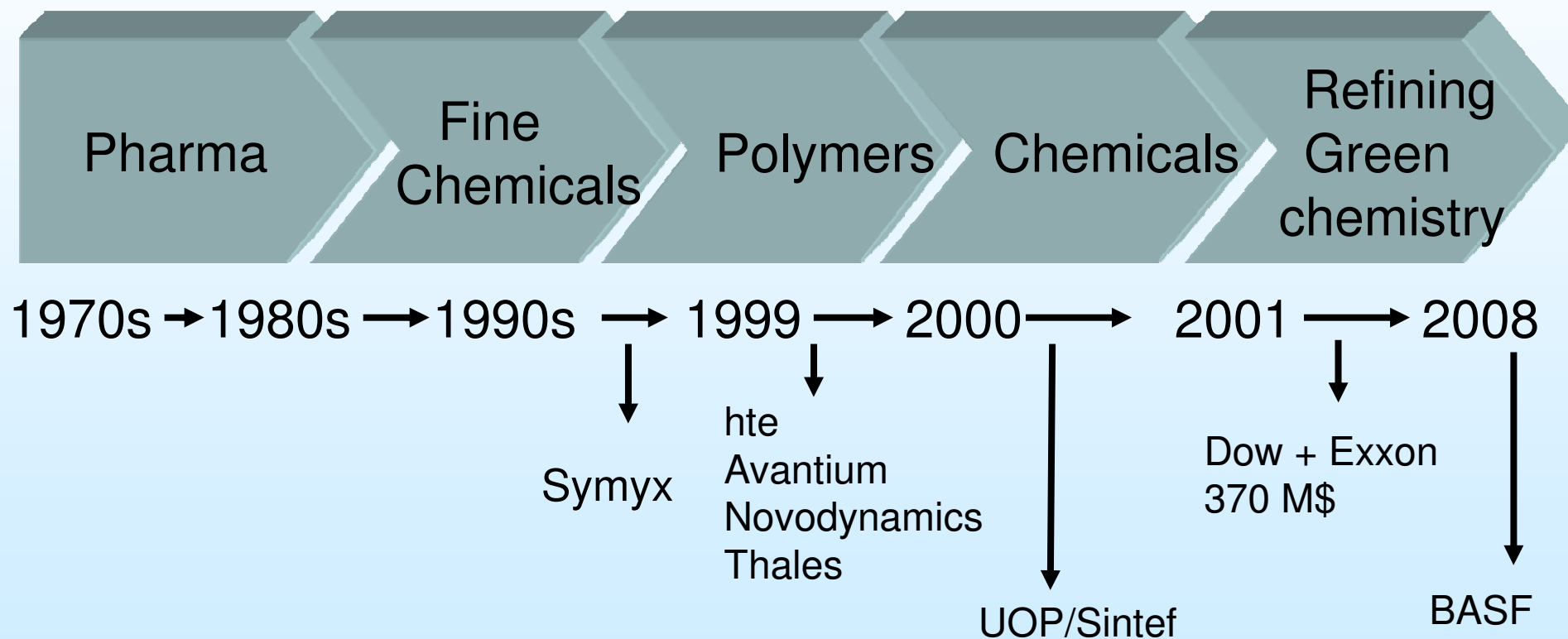


# “Expérimentation haut-débit” Science ou loterie ?

David FARRUSSENG

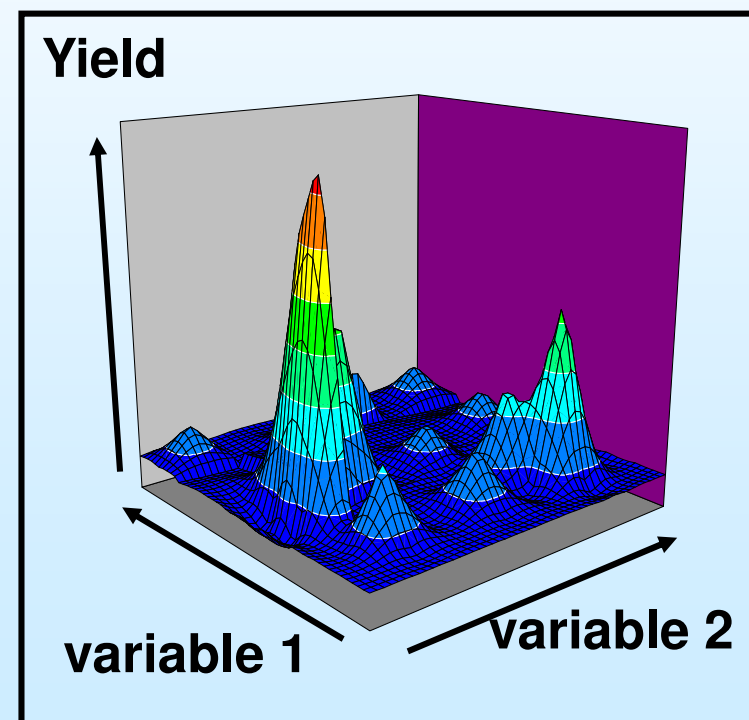
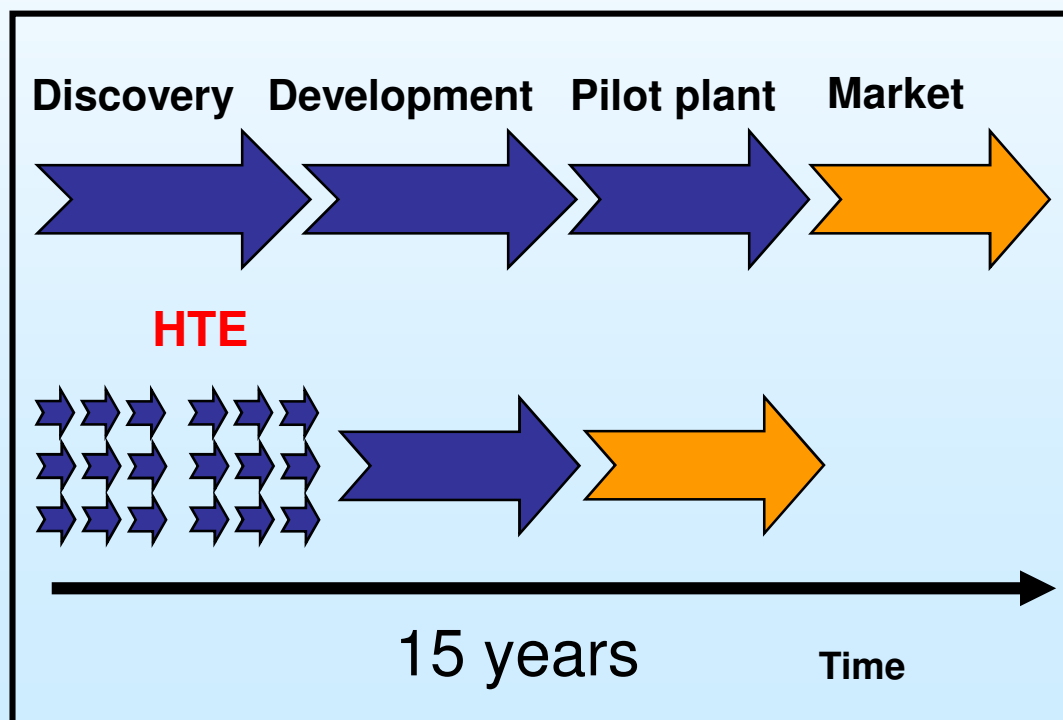
# 10 years of HT Catalysis



*The Catalytic Group Resources,  
JJ Murphy, Combicat2002 Europe,  
Lisbon, April 11-12, 2002*

# Why HT experimentations ?

- To shrink time-to-market
- To increase discovery rates



# Discovery of NH<sub>3</sub> synthesis catalyst in 1903

- 2.500 catalysts and 6.500 experiments within 5 years



“Systematic investigation of the periodic table”

1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110								
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun								
58	59	60	61	62	63	64	65	66	67	68	69	70	71				
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
90	91	92	93	94	95	96	97	98	99	100	101	102	103				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

- Highly complex formulation (ICI 35-4)

Fe<sub>3</sub>O<sub>4</sub>, 0.8% K<sub>2</sub>O, 2% CaO, 0.3% MgO, 2.5%Al<sub>2</sub>O<sub>3</sub>, 0.4%SiO<sub>2</sub>, traces of TiO<sub>2</sub>, ZrO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>

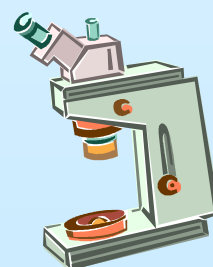
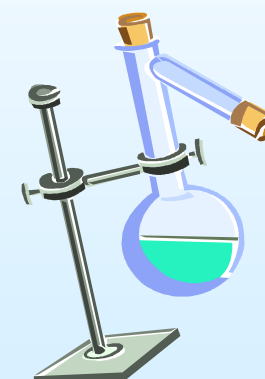
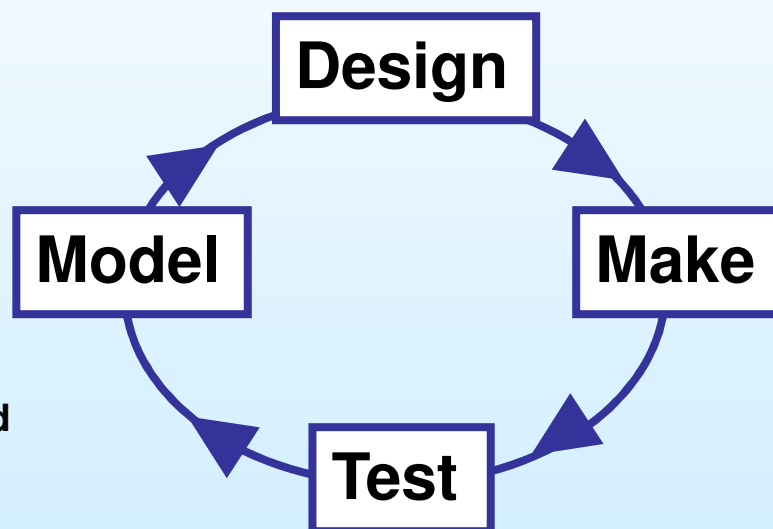
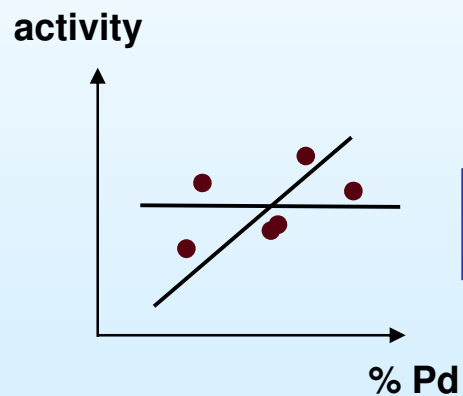
- Rapid dissemination of this empirical oriented approach 4/20

# Rational approach



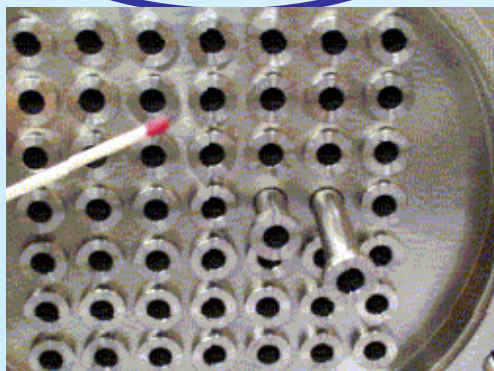
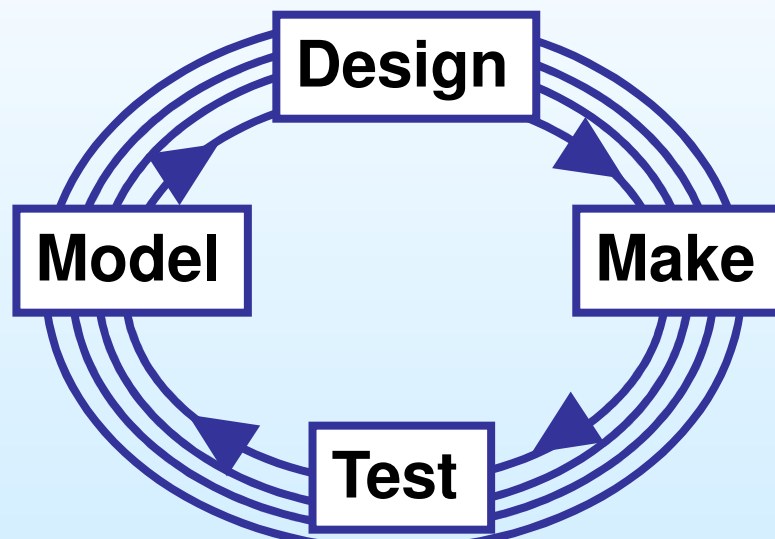
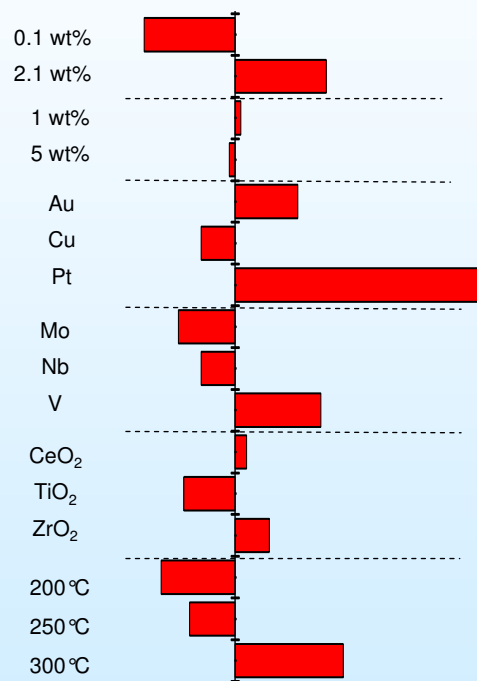
temperature,  
solvent, composition,  
pressure,...

→ composition

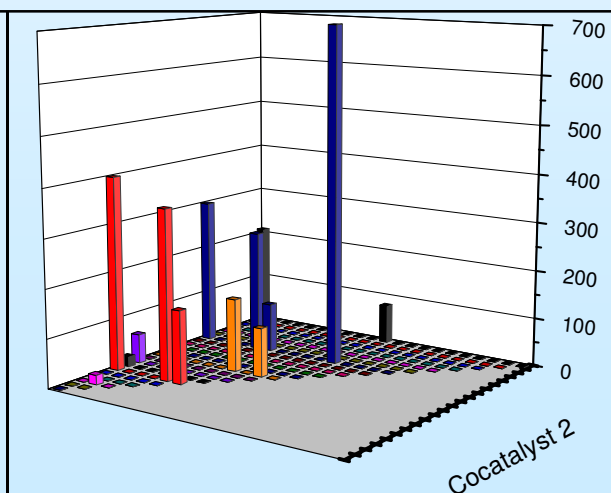
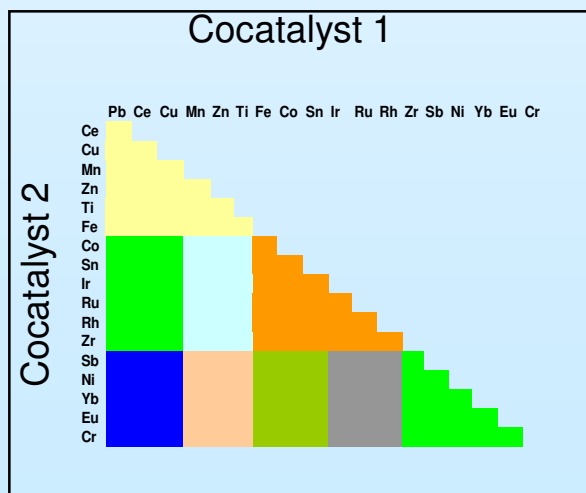
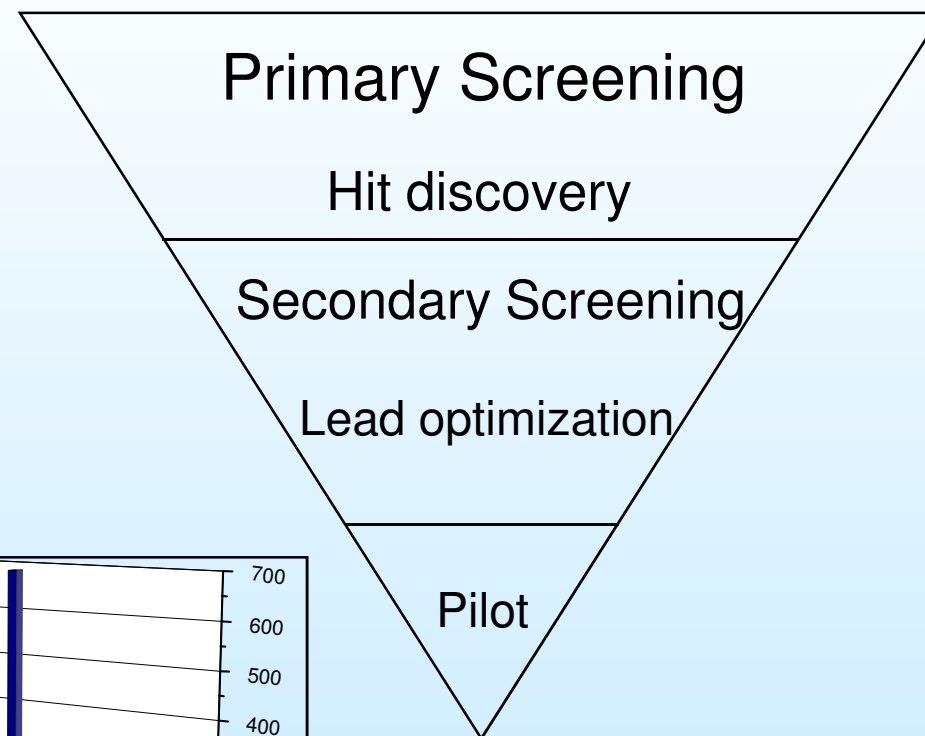
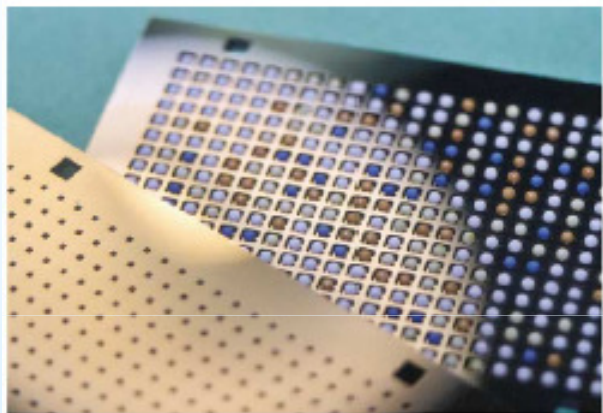


# HT & multivariate approach

temperature,  
solvent,  
composition,...

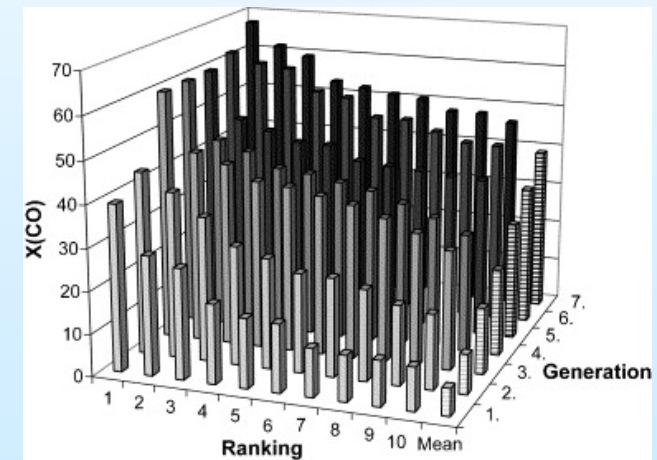
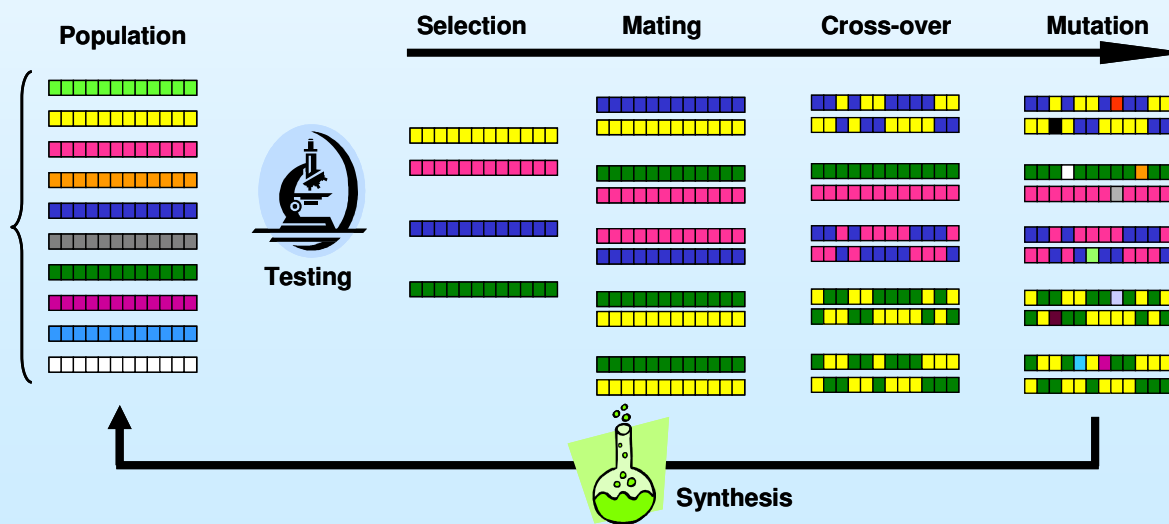
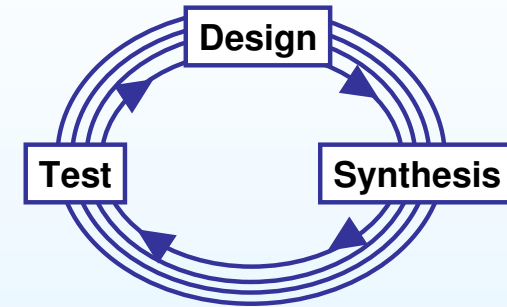


# The combinatorial approach



# The evolutionary approach

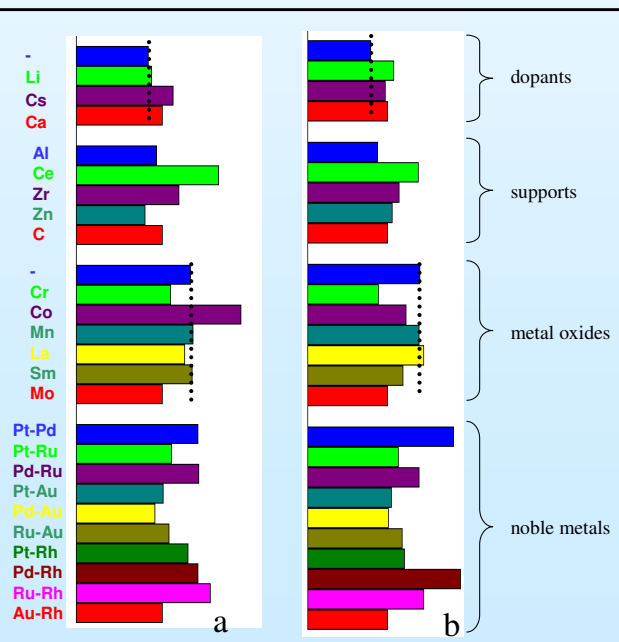
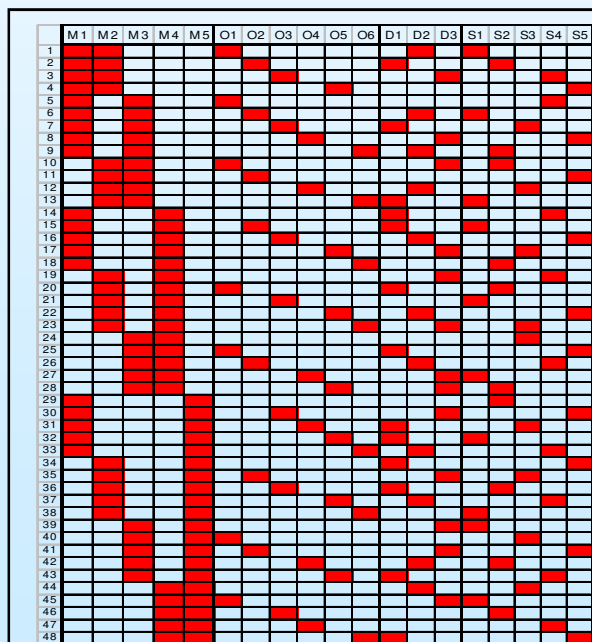
- Combining discovery & optimization
- Exploration & exploitation





# How can HTE generate Knowledge ?

- Quantification of the variable effects on performances
- Maximising knowledge gain while minimizing trials
- DoE : Selox case study



3 alkalis  
 5 supports  
 6 oxides  
 10 metallic binaries



# Issues of library design in Catalysis

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- FAQs

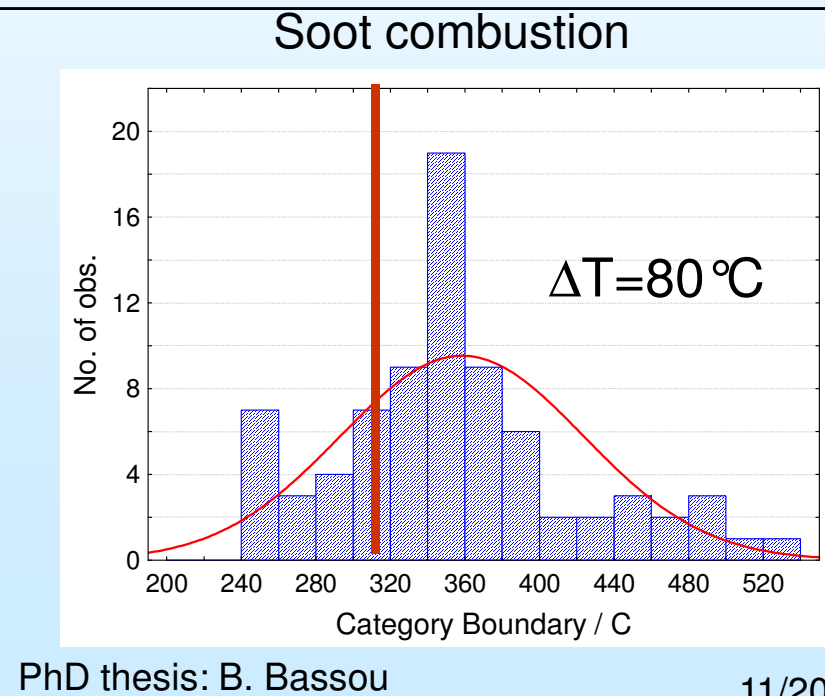
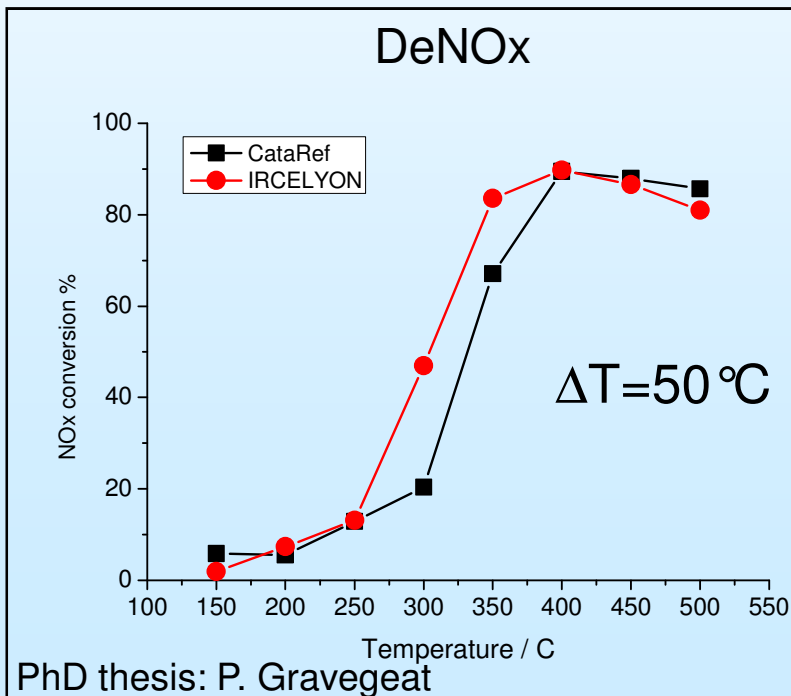
- Which is the best algorithm ?
- How reliable is the methodology ?
- How many experiments shall be performed to solve my problem ?
- How to handle experimental errors ?
- How to get clear information although all parameters are varied ?
- What is the most relevant 101<sup>th</sup> experiments to perform ?

F. Clerc et al *Review of Scientific Instrument*, **2005**, 76, 062208

D. Farrusseng et al , *Appl. Surf. Sci.*, **2007**, 254, 772

# Success stories

- D. Farrusseng, *Surface Sciences Reports*, **2008**, *in press*.
- IRCELYON: exhaust car applications
  - HT discoveries -> pilot tests
  - Microkinetic investigations



# Rational selection of samples



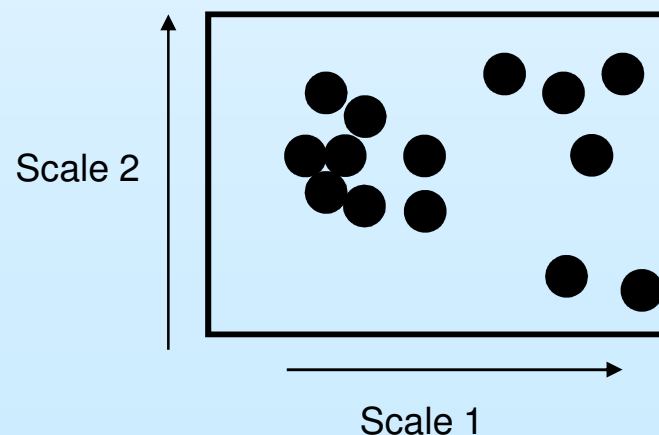
100-1000 samples

How ?



5-10 samples

- Bank of catalyst
  - Uncompleted characterization
  - Inconsistent methods
  - Missing data
- How to quantify diversity in a library of “diverse” catalysts ?

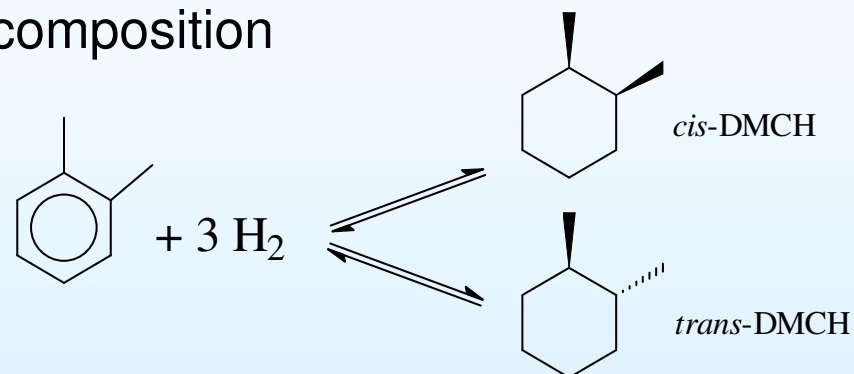


# Hydrogenation properties of bifunctional catalysts

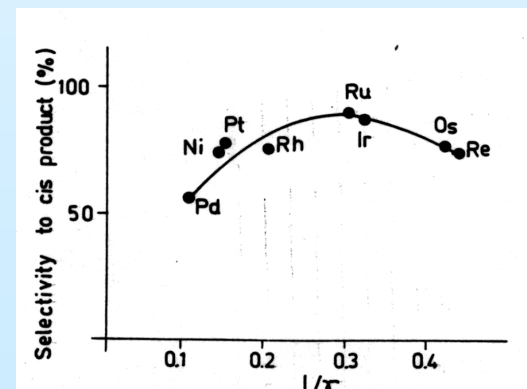
- Hydrogenation of o-xylene
- Activity: highly sensitive to metallic composition

Catalysts	Hydrogenation rate ( $10^{-3}$ mol.h <sup>-1</sup> .g <sup>-1</sup> )
Pt	230
Pt <sub>0.5</sub> Pd <sub>0.5</sub>	30
Pt <sub>0.5</sub> Ge <sub>0.5</sub>	10
Pd	4

Guillon *et al.* Cat. Today 65(2001)



- Selectivity : sensitive to “electrophilic” features
  - Selectivity correlated to “calorific capacity of cond. e”
  - Electronic density of Fermi level  $D(\varepsilon F)$



# « Semi-empirical » model

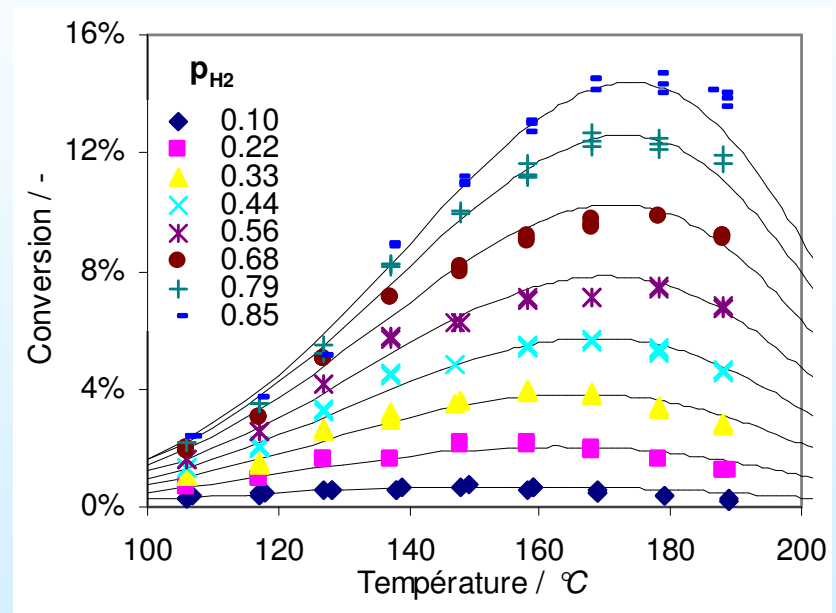
- Langmuir based model
  - H<sub>2</sub> dissociate adsorption
  - Competitive adsorption
  - Fast product desorption

$$r_i = A_i e^{-\frac{E_i}{RT}} \frac{K_{oX} p_{oX} (K_{H_2} p_{H_2})^{n_i}}{\left(1 + K_{oX} p_{oX} + \sqrt{K_{H_2} p_{H_2}}\right)^2}$$

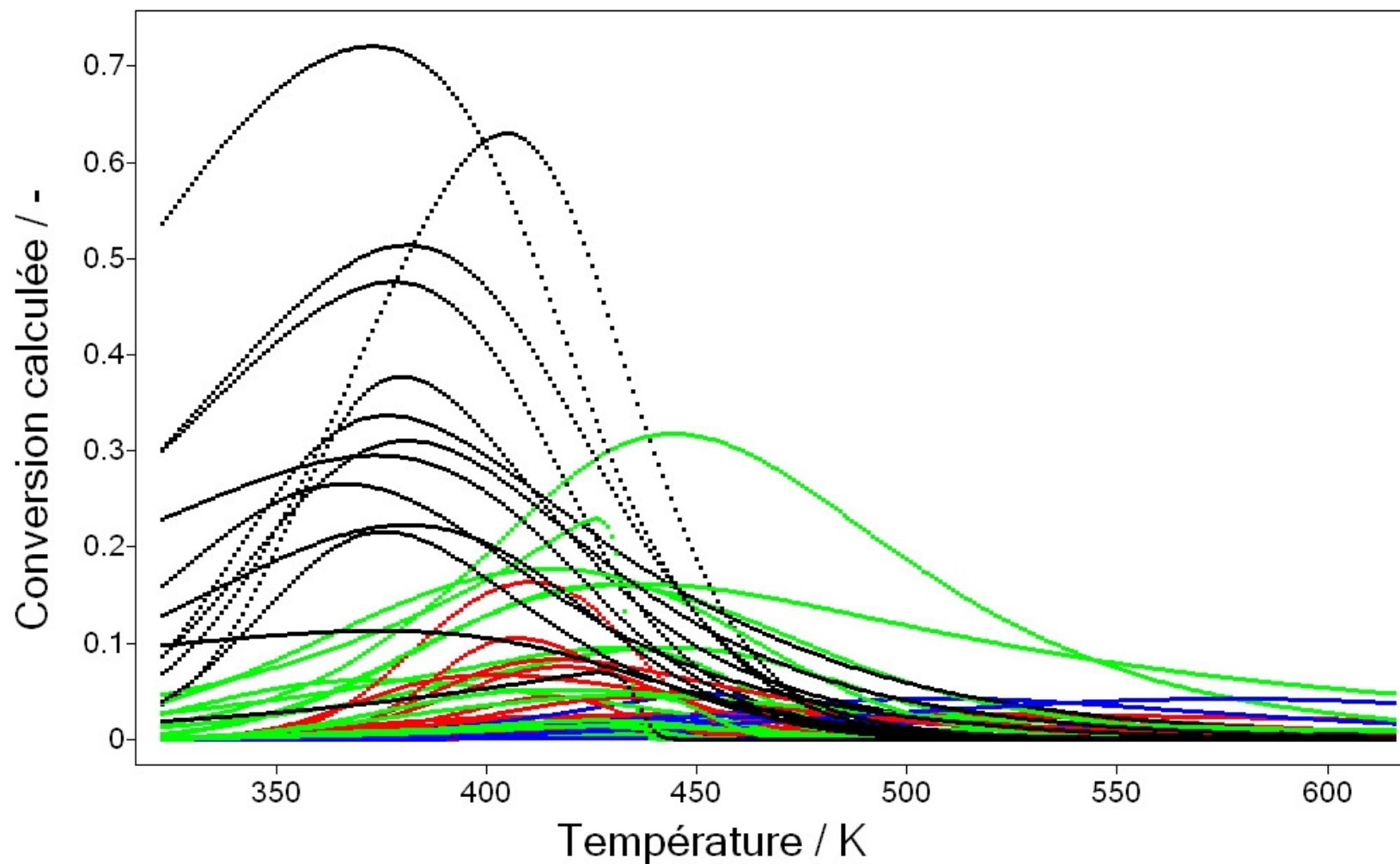
Where  $i = cis$  or  $trans$

- 10 parameters
  - 8 « physico-chemical » ( $E_a$ ,  $A$ ,  $\Delta H_{ads}$ ,  $\Delta S_{ads}$ )
  - 2 semi-empirical ( $n_{cis}$ ,  $n_{trans}$ )

Reference catalyst 0.3%Pd/Al<sub>2</sub>O<sub>3</sub>



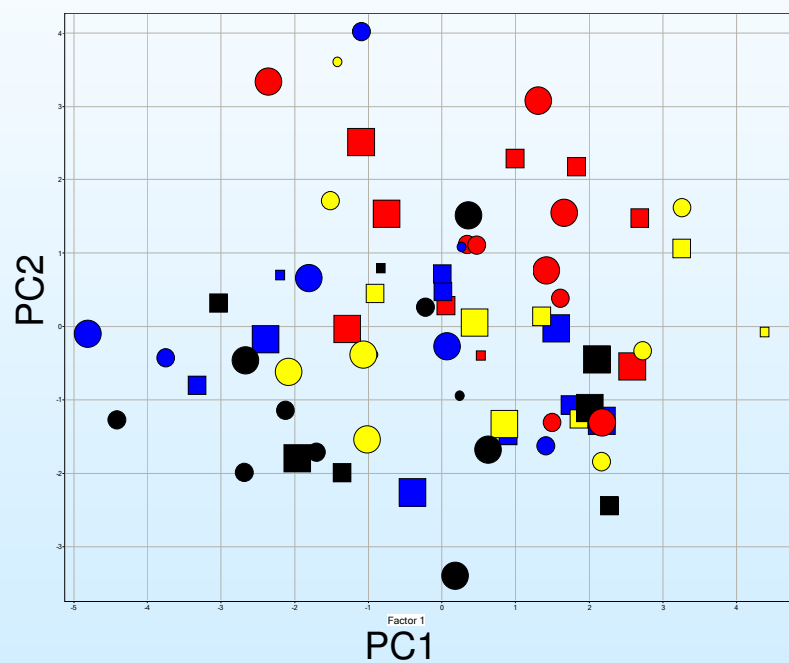
# Hydrogenation profile visualization



■ Pd ■ Ni ■ Pt ■ Rh

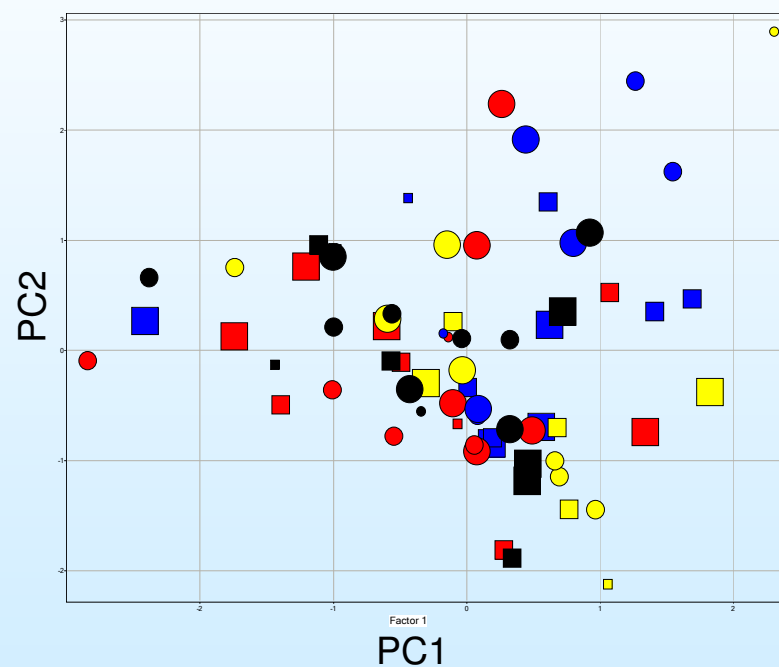
# Catalyst mapping

- 2D activity plot



- Distance = diversity quantification
- High effects of doping and supports
- Rational selection

- 2D selectivity plot

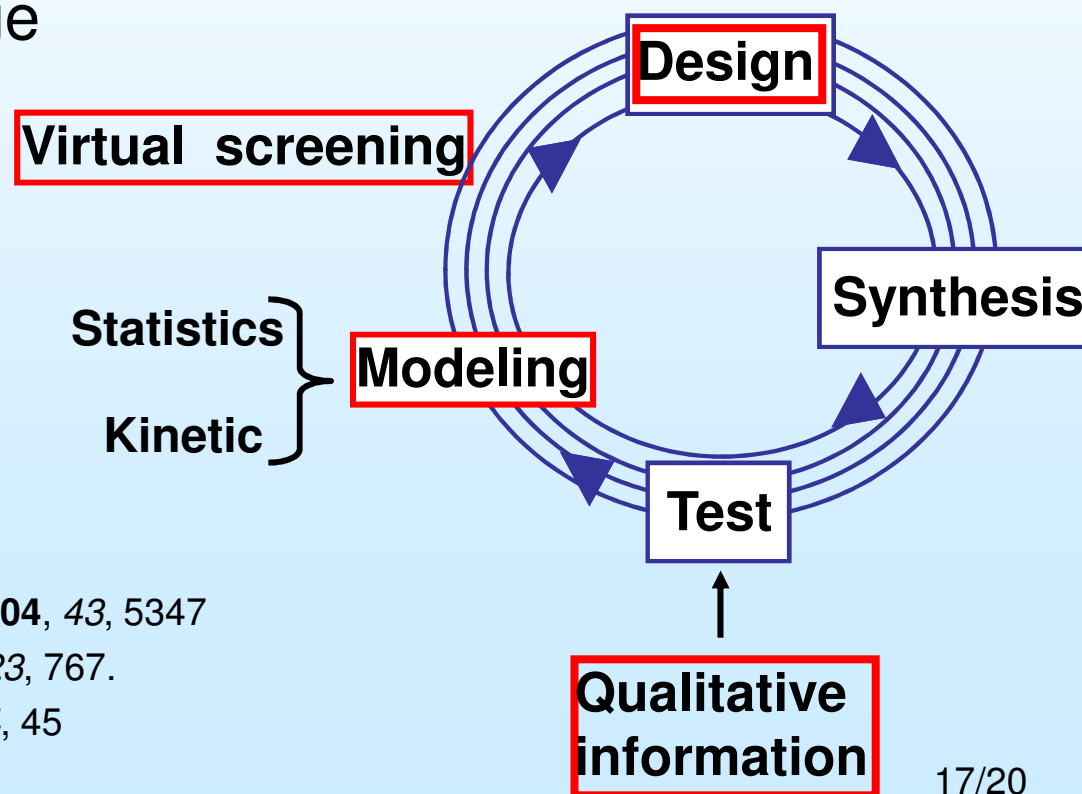


Ni Pd Pt Rh  
□  $\delta$ -Al<sub>2</sub>O<sub>3</sub>  
○  $\alpha\theta$ -Al<sub>2</sub>O<sub>3</sub>



# Conclusions

- To Maximize information by mastering sample diversity
- To capture information
- To generate knowledge



C. Klanner et al *Angew. Chem.-Int. Edit.*, **2004**, 43, 5347

L. Baumes, et al *QSAR Comb. Sci.*, **2004**, 23, 767.

S. Pereira et al *QSAR Comb. Sci.*, **2005**, 24, 45

G. Morra et al *Chem. Eng. J.*, **2008**, 379

# Conclusions

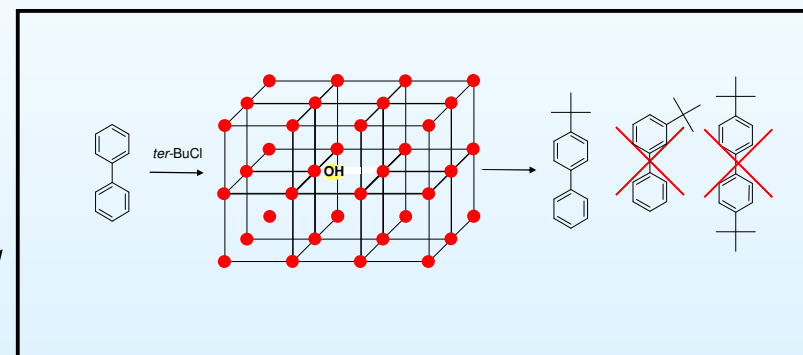
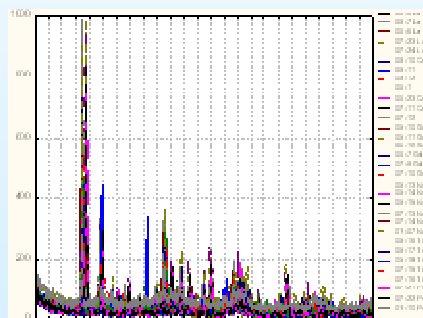
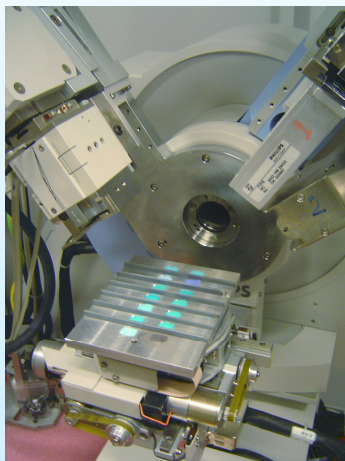
- Concept development
  - Diversity management for material optimization
  - Knowledge discovery by modeling (kinetic & QSAR)
- Tool development
  - SWITCH-16 for HT transient characterization and screening
  - OptiCat, e-library design platform
- New paradigm in HT Catalysis ?  
INTEGRATION OF:
  - Molecular modeling (DFT,QM, MM...)
  - Quantitative screening & characterization
  - Kinetic modeling
  - Statistical modeling (QSAR)



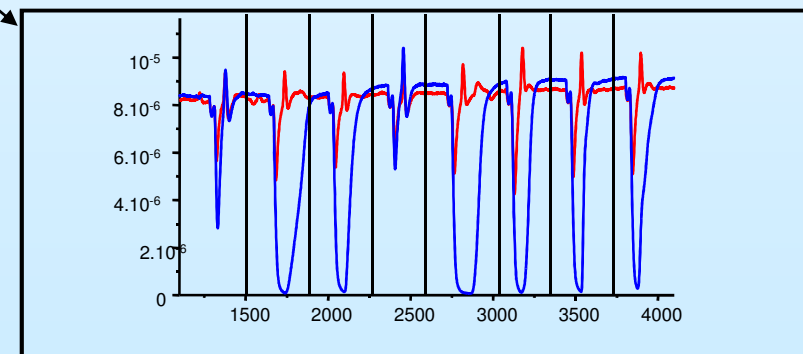
AMTEC GmbH

# Perspectives

- Screening unexplored domains
- MOF : “New” metal-organic molecular sieves



U. Ravon et al *NJC*, **2008**, in press



D. Farrusseng, “Handbook of Catalyst Design”, Wiley, **2008**, in press

# THANKS

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E. Burello



Y. Vauthey, D. Tibiletti, C. Hoffmann, C.  
Klanner, U. Ravon., A. Desmartin-  
Chomel , G. Morra, P. Gravegeat, B.  
Bassou, E. Iojoiu, S. Pereira



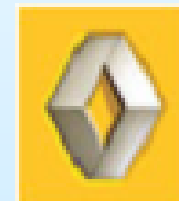
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Dr. G. Rothenberg

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Dr. van der Waal

Dr. S. Morin, Dr. N. Bats



Dr. C. Mirodatos

“Engineering Team”

