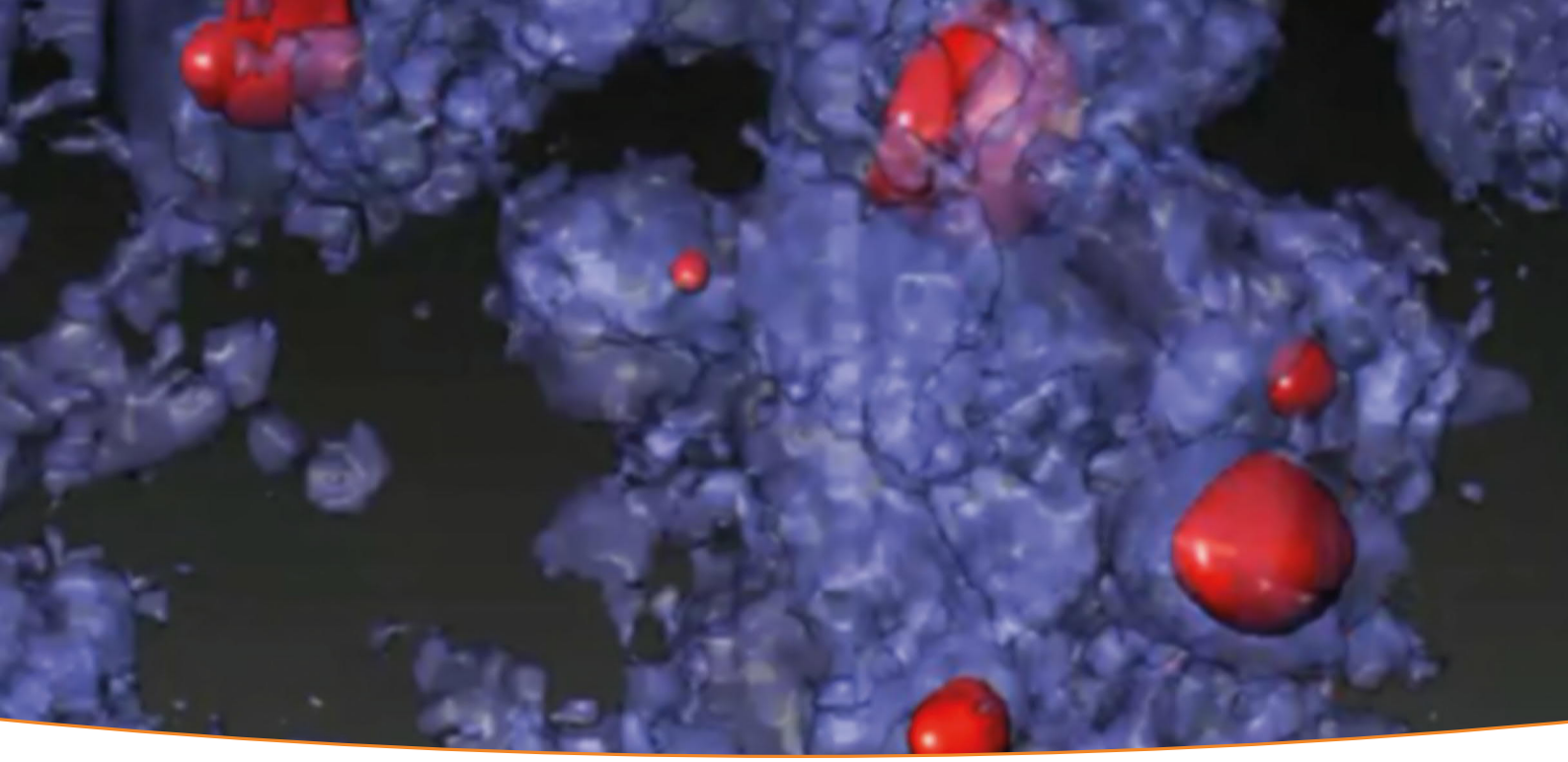

How to determine the reason for catalyst poor performance?

Investigation on catalyst structure using high resolution imaging techniques.

Executive Summary

Catalysts play an essential role in chemical industry, not only in economic terms but also in energy reduction and pollution control. Improvement of catalyst performance will only increase these benefits. The performance of a catalyst is closely related to its architecture at the micro and nanoscale. Advanced analytical imaging techniques are important tools to obtain structural, compositional and mechanistic understanding, paving the way for targeted product improvement. This article demonstrates how scientists in the Expert Capability Center Deventer (ECCD) of Nouryon (formerly AkzoNobel Specialty Chemicals) contribute to design and production of more active (yield), stable (lifetime) and selective (efficiency) catalysts.

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Key facts

>100	Analytical Techniques
>1000	Customer Requests per year
>10000	Samples Analyzed per year

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Nouryon

How to determine the reason for catalyst low performance?

A heterogeneous catalyst typically consists of a substrate (a porous support material) on which the catalytically active phase (e.g. metal, alloy) is sited. In practice, catalyst heterogeneity is present at several levels, either intended or unintended. Some reactions require a homogeneous distribution of the active phase across the supporting extrudate, others benefit from a localized presence of the active phase. At the level of individual extrudates, the distribution of the active phase can be determined with a Scanning Electron Microscope (SEM), using either a backscatter detector (BSE) or by local chemical analysis using Energy Dispersive X-Ray analysis (EDX) (figure 1). When the distribution of the active phase across the diameter of the extrudate is important, preparative methods are required to obtain smooth cross-sections of the extrudates. In such cases the extrudates are embedded in a resin, followed by cross-sectioning using an (ultra-) microtome, for which either a glass knife or a - much harder - diamond knife is used. The choice of the embedding resin is important as it may affect the catalyst structure and should result in a hardness which is comparable to that of the catalyst. The quality of resin embedding can be improved by vacuum impregnation. Alternatively, smooth cross-sections can be obtained by polishing or ion milling. The actual determination of the metal profile can then be done with SEM-EDX, either as line scans or as 2D element mappings (figure 2).

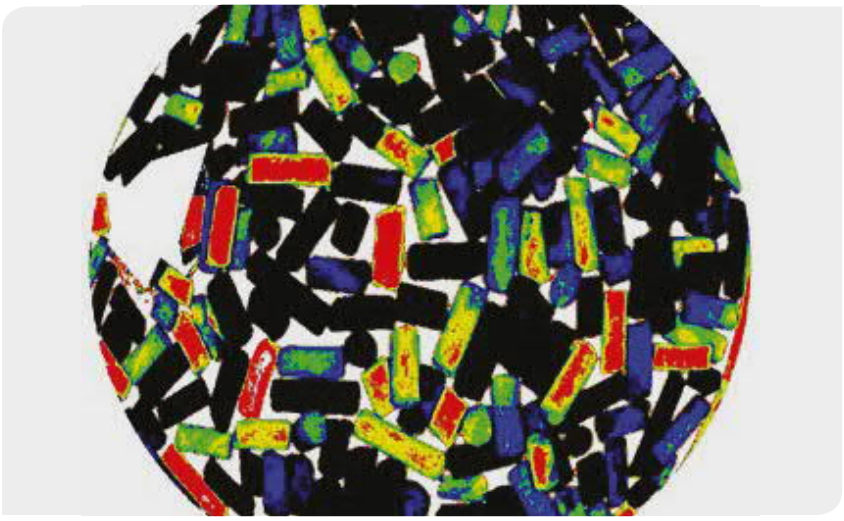

Figure 1. Normalized SEM-BSE image of a hydrogenation catalyst, showing the variation in metal loading between and on extrudates
(black = low loading; red = high loading)

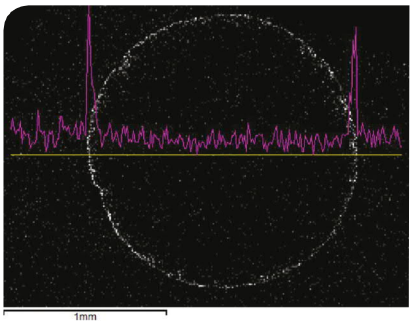

Figure 2. Metal line profile of an egg-shell catalyst, as determined by SEM-EDX.

Much higher magnifications are required to obtain information on the active phase dispersion in fresh catalysts and the changes occurring during use. Depending on the specific requirements of the customers either a STEM detector mounted in a SEM or the dedicated Scanning Transmission Electron Microscope (STEM) instrument can be used for particle size determination, chemical analysis of the individual (nano-) particles (figure 3) or 3-dimensional distribution information, as provided by tomography.

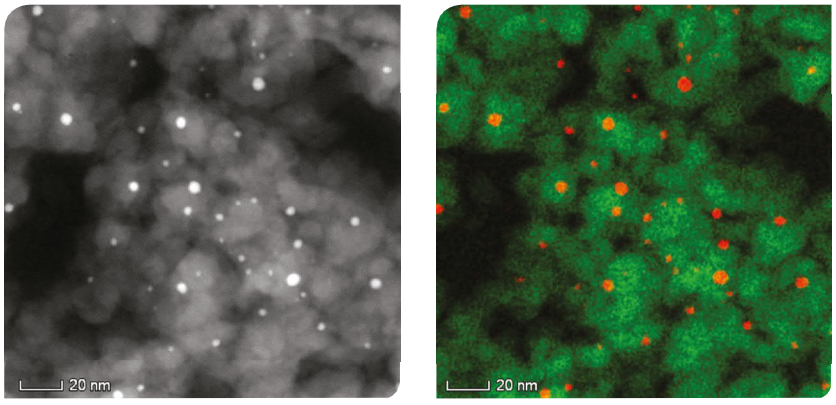

Figure 3. STEM-HAADF image (left) and EDX overlay of element maps (right) of a metal catalyst on a porous support.

Transmission Electron Microscopy (TEM) analysis requires samples that are very thin (e.g. 50-100 nm). The simplest method to achieve that is grinding of the extrudates and looking at the thinner parts of the fragments created. The disadvantage of this method can be that these areas are not representative or do not originate from the relevant area of the extrudate. In those situations, it is beneficial to embed the extrudates (fragments) in resin and make ultrathin sections of the relevant area with an ultramicrotome (figure 4). Thin sections can be also created with the Focused Ion Beam (FIB) facility on a SEM.

For catalysts containing a multitude of chemical phases multivariate analysis of the STEM-EDX data is of great help (figure 5).

Supporting information on the architecture of catalysts can be obtained by the surface analytical techniques XPS and ToF-SIMS, by the crystallographic technique XRD and by the spectroscopic techniques imaging IR and Raman.

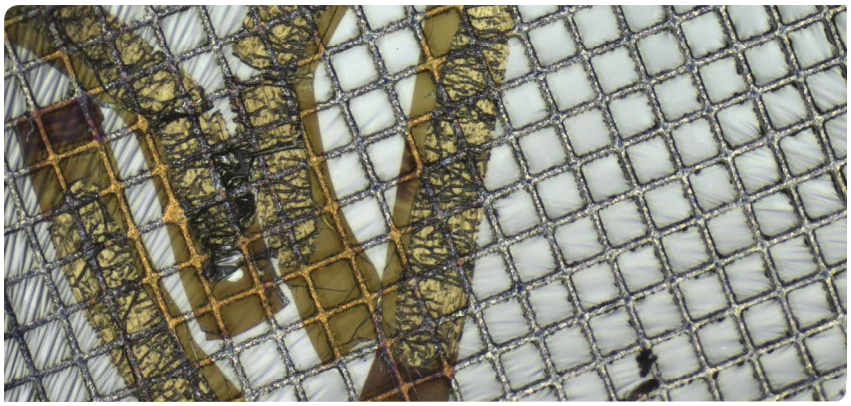

Figure 4. Thin ultra-microtomed sections of resin embedded catalyst particles on a Cu grid for (S)TEM-EDX analysis.

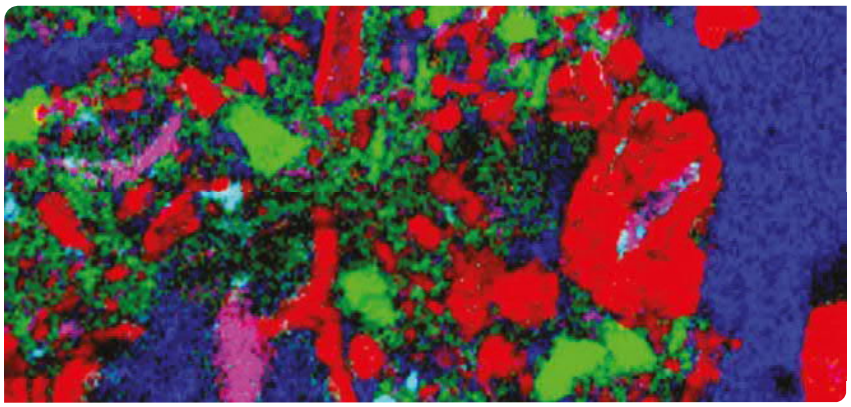

Figure 5. Phase map of a catalyst, as determined by multivariate analysis of STEM-EDX maps.

Conclusion

The scientists at the ECCD have many years experience in successfully investigating catalyst architecture using a wide variety of imaging techniques and related sample preparation. The insights obtained from these advanced analytical nanoscale characterizations enable catalyst designers to develop catalysts with better performance. ECCD scientists have the right knowledge and technical capability to connect your hypotheses on catalyst structure with reality.

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