CHARACTERIZATION OF CATALYSTS: BULK AND TEXTURE

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Contents

Summary

Most of the catalysts used in the chemical industry are high-surface-area solids onto which an active component is dispersed in the form of very small particles. These moieties have dimensions of 1 to 20 nm and are often referred to as nanoparticles. These particles are distributed over the internal surface of the substrate. Given that most substrate surfaces are structurally non-uniform, and because supported particles are extremely small and irregular in both size and shape, an understanding of catalyst structure and texture is of vital importance for optimizing catalysts with respect to performance and lifetime. Thus, this chapter offers the non-specialist reader an account of the most relevant methods employed to characterize the size, shape, structure, and composition of the nanoparticles, as well an assessment of the specific area and pore size of the catalysts. Various types of spectroscopy, diffraction and imaging techniques can therefore be used to achieve the ultimate goal of determining and understanding quantitative structure/composition-activity/selectivity relationships. Accordingly, such detailed knowledge should enable scientists to rationally design new and efficient catalysts for the sustainable production of chemicals, as well as for the removal of

harmful compounds in industrial processes. Finally, a brief description is provided for each technique of its physical basis and relevant information, and a few examples have been selected in each section in order to illustrate the relevance of such techniques and the information gathered from each catalyst system.

1. Introduction

Most commercial catalysts are powdered, consisting of either one or more phases or of supported metallic (or bimetallic) components on large-area supports of different composition and nature, usually oxides. When these systems are used in a given catalytic reaction, activity and selectivity are two important parameters that indicate how good a catalyst is. However, these parameters stem from measurements carried out at macroscopic scale, which is considerably greater than the atomic scale of the molecular events taking place on the catalyst surface. From a scientific point of view, research into catalyst composition, the structure of the framework of the solid and the nature of its porosity are essential parameters to correlate with catalyst performance. In most cases, this provides a way of understanding the role that surface atoms play in the catalytic reaction. This basic information on the structure-property relationship for existing catalysts is valuable in the design of more efficient ones. The objective of understanding catalyst structure and texture has been pursued for nearly thirty years with the advent of many new physical tools developed through surface science and often reiterated.

The analysis of heterogeneous catalysts involves three different quantities. The most important of these is the qualitative identification of the catalytic ingredient, i.e. what atom-type is at the catalyst surface. The second concerns the chemical state of these atoms, i.e. the oxidation state of the atoms involved in the active phase. Finally, it is crucial to determine how the active ingredient is distributed across the catalyst particles. A disappointing feature, however, is the non-planar nature of catalyst systems. This is illustrated by supporting catalysts consisting of small crystallites dispersed on high specific area carriers, such as Al_2O_3, SiO_2, zeolites, etc., mostly within the pores. Thus, this chapter aims to examine the main methods available for the study of both structural and textural characteristics and to analyze the data derived from them.

2. Structure Determination

2.1. Topography

Electron microscopy allows for the direct observation of catalyst morphology over the entire range of particles sizes present in solid catalysts. Electron microscopy images identify phases and provide structural information on crystals, direct images and elemental composition and distribution. Routine applications, however, may be hampered by complexities of image interpretation and by constraints on the type and preparation of specimens and on the environment within the microscope. The aim of this section is to briefly outline the fundamentals and use a few examples to describe the potential techniques have for characterizing catalyst topography. Under the heading electron microscopy, three types of electron microscopy methods are considered: (i) conventional transmission electron microscopy (TEM), which is the most useful tool for particle size measurement; (ii) scanning transmission electron microscopy (STEM); and (iii) scanning electron microscopy. Electron microscopes are often equipped with X-ray detection devices working in the energy-dispersive mode (EDX), and sometimes with electron spectrometers for measuring electron energy-loss spectra (EELS).

Basically, unscattered and scattered electrons are focused with the objective lens in the back-focal plane where the diffraction pattern is formed. After passing through this plane, both unscattered and scattered waves interfere to form an intermediate image in the image plane. The projection lenses are focused either on the diffraction pattern or on the intermediate image to form the final diffraction pattern or image. The 2D image is a projection of the structure on the plane perpendicular to the electron beam.

Conventional transmission electron microscopy (TEM) is suitable for examining supported catalysts with particle sizes down to 2-3 nm, giving information on particle location over the support, on particle size distribution, on particle and support morphology and on the nature and distribution of deposits with a thickness of around 23 nm. Surface topography can be examined using replication techniques. For particles smaller than about 2 nm, the routine analysis of micrographs is not possible, and even in the 2-10 nm range interpretation must be approached with caution.

The periodic structure of a crystal is not feasible in a conventional TEM image, although it is revealed to a limited extent if the technique is converted to high resolution (HRTEM) by modifying the method of image formation either in the TEM instrument or in specialized electron microscopes operating at around 500,000 V. Lattice fringe images represent the simplest case and record an intense modulation that gives the spacing of the atomic planes lying parallel to the incident beam, enabling catalyst particles to be identified. In certain instances, fringes from the support can be used for an accurate assessment of small particle sizes, as well as to determine pore dimensions and interlayer distances. In the case of heavy metals, the crystal structure of particles of this size can also be studied. The amount of crystallographic information is increased by the formation of structure images, but interpretation then requires comparison with images reconstructed by computer.

Electron tomography is a powerful new tool, now commercially available, for three-dimensional structural investigations using three-dimensional TEM. The method enables the characterization of structures hundreds of nanometers in size at nanometer-scale resolution. Electron tomography enables the non-destructive investigation of the interior of truly unique structures. Possible applications for heterogeneous catalysis include the determination of the 3D shape, volume, connectivity and location of meso- and macropores inside a support material. Moreover, the size and location of metal particles inside the material can be visualized unambiguously and subjected to statistical evaluation. The unique possibilities of electron tomography can be understood taking into account the method's two basic steps: (i) acquisition of projection images of the structure under investigation at different tilt angles; and (ii) calculation of the 3D reconstruction (tomogram) of the sample volume from these projections.

Figure 1 illustrates the tomogram for an Au/SBA-15 model catalyst particle (ca. 256 x 256 nm). The centre panel of the top three images displays the reconstructed density of this catalyst. Thus, tomograms like this can be used to determine the 3D shape, volume, connectivity and location of pores inside a support material. Moreover, the size and location of Au particles inside the material can be seen clearly (left: virtual cross-section (thickness 0.64 nm through the reconstruction, and right: surface rendering of 8 nm gold particles) and subjected to statistical evaluation. This kind of information could not be obtained from a single TEM micrograph due solely to the overlapping of structures in projection. The slices at the bottom display three of the 151 electron microscopy projection images (−55°, 0° and +55° tilt angle) that were used to calculate the volume. The two-sided arrows indicate the reversible process of projection and back-projection.

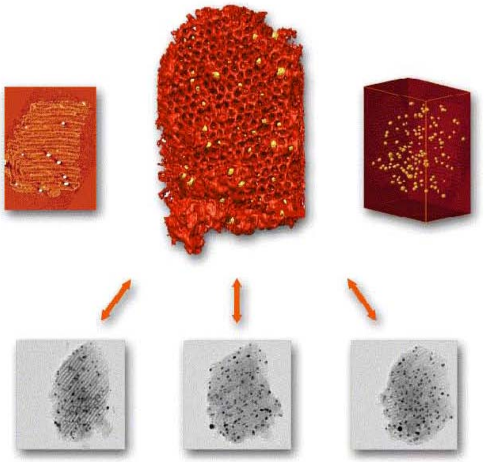

Figure 1. The center panel of the top three images shows the surface rendered visualization of the reconstructed density of an Au/SBA-15 catalyst particle (256 nm×256 nm×166 nm). The size and location of Au particles inside the material can be seen (left: virtual cross-section, thickness 0.64 nm, through the reconstruction; right: surface rendering of gold particles, size 8 nm). The slices at the bottom display three of the 151 electron microscopy projection images (−55°, 0° and +55° tilt angle) that were used to calculate the volume. The two-sided arrows indicate the reversible process of projection and back projection.

An important advantage of electron tomography is that it does not depend on averaging over unit cells or particles. The method enables the investigation of truly unique structures and is thus capable of displaying internal sample irregularities (e.g. distribution of metal particles in catalyst pores in three dimensions). In addition, it can complement the method of physical adsorption of nitrogen at low temperature to elucidate the relationship between microscopic structure and bulk characteristics of heterogeneous catalysts. Since the method does not include averaging over unit cells or particles, the resolution is in the nanometer rather than in the atomic range, as in the case of electron diffraction.

The potential of electron tomography in the determination of the location of silver particles with a diameter of 10–40 nm inside or on the surface of a supporting material was obtained with Y zeolites (NaY). The experiments with SBA-15 model catalysts, which were either loaded with gold or contained 2–3 nm zirconia particles, provided unequivocal information on the location of these particles inside the support, and the non-uniform distribution of particles over the mesopores explained the two-step nitrogen desorption-isotherm. Regarding alumina distribution, an indication for the generation process of mesopores in zeolites was obtained by comparing the reconstructions from steamed zeolite Y (USY) and steamed and acid-leached zeolite Y (XVUSY). While the external surface and the walls of the mesopores in USY were covered with a darker layer, which was assumed to be amorphous alumina that was deposited during steaming, no such features were observed, and thus had probably been removed, in the acid-leached XVUSY.

2.2. Microanalysis

Topographical images in a SEM are formed by back-scattered primary or low-energy secondary electrons. The best resolution is about 2-5 nm, but many routine studies are satisfied with a lower value and exploit the case of image interpretation and the extraordinary depth of field to obtain a comprehensive view of the specimen. With non-crystalline catalysts, SEM is especially useful for examining the distribution and sizes of mesopores.

A merging concept of both SEM and conventional TEM techniques is STEM. In STEM, the incident beam is convergent and areas from 50 nm (microdiffraction) down to less than 1 nm (nanodiffraction) can be examined. In addition, the region of reciprocal space sampled in a convergent beam diffraction pattern can provide very accurate three-dimensional crystal symmetry information, allowing a full analysis of the point and/or space group of the material.

Thus, electron microscopy can not only provide images but also comprehensive structural and chemical analysis of samples at a submicron scale. To achieve this, modern electron microscopes are equipped with three valuable tools: electron diffraction, X-ray microanalysis and energy loss spectroscopy (EELS).

In electron microdiffraction, a fraction of the electron beam is diffracted by the nanocrystals present in supported catalysts, and hence the diffraction pattern should provide crystallographic data down to the scale of a few nanometers if the diffracted electron intensity can be suitably recorded. According to Bragg’s law (see below), the lattice spacings may be easily determined by measuring the recorded spot pattern. This requires simply calibrating the instrument on a specimen of known crystal structure. It is worth stressing that the precision of such lattice spacing measurements on sharp spot patterns is usually only a few percent.

To illustrate this, the morphology and compositions of a sample consisting of nanocables composed of crystalline SiC core coated with a shell of amorphous SiO2 are selected. Figure 2(a) is a low-magnification TEM image of this sample, in which a large quantity of wires with lengths up to several tens of µm and high purity are observed.

The HRTEM image (Figure 2(c)) shows that the wires are a core–shell structure with two different parts. In situ EDX (Figure 2(b)) on a single nanocable recorded the bright ring in the corresponding small area electron diffraction pattern (inset in Figure 2(a)) that can be attributed to the crystalline structure in the sample. In Figure 2(d), the lattice fringes with *d* spacing of 0.25 nm on the HRTEM image of SiC core correspond to the distance of the (111) plane in β-SiC.

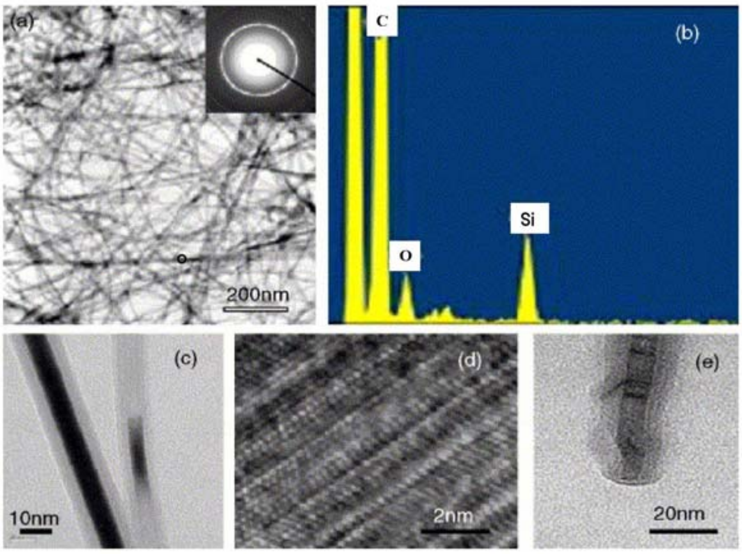

Figure 2. (a), Low-magnification TEM image of the as-prepared SiC/SiO$_2$ nanocable samples and the corresponding SAED pattern (inset). (b), EDS results recorded on the single nanocable. (c), HRTEM image of the SiC/SiO$_2$ nanocables, showing the core-shell structure. (d), HRTEM image of the SiC core. (e), The tip of the nanocable.

The second analytical tool is X-ray microanalysis. Along the path across a thin specimen, high energy electrons may suffer various inelastic scattering processes. It may happen that enough energy is transferred to an inner-shell electron from its atomic energy level. The transition of an outer-shell electron to the vacant site may then induce the emission of an X-ray photon with an amount of energy equal to the energy difference between the excited and final atomic states. The energy (or wavelength) of the photon is thus characteristic of the emitting atom. Measurement of this energy on an X-ray spectrum allows for identifying the nature of the atoms present in the sample (see Figure 2(c)). Film X-ray microanalysis is probably the most used microanalytical tool on an analytical electron microscope. For more details, the reader is referred to dedicated monographs.

The third analytical device is electron energy loss spectroscopy (EELS). The EELS technique needs only to incorporate an electron spectrometer to the STEM, which allows for the analysis of the kinetic energy of transmitted electrons. The inelastic scattering phenomena experienced by the electrons when passing through the thin specimen may be studied when recording electron intensity as a function of energy loss with respect to the incident energy. At loss energies above 50 eV, the spectrum consists of a smoothly decreasing background on which abrupt edges are superimposed. These edges arise at an energy loss corresponding to the transfer of an inner-shell electron up to the vacuum level. The energy loss values of the various edges recorded in the spectrum are equal to the ionization energy of the corresponding shells of the appropriate atoms and may be used to identify the chemical composition of the sample. Indeed, EELS spectra very efficiently display K-shell edges for elements with atomic number Z below 9, which cannot be detected by energy dispersive X-ray spectrometry. Heavier elements may be detected by their L, M, N edges, although superposition with the strong K-edges from light elements may complicate spectra interpretation. Thus, EELS appears as a complement to X-ray microanalysis.

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