

**UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
INSTITUTO DE FÍSICA**

**A new proposal for avoiding sintering of
nanoparticles in catalysis**

Fabio Raserá Figueiredo

M.Sc. dissertation taken under the supervision of Dr. Fabiano Bernardi and Dr. Carolina Brito submitted to the Graduate Program of Instituto de Física - Universidade Federal do Rio Grande do Sul (UFRGS) as part of the fulfillment to obtain the Master's degree in physics.

Porto Alegre, RS, Brazil

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*“In my head there are several windows, that I do know,
but perhaps it is always the same one,
open variously on the parading universe.*

Samuel Beckett

(Molloy, 1951.)

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Above all, I thank my mother, Ivani Cristina Rasera, without whom I would never have the chance to enter an university. She has taken many more roles than she was supposed to, as the ones of my absent father and many times of a friend, when I was still unable to reach other people. She struggled to maintain the most nurturing environment she could, even when violence and scarcity were threatening our home. I truly admire her strength and never-ending love. I know that, in her eyes, the hard times will be worth it if she can see her sons and daughter succeed. And I surely can not find a bigger motivation to succeed.

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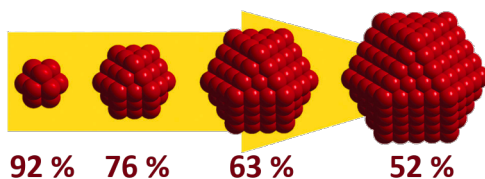
I need to make a honorable mention to my dog, Antonella, because she brought a lightness to these hard times of pandemic and careless government. This little dog has no idea of how good of a companion she is.

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Resumo para Público Leigo

Os catalisadores são substâncias que aumentam a velocidade de reações químicas e por isso são utilizados em mais de 90% de todos os processos químicos da indústria. Sem os catalisadores, seria praticamente inviável suprir a grande demanda de alimentos e fármacos que a sociedade exige. Os catalisadores ainda se destacam no controle de poluentes, como na quebra de moléculas que constituem gases nocivos para o ser humano e contribuem para agravar o aquecimento global.

Com o advento da nanociência, o estudo e desenvolvimento de catalisadores foram revolucionados. A nanociência trabalha com materiais na escala nanométrica, tais como nanopartículas, onde 1 nanômetro corresponde a bilionésima parte do metro. Para compreender melhor o significado de tal quantidade, o tamanho de uma bola de futebol está para o tamanho da Terra assim como 1 nanômetro está para o tamanho de uma bola de futebol. Por conta disso, a maior parte dos átomos das nanopartículas se encontram em sua superfície. Como as reações catalíticas ocorrem na superfície dos catalisadores, o alto percentual de átomos superficiais das nanopartículas as tornam catalisadores muito mais eficientes que materiais comuns. No entanto, reações catalíticas exigem altas temperaturas e isso ocasiona a migração e aglomeração das nanopartículas, que aumentam irreversivelmente de tamanho. Este fenômeno é chamado de *sintering* e devido a ele o percentual de átomos superficiais das nanopartículas diminui, causando prejuízos a sua atividade catalítica.



Percentual de átomos na superfície em relação ao número total de átomos de uma nanopartícula conforme seu aumento de tamanho.

Este trabalho busca evitar *sintering* de nanopartículas através de uma estratégia inédita, que se baseia em criar obstáculos para que as nanopartículas tenham menor probabilidade de entrarem em contato e aumentarem de tamanho. Os experimentos demonstram que o método é muito eficiente na prevenção de *sintering* sem causar danos secundários às nanopartículas. Ainda, foi possível descrever com clareza como a inclusão de obstáculos previne *sintering* e quais as condições importantes para que o método seja efetivo.

Sintering é a principal causa de desativação de catalisadores e a facilidade de aplicação do método proposto, em conjunto com a possibilidade de adaptação para diversos tipos de catalisadores, o tornam extremamente promissor.

Abstract

Sintering is a process whereby nanoparticles increase their size and reduce their number under high temperatures. Since catalytic activity depends on the number of active sites, and those lie on the surface of nanoparticles, the most detrimental consequence of sintering for catalysis is the loss of surface area, which reduces the number of active sites. Sintering is the main cause of catalyst deactivation and the current prevention strategies demand specific synthesis methods, modification of the chemical properties of the nanoparticles or nanostructuring of supports. A new proposal for the prevention of sintering of nanoparticles, easily reproducible, is presented and applied to Cu nanoparticles supported on MgO. A combination of XRD, *in situ* EXAFS and TEM shows the prevention of sintering of Cu nanoparticles under H₂ atmosphere at 300 °C. *In situ* time-resolved XANES and XPS techniques were used to investigate the possibility of catalyst poisoning due to the strategy employed. The results show no evidence of poisoned species. Furthermore, by modelling the system with Monte Carlo simulations, it was possible to reproduce sintering prevention and to propose a possible mechanism whereby the method operates, besides getting a better picture of the pertinent parameters value range that allows sintering prevention.

Keywords: Sintering, nanoparticles, heterogeneous catalysis, catalyst deactivation, catalyst poisoning.

Resumo

Sintering é um processo pelo qual nanopartículas aumentam o seu tamanho e reduzem seu número sob altas temperaturas. Como a atividade catalítica depende do número de sítios ativos, e estes se encontram na superfície das nanopartículas, a consequência mais prejudicial do *sintering* para catálise é a perda de área superficial, que reduz o número de sítios ativos. *Sintering* é a principal causa de desativação de catalisadores e as estratégias de prevenção atuais demandam métodos de síntese específicas, modificação das propriedades químicas das nanopartículas ou nanoestruturação dos suportes. Uma nova proposta para a prevenção de *sintering* de nanopartículas, facilmente reproduzível, é apresentada e aplicada a nanopartículas de Cu suportadas em MgO. Uma combinação de medidas de XRD, EXAFS *in situ* e TEM demonstra a prevenção de *sintering* das nanopartículas de Cu sob atmosfera de H₂ à 300 °C. As técnicas de XANES *in situ* resolvido no tempo e XPS foram utilizadas para explorar a possibilidade de envenenamento do catalisador devido à estratégia empregada. Os resultados indicam que não há qualquer composto envenenado. Ademais, modelando o sistema utilizando simulações de Monte Carlo foi possível reproduzir a prevenção de *sintering* e propôr um mecanismo pelo qual o método opera, além de se obter uma figura mais ampla do intervalo de valores de parâmetros que permitem a prevenção de *sintering*.

Palavras-chaves: Sintering, nanopartículas, catálise heterogênea, desativação de catalisadores, envenenamento de catalisadores.

Contents

Contents	VII
List of Figures	IX
List of Tables	XI
1 Introduction	1
2 Bibliographic Revision	3
2.1 Catalysis and Nanoparticles	3
2.1.1 Cluster Size Effect in Catalysis	4
2.1.2 Supported Nanoparticles	5
2.1.3 Catalyst Deactivation	6
2.2 Poisoning	8
2.2.1 Poisoning Mechanisms	8
2.2.2 Poisoning Prevention	10
2.3 Sintering	11
2.3.1 Sintering Mechanisms	11
2.3.2 Sintering Prevention	19
(a) Cluster-cluster and Cluster/support Interface Modifica- tion	20
(b) Alloying	20
(c) Support Nanostructuring	22
3 Experimental and Numerical Techniques	24
3.1 X-Ray Diffraction	24
3.1.1 Rietveld Refinement	30
3.2 X-Ray Photoelectron Spectroscopy	31
3.3 X-Ray Absorption Spectroscopy	37

3.4	Transmission Electron Microscopy	41
3.5	Monte Carlo Simulations of Cluster Diffusion	44
3.5.1	Random Walks	44
3.5.2	Anomalous Diffusion	45
	References	46

List of Figures

2.1	Illustration of reaction paths with and without a catalyst.	4
2.2	Schematic representation of reaction steps in heterogeneous catalyst . . .	5
2.3	Schematic representation of the change on the percentage of surface atoms as a function of the nanoparticle size.	5
2.4	Illustration of how supported nanoparticles compose a real catalyst. . . .	6
2.5	Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration	9
2.6	Conceptual model of nonselective poisoning by sulfur atom of a metal surface during ethylene hydrogenation	10
2.7	Schematic representation of sintering mechanisms.	12
2.8	<i>In-situ</i> TEM images of coalescence.	14
2.9	Schematics of self-recrystallization after oriented attachment	15
2.10	<i>In situ</i> TEM and HRTEM images of the coalescence by the Oriented Attachment mechanism.	16
2.11	<i>In situ</i> TEM image of the Ostwald Ripening mechanism.	17
2.12	Ni surface area as a function of time for different temperatures.	18
2.13	TEM images of nanoparticle encapsulation by oxide shells.	21
2.14	Schematic illustration of the relationships between support topology and cluster sintering	23
3.1	Bragg's Law schematic representation.	25
3.2	Bragg-Brentano Geometry for XRD	26
3.3	Diffraction patterns of Cu ₂ O standard and nanoparticles.	26
3.4	Schematic representation of size effect in X-Ray diffraction	28
3.5	X-ray diffraction line broadening.	29
3.6	Conceptual scheme of diffraction profile simulation.	31
3.7	Schematic example of Auger emission, spectrum of a silicon wafer and scheme of a concentric hemispherical analyzer.	33

3.8	Universal curve of electronic inelastic mean free path	34
3.9	Scheme to illustrate the Fermi level alignment of the sample and analyzer work functions in XPS measurements.	35
3.10	Diagrammatic view of the effects in the electronic binding energy from XPS.	36
3.11	XPS spectrum of the Cu $2p$ region for Cu, Cu ₂ O and CuO	37
3.12	Schematic representation of XAFS transmission mode setup and typical XAFS spectrum.	37
3.13	Pictorial view of the interference between the waves associated to the emitted photoelectron and backscattered by the neighboring atoms.	40
3.14	Schematic representation of a TEM instrument	42
3.15	TEM images of Cu and Ni nanoparticles.	43
3.16	Bright field and dark field modes in TEM.	43

List of Tables

2.1	Mechanisms of catalyst deactivation	7
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Chapter 1

Introduction

In the 20th century physicists dove in the invisible universe of small scale. The consolidation of quantum mechanics allowed the modeling and experimental probing of low dimensional systems, leading to the development of new scientific fields. Nanoscience emerged within this context and gave rise to impacting applications, not only for the scientific community, but for the development of new technologies for the society. Since its arrival, nanoscience has pushed boundaries in physics (Fomin, 2013, Dupas & Lahmani, 2007), chemistry (Park, 2007, Whitesides, 2005), geology (JU et al., 2015, Ju et al., 2016), materials science (Chong, 2004), bioscience (Khawaja, 2011), electronics (Lieber, 2011, Chappert et al., 2010), among other fields.

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scale, where system properties differ significantly from those at a larger scale (Pidgeon et al., 2004). The *nano* prefix comes from the greek word "nanos", meaning dwarf, and represents one billionth of an unit. That means nanoscience deals with materials with sizes around 10^{-9} m. For comparison purposes, a strand of human hair has a diameter of approximately 80000 nm, a red blood cell diameter is around 7000 nm and a single water molecule lengths around 0.3 nm. In low dimensional systems quantum mechanics reigns, replete of phenomena which are strange to the macroscopic scale where our intuition is molded. Size-dependent properties have actually been exploited for centuries, although without the knowledge of the underlying physics. For example, gold and silver nanoparticles have been used as coloured pigments in stained glass and ceramics since the 10th century AD (Erhardt, 2003). Depending on their size, gold particles appear red, blue or gold in colour. The challenge was to make all nanoparticles with the same size (and hence the same colour), which is still today a non trivial task. Naturally, nanoscience developed side by side with advances in quantum mechanics and the conception of high precision instruments. In the 1930's the inven-

tions of the Scanning Electron Microscope and the Transmission Electron Microscope brought the possibility of atomic imaging and manipulation (Lindsay, 2010). However it was only later, around the 1980's, that nanoscience gained popularity and started to become established as a new scientific field. A lecture given by the physicist Richard Feynman at the annual American Physical Society meeting at Caltech on December 1959 (Feynman et al., 1960) is frequently reminded as one of the sparks that ignited the advent of nanoscience. In this lecture, entitled "There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics", Feynman speaks with excitement about the promising achievements blooming from the ability to manipulate materials at the nanoscale.

From nanoscience came the branch of nanotechnology, where nanostructures are designed for diverse applications. The aim is to create materials, devices, and systems with fundamentally new properties and functions by engineering their small structure. Key issues are being approached through the use of nanotechnology, such as the early detection, diagnostics, prognostics and selection of therapeutic strategies for cancer (Ferrari, 2005) and the increase in Nitrogen use efficiency by crops, which directly improves world food production and reduces waste generation (DeRosa et al., 2010). The nanotechnology arrival has already been consolidated as the latest big technological revolution (Hochella Jr, 2002, Keiper, 2003, Mirkin, 2005). It was even compared to the industrial revolution that took place at the 18th century due to its huge industrial and social impacts Peterson (2000). Today, it is still a rapidly growing sector. In 2016 the global nanotechnology market was evaluated at US\$ 39.2 billion and estimated to reach US\$ 90.5 billion by 2021. (McWilliams, 2016).

The study and development of catalysts was highly impacted by nanoscience. The scientific production regarding nanoparticle-based catalysts grew largely and today constitutes a very relevant niche of science (Bell, 2003, Campelo et al., 2009, Astruc et al., 2005). As nanoscience brought great advances to the field of catalysis, it also brought a number of new issues that need to be fixed. The sintering of nanoparticles, which is the irreversible increase in mean nanoparticle size due to high temperatures, is one of the main impairments in nanomaterial-based catalysts.

This work is focused on introducing a pioneering method to prevent sintering. The following chapter is dedicated to defining the research motivations, carrying a detailed review of the bibliography used to study and introduce the problem. Then, the experimental and numerical techniques used for analysis are explained followed by the methodology description and results analysis. Finally, a brief conclusion summarizes the main results and discuss the perspectives.

Chapter 2

Bibliographic Revision

This chapter introduces the main concepts involved in this work, presenting the scientific literature used for research.

2.1 Catalysis and Nanoparticles

Catalysts are used in most of the current technological processes of the society. Today is estimated that over 90% of all industrial chemicals are produced with the aid of catalysts (de Vries & Jackson, 2012). Its use spurred major improvements in key industries such as pharmaceuticals and foods. However, its relevance goes beyond the industrial applications. Catalysts have been studied and applied in the control of pollutants, as for example in the cleaning of toxic gases from exhaust systems (Whittington et al., 1995), the production of clean fuels as alternative to oil-based ones (Maxwell & Naber, 1992) and more recently in the essential task of reducing greenhouse gas emissions (van der Hoeven et al., 2013, Centi et al., 2003), which are directly related to global warming (Lashof & Ahuja, 1990, Satterthwaite, 2008).

Catalysis was first conceptualized in the 1830s by Berzelius, who collected experimental evidence from many laboratories that identified the phenomenon (Somorjai & McCrea, 2001). A catalyst is defined by The International Union of Pure and Applied Chemistry (IUPAC) as a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change (ΔG) of the reaction (McNaught et al., 1997) and without consumption of catalyst, i.e., catalysts increase a reaction rate without affecting the equilibrium state of the reaction. Fig. 2.1 shows an illustrative energy diagram of a reaction with and without a catalyst, where X and Y represent the reactants and Z the product. The catalyst increases the reaction rate by lowering the activation energy. Catalysis is classified into homogeneous, where only one phase is involved,

and heterogeneous, where the reaction occurs at or near an interface between phases. Besides artificial catalysts, there are also natural catalysts (biocatalysts) present in the human body like enzymes. One example of a catalytic reaction is the decomposition of hydrogen peroxide to water and oxygen when in contact with human blood. The reaction is catalyzed by an enzyme called *catalase* which is present in blood. One catalase molecule can convert millions of hydrogen peroxide molecules to water and oxygen each second (Kaushal et al., 2018). The main goal in the study of catalysts is to increase their selectivity, which is the capability to steer a reaction to produce a desired product, and activity, which is the ability to increase a given reaction rate.

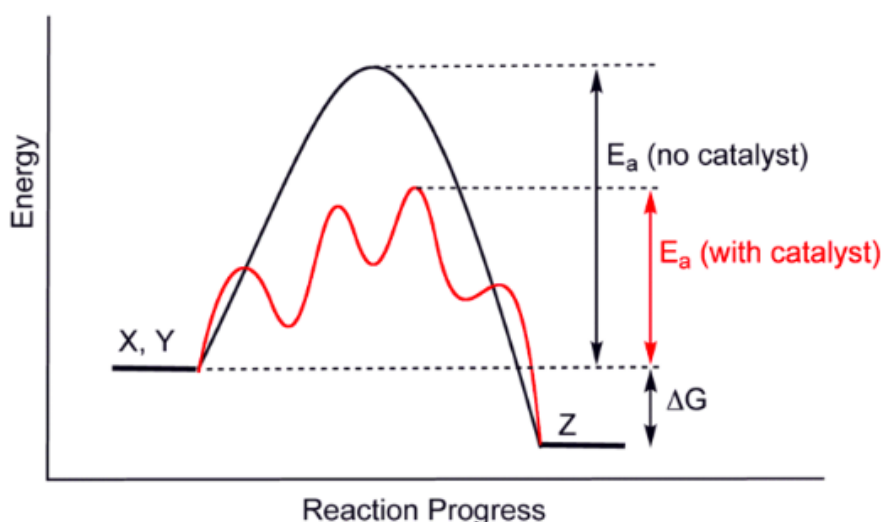


Figure 2.1: A catalyst speeds up a reaction by lowering the activation energy required for the reaction to proceed. Adapted (Learning, 2021).

2.1.1 Cluster Size Effect in Catalysis

In heterogeneous catalysis, the catalytic reaction occurs in the active sites (Taylor, 1925). As exemplified in Fig. 2.2, a catalytic reaction occurs in three main steps: the reactants first adsorb onto active sites, then react to form a product, and finally the product desorbs leaving the active site clear.

The concentration of active sites where catalytic reaction steps occur is much smaller than the total concentration of available surface sites (Somorjai et al., 2002). Since the active sites are composed by surface atoms, and smaller clusters have higher percentage of surface atoms (Fig. 2.3), the use of nanoparticles instead of bulk materials enhances catalytic activity. However, it is important to note that for some reactions the increase in cluster size can improve catalytic activity too (Shtyka et al., 2020), then the nanoparticle

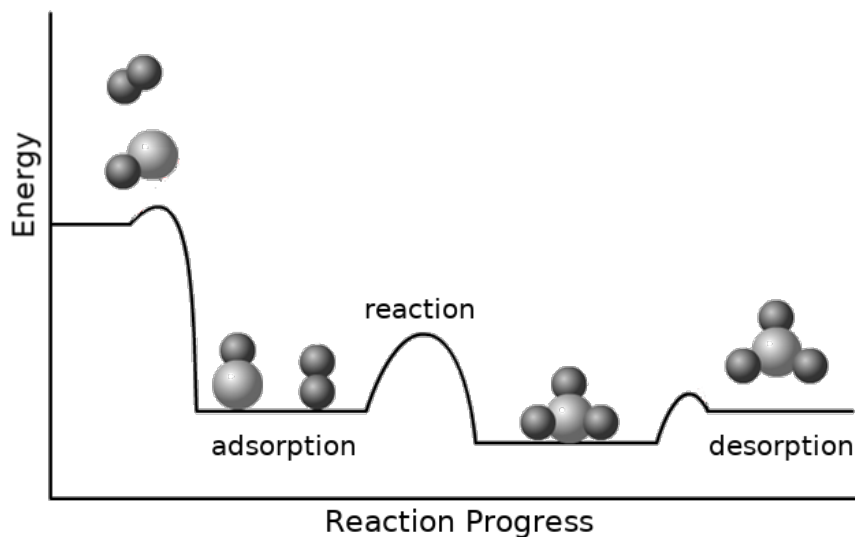


Figure 2.2: Schematic representation of a catalytic process in heterogeneous catalysis. First, the reactants adsorb into the active sites. Then the reaction occurs forming a product. Finally, the product desorbs leaving the active site available. Adapted (ESA, 2018).

size should be optimized for each catalytic reaction and catalyst. Cluster size can also affect catalytic performance because of surface and electronic properties changes with the cluster size.

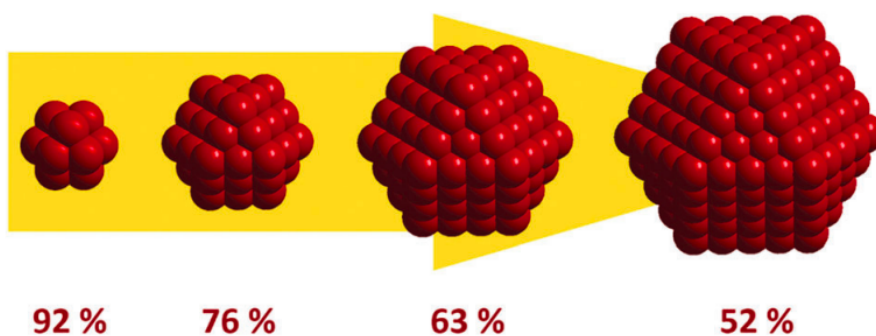


Figure 2.3: Schematic representation of the change on the percentage of surface atoms as a function of the nanoparticle size. Adapted from Sonström & Bäumer (2011).

2.1.2 Supported Nanoparticles

To achieve high dispersion and enhanced thermal stability in catalysts, in heterogeneous the nanoparticles (which are usually metals) are generally anchored over the surface of a less active materials such as carbon black and metal oxides with high surface area,

for instance mesoporous zeolites (Navalón & García, 2016, Haruta, 1997). The material in which the nanoparticles are anchored is called support and is typically composed of particles in the order of hundreds of nm to few μm . Supported catalysts can be prepared in several ways (Delmon et al., 1997), one of the most common being deposition by impregnation. It can be made via several methods, including impregnation by soaking (Poncelet et al., 1995), dry or pore volume impregnation (Ertl et al., 2008), incipient wetness impregnation (Ertl et al., 2008), co-impregnation (Qiu et al., 2013) and successive impregnation (Del Angel et al., 2003). In this method, the nanoparticles are adsorbed by Van der Waals forces. Fig. 2.4 shows an illustration of how supported nanoparticles compose a real catalyst. Supports are usually inert during the reaction, however certain nanoparticle/support combinations can highly improve or impair the catalytic activity. Mostly, the influence of the support will be on the electronic density of states of the nanoparticles, and in particular its surface (Joyner et al., 1984). The magnitude of this interaction can be very high, e.g. in the strong metal support interaction (SMSI) effect, where the oxide moieties from support can migrate into the surface of the nanoparticles encapsulating them (Figueiredo et al., 2019).

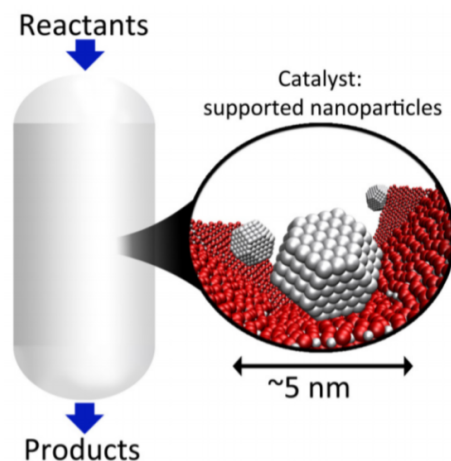


Figure 2.4: Structural representation of an industrial catalyst. The catalytic phase is found inside a reactor into which a flow of reactant gases enter. The products are ejected on the opposite end to which the reactants enter. This reactor can be heated to provide the required energy for the reaction. The nanoparticles are usually synthesized with a mean size of a few nanometers whereas the support is made of bigger particles with a large surface area available for nanoparticle adsorption. Adapted from Mom (2017).

2.1.3 Catalyst Deactivation

Besides optimal selectivity and activity, a long lifespan is highly desirable for catalysts. However, their degradation is unavoidable after many cycles, specially due to the

high temperatures in which most catalytic reactions occur. The time for deactivation can range from seconds to years, depending on the reaction (Moulijn et al., 2001). There are several mechanisms of catalyst deactivation, which can be of chemical, mechanical or thermal nature (Bartholomew, 2001, Forzatti & Lietti, 1999, Argyle & Bartholomew, 2015). Table 2.1 gives a brief description of the main mechanisms. In the simplest models, the catalytic activity is proportional to the number of active sites (Moulijn et al., 2001)

$$k_{obs} = N_T k_{intr} \eta \quad (2.1)$$

where k_{obs} and k_{intr} are the observed and intrinsic rate constants for the reaction (per active site), N_T the total number of active sites, and η the effectiveness factor. Catalyst deactivation can be caused by (i) a decrease of the number of active sites (N_T decreases); (ii) a decrease of the quality of the active sites (k_{intr} decreases); and (iii) a degradation in accessibility to the sites (η decreases). In the present work, sintering and poisoning mechanisms will be discussed in more details.

Table 2.1: Mechanisms of catalyst deactivation (Argyle & Bartholomew, 2015).

Mechanism	Type	Description
Poisoning	Chemical	Strong adsorption of species on active sites which block sites for catalytic reaction, e.g Pt _x Pd _{1-x} ($x = 1, 0.7,$ or 0.5) under H ₂ S sulfidation (Bernardi et al., 2009)
Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores, e.g mechanical deposits of carbon and coke (Lange, 2015)
Thermal degradation and sintering	Thermal Thermal/chemical	Thermally induced loss of catalytic surface area, support area, and active phase-support reactions, e.g growth of Pd nanoparticles above 300 K Tait et al. (2005)
Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound, e.g Al ₂ (SO ₄) ₃ formation in CO oxidation by Pt/Al ₂ O ₃ catalyst (Bartholomew & Farrauto, 2011)
Vapor–solid and solid–solid reactions	Chemical	Reaction of vapor, support, or promoter with catalytic phase to produce inactive phase, i.e formation of K ₂ O film in catalytic combustion by Co/K supported on CeO ₂ (Froment & Delmon, 1994)
Attrition/crushing	Mechanical	Loss of catalytic material due to abrasion; loss of internal surface area due to mechanical-induced crushing of the catalyst particle, e.g carbiding of primary Fe ₃ O ₄ particles increases their specific volume and micro-morphology, breaking up these particles (Kalakkad et al., 1995)

2.2 Poisoning

Catalyst poisoning is caused by the strong adsorption of impurities on active sites, making them unavailable for reactions. It is one of the longest known issues in catalysts and, although it has been widely studied, it is still subject of intense research nowadays (Chernyshev et al., 2019). Due to poisoning the number of active sites in Eq. (2.1) decreases as

$$N_T = N_{T_0}(1 - \alpha) \quad (2.2)$$

where N_{T_0} is the initial number of active sites and α is the fraction of the sites poisoned. Furthermore, the poisoner molecules are predominantly present in the outer shell of the cluster. This implies that the accessibility to the sites decreases (η decreases, Eq. (2.1)).

Undesired compounds are very commonly adsorbed into catalyst surfaces. However, if they are easily removable by a thermal treatment, poisoning is reversible and hence less harmful. When the contaminants are strongly adsorbed in such a way that they cannot be easily removed (thermal treatments at low temperatures), the poisoning effect is irreversible and leads to catalyst deactivation (Dunleavy, 2006). Poisoning is not always detrimental, it can be used to enhance selectivity, although usually at the expense of activity (Argyle & Bartholomew, 2015). It is also possible that a strongly adsorbing species leads to an increase in activity, in this case the species is called a promoter instead of a poisoner (Moulijn et al., 2001).

The toxicity of a species will depend on the oxidation state of the catalyst. In general, toxicity increases with increasing atomic or molecular size and electronegativity (Argyle & Bartholomew, 2015). Sulfur species interact with metals via s and p orbitals, and are one of the main poisoning sources for metallic catalysts. It affects many important catalytic processes like hydrogenation, methanation, Fischer–Tropsch synthesis, steam reforming and fuel cell power production. Nevertheless, the rate of sulfur poisoning and hence sulfur resistance varies from catalyst to catalyst and it is a function of catalyst composition (Bartholomew et al., 1982) and reaction conditions (Erekson & Bartholomew, 1983).

2.2.1 Poisoning Mechanisms

Catalyst poisoning is divided into three categories: selective, anti-selective and non-selective. Selective poisoning involves preferential adsorption of the poisoner at the most active sites at low concentrations. It can be useful when needed to inhibit reactions with

specific functional groups (e.g. selective catalytic reduction of NO_x with NH_3 by Peng et al. (2012)). When sites of low activity are blocked, the poisoning is called anti-selective. If the poisonous species adsorbs to sites without preference, the poisoning is nonselective (Bartholomew, 2001). Fig. 2.5 shows the normalized activity (the reaction rate normalized to initial reaction rate) versus normalized poisoner concentration patterns for each type of poisoning. It is based on the assumption of uniform poisoning of the catalyst surface and surface reaction rate controlling, i.e. negligible degradation of accessibility to the sites. However, for cases where these assumptions do not hold the activity versus poisoner concentration can produce a non-linear curve even for nonselective poisoning (Forzatti & Lietti, 1999).

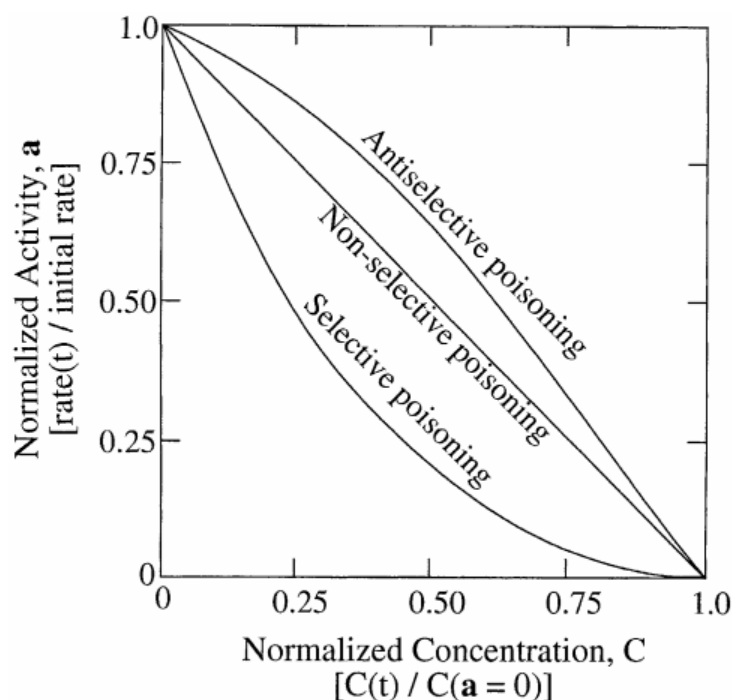


Figure 2.5: Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration (Bartholomew, 2001).

The adsorption of poisonous species affects catalytic activity through competitive adsorption, i.e. the contaminants obstruct adsorption/reaction sites at the metal surface. There are several consequences triggered by the adsorption of poisonous species (Argyle & Bartholomew, 2015, Delmon, 2000). It follows that, by virtue of its strong chemical bond, the poisoner can electronically modify its nearest neighbor metal atoms and possibly its next-nearest neighbor atoms, thereby modifying their abilities to adsorb and/or dissociate reactant molecules. Another effect may be the atomic restructuring at the surface induced by the adsorbed poisoner (Bernardi et al., 2009), possibly causing dramatic

changes in catalytic properties, especially for reactions sensitive to surface structure. In addition, the adsorbed poisoner blocks access of adsorbed reactants to each other and prevents or slows the surface diffusion of adsorbed reactants. In Fig. 2.6, sulfur poisoning of a metal surface on a reaction of ethylene hydrogenation is illustrated. The sulfur atom hinders reactants interaction, while occupying active sites on the metal catalyst.

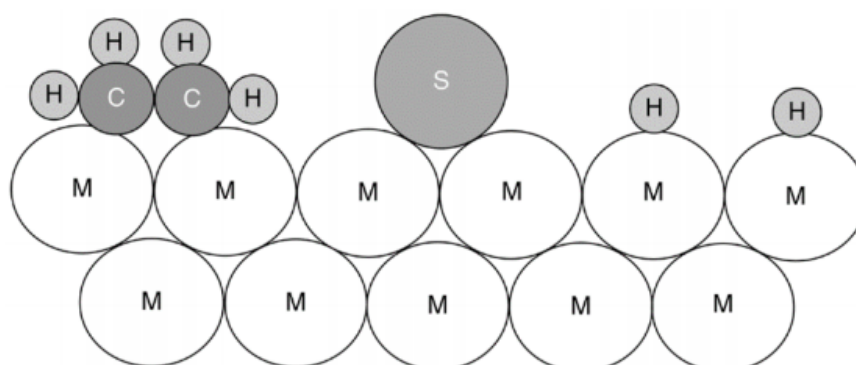


Figure 2.6: Conceptual model of nonselective poisoning by sulfur atoms of a metal surface in ethylene hydrogenation (Bartholomew et al., 1982). In this reaction ethylene (C_2H_4) reacts with H_2 to form ethane (C_2H_6) and is usually catalysed by Ni.

2.2.2 Poisoning Prevention

The main issue originated by poisoning is the loss of active sites, blocked by strongly adsorbed impurities. Hence, it is best prevented by removal of impurities from the feed to levels that enables catalysts operating at its optimal lifetime.

When the environment can not be thoroughly controlled or the presence of possible poisonous species is unavoidable, it may be possible to lower the rate of poisoning through careful choice of reaction conditions that weak the strength of poisoner adsorption, specially with carbon species (Bartholomew, 1982).

Some reactions can present an undesired metal species that produces residuals which lower the catalytic performance. The poisoning of catalysts by metal impurities can be moderated by selective poisoning of the unwanted metal (Parks et al., 1980).

Another strategy that has been employed to reduce the impact of poisoning, particularly for sulfur, is the inclusion of traps (commonly referred to as "getters" in literature) as part of the catalyst, which act as sacrificial stoichiometric reactants to protect the active metal by preferentially adsorbing the poisoner (Jacobs et al., 2000).

2.3 Sintering

Thermal induced deactivation of catalysts is very difficult to prevent and mostly irreversible. This deactivation process results from: (i) loss of catalytic surface area due to crystallite growth; (ii) loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase; and/or (iii) chemical transformations of catalytic phases to noncatalytic phases (Argyle & Bartholomew, 2015). While (iii) is a strictly chemical process, which depends on the catalytic and reactive species, (i) and (ii) have a higher range. Processes (i) and (ii) constitute a phenomenon called sintering (also called coarsening, or grain growth in the ceramics literature). In summary, sintering is a process whereby clusters increase their size and reduce their number, and the most detrimental consequence for catalysis is the loss of surface area, which reduces the number of active sites.

Sintering is the predominant mechanism of catalyst deactivation. Its high recurrence is in part because sintering is not limited to specific reactions, although the sintering rates vary according to the reaction (Vogelaar et al., 2010, Teixeira & Giudici, 1999, Sadeqzadeh et al., 2013, Euzen et al., 1999). In addition, catalytic reactions are usually carried out at high temperatures, and sintering rates grow exponentially with temperature. Empirical correlations have been proposed for the catalytic activity as a function of time and temperature,

$$\frac{da}{dt} = -k_d a^m \quad (2.3)$$

$$k_d = k_{d0} e^{-E_a/(RT)} \quad (2.4)$$

in which a is the catalytic activity, and k_d the deactivation rate constant (Moulijn et al., 2001). The exponent m often has a value of 2. Besides temperature, which affects sintering rates according to Eq. (2.4), other factors such as atmosphere, metal type, metal dispersion, promoters/impurities and support surface area, texture and porosity also contribute to deactivation. Although many of these parameters can be controlled to some extent, the reaction temperatures are almost impossible to decrease for a given system because it would decrease the catalytic activity as well.

2.3.1 Sintering Mechanisms

For supported nanoparticles, there are two main mechanisms of sintering: crystallite migration and atomic migration (also known as Ostwald ripening). Crystallite migration

involves the diffusion of entire crystallites over the support surface, followed by collision and coalescence (process in which two phase domains come together and form a larger phase domain). Atomic migration involves detachment of metal atoms or molecular metal clusters from crystallites, diffusion of these atoms over the support surface (or through vapor phase), and ultimately, capture by other crystallites (Bartholomew, 2001). The driving force for both mechanisms is the minimization of the total surface energy of the system, and both can act simultaneously. When the cluster adhesion to the support is weak, the coalescence mechanism is favored, whereas the atomic diffusion mechanism is favored for strongly adhered clusters (Jose-Yacamán et al., 2005). Fig. 2.7 illustrate both mechanisms.

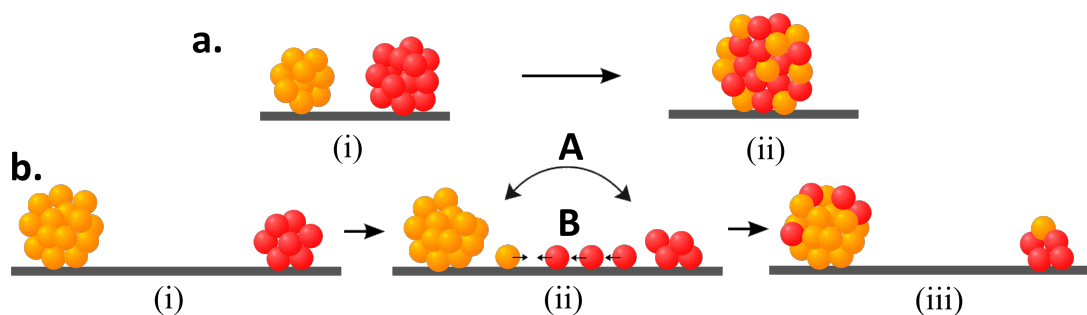


Figure 2.7: Schematic representation of sintering mechanisms. **(a)** Crystallite diffusion: whole clusters migrate along the support surface. When two clusters are close enough (i) a bigger cluster is formed by coalescence (ii). **(b)** Atomic diffusion: Clusters are not required to be in close contact (i). Atoms (or clusters of few atoms) migrate from one cluster to another cluster (ii), in vapor phase (A) or diffusing along the surface (B). The net mass transport is from smaller to larger clusters, because of the lower average coordination of atoms at the surface. Thus big clusters get bigger at the expense of smaller clusters (iii).

Nanoparticles are known to present Brownian motion under high temperatures. Through cluster shape oscillations, provoked by small dislocations of multiple atoms with time, mostly due to thermal energy, small changes in the center of gravity of the nanoparticles occur. Together with the weak adhesion to the substrate, it leads to slight positional shifts of this cluster with each oscillation. Such motions may be described by the classic Frank-Read mechanism (Frank & Read Jr, 1950) for slip. Slip the displacement of one part of a crystal relative to another part along crystallographic planes and directions. The result of the slip is a distortion, viewed as a structural fluctuation, which changes the center of gravity of the nanoparticle on the substrate, thus changing its point of contact. This appears, over time, as small, random displacements across the surface, i.e. Brownian motion, which is microscopically manifested as diffusion. Diffusion coefficients for

supported clusters have been derived based on bubble diffusion theory. Relations between the cluster diffusion coefficient D_p and the surface atomic diffusion coefficient D_s of the type

$$D_p = C \left(\frac{a}{d} \right)^4 D_s \quad (2.5)$$

have been proposed (Gruber, 1967, Harris, 1995), where a is the atomic diameter and d is the cluster diameter, and C is a constant that depends on the cluster shape. Eq. (2.5) indicates that the diffusion of clusters is proportional to the diffusion of its surface atoms and that cluster diffusion grows with decreasing cluster size. The surface atomic diffusion is strongly dependent on temperature and is given by

$$D_s = D_0 e^{-E_a/(RT)} \quad (2.6)$$

where D_0 is a constant, E_a is the activation energy for surface diffusion, R is the gas constant and T is the temperature (Somorjai & Klerer, 1972). Other types of expressions have been proposed in bubble diffusion theory and were later applied to nanocrystal diffusion (Chen & Cost, 1974, Willertz & Shewmon, 1970), where D_p has exponential growth with decreasing d . The variation in migrated distances can be very significant for only few tens of nm difference in cluster size. Considering various models proposed for cluster migration, Harris (1995) suggested that for Pt/Al₂O₃ at 600°C, spherical clusters of ~5 nm in diameter would migrate about 540 nm in 2 h, while large clusters around 24 nm would move at most a distance equal to their diameter.

Coalescence is a process driven by surface energy minimization: the surface area of a coalesced nanoparticle is smaller than that of the sum of the surface areas of the two original nanoparticles. The melting points of nanoparticles are substantially lower than the bulk value, increasing with nanoparticle diameter asymptotically to the bulk value (Buffat & Borel, 1976). The heat created at the coalescing interface melts crystalline material, with heat transferred to the volumes of the coalescing clusters as well as to the surroundings. This facilitates the coalescence mechanism due to the formation of a liquid-like surface layer in the nanoparticles (Sun et al., 2002). In addition to the high percentage of surface atoms, which will conduct the mass transfer through grain boundaries in coalescing clusters, this property makes the coalescence easier for nanoparticles than for macroscopic particles. Fig. 2.8 shows *in situ* sequential TEM images obtained in an 1h window, where the migration and coalescence of Ni nanoparticles supported on MgAl₂O₄ under an atmosphere of H₂O:H₂ 1:1 at 750 °C can be seen.

Recently, a new mechanism in nanoparticle growth has gained notoriety: the ori-

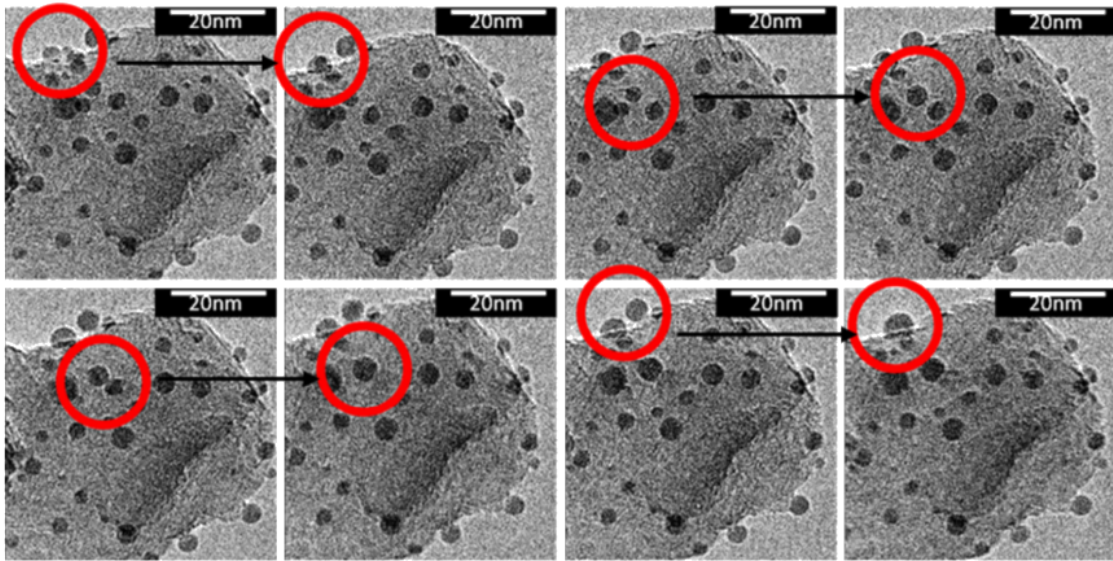


Figure 2.8: *In situ* TEM images of Ni/MgAl₂O₄ nanoparticles exposed to H₂O:H₂ 1:1 atmosphere at 750 °C (Hansen, 2006).

ented attachment mechanism, first proposed by Penn & Banfield (1998). The oriented attachment mechanism propose that, when in contact, nanocrystals rotate to align their crystalline planes while coalescing. For this reason it is also called grain-rotation induced grain coalescence (GRIGC) mechanism. From the thermodynamical point of view, combination in a coherent crystallographic orientation will eliminate the interfaces of nanocrystals, thereby reducing surface energy (Zhuang et al., 2009). When two nanoparticles just attached without self-recrystallization, the curvature radius at the joint is negative. According to the Gibbs–Thompson relation,

$$\mu(R) = \mu_0 + \frac{2\gamma\Omega}{R} \quad (2.7)$$

where $\mu(R)$ is the chemical potential, μ_0 is the chemical potential at a flat interface, γ is the surface free energy, Ω is the volume per atom, and $1/R$ is the curvature radius, the chemical potential at the joint is negative (Zhang et al., 2010). Thus atoms sited on other places are thermodynamically favored to move to the joint. As shown in Fig. 2.9, clusters collide (i), reorient (ii) and coalesce (iii) to a final cluster that adjusts its morphology to minimize surface energy (iv). Steps (ii) to (iii) are very rapid. But the process from state (iii) to state (iv) might be slow, thus irregular small cluster attachment geometries can be seen when the sizes of the assembling units are small. The orientation of the clusters is not always perfect. Coalescence by oriented attachment can result in nanoparticles with irregular morphologies and typical defects of twins, stacking faults, and misorientations

(Tang et al., 2002, Penn & Banfield, 1998). On the other hand, when the sizes of the assembling units become larger, the possibility of oriented attachment decreases, so there is enough time for nanoparticles to self-organize into round shapes.

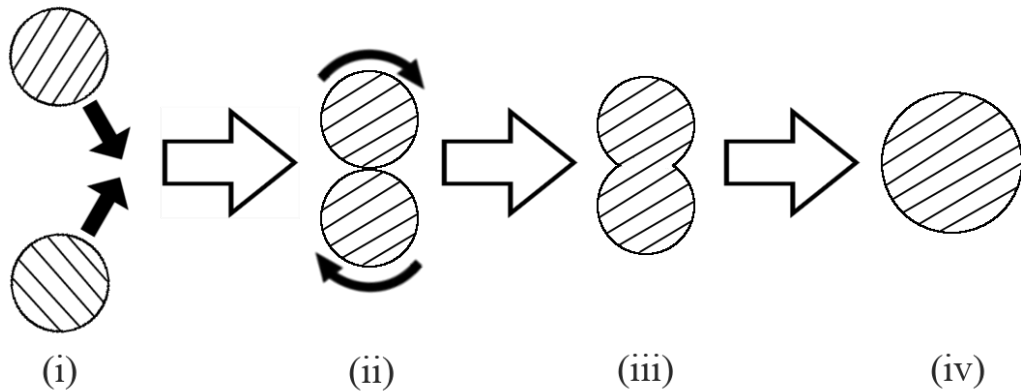


Figure 2.9: Schematics of self-recrystallization following oriented attachment. The diffusing nanoparticles collide (i) and then rotate to have coherent crystallographic orientation (ii). Following reorientation, they coalesce (iii) and adjust morphology (iv) in a process called re-crystallization. Adapted from Zhuang et al. (2009).

Li et al. (2012) used a liquid cell mounted within a high resolution transmission electron microscope (TEM) for the direct *in situ* observation of iron oxide nanoparticle growth by the Oriented Attachment mechanism at room temperature, as seen in Fig. 2.10. The surfaces of adjoining nanoparticles made transient contact at many points and orientations before finally attaching and growing together. Irrespective of how many times nanoparticles made contact, at the time of attachment they either shared the same crystallographic orientation or their orientations were twin-related (a mirrored image of the other particle crystallographic orientation). Molecular dynamics (MD) simulations have been frequently used to study coalescence (Song & Wen, 2010, Zhu, 1996, Ding et al., 2009), and they also show the oriented attachment mechanism. Classical molecular dynamics simulations with a simple two dimensional Lennard-Jones model (Ding et al., 2009) and the Matsui-Akaogi force field (Alimohammadi & Fichthorn, 2009) have demonstrated that the nanoparticles may reorient themselves to match their crystalline orientations at the beginning of the sintering.

In the same way than crystallite migration, the driven force of Ostwald Ripening is the decrease in total surface free energy. The mechanism bears the name of Ostwald, who reported at 1900 the first systematic study of a two phase dispersion coarsening by transfer of matter from small nanoparticles to larger ones (Ratke & Voorhees, 2013).

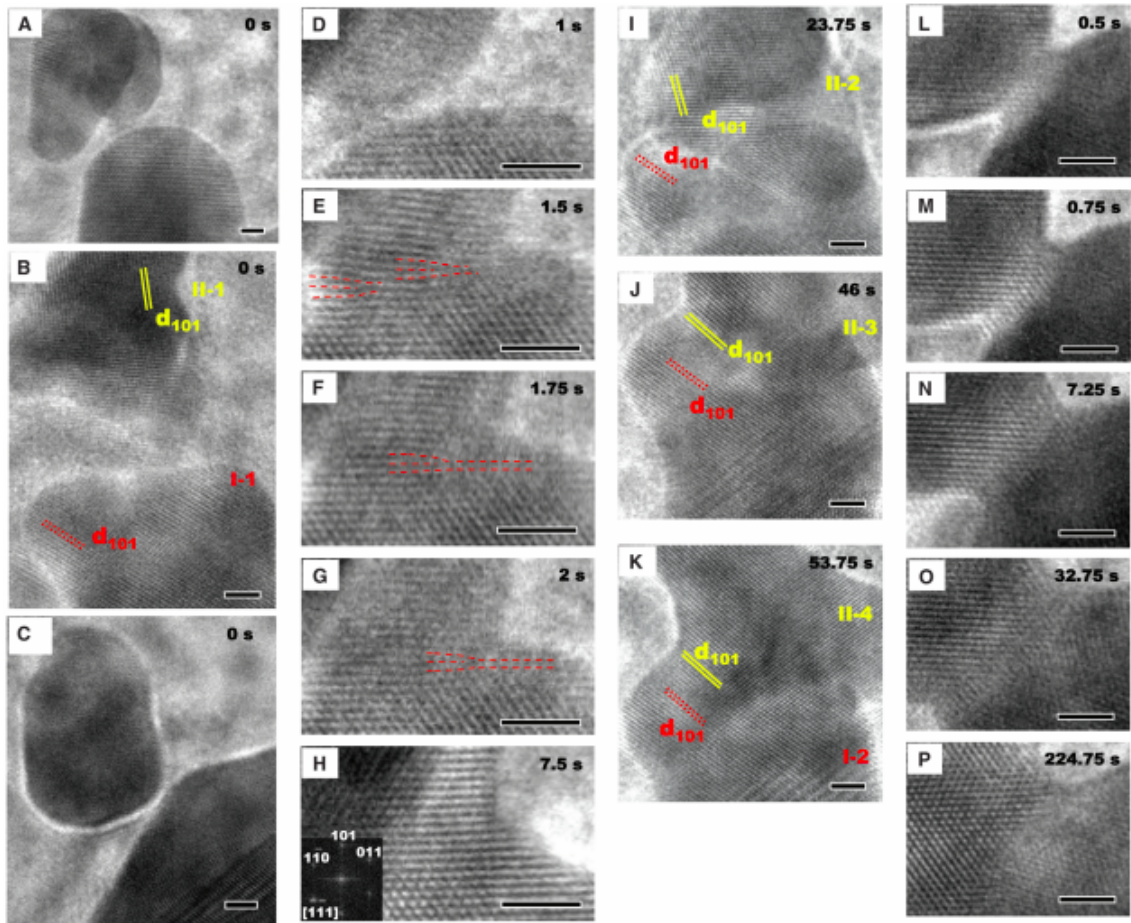


Figure 2.10: Sequences of *in situ* TEM images show the details of the oriented attachment process. (A) and (D to H) Sequence showing attachment at a lattice-matched interface. (A) shows the arrangement of nanoparticles before attachment. The asymmetric nanoparticle in front of the smaller spherical nanoparticle is not involved in the attachment process. (D) to (G) show formation of the interface. Two edge dislocations denoted in (E) to (G) by red dashed lines translate to the right, leaving a defect-free structure in (H). (B) and (I to K) Sequence of images showing relative rotations of nanoparticles during the attachment process, leading to a lattice-matched interface. Nanoparticles I and II have their (-121) plane axes perpendicular to the viewing plane. (C) and (L to P) Sequence showing how the interface expands laterally after attachment. All scale bars are 2 nm. Reproduced from Li et al. (2012).

In the Ostwald model cluster growth occurs as a result of the Gibbs-Thomson equation (Eq. (2.7) which describes the equilibrium concentration at the surface of a cluster. The difference in the chemical potential of the clusters within the distribution will determine the net rate of mass transport. As the chemical potential varies with $1/R$, the net mass transport will be from small to larger clusters. In this way, small nanoparticles tend to vanish and large particles tend to grow (Challa et al., 2011).

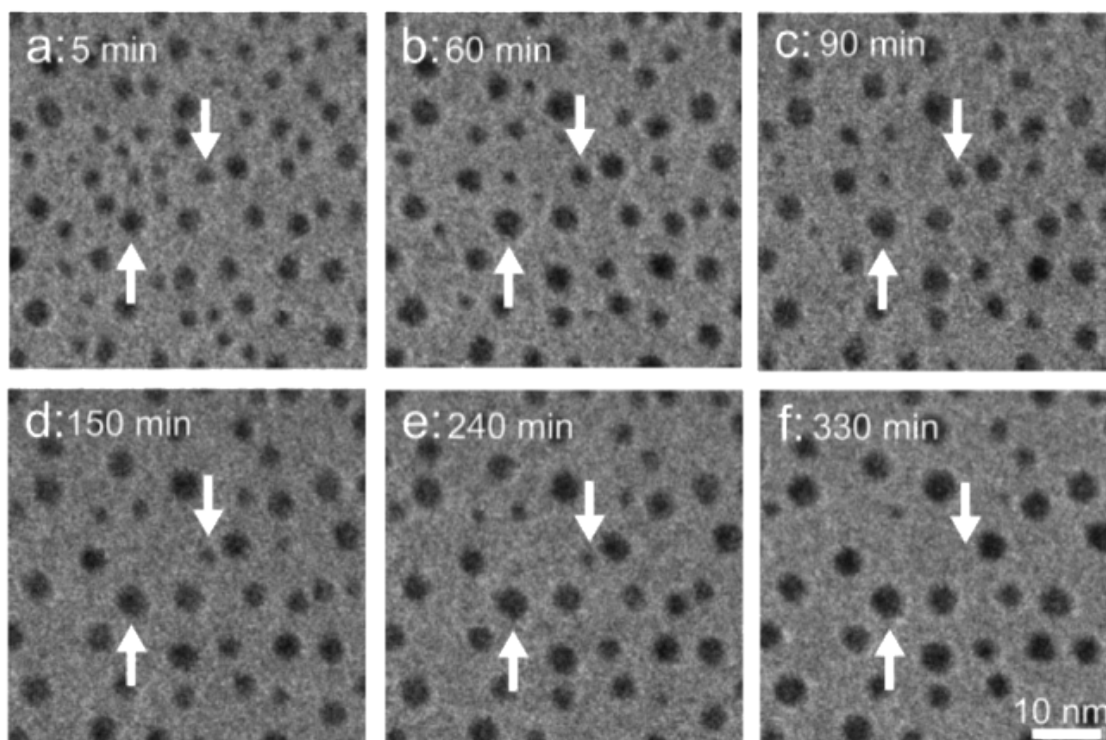


Figure 2.11: (a-f) *In situ* TEM images of Pt nanoparticles supported on SiO₂ exposed to an O₂ atmosphere under 10 mbar pressure and 650 ° C. The arrows indicate two nanoparticles, one increases in size while the other decreases. The images were taken from Simonsen et al. (2011).

There are two kinds of Ostwald ripening, depending on the mobile species involved: a surface-mediated ripening and a gas-phase-mediated ripening. For the former, atomic species, after being emitted from a nanoparticle, diffuse through the support surface and attach to another nanoparticle. In this case, the interaction between the support and the nanoparticle in comparison to the mobile species has significant effect on sintering (Cargnello et al., 2013). In the gas-phase mediated sintering the volatile species are emitted from nanoparticles and the growth is caused by re-adsorption of those volatile species on large nanoparticles (Plessow & Abild-Pedersen, 2016). Fig. 2.11 shows a time-lapsed TEM image series of Pt nanoparticles, acquired during the exposure to 10 mbar synthetic air at 650 °C, where the Ostwald ripening mechanism is evidenced (Simonsen et al., 2011).

Experimental observations, such as shown in Fig. 2.12, where Ni nanoparticles surface area is measured as a function of time during sintering of Ni/SiO₂ nanoparticles under H₂ atmosphere at 650, 700, and 750°C, demonstrate that sintering is strongly temperature dependent. The absolute melting point temperature T_{mp} has a crucial role in sintering rates since the driving forces for dissociation and diffusion of surface atoms

are both proportional to the fractional approach to T_{mp} . The Hüttig and Tamman temperatures are often used to empirically describe the temperatures at which the two migration mechanisms occur. As temperature increases, the mean lattice vibration of surface atoms increases; when the Hüttig temperature ($0.3 T_{mp}$) is reached, less strongly bound surface atoms at defect sites (e.g., edges and corner sites) dissociate and diffuse across the surface, while at the Tamman temperature ($0.5 T_{mp}$), atoms in the bulk become mobile (Argyle & Bartholomew, 2015).

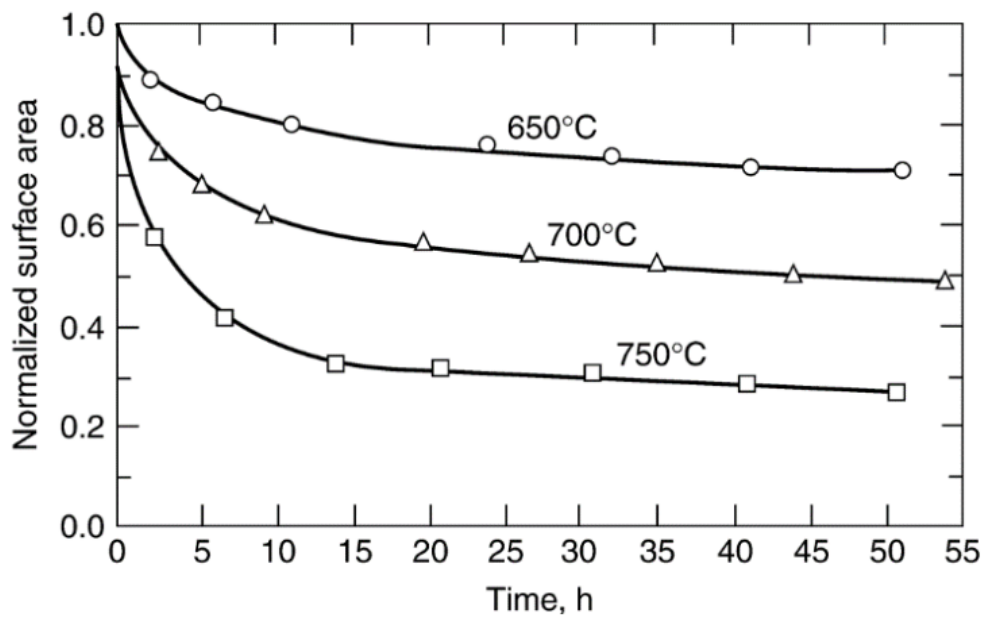


Figure 2.12: Normalized Ni surface area as a function of time during sintering of Ni/SiO₂ in H₂ atmosphere at 650, 700, and 750°C. Reproduced from Bartholomew & Sorensen (1983).

There have been a number of attempts to develop models of sintering. The coalescence models are largely based on the classic work of Smoluchowski (1916), describing the cluster density due to binary encounters of diffusing clusters. Whereas, the Ostwald ripening models go back to the works of Lifshitz & Slyozov (1961) and Wagner (1961) on the condensation of droplets. Theories for the migration and coalescence of supported metal crystallites (Ruckenstein & Pulvermacher, 1973), and the mean growth of clusters by Ostwald ripening (Voorhees, 1985) have been accomplished and both result in a growth law of the type

$$\langle d \rangle^n - \langle d_0 \rangle^n = kt \quad (2.8)$$

where $\langle d \rangle$ is the mean diameter after time t , $\langle d_0 \rangle$ is the initial mean diameter, n an integer,

and k a temperature dependent constant.

Although these models are widely used, studies have shown that they do not accurately predict the sintering behaviour of very small nanoparticles. Campbell et al. (2002) showed that taking into account the very large change of energy per metal atom as a function of size, measured for the first time by single-crystal adsorption microcalorimetry, the sintering behaviour of nanoparticles is better described. The surface energy increases substantially as the radius decreases below ~ 3 nm, which could be expected because the average coordination number of the surface atoms decreases. This makes Eq. (2.7) overpredict the stability of small clusters. Therefore, for more accurate models, it seems necessary to include a proper treatment of the cluster size effect on $\mu(R)$. Furthermore, stochastic cluster models have been implemented to simulate nanoparticle sintering for both coalescence (Sander et al., 2009, Morgan et al., 2005, Akhtar et al., 1994) and Ostwald ripening (Schwind & Ågren, 2001).

The regime of each mechanism should be determined by their activation energy. However, it is highly difficult to observe the reaction stages in which each sintering mechanism prevails over the other, since *in situ* TEM imaging of sintering processes are limited to small areas and time frames. In addition, there are several factors that unpredictably influence on sintering rates (even the electron beam in TEM measurements may have some influence). Previous literature (Beck & Carr, 1988, Wynblatt & Gjostein, 1975) has suggested that the operative mechanism may change from cluster migration, in the early stages when the nanoparticles are very small, to Ostwald ripening, when the clusters become large and effectively immobile. However, recent evidence of early disappearance of small clusters are being related to Ostwald ripening at initial stages of sintering (Hansen, 2006). Because the sintering dynamics is very dependent of the metal, support, and gas atmosphere, the precise stages of sintering are still undetermined, although the mechanisms are known.

2.3.2 Sintering Prevention

There are three main approaches used for sintering prevention: (a) modification of the interface between clusters and between clusters and the support, (b) modification of the metallic nanoparticle electronic structure by bonding with other metals (*alloying*) and (c) modification of the support by nanostructuring.

(a) Cluster-cluster and Cluster/support Interface Modification

Nanoparticle coating is a method that modifies the interface between clusters and it is the most widely used for sintering prevention. To inhibit sintering, the nanoparticles are usually coated by a porous oxide shell, which acts as shield. This shell can be inert (Joo et al., 2009, Park et al., 2008, Vystavel et al., 2005) or catalytically active (Lee et al., 2016). SiO_2 , ZrO_2 , Al_2O_3 are among the most used inert oxide shells, while CeO_2 is widely used for active shells. CeO_2 exhibits high surface ion mobility and a great capacity to store and release oxygen atoms (Trovarelli, 1996), where the Ce(III)/Ce(IV) ratio can be modified by tuning the oxygen vacancies amount of CeO_2 (Della Mea et al., 2017). Although the coating method is effective in reducing sintering rates, these coatings inevitably cover a portion of the nanoparticles surface, thus harming reactivity. Furthermore, they are susceptible to decomposition at high temperatures and the inherent interconnectivity between pores often serves as a sintering pathway for metal nanoparticles (Lee et al., 2016). The nanoparticle coating is accomplished in the synthesis and typically produces a core-shell structure with a nanoparticle in the core region and the oxide in the shell region. The oxide shell must be permeable to expose the active sites in the nanoparticles. Fig. 2.13 shows TEM images of Pt nanoparticles encapsulated by SiO_2 after calcination at 350, 550 and 750 °C, where the silica shell was confirmed to present mesopores 2-3 nm size (Joo et al., 2009). Surfactants are also employed in nanoparticle synthesis to produce thermally stable nanoparticles, and many times as a template to produce oxide shells. Surfactant coatings can not hold temperatures much higher than 300 °C (Ding et al., 2004). In applications where the bulk properties are important, coating is a reliable method. However, for catalysis, where the nanoparticles surface area is of extreme importance, surfactants passivate surface active sites of the nanoparticles and are often accompanied by decrease in mass and/or energy transfer, resulting in diminished catalytic activity. Hence, the encapsulation method restricts catalysis by steric effects (Suryanarayanan et al., 2004), with exception of very specific cases in which the shell can be catalytically active. On the other hand, active shells are made of oxides instead of metal surfaces, then changing the reaction pathways of a given catalytic reaction.

(b) Alloying

As previously mentioned, the melting point of the specific metal nanoparticle plays a key role in sintering. Metals with higher melting points tend to show better thermal stability. Hence, strategies to increase the melting point of a nanoparticle can be expected to mitigate sintering (Cao et al., 2010). The main strategy to achieve this is by combining

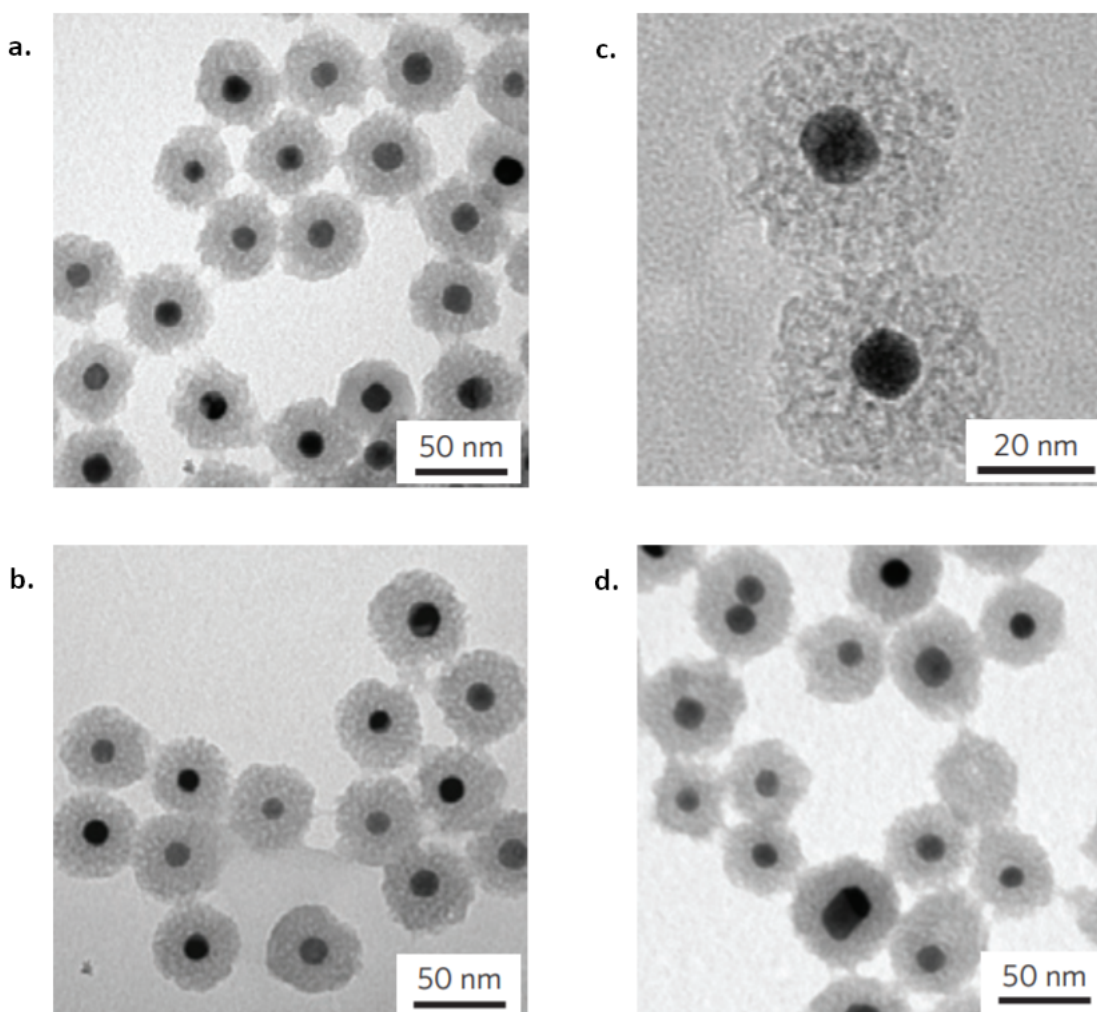


Figure 2.13: TEM images of Pt nanoparticles encapsulated by SiO₂ shells after calcination at (a, b) 350°C, (c) 550 °C and (d) 750 °C. Adapted from Joo et al. (2009).

a metal nanoparticle with another metal whose melting point is higher. This process is called alloying. The bimetallic clusters thus formed will have different chemical composition and atomic arrangements in relation to separated nanoparticles. Cao & Vesper (2010) have synthesized a thermally stable nanocatalyst with a PtRh alloy. The authors showed that the thermal stability of these nanoparticles depends critically on the Pt/Rh ratio, with higher Rh contents leading to increased thermal stability. However, thermally induced de-alloying phenomena are not rare (Jeon et al., 2010), causing metal clusters to sinter. Moreover, this strategy limits the range of available chemical compositions and therefore their activity and/or selectivity.

(c) Support Nanostructuring

Finally, there is an approach to prevent sintering which is based on designing supports that can restrain nanoparticles diffusion. The easiest and most common approach is to produce a mesoporous support (Gabaldon et al., 2007). The presence of pores in the scale of a few to a few tens of nanometers creates confining spaces for the nanoparticles, suppressing their mobility (De Vos et al., 2002). These pores must be stable under high temperature reactions for this procedure be applicable for catalysis. Some issues like pore collapse and the appearance of interconnectivity between pores are prone to happen at high temperatures and enables cluster and atomic migration (Cao et al., 2010). Beyond mesoporous supports, there are several support topologies which can overcome or hinder sintering, although the practical tailoring of these supports are usually challenging. Carbon nanotubes have been used as an alternative to limit nanoparticle collisions (Pan et al., 2007), although it does not prevent sintering from happening, only delays it. Fig. 2.14 shows the advantage of a design with wide-mouthed compartments in preventing sintering by optimizing the distance d between clusters (Liu et al., 2017).

All the alternatives above have limitations in applications for catalysis. Sintering is still an open issue and research aimed to avoiding it with minimal loss of catalytic activity and selectivity, little change in nanoparticles chemical composition and ease of reproduction is of great importance. In this work it is presented a new proposal for preventing sintering without the need of encapsulation, alloying or nanostructuring of supports.

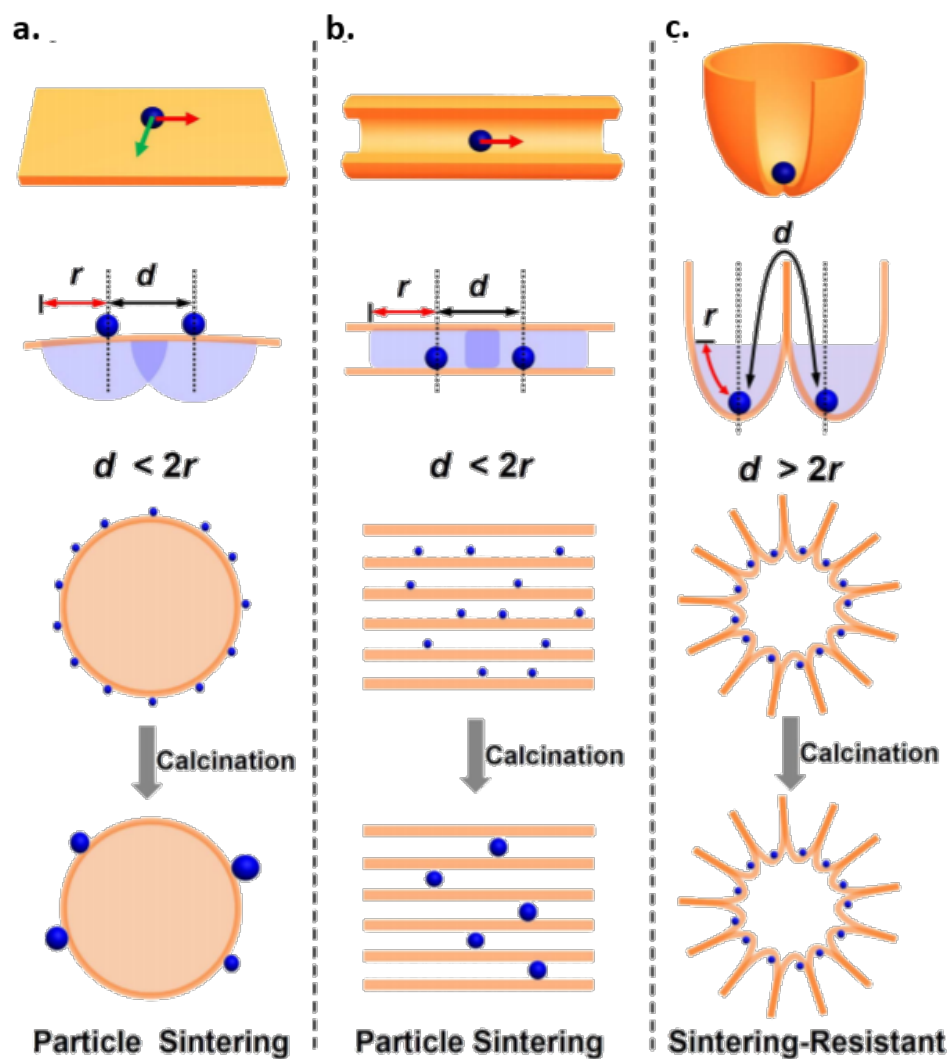


Figure 2.14: Schematic illustration of the relationships between support topology and cluster sintering. Nanoparticles dispersed on (a) the solid supports with two-dimensional open surface, (b) the porous supports with one-dimensional nanochannels, and (c) the supports enriched with wide-mouthed compartments at the surface. d stands for the cluster-to-cluster traveling distance of neighboring two clusters, while r denotes the migration length of individual clusters at a given temperature. Reproduced from Liu et al. (2017).

Chapter 3

Experimental and Numerical Techniques

In this chapter the experimental and numerical techniques used in this work are described. Their theoretical foundations and basic instrumentation are presented as well a brief historical background.

3.1 X-Ray Diffraction

X-Ray diffraction (XRD) by crystals is known since 1912, when it was discovered by Max Laue and earned him a Nobel Prize (Eckert, 2012). XRD is used for non-destructive analysis of materials and it consists on focusing a X-ray beam into a crystalline sample varying the incidence angle or the X-ray wavelength and detecting the intensity of the diffracted X-rays. Since the wavelength range of X-rays can reach the atomic scale, their interaction with a material is sensible to its atomic arrangement. Therefore, the diffraction pattern makes a reliable fingerprint for crystal structures.

The interatomic distance in materials is around a few Å, therefore it is needed incident radiation with wavelength of the same order to produce significant diffraction effects related to the atomic structure. One year after Laue's discovery of X-ray diffraction, W. L. Bragg described X-ray diffraction by representing crystals as a set of parallel atomic planes in which incident radiation is scattered. Bragg et al. (1913) showed that coherent X-rays scattered from these parallel crystal planes interfere each other.

Let d be the distance between two crystal planes and θ the angle between the incident X-ray and the material surface. Fig. 3.1 shows that the scattered X-rays from both planes will have an optical path difference of $2d \sin \theta$. Therefore, the condition for constructive interference is that the optical path difference be equal to an integer multiple of the

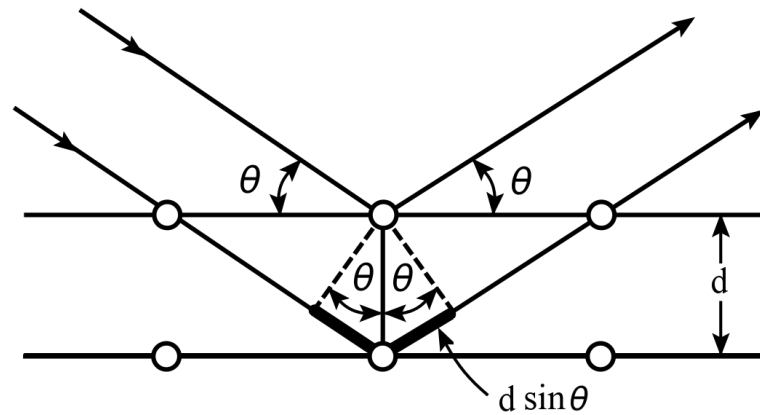


Figure 3.1: Illustration of X-rays scattering by parallel planes.

incident X-ray wavelength. Thus, Bragg's Law is formulated:

$$n\lambda = 2d \sin \theta \quad n = 1, 2, 3, \dots \quad (3.1)$$

The interplanar distance d is an structural characteristic of the material, while λ and θ can be experimentally controlled. However, a crystal structure contains several crystal planes with different interplanar distances. The characterization of a material using the Bragg's Law can be conducted varying λ or θ . The experimental methods of X-ray diffraction are distinguished by the quantity varied. In the Laue's method, λ varies while θ is fixed. In the rotating crystal method λ is fixed and θ is varied by rotating a single crystal around an axis. In the powder method, λ is fixed and θ is varied. However, the way θ is varied is significantly different from the rotating crystal method. The crystal to be examined is reduced to a very fine powder, so that each particle of the powder is a tiny crystal, or assemblage of smaller crystals, randomly oriented with respect to the incident beam. Then θ is varied by changing the incidence angle of the X-ray beam on the sample. The result is that every set of lattice planes in the material will statistically contribute to the diffraction pattern (Cullity & Stock, 1978). One of the most common geometry configurations for powder measurements, and that is used in this work, is the Bragg-Brentano geometry (Fig. 3.2). In this configuration, the X-rays source and the detector are scanned synchronously such that the X-ray incidence angle and the diffracted angle remain the same throughout the scanning. Therefore, in such a geometry only the crystal planes which are parallel to the sample surface may be probed. The detector will record intensity maxima at the θ angles that fulfill Bragg's Law for each crystal plane in the sample. The diffraction intensity as a function of the scattering angle 2θ constitutes the diffraction pattern, also called diffractogram (Fig. 3.3). The maxima regions are denominated Bragg reflections,

that are located in the Bragg's angles. The diffraction pattern is usually exhibited as a function of 2θ , which is the angle between the incident and diffracted beams.

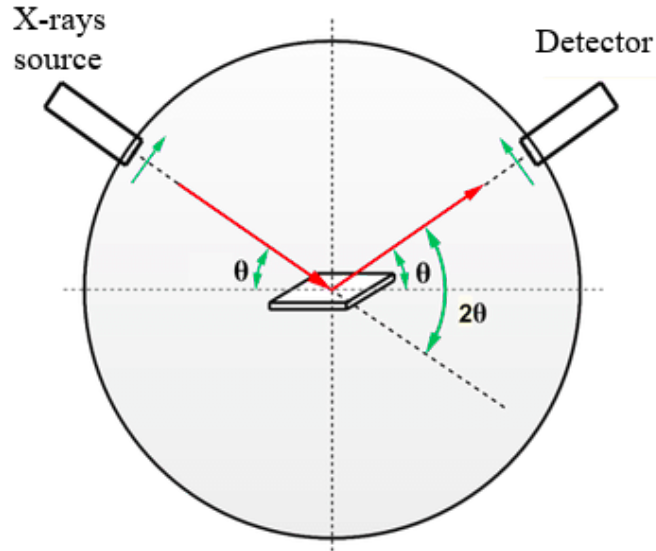


Figure 3.2: Schematic representation of the Bragg-Brentano Geometry used in XRD measurements. Adapted from Raza (2017).

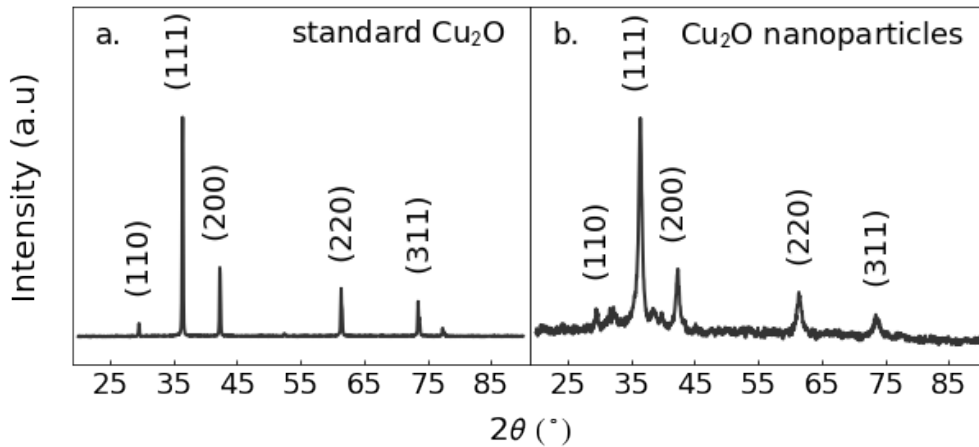


Figure 3.3: Diffraction patterns of (a) standard Cu₂O and (b) Cu₂O nanoparticles.

Any characteristic that makes a crystal deviate from a perfect lattice will shape the diffraction profile. (Fultz & Howe, 2012). The finite size of a real crystal, for example, turns the diffraction lines into peak-shaped functions. The smaller the size of a crystal the broader the peaks, due to the number of crystal planes involved in diffraction. Cullity & Stock (1978) present the following construction to illustrate this relation: suppose, for example, a crystal with finite width t , measured in the perpendicular direction to $(m + 1)$

atomic planes, as demonstrated in Fig. 3.4. Let θ_B be the angle which exactly satisfies the Bragg's Law, then rays **A**, **D**, ..., **M** arrive at planes $0, 1, \dots, m$ at a θ_B angle, so that the rays **A'**, **D'**, ..., **M'** which are scattered at a $2\theta_B$ angle are completely in phase and produce constructive interference. Now, for rays reaching the planes at angles slightly different than θ_B the optical path difference which gives total destructive interference lies deep in the crystal. If rays **B** and **L** arrive at an angle θ_1 , the scattered ray **L'**, from the m^{th} plane, will be $m + 1$ wavelengths out of phase from **B'**. Hence, there must be a crystal plane between the surface and the m^{th} plane for which there is total destructive interference, given that the optical path difference between the incident and scattered rays gradually grows with depth. Therefore, there will be pairs of crystal planes for which the scattered rays at $2\theta_1$ cancel each other, in such a way that rays scattered by the upper half of the crystal cancels those scattered by the lower half. Thus, θ_1 constitutes an angle for which the diffracted ray has null intensity. The same logic applies to $2\theta_2$, being the angle for which a ray **N'**, scattered by the m^{th} atomic plane, is $m - 1$ wavelengths out of phase with ray **C'**, scattered at the surface. These are defined as the limiting angles $2\theta_1$ and $2\theta_2$, where the intensity drops to zero. For angles between them, the intensity is not null but lower than for $2\theta_B$. For an infinite crystal, there will always be pairs of cancelling planes at an infinitesimal distance from θ_B , thus the Bragg reflections are Dirac delta functions (Fig. 3.5.a). For a finite crystal, the smaller the m , the larger the extensions $2\theta_1 - 2\theta_2$ (Fig. 3.5.b). Since less crystal planes are involved in the diffraction process, only partial destructive interference is produced in angles close to θ_B .

The finite size will then introduce a broadening B in the diffraction lines (Fig. 3.5.b). Hence, writing the Bragg's Law (3.1) for the entire thickness of the crystal gives

$$2t \sin \theta_1 = (m + 1)\lambda \quad (3.2)$$

$$2t \sin \theta_2 = (m - 1)\lambda \quad (3.3)$$

which are combined to

$$2t \cos \left(\frac{\theta_1 + \theta_2}{2} \right) \sin \left(\frac{\theta_1 - \theta_2}{2} \right) = \lambda. \quad (3.4)$$

But θ_1 and θ_2 are nearly equal to θ_B , so $\theta_1 + \theta_2 \simeq 2\theta_B$. Therefore with this approximation the length of a crystallite domain becomes

$$t = \frac{K\lambda}{B \cos \theta_B} \quad (3.5)$$

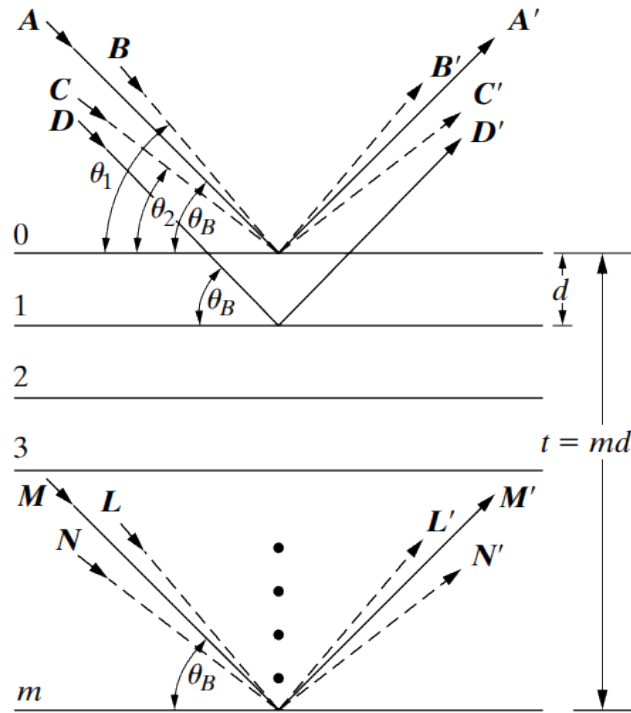


Figure 3.4: Schematic representation of $m + 1$ crystal planes in a crystal of size t . Adapted from Cullity & Stock (1978)

which is known as Scherrer's equation. The proportionality constant K is here introduced *a posteriori* to account for different cluster geometries and specific choices of peak width measurements. This equation gives the mean volume-weighted crystallite size, since the diffraction pattern contains contributions from several crystal planes along the depth of a cluster, and clusters with several sizes are measured.

Several other factors influence on the diffraction profile, not only in the Bragg's reflections shape, but also in its position and intensity (Cullity & Stock, 1978, Warren, 1990). The polarization factor describes the effects in the diffraction intensity when the incident X-ray is polarized. When electromagnetic waves are scattered by a crystal plane, the beam component which has its polarization vector parallel to the plane is scattered without losing intensity. The portion which is perpendicular to the plane is attenuated by a factor $\cos^2 2\theta$. The Lorentz factor is a geometrical correction due to X-ray beam divergence and partial monochromatization. The intensity of the scattered beam is proportional to the Lorentz Factor, given by $1/(4 \sin^2 \theta \cos \theta)$. The multiplicity factor is the number of equivalent crystal planes, i.e., the number of planes with the same interplanar spacing in a family of planes. This factor multiplies the diffraction intensity. The absorption factor describes how a sample absorbs the incident radiation. This induces an exponential

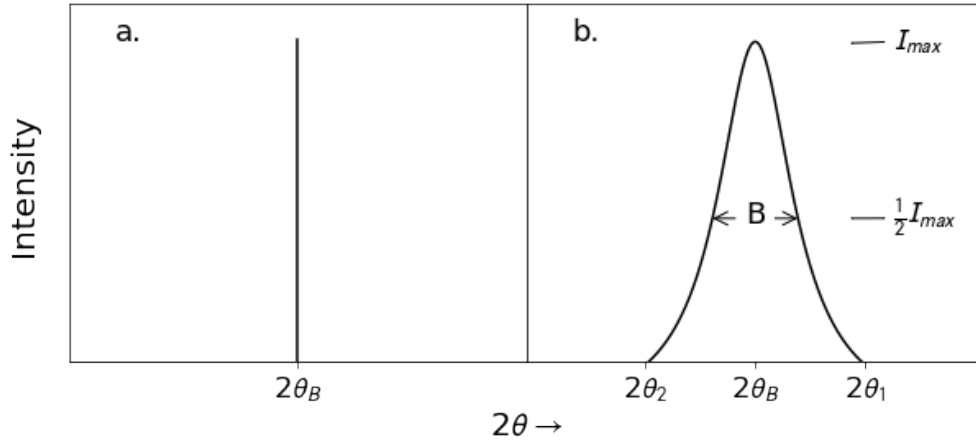


Figure 3.5: Schematic effect of finite cluster size on diffraction curves, where I_{max} is the maximum intensity and B is the full width at half maximum intensity (FWHM). Adapted from Cullity & Stock (1978).

attenuation in intensity as a function of the distance traveled by the X-ray inside the material. The temperature factor describes the effects in the diffraction lines due to the thermal oscillation of the atoms. The main effects of temperature in the XRD patterns are expansion of the unit cell; changing of the Bragg's angles; attenuation of the intensity of the diffracted X-rays, due to the atomic disorder induced by the temperature; increase in the background between consecutive Bragg reflections. The intensity attenuation is not trivial but it can be modeled as exponentially dependent of the mean square atomic displacement.

X-rays are not scattered only by electrons or single atoms, but by a collection of periodically arranged atoms. This introduces a dependence of the scattered intensity with the Miller indices:

$$I(hkl) \propto F^2(hkl) \frac{\sin^2(U_1 h \pi)}{\sin^2(h \pi)} \frac{\sin^2(U_2 k \pi)}{\sin^2(k \pi)} \frac{\sin^2(U_3 l \pi)}{\sin^2(l \pi)} \quad (3.6)$$

where U_1 , U_2 and U_3 are the numbers of the unit cells in the corresponding directions and $F(hkl)$ is called the structure factor, which describes the scattering function of one unit cell (Pecharsky & Zavalij, 2008). The structure form is defined as

$$F(hkl) = \sum_j f_j e^{-2\pi i(hx_j + ky_j + lz_j)} ,$$

where \vec{r}_j is the position of the j^{th} atom in the unit cell, f_j is the form factor of the j^{th} atom and h, k, l are the Miller indices. The form factor is defined as the ratio between the

scattering amplitude by a single electron to the scattering amplitude of the single atom.

The theoretical positions of a Bragg reflection can be calculated from the Miller indices of the respective crystal plane if the unit cell parameters are known. The Bragg's Law can be more conveniently written as

$$2\theta_{hkl} = 2 \arcsin \left(\frac{\lambda}{2d_{hkl}} \right) \quad (3.7)$$

For an orthorombic system, for example, we have:

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2} \quad (3.8)$$

There are two crystallographic parameters which define the basic structure of a diffraction pattern: the unit cell content and the spatial distribution of atoms in the unit cell. Thus a theoretical diffraction line pattern can be simulated using known crystallographic information. If the contributions of the instrumental and specimen conditions are well modeled, the convolution of the individual functions fits the data. However, *ab initio* modeling is difficult and most often a fit is performed using various empirically selected peak shape functions and parameters.

3.1.1 Rietveld Refinement

The Rietveld Refinement is a fitting method that seeks to use the entire diffraction profile, and not just the integrated intensities of the Bragg reflections, to refine the parameters of the structural model (Rietveld, 1969). It requires prior knowledge of the possible crystal structures contributing to the pattern and the instrumental parameters involved in the measurements. Initially the indexing of the XRD pattern is conducted with a database. Then, an initial model is built for each phase. However, instrumental parameters and specimen properties affect the pattern components, producing Bragg reflections with peak like shapes. Proposing a peak function to describe the Bragg reflections, a non-linear least square fitting method can be used to fit the profile. Crystal structure, instrumental, peak function and background function parameters can be involved in the fit. Since the number of parameters can be very high in the full profile fitting, the optimization is done in cycles of few non-fixed parameters until reaching a satisfactory result. This is called a refinement procedure.

After the convergence of the refined parameters, the full diffraction profile is given by the sum of the calculated profiles of each phase. Then the final parameters give valuable information about each component. Fig. 3.6 summarizes the described process

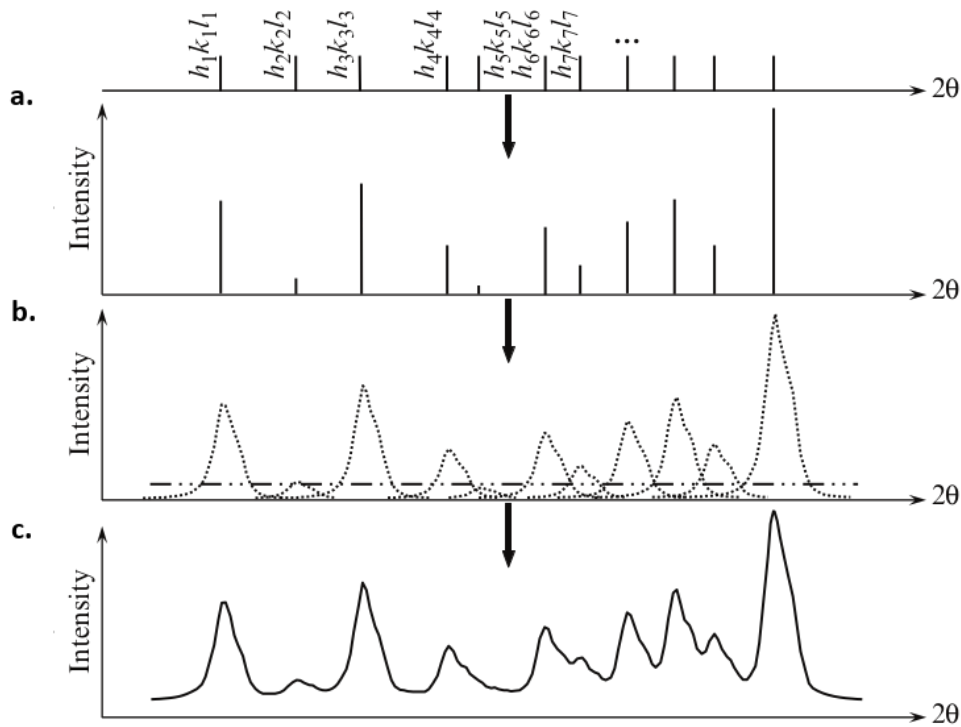


Figure 3.6: (a) Only Bragg reflections positions are represented by the vertical bars of equal length. (b) The intensity of the Bragg reflections is calculated, indicated by the length of the bars. (c) Peak shapes have been introduced, which are the convolution of instrumental and specimen contributions with appropriate peak-shape functions. A constant background is indicated by the dash-double dotted line. (d) The resultant powder diffraction pattern is the sum of all components shown separately in c. Adapted from (Pecharsky & Zavalij, 2008).

of simulating a diffraction profile to adjust the data. It is important, however, to remember that the Rietveld method requires a model of a crystal structure and by itself offers no hints on how to create such a model from first principles. Thus, the Rietveld technique is nothing else than a powerful refinement and optimization tool, and requires knowledge of the possible structures in a sample and the limiting values of the refined parameters.

3.2 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is one of the most used techniques for defining the elemental composition of a solid surface. It probes a depth around 5 nm from the surface of any solid (van der Klink & Brom, 2000). XPS analysis also reveals the chemical environment where the respective element is present, elucidating its oxidation state and existent bonds. It originates from the photoelectric effect, which was explained

by Einstein (1905), that arises from the energy transfer from photons to bound electrons if this energy is greater or equal to the electronic binding energy to the respective atom summed to the material's work function, which represents the minimum energy necessary to remove an electron from it, i.e., the difference between the Fermi energy E_f and the vacuum energy E_{vac} . In this case, the electron is ejected from the atom and this electron is called photoelectron. The kinetic energy (K.E.) of this photoelectron is given by

$$K.E. = h\nu - \phi - B.E. \quad (3.9)$$

where $h\nu$ is the X-ray photon energy, $B.E.$ is the electronic binding energy and ϕ is the material's work function.

XPS is a very straightforward technique. It consists of focusing a X-ray beam into a sample and measuring the kinetic energy of the photoelectrons emitted. Monochromatization is not mandatory, as long as the X-ray spectrum has narrow lines. The kinetic energy is directly related to the binding energy by Eq. 3.9, which allows identify the elemental composition and chemical components present in the sample's surface. However, not only photoelectrons can be emitted from a sample irradiated by X-rays. When a core electron is removed, leaving a vacancy, an electron from a higher energy level may occupy this vacancy releasing energy. Although most often this energy is released in the form of a photon (fluorescence), the energy can also be transferred to another electron, which is ejected from the atom. This second ejected electron is called Auger electron. The photoelectron peaks are labeled according to the electronic level, as seen in Fig. 3.7.a. The Auger peaks are labeled with the electronic levels of the core hole, the bound electron that occupies the core hole and the Auger electron. For example, in Fig. 3.7.a the core hole resides in the O $1s$ level (K notation), while the electron that occupies the core hole and the Auger electron come from the O $2p_{1/2}$ and $2p_{3/2}$ levels (L_2 and L_3 notation, respectively). Fig. 3.7.b. shows this Auger emission identified as O KL_2L_3 .

The depth scale of XPS measurements is controlled by the electronic inelastic mean free path, which is dependent on the kinetic energy of the photoelectron emitted. The electronic inelastic mean free path is defined as the mean distance traveled by an electron before suffering an inelastic collision. As Fig. 3.8.a shows, when a photoelectron is emitted from a depth Z within the material, if its inelastic mean free path is big it will have a higher probability of leaving the material without losing energy, whereas for a small inelastic mean free path it will have a higher chance of leaving the material with energy loss or not leaving at all. In Fig. 3.8.b is shown the universal inelastic mean free path curve, where it can be seen that for photoelectrons traveling in most materials the inelastic mean free path is around 10 Å for the typical kinetic energies of photoelectrons

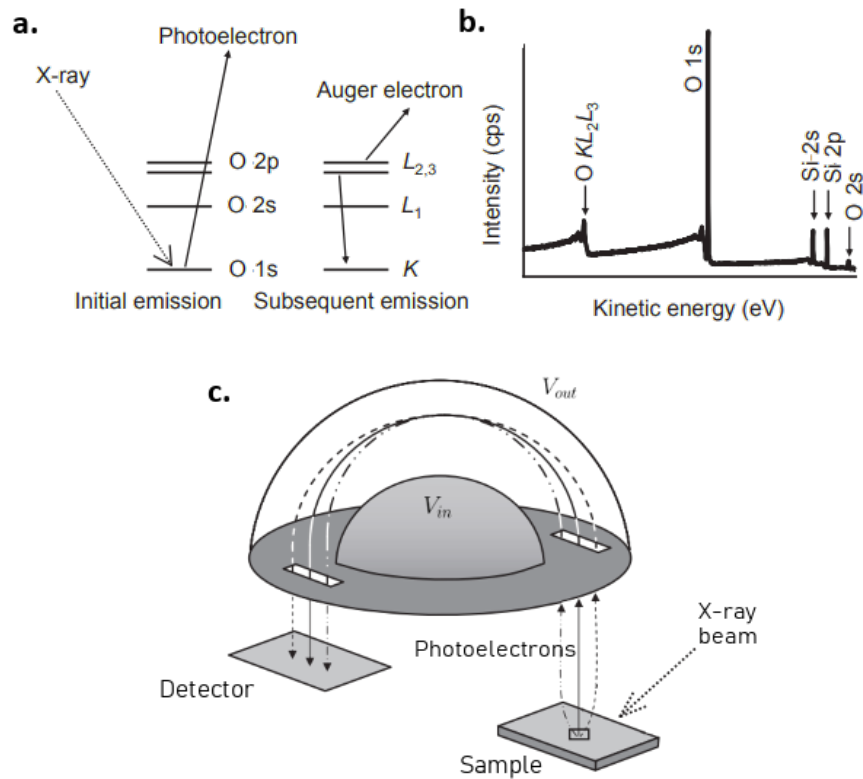


Figure 3.7: (a) Schematic example of a photoelectron and subsequent Auger electron emission. (b) Spectrum collected from a silicon wafer bearing a surface oxide as analyzed under Mg $K\alpha$ irradiation. (c) Scheme of a concentric hemispherical analyzer. Adapted from van der Klink & Brom (2000).

in the XPS technique. At a distance of around three times the inelastic mean free path, 95% of all photoelectrons are scattered before reaching the surface. Due to this small value, XPS probes mostly the surface of materials.

As depicted in Fig. 3.7.c, the XPS instrument consists mainly in an X-ray source, an electron analyzer and a detection system. The electron analyzer consists typically on two concentric hemispheres, one inside the other, of radius R_{in} and R_{out} . Applying specific potentials V_{in} and V_{out} to these hemispheres results in the deflection of photoelectrons of specific kinetic energy arriving in the multichannel detector, which is coupled to a photomultiplier. The photoelectrons are accelerated or retarded to reach this user-defined kinetic energy which is the energy that the photoelectrons must have when passing through the electron analyser in order to reach the multi-channel detector. A schematic illustration is shown in Fig. 3.7.c. In this way, the number of emitted electrons as a function of the kinetic energy can be counted.

Considering the experimental setup of the XPS measurements, the relation between kinetic energy and binding energy should be modified to

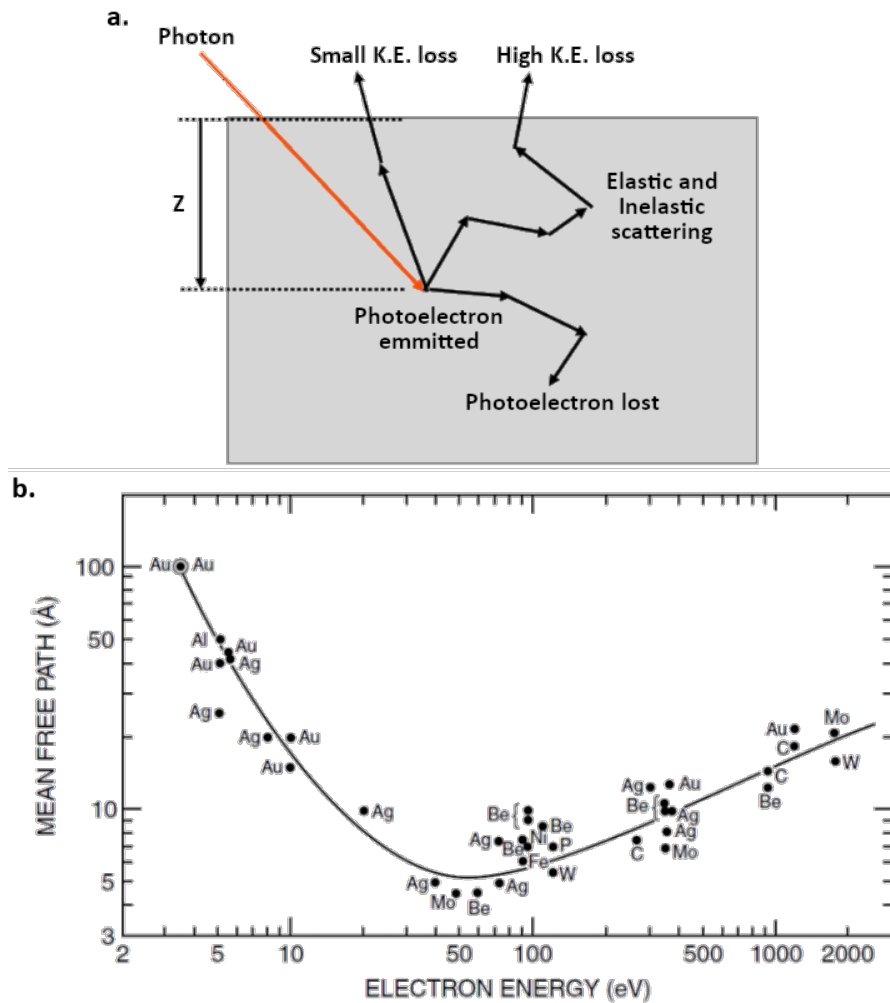


Figure 3.8: **(a)** Schematic representation of the photoelectron scattering after emission, where Z is the material depth. **(b)** Universal curve of electronic inelastic mean free path. Adapted from Somorjai (1990).

$$K.E.XPS = h\nu - \phi_{XPS} - B.E.XPS . \quad (3.10)$$

The change relies on the use of the electron analyzer work function (ϕ_{XPS}) instead of the sample one (ϕ_s). It occurs because if a conductive sample is in physical contact with the instrument, the Fermi level of the instrument and the sample aligns. Then only ϕ_{XPS} needs to be known, as shown in Fig. 3.9.

In XPS analysis, photoemission never comes from an unperturbed free atom, hence the $B.E.XPS$ in Eq. (3.10) should not be expected to describe such a scenario. In fact, it is usually studied the variations in binding energies and signal intensities and widths when comparing data. There are several factors affecting the measured electronic binding

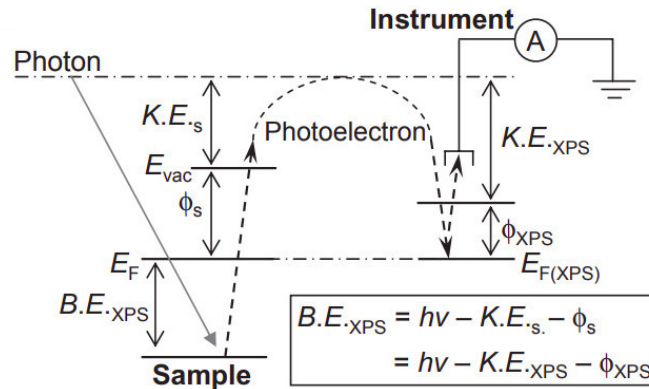


Figure 3.9: Relation between ϕ , E_f and $K.E$ from the sample (subscript s) and instrument. Adapted from van der Klink & Brom (2000).

energy that create distinct features in a typical XPS spectrum, which can be aggregated in two categories: initial state effects and final state effects (schematized in Fig. 3.10). Initial state effects describe the effects induced by the bonding that occurs with other atoms/ions prior to the photoelectron emission process, whereas final state effects are related to the perturbation of the electronic structure resulting from photoelectron emission.

Regarding the initial state effects, the Coloumbic interactions describe the charge density influence on the B.E. values. Prior photoemission, the electronic interactions from the atoms with the chemical environment (interatomic), and within the atoms/ions (intra-atomic) influence on the binding energy, which enables probing of the chemical components and oxidation states (Bagus et al., 2013). The spin orbit splitting, which comes from the interaction of the spin magnetic moment with the orbital magnetic moment of the electrons, gives different binding energies for electrons at the same electronic level, depending on the spin and angular momentum orientations.

The core hole formation from photoionization instantly creates a charge polarization which affects the kinetic energy of the emitted photoelectron. It is supposed to have a kinetic energy that includes all relaxation effects of the ionized atom (except Fluorescence and Auger effects). This is the so called adiabatic approximation but it is not always true. In the opposite regime, the emitted photoelectron respects the sudden approximation, where it leaves the atom before relaxation and its kinetic energy decreases due to a transfer to the ionized atom or material, then increasing the measured binding energy. Note that the real binding energy is the same. The energy transfer from the emitted photoelectron to the ionized atom or material may occur by shake-up, shake-off, plasmon losses and multiplet splitting effects. The plasmon losses comes due to an energy transfer from the emitted photoelectron to the collective excitations (plasmons) existing in the material.

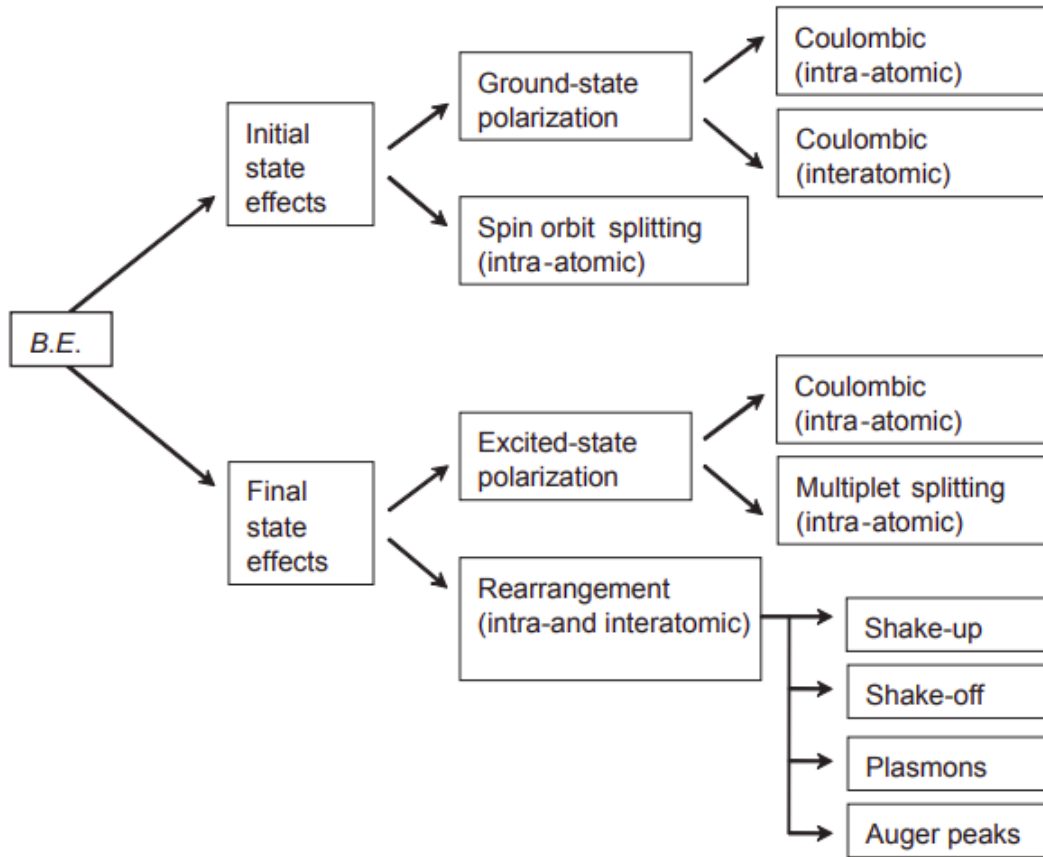


Figure 3.10: Diagrammatic view of all the effects that can be experienced by photoelectron emissions from a bound atom/ion with respect to the B.E. value of an unperturbed free atom.

The shake-up and shake-off effects occur due to the energy transfer from the emitted photoelectron to a valence band electron of the ionized atom. If the energy transfer is enough to unbound the valence electron, the effect is called shake-off while the energy transfer without ionizing the atom is called shake-up. Shake-up features can be useful in providing information on the chemical components existing, especially for metal oxides, since they are directly affected by the valence band structure. Fig. 3.11 shows how the shake-up features (identified as satellites) of Cu and its oxides are easily distinguishable. Multiplet splitting effects may occur whether the atom presents unpaired electrons. After photoemission, the unpaired electron may interact with the unpaired electron at the core level in a similar way than the spin orbit splitting effect. However, the main difference is that the spin orbit splitting effect is an initial state effect and the multiplet splitting is a final state one.

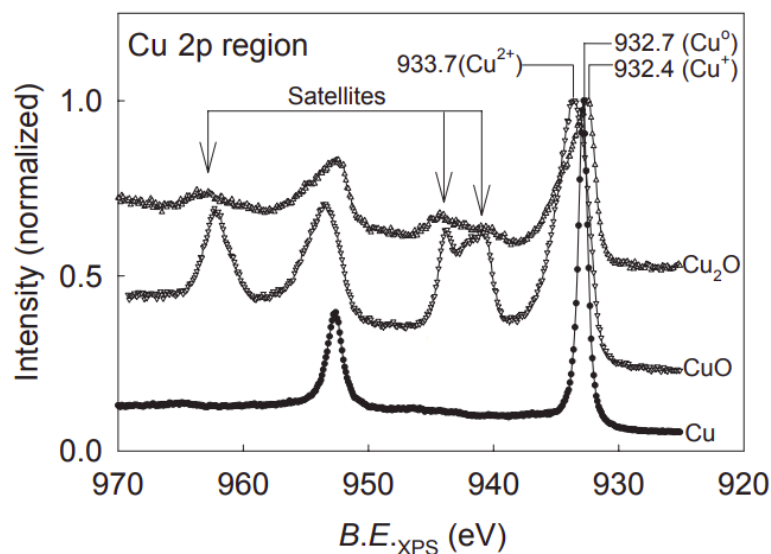


Figure 3.11: XPS spectrum of the Cu 2p region for Cu, Cu₂O and CuO. Adapted from van der Klink & Brom (2000).

3.3 X-Ray Absorption Spectroscopy

X-ray Absorption Spectroscopy (XAS) is a technique for studying, at the atomic and molecular scale, the local structure around selected elements. It is a very versatile tool because it does not require long range translational order (Bunker, 2010). XAS technique is also used *in situ*, which makes it a very useful technique for the study of reactive systems under high temperature and pressure of gas, such as catalysts (Fernández-García, 2002).

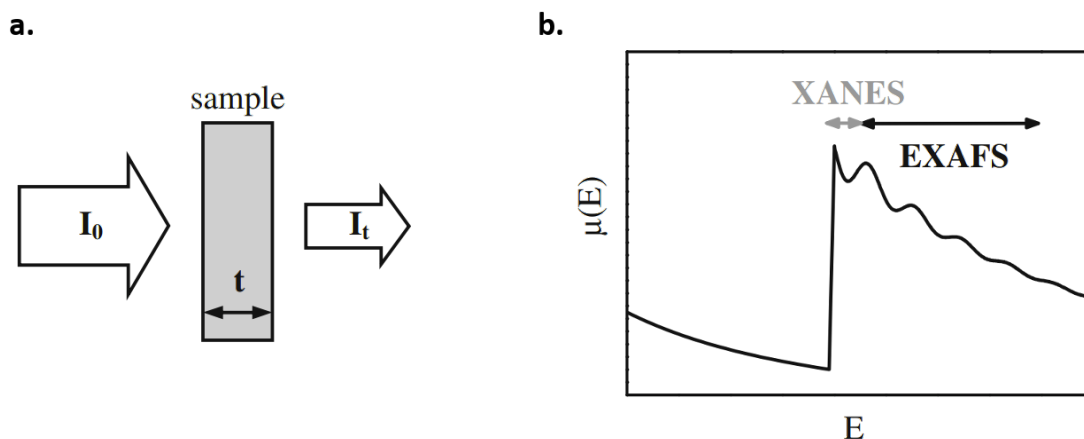


Figure 3.12: (a) Schematic representation of incident and transmitted X-ray beam. (b) Absorption coefficient $\mu(E)$ versus photon energy around an absorption edge. The XANES and EXAFS regions are demarcated. Adapted from (Schnorr & Ridgway, 2015).

The XAS technique is based on measuring the absorption coefficient of X-rays by the sample as a function of the X-ray energy. Then the measurement consists on the incidence of a monochromatic X-ray beam in the sample with the detection of the transmitted intensity. The intensity I attenuation for a sample of thickness t is described by the Beer-Lambert's law:

$$I = I_0 e^{-\mu(E)t} \quad (3.11)$$

where I_0 is the intensity of the incident X-ray and $\mu(E)$ is the absorption coefficient. Fig. 3.12.a shows a schematic representation of the XAS measurement setup in transmission mode. Generally, $\mu(E)$ decreases smoothly with energy. However, there are sharp rises in $\mu(E)$ for well defined energies related to specific atoms in the material. These are called absorption edges and they arise when the X-ray energy is sufficient to emit photoelectrons from bound states in the atoms. For energies just above the absorption edge, $\mu(E)$ presents an oscillatory pattern, which is called X-ray Absorption Fine Structure (XAFS), and it is categorically divided into the X-ray Absorption Near Edge Structure (XANES) and the Extended X-Ray Absorption Fine Structure (EXAFS) (Fig. 3.12.b). Although absorption edges were first measured in 1913 by Maurice De Broglie, it was much later that Stern et al. (1974, 1975), Sayers et al. (1971), and Lytle et al. (1975) synthesized the essential aspects of a viable theory of XAFS, making it a practical tool.

XAS is described by quantum mechanics since it arises from the absorption of photons, which gives an electronic transition between quantum states. The absorption coefficient $\mu(E)$ has to be proportional to the probability of an electronic transition induced by an electromagnetic wave with energy E . In the atomic context, electromagnetic waves can be treated as a weak time-dependent perturbation. Time-dependent perturbation theory describes that the transition rate, to first order in the perturbation, is proportional to the squared modulus of the transition amplitude (matrix element). This is known as the Fermi's Golden Rule. Hence, using the interaction Hamiltonian between an electromagnetic field with the electrons in the dipole approximation:

$$\mu(E) \propto \sum_f |\langle f | \hat{\epsilon} \cdot \hat{r} | i \rangle|^2 \delta(E_i - E_f - E) \quad (3.12)$$

where $|i\rangle$ and $|f\rangle$ are, respectively, the initial and final electronic states. The quantities \hat{r} , $\hat{\epsilon}$ and E are the electron position and the X-ray's electric polarization vector and energy. Eq. (3.12) describes the probability of transition from the electronic state $|i\rangle$ to any of the vacant electronic state $|f\rangle$ for a single electron in an isolated atom.

The EXAFS oscillations arise from the interference between the waves associated to the photoelectron emitted and photoelectron backscattered by the neighboring atoms. Depending on the existence of constructive or destructive interference the absorption coefficient increases or decreases, respectively, then explaining the oscillatory behaviour after absorption edge. It is schematically shown in Fig. 3.13. The mathematical description can be done by a high order multiple scattering formalism (Lee & Pendry, 1975), and results in the factoring of $\mu(E)$ in terms of the absorption by an isolated atom $\mu_0(E)$ modulated by an oscillatory function $\chi(E)$:

$$\mu(E) = \mu_0(E) (1 + \chi(E)) \quad (3.13)$$

The $\chi(E)$ function is the EXAFS oscillations, which is analyzed to obtain structural information. In order to separate the structural information from the energy dependence of the absorption coefficient, Eq. (3.13) is rewritten as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \approx \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0} \quad (3.14)$$

where the energy-dependent denominator is approximated by a constant typically chosen as the height of the absorption edge. Instead of using $\chi(E)$, the EXAFS oscillations are usually written as a function of the photoelectron wave number $k = \sqrt{2m_e(E - E_0)}/\hbar$, where m_e stands for the electron mass. The position representation of the states in Eq. 3.12 can be expressed in terms of an outgoing wave emitted at the absorbing atom plus incoming waves that are scattered back by neighboring atoms and used to calculate the dipole transition matrix element from which $\chi(k)$ is calculated (Sayers et al., 1971). Then the EXAFS oscillations can be expressed as

$$\chi(k) = \sum_j S_0^2 N_j \frac{F_j(k) e^{-2R_j/\lambda(k)}}{k R_j^2} e^{i2kR_j + i\delta_j(k)} e^{-2\sigma_j^2 k^2} \quad (3.15)$$

where the j index represents the atomic shell at a given distance from the central atom. Here the structural parameters are the interatomic distance R_j (half the total length of the scattering path), the coordination number N_j (number of equivalent single scattering paths) and the Debye-Waller factor σ_j^2 (temperature dependent fluctuation in bond length, which includes also the effects due to structural disorder). In addition, $F_j(k)$ represents the effective scattering amplitude, $\delta_j(k)$ is the effective total phase shift (including contributions from the central atom and all scattering atoms), $\lambda^{-1}(k)$ is the sum of the inverses of the inelastic mean free path and the length associated to the finite lifetime of the hole created at the core level, and S_0^2 is the amplitude reduction factor.

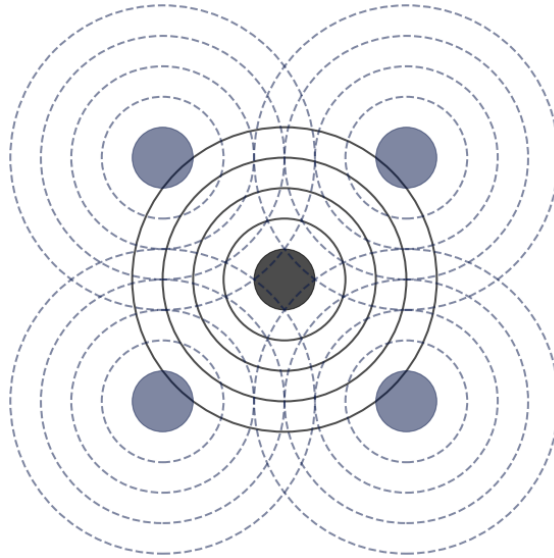


Figure 3.13: Pictorial view of the interference between the waves associated to the emitted photoelectron (black solid circles) and backscattered by the neighboring atoms (gray dashed circles).

For data analysis, firstly the EXAFS oscillations should be extracted from the XAS spectrum. After this, the EXAFS oscillations are Fourier transformed in order to facilitate the interpretation of the results. The next step is the fitting of the EXAFS oscillations and Fourier Transform. For this purpose, *ab initio* calculations of the scattering phase shifts and amplitudes have become the standard procedure. The FEFF program (Zabinsky et al., 1995) is commonly used to implement this calculation. It starts with a model structure that specifies the absorbing atom and the positions and types of the surrounding atoms to be considered. Then, it determines the scattering paths from the geometrical distribution of the atoms, creates spherically symmetric muffin-tin potentials, overlaps the atomic wavefunctions, and calculates the effective scattering phase shifts based on the potentials. FEFF implements a path filter that efficiently (and approximately) estimates the importance of each scattering path. Once the paths are enumerated, the effective scattering amplitudes for each path are calculated using the algorithm of Rehr & Albers (1990), and the EXAFS oscillations are generated by summing the paths. With the effective scattering amplitude and phase shift of one or more paths, a least-squares minimization method is used to fit Eq. 3.15 (and its Fourier Transform) to the EXAFS oscillations, where the path parameters R_i , N_j , S_0^2 , σ_j^2 (and also an adjustment in energy E_0) are used as variables. EXAFS is complementary to XRD, since the latter establishes all periodic structural features of solids with long range order, while EXAFS can elucidate local atomic order structure even for very low concentrations (Grünert & Klementiev, 2020).

The XANES region is often comprised of intense absorption peaks that come due to the photoelectron scattering in the near vicinity of the absorbing atom (Bunker, 2010). They are sensitive to chemical bonding and the oxidation state of the absorbing atom. XANES region analysis is usually carried out by linear combination of standards which are suspected to be in the sample. Linear Combination Fitting (LCF) is severely limited if a large number of possible standards has to be considered and if the spectra of different standards are very similar to each other. Characteristic features such as the intensity after the absorption edge can be quantified by peak fitting procedures. To that end, the absorption edge itself is typically approximated by an arctangent function while the peaks are modeled by a pseud-Voigt function to account for experimental broadening (Bunker, 2010).

3.4 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is the most used technique to acquire images of objects with submicrometer dimensions. The electron microscope arose due to the limited resolution in optical microscopes, which is imposed by the wavelength of visible light (380-700 nm). Soon after Louis de Broglie theorized the wave-like characteristics of electron (De Broglie, 1925), Knoll and Ruska developed the idea of an electron microscope, which awarded Ruska with the ("somewhat late" as himself said) 1986 Nobel prize (Ruska, 1987). Relativistic electrons have an approximate de Broglie wavelength given by

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E\left(1 + \frac{E}{2m_0c^2}\right)}} \quad (3.16)$$

where E is the electron energy and m_0 its rest mass, while h and c are the Planck and speed of light constants. In a typical electron microscope electrons have energy in the range 100-300 keV. From Eq. (3.16), these energies result in wavelengths smaller than the typical interatomic distance in crystals, which is on the order of a few Å. Therefore these electrons are able of probing materials with atomic resolution. The instrumental limitations of a TEM equipment operating in typical settings decrements this resolution, making it closer to the order of the nanometers. However, there are high resolution techniques that are able to resolve individual atoms and show discernible crystalline planes.

The TEM technique consists on focusing an electron beam into a sample and detecting

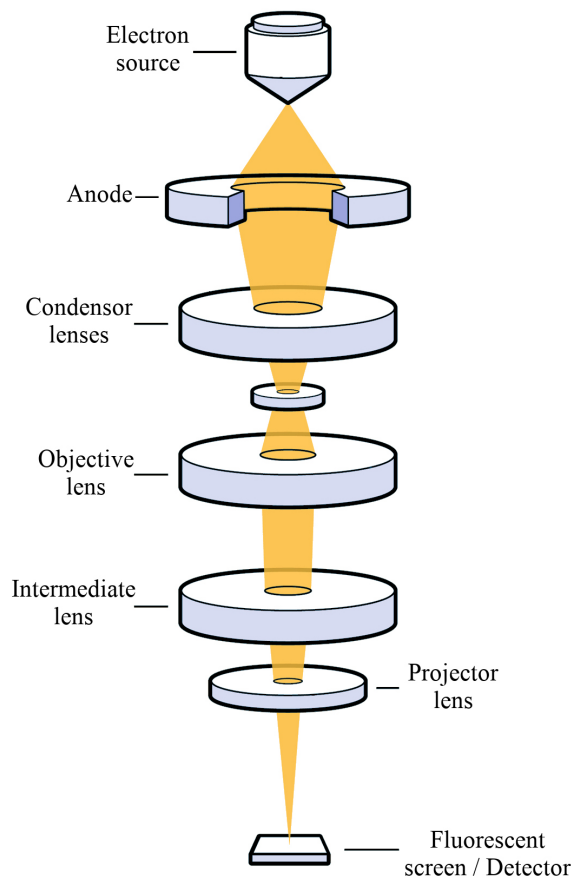


Figure 3.14: Schematic representation of a TEM instrument. The sample is positioned between the condenser and objective lenses.

the transmitted electrons. The microscope is made by an electron gun, a set of lenses and a detection system, as schematized in Fig. 3.14. The electron gun is made of an electron source and an anode to accelerate the electrons. The electron beam that leaves the electron gun enters in a system of condenser lenses where it is collimated to a coherent beam and directed to the sample. Then, the transmitted electrons enter the imaging set of lenses, which consist of an objective, an intermediate and a projector lens, and finally reach a fluorescent screen or detection system.

TEM images are a bidimensional projection of the region in the sample on which the electron beam is focused. The incoming electrons undergo scattering, and thus the electron wave can change both its amplitude and phase as it traverses the specimen. By positioning an objective aperture at a specific location in the back focal plane, an image is made with only those electrons that have been transmitted in a specific angle in relation to the direction beam. This defines two imaging modes, as shown in Fig. 3.16. When the aperture is positioned to pass only the transmitted electrons in a small angle in

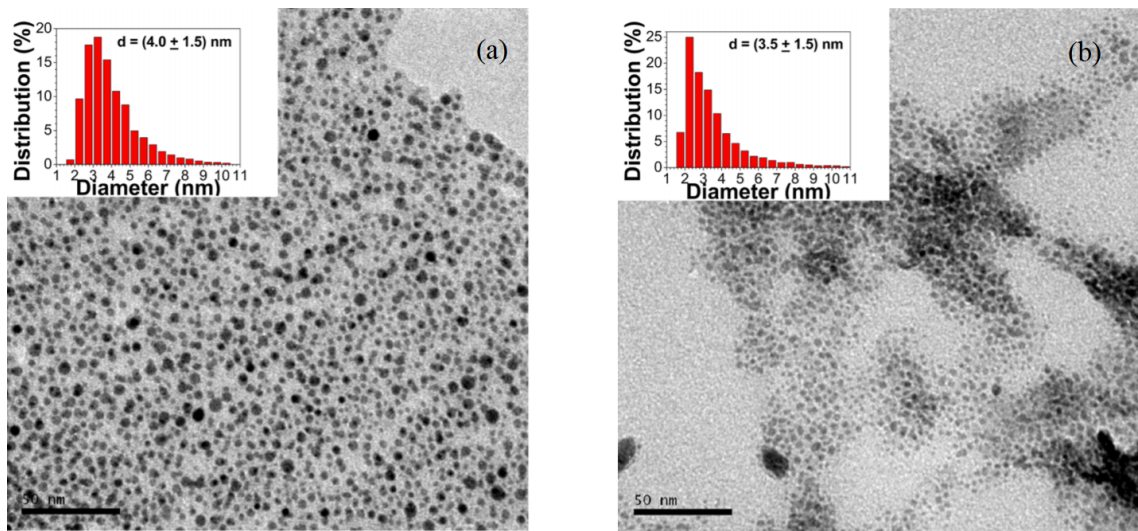


Figure 3.15: Transmission electron microscopy images of (a) Cu and (b) Ni nanoparticles. The inset represents the size distribution of the nanoparticles. Adapted from Matte et al. (2015).

relation to the direction beam, a bright-field image is formed, whereas when the aperture is positioned in high angles, a dark-field image is formed (Fultz & Howe, 2012). Fig. 3.15 shows bright field TEM images of Cu and Ni nanoparticles (Matte et al., 2015).

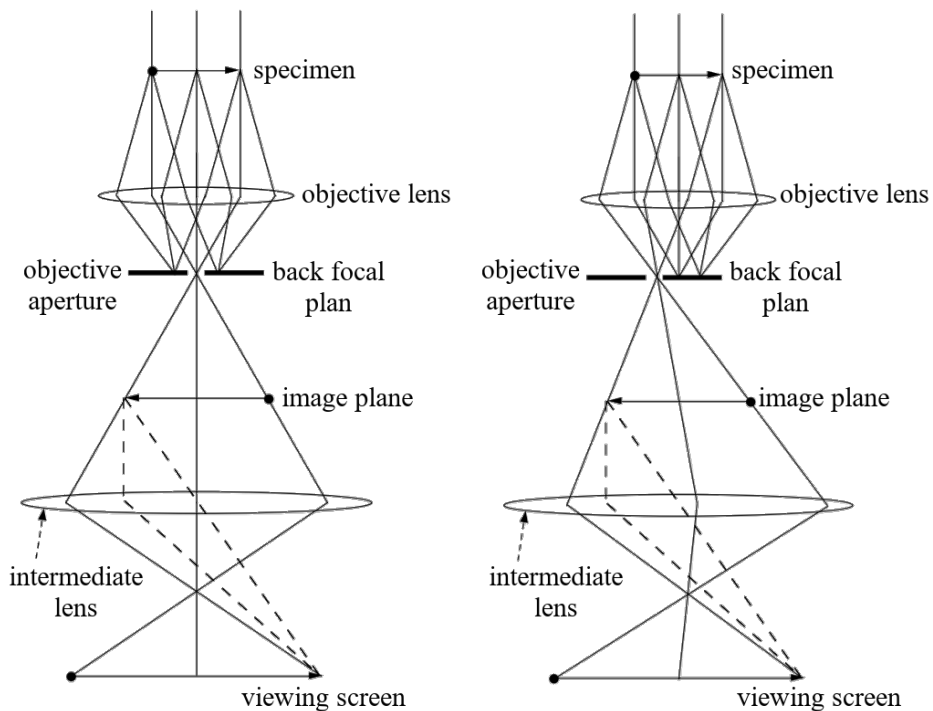


Figure 3.16: On the left, the schematics for a bright field mode. On the right, a dark field mode. Image from Fultz & Howe (2012).

3.5 Monte Carlo Simulations of Cluster Diffusion

The Monte Carlo methods are a broad class of computational algorithms which rely on random sampling to obtain statistical results. Monte Carlo simulations sample from a probability distribution for each variable to produce possible outcomes. It can be used to study thermodynamic quantities or statistical properties of a large variety of systems. Some examples range from the computation of the specific heat of materials to spatial correlations in a system (Newman & Barkema, 1999). Supported small clusters, such as nanoparticles, present thermally activated Brownian motion due to weak nanoparticle interfacial adhesion (Jose-Yacamán et al., 2005). A simple way to study Brownian Motion of clusters is by a Monte Carlo simulation which use random numbers to perform random walks.

3.5.1 Random Walks

A random walk is a path that consists of a succession of random steps. Lets consider a random walker, who initially starts at the origin in d dimensions. At each step, the walker has equal probability $1/(2d)$ to move in any direction within any of the d axis with a step size Δ . Let \vec{R}_N be the position of the walker after N independent steps and τ the time interval between the steps. Then time is defined as $t = N\tau$. It can be shown that in the limit where $\Delta \rightarrow 0$, $\tau \rightarrow 0$ and $N \rightarrow \infty$ the probability density to find the walker in a position interval $(\vec{r}, \vec{r} + d\vec{r})$ at time t is:

$$\rho(\vec{r}, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left[-\frac{r^2}{4Dt}\right] \quad (3.17)$$

where

$$D = \frac{\Delta^2}{2d\tau} \quad (3.18)$$

D the diffusion coefficient (Reichl, 1999). Eq. 3.18 is also known as the Einstein-Smoluchowski relation. The diffusion coefficient is a measurable quantity that gives information on the average behaviour of clusters.

When modeling a dynamic physical problem, random walks with variable jump length can be more adequate. A numerical implementation of random walks with variable jump length requires a sampling method for non-uniform distributions. The inverse transform method (Devroye, 2006) generates sample numbers at random from a probability distribution given its cumulative distribution function. Let X be a random variable whose

distribution f_X can be described by the cumulative distribution function F_X . By generating a random number u from the standard uniform distribution in the interval $[0,1]$, X can be computed by taking $F_X^{-1}(u)$. The only requirement is that the cumulative distribution F_X be invertible. Furthermore, if the distribution has finite first and second moments, the central limit theorem states that the probability distribution of a large number of measurements of X is a Gaussian centered at the mean, regardless of the form of f_X (Reichl, 1999).

3.5.2 Anomalous Diffusion

Eq. 3.17 is a Gaussian function centered at $\langle r \rangle$ (zero in this case) with standard deviation $\sigma = \sqrt{\Delta^2 N} = \sqrt{2Dt}$. Hence, in free diffusion the mean-square displacement of the diffusing cluster grows linearly with t ,

$$\langle r^2 \rangle = 2d Dt \quad (3.19)$$

However, for diffusion in inhomogeneous medium, such as clusters within crowded systems, diffusion is described by a power law (Havlin & Ben-Avraham, 1987)

$$\langle r^2 \rangle \propto t^\alpha \quad (3.20)$$

and a normalised, time dependent diffusion coefficient can be defined (Saxton, 2001)

$$D(t) = \Gamma t^{\alpha-1} \quad (3.21)$$

where Γ is a constant. When $\alpha > 1$, super-diffusion is described, while $\alpha < 1$ describes sub-diffusion. For $\alpha = 1$, $\langle r \rangle \propto t$, D is constant and diffusion is normal.

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