Catalysis Today 137 (2008) 36–43

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Structure oriented library design in gas phase oxidation catalysis

Stephan Andreas Schunk [a,*], Andreas Sundermann [a], Hartmuth Hibst [b]

[a] *hte Aktiengesellschaft[1], Kurpfalzring 104, 69123 Heidelberg, Germany*
[b] *BASF Aktiengesellschaft[2], GCC/S, M 301, 67957 Ludwigshafen, Germany*

ARTICLE INFO

Article history:
Available online 23 May 2008

Keywords:
High throughput experimentation
Library design
Oxidation catalysis

ABSTRACT

Structure oriented screening techniques are discussed with regard to their usefulness and applicability in catalyst screening in research projects with different degrees of exploratory character. Structure oriented screening approaches were applied to build libraries for two target reactions in two case studies presented in this paper one challenging exploratory ammon-oxidation reaction for the conversion of C_6-feedstocks to adipodinitrile precursors with currently no relevant useful materials and no technical solution known. In this study the structure driven approach helped to identify lead structures for the conversion. The second case study focuses on the oxidation of acrolein and methacrolein to the corresponding unsaturated acids. Here technical catalyst candidate materials are known and are applied in the actual industrial applications. Therefore, the focus of the second case study is to find a superior material or alternative candidate materials with improved properties with this research strategy. For both case studies the effectiveness of the structure based approach is evaluated and put into perspective with state of the art library design and research strategies in high throughput experimentation and combinatorial catalysis.

1. Introduction

High throughput experimentation and Combinatorial Chemistry have evolved to broadly accepted methods and technologies applied both in industry and academia. A remaining challenge in this field is connected with the question of what the most efficient approaches are for using these highly time- and resource-saving techniques in the related research programs. In order to increase efficiency, the process of lead structure identification has to be streamlined, in order to detect candidate materials with the potential of further optimization. Two general cases can usually be discriminated in catalysis research: (a) new catalytic reactions where no useful catalysts are known or (b) known catalytic reactions where the performance data of known structures reveals deficiencies or potential for improvement. In both cases it is necessary to set up libraries of candidate materials in the research process so that the diversity of these libraries employed for the study is adequate and in accord with the research target. A number of groups successfully developed methods to tackle challenges in library design and the finding of optimal catalyst recipes, nevertheless in many cases the compositional space or the aspect of recipe parameter modification during library design seems to overrate the structural aspects in these studies [1–6]. In this paper we will discuss and illustrate two complimentary approaches for the identification of complex multi-element lead structures of mixed metal oxides, namely the retrospective deconvolution on the basis of simple binary and ternary oxides [7] and the compositional derivatisation of a highly complex mixed metal oxide target candidate structure. Both approaches will be discussed for two catalytic target reactions, the first being the conversion of C_6-feedstocks as *n*-hexane, cylcohexane and benzene to adipodinitrile derivatives over solid oxides under ammonoxidative conditions [7]. The second reaction is the oxidation of unsaturated aldehydes such as acrolein and methacrolein to the corresponding unsaturated acids over solid oxides synthesized by hydrothermal techniques [8,9].

Both case studies rely on the fact that structural diversity can be introduced into the screening deliberately and that structural changes should be tracked by analytical methods instead of assuming that the mere change of variables in a compositional or physical treatment synthetic plan is the only source of diversity. The discriminator for the structural diversity of samples is in both case studies X-ray powder diffraction before and after the catalytic test. The powder X-ray diffractogram is used to identify the bulk structures (if possible), the degree of crystallinity and the amount of semi-crystalline or amorphous content of the solid oxides. The

---

* Corresponding author. Tel.: +49 6221 7497111; fax: +49 6221 7497134.
E-mail address: stephan.schunk@the-company.de (S.A. Schunk).

[1] www.hte-company.de.

[2] www.basf.com.

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.03.034

additional information gained by the structural discriminator can either be used for data evaluation with the aid of neural networks or together with conventional design of experiments.

In the past, different groups have mainly employed the variables stemming from the compositional space using multi-element combinations as diversity criterion for library design in the experimental planning stage. One main reason for choosing this approach is undoubtedly the reduction in the logistical impact by using only a limited number of fixed preparation recipes for the synthesis of candidate materials. The alternative approach presented here does not have this logistical advantage of a limited number of preparation pathways by a fixed recipe, but either involves frequent change and adaptation of automated preparation sequences and/or a higher proportion of manual work. The impact on manual preparation sequences generally has a high impact on the logistics of operating one or more automated preparation platforms and it is evident that a high degree of flexibility with regard to the platform functionality is demanded [10]. Looking at the effectiveness of screening of a multidimensional experimental space, a different picture is obtained by using the approach presented here: from the compositional and X-ray diffraction data structural data together with the catalytic performance data are analysed in classical statistical designs and composite designs. Therefore, direct conclusions to structure-property relationships can be drawn on the basis of the X-ray diffractional data obtained, with the restriction that the structural data represent the bulk structure of the samples analysed. In order to deepen insight, this approach is of course expandable to numerous analytical techniques, and as the authors envision, it is in principle also in accord with "in situ"-analytical observations [11,12].

The approach of structure directed library design and catalyst screening bears similarities with library design and testing of molecular entities like molecular catalyst candidates or drug candidates [13,14]. In both cases, namely the synthesis and testing of molecular catalysts and drug candidates, the structure directed library design focuses upon limiting the degrees of freedom in test candidate diversity space by combining the synthetic effort with an analytical control of the target candidate library elements before screening for useful properties. The major difference remaining between the structure directed approach and the screening of molecular compounds as target materials is based on the fact that three-dimensional extended solids can only, to a certain extent, be characterised by structure analysis through X-ray diffraction with the surface being the main locus of the catalytic reaction still left obscure. At least powder X-ray diffraction offers partial control of the sample quality and offers a medium for sample classification, discrimination and quality control of the libraries obtained. A useful extension for the structure controlled screening approach would therefore be the coupling with a highly sensitive technique that retrieves a maximum amount of information on the surface structure. Results of Wachs suggest that Raman spectroscopy could be a useful piece in the puzzle to further reduce the redundant degrees of freedom and true diversity control in the structure directed screening approach [12]. Additionally, Raman spectroscopy offers the option of truly characterising surface species or surface environments that contribute to the catalytic "action", a fact that can contribute to insight into elementary steps in heterogeneous catalysis.

In the design and evaluation of libraries for high throughput test campaigns, other groups have chosen approaches that rely on gathering the maximum amount of data available in open literature, including structural data, of test candidates employed in the studies in order to establish QSAR ("quantitative-structure-property relationships") on the basis of high throughput catalyst screening [15,16]. The main target of this approach is to develop so called descriptors that allow correlations throughout the candidate materials tested and derive insight into properties which appear useful. An important feature of this approach is the fact that library diversity can be expressed in terms of numerical values, rendering different libraries comparable. In our paper the additional information that is taken into account for the discrimination of catalyst candidates is limited to structural parameters that can be estimated by X-ray diffraction techniques prior to and post-catalytic testing. The choice of target structures to be evaluated is crucial to the success of any given program, therefore we describe how the target structures were chosen together with the case studies.

It is evident, that in order to bring to bear the full power of a screening approach focussed on structural identities, a number of elements have to come together that go beyond flexible and automated synthesis platforms, high throughput capable analysis instruments and screening equipment for adapted throughput and delivering test data of adequate quality [17,18]. The essential part that embraces the workflow is a software platform that is able to bring all test data together in one database and capable of data correlations based on the results retrieved [19]. Without the suitable automation and software environments the effort becomes a tremendous endeavour consuming massive amounts of manual workforce and personal control of data.

In order to execute the two case studies mentioned in this paper fully automated screening units were employed which utilize catalyst quantities of approximately 1 ml and a 48-fold degree of parallelisation, automated synthesis platforms and a suitable software environment also came to bear in both cases.

2. Retrospective hit deconvolution: a case study for a highly exploratory target reaction

For the target reaction of ammonoxidative conversion of a C_6-feedstock with the goal of obtaining adipodinitrile or a related derivative an approach was chosen where highly complex materials known to be useful in related oxidation and ammoxidation reactions were tested with regard to their performance in the target reaction [7]. A major part of the initial library was set up by a mix of candidate materials that are structurally well characterised and known to be catalytically active and selective in related ammon-oxidation reactions. Special focus in the library planning was put on the inclusion of complex catalyst candidates known to be useful in allylic oxidation of olefins [20–22] or benzylic oxidation of aromatics [23]. The aforementioned catalyst classes were described as candidate materials for allylic and benzylic functionalization in the open and patent literature were therefore thought to be potentially prospective for the target reaction and. For this library not only pure phase compounds were included after X-ray diffractometric characterisation but also phase mixtures or materials with high amorphous content. The synthesis of these materials was carried out closely repeating the recipes described in the respective patents and papers and controlling the synthetic quality of the candidate samples, with the data reported in the original papers and patents as quality criteria. The setup of the experiments was conducted as factorial designs (mainly Box-Behnken) with the structural identity as variable and ternary and quaternary compositional designs for the compositional variation of iso-structural compounds.

Within the early phase of the screening campaign a complex lead candidate with the compositional formula $Mo_{12}Sb_3Co_1V_1Nb_1Ta_1Ti_1O_x$ was identified as a useful candidate material, being able to convert benzene and cyclohexane into 1,4-dicyanobutadiene (muconitrile). The structural analysis of the catalyst sample revealed a largely amorphous oxide content with crystalline

Table 1
The table illustrates the products that are formed over the various mixed metal oxides that were evaluated as catalyst candidates in the ammonoxidative conversion of benzene [7]

Ternary oxide systems	Products found	Quarternay oxide systems	Products found	Pentenary oxide systems	Products found	Hexenary oxide systems	Products found
V-Sb-O	C4-DN	V-Sb-Ti-O	C4-DN	V-Sb-Ti-Nb-O	C4-DN	V-Sb-Ti-Nb-W-O	C4-DN
Mo-V-O	C4-DN MLI	Mo-V-Nb-O Mo-V-Ta-O	C4-DN MLI	Mo-V-Nb-Ta-O	C4-DN MLI		
Mo-Sb-O	C4-DN C6-DN	Mo-Sb-Ti-O	C4-DN C6-DN	Mo-Sb-V-Ti-O	C4-DN C6-DN	Mo-Sb-V-Nb-Ti-O	C4-DN
		Co-Mo-Sb-O	C4-DN	Co-Mo-Sb-Ti-O	C4-DN	Co-Mo-Sb-Nb-Ti-O	C4-DN

For simplicity, oxidation products with a carbon backbone smaller than C_4 are left out (abbreviations C4-DN, C_4-dinitriles; C6-DN, C_6-dinitriles; MLI, maleinimide). Reaction conditions: 2% benzene, 4% ammonia, 14% oxygen, balance nitrogen, GHSV 1000 h^{-1}, temperature range 420–440 °C.

portions of shear structures of Mo_5O_{14}-type oxides in mixture with β-Co-molybdate and traces of MoO_3. Although the material only gave small yields of the product, no other catalyst candidate showed the same or comparable performance in the target reaction. Following this screening strategy, a positive output was gained from this initial phase of the screening campaign: a large amount of catalyst materials, which were well characterised by structure and composition, could be ruled out as being prospective candidates in the target reaction and a lead candidate material, displaying a complex composition from an elemental and crystallographic point of view was identified. In order to further develop this lead candidate material again a structure based approach was chosen which built on the detectable structures and the composition of the lead material. To gain more insight into the structure-property relationship, on the basis of a structure directed screening approach, the deconvolution of the lead compound into binary, ternary and quaternary oxides based on the elemental composition of the lead structure was undertaken. In order to establish a structure-property relationship, potential element combinations of the catalyst candidate, which were reported in structural databases to form crystalline or semi-crystalline oxide materials upon synthesis, were taken as base points for the deconvolution. These base points became the centerpoints of the compositional designs, where within a certain degree the elemental stoichiometry was varied for the reported compounds first of all to vary the composition for iso-structural compounds and second to allow for formation of phase mixtures, side phases or potential amorphous content. From a graphic multidimensional viewpoint one could say that the highly crystalline multinary candidate materials were used as reference points to build a complex multidimensional grid of complex oxide materials (see Table 1).

The deconvolution of the compositional formula of the lead candidate material into multinary oxides starting from binary compositions, allowed to establish structure-property relationships that contributed to a better understanding of the complex multi-element material found in the initial screening: it was discovered that muconitrile (1,4-dicyanobutadiene) could only be obtained using Mo-Sb-O_x, Mo-Sb-Ti-O_x and Mo-V-Sb-Ti-O_x type oxides as catalysts, which structurally display mainly a amorphous to semi-crystalline character similar to oxides of the bronze-type Mo_5O_{14}. Rutile type oxides like V-Sb-O_x, V-Sb-Ti-O_x produce mainly unsaturated C_4-dinitriles. An essential feature of Mo-Sb-O_x, Mo-Sb-Ti-O_x and Mo-Sb-V-Ti-O_x seems to be the semi-crystalline nature, which also leads to a partial instability of the oxide.

The study illustrates that, in principle, highly complex multiphase candidate materials can be deconvoluted, on a structure based approach, into compounds of compositionally and structurally less complex nature, taking structurally well characterised and previously reported compounds as reference points for the library setup. A variation of these compounds in stoichiometry and respectively phase composition and crystalline nature adds to further diversity in library constituents on a systematic basis. The evaluation of the results can largely be eased by the use of classical design of experiments, composite designs or alternatively more complex methods which were not used within this context like neural networks or genetic algorithms.

3. Structural and compositional derivatisation for a closely related family of bronze structures: a case study about the search for an improved catalyst system

The extensive research performed by numerous groups on the structural identity of Mo-V-Nb-Te-O type oxides [24] has revealed a number of important findings that have led to a better understanding of the structure-property relationships that render these materials active and selective compounds in the direct conversion of alkanes, especially propane to propylene, acrolein and acrylic acid [25]. A core finding was the identification of two phases, namely i- and k-phase, which are the two crystalline products that can be obtained phase-pure or may evolve as phase mixture under non-optimum synthesis conditions [26]. Optimum synthesis conditions will deliver both i- and k-phase as phase-pure compounds, which both have very different catalytic behaviour in alkane oxidation [8]. The phase which is attributed to being catalytically active and selective in propane oxidation is the i-phase which is usually synthesized using the elemental composition Mo-V-Nb-Te-O. This i-phase is iso-structural with the oxidic bronze $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ [27] which can also be obtained in highly crystalline and phase-pure form by hydrothermal synthesis. The $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ bronze structure shows typical structural motifs of six and seven ring channels which are also found together with the channel forming oxide species of groups V and VI. Based on the observation of the isotypic crystallization of Mo-V-Nb-Te-O and $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ a synthetic method was developed offering access to a wide range of structurally identical but compositionally largely varying bronzes: the introduction of Cs into the channel lattice of Mo-V-Nb-Te-O type oxides using hydrothermal or conventional synthetic techniques opens up a wide range of synthetic possibilities [8]. A large compositional variety of isotypic bronze-type oxides can be synthesized using this methodology, using elements of groups V and VI as base constituents of the framework lattice, as long as a few boundary conditions for the synthetic effort are kept constant. First and most important rule is that the stoichiometric ratio of Cs and the other metal constituents of the bronze is kept at the same level as in the oxide system $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ namely 1/10. The second rule that has to be obeyed in order to obtain oxides which are isotypic to the i-phase, is that the sum of the oxidation states of the framework building bronze constituents multiplied with the respective stoichiometric coefficients of the constituents must be close to the range of niobium and tungsten the compound $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$, in this case based on the given stoichiometric formula 27,5 (2,5 × 5[Nb] + 2,5 × 6[W]). By sticking to both rules it is possible to synthesize a large variety of oxidic bronzes and to introduce various transition metals and main group elements into the bronze structure. The main focus of the study presented here was Cs-containing bronzes, that had molybdenum and vanadium as main framework building constituents of the type $Cs_{0,5}(Mo\text{-}V\text{-}X)_5O_{14}$.

This synthetic development propelled our research focussed on the development of alternative candidate systems for the oxidation of methacrolein to methacrylic acid largely. The focus of our program was directed towards compositional variation of classical heteropolyacids, Cs/P-doped Mo-V-W bronzes which have a largely semi-crystalline character and P-doped bronzes of the type $Cs_{0,5}(Mo\text{-}V\text{-}X)_5O_{14}$ which are highly crystalline compounds. These three structures were again taken as basis of our structure directed approach and composite designs were used to establish an understanding towards structure-property relationships.

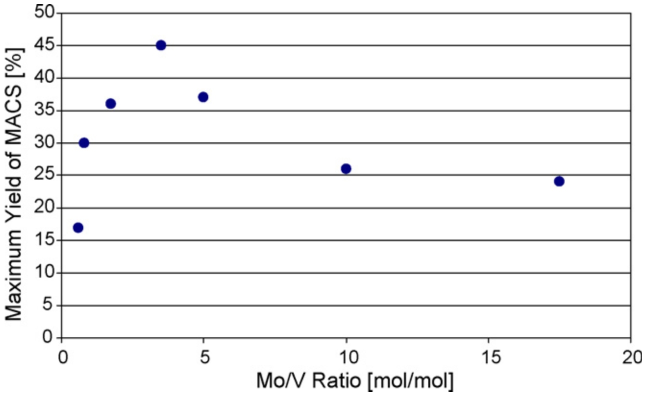

Fig. 1. Display of the catalytic performance expressed as the maximum yield of methacrylic acid per pass of various Cs/P-doped Mo_5O_{14}-type bronzes. The window of reaction conditions at which these yields were obtained was in the range of 1–5% methacrolein, 7–16% oxygen, 2–40% water, balance nitrogen in a GHSV range of 500–4000 h^{-1}. On the *x*-axis the different levels of vanadium that were employed at a constant ratio of Mo/W of 7 are plotted.

4. Reference systems in the study: Cs/P-doped Mo-V-W bronzes and heteropolyacids

The standard industrial catalyst system for the oxidation of methacrolein to methacrylic acid are molybdenum based heteropolyacids of the type $H_{3\text{-}A}Cs_A(Mo_{12-(B+C)}V_BX_C)P$ [28–30]. A variety of elements are claimed to be beneficial for this catalyst system for performance enhancement, among others most important caesium as counter ion and vanadium. Both serve as elements which are beneficial for the enhancement of the oxidation properties of the catalyst, improving selectivity and yield. A number of other elements are claimed to be useful for performance improvement, such as antimony, iron or arsenic, in many cases fine details in the preparation recipe are decisive as to whether or not the beneficial properties will manifest or not.

The general challenge with the industrially important heteropolyacid based catalyst system is based on the fact that the lifetime of the industrial catalyst is relatively short compared to other industrially important oxidation catalyst systems, while the price of the catalyst is reasonably high, especially due to expensive elements contained in the catalyst like caesium. Why is the catalyst lifetime for this extended solid comparatively short? The current picture of the working heteropolyacid catalyst is that the intact heteropolyacid appears to be the catalyst precursor, decomposing into lacunary heteropolyacids and the respective fragments which are thought to be responsible for the catalytic "action". Due to the decomposition of the heteropolyacids to thermodynamically more stable phases like MoO_3, which are catalytically active but mainly responsible for the total oxidation of methacrolein to CO_x, a degradation in the performance of the catalyst system is observed.

Looking at related heterogeneously catalyzed gas phase oxidations it is striking to see that the oxidation of acrolein to acrylic acid, which on first impressions, seems to be a closely related reaction and appears over totally different type of solids, namely Mo-V-W based bronzes of Mo_5O_{14}-type [31–34]. Heteropolyacids are also very selective catalysts in acrolein oxidation, but show a lack of activity with regard to the bronze systems. The bronzes are very stable catalysts with regard to their lifetime and are by far not liable to suffering from similar degradation mechanisms as the heteropolyacids. From point of view of the related oxidation reactions, Gaube et al. have tried earlier to modify these Mo_5O_{14}-type bronzes with caesium and phosphorous in order to improve their performance in the oxidation of methacrolien to methacrylic acid. In an extended study we have systematically varied the vanadium content of these bronzes, and doped the resulting iso-structural bronzes with various Cs/P levels and ratios. For our study it was important to conserve the structural identity of the Mo-V-W bronze systems in the form of a ternary experimental design. Fig. 1 illustrates that the highest yield of methacrylic acid can be achieved with a molybdenum to vanadium ratio of Mo/V = 3,5 and a ratio of Mo/W of 7. The plot only shows the dependence on the variation of the molybdenum to vanadium ratio of the bronze, as it has the most pronounced effect on the performance of the candidate material. Changes in the molybdenum to tungsten ration outside Mo/W of 7 result in extreme changes with regard to performance, the yield of methacrylic acid drops dramatically at higher and lower ratios. With varying Cs/P ratio in a range of 0.5–2 yields in a similar range to the target product can be achieved, while this is not possible if the Mo/V- and the Mo/W ratio is not in the adequate range. Generally it can also be said that increasing ratio of Mo/P also leads to a lower activity of the doped samples.

Yields of over 40% of methacrylic acid on a carbon basis are achievable with these catalyst systems, as can be seen from Fig. 1. The reaction conditions needed to achieve these yields are either connected to high water contents of approximately 40% water (64% conversion, 70% selectivity to methacrolein at a feed of 5% methacrolein, 40% water, 9% oxygen, balance nitrogen, 310 °C, GHSV 1500 h^{-1}), or a reduction in methacrolein feed concentration in combination with a reduction in water content (67% conversion, 60% selectivity to methacrolein at a feed of 2% methacrolein, 4% water, 15% oxygen, balance nitrogen, 310 °C, GHSV 1500 h^{-1}). We have previously reported about the structural integrity of similar bronze based oxides and the effect of Cs/P-doping on these complex structures. Apparently Cs/P doping leads to a partial decomposition of the bronze and formation of heteropolyacid layers on the surface of the bronze [35]. It is interesting to see that although the basic bronzes are catalyst systems that can withstand the conditions of oxidation of acrolein to acrylic acid for a prolonged lifetime, an insufficient performance is observed for the oxidation of methacrolein to methacrylic acid after several hours on stream. Fig. 2 illustrates the behaviour of a bronze-type sample doped with Cs and P of the composition $Mo_{0,7}W_{0,1}V_{0,2}Cs_{0,04}P_{0,02}O_x$. It can clearly be seen that the aged sample shows a massive loss in selectivity to the target product and is also less active after 24 h already. The degradation of the sample is not finished at that point and further loss in activity and selectivity can be observed. The X-

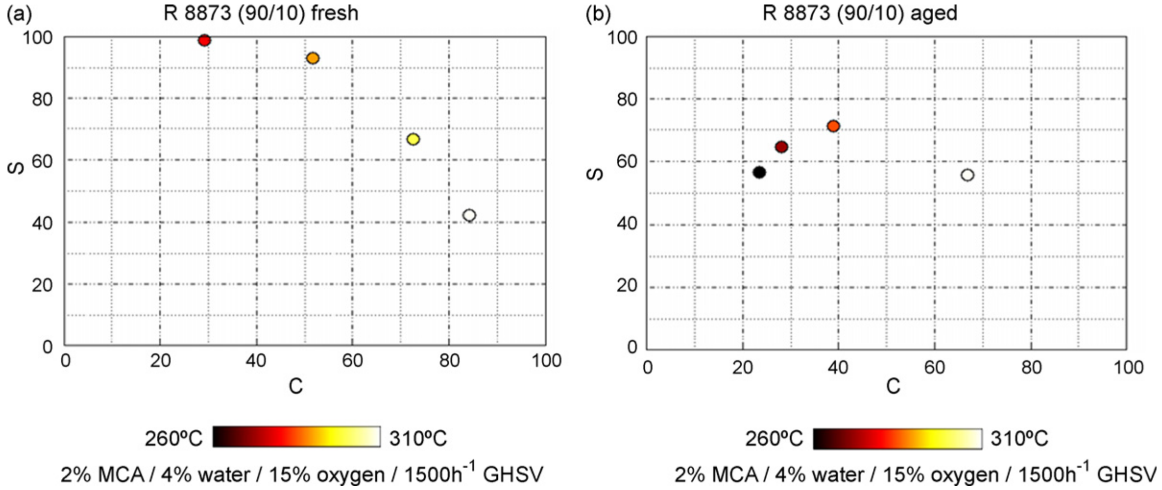

Fig. 2. (a and b) Performance change for a Cs/P-doped sample of the composition $Mo_{0,7}W_{0,1}V_{0,2}Cs_{0,04}P_{0,02}O_x$ displayed in a conversion/selectivity plot at a feed-composition of 2% methacrolein, 4% water, 15% oxygen, balance nitrogen, GHSV 1500 h^{-1}. (Left (a)) shows the performance of the fresh sample at 280, 290, 300 and 310 °C and (right (b)) shows the performance of the aged catalyst after 24 h of time on stream at 260, 270, 280 and 300 °C.

ray diffractometric analysis of the sample prior to the catalytic test showed the typical diffractogram of an Mo_5O_{14}-type bronze with some heteropolyacid as side phase, the post-catalytic analysis via X-ray diffraction showed that the Mo_5O_{14}-type bronze remained only as side phase, main phases that could be identified were heteropolyacids and hexagonal and orthorhombic Mo-V-oxides. The transformation of the doped bronze to these other phases can be seen as an effect of the combination of the hydrothermal treatment in combination with the presence of the organic feed.

The lack of selectivity to the target product and the lack of inherent stability make the Cs/P-doped Mo_5O_{14}-type bronze systems not very competitive with regard to the standard catalyst system, which is more stable and selective.

5. Cs-containing Mo-V-X-O_x bronzes: a structural alternative to Mo_5O_{14} bronzes

In the second part of the study it was attempted to synthesize bronze-type structures in the compositional range of Keggin type heteropolyacids like Cs-P-Mo-V-X-O based on the synthetic recipe developed by Hibst et al. [8]. The synthetic recipe in the original recipe by Hibst was used to synthesize the bronzes, which were then impregnated with aqueous solutions of H_3PO_4 following an incipient wetness procedure. As mentioned above heteropolyacids are currently the only satisfying catalytic system and the industrial benchmark for the selective oxidation of methacrolein to methacrylic acid. Indeed, it was possible to prepare new bronze-type compounds based on Cs-Mo-V-X-O type bronzes, which are isostructral with $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ and the well known Mo-V-Nb-Te i-phase over a wide compositional range. Especially the bronze-type systems Cs-Mo-V-Nb-O, Cs-Mo-V-Se-O, Cs-Mo-V-Nb-Zr-O, Cs-Mo-V-Sb-O and Cs-Mo-V-Bi-O showed interesting performance data in the target reaction. Again in our study the structural integrity of the samples was a core design parameter. The elemental compositions were varied, along the lines of isostructural compounds, using the identity and amount of the substituted element as variable in the design. For a number of lead compositions ternary designs were taken as an experimental basis.

In Fig. 3(a) and (b) the performance of a pure Cs-containing bronze is compared with a P-doped bronze structure. It is clearly visible that doping with low levels of phosphorous, leads to a major improvement in performance of the catalyst candidate. Maximum selectivities up to 90% at approximately 40% conversion of methacrolein could also be obtained for catalysts of the composition $Cs_{0,5}Mo_{3,83}V_{1,17}Bi_{0,06}O_{14}P_{0,06}$ (39% C, 87% S, 2% methacrolein, 4% H_2O, 9% O_2, 2000 h^{-1} GHSV), similar values with regard to

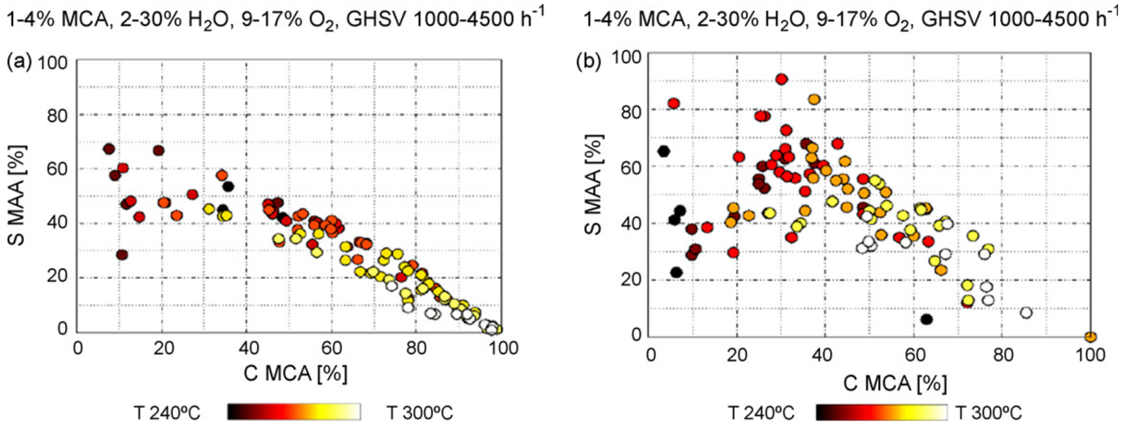

Fig. 3. (a and b) Performance change illustrated in a conversion selectivity plot for a Cs-containing bronze of the composition $Cs_{0,5}Mo_{3,44}V_{1,22}W_{0,39}O_{14}$ (left (a)) and $Cs_{0,5}Mo_{3,44}V_{1,22}W_{0,39}O_{14}P_{0,17}$ (right (b)) in the feed-range of 1–4% methacrolein, 2–30% water, 9–17% oxygen, balance nitrogen, GHSV 1000–4500 h^{-1}. Both catalysts are isostructural with $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ and display no notable ageing behaviour during the test time of 1 week.

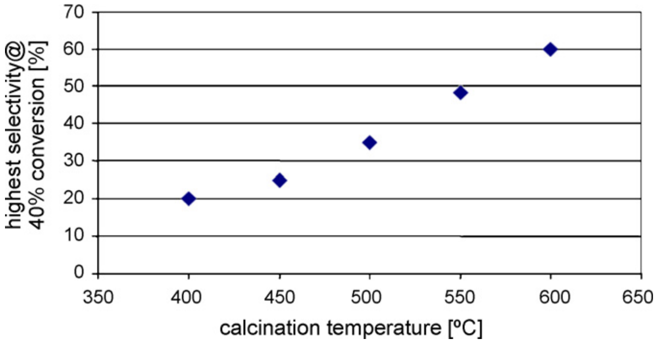

Fig. 4. Influence of the calcination temperature of the bronze-type sample $Cs_{0,5}Mo_{3,72}V_{1,22}Se_{0,05}O_{14}P_{0,17}$ on the level of selectivity of methacrolein oxidation to methacrylic acid at a conversion level of 40% for a feed-composition of 2% methacrolein, 4% water, 15% oxygen, balance nitrogen, GHSV 1500 h^{-1}. An increase in calcination temperature is also accompanied with increased crystallinity of the catalyst sample.

conversion and selectivity under the feed conditions indicated were obtained for bronzes containing W, Nb, and Se. Unfortunately, these high values for the selectivity to methacrylic acid are not visible at conversions higher than 40%. Nevertheless, the improvement of the catalytic properties which renders the materials industrially interesting by doping the phase-pure Cs-containing bronze structures with phosphorous is clearly visible without compromising the structural integrity of the material. It is even more important that these materials are long term stable and not susceptible to the same degradation mechanisms as the Cs/P-doped Mo_5O_{14}-type bronzes.

From the X-ray diffractometric analysis of the samples no heteropolyacid-formation could be observed prior or post the catalytic test if the P-content in relation to the metal content (excluding Cs) was kept at a ratio of the stochiometric formula Me/P of 18–30. This range is also the optimum range with regard to the catalytic performance for maximum yields and selectivities to the target product. If the P-content is raised to a higher level in the range of Me/P of 10–15, samples would still display pure i-phase diffractograms prior to the catalytic test, samples after the catalytic test would display diffractograms indicating the presence of heteropolyacids and nanocrystalline Mo_5O_{14}-bronze-type structures.

Another essential factor for obtaining high selectivities to the target product is the degree of cystallinity of the bronze-type samples. Generally speaking a higher calcination temperature will deliver a sample of higher crystallinity, visible by diffraction lines of lower width at half height in the powder diffractogram. In Fig. 4 the final calcination temperature of the catalyst sample $Cs_{0,5}Mo_{3,72}V_{1,22}Se_{0,05}O_{14}P_{0,17}$ was varied in the range of 400–600 °C prior to impregnation with phosphorous and exposure to the catalytic test. It can clearly be seen that the impact on the selectivity to methacrylic acid is dependent on the calcination temperature, along with higher calcination temperatures, a reduction in the width of peaks in the diffractogram and higher peak intensities were observed.

In order to achieve a better understanding of the interaction of the organic substrate with the material, a comparative test series with exchange of methacrolein against acrolein oxidation was undertaken. There are two reasons behind using a different substrate for the oxidation reaction. First, as Hibst et al. have illustrated [8] Cs-containing bronzes of the type $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ can be regarded as highly crystalline derivatives of the nanocrystalline Mo_5O_{14}-bronze-type structures, which are used on an industrial basis for the oxidation of acrolein to acrylic acid. The exchange of the organic substrate can give insight to how the highly crystalline Cs-containing bronzes $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ react to the C3-substrate acrolein in comparison to the nanocrystalline Mo_5O_{14}-bronze. The second question that light can be shed on is the role of potentially undetected fractions by X-ray diffraction of heteropolyacids on the $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ type bronzes post-doping with phosphorous. In Fig. 5(a) and (b) the difference with regard to the response to the substrates acrolein and methacrolein is illustrated for the sample $Cs_{0,5}Mo_{3,55}V_{0,28}Zr_{0,72}Nb_{0,49}O_{14}P_{0,28}$. It can be clearly seen that the dependence on the organic substrate with regard to activity and selectivity is tremendous. Acrolein is by far converted at a much higher rate and with much higher selectivity to the corresponding unsaturated acid than methacrolein. The comparison of the performance of these samples with regard to the two different feed molecules provokes the question as to what the generic differences in oxidation of methacrolein and acrolein and whether general difficulties of in methacrolein oxidation arise from these differences with regard to the molecular structure.

6. Computational study of the substrate reactivity

In order to compare the reactivity of methacrolein with that of acrolein substrate a supplementary computational study utilizing quantum chemical methods was performed [36]. In terms of reaction energies, our calculations showed, that according to our

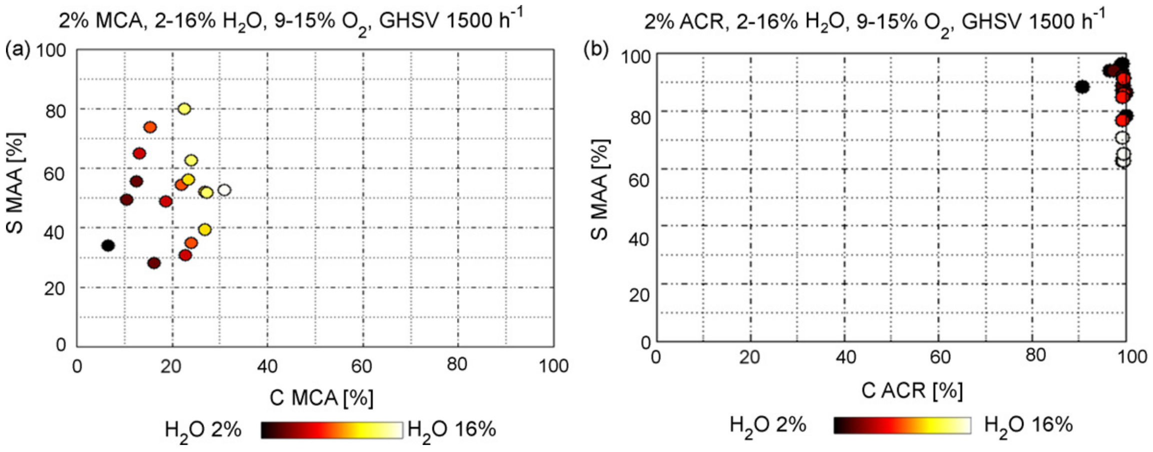

Fig. 5. (a and b) Performance difference for the sample $Cs_{0,5}Mo_{3,55}V_{0,28}Zr_{0,72}Nb_{0,49}O_{14}P_{0,28}$ in the oxidation of methacrolien to methacrylic acid (left (a)) at 300 °C and in the oxidation of acrolein to acrylic acid at 290 °C (right (b)).

Table 2

R-CHO + $0.5O_2$ → R-COOH (ΔG (values for ΔE without zero point energy correction are given in parentheses)) calculated with the B3LYP density functional as implemented in GAMESS [37] and a series of correlation consistent basis sets [38] to estimate the basis set error

	cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ
Acrolein	−193.1 (−248.7)	−197.1 (−252.7)	−198.7 (−254.3)	−198.8 (−254.4)
Methacrolein	−192.4 (−247.8)	−194.5 (−249.9)	−196.3 (−251.8)	−195.8 (−251.3)

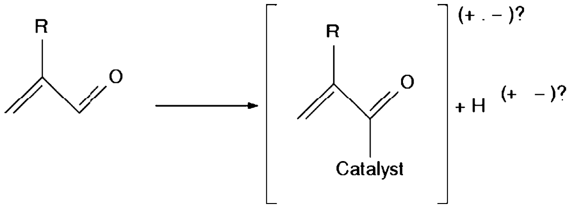

Fig. 6. Schematic drawing of the reaction scheme for the H-activation step.

Table 3

Energies for hypothetical H-abstraction reactions relative to the analogue reaction of acrolein (negative numbers = the reaction for methacrolein is more favourable than the corresponding reaction for acrolein)

	Anion ($R^- + H^+$)	Radical ($R^\bullet + H^\bullet$)	Cation ($R^+ + H^-$)
Methacrolein (carbonyl H)	−6.7	12.4	−23.8
Methacrolein (methyl H)	−87.9	1.5	134.9

Calculations were performed at B3LYP/aug-cc-pVTZ level.

calculations [36], both substrates are oxidized in an exothermic reaction with almost identical reaction energies differing only by 2 kJ/mol (see Table 2). More impact can be expected from the role the additional methyl group in methacrolein can play (see Fig. 6) in potential side reactions (i.e. decreasing the yield of the desired product). For numeric results of these calculations see Table 3. A graphical representation is shown in Fig. 7. Accordingly, the carbonyl H-abstraction step in methacrolein is always quite similar to the result found for acrolein. H abstraction from the methyl group on the other hand, strongly depends on the electron count in the system. Our computational findings give hints to some desired properties of a potential catalytic system of methacrolein oxidation. To suppress methyl H-activation, the system should operate in the hydride abstraction regime (i.e. having a high Lewis acidity) rather than supporting a radical like or proton abstraction type reaction pathway. Apparently heteropolyacids are superior with regard to this property of hydride abstraction when compared to Cs/P-doped nanocrystalline Mo_5O_{14}-bronze and P-doped $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ type bronzes. This goes very well along with the finding that the latter two materials classes are superior candidate materials in acrolein oxidation.

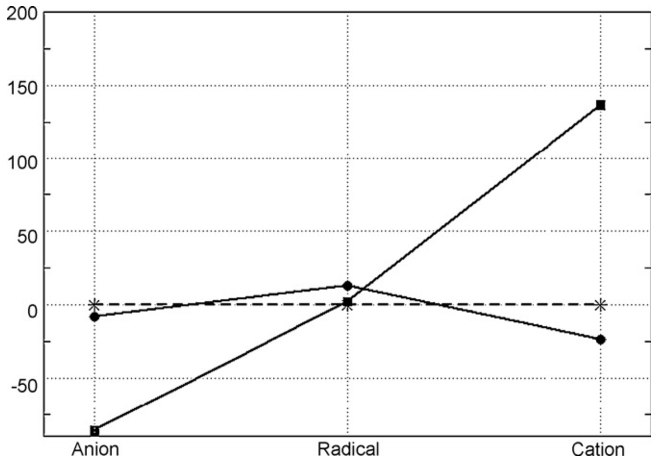

Fig. 7. Energies for H-abstraction ((*) acrolein, set to 0.0 kJ/mol, (●) methacrolein, carbonyl H, (■) methacrolein, methyl H). Due to charge transfer from/to a transition metal center, an actual catalytic system is situated between the extreme points. This is indicated by the interpolating lines.

7. Conclusions

In the studies included in this paper we tried to illustrate that both the retrospective hit deconvolution of complex lead compounds and the compositional derivatisation of iso-structural compounds can be helpful tools for uncovering structure-property relationships. For the case study of the retrospective deconvolution the catalytic functions of the complex hit could be assigned to more simple mixed metal oxides. For the successful oxidation of cyclohexane and benzene to muconitrile, Mo-Sb-O_x, Mo-Sb-Ti-O_x and Mo-Sb-V-Ti-O_x bronze-type oxides of partially amorphous character could be identified as most simple lead compounds.

For the case study compositional derivatisation for the target structures heteropolyacid, Cs/P-doped nanocrystalline Mo_5O_{14}-bronze and P-doped $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ type bronzes the most useful elemental was a straightforward exercise. Here the structural family of Mo_5O_{14}-type bronzes could successfully be excluded as useful candidates due to lack of stability under reaction conditions. The derivatisation of the alternative family of P-doped $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ type bronzes lead straight to a range of interesting elemental compositions and a handful of useful doping elements which could be included in the structure. The comparative study with acrolein oxidation on P-doped $Cs_{0,5}[Nb_{2,5}W_{2,5}O_{14}]$ type bronzes revealed their superior performance for the C3-substrate. Our computational findings to compare reactivities of acrolein and methacrolein indicate that the pronounced differences for the three materials classes derive from the fact that only for heteropolyacids a preference for hydride abstraction in the absence of methyl activation occurs.

References

[1] D. Wolf, O. Buyevskaya, M. Baerns, Appl. Catal. 200 (2000) 63.
[2] Y. Sun, B.C. Chan, R. Ramnarayanan, W.M. Leventry, T.E. Mallouk, S.R. Bare, R.R. Willis, J. Comb. Chem. 4 (2002) 569.
[3] T. Johann, A. Brenner, M. Schwickardi, O. Busch, F. Marlow, S. Schunk, F. Schüth, Catal. Today 81 (2003) 449.
[4] J. Klein, O. Laus, J.M. Newsam, A. Strasser, A. Sundermann, U. Vietze, T. Zech, S.A. Schunk, Petrol. Chem. Division Preprints 47 (2002) 254.
[5] J. Klein, T. Zech, J.M. Newsam, S.A. Schunk, Appl. Catal. A: Gen. 254 (2003) 121.
[6] S.A. Schunk, A. Haas, J. King, J. Klein, Conference Proceedings of AIChE Spring National Meeting, Altanta, USA, 2005.
[7] S.A. Schunk, A. Sundermann, H. Hibst, Comb. Chem. High Throughp. Screen. 10 (2007) 51.
[8] H. Hibst, F. Rosowski, G. Cox, Catal. Today 117 (2006) 234.
[9] S.A. Schunk, H. Hibst, in: Proceedings of the 5th WCOC, 2005, p. 366.
[10] T. Zech, CHEManager 5 (2007).
[11] I. Wachs, Catal. Today 100 (2005) 79.
[12] I. Wachs, Smart Combinatorial Operando Spectroscopic Catalytic Reactor System, Talk given at 2006 Aiche Meeting.
[13] N.K. Terret, Combinatorial Chemistry, Oxford University Press, Oxford, 1998.
[14] P. Kolb, D. Demuth, J.M. Newsam, M.A. Smith, A. Sundermann, S.A. Schunk, S. Bettonville, J. Breulet, P. Francois, Macromol. Rapid Commun. 25 (2004) 280.
[15] L. Baumes, D. Farrusseng, C. Klanner, C. Mirodatos, F. Schüth, QSAR Comb. Sci. 22 (2003) 729.
[16] C. Klanner, D. Farrusseng, L. Baumes, C. Mriodatos, F. Schüth, Angew. Chem. Int. Ed. 43 (2004) 5347.

[17] S.A. Schunk, D. Demuth, A. Cross, O. Gerlach, A. Haas, J. Klein, J.M. Newsam, A. Sundermann, W. Stichert, W. Strehlau, U. Vietze, T. Zech, High-Throughput Screening in Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2004.
[18] S.A. Schunk, O. Busch, D.-G. Demuth, O. Gerlach, A. Haas, J. Klein, T. Zech, Surface and Nanomolecular Catalysis, CRC Taylor and Francis, New York, 2006.
[19] M. Saupe, R. Födisch, A. Sundermann, S.A. Schunk, K.-E. Finger, QSAR Comb. Sci. 24 (2005) 66.
[20] R.K. Grasselli, Catal. Today 49 (1999) 141–153.
[21] G. Centi, S. Perantoner, F. Trfiro, Appl. Catal. A: Gen. 136 (1996) 205–229.
[22] R.K. Grasselli, D.D. Surech, K. Knox, J. Catal. 18 (1997) 356–364.
[23] A. Anderson, J. Catal. 100 (1986) 414–428.
[24] M. Hatano, K. Kayou, Eur. Pat. 318 295, 1988.
[25] T. Ushikobo, K. Oshima, A. Kayou, M. Vaarkamp, M. Hatano, J. Catal. 112 (1997) 479.
[26] M. Aouine, J.L. Dubois, J.M.M. Millet, Chem. Commun. (2001) 1180.
[27] M. Lundberg, M. Sundberg, Ultramicroscopy 52 (1993) 429.
[28] S. Berndt, D. Herein, F. Zemlin, E. Beckmann, G. Weinberg, J. Schütze, G. Mestl, R. Schlögl, Ber. Bunsenges. Phys. Chem. 102 (1998) 763.
[29] F.C. Jentoft, S. Klokishner, J. Kröhnert, J. Melsheimer, T. Ressler, O. Timpe, J. Wienold, R. Schlögl, Appl. Catal. 256 (2003) 291.
[30] M. Sultan, S. Paul, M. Fournier, D. Vanhove, Appl. Catal. 259 (2004) 141.
[31] H. Vogel, R. Böhling, H. Hibst, Catal. Lett. 62 (1999) 71.
[32] G. Mestl, Ch. Linsmeier, R. Gottschall, M. Dieterle, J. Find, D. Herein, J. Jäger, Y. Uchida, R. Schlögl, J. Mol. Catal. A: Chem. 162 (2000) 455.
[33] M. Dieterle, G. Mestl, J. Jäger, Y. Uchida, H. Hibst, R. Schlögl, J. Mole. Catal. A: Chem. 174 (2001) 169.
[34] J.C. Petzold, H. Böhnke, J.W. Gaube, H. Hibst, in: Proceedings of the 4th WCOC, Volume II, 2001, p. 127.
[35] J.B. Wagner, D.S. Su, S.A. Schunk, H. Hibst, J. Petzoldt, R. Schlögl, J. Catal. 224 (2004) 1–28.
[36] All structures were completely optimized at the given level of theory. The stationary points were verified as local minima on the energy hypersurface by a numerical calculation of the Hessian matrix. Zero point energy corrections and estimated contributions of rotational and vibrational degrees of freedom to the partition function were estimated within the static rotor/harmonic oszillator approximation at cc-pVDZ/B3LYP level of theory. The calculations were carried out on an Intel T7600 dual core CPU in parallel mode on a linux operated machine.
[37] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347–1363.
[38] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.