Characterization of Nanostructured Catalysts

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Most of the catalysts used in the chemical industry are high-surface-area solid onto which an active component is dispersed in the form of very small particles. These particles have dimension of 1 to 20 nm and often referred to as nanoparticles. The rapid developments in atomic-resolution electron microscopy over the last decade have revolutionized the understanding of catalyst structures at the nanoscale. Modern catalysis laboratories now routinely utilize a broad suite of characterization methods such as scanning and transmission electron microscopy and scanning transmission electron microscopy. Major progress has been made in characterizing catalysts in their working state, not simply prior to or after a catalytic reaction, with increased realization that catalysts are highly dynamic solids that often restructure under reaction conditions. In this chapter we will discuss about microscopy techniques used for characterization of catalyst.

Keywords: Catalyst; Nanoparticle; TEM; SEM; STEM etc.

1. Introduction

Most catalysts are fine powder; consist of either one or more phase or of metal (bi-, tri-metallic) components on large-area. These particles have dimension of 1 to 20 nm. These catalyst particles are distributed over the internal surface of the substrate. Mostly substrates are structurally non-uniform because supported metal particles are small and irregular in size and shape. When these catalysts are used in the catalytic reaction, activity and selectivity are the two important parameter that indicates the effectively of the catalyst.

Characterization is a central aspect of catalyst development [1-3]. The elucidation of the structure, composition, and chemical properties of both the solids used in heterogeneous catalysis and the adsorbates and intermediates present on the surfaces of the catalysts during reaction is vital for a better understanding of the relationship between catalyst properties and catalytic performance. This knowledge is essential to develop more active, selective, and durable catalysts, and also to optimize reaction conditions [2-4].

Important parameters of catalyst, like texture and chemical surface, are determined to able to relate their catalytic activity to their properties. Thus characterization of catalysts becomes a key point in any study in the field of catalysis. Thus this chapter discusses the several techniques available for the study of both structural and textural characteristics and to analyze the data derived from them [4].

2. Characterization Techniques

2.1 Electron Microscopy

Electron microscopy (EM) is a straightforward technique useful for the determination of themorphology and size of solid catalysts [1-6]. Electron microscopy can be performed in one of two modes.

Scanning Electron Microscopy (SEM)

Morphology of catalysts on the nanometer and micrometer scale can be characterized SEM and get 3-D image of the surface. An extremely fine beam of electron is directed at the specimen, scanning across the specimen by the scan coils. In scanning electron microscopy (SEM), the yield of either secondary or back-scattered electrons is recorded as a function of the position of the primary electron beam, and the contrast of the signal used to determine the morphology of the surface: the parts facing the detector appear brighter than those pointing away from the detector [5]. Dedicated SEM instruments can have resolutions down to 5 nm; but in most cases, SEM is only good for imaging catalyst particles and surfaces of micrometer dimensions. Additional elemental analysis can be added to SEM via energy-dispersive analysis of the x-rays (EDX) emitted by the sample [4-6].

Transmission electron microscopy (TEM)

The internal structure of solids and their microstructural and ultrastructure detail are able to be probed by Transmission electron microscopy (TEM). TEM resembles optical microscopy, except that electromagnetic instead of optical lenses are used to focus an electron beam on the sample. An electron gun at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. A system of condenser lenses demagnifies the beam emitted by the gun and controls its diameter as it hits the specimen. The specimen should be thin enough to transmit the electron

beam. The objective lenses form an intermediate magnified image, which is enlarged by the subsequent projector lenses on a fluorescent screen. The image can be visualized by the operator or photographed with a camera. Two modes are available in TEM, a bright-field mode where the intensity of the transmitted beam provides a two dimensional image of the density or thickness of the sample, and a dark-field mode where the electron diffraction pattern is recorded. A combination of topographic and crystallographic information, including particle size distributions, can be obtained in this way [3, 7, 8].

2.2 X-Ray diffraction

X-ray diffraction (XRD) is commonly used to determine the bulk structure and composition of heterogeneous catalysts with crystalline structures [1-4, 9, 10]. Because most catalysts are in the form of polycrystalline powders, the XRD analysis is typically limited to the identification of specific lattice planes that produce peaks at their corresponding angular positions 2θ, determined by Bragg's law, $2d \sin \theta = n\lambda$. In spite of this limitation, the characteristic patterns associated with individual solids make XRD quite useful for the identification of the bulk crystalline components of solid catalysts [2-4].

X-ray diffraction can also be used to estimate the average crystallite or grain size of catalysts [9,10]. The XRD peaks are intense and sharp only if the sample has sufficient long-range order, and become broader for crystallite sizes below about 100 nm. Average particle sizes below about 60 nm can be roughly estimated by applying the Debye–Scherrer equation, $D = 0.89\lambda/(B_0^2 - B_e^2)^{1/2}\cos\theta$, where B_0 is the measured width (in radians) of a diffraction line at half-maximum, and B_e the corresponding width at half-maximum of a well-crystallized reference sample [14,20, 21]. In spite of the large success of XRD in routine structural analysis of solids, this technique does present some limitations when applied to catalysis [9, 10].

X- ray powder diffraction patterns of samples were collected in a diffectometer using nickel filtered Cu-Kα radiation ($\lambda = 0.15406$ nm). Data were collected in the 2θ range of 10- 70 degrees. The crystalline phase was identified by using the diffraction pattern of Joint Commettee on Powder Differection Standards (JCPDS) of the International Centre for Diffraction Data (ICDD). First, it can only detect crystalline phases,and fails to provide useful information on the amorphous or highly dispersed solid phases so common in catalysts [10]. Second, due to its low sensitivity, the concentration of the crystalline phase in the sample needs to be reasonably high in order to be detected. Third, XRD probes bulk phases, and is not able to selectively identify the surface structures where catalytic reactions take place. Finally, XRD is not useful for the detection of reaction intermediates on catalytic surfaces.

2.3 Fourier-transform infrared spectroscopy (FTIR)

In catalysis, infrared (IR) spectroscopy is commonly used to characterize specific adsorbates. Because of the localized nature and particular chemical specificity of molecular vibrations, IR spectra are quite rich in information, and can be used to extract or infer both structural and compositional information on the adsorbate itself as well as on its coordination on the surface of the catalyst. In some instances, IR spectroscopy is also suitable for the direct characterization of solids, especially if they can be probed in the far-IR region [4, 11].

Several working modes are available for IR spectroscopy studies [11]. The most common arrangement is transmission, where a thin solid sample is placed between the IR beam and the detector; this mode works best with weakly absorbing samples. Diffuse reflectance IR (DRIFTS) offers an alternative for the study of loose powders, strong scatters, or absorbing particles. Attenuated total reflection (ATR) IR is based on the use of the evanescent wave from the surface of an optical element with trapezoidal or semispherical shape, and works best with samples in thin films. Reflection–absorption IR spectroscopy (RAIRS) is employed to probe adsorbed species on flat reflecting surfaces, typically metals. In the emission mode, the IR signal emanating from the heated sample is recorded. Finally, both photoacoustic (PAS) and photothermal IR spectroscopies rely on temperature fluctuations caused by radiation of the sample with a modulated monochromatic beam. The availability of all these arrangements makes IR spectroscopy quite versatile for the characterization of catalytic systems.

The applications of IR spectroscopy in catalysis are many. For example, IR can be used to directly characterize the catalysts themselves. This is often done in the study of zeolites, metal oxides, and heteropolyacids, among other catalysts [11]. Further catalyst characterization can be carried out by appropriate use of selected adsorbing probes [11]. For instance, the acid–base properties of specific surface sites can be tested by recording the ensuing vibrational perturbations and molecular symmetry lowering of either acidic (CO and CO_2) or basic (pyridine and ammonia) adsorbates. Another common application of IR is to characterize reaction intermediates on the catalytic surfaces, often *in situ* during the course of the reaction [2-4, 11].

New directions have been recently advanced in the use of IR spectroscopy for the characterization of adsorbates, including the investigation of liquid–solid interfaces *in situ* during catalysis. Both ATR [2-4] and RAIRS [2-4] have been recently implemented for that purpose. RAIRS has also been used for the detection of intermediates on model surfaces *in situ* during catalytic reactions [11]. The ability to detect monolayers *in situ* under catalytic environments on small-area samples promises to advance the fundamental understanding of surface catalytic reactions.

2.4 Temperature-Programmed Desorption and Reaction

When probes with specific adsorption characteristics are used, additional chemical information can be extracted from adsorption–desorption experiments. Temperature-programmed desorption (TPD), in particular, is often employed to obtain information about specific sites in catalysts [4, 12]. The temperature at which desorption occurs indicates the strength of adsorption, whereas either the amount of gas consumed in the uptake or the amount of desorption upon heating attests indicates the concentration of the surface sites. The most common molecules used in TPD are NH_3 and CO_2, which probe acidic and basic sites, respectively, but experiments with pyridine,O_2, H_2, CO, H2O, and other molecules are often performed as well [12]. As an example, the Ammonia [12].

Some solid samples may decompose or react with the probe molecules at elevated temperatures, causing artifacts in the TPD profiles [12]. However, this conversion can in some instances be used to better understand the reduction, oxidation, and reactivity of the catalyst. In this mode, the technique is often called temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), or, in general, temperature-programmed surface reaction (TPSR or TPR) [1-4, 12]. The principles of TPR, TPO, and TPSR are similar to those of TPD, in the sense that either the uptake of the reactants or the yields of desorption are recorded as a function of temperature. Nevertheless, there can be subtle differences in either the way the experiments are carried out or the scope of the application. TPSR in particular often requires the use of mass spectrometry or some other analytical technique to identify and monitor the various species that desorb from the surface.

These TPD techniques reflect the kinetics (not thermodynamics) of adsorption, and are quite useful for determining trends across series of catalysts, but are often not suitable for the derivation of quantitative information on surface kinetics or energetics, in particular on ill-defined real catalysts. Besides averaging the results from desorption from different sites, TPD detection is also complicated in porous catalysts by simultaneous diffusion and re-adsorption processes [12].

2.5 Thermogravimetry and Thermoanalysis

Changes in catalysts during preparation, which often involves thermal calcination, oxidation, and reduction, can also be followed by recording the associated variations in sample weight, as in normal thermogravimetry (TG) or differential thermogravimetry (DTG); or in sample temperature, as in differential thermal analysis (DTA) [3, 4]. Although these thermal methods are quite traditional, they are still used often in catalysis research.

Besides the prediction of calcination temperatures during catalyst preparation, thermal analysis is also used to determine the composition of catalysts based on weight changes and thermal behavior during thermal decomposition and reduction, to characterize the aging and deactivation mechanisms of catalysts, and to investigate the acid–base properties of solid catalysts using probe molecules. However, these techniques lack chemical specificity and require corroboration by other characterization methods.

2.6 Raman Spectroscopy

Raman spectroscopy offers an alternative for the vibrational characterization of catalysts, and has been used for the study of the structure of many solids, in particular of oxides such as MoO_3, V_2O_5, oxides such as SiO_2, Al_2O_3, and zeolites give low Raman signals, this technique is ideal for the identification of oxygen species in covalent metal oxides. Surface-enhanced Raman spectroscopy (SERS) has also been employed to characterize metal catalyst surfaces [13]. The low sensitivity and severe conditions required for the signal enhancement have limited the use of this technique [14], but some interesting work has been published over the years in this area, including studies on model liquid–solid interfaces [13, 14].

Raman spectroscopy does suffer from some severe limitations. For example, Raman intensities of surface species are often quite low. Also, the high laser powers needed for Raman characterization tend to heat the sample, and often cause changes in the physical properties of the solid. Finally, strong sample fluorescence typically masks the weaker Raman signals [14]. Fortunately, some of these difficulties have been recently minimized via the implementation of Fourier transform [1-4, 13, 10] and UV [13, 14] Raman spectroscopy arrangements. There are also new efforts new on the use of Raman spectroscopy *in situ* and under *operando* (in conjunction with activity measurement) conditions [13, 14].

2.7 Ultraviolet–Visible Spectroscopy

Compared with IR and Raman spectroscopies, ultraviolet–visible (UV–Vis) spectroscopy has had only limited use in heterogeneous catalysis. Nevertheless, this spectroscopy can provide information on concentration changes of organic compounds dissolved in a liquid phase in contact with a solid catalyst, be used to characterize adsorbates on catalytic surfaces, provide information on the absorption spectra and band gap of photocatalysts, or map the electronic structure of transition metal cations in inorganic materials [1–4]. Figure 1.15 displays an example where Cr^{3+} andCr^{6+} species in calcined, hydrated, and reduced chromia/alumina catalysts are differentiated by UV–Vis [15]. This information was used to optimize the preparation method for Cr^{6+}-based catalysts for alkane dehydrogenation.

The main drawback of the use of UV–Vis spectroscopy for catalyst characterization is that the data commonly show broad and overlapping absorption bands with little chemical specificity. Also, it is often quite difficult to properly interpret the resulting spectra. Lastly, quantitative analysis is only possible at low metal oxide loadings [15].

2.8 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is most frequently used to analyze liquid samples, but in the magic angle spinning (MAS) mode, this spectroscopy can also be employed to characterize solid catalysts, zeolites in particular [2-4, 16–17]. For example, the 29Si NMR signal can be used to determine the coordination environment of Si in the framework of the zeolite, taking advantage of the fact that the coordination of each additional Al atom to a given Si center results in a shift of about 5 to 6 ppm from the original peak position in $Si(OSi)_4$ at - 102 to - 110 ppm [16, 17].

Nuclear magnetic resonance is certainly a versatile analytical tool with wide applicability to catalysis. Nevertheless, it does have some notable shortcomings. For example, NMR is not a very sensitive spectroscopy technique, and requires catalytic samples with high surface areas. This is often not a big problem, given that most catalytic phases are highly dispersed, but these too have a large number of types of sites, which get averaged in the NMR spectra. In addition, different NMR peaks may overlap in complex mixtures of reactants, intermediates, and products, making the analysis of catalytic systems difficult [17].

2.9 Electron Spin Resonance

Electron spin resonance (ESR), also called electron paramagnetic resonance (EPR), is used in heterogeneous catalysis to study paramagnetic species containing one or more unpaired electrons, either catalytic active sites or reaction intermediates [18,19]. For instance, a number of ESR studies have been dedicated to the detection and characterization of oxygen ionic surface species such as O_2^-, O^-, O_2^{2-}, and O^{2-}, key intermediates in catalytic oxidation processes [4, 18, 19]. Another important use of ESR in catalysis is for the study of the coordination chemistry of transitionmetal cations incorporated into zeolites or metal oxides [18, 19].

Special spin-trapping techniques are also available for the detection of short-lived radicals in both homogeneous and heterogeneous systems. For instance, _-phenyl *N-tert*-butyl nitrone (PBN), *tert*-nitrosobutane (*t*-NB), _-(4-pyridyl *N*-oxide) *N-tert*-butyl nitrone (4-POBN), or 5,5-dimethyl-1- pyrroline *N*-oxide (DMPO) can be made to react with catalytic intermediates to form stable paramagnetic adducts detectable by ESR [18]. Radicals evolving into the gas phase can also be trapped directly by condensation or by using matrix isolation techniques [19].

Although ESR has the advantage over NMR of its high sensitivity toward low concentrations of active sites and intermediates, this method is only applicable to the characterization of paramagnetic substances. In addition, the widths of the ESR signals increase dramatically with increasing temperature, making the *in situ* characterization of catalytic systems at reaction temperatures difficult. Finally, ESR methods cannot distinguish surface and bulk species [18, 19].

2.10 X-Ray and Ultraviolet Photoelectron Spectroscopies

X-ray photoelectron spectroscopy (XPS) is a useful technique to probe both the elemental composition of the surface of catalysts and the oxidation state and electronic environment of each component [4, 20, 21]. Qualitative information is derived from the chemical shifts of the binding energies of given photoelectrons originating from a specific element on the surface: in general, binding energies increase with increasing oxidation state, and to a lesser extent with increasing electronegativity of the neighboring atoms. Quantitative information on elemental composition is obtained from the signal intensities. The principles of ultraviolet photoelectron spectroscopy (UPS) are similar to those of XPS, except that ultraviolet radiation (10 to 45 eV) is used instead of soft x-rays (200 to 2000 eV), and what is examined is valence rather than core electronic levels [20, 21].

X-ray photoelectron spectroscopy is indeed quite informative, but requires the use of expensive instrumentation. Also, the detection of photoelectrons requires the use of ultrahigh vacuum, and therefore can only be used for *ex situ* characterization of catalytic samples (although new designs are now available for *in situ* studies [1-4, 20, 21]). Finally, XPS probes the upper 10 to 100 Å of the solid sample, and is only sensitive to the outer surfaces of the catalysts. This may yield misleading results when analyzing porous materials.

2.11 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is based on the ejection of the so-called Auger electrons after relaxation of photoionized atoms. This technique is quite complementary to XPS, and also provides surface-sensitive information on surface compositions and chemical bonding [1-4].

As opposed to XPS, AES signals typically exhibit complex structure, and sometimes require elaborate data treatment.

Also, AES does not easily provide information on oxidation state, as XPS does. On the other hand, AES is often acquired by using easy-to-focus electron beams as the excitation source, and can therefore be used in a rastering mode for the microanalysis of nanosized spots within the surface of the catalyst. Given their different sampling depths, XPS and AES can also be combined to obtain a better picture of the profile of the different elements in the solid as a function

of distance from the surface. The latter task can be aided by adding sputtering capabilities to the experimental setup [22].

2.12 Secondary-Ion Mass Spectroscopy

Secondary-ion mass spectroscopy (SIMS) is based on the mass spectrometric detection of the secondary ions emitted upon bombardment of the sample with a primary ion beam. The composition of the ion clusters detected provides an indication of the molecular arrangement of the atoms on the surface [1-4, 23]. SIMS experiments may be performed in one of two modes— static, where a low sputtering rate is used in order to analyze the top most surface, and dynamic, in which case the primary ion current density is sufficient to erode the surface for depth profile analysis.

Although SIMS can provide quite valuable information on the molecular (rather than atomic) composition of the surface, this is a difficult technique to use. Moreover, the resulting spectra are complex, and quantification of the data is almost impossible. To date, SIMS remains a special and seldom-used technique for catalyst characterization [23].

3. Conclusion

In this chapter, we have briefly introduced a selection of techniques used to characterize catalysts. Only the most common and useful techniques have been reviewed since a comprehensive list of all the characterization methods available would be never ending. Moreover, although modern surface science studies with model catalysts were only mentioned briefly toward the end of the review, this in no way suggests that these are of less significance. In fact, as the ultimate goal of catalyst characterization is to understand catalytic processes at a molecular level, surface studies on well-defined model catalysts is poised to be central in the future of the field.

References

[1] Weckhuysen BM (Ed.), In-Situ Spectroscopy of Catalysts, American Scientific Publishers, StevensonRanch, 2004.

[2] Haber J, Block JH, Delmon B, Methods and Procedures for Catalyst Characterization Part 3. Characterization of Solid Catalysts, 2008 Wiley-VCH Verlag GmbH & Co. KGaA. DOI: 10.1002/9783527610044.hetcat0066.

[3] Imelik B, Vedrine J C. (Eds.) Catalyst Characterization Physical Techniques for Solid Materials, 1994 ISBN 978-1-4757-9589-9 Springer.

[4] Leofanti G, Tozzola G, Padovan M, Petrini G, Bordiga S, Zecchina A, Catalyst characterization: characterization techniques, Catalysis Today, Ch 4, 34, 1997; 307-327.

[5] Lomić GA, Kiš EE, Bošković GC and Marinković-Nedučin RP, APPLICATION OF SCANNING ELECTRON MICROSCOPY IN CATALYSIS; BIBLID: 1450–7188, 2004, 35, 67-77.

[6] Otto TN, Habicht W., Dinius E, Zimmerman M, Catalyst Characterization with FESEM/EDX by the Example of Silver-Catalyzed Epoxidation of 1,3-Butadiene, "Scanning Electron Microscoopy" Viachelav Kazmiruk (Eds) 2012; ISBN 978-953-51-0092-8.

[7] Bele P and Stimming U, Advanced TEM Characterization for Catalyst Nanoparticles Using Local Adaptive Threshold (LAT), Image Processing MRS Proceedings, Volume 1184 January 2009; 1184-HH01-05.

[8] Villa A Dimitratos N, Chan-Thaw CE, Hammond C, Veith GM, Wang D, Manzoli M, Prati L and Hutchings GJ, Characterisation of gold catalysts, *Chem. Soc. Rev.*, 45, 2016; 4953-4994.

[9] Rioux RM, Song H, Hoefelmeyer JD, Yang P, and Somorjai GA, High-Surface-Area Catalyst Design: Synthesis, Characterization, and Reaction Studies of Platinum Nanoparticles in Mesoporous SBA-15 Silica; *J. Phys. Chem. B, 109,* 2005; 2192-2202.

[10] Beale AM, Stavitski ES, Weckhuysen BM (2015). Characterization of catalysts: Surface and in-situ methods. Encyclopedia of life support systems (EOLSS). Available at: http://www.eolss.net/samplechapters/c06/e6-190-13-00.pdf Retrieved on 9/04/2015.

[11] Zaera F, New advances in the use of infrared absorption spectroscopy for the characterization of heterogeneous catalytic reactions Chem Soc Rev. 2014 21;43(22):7624-63.

[12] Di Cosimo JI, Díez VK, Ferretti C and Apesteguía CR, Chapter 1 : Basic catalysis on MgO: generation, characterization and catalytic properties of active sites, in *Catalysis: Volume 26*, 2014, **26**, pp. 1-28 DOI: 10.1039/9781782620037-00001eISBN:978-1-78262-003-7 From Book Series : SPR - Catalysis.

[13] Bañares MA, Mestl G, Chapter 2 Structural Characterization of Operating Catalysts by Raman Spectroscopy Advances in Catalysis; 52, 2009; 43–128.

[14] Mestl G, *In situ* Raman spectroscopy for the characterization of MoVW mixed oxide catalysts, Journal of Raman Spectroscopy, 33 (5) 2002; 333–347.

[15] Tabares Suarnaba EG, Lee YF; Yamada H, Tagawa T; Ultraviolet–Visible (UV-Vis) Microspectroscopic System Designed for the In Situ Characterization of the Dehydrogenation Reaction Over Platinum Supported Catalytic Microchannel Reactor, 2016, doi:10.1177/0003702816671071.

[16] Zheng A, Liu SB, Deng F. Acidity characterization of heterogeneous catalysts by solid-state NMR spectroscopy using probe molecules.Solid State Nucl Magn Reson. 2013; 55-56:12-27.

[17] Lang S, Benz M, Obenaus U, Himmelmann R, Hunger M, Novel Approach for the Characterization of Lewis Acidic Solid Catalysts by Solid-State NMR Spectroscopy *ChemCatChem* 8, 2016; 2031.

[18] Shukla AK (Eds) EMR/ESP/EPR Spectroscopy for Characterization of Nanomaterials; Vol 62 of advanced structured Materials, Springer, 2016; ISBN 813226556, 9788132236559.

[19] Narayana KV, B David Raju BD, Masthan SK, V Venkat Rao VV, P Kanta Rao PK, Subrahmanian R, Martin A, ESR spectroscopic characterization of V_2O_5/AlF_3 ammoxidation catalysts, Catalysis Communications, 5 (8) 2004; 457–462.

[20] Cheng DG, Chong M, Chen F, Zhan X, XPS Characterization of CeO2 Catalyst for Hydrogenation of Benzoic Acid to Benzaldehyde; Catalysis Letters, 120 (1) 2008; 82–85.

[21] Venezia AM, X-ray photoelectron spectroscopy (XPS) for catalysts characterization, Catalysis Today, 77 (4) 2003; 359–370.

[22] Riviere JC, Myhra S (Eds) Handbook of Surface and Interface Analysis: Methods for Problem-Solving II Edition; 2009 by CRC Press ISBN 9781420007800.

[23] Hofmann JP, Rohnke M, Weckhuysen BM, Recent advances in secondary ion mass spectrometry of solid acid catalysts: large zeolite crystals under bombardment., Phys Chem Chem Phys. 28, 16(12), 2014; 5465-74.