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Introduction

Keywords

Heterogeneous catalysis
The aim of catalyst characterization
Spectroscopic techniques
Research strategies

1.1

Heterogeneous Catalysis

Today, catalysis plays a prominent role in our society, and the majority of all chemicals and fuels produced within the chemical industry has been in contact with one or more catalysts. In fact, catalysis has become indispensable in environmental pollution control, with selective catalytic routes replacing stoichiometric processes that generate waste problems. One clear example is the way in which a three-way catalyst leads to an effective reduction in the pollution from car engines, and catalytic processes to clean industrial exhaust gases have now been developed and installed. In short, whilst catalysis is vitally important for our economies of today, it will become increasingly important in the future.

A heterogeneous catalytic reaction begins with the adsorption of the reacting gases onto the surface of the catalyst, where intramolecular bonds are broken or weakened (exactly how this happens on metals in terms of simplified molecular orbital theory is explained in the Appendix). Next, the adsorbed species react on the surface, often in several consecutive steps. Finally, the products desorb from the surface into the gas phase, thereby regenerating the active sites on the surface for the following catalytic cycle. The function of the catalyst is to provide an energetically favorable pathway for the desired reaction, in which the activation barriers of all intermediate steps are low compared to the activation energy of the gas phase reaction. The sequence for the catalytic oxidation of carbon monoxide is illustrated schematically in Figure 1.1. Here, the key role of the catalyst is to dissociate the O_2 molecule, which occurs at the surface of many metals. For some introductory texts on the theory of catalysis, see [1–10].

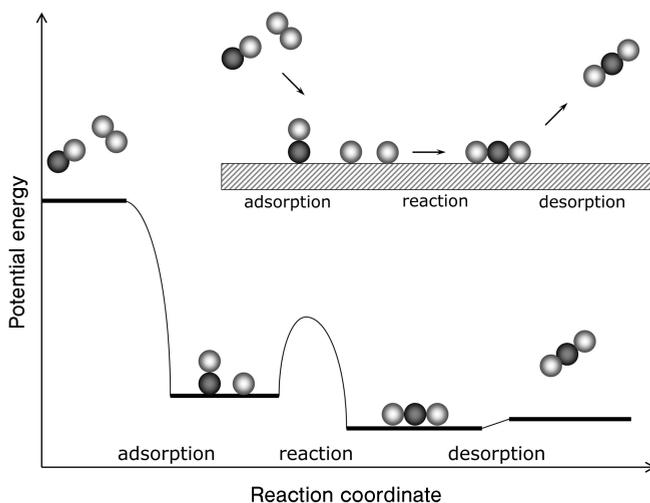


Fig. 1.1 Schematic representation of a well-known catalytic reaction, the oxidation of carbon monoxide on noble metal catalysts: $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$. The catalytic cycle begins with the associative adsorption of CO and the dissociative adsorption of O_2 onto the surface. As adsorption is always exothermic, the potential energy decreases. Next, CO and O combine to form an adsorbed CO_2

molecule, which represents the rate-determining step in the catalytic sequence. The adsorbed CO_2 molecule desorbs almost instantaneously, thereby liberating adsorption sites that are available for the following reaction cycle. This regeneration of sites distinguishes catalytic from stoichiometric reactions.

As catalysis proceeds at the surface, a catalyst should preferably consist of small particles with a high fraction of surface atoms. This is often achieved by dispersing particles on porous supports such as silica, alumina, titania or carbon (see Fig. 1.2). Unsupported catalysts are also in use; examples of these include the iron catalysts for ammonia synthesis and CO hydrogenation (the Fischer–Tropsch synthesis), or the mixed metal oxide catalysts used in the production of acrylonitrile from propylene and ammonia.

The important properties of small particles are defined in Figure 1.3. For unsupported catalysts and for support materials, it is necessary to know how much material is exposed to the gas phase. This property is expressed by the specific area, in units of $\text{m}^2 \text{g}^{-1}$. Typical supports such as silica and alumina have specific areas on the order of 200 to 300 $\text{m}^2 \text{g}^{-1}$, while active carbons may have specific areas of up to 1000 $\text{m}^2 \text{g}^{-1}$, or more. Unsupported catalysts have much lower surface areas, typically in the range of 1 to 50 $\text{m}^2 \text{g}^{-1}$.

Surface areas are determined by *physisorption*. The most common procedure to determine surface area is to measure how much N_2 is adsorbed onto a certain amount of material. The uptake is measured at a constant low temperature (i.e., 80 K) as a function of N_2 pressure, and is usually very well described by the Brunauer–Emmett–Teller (BET) isotherm. After determining the number of N_2

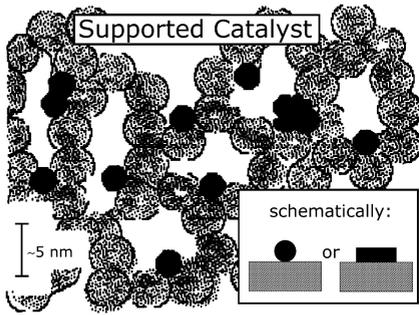


Fig. 1.2 An impression of a silica-supported catalyst. The inset shows the usual schematic representations.

molecules that form a monolayer on the support, one obtains the total area by setting the area of a single N_2 molecule to 0.16 nm^2 [11].

For particles on a support, dispersion is an important property, and is straightforwardly defined as the fraction of atoms in a particle located at the surface. The dispersion is usually determined by chemisorption of a gas that adsorbs only on the supported particles, and not on the support. For metals, hydrogen or CO are the obvious choices. It is necessary to adopt a certain stoichiometry for the number of H-atoms or CO molecules that can be accommodated per surface atom in the particle (this is usually taken as one CO or H-atom per metal atom) [11].

Supported catalysts can be prepared in several ways [12], but the simplest is that of *impregnation*. A support has a characteristic pore volume (e.g., 0.5 mL g^{-1}); hence, adding this volume of a solution containing the appropriate amount of a convenient catalyst precursor (e.g., nickel nitrate in water to prepare a supported nickel catalyst) to the support will simply fill all the pores. However, by allowing the system to dry, and then heating it in air to decompose any undesired salts, the supported material will be converted to the oxidic form. Reduction in hydrogen then converts the oxidic precursor – at least partially – into a supported metal catalyst.

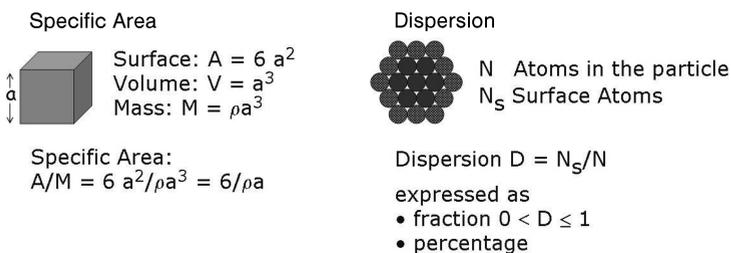


Fig. 1.3 Specific area and dispersion are important characteristic properties of a supported catalyst.

Catalysts may be metals, oxides, zeolites, sulfides, carbides, organometallic complexes, and enzymes [1–10]. The principal properties of a catalyst are its activity, its selectivity, and its stability. *Chemical promoters* may be added to optimize the quality of a catalyst, while *structural promoters* improve the mechanical properties and stabilize the particles against sintering. As a result, catalysts may be quite complex. The state of the catalytic surface often also depends on the conditions under which it is used, and in this respect spectroscopy, microscopy, diffraction and reaction techniques represent methods by which the appearance of the active catalyst can be investigated.

1.2 The Aim of Catalyst Characterization

The catalytic properties of a surface are determined by its composition and structure on the *atomic scale*. Hence, it is not sufficient to know that a surface consists of a metal and a promoter – perhaps iron and potassium – but it is essential to know the exact structure of the iron surface, including any defects and steps, as well as the exact location of the promoter atoms. Thus, from a fundamental point of view, the ultimate goal of catalyst characterization should be to examine the surface atom by atom, and under reaction conditions. The well-defined surfaces of single crystals offer the best perspectives for atom-by-atom characterization, although occasionally atomic scale information can also be obtained from real catalysts under *in-situ* conditions (for some examples, see Chapter 9). The many aspects that we need to study in order to properly understand supported catalysts on a fundamental level are shown schematically in Figure 1.4 [13].

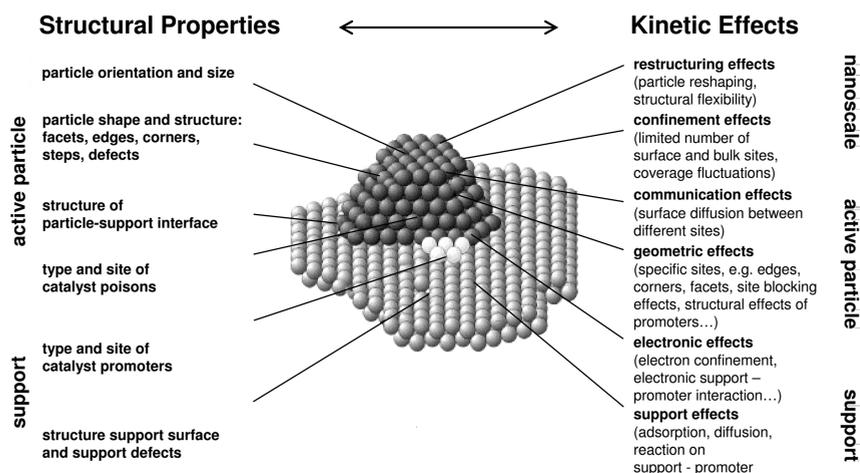


Fig. 1.4 Scheme of the many aspects of supported catalysts that call for characterization on the molecular level. (Adapted from [13]).

The industrial view on catalyst characterization is different, however. Here, the emphasis is placed mainly on developing an active, selective, stable and mechanically robust catalyst. In order to accomplish this, tools are needed which identify those structural properties that discriminate efficient from less-efficient catalysts, and all spectroscopic information that helps to achieve this is welcome. The establishment of empirical relationships between the factors that govern catalyst composition, particle size and shape and pore dimensions on the one hand, and catalytic performance on the other hand, are extremely useful in the process of catalyst development. However, such relationships may not provide much fundamental insight into how the catalyst operates in molecular detail.

Van Santen [14] identifies three levels of research in catalysis:

- The *macroscopic* level is the world of reaction engineering, test reactors and catalyst beds. Questions concerning the catalyst deal with such aspects as activity per unit volume, mechanical strength, and whether it should be used in the form of extrudates, spheres, or loose powders.
- The *mesoscopic* level comprises kinetic studies, activity per unit surface area, and the relationship between the composition and structure of a catalyst versus its catalytic behavior. Much of the characterization studies belong to this category.
- The *microscopic* level is that of fundamental studies, and deals with the details of adsorption on surfaces, reaction mechanisms, theoretical modeling, and surface science.

In simplifying, one could say that catalyst characterization in industrial research deals with the *materials science of catalysts* on a more or less mesoscopic scale, whereas the ultimate goal of fundamental catalytic research is to characterize the surface of a catalyst at the microscopic level – that is, on the *atomic* scale.

Catalyst characterization is a lively and highly relevant discipline in catalysis, with the literature revealing a clear desire to work with defined materials. For example, about 80% of the 143 oral reports at the 11th International Congress on Catalysis [15] contained at least some results on the catalyst(s) obtained by characterization techniques, whereas only 20% of these reports dealt with catalytic reactions over uncharacterized catalysts. Another remarkable fact obtained from these statistics is that about 10% of the reports included the results of theoretical calculations. Clearly, the modern trend is to approach catalysis from many different viewpoints, using a combination of sophisticated experimental and theoretical tools.

1.3 Spectroscopic Techniques

There are many ways to obtain information on the physico-chemical properties of materials. Figure 1.5 presents a scheme from which almost all techniques can be

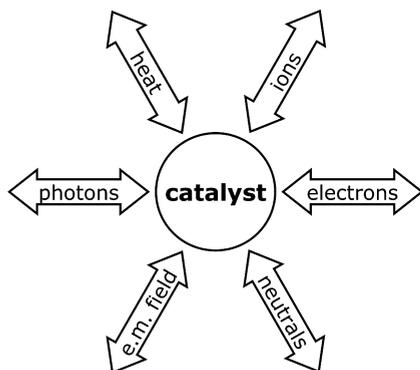


Fig. 1.5 Diagram from which most characterization techniques can be derived. The circle represents the sample under study, the inward arrow represents an excitation, and the outward arrow indicates how the information should be extracted.

derived. Spectroscopies are based on some type of excitation, represented by the in-going arrow in Figure 1.5, to which the catalyst responds, as symbolized by the outgoing arrow. For example, one can irradiate a catalyst with X-rays and study how the X-rays are diffracted (X-ray diffraction, XRD), or one can study the energy distribution of electrons that are emitted from the catalyst due to the photoelectric effect (X-ray photoelectron spectroscopy, XPS). One can also heat up a spent catalyst and examine which temperatures reaction intermediates and products desorb from the surface (temperature programmed desorption, TPD).

Characterization techniques become surface sensitive if the particles or radiation to be detected are derived from the outer layers of the sample. Low-energy electrons, ions and neutrals can only travel over distances of between one and ten interatomic spacings in the solid state, which implies that such particles leaving a catalyst may reveal surface-specific information. The inherent disadvantage of the small mean free path is that measurements must be carried out *in vacuo*, which conflicts with the wish to investigate catalysts under reaction conditions.

Photons that are scattered, absorbed or emitted by a catalyst form a versatile source of information. Figure 1.6 shows the electromagnetic spectrum, along with a number of techniques involving photons. In addition to the common sources of photons (lamps, lasers, helium discharge and X-ray sources) available for laboratory use, synchrotrons offer a broad spectrum of highly intense, polarized light. Electromagnetic radiation penetrates solids significantly, although if the solid responds by emitting electrons – as in the photoelectric effect – one obtains nevertheless surface-specific information.

In this book, we describe some of the most often-used techniques in catalyst characterization, and also provide some statistics showing how often certain methods have been described in the most important catalysis journals since 2002 (see Fig. 1.7) [16]. In the following chapters we will highlight those methods that have been particularly useful in studies of metal, oxide and sulfide catalysts, and re-

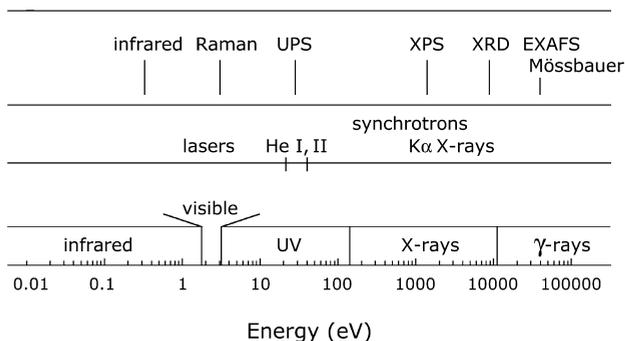


Fig. 1.6 The electromagnetic spectrum, along with common photon sources and a number of characterization techniques based on photons.

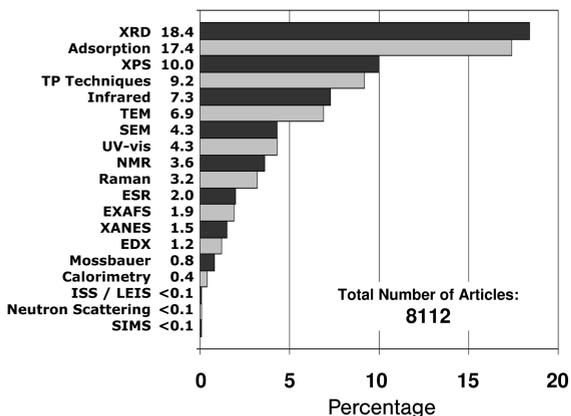


Fig. 1.7 Percentage of articles in *Applied Catalysis A and B*, *Catalysis Letters* and *Journal of Catalysis* between 2002 and 2006 (end October) that cite results obtained with various characterization techniques. Typical surface-science methods have been excluded. (Reproduced from [16]).

ISS: ion-scattering spectroscopy; LEIS: low-energy ion scattering; SEM: scanning electron microscopy; SIMS: Secondary ion mass spectrometry; TEM: transmission electron microscopy; TP: temperature-programmed; XANES: X-ray absorption near edge spectroscopy.

lated model systems. Zeolites and techniques such as nuclear magnetic resonance (NMR) fall beyond the scope of this book. Several books covering the subject of catalyst characterization are included among the references [17–21].

1.4 Research Strategies

Bearing in mind that the aim of characterization in fundamental catalysis is to obtain information concerning the active surface under reaction conditions in

molecular detail, one might consider that surface science would be the discipline to offer the best opportunities. However, many of the tools do not work on technical catalysts, and consequently one must resort to model systems. For example, one can model the catalytic surface with that of a single crystal [5], and by using the appropriate combination of surface spectroscopies the desired characterization on the atomic scale is certainly possible in favorable cases. The disadvantage here, however, is that although one may be able to study the catalytic properties of such samples under realistic conditions (pressures of 1 atm or higher), most of the characterization is by necessity carried out in ultra-high vacuum, and not under reaction conditions.

The other approach is to study real catalysts by using *in-situ* techniques such as infrared and Mössbauer spectroscopy, extended X-ray absorption fine structure (EXAFS) and XRD, either under reaction conditions, or – as occurs more often – under a controlled environment after quenching the reaction. These *in-situ* techniques, however, are usually not sufficiently specific to yield the desired atom-by-atom characterization of the surface, and often they determine the overall properties of the particles. The situation is represented schematically in Figure 1.8.

The dilemma is thus that investigations of real catalysts, when conducted under relevant conditions by *in-situ* techniques, provide little information on the surface of the catalyst, and that the techniques which are surface-sensitive can often only be applied on model surfaces under vacuum. Model catalysts consisting of particles on flat, conducting supports often present an alternative with respect to surface analysis [22–26], as several examples in this book show. Also, *in-situ* tools that work on single crystals or model surfaces can in some cases be used to assess the significance of results obtained in vacuum for application in the real world [27]. Bridging the gap between ultra-high vacuum and high pressure – as well as the gap between the surface of a single crystal and a that of a real catalyst – are important issues in catalysis.

	Real catalyst	Single crystal
Reaction conditions	XRD, TP techniques Infrared and Raman EXAFS, XANES, AFM Mossbauer, ESR, NMR	Infrared TP techniques STM, AFM
Vacuum	XPS, SIMS, SNMS LEIS, RBS, TEM, SEM	All surface science techniques

Fig. 1.8 Possibilities for spectroscopic research in catalysis (for abbreviations, see Fig. 1.7). AFM: Atomic force microscopy; ESR: Electron spin resonance; RBS: Rutherford backscattering; SNMS: secondary neutral mass spectrometry.

Another point that concerns the relevance of spectroscopic research in catalysis is the following. Both catalysis and spectroscopy are disciplines that demand considerable expertise. For instance, the state of a catalyst often depends critically on the method of preparation, its pretreatment, or its environment. It is therefore essential to investigate a catalyst under carefully chosen, relevant conditions, and after the proper treatment. Catalytic scientists recognize these requirements precisely.

Spectroscopy, on the other hand, is by no means simple, and quick and easy experiments barely exist for catalyst characterization. The correct interpretation of spectra requires experience based on practice, together with a sound theoretical background in spectroscopy, in physical chemistry, and often also in solid-state physics. Intensive cooperation between spectroscopists and experts in catalysis is the best way to warrant meaningful and correctly interpreted results.

It is good to realize that, although many techniques undoubtedly provide valuable results on catalysts, the most useful information is almost always derived from a combination of several characterization techniques. The case studies in Chapter 9 present some examples where such an approach has been remarkably successful.

In conclusion, the investigation of catalytic problems by using a combination of spectroscopic techniques, applied under conditions which resemble as closely as possible those of the reaction in which the catalyst operates, according to an integrated approach in which experts in catalysis and spectroscopy work in close harmony, offers the best perspectives for successful research into catalysts.

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