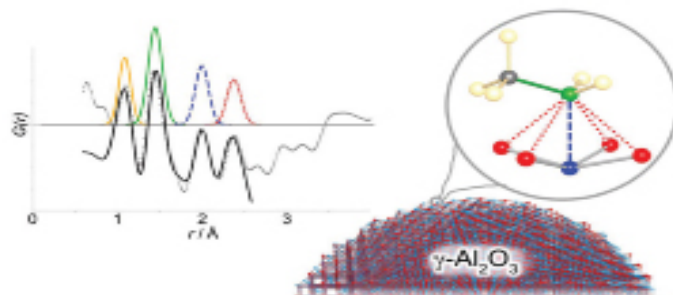
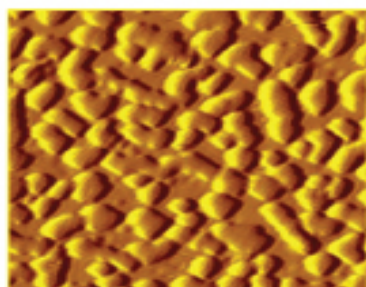
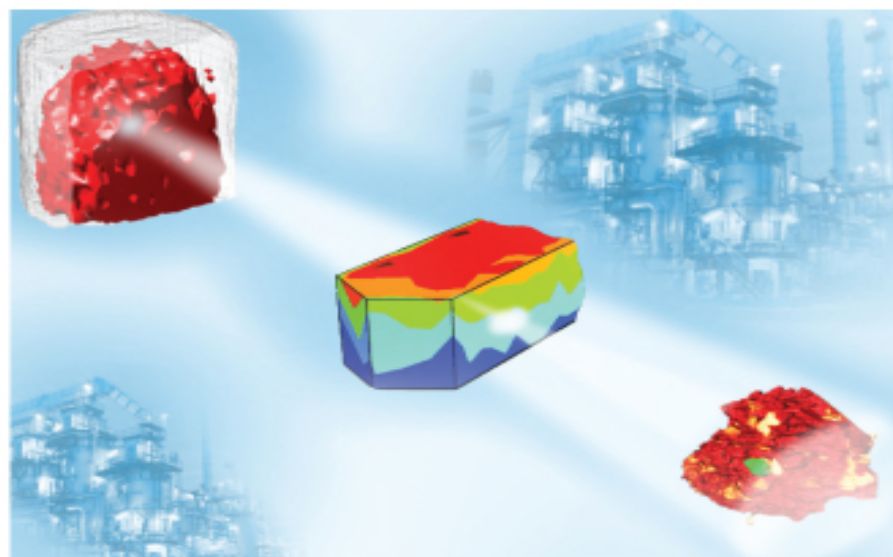


# *In-situ* Characterization of Heterogeneous Catalysts

*Edited by*  
José A. Rodríguez, Jonathan C. Hanson,  
and Peter J. Chupas



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# ***IN-SITU*** **CHARACTERIZATION OF HETEROGENEOUS CATALYSTS**

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# Introduction: Goals and Challenges for the *In-situ* Characterization of Heterogeneous Catalysts

José A. Rodriguez, Jonathan C. Hanson, and Peter J. Chupas

## **Catalysis and the Need to Characterize Active Sites in Different Types of Materials and Chemical Environments**

Catalysis is central to the production of fuels and chemicals, including more than 70% of today's chemical products. About 20% of the value of all commercial products manufactured in the United States is derived from processes involving catalysis [1-3]. Thus, the understanding and optimization of heterogeneous catalysts is a critical need within the chemical industry [2, 3]. The most important considerations when designing a new catalyst or when optimizing the performance of an existing one are activity, selectivity, and durability [3]. The catalyst must be able to perform a reaction of interest at an acceptable rate under a practical set of temperatures and pressures. There is a commercial incentive to tune catalysts to operate at low temperatures and pressures [2, 3]. It is concurrently important that the rate of side reactions be minimal, and the catalyst must be able to sustain the desired reaction

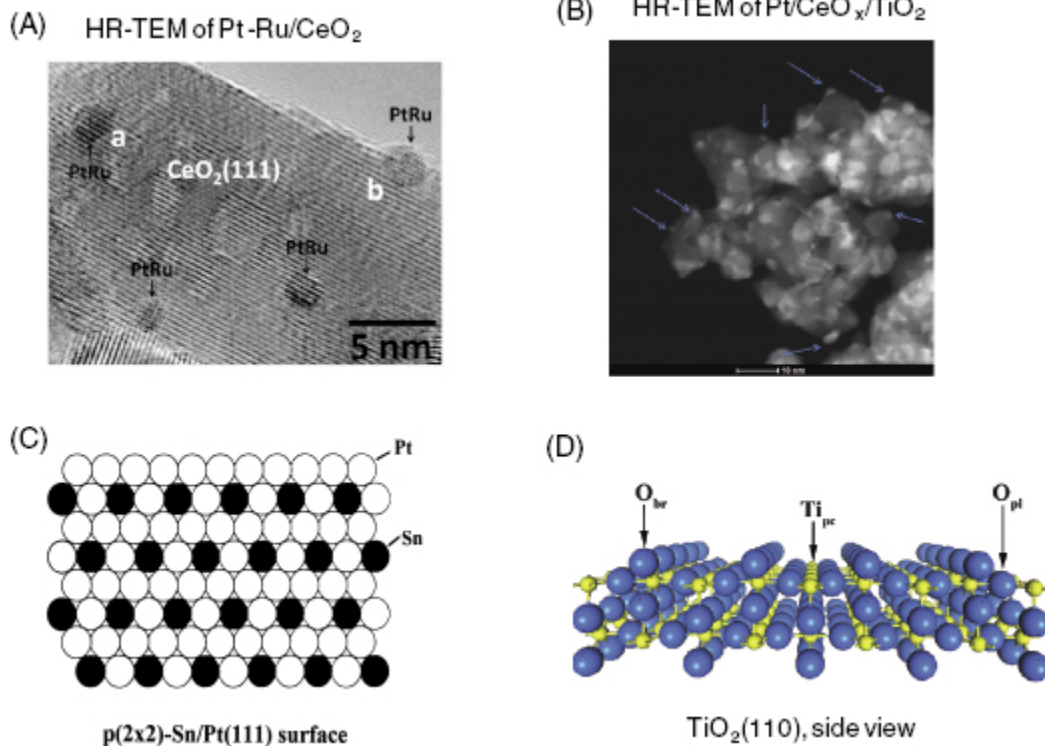
over long periods of time [3]. When designing or optimizing a catalyst, one must know the nature of its active sites and how they interact with the reactants, intermediates, and products of a catalytic process. The structural and electronic properties of the active sites are usually affected by the chemical environment in which they operate. This book describes experimental techniques that have been developed to characterize catalysts and study reaction mechanisms *in situ* under academic and technical or industrial conditions.

Heterogeneous catalysts can be metals, oxides, carbides, sulfides, nitrides, practically any type of material [1-3]. In the nineteenth century it was already known that all the regions or atoms in the surface of a heterogeneous catalyst are not involved in the real catalytic process. The concept of the “active site” in catalysis has been used since its introduction in the 1920s by Taylor and Langmuir [4, 5]. However, despite considerable scientific effort over many years, our knowledge of what exactly the active sites are and how they really work is in most cases very primitive [6]. First, it is necessary to identify the active site and fully characterize its electronic and structural properties under reaction conditions. Since industrial catalysts and catalytic processes are extremely complex [2, 3], the development of techniques for the characterization of catalytic systems *in situ* as they evolve in time with a changing chemical environment is a very challenging task. [Figure I.1](#) shows four different types of systems which are frequently used in catalytic studies. [Figure I.1A](#) displays an image of high-resolution transmission electron microscopy (HR-TEM) for a high surface area Pt-Ru/CeO<sub>2</sub> catalyst [7]. One sees particles of a Pt-Ru alloy (1.5–3 nm in size) on top of a ceria support that mainly exhibits the (111) face of the oxide. In the case of [Figure I.1B](#), the HR-TEM image corresponds to a Pt/CeO<sub>x</sub>/TiO<sub>2</sub> catalyst [8]. The loading of Pt is very low

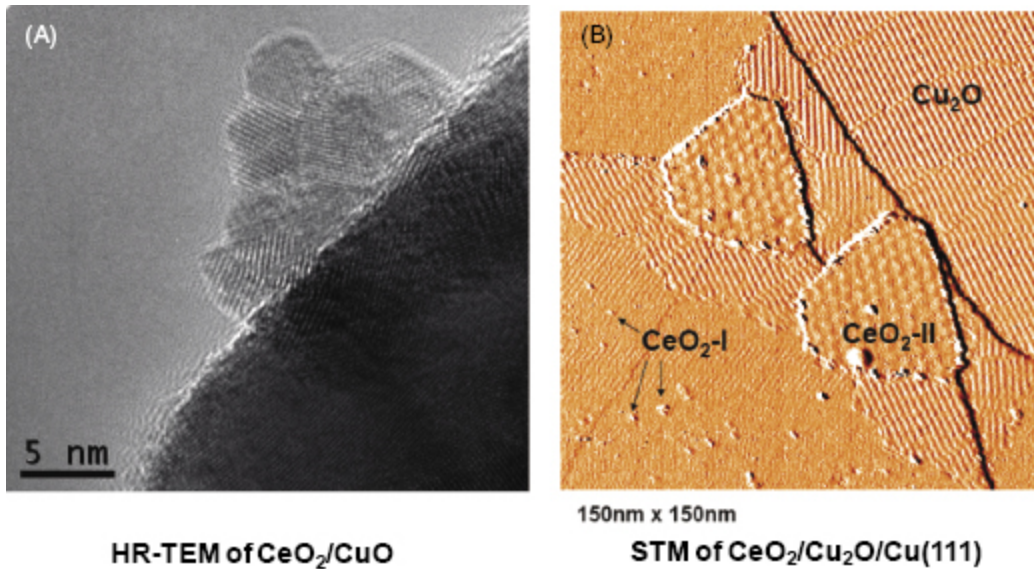
(0.5 wt%) and the small particles of the metal (0.4–0.5 nm) are difficult to detect with HR-TEM. The  $\text{TiO}_2$  support nanoparticles are monocrystalline and present an average size of 10–15 nm. The bright spots as indicated by the arrows represent  $\text{CeO}_2$  nanoparticles with an average diameter of about 4–5 nm. In the  $\text{Pt/CeO}_x/\text{TiO}_2$  catalyst, the very low content of Pt points to the need for characterization techniques with a high sensitivity. Many catalytic processes are carried out on the type of metal/oxide powder catalyst shown in [Figure I.1A,B](#), with the surface exhibiting a high degree of structural heterogeneity [1–3]. In contrast, when studying correlations between surface “structure” and reactivity, it may be advantageous to do experiments on well-defined single-crystal surfaces such as those displayed in [Figure I.1C,D](#) [9, 10]. Furthermore, the system in [Figure I.1A](#) has the typical metal/oxide configuration seen in many industrial catalysts [1–3]. However, to enhance the participation of ceria in catalytic reactions, one may adopt an inverse configuration in which nanoparticles of this oxide are deposited on top of the surface of a metal or another oxide [11]. Thus, the inverse  $\text{CeO}_2/\text{CuO}$  and  $\text{CeO}_2/\text{CuO}_x/\text{Cu}(111)$  catalysts shown in [Figure I.2](#) exhibit a very high activity for the low-temperature oxidation of CO and the CO preferential oxidation (PROX) reactions [12, 13]. In practical terms, one needs to develop techniques for the *in-situ* characterization of all the systems shown in [Figure I.1](#) and [Figure I.2](#), and even much more complex materials in which there are multiple phases coexisting in a three-dimensional space [14]. When focusing on spatial resolution, characteristic length scales relevant for catalytic materials range from a few millimeters (usual sample size) to nanometers (typical size of catalytic nanoparticles). If one is interested in the geometrical structure of molecules adsorbed on the surface of the catalyst as reactants or intermediates, then the

significant length scale is in the order of angstroms or picometers.

**Figure I.1.** Different types of systems investigated in studies in the area of catalysis. (A) Image of HR-TEM for a Pt-Ru/CeO<sub>2</sub> catalyst. Reprinted with permission from Reference 7. Copyright (2012) Elsevier. (B) Image of HR-TEM for a Pt/CeO<sub>x</sub>/TiO<sub>2</sub> catalyst. Reprinted with permission from Reference 8. Copyright (2012) American Chemical Society. (C) Top view of a Sn-Pt(111) model catalyst. (D) Side view of a TiO<sub>2</sub>(110) surface.



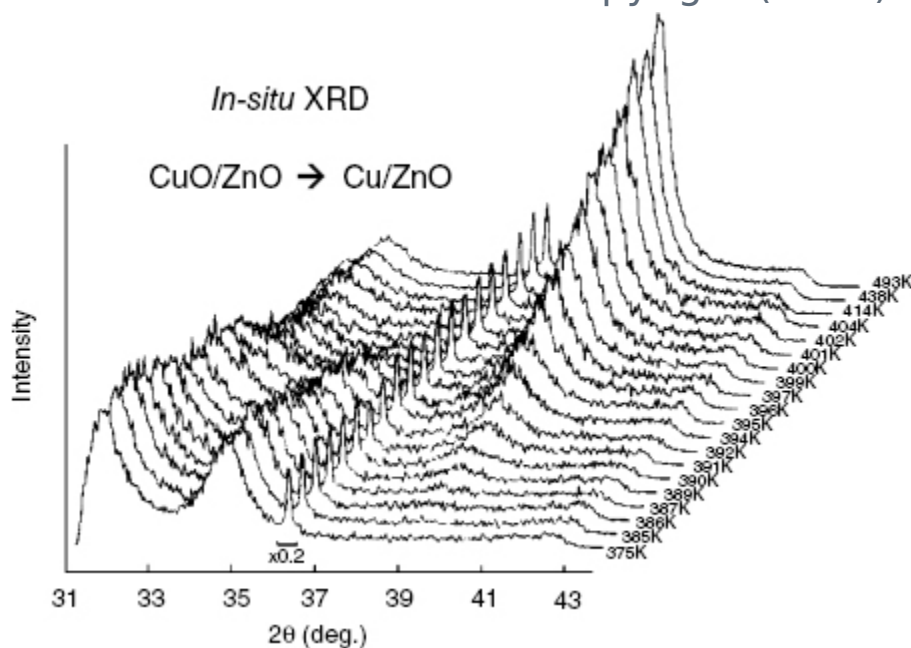
**Figure I.2.** Inverse ceria/copper oxide catalysts. (A) Image of HR-TEM for a CeO<sub>2</sub>/CuO powder catalyst. Reprinted with permission from Reference 12. Copyright (2010) American Chemical Society. (B) Image of STM for a CeO<sub>2</sub>/CuO<sub>x</sub>/Cu(111) model catalyst. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society.



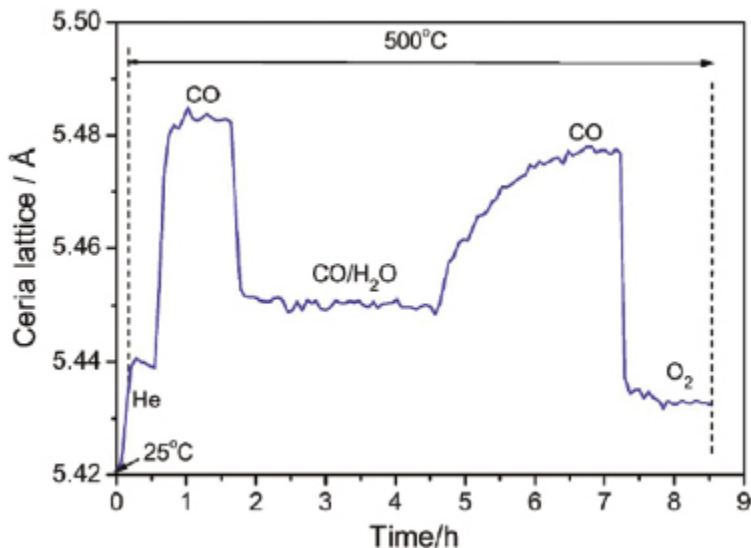
Time is a very important parameter when studying a catalytic process. A phenomenological rate law gives the disappearance of reactants or appearance of products as a function of time for a particular set of reaction conditions (pressure, temperature, and chemical concentrations) [6]. At a microscopic level, molecules are transformed and the chemical environment around the active sites of a catalyst changes as a function of time [6, 10]. In order to obtain a full understanding of the key transformations associated with a catalytic process, one must be able to track the time evolution of the structural and electronic properties of the active site. The activation and breaking of a chemical bond inside a molecule occurs in the picosecond regime but the completion of a full reaction cycle on the surface of a catalyst usually takes longer times. Based on turnover rates for typical reactions ( $10^{-2}$ - $10^3$  molecules/site•second) [9, 10], one can estimate that the timescale for a catalytic transformation on the surface of a catalyst is usually in the range of minutes to milliseconds under typical reaction conditions. Ideally, one must be able to track transformations of the catalytic material in this time range. Very valuable information about catalytic processes can be obtained under steady-state conditions (i.e., no variations in

temperature, pressure, and reaction rate), but to obtain a detailed understanding of reaction mechanism one frequently has to do experiments in a non-steady-state or transient mode in which the properties of the catalytic system are perturbed by changing the temperature (see [Fig. I.3](#)), or by pulses (fluctuations) in the pressures of the reactants [5, 6, 15]. In principle, the perturbations in the reaction conditions can affect the structural properties of the catalyst ([Fig. I.3](#) and [Fig. I.4](#)) and the lifetime of surface intermediates that are produced during the reaction.

**Figure I.3.** Three-dimensional plot of *in-situ* XRD patterns collected during the reduction/activation of a powder CuO/ZnO catalyst in a mixture of 0.25% CO, 0.25% CO<sub>2</sub>, and 4% H<sub>2</sub> in argon. The XRD patterns were collected at temperatures between 375 and 493 K. A CuO → Cu structural transformation was seen around 400 K. Reprinted with permission from Reference 5. Copyright (1991) Elsevier.



**Figure I.4.** Variation of the lattice constant of ceria after exposing a powder Au-CeO<sub>2</sub> catalyst to CO, the reaction mixture for the water-gas shift reaction (CO/H<sub>2</sub>O), CO, and O<sub>2</sub>. The reported values were obtained after analyzing results of time-resolved XRD by Rietveld refinement. Reprinted with permission from Reference 15. Copyright (2006) American Chemical Society.



On the basis of the considerations discussed in the previous paragraphs, one finds that the ideal tool for a detailed study of typical catalytic processes should have high sensitivity and allow us the fast acquisition of data in a milliseconds timescale with a spatial resolution in the range of nanometers or smaller, monitoring simultaneously the properties of the catalyst active sites and the adsorbed reaction intermediates. This is a highly demanding set of requirements. At the present time, no single technique can accomplish all of these tasks. For a complete characterization of a catalytic process, one must combine different techniques. Many of the existing techniques focus only on examining the properties of the catalyst, while others are better suited for studying the surface chemistry associated with the reaction process. In practical terms, it is necessary to find a reasonable balance between temporal



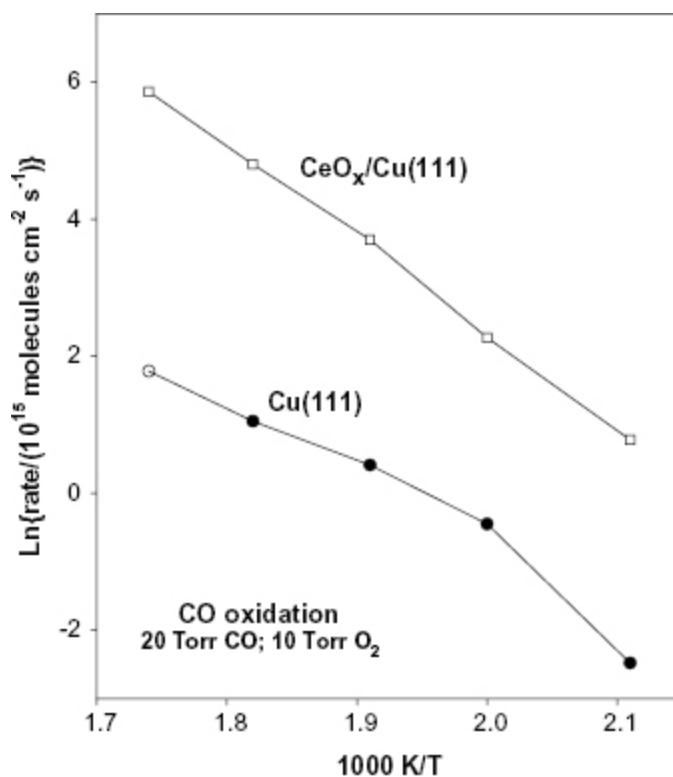
and spatial resolutions. Techniques which can provide morphological information at the nanometer or subnanometer range do not have the time resolution required for most transient or kinetic studies. Most characterization techniques give average properties for relative large areas (from micrometers to millimeters) of the catalyst sample, making emphasis on obtaining high sensitivity for dealing with low concentrations of elements and for allowing the fast data acquisition necessary for transient experiments.

Nowadays surface science offers a quite impressive array of experimental techniques to investigate the properties of surfaces [6, 10]. Many of these techniques are based on some type of excitation (photons, electrons, neutrons, ions, electromagnetic field, heat, etc.) to which the catalyst responds. A similar type of excitation can be associated with different types of phenomena yielding information about different properties. For example, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS) all use photons for probing the sample and are among the most frequently employed techniques for catalyst characterization [5, 6]. XRD occurs in the elastic scattering of X-ray photons by atoms in a periodic lattice and can be used to obtain structural information. In contrast, irradiating a catalyst with X-ray photons can induce excitation of electrons from occupied core levels to empty valence levels (XAS) or generate photoelectrons (XPS), yielding information about the composition of the sample and the electronic properties of the elements present.

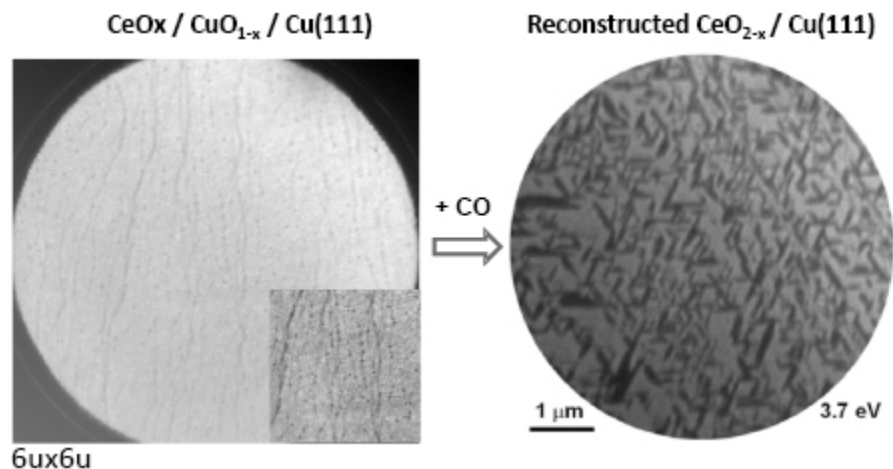
Many surface science techniques operate under vacuum or high-vacuum conditions [6, 10] and cannot be applied in the characterization of catalysts under normal reaction conditions. In order to overcome this problem, several laboratories have developed experimental systems which

combine a high-pressure system with an ultra-high-vacuum (UHV) analysis chamber [9, 10, 16]. The high-pressure reactor allows the kinetics of catalytic reactions to be measured on a given surface (see [Fig. I.5](#)), while analysis of the structure and composition of the surface both before and after reaction can be accomplished in the UHV chamber. This approach has provided valuable insights into many catalytic processes [9, 10, 16], but it is now clear that the combination of *prenatal* and *postmortem* analysis can miss important changes that occur to the surface of a catalyst under reaction conditions [17-19]. Since surfaces are flexible entities which can reconstruct after interacting with adsorbed molecules (see [Fig. I.6](#) and References [17-19]), one must perform an *in-situ* characterization of the catalyst. In recent years, notable advances in design and instrumentation have added moderate-pressure XPS ([Fig. I.7](#)) and high-pressure scanning tunneling microscopy (HP-STM) [17, 20, 21] to the arsenal of techniques that is available for the *in-situ* characterization of catalysts. Furthermore, there has been an extraordinary effort to develop or improve characterization techniques which take advantage of synchrotrons or neutron facilities. It is in these facilities where major advances have been made in the development of techniques which allow us the structural characterization of crystalline or amorphous materials [22-26], dealing with diluted samples [26, 27], the fast acquisition of data [27-29], and catalyst imaging [24, 26, 30]. There has also been substantial progress in the integration of techniques for the simultaneous study of the catalyst properties and reaction mechanism [25, 30-34].

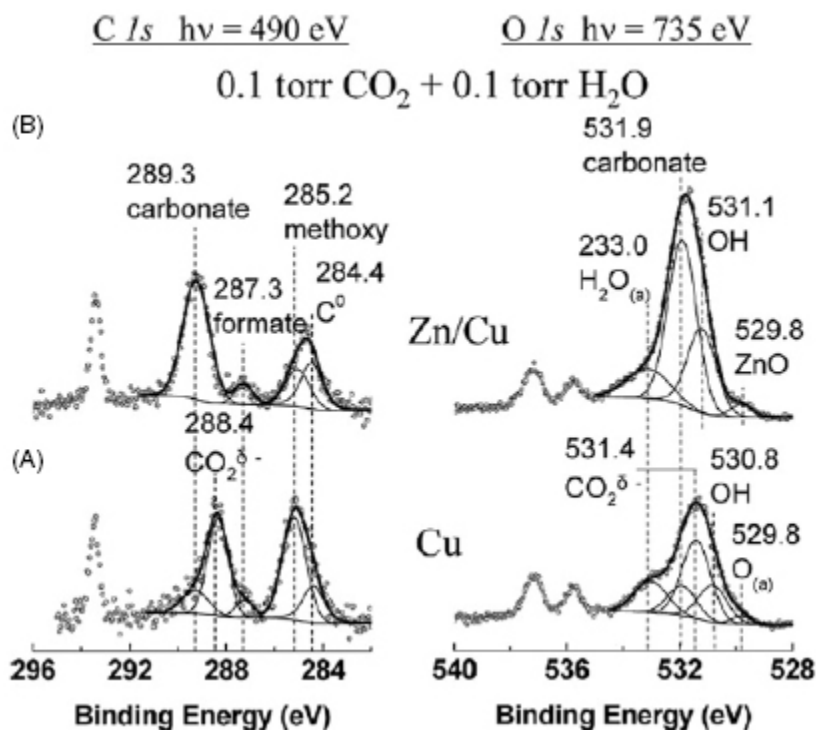
**Figure I.5.** Arrhenius plots for the  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$  reaction on Cu(111) and on a surface in which ceria nanoparticles covered  $\sim 18\%$  of the copper substrate.  $P_{\text{CO}} = 20$  Torr,  $P_{\text{O}_2} = 10$  Torr. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society.



**Figure I.6.** Images of *in-situ* low-energy electron microscopy obtained before and during the exposure of a CeO<sub>x</sub>/CuO<sub>x</sub>/Cu(111) model catalyst to CO [19]. In the final step, the system consisted of ceria nanoparticles dispersed on a reconstructed Cu(111) surface. Reprinted with permission from Reference 19. Copyright (2012) American Chemical Society.



**Figure I.7.** Carbon and oxygen 1s XPS spectra of (A) pure Cu and (B) Zn/Cu (0.1 mL Zn) in the presence of 0.1 Torr of CO<sub>2</sub> and 0.1 Torr of H<sub>2</sub>O at room temperature. Two carbonaceous species, formate and methoxy, are shown to form on both surfaces. Activated CO<sub>2</sub> and carbonate species present in pure CO<sub>2</sub> remain visible on each surface. In addition, molecularly adsorbed H<sub>2</sub>O is also observed in both spectra. The presence of Zn makes carbonate the majority species on the surface. Reprinted with permission from Reference 20. Copyright (2009) Elsevier.

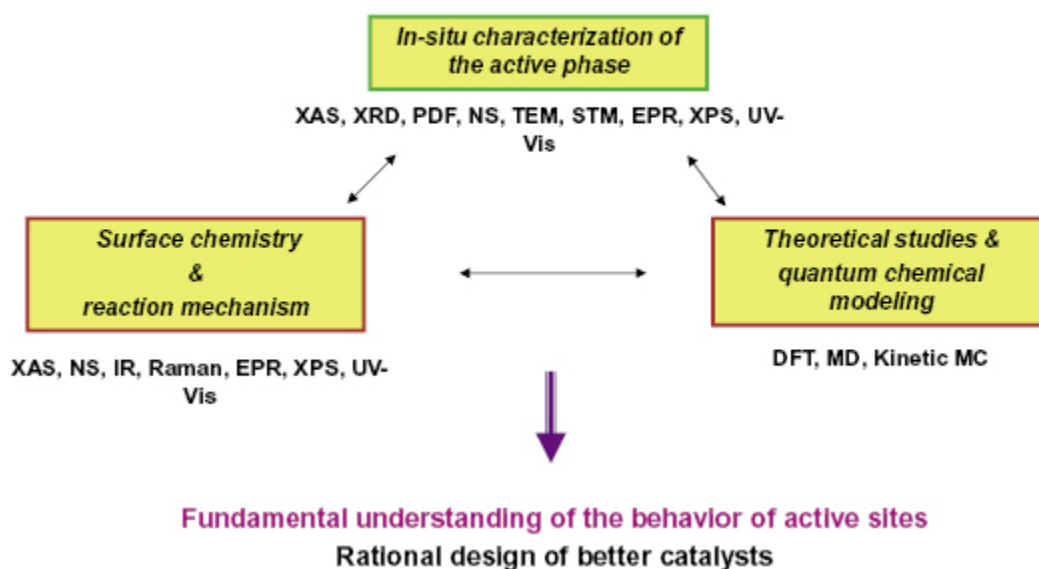


This book is divided in 16 chapters which cover recent advances in an array of techniques which can be used to study *in-situ* catalytic processes taking place on high-surface area powders or on well-defined model catalysts. Using these techniques, one can perform fundamental studies of the physical and chemical properties of a catalyst obtaining information about composition, structural features, surface morphology, electronic states, and chemical reactivity. [Figure I.8](#) shows a typical approach followed nowadays in the study of catalytic processes. First, one must identify and characterize the active phase of the catalyst. This is usually followed by studies of surface chemistry aimed at obtaining the details of the reaction mechanism. Theoretical studies can provide a conceptual frame for understanding the properties of the catalyst or the steps in the reaction mechanism [35, 36]. The integral approach shown in [Figure I.8](#) eventually can yield a fundamental understanding of the behavior of active sites which can be used for the rational design of better catalysts.

This approach usually takes advantage of the *in-situ* techniques described in this book.

**Figure I.8.** Different areas of research during the study of catalytic processes. A fundamental understanding is obtained by combining *in-situ* characterization of the active phase in the catalyst with experimental and theoretical studies of the surface chemistry associated with the catalytic process. NS, neutron scattering; TEM, transmission electron microscopy; EPR, electron paramagnetic resonance; UV-Vis, ultraviolet-visible spectroscopy; IR, infrared; DFT, density functional theory; MD; molecular dynamics; MC, Monte Carlo.

**Integral approach to catalysis:**



## Catalyst Composition and Active Phase Identification

The first step in any catalytic study is to identify the composition and active phase of the catalyst under reaction conditions. XAS is perhaps the technique most frequently used for this task. The first three chapters in the book show