

Seeing Beyond Bragg's Law

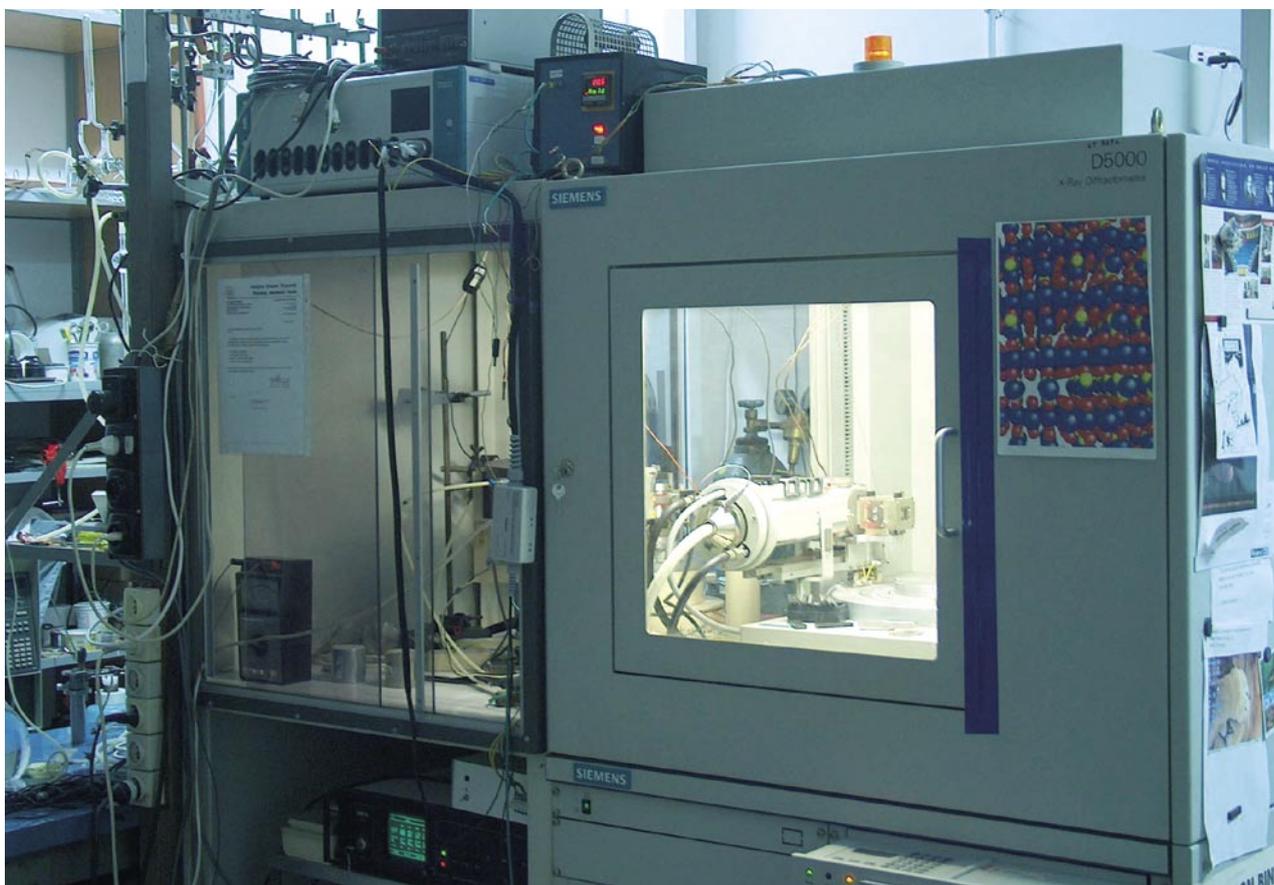
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Recent years have seen a swift rise in the significance of new materials produced by nanotechnology, i.e. materials consisting of structural elements on the order of a few to a few hundred nanometers. Here we take a look at methods for studying the behavior of metallic nanoparticles, or tiny lumps of metal

Materials that contain metallic nanoparticles have so far found uses as superparamagnetics, metallic liquids,

nanocolloids, and antimicrobe layers. However, they play their most crucial role in the field of chemistry, as catalysts in a range of chemical processes used in industry.

Catalytic processes frequently employ transition metals, such as palladium (Pd), platinum (Pt), nickel (Ni), and cobalt (Co). Because metal surfaces play an active role in catalysis, the objective has naturally been to strive to maximize this surface area (per gram of material). This entails fragmenting the surface, down to the scale of nanometers. The vast material area so obtained interacts with the reaction gasses, which bond strongly to it, modifying both their own properties and the properties of the metal itself. At present, much experimental evidence indicates that the metal surface undergoes significant transformations during the reaction itself, and if we wish to understand how the elementary chemi-



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Of all physical analysis methods, X-ray diffraction techniques exerted the greatest impact on the development of 20th-century chemistry and materials science. It turns out that the proper modification of such techniques for use with nanopowders makes it possible to register very subtle surface changes

cal processes proceed we will have to understand these transformations.

Performing experimental observations of a metal surface's structural evolution, i.e. the rearrangements in the atoms' positioning, is no easy task. The way in which reaction gasses interact with a metal surface depends greatly on the gas pressure. Moreover, the threshold energy required to stimulate spontaneous surface reconstruction is lower in the case of nanoparticles, where the surface of individual exposed crystal walls is significantly smaller, even though the overall surface of the metal is considerably greater.

How should we strive to observe such subtle surface processes? In fact, we can find a way using the well-known technique of X-ray powder diffraction. It turns out that the proper modification of this technique for use with nanopowders, makes it possible to register very subtle changes.

One fundamental methodological problem is how to interpret the detected changes in the diffraction image, indicating the structural modification of the nanoparticle surface. Unfortunately, the traditional 20th-century tools for interpreting powder diffraction, based on the fundamental principle of crystal lattice diffraction identified by W. L. Bragg, cannot be successfully employed for the structures we are concerned with here.

Taking diffraction beyond Bragg's law

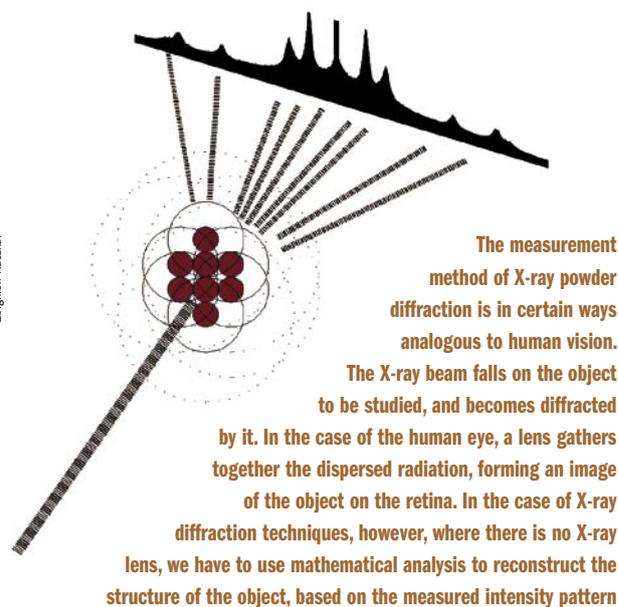
Bragg's law describes the relationship between the distance separating individual planes and the angle of diffraction, in the case of well-structured sequences of atom layers (e.g. crystal lattices) with long rows of equidistant atoms.

It turns out that as the atom rows grow shorter (i.e. down to the size of nanoparticles), the diffraction image not only shows broadened diffraction reflexes, it also evidences a small shift in them. This shift in diffraction reflexes caused by nanocrystallinity is not great, but it means that the position of the entire set of observed expanded reflexes is not consistent with any crystallographic system. The extent to which various diffraction reflexes are shifted depends on such factors as the state of the nanocrystal surface. One natural phenomenon that is observed for pure transition-metal nanocrystals involves reduced inter-atomic distances on the surface.

The intensity of the diffraction reflexes observed from nanocrystals likewise depends significantly on the structure of their surface. While monitoring the intensity of diffraction maximums *in situ*, one can observe changes during the course of such processes as the surface chemisorption of gas.

Interpreting diffraction images from nanocrystals

All of these phenomena, confirmed by measurements, provide irrefutable evidence that metallic nanocrystals can considerably modify their surface structure under the influence of chemical media. X-ray powder diffractometry



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interpreted with the use of atomistic simulations has enabled us to observe the swelling of metallic nanoparticles under the influence of oxygen chemisorption. The surface bonds are then saturated, and the average inter-atomic distances increase. A similar approach has also enabled us to structurally interpret noncrystalline nanostructures, associated with the presence of atoms in an environment showing local fivefold symmetry. Such structures, sometimes observed by microscope, may demonstrate a more favorable bonding energy in the case of small clusters of atoms, and could thus be frequently observed in a population of very small nanoparticles.

One natural phenomenon that has a significant impact on the structure of bimetallic nanoparticles, i.e. nanofragments of the alloys of two metals, is the surface segregation of one of the metals. However, when the gaseous atmosphere is changed this phenomenon can reverse, and the more favorable energy configuration might be one in which the atoms of the metal which previously remained inside the nanoparticle emerge to the surface. Using the methods described here, we have managed not only to confirm the model of segregation in platinum-cobalt (Pt-Co) alloys, but also to observe the dynamics of the same phenomenon of metal concentration reversal in a nanocrystalline alloy of palladium and gold (Pd-Au).

It seems that research methods of this sort could play a significant role in gleaning an understanding of real chemical processes, helping us to propel the field of chemistry along its journey from the Periodic Table towards an ultimate, full, quantum-mechanical description of reactions. The first step towards such a description must be an awareness of a catalyst surface's real structure during the course of a reaction. ■

Further reading:

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