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CATALYSTS LIVE AND UP CLOSE: MASTERING HETEROGENEOUS CATALYSIS AT DIFFERENT LENGTH SCALES

Determining the active site in a catalyst material and elucidating the related reaction mechanism are intellectual challenges and of paramount importance for the rational development of new or better catalysts. This short article gives an overview of the field of in-situ spectroscopy of catalytic solids and illustrates some trends by using recent showcases from our group.

Catalysts are the workhorses of chemical industry: more than 80% of chemicals have come into contact with at least one catalyst material during their manufacturing process. Catalytic solids can also be extremely complex: solids with high surface areas, for examples, possess many different potential active sites in their structure. Determining the active site in these catalysts and elucidating their related reaction mechanism remain intellectual challenges and are of paramount importance for the road to the so-called rational design of catalysts, offering prospects of improved formulations of existing catalysts, and the possibility to create more effective and

selective catalysts from scratch. Rational design remains in most cases a pipe dream: the experimental tools available for monitoring catalysts as they work are still, in the main, too rudimentary. Therefore, spectroscopy should ideally be performed under realistic catalytic conditions. This is the field of in-situ spectroscopy; i.e., spectroscopy of the catalyst material, while the catalytic reaction is running [1, 2]. Unfortunately, performing an ideal in-situ experiment is not easy and may remain a fantasy as suggested by J.F. Haw in his textbook on in-situ spectroscopy of heterogeneous catalysts [3]. According to this author, a perfect in-situ experiment would look inside an industrial reactor and reveal the most intima-

te details of a surface chemical reaction, including transition states of reactions. The envisaged sensor would profile chemical compositions on the scale of catalyst particles as well as spatial variations over the volume of the reactor with a high time resolution. Haw differentiates therefore between the “purest” definition of the term “in-situ spectroscopy”, in which the spectroscopic measurement should be made under reaction conditions and a more inclusive definition, which refers to any spectroscopic result that is relevant to reaction conditions and teaches us about catalytic chemistry. This - although valuable - argument by J.F. Haw, together with the fact that the word “in-situ” is used in connection with a specific catalyst handling, such as in situ regeneration and in situ activation, has led to the launch of a new name for the field of Haw’s “purest” definition of “in-situ spectroscopy”. This name is “operando spectroscopy” and it originates from the Latin gerund, meaning operating or working. The advantage of the name “operando” is a clear distinction between in-situ spectroscopic studies of a working catalyst under realistic reaction conditions and other interesting - but defined according to the more inclusive definition - in-situ studies. The field of operando spectroscopy is under intense development and the ultimate dream is still to perform the ideal in-situ - or better operando - experiment as outlined by J.F. Haw [3]. This should be possible if we can develop technology to such advanced levels that no

or only minor concessions in time scale, temperature, pressure and reactor design have to be made and that the related data processing and handling becomes less cumbersome.

The aim of this paper is to give a brief overview of the field of in-situ or operando spectroscopy of catalytic solids and more in particular illustrate with specific examples what Utrecht University has been doing over the last 5 years in this research area.

Potential roadmap for in-situ spectroscopy studies

A lot of spectroscopic techniques are or have been used under experimental conditions far from relevant catalytic conditions. In cases where realistic catalytic conditions were chosen, the characterization studies were mostly limited to the use of one particular in-situ spectroscopic technique measuring the catalyst under steady-state conditions, leading to spectroscopic data, which do not change with increasing reaction time. The disadvantages of this approach are threefold:

- 1) the spectroscopic information obtained from a catalyst material under ex-situ conditions is only of little relevance since important structural and physicochemical changes can take place in the catalyst material when present in the chemical reactor. Indeed, it is known that the presence of water, oxygen or other molecules may completely alter the molecular structure of a catalyst. The concessions made for reactor design and reaction temperature/pressure lead to information with sometimes little relevance for the operating catalyst;
- 2) each spectroscopic technique has its own sensitivity and limitations, which mean that one technique will not provide all necessary chemical information (e.g. oxidation state) about the working catalyst. Thus, more research has to be directed towards an intelligent combination of two or more spectroscopic techniques, which provides complementary information on the molecular structure and composition of a catalyst under working conditions;
- 3) the time resolution is often too low to detect reaction intermediates.

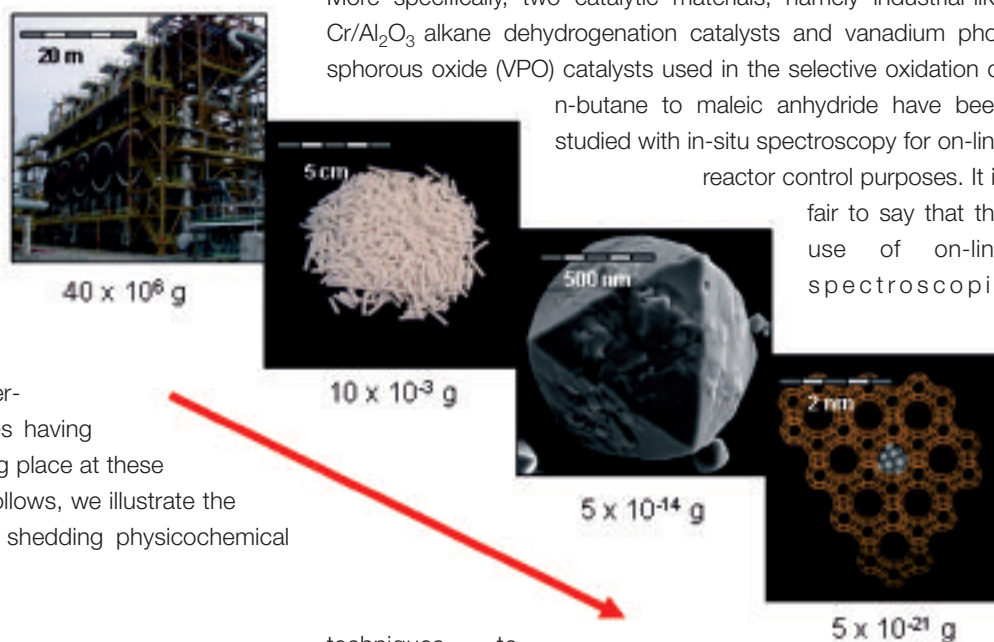
One of the challenges is to discriminate between spectator species and species actively involved in the catalytic event and to decrease the time necessary for measuring unusual states and reaction intermediates in an active catalyst. This requires the development of time-resolved techniques for measuring catalysts in the sub-second region in combination with fast on-line product analysis and transient kinetic experimentation. Based on these observations, one can try to make an attempt of a roadmap for in-situ spectroscopy, setting the field for the years to come [1, 2]. I am fully aware that such an attempt has the risk to fail or to be incomplete.



Nevertheless, it has the advantage that it may stimulate some discussion in the catalysis community. My ideas concern three areas of future research. Area 1 can be coined as “measuring better, measuring faster and measuring more”, whereas Area 2 concerns the logic extension of the operational window of in-situ studies to catalytic liquid-solid and liquid-gas-solid reaction systems. Area 3 of the proposed roadmap can be named “single-molecule and single-site in-situ spectroscopy-microscopy”.

In-situ spectroscopy for studying catalytic phenomena at different length scales

There are four different length scales of importance when considering a catalytic process. This is illustrated in the Figure in this page. The first level of interest is the reactor, in which the catalyst material is placed and is of the orders of centimeters to meters, in case a full-scale installation is considered. Catalyst materials are pre-shaped in e.g. extrudates of millimeter-dimensions to avoid pressure drops in the reactor. The third level constitutes e.g. zeolite crystals of micron or submicron dimensions, which contains active sites of the dimensions of nanometers or Angstroms. Mastering the performance of a catalytic solid requires having full control over the phenomena taking place at these four different length scales. In what follows, we illustrate the use of in-situ or operando tools in shedding physicochemical insight at the first three length scales.



In-situ spectroscopy of a reactor

Large-scale reactors loaded with catalytic solids are employed in a wide variety of chemical plants all over the world for the production of transportation fuels, bulk and fine chemicals. Monitoring the chemicals that are leaving the catalytic process commonly controls these reactors. Once the product composition deviates from the desired one, process control actions are taken to correct for this change. Important parameters for running large-scale industrial reactors based on heterogeneous catalysis for bulk chemicals production most economically are the reaction temperature and pressure as well as the chemical composition and physical properties of the reaction mixture. Often such corrective scenarios are based on empirical models, which are obtained from plant test runs. A

better approach would be to on-line monitor the physicochemical phenomena of the catalyst material taking place in the reactor by means of in-situ spectroscopy and to develop an “expert system” based on such spectroscopic measurements. Examples include coke formation (e.g. leading to active site blocking), catalyst reduction (e.g. over-reduction of the catalyst surface, change of catalyst dispersion (e.g. metal oxide clustering), migration of the oxide phase into the oxide support (e.g. metal ion migration into the support oxide), and change of phase (e.g. solid phase transformation during a redox reaction). With such expert system, it should then be possible to make a corrective action once a spectroscopically visible change occurs in the catalyst material. This is faster than monitoring the off-spec product leaving the reactor. Recently, this concept has, to the best of our knowledge, for the first time successfully developed to on-line control a catalytic solid at work [4]. More specifically, two catalytic materials, namely industrial-like $\text{Cr}/\text{Al}_2\text{O}_3$ alkane dehydrogenation catalysts and vanadium phosphorous oxide (VPO) catalysts used in the selective oxidation of n-butane to maleic anhydride have been studied with in-situ spectroscopy for on-line reactor control purposes. It is

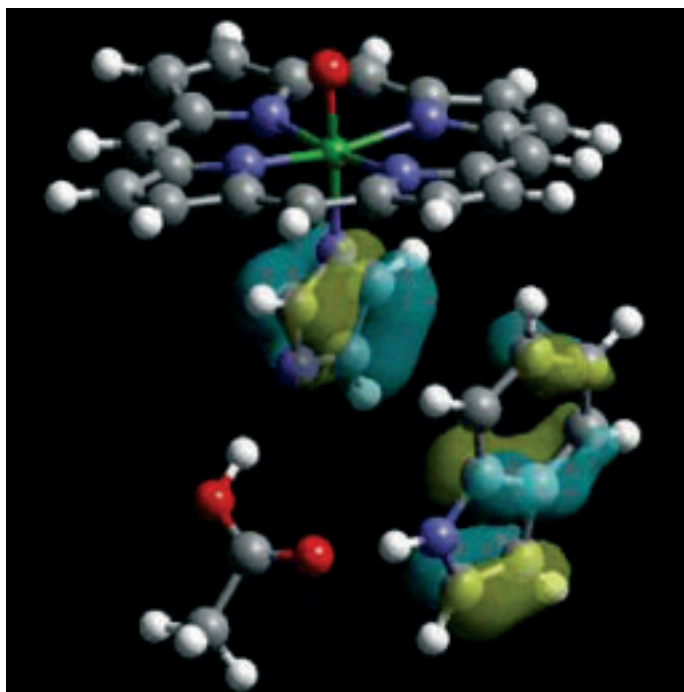
fair to say that the use of on-line spectroscopic

techniques to obtain data for process trend monitoring have already been applied in polymer science, while the only catalytic process in which in-situ spectroscopy is used as a means of process control is the production of 1,3-propanediol, making use of a homogeneous catalyst. The novelty of the developed approach is therefore linked to the use of in-situ spectroscopy to on-line control heterogeneous catalytic systems.

In-situ spectroscopy of an extrudate

The preparation of supported catalysts is an important industrial process since these systems are employed in crucial chemical processes such as hydrogenation reactions, Fischer-Tropsch synthesis and

the hydrotreatment of transportation fuels. The vast scale, on which these systems are employed, makes that their preparation needs to be achieved by simple means. In general, porous support bodies are impregnated with a solution containing metal-ion complexes, after which drying is carried out to deposit the active phase precursor salts on the support. Variations in the procedures used for impregnation and drying can have severe consequences for the activity of the final catalyst. The dispersion of the active phase and its macro-distribution inside the catalyst bodies are important parameters in this respect. The analysis of bisected catalyst bodies with spatially resolved spectroscopic techniques makes it possible to determine the distribution of the different components of the impregnation solution inside these samples during the preparation process. Recently, an indirect Magnetic Resonance Imaging (MRI) method has been developed to determine in a non-invasive manner the distribution of paramagnetic Co^{2+} -complexes inside $\text{Co}/\text{Al}_2\text{O}_3$ catalyst extrudates after impregnation with Co^{2+} -citrate solutions of different pH and citrate concentrations [5]. This method is based on the destructive effect of these complexes on the ^1H NMR signal of the water solvent in MRI measurements. UV-Vis-NIR micro-spectroscopy measurements were carried out simultaneously to obtain complementary information on the nature of the Co^{2+} -complexes. In this way, it could be confirmed that the actual distribution of Co^{2+} inside the extrudates could be derived from the MRI images. By the combination of these space- and time-resolved techniques, information was obtained on both the strength and the mode of interaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$



and different Co^{2+} -citrate complexes with the Al_2O_3 support. Complexation of Co^{2+} by citrate was found to lead to a stronger interaction of Co with the support surface and the formation of an egg-shell distribution of Co^{2+} -complexes after impregnation. By the addition of free citrate and by changing the pH of the impregnation solution, it was possible to obtain the rather uncommon egg-yolk and egg-white distributions of Co^{2+} inside the extrudates after impregnation. In other words, by carefully altering the chemical composition and pH of the impregnation solution, the macro-distribution of Co^{2+} -complexes inside catalyst extrudates could be fine-tuned from egg-shell over egg-white and egg-yolk to uniform.

In-situ spectroscopy of a single zeolite crystal

Zeolites represent a group of catalytic solids, which are heavily used in petrochemical and refining industries. Since their discovery in the 1970s, zeolites with MFI topology, such as H-ZSM-5, have been utilized in different large-scale applications due to unique combination of the acidic properties and the pore architecture. In order to obtain more information from particles or grains on how the catalytic processes take place in distinct places of a catalyst, micro-spectroscopic techniques should be employed. As of to-date, a number of microscopic methods, such as IR, UV-Vis, Raman and interference microscopy have been applied to study various steps in catalyst preparation and diffusion of organic compounds in the microporous materials. Recently, in our laboratory a combination of in-situ optical and fluorescence micro-spectroscopy has been employed to investigate the oligomerization of styrene derivatives occurring in the micropores of coffin-shaped H-ZSM-5 zeolite crystals in a space- and time-resolved manner [6]. The carbocationic intermediates in this reaction act as reporter molecules for catalytic activity, since they exhibit strong optical absorption and fluorescence. In this way, reactant selectivity and restricted transition state selectivity for 14 substituted styrene molecules can be visualized and quantified. Based on a thorough analysis of the time- and space-resolved UV-Vis spectra, it has been revealed that two main parameters affect the reaction rates, namely, the carbocation stabilization effect, and the diffusion hindrance. The stabilization effect was tested by comparison of the reaction rates for 4-methoxystyrene vs. 4-methylstyrene and in the row of 4-bromo-, 4-chloro and 4-fluorostyrene; in both cases less electronegative substituents were found to accelerate the reaction. As to the steric effect, bulkier chemical groups bring down the reaction rate, as evident from the observation that 4-methoxystyrene is more reactive than 4-ethoxystyrene due to differences in their diffusivity, while heavily substituted styrenes, such as 3,4-dichlorostyrene and 2,3,4,5,6-pentafluorostyrene, cannot enter the zeolite pore system and therefore do not display any reac-

tivity. Furthermore, β -methoxy-styrene and trans- β -methylstyrene show limited reactivity as well as restricted reaction product formation due to steric constraints imposed by the H-ZSM-5 channel system. Finally, polarized light optical micro-spectroscopy and fluorescence microscopy demonstrate that dimeric styrene compounds are predominantly formed and aligned within the straight channels at the edges of the crystals, whereas a large fraction of trimeric carbocations along with dimeric compounds are present in the straight channels of the main body of the H-ZSM-5 crystals. Our results reinforce the observation of a non-uniform catalytic behavior within zeolite crystals with specific parts of the zeolite grains being less accessible and reactive towards reactant molecules.

Concluding remarks and look into the future

Many catalyst discoveries are based on serendipity or on a trial-and-error approach often accelerated these days by the use of high-throughput experimentation and design of experiment techniques. They have led repeatedly and will still lead in the future to new industrial catalytic processes. However, rational catalyst design should still be the ultimate goal of catalyst scientists simply because it is an intellectual challenge to design new catalytic materials based on fundamental knowledge about the active site. This ambition requires fundamental insight in the molecular structure of the active site and in the reaction and deactivation mechanism of a catalytic process. To do so, researchers are nowadays developing spectroscopic tools to study catalyst materials inside a reactor without making major concessions in e.g. time scale, reaction temperature, reaction pressure and reactor design. This approach allows creating relevant quantitative structure-activity relationships and expert systems for on-line process control. The main challenges in this exciting field are:

- a) the development of time-resolved spectroscopy, in conjunction with the design and construction of high quality spectroscopic-reaction cells, which allow combining complementary information of two or more characterization techniques;
- b) the study of catalytic solid-liquid and gas-liquid-solid reaction systems and the development of tools enabling the study of these



catalytic interfaces;

c) the combination of in-situ microscopy and spectroscopy with the possibility to focus on the catalytic chemistry of one single active site of nanometer dimensions. This requires the development of site-selective nanoscopic techniques.

Finally, it should be clear that in-situ characterization cannot be just regarded as the King's new clothes because it clearly defines the experimental conditions how a combined spectroscopic-catalytic experiment should be done. It therefore differentiates itself from the more inclusive definition of in situ spectroscopy, as discussed by J.F. Haw. In-situ or operando spectroscopy is considered to be very important for the future development of catalysis science and engineering. The developed techniques will also be valuable to better understand the fundamentals of catalyst synthesis.

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