Design of mesoporous USY zeolites for superior hydrocracking

24th October 2024

ZEOPORE

From KU Leuven, Belgium, °2017

Superior catalytic performance for refining and chemical industry: fossil and circular

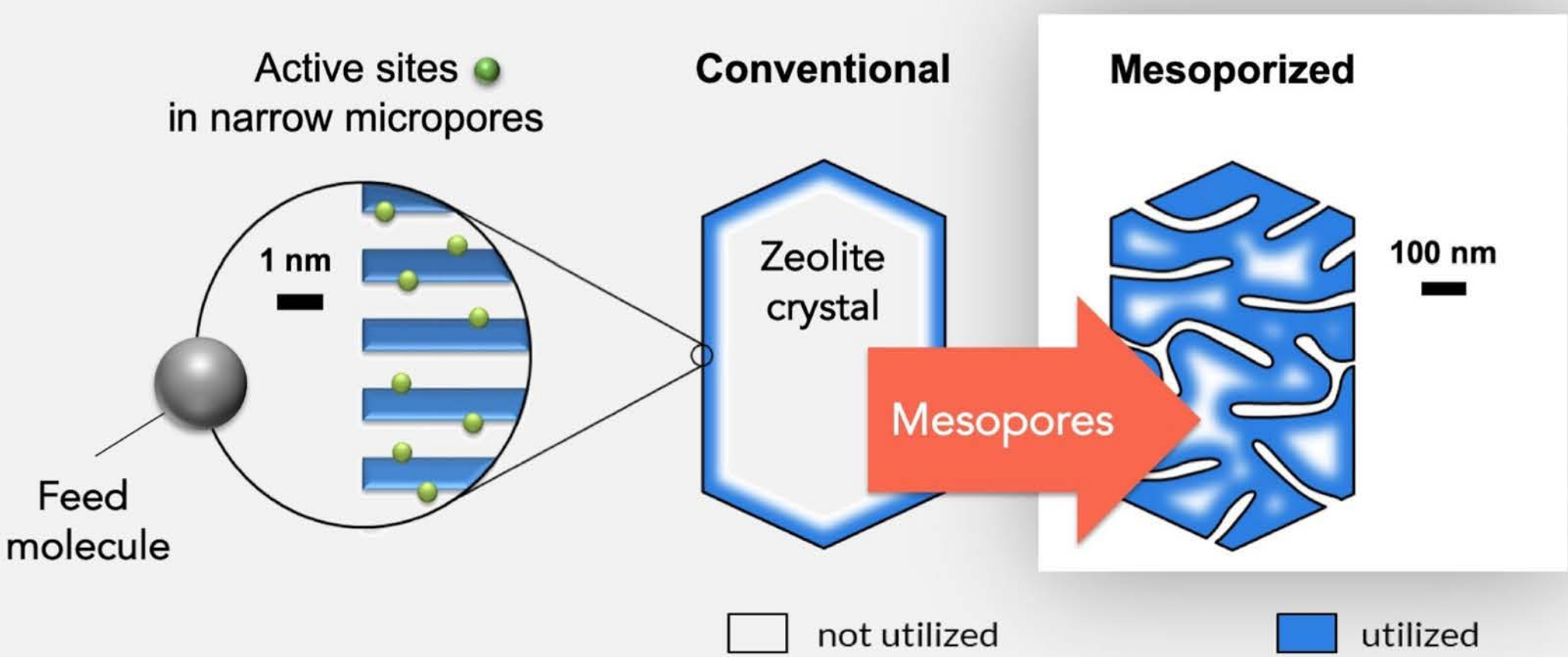
Chemical treatments on standard commercial zeolite powders

high performance zeolites in global catalyst market

gram to ton scale

Controlled zeolite pore modification

Enhances catalytic processes



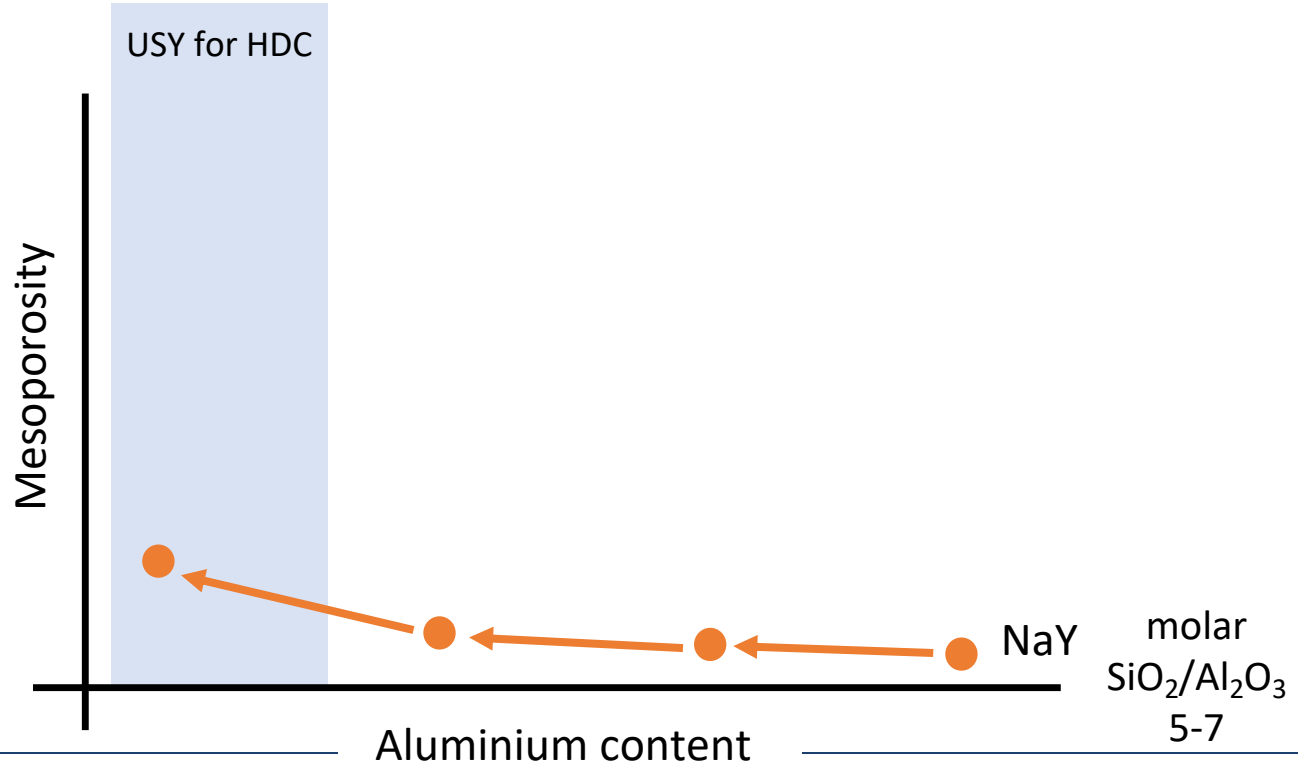
Benefits of mesoporous USY

- Increased middle distillates
- Higher activity

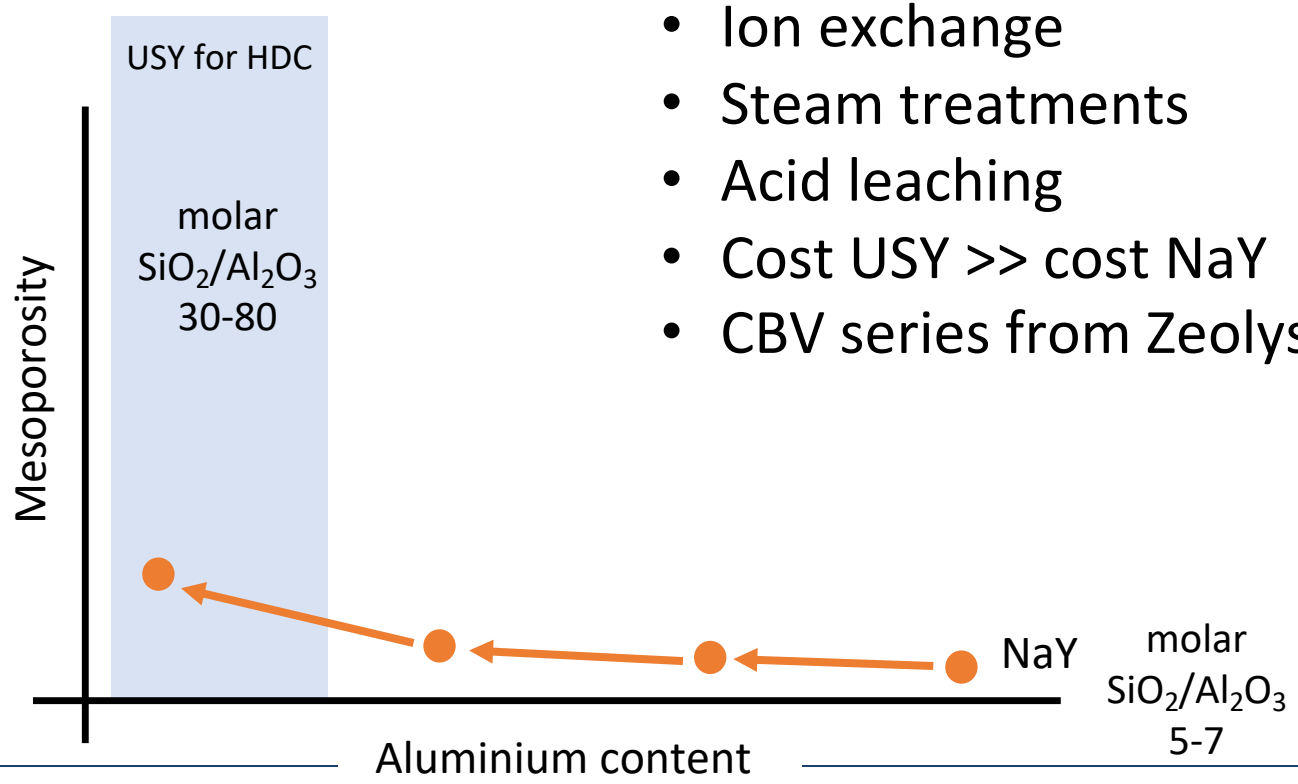
- Reduced hydrogen consumption
- Higher plant capacity
- Higher stability and longer cycle time
- Tolerance to more difficult feedstocks
- Higher quality of products
  - higher viscosity index, lower polycyclic aromatics, and higher H-content
- Increased residue conversion

State of the art

USY zeolites obtained via dealumination



USY zeolites obtained via dealumination

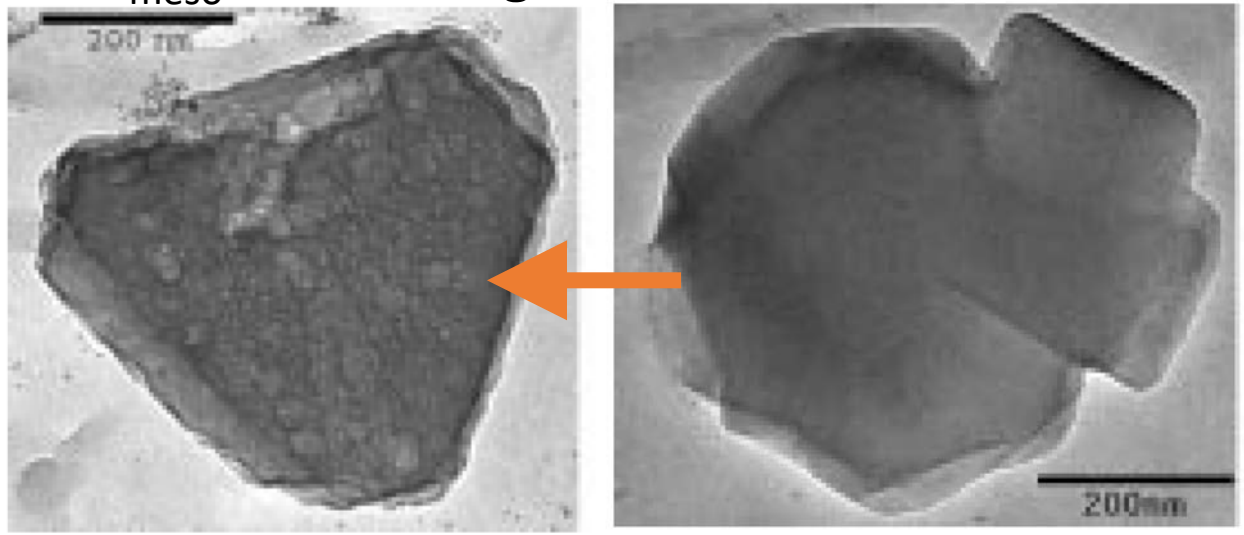


- Established unit operations:
  - Ion exchange
  - Steam treatments
  - Acid leaching
  - Cost USY >> cost NaY
  - CBV series from Zeolyst industrial reference

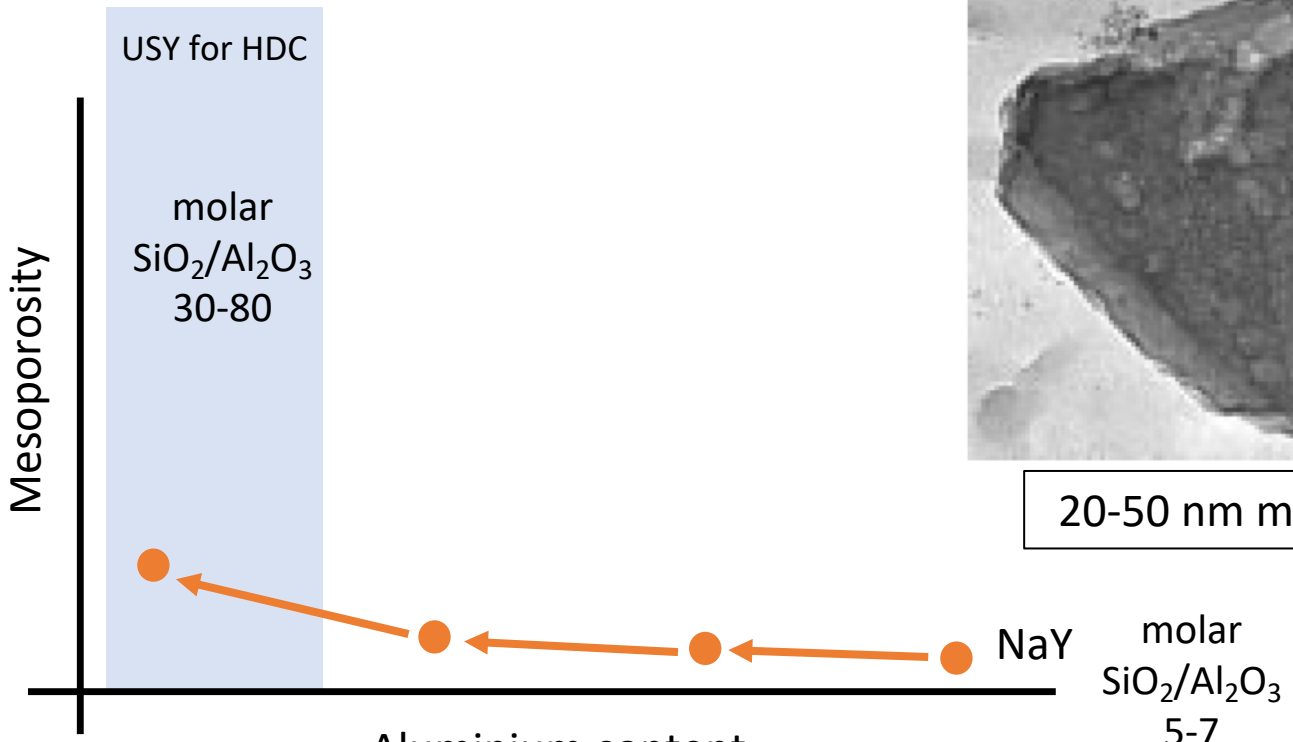
Dealumination generates some mesoporosity

USY
V_{meso} ~ 0.20 ml/g

NaY
V_{meso} ~ 0.05 ml/g



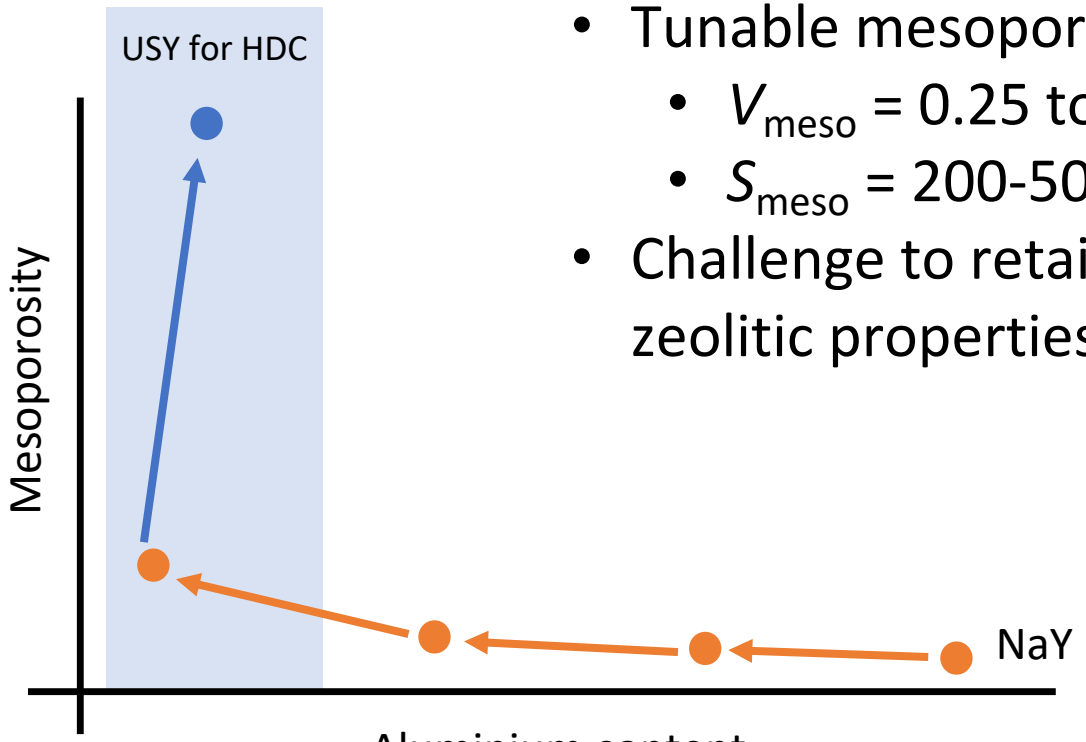
20-50 nm mesopores



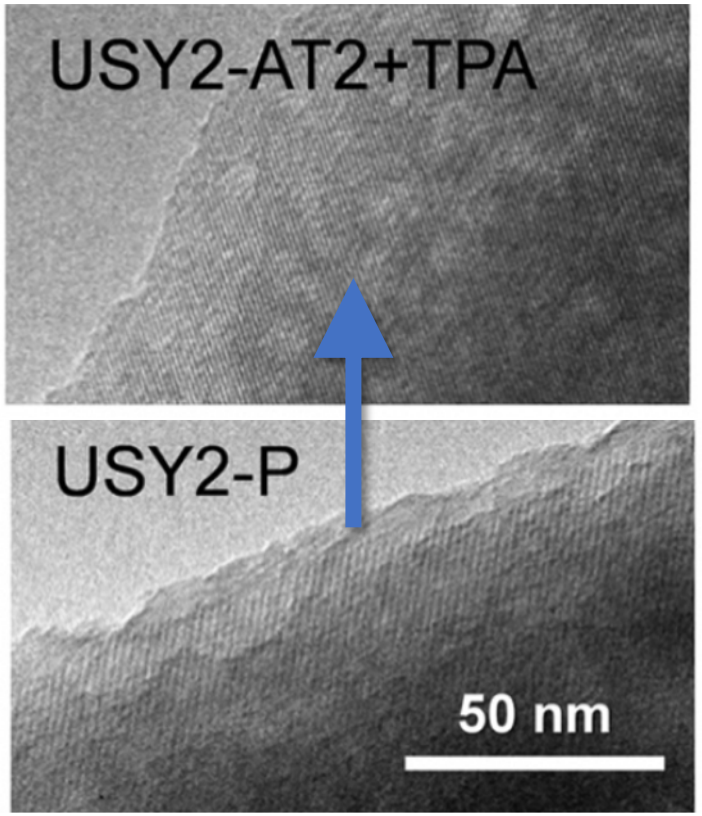
Targeted mesoporization known for a decade

3-10 nm mesopores

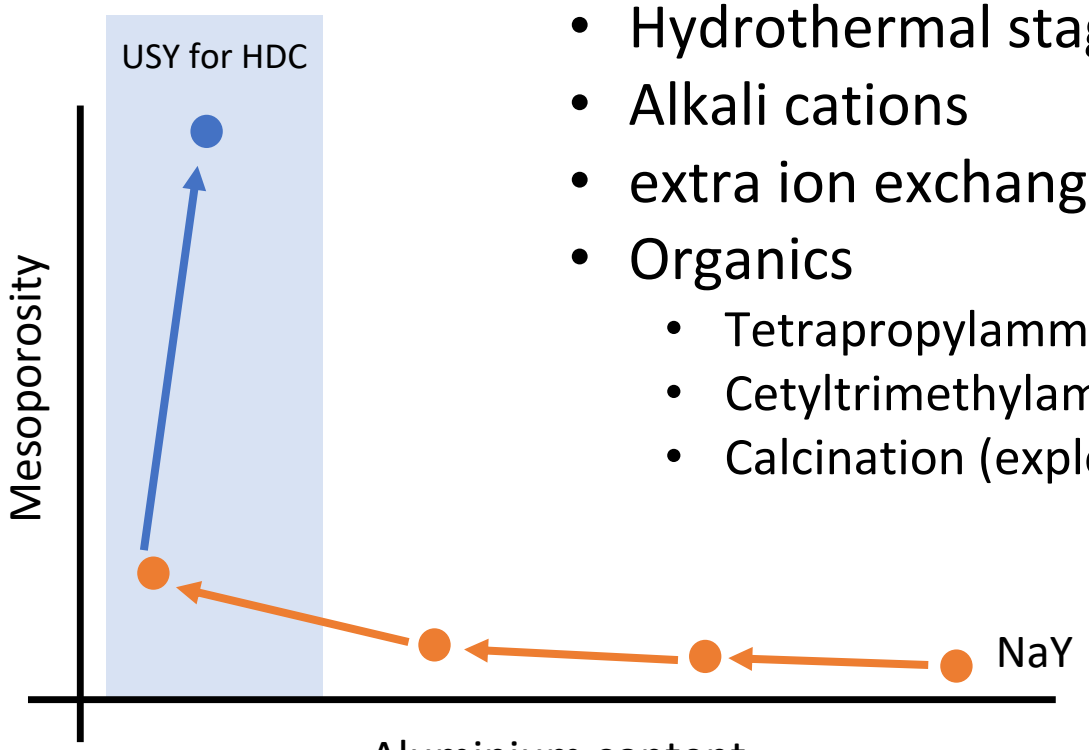
Adv. Funct. Mater. **2012**, *22*, 916–928



- Base treatment common
- Tunable mesoporosity:
  - V_{meso} = 0.25 to 1.00 ml/g
  - S_{meso} = 200-500 m^2/g
- Challenge to retain intrinsic zeolitic properties

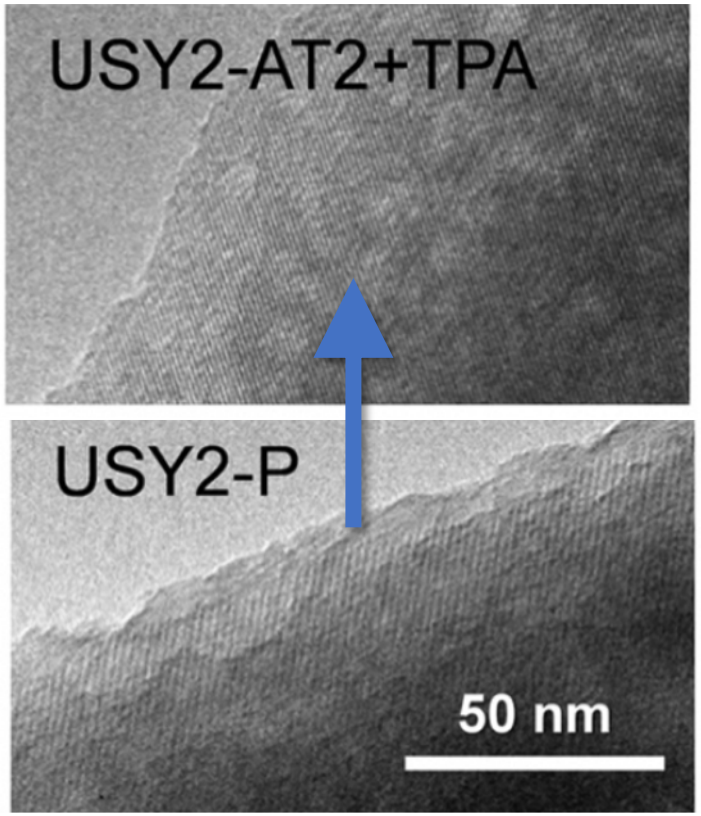


Mesoporization has a bad reputation



- Expensive dissolution
- Hydrothermal stages
- Alkali cations
- extra ion exchanges
- Organics
  - Tetrapropylammonium (TPA)
  - Cetyltrimethylammonium (CTA)
  - Calcination (explosivity)

Adv. Funct. Mater. **2012**, *22*, 916–928



Cases on VGO hydrocracking

Case 1: Mesoporization USY with NaOH

	Base CBV760	Mesoporous
S_{meso} / m^2/g	213	339
V_{meso} / ml/g	0,16	0,25
V_{micro} / ml/g	0,21	0,16

3 nm mesopores

- Base and ion exchange
- Increased mesoporosity vs microporosity

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- Base and ion exchange
- Increased mesoporosity vs microporosity
- Increased middle distillates
- Reduced activity

Table 3: Comparison of hydrocracking of VGO over $NiMoS_2$/HY-A/alumina and over a commercial catalyst.[a]

activity[b] ΔT [°C]		+13
selectivity[c] [Δ wt %]	lights (<65 °C)	−4.3
	naphtha (65–145 °C)	−5.6
	kerosene (145–250 °C)	+5.2
	diesel (250–375 °C)	+4.7
coke formation[d] [Δ wt %]		−22

Case 2: Mesoporization USY with NaOH + CTA

	Base CBV760	Mesoporous
V_{meso} (2-8 nm) / ml/g	0,01	0,62
Crystallinity / %	100	33

2-8 nm mesopores

- Base + CTA and ion exchange
- Increased mesoporosity vs crystallinity

Case 2: Mesoporization USY with NaOH + CTA

	Base CBV760	Mesoporous
V_{meso} (2-8 nm) / ml/g	0,01	0,62
Crystallinity / %	100	33
Delta T / deg.C	base	+13
Delta middle distillates / wt%	base	+1,2

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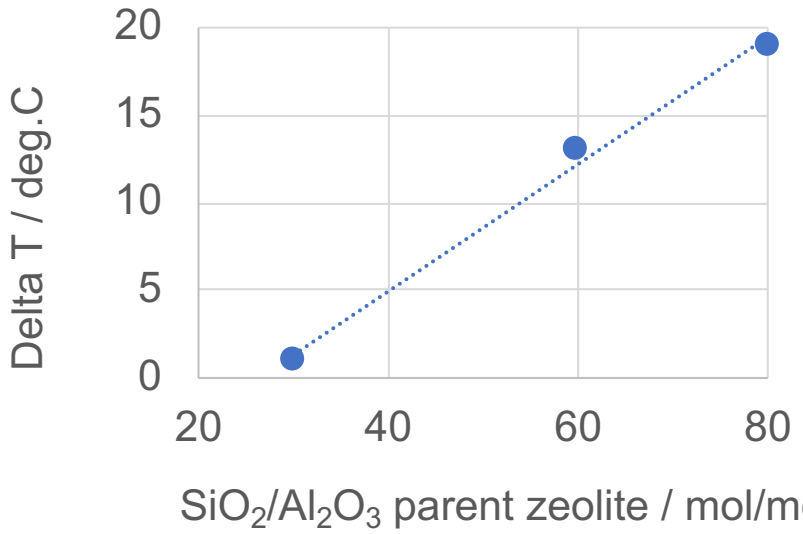
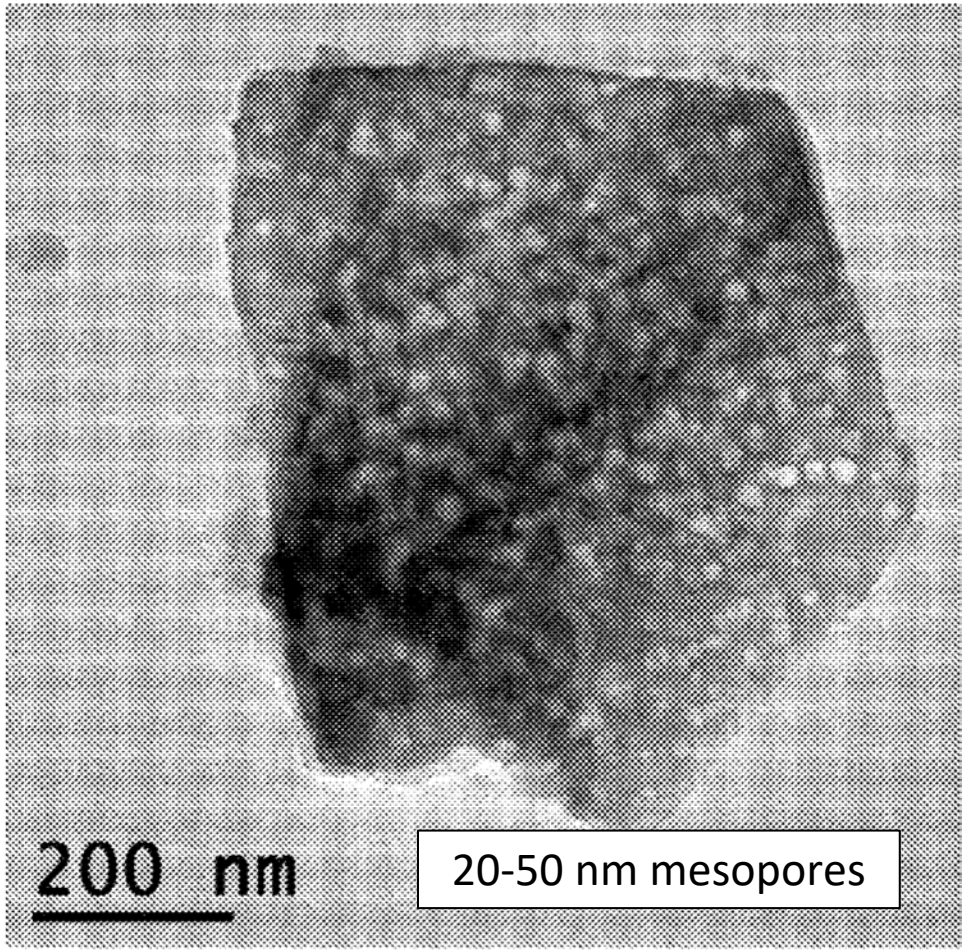
- Base + CTA and ion exchange
- Increased mesoporosity vs crystallinity
- Increased middle distillates
- Reduced activity with molar SiO_2/Al_2O_3 ratio



Case 3: Hydrothermal mesoporization in acid

	Base	Mesoporous
V_{meso} / ml/g	0.11	0.18
acidity / mmol/g	0.32	0.22

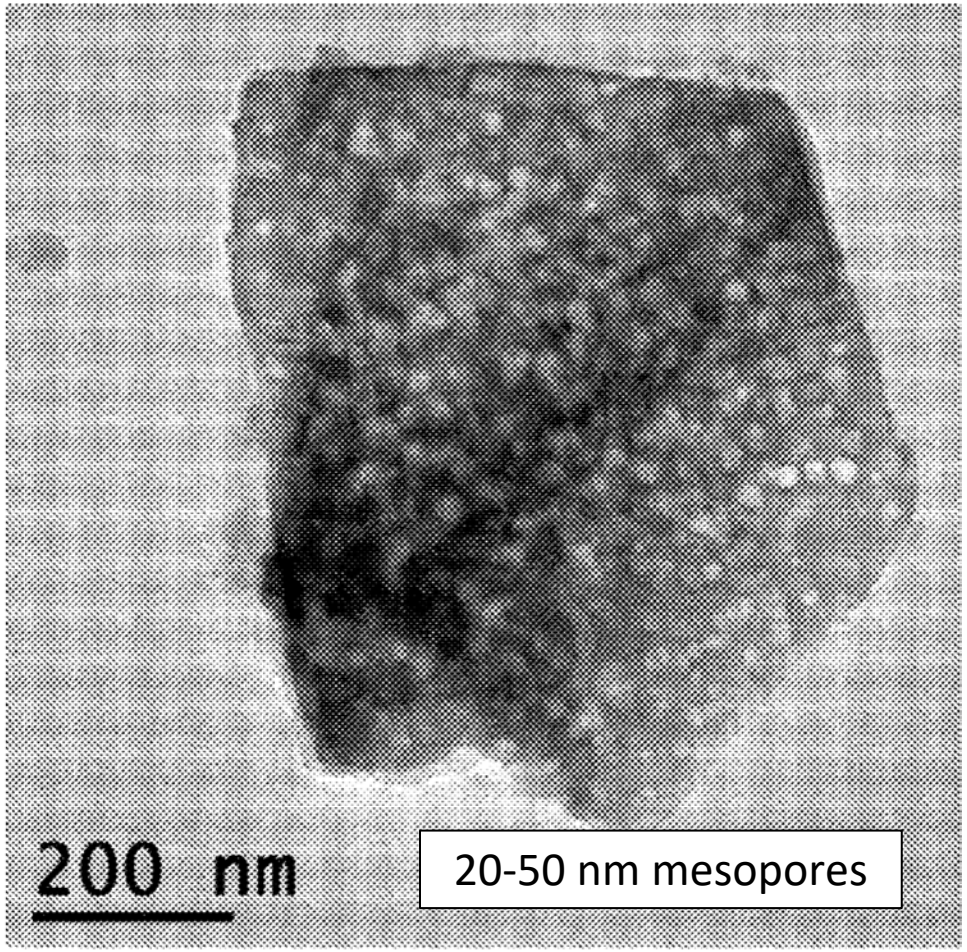
- Hydrothermal synthesis
- Increased mesoporosity vs acidity



Case 3: Hydrothermal mesoporization in acid

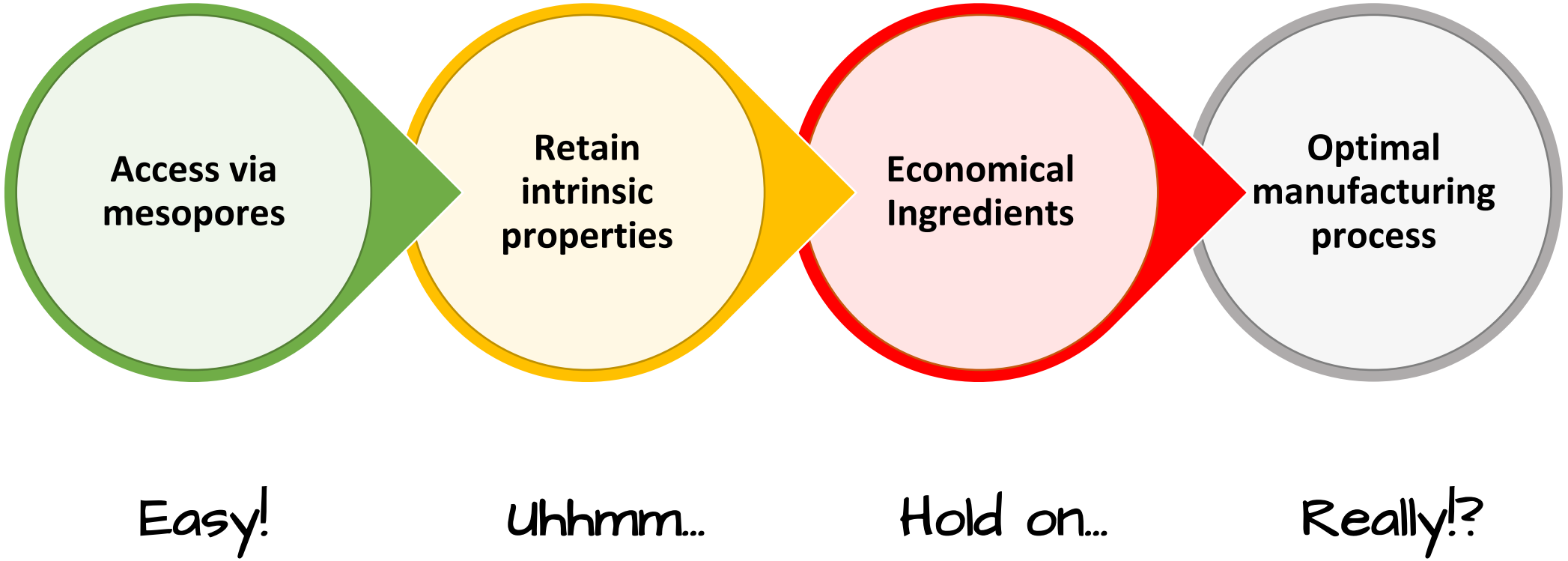
	Base	Mesoporous
V_{meso} / ml/g	0.11	0.18
acidity / mmol/g	0.32	0.22
Delta T / deg. F	Base	-5
Delta middle distillates / wt%	Base	+2.6

- Hydrothermal synthesis
- Increased mesoporosity vs acidity
- Increased middle distillates
- Increased activity



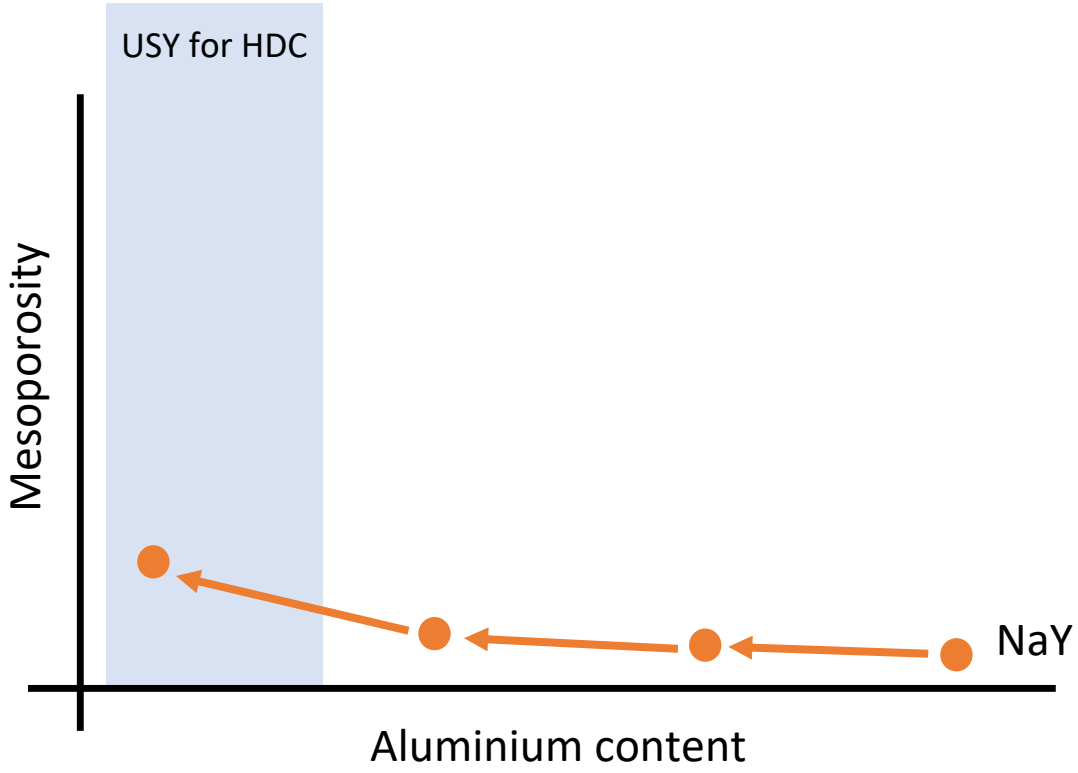
Challenges

SUPERIOR HYDROCRACKING USY ZEOLITES

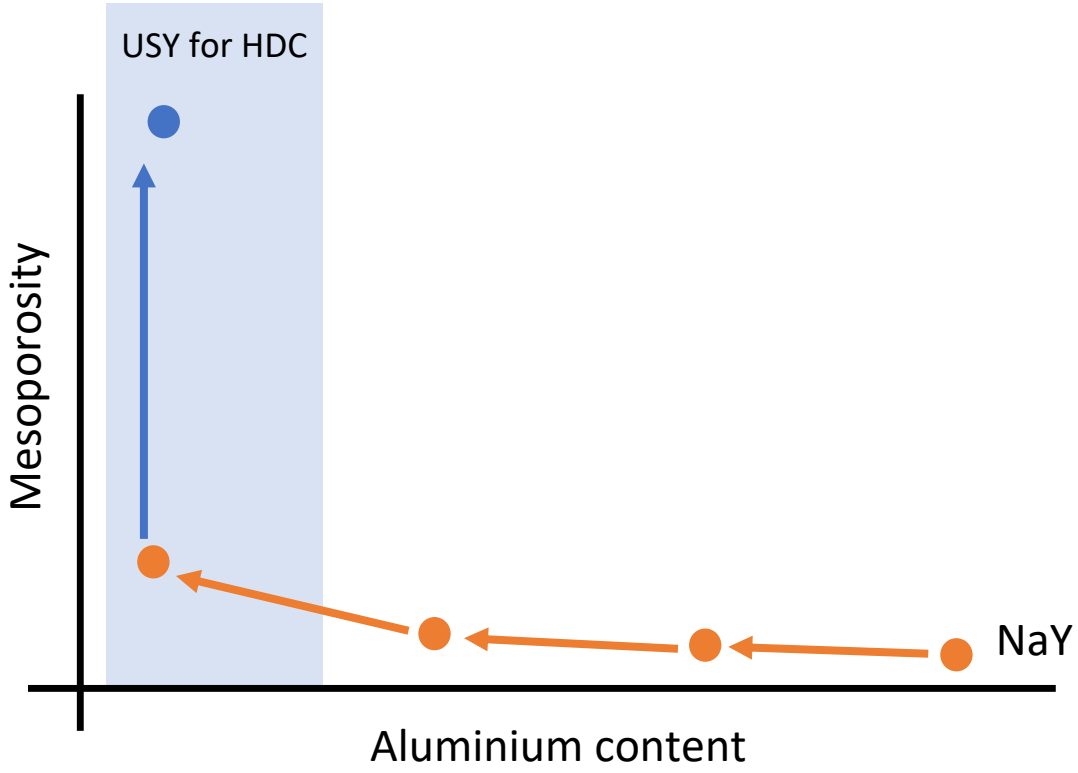


and the faujasite landscape

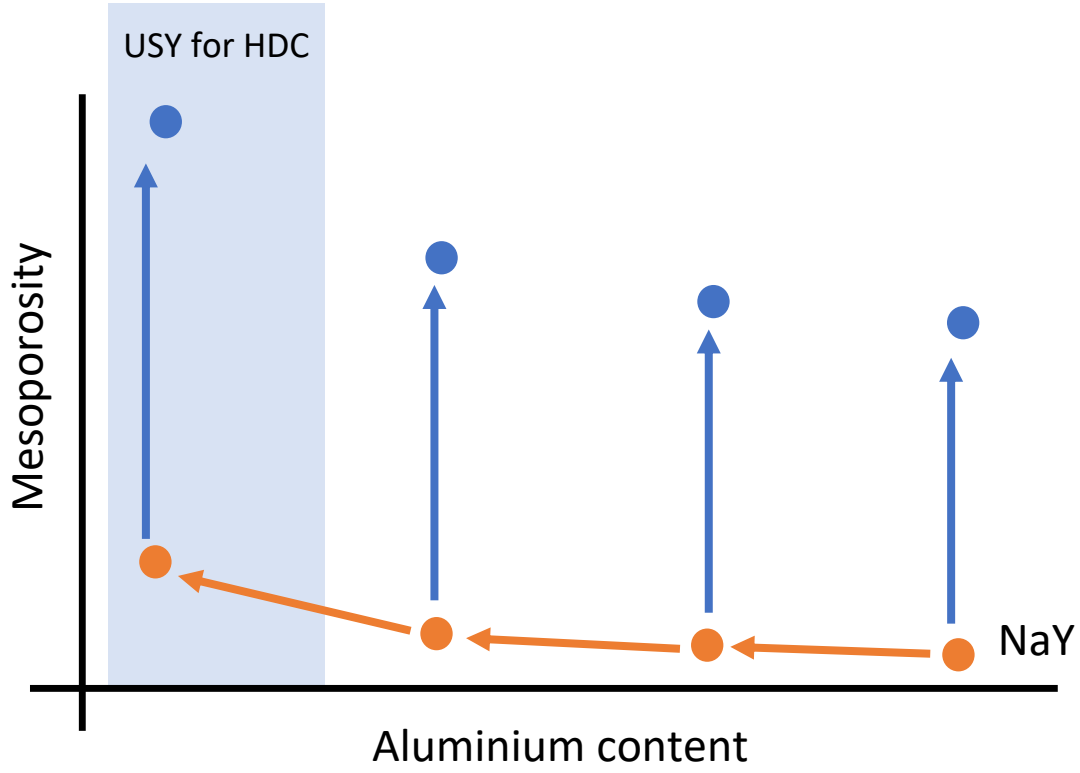
Make any standard USY



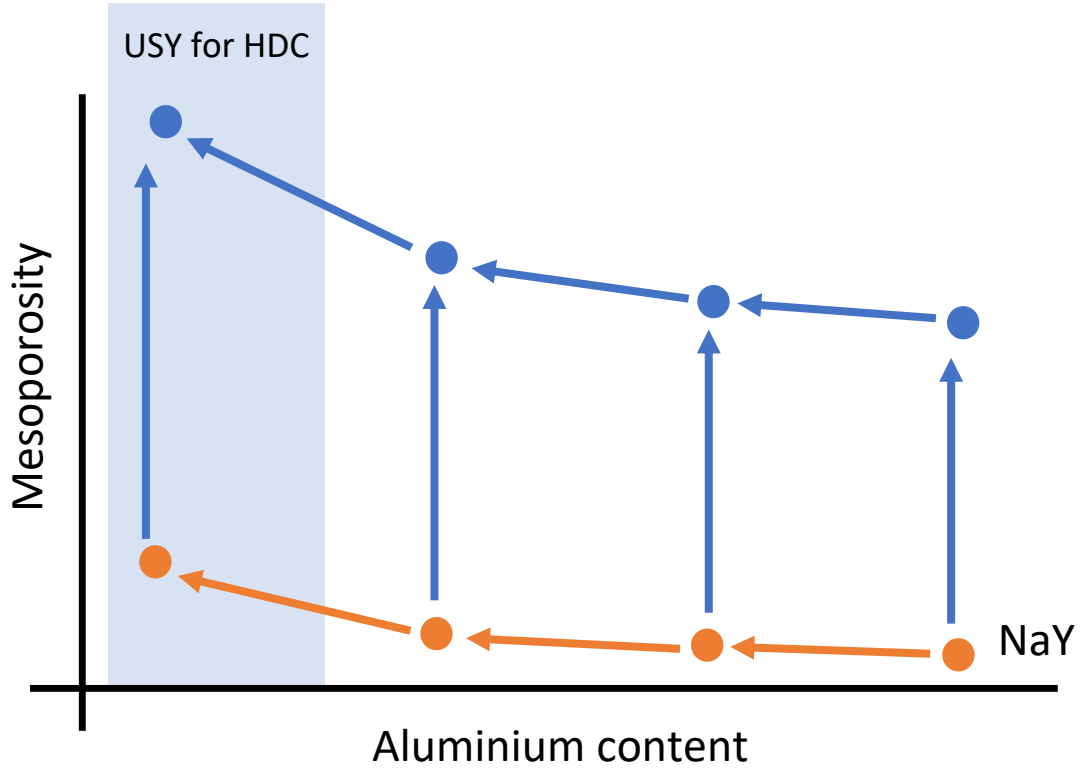
Mesoporizing since 2008



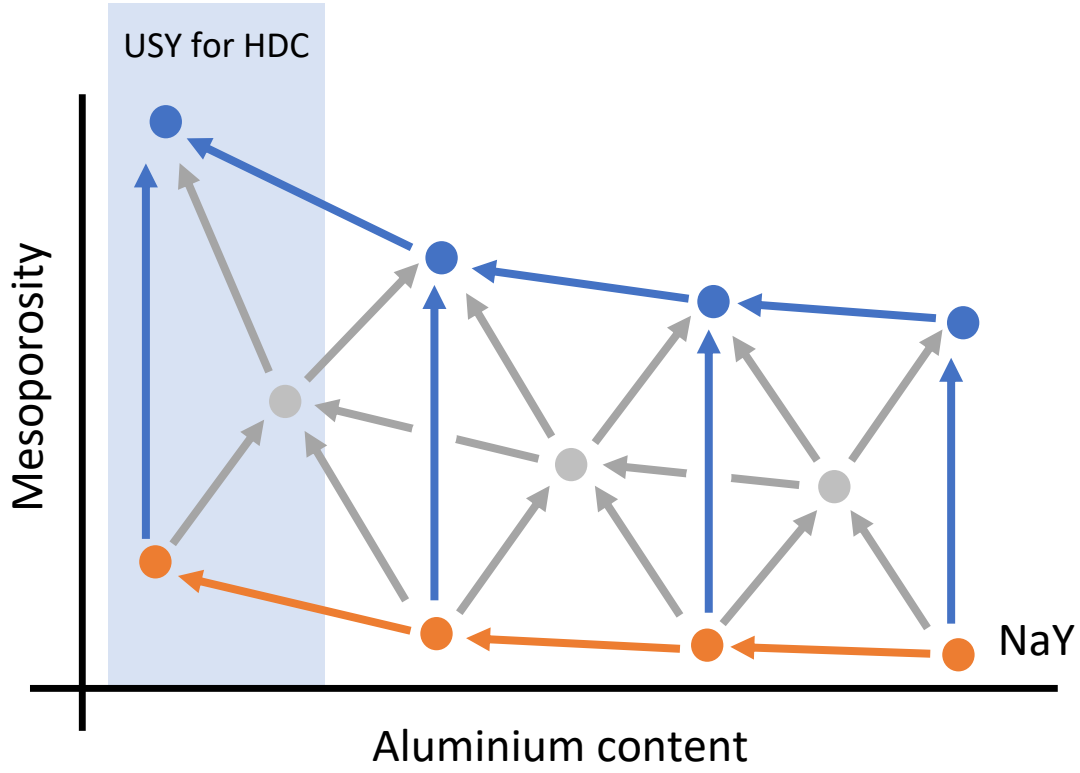
Mesoporize any zeolite



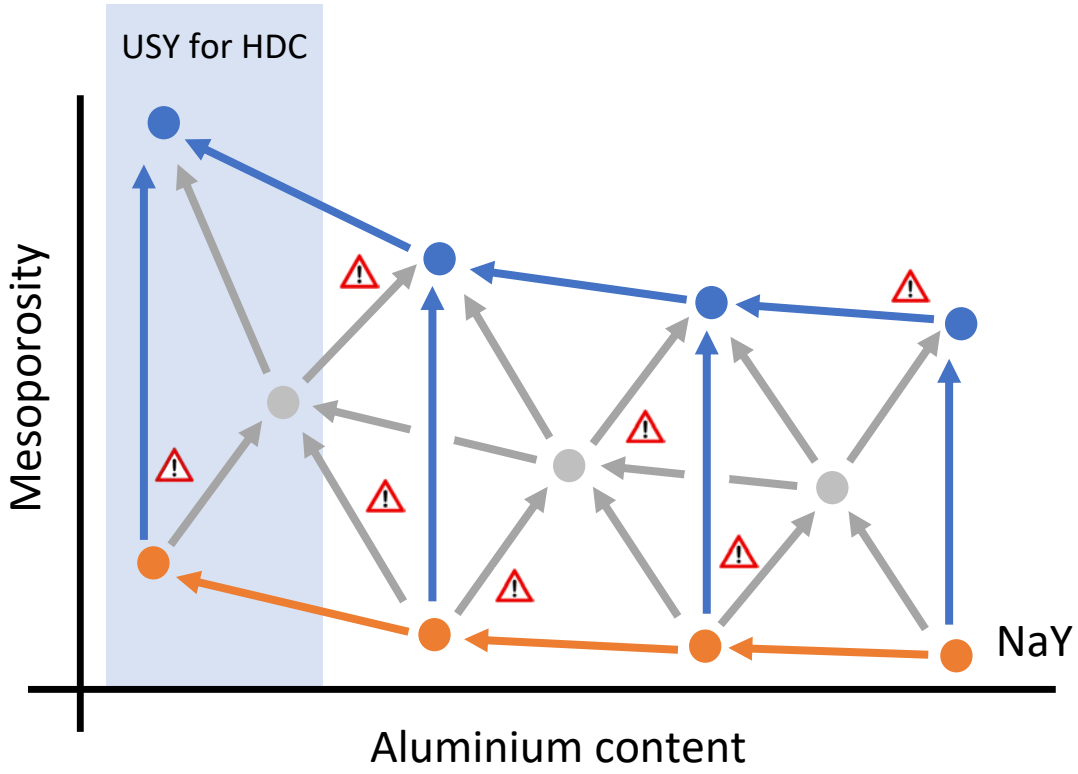
Unique steam stabilization



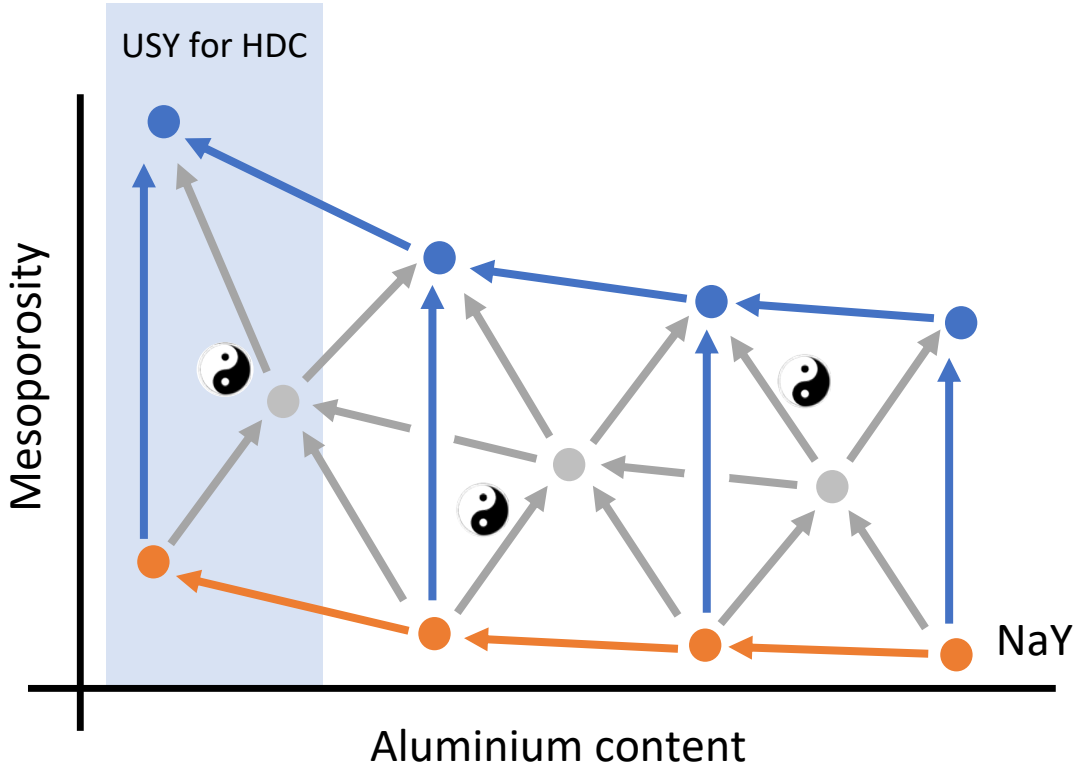
2D landscape



2D landscape: many pitfalls



2D landscape: ample synergy



Synergy fronts:

- Materials properties
- Process cost
- Ease of manufacture

Two different routes

Similar materials prepared using distinct routes

Aspect	Parent USY
V_{micro} / %	100
V_{meso} / %	100
All Bronsted acidity umol/g	129
SiO_2/Al_2O_3 / mol/mol	60

Similar materials prepared using distinct routes

Aspect	Parent USY	Mesoporous Sub-optimal	Mesoporous optimal
V_{micro} / %	100	80	85
V_{meso} / %	100	191	193
All Bronsted acidity umol/g	129	90	105
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MD / wt%	Base	+1.5	+3.8

Conventional descriptors of limited value

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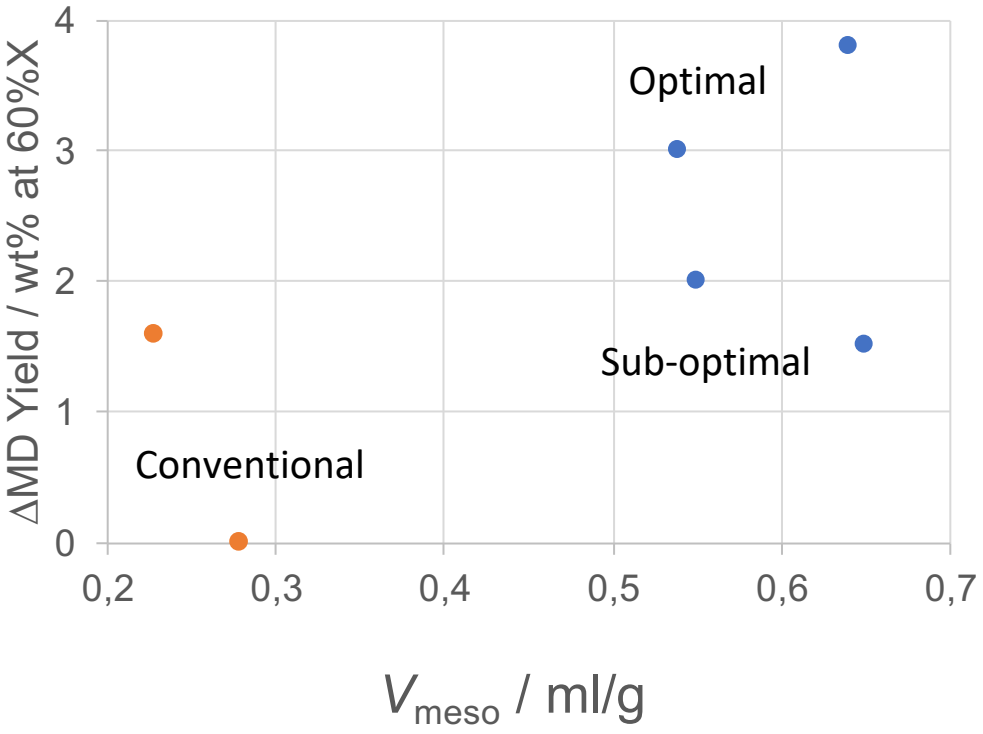

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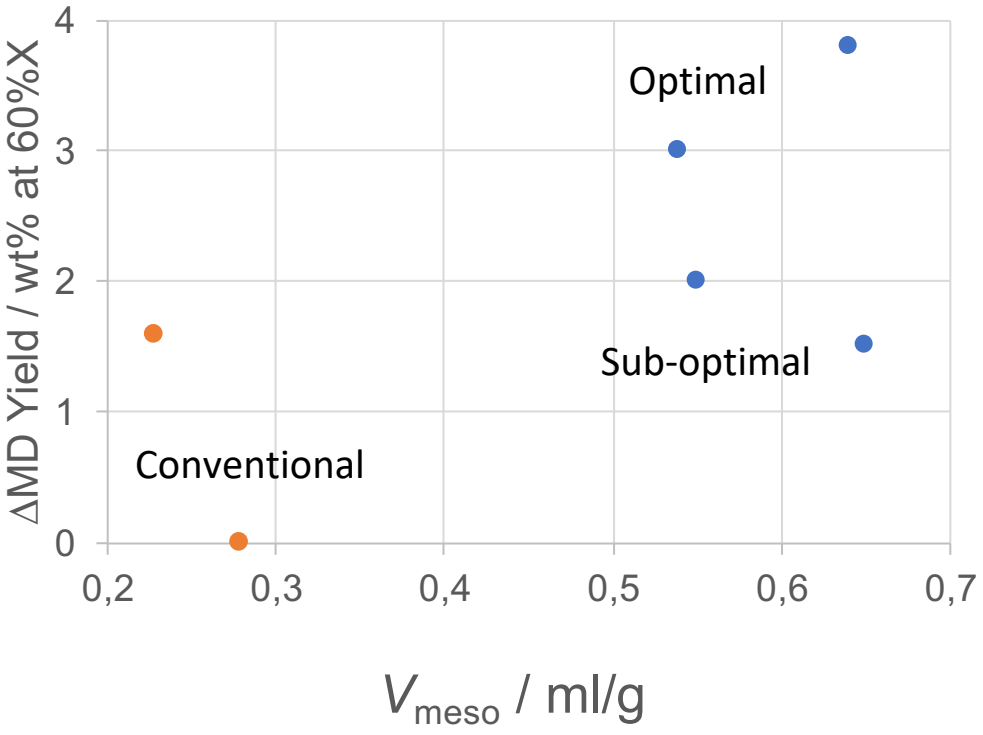
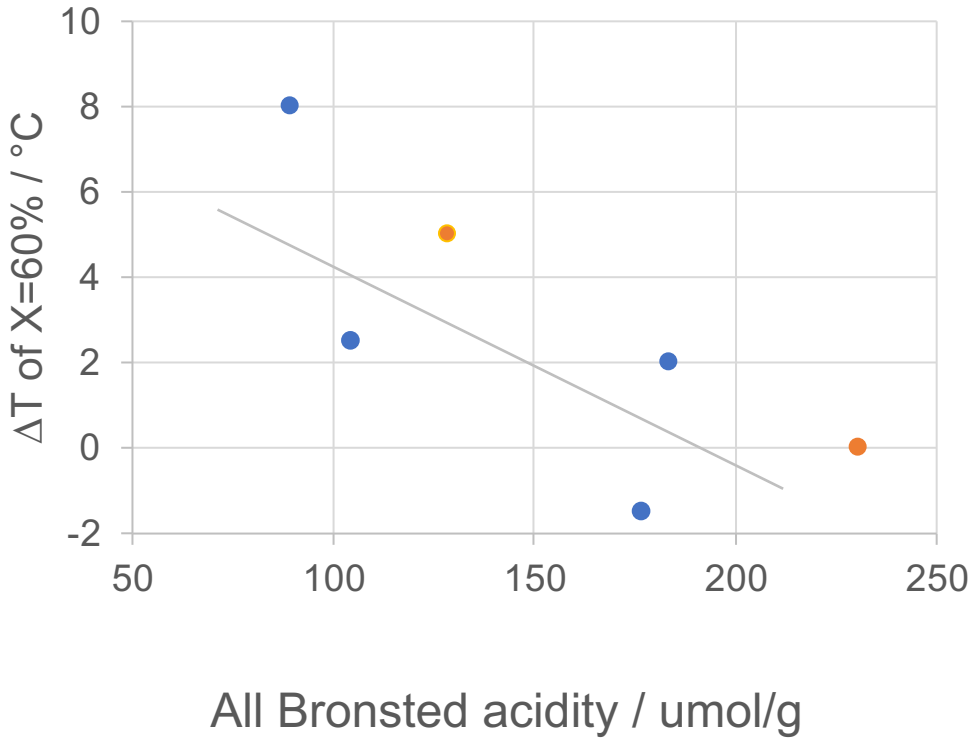




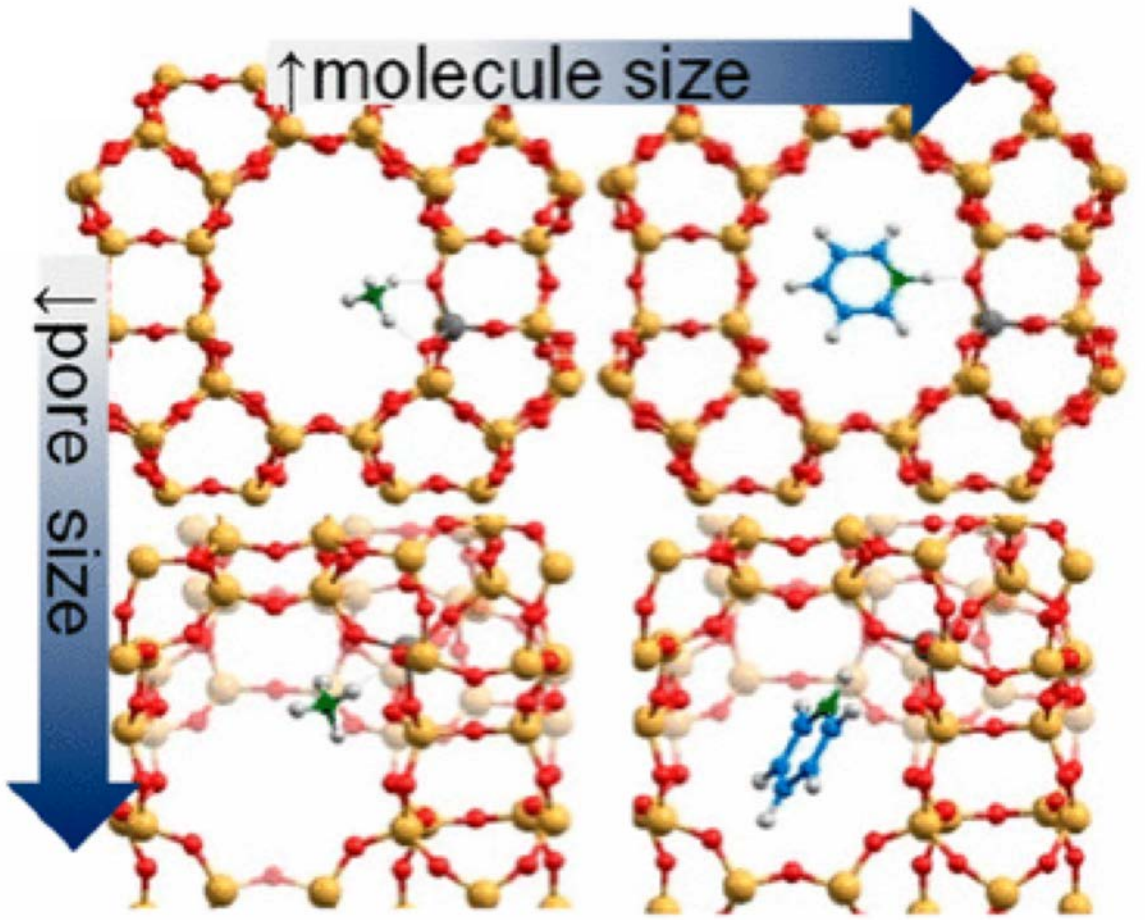
Need for better understanding

Advanced acidity analysis

ACS Catal. 2019, 9, 1539−1548

Zeolite acidity: a complicated reality

- Type of zeolite
- Type of probe molecule
- Bronsted vs Lewis
- Static vs dynamic
- Sample preparation
- Powder vs catalyst



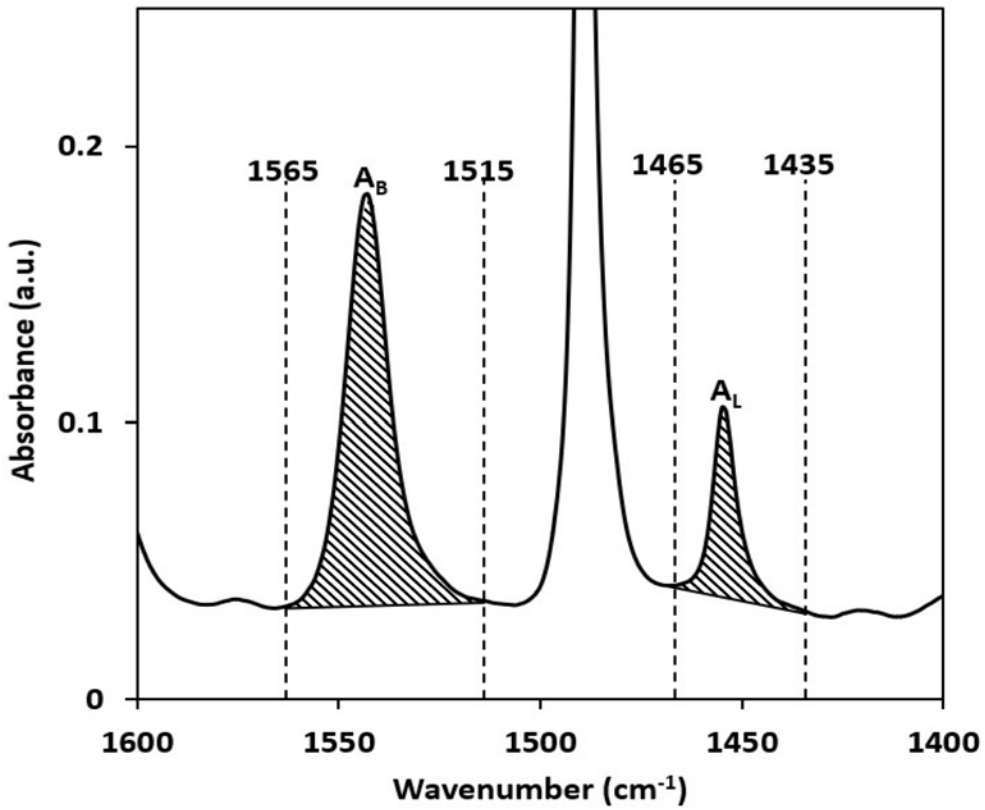
Journal of Catalysis 385 (2020) 52–60

Zeolite acidity: potential of pyridine sorption

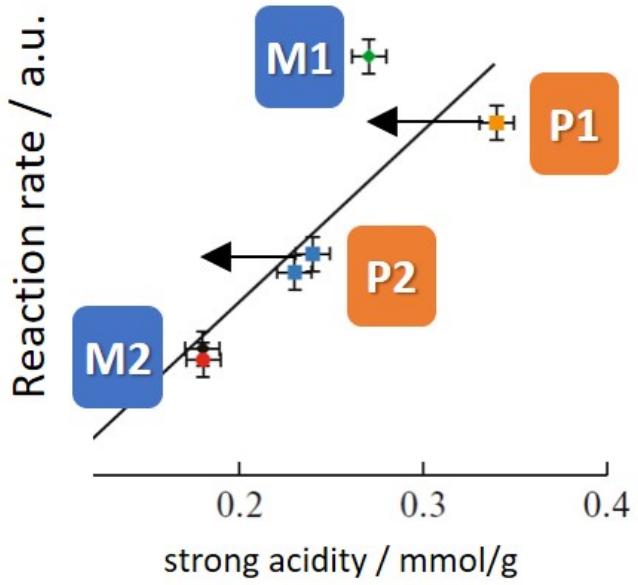
- Type of zeolite
- Type of probe molecule
- Bronsted vs Lewis
- Static vs dynamic
- Sample preparation
- Powder vs catalyst

FTIR pyridine spectroscopy:

- Quantity
- Type: Lewis vs Bronsted
- Strength



Known mesoporization yields reduced acid strength



doi.org/10.1134/S0965544120040180

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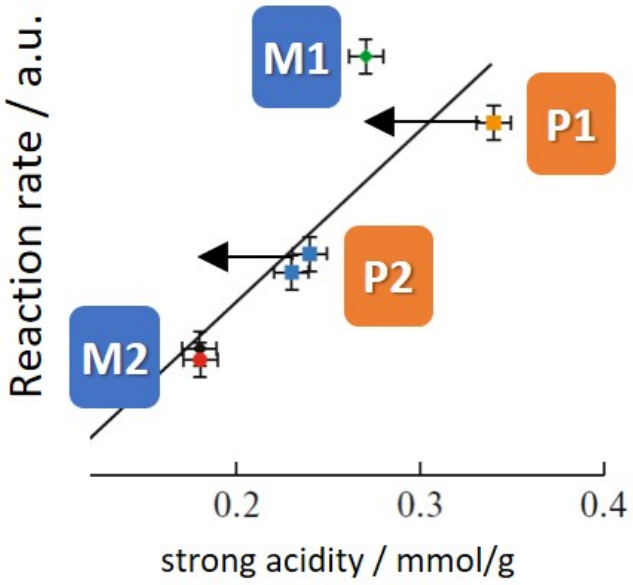

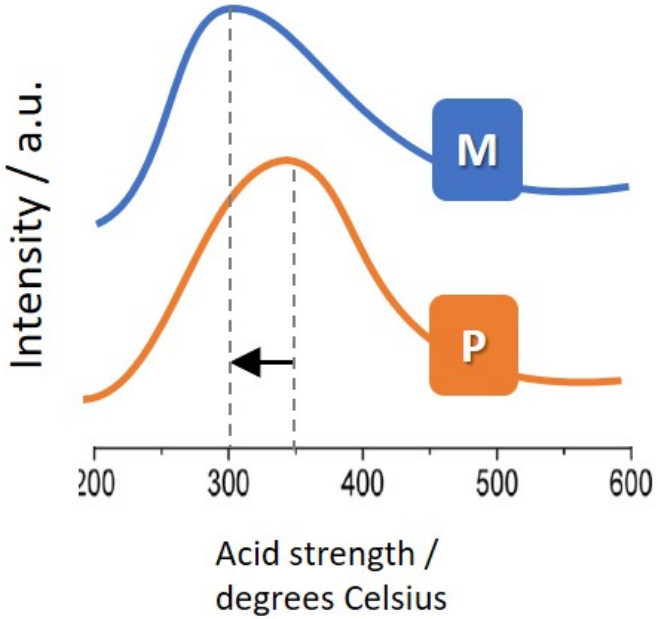

doi.org/10.1134/S0965544120040180

doi.org/10.1021/cs5017694

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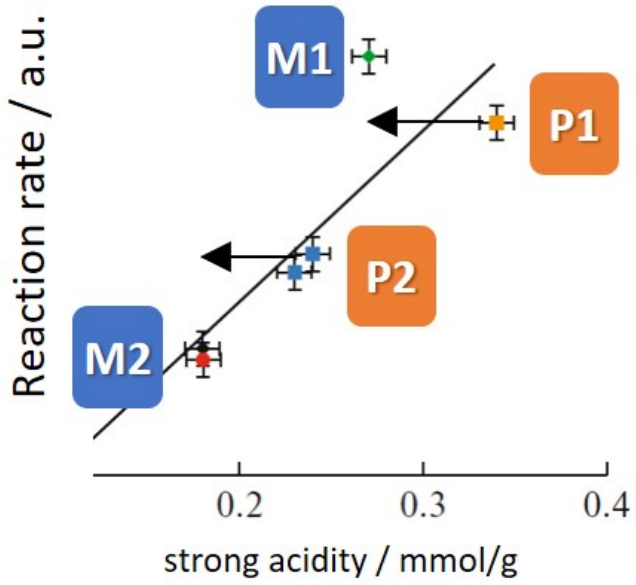
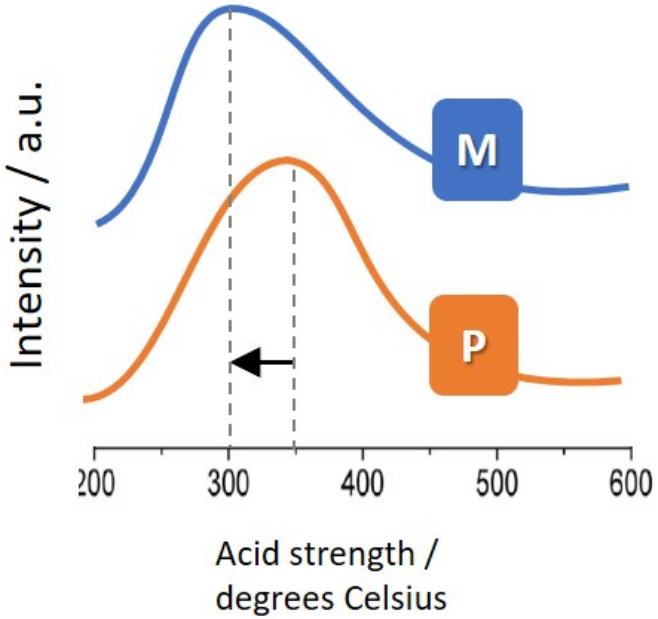
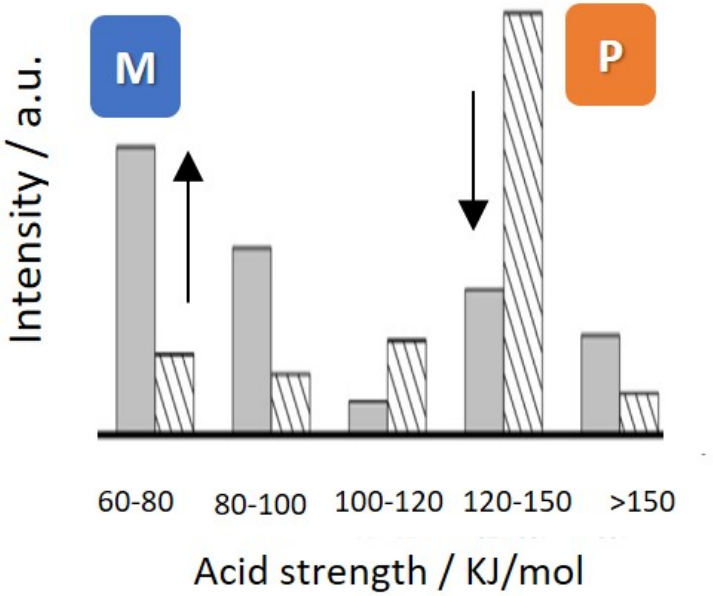






doi.org/10.1134/S0965544120040180

doi.org/10.1021/cs5017694

doi.org/10.1016/j.micromeso.2014.04.003

Acid strength key differentiator

Aspect	Parent USY
V_{micro} / %	100
V_{meso} / %	100
All Bronsted acidity umol/g	129
Strong Bronsted acidity umol/g	77

Acid strength key differentiator

Aspect	Parent USY	Mesoporous Sub-optimal
V_{micro} / %	100	80
V_{meso} / %	100	191
All Bronsted acidity umol/g	129	90
Strong Bronsted acidity umol/g	77	36

Strong acidity strongly influenced

Acid strength key differentiator

Aspect	Parent USY	Mesoporous Sub-optimal	Mesoporous optimal
V_{micro} / %	100	80	85
V_{meso} / %	100	191	193
All Bronsted acidity umol/g	129	90	105
Strong Bronsted acidity umol/g	77	36	66

Preservation acid strength: unique Zeopore result

Advanced hydrocracking descriptors

Advanced hydrocracking descriptors

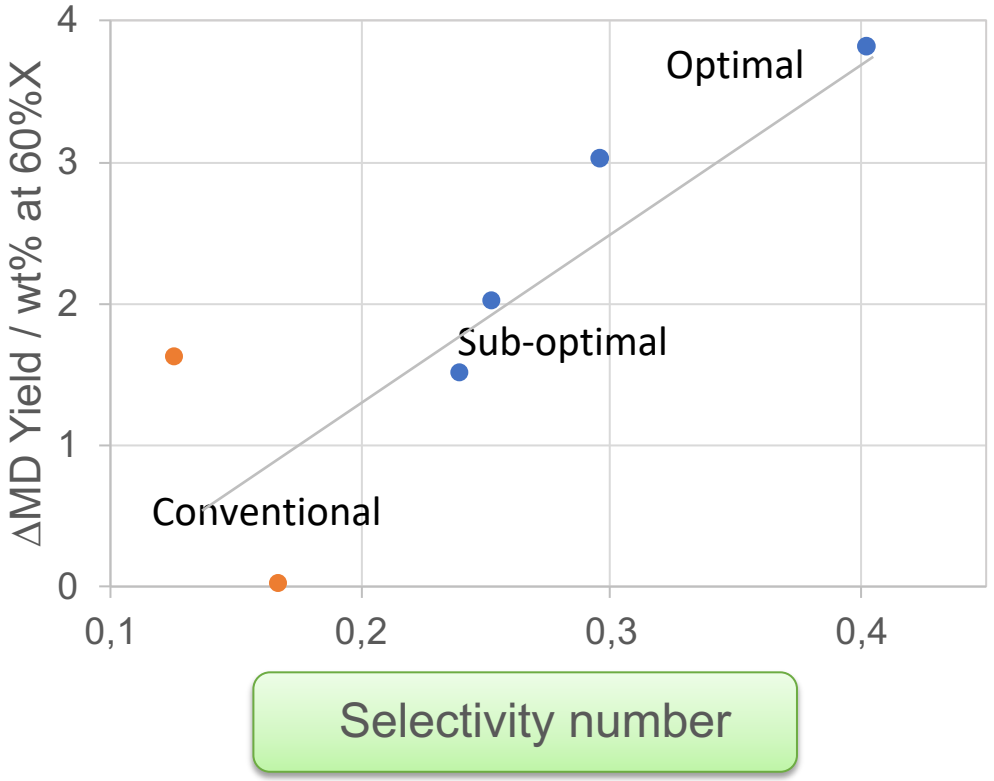
Selectivity number

Mesoporisity and acid strength

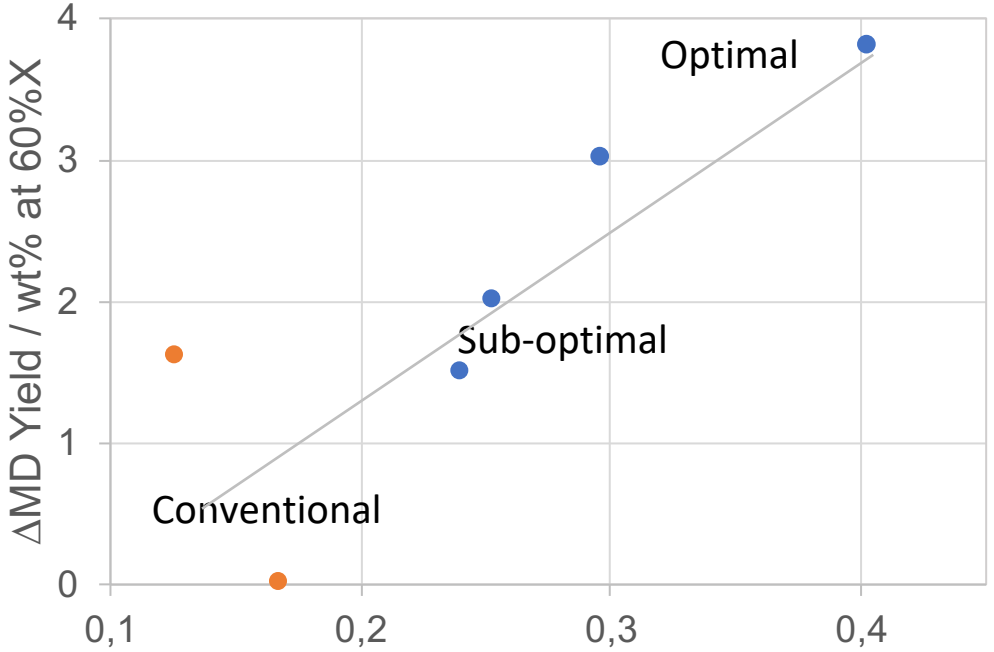
Activity number

Overall acidity and acid strength

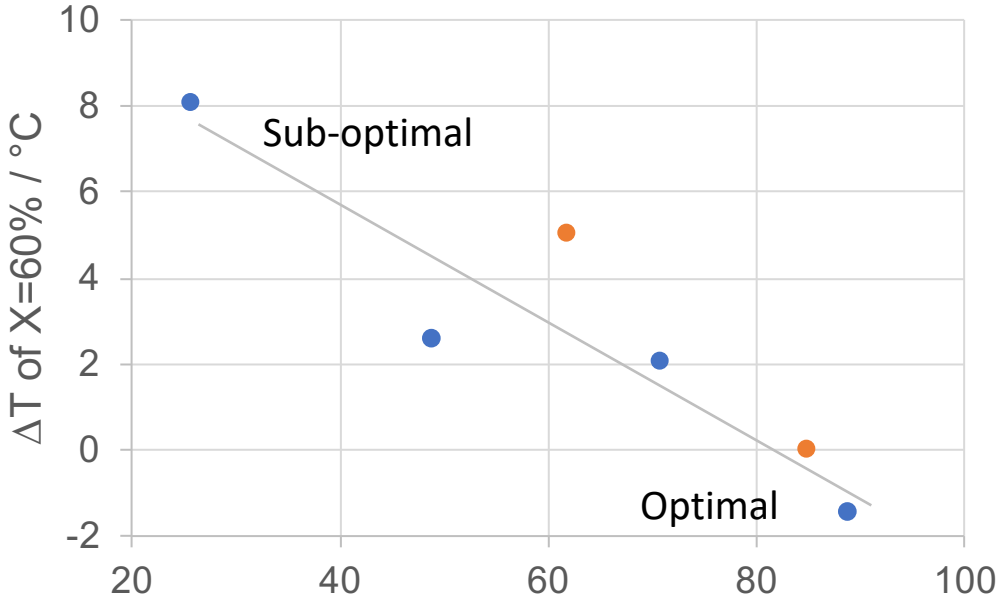
Advanced hydrocracking descriptors



Advanced hydrocracking descriptors



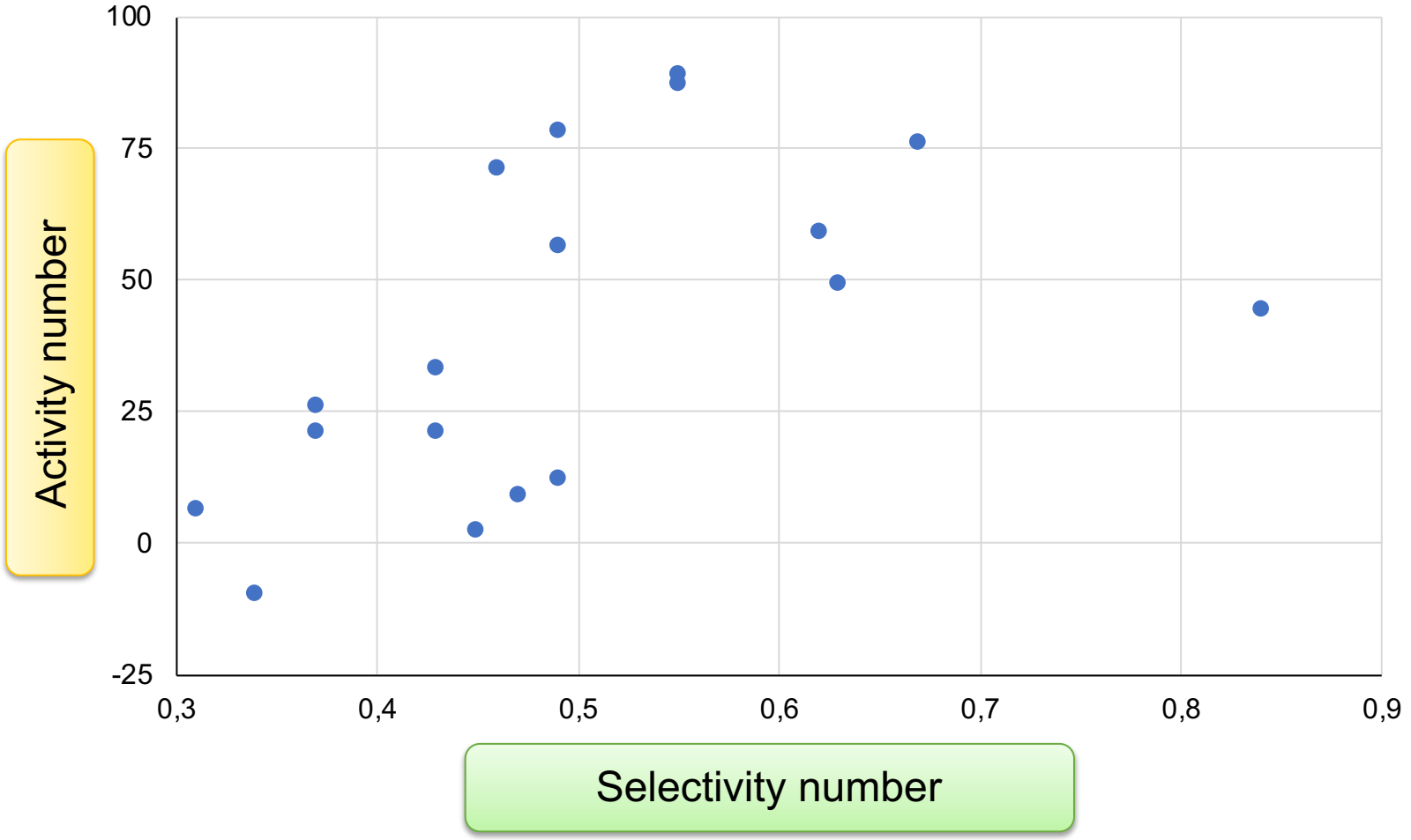
Selectivity number



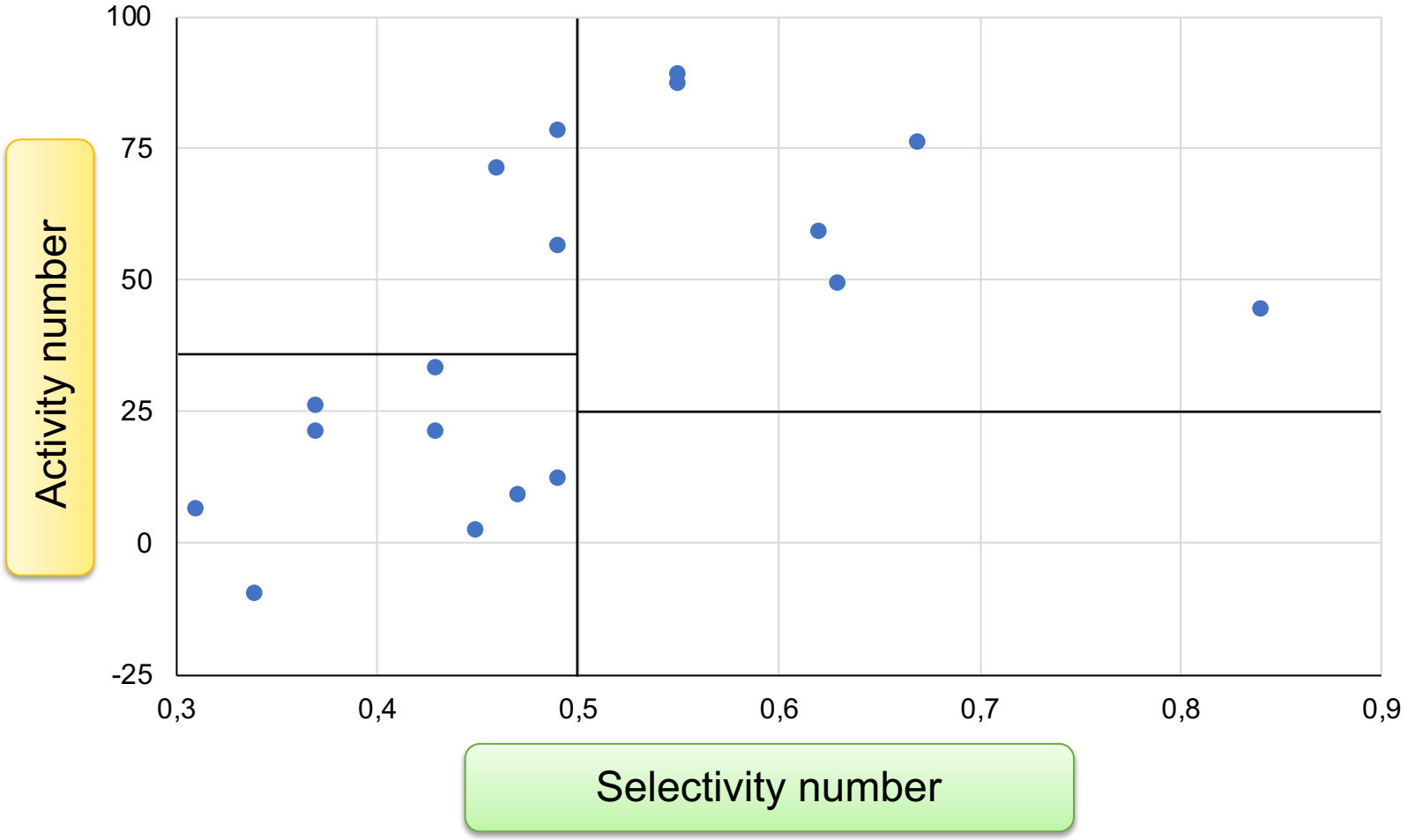
Activity number

Selectivity and activity number relate better to observed performance

Acidity descriptors create performance landscape



Acidity descriptors create performance landscape



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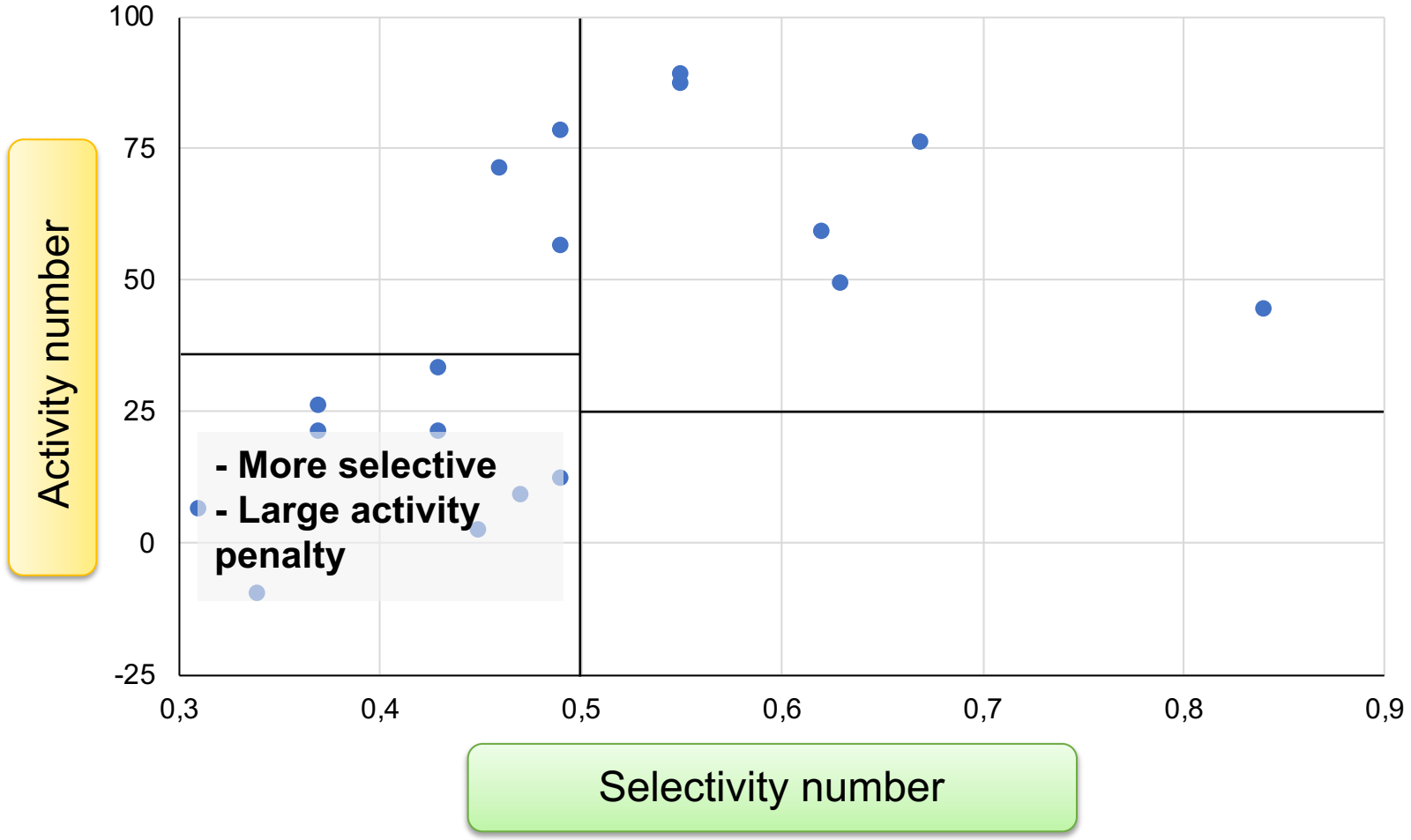
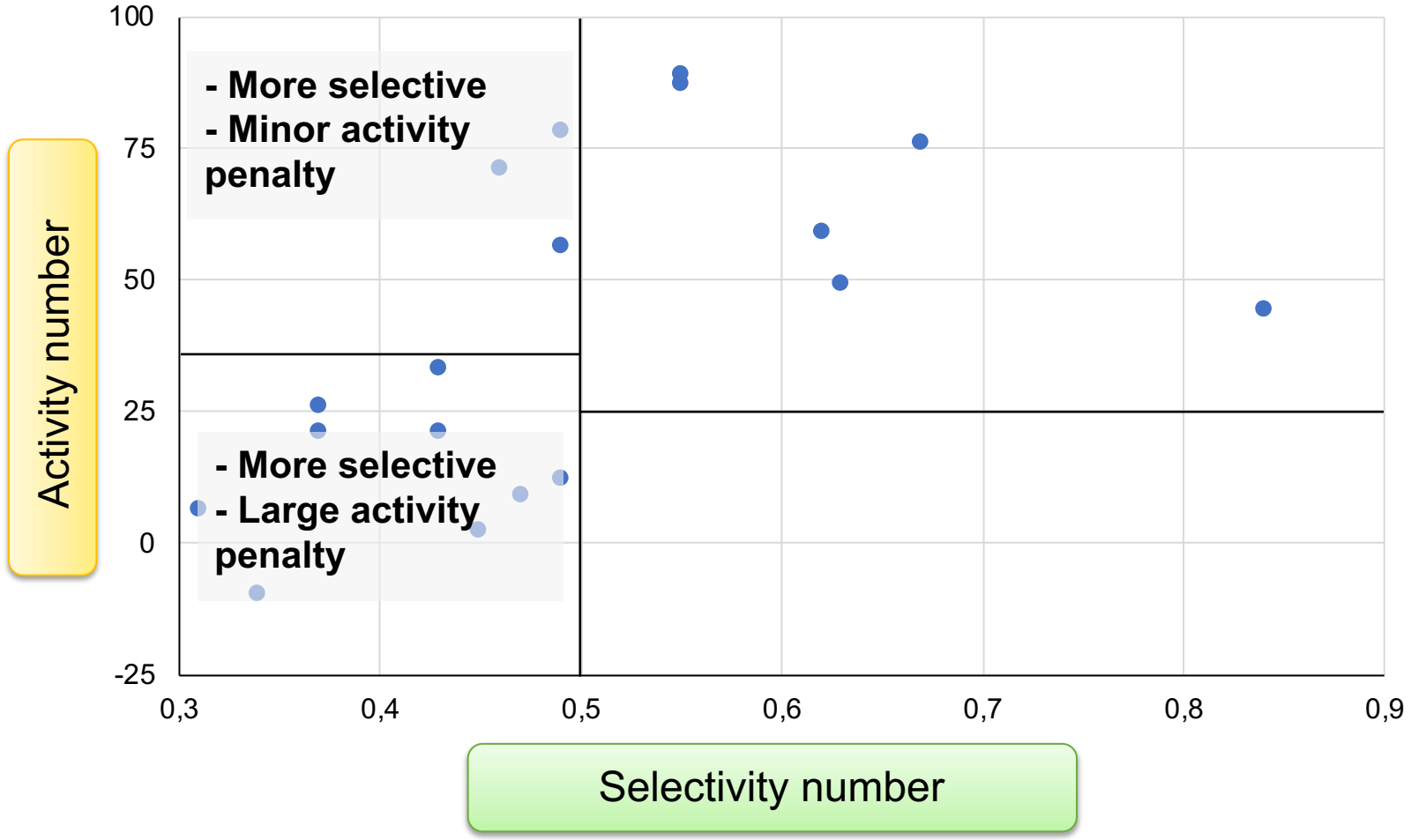
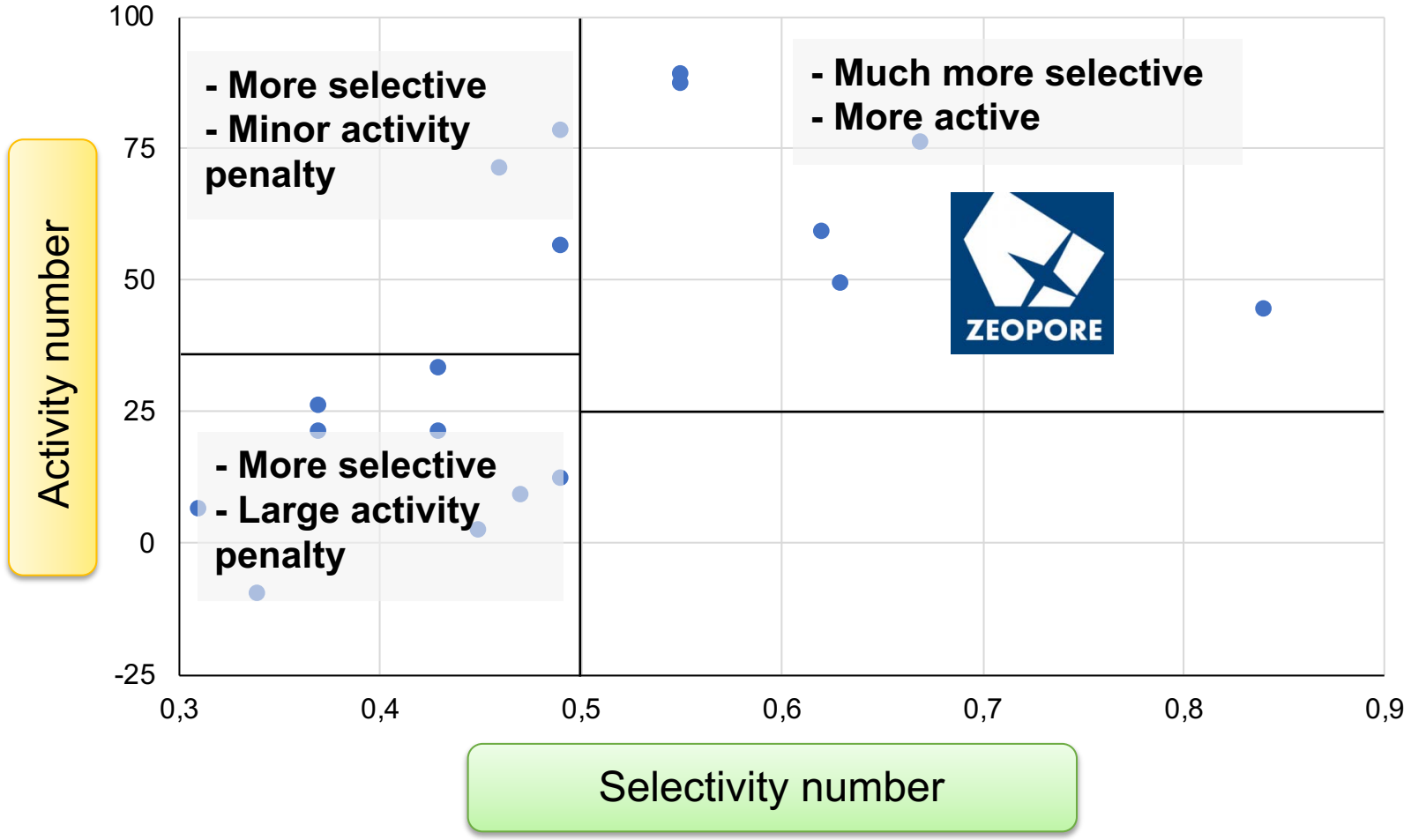


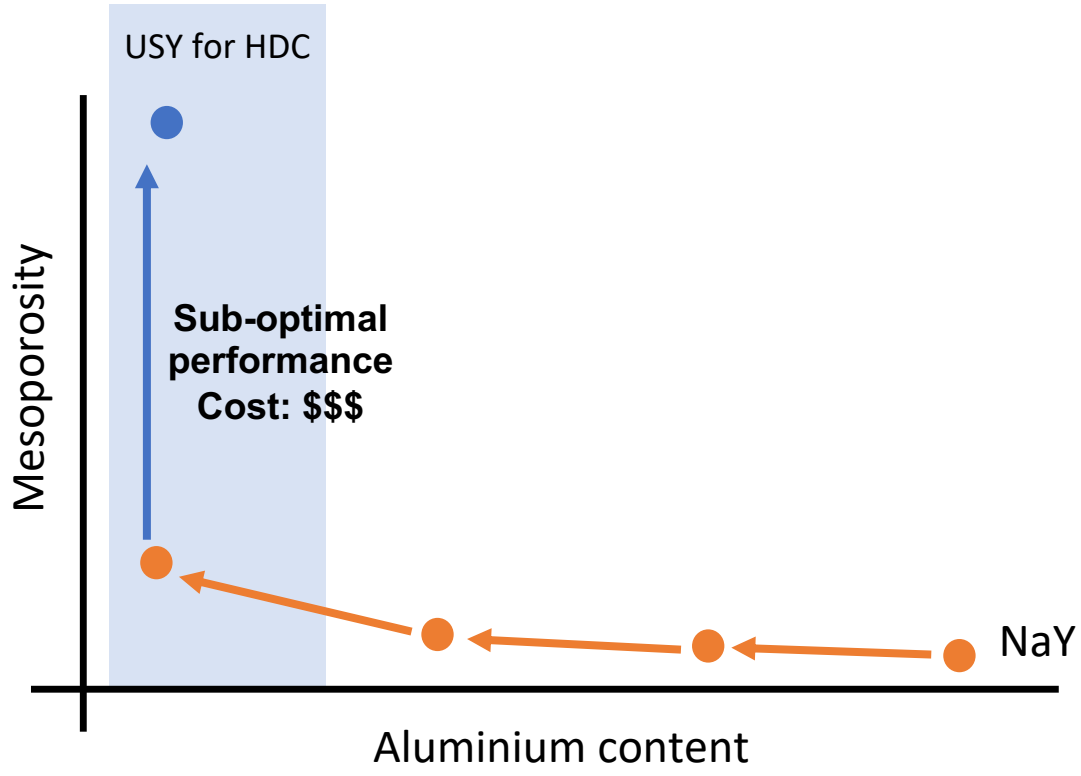
Acidity descriptors create performance landscape



Acidity descriptors create performance landscape



Zeopore enables unique hydrocracking business case



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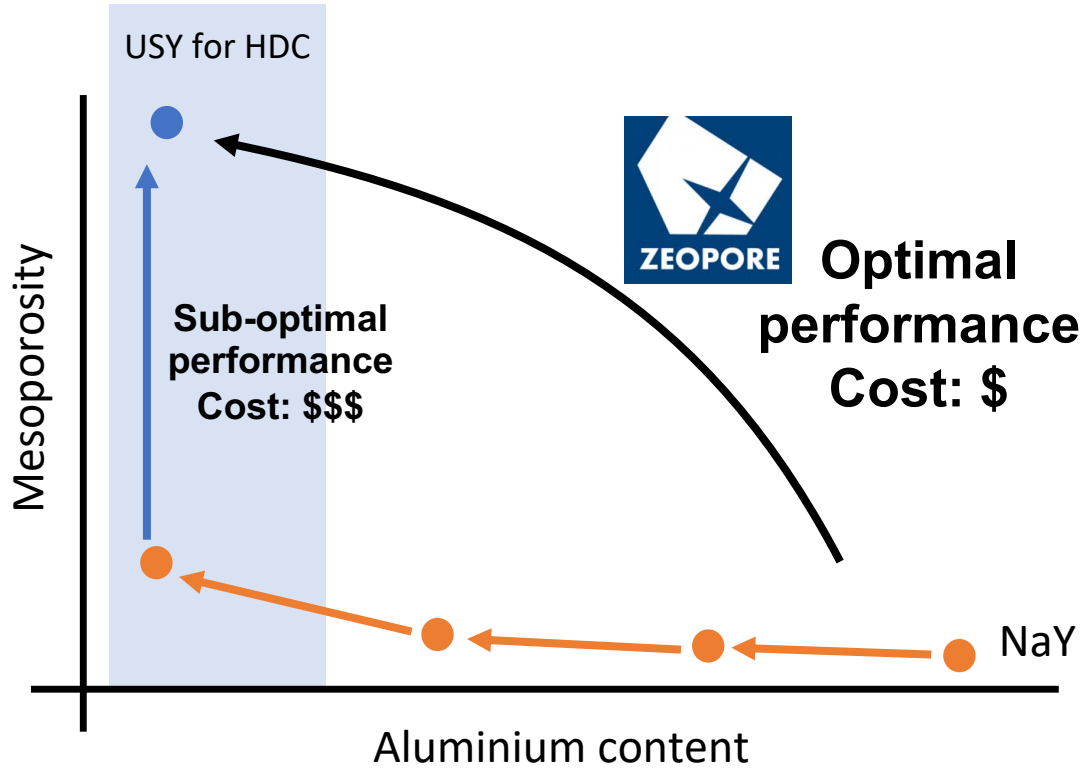
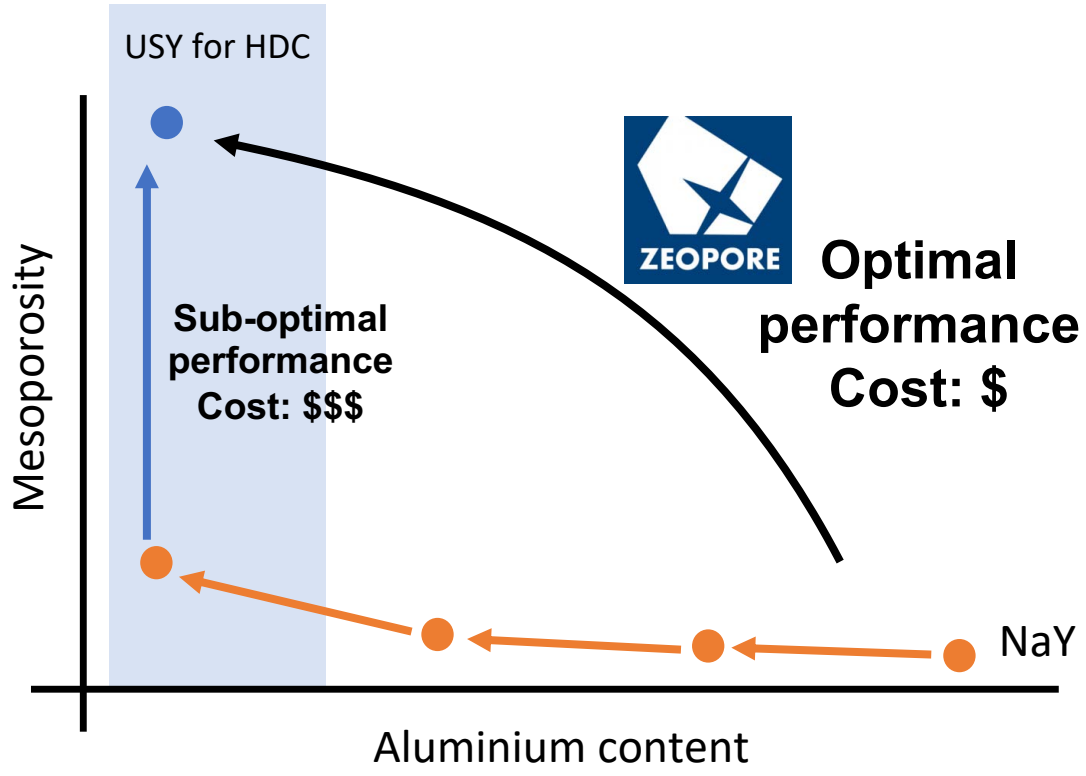
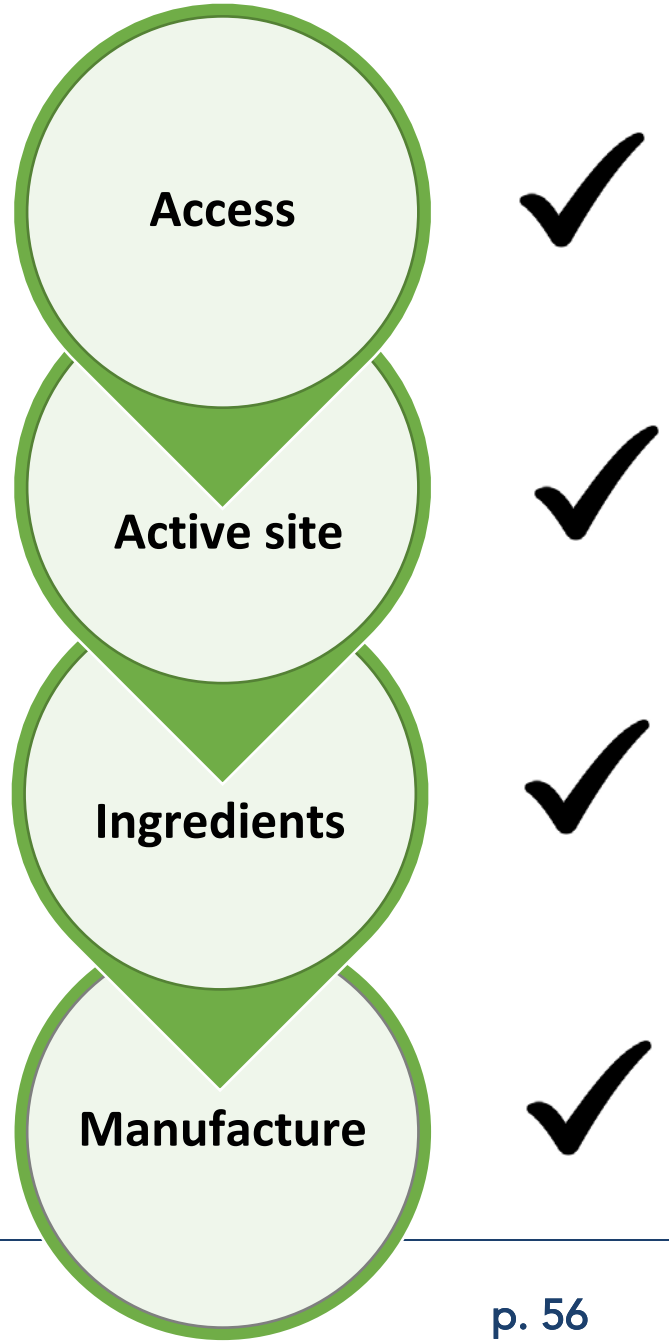


Zeopore enables unique hydrocracking business case





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Customer Validation

Proven Benefits

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Financials

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Q&A session

Thank you!

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