

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

Oliver Christian Gobin, Alberto Martinez Joaristi, Ferdi Schüth *

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr, Germany

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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 C₃H₆. 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

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 $\mathbf{f} : \mathbf{X} \rightarrow \mathbf{Y}$ 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

* Corresponding author.

E-mail address: schueth@mpi-muelheim.mpg.de (F. Schüth).

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 \mathbf{x} to the objective vector \mathbf{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: $\text{Ni}(\text{NO}_3)_2$ from Fluka, purum p.a.; $\text{Cu}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$ from Fluka puriss p.a.; $\text{Al}(\text{NO}_3)_3$, $\text{K}(\text{NO}_3)$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ from Merck, GR for analysis; $\text{Ce}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ 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 $\text{CuK}\alpha$ radiation (1.54056 Å), a secondary Ni-filter, and an X’Celerator detector. Patterns were recorded in the range of 15–70° 2θ 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 microscopy (SEM) using a Hitachi S-3500N 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 C_3H_6 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 C_3H_6 , 1500 ppm NO, and 5% O_2 at GSHV $\sim 20,000 \text{ h}^{-1}$ 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.

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