Lectures on

Modern Methods in Heterogeneous Catalysis Research

Fritz-Haber Institute of Max-Planck Society

Combinatorial Methods in Catalyst Development By High-Throughput Experimentation

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High-Throughput Experimentation in Synthesis and Testing of Catalytic Performance of Materials

Surface & bulk properties

- Structural properties
- Electronic properties
- Photonic properties

Comprehensive knowledge

Methodology

Instrumental techniques

Data evaluation

Catalytic Materials

- Selection of primary elements
- Preparation
- Testing

Optimized catalyst composition

Science

Application

Table of Content

Methodologies

- **Experimental**
  - Catalyst preparation & testing (sreening)
- **Eperimental Design**
  - Evolutionary Approach (Genetic algorithm) for designing generations of different catalyst compositions
  - Artificial Neural Networks (ANN) for correlating catalytic performance with catalyst properties

Case Studies

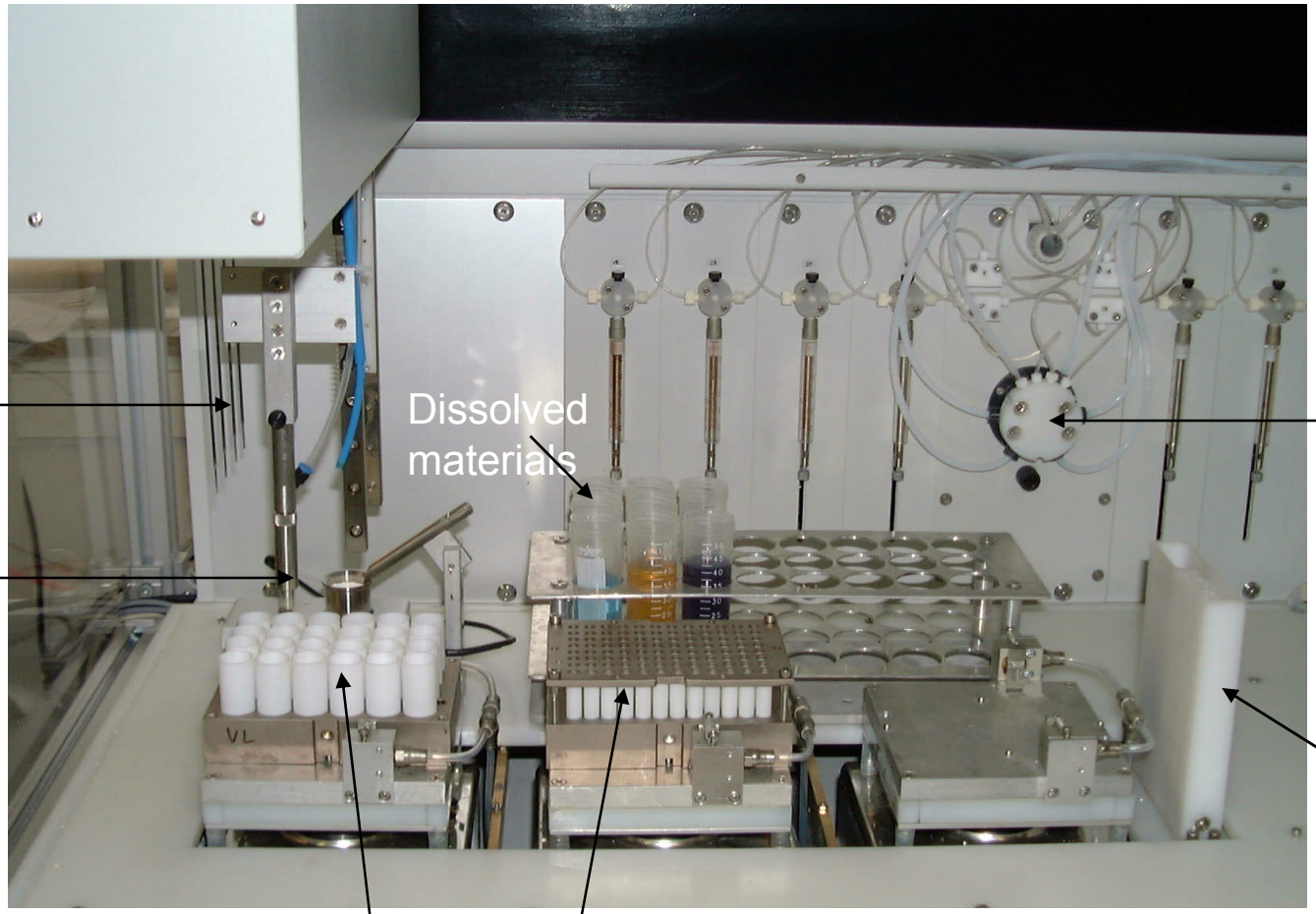
- Oxidative dehydrogenation of alkanes
- Ammonia + methane to hydrocyanic acid

Automated Preparation of Catalysts

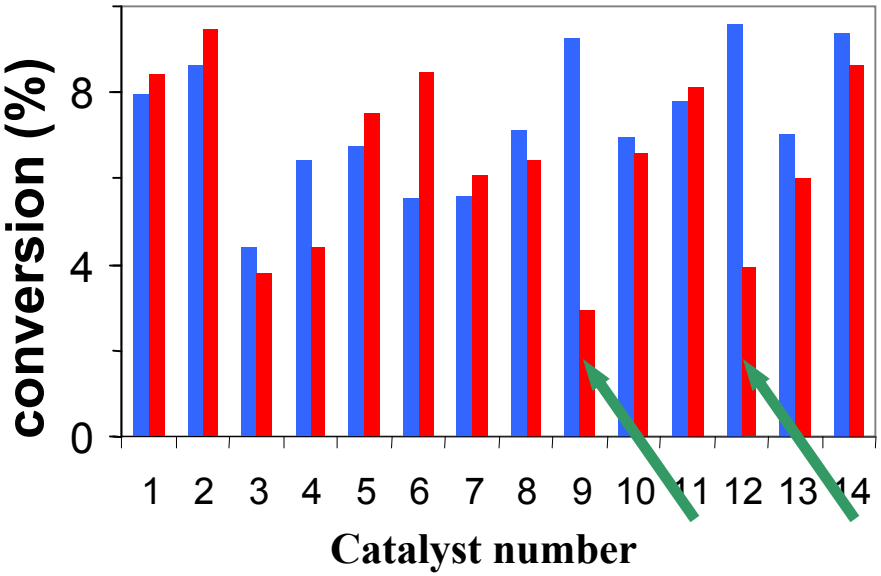
Automated liquid handler GILSON 215

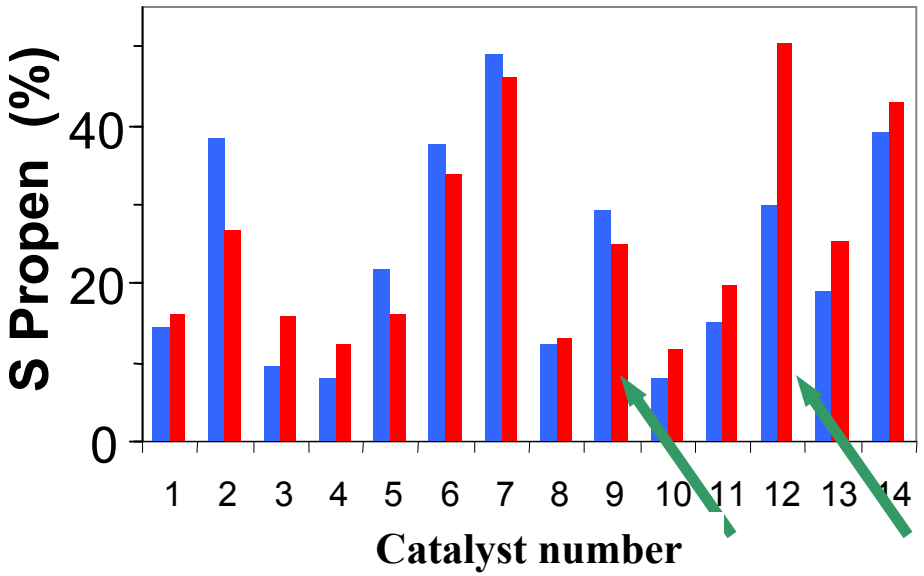
- free positioning in x, y, z direction
- Positioning accuracy 0.1 mm
- liquid transfer volume 20 µl – 5 ml

Preparation of Catalytic Materials in Parallel
- Sophas-Kat by Zinsser -



Comparison of Manual and Automatic Preparation of Catalysts of Different Composition



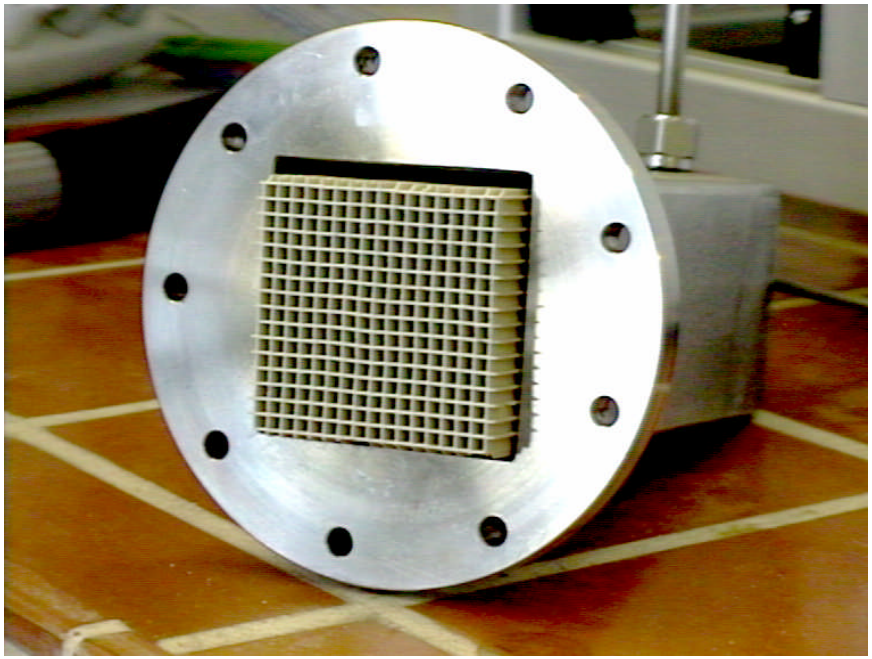


- Reaction: Oxidative Dehydrogenation of Propane
- Preparation: Impregnation

→ similar catalytic properties of manually and automatically prepared catalysts

Multi-Channel Reactor Modules

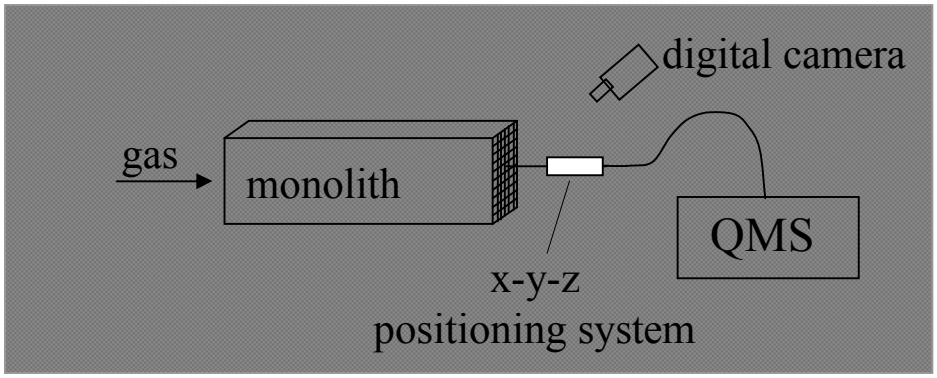
Monolithic Reactor Module - One Catalyst in Each Channel

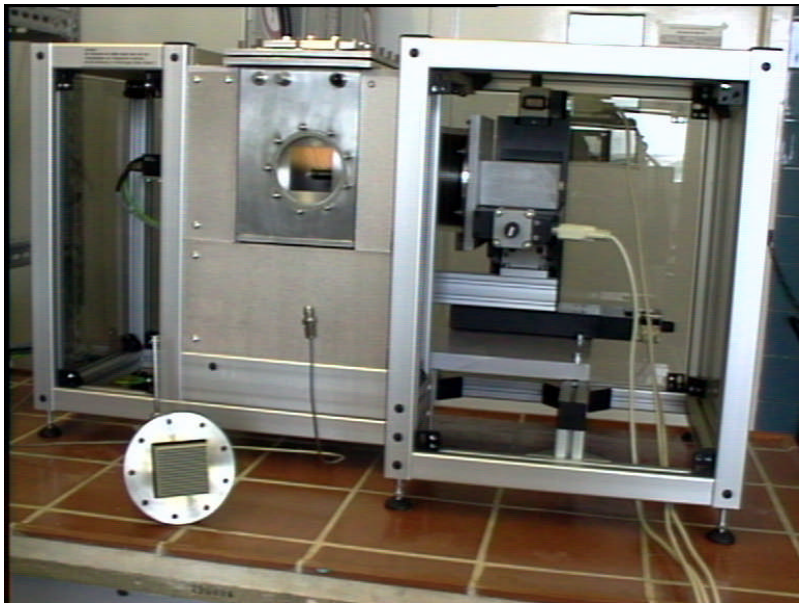


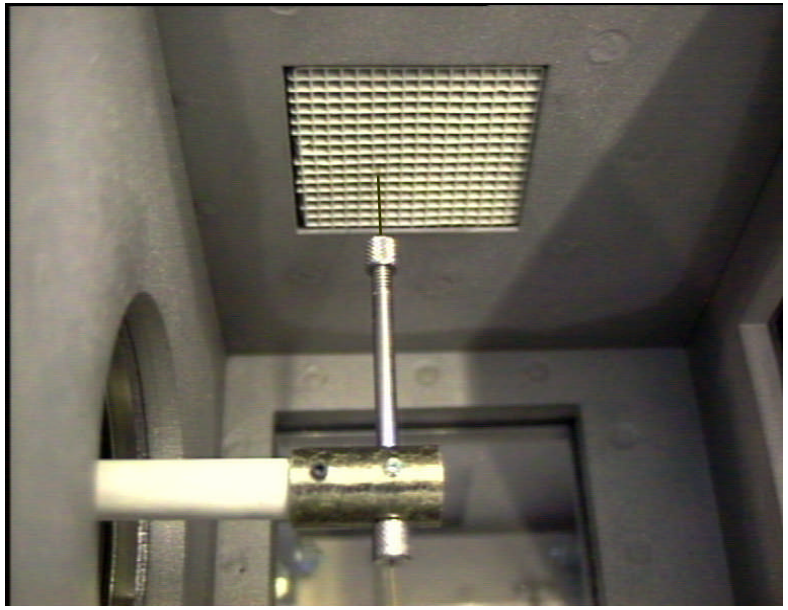
Catalyst library in a monolithic reactor module

- Charging with catalyst precursors
- Charging with carrier material, preparation of catalysts by incipient wetness
- Covering of the channel walls by a washcoat and soaking by metal salts

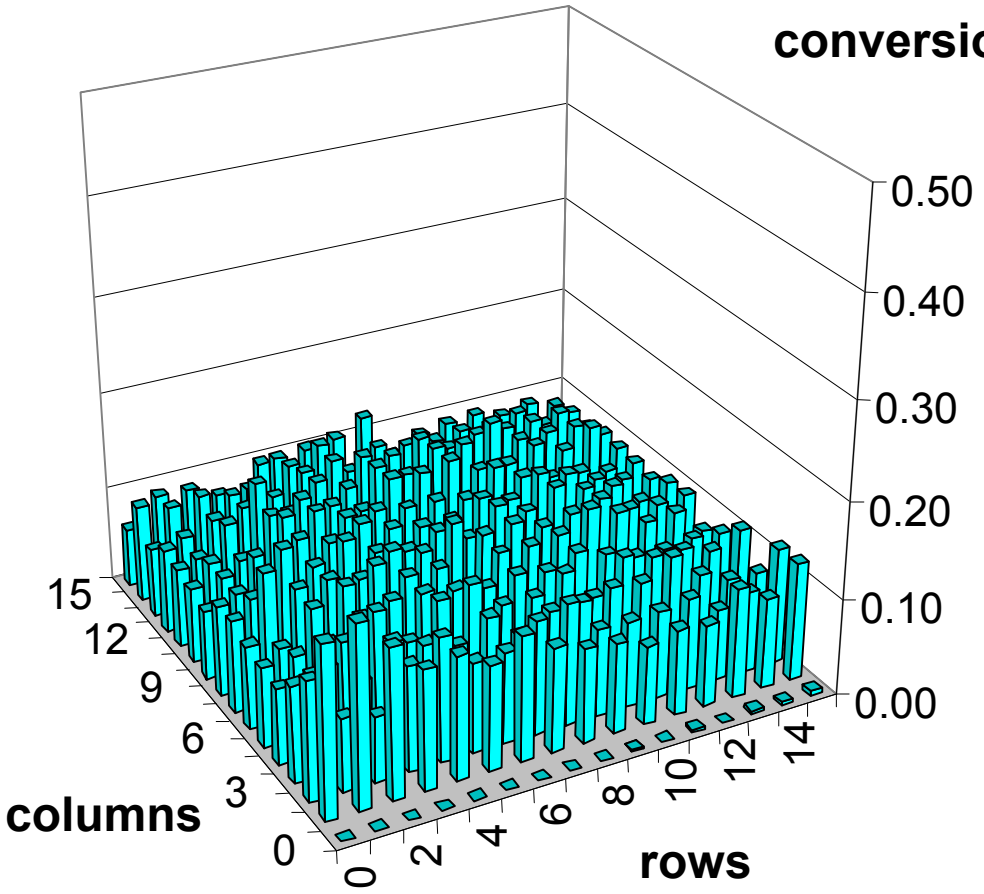
Parallel Screening of Catalysts in a Monolithic Reactor Module







Reproducibility



Oxidation of Methane at 340 °C

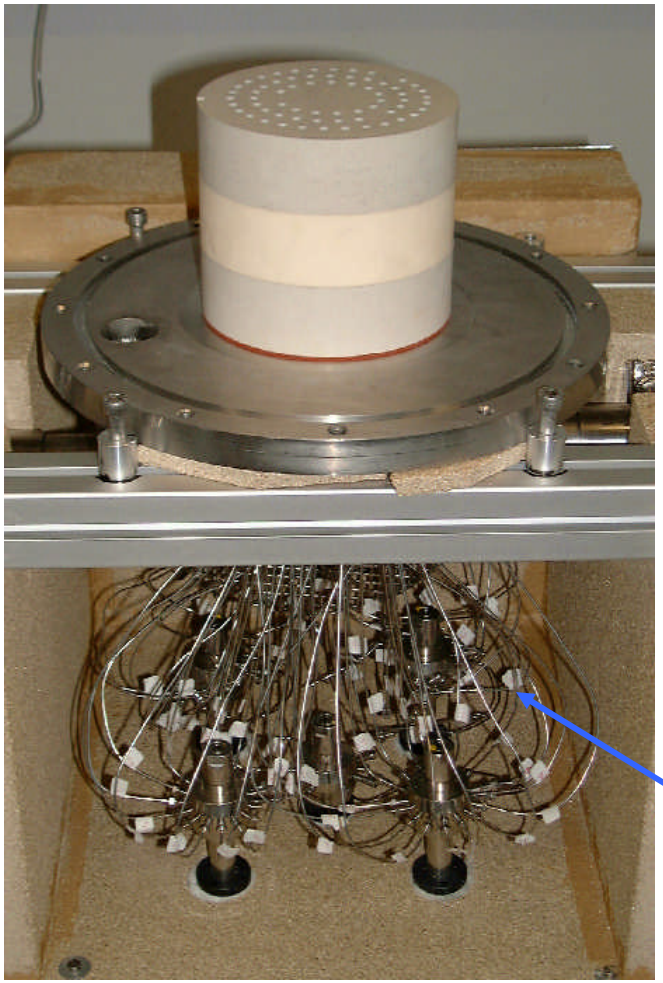
All catalysts are identical (0,5% Pt/Al_2O_3)

Standard deviation of conversion degrees

different channels: 17 %

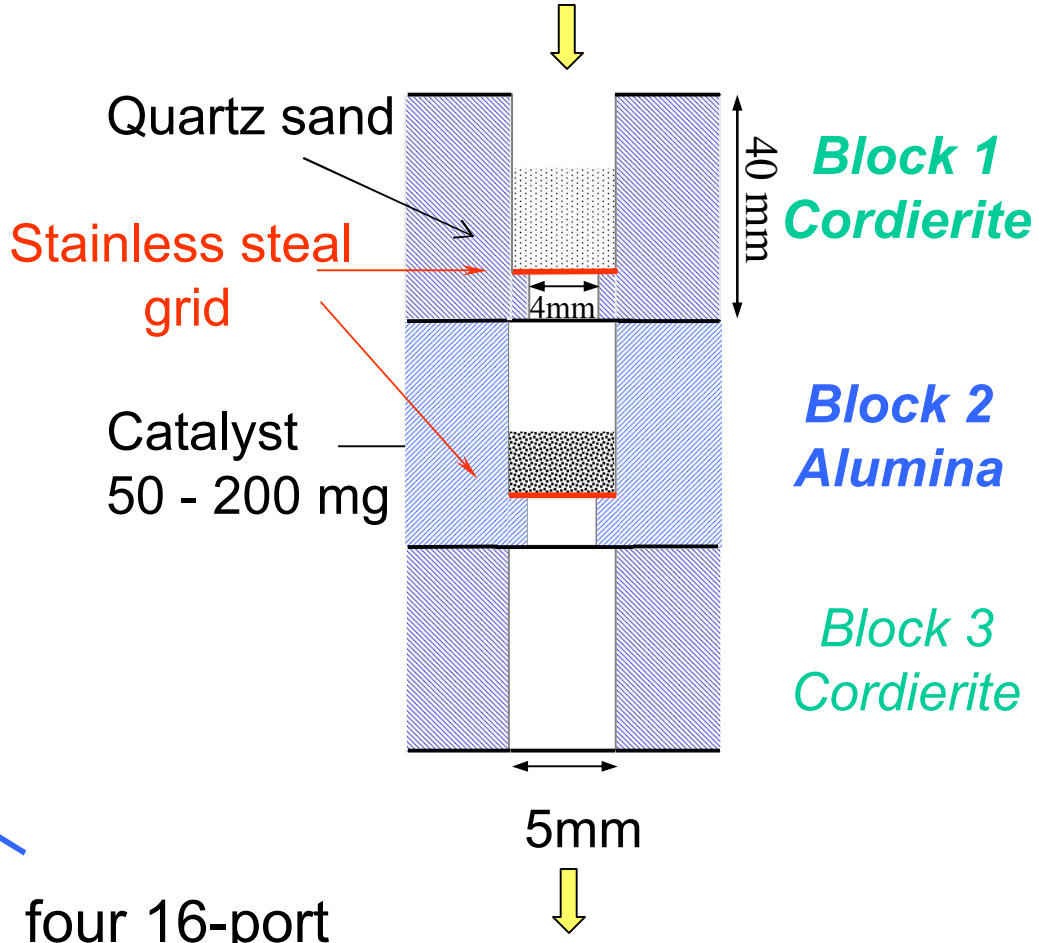
different measurements in the same channel: 2 %

64 Channel Parallel Reactor



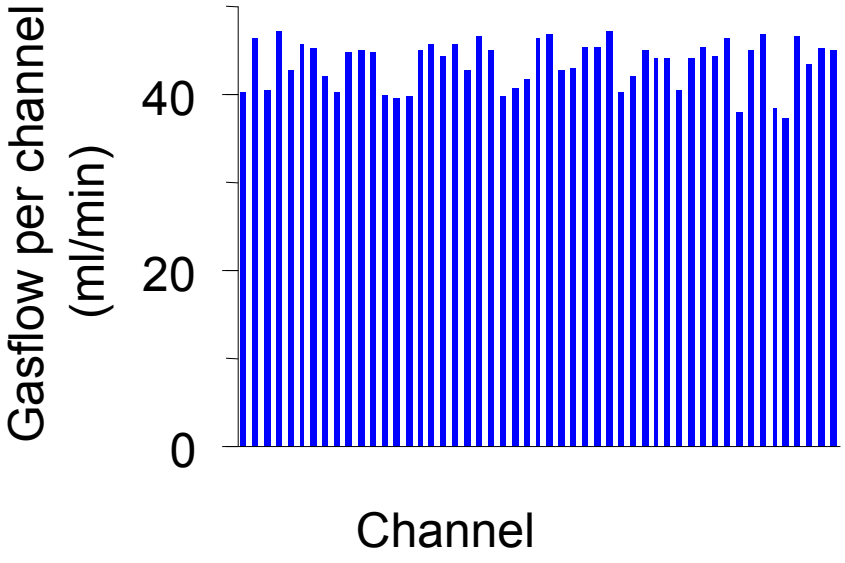
four 16-port valves

1 channel:



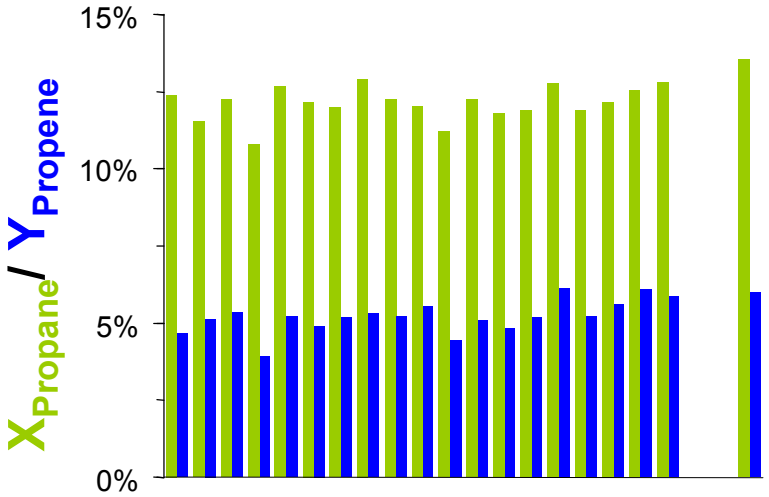
Present Reactor Set-up: 64 Channel Reactor

Performance of 64 parallel reactor channels, each contains the same catalyst material for the oxidative dehydrogenation of propane to propylene



standard deviation 5%

comparable flow rates through each channel



	parallel reactor	single tubular reactor
S / %	47.0 ± 5	44.5
Y / %	5.8 ± 1	6.0

comparable yield and selectivity

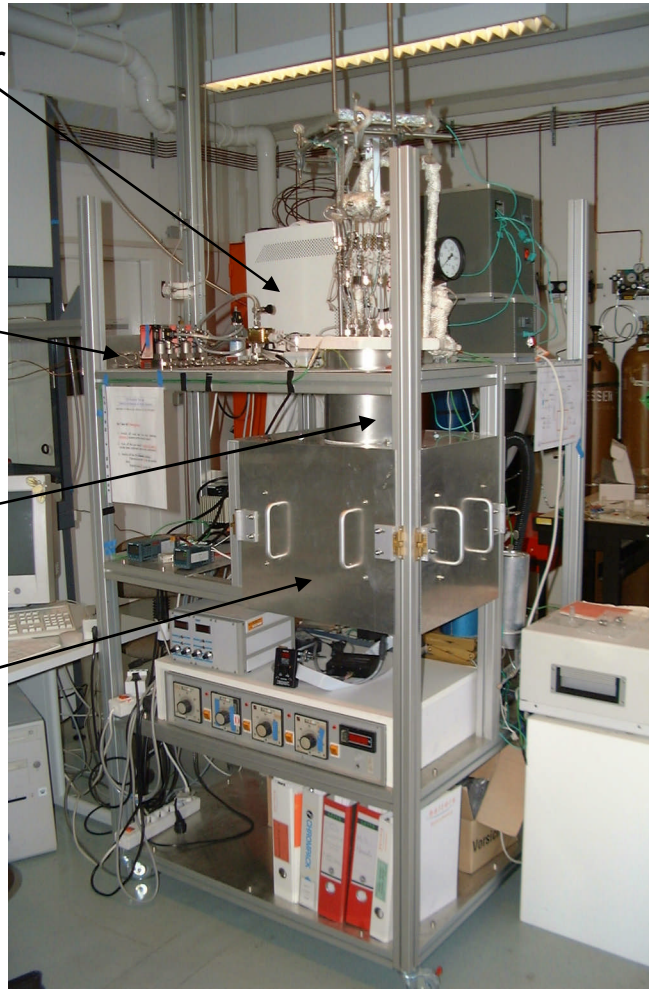
Testing of catalytic Materials in Parallel
- Alkanes to Oxygenates -

Mass spectrometer

Gas supply

10-Channel reactor module

Hotbox

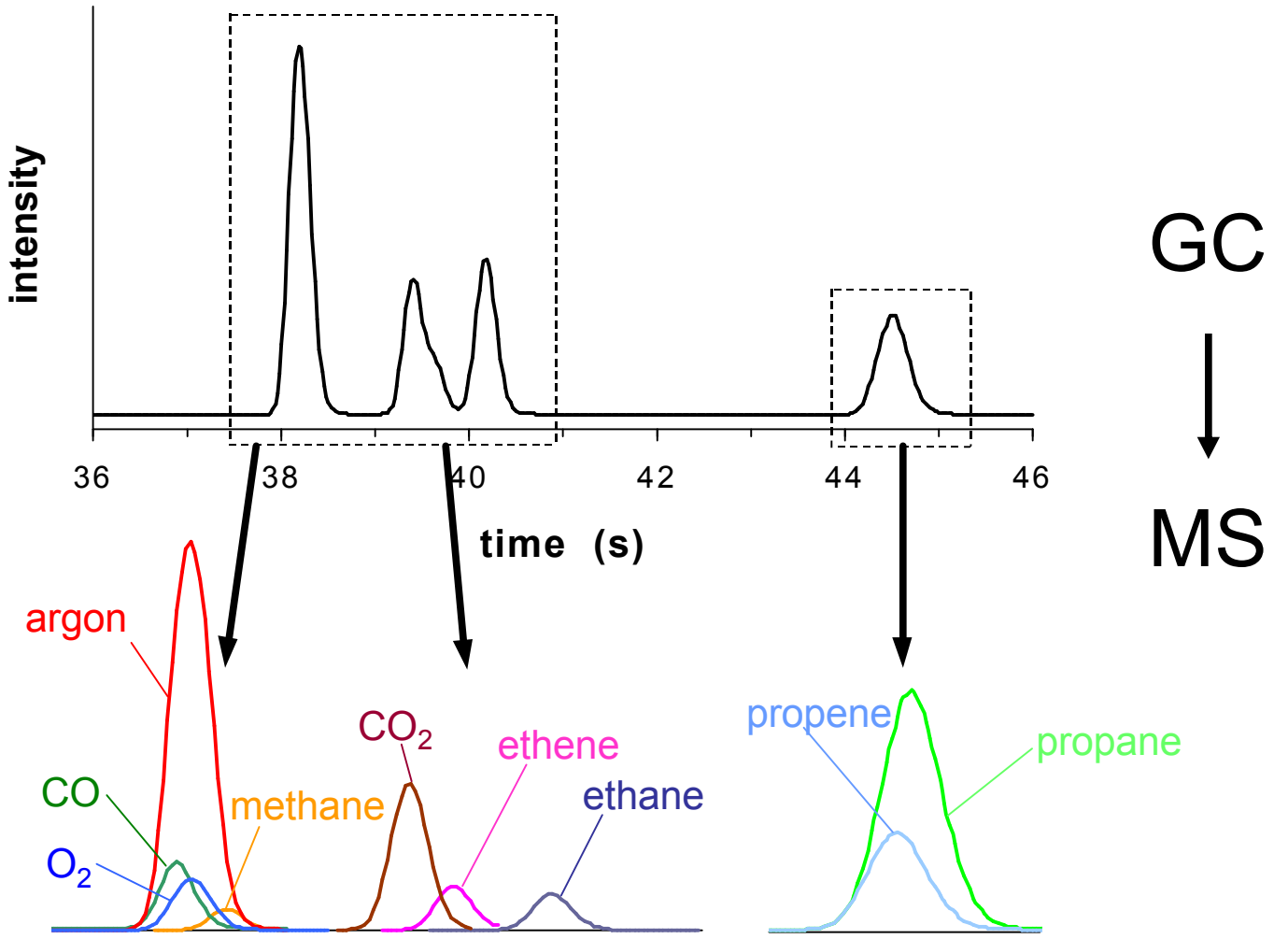


Gas distributor

Flow restrictor

Rapid Analytical Tools for Reactor Effluent Composition

Fast Effluent Analysis as Applied for the Oxidative Dehydrogenation of Propane



Fast Analysis by GC - TOF MS - coupling

- Disadvantages of classical analytic methods:
  - GC - analysis is often not fast enough for HTS-applications
- new principle:
  - MS - analysis is uncertain due to overlapping masses
  - Using a TOF (time of flight) MS as detector for a GC
  - ↳ Fast GC-separation by using short columns
  - ↳ very high scan rates (up to 500 scans/s) enable detection of narrow GC - peaks (< 0,5 s)
  - ↳ Baseline separation of GC - peaks is not always necessary due to the mass selective detection
  - ↳ Overlapping masses are reduced by the GC separation

⇨ **Complete analysis in short times**

(Analysis of all products of the propane ODH reaction < 40 s)

Variables and Objectives in the Selection of Catalytic Materials

Variables

- Qualitative and quantitative composition of the catalytic materials
- Method and conditions of materials preparation
- Forming procedure of materials before catalytic testing
- Testing conditions (temperature, space velocity, shape and size of material, ...)

Objectives

- Descriptive: Activity (degree of conversion), selectivity ($S \overset{!}{=} f(X)$), yield, catalyst stability)
- Kinetics and transport processes
- Quantitative relationships: kinetic parameters and their dependence on “composition”

Case Studies

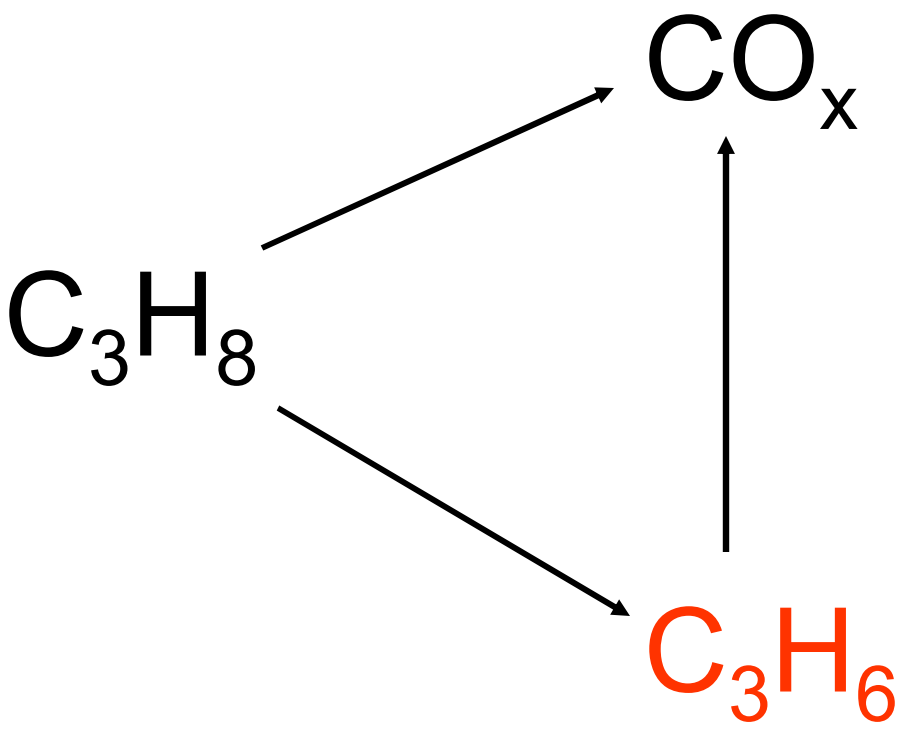
Illustrating

***Combinatorial Catalysis* and a Supplementing**

Fundamental Approach

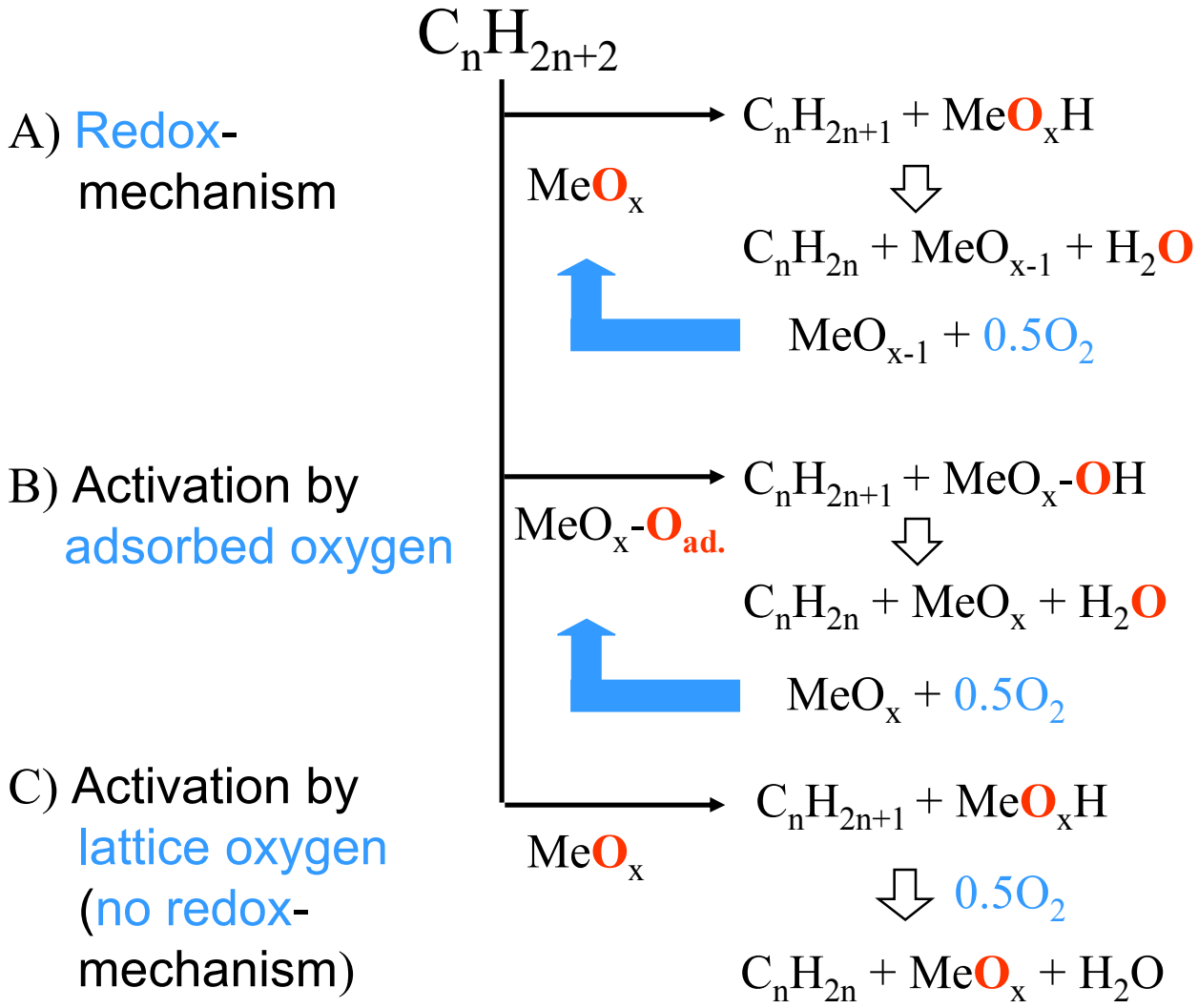
- **Oxidative dehydrogenation of light alkanes**
- **Low-temperature total oxidation of low-concentration propane**
- **Water-gas-shift reaction**
- **Ammonia + methane to hydrocyanic acid**
- **Selective hydrogenation of hydrocarbons with multiple bonds**

Illustration of Approach
- Oxidative Dehydrogenation of Propane to Propene -



Defining a Pool of Primary Potential Catalytic Elements/Compounds

Primary reaction steps of the oxidative dehydrogenation of alkanes on metal oxides



Mixtures of Metal Oxides as Potential Catalysts for the Oxidative Dehydrogenation of Propane

1. Evolution

Redox metal oxides of medium metal-oxygen binding energy in the range from –400 to –200 kJ/mol from various groups of the Periodic Table

V B	VI B	VII B	VIII	II B	III A	IV A
V_2O_5	MoO_3	MnO_2	Fe_2O_3	ZnO	Ga_2O_3	GeO_2
Nb_2O_5	WO_3		Co_3O_4	CdO	In_2O_3	
			NiO			

2. Evolution

Survivors from the first evolution plus

basic metal oxide	MgO
acidic metal oxide	B_2O_3
metal oxide on which O_2 dissociates	La_2O_3

Combinatorial Process

Systematic combination

- e. g. binary and ternary compositions

Stochastic combinations

- multi-element/compound compositions

Optimization procedures in the combinatorial process

- common optimization procedures (for local search problems only)
- evolutionary processes (e. g. rondom search, genetic algorithms)
- neural network
- factorial design (less suited for multi-element/compound compositions)

Methodical Basis of Evolutionary Strategies for the Development of Solid Catalysts

Applied CAtalysis

Optimization processes in Nature and their Adaptation to the Development of Catalytic Materials

Optimization processes in the nature

→ **Evolution**
Aim: Optimization of properties of living individuals to adapt to environmental conditions

Which are the mechanisms of these processes?

→ Change of genetic make-up by **Selection, Cross-over, Mutation**

Can these processes analogously be applied to catalyst development?

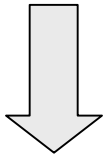
→ Yes

Populations of catalysts with different composition, which are optimized with respect to their performance by genetic operators (cross-over, mutation) in analogy to the nature

Why Evolution in Catalyst Development?

Combinatorial Explosion of the parameter space for complex systems (composition; mode of preparation, conditions of testing …)

Strict combinatorial approach as well as factorial design of experiments lead to very high test effort:



Requirement - intelligent search algorithm:

- self-adaptive
- autonomic (unsupervised)
- universal (discrete as well as continuous values)

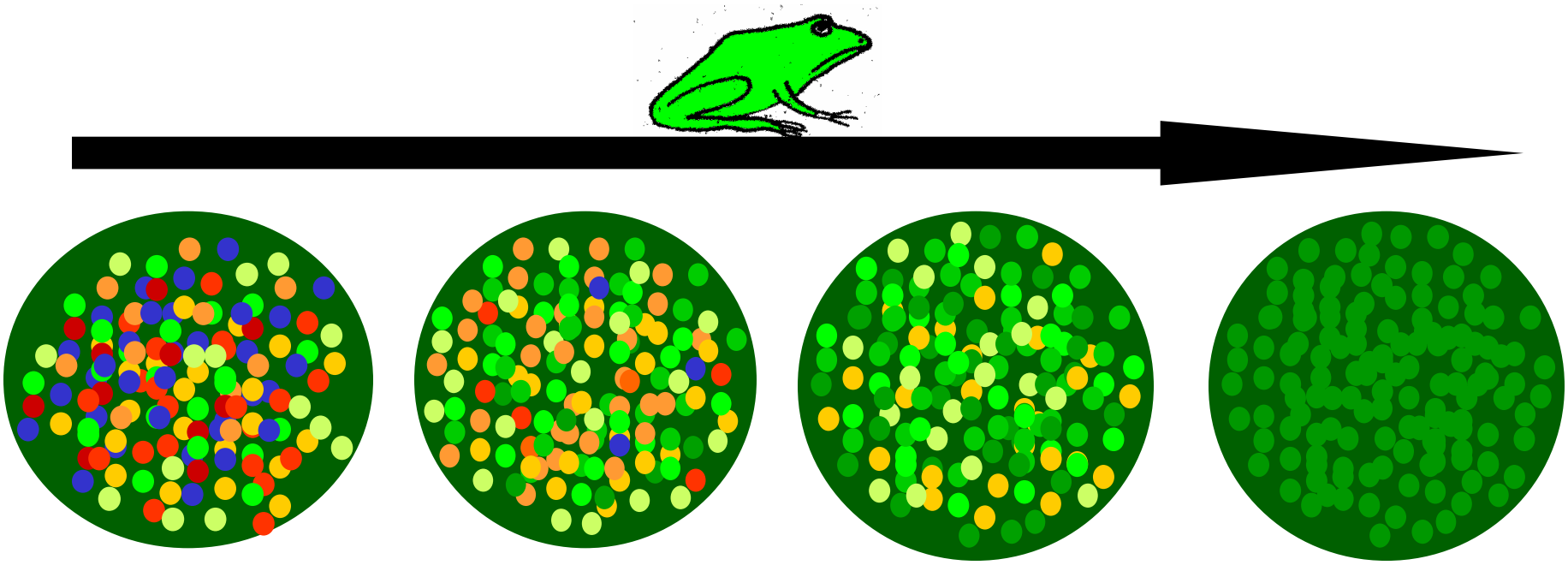
How Evolutionary Principles can be applied to Catalyst Development?

- **Design of an Evolutionary Algorithm**
  - Mode of encoding Catalyst composition
  - Mode of Cross-over and Mutation
  - Mode of Selection and Reproduction
- **Testing and phenomenological understanding**

D. Wolf, O. Buyevskaya, M. Baerns, Appl. Catal. 200 (1-2) (2000) 63

Evolution: Optimization by Natural Selection and Adaptation

Favored selection and reproduction of green individuals for adaptation to green environment



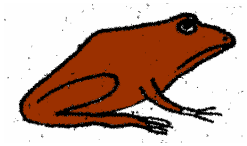
Applied CAtalysis

Evolution - Description of complex phenomenons based on simple structural units

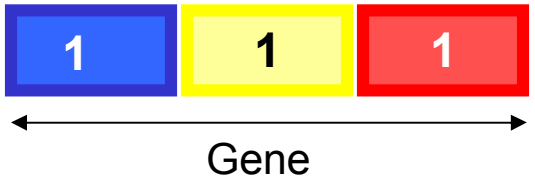
Gene-analogous Encoding:

1 = present
0 = not present

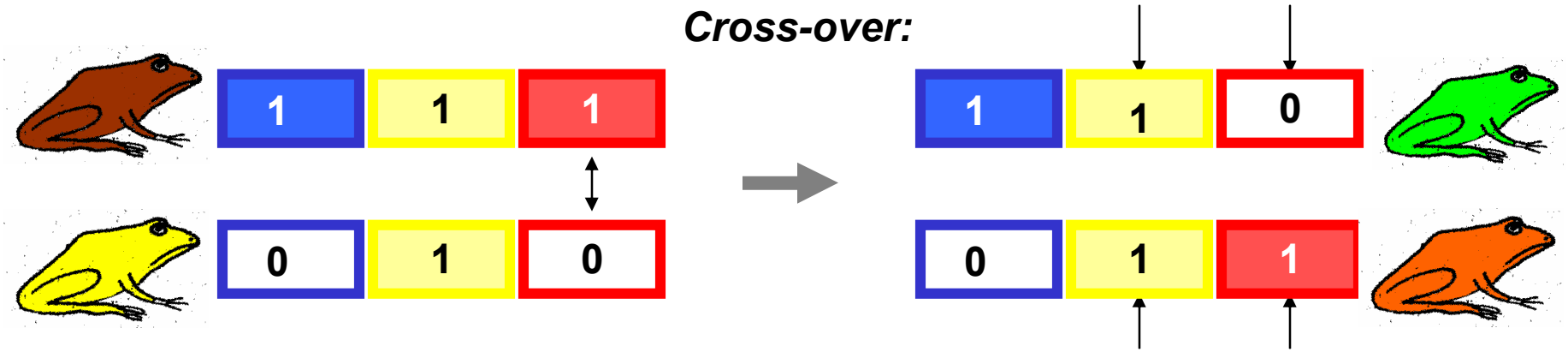
Phenotype



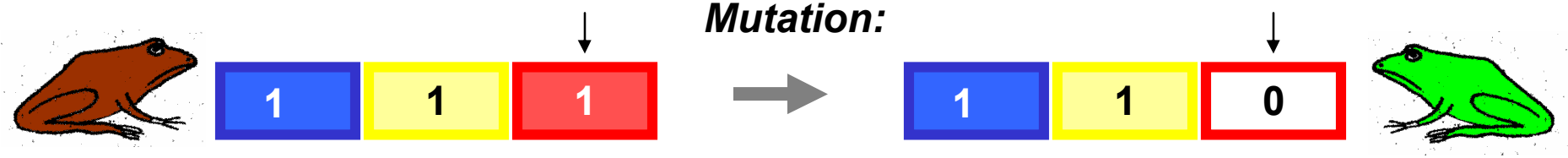
Genotype



Cross-over:



Mutation:

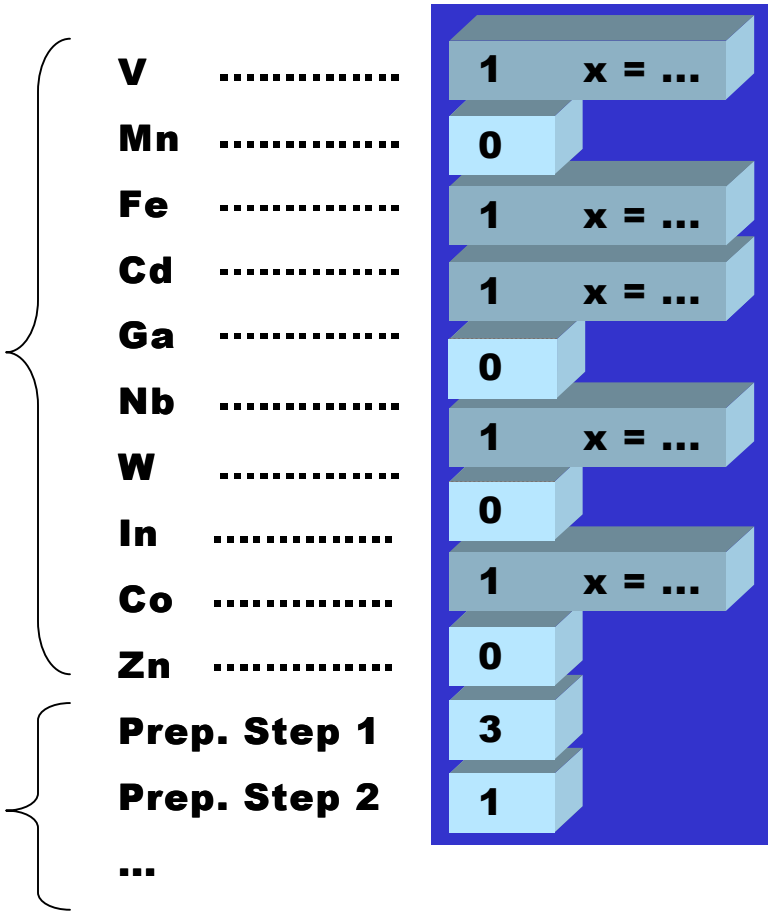


Applied CAtalysis

Design of an Evolutionary Algorithm for Catalyst Development – Mode of Encoding

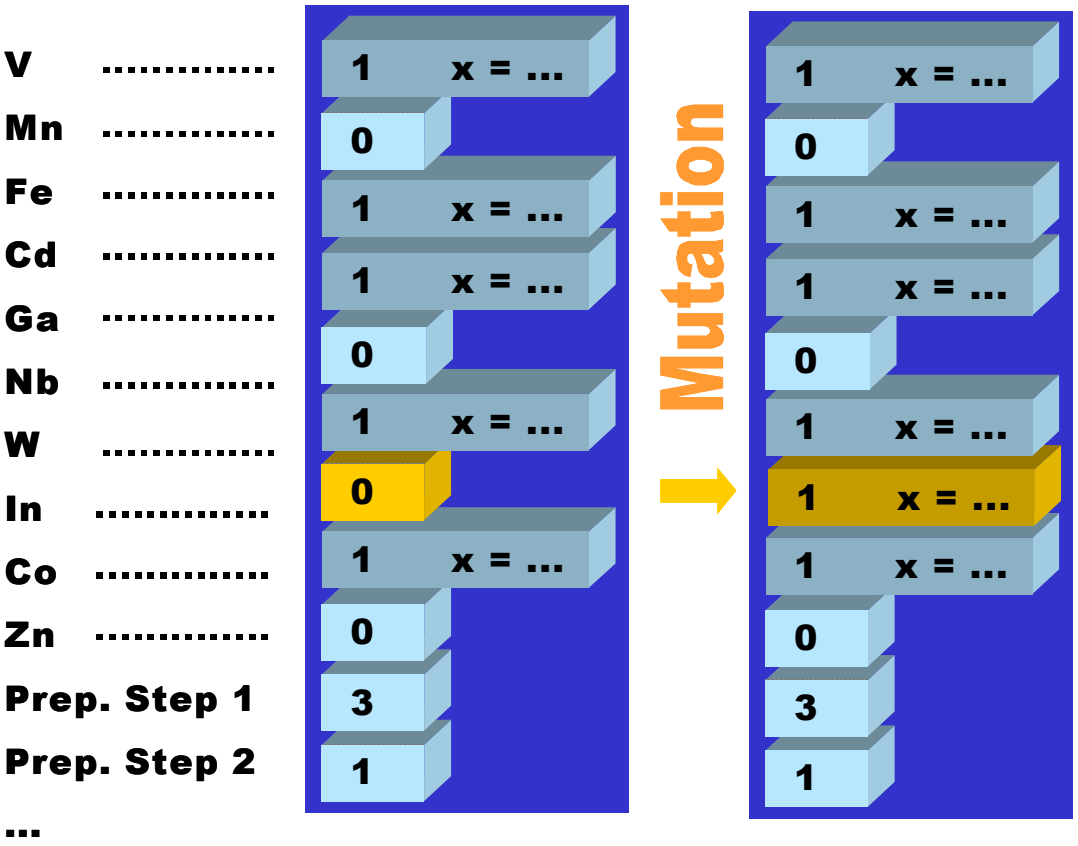
Consideration of:

- composition
- Mode of various preparation steps



Applied CAtalysis

Design of an Evolutionary Algorithm for Catalyst Development – Mode of Mutation



Quantity:

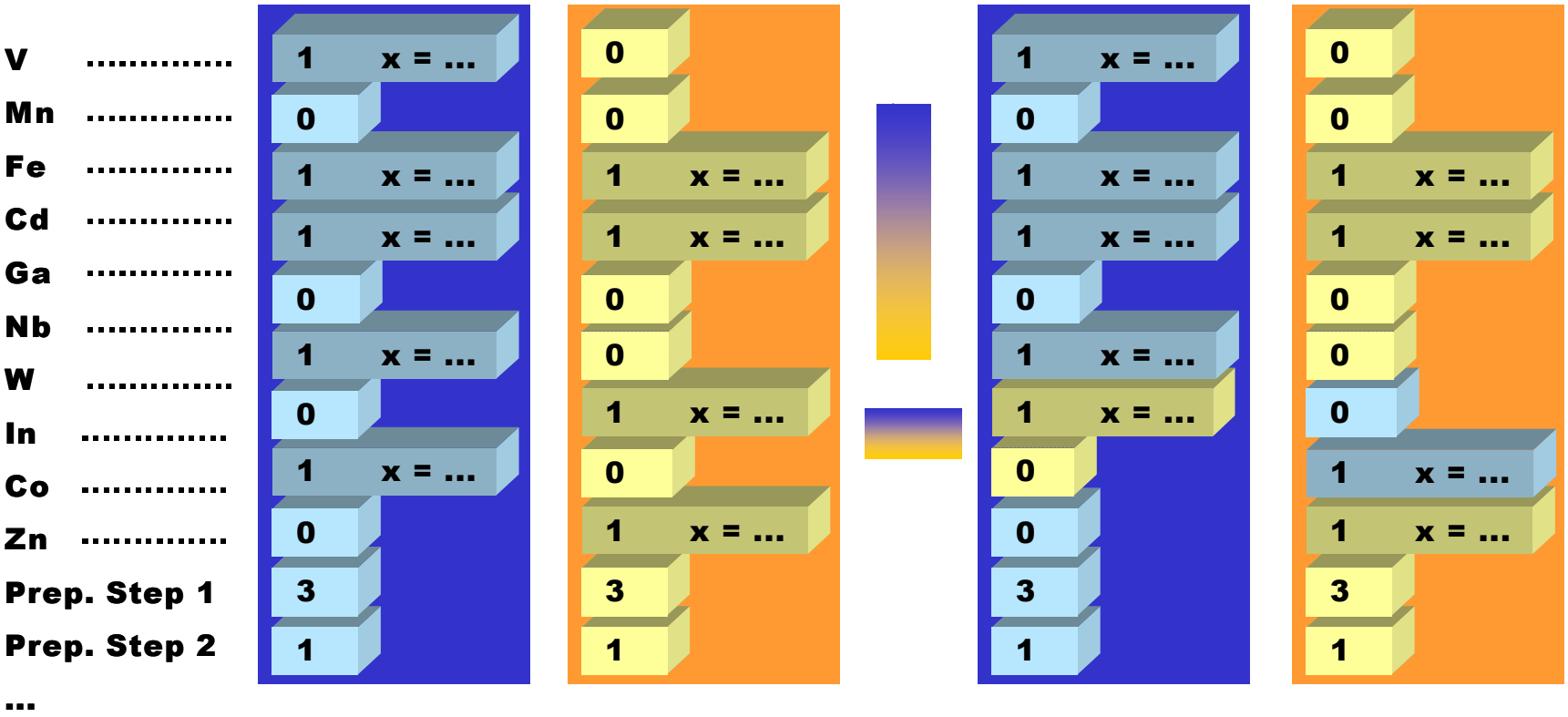
$$s_i = (-1)^t \frac{x_i^n}{d}$$

$$x_i^{n+1} = x_i^n + s_i$$

Optimal size of mutation segments and number of mutation points?

Applied CAtalysis

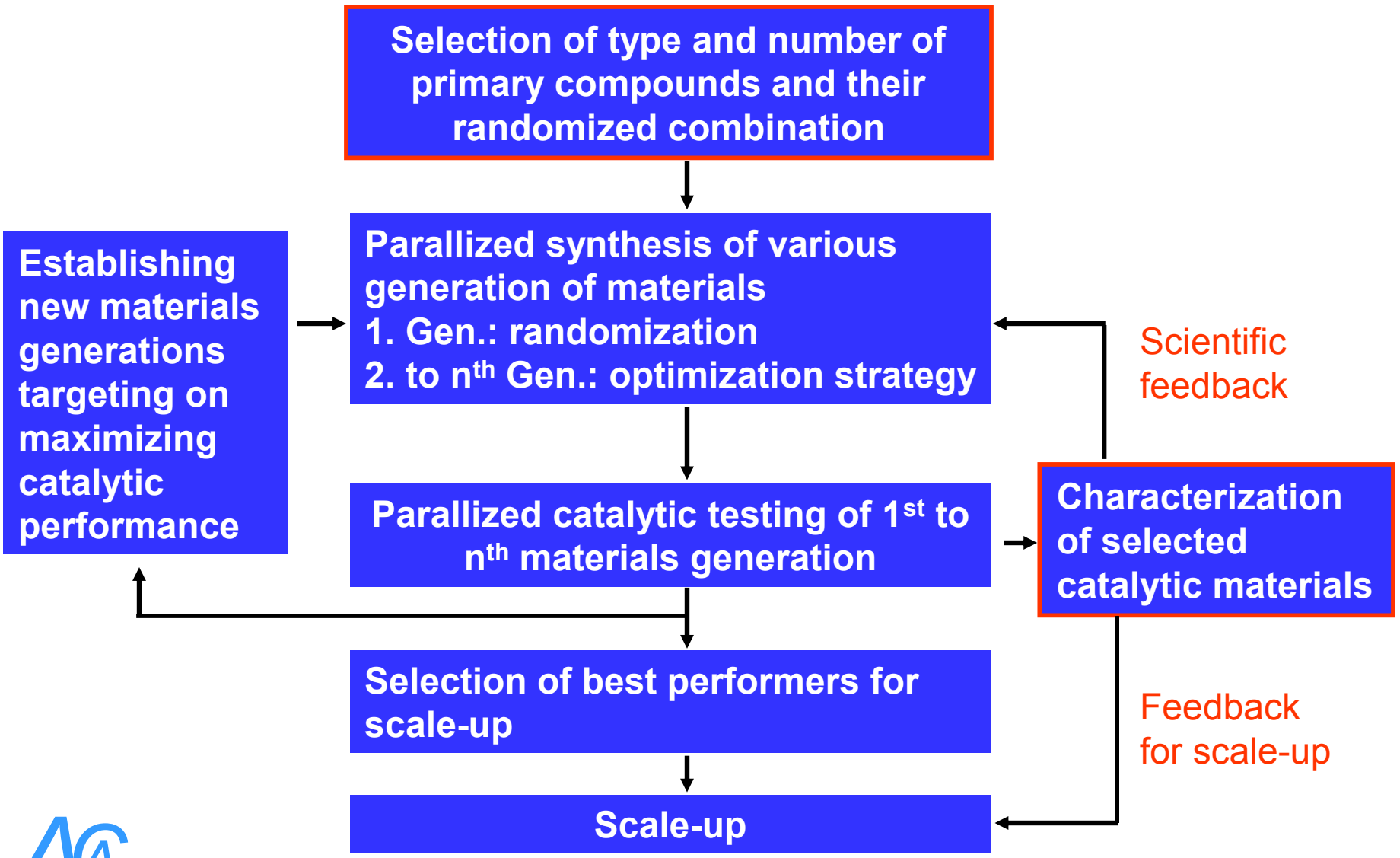
Design of an Evolutionary Algorithm for Catalyst Development – Mode of Cross-over



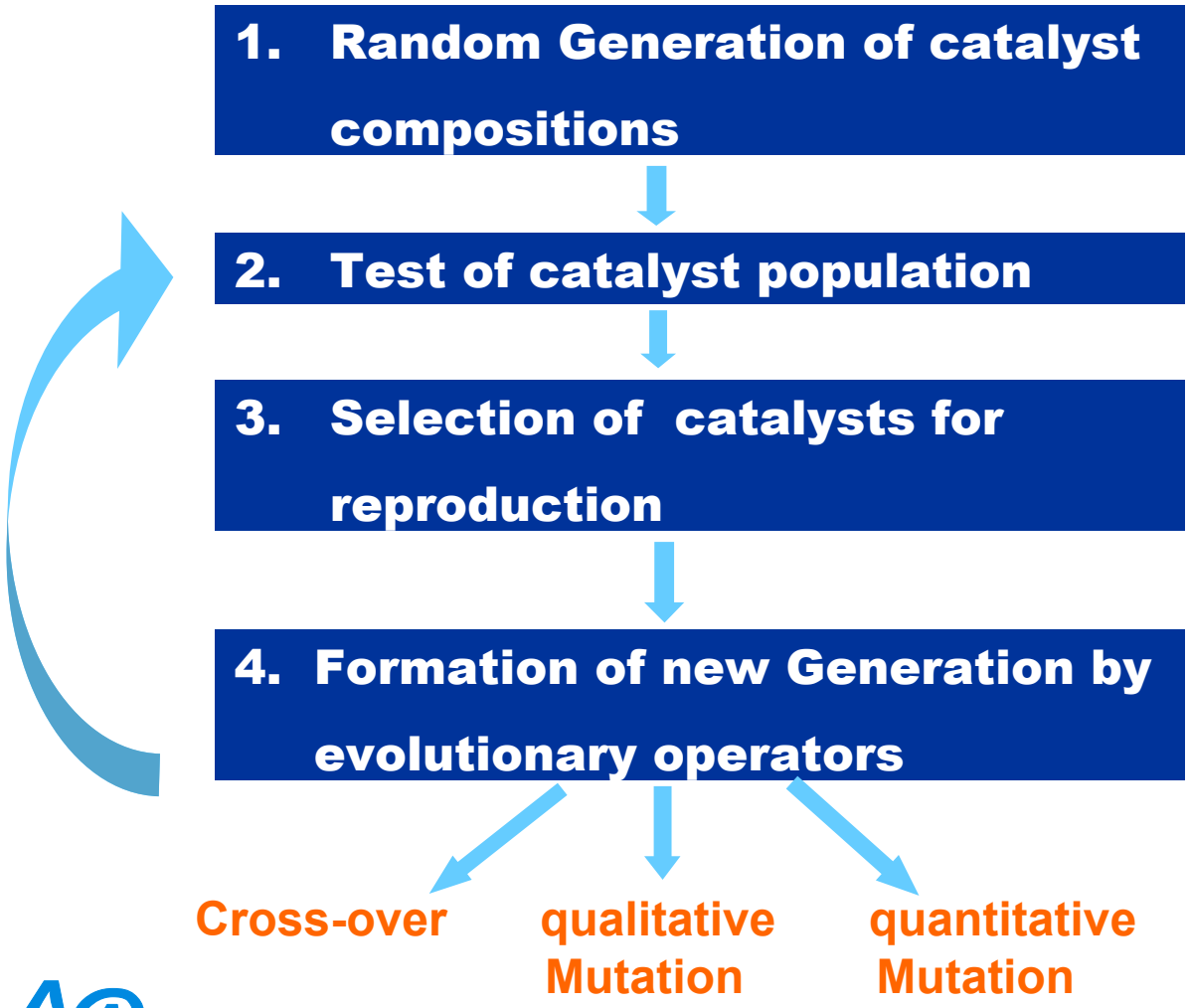
Optimal size of crossover segments and number of crossover points ?

Applied CAtalysis

Methods in the Search and Optimization of Catalytic Materials Applying an Evolutionary Procedure



Design of an Evolutionary Algorithm for Catalyst Development – Mode of Operation

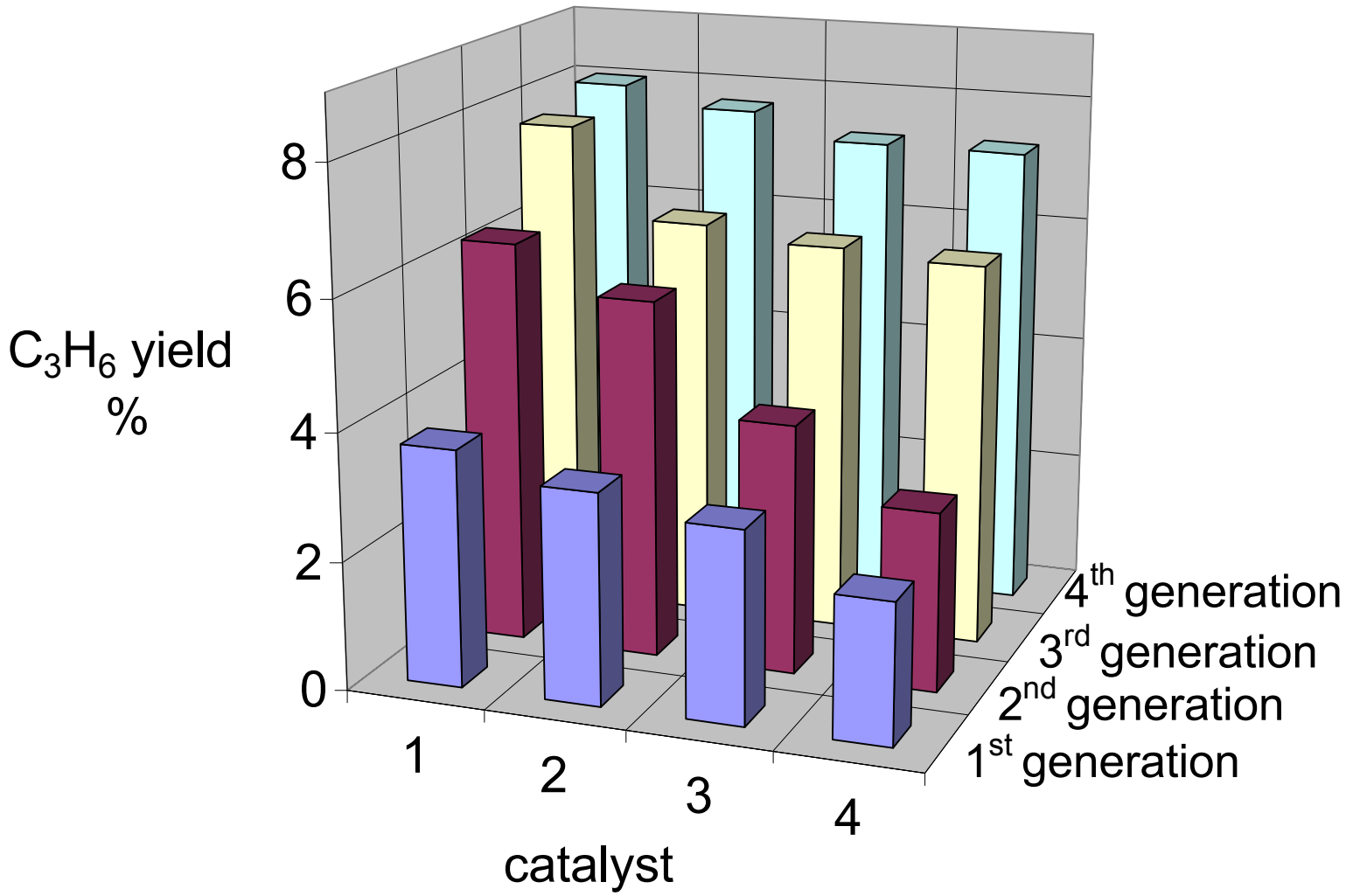


How much?

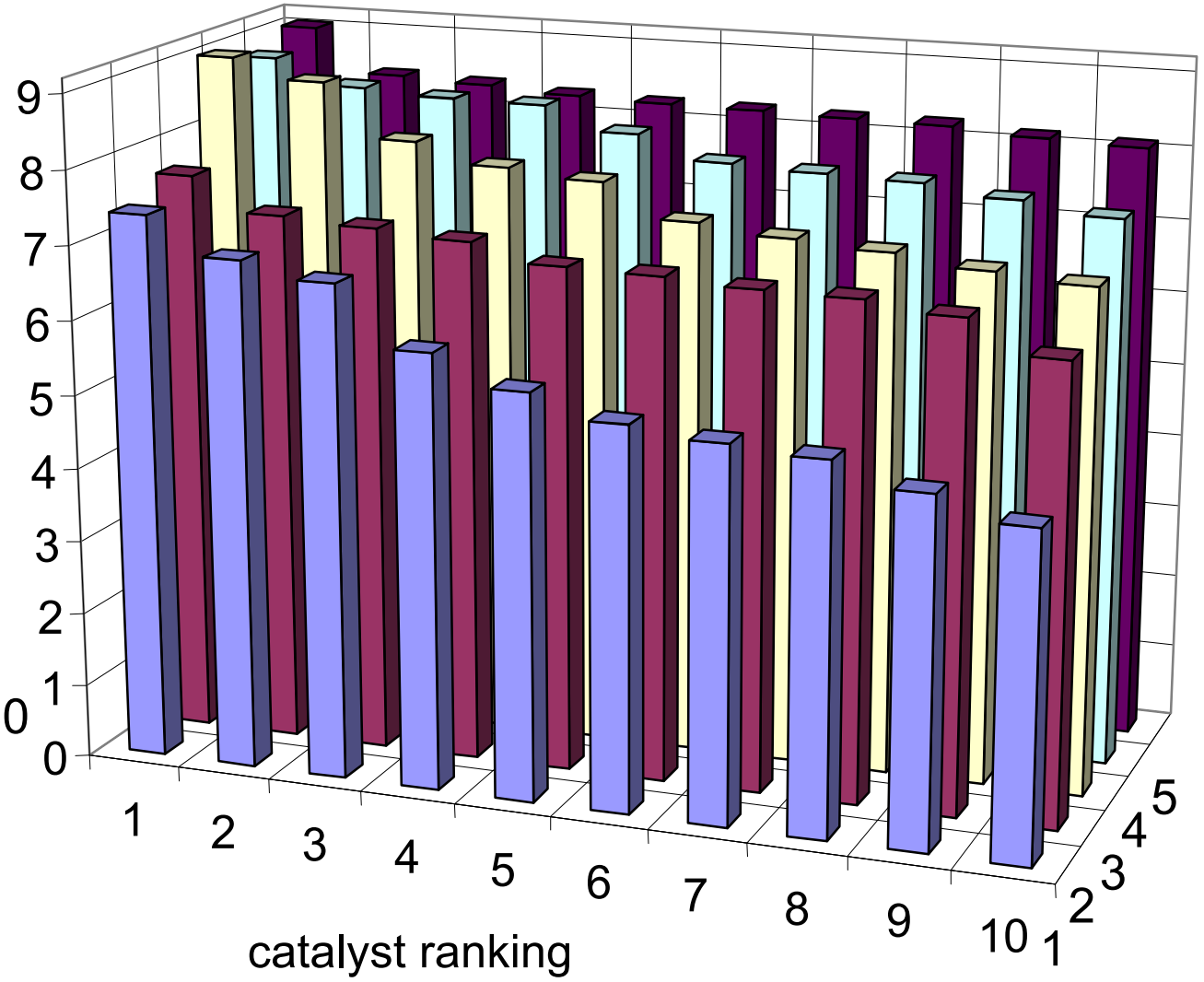
How?

Applied CAtalysis

Best propene yields achieved in each generation in the order of decreasing catalyst quality (Case A):



The 10 best performers with respect to propene yields in each generation



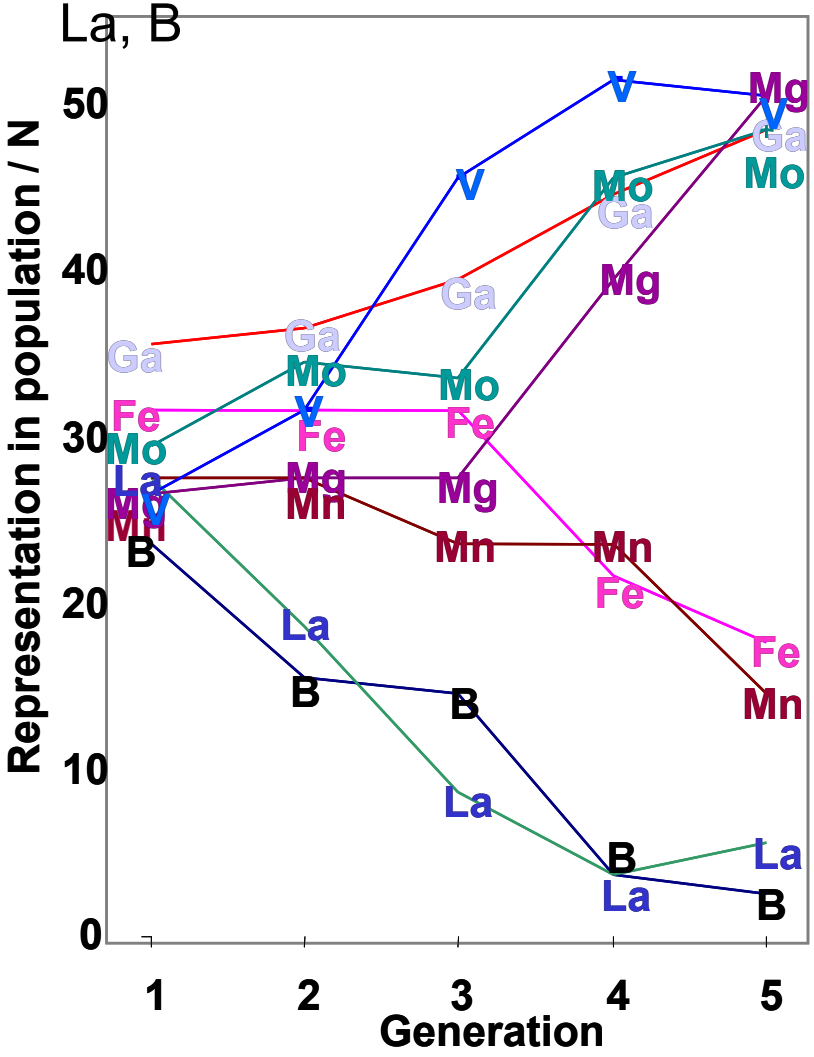
$C_3H_8/O_2/N_2$=30/10/60
T=500°C
τ=0.12-0.6 s·g_{cat}/ml

Stoichiometric composition of the best catalytic materials in each generation

	V	Mg	B	Mo	La	Mn	Fe	Ga
1st generation	0.24				0.33		0.15	0.28
	0.44			0.11		0.26		0.19
	0.42	0.40					0.04	0.14
2nd generation	0.47			0.05		0.27		0.20
	0.35	0.33					0.03	0.28
	0.39			0.22		0.23		0.17
3rd generation	0.22	0.47		0.11				0.20
	0.30	0.63						0.07
	0.14	0.20		0.15			0.08	0.42
4th generation	0.27	0.37		0.12			0.13	0.11
	0.29	0.31		0.14				0.26
	0.19	0.39		0.09				0.33
5th generation	0.32	0.18		0.04		0.09		0.33
	0.16	0.11		0.17			0.09	0.47
	0.38	0.40		0.18				0.04

Change in catalyst composition during 2nd evolution

Number of catalysts N containing the elements V, Mg, Mo, Ga, Fe, Mn, La, B as function of generation 1 to 5



Result:

GA focusses on Mg-V-Ga-Mo catalysts

J.N. Cawse, M. Baerns, M. Holena
unpublished results

High-Throughput Experimentation

and

Fundamental Knowledge

Selected catalytic materials from the evolutionary procedure and from supplementary experiments

Best performing α–Al_2O_3-supported materials from the 3rd and 5th generations

3rd generation
- $V_{0.22}Mg_{0.47}Ga_{0.20}Mo_{0.11}O_x$
- $V_{0.30}Mg_{0.63}Ga_{0.07}O_x$

5th generation
- $V_{0.32}Mg_{0.18}Ga_{0.33}Mo_{0.04}Mn_{0.09}O_x$
- $V_{0.16}Mg_{0.11}Ga_{0.47}Mo_{0.17}Fe_{0.09}O_x$

Supplementary materials

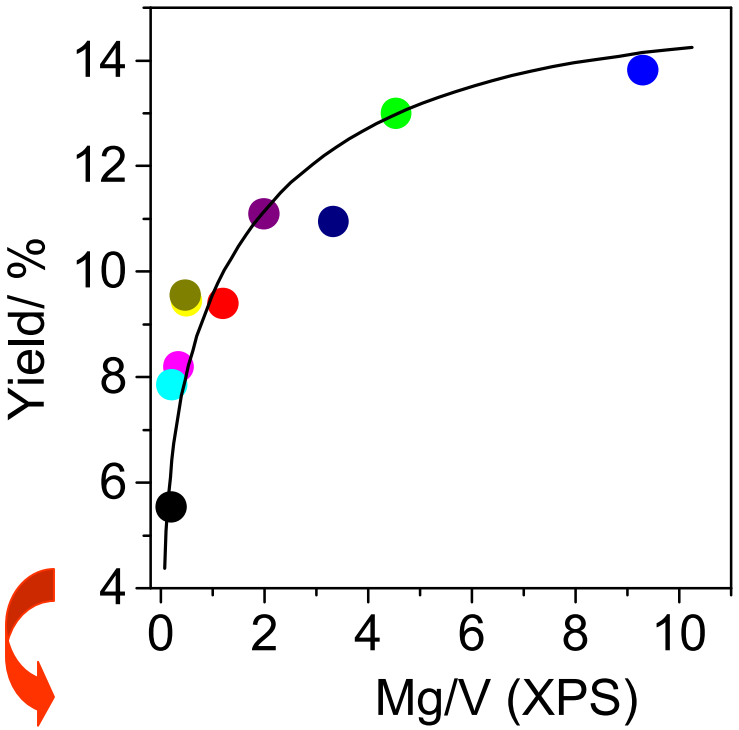
a) **V-Mg-Ga-O**/α–Al_2O_3
36 combinations

b) **V-Ga-O**
11 combinations
V/Ga : 0.01 - 100

c) **V-Mg-O**
4 catalysts of different phase compositions

Relationship between catalytic performance and surface ratio of Mg/V

Reaction conditions: C_3H_8-O_2-N_2=40-20-40; T=773K; X(O_2) ≈100 %



- $V_{0.3}Mg_{0.63}Ga_{0.07}O_x$
- $V_{0.22}Mg_{0.47}Ga_{0.2}O_x$
- $V_{0.32}Mg_{0.18}Mo_{0.04}Mn_{0.09}Ga_{0.33}O_x$
- $V_{0.16}Mg_{0.11}Mo_{0.17}Fe_{0.09}Ga_{0.47}O_x$

} from the evolutionary procedure

- $V_{0.2}Mg_{0.5}Ga_{0.3}O_x$
- $V_{0.2}Mg_{0.2}Ga_{0.6}O_x$

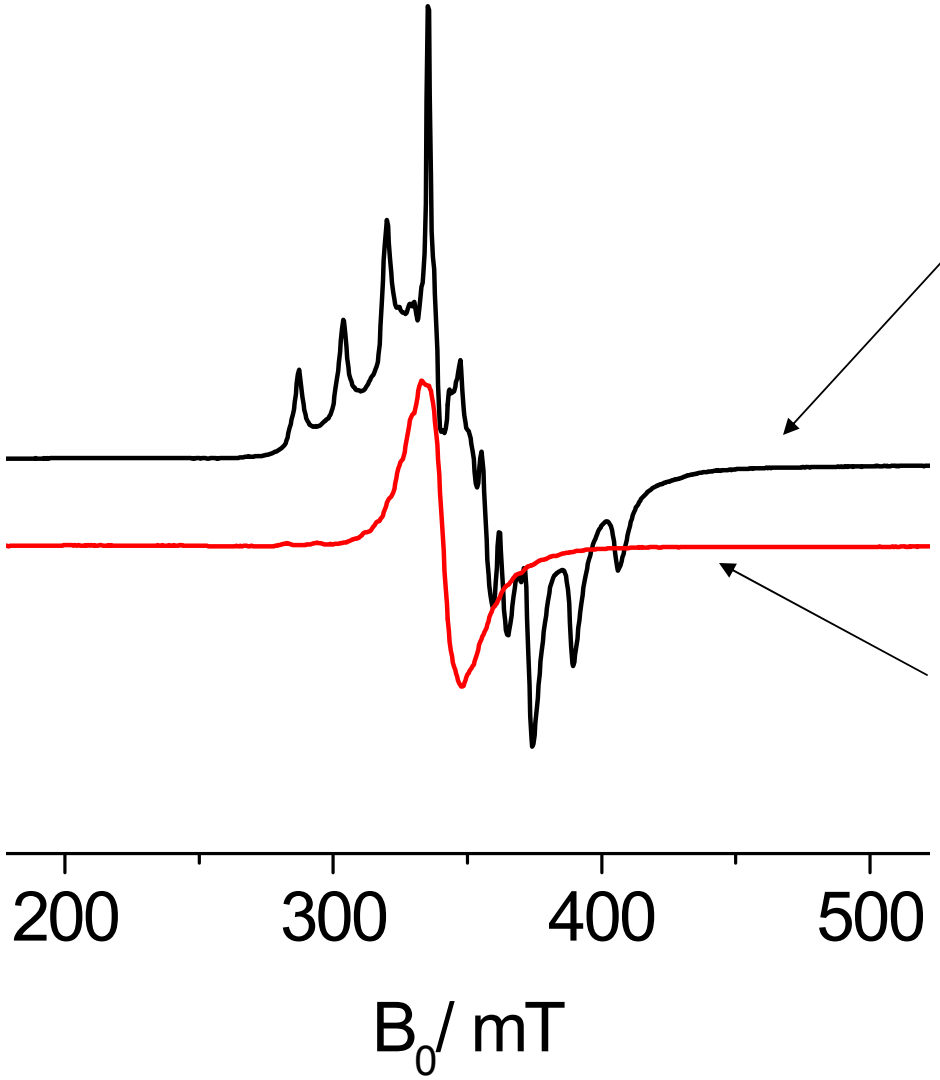
} best from V-Mg-Ga-O/αAl_2O_3

- $V_{0.8}Mg_{0.2}O_x$
- $V_{0.5}Mg_{0.5}O_x$
- $V_{0.2}Mg_{0.8}O_x$
- $V_{0.1}Mg_{0.9}O_x$

} Not supported V-Mg-O

EPR measurements show increasing concentration of octahedral isolated VO^{2+} centres with increasing the Mg/V ratio (XPS). The more dispersed active vanadium species, the higher the selectivity that can be achieved.

EPR Spectra of VMgO catalysts



$V_{0.1}Mg_{0.9}O_x$

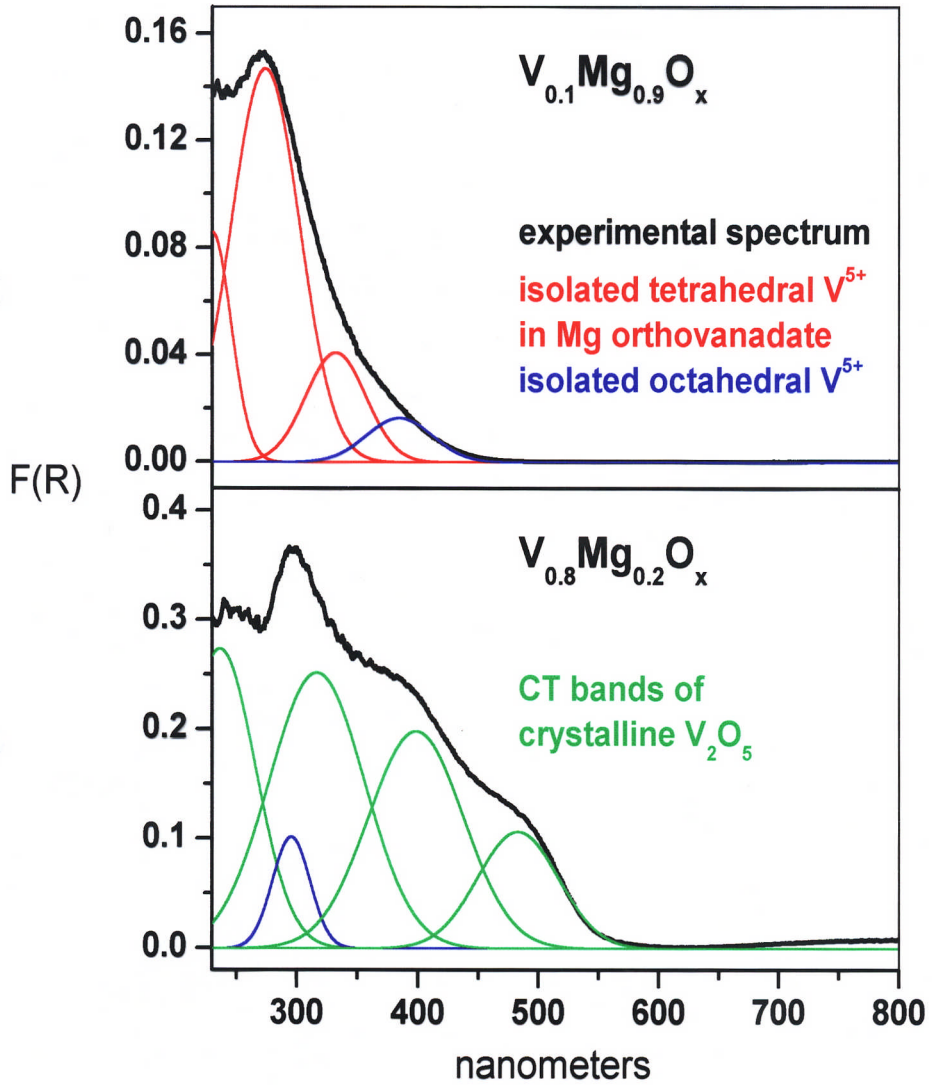
Isolated VO^{2+}

weakly interacting VO^{2+}

$V_{0.8}Mg_{0.2}O_x$

Strongly interacting VO^{2+}

UV/VIS-DRS spectra of VMgO catalysts



Applied CAtalysis

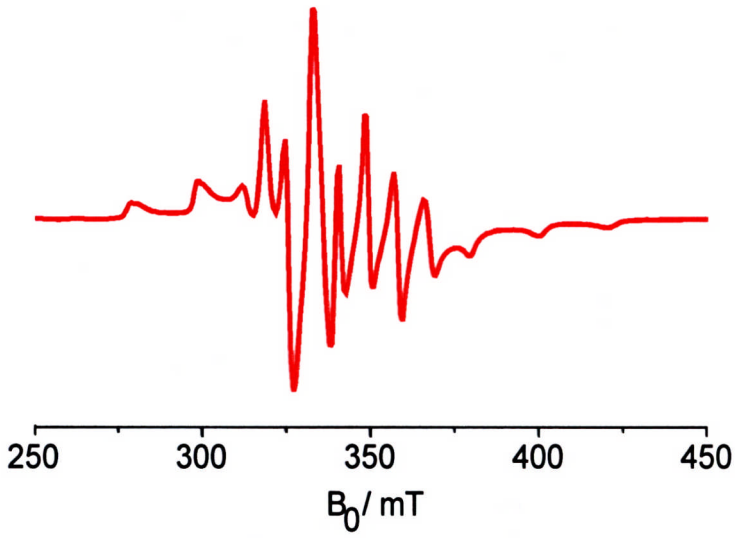
Characterization of VO_x (5.5 at. %) MCM-41

TPR

(5 % H_2-Ar, 50 ml/min, 10 k/min)

peak at 800 K resulting from monomeric or low-oligomieric VO_x

ESR



isolated octahedral VO^{2+} sites (16.8 % of ESR signal intensity, hyperfeine structrure)

VO^{2+} sites coupled by weak dipolar interactions (83.2 % of ESR signal intensity, isotropic broad singlet superimposed)

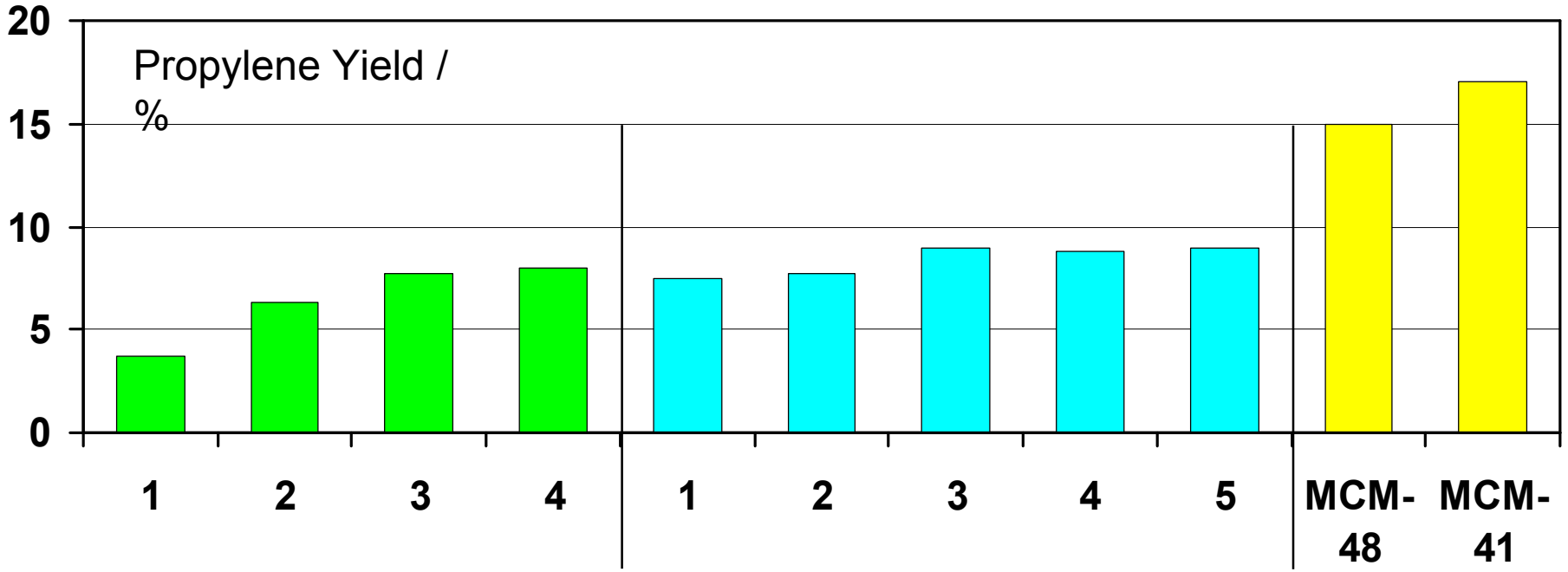
Mean vanadium valence state

4.7

Catalytic performance of VO_x/MCM-41 and VO_x/MCM-46 in the oxidative dehydrogenation of propane

$C_3H_8/O_2/N_2$	τ/s·g_{cat}·cm^{-3}	$X(C_3H_8)$/ %	$S(C_3H_6)$/%	$S(CO_x)$/%	$Y(C_3H_6)$/%
		VO_x(2.8 wt.%)/MCM-41			
30/25/45	0.04	44.6	32.7	42.2	14.6
30/20/50	0.04	34.2	42.3	41.4	14.5
40/20/40	0.04	30.3	49.1	32.8	14.9
		VO_x(2.8 wt.%)/MCM-48			
30/25/45	0.08	46.6	34.6	37.3	16.1
30/20/50	0.08	37.3	45.8	36.9	17.1
40/20/40	0.08	32.8	53.0	28.8	17.4

Evolutionary Development of Catalyst Performance



Generation → 1st Evolution

Oxides of
V, Nb, **Mo**, W, **Mn**, **Fe**,
Co, Ni, Zn, Cd, **Ga**, In, Ge

Generation → 2nd Evolution

Oxides of
V , (Mo, Mn, Fe), **Ga**,
Mg, B, La

Scientific Knowledge →

Highly dispersed VO_x on MCM

Applied CAtalysis

Conclusions

- High-throughput synthesis & testing of catalytic materials
  is a means of accelerating the search for new catalytic materials or further optimizing already existing catalyst compositions
- A scientific input in the initial development process and a concomitant fundamental approach is required
- Pitfalls in high-throughput testing exist
  - standard versus optimized reaction conditions
  - hot spots & run-away for exothermic reactions
  - inter- and intra-particle heat- and mass-trans-port limitation

Applied CAtalysis

Institute for Applied Chemistry
Berlin-Adlershof

High-Throughput Experimentation at High Temperatures Search and Discovery of New Catalytic Materials for the Synthesis of Hydrocyanic Acid

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High temperature reactions (>800°C) with a possible implementation for high-throughput experimentation

Oxidative coupling of methane: $2CH_4 + ½O_2 \rightarrow C_2H_6 + H_2O$

up to 880°C; supported metals and metal oxides; no large-scale application

Production of synthesis gas: $CH_4 + H_2O \rightarrow CO + 3H_2$

>900°C; supported Ni-catalyst; fixed bed

Synthesis of hydrocyanic acid: $NH_3 + CH_4 \rightarrow HCN + 3H_2$

1000-1300°C; Pt-catalyst; tube bundle

$NH_3 + CH_4 + 1½O_2 \rightarrow HCN + 3H_2O$

1000-1100°C; Pt/Rh-gauze; tube reactor

Challenges for high temperature - high-throughput experimentation

- Heating provision for high temperatures (>800°C)

  - comparable temperatures within the different reaction channels

  -avoidance of mutual influences of adjacent channels (exothermic reactions)

- -Inert, gas proof and thermally stable reactor materials

  - low rate of reactions with the reactor material

- Prevention of product condensation

  - if necessary heating of the tubes, capillaries, valves etc.

- Fast on-line analysis

  - depending on the number of channels analytical speed of 1 - 3min per reactor

State of the art

- No multi-channel reactors for temperatures >800°C known

- High-throughput experimentation for temperatures <800°C:

  - Monolithic reactors

    high-throughput applications up to 600°C; heating time for module and cross

    communication between channels due to thermal conductivity

  - Tube reactors

    high-throughput applications usually between 400 to 600°C;

    shortcoming: non-homogeneous temperature distribution

Equipment for a high-temperature reaction of industrial importance - Conversion of ammonia and methane to hydrocyanic acid -

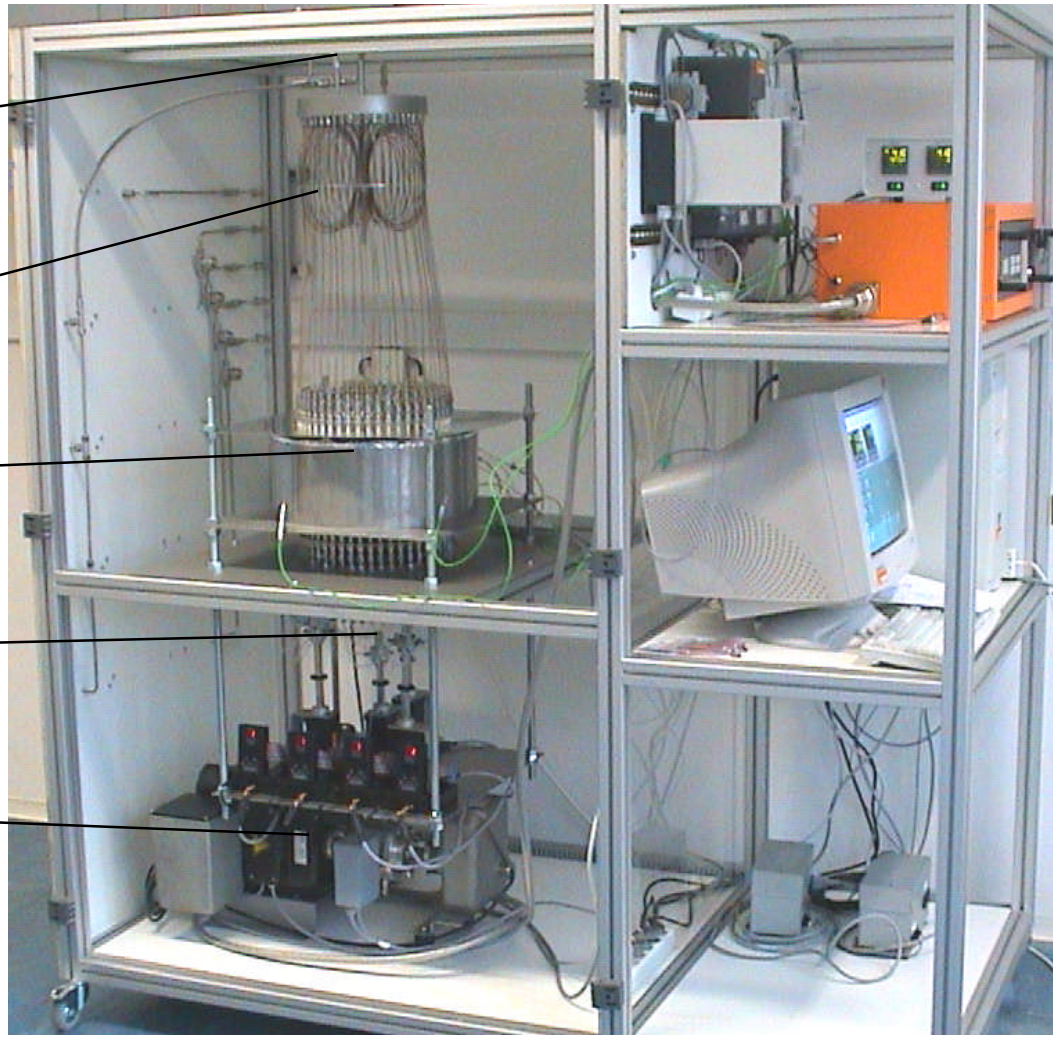
Gas distributor

Capillaries

48-channel reactor

Multi-port valves

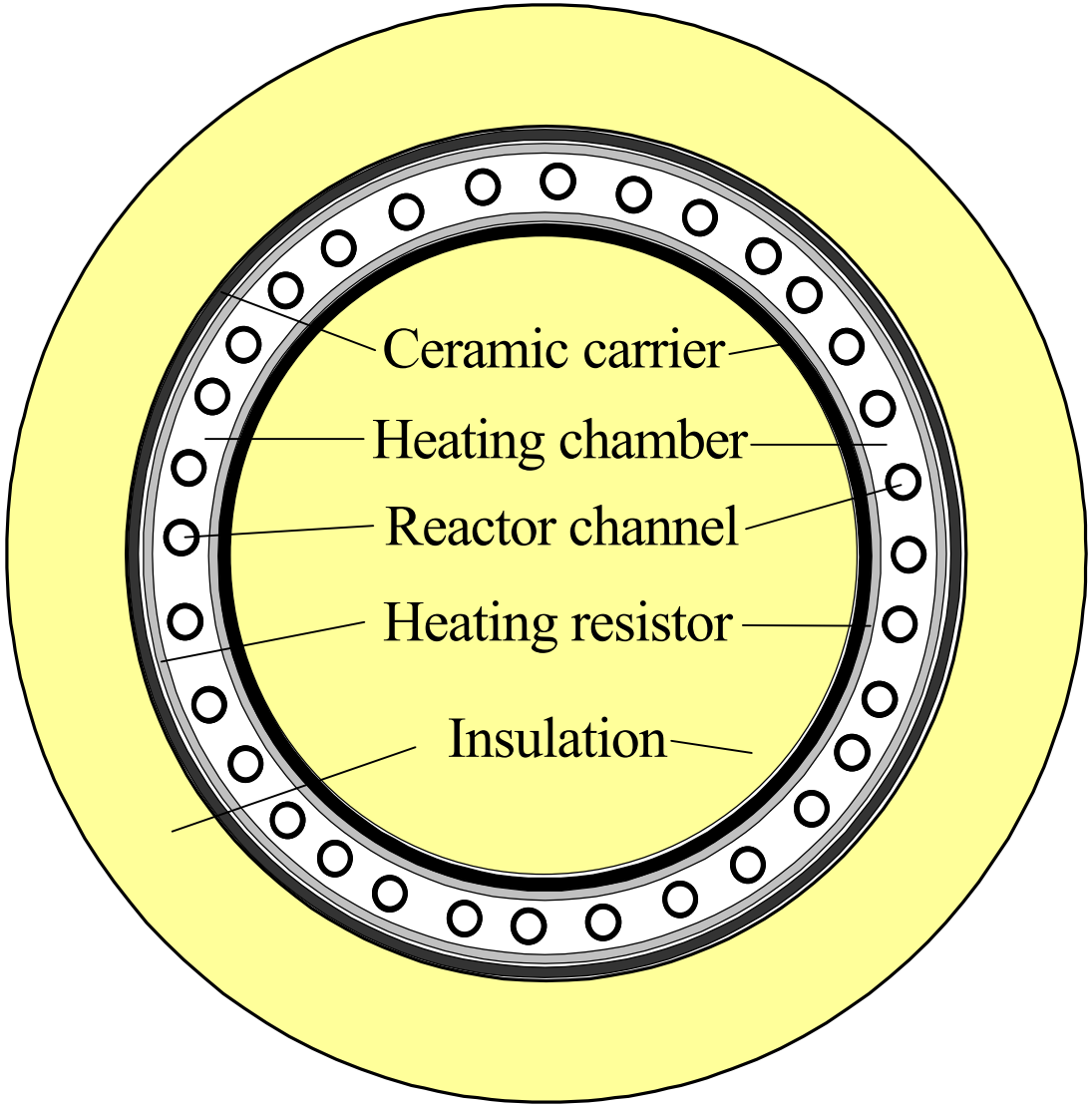
IR-spectroscopy (analysis of NH_3, CH_4 and HCN)



Applied CAtalysis

Solutions in equipment development - the heating system

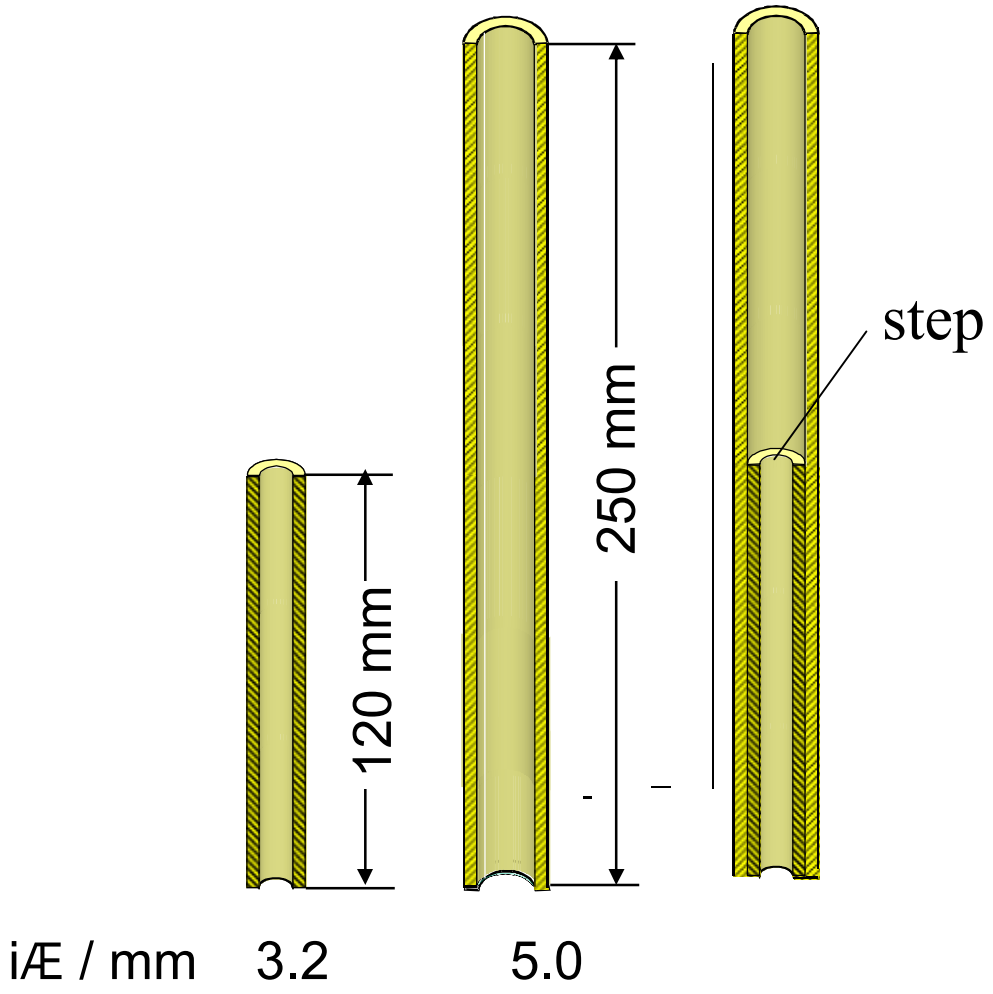
- Small concentrically heating chamber only 20 mm wide and 30 mm high
- Separately controlled heating resistor on the inner and outer side
- The reactor channels are arranged vertically through the chamber



Applied CAtalysis

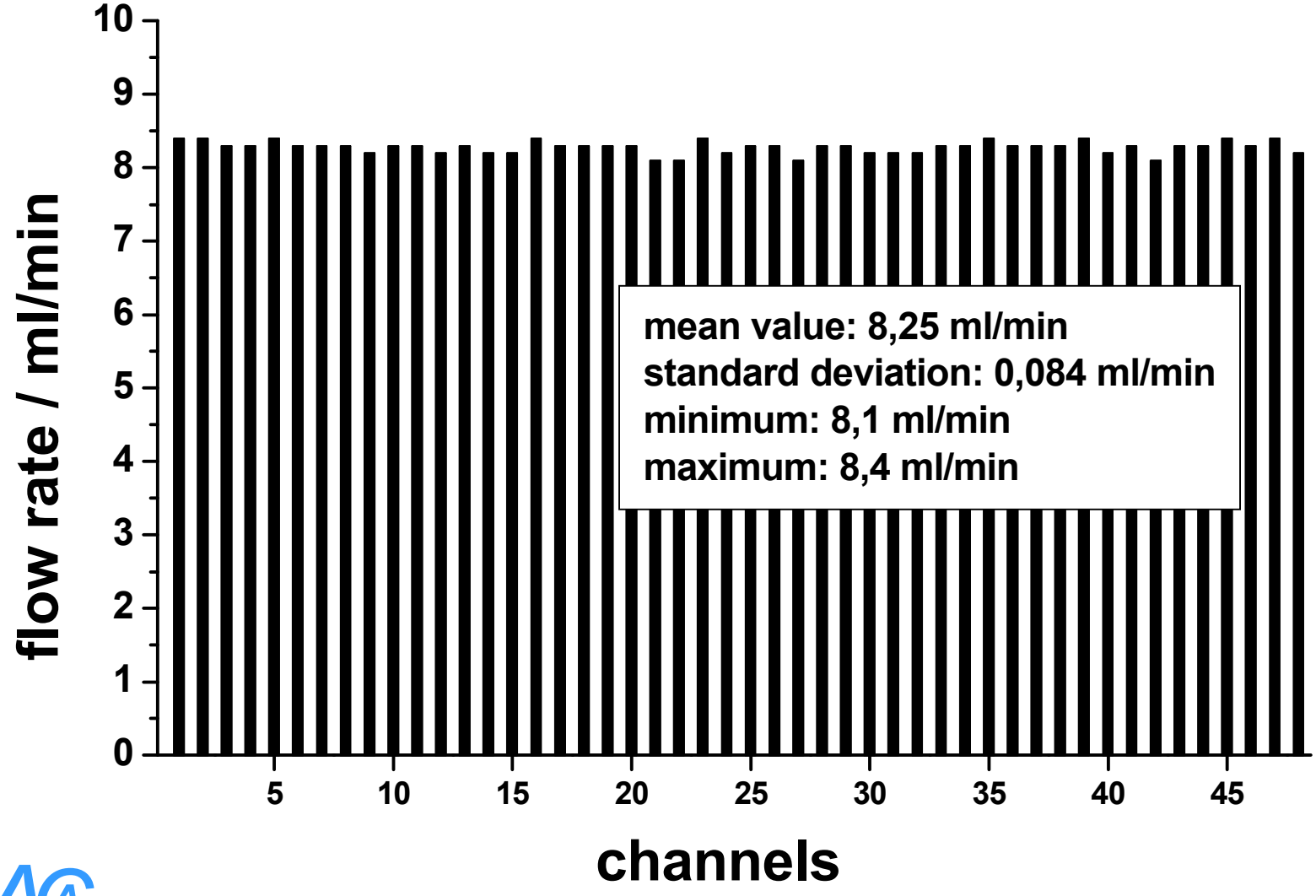
Solutions in equipment development - the reactor tube

- Using alumina as reactor material
- A small alumina tube is fitted into a bigger one
- The catalytic material is placed on an inert “sieve” lying on the step between the tubes



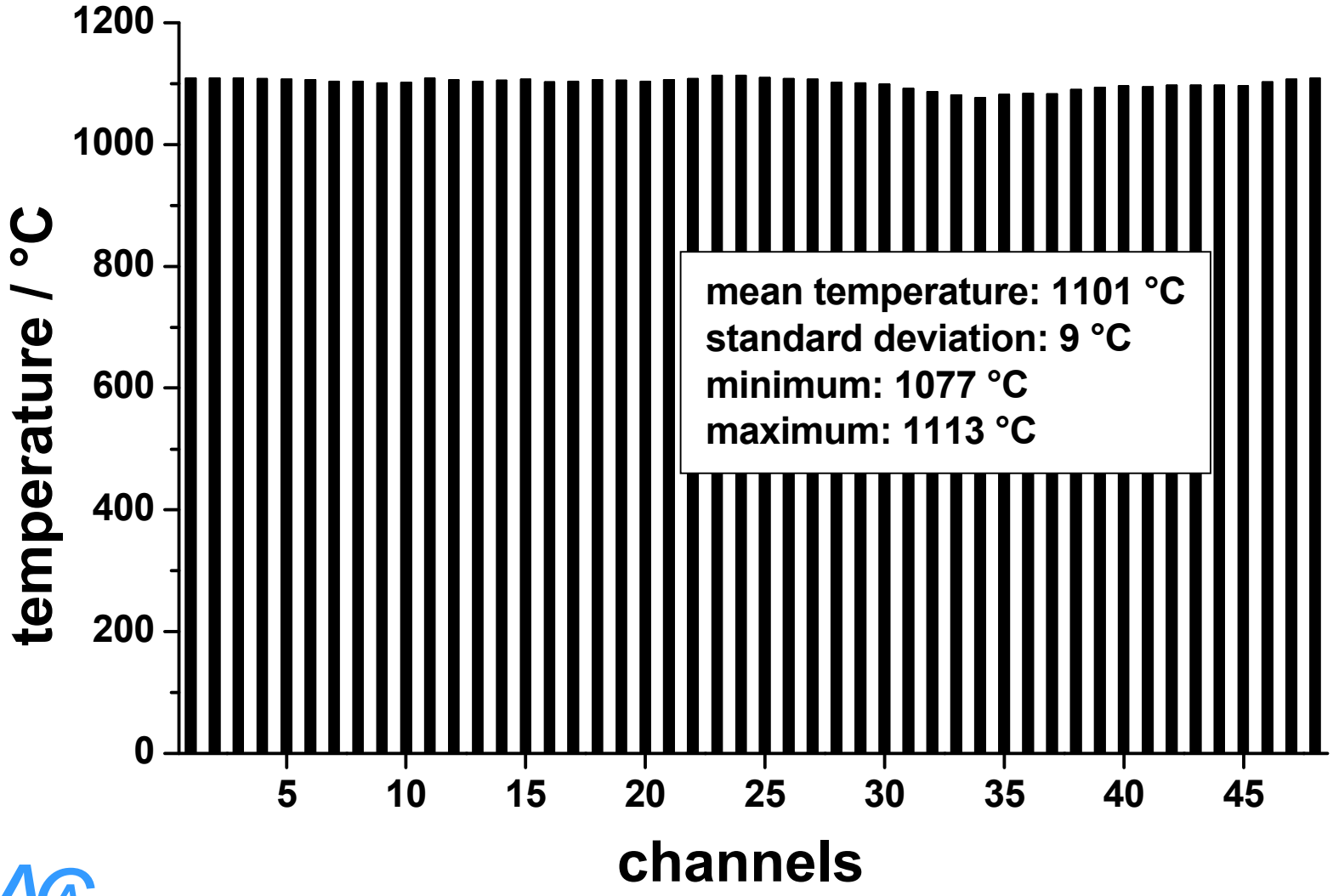
Applied CAtalysis

Validation of equipment for a high-temperature reaction
Comparison of the flow rates in the 48 different channels



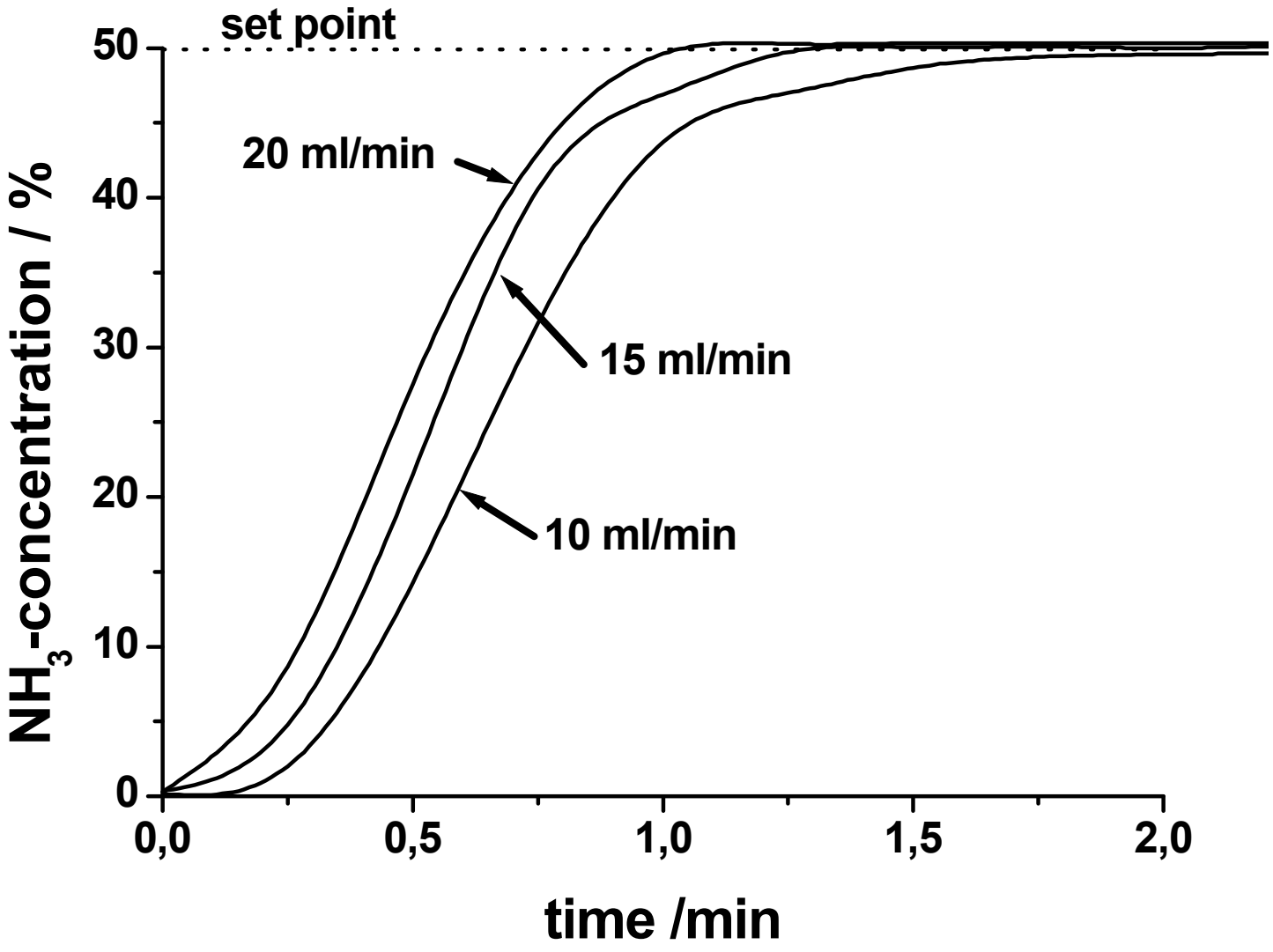
Applied CAtalysis

Validation of equipment for a high-temperature reaction
Temperature distribution in the 48 parallel channels



Applied CAtalysis

Validation of equipment for a high-temperature reaction
Time dependence of the response signal of the IR-spectrometer



Applied CAtalysis

Range of experimental conditions

- 48 fixed bed reactors

  catalyst-mass between 0.5 and 0.01g

- Temperatures up to 1150°C

  standard deviation less than 10°C between different channels

- Fast on-line analysis

  one analysis - including swiching and rinsing time - within 2 min

- Flow rates usually at 10 ml/min

  standard deviation <0.1ml/min between different channels

Applied CAtalysis

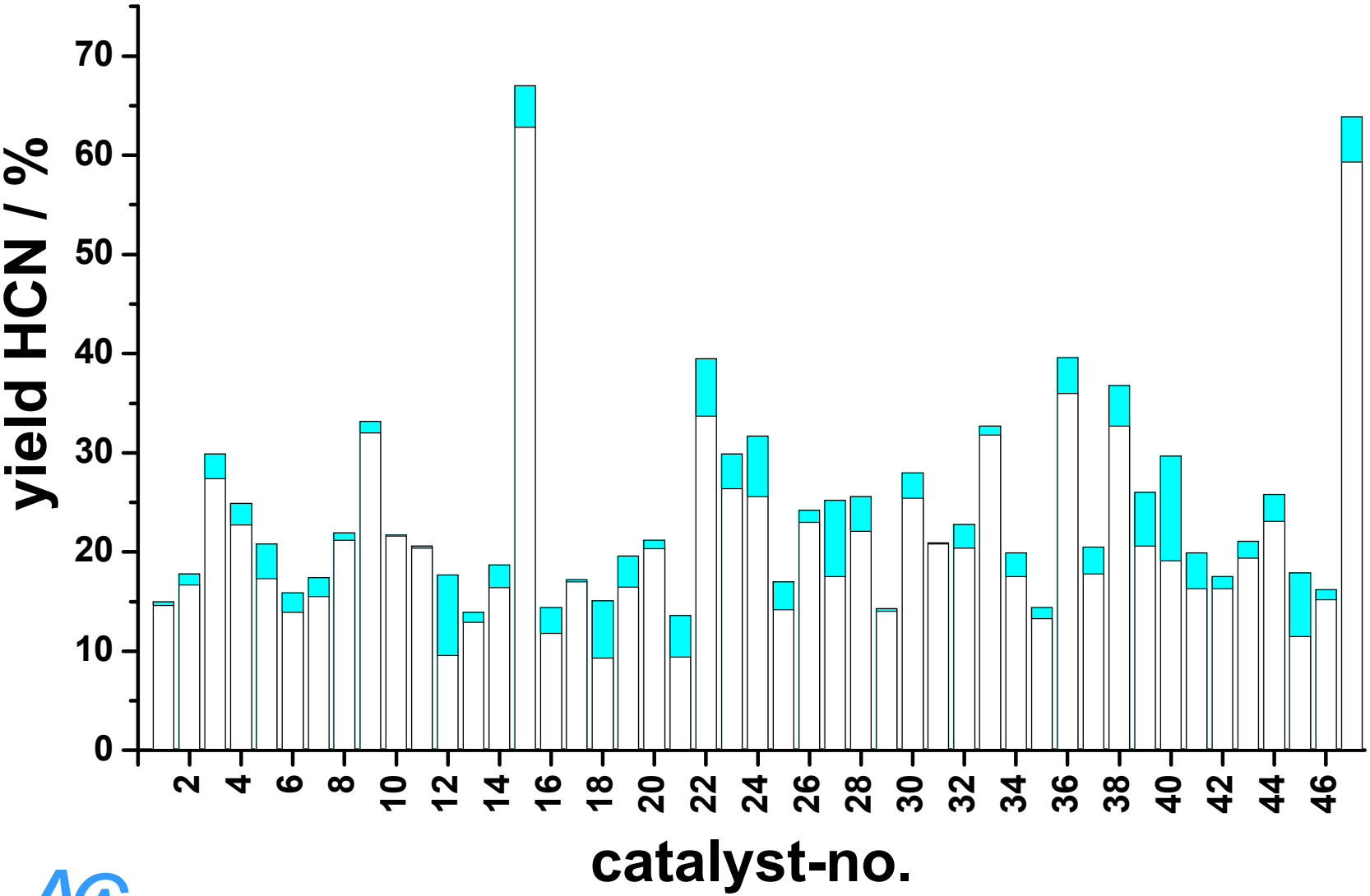
Potential catalytic compounds

- Support Materials
  thermally stable compounds with predominantly basic character (oxides, nitrides, carbides, borides)

- Active Components
  metals especially of the 7th but also of the other subgroups of the periodic table (noble metals, heavy metals)

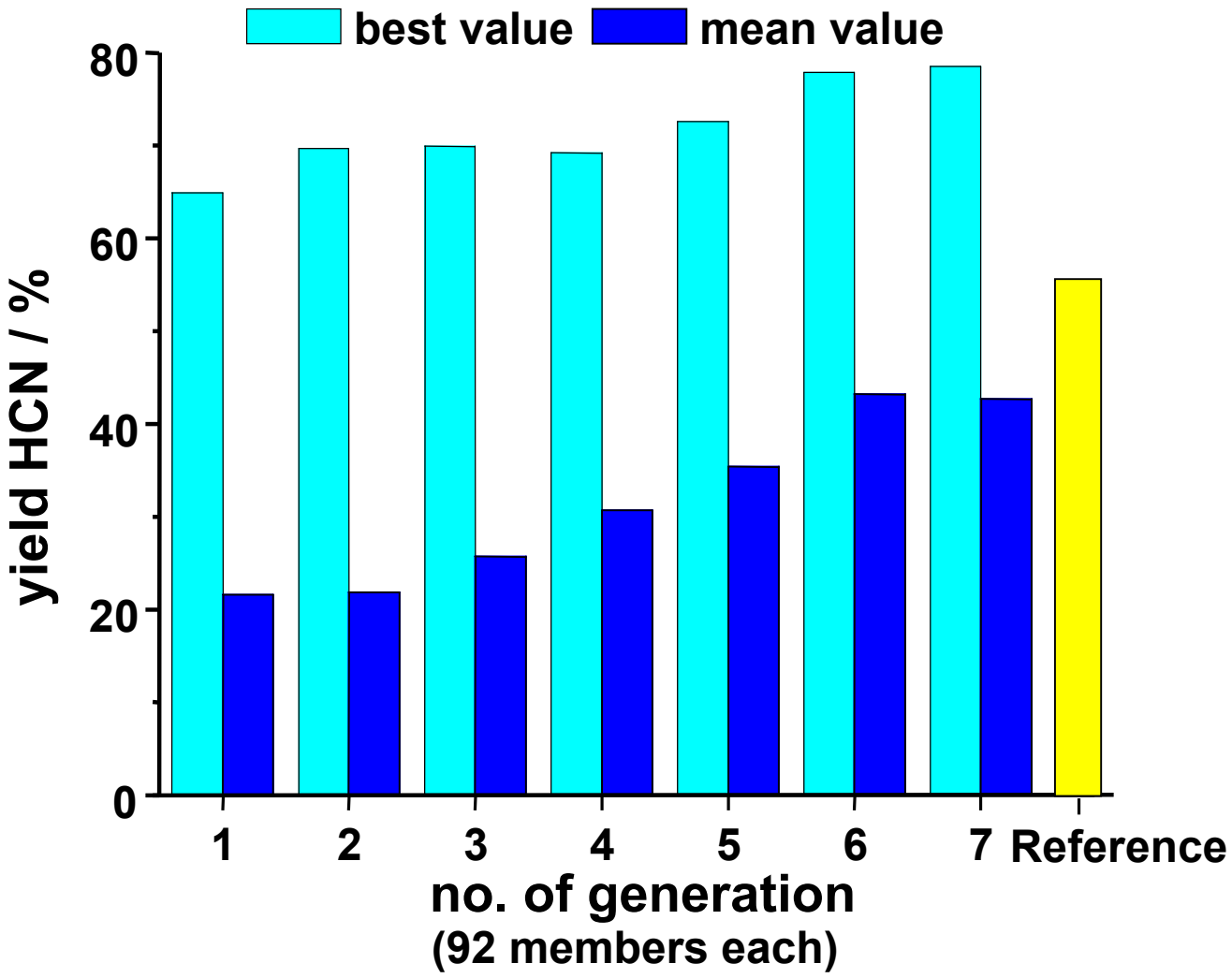
- Metal Coverage
  mixtures of up to 6 elements in one catalytic material; (1 to 10 hypoth. monolayers)

Reproducibility of the catalytic results
Identical catalyst compositions - twice synthesized and tested



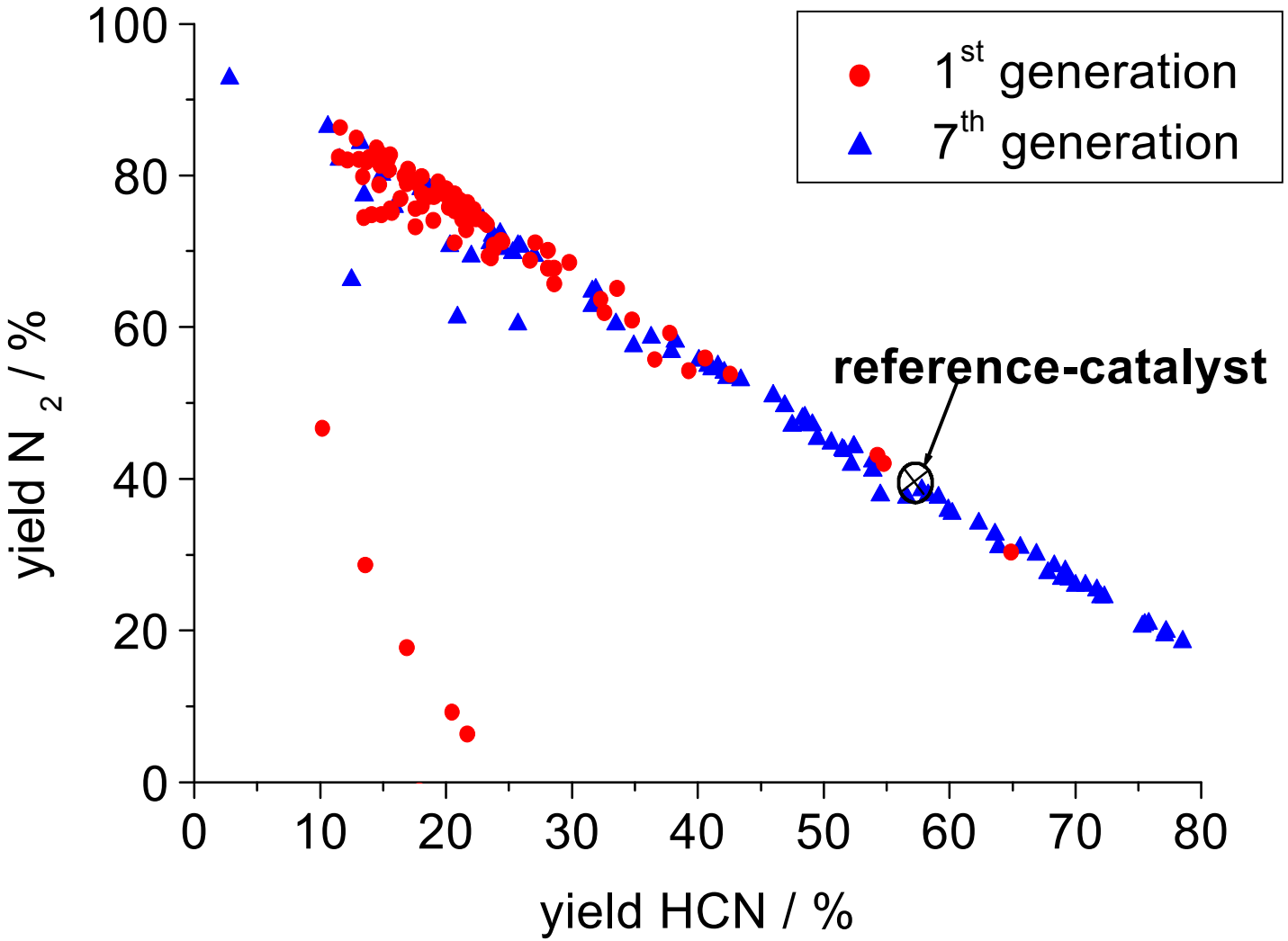
Applied CAtalysis

Development of the mean and best yields in subsequent catalyst generations



Applied CAtalysis

Improvement in catalytic performance - Correlation between N_2 and HCN yield



Applied CAtalysis

Conclusions

- Successful development of a new multi-channel reactor for high temperature reactions up to 1150°C
- The validation of the equipment shows good reproducibility of obtained catalytic results
- New promising catalyst compositions were detected for the reaction of methane and ammonia to hydrocyanic acid

A combinatorial approach using the high-temperature 48-channel reactor as well as parallel catalyst synthesis and evolutionary optimisation strategy is an effective way to search for better catalytic materials.

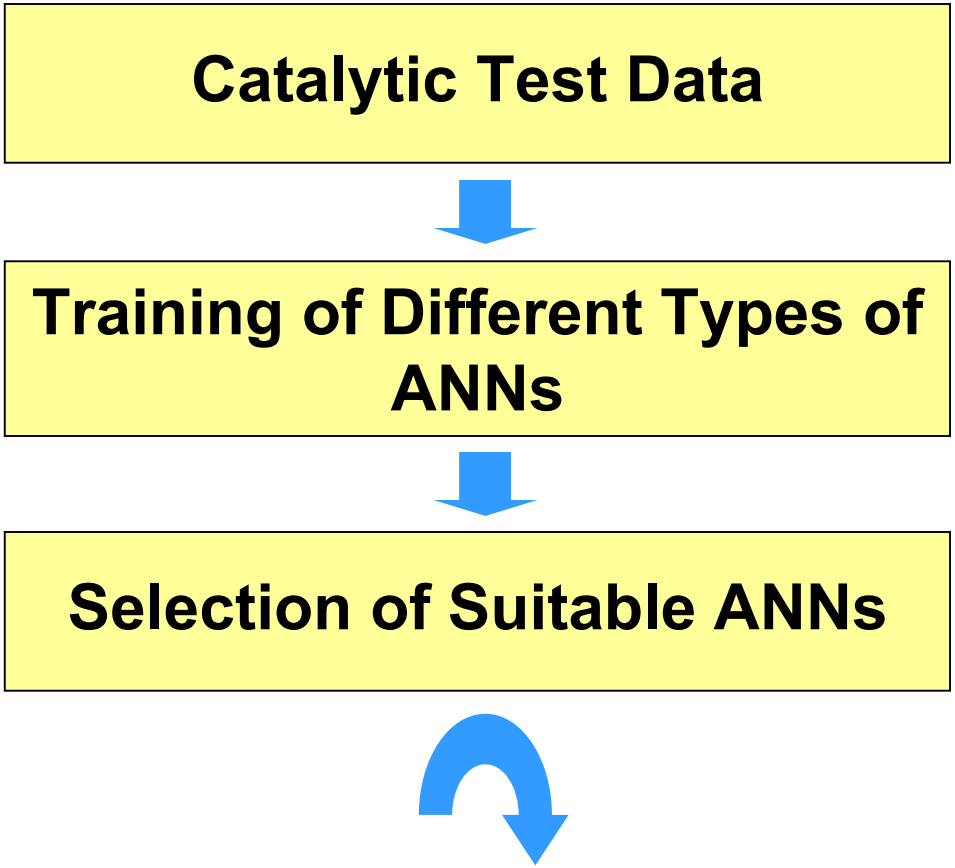
Artificial Neural Networks (ANN)
- Data approximation and knowledge extraction -

- ***Inspiration*** – biological neurons and neural systems
  - *signal (+information) processing: distributed*, not sequential
- ***Architecture*** – neurons, connections, layers (perceptron)
  - *input* | *hidden* | *output* neurons **~** signal processing
- ***Computed function***: input space → output space

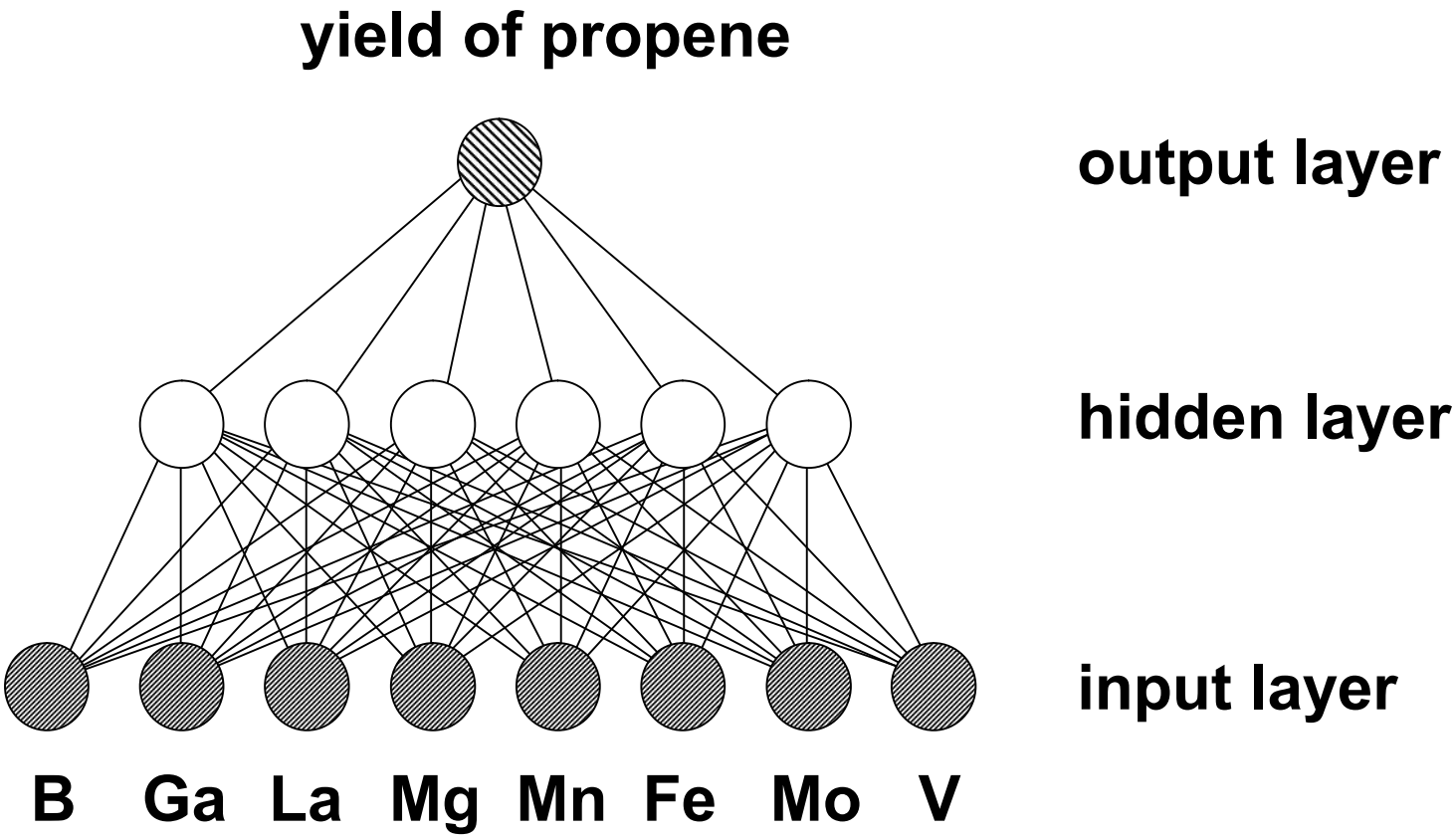
Why ANNs in Combinatorial Catalysis ?

- Mathematical description of the parameter space
- Establishing *complicated relationships* between
  - composition, chemical + physical properties, test conditions
    and
  - performance (yield, conversion, selectivity, deactivation, …)
- *Extraction of knowledge* available from test data
- Use of knowledge as driving force in the search for good catalysts

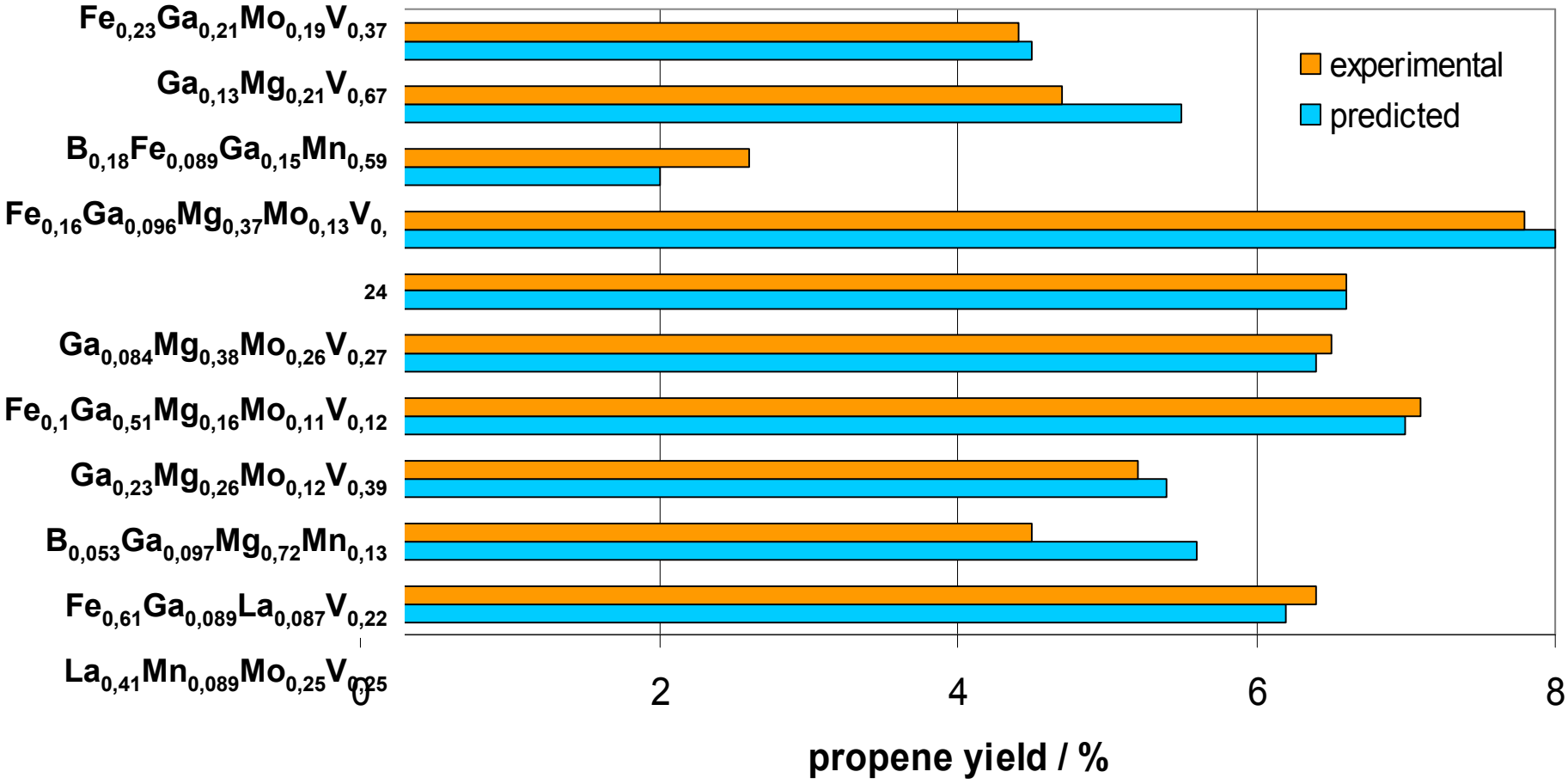
ANNs for Test-Data Analysis



Example of a Multilayer Perceptron



Validation of the ANN
Experimental and predicted data



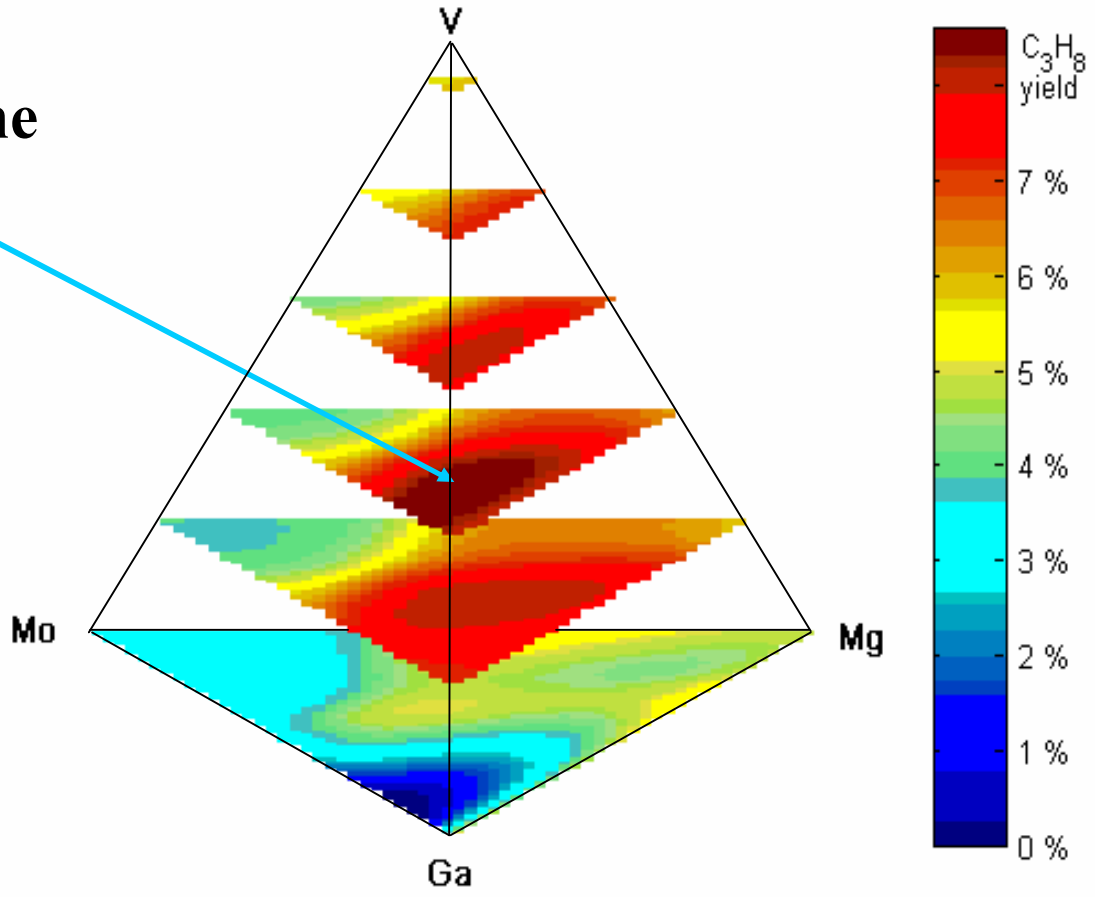
Applied CAtalysis

Knowledge extraction from data

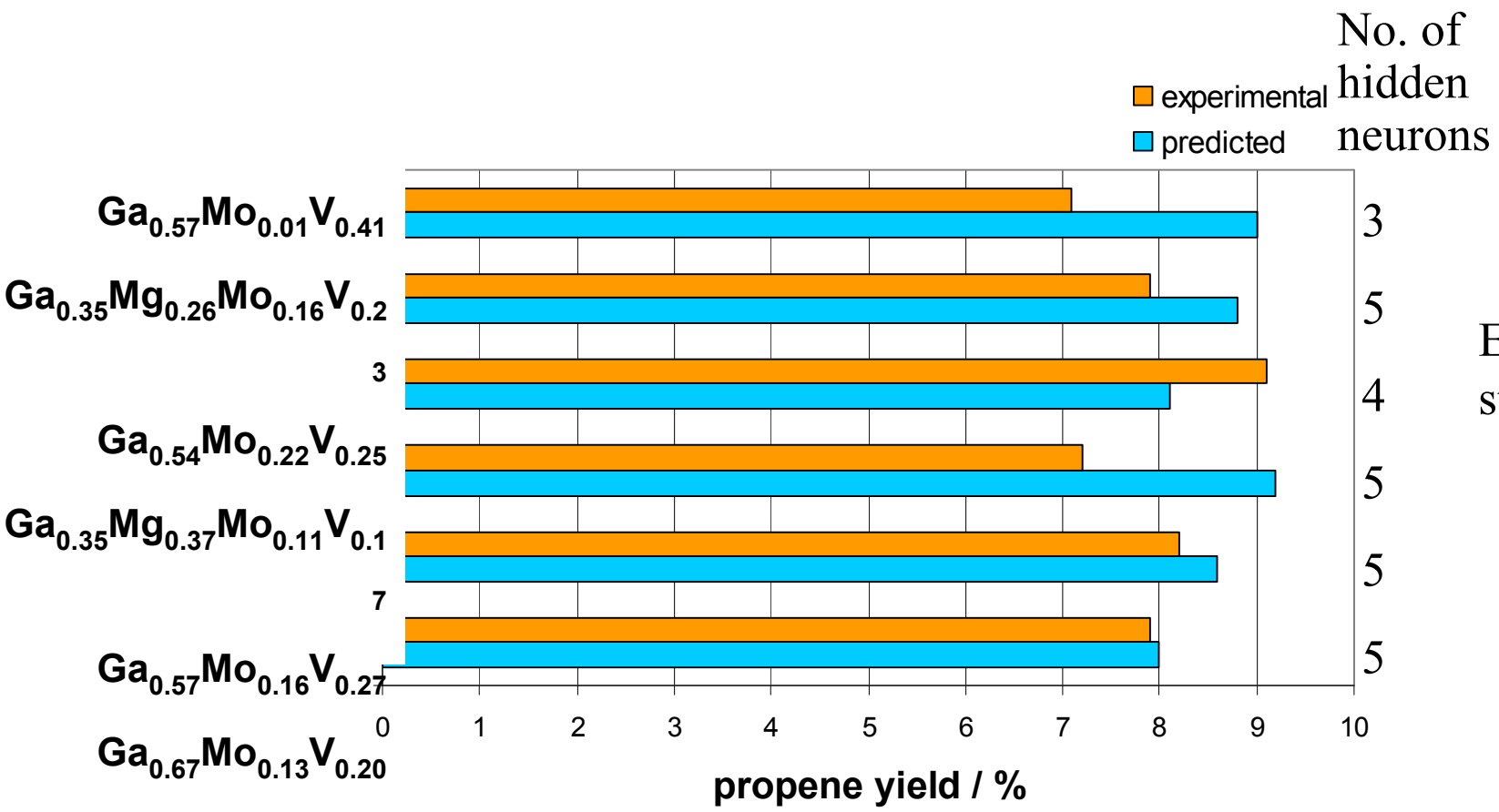
- **Prediction of catalytic performance for a given catalyst composition (interpolation)**
- **Prediction of optimal catalyst composition for maximum catalyst performance**
- **Logical rules about dependences**

Visualization of Knowledge from ANN

highest propene yields in the V-Mo-Ga-Mg system



Experimental Validation of Predicted Optimal Catalyst Composition
- Predicted and experimental results -



Applied CAtalysis

Extraction of Rules from ANNs

Rules for catalyst compositions showing propene yields > 8 %

Rule 1
Ga: 24 - 33 %
Mg: 31 - 39 %
Mo: 0 - 7 %

Rule 2
Ga: 38 %
Mg: 29 - 36 %
Mo: 0 - 9 %

Experimental validation of rules 1 and

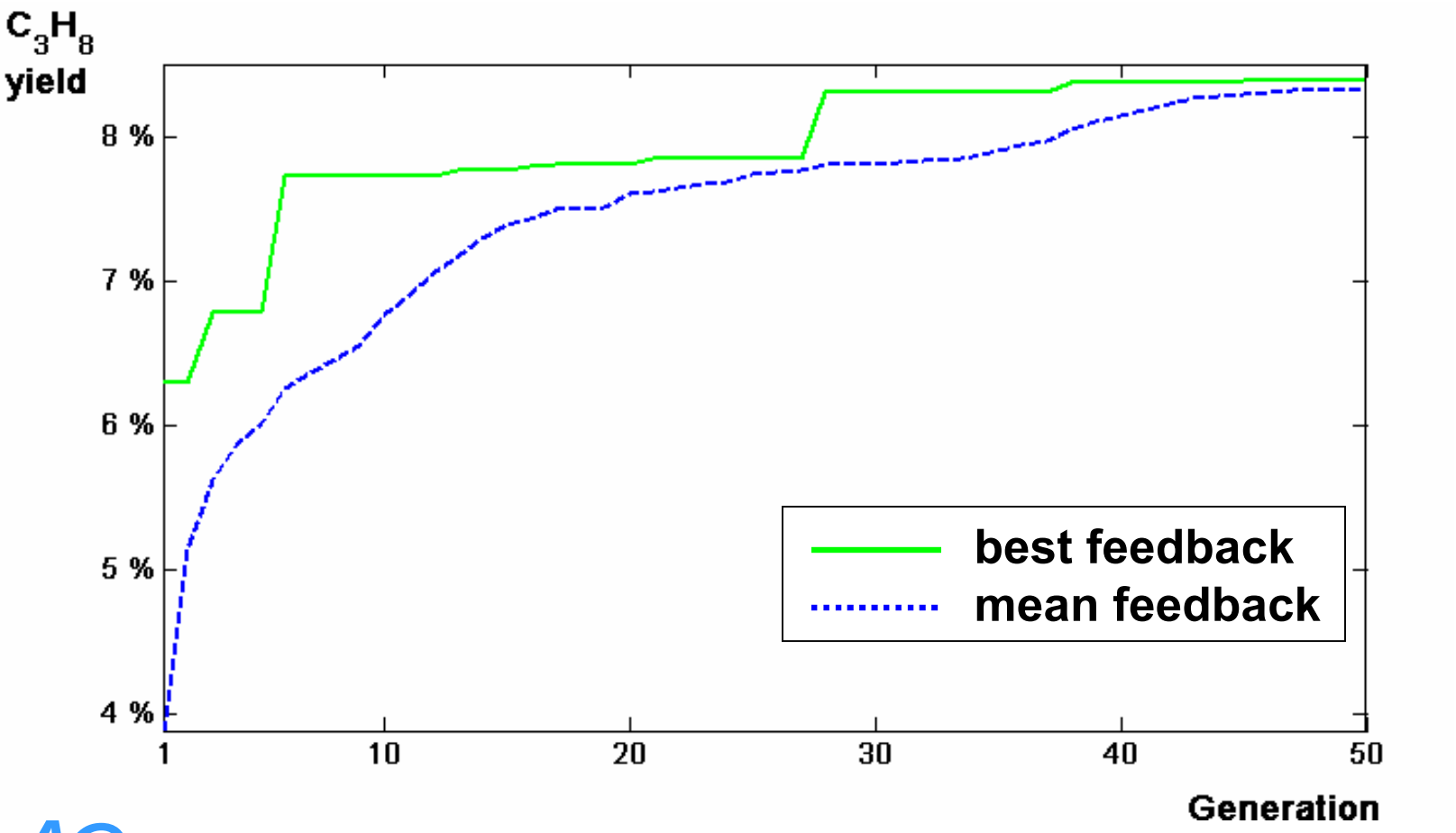
composition [mol %]				propene yield [%]	
Ga	Mg	Mo	V	predicted	experimental
32	32	7	29	8.1	8.2
27	36	6	31	8.1	8.4
32	33	5	30	8.3	8.0
38	31	8	23	8.3	7.9
38	31	9	22	8.4	8.3
38	32	9	21	8.4	8.2

Good agreement between prediction and experimental results

Applied CAtalysis

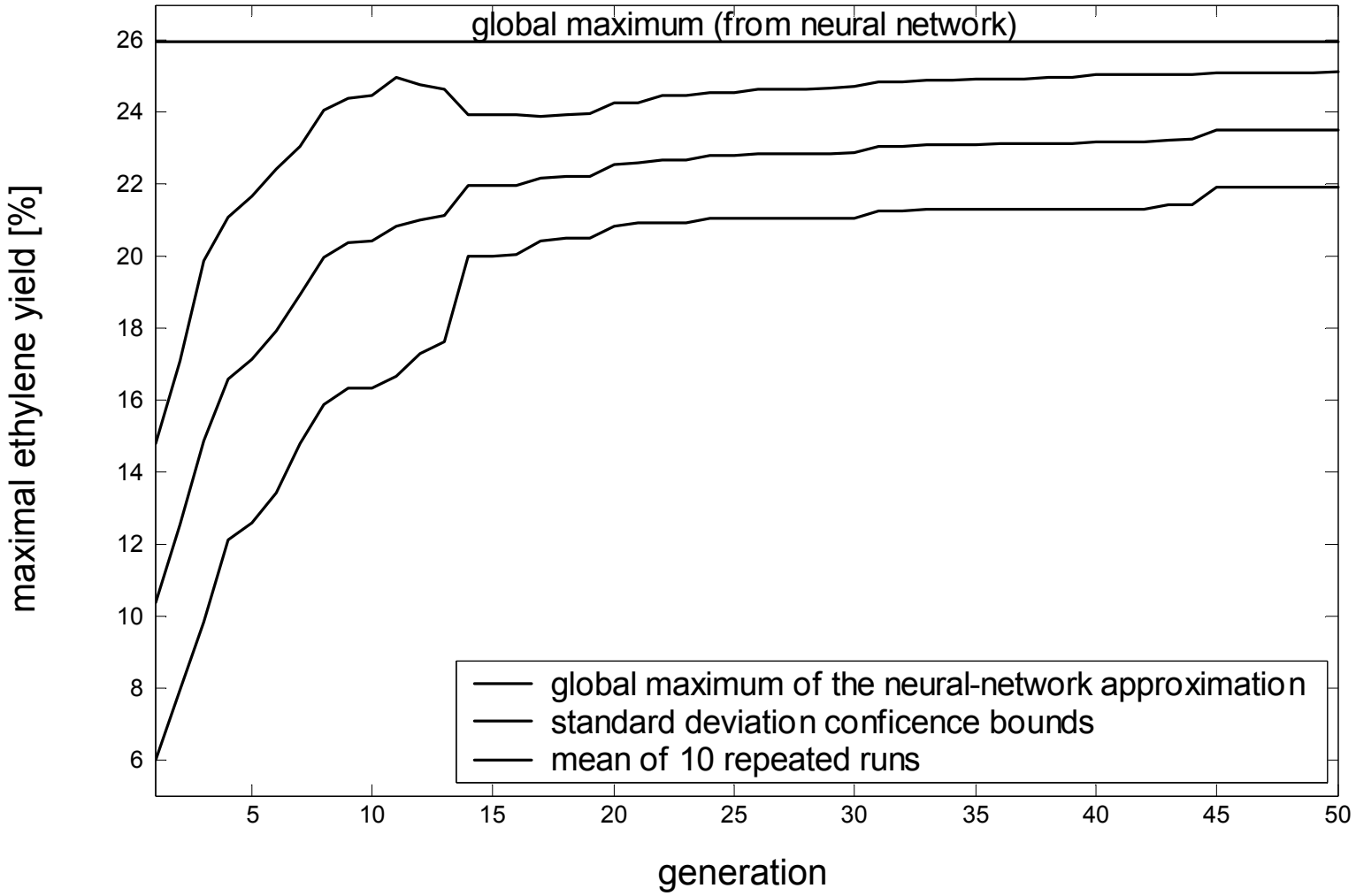
Combination of GA and ANN

Examplary visualization of convergence of a virtual GA run



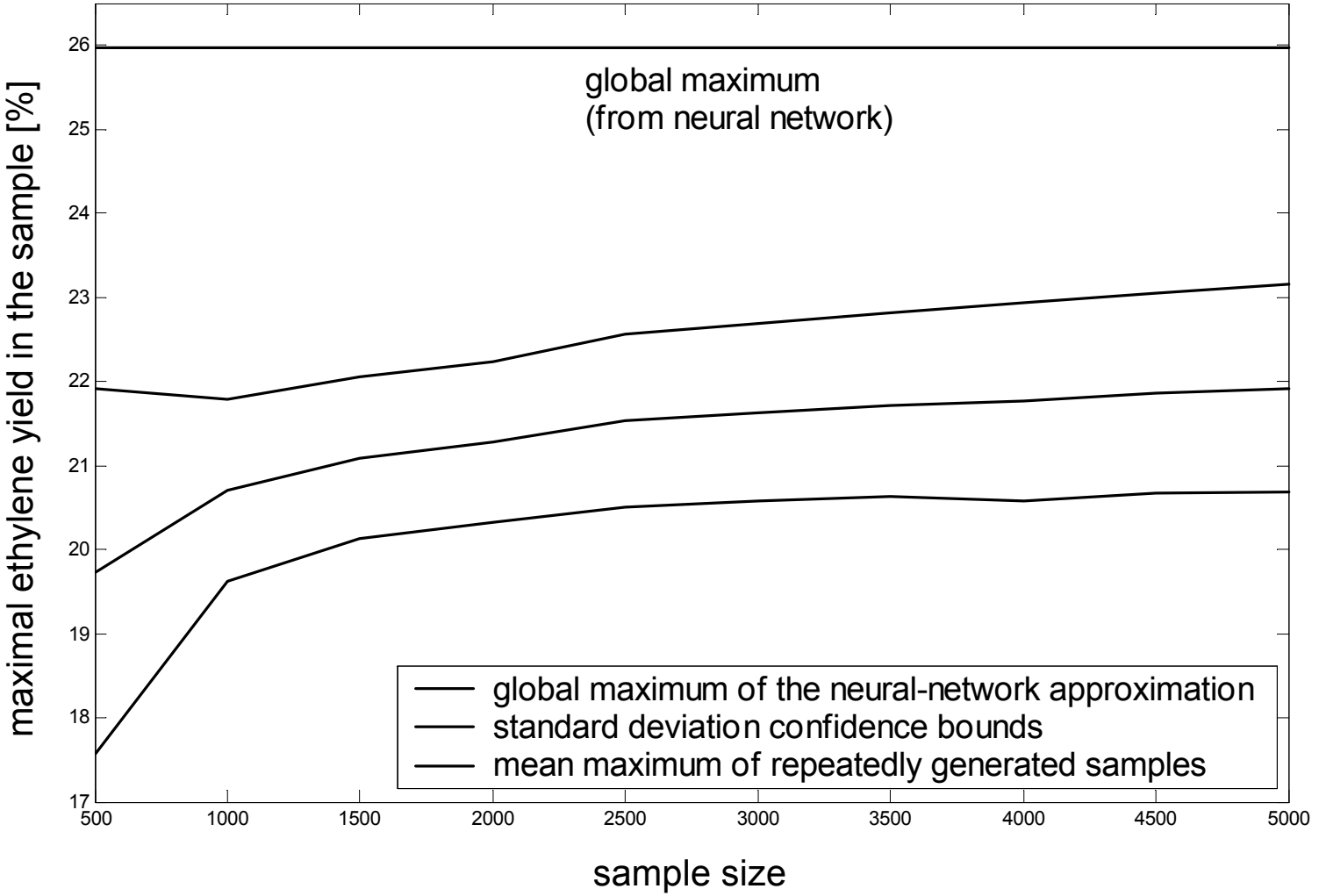
Applied CAtalysis

Application of ANN and GA for Predicting Catalyst Performance



Maximal catalyst performance in each 60-samples generation being prepared by an evolutionary approach (GA)

Application of ANN for Predicting Catalyst Performance



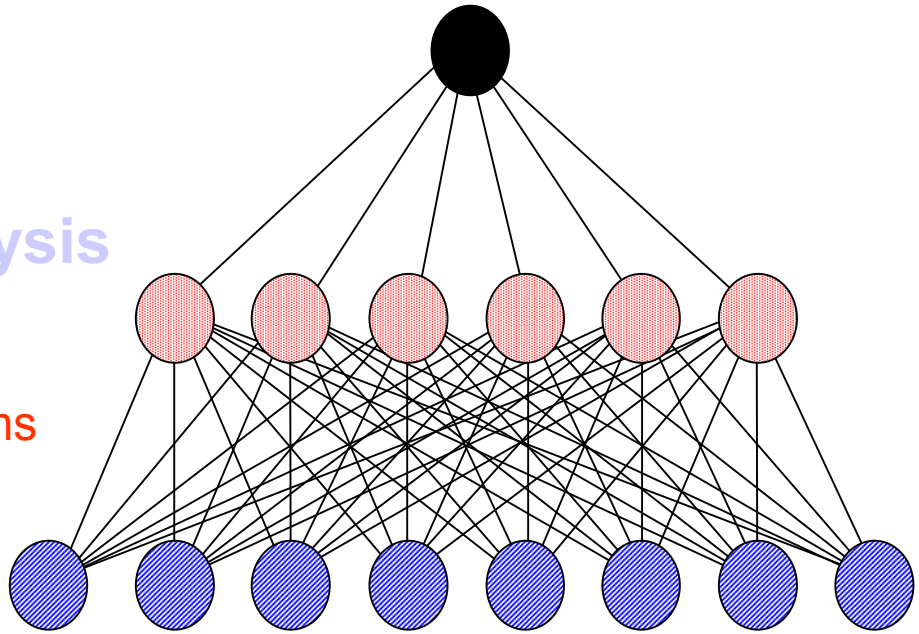
Maximal catalyst performance as a function of size of a generation of randomly-composed samples

Conclusions

- The GA approach is suited for improving and discovery of catalytic compositions
- For large data pools an ANN can be used as a tool for
  - knowledge extraction
  - setting up of relationships between catalytic performance and materials properties
  - predicting optimal catalyst compositions
  - testing of different optimization strategies as a basis
    for further experiments on the basis of pre-existing knowledge
- Combination of GA and ANN for setting up “virtual” experiments

Future Application of Neural Networks

Output Variables
Catalyst performance



outer layer

hidden layer

input layer

Descriptors
Catalyst properties

Science of Catalysis
Property-reactivity relationships
Kinetics and Mechanisms

Selection of Descriptors of Catalytic Materials

Synthesis parameters

- preparation method
- support material
- percentage of catalytic material
- mass of catalyst (scale-up)
- calcination temperature and time

Chemical composition

Reaction conditions

-
-

Physico-chemical properties

- acidity and basicity; electronegativity
- redox properties
- adsorption capacity for reactants
- crystallinity/amorphicity; crystal size; phase composition
- electronic and ionic conductivity
- BET surface area
- melting temperature, heat capacity, enthalpy of formation

Provision of kinetic data in high-throughput catalytic testing of solid materials

Standard conditions

First approximation for identifying a number of suitable materials which catalyze the chemical reaction towards the desired products

Full Kinetics

Change of reaction conditions in catalytic testing over the whole range of potential catalyst operation

The End