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Pitfalls in heterogeneous thermal, electro- and photocatalysis

Ulrike I. Kramm,[a] Roland Marschall,[b] and Marcus Rose*[c]

Abstract: Catalysis is the key technology of our well-established chemical industry. Also, it is considered one of the most interdisciplinary and fundamental sciences with enormous potential for future research and development. Hence, a high number of manuscripts dealing with all different aspects of catalysis topics are published each day. Unfortunately, certain pitfalls that became quite common by now are found in submitted manuscripts and sometimes (and too often) even pass the peer reviewing process. This is especially a problem at the forefront of catalysis research at which novel catalysts are developed and novel reaction systems are described from scratch. Hence, in this concept paper common pitfalls in carrying out and reporting catalytic experiments ranging from heterogeneous thermal catalysis to photo- and electrocatalysis are briefly summarized and solutions how to avoid these issues are presented.

Introduction

Catalysis is a key technology for chemical production and nowadays one of the most interdisciplinary research fields. R&D activities range from fundamental understanding of catalytic reactions, novel catalyst materials and reaction systems to versatile aspects related to reaction engineering. According to Web of Science (August 30nd 2018) approximately 4.000 manuscripts on the topic “catalysis” are published each month. Overall, a high quality of research is shown. However, there are several pitfalls that unfortunately occur too often and that also get by the peer-reviewing process on a regular basis. This not only includes details of experimental procedures that are not reported in sufficient detail to enable reproducibility but also more severe aspects in catalyst testing especially regarding mass and heat transfer limitations, stability tests, benchmarking, and the three key parameters describing the catalyst performance: activity, selectivity and stability. With regard to novel catalytic materials the most important common pitfalls were summarized recently by Schüth et al.[1] while the characterization of catalyst stability, recyclability and the “lifetime” in general was summarized briefly by Scott.[2] With a special focus on metal-organic frameworks (MOF) and porous polymers as a comprehensive new class of solid catalysts recent review papers of Gascon et al.[3] and Rose[4] addressed the most common issues in individual chapters, respectively.

Hence, in this contribution we summarize the most common pitfalls. Most of them can be considered rather general and being important for all fields in catalyst testing ranging from conventional heterogeneous thermal catalysis towards photo- and electrocatalysis. The latter two types of catalysis attracted increasing attention in the past years. As they have special requirements especially regarding the energy transfer (either by UV/Vis radiation or by applying a potential and use of a direct electron transfer) the most important pitfalls are addressed in separate chapters.

General considerations and thermal heterogeneous catalysis

Heterogeneous thermal catalysis covers a wide field of research with enormous potential for future innovative technologies. Not only new catalytic systems are exploited to deal with the transition from fossil to renewable resources and energy, but also catalyst development in close proximity to materials chemistry has seen major advances in the recent past. Hence, often newly developed catalysts and catalytic systems are experimentally investigated on a rather small lab scale. Of course, publications that report these initial results cannot address all aspects for future scale-up and technological implementation. Nevertheless, to avoid misconceptions and incorrect interpretation of data the following aspects have to be taken into account. A detailed description on laboratory testing of solid catalysts was summarized earlier by Kapteijn et al. in the *Handbook of Heterogenous Catalysis*.[5]

Mass transfer limitations

First of all, when applying solid catalysts always multiphasic reaction systems are present, as at least one fluid phase is involved being a gas or a liquid phase together with a solid catalyst. Often the reaction involves even more fluid phases, adding at least one more phase boundary that can play a key role in the catalytic performance. Hence, mass and heat transfer at all interfaces of the solid and the fluid phases require utmost attention. Fortunately, heat transfer limitations can often be neglected in small lab-scale catalytic reactors as they typically can be run close to ideal isothermal conditions, at least at rather low reaction temperatures and with a rather small reaction enthalpy, independent from the reaction being exothermic or endothermic. Nevertheless, this has to be verified by control of the temperature of the reaction mixture or in case of fixed bed reactors by proper temperature measurement at several points in the axial direction of the catalyst bed. Depending on the

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dimensions of the reactor also radial temperature gradients have to be taken into account and ideally eliminated. This is possible by either decreasing the reactant concentration or the catalysts amount by dilution with inert material.

Mass transfer limitations pose a more serious issue that is often encountered but neglected in catalytic experiments. Hence, when catalysts are compared regarding their activity and productivity often the overall effective performance of the catalyst or the whole reaction system is measured, i.e., the macrokinetics. However, when catalysts are compared they might exhibit a similar performance in case mass transfer limitations occur, although the intrinsic catalytic properties, i.e., the microkinetics, might be significantly different.

How to identify mass transfer limitations? In case of two fluid phases, e.g., a liquid and a gas phase, the transport of the gas as a reactant can limit the performance of the catalyst when the gas solubility is comparably low and mass transfer from the gas into the liquid phase too slow compared to the reaction kinetics. This can be determined experimentally by varying the amount of catalyst under otherwise constant reaction parameters (Figure 1a). In case the reaction is limited by mass transfer at this phase boundary, the reaction rate remains constant. In case no limitations occur, the rate varies and directly correlates to the applied catalyst amount.

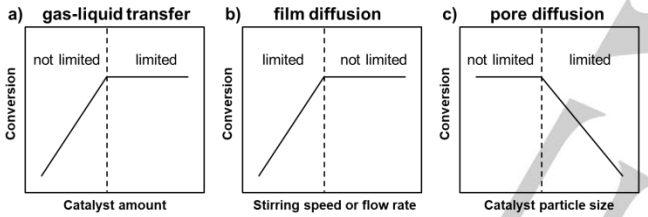


Figure 1. Schematic diagrams showing the influence of the reaction parameters on typical mass transfer limitations that might occur during catalyst testing.

The further phase boundaries are directly related to solid catalyst particles where the following steps are essential and determine the course of the reaction and possible limitations. The substrates are initially subjected to convective mass transfer in the bulk fluid phase. In close proximity to the catalysts external surface a film is formed that is characterized by a laminar flow that results in a concentration gradient and hence, mass transfer limited by diffusion through the film layer. The thickness of the film is majorly determined by the flow/mixing regime of the bulk phase that can range from laminar to a highly turbulent behavior and is typically characterized by the dimensionless *Reynolds* number. It can be influenced by the stirring speed in a stirred tank reactor or the flow velocity in a fixed-bed tube reactor. In electrocatalysis, the rotating disc electrode (RDE) technique uses the application of a laminar flow to decrease the diffusion layer thickness. In general, the mass transfer limitation by film diffusion can be easily identified by varying the stirring speed or the flow velocity in batch or continuous testing, respectively (Figure 1b). If the reaction rate varies with a more vigorous mixing obviously the thickness of the film plays a crucial role. If the activity does not depend on film diffusion it is independent from the stirring speed/flow velocity.

The next and very often most limiting mass transfer step is the diffusion in the pore system, especially in case of catalysts with an intrinsic porosity and rather small micro- (<2 nm) and mesopores (2-50 nm). In this case the mass transfer directly depends on the pore diameter and pore length. While the former can typically not be varied very well, the pore length and hence, the maximum pathways the substrates have to be transported to the inner catalytic active sites directly correlate with the particle size. Hence, by fractioning the catalyst particles according to their particle size and individually testing them in the catalytic reaction pore diffusion limitations can be easily accessed (Figure 1c). In case the reaction rate decreases with increasing particle size, the reaction is definitely limited by mass transfer. In the absence of limitations the activity is independent of the particle size. In case particle size variation is challenging or not possible, e.g., for core shell catalysts, the occurrence of pore diffusion limitation should be at least estimated using the Weisz-Prater criterion based on the characterization of physical and textural properties of the catalyst.[6]

Transient behavior

When catalysts are tested in continuously operated reactors they often show a transient behavior for a certain amount of time before they reach dynamic steady state conditions (quasi-steady state). Two different behaviors are observed: Either the initial activity increases or it decreases for a certain time-on-stream until steady state conditions are reached. This can have various reasons. The most common one in heterogeneous catalysis is probably the *in situ*-formation of the actual catalytically active species, e.g., when a metal oxide is first reduced into the main active surface species or surface restructuring occurs. Furthermore, the mass transfer and desorption of the products might play a significant role. Initially, the pore system is empty and mass transfer less or even not limited while after reaching steady state conditions the mass transfer of the substrates and the product might be significantly limited, and hence, also rate limiting. Lastly, especially when nanoporous catalysts are applied, confinement effects can occur, that might result in different concentrations in the pore system and in the bulk fluid phase. This behavior has, however, been studied only very seldom.

Wettability

For liquid phase reactions the wettability of the surface and especially of the nanosized pores is an often neglected parameter with a strong impact on the catalytic performance, as previously discussed in detail by Wang and Xiao.[7] On the one hand, this is motivated by catalytic materials with surface properties that can range from super-hydrophobic to super-hydrophilic and that ideally can be tailored to a certain extend. On the other hand, especially polar molecules such as water tend to show unusual chemical and physical properties in confined nano-spaces as was shown, e.g., for zeolites, MOFs

and carbon-based materials.[8] Hence, experimentally in the liquid phase not well accessible, there are mainly two approaches to unravel an influence of the wettability independent from all other reaction parameters: 1) reactions that occur in the liquid phase with no reactants from a gas phase involved should be majorly independent from the reaction pressure. Hence, varying the pressure with an inert gas would exhibit a varying catalytic performance as also smaller pores are filled and more catalytic sites get in contact with the reaction solution. This would be expected especially in the case when the contact angle of the liquid phase and the solid surface are significantly above 90 ° and hence, pore filling directly depends on the pressure as can be calculated from the *Washburn* equation. In the opposite case, with a high wettability the pore filling would occur by capillary forces. In this case a pressure dependence is less likely. 2) In case the reaction also depends on a component from the gas phase and hence, is also pressure depended, a qualitative statement on the wettability might only be feasible if inert solvent mixtures are applied with varying polarity. E.g., adding defined amounts of a less polar alcohol to an aqueous solution can increase wettability. Trends in the activity can point towards a wettability-dependence.

Key performance indicators: activity and selectivity

The most important measure for the catalyst performance is often acclaimed to be the activity. This holds true only to a certain extent, as for every application a lower activity can simply be compensated by using more catalyst. Much more important are thus, the selectivity and stability of catalysts. They determine the amount of by-products formed and the maximum time-on-stream a catalyst can be applied.

The catalyst activity is typically characterized by the measureable reaction rate, i.e., the amount converted per unit of time, e.g. mol h^{-1}. When solid catalysts are applied it is useful to refer the rate to either one of the following parameters: mass of catalyst (e.g. mol h^{-1} g^{-1}, most often used and referred to as *productivity*, sometimes the amount of product instead of conversion), volume of the catalyst (bed) (e.g. mol h^{-1} L^{-1}), or the surface area (e.g. mol h^{-1} m^{-2}). In case of supported metal catalysts the specific activity can also refer to the mass of metal instead of the overall catalyst mass. Industrially most often the integral specific activity is used and given in $kg_{Product}$ $kg_{Catalyst}^{-1}$ h^{-1}. Using the available surface area is often problematic and prone to severe errors as it can change dramatically under reaction conditions and by far not all surface sites are catalytically active.

In homogenous as well as in biocatalysis catalysis the amount of catalytic active species is typically exactly known. Hence, the catalyst performance can be referred to the amount catalytic active site, i.e., a rate measured in mol h^{-1} mol^{-1}. This is typically referred to as *turn over frequency* (TOF). The total amount of turnovers until deactivation occurs (mol mol^{-1}) is called *turn over number* (TON). In literature often slightly different definitions are used. Kozuch and Martin reported a details discussion on that topic and suggestions for “best practice”.[9]

To provide TOF and TON when working with solid catalysts is a challenging task, as the amount of active sites under reaction conditions is basically not accessible. Of course, e.g., in case of supported metals, chemisorption methods can be applied to estimate the amount of available sites. However, under the specific reaction conditions in the presence of various species in the reaction mixture as well as surface intermediates a reliable determination seems not possible. Hence, such data should be handled carefully. Electrocatalysis might be one exception in this case, as determination of active surface area is possible even under reaction conditions. Still some limitations apply that are addressed in the electrocatalysis section.

Another issue with TOF and TON, but also with determined reaction rates of solid catalysts is the fact that they depend on reaction parameters temperature and pressure (at least in case a gaseous species is involved), and most importantly on the concentration range and conversion level. Hence, for a reliable comparison of different catalysts the characteristic values should be determined under identical conditions. All reaction parameters have to be reported for reasons of comparability. Furthermore, reaction rates and TOF have to be determined at the beginning of reactions at low conversion levels, in a range, in which they can be assumed to be rather constant.

Although stability issues are discussed in the next chapter, issues related to reporting TON as a measure of stability are briefly discussed here. As mentioned before, TON are a measure of the overall achievable turnovers of the active sites until deactivation. However, in literature way too often TON are reported at an arbitrary reaction time far away from deactivation. Unfortunately, this is too often used to compare different catalysts and hence, conveys a wrong message unintentionally or on purpose.

As mentioned above, the selectivity is the major performance criterion, as only a very minor amount of reactions do not yield by-products. Hence, comparison of selectivity can be found in most catalysis papers. In general their calculation is carried out correctly according to text book methods. However, comparison with reference catalysts and previously reported literature results often contains a major issue: the selectivity depends on the conversion of every reaction.

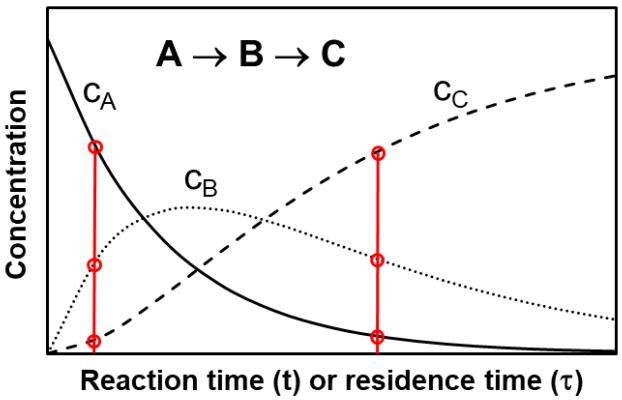


Figure 2. Schematic concentration-time profile that illustrates the importance of comparing selectivity at equal levels of conversion.

Hence, the comparison of selectivity at different levels of conversion is prone to misinterpretation of experimental results as performance criteria of different catalysts that are not reliable. Figure 2 shows schematically a concentration time profile of two subsequent non-reversible reactions. When the selectivity for the intermediate B and the final product C are compared at different conversion levels (red lines) major differences are found. Hence, when comparing selectivity data of different catalysts, although the reaction parameters might be equal and even the reaction or residence time is the same, with a varying activity conversion levels can vary significantly. Therefore, the selectivity cannot be compared at all. It has to be assured that the conversion levels under these conditions are equal for a reliable comparison. It is also of utmost importance to close the mass balance by confidential analytical techniques to reliably determine selectivities.

Another issue arises for reactions with more than one reactant. In this case the selectivity for the formation of the product can be calculated with respect to each of the reactant individually and thus, also possess significantly different values. Hence, in case of multiple reactants all of the product selectivities should be calculated and compared.

Stability, deactivation and leaching

Regarding application-related catalyst development the stability is one of the major measures to characterize novel materials. On the one hand, “stability” can simply refer to the mechanical stability, e.g., in fluidized bed (gas-solid) or suspension (liquid solid) reactors, less pronounced in fixed bed reactors filled with catalyst particles or shaped bodies. By a permanent flow of the reaction mixture attrition is a major issue and has to be addressed sufficiently. However, more often “stability” refers to the long term performance of novel catalysts regarding deactivation. Here, two different lifetimes have to be considered: operating time between regenerations (as in the case of, e.g., FCC catalysts which are regenerated on a time scale of seconds to minutes) and total life time until the catalyst has to be replaced in the reactor by a fresh charge.

In this context, “long term” is apparently considered by research-oriented vs. application-oriented scientists on very different time scales. While industrial applications typically refer to time-on-stream of several months up to several years, the scientific community in the development of novel catalysts uses the term “long term” rather on a basis of hours to days maximum. This is rather misleading. Of course, lab research on novel materials often does not have the capabilities and resources for in depth-investigations of the actual long term-stability. With that in mind, manuscripts reporting reliable long-term data should receive greater attention and appreciation.

One important fact to keep in mind is that the long term-performance of a catalyst depends significantly on the process conditions. Especially the composition of the feed stream often differs significantly in the lab testing setup and the industrial plant. Hence, a reliable evaluation can only be carried out when all the real process conditions can be experimentally realized.

Nevertheless, of course innovative approaches to novel catalysts are often not tested in reactor setups in that great detail. Often, even only batch reactors are applied. In this case the claim of stability of a catalyst is derived from recycling experiments. In this case all necessary information has to be reported, especially on the treatment of the catalyst in between the cycles. Washing, drying, calcination and so on can have a significant impact on the performance in subsequent cycles. Basically all typical reasons for deactivation, i.e., depositions/coking, poisoning, sintering or leaching into the fluid phase, can occur during the reaction as well as during the treatment in between cycles. Their mechanisms and consequences should be experimentally investigated when being observed. In this context it is also of utmost importance to consider the fact that in case of newly developed catalysts often a comprehensive characterization of the as synthesized material is reported while the catalytic experiments are poorly described. This should, however, be in the focus: the initial activity, changes over time and issues such as a closed mass balance especially for new catalytic reaction systems with high complexity, e.g., in biomass conversion. For the latter also more difficult to find by-products should be pursued to be identified although they might be much more challenging.

The major pitfall in reporting stability and long term-performance of catalysts is to carry out the reaction at full or equilibrium conditions. When a recycling in batch operation is conducted and each cycle the reaction mixture reaches full conversion, no reliable conclusion on catalyst performance can be drawn (Figure 3a). The problem is that the conversion is simply limited by the availability of substrate. If more would be present, more could be converted in the same time. In other words, the amount of catalyst is too high or the reaction time too long. Therefore, a deactivation could not be observed and will only then become visible in the conversion when enough cycles were run and the activity has decreases so significantly, that conversions below 100% can be observed (Figure 3a). Often, that is not reported and a high stability and recyclability is claimed. The same artefact is found for continuous testing. In this case the conversion is reported vs. time on stream. Also, here a decrease could not be observed due to the “excess activity” (Figure 3b).

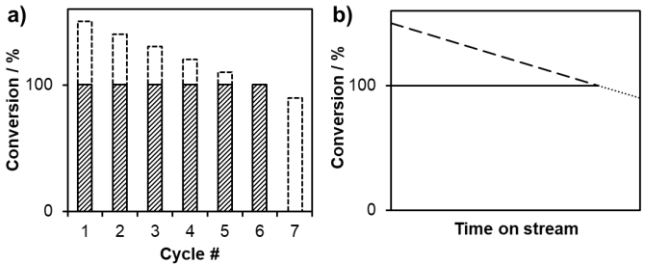


Figure 3. Schematic diagrams that illustrate why comparing catalyst performance by recyclability in batch (a) and in continuous (b) operation at maximum conversion or yield provides non-reliable and even wrong information. The full lines (b) and columns (a) show the typically reported data. Dashed lines/columns show the reality in case the substrate-to-catalyst ratio would be higher and changes could be directly observed.

What can be done to avoid that? Recycling in batch reactions or continuous experiments have to be carried out at conversion levels significantly (at least 10-20 % and considering the overall experimental error) below full conversion, or, in case of reactions limited by a thermodynamic equilibrium, below the maximum conversion that is possible. This can be achieved by decreasing the amount of catalyst or *vice versa* increasing the amount of substrate. Alternatively, shorter reaction or residence times can be applied. Also, the reaction temperature can be reduced to slow down the reaction. Which way to go is mainly determined by the key reaction parameters, that should be as close to the real process conditions as possible. Overall, it would be beneficial to report rather concentration time profiles instead of individual single activity/selectivity points.

Besides the stability and long term performance the leaching of active species is also crucial and should be reported. Ideally, complementary methods are applied. Of course, the leaching of, e.g., a supported metal species can be characterized by measuring trace amounts of the metal in the reaction solutions. Complementary, also the reduced amount of metal on the catalyst support can be determined. Although in this case small changes can only be determined with a much lower reliability. Of great importance are filtration or hot filtration experiments, which are of course hard to perform at higher temperatures, especially above 100 °C. It is assumed, that no active species leaches from the solid catalyst. Hence, the solid material should be filtered off, especially in batch liquid phase reactions, and the reaction should be continued under identical conditions. Ideally, no further conversion is observed by leached active species. But also in this case, there has to be sufficient substrate left in the solution to enable a further reaction. Otherwise, the same limitations would occur as mentioned above. If the catalyst is operated continuously the active metal should be characterized comprehensively after operation.

An alternative option to exclude leaching of metal-species from a solid support is the three-phase test. Therein, a reaction is carried out with one substrate bound to another solid support, such as a polymeric resin. In case leaching occurs a reaction takes place at the surface-bound substrate of the second solid. In case no leaching occurs no reaction is observed. A paper nicely demonstrating the principle of hot filtration, the three-phase test as well as Hg poisoning as complementary methods to prove the formation of metal nanoparticles as active species on a support was reported by Park et al.[10]

Reproducibility and benchmarking

A major issue in reporting catalytic results is the reproducibility and reliability of results. On a regular basis results are reported that seem to be derived from single experiments without any assessment of the reliability. Hence, it is of great importance to report values such as a standard deviation for the reported experiments. Last but not least, to provide the reader with information about the importance of observed and reported trends. However, sometimes very minor standard deviations are reported that seem to be great regarding the experimental procedure. On a closer look, however, that is only the standard deviation of, e.g., the analytical technique used for quantification such as gas chromatography. This, however, neglects the influence of the overall experimental procedure with all the versatile sources for random errors including even the preparation of catalysts. It should become customary to report such data to increase reliability of catalytic results.

In the past two decades a vast amount of materials innovations resulted in a high number of novel catalyst materials. In many manuscripts that report new catalysts comparison and benchmarking with known catalysts for the same reaction is missing or insufficient. However, to really evaluate the novelty and increase in performance, first of all, a comprehensive comparison to literature data is inevitable. Of course, especially the points mentioned above have to be taken into account when comparing key performance indicators. The most crucial reactions parameters have to be compared. Even more important to literature comparison is the experimental prove of comparability. Hence, depending on the reaction system, typical commercial catalysts or similar literature-known materials have to be tested under identical conditions. This will also help in identifying previously reported work with less reliable data. Despite vigorous peer reviewing this is, unfortunately, published way too often.

Besides benchmark catalyst it could be of interest to test other similar substrates as benchmark reaction. This is more common in homogeneous catalysis, especially to prove the broad applicability of various functional groups on the substrate. In heterogeneous catalysis it is always a question of the major motivation of the work, whether a new catalytic material is developed in general or rather specific for a certain reaction.

Photocatalysis

In heterogeneous photocatalysis, an absorber material is irradiated with light, and when the energy of light is higher than the band gap energy of the used semiconductor absorber, charge carriers inside the material are generated. Those charge carriers (photoexcited electrons and holes), after separation, need to diffuse to the surface of the semiconductor to perform reactions, namely reduction and oxidation reactions. Indeed, many charge carriers recombine during this process, usually at defects, grain boundaries, or at the surface.

An exemplary reaction could be the overall water splitting reaction, the half reactions being reduction of protons with electrons to dihydrogen (H_2) and oxidation of water to dioxygen (O_2). Since many different types of reactions can be performed with photocatalysis, the different occurring issues and pitfalls that are regularly found in literature are discussed as follows.

Pollutant degradation

One of the most popular type of photocatalytic investigations found in literature is the dye degradation reaction. In this case, dyes are used a model pollutants to investigate the oxidative decomposition of organic compounds in waste waters. The reason why dyes such as methylene blue (MB), rhodamine B or others are often used is probably that following the decolorization of a dye upon light irradiation of a semiconductor

suspension is rather easy to perform. The filtrated solution can be easily analyzed with absorption spectroscopy, and samples taken in a constant interval usually show deteriorating absorption spectra of the dyes. In the ISO 10678 norm, MB is used as test pollutant to assess the activity of self-cleaning films.[11]

However, there are some issues that can be found in literature that should be avoided. For example, already in 2014 Choi et al. showed that the decolorization of a dye should not be performed when a visible-light absorbing photocatalyst is investigated.[12] The reason is that in such a case, the absorption of the semiconductors and the dye can overlap, and it is not possible to differentiate whether the dye or the semiconductor absorb the irradiated light. Moreover, it becomes impossible to investigate possible dye sensitization effects. Dye degradation can be used as model reaction when the semiconductor absorption and the dye absorption do not overlap, and the emission spectrum of the used lamp cannot excite the dye.

In many reports, control experiments are presented in order to show no decay in the absorption of dye solutions under irradiation without catalyst. However, in many cases this analysis gives no straight line, but a slight decomposition. In that case, the often performed kinetic analysis is problematic, since in that case photochemical and photocatalytic degradation of the dye occur simultaneously, and thus, influence the kinetics of each other. Simple pseudo-first order kinetics, as usually considered in pollutant degradation reactions, are not valid in that case.[13]

Moreover, the experimentalist has to prove that the adsorption/desorption equilibrium of the model pollutant in the dark has actually been reached before irradiation. This is especially important when using mesostructured photocatalysts. Results for photocatalytic degradation should show that the concentration-related absorption of the model pollutant under dark conditions does not change anymore before starting light irradiation, with at least two data points showing constant absorption (Figure 4).

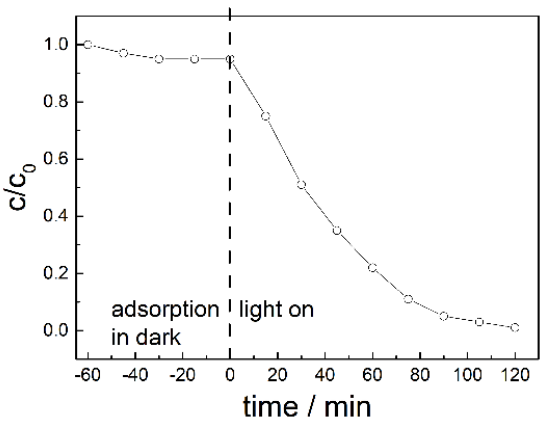


Figure 4. Fictive data indicating ideal control condition in the dark before light irradiation, and first order kinetics (logarithmic decay) degradation curve.

In some cases, e.g. mesoporous semiconductors, that might take hours.[14] Please note that pseudo-first order kinetics analysis for model pollutant degradation are only valid at sufficiently low concentrations when the process is “diffusion-limited”,[15] and when the observed decay is actually logarithmic, not linear.

Nevertheless, in many reports no additional characterization of the reaction besides absorption spectroscopy is performed. However, many dyes lose their color immediately if one functional group is cleaved. Thus, simply following the decolorization of a dye solution as photocatalytic test is not enough. Aim of pollutant degradation is the total mineralization of the compound, the decomposition into water, carbon dioxide and mineral acids. As a result, no residual organic carbon should remain in solution upon total mineralization. This can be controlled with total organic carbon (TOC) analysis, and should always be performed in addition to the absorption experiment, to investigate the degree of mineralization of the photocatalytic reaction. In addition, GC-MS or ESI-MS studies can be performed to analyze the colorless reaction products to understand the decomposition reaction, in order to improve it towards total mineralization.[14]

Hydrogen production & Water splitting

For an economy based on renewable energies, intermitting solar irradiation results in the need to store solar energy on a large scale. In search for clean future energy carriers, solar hydrogen as a solar fuel is often discussed as energy carrier for a fossil fuel-free economy. Photocatalytic hydrogen produced from water splitting is one possible way to generate solar hydrogen.

The term *water splitting* in heterogeneous photocatalysis is only valid for an absorber dispersion in pure water. In case of using a sacrificial agent, either *hydrogen generation* or *oxygen generation* have to be used.[16]

In the last decade, several propositions for the normalization of photocatalytic water splitting reactions have been made. Until today, the most popular way reporting water splitting or hydrogen generation is still in production rates, often in mol h^{-1}, although it is generally accepted that reporting apparent quantum yields or photonic efficiencies is the favorable practice.[17] In some cases, the authors recognize that such rates are still very often also normalized to the amount of photocatalyst, resulting in rates like mol $h^{-1}g^{-1}$. However, it is well-known that the reaction rate of a photocatalytic reaction is in general not proportional to the amount of photocatalyst, since light absorption, scattering and shading in the reactor have to be considered.[18] Rates should only be reported at the optimum amount of photocatalyst,[19] and as steady-state rates shown in a time-dependent rate curve. Moreover, reported rates measured with very low amounts of photocatalyst (1-10 mg L^{-1}) result on the one hand in very large rates when normalized per catalyst mass, suggesting high activities at a first glance. But consequently the average measurement error also increases, and the total amount of products could fall into the error regime of the measurement device. Overall, the probability of reporting too high activities increases, and hence, should be avoided.

Taking the measurement at optimum photocatalyst loading with optimum light absorption for granted, tailored co-catalyst decoration of semiconductors is often performed as a viable strategy to improve charge carrier separation in photocatalytic water splitting,[20] and in photosynthetic reactions to avoid the back reaction.[21] Co-catalyst loadings are often reported in wt.-%, and then different co-catalysts are compared in their effect. As a result, however, the *molar* loading of the co-catalyst on the semiconductor absorber is different, due to the different molar weights of the varying co-catalyst materials. For example, comparing Rh with Pt loading with the same 0.01 wt.-% on a typical absorber (mass = 1 g, same surface area and crystallite size) would result in 0.98 µmol g^{-1} Rh loading, but only half the amount of Pt (0.51 µmol g^{-1}). As a results, the distribution of the cocatalyst and its crystallite size can also vary strongly.

Additionally, loading in wt.-% becomes even more problematic when the same wt.-% of one co-catalyst is loaded on differently mesostructured semiconductors with strongly varying surface area. In such a case, we suggest that co-catalyst loadings should be reported in moles per absolute surface area (e.g. µmol m^{-2}) of the used amount of semiconductor for the photocatalytic reaction.[22] In that case, the effect of different co-catalysts or specific surface areas (when the same co-catalyst material is used) could be compared.

Considering hydrogen production, recently addressed in an excellent editorial by Kamat and Jin,[23] the reaction products of the oxidation reaction with sacrificial electron donors should be analyzed to close the mass balance for scientific clarification. Moreover, in such reactions hydrogen will be generated both *via* direct reductive and indirect oxidative pathways,[16] and even photocurrent doubling can occur.[24] A more detailed control of the oxidation products in photocatalytic hydrogen generation, as in carbon dioxide (CO_2) reduction, is necessary. Obviously, the same is required for the reduction products during sacrificial oxygen generation.

Unfortunately, in some rare cases the authors even found that sacrificial reagents in hydrogen generation were used that were extremely close in composition to the used absorber, making it impossible to clarify possible material degradation (because the sacrificial reagent consisted of compounds that could be possible degradation products of the investigated absorber material), and no oxidation products in general were analyzed. Hence, we strongly recommended to avoid such practice. In general, we also suggest that post-photocatalytic analysis of semiconductor absorber materials becomes a standard in materials research for photocatalysis, including at least surface analysis (physisorption, XPS, residual products/educts by IR, etc.), absorption spectra, and phase analysis (by X-ray diffraction, Raman spectroscopy, etc.) after the photocatalytic reaction.

CO_2 reduction

Heterogeneous photocatalysis can be used to convert CO_2 into carbon-based solar fuels, reducing the amount of this greenhouse gas in the environment. In heterogeneous photocatalytic CO_2 reduction, it can be even more regularly observed that the oxidation products are not fully analyzed. This is especially problematic since the reaction comes, like water splitting, with a large positive shift in Gibbs free energy, and the back reaction towards CO_2 has to be avoided. The oxidation reaction needs to be investigated in detail, since it might be the rate-determining step of the whole reaction. Due to the low solubility of CO_2 in water leading to a bad substrate-photocatalyst contact time, gas-phase CO_2 reduction should be favored, also to investigate reaction products in more detail. Labelling the reaction substrate CO_2, using $^{13}CO_2$ should become standard to prove the origin of the photoproducts, especially since CO_2 reduction products could also arise from carbon impurities (see below). Moreover, the back reaction of the observed carbon-based reaction products has to be controlled. As shown by Mul et al., a photocatalyst active for CO_2 reduction can also oxidize the reaction products, due to thermodynamic reasons (see above).[25] Finally, as pointed out by Strunk and Moustakas, working under high purity conditions to avoid impurities from the reactor and the sample is of utmost importance to improve and tailor better photocatalysts in a knowledge-based fashion.[26]

Electrocatalysis

When catalytic reactions at the interface of an electronic and ionic conductor are investigated electrocatalysis comes into play. The educts of the related reactions are either gaseous or liquid. The catalytic parameters of such catalyst materials can be investigated in either three-electrode setups (intended to focus on microkinetics) or two-electrode arrangement as commonly found in real devices such as fuel cells or electrolysers. Just recently, A.R. Zeradjanin summarized frequent pitfalls in electrochemical energy conversion reactions.[27] Thus, this paragraph should be suggested in addition to that previous work, possibly shining light from another view on similar challenges.

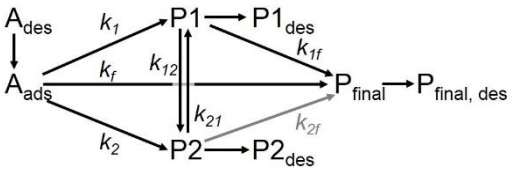
Testing methods

The selection of the applied evaluation method depends on the intended conclusions that should be made. Evaluation of the catalytic activity is often made with the rotating disc electrode (RDE) setup. For reactions that undergo mass-transport limitation at certain overpotentials the application of the floating electrode technique might be useful.[28] Similar to RDE, this is a dynamic technique to measure current voltage characteristics. However, the achievable current densities are closer to operation conditions in the real device, whereas at the same time only very low catalyst loadings are required. Therefore, this technique seems very well suited within the development of new catalysts. In order to enable conclusions on the behavior of a catalyst under operating conditions, at a certain point optimization of the performance should be made in the real device. Up to a distinct catalyst loading, increasing the catalyst loading could be one option to enhance the overall performance. Above a specific loading, however, mass transport can become a serious issue. In such cases, it is more the electrode engineering than the optimization of active site structures that will help to achieve best performance. However, as described

below, catalyst loading can become a crucial issue even under RDE conditions, for example when non-precious metal catalysts (NPMC) are used.

Catalytic activity and selectivity

NPMC play a growing role within the search of new, earth abundant and cheap electrocatalysts. Often, the activity of such systems is not as good. To enhance the performance the catalysts are tested at high catalyst loading. However, caution need to be taken, when for such high loadings intrinsic materials properties should be extracted.



Scheme 1. Reaction pathways for a fictive reaction of A to P_{final}. P1 and P2 are possible intermediates in the given reaction. They can either react to each other, to the intended product P_{final} or being released into the electrolyte.

In Scheme 1 the reaction pathway of a fictive reaction A → P_{final} is given. In this example, there are two intermediates that can be formed in parallel to the formation of the desired product P_{final}. If we can assume that $k_f >> k_1 \approx k_2$, the catalyst has a high selectivity for the formation of P_{final}. Measurements on selectivity should lead to similar selectivity values, independent of the catalyst loading.

However, if the reaction towards P1 (or P2) is more favorable, beside the further reaction to P_{final}, desorption of these products or reactions to each other are possible. If the catalyst layer thickness is increased the residence time of any desorbed species $P1_{des}$ (and $P2_{des}$) increases. The probability that it get re-adsorbed on another active site to react further to P_{final} (or to each other) increases. As a consequence the selectivity towards the product P_{final} will increase with increasing catalyst loading.
Thus, playing with the catalyst loading can on the one hand be used to tune the product formation in the one or other direction. On the other hand, in case a fundamental understanding of the reaction mechanism is desired, measurements with high loadings should be avoided, as they might mask the real performance behavior of the catalyst.

Beside typical selectivity measurements with the rotating ring disc electrode (RRDE) technique, in best case also measurements of the catalytic activity towards reaction of P1 and P2 should be performed to clarify the reaction mechanism. Product distribution can be analyzed by coupling EC to mass spectroscopy or chromatography.[29]

As an example, for the oxidation of hydroxymethylfurfural (HMF) to furandicarboxylic acid (FDCA), first either the aldehyde group or the alcohol group is oxidized.[30] In order to understand the reaction mechanism, the oxidation reaction of the possible intermediates, hydroxymethylfurancarboxylic acid and furan-dicarboxaldehyde, need to be investigated as well. This will illustrate whether the catalyst is more capable in aldehyde or alcohol oxidation.[30a] This is common for more complex reactions, but should be applied more general, as single selectivity measurements with the RDE technique might be misleading.

For example, the Levich equation shows the proportionality of the diffusion limiting current density j_{Diff} and the number of transferred electrons n. While the theoretical diffusion limiting current densities assigned to the oxygen reduction reaction (ORR) on platinum (n = 4) or gold (n = 2)[31] are good in line with the respective measured values, in case of non-precious metal catalysts (NPMC) diffusion limiting current densities depend on the catalyst loading.[32] In order to reach a good diffusion current density plateau, often loadings of 0.5 mg cm^{-2} to 0.8 mg cm^{-2} are required. The effects were explained by a 2x2 electron transfer reaction rather than 4 electron transfer reaction as on platinum.[32b, 32c]

Considering the problematic as stated above, Zhou et al. recommend the determination of n by the RRDE method with collection efficiencies determined for the given experimental conditions and at low catalyst loadings (0.1 – 0.2 mg cm^{-2}).[33]

In an extreme case, the H_2O_2 quantities might be an order of magnitude larger at low catalyst loadings (e.g.[32a, 32d]). Nevertheless, as degradation in fuel cells is strongly affected by hydrogen peroxide release [34], the real H_2O_2 quantities are important to know and so far selectivity is reported, data should be provided at low catalyst loading.

Other, very common examples are related to the oxygen evolution reaction (OER) or CO_2 reduction reaction (CO_2RR).
The OER takes place during the process of water oxidation at sufficiently high potentials (typically U > 1.5 V to obtain 10 mA cm^{-2}). For carbon-supported catalysts beside oxygen evolution also carbon oxidation (formation of CO or CO_2) need to be considered as a competing reaction. In case of CO_2RR, the applied potentials are << 0 V. Based on this, the hydrogen evolution reaction (HER) can take place as well.

Faradaic efficiencies need to be detected, but require a quantitative analysis of the reaction products. The coupling of electrochemistry with mass spectroscopy (MS), chromatography or RRDE might provide a solution.

When the RRDE is used, the (platinum) ring electrode should be fixed to a potential suitable for efficient detection of the desired product. In case of OER, it should be in the ORR regime but avoiding side reactions (e.g. 0.4 - 0.6 V vs. RHE). In this respect, under potential adsorption of hydrogen, the HER and the CO_2RR need to be avoided.

For dynamic measurement conditions where gaseous or liquid products should be detected, the ring current densities (or mass signals) might be delayed as the products might be trapped in porous electrodes. Based on this, for example determination of the faradaic efficiency for a current density of 1 mA cm^{-2} was recommended for the OER.[35] Again, also here, the use of thinner electrodes or flat films can help to avoid this problem. Nevertheless, as mentioned above, the catalyst loading can be used for “reaction engineering”. However, this should then not be discussed in terms of selectivity of a distinct catalyst but as electrode engineering.

Determination of the electrochemical active surface area (ECSA)

One major advantage in comparison to other heterogeneously catalyzed reactions is the accessibility of the electrochemically active surface area (ECSA) that can be determined from specific adsorption/desorption on the catalyst. In relation to precious metals often hydrogen adsorption and desorption (HAD) or CO stripping are the methods of choice that are applicable from laboratory scale half-cell measurements using the RDE technique to device application. In relation to this, the catalytic activity can be directly related to the ECSA and active site density in order to determine TOF values.

The ECSA value might appear smaller, when impurity species are present during the measurement, either from the electrolyte or the gas.[36] It might also be underestimated for small nanoparticles as adsorption is suppressed by an ensemble effect.[27, 37]

In case of NPMC often even no specific adsorption of hydrogen or CO is visible.[38] In this case the double layer capacity[39] or area under observed redox peaks[40] might give indication of the active site density. It was also shown that changing the pH can help to enable specific adsorption of small gas molecules.[41]

Stability testing

When it goes towards application, stability (constant current or constant voltage) and durability (cycling conditions) of a catalyst become important.

In a recent article, the activity and durability of a Pt/C catalyst in RDE (under different conditions), in a fuel cell and using the floating electrode technique were compared.[36b] The authors came to the main conclusion, that when different pitfalls related to the RDE technique are avoided, similar conclusions can be made in comparison to FC.

a) In half-cell measurements

There are different aspects where (metal ion) impurities in the electrolyte can cause misleading conclusions with respect to stability of electrocatalysts. Such impurity species might either be present directly in the electrolyte (e.g. iron in KOH [42]) or be formed during the reaction by partial leaching of the counter electrode, in case platinum or gold are used.[43] In both referred cases the deposition of impurity species can led to an improved performance as more active catalytic sites are formed (in case of NiFeOOH) or deposited on the original catalyst layer. Thus, for stability tests it should be ensured that the counter electrode material, or possible impurities in the electrolyte are not of relevance for the reaction.

While impurity species can improve the performance of NPMC, they can block active catalyst sites in case of PGM catalysts (compare ECSA part). As a consequence, the increasing amount of adsorbed impurity species can lead to a seemingly stronger decrease in activity, as e.g. observed by Martens et al. for the ORR on Pt/C.[36b] Repeating the initial conditioning steps prior to the final ORR activity measurement showed that most of the activity decay could be recovered. Only measurements in highest purity electrolytes (and cleaned glass ware) gave clear trends of the real performance decay and underlines the importance especially for precious metal catalysts.

Another issue is the presence of “spectator species” (as defined as not of relevance for catalysis), within NPMC. They are typically found when the preparation is not finished by an acid leaching step. If for such catalysts a possible activity decay might be assigned to the loss of metal ions from the catalyst layer caution need to be taken, as those ions might not necessarily come from active sites or a significant smaller fraction is indeed related to active site de-metalation.[44] Nevertheless, also metal ions from spectator species can be involved in the degradation, e.g., of the membrane, but could easily be avoided by an improved cleaning of the initial catalyst.

b) In fuel cell application

Limitation in mass transport is one general problem that has to be faced with NPMCs in FC application. Common loadings are 3-4 mg cm² or above.[45] As visible from several publications in this area, limited transport properties come into play even at potentials of 0.6 V or higher (depending on the activity of the catalyst). If potentiostatic stability tests are performed in a region of mass transport limitation, a loss in active sites might not directly be detectable, as still the transport properties but not the number of active sites limit the overall current density (cf. Fig. 3).

As mass transport becomes crucial especially at higher loadings, the use of lower loadings might help to get better insights. This might especially be of interest for the comparison of catalysts that differ much in their initial performance. In anyway, the selected potential needs to be ideally representative for the later application of the catalyst.

In-situ measurements

The coupling of electrochemistry with various spectroscopic techniques can give useful insights in the reaction mechanism, active site identification or degradation. There are some important issues that have to be considered in this respect:

The catalyst should remain stable under the applied conditions at least for the time of the measurement. Possible changes in activity should be checked after the in-situ tests. The area of electrochemical response should be similar to the probed range of the spectroscopic technique. E.g., Raman spectroscopy enables a very high resolution and spectra can be recorded on small spot sizes. In this case, local changes should be correlated with local variations of the current density. If this is not available, it might be better to correlate the overall current density changes with the average of the Raman changes. Whereas of course, the local variations (and their magnitude) can give indications for further electrode optimization.

Another extreme is the application of Mössbauer spectroscopy coupled with electrochemistry. Typically, large quantities of catalyst are required and relatively large loadings to enable a good resolved Mössbauer spectrum within a reasonable timeframe. In an early work by Bouwkamp-Wijnoltz, however, it was shown, that only a small fraction of this electrode participated in the electrochemistry.[46] Based on this, a profound optimization of the measurement conditions is required to balance the Mössbauer signal and electrochemical response.

Conclusion

The experimental approach to test solid catalysts and the evaluation of the obtained data are prone to numerous mistakes that are commonly found in the scientific literature during peer-review but also in already published articles. That applies equally to thermal, photo- and electrocatalysis. The major issues result from ignoring effects that overlap with the actual catalytic reaction, the catalysts itself and all observed species. Most often, all kinds of mass transfer limitations occur that can be ruled out or avoided with simple control experiments. Also of great importance is a comprehensive benchmarking especially of new catalysts to reliably proof an advance over the state of the art. Overall, we hope this concept article gives sufficient and comprehensive insights into the most common pitfalls and how to avoid them to assure a high quality of catalysis research in the future.

Acknowledgements

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Keywords: Catalyst testing • Heterogeneous catalysis • Electrocatalysis • Photocatalysis • Pitfalls

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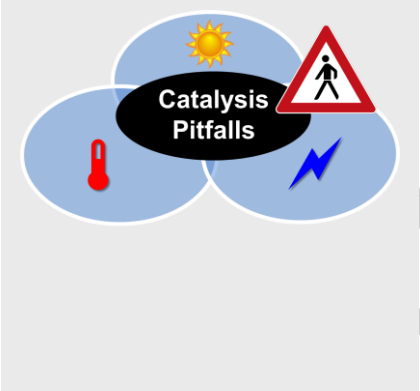
Entry for the Table of Contents (Please choose one layout)

Layout 1:

CONCEPT

Catalytic experiments and data evaluation in thermal, photo- and electrocatalysis are prone to numerous pitfalls. This article provides a summary of the most common ones and how to avoid them.



*Ulrike I. Kramm, Roland Marschall, Marcus Rose**

Page No. – Page No.

Pitfalls in heterogeneous thermal, electro- and photocatalysis

Layout 2:

CONCEPT

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*Author(s), Corresponding Author(s)**

Page No. – Page No.

Title

Text for Table of Contents

Author profiles:

Marcus Rose studied chemistry at Technische Universität Dresden and obtained his PhD with Stefan Kaskel working on novel porous materials for adsorption and catalysis. After research stays at Georgia Institute of Technology and Max-Planck-Institut für Kohlenforschung he became group leader at RWTH Aachen University with Regina Palkovits. Since 2017 he is full professor of chemical technology at Technische Universität Darmstadt. His research is focused on catalysis for the conversion of renewable resources at the interface of catalyst development, characterization, testing and reaction engineering.

Ulrike Kramm studied Applied Physics at the University of Applied Science in Zwickau. From 2006 – 2009 she did her PhD thesis in the group of Sebastian Fiechter at the Helmholtz-Center Berlin (HZB) working on the structural characterization of porphyrin based catalysts. For about 1 ½ years she worked in parallel as a postdoctoral researcher in the group of Jean-Pol Dodelet (INRS-EMT, Varennes, Canada) and at HZB, before she went to the group of Dieter Schmeißer at BTU Cottbus. Since 2015, she has a junior professorship at TU Darmstadt. In 2017 she was awarded a BMBF young researcher group & a young scientist award of the Mössbauer society, 2018 she received the Adolf-Messer award. Her work focusses on the development and optimization of non-precious metal catalysts as well as their spectroscopic characterization.

Photo: Fotostudio Hirch, Darmstadt

Roland Marschall obtained his PhD in Physical Chemistry from the Leibniz University Hannover in 2008, working on mesoporous materials for fuel cell applications. After a one year postdoctoral research at the University of Queensland in the ARC Centre of Excellence for Functional Nanomaterials, he joined in 2010 the Fraunhofer Institute for Silicate Research ISC as project leader. In 2011, he joined the Industrial Chemistry Laboratory at Ruhr-University Bochum as young researcher. In 07/2013, he became Emmy-Noether Young Investigator at the Justus-Liebig-University Giessen. Since 08/2018, he is full professor at the University of Bayreuth. His current research interests are heterogeneous photocatalysis, especially photocatalytic water splitting using semiconductor mixed oxides, and synthesis of oxidic mesostructured materials for renewable energy applications.