Multi-objective Optimization in Combinatorial Chemistry Applied to the Selective Catalytic Reduction of NOx.

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Motivation

- Need to focus on inventing new catalyst composition that allow to break away from current limits.
- High-throughput experimentation allows to explore a vast combination of new catalytic materials.
- Intelligent design of experiments and libraries is essential in order to find new and improved catalysts.
- The screening has to be directed to the desired direction and the number of experiments has to be minimized.
- Evolutionary methods such as genetic algorithms are highly flexible optimization methods [1].
- Genetic algorithms can be adapted in order to screen for improved combinations of mixed oxide metal catalysts with respect to multiple objectives.
- Combinations of Al, Cu, Ni, Co, Fe, Mn, K, Sr, La, Ce and Sm are used to prepare the new catalyst compositions.

Methods

- Automated synthesis of oxide nanoparticles by the activated carbon route [2] (fig. 1).
- High-throughput screening using a 49 parallel pass flow stage II reactor (fig. 2) in combination with a FTIR analysis of the exhaust gas stream (not shown).
- The combined error of the synthesis and of the catalytic test is 6 % (std. dev.).
- Multi-objective design of experiments by evolutionary optimization based on genetic algorithms.

Precursors

Mixing

Impregnation

Fig. 1: ABIMED liquid handling robot robot for automated precursor mixing and impregnation of activated carbon particles.

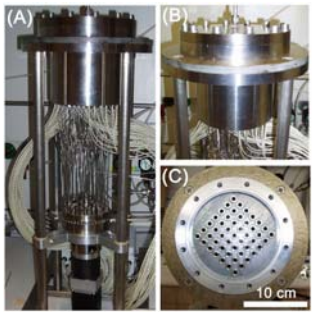


Fig. 2: Images of the 49 parallel channel reactor set-up (hte AG Heidelberg): (A) side view on the complete setup, (B) closed reactor and (C) top view on the open reactor.

Multi-objective evolutionary optimization

- Single objective optimization is a special case of multi-objective optimization (and not vice versa).
- Implementation of the optimization framework using PISA [3].
- Multi-objective algorithms: SPEA2 [4] and IBEA [5].
- Variators: bit-flip mutation and one point binary crossover.

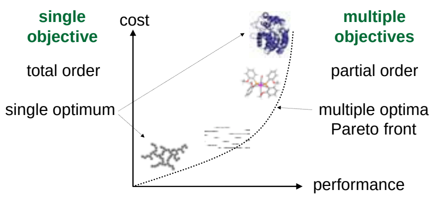


Fig. 3: Schematic representation of a Pareto-optimal front for two objectives.

Encoding of solid multi-component catalysts

- Encoding of the catalysts by binary chromosomes of 27 bits: **11 bits** for the combinations of the elements and **16 bits** for the concentrations (fig. 4).
- Selected boundary conditions and constraints in order to reduce the search space:
  1. The maximum number of main elements in a catalyst is less or equal than four.
  2. The sum of the concentrations of the promotor elements is limited to 5.0 mol%.
  3. The sum of all concentrations equals 100 mol%.
  4. Two systems are considered: systems with and without Al as support; for both systems Al constitutes the remainder, but the concentration ranges are different (table 1).

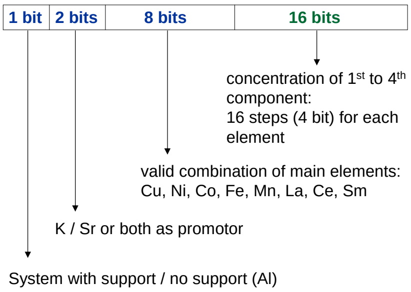


Fig. 4: Encoding scheme using 11 bits for the combinatorial and 16 bits for the continuous part of the problem.

Genotype	support	no support
0000	0.5	2.0
0001	1.0	4.0
0010	2.0	8.0
(…)	(…)	(…)
0111	12	30
1000	16	33.3
(…)	(…)	(…)
1100	32	63
1101	33.3	75
1110	34	88
1111	35	100

Table 1: Discrete encodings of the element concentrations (in mol%).

Constraint handling technique

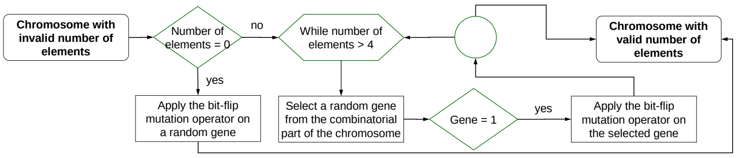


Fig. 5: Flowchart of the repair algorithm for the combinatorial part of the chromosome.

Application to the HC-SCR

- Application: the problem of finding the best combination and composition of elements in a catalyst active at low temperature in HC-SCR (hydrocarbon selective catalytic reduction of NO).
- The catalysts are optimized with respect to the conversion to N_2 and the temperature at which the yield is maximal.
- Reaction conditions: 1500 ppm NO, 2000 ppm C_3H_6, 5% O_2, rest N_2, GSHV 20.000 h^{-1}

Results

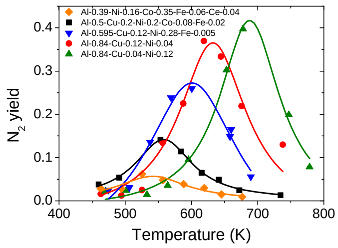


Fig. 6: NO to N_2 conversion curves as a function of the temperature for selected Pareto-optimal solutions.

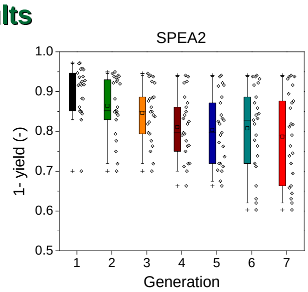
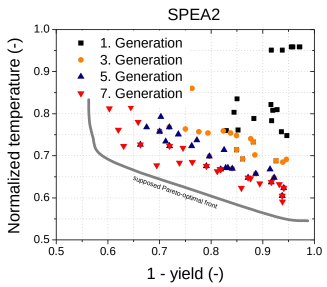


Fig. 7: Evolution of the objective function (1- yield) for the solutions of the archive population for SPEA2.



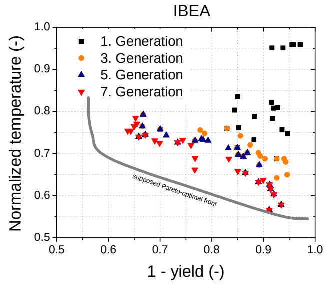
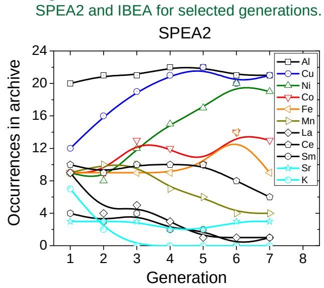


Fig. 8 and 9: Visualisation of the evolution of the archive population in the objective space for SPEA2 and IBEA for selected generations.



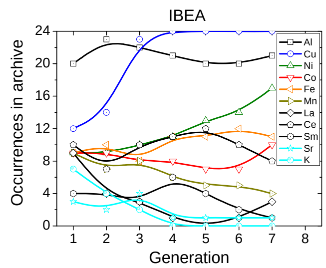


Fig. 10 and 11: Evolution of the occurrences of elements in the archive population for SPEA2 and IBEA.

Conclusions

- Stage II screening approach in combination with genetic algorithms is a valuable tool for high-throughput investigations of catalysts also with respect to multiple objectives.
- The full strength of these techniques can be played off especially for the screening of unknown, high dimensional and constrained spaces.
- “Simple” catalyst compositions (ternary oxides) show better performance than more complex compositions.
- The best noble metal free catalysts are combinations of Cu and Ni. Catalysts, which are active at low temperature, furthermore include Co and Fe.

Literature

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[5] E. Zitzler, S. Kunzli, in Parallel Problem Solving From Nature - Ppsn Viii. (2004), vol. 3242, pp. 832-842.

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