(photovoltaics) and thermal energy (solar heat), solar energy to chemical energy conversion to produce solar fuels by photocatalysis has some unique advantages in terms of energy storage, transportation and utilization, because the photocatalytically converted chemicals (solar fuels) can be conveniently activated for use. Though current research on this field is still in the stage of laboratory research, it can be envisioned that some breakthroughs may be achieved in the near future with extensive research input. And it is necessary to take the research on solar fuel production in a high priority to secure the national renewable energy development.

FUNDING

This work was supported by the National Natural Science Foundation of China (21473189, 21361140346), the National Basic Research Program of China (2014CB239403), and the Collaborative Innovation Center of Chemistry for Energy Materials (iChEM).

Hongxian Han and Can Li
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences and Dalian National Laboratory for Clean Energy, China
*Corresponding author
E-mail: canli@dicp.ac.cn

REFERENCES

1. Kudo, A, Nishiro, R and Kato, H et al. Chem Phys 2007; 339: 104–10.
2. Maeda, K, Inoue, Y and Domen, K et al. Nature 2006; 440: 295.
3. Kim, ES, Domen, K and Lee, JS et al. J Am Chem Soc 2013; 135: 5375–83.
4. Wang, X, Han, HX and Li, C et al. Angew Chem Int Ed 2012; 51: 13089–92.
5. Yang, JH, Han, HX and Li, C et al. Acc. Chem. Res. 2013; 46: 1900–09.
6. Li, RG, Zhang, FX and Li, C et al. Nat Commun 2013; 4: 1432.
7. Liu, GJ, Shi, JY and Li, C et al. Angew Chem Int Ed 2014; 53: 7285.
8. Ding, CM, Shi, JY and Li, C et al. Phys Chem Chem Phys 2014; 16: 15608.
9. Kanan, M and Nocera, DG. Science 2008; 321: 1072–5.
10. Luo, JS, Im, JH and Grätzel, M. Science 2014; 345: 1593–6.

doi:10.1093/nsr/nwv016
Advance access publication 20 April 2015

CHEMISTRY

Special Topic: Catalysis—Facing the Future

Studying birth, life and death of catalytic solids with operando spectroscopy

Bert M. Weckhuysen

Catalytic solids are arguably the most important catalysts used in pharmaceutical, (petro)chemical and environmental industries: most transportation fuels, materials as well as fine and bulk chemicals are produced by heterogeneous catalysts [1,2]. Despite their widespread use, the intricate details how they are composed, function, change and ultimately deactivate are still not well understood. One of the reasons is that catalytic solids are hierarchically structured, multicomponent and multielement materials. They are very dynamic under true reaction conditions, which often comprise high temperatures and pressures. This dynamic aspect is further underlined by the fact that most often a freshly prepared catalyst material loaded in a chemical reactor structurally changes during a period of activation. Such period of reaction environment-induced changes, very similar to the behavior of a chameleon, can easily take a few days in an industrial setting, a period in which the catalyst unfortunately suboptimally performs. These inherent dynamics make it a real tour de force to study and understand how catalytic solids are formed (‘birth’), function (‘life’) and deactivate (‘death’), an ambition which is already around since the early days of catalysis.

Fig. 1 pictorially illustrates how catalyst scientists may use of a ‘photocamera’ to make real-life 3D movies of the entire lifespan of a heterogeneous catalyst. This photocamera including an extremely powerful lens should have the potential to zoom-in and -out with the capability to focus on both the chemical reactor and individual catalyst particles. Moreover, it should track individual atoms and molecules in real-time, while bond-breaking and -making processes are occurring. All this has then do be done under realistic reaction conditions. Unfortunately, such powerful ‘photocamera’ is not yet on
Figure 1. Pictorial illustration of the use of a powerful ‘photocamera’ to make a real-life 3D movie of the entire lifespan of a catalytic solid.

the market nor even close to a practical stage of development. Fortunately, in the past decade several research groups have made important steps forward to take nanoscale ‘photographs’ and ‘movies’ of e.g. fluid catalytic cracking, methanol to olefins and Fischer–Tropsch synthesis catalysts, shedding fundamental insight in their working and deactivation [3]. This perspective aims to highlight some of the recent developments in this field of research and provides some outlook of what may become feasible in the foreseeable future. By no means this article intends to be a comprehensive (mini) review, and consequently several of the described trends are only highlighted making use of examples from my own research group.

About 15 years ago, Eric Gaigneaux (Belgium), Gerhard Mestl (Germany), Miguel Banares (Spain) and myself have launched the ‘operando spectroscopy’ methodology for catalysis research [4,5]. We felt that spectroscopic approaches should be (further) developed in such a way that they really could tell how an operating catalyst was functioning. Since then two promising subfields in the area of operando spectroscopy have emerged and subsequently developed to different levels of sophistication. A testimony of all these activities can be found in the proceedings of the preceding editions of the International Conference on Operando Spectroscopy, held subsequently in Lunteren (The Netherlands, 2003), Toledo (Spain, 2006), Rostock-Warnemünde (Germany, 2009) and Brookhaven (USA, 2012).

The first successful direction in operando spectroscopy research deals with the inherent complexity of industrial-like catalysts and the related reaction conditions of high temperature and pressure. As a result, many research groups worldwide have developed operando set-ups to collect IR, Raman, UV-Vis, fluorescence and X-ray spectra, often in a combined fashion [6]. A nice, and very recent example of such operando approach originates from a Chinese research group and includes Raman spectroscopy to probe iron-based Fischer–Tropsch catalysts at work [7].

A more recent trend is the implementation of operando spectroscopy tools for monitoring pilot-scale reactors and evaluate the catalyst behavior along the reactor bed [8]. A second line of research activities has been operando spectroscopy measurements of liquid-phase catalytic reactions. Although still relatively underdeveloped in comparison to gas-phase catalytic reactions, it is clear that the additional complexity of the system requires more clever approaches to distinguish the reactant, reaction intermediates and reaction products from solvent molecules. Within this context, ATR-IR methodologies have proven to be a very promising avenue [9], although other spectroscopic techniques will have to be explored to gather information of both the catalyst material and reaction environment.

With these operando approaches for liquid- and gas-phase catalytic reactions in hand, it also came to the attention of researchers that it is of utmost important to verify if the operando spectroscopy cell indeed performs in an analogous manner than a real reactor set-up. This has turned out not always to be the case as the conditions for proper spectroscopy and catalyst testing are not identical. Differences may occur due to e.g. deviations in temperature and hydrodynamics around the catalyst sample, leading to even deviations in the catalytic performances of the same catalyst material tested in different operando spectroscopy set-ups. Furthermore, measuring implies perturbing, which means that e.g. (laser) light may induce local heating or even the introduction of artifacts in the catalyst material under study. Cross-validations as well as post-mortem characterization of the catalyst material remains then essential to determine the origin of spurious data, or any other noted deviations from literature data.

A second important line of development has been the merge between microscopy and spectroscopy tools [3]. With the so-called micro-spectroscopy approaches, it has been possible to investigate in great detail the spatiotemporal heterogeneities taking place within catalytic solids. Examples include fluorescence microscopy, Raman, IR and
synchrotron-based X-ray microscopy. Advanced fluorescence spectroscopy now enables the detection and tracking of single molecules during catalysis within a catalyst particle [10,11], while with X-ray nanotomography one can assess the 3D structure, composition and accessibility of an individual catalyst particle down to tens of nanometer [12]. An illustrative example of this operando X-ray nanospectroscopy approach entails the study of a single iron-based Fischer–Tropsch catalyst particle at elevated pressure and temperature in a flow of synthesis gas [13].

The same microspectroscopy approach can be done for an entire reactor tube. The merge of spectroscopy and microscopy is just showing its merits, and one may expect that further steps can be taken by improving the spatial resolution so that more local details of a catalyst particle could become visible. A recurring question with microspectroscopy research is how relevant the gathered knowledge for a single catalyst particle is for the bulk catalyst sample. This implies the development of multiple catalyst particle research, as well as bulk characterization methods to validate the main observations made by single catalyst particle spectroscopy. One way to address this issue is to make use of correlative microspectroscopy techniques, which aims to chemically image the very same selected catalyst particle or catalyst domain with two or more microscopy methods. Following this approach, a more detailed picture of the chemistry taking place during catalysis emerges. An example is integrated light and electron microscopy in which in a first step fluorescence microscopy (FM) data are gathered, and in a subsequent step electron microscopy (EM) data are measured [14]. Overlaying both types of microscopy data allows us to relate the ultrastructures, as measured by EM, with the reactivity maps, as measured by FM.

It is fair to note that the typical ‘frame rates’ of current operando set-ups are still in the millisecond time domain. If the goal is to investigate bond-breaking and -making processes as well as electron fluctuations during a catalytic processes, we will have to aim to build a much faster ‘photocamera’ enabling to explore the femto- and attosecond time domain. If this becomes reality, ‘molecular movies’ of a real-life catalytic process could provide unprecedented insights in the reaction mechanisms of heterogeneous catalysts [3]. Knowing the pace with which spectroscopy methods develop such dream experiments may become reality within the next decade or two.

With the above-described promising analytical developments, including the in-parallel conducted catalyst performance measurements, proper and statistically sound data analysis protocols are becoming a necessity. Clearly, data mining approaches have to be further developed and applied to better appreciate the outcome of a particular operando spectroscopy approach taken, finally leading to the development of quantitative structure–performance relationships. Future studies have then to focus on translating these fundamental insights into the synthesis of new or improved catalyst materials, and on further increasing the time and spatial resolution to observe the intimate details of catalytic events [3].

REFERENCES

1. Ertl, G, Knozinger, H and Schuth, F. et al. (eds). Handbook of Heterogeneous Catalysis, 2nd edn. Weinheim: Wiley-VCH, 2008.
2. Hagen. J. Industrial Catalysis: A Practical Approach. Wiley-VCH, Weinheim, 1999.
3. Buurmans, ILC and Weckhuysen, BM. Nat Chem 2012; 4: 873–86.
4. Banares, MA. Catal Today 2005; 100: 71–7.
5. Weckhuysen, BM. Phys Chem Phys Chem 2003; 5: doi: 10.1039/B309654H.
6. Bontrup, U. Chem Soc Rev 2010; 39: 4718–30.
7. Fu, D, Dai, W and Mao, W et al. ChemCatChem 2015; 7: 752–6.
8. Sattler, JJHB, Mens, AM and Weckhuysen, BM. ChemCatChem 2014; 6: 3139–45.
9. Mojet, BL, Ebbesen, SD and Lefferts, L. Chem Soc Rev 2010; 39: 4643–55.
10. Janssen, KPF, De Cremer, G and Naely, RK et al. Chem Soc Rev 2014; 43: 990–1006.
11. Ristanovic, Z, Kerssens, MM and Kubarev, AV et al. Angew Chem Int Edit 2015; 54: 1836–40.
12. Meirer, F, Morris, DT and Kalirai, S et al. J Am Chem Soc 2015; 137: 102–5.
13. Gonzalez-Jimenez, ID, Cats, K and Davidian, T et al. Angew Chem Int Edit 2012; 51: 11986–90.
14. Karreman, MA, Buurmans, ILC and Geus, JW et al. Angew Chem Int Edit 2012; 51: 1428–31.

Bert M. Weckhuysen
Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, the Netherlands
E-mail: b.m.weckhuysen@uu.nl

doi: 10.1093/nsr/nwv020
Advance access publication 24 April 2015