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High throughput experimentation in oxidation catalysis: Higher integration and ''intelligent'' software

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Abstract

High throughput experimentation methods are well established in many companies and in research groups in academia. Recent advances were primarily achieved in the fields of innovative synthesis methods for bulk catalysts, using amongst other techniques split-and-pool methods, in miniaturization of reactors while increasing parallelization up to 625-fold on an approximately 7 cm × 7 cm footprint, and in development of novel software for ''intelligent'' design of libraries. Developments in these fields will be highlighted with a focus on applications in oxidation catalysis.

Keywords: High throughput experimentation; Microreactor; Descriptor; Split-and-pool; Activated carbon route

1. Introduction

High throughput experimentation has developed over the last 5 years to become almost a routine set of methodologies in catalysis research laboratories in industry as well as in academia [1–4]. The main challenges in homogeneous catalysis lie in the development of sufficiently general and reliable synthesis protocols for the creation of typical molecular catalysts, while the challenges in heterogeneous catalysis are more diverse, ranging from suitable synthesis techniques for preparation of bulk catalysts to the development of descriptors for solids to represent such materials in computer-usable form. This contribution will focus predominantly on the problems encountered in heterogeneous catalysis.

Full implementation of a high throughput workflow needs all the necessary components, i.e. a software environment for sample and results tracking, synthesis capabilities, analytical tools, high throughput reactors, and software for data mining and library design. The tools for the different parts of the workflow are in different stages of their development. While reactors for close-to-conventional catalyst screening are yielding data with a quality coming close, sometimes even exceeding, that of single channel reactors, more highly integrated reactors are not as well developed although a number of stage I screening technologies has been developed. Major shortcomings also exist in the fields of catalyst synthesis, especially when methods beyond impregnation or ion exchange are to be used. This concerns especially the synthesis of bulk catalysts, which is conventionally often done by precipitation, co-precipitation, spray drying and related techniques, which are very difficult to parallelize. Deficits also exist with respect to software for data mining and intelligent library design which would go beyond statistical optimization. In the following, we will highlight recent advances in synthesis, reactor integration, and library design using a descriptor based method. These tools are expected to be integrated in the technology suite available in high throughput programs in heterogeneous catalysis.

2. Synthesis methods: the activated carbon route and split-and-pool protocols

Synthetic methods such as impregnation and ion exchange are reasonably well developed and suited for parallelization, and it

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has been shown early on in the development of the field, that reliable catalyst synthesis is possible following such methods [5]. Even more complex protocols, such as the synthesis of zeolitic materials via hydrothermal methods have been successfully parallelized [6–9]. However, many important catalytic materials, especially for oxidation reactions, are bulk materials, such as mixed metal oxides. The synthesis of such samples is difficult to parallelize. Typically, such oxides are formed by precipitation or co-precipitation. Although these synthesis steps can in principle be parallelized, as has been shown for the synthesis of gold based catalysts for low temperature CO-oxidation [10], it is still difficult to create a wide variety of different samples using such techniques, or to produce larger amounts of such catalysts, since the solution volumes involved in their synthesis are typically rather high. In addition, also methods to produce a vast amount of different catalysts with a small number of steps – comparable to the split-and-pool synthesis known in medicinal chemistry – are difficult to implement for solid catalysts, although this would be highly interesting for the creation of discovery libraries, which typically have several hundred to several thousand members. Therefore, bulk catalysts are often still "manufactured" in the literal sense of the word in many academic and industrial laboratories, even if equipment for parallelized synthesis is available.

Over the last years we have developed two methods which can be used to produce bulk oxide catalysts using highly parallelized and automated protocols. One of these techniques is the activated carbon route for the synthesis of high surface area binary, ternary or multinary mixed metal oxides, either as defined phases or as phase mixtures, including amorphous materials [11]. The activated carbon route is based on the impregnation of activated carbon with highly concentrated metal salt solutions and subsequent combustion of the carbon. Due to the fact that the carbon pore system provides a confined space during the generation of the oxide from the precursor, the oxide particles do not grow to large sizes and typically small particles in the size range of about 10 nm are obtained, with the correspondingly high surface areas of about 100 m^2/g. For a high throughput implementation of the method, known amounts of activated carbon are placed in the wells of a preparation module. Then, known amounts of the desired metal precursor solutions are added to the carbon according to the water uptake capacity. Subsequent combustion of the carbons yields the oxides. Since the solubility of the metal salts differ, also different amounts of solid are generated for each well. However, the amounts formed are known, so that these differences can be taken into account in subsequent catalytic tests. Libraries synthesized following this synthetic pathway have been investigated for the catalytic potential in CO-oxidation [12], NO reduction [13], and hydrocarbon steam reforming and partial oxidation. Results for one example, NO reduction under oxidizing conditions, will be shown below.

So-called Kugelkohle, an activated carbon in form of submillimeter sized spheres produced by Blücher GmbH, Erkrath (Germany), was found to be an especially interesting carbon matrix for this method. The Kugelkohle has a high surface area, high pore volume, and, depending on the type, contains almost no impurities. Oxides templated with the Kugelkohle are often also obtained in the form of small spherical particles, i.e. they maintain the shape of the carbon template, which is very interesting for direct use in miniaturized high throughput reactors (see below), and could also be very suitable for the production of split-and-pool libraries. Fig. 1 shows an electron scanning micrograph of an alumina based mixed metal oxide synthesized with Kugelkohle as the hard template.

High throughput synthesis using the activated carbon method typically relies on spatially addressable wells in a synthesis module, which are sequentially or in a semi-parallel fashion supplied with the necessary precursor solutions. A conceptionally much more powerful approach for the synthesis of a multitude of compounds with relatively few synthetic steps is the split-and-pool technology. Such concepts were originally developed in the pharmaceutical industry [14] for the synthesis of large libraries of molecules. The split-and-pool method follows a relatively straightforward protocol. (i) For the introduction of different functional groups in a bead-bound scaffold molecule, a batch of the beads is divided into as many parts (n) as different functional groups shall be introduced in a first position on the scaffold molecule. The corresponding reactions are then carried out in different reaction vessels. After this step, n different compound have been generated. (ii) Then, the beads from all the different batches are pooled and mixed again. (iii) These beads are again divided into as many parts as different functional groups shall be introduced in a second position on the scaffold molecule (m) and the reactions are carried out in different batches. Since in each of the m batches there were n different molecules before the reaction (if there are enough beads and mixing after pooling was effective), after reaction there are $m \times n$ different compounds although only $m + n$ reactions have been carried out. If there is a third (with o different groups) or fourth position (with p different groups) in the scaffold molecule which shall be functionalized, the sequence can be repeated, resulting in the formation of $n \times m \times o$ or $m \times n \times o \times p$ different compounds,

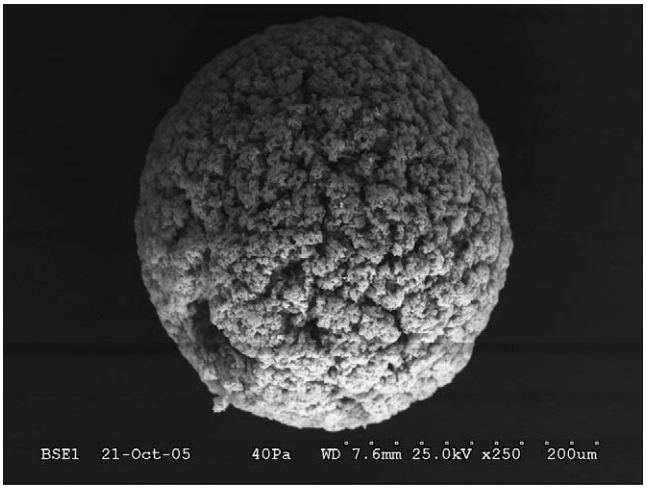

Fig. 1. Scanning electron micrograph of a high surface area, alumina (60%) based oxide (AlMgFeNiCoMnCuLaZr-oxide) obtained by the activated carbon route from Kugelkohle as hard template. The diameter of the particle is about 250 μm.

respectively. The disadvantage of the method is the fact that one does not know without analysis, which compound is on which bead. Since often the different compounds are formed in minute amounts which are difficult to analyze, various encoding strategies have been developed for easy tracking of the beads.

The concepts developed for the split-and-pool synthesis of molecules are not directly transferable to the synthesis of solids, since neither defined building blocks nor defined scaffolds exist in the synthesis of solids. However, the general idea, i.e. the synthesis of a vast number of different solids with a relatively small number of steps by using split-and-pool protocols can be realized. This has been done by the team at hte Aktiengesellschaft [15,16] and the group of Mallouk [17]. The approach resembles the one pursued in the pharmaceutical industry, but employs differently concentrated metal precursor solutions, instead of organic groups which are coupled to a scaffold. Encoding, which is crucial in drug discovery, is not necessary for catalysts composed of different metal oxides, since readout of the beads can simply be done by spatially resolved chemical analysis, for instance by XRF (Fig. 2). As supports, one can use non-porous ceramic spheres, for instance made of alumina, or porous ceramic or polymeric spheres. In between different impregnation steps a calcination step may be advisable in order to prevent redissolution of compounds deposited in a first step. Possible cross-contamination is a drawback of the split-and-pool method for the deposition of solids, since other than the covalent bond formed in molecules which is essentially irreversible if conditions are properly chosen, solid compounds have a certain solubility in most solvents. However, by proper means, such as carefully chosen solvents and reaction conditions, or compartmentalization of the supports, this problem can almost fully be solved.

It is not sufficient, though, to be able to produce vast numbers of catalytic materials, such as it is possible with the split-and-pool technology. Such an approach requires also adapted reactors with which the catalysts thus generated can be as efficiently tested as they are synthesized. This problem will be addressed in the following section.

3. Highly integrated reactors

Reactors which give data of similar quality as conventional single channel reactors are well developed [5,10], in routine operation in several laboratories, and are nowadays commercially available. Degrees of parallelization in such systems for stage II screening are up to about 50-fold. However, for primary screening, more highly integrated reactors would be desirable. Such reactors cannot any longer be constructed by parallelizing conventional multi-channel reactors higher and higher; instead principally different approaches have to be chosen. In addition, reactors for primary screening often need to have a format which is best suited for the analytical technique used, or the method used for solids synthesis for optimum performance. In the following we will describe two reactor systems which have recently been developed. One relies on the use of a ceramic monolith as it is normally employed as support for selective catalytic reduction catalysts in power plants, the other is manufactured by micromachining techniques in a silicon wafer.

The reactor system based on the ceramic monolith is designed to operate in connection with the color detection system recently developed by Busch et al. [13]. The reactor body consists of a 25×25 channel ceramic monolith, of which only the inner 23×23 channels are used, resulting in a parallelization degree of 529. This monolith is cut in the middle normal to the channels, and a catalyst support plate made of brass having the same type and pattern of channels as the monolith is placed in this position and sealed with a suitable sealing material for the desired application (Fig. 3). At the exit of the reactor, a filter paper impregnated with

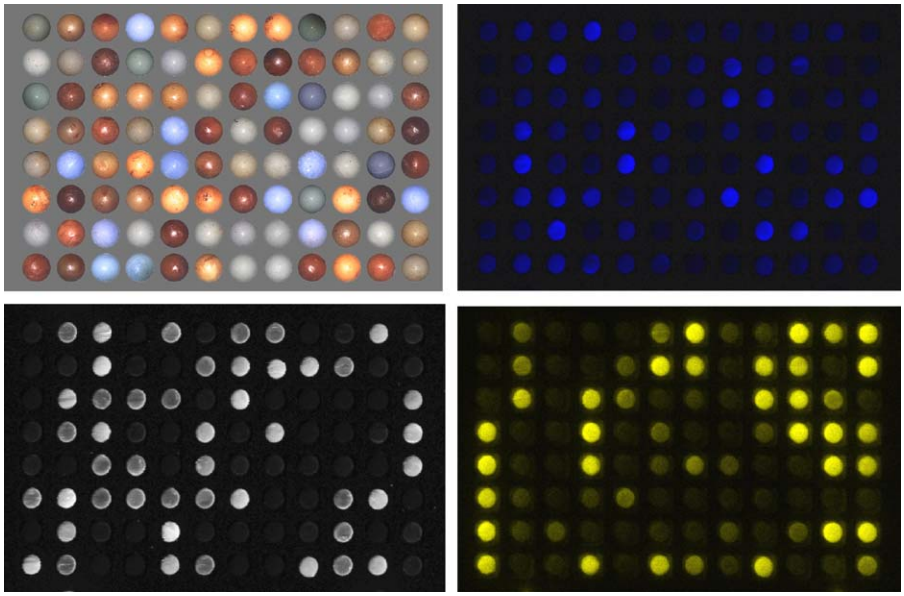

Fig. 2. The 96 catalyst spheres prepared by the split-and-pool protocol. From upper left clockwise: optical image, XRF mapping of Co, XRF mapping of Mo, XRF mapping of Fe. The different levels at which the elements are present are detectable.

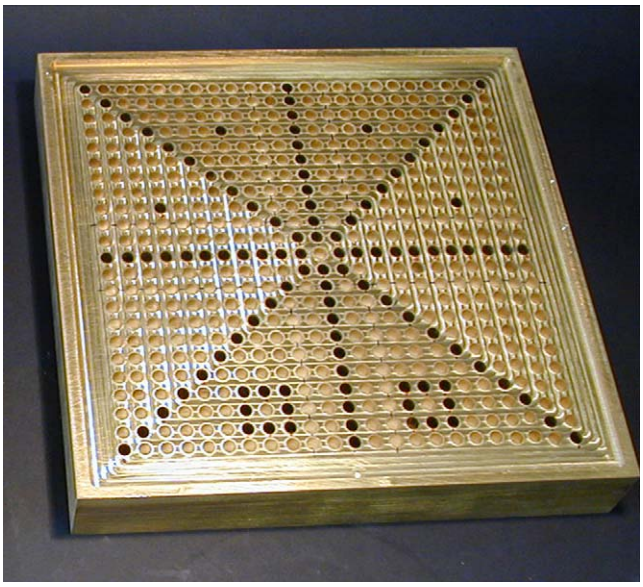

Fig. 3. Sample holder plate of the 529 reactor. The dark spots are channels filled with Pt/Al_2O_3, the other channels contain alumina. The size of the plate is 150 mm × 150 mm.

the detection dye can by tightly attached to the channel outlets by means of a vacuum system, so that the outlet gas of each channel passes through a clearly defined section of the impregnated filter paper. The filter paper is exposed to the gas stream typically for 5 min during reaction. The system is used in our laboratory for screening of DeNOx catalysts, i.e. the dye (ABTS) is NO-sensitive [13]. If NO is present in the gas stream, the ABTS dye reacts and turns blue. If, on the other hand, an efficient catalyst is placed in the corresponding channel, all NO is removed, and no color signal is obtained. The impregnated filters can easily be changed during operation of the reactor, so that also the development of activity over time can be analyzed. Fig. 4a shows the developed filter paper after a test pattern of catalysts (as visible in Fig. 3) had been placed in the reactor for a gas mixture consisting of propene, NO, and nitrogen as balance. Fig. 4b shows the results obtained in NO reduction with propene in the presence of 5% O_2 with a real catalysts library of high surface area mixed metal oxides which had been synthesized using the activated carbon route discussed in Section 2. In this library, the white spots for several channels indicate that catalysts with some DeNOx activity are present. These formulations were tested subsequently in a single channel reactor with IR analysis, and the DeNOx activity could be confirmed. The best system was a AlMgZrNiFe mixed oxide which reached 25% NO conversion at about 350 °C, however, at much higher space velocity than in the 529 channel reactor, which is quite remarkable for a noble metal free system. The temperature range for selective NO removal was rather broad (above 15% conversion between 300 and 400 °C) for this catalyst compared to a 5% Pt/Al_2O_3 which reached close to 50% conversion at 200 °C. In addition, several other promising mixed metal oxides were identified in the 529 channel screen and confirmed in the single channel reactors. These systems are now studied in detail, and the results will be reported in a forthcoming publication.

The reactor based on the ceramic monolith is designed to operate with the color detection method. However, this means that for each new project, a new detection scheme would have to be developed, in that a dye or a fluorescent dye reacts with a reagent or a product. This can be rather time consuming, for some projects it will not be possible to develop a specific dye detection. It is thus desirable to have more generic, highly parallelized reactors available. Such a system was developed on the basis of silicon wafer technology [18]. The techniques used for the construction of such higher integrated system are well developed in micromachining, and microstructured reactors have now been built reaching parallelization degrees of up to 625, after a first generation with 105 channels and a second system with 384 channels. Fig. 5 shows a photograph of such a reactor with 625 wells. It is constructed from silicon by standard microstructuring techniques, such as masking, selective etching, controlled oxidation, reactive ion etching, or micro powder blasting of the silicon [18]. Silicon is a highly suitable construction material for such reactors, since due to the thin, dense SiO_2 coating present on the silicon surface, it is highly stable and inert under oxidizing conditions. Reactors consist of two identical semi-systems with the desired number

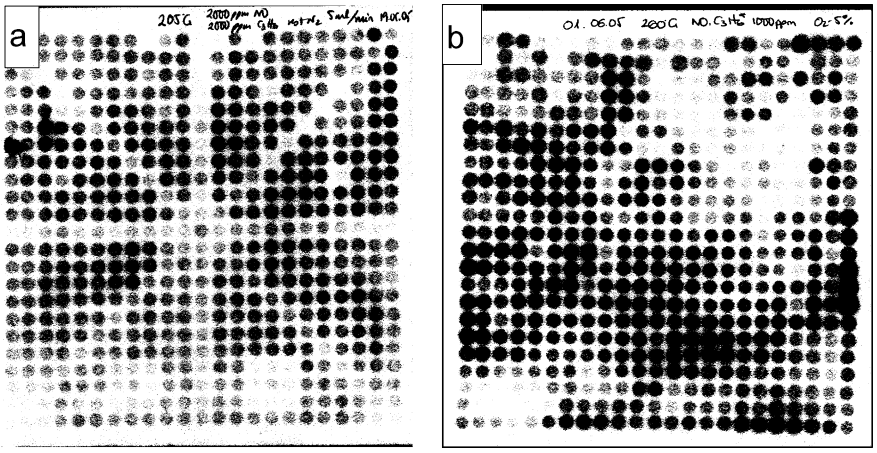

Fig. 4. (a) Dye impregnated filter paper after exposure to the gas flow exiting the reactor with the test pattern of catalysts shown in Fig. 3, 205 °C, gas composition 2000 ppm NO, 2000 ppm C_3H_6, nitrogen as balance, flow in each channel 5 ml/min. (b) Dye impregnated filter paper after exposure to the gas flow exiting the reactor filled with different high surface area mixed metal oxides, 260 °C, gas composition 1000 ppm NO, 1000 ppm C_3H_6, 5% O_2, nitrogen as balance, flow in each channel 5 ml/min.

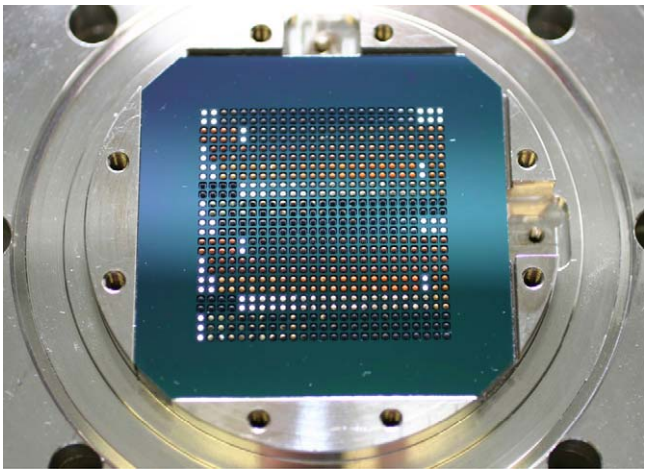

Fig. 5. Photograph of the 625 wafer reactor filled with catalyst spheres. The silicon wafer is mounted in a flange for gas connection, under reaction conditions it is covered by a top wafer which is constructed similarly. The size of the wafer is 70 mm × 70 mm, catalysts are located in a 50 mm × 50 mm area.

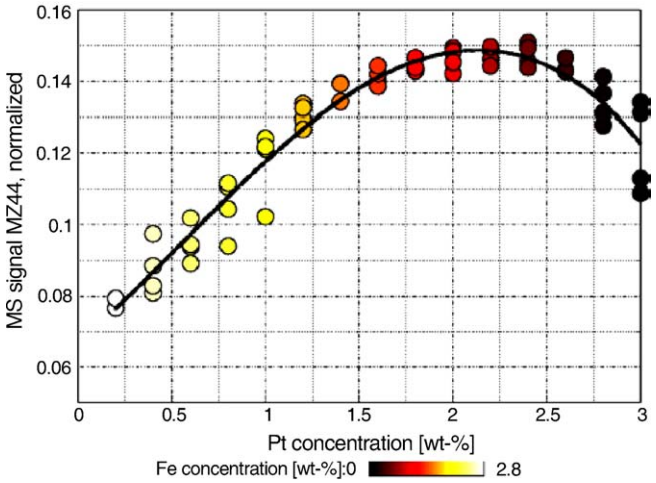

Fig. 6. Performance of $PtFe/Al_2O_3$ catalysts in preferential CO-oxidation as measured in the 625 wafer reactor. Total metal loading 3 wt.%, 150 °C, GHSV 100 000 h^{-1}, 1% CO, 1% O_2, 5% H_2O, 5% Ar, H_2 balance.

of wells and membranes on the bottoms of the wells. The catalyst is placed in the wells of the reactor in form of single beads, which can be synthesized by the split-and-pool technology described above, thus allowing an integrated workflow. The gas is distributed via a lid on top of the reactor which is fully symmetrical to the bottom plate and which seals the wells against each other reasonably well even without bonding, but simple pressing. However, if necessary, the systems can also be permanently bonded to achieve a fully gas-tight sealing. Analysis proceeds via a sampling capillary for a mass spectrometer or other suitable techniques. This reactor has been used and validated for hydrocarbon oxidation and preferential CO-oxidation in hydrogen. $PtFe/Al_2O_3$ catalysts were identified out of a test library as active and selective for the preferential CO-oxidation, a composition which was known from literature before [19,20]. Fig. 6 gives data for selected compositions focussing on the PtFe-system, which shows that a metal concentration of about 2% Pt and 1% Fe is optimal at a total metal loading of 3%. This result was shown to be independent of the type of reactor used, i.e. similar results were obtained in the 384 well as well as in the 625 well reactor. Although for detailed analysis of the catalysts use of a stage II reactor is still necessary, the microstructure reactors described here are a very valuable screening tool for the analysis of vast numbers of catalysts in short times.

4. Software environments and library design tools

Integrated high throughput programs in catalysis research present a formidable challenge for an informatics environment. HTE workflows typically consist of a number of stations or modules, which are connected by materials and informatics flow. The task of a data management system consists of collecting all the information and relating it to sample identity, storing the data in a format that can later be easily retrieved and cross-correlated, and in providing a user-friendly interface. The complexity of this task is enormous. The data comes from very different sources (user input, output of analytical instruments which are often vendor specific, physical and chemical data from data bases and so on), and the amount of data can be exceedingly high on the giga- to terabyte level for complex programs. In addition, the workflow can be highly project specific, so that the software environment needs to be sufficiently flexible to allow easy adaptation to new project requirements.

In spite of these problems, several solutions have been described already. For an academic environment, a software suite has been developed in the framework of the EU Combicat program [21,22]. An industrial solution has been introduced by hte [23], which consists of a suite of modular software components based on a standardized language called hteML which itself is based on XML, one of the standard languages for exchanging data on the web. Symyx Technologies provides a proprietary software environment named Renaissance® to support a high throughput workflow. Considering these developments, one can probably safely say that all major problems concerning a data management structure even for complex high throughput environments are solved, although continuing development work and adaptation will remain necessary.

This is different, though, for the fields of intelligent data analysis and library design. In these fields there is still an urgent need for novel methods and approaches. There are in principle many methods which can be used for library design, simple ones, such as random selection of elements, approaches based on statistical methods, such as design-of-experiments which are implemented in the commercial software suites, or more advanced techniques, such as evolutionary algorithms which have, for instance, been used in optimizing catalysts for oxidative dehydrogenation of propane [24] or the oxidation of isobutene to methacrolein [25]. Combined with the holographic search strategy [26], a very powerful visualization tool, these techniques make a highly appropriate software suite for high throughput screening. A toolbox for library design including a number of tools has been developed at IRC and is available on the web [27].

However, as valuable as these methods are also in the discovery of novel formulations, their application often results more in an incremental improvement of known compositions, even if they may be very efficient for this purpose. For a true discovery library, these approaches are not suitable, since as broad as possible coverage of chemical space is desirable for such libraries. In the pharmaceutical industry, so-called descriptors [28] are used, via which in silico screening is possible to construct an optimal library. For molecular catalysis, such methods can be adapted to describe the catalysts and ligands, although, surprisingly, this approach is up to now only rarely used [29]. For solids, however, implementation of similar techniques is much less straightforward.

We have implemented a methodology [30,31] to develop descriptors for solid catalysts, which contain information on elemental composition of the catalysts, on the synthesis procedure, chemicals used in the synthesis, and physico-chemical parameters of the catalysts selected from about 3000 possible parameters. The descriptor vector was obtained by a ''learning'' process, in which a diverse library (diversity judged by chemical intuition) was tested in the oxidation of propene, and catalytic behaviour was classified in five classes after principal components analysis and a classification routine. The classes can roughly be characterized as: (i) low activity total oxidation, (ii) medium activity total oxidation, (iii) high activity total oxidation, (iv) partial oxidation, and (v) oligomerization. The catalysts performance was then correlated with the parameters by different techniques, i.e. neural networks or classification trees, and the best correlations taken as the descriptor vector, containing about 40 parameters. For the neural networks, a number of different architectures have been tested, and interestingly, several parameters were selected as part of the descriptor vector by most or even all networks. These parameters include atomic radius, electron affinity, normalized formation free enthalpy for the most stable metal oxide, the smallest energy difference between the most stable oxide and another oxide in the catalyst, the number of elements in the catalyst, and eight parameters related to the synthesis. In addition, when examining the attributes related to the element oxides, only two attributes based on the melting point are included. For the element ions, ionic radius, coordination number, and ionic covalent parameter seemed to be the most important variables. Inspecting these parameters, chemical intuition would suggest that they could indeed in some complex way correlated in the performance of a catalyst in propene oxidation. Especially significant appears to us, that many parameters describing features of the synthesis enter the descriptor, because experience tells us, that the synthesis is crucial for the performance of a catalyst. Any correlation method in heterogeneous catalysis, which does not take into account the synthesis will have a high probability to fail in obtaining reasonable predictive power.

The prediction of performance of a solid in propene oxidation based on such descriptors as described above is far superior to random prediction (about three times as many correct classifications), so that one can with some justification state, that chemical intuition has been implemented in a software program [30,31].

This system is now in use for virtual screening of solid catalysts, i.e. catalysts are at random generated by a software program, then the descriptor is calculated and performance is predicted. The challenge here is to expand the software so that chemical knowledge is incorporated. While the power of the program lies in the fact that it does not just provide the user with the descriptors a catalyst should meet, but instead with an actual, albeit general, synthesis protocol, the disadvantage is that these protocols often describe ''impossible'' catalysts. An example could be a synthesis recipe as follows: prepare by a precipitation process a solid consisting of 30% Ba, 50% Na, and 20% V (oxygen is excluded), using inorganic, non-halide precursors from aqueous solution. Using suitable precursors and finding a precipitation agent which would precipitate all three metals at the same time is virtually impossible. So one either has to discard such a formulation, or make it synthesizable by adapting the synthesis process and thus changing the software suggested recipe. Both alternatives are not optimal, and we are presently trying to incorporate chemical knowledge into the system in a way, that a high fraction of immediately synthesizable catalysts is suggested by the program.

5. Conclusion

HTE approaches in catalysis, and especially also in oxidation catalysis, have become practically useful over the last decade and are industrially implemented. A framework allowing the synthesis and evaluation of a wide range of different catalytic materials in a variety of reactions is available. There are still gaps and needs, such as higher integration and improved and accelerated generic analytical tools, and especially novel approaches in data analysis and library design. However, as the preceding discussion of some advances of the last years has shown, these developments are forthcoming and will be implemented in the routine workflow of HTE programs.

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