

## CHAPTER 1

# SPECTROSCOPIC CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

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Transition metal ions - elements with a partially filled *d* shell – on surfaces of inorganic oxides possess a wide variability in oxidation state, coordination number and molecular structure. This variability forms the basis for their diverse chemical behavior, which is especially important in the field of heterogeneous catalysis. The characterization of supported transition metal ions is a very demanding job, which requires the use of a battery of advanced preferably *in situ* spectroscopic techniques.

### 1.1. Transition metal ions on surfaces as heterogeneous catalysts

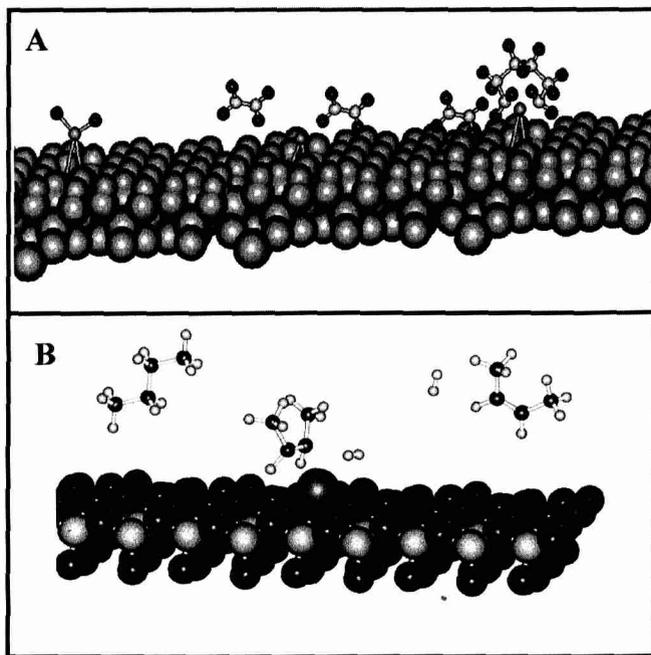
Transition metal ions (TMI) on surfaces are not in their most stable situation, because the surface atoms provide only an incomplete coordination shell. Complete coordination is achieved with additional ligands such as water molecules, resulting in tetrahedral or octahedral complexes. If these ligands are stronger than the surface atoms, they will (partially) replace the surface atoms in the first coordination sphere. The coordination complex is then bound to the surface by ionic interaction in the case of a cationic complex and an anionic surface and/or by van der Waals forces in the case of neutral complexes and surfaces. Another way to complete the coordination shell is clustering of the TMI into oxidic aggregates at the surface. The actual state of the TMI depends on the balance between the TMI-surface interactions and the driving forces to complete the coordination shell. If the former predominate, atomic dispersion can be achieved; if the latter predominate, clusters of TMI will be

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formed at the surface. The situation is further complicated by the heterogeneity of the surface as expressed by the number of surface defects and the large variety of surface sites that may be present. The result is usually an inorganic surface with atomically dispersed TMIs, physically or chemically anchored to the surface and with all kinds of clusters going from dimers to large (crystalline) aggregates of TMIs. It is clear that useful characterization techniques, which can provide detailed information about the molecular structure of supported TMI, must be capable of discriminating between (1) isolated TMI; (2) a two-dimensional overlayer of TMI and (3) three-dimensional TMI clusters or crystallites.

It is also remarkable to see that the same metal ion; *e.g.*, Cr, can catalyze two totally different type of reactions depending on the type of support [1,2]. A pictorial representation of two industrially important Cr-based catalysts, catalyzing the polymerisation of ethylene and the dehydrogenation of alkanes, is given in Fig. I.1. Thus, the relation between the properties of a surface TMI and those of the support has also to be addressed.



*Figure. I.1. Pictorial representation of (A) an industrial Phillips Cr/SiO<sub>2</sub> polymerisation catalyst and (B) an industrial Cr/Al<sub>2</sub>O<sub>3</sub> dehydrogenation catalyst. In case A, ethylene molecules enter the first coordination sphere of a reduced Cr ion and transform into a polyethylene chain, while in case B n-butane enters the first coordination sphere of a reduced Cr ion on an alumina surface. The two hydrogen atoms are then abstracted from the alkane, and the formed H<sub>2</sub> and butene are released from the surface.*

Table I.1: Questions to be answered.

Oxidation state of the TMI?
Coordination environment of the TMI?
Surface or bulk species?
Atom or cluster?
Number of active TMI?
Oxidation state and coordination under catalytic action?

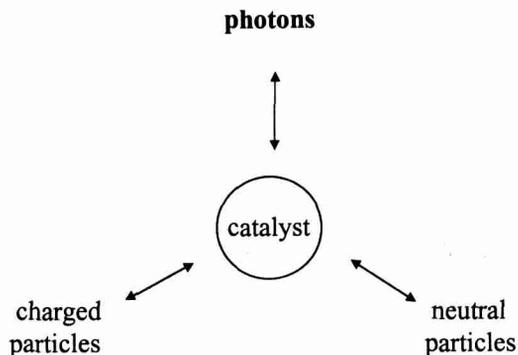
The questions for scientists working in the field of heterogeneous catalysis are then:

- (a) What is the catalytic active site?
- (b) How many active sites are present at the surface?
- (c) What is the chemistry going on at the active site?
- (d) How does the chemistry relate to the properties of the support?

If significant answers can be formulated to all of them, one can formulate quantitative structure/composition–activity/selectivity relationships for heterogeneous catalysts. This is – to our best knowledge - not yet the case for any existing catalyst. Indeed, the detection of the active site is not easy. Table I.1 summarizes the problems involved. One usually relies on direct spectroscopic measurements, but it is impossible to formulate answers on the basis of results obtained with one technique only. The usual strategy is then to use several spectroscopic techniques, which give complementary information. This strategy is often coined the multitechnique approach.

## 1.2. Spectroscopic characterization of heterogeneous catalysts

There are many ways to gather information about the physicochemical properties of transition metal ions on surfaces, but almost all characterization techniques can be derived from the scheme given in Figure I.2. This pictorial representation is generally known as the Propst diagram [3], and the circle in the center represents the sample to be analysed. Ingoing arrows indicate the various methods used to excite the catalyst sample, while the possible responses of the heterogeneous catalyst to that excitation are indicated by the outgoing arrows. Thus, every spectroscopic technique can be represented by a combination of an arrow in and an arrow out. For example, one can irradiate with photons and measure the energy distribution of electrons that are emitted from the catalyst surface due to the photoelectron effect. This forms the basis of X-ray photoelectron spectroscopy. It is also important to stress that a single combination of inward and outward arrow may lead to distinct spectroscopies depending on what property of the sample is measured. This is the case for infrared and Raman spectroscopy.



*Figure I.2. The modified Propst diagram for characterizing transition metal ions on surfaces: The circle is the heterogeneous catalyst, the inward arrow stands for an excitation of the transition metal ion, while the outward arrow indicates how the information can be extracted.*

This textbook is limited to the interaction of photons with catalysts, and more in particular, to electron spin resonance (ESR), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), Raman spectroscopy (RS), diffuse reflectance spectroscopy (DRS) in the UV-Vis-NIR region and X-ray photoelectron spectroscopy (XPS).

In order to appreciate better the selection of these spectroscopic techniques, we have performed a literature survey [4]. Up to July 1999, about 63000 research articles have been published about transition metal ions. More than 43000 of them were in the field of homogeneous, heterogeneous and enzymatic catalysis. An overview of the number of literature hits for each transition metal ion is given in Figure I.3. It is clear that Cu and Fe ions are most studied. The second and third row transition metal ions, such as Mo, W and Re ions, are much less investigated. Combining this search with the keywords 'spectroscopy' and 'surfaces, oxides or supports' results in 2312 papers. The relative use of the ESR, NMR, IR, DRS, RS and XPS techniques for characterizing TMI on surfaces is illustrated in Figure I.4. Magnetic resonance techniques, such as ESR and NMR, are most frequently used, although we have to take into account that NMR has been mostly used for characterizing the supports or oxides instead of the TMI itself. The same most probably holds for IR spectroscopy. The relative use of the XPS, RS and DRS techniques is almost equal.

Figure I.5 illustrates the various, rather arbitrary regions into which electromagnetic radiation has been divided [5]. The boundaries between the regions are by no means precise, although the fundamental molecular processes associated with each region are quite different. Each chapter in this textbook is devoted to one or more spectroscopic techniques with the exception of Chapter 1.

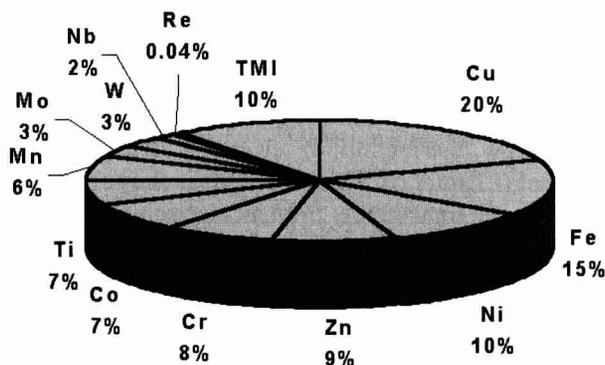


Figure I.3. Overview of the number of literature hits for each transition metal ion up to July 1999 (the total number of hits is 62906, while the group of TMI refers to other transition metal ions or to transition metal ions in general).

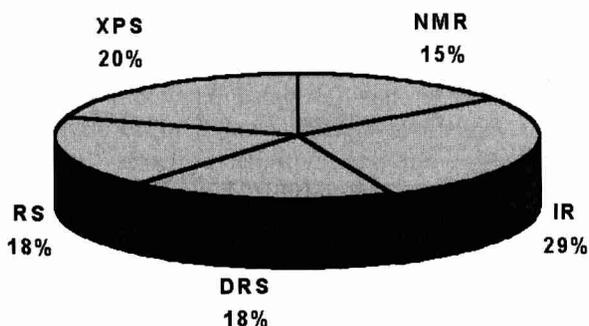


Figure I.4. Relative use of ESR, NMR, IR, DRS, RS and XPS in the literature for characterizing TMI on surfaces.

All the described spectroscopies can be essentially related to one of these fundamental molecular processes. This can be done as follows:

- (1) *Radio and microwave region* ( $3 \cdot 10^6$ - $3 \cdot 10^{11}$  Hz): Magnetic resonance techniques, including nuclear magnetic resonance (NMR) and electron spin resonance (ESR) are measuring the energy change that arises from an electron or nuclear spin change (Chapter 2).
- (2) *Infrared region* ( $3 \cdot 10^{12}$ - $3 \cdot 10^{14}$  Hz): Vibrational spectroscopies (IR and RS) measure the energy change due to changes in molecular configuration (Chapter 3). RS is a spectroscopic method used to observe changes in molecular configuration in the ultraviolet, visible or near infrared region (use of laser light), which are analogous to what is observed by IR in the infrared region of the electromagnetic spectrum.

- (3) *Visible and Ultra-violet regions* ( $3 \cdot 10^{14}$ - $3 \cdot 10^{16}$  Hz): Electronic spectroscopy (DRS) measures the separations between the energies of valence electrons (Chapter 4).
- (4) *X-ray region* ( $3 \cdot 10^{16}$ - $3 \cdot 10^{18}$  Hz): X-ray photoelectron spectroscopy (XPS) measures the energy distribution of electrons that are emitted due to the photoelectric effect (Chapter 5). This technique is thus an exception to the above generalization since the transition is from an electronic level to an unbound state; *i.e.*, an ejection of an electron. As a consequence, the mode of detection is different. That is, in all of the other spectroscopies the absorption, emission or scattering of electromagnetic radiation is measured as a function of energy (wavelength), while in XPS it is the kinetic energy of the emitted electrons, which is measured.

<b>Magnetic resonance techniques: NMR and ESR</b>	<b>Vibrational spectroscopies: IR and RS</b>	<b>Electronic spectroscopies: DRS</b>	<b>X-ray photoelectron spectroscopy: XPS</b>
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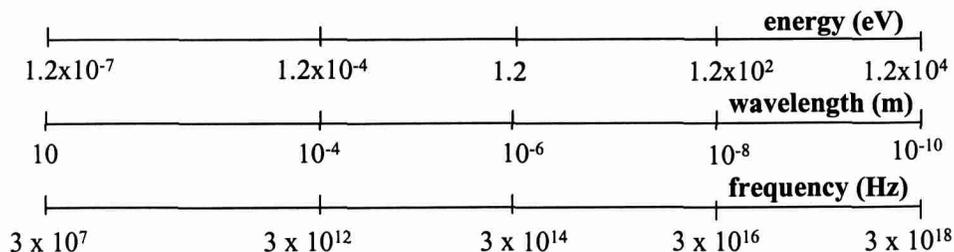


Figure 1.5. The regions of the electromagnetic spectrum, and the spectroscopic techniques discussed in this textbook : energy scale (eV); wavelength scale (m) and frequency scale (Hz) (After ref. [5]).

The applicability of the individual spectroscopies, and the obtained information on the coordination, oxidation states and dispersion of supported transition metal ions are summarized in Table I.2. It is clear that no characterization technique will be capable of providing all the information needed for a full characterization of TMI on surfaces, and a successful characterization of such materials requires the multitechnique approach. Other relevant books on this subject can be found in the literature [6-12]. The applicable range of temperatures and pressures are not controlled by the spectroscopic technique itself, with exception of XPS. The ranges of temperature and pressure are fully controlled by the devices or cells attached to the spectrometers. Further progress in the design of these cells will lead to a wider range of measurement conditions.

Table I.2. The applicability of the individual spectroscopies, and the obtained information on the coordination, oxidation states and dispersion of transition metal ions on surfaces.

Spectroscopy	Coordination	Oxidation state	Dispersion
NMR	+	+/-	-
ESR	+	+	+/-
IR	+	+	+
RS	+	+	+
DRS	+	+	-
XPS	-	+	+

### 1.3. In situ spectroscopy

Until recently, most spectroscopic characterization studies were conducted under conditions often far away from real catalytic conditions [13]. Indeed, knowing only the before-reaction part (activated catalysts) and after-reaction part (deactivated catalysts) of the catalytic event is not sufficient to identify the active site, and to develop quantitative structure-activity/selectivity relationships. Therefore, researchers try nowadays to develop spectroscopic methods that allow them to study supported TMI, while they are in (re)action. This is the field of *in situ* spectroscopy, which – in the strict sense – refers to the study of a heterogeneous catalyst at its working place (e.g., in a stream of reactants at high temperatures). A schematic representation is given in Figure I.6.

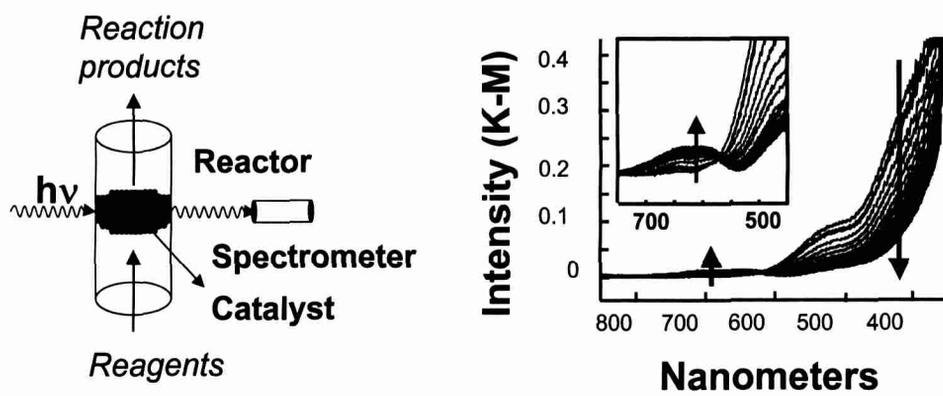


Figure I.6. Scheme of an experimental set-up for *in situ* catalyst characterization, in combination with on line activity/selectivity measurements.

Table I.3. Conditions for obtaining well-resolved DRS, RS, IR, ESR and XPS spectra.

DRS	RS	IR	ESR	XPS
Room temperature	Room temperature	Room temperature	Liquid N <sub>2</sub> or He temperature	Room temperature
Low-medium metal loading	Medium-high metal loading	Medium-high metal loading	Low metal loading	Medium-high metal loading
Vacuum-low pressure	Vacuum-low to medium pressure	Vacuum-low pressure	Vacuum-low pressure	Ultra high vacuum

Thus, *in situ* spectroscopy is defined as spectroscopy under reaction conditions and the reaction is to be interpreted in a very general way. It includes the activation of the catalysts as well as the catalytic reaction itself, and spectroscopic and catalytic measurements have to be done on the same catalyst at the same time under optimal spectroscopic and catalytic conditions. This requires special cells, usually called catalytic cells. It is clear that the design of the *in situ* spectroscopic cell is a crucial step because the optimal conditions for performing spectroscopic and catalytic measurements are mostly not identical, and there will mostly be a compromise between both, which results in lower catalytic performances and less resolved spectra. Table I.3 summarizes the experimental conditions for obtaining well-resolved spectra of supported TMI with DRS, RS, IR, ESR and XPS. One drawback is, of course, band broadening, which can go as far as a complete loss of the band intensity in the background signal at high temperature.

#### 1.4. References

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