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Multi-objective optimization in combinatorial chemistry applied to the selective catalytic reduction of NO with C₃H₆

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Abstract

A high-throughput approach, aided by multi-objective experimental design of experiments based on a genetic algorithm, was used to optimize the combinations and concentrations of a noble metal–free solid catalyst system active in the selective catalytic reduction of NO with C_3H_6 . The optimization framework is based on PISA [S. Bleuler, M. Laumanns, L. Thiele, E. Zitzler, Proc. of EMO'03 (2003) 494], and two state-of-the-art evolutionary multi-objective algorithms—SPEA2 [E. Zitzler, M. Laumanns, L. Thiele, in: K.C. Giannakoglou, et al. (Eds.), Evolutionary Methods for Design, Optimisation and Control with Application to Industrial Problems (EUROGEN 2001), International Center for Numerical Methods in Engineering (CIMNE), 2002, p. 95] and IBEA [E. Zitzler, S. Künzli, Conference on Parallel Problem Solving from Nature (PPSN VIII), 2004, p. 832]—were used for optimization. Constraints were satisfied by using so-called "repair algorithms." The results show that evolutionary algorithms are valuable tools for screening and optimization of huge search spaces and can be easily adapted to direct the search towards multiple objectives. The best noble metal free catalysts found by this method are combinations of Cu, Ni, and Al. Other catalysts active at low temperature include Co and Fe.

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1. Introduction

High-throughput experimentation (HTE) and combinatorial methods for the development of new catalysts are attracting increasing attention in both industry and academia [1–6]. One important element in HTE, common to both homogeneous and heterogeneous catalysis, is the design of experiments and of libraries to find new and improved catalysts. The need is for intelligent methods that are able to direct the screening to the desired direction and minimize the number of experiments needed to achieve a significant improvement. Evolutionary methods, such as genetic algorithms, have been found to be efficient and highly flexible in solving various combinatorial and global optimization problems in complex and multidimensional spaces [7]. Directed evolution has proven a versatile and powerful method for the generation of combinatorial libraries and development

Corresponding author. *E-mail address:* schueth@mpi-muelheim.mpg.de (F. Schüth). of biocatalysts [8–10]. The design of combinatorial libraries in the drug industry has one application of this method [11–13]. In the field of heterogeneous catalysis, Wolf et al. [14] were the first to use an evolutionary approach to optimize the combinations of elements of multicomponent solid catalysts. Since then, several groups have optimized solid catalysts with the aid of genetic algorithms [15–19]. However, up to now, the search has been conducted toward one sole objective. In real world problems and especially in catalysis, several, often conflicting objectives generally must be taken into account. Thus, methods that are able to find optimal solutions with respect to several goals are needed.

In general, a multi-objective optimization problem can be defined as finding a vector of decision variables, $\mathbf{x} = (x_1, x_1, \dots, x_m) \in \mathbf{X}$, in the decision space \mathbf{X} that optimizes a vector function $\mathbf{f} : \mathbf{X} \to \mathbf{Y}$ by assigning the quality of a specific solution \mathbf{x} to a vector of objective variables $\mathbf{y} = (y_1, y_1, \dots, y_n) \in \mathbf{Y}$ in the multidimensional objective space \mathbf{Y} . In the case of a solid catalyst, the decision variables can be any

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set of appropriate descriptors to be optimized. A functional relation should exist between the *m* decision variables and the *n* objective functions. A quantitative structure activity relationship (QSAR) model, which can assign the quality of a solution **x** to the objective vector **y**, can be used for modeling such a problem [20–22]. However, up to now QSAR, modeling of complex systems, such as solid catalysts, carries a high error in prediction. Thus, a model must first be developed. For this reason, when screening for new solutions in unknown decision spaces, evaluation of the objective functions can be done only experimentally or using a hybridization of an experimental and a QSAR approach. In the present work, we focus on the purely experimental approach.

In the last few years, in the light of the energy problem and global warming, additional efforts have been made to prevent the release of substances that amplify these environmental problems. Therefore, diesel and lean-burn gasoline engines are becoming more and more attractive compared with regular gasoline engines due to the higher efficiency with respect to fuel consumption. Also, increasingly stringent emission regulations of harmful substances for vehicles urgently require new catalysts that are highly active for the selective reduction of nitrogen oxides in oxygen-rich conditions. One group of possible catalysts are noble metal–free metal oxides. The number of possible combinations is vast, and some have been investigated on various supports in recent years [23–25].

In this work, we present a method for experimental optimization with respect to multiple objectives. We focus on the optimization of metal oxides consisting of combinations of 11 elements, selected from the transition metal (Cu, Ni, Co, Fe, Mn), lanthanide (La, Ce, Sm), and alkali metal (K, Sr) groups. Alumina was used as the support, because of its ability to develop high surface area and its high hydrothermal stability. A combinatorial, evolutionary directed, high-throughput multi-objective optimization approach was applied to this system. Due to its importance in industry, the selective catalytic reduction of nitrogen oxide with C_3H_6 is used as a test case for this approach.

Two important factors that determine the quality of a catalyst include the maximum conversion that can be achieved and the temperature at which high conversion is possible. Due to the fact that most of the restricted compounds are emitted in the early phase of the driving cycle, when the catalyst is still cold, a low temperature for high conversion is preferable. Thus, the catalysts will be optimized with respect to two objectives: the conversion to nitrogen and the temperature at which the yield is maximal (the so-called "peak" or "light-off" temperature). We applied two different multi-objective algorithms—SPEA2 [26] and IBEA [27]—to this problem. We compare and discuss the results of the two algorithms, emphasizing some implementation and encoding issues common to heterogeneous catalysis.

2. Experimental

2.1. Catalyst synthesis

The mixed oxide catalysts were prepared by the activated carbon route [28,29], using metal nitrates as precursors. Acti-

vated carbon (R1424, Carbotec/Rütgers) from the same activation batch was used as an exotemplate because of its exceptional properties: high purity (ash content <0.5 wt%) and very high BET surface area (1800 m^2/g) and pore volume (0.9 cm^3/g). The pore system consists of a very high fraction of micropores with diameter <1 nm, with particles almost uniform spheres 200-400 µm in diameter. The impregnation was carried out by an automated liquid-handling robot (ABIMED) using 2 M precursor solutions of the corresponding metal nitrates: Ni(NO₃)₂ from Fluka, purum p.a.; Cu(NO₃)₂, Co(NO₃)₂, La(NO₃)₃ from Fluka puriss p.a.; Al(NO₃)₃, K(NO₃), Sr(NO₃)₂, Mn(NO₃)₂, Fe(NO₃)₃ from Merck, GR for analysis; Ce(NO₃)₃ and Sm(NO₃)₃ from Acros Organics (99.9% pure). After the precursor solutions were mixed by the robot, the mixed solutions were used to impregnate the activated carbon using a slight excess of solution (for 1 g of activated carbon, 0.99 mL of solution). Calcination was performed without additional drying at 973 K for 3 h in air to combust the carbon, resulting in the formation of the mixed metal oxides. The resulting mixed oxide particles were also uniform and spherical in most cases, and of similar diameter as the carbon exotemplate, as can be seen in Fig. S1 for a representative Cu/Ni/Al particle.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained using a Bragg–Brentano diffractometer (PANalytical, X'Pert Pro). The data were collected using CuK_{α} radiation (1.54056 Å), a secondary Ni-filter, and an X'Celerator detector. Patterns were recorded in the range of 15–70° 2 Θ and a step width of 0.0167°. Nitrogen physisorption isotherms were measured using a Quantachrome NOVA 3000e sorptometer at liquid nitrogen temperature (77 K), after outgassing under vacuum at 523 K for at least 2 h. Particle shape and size were estimated by scanning electron microscope operating at 10 kV. The samples were coated with a thin layer of gold before analysis.

2.3. Catalytic testing

A stage II high-throughput screening concept using a 49 parallel stainless steel gas-phase reactor from hte Aktiengesellschaft, built according to the principles described in Kiener et al. [30], was used for testing the catalytic activity of the mixed oxide catalysts in the selective catalytic reduction of NO with C₃H₆ under lean-burn conditions. Fig. 1 shows several images of the reactor setup. The catalysts were activated at 573 K under a nitrogen flow for at least 2 h before catalytic testing. The measurements were performed under a mixture of 2000 ppm C₃H₆, 1500 ppm NO, and 5% O₂ at GSHV \sim 20,000 h⁻¹ and a reactor pressure of 1.2 bar at up to 10 different temperatures for each catalyst. To reduce the time needed for the catalytic testing of all 49 catalysts, the temperature of the reactor was increased steadily from 473 to 773 K at a rate of 12 K/h. Thus, the complete testing of all 49 catalysts at up to 10 different temperatures took about 25 h.



Fig. 1. Images of the 49 parallel channel reactor set-up: (A) side view on the complete setup, (B) closed reactor and (C) top view on the open reactor.

The exhaust gas compounds were analyzed by Fourier transform infrared (FTIR) spectroscopy, using a Thermo Electron Nicolet Avatar 370 with a 17-mL gas cell heated to 303 K. The resolution of the system was set to 1.0 cm^{-1} , the aperture to 100, and the gain to 8. The pressure at the outlet of the gas cell was set to 1.2 bar. Eight scans were obtained for each spectrum, and a total of four spectra were recorded for each analysis.

2.4. Calculations

From the IR spectra, the gas concentrations of NO, NO₂, N₂O, C₃H₆, CO, CO₂, and H₂O were evaluated at two characteristic wavelengths. The N₂ concentration was calculated from the NO, NO₂, and N₂O concentrations using the nitrogen mass balance; it was assumed that no additional nitrogen compounds were formed. Both objective functions are to be minimized and are obtained by normalization of the maximum conversion of NO to N₂ and of the temperature at which the conversion is maximal:

$$1 - \text{yield to } N_2 = 1 - \frac{[\text{NO}]^{\text{out}} - [\text{NO}_2]^{\text{out}} - 2[\text{N}_2\text{O}]^{\text{out}}}{[\text{NO}]^{\text{in}}}$$

normalized temperature =
$$1 - \frac{T_{\text{max,yield}} - 800 \text{ K}}{150 \text{ K} - 800 \text{ K}}.$$

The normalization parameters were chosen to have the same scale for both objectives.

3. Experimental design by evolutionary multi-objective optimization

Evolutionary techniques such as genetic algorithms are global search techniques, which can be used for experimental design. They include heuristic strategies for searching for new and improved solutions in an intelligent way. Interactions among design variables or components are intrinsically considered. These techniques are inspired by evolutionary biology; they maintain several potential solutions in parallel (a population), and the solutions undergo recombination, mutation, and selection steps during each iteration. One iteration loop is called a generation. After a certain number of generations, the algorithm converges, and, ideally, it finds the globally optimal solution.

Genetic algorithms are also suited for experimental design with respect to several goals or objective functions. In singleobjective optimisation, the optimal solution is clearly defined, and only one possible solution exists. In the case of multiobjective optimization, where we attempt to optimize all of the objectives at the same time, the situation is completely different, because two optimal solutions may differ. Thus, the optimal solution is a composite of all optimal solutions with respect to multiple objectives and usually forms a set of optimal trade-off surfaces that also includes the single objective optimum. This set of optimal solutions is designated the Pareto-optimal set. In multi-objective optimization, generally the goal is to approximate this set and keep the population as diverse as possible.

The platform and programming language independent interface for search algorithms (PISA) [31] was chosen to build up the optimization framework. PISA was recently developed by Bleuler et al. [31] to reduce the programming and implementation overhead for application engineers and to facilitate the use of different optimization methods on different test problems. The idea behind PISA is to divide the implementation of an optimization method into an application-specific part (e.g., screening for new catalysts) and in an algorithm-specific part. The application-specific part is written in Matlab and is designated the variator, because it includes all of the variation operators. The algorithm-specific part is designated the selector, because it performs the ranking and selection of solutions. Random numbers were obtained from RANDOM.ORG [32], which offers true random numbers generated from atmospheric noise. SPEA2 [26] and IBEA [27] were used as selector algorithms. For IBEA, an ε -indicator was used. The IBEA parameters κ and ρ were set to 0.05 and 1.1, respectively. Elitism is implemented in both algorithms using an additional population, the so-called "external" or "archive" population. In SPEA2, diversity along the Pareto-optimal front is preserved through a density estimation technique that uses a k-nearest-neighbor clustering algorithm. The fitness assignment of IBEA is already diversity-preserving, and thus no additional density estimation technique is needed.

In this work, to ensure robustness to noise, new solutions were preferred to old solutions during the selection process, to reduce the impact of fortuitously good solutions. In addition, population size is a critical factor [33,34], and the selection intensity [35] should be correctly chosen to reduce the effects of a noisy environment. A low selection intensity was obtained using a binary tournament selection algorithm. A detailed study of the behavior of different algorithms in the presence of noise was conducted by Hancock [36].

The initial population size (α) , parent population size (μ) , and offspring population size (λ) were all set to 24 individuals. Also, the archive size was set to 24. In a preliminary test, 48 randomly chosen catalysts were tested, and 19 catalysts covering the whole decision space were selected to build up the initial population. Along with these 19 randomly created catalysts, five selected single-oxide catalysts (10 and 33 mol% Cu, 10 mol% Mn, 10 and 33 mol% Ni, and Al as remainder) were included in the initial population. It was the same for both algorithms, to ensure the same starting point for the optimization process. The catalysts were encoded using binary vectors of 27 bits. We discuss this decision in more detail and provide an exact definition of the space explored in the next section. An extended version of this section with a more detailed explanation of the algorithm and additional implementation guidelines is available in the supplementary material.

4. Representation of solid catalysts and definition of the space to be explored

A total of 11 elements in different combinations and varying concentrations compose the search space of the so-called "deNOx problem"-finding the best combination and composition of elements in a catalyst active at low temperature in HC-SCR. The elements can be classified into three groups: (1) elements acting as support with a high molar fraction in the catalyst, (2) the main elements with likely a major contribution to the catalytic reactivity of the catalyst, and (3) elements acting as promoter, with only a small molar fraction in the catalyst. As stated before, Al was chosen as the element for the support; Cu, Ni, Co, Fe, Mn, La, Ce, and Sm were chosen as the main elements; and K and Sr were chosen as the promoters. Some boundary conditions (denoted as constraint C.i) were introduced to reduce the search space and incorporate chemical knowledge into the encoding. Systems with and without support were treated separately; the maximum number of main elements in a catalyst was four or fewer (constraint C.1). For systems with support, the Al concentration had to be > 33.3 and <95.0 mol%. The concentration of each main element was limited to 35 mol% (C.2). For systems without support, the maximum allowed Al concentration in a catalyst was 33.3 mol%, and the concentration for each main element was unrestricted (C.3). Only a maximum of two elements from the lanthanides series could be present simultaneously in a catalyst (C.4). The sum of the concentrations of the promoter elements was limited to 5.0 mol%; a catalyst could contain both promoter elements (C.5). Superimposed on these self-introduced boundary conditions was the trivial requirement that the sum of all concentrations equal 100 mol%. For both systems, Al constituted the remainder (C.6).

It is important to note due to the premixing of the metal nitrates before impregnation, the resulting metal oxides are not really supported on Al. Al atoms may be part of the active phase. However, Al is important for obtaining high surface areas, and by itself has very low activity; therefore, Al is designated a support if constraint C.2 is fulfilled.

Table 1	
Discrete encodings of the element concentrations	

Genotype	Phenotype (mol%) with support	Phenotype (mol%) without support
0000	0.5	2.0
0001	1.0	4.0
0010	2.0	8.0
0011	4.0	12
0100	6.0	16
0101	8.0	20
0110	10	25
0111	12	30
1000	16	33.3
1001	20	35
1010	24	40
1011	28	50
1100	32	63
1101	33.3	75
1110	34	88
1111	35	100

4.1. Encoding of the element combinations and concentrations

Various encodings can be considered for encoding the combinations of the elements. For such combinatorial problems, a binary representation is generally chosen [37]. Vectors of integer numbers also could be used, but special genetic operators would be required. We chose to encode the combinatorial part of the problem by a binary vector. The most direct way to do this is to use 1 bit for each element [14].

In contrast to encoding the combinations, encoding of the element concentrations is a continuous problem. For such problems, using an evolution strategy with floating point vectors as data type seems to be the natural way to represent the search space properly. But using binary vectors has some important advantages, especially when dealing with experimental optimization problems. Using continuous data structures in experimental optimization makes sense only if the experimental error of the design variables tends toward zero. Typically, the experimental procedures are not as accurate, and an unintentional discretization of the search space occurs; therefore, binary encoding seems more reasonable. The step size should be significantly larger than the expected experimental error. Thus, an advantage of the discretization of a continuous problem is reduced accuracy and dimension of the search space to promote faster convergence [38]. Moreover, if both the combinatorial and the continuous part of the problem are represented by a single binary vector, then no special variation operators are required, and adaptation by building blocks as described by the schema theorem is valid [39].

We chose to discretize the concentrations into 16 steps by using a binary representation of 4 bits for each main element. Due to the maximal number of four main elements in a catalyst (constraint C.1), 16 bits are required for encoding the concentrations. Using the ABIMED robot for synthesis of the catalyst, the minimal volume that can be handled is about $1-3 \mu$ L; thus, a minimal step size of 5 μ L (roughly 0.5 mol%) is reasonable. The discretization of the problem also allows the use of different step sizes and incorporation of some problem-specific



System with support / no support (AI)

Fig. 2. Final encoding using 11 bits for the combinatorial and 16 bits for the continuous part of the problem.

knowledge. Most of the metal oxides form spinel phases at 33 mol%; thus, these concentrations should be encoded regardless of the step size. Also, it could make sense to use a smaller step size for the region below 15 mol%. In contrast, around the spinel concentrations, the step size at high loading can be coarser. Table 1 gives the discrete concentration encodings (genotypes) with the corresponding decoded values (phenotypes).

Fig. 2 shows the complete encoding. A binary one-point crossover operator with a crossover probability of $p_c = 1$ and a binary bit-flip mutation operator with a mutation probability of $p_m = 1/27 = 0.037$ were applied on the whole chromosome to recombine and to mutate the parent solutions.

4.2. Handling constraints

Michalewicz [37] investigated several techniques for dealing with constrained problems, including (a) the design of two evaluation functions for the feasible and infeasible domains, (b) the rejection of infeasible solutions (death penalty), (c) the penalization of infeasible solutions by penalty functions, (d) the use of so-called "repair functions" to repair infeasible solutions, and (e) the adaptation of genetic operators and the use of special representations to maintain a feasible population. Although certainly not complete, this list summarizes some of the most popular techniques. Only options (d) and (e) (i.e., maintaining a feasible population by special representations, genetic operators, or repair functions) seem to be good choices in the case of experimental optimization, as the evaluation system is used at maximal capacity. Because repairing infeasible solutions in the deNOx problem is relatively easy, we chose to use repair functions to repair both invalid combinations of elements and invalid concentration ranges. Fig. 3 shows a general flowchart of a multi-objective optimization algorithm for constrained problems. Figs. S2 and S3 illustrate the repair algorithms for the combinatorial and the continuous part of the deNOx problem in flowcharts.

5. Results and discussion

5.1. Errors of the reactor setup and synthesis

The conversion distribution of the reactor was obtained by placing the same amount of a reference Pt/Al₂O₃ catalyst from the same batch into 24 channels of the reactor. The other 25



Fig. 3. Flowchart of a multi-objective optimization algorithm for constrained problems (see Section 3 and Zitzler et al. [26] for explanation).



Fig. 4. NO to N_2 conversion distribution in the reactor. Even positions are filled with with Pt/Al_2O_3 , and uneven positions with Al_2O_3 .

channels were left empty to determine whether the reactor channels were influencing each other, which should not be the case if the flow rate and the dead time are sufficiently high to guarantee stable conditions. Fig. 4 shows the distribution of the maximum conversion of NO to N₂ at the temperature at which the conversion is maximal (the peak temperature). The conversion distribution shown in Fig. 4 is very narrow with a standard deviation of 0.0167, corresponding to an error of about 3.4%. The maximum deviation from the average value was about 0.03 (6%). This error can be interpreted as the error of the reactor system and is sufficient for a stage II screening. In the distribution of the peak temperature of the NO to N₂ conversion, the error was about 2 K (0.4%), as shown in Fig. S4. The flow rate distribution is shown in Fig. S5. From Figs. 4 and S4, it can be seen that the channels did not influence each other. In no case was the maximal conversion of the empty channels >0.03.

The reproducibility of the synthesis was checked by performing several tests on a series of 10 equal catalysts composed of a ternary metal oxide supported on Al oxide. The catalysts were impregnated with a nitrate mixture consisting of 70 mol% Al, 12 mol% Cu, 6 mol% Fe, and 12 mol% Ce. The results indicate that the reproducibility was sufficiently high for a stage II screening approach. The maximum NO to N₂ conversion was 0.133 ± 0.007 , and the peak temperature of the maximal conversion was 618.6 ± 7.1 K, corresponding to errors of about 5% (standard deviation) in the peak conversion and of <1.5% in the peak temperature. The maximum error in the case of the peak conversion was roughly 9%, corresponding to the maximum possible error of the catalytic test together with the synthesis procedure, because the different catalysts were synthesized in individual batches.

5.2. Experimental optimization of the deNOx problem

In this section, we first present and discuss the experimental results obtained by two independent single runs for each algorithm. As already mentioned in Section 3, both initial populations were identical; however, it is important to note that these evolutionary processes are stochastic, and a fully valid comparison of the performance of the algorithms is not possible by only carrying out a single run. Only the results observed here that can be influenced by random effects can be compared. For a reliable comparison, many experimental optimization programs with random initial populations must be compared, which is not feasible in a reasonable time frame even with high-throughput methods. But before the experimental optimization was done, the performance of the algorithms was evaluated using test functions and encodings with similar properties than the de-NOx problem by carrying out 100 runs with different random seeds [40].

In addition, it is very important to point out that in our case, only a specific system—combinations of 11 elements with certain restrictions synthesized by the activated carbon route— was optimized. When using other synthetic protocols, different combinations of elements or different concentrations may form the optimal set. However, for the bounded problem given here, we are fairly confident that the system cannot be improved much further.

Fig. 5 shows the evolution of the archive population with boxplots for the objective function (1 - yield) for SPEA2. In addition, Fig. S6 shows the evolution for both objectives and both algorithms. As can be clearly seen, the average fitness improved with each generation. The best solution of each generation is represented by the lower outlier of the boxplot; they demonstrate that the best solutions did not improve steadily (like the average fitness of the archive population), but rather in a step-



Fig. 5. Evolution of the objective function (1 - yield) for the solutions of the archive population for SPEA2.

wise manner. The boxes representing 50% of the data increased in most of the cases, and the lengths of the upper and lower whiskers tended to decrease during the evolution due to the improved distribution of the solutions along the (1 - yield) axis and along the peak temperature axis. This is another an indication of successful convergence toward the Pareto-optimal front and of the good diversity preservation of both algorithms.

Fig. 6 shows the archive populations of SPEA2 and IBEA for selected generations in Pareto plots in the objective space. Because both objective functions are to be minimized, the nondominating solutions formed a trade-off front from the upper left to the lower right part of the plot. Both algorithms approached the Pareto-optimal front with each generation. The convergence process can be clearly distinguished, and it also can be seen that each algorithm approached the Pareto-optimal front in a different way. SPEA2 was able to find a better solution for the NO conversion after seven generations than IBEA. In contrast, IBEA found a better solution with respect to the peak temperature of NO conversion. IBEA tended to converge strongly toward Cu-containing catalysts. In Fig. 6, this effect is illustrated by cluster formation in the region with a high conversion to N₂. For SPEA2, some clustering can be observed, but it is less pronounced. After the seventh generation for both algorithms, the solutions were well distributed along the Pareto-optimal front. However, SPEA2 was able to approach the Pareto-optimal front better than IBEA, and, in addition, the distribution was slightly better.

It is noteworthy that the Pareto plots in Fig. 6 provide very efficient visualization of the objective space, useful for extrapolating the solutions and estimating the shape of the Pareto-optimal front. In addition, the Pareto plots give an estimate how far one can probably optimize a certain system, since one can guess by extrapolation of the incremental improvements of the different populations where the asymptotic Pareto-optimal front lies. This is a very important information for the screening of





Fig. 7. Evolution of the occurrences of elements in the archive population for SPEA2 and IBEA.

Fig. 6. Visualization of the evolution of the archive population in the objective space for SPEA2 and IBEA for selected generations.

new catalytic compositions. In Fig. 6, an extrapolated guess of the Pareto-optimal front of this system is represented by a gray line. The shape is linear to spherical, and the front is continuous.

Fig. 7 shows the evolution of the occurrences of the archive population up to the seventh generation. The maximum number of occurrences is 24 (the size of the population). As stated before, the initial population was created randomly, but nevertheless the constraints C.1 to C.6 must be satisfied. This lead to the elemental distribution of the first generation, as can be seen in Fig. 7. The evolution demonstrates a clear trend for most of the elements: Systems with support (constraint C.2) were preferred over systems without support (C.3); both algorithms converged toward Cu- and Ni-containing catalysts. But SPEA2 and IBEA had different convergence rates. The trends for the promoter elements Sr and K were slightly different; K showed a clear negative trend and disappeared completely after three or four generations in the case of SPEA2

and IBEA. In contrast, Sr did not disappear during the evolution, but neither did it increase. Its occurrence was constantly in the range of two to three catalysts in the archive. The trends for Mn, Sm, La, and Ce at higher generation numbers were negative. The elements did not disappear completely, but clear decreases in Mn, Sm, and La occurred. The trends for Co- and Fe-containing catalysts are not clear. The occurrences of both elements seemed to fluctuate, with only a slightly positive trend demonstrated.

Table 2 gives the NO-to-N₂ yield of selected solutions from the archive populations of SPEA2 and IBEA. It can be seen that the Pareto-optimal trade-off front was composed predominantly of Cu- and Ni-containing catalysts of varying concentrations and a higher concentration of Al. Interestingly, these binary oxides were more active than the corresponding single-element oxide catalysts. The incorporation of a third element, such as Co or Fe, generally resulted in activity loss; however, at temperatures below 600 K, Cu and Ni catalysts in combination with Co, Fe, and sometimes also Mn were optimal solutions, as shown in Fig. 8 and Table 2.

Table 2 Peak conversion of NO to N_2 and peak temperature of selected catalysts from the SPEA2 and IBEA archive populations

Catalysts	X _{max}	T _{max}
(concentrations in mol%)	(%)	(K)
Al-84-Cu-4-Ni-12	44	678
Al-88-Cu-8-Ni-4	39	645
Al-84-Cu-12-Ni-4	37	620
Al-66-Cu-10-Ni-24	31	585
Al-64-Cu-20-Ni-16	21	589
Al-66-Cu-12-Ni-12-Co-8-Fe-2	23	580
Al-54-Cu-12-Ni-28-Co-6	19	581
Al-50-Cu-20-Ni-20-Co-8-Fe-2	14	555
Al-39-Ni-16-Co-35-Fe-6-Ce-4	6	534
Al-40-Cu-2-Ni-33-Co-24-Sm-1	7	526



Fig. 8. NO to N_2 conversion curves as a function of the temperature for selected Pareto-optimal solutions.

IBEA was not able to approach the Pareto-optimal front as well as SPEA2. It is very likely that the fast convergence of IBEA toward Cu-containing catalysts, as shown in Fig. 7, had a negative effect on the overall performance of the algorithm. Nevertheless, in the last two generations, IBEA was able to find promising Cu and Ni catalysts and showed a strong convergence toward Ni in addition to Cu. In conclusion, it seems important that a genetic algorithm not strongly favor a single solution. However, a properly working algorithm still should be able to find optimal solutions after a few more generations.

In the following a discussion of the underlying physicochemical properties of the catalysts and their correlation with catalytic activity will be given on the basis of the catalytic screening and on characterisation by adsorption, and XRD investigations. Cu and Ni were the only elements in this system, which showed high SCR activity. These two elements predominately formed the Pareto-optimal trade-off front. Cu was especially active at low metal loadings (around 8–12 mol%); higher Cu loadings led to a distinct activity drop, although the maximal conversion happened at lower temperatures. This is somewhat different than for the Ni-containing catalysts, which were highly active at metal loadings up to 30–35 mol%, depending on the catalyst composition. Catalysts with a peak activity



Fig. 9. XRD patterns of two selected highly active Al/Cu/Ni catalysts (A) and (B). In contrast two XRD patterns of Mn and K containing catalysts (C) and (D) are shown.

at low temperatures generally had a relatively high Ni loading (15 to 30 mol%), whereas those with low metal loading (5 to 15 mol%) were located in the upper left region (the highactivity region) of the Pareto front. The XRD pattern of the most active catalyst (Al-84-Cu-04-Ni-12), with a NO-to-N2 conversion of 44%, is shown in Fig. 9A. As shown, the dominant phase was composed of large Ni-oxide crystallites. The other reflexes cannot be unambiguously ascribed to pure Cu-spinel, pure Nispinel, or a simple combination of both. A higher amount of Al compared with the pure spinel seems to be included in the spinel phase. The prominent crystalline phase in the case of a similar catalyst, synthesized with 8 mol% Cu and 6 mol% Ni (Al-84-Cu-08–Ni-6) was a $Cu_x Ni_{x-1} Al_2 O_4$ mixed spinel with similar crystallite sizes as can be seen in Fig. 9B. The decrease in the Ni concentration led to not so large Ni-oxide crystallites as in Fig. 9A and the increase in Cu allowed the formation of a small fraction of Cu-oxide. In both samples a significant amount of amorphous phase also was present. The activity of this sample was slightly lower (yield \sim 38%) than that of Al-84–Cu-04–Ni-12. In both samples, practically no crystalline Cu-oxide was present. Therefore, the active phase in the case of Cu seems to be amorphous Cu-oxide, along with crystalline spinel but not crystalline Cu-oxide. In contrast, crystalline Ni-oxide and Nispinel are highly active phases. The activity can be increased by formation of mixed Cu/Ni spinels.

Fig. 10 compares a highly crystalline Al/Cu catalyst and a corresponding catalyst with La. The catalyst with La had SCR activity of only about 7%, whereas without La, the activity increased to 18%. Crystalline Cu-oxide is present in both samples, but the formation of Cu-spinel on calcination was significantly hindered in the presence of La. In this case, it is evident that the active phase was crystalline Cu-spinel. The negative influence of La during the formation of a crystalline spinel phase is likely related to the dimension of the La ions, which makes fitting them into the framework difficult. This is also valid for Sm. A significant activity drop was observed in most of the La-



Fig. 10. XRD patterns of a Al/Cu (A) and Al/Cu/La catalyst (B).

or Sm-containing catalysts. During the optimization process, both algorithms were able to identify the negative influence of La and Sm, as shown in Fig. 7. In contrast, the Ce in the archive population was stable during the evolution up to high generation numbers. For Ce, even for materials with a very low amount of Al (<10 mol%) but a significant amount of Ce, the resulting particles exhibited a high BET surface area (at least $80 \text{ m}^2/\text{g}$). The addition of Ce improved the formation of oxide particles with a high BET surface area and did not seem to significantly affect the properties of the other elements. Also, XRD investigations of Ce containing catalysts showed the formation of a crystalline Ce-oxide phase in addition to the other phases. Thus, if the Ce metal loading is high, then Ce-oxide itself can be considered a support.

As described previously, the addition of Co and Fe to a catalyst did not result in a clear trend. Sometimes the addition resulted in an improved activity, and other times, no clear change in activity could be seen. However, in most cases, the catalyst activity decreased. For Mn, in all cases, an addition resulted in decreased activity, although Mn by itself showed an SCR activity of about 15%. For instance, the addition of 4 mol% Mn to sample Al-86-Cu-08-Ni-06 resulted in an activity loss of 8-10%. The XRD pattern C in Fig. 9 shows no strong inhibition of the formation of crystalline phases. The addition of Mn even led to a slightly better crystallization. However, in this case, the dominant spinel phase was nearly pure Ni-spinel, not a mixed spinel phase as in the case of Al-86-Cu-08-Ni-06. This might be one explanation for the activity drop. The formation of Mn-oxide also could lead to catalysts that are more selective to the oxidation of C₃H₆. For instance, as seen during the experiments, most of the Mn-containing catalysts were highly active at low temperatures for the oxidation of C_3H_6 by oxygen.

Co and Fe do not significantly decrease the activity of a catalyst. At higher metal loadings, a crystalline Co-oxide emerged (XRD not shown) that is known to be highly active at low temperatures for the NO oxidation to NO₂ [41,42]. NO reduction over Co-oxide only occurs at higher temperatures when NO oxidation is thermodynamically limited. However NO₂ can be an intermediate species with a higher activity than NO in HC-SCR [43,44]. In combination with a highly active element for the SCR such as Cu or Ni, this can lead to catalysts, which are active at low temperatures. Fe is known to be highly active in the SCR of NO by NH_3 [45,46]. In this work, adding Fe to a catalyst generated no clear increase in activity.

Both K and Sr were initially defined as possible promoter elements, and the maximum concentration of these elements was limited to 5 mol%. For Sr, no clear conclusion can be drawn; the element did not seem to have any positive or strongly negative effect on the performance. In contrast, the addition of K resulted in a very pronounced drop in the activity of the corresponding catalyst in all cases. It was observed that after calcination, the resulting catalysts containing K were differently colored and sometimes very inhomogeneous. Thus, it can be assumed that the activity drop was due to a negative influence during catalyst synthesis. K is known to strongly promote combustion of the activated carbon. Thus, a possible explanation for the difficulties encountered during the synthesis of K-containing catalysts could be the formation of hot spots during the calcination process, which disturb the formation of an active phase and lead to inhomogeneous particles. This can be confirmed by XRD, as can be seen in Fig. 9D for a sample consisting of 85 mol% Al, 10 mol% Cu, and 5 mol% K. The SCR activity of this sample was 8%, more than three times less than the activity of the corresponding catalyst without K. No evident crystalline phase could be identified. The sample was predominantly amorphous, with small amounts of crystalline Cu-oxide and Cu-spinel.

6. Conclusion

Genetic algorithms or evolutionary optimization techniques have been found to be highly flexible methods for the development of catalysts in multi-objective optimization problems. The stochastic nature and the incorporation of heuristics based on evolutionary biology better direct the search in the desired direction compared with, for instance, a random search approach, and makes the technique robust to noise and to the undesired convergence toward suboptimal solutions. The full strength of these techniques can be played off, especially for the screening of unknown, high-dimensional, and constrained spaces. In addition, they are easily scalable to an arbitrary number of objectives, which make them suitable for many problems in catalysis.

In this work, we investigated the ability to direct the search toward two independent objectives using a multi-objective approach to optimize a noble metal-free solid catalyst system active in the selective catalytic reduction of NO with C_3H_6 . Combinations of Cu, Ni, and Al were the best catalysts synthesized through the activated carbon route found by this method. Other catalysts active at low temperature include Co and Fe. Visualizing the solutions in the objective space using Pareto plots allowed us to estimate of the shape and location of the Pareto-optimal front and determine to what extent this noble metal-free system is active in the SCR with C_3H_6 .

A hybridization of the developed optimization framework with neural networks, acting as local search during the evolution, could improve the optimization process. In addition, the problem of encoding solid catalysts and the impact of such encoding on the performance of the experimental evolution should be investigated in more detail in future studies.

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Supplementary material

The online version of this article contains additional supplementary material.

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