Comparison of Single- And Multiobjective Design of Experiment in Combinatorial Chemistry for the Selective Dehydrogenation of Propane

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Two genetic algorithms for the single- and multiobjective design of combinatorial experiments were applied to the optimization of a solid catalyst system active in the selective catalytic oxidation of propane to propylene. The two different optimization strategies, namely, the single objective optimization of the yield and the multiobjective optimization of the conversion and selectivity were implemented and compared. It was observed that the multiobjective approach optimized the yield in a similar way compared to the single objective approach. With respect to the selectivity, however, the multiobjective outperformed the single objective approach. It was also found that by applying the multiobjective optimization more interesting possible combinations were discovered.

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] The challenge of finding an optimal catalyst composition and preparation method for a specific reaction has, during the last 10−15 years, led to the preparation of catalysts with active elements, supports, and dopants selected from increasingly large pools and preparation methods. Consequently, the optimal formulations have to be searched for in high-dimensional descriptor space. Nowadays, 20−30 descriptors are not exceptional. For high dimensional spaces, the traditional designs of experiments (DoE) methods are no longer reasonable as many prescreening experiments are required. The need is for intelligent methods able to perform an efficient screening in multimodal search spaces by only performing a minimum number of experiments.

For such purpose, evolutionary global optimization methods, such as genetic algorithms,[7,8] have become very attractive in heterogeneous catalysis, mainly because of the possibility to establish a straightforward correspondence between optimization paths followed by the algorithm and the channels of the high-throughput reactor in which the catalysts proposed by the algorithm are subsequently tested.

In materials science and in heterogeneous catalysis, genetic algorithms have been used for approximately ten years[9−24] with Wolf et al.[25] being the first to establish an evolutionary approach to optimize the combinations of elements of multicomponent solid catalysts. However, up to recently,[26] the search has been conducted toward one sole objective as Wolf and co-workers described for the oxidative dehydrogenation of propane.[25] In real world problems and especially in catalysis, several, often conflicting objectives generally must be taken into account. In addition, there is the need not only to find the optimal catalyst composition, but various compositions with similar efficiency to the best one, for instance, to allow more robust further development or the circumvention of patent constraints. Thus, methods that are able to find many optimal solutions with respect to several goals are needed. In our group, a multiobjective GA was applied with respect to two conflicting objectives: the conversion to nitrogen and the temperature at which the yield is maximum, that is, the so-called “peak” or “light-off” temperature, for the reduction of NO with C_3H_6.[26] Because 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. Also Baumes investigated in his thesis and in several recent studies the application of multiobjective optimization in heterogeneous catalysis.[27−29] However, one question is currently unanswered, that is, if the multiobjective approach is superior to the single-objective, as the complexity of the problem may increase considerably as a function of the objectives. In addition, it is unclear, if there is really a need for sophisticated algorithms in catalysis, which are able to deal with several objectives or if a reformulation of the problem definition to result in only one objective is more reasonable because of the much simpler implementation of the algorithm.[25]

Propene is an important intermediate in many chemical processes like the production of polymers, including polypropylene, polyurethane, and epoxy resins along with other materials such as acrylonitrile, propene oxide, and isopropanol. The main process for the production of propene is steam cracking of hydrocarbons.[30] Very high temperatures (∼750 °C) are needed to overcome the thermodynamic limitations. When exposing hydrocarbons to high tempera-

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tures, there is always a possibility of coke formation and therefore regeneration of the catalyst by burning off the coked deposits, as well as periodic process shutdown are required. The oxidative dehydrogenation (ODH) of propane may offer a promising alternative for the production of propylene compared to the conventional route described above. There are no thermodynamic limitations and propane can be oxidized at lower temperatures. Beside that, the reaction mixture contains oxygen. Therefore, the risk of catalyst deactivation by coking is reduced, which is very important from the industrial point of view.

In this work, we focus on a comparison of a single- and a multiobjective, evolutionary approach to experimental optimization of oxidative propane dehydrogenation (ODH). The composition and combination of metal oxide catalysts consisting of combinations of 12 elements, (Te, Nb, Al, V, Ni, Cr, Co, Fe, Mo, Li, Sr, Mg), which could present a high catalytic activity and lifetime, was chosen as the system to optimize. The pool of information has been chosen on the basis of knowledge collected from the literature.[31−39] In the oxidative dehydrogenation, the products from total combustion are thermodynamically favored. The viability of the process relies heavily on the design of a catalyst to overcome the selectivity challenge. Therefore, two important factors that determine the quality of the catalyst for the ODH are the activity and the selectivity. On the other hand, activity and selectivity can be combined to the single parameter yield of the desired product, which is often what is optimized in industrial practice. Therefore, we follow two strategies for the optimization of the catalytic process: in the single-objective approach, the yield to propylene was chosen as the objective, whereas in the multiobjective approach, both the conversion and the selectivity were selected.

The difference in the multiobjective optimization is that catalysts with high selectivities presenting low yields will not be discarded. We compare and discuss the results of the different approaches applying the two different algorithms, emphasizing the differences in the activity and catalytic composition.

2. Experimental Section

The mixed oxide catalysts were prepared by the activated carbon route[40,41] using metal nitrates as precursors. Activated carbon (KK 1407 Carbotec/Rutgers) from the same activation batch was used as exotemplate because of its exceptional properties: high purity (ash content <0.5 wt %) and very high BET surface area (1656 m^2/g) and pore volume (0.79 cm^3/g). The pore system consists of a very high fraction of micropores with diameters <1 nm. The particles are almost uniform spheres with diameter of 200−400 μm. The impregnation was carried out manually using differently concentrated solutions, depending on the solubility of the precursors. The metal precursors used were $Co(NO_3)_2$, $Fe(NO_3)_3$, $Ni(NO_3)_2$, $Al(NO_3)_3$, $Cr(NO_3)_3$, $Mg(NO_3)_2$, $LiNO_3$, Na_3VO_3, all from Fluka, puriss p.a; H_6TeO_6, $(NH4)_6$ Mo_7O_{24}, $NH_4NbO(C_2O_4)_2$, from Sigma-Aldrich.

After the precursor solutions were mixed in a beaker, impregnation of the activated carbon was carried out using a slight excess of solution, that is, for 1 g of activated carbon 0.89 mL of solution was used. The wet carbon was furthermore mixed to get a homogeneous distribution over the carbon support. Later on, the solid material was dried at 60 °C overnight and calcined at 550 °C for 45 min in air to combust the carbon, resulting in the formation of the mixed metal oxides.

2.1. 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.,[42] was used for testing the catalytic activity of the mixed oxide catalysts in the selective oxidation of propane. The catalysts were activated at 400 °C for 15 min before catalytic testing. The measurements were performed using a reaction mixture ($C_3H_8/O_2/N_2 = 4/3/293$) at GSHV 12.255 h^{-1} and a reactor pressure of 1.2 bar. The catalytic activity was evaluated at 400, 450, and 500 °C. Each catalyst was analyzed twice, and the analysis took 5 min for each sample. The complete testing of all 49 catalysts at up to 3 different temperatures took about 24 h.

The effluent gas was analyzed by an on line gas chromatograph (Agilent Technologies 6890N) equipped with a Restek RTX-1 #10187 column, methanizer, and a flame ionization detector. The carbon mass balance on the carbon atoms of propane was monitored and typically closed to 100 ± 5%.

3. Genetic Algorithms for Evolutionary Experimental Design

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. In general, GAs are a class of nonlinear, adaptive, and heuristic methods for solving optimization and search problems. In nature, populations evolve over many generations following the principle of natural selections and the “survival of the fittest”. By adapting this principle from nature, genetic algorithms can generate artificial populations to undergo an evolution that approach an optimal solution of a predefined problem.

Genetic algorithms are also suited for experimental design with respect to several goals or objective functions. In single objective optimization, the relative order of the solutions in a population is clearly defined in the objective space, and only one global best fitness exists. The situation is completely different in the case of multiobjective optimization as two optimal solutions may differ from each other in the objective space. Several strategies have been developed over the last decades in order to deal with multiobjective optimization problems. Weight based techniques are the oldest techniques. The basic concept is to combine several objective functions into one overall objective function. The multiobjective problem is reduced to a single-objective problem and methods for solving single-objective optimization problems can be applied without modification. Thus, the implementation is very simple; however, a major drawback is how to normalize, prioritize, and weight the contribution of the various objectives. In catalysis, this approach was used by Wolf et al.[25] In the case of modern evolutionary multiobjective optimization techniques all the objectives are optimized at the same time. The optimal solution is a composite of all optimal solutions with respect to the multiple objectives and usually forms a set of optimal trade-off surfaces that includes the single objective optimum. This set of optimal solutions is designated the Pareto-optimal set. In multiobjective optimization, generally the goal is to approximate this set and to keep it as diverse as possible.

3.1. Optimization Framework. To compare the mere differences of the single- and multiobjective approaches, in both cases standard implementations that are known to perform well in literature were used. The optimum size of the population depends on many factors and is a critical factor as a too big population leads to a low convergence and a too small population is more likely to converge toward a local optimum. In catalysis, in addition, the reactor or testing size has to be considered. A good choice for the minimum population size for expensive problems is given by the probability to reach each point in the search space as defined for binary encodings by Reeves.[43] In this study, the initial population size, parent population size, and offspring population size were all set to 24 individuals, which represents a good compromise between speed of convergence and the probability to reach each point in the search space, which is in this case >99.99%. In a preliminary test, 48 randomly chosen catalysts were tested. This population was identical for both algorithms to ensure the same starting point for the optimization process. Based on the results obtained in our previous paper,[47] a binary representation was chosen, which has the advantage of tailoring the minimum distance of the individuals in the search space by the possibility to choose the number of bits for the representation. This, in addition, reduces the tendency to form clusters.[47] The genetic variation operators were in both cases the classic bit-flip mutation operator with a probability of 0.067 and a one-point crossover operator with a probability of 1. Maintaining diversity in the population is another critical factor and several diversity preservation methods exists, some of them were investigated and summarized in a recent study by Farruseng and Clerc.[44] By using a binary tournament selection operator it is guaranteed to keep the diversity in the population as high as possible during the mating selection step. In addition, in the case of the single objective approach, a restricted tournament replacement strategy[45,46] with a window size of 5 was applied to control the diversity in the population by not only searching for the one single best catalyst but also for differently composed solutions as in the case of a multiobjective approach. Elitism was implemented by a deterministic addition of the best catalyst to the mating pool. The multiobjective implementation was performed according to our previous studies.[47] The strength Pareto evolutionary algorithm (SPEA-2)[48] was used and implemented based on the platform and programming language independent interface for search algorithms (PISA).[49] SPEA-2 is a so-called Pareto-based algorithm, which operates toward two goals: minimization of the distance toward the Pareto-optimal set, and maximization of the diversity within the Pareto-optimal set. Elitism is implemented in SPEA-2 by using an additional population, the so-called "external" or "archive" population that is composed of the best 24 nondominated individuals during the search and is used in combination with the regular population as mating pool. If less than 24 nondominated individuals were found, the archive is filled up with dominated individuals. In contrast, in the single objective approach only the last population is used to generate the offspring population and only the best individual found so far is preserved. The diversity along the Pareto-optimal front is preserved through a density estimation technique that uses a *k*-nearest neighbor clustering algorithm. For details about the implementation, we refer to the original publications.[48] For both algorithms, random numbers were obtained by RAMDOM.ORG,[50] which offers true random numbers generated from atmospheric noise. It should be noted that it is technically possible to use SPEA-2 as a single objective optimization algorithm. It can be easily shown that a single objective SPEA-2 performs poorly compared to a standard single objective GA. We tested this on a number of test function. The reason is that the concept of Pareto selection can not be directly applied to single objective problems because the Pareto-front is composed by only one (the best) solution. All other solutions are dominated by this solution. In addition, the *k*-means clustering algorithm, which is used to keep diversity along the Pareto front, also does not operate in the desired way.

4. Representation of Solid Catalyst and Definition of the Space to Be Explored

The codification of the catalysts was performed according to the rules described in detail in Gobin's work.[47] A 4b-10b-16b type of encoding was used, that is, four bits for the promotor elements, 10 bits for the main elements, and 16 bits for the concentrations of the elements. The main elements were Al, V, Ni, Cr, Co, Fe, Mo, Li, Sr, and Mg; in addition, Te and Nb were chosen as the promoters. Thus a total of 12 elements in different combinations and varying concentrations compose the search space. Three boundary conditions were defined to furthermore reduce the search space: the maximum number of main elements in a catalyst was limited to four or fewer (constraint C.1). The sum of the concentration of the promoter elements was limited to 10%; a catalyst could contain both promoter elements (C.2). Superimposed on these self-introduced boundary conditions was the requirement that the sum of all concentrations was equal to 100% (C.3). The boundary conditions were satisfied by applying repair algorithms as additional stochastic variation operators after performing the standard variation by crossover and mutation.[26,47]

5. Results and Discussion

5.1. Errors of the Reactor Set up and Synthesis. The conversion distribution of the reactor was obtained by placing the same amount of a reference 5 wt % Pt/Al_2O_3 catalyst from the same batch into 24 channels of the reactor. The other 25 channels were left empty to determine whether the reactor channels are influencing each other, which should not be the case if the flow rate and the dead time are sufficiently high to guarantee stable conditions. Figure 1

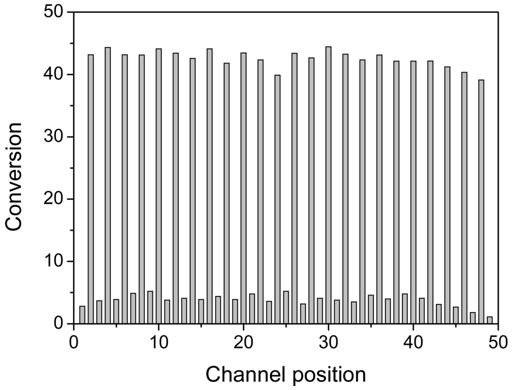

Figure 1. Distribution of measured propene conversion to carbon dioxide in the reactor at a reaction temperature of 500 °C. Even positions are filled with 5% Pt/Al_2O_3, and uneven positions with quartz.

shows the distribution of the maximum conversion of propane combustion at operating conditions.

From Figure 1, it can be seen that the channels did not influence each other. The average conversion is 42.57%. The conversion distribution shown in Figure 1 is very narrow with a maximum error of 4% (1.4% standard deviation). In no case was the maximal conversion of the empty channel >6%. The Pt/Al_2O_3 catalyst was used to test the reactor because of its long time stability.

The reproducibility of the synthesis was checked by performing several tests on two series of 3 equal catalysts, composed of 3.33 mol % Te, 6.66 mol % Nb, 9.00 mol % Al, 63.01 mol % Cr, 18.00 mol % Fe and 3.33 mol % Te, 6.66 mol % Nb, 31.11 mol % Ni, 44.45 mol % Cr, 17.78 mol % Fe. The maximum conversions were 21.10 and 26.27, with errors of 2%.

5.2. Experimental Optimization of the Propane Dehydrogenation. In this section, we first compare and discuss the experimental results obtained by the single objective (yield) and multiobjective (selectivity and conversion) approach, by comparing the two populations, which are used as mating pool to generate offspring populations. These are the single objective population and the SPEA-2 archive population.

Figure 2A/B shows the evolution of the yield, the conversion, and the selectivity of the two populations. As can be clearly seen in Figure 2A-1/B-1, the average yield improved with each generation in both cases. The best solution of each generation is represented by the outlier of the boxplot. The best catalysts with yields close to 12% were found by SPEA-2 after 5 generations. The same trend was observed for the selectivity and conversion. As shown in Figure 2A-3/B-3, the average selectivities are 28% for the single and 45% for the multiobjective algorithm after six generations. Also the average conversions are higher in the case of the multiobjective approach. The apparently poor results of the single objective approach are in parts caused by the comparison of the single objective population and the archive population of SPEA-2. The archive keeps track of the best individuals along the optimization with respect to both objectives. In contrast, the single objective population is strongly influenced by the stochastic and heuristic nature of the algorithm, that is, for instance, poor solutions may emerge, and good solutions may disappear.

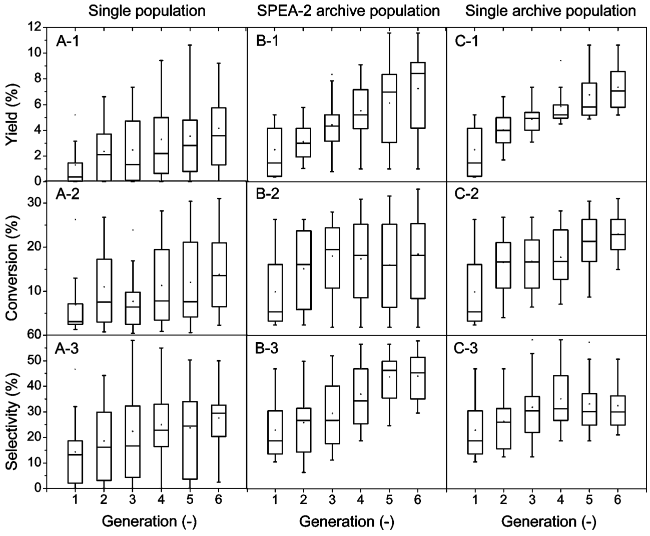

Figure 2. Evolution of the yield, conversion, and selectivity for the solutions of the single, the SPEA-2 archive, and the single archive population.

To have a fair comparison, we created a new population, denoted as the archive population of the single objective approach. Similar to the way the multiobjective archive population is created, the single objective archive population consists of the 24 best catalysts found so far. The major difference compared to the SPEA-2 archive is that no Pareto-selection is performed and the catalysts are only selected with respect to their yield. However, one should note that this population is not used by the algorithm, in contrast to the SPEA-2 archive population, which is directly used to generate the offspring population. By comparing the yields of the archive populations in Figure 2B-1/C-1, one can clearly see that the single objective algorithm performed as good as the SPEA-2 algorithm. The slightly better yields found by SPEA-2 are not significant to be discussed on the algorithmic level. Likely, the inferior results are due to the stochastic nature of the algorithm. However, it is remarkable to note, that even if the yield was not directly optimized in the case of the multiobjective algorithm, that is, at no time the yield is explicitly calculated, the results are comparable and even slightly better. This gives already evidence that the multiobjective approach does not perform worse. To gain a deeper insight in the way the algorithms evolved the catalyst populations, conversion and the selectivity of the archive populations will be compared in the following.

In Figure 2B-2/C-2, the evolution of the conversion is shown. The average results are higher and the distribution more narrow in the single objective case. In contrast, the average selectivities shown in Figure 2B-3/C-3, are higher in the case of the multiobjective algorithm. For the single objective algorithm, a decrease can be observed after the fourth generation as can be seen in Figure 2C-3. These results clearly indicate that the single objective algorithm predominantly evolved by improving the conversions and not the selectivities. In contrast, the multiobjective approach, improved the yields by improving both conversion and selectivities, however, stronger focusing on the improvement of

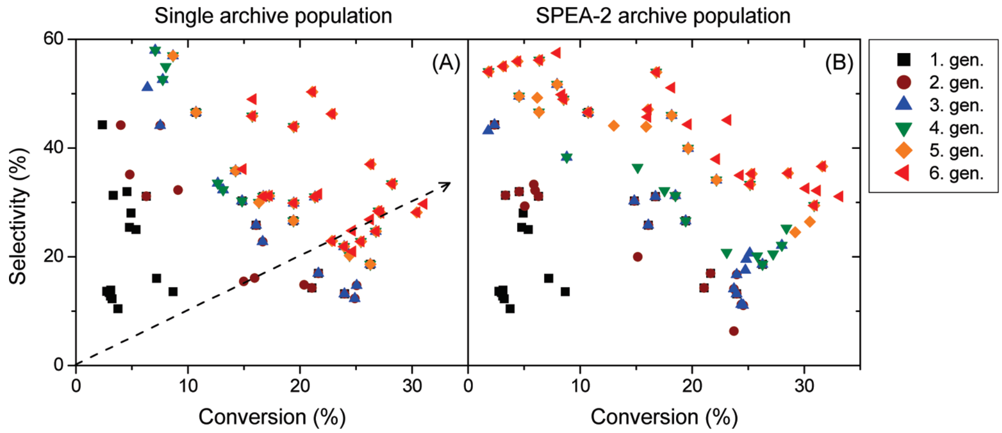

Figure 3. Visualization of the evolution of the archive populations in the objective space.

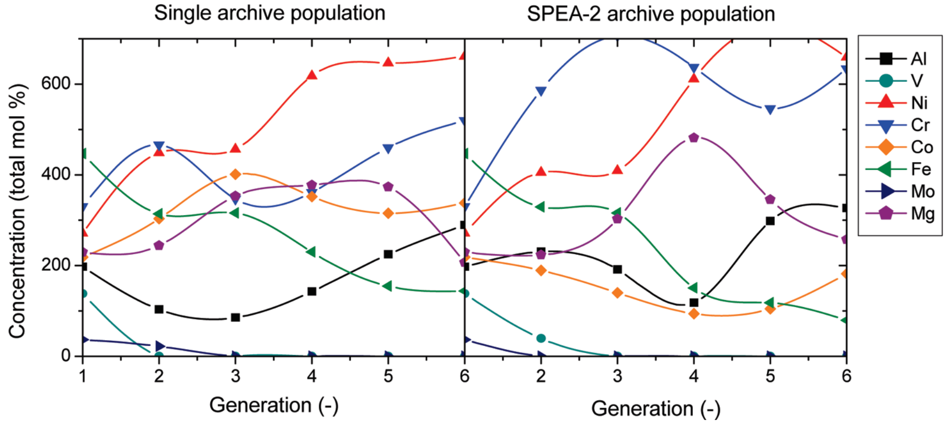

Figure 4. Evolution of the concentration of elements in the archive populations.

the selectivities as can be seen in Figure 2B-2 compared to Figure 2B-3.

This situation can also be seen in Figure 3, which shows the archive populations of both approaches for the six generations in the two-dimensional objective space, that is, plotted as the conversion versus the selectivity. Such kinds of plots are generally denoted as Pareto plots, as Pareto optimal solutions can be easily identified. The SPEA-2 solutions are well distributed along the Pareto space, and even solutions which show a high selectivity but a low conversion are kept in the archive population of the sixth generation. In contrast, this was not the case for the single objective approach. The strongest direction of attraction is visualized Figure 3A by an arrow. The arrow corresponds to the product selectivity times conversion. Solutions in the boundary region, that is for instance, the high selectivity region, were lost and the evolution only took place toward catalysts showing a high conversion. This is perfectly in line with the previously discussed results and furthermore shows that the single objective algorithm is converging toward different catalysts than the multiobjective. In the following, we will analyze the results of the archive populations in terms of catalyst compositions and compare them to the catalytic results.

In Figure 4, the evolution of the total concentration of elements in the populations is shown for the most significant elements. Both algorithms are clearly converging toward Ni and Cr containing catalysts showing the highest fraction of around 650 mol % (This value represents the sum of the concentrations of one specific element of all catalysts in a single generation) in the populations; however, the trend is more pronounced for the multiobjective algorithm. In addition to these two elements, the single objective algorithm also keeps a high fraction of Co-containing catalysts in the population. In contrast, for the multiobjective algorithm only a minor fraction of catalysts contains Co, which is, in addition, showing a slightly negative trend. In summary, Ni, Cr, and Co compose the elements which have a high influence on the catalytic activity and were found by both algorithms. Al seems to be an important element with an increasing amount in the populations. In contrast, V and Mo showed a clear detrimental effect in the catalytic activity disappearing completely after two or three generations contrary to the active catalysts in literature, which mainly are composed of these two elements; the trend for Fe is similar in both approaches having a higher negative convergence rate for the multiobjective algorithm although in both cases the incidences do not disappear completely. As we will show later, however, Fe composes an important element to obtain high selectivities. The trend for Mg is not clear for both algorithms. The occurrence of Mg fluctuates keeping a high fraction of Mg in the populations. The reason can be that the addition of Mg to the catalysts produces a decrease in the catalytic activity. On the other hand, the selectivity increases remarkably. The trends for Li and Sr (not shown in Figure 4) were quite similar in both approaches showing a distinct negative effect, while only keeping a low fraction of these elements in the catalysts. The analysis of

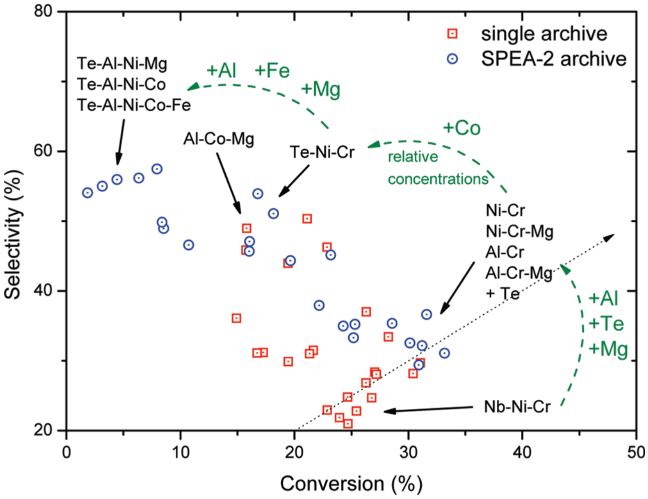

Figure 5. Visualization of catalyst composition of the sixth archive populations in the objective space.

the evolution of the element concentration in the population, does not explain the trends shown and discussed in Figure 2. To obtain a deeper understanding why the single objective approach evolved predominantly through improvement of the conversion, contrary to the multiobjective approach, the catalyst combinations in the objective space will be discussed in the following.

In Figure 5, the archive populations of the sixth generation are shown in the objective space. The most important catalyst combinations in the high conversion and high selectivity region are highlighted. It can easily be seen that most of the individuals of the single objective population are located in the high conversion region around the area with the strongest direction of attraction as shown in Figure 3 or Figure 5 by an arrow. In contrast, the individuals of the SPEA-2 archive are well distributed along the objective space. Ni composes the major component in nearly all catalysts, in the high conversion region as well as in the high selectivity region. By adding Cr to Ni, highly active catalysts are obtained, predominantly with selectivities below 30%. Te, Mg, and Al increase the selectivities to up to 40%, without resulting in a decreased activity. These catalysts compose the majority of the population of the single objective approach as can be seen in Figure 5. The selectivities can be further improved up to 50% by addition of Co and by fine-tuning the relative concentrations of the elements in the catalysts. Further increase of the selectivities up to 60% is possible by forming Te−Al−Ni catalysts with Mg, Co, and Fe. The conversion, however, drops to below 20% or even 10%. These combinations were only found by the multiobjective approach, because of their poor performance with respect to their activities, and thus their yields. Another interesting range of catalysts are the Ni−Cr combinations, which were found by both algorithms. Addition of Nb to Ni−Cr leads to catalysts with low selectivities of below 25%, while an addition of Te leads to catalysts with selectivities up to 50%. The catalyst showing the highest selectivity in the single archive population is a combination of Al, Co, and Mg with selectivities slightly below 50%. From the chemical point of view, combinations of elements, showing high selectivities are more important than catalysts with a similar yield but a low selectivity.

Interestingly, the catalyst formulations shown above are completely different to the ones obtained by Wolf et al.[25] Their catalysts are based on vanadium and molybdenum. In our system, these elements had a negative influence on the catalytic activity. Also our best catalysts are slightly better than ones discovered by Wolf et al.[25] We tested some of the best catalysts, such as $\mathrm{Te_{3,33}Nb_{9,99}Ni_{28,89}Cr_{26,49}Co_{31,3}}$ and $\mathrm{Nb_{6,66}Ni_{20,01}Co_{33,33}Mg_{40,03}}$, in a single tube reactor to have more accurate data and observed yields of ∼12%.

One should note that the results observed and compared in this contribution are at an early state of the optimization. Further evolution, however, would accentuate the results, that is, the single objective population would be strongly attracted to the high conversion region along the strongest direction of attraction (see Figure 3 or 5). SPEA-2, in contrast, would furthermore diversify and improve the results through optimization of both objectives. In conclusion, the most significant benefit of the multiobjective approach is the way catalysts in the boundary region of the objective space are treated. By only performing a single objective optimization, catalysts combination showing a low yield will be removed from the population, although possibly performing very good in terms of selectivity or conversion. It is therefore more likely to find more interesting possible combinations by performing a multiobjective approach.

6. Conclusions

Genetic algorithms or evolutionary optimization approaches have been found to have a significant potential toward the identification of improved catalyst materials. As has been shown for the selective propane dehydrogenation, GAs are a fast and convenient way, as they do not need to be trained and do not need information about gradients or other specific information on the problem to be solved.

In this work, we have applied two different strategies using single objective optimization (yield) and multiobjective optimization (conversion vs selectivity). Although optimizing two objectives simultaneously, the multiobjective approach performed slightly better compared to the single objective approach with respect to the optimization of the yield. This is remarkable, as the yield is not explicitly calculated during the multiobjective optimization and, therefore, not directly optimized. In addition, the multiobjective algorithm was able to find catalysts in the extreme regions, which were not found by the single objective algorithm. The reason is, that the single objective approach only optimizes in one direction, whereas the multiobjective approach optimizes all objectives simultaneously and is able to keep individuals at the extreme boundaries. Generally speaking, the multiobjective approach should be preferred to the single objective as it performs at least as good with respect to the optimization of the yield, and, in addition, it is more likely to find more interesting possible combinations, as also selectivity and conversion are optimized simultaneously.

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