

Electron Microscopy in Heterogenous catalysis

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Electron Microscope is popular and powerful techniques used to characterize heterogeneous catalysts. In heterogeneous catalysis, frequently used catalysts are metal particles supported on an oxidic material. The size of the metal particles plays a crucial role for the catalyst efficiency, and the determination of size distribution is one of the main tasks of electron microscopy in catalysis. The purpose of this review is to summarize the significant developments and achievements in this field with particular emphasis on the characterization of catalysts.

Keywords: Catalyst; Heterogenous Catalysis; Electron microscopy; TEM; SEM

1. Introduction

Catalysis plays a key role for the sustainable development of our society. The characterization of morphology, chemical composition, surface, and internal structure of catalysts is of great importance for the synthesis of materials of high selectivity, high conversion rate, with long cycle times favored for their reduced environmental impact. Modern electron microscopy with its arsenal of imaging and spectroscopic techniques gives access to the collective and individual properties of such materials.

Most industrial catalysts are multicomponent systems. This fact is making heterogeneous catalyst characterization very difficult, since it is necessary to know the chemical content and structure on a nano-scale level, oxidation states of active centers and their environment. The research in the field of catalysis is also specific because it is necessary to have a large and easily accessible surface area, due to the fact that the actual catalytic act takes place in the thin surface layer. Most often this is achieved by reducing the size of catalyst particles. Therefore, for industrial catalysts, small, very often nano-sized, crystallites are widely used, i.e. they represent the active catalytic substance. It should be emphasized that very often catalysts or catalyst supports were required to have nanostructured material properties, like in the case of sponge-like structure catalysts [1, 2]. This is the reason why only the use of various sophisticated instruments can yield successful investigation

Electron microscopy has potential to reveal the microscopic details of catalysts. In 1940, M. von Ardenne and D. Beischer published in *Angewandte Chemie* possibly the first paper to describe the usefulness of transmission electron microscopy (TEM) for extracting morphological and structural information on supported and unsupported catalysts.[3] J. Turkevich reported in 1945 the use of the electron microscope for the study of several important catalysts.[4, 5] Catalysis, together with the materials science of semiconductors, have been the driving force for the continuous improvement of electron optics and microscopic design for transmission electron microscopes.

Advanced electron microscopes are not only marked by their high resolution, they are also defined by their high brightness field emission gun with its highly coherent electron beam. Aberration correction significantly improves the quality of high-resolution images by eliminating the Fresnel fringes and delocalization effects, so that the surface structure of industrial catalysts can be determined [6, 7]. The implementation of monochromators, and the development of high resolution electron-energy loss spectrometry (EELS), mark a new generation of analytical electron microscopy. Modern, advanced, analytical electron microscopes with aberration correctors provide genuine atomic and energy resolution and high sensitivity to heavy or light atoms.

2. Characterization

Atomic resolution imaging can now be routinely achieved in the modern electron microscope and has been widely applied to characterizing the atomic structure of a plethora of materials [8]. Although scanning tunneling microscopy and atomic force microscopy techniques can provide atomic resolution information and have provided invaluable information on the fundamental processes of heterogeneous catalysis [9], these techniques have not been successfully applied to the study of practical industrial catalysts. On the other hand, most heterogeneous catalysts can be directly examined in an electron microscope. Applications of high-resolution TEM to the characterization of heterogeneous catalysts have been discussed in several recent reviews [10-13]. With the recent explosive initiatives in nanoscience and nanotechnology, atomic resolution TEM (ARTEM) will play an even more important role in understanding the structure and properties of nanoparticles, nanostructured catalysts, and other nanoscale systems.

Transmission electron microscopy or more broadly analytical transmission electron microscopy is the unique method for this purpose because it provides most of necessary fundamental information on morphology and microstructure of the material.

Microstructure characterization is crucial for understanding and optimization of any heterogeneous catalyst performance. At the preparation stage, it is important to find procedures providing homogeneous distribution of the active phase in highly dispersed state over the surface of the support. In the case of multicomponent catalysts it is also important to check if the components are properly mixed (alloy formation vs. phase separation). At the utilization stage various microstructure changes may occur that degrade the catalyst performance (deactivation). Most important processes causing the deactivation are sintering, poisoning and phase transformations. The first process describes decline of the surface area of the active phase and the support as the result of particle growth and/or filling up the pores. Poisoning usually is the process of blockage of the active surface of the catalyst by pollutants present in the feedstock or by the by-products of the catalytic reaction. Finally, phase transformations mean solid state reactions occurring in the catalyst such as changes of allotropic forms, phase decomposition or reactions between the active phase and the support. Very often the processes described above occur at nanometer length scale and amounts of analyzed materials are very small so that suitable micro-analytical methods are necessary. Transmission electron microscopy or more broadly analytical transmission electron microscopy is the unique method for this purpose because it provides most of necessary fundamental information on morphology and microstructure of the material.

2.1 Phases identification

Identification of phases present in any catalyst formulation is undoubtedly necessary for its characterization. At macroscopic scale the problem is usually solved by using “bulk” techniques such as X-ray diffraction or vibrational spectroscopy, but in many cases local information at below nanometer scale is needed. Moreover, to understand the catalyst activity or deactivation a spatial correlation of various phases is crucial. TEM is a unique method for that purpose because it provides direct imaging, diffraction pattern and spectroscopic information from the same point of the sample with very high spatial resolution. Generally, phase identification in TEM can be done based on the atomic (crystal) structure or elemental composition. The former method uses usually one of a spectrum of electron diffraction techniques (selected area electron diffraction, micro-(nano) electron diffraction, convergent beam electron diffraction) [14] and rely on the comparison of obtained diffraction patterns with those expected for compounds with known crystal structure. It should be noticed however, that generally electron diffraction is not very precise as to determination of unit cell parameters (at least much less precise than X-ray diffraction) and large number of crystals may be possible candidates. In such cases an information on chemical composition (available in some TEM instruments – see below) is helpful. A great advantage of electron diffraction as compared to X-ray diffraction is sensitivity, i.e. very small amount of material is required to get interpretable diffraction pattern. Using nano-diffraction technique ED patterns from individual few nanometers big crystals can be obtained. For even smaller crystallites identification is possible via high resolution (structure) imaging. In this case distances between fringes in the images and angles between various sets of fringes correspond to inter-planar distances and angles in the crystal lattice [15, 16]. A careful measurement of the fringes (preferably using fast Fourier transformation FFT) and their comparison with calculations for known structures enables phase identification.

2.2 Spatial distribution of phases

The distribution of various phases (e.g. the active metal over the support) is clearly important issue for catalyst characterization. In a simple case of crystalline phase dark field imaging in TEM mode can be used [17]. A drawback in this case is that in one setting only small fraction of crystallites of the phase is identified. Much more effective is scanning TEM (STEM) method, where the electron is tilted electronically describing a hollow cone. In the case of non-crystalline materials phase distribution can be determined by using high angle annular dark field (HAADF) or Z-contrast method in STEM [18]. The method is based on high-angle incoherent scattering of electrons, which depends very strongly on atomic number (Z^2). In modern STEM instruments HAADF images with atomic resolution can be obtained, so that even individual metal atoms on oxide supports can be identified [19]. Important limitation of classical TEM as a tool for studying distribution of particles of active phase deposited on the support (especially with high porosity) is that TEM images are the projections of the object. It is not easy therefore to find the distribution of the particles within the pores of the support. Recent advances in microscopy technique as well as in computation enabled to overcome this limitation through application of the electron tomography [20, 21]. The method requires the acquisition of large amount of images (projections) taken over a broad range of tilt values. From this a three dimensional map of the object is constructed enabling visualization of two dimensional slices presenting position of the particles within the pores. Spatial distribution of various phases in the catalyst must be known in order to understand and to control the process of catalyst poisoning.

2.3 Shape and size distribution of particles

Ability of TEM to reveal directly shape and size distribution of nanometer sized objects is of vital importance for characterization of catalysts [22]. The information on the particle shape and size distribution is needed for determination of mechanism of catalytic reactions including the dependence on the crystal faces exposed at the surface. On the other

hand observations of the evolution of shape and size distribution of particles of the active phase during catalyst use provide information on the mechanism of deactivation. It is important to realize that TEM has limitations as to the source of information on particles present in the catalyst. From small particle size the limit depends strongly on the active phase – support composition. For typical catalysts and classical HRTEM 1 nm is a safe limit.

2.4 Structure and Shape of Metal Nanoparticles

The shapes of metal nanoparticles play an important role in determining the performance of supported metal catalysts. In structure-sensitive catalytic reactions, only certain faces of metal nanoparticles are dominant active sites for the desired products; other faces of the nanoparticles are either not active or are active for producing undesired side products. For example, in the synthesis of ammonia reaction, rate differences of over an order of magnitude were observed with the (111) and (210) faces providing the highest activity [23, 24]. The relative portion of edge, corner, and surface atoms also varies with the shape of the nanoparticles.

ARTEM images can provide information on the shape and, in some cases, the surface atomic structure of the metal nanoparticles. Internal structural defects such as twins can also be revealed; dislocations and stacking faults are rare in small metal nanoparticles although they do exist in large particles.

The shapes of metal nanoparticles in supported metal catalysts depend on many parameters, including their sizes, the method of preparation, the history of the catalyst treatment, and their interaction with the support. Even for model supported nanoparticles, it is difficult, if not impossible, to obtain statistically meaningful results on the shape distributions of the metal nanoparticles. Therefore, we have not been able to meaningfully correlate the shape of metal nanoparticles to their catalytic properties. Extensive research, however, has been conducted on the fundamental understanding of the structure and shape of metal nanoparticles and their formation mechanisms, with a focus on those nanoparticles that have five-fold symmetry [25, 26].

2.5 Atom ordering

Determination of the atomic structure (i.e. atomic positions in the unit cell) of a crystal can be done using electron diffraction or HRTEM. As in X-ray crystallography information on the atomic positions is coded in intensities of reflections in the electron diffraction pattern. The problem is that in most cases the intensities of reflections in electron diffraction patterns are disturbed by the effect of dynamic (multiple) diffraction and cannot be treated within ordinary kinematical theory [14]. The effect of dynamical scattering may be restricted to some extent by using a special method of precession electron diffraction [10] or the diffraction is treated as fully dynamic phenomenon as in the method of convergent beam electron diffraction (CBED) [14].

The atomic structure of crystal can also be determined from a series of HRTEM images taken at various crystallographic orientations. The idea is that HRTEM image represents a projection of the crystal lattice (in fact its electrostatic potential) so that an analysis of a set of images (projections) can provide an information of the crystal lattice [11]. In this case a critical issue is an image resolution that must be better than interatomic distances in the crystal. It should be mentioned however, that despite of resolution, interpretation of HRTEM images is not straightforward. The reason is the presence of image aberrations due to non-ideal imaging by the microscope, but also the effect of dynamical diffraction mentioned above [11]. Of special importance for studies on heterogeneous catalysts (small particles) is a spherical aberration which causes delocalization of information. This effect may result in appearance of the lattice fringes outside the crystal, thus making impossible precise localization of the crystal. A huge step ahead in the microscopy was thus introduction of the aberration correctors in the modern instruments, which enabled qualitative improvements in visualization at atomic scale [12]. The effect of dynamical diffraction is taken into account by image calculations, i.e. comparison of the experimental images with those calculated for various crystal models and imaging conditions. The effect of dynamical diffraction increases strongly with increasing crystal thickness. In addition to “bulk” crystal structure HRTEM, especially when equipped in Cs corrector, provides information on the structure of the surface of small particles. In particular effects of the surface relaxation (contraction or expansion of outermost atomic layers) or the surface reconstruction (e.g. faceting) may be observed [13]. HRTEM enables also detail investigation on the atomic structure of the interface between particles of the active phase and the support. The character of the interface determines the strength of interaction between the particles and the support and thus their stability (resistance to sintering) but also may influence catalytic activity. For example it is well known that preferred, epitaxial orientation of metal nanocrystals on crystalline supports is responsible for enhanced resistance to sintering [14].

2.6 Local elemental composition and electronic structure

Knowledge of a local elemental composition and electronic structure is important for characterization of heterogeneous catalysts and supplement structural information provided by TEM. Two spectroscopic techniques: EDS (energy dispersive spectroscopy) and EELS (electron energy loss spectroscopy) are normally used for this purpose and works as attachments to STEM instruments. Such multipurpose instruments are often called AEM (analytical electron

microscope) [15]. Information on elemental composition on nanometer or better atomic scale are required for studies on composite (alloy) metallic catalysts, on mechanism of poisoning of catalysts or on catalysts deactivation. Knowledge of elemental composition is also the only way for identification of poorly ordered or amorphous phases often occurring in real heterogeneous catalysts. Due to its operation principle spatial resolution of EDS is limited to few nm range and it is more sensitive to heavier elements.

On the other hand EELS approaches now a spatial resolution of 0.1 nm and is more sensitive for light elements. Moreover, contrary to EDS EELS provides also information on electronic structure of the atoms, in particular on their valences but also on their surroundings. Fine structure of the EELS spectra contains information similar to that present in XAFS (X-ray absorption fine structure) spectroscopy. In conjunction with fast computers and advanced software EDS and EELS can also be used to produce two dimensional mappings (elemental, oxidation state etc).

2.7 Particle Visibility

Two imaging modes are commonly used to examine the structure of small particles or clusters in supported catalysts: plan view imaging and profile view imaging. In the plan-view imaging mode, the contrast of the metal nanoparticles can be obscured by the underlying support. The visibility of metal nanoparticles supported on light-element carriers depends on the atomic number of the metal, the shape of the particle, and strongly on the ratio of the size of the metal particle to the thickness of the support. When the thickness of the support increases, the visibility of very small metal clusters drastically decreases; details of the shape and structure of the nanoparticles are often overshadowed by the dominant phase contrast of the support and sub-nanometer particles can become completely invisible. When the support material is amorphous, a so-called “minimum contrast” technique can be applied to enhance the visibility of supported metal nanoparticles (Heinemann & Soria, 1986).

2.8 Measurement of Lattice Parameters and Surface Rearrangement of Atoms

ARTEM is well established for accurately measuring lattice parameters, distortions of atomic arrangements near defect sites and interfaces, and surface reconstructions [27] (Smith, 1997). For supported metal catalysts, however, the metal nanoparticles are usually of irregular shape and randomly oriented. In the reciprocal space, small particles are associated with large diffraction volumes at each reciprocal lattice (the so-called shape and size effect). The consequence of this large diffraction volume is that even if the nanoparticle is tilted away from the exact zone axis, lattice fringes can still be observable in ARTEM images. This is why most small particles show lattice fringes in ARTEM images even if the particles are randomly oriented. For FCC metal particles, the observable fringes are usually (111) lattice planes because of their larger lattice spacings. Image simulations show that simple interpretation of ARTEM images of randomly oriented nanoparticles can be problematic because the observed fringe spacings may not correspond to the true lattice spacings of interest [28-30] (Malm & O’Keefe, 1997; Crozier et al., 1999; Tsen et al., 2003). The variations in the measured fringe spacings can be as large as 12% from the true lattice spacings, especially for very small clusters and for fringes near the edges of a nanoparticle [30] (Tsen et al., 2003). Therefore, one has to be cautious to claim surface relaxations/ distortions of small nanoparticles simply based on the measured fringe spacings in the ARTEM images. To correctly determine the lattice spacings in ARTEM images of small nanoparticles, a statistical method such as the one proposed by Tsen et al. 2003 has to be used. By following the proposed procedures and measuring 100 Pt nanoparticles, the mean fringe spacing from ARTEM images of small nanoparticles could be determined to within 1 pm or better. With accurate measurement of the average lattice fringes, the above authors, based on Vegards’ law, were able to determine the alloy composition of a model bimetallic catalyst. Differentiation of different alloy compositions, however, proved to be difficult due to the statistical distribution of measured lattice fringes from different alloy compositions.

3. New Improved TEM

Though TEM is an advanced technique (was invented 74 years ago) it is still rapidly progressing and opens new possibilities. Of particular importance in the field of studies on solid catalysts is a technique known as environmental transmission electron microscopy (E-TEM). Contrary to ordinary TEM, where the sample is studied under high vacuum, ETEM makes possible to examine sample at temperatures up to 1000 0C at elevated gas pressures (few tens Tr). What is important even is such conditions high resolution (~0.1 nm) is still possible [31]. Main importance of this technique is for catalysis because it brings us closer to an ultimate goal of seeing the atomic structure of a working catalyst. When combined with high resolution EELS, E-TEM constitutes a complete laboratory for studies on the atomic and electronic structure of the active sites at the surface of the active phase. Recently, yet another step ahead was made in the direction of full understanding of the mechanism of catalytic reactions at the surface. Aside of high spatial and energy resolution TEM has a chance to become also a time resolution technique. The new technique known as ultrafast or 4D transmission electron microscopy uses a very short pulses of electrons to generate images and electron diffraction patterns. Thanks to very fast detectors a picosecond time resolution should be possible [32].

4. Limitations of EM as a method of studying catalysts

As each experimental method EM has its own limitations that should be taken into account during interpretation of the results obtained for particular kind of materials studied. The limitations have two sources: physical (chemical) phenomena occurring during observation and specific problems connected with preparation of the samples. In the first group the most important are beam induced phenomena. In modern HRTEM instruments energy of electrons in the incident beam is typically 200 or 300 keV so the beam can seriously influence the material investigated. Moreover, in order to get interpretable information from extremely small particles, the intensity of the beam must be very high. Electron beam induced changes in the sample are due to shift of the atoms from equilibrium positions (knock-on)-structure modification or breaking of chemical bonds – chemical modification. If, however the structure or the chemistry of the sample is changed, the specimen is not representative of the parent material anymore. The structure modifications may involve amorphization, structure fluctuations, decomposition or even evaporation of the material. Amorphization is frequently observed during TEM observations of zeolites (e.g. ZSM-5), crystalline silicas or ordered carbons. Despite being generally unwanted phenomenon (artifact) amorphization of zeolites can be used in positive way. For metal catalysts supported on zeolites visibility (and detectability) of small metal particles is greatly improved after the support amorphization. It is worth to note, that reversible process i.e. crystallization of an amorphous materials is also sometimes observed. It happens e.g. for metastable phases, where disorder is frozen during preparation. In such cases crystallization may occur due to activation by electron impact or by local heating. The structure fluctuations were observed for small crystalline particles as structure (e.g. fcc – bcc) or morphology change. It is believed, that despite direct electron impact, the effects are due to very short temperature jumps above melting point. Phase decomposition under electron beam is usually observed for organic compounds, but happens also for inorganics. Typical examples are hydroxides (transformation to oxides) or hydrated salts (dehydration). Removal of atoms from the sample under irradiation may cause formation of nanometer size voids or holes. For crystalline materials the voids often have regular outlines determined by crystal planes. Finally, irradiation with electron beam may cause contamination of the sample. Most frequent effect is a buildup of an amorphous carbon overlayer at the surface of the sample. The source of the contamination could be poor vacuum in the microscope (hydrocarbons, CO) or the sample itself. Contamination rate increases rapidly with the beam intensity and thus often is a problem when strongly focused beam is used (nano-diffraction, STEM, etc.). The presence of contamination layer degrades the quality of high resolution images but may also lead to misinterpretation of results. An example could be studies on catalyst deactivation where contamination layer may easily be consider as effect of carbonization or decoration of the active phase. Another limitation of TEM as analytical method applied in studies on highly inhomogeneous systems such as heterogeneous catalysts is poor sampling (poor statistic value). Typical HRTEM micrograph (60x90 mm) taken at 500 000 magnification covers an area of about 25 000 nm². Assuming that useful images are obtained for sample thickness at most 50 nm the volume recorded in a single image is 1.25x10⁶ nm³. It means therefore that 10¹² micrographs are needed to record a 1 mm³ of the material. On the other hand, 1 mm³ of industrial (e.g. Pt/Al₂O₃) catalyst contains around 10⁹ metal particles, from which maybe 10³ are analyzed in TEM study. It is clear therefore that whenever possible, the data obtained by TEM should be supplemented by other “bulk” techniques such as X-ray powder diffraction, gas adsorption, Raman spectroscopy, EXAFS, etc.

5. Conclusions

Modern advanced electron (TEM/STEM) microscopy utilizing combination of HRTEM, HAADF, EDS, EELS, and electron diffraction techniques can be successfully applied for complete characterization of heterogeneous catalysts. Strongly developed nowadays techniques of environmental TEM and dynamical ultra-fast microscopy give chance for atomic scale characterization of the “working” catalysts during catalytic reaction. The very high spatial resolution of electron microscopy and highly energetic probe pose however the significant challenge for the future. How to overcome the most important drawbacks of the methods: very poor statistical value and possibility of beam induced artifacts.

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