

Transmission Electron Microscopy as indispensable tool
for imaging and chemical characterization
of heterogeneous catalysts*

L. Kepiński

*Division of Nanomaterials Chemistry and Catalysis,
Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, Okólna 2, 50-412 Wrocław, Poland
tel: 48-71 34 350 21 ext.155, e-mail: l.kepinski@int.pan.wroc.pl*

Transmission Electron Microscopy (TEM) and its mutation Scanning Transmission Electron Microscopy (STEM) is one of the most important methods providing unique information on structure and chemistry of solid catalysts at length scale down to level. The principal reason is its high spatial resolution (below 0.1 nm) but also universality, i.e., ability of observation of both images and diffraction patterns of individual nanometer size objects. Recent advances in TEM in particular application of image and beam correctors, possibility of studying specimens at non vacuum conditions (environmental TEM) and possibility of dynamic (time resolved) studies even further broadened the applicability of the method in catalysis.

1. INTRODUCTION

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

*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65th birthday

(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 including:

1. identification of phases present
2. spatial distribution of the phases
3. shape and size distribution of particles
4. atom ordering (crystal structure)
5. local elemental composition
6. local electronic structure.

In this review we shortly describe how above goals can be achieved using modern TEM techniques and give examples of their use for catalyst characterization. New advances, opportunities and challenges in TEM will also be presented. Finally, fundamental and practical limitations of the method of transmission electron microscopy will be shortly discussed.

2. CHARACTERIZATION OF HETEROGENEOUS CATALYSTS BY TEM

Identification of phases present. 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 a 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) [1] 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 [2]. Careful measurements of the fringes (preferably using fast Fourier transformation FFT) and their comparison with calculations for known structures enables phase identification. Figure 1 shows as example identification of phases present in Co/C model catalyst subjected to oxidation-reduction treatment [3].

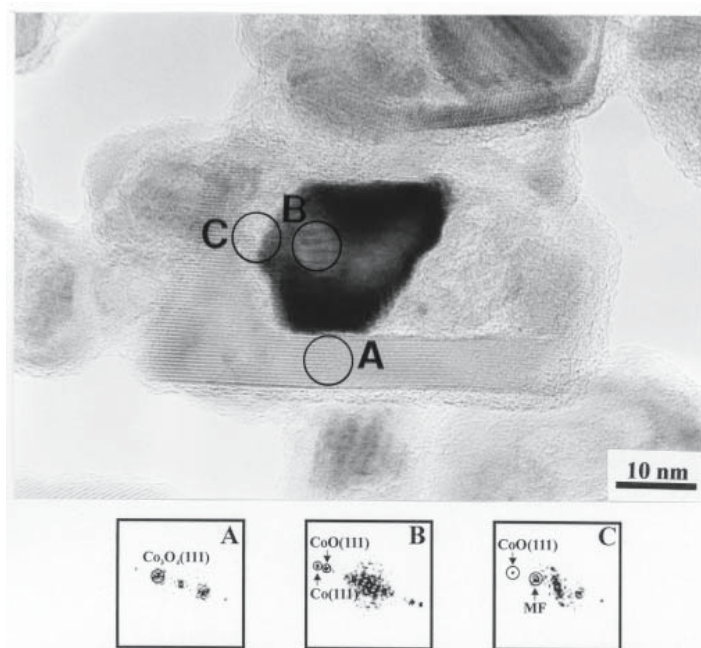


Fig. 1. Identification of various Co oxides in Co/C model catalyst [3].

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 (Figure 2) [4].

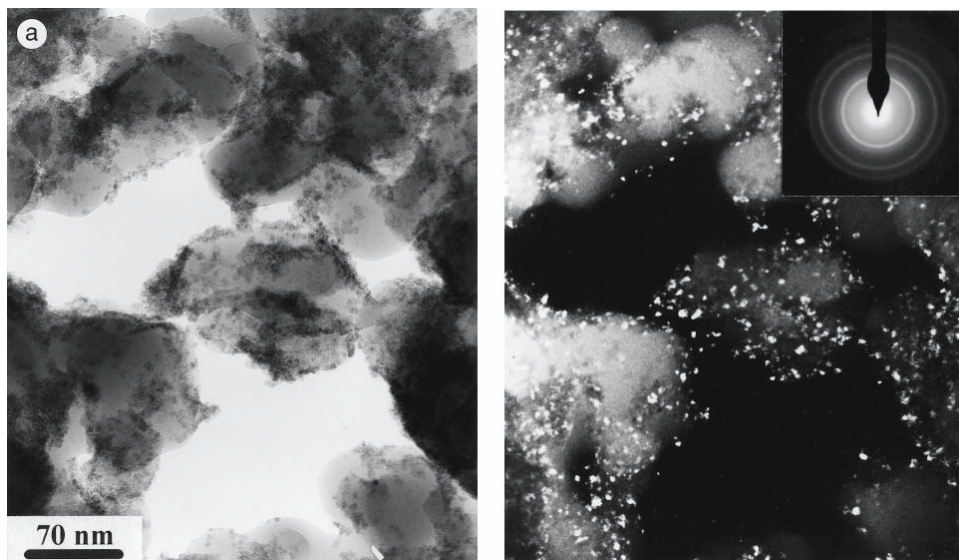


Fig. 2. Comparison of bright (left) and dark (right) field images of CeO_2 nanoparticles supported on SiO_2 [4].

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 [5]. 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 [6]. 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 [7]. 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. An example is formation of carbon deposits on the surface of metal catalysts used for steam reforming of hydrocarbons. It has been found that addition of small amount of Mo to Ni/Al₂O₃ catalyst significantly reduces the amount Ni particles active in the process of filamentous carbon growth [8].

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 (Figure 3) [9].

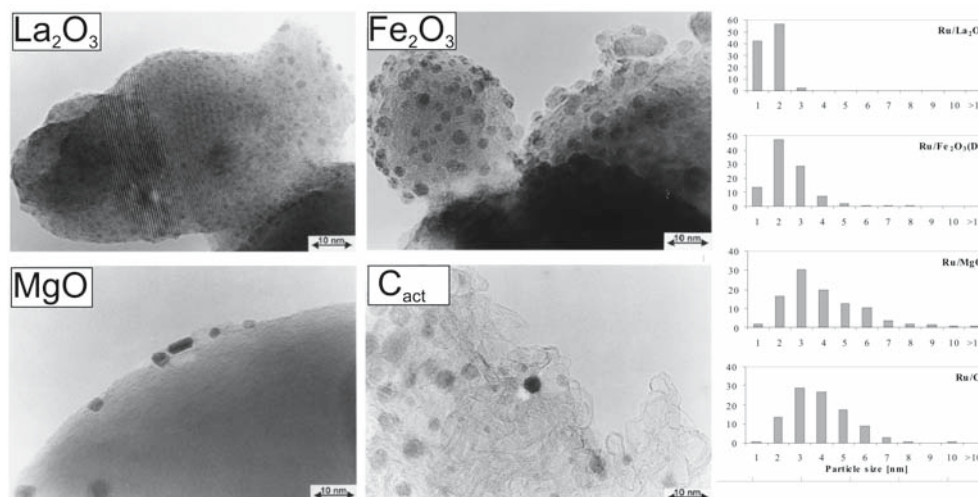


Fig. 3. Distribution of Ru particles on various supports [9].

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.

Atom ordering (crystal structure). 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 can not be treated within ordinary kinematical theory [1]. 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) [1].

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.

Tab. 1. Number of various crystal orientations that can be resolved in HRTEM at a given resolution.

Material	Number of orientations available for a given resolution			
	0.2 nm	0.16 nm	0.1 nm	0.06 nm
diamond	1	1	2	9
Al	2	2	6	10
Si	1	2	7	13
Fe (bcc)	1	1	4	12
W	1	1	5	13

Table 1 shows for few examples how many different orientations can be resolved in HRTEM images for a given resolution. It is clear therefore that resolution 0.1 nm or better is not just a whim. 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 Figure 4 [14].

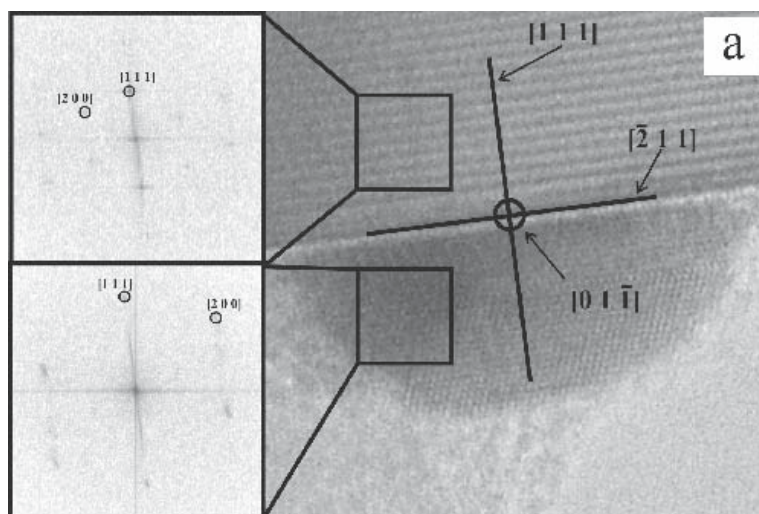


Fig. 4. Metal- support interface – Au/CoCr₂O₄ catalyst. Epitaxial orientation between Au particle and the support is seen [14].

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 valencies 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).

3. NEW ADVANCES IN TEM

Though TEM is a mature 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 [16]. This technique is of vital importance 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 [17].

4. LIMITATIONS OF TEM AS A METHOD OF STUDYING SOLID CATALYSTS

As each experimental method TEM 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 was 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 considered 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 nm) 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 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” catalyst 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.

6. REFERENCES

- [1] *Electron Diffraction Techniques*. ed. by J. M. Cowley, Oxford University Press, Oxford, 1992 vol. I and II.
- [2] W. Qin and P. Fraundorf, *Ultramicroscopy* 94, 245 (2003).
- [3] D. Potoczna-Petru and L. Kępiński, *Catal. Lett.*, 73, 41 (2001).
- [4] L. Kępiński and M. Wołczyr, *J. Solid State Chem.*, 131, 121 (1997).
- [5] M. Varela, A. R. Lupini, K. van Benthem, A.Y. Borisevich, M. F. Chisholm, N. Shibata, E. Abe and S. J. Pennycook, *Annu. Rev. Mater. Res.* 35, 539 (2005).
- [6] A. A. Herzing, C. J. Kiely, A. F. Carley, P. Landon and G. J. Hutchings, *Science* 321 1331 (2008).
- [7] H. Friedrich, P. E. De Jongh, A. J. Verkleij and K. P. De Jong, *Chem. Rev.*, 109 1613 (2009).
- [8] L. Kępiński, B. Stasińska and T. Borowiecki, *Carbon* 38, 1845 (2000).
- [9] A. Basińska, L. Kępiński and F. Domka, *Appl. Catal. A*. 183, 143 (1999).

- [10] A. Avilov, K. Kuligin, S. Nicolopoulos, M. Nickolskiya, K. Boulahya, J. Portillo, G. Lepeshov, B. Sobolev, J. P. Collette, N. Martin, A. C. Robins, P. Fischione. *Ultramicroscopy* 107, 431 (2007).
- [11] J.C.H. Spence, *Experimental High Resolution Electron Microscopy*, Oxford University Press, Oxford, 1989.
- [12] M. Lentzen, B. Jahnen, C. L. Jia, A. Thust, K. Tillmann, and K. Urban, *Ultramicroscopy* 92, 233 (2002).
- [13] D. S. Su, et al. *Angew. Chem.-Int. Ed.* 47, 5005 (2008).
- [14] M. Małacka and L. Kępiński, *J. Microscopy-Oxford* 237, 282 (2010).
- [15] J. Liu, in *Nanotechnology in Catalysis* (B. Zhou, S. Hermans and G. Somorjai eds.) vol 2, Kluwer Academic, New York 2004, p. 361.
- [16] P.A. Gai and E.D. Boyes, *Microscopy Research and Technique*, 72, 153 (2009).
- [17] A.H. Zewail and J.M. Thomas, *4D Electron Microscopy: Imaging in Time and Space*, Imperial College Press, London 2009.

CURRICULUM VITAE



Leszek Kępiński. Born in Wrocław, Poland in 1953. Diploma in Electronics from Wrocław University of Technology. Ph.D. in Physics in 1980 and D.Sc. degree (Habilitation) in Chemistry in 2000 from the Institute of Low Temperature and Structure Research of Polish Academy of Sciences in Wrocław. Since 2000 he is an Associate Professor of Chemistry and since 2003 head of the Division of Nanomaterials Chemistry and Catalysis and the Laboratory of Electron Microscopy in the Institute of Low Temperature and Structure Research of Polish Academy of Sciences in Wrocław. Member of Polish Chemical Society and Polish Catalysis Club.

His activity is focused on experimental studies on the relationship between microstructure and chemical activity of highly dispersed systems: thin metal film, heterogeneous catalysts and nanoparticles. He is the author of more than 100 papers the peer-reviewed journals.