CHARACTERIZATION OF CATALYSTS: SURFACE AND *IN-SITU* METHODS

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Keywords: catalysis, *in-situ* spectroscopy, UV-VIS, infrared, Raman, nuclear magnetic resonance, electron paramagnetic resonance, X-ray absorption, diffraction and scattering, Mössbauer microspectroscopy, combined techniques, calorimetry, SSITKA

Contents

Summary

The study of catalysts under *in-situ* conditions enables the catalyst scientist to identify and understand the important steps, e.g., the formation of important reaction intermediates and active sites, and stages in a catalyst's lifetime, such as activation/deactivation. The development of characterization methods as well as the design and construction of appropriate *in-situ* cells and reactor probes are inevitable in order to obtain such insight. Both spectroscopic and scattering techniques have been used in attempt to understand quantitative structure/composition-activity/selectivity relationships in catalysis. Armed with such detailed knowledge about the catalyst, it is then possible for scientists to design, in a more rational way, new and efficient catalysts for sustainable production of bulk and fine chemicals as well as for the removal of harmful compounds in industrial catalytic processes. This chapter provides an overview of the *in-situ* characterization techniques available for investigation of catalytic materials. The possibilities and limitations of the methods are discussed and illustrated with numerous case studies.

1. Introduction

The term catalyst was coined as early as 1835 by the Swedish scientist Jöns Jacob Berzelius to describe the process by which a chemical reaction is sped up by an additional body. It does this by reducing the activation energy of a specific chemical reaction and is thus able to control the direction of a particular process thus bringing about selectivity to the chemical process. As such nowadays as much as 85% of all synthetic bulk and fine chemicals will have been in contact at some point during their manufacture with a catalyst, the majority of which will be solids and used to catalyze the reactants in either the gas or liquid phase (commonly described as a heterogeneous catalytic process).

Catalyst scientists are always looking to either improve upon a catalytic process (e.g. better selectivity/lower operating temperatures) or develop new reactions in order to meet the demands an ever-changing world requires. Often this process is more trial and error based rather than rational and as such is something of a hit and miss affair. In order to improve on this situation, catalyst scientists require better insight into the key stages of the reaction process and in particular, the catalyst's *modus operandi*. Armed with a rigorous understanding of this it could then be possible to prepare the archetypal designer catalyst with the desired superior performance for the reaction in question. However, such information can only be obtained reliably by monitoring a catalyst "in action". In order to do this it is essential to adapt catalytic reactors and/or spectroscopic/scattering techniques to study the processes in real time – an approach which gives rise to the field of *in-situ* methods.

A catalytic cycle typically consists of a sequence of reaction steps that describe the transformation of substrate molecules into a final reaction product at a catalytically active site. Although scientists have been working for decades to decipher such events, only in a limited number of cases has a deeper understanding of the processes involved been achieved. If such information is to be obtained one requires sufficient, detailed information about the catalyst material at each step in its lifecycle: i.e., *synthesis → calcination → activation → reaction → deactivation → regeneration (where possible)*. Conventional characterization (hereby termed accordingly *ex situ* characterization) focuses on the study of the catalyst materials at these various stages, away from the reactor and is often performed under ambient conditions; i.e., at room temperature and atmospheric pressure. Although this approach yields interesting information, it is incapable of providing direct insight into the processes occurring in the catalyst during the course of the reaction. Therefore, the catalyst scientist is forced to develop analytical tools that enable the continuous monitoring of the catalyst "in action", in other words, to be able to track the physicochemical processes taking place in an active catalyst in real time under operating conditions [1, 2]. However, we observe that at this stage a drawback of *in-situ* methods is that the gas and/or liquid phase surrounding the catalyst are probed simultaneously, including both the active surface and the inactive bulk of the material in question, making the interpretation prone to ambiguities.

It is possible to trace the origin of *in-situ* spectroscopy in catalysis back to 1954 with two seminal papers from the R. P. Eischens group [3, 4]. In these reports, the interaction of carbon monoxide with Cu, Pt, Pd and Ni supported on SiO_2 and of ammonia molecules with cracking catalysts were studied with infrared (IR) spectroscopy. It is noteworthy that from the modern viewpoint, these studies may still not be regarded as real *in-situ* investigations of catalysts since the ‘reaction conditions’ were far removed from those that are actually found in a catalytic process. Nevertheless, they represented an important step forward for the *in-situ* approach since for the first time they considered the importance of the dynamics of a catalyst surface in the presence of adsorbates. Indeed, R. P. Eischens was most probably the first to construct a spectroscopic-reaction cell for measuring IR spectra of heterogeneous catalysts. Since these pioneering studies, continuous progress towards the use of *in-situ* spectroscopic techniques can be observed. This is illustrated in Figure 1, which shows the evolution of the number of *in-situ* spectroscopy papers in the catalysis literature.

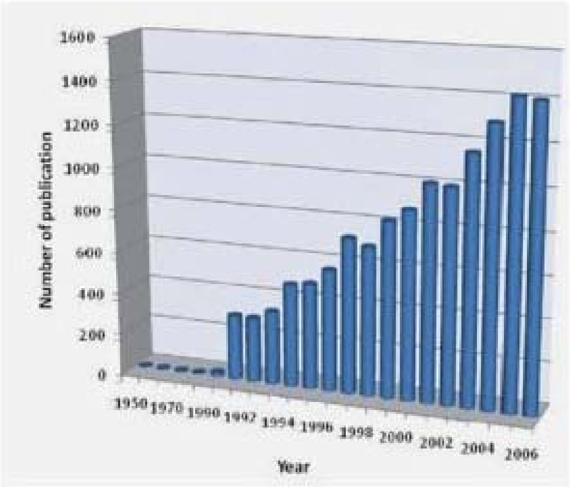

Figure 1. Estimated number of publication on *in-situ* characterization of catalysts (based on the results of an ISI and Chemical Abstracts database search using the terms ‘*in-situ*’ and ‘catalyst’).

Several research strategies can be applied to investigate the fundamental relations between the physicochemical properties of a catalyst material and its catalytic activity and selectivity. Scientists are always faced with the dilemma between the level of information they would like to obtain about a catalyst and the relevance of this information regarding the real catalytic event. One approach is to consider a well-defined single crystalline surface as a model of the catalytic material. Such an approach represents the underlying idea upon which surface science techniques are based and whilst it may lead to valuable information at the atomic scale, the pressure range (ultra-high or high vacuum) is often a far cry from relevant reaction conditions. In this respect, we observe that recent developments in some surface science techniques, such as X-ray photoelectron spectroscopy and electron microscopy, are inching towards pressure regimes that allow for the introduction of reactants and thus offer the potential for obtaining very important new insight into catalytic processes. A typical approach used to investigate catalysts by these methods is to first subject the real catalyst system to the appropriate reaction conditions or, as is still often done, under a controlled environment after reaction quenching. The disadvantage of this approach lies in the fact that generally the information is not yet high enough (although we note that such techniques as soft X-ray transmission microscopy is pushing the boundaries with what can be achieved with microscopy techniques in terms of both the resolution (currently ~ 20 nm) and the reactant conditions which can be applied *in-situ*) so that one ends up with at best an overall picture of the active catalyst material. However, we observe that such a situation illustrates that each technique has its own advantages and disadvantages to reveal details on the active catalyst surface. Each technique has a specific potential for quantitatively or qualitatively probing the oxidation state, the coordination environment and the dispersion of a metal ion. Needless to say, none of the characterization techniques reviewed in this chapter is capable of providing all the information needed for complete characterization of the catalytic solid under reaction conditions.

Solid catalyst materials often possess a complex composition upon which several species can be simultaneously present at the catalyst surface. They include: a) active sites; i.e., surface species, which bind a substrate, giving rise to an active site-reaction intermediate surface complex and catalyze a chemical reaction. The different active sites may exhibit a different activity and selectivity pattern toward substrate molecules and a particular active site may be responsible for an unwanted side reaction as well, resulting in by-product formation; b) reaction intermediates which are mostly short-lived and therefore difficult to detect; and c) spectator species; i.e., surface species which do not actively participate in the catalytic reaction, but are formed during the reaction and thus are in an appreciable amount at the surface, complicating the spectroscopic analysis. It is clear that it is necessary to distinguish between true active sites and spectator species; however, this is only possible through the careful selection of complementary characterization techniques and the development of site-selective spectroscopic techniques with a sufficient discriminative power. Another challenge is the quantification of active sites in a working catalyst. The ideal situation would be a quantitative determination of each fraction of surface species on the basis of spectroscopic data only, but this has been unachievable so far due to the lack of data on the extinction coefficients of mostly unusual surface species formed in an active catalyst. The extinction coefficients of such species cannot be simply found in spectroscopic textbooks nor can they be measured independently in a specific experiment. What is equally important to consider is the fact that the surface species formed in a working catalyst mostly possess unusual identities, and consequently, the interpretation of the spectroscopic data in terms of active sites, reaction intermediates and spectator species is far from trivial. A solution can be obtained from advanced theoretical tools for calculating experimental spectroscopic data. This requires the generation of theoretical spectra of relevant computer cluster models on a series of potential active sites. A close match between the theoretical and experimental spectra allows a detailed description of the structure of the active site or reaction intermediate. Based on this knowledge, a reaction cycle can be proposed and mechanistic insight can be obtained.

In order to obtain relevant information about the catalyst material, spectroscopic and catalytic measurements ought to be carried out at the same time. The catalyst material has to be placed in a catalytic reactor, which allows for the obtaining of spectroscopic data at e.g. high temperatures and pressures in the presence of a substrate. The catalytic activity and selectivity of the catalyst material can then be determined via on-line product analysis, mainly using chromatographic/mass spectrometric methods; thus making it possible to identify important structure-activity relationships. The appropriate design and construction of *in-situ* cells is a crucial step in obtaining interrelated spectroscopic and catalytic data. One challenge in designing *in-situ* cells is that the optimal conditions for performing spectroscopic and catalytic measurements are not identical and thus a compromise is often made. Generally speaking, high measurement temperatures always give rise to less resolved spectra making their analysis difficult. Furthermore, finding a good compromise between spectroscopy and catalysis often implies that non-optimal catalytic performances are measured in a spectroscopic-reaction cell. Nevertheless, there are now *in-situ* cells available enabling the study of catalytic processes up to 700-1000°C and 50-100 bar with properties very close to those of real catalytic reactors. Amongst many aspects of designing a high quality *in-situ* cell for investigating catalysts in action the following aspects can be considered to be the most important: the operating temperature of the catalyst, the catalyst form, irradiation damage, activity and selectivity, the cell volume, the cell window material and the safety [5].

We now illustrate the application of *in-situ* techniques for the study of catalytic processes by highlighting some relevant examples in the literature, which have been classified below by technique. Our overview begins with a focus on the more ‘classical’ spectroscopic and scattering techniques before moving onto the comparatively younger fields of *in-situ* microscopy and multi-technique methods. Finally, we briefly discuss a number of approaches which make use of atypical techniques to yield valuable insight into a catalytic process.

2. UV-Vis Optical Spectroscopy

Spectroscopy in the ultraviolet (UV), visible (Vis) and near-infrared (NIR) region of the electromagnetic spectrum is often called electronic spectroscopy because electromagnetic radiation in this spectral region drives the outer shell electrons to the excited energy levels [6]. Optical spectroscopic measurements in a gas and liquid phase are usually conducted in transmission mode, while for the investigations of powders and solids the light reflected from the sample is usually collected using the technique named diffuse reflectance spectroscopy (DRS) [7]. One of the advantages of DRS is that the obtained information is directly chemical in nature since outer shell electrons of the transition metal ions are probed. This provides information about the oxidation state and coordination environment of transition metal ions in catalytic solids. The same holds for the nature of adsorbed species and different hydrocarbon species can be investigated due to specific $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

DRS is based on the reflection of light by a powdered sample, when the diffuse reflected photons are scattered in all directions. Quantitative treatment of the spectra is based on the Schuster-Kubelka-Munk (S-K-M) theory. It has to be emphasized that this approach is valid under the following conditions of (a) a low abundance and uniform distribution of absorbing centers; (b) isotropic and diffuse monochromatic irradiation and scattering; and (c) infinite sample layer thickness (is usually reached for sample layers of a few mm thickness). Specially designed cells are necessary to fulfill these requirements. Several modes of operation can be used to measure *in-situ* DRS spectra of catalytic solids under working conditions:

(1) An integration sphere, which is capable of collecting > 95% of the scattered light over a wide range of wavelengths [8, 9]. To minimize the light losses, the sphere is coated with a perfectly reflecting material such as MgO and $BaSO_4$. An *in-situ* DRS cell is placed in front of this classical setup, as illustrated in Figure 2.
(2) An accessory consisting of two ellipsoidal mirrors so that about 20% of the diffusively reflected light is collected and the specular component is minimized. An *in-situ* cell can be placed in the center of the setup.
(3) A fiber optics attachment equipped with a high-temperature probe. This probe can be easily introduced into a catalytic reactor [10-12]. The potential of this method in catalysis is illustrated in the following examples.

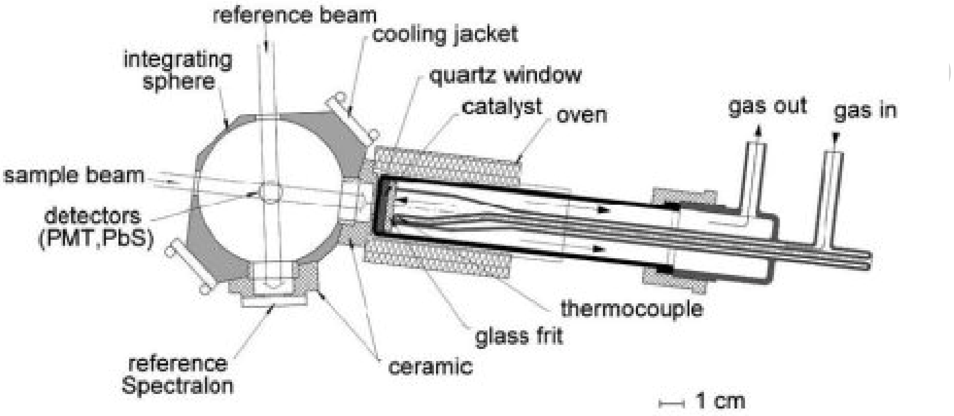

Figure 2. Integrating sphere, equipped with ceramic spacer in sample and reference position, microreactor, and oven. The detectors are located at the top (PbS detector for NIR range) and at the bottom of the sphere (photomultiplier tube for UV-vis range (from [8])

2.1 Active Dehydrogenation Site and Structure-Activity Relationship for Cr/Al2O3 Catalysts

The catalytic dehydrogenation of alkanes is of great importance as an effective route for the direct production of light alkenes [13]. A Cr/Al_2O_3 catalyst doped with an alkaline earth metal oxide is industrially used for this process, and much research has been devoted to elucidate its active dehydrogenation site as well as its reaction and deactivation mechanism [14]. Both Cr^{3+} and Cr^{2+} have been proposed to be the active species. The speciation of chromium oxide species present under reaction conditions was measured by *in-situ* UV-Vis spectroscopy [15]. The spectra dataset, given in Figure 3 shows a gradual decrease of absorption maxima around 360 and 450 nm (ligand-to-metal charge transfer (LMCT) transitions of Cr^{6+}) ,with increasing reaction time at the expense of a new weak absorption band with a maximum at around 625 nm (d-d transition of $Cr^{2+/3+}$). The correlation between the dehydrogenation activity and the amount of $Cr^{2+/3+}$ allows a conclusion to be made that the alkane dehydrogenation activity is directly proportional to the amount of reduced chromium oxide species formed under reaction conditions. The difference in catalytic activity between Cr/Al_2O_3

catalysts at different times on stream was explained in terms of coke deposited on the catalyst surface.

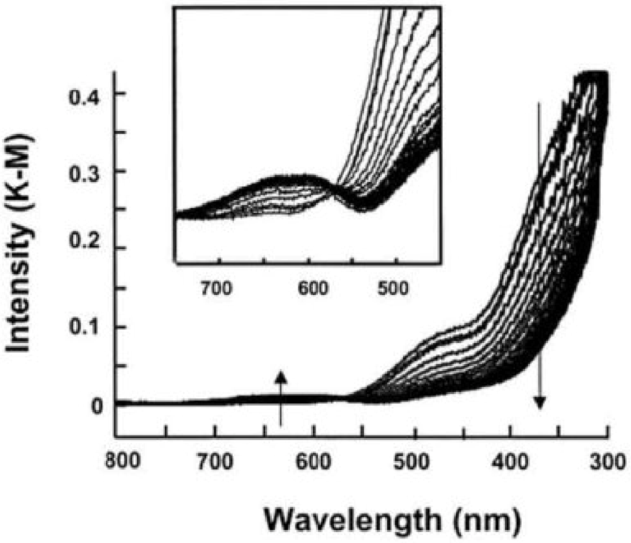

Figure 3. *In-situ* UV–Vis diffuse reflectance spectra of 0.5 wt.% Cr/SiO_2 catalyst treated at 350°C in 2% isobutane in N_2 as a function of time (from [15])

The same reaction was probed using a fiber-optics setup which enables the temperature range to be extended up to 800°C and to reduce the measurement time per spectrum to 6 ms, with extended spectral range and improved signal-to-noise ratio. Using this approach, the LMCT bands were shown to decrease within the first 15 s of the reaction, due to Cr^{6+} reduction to a lower oxidation state in the presence of propane. This Cr species emerging in the reaction were identified as pseudo-octahedral Cr^{3+}, characterized by d-d transitions at 465 and 650 nm. No indication of Cr^{2+} species could be observed in the NIR region, ruling out its presence in the working catalysis.

2.2 NO Decomposition on Cu-ZSM-5 Zeolites

Direct decomposition into molecular nitrogen and oxygen is an appealing way of NO abatement. Among the whole series of materials which have been investigated as potential catalysts for this reaction, copper-exchanged ZSM-5 zeolite was found to exhibit high and stable catalytic activity. A considerable effort has been put into identifying the active sites of Cu/ZSM-5 and elucidating NO decomposition mechanism. *In-situ* UV-Vis spectroscopy investigation has shown that upon pretreatment in helium the spectra show the presence of $Cu^{2+}\cdot Cu^{2+}$ pairs [16]. At temperatures below 400 °C the spectra exhibit bands at 13000 cm^{-1} and 30000 cm^{-1}, respectively, which could be assigned to d-d and charge transfer transitions of Cu^{2+}–O^{2-} – Cu^{2+} complex, while at higher temperatures the spectra features the band at 21500 cm^{-1}, characteristic of Cu^{2+}–μ(O^-)2– Cu^{2+} (Figure 4a). Upon admission of NO to the catalyst pretreated in helium, the band at 21500 cm^{-1} arises at the later times compared to that at 13000 cm^{-1} band. An isobestic point between the 13,000 and 21,500 cm^{-1} feature was observed. Based on this information in conjunction with the product analysis, it was possible to devise a reaction scheme (Figure 4b). According to the proposed mechanism, $Cu^{2+}\cdot Cu^{2+}$ pair interacts with two NO molecules giving rise to the

$Cu^{2+}–O^{2-}– Cu^{2+}$ and N_2O. Upon interaction with N_2O the $Cu^{2+}–O^{2-}– Cu^{2+}$ is transformed into μ-oxo cluster. Molecular oxygen is released upon subsequent decomposition of the latter. Below 400 °C formation of μ-oxo complexes was found to be rate-limiting while above this temperature O_2 desorption is becoming rate-limiting, implying that the activation energy for N_2O decomposition is higher than that of O_2 desorption.

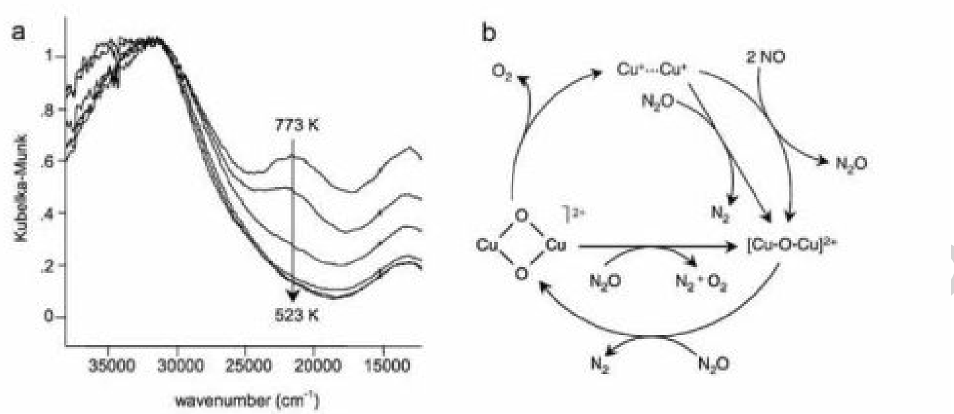

Figure 4. (a) *In-situ* UV-Vis spectra of Cu-ZSM-5 taken during NO decomposition reaction in the temperature range 523-773 K. (b) Proposed reaction mechanism for the decomposition of NO and N_2O on Cu-ZSM-5 (from [16]).

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