



Recent research advances and critical assessment of methods to determine the particle size in supported metals



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ABSTRACT

Physicochemical characterization of catalysts in surface and bulk manners is an area of vital importance in experimental heterogeneous catalysis. The knowledge of physicochemical properties such as overall surface area (internal and external), pore size distribution (distribution of micro-, meso-, and macro-pores) and pore volume, elemental composition, particle size and dispersion (and active metal surface area), coupled with the chemical surface reactivity, acid-base characteristics, and surface structures/bonding of the adsorbates, etc., enables one to decipher the important structure-property-performance relationships, or, the catalytic performance as a function of the physicochemical properties, as well as elucidate the reaction mechanisms and catalytic turnover cycles, to be able to design better (i.e., more efficient and chemo-selective) catalysts. The basic principles of characterization including physisorption, chemisorption, temperature-programmed techniques, X-ray techniques, analytical electron microscopy, and vibrational spectroscopies, are all drivers for development of a complete collage or suite of physicochemical properties, important for structure-property-performance relationships.

A critical assessment first and then a comparative evaluation of the different methods available currently for the determination of metal particle size in supported metals is given. The determination of metal particle size is important to evaluate the so-called structure sensitivity of chemo-catalytic reactions. The methods that are currently available include substrate-specific selective chemisorption of suitable probe molecules, X-ray powder diffraction, analytical high-resolution transmission electron microscopy (in bright and dark field), small-angle X-ray scattering (SAXS and ASAXS) and X-ray absorption spectroscopy (XAS). Based on the state-of-the-art, selective chemisorption is perhaps the most sensitive technique, as all atoms are probed at the atomic level, independent of the crystallite size. Selective chemisorption also yields a surface-averaged particle size, which is more pertinent from the standpoint of catalytic science; X-ray diffraction and TEM measurements give volume- and particle number-averaged particle sizes. Some recent advances in the determination of particle sizes and in-situ evolutions of particle size distributions, structure of the metal-support interface, and the electronic properties of small metal clusters are also discussed.

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1. Introduction

Physicochemical characterization of catalysts in surface and bulk manners is an area of vital importance in experimental heterogeneous catalysis. The knowledge of physicochemical properties such as overall surface area (internal and external), pore size distribution (distribution of micro-, meso-, and macro-pores) and pore volume, elemental composition, particle size and dispersion (and active metal surface area), coupled with the chemical surface reactivity, acid-base characteristics, and surface structures/bonding of the adsorbates, etc., enables one to decipher the important structure-property-performance relationships, or, the catalytic performance as a function of the physicochemical properties, as well as elucidate the reaction mechanisms and catalytic turnover cycles, to be able to design better (i.e., more efficient and chemo-selective) catalysts. The basic principles of characterization including physisorption, chemisorption, temperature-programmed techniques (such as temperature-programmed desorption (TPD), temperature-programmed reduction (TPR), temperature-programmed oxidation (TPO), and temperature-programmed reaction (TPRe)), and X-ray techniques (such as X-ray diffraction (XRD), low energy electron diffraction (LEED), the several variants of X-ray absorption spectroscopy (XAS), such as extended X-ray absorption fine structure (EXAFS), XANES (X-ray absorption near edge spectra) and Quick EXAFS (or, QEXAFS), analytical electron microscopy, and vibrational spectroscopies, are all drivers for development of a complete collage or suite of physicochemical properties, important in catalyst design and in evaluation of structure-property-performance relationships [1–14].

The textural properties including surface area and pore size distribution (and porosity or pore volume) are important features of a catalyst or an inorganic support. The overall or total surface area is an important feature as it controls the accessibility (via pore architecture) of substrates to the active sites and is often related to the catalyst activity. For supported metals, the active metal components are distributed throughout the interpenetrating network of pores, in some manner (such as cherry or core and egg-shell (or, even uniform), as stated above). The size of the metal particles is important and a distinction and a definition of two specific subgroups is in order here. Metal particles dispersed in the size range of 1–5 nm are perhaps of the most interest in catalytic science studies as there is a marked sensitivity in this range of the reaction turnover frequency (the single most important arbiter of catalytic performance) to the particle size.

The focus of this article is to offer a critical assessment at first and then a comparative evaluation of the different methods currently available for the determination of metal particle size in supported metals. The determination of metal particle size is important to evaluate the so-called structure sensitivity of chemo-catalytic reactions. The methods that are currently available include substrate-specific selective chemisorption of suitable probe molecules, X-ray powder diffraction, analytical high-resolution transmission electron microscopy (in bright and dark fields), Small-angle X-ray scattering (SAXS), and X-ray absorption spectroscopy (XAS). The metal dispersion is defined as the fraction of the total metal atoms that reside on the surface, and are thus available for titration with a suitable probe molecule (adsorbate) such as H₂, CO, NO, and N₂O. Thus, the dispersion, D, can be determined by chemisorption measurements with adsorbates such as above that bind strongly to the metal atoms, but interact in a negligible way with the inorganic support. The values of dispersion enable one to calculate the average particle size which is related to the metal surface area. The structure-sensitivity of the chemical reactions can be assessed by the particle size effects, and thus the catalytic reactions as defined by the turnover fre-

quencies (TOF, s⁻¹) and areal rates (rates on the bases of metal surface areas) that are not a function of the particle size are termed as structure-insensitive (often termed as “facile”—but quite incorrectly, we believe). Of course, for reactions deemed to be structure-insensitive or facile from particle size studies, it is always a good practice to rule out confounding features such as experimental artifacts, metal-support interaction as a function of particle size, or even spillover, in some cases. The particle size distribution and average particle size can also be discerned by power X-ray diffraction (PXRD) and analytical electron microscopy (HRTEM), however, selective chemisorption is perhaps the most sensitive technique, as all atoms are probed at the atomic level, independent of the crystallite size. Thus, selective chemisorption methods are especially useful for highly dispersed catalysts, and offer the added benefit of being quick and inexpensive, compared to the other two. Selective chemisorptions also yields a surface-averaged particle size, which is more pertinent from the standpoint of catalytic science; X-ray diffraction and TEM measurements give volume- and particle number-averaged particle sizes.

2. Selective chemisorption

Chemisorption of H₂ is the most widely used method to determine dispersion, D, and the metal surface areas, and is studied on all Group VIII metals [15]. The adsorption is dissociative at 300 K for all metals, and is represented by the following stoichiometry:



The stoichiometry for Pt also follows the above equation, and adsorption values of H_{ads}/Pt_s are close to unity. However, it is instructive to note that the metal adsorption stoichiometries are frequently determined for bulk metals, i.e., large crystals that are not supported on any support. Thus, for small metal clusters and crystallites (0.1–2 nm), the adsorption stoichiometry value can increase, even to 2, because these atoms have low surface coordination numbers and reduced steric constraint. The diameter of the H₂ molecule is 2.89 Å or 0.29 nm, and thus for small crystallites of the order of 1–2 nm, it is conceivable that more than one H₂ atom can attach or adsorb on the surface metal atom. From a historical perspective, the use of selective chemisorption to measure active metal surfaces was first proposed and demonstrated by Emmett and Brunauer, on their studies on Fischer–Tropsch iron catalysts [5].

The representative adsorption isotherms of H₂ on Pt dispersed on Al₂O₃ are given in Fig. 1 [4]. Line 1 represents the total uptake (μmol/g) and saturation coverage is reached at pressures in excess of 200 Torr. In this range, the adsorption of H₂ on alumina support is represented by line 3, and is reflective of the weak and reversible adsorption in the Henry's law region. The difference isotherm, Line 2, is the adsorption of H₂ on Pt. It is interesting to note that most adsorbate/support systems follow Henry's law, and thus the line 1 isotherm can be extrapolated to zero pressure intercept to determine the adsorption/chemisorption on pure Pt. It should be noted that this does not represent gas uptake at zero pressure (as misstated sometimes, especially without “extrapolated”). The metal surface area, particle size, and dispersion are then assessed and calculated by the formulae given in prior works [4,15]. This requires a-priori knowledge or approximations of parameters such as site density or the number of surface metal atoms per unit area on the bases of some combinations of low-index planes for the metal structure, such as (1 1 1), (1 0 0), and (1 1 0) faces for an fcc metal such as Pt, area per metal atom, volume, and bulk density [15].

It is now instructive to look at some recent research reports that cover different aspects of these characterization analyses and their use in study of catalytic reactions. In one such study, the objective

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