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"Gh. Asachi" Technical University of Iasi, Romania

Book Review

HANDBOOK OF HETEROGENEOUS CATALYSIS

Second, Completely Revised and Enlarged Edition
Volume 2

Gerhard Ertl, Helmuth Knözinger, Ferdi Schüth, Jens Weitkamp (Editors)

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The second volume of the *Handbook of Heterogeneous Catalysis* deals with the characterization of solid catalysts.

The characterization methods are grouped in two categories, devoted to the analysis of the physical and chemical properties, respectively. The third part of the second volume contains the IUPAC recommendations on the methodologies used for catalyst characterization.

The first group of methods for the characterization of the physical properties is focused on surface area and porosity. It is known that the textures of many catalysts and supports are extremely complex, and no single experimental technique is able to provide an evaluation of the "absolute" surface area. The BET-nitrogen method, widely used for determining the surface area of porous catalysts, is presented from a critical point of view. This method is considered appropriate for the characterization of mesoporous and macroporous materials while the data obtained for the microporous catalysts should be regarded only as an apparent or equivalent surface area. The recent developments based on advanced theoretical procedures, such as non-local density functional theory (NLDFT) and molecular simulation, for the nanopore size analysis are also presented. Mercury porosimetry, despite its drawbacks, is described as a standard method for investigating the macropore structure of a catalysts or support.

The methods for particle size and dispersion measurements are presented in the next chapter. Concerning particle size measurement both chemical and physical methods are described. Chemical methods, based on the determination of the amount of gas chemisorbed on the surface of particles, are widely used for metals and do not require expensive equipment or special skills. As far as physical techniques are concerned, emphasis is placed on electron microscopy, which is the most powerful method for particle size measurements. Techniques based on X-ray diffraction such as line broadening analysis (LBA) and small-angle X-ray scattering (SAXS) are also useful methods since they lead to both mean size and size distribution. The first method probes the crystallite sizes, whereas SAXS probes the particle sizes; these techniques are complementary since a particle can be polycrystalline. However, except from simplified LBA these methods are not in widespread use because they require special equipments and complicated calculations and are carried out only by a few specialists. Similar comments hold for particle size measurements by magnetic methods. These techniques are discussed in less detail than electron microscopy.

In the following chapter the methods employed for the characterization of the structure and morphology of the solid catalysts are described. The X-ray powder diffraction – an important characterization tool in catalysis - is shortly presented but the chapter contains many references for a more detailed description of this technique. In addition, XRD is presented as a powerful tool for in situ investigations of working catalysts, able to elucidate the structure and element composition of catalytically active phases.

The applications of X-ray Absorption Spectroscopy (XAS) in heterogeneous catalysis are focused on the extended X-ray absorption fine structure (EXAFS), atomic XAFS and delta XANES. This chapter describes the physical principles of XAS

at a sufficiently basic level to allow scientists working in catalysis to evaluate critically recent articles in the literature dealing with the application of the XAS in catalysis research. The three basic analysis techniques to unravel the structural, electronic and surface properties of heterogeneous catalysts are also described.

The next part, devoted to electron microscopy techniques, contains a description of the principal modes of operation of electron microscopes, as they are applied in the study of solid catalysts. Besides imaging techniques (TEM, SEM, STEM, ACEM, Electron tomography and holography, other electron microscopy methods, such as electron diffraction and electron beam microanalysis are also presented. The final part deals with the application of electron microscopy *in situ*. Each method is illustrated with examples showing how this technique yields information about solid catalysts. Thus, the selection of topics is limited to those which are most relevant to the study of catalysts.

The next chapter, on scanning probe methods (SPM) , describes the basic principles and the mode of operation behind the scanning tunnelling microscope (STM) and atomic force microscopy (AFM) techniques, and the framework needed to understand the electronic and geometric information contained in SPM images. The importance of electric fields in chemical systems and in heterogeneous catalysis is outlined in the following chapter. Experimental methods that display ultimate detection limits of individual atoms and molecules in both imaging and chemical probing are clearly presented. Different applications, including studies on surface morphology, surface mobility, reaction mechanisms and kinetic and field effects are also reported. Among these methods, the application of field electron microscopy (FEM) and field ion microscopy (FIM) to image spatio-temporal patterns with nanoscale resolution is opening new perspectives for further studies. Mössbauer spectroscopy and time-differential perturbed angular correlation (TDPAC) belong to a class of techniques which detect solid-state properties mediated by hyperfine interactions via nuclear spectroscopy. The application of Mössbauer spectroscopy to the study of iron-containing and – in the case of emission spectroscopy – also to cobalt-containing solid catalystsand to a lesser extent to catalysts containing tin, iridium, antimony and gold is presented in the first part. Then, the use of TDPAC to the study of molybdemun systems is also discussed.

The chapter devoted to solid-state NMR gives a brief review on the basic principles of the technique, methods of high resolution solid-state NMR and special techniques for the preparation of solid catalysts investigated by these methods. As a typical application of solid-state NMR spectroscopy in heterogeneous catalysis, investigations of solid catalysts by ^{29}Si, ^{27}Al and ^{17}O NMR spectroscopy are demonstrated. A further objective of this chapter is the description of *in situ* NMR experiments that allow one to study the mechanisms of heterogeneously catalyzed reactions. Throughout the chapter, special attention has been devoted to the applications of zeolites as solid catalysts.

The next chapter outlines the opportunities of vibrational spectroscopies (infrared transmition-absorption, diffuse-reflectance, infrared emition, laser Raman spectroscopies etc) that can be used for the structural characterization of catalytic materials. Representative examples for the characterization of selcted materials such as bulk oxides (binary oxides, multicomponenet materials, zeolites and molecular sieves) and supported catalysts are presented. In the following chapter on neutron scattering, apart from its well-known application in structure determination, recent developments in inelastic and quasi-elastic scattering are presented as new possibilities to probe molecular motion at microscopic level. In the next chapter the methods for the identification of the morphological characteristics of solid catalysts, covered hierarchically by many orders of magnitude from nanometers to millimeters, are discussed. Eggshell morphology and the special case of a monolith are discussed in detail. The first part, dedicated to the characterization of the physical properties of a solid catalyst, end with a short description of some important mechanical characteristics.

The second part, dealing with the chemical properties of heterogeneous catalysts, starts with the methods used for the determination of the bulk chemical composition of catalytic materials. Bulk sampling procedures and the typical instrumental methods for the determination of the bulk chemical composition of catalysts are shortly described. Next, the pertinent techniques for analyzing the chemical composition of solid surfaces are described. These are grouped in electron spectroscopies (AES, XPS), ion-scattering spectroscopies (LEIS, ISS, RBS) and spectroscopic methods analyzing secondary particles (SIMS, SNMS, LAMMA).

In the next chapter the characterization of the chemical states of solids and their surfaces by different instrumental methods is presented in detail. Five categories of methods are discussed and the typical information specific for each method are clearly outlined: electron spectroscopies (XPS, AES), UV-VIS-NIR and EPR spectroscopies, photoluminescence spectroscopy, Muon spin spectroscopy and temperature-programmed reduction and oxidation.

The acidity and basicity of solid catalysts is an important topic in heterogeneous catalysis and is covered in detail. After an introductory part presenting the concepts of acidity-basicity, different well-established techniques are described. The sub-chapter on termochemical characterization covers the temperature-programmed desorption (TPD) and adsorption microcalorimetry. Both methods employ probe molecules to examine interactions of surfaces with gas or liquid-phase molecules. Infrared spectroscopy of adsorbed probe molecules is shown to provide information on the intensive and extensive

properties of solid acids and bases when appropriate probe molecules are used. Finally, the use of NMR spectroscopy for the characterization of Bronsted acid sites, Lewis acid sites and base sites, either directly or by application of probe molecules is reviewed. It is shown that solid-state NMR spectroscopy allows the determination of the type, strength, accessibility and concentration of surface sites. By using sophisticated one and two-dimensional solid-state NMR techniques, structural parameters are also available. The next part is focused on active phase-support interactions and two special cases are presented in detail: metal-support and oxide-support interactions.

The topic of carbonaceous deposits and catalyst coking is presented in the following chapter. The broad spectrum of analytical methods applied to study the physico-chemical properties of coke on and inside catalysts, such as analytical chemistry methods, spectroscopic and surface science techniques, chromatographic and kinetic studies and online process control, is reviewed under this chapter.

In the last part of the second volume includes some important IUPAC recommendations for reporting physisorption data for gas-solid systems and for the methods and procedures for catalysts characterization. The objective is to provide recommendation on methodology (rational approaches to preparation and measurement) and not to provide specific methods for preparation or measurements.

Cezar Catrinescu
Department of Environmental Engineering and Management
Technical University of Iasi