are very different than FRESH, the polarity is not regained and very high apolar properties result.

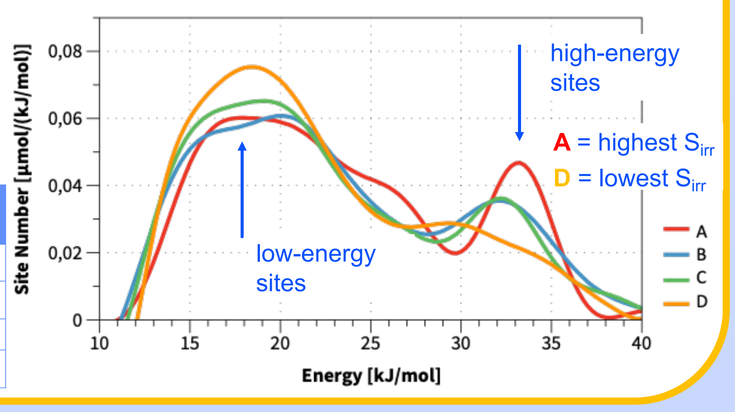
Zeolites are used for methanol adsorption – what are the quantitative differences?

Is there irreversible adsorption of methanol? How does this influence the adsorption isotherms? Does the behaviour reflect the adsorption energy distribution?

In an IGC finite-concentration (FC) setup, methanol is passed over the catalyst at a defined p/p0 = 0.24 at 40° C for 6 min. Multiple runs, the desorption isotherms and thermal desorption are further interpreted.

Samples	S_{BET} [m²/g]	C_{BET}	S_{irr} [m²/g]
A	224,1 ± 0,7	39,3	44,6
B	252,9 ± 13,6	32,4	35,9
C	224,7 ± 3,6	25,3	26,7
D	227,0 ± 5,0	25,4	16,1

The adsorption energy distribution function is calculated by the Elution at the Characteristic Point (ECP), see H. Balard [4].



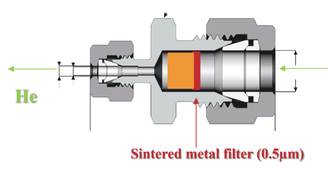
IGC-FC revealed clear differences in methanol adsorption behaviour of four zeolites. Irreversible adsorption of A was highest with 44.6 m²/g equivalent. Sample A showed also the highest number of high-energy sites at 33 kJ/mol while sample D has lowest irreversible adsorption.

Determination of diffusion coefficients by van Deemter are tedious. How does the Zero Length Column (ZLC) method perform?

The ZLC method can be easily performed with the IGC Neuronic instrument to measure diffusion coefficients of toluene, cycooctane and octane on two alumina beads.

ZLC methods:

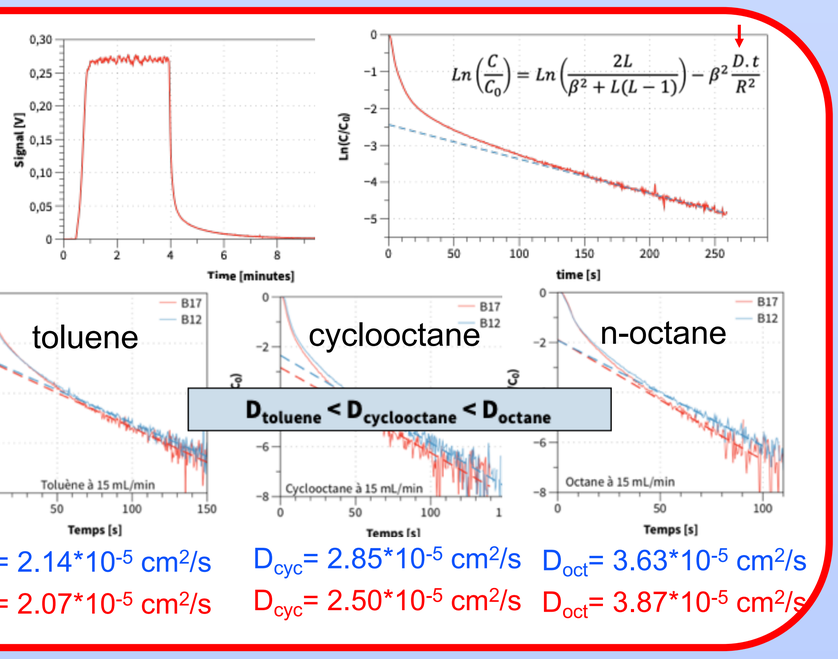
Conversion of the desorption front and fitting the asymptote in a $Ln(C/C_0)$ plot to obtain D, see references [5, 6].



Example: Alumina beads

B12: d_{50}= 1.71 mm

B17: d_{50}= 1.65 mm



D_{tol}= 2.14*10⁻⁵ cm²/s D_{cyc}= 2.85*10⁻⁵ cm²/s D_{oct}= 3.63*10⁻⁵ cm²/s

D_{tol}= 2.07*10⁻⁵ cm²/s D_{cyc}= 2.50*10⁻⁵ cm²/s D_{oct}= 3.87*10⁻⁵ cm²/s

Diffusion coefficients of octane, cyclooctane and toluene could easily be determined using the ZLC method and the IGC-FC setup in the kinetic regime.

Experiments were repeated using alumina beads of two slightly different particle diameters and results were confirmed within experimental error.

References

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Limitations

The IGC physisorption studies are well suited to study an overall surface behaviour. Catalysts with a small, but highly active number of catalytic sites as noble metal catalysts are less suited, unless diffusion rate or the behaviour of the carrier under physisorption conditions are of interest.