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In-situ study of the growth, structure and reactivity of Pt-Pd nanoalloys

Astrid DE CLERCQ

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Christophe PETIT, Université Paris VI, Rapporteur Christian RICOLLEAU, Université Paris VII, Rapporteur Marie-José CASANOVE, CNRS, Toulouse, Examinatrice Olivier MARGEAT, Aix-Marseille Université, Examinateur Christine MOTTET, CNRS, Marseille, Examinatrice Suzanne GIORGIO, Aix-Marseille Université, Directrice de thèse

Resumé

Les propriétés catalytiques des nanoparticules métalliques peuvent être améliorées par effet d'alliages. La synthèse en solution par voie colloïdale permet de préparer des nanoalliages homogènes en taille, en forme et en composition chimique, de structure ordonnée, désordonnée ou cœur-coquille.

La nucléation et la croissance des nanoalliages de Pt-Pd sont étudiées ici par microscopie électronique en transmission (MET), en condition standard, puis in situ dans une cellule liquide formée par des feuilles d'oxyde de graphène. La cinétique de croissance des nanoalliages de structure homogène de Pt-Pd correspond à l'incorporation directe des monomères en solution, compatible avec un processus limité par la réaction de surface, sans phénomène de coalescence (mécanisme de Lifshitz-Slyozov-Wagner). Par contre, la coalescence intervient au cours de la croissance des nanoparticules de Pt pur.

La structure théorique à l'équilibre de nanoalliages de Pt-Pd est déterminée par des simulations Monte Carlo. La structure la plus probable correspond à une surface riche en Pd et à une sous couche atomique riche en Pt, stable à des températures élevées. Ces simulations montrent que des effets électroniques résultant de l'effet d'alliage, sont possibles à la surface.

L'effet de l'adsorption de gaz oxydants ou réducteurs sur la forme de nanocubes de Pd et de nanocubes cœur-coquilles de Pd@Pt, est étudié in situ par microscopie environnementale sous pression de quelques mbar, dans un porte objet environnemental. On observe des changements de formes sous oxygène, dus au développement de facettes d'indices plus élevés.

La réaction d'oxydation du CO est utilisée pour comparer la réactivité des nanoalliages de Pt-Pd et des nanocubes cœurs-coquilles de Pd@Pt en fonction du recouvrement de Pt à la surface. La réactivité maximale pour un faible recouvrement est interprétée par une baisse de l'énergie d'adsorption du CO liée au désaccord paramétrique entre le Pt et le Pd et à la modification de la structure électronique du Pt lié au Pd.

Mots-clés

nanoalliages, structure cœur-coquille, MET in situ (en milieu gazeux et liquide), Pt-Pd, catalyseur modèle, synthèse colloïdale

ii

Abstract

The catalytic properties of metal nanoparticles can be improved by the alloying effect. Nanoalloys homogeneous in size, shape and chemical composition can be prepared with the colloidal synthesis method, with an ordered, random or core-shell chemical structure.

Nucleation and growth of colloidal Pt-Pd nanoalloys were studied by transmission electron microscopy (TEM), in standard conditions and in situ with the aid of a graphene oxide liquid cell. The growth kinetics of homogeneous Pt-Pd nanoalloys corresponds to the direct incorporation of the monomers in solution. It was compatible with a process limited by the surface reaction, without coalescence (Lifshitz-Slyozov-Wagner mechanism). On the contrary, coalescence occurs during the growth of pure Pt nanoparticles.

The theoretical structure of Pt-Pd nanoalloys is determined by Monte Carlo simulations. The most stable structure corresponds to a Pd surface and Pt subsurface layer, which is stable up to high temperatures. These calculations show that electronic effects, resulting from the alloying effect, are possible at the surface.

The effect of adsorption of oxidizing or reducing gasses on the shape of pure Pd nanocubes and core-shell Pd@Pt nanocubes is studied in situ by TEM with an environmental cell. The observed changes in a few mbar of oxygen are due to the development of higher index facets.

The CO oxidation reaction is used to compare the reactivity of homogeneous Pt-Pd nanoalloys and core-shell Pd@Pt nanocubes with increasing coverage of Pt at the surface. A maximal reactivity is attained for a low coverage. The effect is interpreted by a decrease in adsorption energy of CO, due to electronic effects originating from the lattice mismatch between Pt and Pd and the mixed Pt-Pd bonds.

Keywords

nanoalloys, core-shell structure, in situ TEM (in gas and liquid), model catalyst, Pt-Pd, colloidal synthesis

Preface

Particles in the nanometer size range have many remarkable properties due to their large surface area to volume ratio. Palladium (Pd) and Platinum (Pt) nanoparticles are often used as catalysts to improve a chemical reaction. Palladium is important for different hydrogenation reactions, carbon-carbon bond forming and oxidation reactions. Platinum is used in the petroleum industry for cracking, isomerization and reforming processes. A large part of both metals is also currently used in car exhaust catalysts, to reduce the emission of CO, NO_x and hydrocarbons.

Bimetallic nanoparticles (called 'nanoalloys' for the more general combination of several metals) have an extra parameter to control the catalytic properties, which can give benefits in terms of reliability, cost and performance [1]. There is a special interest in reducing the use of platinum, due to its high price, while maintaining or even improving the catalytic properties. This is essential for emerging technologies, such as fuel cells. Although bimetallic Pt-Pd NPs are already used in different catalytic applications, improved properties were mostly found in an empirical way. For example, the industrial application of Pt-only, Pd-only or Pt-Pd combination in car exhaust catalysts was mostly of economic origin, directed by price fluctuations of both metals in the last 40 years. A profound study on the relationships between the different parameters can therefore contribute to a knowledge-based development of cheaper and better heterogeneous catalysts.

In this study, Pt-Pd nanoparticles with different structures are compared. These particles were synthesized in a liquid phase, to improve the control over the size, shape and chemical structure. State-of-the-art techniques were used and further developed to study the nucleation and growth of these nanoalloys. A theoretical study was made, to increase insight in the expected thermodynamic stable chemical structure. Since the structure depends also on the environment, it is important to study these nanoparticles in realistic conditions and with a model catalytic reaction. This 'from A to Z' approach in which the particles are synthesized, characterized, calculated and studied in a model reaction allows getting more information on the structure-reactivity relationship of the Pt-Pd nanoalloys in catalysis.

Chapter 1 introduces the preparation, use and stability of catalytic nanoalloys, prepared through wet chemical synthesis. Benefits in terms of control over the nanoalloy structure are shown. The current status of Pt-Pd alloys is summarized, together with some other examples that are important for a thoroughly understanding of the challenges within this research domain.

Then, the synthesis from solution of two types of Pt-Pd nanoalloys (homogeneous alloy and core-shell) is presented in **Chapter 2**. They are characterized by transmission electron microscopy (TEM) and deposited on oxide supports. A brief study of the removal of the organic stabilizers and the effect on the organization is presented.

Next, in **Chapter 3**, an interesting new in situ method to study the nucleation and growth of nanoalloys in solution in a standard TEM is presented. In a graphene oxide liquid cell, the growth of pure Pt will be compared with Pt-Pd nanoalloys and the growth of a Pt layer on a Pd core is also shown.

In **Chapter 4**, the theoretical chemical structure of Pt-Pd nanoalloys is calculated. Insights in the chemical structure under realistic temperatures are obtained. Pd surface segregation is confirmed, although some specific surface sites would be able to host Pt atoms. A temperature stable Pt subsurface layer, almost independent of the size and shape is demonstrated. Implications on the catalytic performance are discussed.

Chapter 5 aims to determine the influence of oxidation-reduction cycles on the facetting of the nanoalloys, through an in situ environmental TEM study. In this method, the particles are observed in O_2 and H_2 atmospheres.

Then, in **Chapter 6**, the reactivity of these nanoalloys in a test reaction, the CO oxidation, is followed by gas phase chromatography. Possible connections between the catalytic performance and the structure are discussed.

Finally the major results arising from this study are summarized in **Chapter 7**. Further research topics based on current work are suggested, as well as remaining challenges in this field of catalytic nanoalloys and in situ transmission electron microscopy.

Table of Contents

Resumé			i	
Mots-clés			i	
Abstract			iii	
Keywords			iii	
Preface			v	
Table of Conte	ents		vii	
Chapter 1	Introd	luction to nanoalloys in catalysis	1	
1.1	Preparation of supported model catalysts through wet chemical synthesis			
1.2	Struct	ure of nanoalloys influencing the catalytic properties	5	
	1.2.1	Size and shape	5	
	1.2.2	Chemical structure of bimetallic partides	8	
	1.2.3	Oxide support	11	
1.3 Influence of the environment				
	1.3.1	Influence of the environment on the shape	11	
	1.3.2	Influence of the environment on the chemical structure	12	
	1.3.3	Other effects of the environment	13	
1.4	Pt-Pd	nanoalloys in literature	14	
	1.4.1	In creased catalytic activity of Pt-Pd nanoalloys	14	
	1.4.2	Influence of the environment on Pt-Pd nanoalloys	16	
1.5	Summ	nary of the general context and goals		
Chapter 2	Prepa	ration and characterization of Pt-Pd nanoalloys	19	
2.1	Small	homogeneous Pt-Pd nanoalloys	21	
	2.1.1	Nanoparti de synthesis and characterization	21	
	2.1.2	Deposition on oxide supports and deaning	25	
2.2	Towa	rds controlled Pd _{core} @Pt _{shell} structures	29	
	2.2.1	Nanoparti de synthesis and characterization	29	
	2.2.2	Deposition on oxide powders and deaning		
2.3	Condu	usions on the preparation and characterization of Pt-Pd nanoalloys		
Chapter 3	In situ	ITEM study of Pt-Pd nanoalloys from solution		
3.1	State o	of the art of in situ liquid TEM		
3.2	Experi	imental technique	41	

	3.3	Note on synthesis by electron beam i rradiation				
	3.4	Pure Pt and influence of the ligands				
		3.4.1	Observations of Pt + ole vlamine in the liquid cell	44		
		3.4.2	Observations of Pt + octylsilane in the liquid cell	47		
		3.4.3	Interpretation of the observed nudeation	48		
		3.4.4	Condusions on pure Pt with differentligands	49		
	3.5	Small F	Pt-Pd nanoalloys + oleylamine ligands	50		
		3.5.1	Observations in the liquid cell	50		
		3.5.2	Interpretation and comparison with NPs prepared in standard reactor	53		
		3.5.3	Condusions on Pt-Pd(OAm) nanoalloys	55		
	3.6	Growt	n of a Pt layer on a Pd nanosphere	55		
		3.6.1	Observations with a JEOL 3010 at 300kV	55		
		3.6.2	Observations with a JEOL-ARM 200F at 200kV	57		
		3.6.3	Condusions on the growth of a Pt layer on a Pd nanosphere	59		
	3.7	Growt	n ofa Ptlayer on Pd nanocubes	60		
		3.7.1	Observations in the liquid cell	60		
		3.7.2	Interpretation of the shape changes	62		
		3.7.3	Condusions on Pt layer on a Pd nanocube	63		
	3.8	Genera	al condusions on the liquid TEM studies	63		
Chapter	4	Theore	tical structure of Pt-Pd nanoalloys	65		
	4.1	Backgr	ound and state of the art	67		
	4.2	Simula	tion method	69		
		Simara				
		4.2.1	Energetic model (SMA-TB)	69		
		4.2.1 4.2.2	Energetic model (SMA-TB) Initial duster configurations	69 72		
		4.2.1 4.2.2 4.2.3	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method	69 72 73		
	4.3	4.2.1 4.2.2 4.2.3 Results	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method	69 72 73 74		
	4.3	4.2.1 4.2.2 4.2.3 Results 4.3.1	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh	69 72 73 74 74		
	4.3	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2	Energe ti c model (SMA-TB) Initial dus ter configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih	69 72 73 74 74 77		
	4.3	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size	69 72 73 74 74 77 79		
	4.3	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the temperature	69 72 73 74 74 77 79 81		
	4.3	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size ent on the effect of the environment	69 72 73 74 74 77 79 81 85		
	4.3 4.4 4.5	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size ent on the effect of the environment. ent on core-shell Pd@Pt NPs	69 72 73 74 74 77 79 81 85 86		
	4.3 4.4 4.5 4.6	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm Comm	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size Effect of the temperature ent on the effect of the environment ent on core-shell Pd@Pt NPs sion on the theoretical study	69 72 73 74 74 77 79 81 85 86 86		
Chapter	4.3 4.4 4.5 4.6 • 5	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm Comm Condu	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size Effect of the temperature ent on the effect of the environment ent on core -shell Pd@Pt NPs sion on the theoretical study ire of Pt-Pd nanoalloys in gas environment	69 72 73 74 74 77 79 81 85 86 86 86 89		
Chapter	4.3 4.4 4.5 4.6 • 5 5.1	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm Comm Condu Structu Instrur	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size Effect of the temperature ent on the effect of the environment ent on core -shell Pd@Pt NPs sion on the theoretical study re of Pt-Pd nanoalloys in gas environment nent and sample pre paration	69 72 73 74 74 77 79 81 85 86 86 86 89 91		
Chapter	4.3 4.4 4.5 4.6 5.1 5.2	4.2.1 4.2.2 4.2.3 Results 4.3.1 4.3.2 4.3.3 4.3.4 Comm Condu Structu Instrur State o	Energetic model (SMA-TB) Initial duster configurations Monte Carlo simulation method and discussion Low temperature ordering in TOh Low temperature ordering in Ih Effect of the size Effect of the size Effect of the temperature ent on the effect of the environment ent on the effect of the environment sion on the theoretical study re of Pt-Pd nanoalloys in gas environment if the art	69 72 73 74 74 77 79 81 85 86 86 86 86 89 91 92		

		5.3.1 Small homogeneous Pt-Pd nanoalloys				
		5.3.2 Pd nanocubes	96			
		5.3.3 Cubic core-shell Pd@Pt na noalloys				
		5.3.4 Beam effects				
	5.4	Condusion on the ETEM observations				
Chapte	r 6	Reactivity of Pt-Pd nanoalloys for the CO oxidation reaction				
	6.1	Background, principles and state of the art				
	6.2	Experimental technique and optimization				
	6.3	Evaluation of the CO conversion				
		6.3.1 Reactivity of small Pt, Pd and Pt-Pd nanoalloys				
		6.3.2 Reactivity of cubic core-shell Pd@Pt nanoalloys				
	6.4	Apparent activation energy	119			
		6.4.1 Arrhenius plot of small Pt-Pd nanoalloys				
		6.4.2 Arrhenius plot of cubic core-shell Pd@Pt nanoalloys				
		6.4.3 Compensation effect				
	6.5	Preliminary kinetic analysis				
	6.6	Structure after reaction				
	6.7	Condusions on the reactivity studies				
Chapte	6.7 r 7	Condusions on the reactivity studies	125 127			
Chapte	6.7 r 7 7.1	Condusions on the reactivity studies Conclusions Achieved results				
Chapte	6.7 r 7 7.1	Conclusions on the reactivity studies Conclusions Achieved results 7.1.1 Small homogeneous Pt-Pd nanoalloys				
Chapte	6.7 r 7 7.1	Conclusions on the reactivity studies Conclusions Achieved results 7.1.1 Small homogeneous Pt-Pd nanoalloys 7.1.2 Cubic core-shell Pd@Pt nanoalloys				
Chapte	6.7 r 7 7.1	Conclusions on the reactivity studies				
Chapte	6.7 r 7 7.1 7.2	Conclusions on the reactivity studies				
Chapte	6.7 r 7 7.1 7.2	Conclusions on the reactivity studies				
Chapte	6.7 r 7 7.1 7.2	Conclusions on the reactivity studies				
Chapte	6.7 r 7 7.1 7.2	Conclusions on the reactivity studies				
Chapter	6.7 r 7 7.1 7.2	Conclusions on the reactivity studies	125 127 129 129 130 131 132 132 133 133 134			
Chapter Referen List of I	6.7 r 7 7.1 7.2 nces	Conclusions on the reactivity studies	125 127 129 129 130 131 132 132 133 133 134 146			
Chapter Referen List of I	6.7 r 7 7.1 7.2 nces Figures.	Conclusions on the reactivity studies Conclusions Achieved results 7.1.1 Small homoge neous Pt-Pd nanoalloys 7.1.2 Cubic core-shell Pd@Pt na noalloys 7.1.3 General progress in the research field Research outlook 7.2.1 Possible future research topics 7.2.2 Outlook for in situ electron micros copy methods 7.2.3 Outlook for catalytic colloidal nanopartides	125 127 129 129 130 131 132 132 133 133 133 134 146 151			
Chapter Referen List of I List of I	6.7 r 7 7.1 7.2 nces Figures. Tables	Conclusions on the reactivity studies Conclusions				
Chapter Referen List of 1 List of 2 List of 1	6.7 r 7 7.1 7.2 7.2 Figures. Tables Equatio Abbrevi	Conclusions on the reactivity studies	125 			

х

Chapter 1 Introduction to nanoalloys in catalysis

A heterogeneous catalyst is defined as a solid catalyst that can accelerate a chemical reaction in the liquid or gas phase. These catalysts generally consist of (transition) metal nanoparticles of 1-10 nm, homogenously dispersed on a solid support. To improve the contact area with the reactants, this support is mostly a high surface area oxide powder or a nanoporous material. Many preparation methods of these heterogeneous catalysts exist, but in this work, we focus on the wet chemical synthesis route. It will be shown that it is an ideal technique to prepare model catalysts, with controlled size and shape.

Monometallic catalytic nanoparticles often encounter problems such as limited lifetime or high cost. Bimetallic nanoparticles possess many advantages that may help to improve the catalytic properties. It is demonstrated that the wet chemical route can also control the chemical structure of bimetallic nanoparticles.

In this chapter, the different steps to make a supported model catalyst through synthesis from solution are discussed. Then, different structures (size, shape and chemical arrangement) of nanoalloys are illustrated. This is important since the structure can have an influence on the catalytic performance. However, it will become clear that the catalytic reaction itself and the environment that it creates, influences the structure. As such, the need for adequate in-situ experiments is demonstrated. Finally, different studies on Pt-Pd nanoalloys are summarized.

1.1 Preparation of supported model catalysts through wet chemical synthesis

A good preparation technique of a model catalyst is characterized by a very narrow size, shape and composition distribution, in order to obtain homogeneous and controllable properties.

Impregnation of a support by a metal salt and subsequent calcination and reduction is mostly used in industry. However, it results in a rather large particle size and composition distribution. With this technique, it is also difficult to vary the metal loading and particle size independently. Physical vacuum condensation techniques can give narrow size distributions, but the resulting amount of nanoparticles is often too small to test in catalytic reactions at realistic conditions.

Nanoparticles (NPs) can also be prepared from solution, frequently called the colloidal method. The different steps are shown in Figure 1.1. The growth of the NPs is initiated from metal precursors that are dissolved in a solvent, by the addition of a reducing agent. The solution can be aqueous, with mostly metal salts used as precursor (e.g. Na₂PdCl₄) or organic, with dissolved organometallic complexes (e.g. Pd(acac)₂).



Figure 1.1 : Successive steps of the colloidal synthesis method for the preparation of a supported model catalyst.

In this precursor solution, the first challenge is to obtain a stable NP system during the reduction step. This is done by the addition of stabilizers, which are mostly organic ligands, polymers or ionic salts. These stabilize the particles in an electrostatic and/or steric way, and keep the particles well-dispersed.

The stabilizers that were used in this work are oleylamine (OAm) ligands and the long chain polymer poly(vinylpyrrolidone) (PVP) for which the stabilization is schematically represented in Figure 1.2. The functional group is bonded to the NP surface and the long organic chain stabilizes the particle through steric hindrance. The type of interaction of the stabilizers with the metal NP influences the size and shape. Oleylamine stabilizes trough the amine functional group, although it is reported that at high temperature it can undergo metal-ion induced oxidation to nitriles [2]. PVP can adsorb on the NP both with the oxygen and nitrogen atom, depending on the coverage [3]. Moreover, the long chain polymer forms an encapsulating sphere around the particle (Figure 1.2 (b)).



Figure 1.2 : Simplified representation of the stabilization of a nanoparticle with (a) oleylamine ligands and (b) PVP polymer. (from reference [4] and [5])

In the next steps, the NPs can be immobilized on a support (Figure 1.1). Generally, the colloidal solution is first centrifuged, to separate the NPs from the excess of precursors and stabilizers. Then, they are redispersed in the same or another solvent, at the same or another concentration. This centrifuge-redispersion step needs to be optimized, to ensure a minimal

agglomeration of the NPs. The 'washed' colloidal solution can then be mixed with an oxide powder or porous structure, or be dropped on a flat surface, to obtain supported metal NPs.

However, the residual stabilizers can reduce or even completely destroy the catalytic activity of the NPs, by blocking the catalytic active surface sites. Therefore, these stabilizers are often removed before the reactivity tests. It is one of the main disadvantages of this preparation, since it is clear that it is a challenge to maintain the structure and dispersion of the colloidal particles during this deposition and cleaning.

It is important to note that variations on this colloidal method exist, such as synthesis with reversed micelles [6] or the liquid-liquid phase transfer method [7][8]. These types of synthesis can also give controlled NP structures.

1.2 Structure of nanoalloys influencing the catalytic properties

The **structure** of the nanoparticle is in this work defined as the physical parameters including size, shape, composition and chemical arrangement. The properties of the nanoparticles (e.g. catalytic, photonic, magnetic, etc.) can be fine-tuned by controlling the structure. Here, the focus is on the catalytic properties. When a reaction does not depend on the structure of the catalytic NPs, with the activity normalized to the exposed surface area, the reaction is called 'structure-insensitive'. However most catalytic reaction are influenced by the structure and are therefore called **structure-sensitive** reactions. Moreover, the selectivity can be influenced by the type of exposed crystal facet, when there is more than one possible reaction product. In this section, the control of the structure through the wet chemical synthesis and the influence on the catalytic reaction are further discussed.

1.2.1 Size and shape

• Origin of the influence of size and shape on the catalytic performance

A frequently used example to demonstrate the size-effect of NPs in catalysis is the remarkable activity of gold when it is smaller than 5 nm [9], while bulk Au is inert. The influence of the size can have two origins. First, for smaller sizes, the number of under-coordinated atoms (edges, corners) rises exponentially. These sites have a different activity than extended surfaces, due to the different electronic structure. Then for very small NPs of a couple of atoms, often referred to as 'clusters' a quantum confinement effect can occur [10].

The influence of the shape is again related to the modified electronic structure of the exposed facets due to a different amount of nearest neighbors. We focus on metals with a face-centered cubic (fcc) lattice, for which the low energy surfaces are (111), (100) and (110), with atoms having respectively 9, 8 and 7 nearest neighbors.

• Equilibrium size and shape

In the study of nanoparticles, **surface free energy** γ is an important parameter to take into account, since the relative amount of surface varies drastically for small particles. The surface free energy rises when more bonds are broken at the surface and thus $\gamma(111) < \gamma(100) < \gamma(110)$. For a monometallic particle in vacuum, the equilibrium shape is determined by a minimization of the total Gibbs free energy. For an fcc metal, this minimization is described by the Wulff construction [11] and leads to a truncated octahedral (TOh) equilibrium shape, with (100) and (111) facets (Figure 1.3 (a)). This shape was frequently observed. For example for a palladium NP an anisotropy ratio $\gamma_{(100)}/\gamma_{(111)}$ of 1.16 was found after annealing in vacuum [12]. For very small sizes however, icosahedral and decahedral shapes would be able to minimize the energy of the system. These shapes are mainly limited by lowest energy (111) surfaces, but have a strain component due to the twinned structure which makes them unstable at larger sizes (Figure 1.3 (b-c)). A size-dependent crossover between these structures was calculated, depending on the metal [13].



Figure 1.3 : Equilibrium shapes of NPs by minimization of the surface free energy (a) truncated octahedron (b) decahedron (c) icosahedron, with red (100) and blue (111) facets. (adapted from [13])

• Preparation of different sizes and shapes from solution

However particles prepared from solution do not necessarily adopt this equilibrium shape determined for vacuum conditions. This is due to stabilization of certain facets by preferential adsorption of the stabilizers. Also kinetic factors and defect formation play a role.

By (empirical) optimization of the colloidal method, a large variety of shapes could be synthesized with high shape-purity. A first understanding of the formation of a certain

structure in liquid was acquired, although precise mechanisms in the often complex solutions are still under investigation. Especially the synthesis in organic media often lack reproducibility due to the known or unknown contaminations.

Classically, the NP formation is divided into the **nucleation** and **growth** stage and both are important to control. An example of this control is given in Figure 1.4 [14]. It was understood that the initial (twin-) structure of the seed can have a large influence on the subsequent NP shape [14].

In the thermodynamically controlled regime, a statistical distribution of above mentioned equilibrium shapes are formed as seeds. They can then further evolve to different shapes depending on the stabilization and reaction kinetics. For example, cubes and elongated bars were typically found for strong preferential stabilization of the (100) facet, due to stronger bonding of the functional group.

The amount of twinning is also determined by reaction kinetics. For slower atom addition, the multiple twinned structures will prevail. In the kinetically controlled regime, for very slow reduction, planar seeds with stacking faults were observed. These can further grow to plate-like shapes.

Because of the additional degree of freedom, it is generally more complicated to obtain well determined shapes for bimetallic NPs (although possible e.g. [15],[16]). However, as is discussed in the next section, also predefined monometallic shapes can be used to make core-shell NPs with a specific shape.

An important conclusion here is that, to determine the structure-sensitivity of a reaction, surface-science studies often have worked with model extended surfaces or physically prepared equilibrium shaped supported NPs. Now, a new kind of model catalyst can be synthesized from solution, for which both the size and the shape can be varied independently.

7



Figure 1.4 : Frequently observed shapes of nanoparticles of fcc metals prepared by colloidal methods, showing the importance of the initial seed on the further shape evolution. Color code as green= (100), yellow=(111) and purple (110) facets. The parameter *R* is defined as the ratio between the growth rates along the (100) and (111) direction. (extracted from [14])

1.2.2 Chemical structure of bimetallic particles

• Overview of possible chemical arrangements

A bimetallic particle can have a variable chemical compositions (variable mol% of the components), but also have a different spatial distribution of both elements at the surface. Some possible chemical arrangements are illustrated in Figure 1.5. The first two structures are found for metals that have certain miscibility. Then the chemical structure can be (a) a solid solution/homogeneous alloy or (b) have an ordered intermetallic lattice, mostly deduced from bulk phase diagrams. For a well-defined ordered lattice, a predefined stoichiometry is necessary. In this case, it depends on the type of lattice plane at the surface whether one or both metals are visible in the catalytic reaction.



Figure 1.5 : Different chemical structures of a bimetallic nanoparticle: (a) homogeneously mixed (b) ordered (c) core@shell (d) onion-shell (e) Janus segregated structures. (from reference [17])

Demixing (term derived from metals immiscible in the bulk phase) or segregation (often used for local demixing) can give rise to the other chemical structures in Figure 1.5 (c-e). In fact, segregation of one of the metals to the surface, i.e. **surface segregation**, is an often observed phenomenon in nanoalloys. A difference in surface free energy of both metals is one of the origins of this effect. The element with the lowest surface free energy will then move to the surface, to lower the total energy of the system, thereby creating a core@shell structure (Figure 1.5 (c)). In literature it is common to write 'Metal_x@Metal_y' core@shell nanoparticle. Other segregated structures e.g. the so-called Janus structure in Figure 1.5 (e) are less interesting for catalysis, but have applications in other fields.

• Origin of the influence of the chemical structure on the catalytic performance

The active sites in catalysis are usually situated at the surface of the nanoparticle. In bimetallic particles, there is not always an equal distribution of both metals at the surface, so that they do not participate equally in the reaction (**geometric effect**). This has an effect for example if only one of the metals is active and the other one is inactive.

But mixing both metals can also give a better catalytic activity, than what would be expected based on the exposed metal atom fraction at the surface. This synergetic effect is derived from an **electronic effect** that can be related to:

- The formation of bimetallic metal bonds, with possible electron transfer. This is the so called **ligand effect**. (not to be confused with the organic ligands used in synthesis)
- The change in the metal bond length, due to **strain effects**. This is due to a difference in metal bond length of both metals. This last effect is particularly relevant for core@shell alloys with a different lattice parameter and epitaxial growth.

Nørskov and coworkers [18][19] explained the variation of reactivity with the variation of the electronic properties, due to both ligand and strain effects. They calculated that the adsorption strength of reaction intermediates at the metal surface is related to the relative

position of the d-band center compared to the Fermi level (Figure 1.6). This is because the antibonding states of the adsorbate are more filled (weaker adsorption) when the d-band center is has a lower position compared to the Fermi level. They then demonstrated that compressive stress can induce a downshift in the d-band center, with a decrease in adsorption strength, while tensile stress has the reverse effect. Depending on the limiting step in a reaction (e.g. adsorption of reactants or desorption of the products) the reactivity can as such increase or decrease.



Figure 1.6 : Schematic illustration of the variation in binding strength of an adsorbant due to the interaction of the adsorbate valence states and the d-bands of the transition metal. The filling of the antibonding states that weaken the interaction is related to the position of the d-band center compared to the Fermi level.[20]

• Preparation of different chemical structures from solution

Wet chemical synthesis offers new possibilities to prepare different types of chemical structure, also when they are not thermodynamically favored. The optimization of the synthesis is often challenging, since one need to consider the different reduction rates of the metal precursors (and associated nucleation and growth rates) and the different strength of stabilization for both metals.

A first possibility to obtain bimetallic NPs is to introduce the two precursors simultaneously. Normally the precursor with the highest reduction potential (E_0) is reduced first. When the second precursor is reduced, a core(highE₀)@shell(lowE₀) NP is formed. However, this is only true for the same type of precursors. Often one can choose from different metal precursors and as such play with the different reduction rates (for example, zerovalent Pd(dba)₂ is reduced faster than bivalent Pd(acac)₂). Also the ligands can form a more or less stable complex with one of the components and in this way the reduction order can be reversed. However the boundary between the two reduction regimes might not be very strict.

The sequential introduction of the different metal precursors can be used to control precisely the reduction order. This approach is often used to create well defined core@shell structures.

The core@shell structure is particularly interesting in catalysis, to give economic benefits by alloying with a less expensive metal core. A less noble core can however be etched away by the deposition of a more noble metal (galvanic replacement), so again all parameters need to be considered to optimize the synthesis.

1.2.3 Oxide support

The support influences the reaction, but in this work inert SiO_2 powder will be used for the preparation of all model catalysts. Therefore, we will not further discuss this effect. Some general examples of the effect of the support on the catalytic reactivity, including wetting, charge transfer and strong-metal support interaction are given in [21] and [22].

1.3 Influence of the environment

In the aim to control the structure of the nanoalloys, one must take into account that it greatly depends on the physicochemical environment (e.g. temperature, pressure, reactants). Therefore, we need to study the dynamic structural changes with accurate **in situ measurement techniques**. We focus here on two main dynamic changes of nanoalloys that can occur under influence of gas adsorbates: shape changes and chemisorption-induced surface segregation.

1.3.1 Influence of the environment on the shape

In the literature, the shape change under reaction conditions was studied mostly for monometallic NPs. In situ grazing incidence X-ray diffraction (GIXRD) was used to study pure Pt [23], Pd [24] and Ru [25] on MgO. These NPs were mainly limited by (100) and (111) facets in vacuum, but they became rounded in O_2 atmospheres. This rounding was attributed to the formation of high index (e.g. 112) facets (Figure 1.7).



Figure 1.7 : Illustration of the rounding of the faceted corners by high index surfaces that appear with the introduction of O_2 . (from reference [24])

Another powerful method is in situ environmental TEM (ETEM). With this technique, the nanoparticles can be imaged in presence of gasses. For example, the rounding in an oxygen rich environment of a facetted Au NP on CeO₂ was observed by the group of Takeda [26]. Moreover, the particle again became facetted in presence of the reducing CO gas (Figure 1.8). The ETEM technique is used in this work, and more details and examples are therefore given in section 6.1.



Figure 1.8 : Statistical distribution of the shape of Au NPs on CeO₂ support, as a function of the partial pressures of P_{co} and P_{o2} measured by ETEM. (extracted from [26])

Also theoretical calculations for O_2 adsorption on pure metal NPs generally showed a rounding under oxidizing conditions [27][28]. Oxygen gas has higher adsorption energy on high index facets with more open arrangements. It can therefore preferentially stabilize these facets and accordingly change the shape.

1.3.2 Influence of the environment on the chemical structure

Furthermore, for nanoalloys, chemisorption-induced surface segregation can be observed. This can induce an increase or decrease in catalytic activity, depending if the component that is stabilized at the surface is more or less active.

For example, Tao et al. showed a reversible surface segregation effect under different gas conditions for Rh-Pd, Rh-Pt and Pt-Pd NPs by in situ ambient-pressure X-ray photo-electron spectroscopy (XPS) [29][30]. The metal that binds more strongly with the molecules in the environment can as such segregate to the surface, e.g. Rh under influence of NO in Rh-Pt (Figure 1.9).



Figure 1.9 : Evolution of the atomic fractions of both elements in Rh-Pt (1:1) nanoalloys in presence of different gases at 300°C, measured by in situ ambient pressure XPS. (from [30])

ETEM was again useful in the study of chemisorption-induced surface segregation in nanoalloys. For example, a combined in situ ETEM and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) study demonstrated the formation of a Pd surface layer under O_2 and CO/O_2 gas [31] (Figure 1.10).

Again, theoretical calculations confirmed this effect. For example it was calculated for the M-Au case (with M = Ni, Pd, Pt) in the presence of oxygen, that the metal with higher surface energy can segregate to the surface [32]. The higher heat/enthalpy of chemisorption for CO (Pd>Au) explains the Pd surface segregation of Pd under CO environment in AuPd.



Figure 1.10 : Au@Pd core-shell formation in AuPd nanoalloys in O₂ observed by ETEM. (from [31])

1.3.3 Other effects of the environment

It should be noted that the size can change during the reaction (sintering or redispersion). Alloying can have a positive influence on the stability in a certain environment. For example, Grazing Incidence Small Angle X-ray Scattering (GISAXS) experiments showed the increased resistance against shape and size changes for Au-Pd particles in oxygen compared to pure Pd [33].

The catalytic properties of metallic NPs are strongly related to the metal oxidation state of the surface, which can change during the reaction. Mostly, the reduced metal state is associated with catalysis. Therefore noble metals are frequently used as catalysts. On the other hand, the catalytic activity of the associated metal (surface) oxide and its role during the catalytic reaction is still a controversial topic.

Moreover, there is a large interconnection between the different parameters. For example the segregation and shape changes can be kinetically faster for smaller sizes. Also the adhesion energy with the substrate can be of importance and has a larger contribution for smaller sizes. This shows the complexity of the study of the structure-activity relationship and shows the need for well controlled structures obtained with wet chemical synthesis.

1.4 Pt-Pd nanoalloys in literature

1.4.1 Increased catalytic activity of Pt-Pd nanoalloys

Pt and Pd are both powerful catalysts. Both metals have a face-centered cubic lattice structure. In the bulk metal, they form a solid solution in the whole composition range and are thus ideal candidates to prepare different types of catalytic nanoalloys.

Nowadays, Pt-Pd nanoalloys are frequently studied for applications in fuel cells, for the optimization of the oxygen reduction reaction (ORR) [34][35], the methanol oxidation reaction (MOR) [36] or the formic acid electro-oxidation (FAO) [37]. Also other reactions are of interest, such as hydrogenation reactions [38], photocatalytic CO oxidation in presence of humidity [39] and the preferential oxidation of CO in excess H₂ (PROX) [40].

Improved properties were obtained by alloying both metals compared to the pure Pt or Pd catalysts. However because of the great variety of structures, it is difficult to find the origin(s) of the enhanced catalytic properties. We focus now on studies using the NP preparation from solution, with different sizes, shapes and chemical structure. Some examples of different structures reported in the literature are given in Table 1:1.

• Homogeneously mixed alloy chemical structure with different shapes

Some studies described the formation of Pt-Pd homogeneously mixed alloy chemical structure. For example, by adjusting the molar ratio of the precursors, spherical Pt-Pd nanoalloys of different compositions could be compared. Both highest activity and stability was obtained for Pt-Pd structures with 40-60 mol% Pt in the MOR [36]. It was explained by a bi-functional methanol oxidation mechanism (geometric effect): Pd would be responsible for

the water dehydrogenation to form Pd-OH, while Pt catalyzes the methanol dehydrogenation to form Pt-CO. Also other shapes of homogeneously mixed Pt-Pd nanoalloys, such as tetragonal or cubic shapes (with a composition around 1:1) showed improved specific activity in the MOR [16] (i.e. activity normalized to the electrochemically active surface area mostly estimated from hydrogen adsorption-desorption curves). It was attributed to an electronic effect due to the coexistence of surface Pd and Pt sites [16].

Shape	Chemical structure		approximate	test	specific	year	ref
			size (nm)	reaction	activity		
					compared to		
					pure Pt		
sphere	alloy (34,52,67,88,100%Pd)		4-5	MOR	x 1.25	2011	[36]
tetrahedron	alloy (1:1)		5	MOR	x 2.2	2011	[16]
cube	alloy (1:1)		8.5	MOR	x 3	2011	[16]
hollow cube	alloy (1:1)		12	FAO	-	2009	[41]
sphere	core-shell 1-4 Pt layers	Ō	4	ORR	x 2	2009 2010	[42] [43]
cube	core-shell 1-5 Pt layers		18	ORR	x 3	2014	[35]
octahedron	core-shell 2-5 Pt layers	\blacklozenge	20	ORR	x 4	2015	[44]
icosahedron	core-shell 0.7-4.3 Pt layers	Ó	15	ORR	x 8	2015	[45]
dendritic	core-shell 14 nm Pt dendrites	*	23 (9+14)	ORR+ FAO	x 2.5 x 1.5	2009 2010	[46] [47]
dendritic	core-shell 2.5 nm rough Pt	Ű	25.5 (23+2.5)	MOR	-	2015	[48]

Table 1:1 : Overview of some of the reported Pt-Pd nanoalloy structures (alloyed or core-shell) showing an increased activity in electrochemical reactions (red=Pd, blue=Pt).

• Core-shell Pd@Pt with different shapes

Because of the high cost of Pt and its crucial function in fuel cells, there is an increased interest in thin film Pd@Pt core-shell alloys. These core-shell alloys were sometimes prepared by a one-pot method [34], but mostly a sequential reduction was used, with the aim of a homogeneous deposition. To localize the reduction of the Pt-precursor on the Pd core, a hydrogen-sacrificial protective strategy was developed, together with a slow reduction process [49]. This strategy was further elaborated by the group of Adzic with the deposition of an ultrathin sacrificial Cu layer by electrochemical method on Pd [50]. This Cu layer is then

displaced by Pt by galvanic replacement. For the deposition of one monolayer on spherical Pd cores, a twofold increase in the ORR reactivity was observed compared to pure Pt [43]. There was only little variation with the addition of subsequent Pt monolayers (up to 4 layers) [42].

Controlled Pd@Pt NPs with different well-defined shapes such as cubes, bars, icosahedrons, etc. and discrete number of Pt layers were obtained by the group of Xia [35][44][45]. They first developed methods to precisely control the Pd core shape. For example bromide-stabilized Pd nanocubes with different sizes and preferential (100) surface facets, were synthesized [51]. Then, they used the controlled Pd cores as starting point for the synthesis of core-shell Pd@Pt nanoalloys. The highest activity in these studies was obtained with icosahedral Pd cores and 2-3 monolayers of Pt [45]. It was explained by the increased compressive strain in the Pt layer, due to the icosahedral twinned structure. This caused a weakening of the adsorption of O and OH, which is the limiting factor in the ORR.

• Increased stability through alloying Pt-Pd

In addition, the stability of the catalyst can be increased by alloying Pt with Pd. Monometallic Pt is known to be deactivated by particle coarsening [52][53]. In car exhaust catalyst, Pd would slow down the sintering of Pt-Pd nanoparticles as compared to pure Pt (at oxidative conditions at very high temperatures >800°C). This would be related to the formation of stable PdO instead of low vapor pressure PtO₂ [54]. At lower temperatures, sintering would occur through surface migration of mobile atoms, which would also be slowed down in the alloy [54].

1.4.2 Influence of the environment on Pt-Pd nanoalloys

The catalytic activity of Pt-Pd nanoalloys depends on the structure, which is influenced by the environment.

• Pd surface segregation maintained for different gas environments

Experimentally a Pd surface segregation was found in a large number of studies, for different NP preparation methods and different environments. This supports the theory of surface segregation of the metal with the lowest surface energy. For example, NPs prepared by laser vaporization showed Pd surface segregation in high vacuum conditions by low energy ion scattering (LEIS) measurements [55]. NPs prepared by wet-impregnation showed an increased Pd surface composition after annealing at higher temperatures in vacuum [56].

It was explained in section 1.3 that adsorbates can induce a different surface segregation than that determined for vacuum conditions. However, for standard oxidizing and reducing gasses the Pd surface segregation seemed to persist.

As such, a Pd-enriched surface was observed in vacuum, after O_2 [57] or H_2 gas exposure at high temperature [56]. This was explained by a higher heat of adsorption of oxygen and hydrogen on Pd (Table 1:2), so that the Pd surface segregation is not inverted. Other studies of technical air-exposed NPs prepared by sequential reduction in H_2 demonstrated as well this Pd-enriched surface by X-Ray Photoelectron Spectroscopy (XPS) [58] or by extended X-ray absorption fine structure analysis (EXAFS) [59][60].

	O ₂ (dissociative)	H ₂	CO
Pd (111)	230 kJ/mol [61]	87 kJ/mol [62]	134 kJ/mol[63]
Pt (111)	188 kJ/mol [61]	75 kJ/mol [62]	146 kJ/mol [64]

Table 1:2 : Estimations of the adsorption energies of O₂, H₂ and CO on Pt and Pd surfaces.

Only few studies report on in situ measurements of the surface composition of Pt-Pd nanoalloys, directly in the presence of different gasses. No substantial surface reorganization was observed by in situ ambient pressure XPS, under altering NO and CO gas environment at 300°C [29][30]. An almost stable high Pd surface concentration was found, for particles prepared by colloidal methods with different concentrations (Figure 1.11). However, a small concentration of Pt was found at the surface for higher Pt concentrations (Figure 1.11).



Figure 1.11 : Evolution of the atomic fractions of both elements at the surface in Pt-Pd nanoalloys in presence of different gases at 300°C, measured by in situ ambient pressure XPS. (from [30])

Notwithstanding, the existence of stable Pd@Pt core-shell alloys, with Pt at the surface, was shown by HAADF-STEM methods [65][66]. It shows that metastable structures could be stable in different environments. For relatively thick Pt shells made by atomic layer deposition (4 nm core and 1.5 nm shell), the Pd@Pt structure would be even stable up to 400°C in air [67].

• Remark on the precision of the in situ methods

So overall, a Pd segregation tendency was indicated. However each method used has its own limitations and very accurate surface composition determination stays a challenge. For example LEIS methods suffer from preferential sputtering of Pd and ion beam mixing effects with possible irradiation enhanced segregation. EXAFS is based on complicated data analysis and estimations on particle size and shape, with often not perfect fitting [60]. XPS is not extremely surface sensitive. Also chemisorption techniques are not unambiguous, since the adsorbates might influence the chemical structure. This shows the importance of combining experiments with calculations to fully determine the equilibrium structure of the catalytic Pt-Pd nanoalloys.

1.5 Summary of the general context and goals

In the work presented, nanoparticles are prepared by the decomposition of metal precursors in a solvent, in the presence of stabilizers.

Different chemical structures of Pt-Pd nanoalloys were illustrated in this chapter, in order to improve the catalytic performance. We focus further on:

- Homogeneous alloy structures that can show improved reactivity by the ligand effect.
- Core-shell alloys, for which also strain effects can be important.

A first goal is to obtain more insight in the control of the size, shape and chemical composition of Pt-Pd nanoalloys in solution.

A second goal is to prepare reproducible, clean model catalysts through this preparation method and to investigate possible relationships between the structure (size, shape and chemical structure) and the reactivity.

A last goal is to get more insight in the influence of environment (temperature and gas environment) on the structure and reactivity of Pt-Pd nanoalloys, with a focus on shape changes and chemical restructuring induced by the environment.

Chapter 2 Preparation and characterization of Pt-Pd nanoalloys

In this chapter, the synthesis of different Pt-Pd nanoalloys from solution is presented. First, the synthesis of homogeneously alloyed Pt-Pd NPs with narrow size distribution is described. Next, a cubic core-shell Pd-Pt structure is shown. For both, the deposition on oxide powders and the removal of the stabilizers are described. The NPs (size, loading, structure, etc.) need to be unambiguously characterized, for which a variety of techniques were used. These model catalysts were tested for the CO oxidation reaction, which is presented in Chapter 6.

2.1 Small homogeneous Pt-Pd nanoalloys

2.1.1 Nanoparticle synthesis and characterization

• Materials

Commercially available platinum(II)acetylacetonate $Pt(acac)_2$ (98%, Acros Organics) and palladium(II)acetylacetonate $Pd(acac)_2$ (99%, Sigma-Aldrich) were used in all synthesis. Although water based methods are rapidly developing, most controlled NP structures in literature, especially the smaller ones, are obtained in organic solvents. These acetylacetonate precursors are solvable in organic solvents and relatively stable in air.

Oleylamine OAm (technical grade, 70%, Aldrich) was used both as the solvent and capping ligand. Morpholine borane MB (95%, Aldrich) is a mild reducing agent, which was reported to give better control over the reduction kinetics, to obtain a narrow size distribution [68][69].

Different supports (powders and flat surfaces) were used. Amorphous SiO_2 powder was purchased from US Research Nanomaterials (+98%, 60-70 nm, 160-600 m²/g) and cubic MgO powder was home made by burning an Mg ribbon and collecting the fumes. Flat Si-wafers and Al-disks with a thin layer of native oxide (SiO₂ or Al₂O₃) were cleaned in ultrasound with ethanol/H₂O.

Abbreviations and structure of chemical components can be found on p. 153.

• Description of the synthesis

The wet chemical synthesis of both mono- and bimetallic (1:1) Pt-Pd nanoparticles was realized according to a procedure described by the Shouheng Sun's research group [36]. In a three neck reactor $Pd(acac)_2$ and $Pt(acac)_2$ (0.5 mmol in total) were dissolved in 15 ml OAm in a glove box under argon atmosphere. The reactor was closed with rubber septa and transferred to the fume hood. Then, it was put under argon flow with a needle through the

septa. This enables to install the condenser and temperature probe under continuous argon atmosphere (Figure 2.1). Next, the condenser was closed with a septum with a balloon to compensate pressure increase during heating. The solution was heated up to 60°C under continuous magnetic stirring. The precursors were then reduced by a fast injection of 0.2 g MB dissolved in 3 ml OAm at ambient temperature, also prepared in the glove box. All solutions turned black rapidly, slightly faster for pure Pd than pure Pt. The solutions were then heated up to 90°C for 30 min (Pd NPs) and up to 180°C for another 30 min (for Pt and Pt-Pd NPs).





The solutions were cooled down (not to room temperature, otherwise the OAm becomes too viscous) and separated in 6 centrifuge tubes. Isopropanol was added up to 15 ml and the particles were centrifuged at a rotation speed of 7200 revolutions per minute (rpm) for 12 min. The black precipitate was then redispersed in 15 ml heptane. This centrifuge-redispersion step was repeated several times to remove as much as possible the excess OAm. However after 3-4 times some agglomeration started to occur, which is a sign that too much OAm was removed to keep the particles stabilized. If necessary, some ligands can again be added to redisperse the agglomerated particles.

• Standard TEM observations and EDX

This colloid was dropped on a carbon-coated copper grid for characterization by transmission electron microscopy (TEM) with a JEOL 3010 operating at 300kV. As shown in Figure 2.2 the particles were **homogeneous in size and self-organized on the substrate**. Size distributions of around 500 NPs were acquired with the program "ImageJ-Particle Analysis". The average area of the NPs was measured and expressed as an equivalent diameter D, with the approximation of a spherical shape. The corresponding size histograms are given below the images, with the

95% size interval ($\pm 2\sigma$ for all intervals in this thesis). Pure Pt NPs had an average size of 3.7 \pm 1.5 nm (22% size dispersion, defined as σ /D), while the diameter of pure Pd was 5.0 \pm 1.0 nm (10% dispersion). The Pt-Pd particles were even smaller than pure Pt, with an average diameter of 3.2 \pm 0.8 nm (13% dispersion). Pure Pd and Pt-Pd alloys were thus more homogeneous in size than pure Pt. However, the measured equivalent diameter of pure Pt is influenced by the large proportion of elongated shapes, which increases the average size and the size dispersion.

The average composition of Pt-Pd (1:1 precursor ratio) was determined by Energy-dispersive X-ray spectroscopy (EDX) to be $49 \pm 8\%$ Pt/Pd. Although small local variations could not be excluded, the homogeneous alloyed structure is confirmed by the homogeneous size, shape and electronic contrast.



Figure 2.2 : TEM images of the NPs with OAm ligands, organized on a carbon grid and corresponding size histogram below of (a) pure Pt with average size of 3.7 ± 1.5 nm (b) Pt-Pd (1:1) nanoalloy with average size of 3.2 ± 0.8 nm (c) pure Pd with average size of 5.0 ± 1.0 nm. The FFTs in inset illustrate the organization due to the ligands.

• High resolution TEM observations

It can be seen in the HRTEM image of Figure 2.3 (a), that the elongated pure Pt NPs are monocrystalline. In situ TEM observations will show that for pure Pt, coalescence occurs in solution with OAm ligands (Chapter 3 and [70][71][72]). These elongated Pt NPs are thus the result of coalescence. In section 3.5 the origin of these elongated Pt particles and the difference with the alloyed Pt-Pd structure is further discussed. On the other hand, spherical pure Pd NPs were less crystalline than Pt with numerous defects and multiple twins, as can be seen in Figure 2.3 (b).

The Pt-Pd had a spherical shape (a shape closer to pure Pd), but were in general better crystallized. Both monocrystals as defective structures were observed, but also frequent twin structures (HRTEM image. Figure 2.3 (c)).



Figure 2.3 : Representative HRTEM images of the small nanoparticles prepared with OAm ligands (a) monocrystalline elongated pure Pt (b) poorly crystallized pure Pd (c) Pt-Pd with defective, single crystal and twin structure.

• Regular interparticle distance on flat supports

A 2D self-organization, with regular distance between the particles was found when depositing the particles on a flat support (e.g. the carbon TEM grid). This can be noticed in the calculated Fast Fourier Transform (FFT) in Figure 2.2. The distance of the bright ring to the center is related to the average interparticle distance. The spacing due to the oleylamine ligands was as such around 2-3 nm. The 6 diffuse spots in Figure 2.2 for Pt-Pd and Pd represent even a certain hexagonal ordering, although the particles are much less ordered than the so-called 'self-assembled superlattices' [73]. This organization is largely influenced by the density of the particles on the flat support. Sometimes, multiple layers are observed for high densities. For lower densities, the organization became less regular (Figure 2.4).



Figure 2.4 : Variation of the interparticle spacing of Pt-Pd NPs, due to a difference in density of NPs on the TEM grid, with a superposition of multiple 'layers' for very high concentration (left) or a less regular interparticle distance for lower concentrations (right).
2.1.2 Deposition on oxide supports and cleaning

The nanoparticles were then deposited on flat surfaces for a study of the self-organization, and on powders for the reactivity tests presented in Chapter 6.

• Deposition on flat surfaces and effect of ligand removal on 2D organization

The self-organization of colloidal particles on flat surfaces can have potential applications in different domains, such as electrochemical sensors. Moreover, they can be used as model catalyst with regular distance between the particles [74].

As mentioned in section 1.1, the stabilizers can block the catalytic active sites and are often removed before catalytic testing. A method that can be used is annealing at high temperature, but this destroys the 2D organization. Low temperature methods such as plasma or UV-ozone cleaning are preferred, to remove the organic part with little agglomeration or structural changes [75][76][77]. For oleylamine ligands, also an acetic acid cleaning was described [78].

We studied the effect of these different low temperature cleaning methods on the selforganization of the Pt-Pd nanoparticles. Since the particles were too small to observe in the available SEM directly on a SiO₂ wafer, TEM samples were prepared. Small pieces Aluminum disks were immersed in the solution and ultrasonicated for 1h and slowly dried. TEM samples were prepared by scratching the surface of the Al₂O₃ and wiping a TEM grid over the scratched surface. Figure 2.5 shows the evolution of the organization of the Pt-Pd assemblies on Al₂O₃. The inset FFT images show a very diffuse circle, because of irregularities of the Al₂O₃ surface and because the area is not completely covered. A more pronounced FFT circle means a more regular interparticle distance (e.g. Figure 2.5 (a) for as-deposited NPs).

To follow at the same time the cleaning efficiency, Fourier transform infrared spectroscopy measurement (FTIR) were acquired with a nitrogen flushed Bruker Vertex 70 (Figure 2.6). A layer of particles was deposited on the surface of a KBr compressed pellet and subsequently cleaned with the different techniques. The oleylamine ligand was characterized by a v_s -CH₂ stretching peak around 2851 cm⁻¹ and a v_{as} -CH₂ stretching peak around 2924 cm⁻¹.

Both the O_2 plasma and UV-ozone can reduce these oleylamine peaks below the reference level, which was a KBr pellet with no deposition (arrows on Figure 2.6).

It can be seen in the TEM images in Figure 2.5 (a-c) that remote O_2 plasma induces a disordering of the large organized areas of NPs (within 1 min), and finally leads to agglomeration (5 min). A similar break up in smaller organized domains was noticed by Gehl et al. [75] for a direct O_2 plasma.



Figure 2.5 : Pt-Pd NPs on Al₂O₃ thin films (a) as prepared (b) after O₂ plasma cleaning during 1 min (c) and 5 min (d) after cleaning by acetic acid (e) after UV-ozone cleaning during 20 min and (f) after Ar plasma cleaning during 30 s. The calculated FFT in the insets represents the corresponding evolution of the order (visible circle) or coalescence (diffuse circle).

Although acetic acid was reported to be more efficient for OAm cleaning than UV-ozone [79], here we did not find an efficient cleaning. Moreover, the acetic acid induces restructuring in large areas with coalescence (Figure 2.5 (d)).

The UV-ozone cleaning of 20 min at room temperature was able to remove the oleylamine ligands and could conserve a local order and a near constant interparticle distance (Figure 2.5 (e)). The particles seem to be organized in larger domains after UV-ozone treatment than after O_2 plasma. A previous study of the UV-ozone cleaning of Au nanoparticles, organized on SiO_x covered TEM grids [80] also showed a reasonable maintaining of the order, despite of the small disruptions of the 2D ordering and some coalescence.

Short treatment in Ar plasma did not remove the ligands and sputtering damages appeared. This is in agreement with the literature, where inert N_2 direct plasma sources [75] was tested up to complete removal of the ligands, which results in sputtering damage and total agglomeration.

The complete removal of the ligands, while maintaining the organization, is shown to be challenging. Compared to earlier studies, the particle sizes and/or interparticle distances were smaller. In this work, we continued to use UV-ozone treatments as efficient and flexible low temperature cleaning method, with minimal agglomeration effects.



Wavenumber [cm⁻¹]

Figure 2.6 : The FTIR spectra of Pt-Pd NPs deposited on KBr flat substrates and treated to remove the oleylamine ligands by the different techniques. (a) Ar plasma (d) Acetic acid are not efficient, while (b) $1 \min O_2$ plasma and (c) 20 min UV-ozone decreased the OAm characteristic peaks below reference level.

• Deposition on powder supports

The problem with the deposition on powders was that the NPs often agglomerated, as seen in Figure 2.7 (a). To ensure a homogeneous deposition, the colloidal solutions were agitated in an ultrasonic bath for at least 1 h. Then, the colloidal solution was mixed with the oxide powder in an ultrasonic bath for at least 2h. The MgO powder was collected by centrifuging the mixed solution at low speed (1200-1500 rpm). A heptane wash removed of the excess of free nanoparticles (without this washing see Figure 2.7 (b)). This method enabled a homogeneous deposition, as seen in Figure 2.7 (c).

A factor that was found to have large influence on the deposition rate was the centrifugeredispersion step, before mixing with the powder. Increasing the number of centrifugeredispersion steps removed more ligands and thus gave a better contact area for deposition. Increased amount of NPs on MgO were obtained by washing the particles up to 6 times. However, coalescence starts to occur (Figure 2.8). Although loading in catalytic samples is generally low, the ability to homogeneously deposit the colloidal particles can have other applications such as metallization of porous structures.



Figure 2.7 : Importance of different steps in the deposition: (a) agglomeration when not using ultrasound mixing (b) agglomeration when not removing the non-deposited particles by a heptane wash. When using both steps, a homogenous deposition can be obtained as in (c) with an example on SiO₂ powder.



Figure 2.8 : Importance of the centrifuge-redispersion step before the deposition of Pt-Pd NPs on MgO powder: TEM image of the density after (a) 1 time centrifuge-redispersion with 2h ultrasound mixing (b) 5 times (c) 6 times

On powders, it was more difficult to determine if the ligands were completely removed, since FTIR spectroscopy on SiO_2 powder is masked by a too strong absorption of the SiO_2 powder itself. For the reactivity tests in Chapter 6, similar cleaning treatments with 20 min UV-ozone was done, by spreading out the powder in a glass Petri dish in the UV-ozone cleaner. If some ligands are still present after this cleaning, it is interesting to know at what temperature they are removed. It can be seen on the Thermogravimetric analysis (TGA) in Figure 2.9 that the oleylamine is removed between 220°C and 370°C in an argon flow with a heating of 10°C/min.



Figure 2.9 : TGA of OAm-capped Pd NPs on MgO powder under Ar flow

2.2 Towards controlled $Pd_{core}@Pt_{shell}$ structures

The design of core-shell nanoparticles is a promising route to reduce the use of the expensive noble metals, and to tune the properties for better performances (section 1.4.1). Here we will use a sequential reduction to prepare thin layers of Pt on Pd cores with well-defined cubic shapes.

2.2.1 Nanoparticle synthesis and characterization

• Materials

A glass reactor resistant up to 3 bar of pressure was used in this synthesis. PVP (poly(vinylpyrrolidone)) with average molar weight of 130 000 000 (Alfa Aesar) was used as capping layer and the end groups of the PVP polymer were the mild reducing agents [81]. Potassium iodide (KI) was added as additional stabilizer and Dimethyl sulfoxide (DMSO) was the solvent. The same Pt/Pd acetylacetonate precursors were used as in previous synthesis.

• Description of the synthesis

The preparation of these NPs is illustrated in Figure 2.10. The synthesis of cubic Pd cores was inspired on a method of Yang et al. [82]. 25 mg of Pd(acac)₂ (0.08 mmol) was mixed in 2ml DMSO and 77.5 mg PVP and 69 mg KI were dissolved in 2 ml DMSO. Next, both solutions were mixed together under vigorous stirring for 10 min. The glass reactor was then closed and heated up to 140°C for 2h in an oil bath, before cooling down to room temperature. A sample of pure Pd particles was extracted (1ml containing 0.02 mmol of Pd), leaving 0.06 mmol in the solution.



Figure 2.10 : Illustration of the sequential reduction method used to prepare Pd@Pt core - shell NPs

A first quantity of $Pt(acac)_2$ (0.006 mmol, so 0.1 molar equivalent Pt/Pd, in 2 ml DMSO) was then mixed with the cold solution. This mixture was again heated up to 120°C for 1h30 and a new sample containing 0.02 mmol Pd was taken. This procedure of cooling to room temperature and adding a certain molar equivalent Pt precursor was repeated 3 times (0.1, 0.2, 0.5eq in total). During this procedure, the concentration of Pd in the solution decreases, with increasing $Pt(acac)_2$ precursor.

The particles were very sensible to agglomeration during the washing procedure. Therefore the deposition-redispersion procedure was only done once. A certain volume of solution containing 0.02 mmol Pd (and subsequent amounts of Pt) was divided over 2 flasks and completed up to 8 ml with acetone. The nanoparticles were centrifuged for 20-30 min at 3000 rpm. Then, they are dispersed in a mixture of 0.8 ml ethanol and 0.6 ml water.

• Standard TEM observations of the Pd cubic cores

Figure 2.11 (a-b) gives an overview of TEM images of the pure Pd seeds, dropped on a carbon film. Most of them are monocrystalline cubes with (100) facets with an average edge length of 14.6 ± 2.3 nm, or elongated bars along a crystallographic [001] direction. The enlarged image of a cube in Figure 2.11 (c) clearly shows very weak truncations by (110) facets at the edges and truncations by (111) facets at the corners. The extension of these truncations approximately corresponds to an anisotropy ratio between the surface free energies of $\gamma(001)/\gamma(110) \cong \gamma(001)/\gamma(111) \cong 0.7$, which is lower than the values obtained for similar sized Pd crystals on MgO, at the equilibrium in UHV, with $\gamma(001)/\gamma(111) \cong 1.16$ [12]. The selected area electron diffraction (SAED) pattern in Figure 2.11 (d) clearly shows the well crystallized nature of these nanoparticles.



Figure 2.11 : TEM images of the Pd seeds obtained in presence of PVP and KI in DMSO solvent (a-b) collection of cubes (40-60%), bars (40-20%) and other shapes (20%) (c) Magnified Pd cube with visible truncations and (d) high crystallinity demonstrated by the SAED pattern of the fcc crystals.

• Standard TEM observations of the concave Pd@Pt core-shells

The Pd nanocubes with successive amounts of Pt (addition of 0.1, 0.2 and 0.5 molar Pt/Pd equivalent) are shown in Figure 2.12 (a-i). Compared to the pure Pd nanocubes, no noticeable size increase was demonstrated within the limits of detection. This has two reasons. As will be shown by EDX analysis, only very low Pt quantities were deposited. Moreover, the Pt was preferentially deposited at the corners of the Pd cubes. As such, the crystal evolved from a cube to a 'frame concave nanocrystal' as previously described by Lu et al. [66]. This resulted in an overall sharpening of the corners, but negligible size increase. This also means that for the reactivity tests that are presented in Chapter 6, no size effect has to be taken into account. A high resolution image of the edge and the corner of such a frame concave nanocrystal can be seen in Figure 2.13. It shows the epitaxial growth of Pt on the (001) Pd faces. Despite of a small lattice mismatch of 0.77% between Pt and Pd lattices, the (002) lattice planes are continuous at the interface, due to the accommodation of Pt on the Pd substrate. However some distortions are seen near the corners and the deposition of Pt creates higher index facets are believed to be more reactive in catalysis [83].



Figure 2.12 : TEM images of Pd seeds with successive coverage of Pt, with addition of (a-c) 0.1 molar equivalent (d-f) 0.2 molar equivalent (g-i) 0.5 molar equivalent



Figure 2.13 : HRTEM image of the corner of a Pd seeds covered with about 2 equivalent layers of Pt (0.5 eq Pt/Pd precursor), with the creation of higher index surfaces

• EDX analysis of the Pd@Pt core-shells and calculation of the equivalent layers

The results of the EDX analysis of 2 different syntheses are shown in Table 2:1. These values represent the average of 10 measurements on a larger collection of particles. It can be noticed that not all the platinum precursor was reduced under these conditions, with an average of 23% that was actually deposited. However a linear increase in the Pt/Pd atomic ratio was obtained.

sample name	mol eq Pt/Pd added to	EDX measured mol eq Pt/Pd	% deposited	equivalent atomic layers for 14.6 nm	estimated total metal loading (wt.%)
	301011011			cube	on SiO ₂
Pure Pd	0	0	0	0	2.3
Pd@Pt _{0.2eqL}	0.1	0.016±0.004	0.16	0.2	2.4
Pd@Pt _{0.4eqL}	0.2	0.034±0.02	0.17	0.4	2.5
Pd@Pt _{0.5eqL}	0.2	0.044±0.005	0.22	0.5	2.6
Pd@Pt 1.6eqL	0.5	0.13±0.06	0.26	1.6	2.9
Pd@Pt 2.2eqL	0.5	0.18±0.02	0.36	2.2	3.1

Table 2:1 : EDX analysis for different quantities of Pt added to the solution of Pd cubes

From this EDX analysis we calculated the equivalent Pt atomic layers deposited on these 14.6 nm cubes, with the estimation of 8 mol% at the surface. After the controlled deposition of increasing quantities of Pt, samples with 0.2, 0.4, 0.5, 1.6 and 2.2 equivalent monolayers were prepared. In further discussion, the sample names are based on this calculation and written as Pd@Pt_(x-equivalent-layers).

• Information on the growth mode

Compared to other synthesis of core-shell Pd@Pt that have been undertaken, this synthesis showed no homogeneous nucleation¹ of pure Pt NPs. Indeed, it can be a challenge to prepare core-shell alloys with only heterogeneous nucleation² on the Pd cores. Pt has a high cohesive energy, which often leads to homogeneous nucleation or dendritic island growth modes [46][84].

In this synthesis, it is believed that a **galvanic replacement reaction** is at the origin of the localized deposition. The galvanic replacement was previously observed for cubic Pd NPs stabilized with Br⁻ ions, for which the Pd sides were replaced with Pt from $PtCl_6^{2-}$ precursors [36]. Deposition was only noticed in presence of Br⁻. The etching of Pd atoms at (100) facets to replace with Pt atoms at the corners led then to a concave structure.

Here, the Γ ions are preferentially adsorbed at (100) surfaces, which stabilizes the cubic shape [82]. An iodide-assisted galvanic replacement from Pd at the (100) surfaces can in this case be initiated, with a simultaneous reduction of the Pt(acac)₂ precursor at the (111) corner facets.

The relative low temperature (120°C) further limits the diffusion of the deposited Pt at the corners [35]. No deposition was observed when adding $Pt(acac)_2/PVP$ to a solution, in which the Pd particles were washed (so the KI removed). This supports this theory.

The etching/deposition was found more severe for non-cubic seeds as bars and triangles, creating holes in the structures for high Pt(acac)₂ concentrations (Figure 2.14). The presence of these bars and triangles thus induces an error on the calculation of equivalent layers of Pt on the Pd cubes.



Figure 2.14 : TEM images of the etching of the Pd cores when depositing larger amounts of Pt (here: 0.5 eq Pt/Pd precursor), creating irregular structures.

¹ Homogeneous nucleation = nucleation in the liquid phase

² Heterogeneous nucleation = nucleation on a solid surface, here the Pd core surface

2.2.2 Deposition on oxide powders and cleaning

• Deposition on powder supports

For the pure Pd nanocubes, 0.7 ml containing 0.01 mmol Pd was mixed with 45 mg SiO₂, which gives an approximate loading of 2.4 wt.%. Proper mixing was ensured by the ultrasound radiation for at least 1 h. Then 0.1 ml acetone was added to improve the deposition of the particles on the support, and mixed for another 30 min. This solution was centrifuged for 10 min, and dried in vacuum.

The total metal wt.% loading was calculated based on EDX analysis (Table 2:1). The particles were relatively well dispersed, although some local agglomeration could not be prevented (Figure 2.15).



Figure 2.15 : TEM images of the Pd@Pt nanoparticles (a) relatively homogeneously dispersed on SiO₂ powder (b) with some local agglomeration of the particles.

• Cleaning of the particles

The powder was then spread out in a glass Petri dish and put in the UV-ozone generator at room temperature for 2h (with an intermediate mixing step after 1h) to remove the polymer. No major modification of the shape was observed after UV-ozone, as seen in Figure 2.16 for particles on a carbon grid or on SiO_2 powder.

FTIR spectroscopy studies showed that the used cleaning method (1x wash+deposition+2h UVozone) sensibly reduced the peak intensities of PVP (Figure 2.17). However, simple washing the particles several times was found to be more effective to remove the PVP. This explains the fast agglomeration after successive washing, because if the polymer is effectively removed, the particles can agglomerate. Another cleaning strategy in which the particles are first dispersed on SiO₂ and then extensively washed could be considered in the future. Some other small peaks seem to appear after cleaning, which might be an indication of residual carbon fragments.

It was further observed that some contaminants stayed on the surface after one centrifugeredispersion step and can possibly poison the catalytic surfaces. EDX analysis showed approximately 3 mol% Sulfur, 2 mol% Potassium and 4 mol% lodine. Optimization of the cleaning and replacement of the high boiling temperature solvent DMSO can be a future point of interest.



Figure 2.16 : TEM images demonstrating the minimal effect of UV-Ozone on the morphology: (a) Pd@Pt_{2.2eqL} after 1h UVO on a carbon grid and (b) pure Pd cubes on SiO₂ after 2h UVO



Figure 2.17 : The FTIR spectra of Pd@Pt_{0.2eqL}NPs deposited on KBr flat substrates. A decrease of the characteristic PVP peaks was observed after UV-ozone treatment. However only a combination of extensive washing (3x) and successive UV-ozone treatment can completely bring these peaks below reference level.

2.3 Conclusions on the preparation and characterization of Pt-Pd nanoalloys

In this chapter, the synthesis of two types of Pt-Pd nanoalloys was presented.

Homogeneous Pt-Pd nanoalloys were synthesized from an Oleylamine (OAm) solution with a size of around 3 nm. The size and shape of the Pt-Pd nanoalloys was found more homogeneous than elongated Pt NPs. The Pt-Pd nanoalloys were self-assembled on flat oxide surfaces. The organic ligands, that create this self-assembly, were removed by different techniques. UV-ozone is an appropriate technique to remove the ligands, while maintaining a regular interparticle distance with limited coalescence. The particles were deposited on SiO₂, used in the reactivity studies later on in Chapter 6.

Pd cubes, primary limited by (100) faces, were synthesized with PVP/KI stabilization. Then, successive amounts of Pt were deposited on the Pd cubes, verified by EDX and HRTEM. A frame concave shape, which is limited by high index surfaces at the Pt corners, was obtained. The amount of Pt was expressed as equivalent layers on Pd cubes and as such, NPs with 0.2, 0.4, 0.5, 1.6 and 2.2 equivalent Pt layers on Pd cubes were deposited on SiO₂ powder and cleaned by UV-ozone, to test for the CO oxidation reaction in Chapter 6.

Chapter 3 In situ TEM study of Pt-Pd nanoalloys from solution

In this chapter, it is demonstrated how the nucleation and growth mechanisms of nanoalloys in liquid can have an influence on the final structure. This study is conducted with an original in situ technique, using a graphene oxide liquid cell inside the TEM microscope. The field of liquid TEM is rapidly developing, so it is important to describe first the current state of the art, with a focus on nucleation and growth of noble metal NPs. Then, it is shown how to prepare the graphene oxide liquid cell. The advantages and limits of this type of liquid cells are demonstrated by a study of pure Pt NPs with two types of ligands. Next, small Pt-Pd nanoalloys with oleylamine ligands were imaged during nucleation and growth. Also the growth of a thin Pt layer on a pre-synthesized Pd core is discussed. As such, the two different types of Pt-Pd nanoalloys obtained by a standard synthesis in Chapter 2 are compared with similar nanoparticles, grown in situ in the liquid cell.

3.1 State of the art of in situ liquid TEM

The ability to observe liquids at high resolution by TEM has recently received a lot of attention, as evidenced by the increasing number of publications, special journal issues and workshops (e.g. MRS bulletin, January 2015 [85]). This in situ technique has already been used in studies of different domains such as biology, nanomedicine, physics and chemistry. In the field of metal nanoparticles, insights in dynamic motion, growth and coalescence mechanisms were already obtained.

It was shown in previous chapters that it is possible to tune the structure (size, shape, chemical arrangement) of metal nanoparticles in solution. The final structure that can be observed in standard TEM is related to the choice of the stabilizers and metal precursors, since these parameters affect the nucleation and growth kinetics. However, the mechanisms of nucleation and growth in these often complex liquids are still not completely understood. Therefore, liquid TEM is an excellent method to study in direct the formation of these NP structures.

In most studies, micro-fabricated silicon liquid cells are used, to overcome the evaporation of the liquid in the high vacuum TEM environment. They consist of two silicon wafers coated with 10-100 nm silicon nitride, from which the silicon is etched away in a predefined region [86]. Unfortunately the resolution is limited by the high atomic number of the Si₃N₄ windows and the relatively thick liquid layer. A local thinner liquid layer was obtained by deflecting windows, narrow channels or bubble formation, but most of the studies up to now did not attain atomic resolution in the liquid.

The first studies were interested in the dynamic motion (diffusion and coalescence) of presynthesized Au [87],[88] and Pt [71]. Later on, the **direct reducing capability of the electron beam** was used, to reduce in situ the metal precursor and as such **observe in direct nucleation and growth**. This principle, that was used here, is illustrated in Figure 3.1. Similar liquids as for the standard synthesis are encapsulated, with the exception of the chemical reducing agent, which is replaced by the electron beam irradiation.



Figure 3.1 : Illustration of the reduction of metal precursors under electron beam irradiation with subsequent formation of nanoparticles, stabilized by ligands.

As such, the nucleation and growth by atom addition of Pt [70], Pd [89], Ag [90][91] NPs were studied in real time. Also the growth of some bimetallic NPs such as Pt-Fe [92][93] and core-shell structures such as Au@Pd [94] or Pt@Au [95] was demonstrated.

With the development of the **graphene liquid cell** [72], the start was given for the imaging of nanoparticles in a liquid with atomic resolution. With this new type of liquid cell, it was possible to observe the nucleation and growth of pure Pt NPs with OAm ligands [72].

More recently, the in situ growth of NPs with specific shapes was studied. For example the formation of cubic Pt nanoparticles stabilized with oleylamine and oleic acid ligands was demonstrated [96]. After some initial time of coalescence for small Pt particles, (100) facets began to develop for larger particles, which was explained by the reduced mobility of oleylamine on the (100) facets.

But the shape is not only controlled by the stabilizers. The reduction rate, that depends on the electron dose, had a large effect on the shape too [90][97]. It can be controlled by the variation of the magnification. As such, the 2D growth of Au nanoplates and isotropic 3D facetted clusters was initiated at low dose in a thermodynamically controlled regime, while a majority of 3D branched clusters was formed at high dose in a kinetically controlled regime [97]. Moreover, stacking faults were shown to have a crucial influence on the final shape of the Au nanoplates [97].

All these different examples show the interest of liquid TEM studies for the understanding of the nucleation and the dynamic growth of colloidal nanoparticles.

3.2 Experimental technique

For all TEM observations (unless stated differently), a JEOL 3010 operated at 300 kV was used. We used a liquid cell similar to that described by Yuk et al. [72], but in the present case, graphene oxide was used instead of pure graphene. High quality graphene, as used in this previous study [72], was made by chemical vapor deposition on a copper foil. These specific apparatus are not always available, so the advantages of graphene oxide are especially the easier (larger scale) production process and flexible manipulation. It will be shown that chemically prepared graphene oxide can have similar encapsulation properties as graphene.

The preparation of graphene oxide was based on the Hummer's method with additional KMnO₄ [98]. The product was washed by centrifuging and redispersion in ethanol for several times. Before use, the solution was sonicated for a short time. The graphene oxide sheets had sizes of around 10 μ m. Graphene oxide can be seen as sheets of graphene that are decorated with oxygen functional groups at the sides and edges. The exact atomic structure of graphene oxide is however still under discussion. Hydroxyl, carbonyl, carboxyl and epoxide groups would be present in different amounts and be distributed highly inhomogeneous at the nm level. The oxygen content is concluded between 10 and 50 %, depending on the synthesis method. In the method used here, the oxygen level was reported to be around 10 at% [98]. The oxygen content is known to decrease under higher electron dose, but this also means that it is sensible to beam damage.

The preparation of the liquid cell is illustrated in Figure 3.2. It actually consists of a collection of different small liquid cells. The liquid areas stand out due to an increased and irregular contrast in TEM (Figure 3.3). It was made by dropping the graphene oxide solution on two different holey carbon grids. Then, the solution containing the metal precursors and stabilizers was dropped on one of the grids. The cells were closed by simply putting the other grid on top, with the graphene oxide side towards the solution. Van Der Waals forces between the graphene oxide sheets pull the sheets of one side on top of the other grid. Therefore, the top grid can be removed. One can choose to keep both grids, to have higher amount of liquid cells. However it was found that excess of solution limited the resolution by contamination of the imaging area with carbon fragments. Also a large excess of organic stabilizers had this similar detrimental effect, so it was chosen to dilute the precursor+stabilizers, preferably with a high boiling point solvent such as 1,2-dichlorobenzene (bp 180.5°C).



Place a drop of the graphene oxide solution on 2 holy carbon grids.



Place a drop of the precursor solution on one of the grids.



Put the 2 liquid sides together, and take one grid for observation.

Figure 3.2 : Method to make the graphene oxide liquid cell.

It is difficult to make an estimation of the amount of liquid in one cell, since it is variable depending on the chosen liquid area. In areas with large amount of liquid, it is not possible to obtain meaningful images with our microscope due to the strong contrast. It is considered that in this work, the thickness would not exceed few nm, to provide high resolution imaging during the reaction. After 20-30 min of irradiation, the liquid cell is mostly dried out. This means that it is not possible to follow the growth for a longer time with this type of cell. For the growth of larger particles, these limitations should be taken into account.



Figure 3.3 : Typical view of a liquid zone (containing pre-synthesized NPs) in TEM (a) with wrinkled graphene oxide over the holey circular zone and (b) irregular local contrast.

The use of these graphene oxide liquid cells is very interesting, especially for the nucleation phase and for the possible high resolution imaging of the lattice fringes. Since information on the nucleation phase and the start of growth are typically not accessible with a series of standard TEM samples, collected at discrete times during synthesis, it is one of the main advantages of this type of liquid cell. A disadvantage is that the experiments have a rather low success rate, with sometimes no nucleation or lack of a suitable liquid area. Also the 'nanoscale' variation in the liquid cell properties (amount of liquid, local contaminations, etc.) can make the comparison between different experiments challenging.

3.3 Note on synthesis by electron beam irradiation

Even more than for regular solid samples, the effect of the TEM electron beam needs to be taken into account, since it is at the origin of the reduction process. Most previous studies were done with aqueous solutions, for which it was considered that the solvated (or hydrated) electrons play a major role in the reduction of the metal precursors. This is based on the similarities with high energy gamma radiation-induced synthesis methods in water based solutions. For this last synthesis method, radiolysis products are well studied. Mostly reducing hydrated electrons $e^{-}(aq)$, hydrogen radicals H[•] and oxidizing hydroxyl radicals OH[•][99] are created.

However, radiation-assisted synthesis in organic media is much less studied than in aqueous media. The organic molecules can decompose with much more diversity as compared to the radiolysis of water. This results in complex reaction products and processes. Moreover, impurities largely present in organic solvents as compared to ultrapure H_2O can strongly influence the process.

In conventional studies of radiation-induced synthesis, it is common to calculate the dose in Gy/s. This unit is the multiplication of the dose rate in $e^{-}/Å^{2}s$ with the stopping power. For 1,2-dichlorobenzene the stopping power is 2.428 MeV cm²/g at 200keV or 2.054 MeV cm²/g at 300keV [100], similar to water. The dose rate associated to the TEM electron beam is as such 10^{9} - 10^{10} Gy/s, which is orders of magnitude higher than a 'high dose' of 10^{5} Gy described for radiation-induced synthesis methods [101]. At these high doses, the metal ions are rapidly consumed during the nucleation process and small particles are obtained [102], almost independently of the initial precursor concentration [103].

It is also noticeable that the electron beam induces changes of morphology and structure of the metal particles, as previously seen in standard HRTEM [104][105] and in liquid HRTEM [72]. Energy transfer by the high-energy electron beam can cause irreversible degradations such as atom displacement (knock-on) and local heating, although this last effect is probably limited to less than 50°C.

These effects are inherent in beam-induced growth studies, since imaging with lower doses often did not induce nucleation. Microfabricated cells with microfluidic systems, in which the reducing agent can be separated from the growth solution, could provide more understanding of the growth under low dose and flow conditions, independently of the electron beam [106][95].

3.4 Pure Pt and influence of the ligands

Some important phenomena in the liquid cell will be illustrated with the nucleation and growth of pure Pt NPs. First, similar experiments as described by Yuk et al. [72] with Pt(acac)₂ and oleylamine (OAm) were performed, to validate the use of graphene oxide instead of graphene. This experiment was then compared with the growth of Pt in presence of another type of ligand, n-octylsilane (OS). Their different nucleation behavior will illustrate the information that can be extracted from this type of in situ studies, even when the reduction process is different from the synthesis in a standard reactor. The nucleation rate of pure Pd under similar conditions was found to be too fast, so unfortunately, no comparison with pure Pd was possible.

3.4.1 Observations of Pt + oleylamine in the liquid cell

A graphene oxide liquid cell with a drop of a solution containing 20 mg Pt(acac)₂ in 1 ml 1,2dichlorobenzene (0.05M) with oleylamine ligands (9:1 volume ratio) was prepared. The presented results were obtained with a precursor concentration two times higher than Yuk et al. [72], all other solution parameters were the same. As stated before, it was necessary to dilute the OAm ligands with a solvent, because of contamination issues. The solution contained as such 6 times more ligands than Pt atoms (= 6 molecular equivalent = 6 eq OAm). High boiling point 1,2-dichlorobenzene (BP 180.5 °C) was confirmed to be a good solvent.

Figure 3.4 shows the nucleation and growth of Pt NPs in the graphene oxide liquid cell, during electron beam irradiation. It can be seen that the start of nucleation was very fast, with already some small particles visible in the first image. In all observations it was therefore opted to do the beam adjustments in another area, to minimize nucleation before observation. The nucleation of new particles was observed until 4-5 min. However, the particle density remained almost constant, due to the frequent coalescence (see graph in Figure 3.5). This growth mechanism by coalescence was found in parallel to growth by monomer attachment, as was observed in previous studies [70][72]. After about 5 min, no new nucleation occurred, and coalescence became the main growth mechanism. This is represented by a decreasing particle density (Figure 3.5).

For the larger particles lattice fringes could be imaged during coalescence (Figure 3.6), with an oriented attachment along the <111> direction. This orientation specific coalescence was also observed by Yuk et al. [72] and was attributed to minimal ligand obstruction in this direction.



Figure 3.4 : TEM images of nucleation and growth of pure Pt NPs with OAm ligands, by reduction of the electron beam, in a graphene oxide liquid cell. Nucleation started fast and then the particles grew both by monomer attachment and frequent coalescence (beam current 4.10^4 A/m² at a magnification of 300K).



Figure 3.5 : Pt(OAm) particle density in the liquid cell, in a fixed frame of 230 nm² as a function of the time. The increase in particle density by nucleation up to 5 min is limited due to the competition with coalescence during the whole time interval.



Figure 3.6 : TEM images of the coalescence event of two pure Pt NPs, along the <111> direction.

After the disappearance of the liquid, an average particle size of 2.4 \pm 2.2 nm was measured (Figure 3.7). This drying of the liquid cell was probably the limiting factor for further growth by coalescence. The particles were however close to the sizes of those prepared in a standard reactor, by reduction with morpholine borane (pure Pt(OAm) 3.7 \pm 1.5 nm, Figure 2.2, p. 23). The variation in sizes was quite large (σ = 1.1 nm, dispersion 46%), with a mixture of elongated and spherical shapes. Most particles were well crystallized. This was also the case for pure Pt from the standard reactor (section 2.1.1). This means that particles rearranged their structure after coalescence, as was observed by Yuk et al. [72].



Figure 3.7 : TEM image of the final Pt NPs synthesized with OAm ligands in a graphene oxide liquid cell, after electron beam exposure for about 12 min and with corresponding particle diameter histogram.

The beam current density for this experiment was in the range of 10^4 A/m^2 , similar as in the study of Yuk et al. [72] However the effect of a different acceleration voltage (here 300kV instead of 80 kV) is not completely understood [107], since this parameter has an influence on the fundamental physics of the radiation-material interactions. At low voltage, ionization damage is more severe due to the inelastic scattering, while damage by knock-on dominates at high voltage. More quantitative studies are needed to fully understand other processes involved (e.g. concentration of oxidizing radicals might be different).

3.4.2 Observations of Pt + octylsilane in the liquid cell

A graphene oxide cell with a drop of a solution of 0.05M Pt(acac)₂ and 1 eq n-octylsilane (OS) (abcr, 95%) in 1,2-dichlorobenzene was prepared (4 mg in 10 μ l OS and 190 μ l DCB). Some major differences with the previous experiment were observed.

First, the start of nucleation was very slow, only starting after about 10 min of irradiation and continuing for another 10 min. Particle again grew through both monomer attachment and coalescence (Figure 3.8). The octylsilane ligand seemed to protect the particles a little more. Sometimes, coalescence was avoided, even if the particles came very close, especially at larger sizes (Figure 3.9).

The Pt NPs that were formed after drying of the liquid cell at about 20 min were similar in size, but more homogeneous $(2.6 \pm 0.7 \text{ nm})$ than the particles formed with oleylamine ligands. Less elongated shapes were observed (Figure 3.10).



10 min



20 min

Figure 3.8 : TEM images of nucleation and growth of pure Pt NPs with OS ligands, by reduction of the electron beam, in a graphene oxide liquid cell. Nucleation only starts after 10 min irradiation, then the particles grew by both monomer attachment and coalescence (beam current 1.10^4 A/m² at a magnification of 300K)



Figure 3.9 : TEM images of coalescence events of pure Pt NPs with OS ligands. The particles can come very close without coalescence.



Figure 3.10 : TEM image of the final Pt NPs synthesized with OS ligands in a graphene oxide liquid cell (from other series), after electron beam exposure for about 20 min and with corresponding particle diameter histogram.



Figure 3.11 : Pt(OS) particle density in the liquid cell, in a fixed frame of 650 nm², as a function of the time. Nucleation started only at about 10 min of irradiation and continues for another 10 min, with some coalescence events.

It was reported that pure Pt particles with a very narrow size distribution could be prepared with n-octylsilane ligands and Pt(dba)₂ precursor, under 3 bar of H₂ [108]. The Pt-SiCxHy bond would have a covalent nature, indicating the strong bond of the ligand at the Pt surface. A similar synthesis was done with Pt(acac)₂ and OS ligands in a glass reactor, with addition of morpholine borane and very small spherical particles (2-3 nm) were obtained.

3.4.3 Interpretation of the observed nucleation

The classical LaMer's theory of nucleation [109] describes that monodispersity can be obtained with a high nucleation rate in a short time and an initial rapid growth to reduce concentration below supersaturation. Although with this strategy to separate nucleation and growth stage ('burst' nucleation), often monodisperse sizes could be obtained, it was also reported that it may not be a sufficient, nor a necessary condition [110]. The study of Pt with

two types of ligands seems to support this last statement. Nucleation was faster in the Pt(OAm) system, but more monodisperse sizes were found for Pt(OS). This is due to the strong ligand protection of octylsilane, with formation of covalent bonds [108] and the less strong protection of OAm, which resulted in frequent coalescence and elongated shapes.

In the supplementary information of the publication of Zheng et al. [70] possible reduction mechanism for pure Pt(OAm) are discussed. They state that oleylamine based reduction only occurs at high temperatures and that the heating in the cell is limited; therefore they attribute the reduction to solvated electrons.

$$Pt^{2+} + 2RNH_2 \rightarrow Pt^0 + 2RNH_2^+$$
 (oleylamine based reduction)
 $Pt^{2+} + 2e^- \rightarrow Pt^0$ (solvated electron based reduction)

However, it is also known that OAm can form a complex with the metal ions of the precursor [111]. If the reduction would only be dependent on the solvated electrons, differences in stabilization/shape formation might occur by changing the ligands, but nucleation should start at the same time (for a same Pt precursor). Because we noticed here a large difference in time of the start of nucleation, it is therefore necessary to include the metastable OAm complex formation in the explanation of the observed phenomena.

3.4.4 Conclusions on pure Pt with different ligands

The use of graphene oxide instead of graphene does not seem to influence the growth of Pt with oleylamine ligands, since compared to the study of Yuk et al. [72] similar mechanisms were observed. Growth by both monomer attachment and frequent coalescence was demonstrated. The final pure Pt NPs with oleylamine ligands were monocrystalline, quite disperse in size and with some elongated shapes.

These Pt particles were compared with the formation of Pt NPs with octylsilane ligands. These are known to be strongly bound to the Pt surface. The nucleation process was remarkably slower, but this did not impede to obtain particles with homogeneous size. The strategy to create monodisperse particles based on the LaMer theory of nucleation [109] was therefore not applicable.

It was shown that pure Pt nanoparticles could be grown by in-situ electron irradiation in a graphene oxide liquid cell, with final structures that resemble those obtained in a standard synthesis. This shows the possibilities of the use of this type of liquid cells in the study of nucleation and growth of colloidal NPs.

3.5 Small Pt-Pd nanoalloys + oleylamine ligands

3.5.1 Observations in the liquid cell

Next, the solution encapsulated between two graphene oxide layers was made by mixing 10 mg of $Pd(acac)_2$ and 10 mg $Pt(acac)_2$ in 2 mL of 1,2-dichlorobenzene with oleylamine (9:1 volume ratio). This gives a molar ratio of 57% Pd precursor and 43% Pt precursor, with a total concentration of 0.029M. The reduction of the Pt and Pd precursors by the electron beam and subsequent nucleation and growth of Pt-Pd nanoalloys can be seen in Figure 3.12. These TEM images were taken from the same area during 180 s of beam exposure. During this time, no coalescence occurred. The time t= 0 s in Figure 3.12 (a) represents the origin of the series of images. Before this time, adjustments were again done in another area to minimize the irradiation effect in the area of interest.



Figure 3.12 : (a–g) In situ nucleation and growth of Pt-Pd NPs in the liquid cell with time, by reduction of the electron beam. The density of particles is stable after approximately 70 s of irradiation. The inset of (g) shows a faceted cluster, mostly limited by (111) and (100) facets (beam current 1.5. 10^4 A/m² at a magnification of 300K).

The Pt-Pd nanoalloys start to be visible around 40 s of irradiation. However, the nucleation kinetics is very fast and it is not possible to determine the size of a stable nucleus with the achieved time and space resolution.

The density of clusters was measured as a function of irradiation time, in a fixed area that was compensated for the drift (Figure 3.13). The density increased until 70 s of observation (in Figure 3.12 (a-d)). After this time, no more nucleation was observed. No coalescence was observed either, which resulted in a stable particle density after 70 s.

The mean particle size increased as a function of irradiation time. In the case of the marked particle in Figure 3.12 (e), the cluster size as a function of time (t) during the growth process is represented in Figure 3.13 (b). After about 80 s, the cluster size is constant around 2 nm, which is close to the size measured in the assembly of NPs obtained in the standard solution synthesis (see Pt-Pd(OAm), 3.2 nm, Figure 2.2, p. 23). It appeared that the increase in particle size depends on $t^{1/2}$, as previously reported for Ag NPs growing in a liquid cell [90].

As the clusters were free to move in the liquid, their orientation changed frequently during the growth, so that different lattice fringes frequently appeared or disappeared during the observation. Figure 3.14 displays the evolution for 180 s of a particle from another series of observation. With time, the contrast increased and the crystalline order improved. Later on, the clusters became faceted. The lattice fringes correspond well to those of Pt and/or Pd (111) and (200) spacings.



Figure 3.13 : (a) Density of clusters in the liquid as a function of the irradiation time during the nucleation and growth process of Pt-Pd NPs. (b) Cluster diameter as a function of the irradiation time during nucleation and growth process, for one isolated cluster with t^{1/2} exponential fit.



Figure 3.14 : Structure and morphology evolution with time of the same Pt-Pd NP in the liquid cell between 50 and 180 s as they rotate in the solution.

Most of the final clusters were single crystals, although some had a twinned structure, as seen in Figure 3.15 taken at 500 (a), 530 (b), and 540 s (c). At this stage, nucleation and growth are finished.

Both in Figure 3.14 and Figure 3.15, the size of the particles was almost constant, but from the lattice resolution, it can be observed that they still rotate and make translations at short distances, due to their movements in the liquid phase. After about 10 min of beam irradiation, the particles stopped their movement and the cell was dried out. The final average size was measured to be 3.2 ± 1.4 nm (Figure 3.16).



500 s 530 s 540 s Figure 3.15 : Shape and crystal structure of Pt-Pd nanoalloys in liquid after longer time of observation. Both single crystals and twins are visible.



Figure 3.16 : Size distribution of Pt-Pd nanoalloys with OAm ligands in the liquid cell (10min).

3.5.2 Interpretation and comparison with NPs prepared in standard reactor

Once again, it is shown that it is possible to reproduce in situ in the liquid cell similar nanoalloys than those obtained in a standard reactor (compared to small homogeneous Pt-Pd(OAm) nanoalloys in section 2.1.1).

In Table 3:1, the final sizes and standard deviations of pure Pt and Pt-Pd in the standard reactor and in the liquid cell are listed. It can be noticed that the particle sizes were generally in the same size range, around 3 nm. The average final size of Pt-Pd in the liquid cell was larger than that of Pt, in contrast to the trend in the standard reactor. However, cell volumes are not necessarily the same and time of growth in the liquid cell is limited. More interesting, the size dispersion in the liquid cell was much larger for Pt than for Pt-Pd. This was also the case in the standard reactor. This is clearly related to the decreased amount of coalescence events in the case of Pt-Pd, which resulted in a more homogeneous growth and smaller size distribution. In addition, the faster and more homogeneous nucleation resulted in a small dispersion, as predicted by the LaMer theory of nucleation [109].

Larger size dispersion was generally found in the liquid cell, compared to the standard reactor, which can be due to the absence of stirring in the graphene liquid cell. In addition, conditions were not completely the same, since much more ligands were present in the standard reactor (pure Oleylamine solution). It was not possible to image growth with much more ligands in this type of liquid cell, due to contamination of the imaging area. It is also clear that reducing agents are not the same (chemical reducing agent MB vs. e-beam). The concentration of reducing agents in the liquid cell is difficult to quantify because of the unknown cell volume. However both reducing mechanisms are able to produce NPs within the minute range, which suggests a similar reducing speed.

	Average size standard reactor	σ	Cv	Average size liquid cell TEM	σ	C _v
Pt	3.7 nm	0.8 nm	22%	2.4 nm	1.1 nm	46%
Pt-Pd	3.2 nm	0.4 nm	13%	3.2 nm	0.7 nm	22%

Table 3:1 : Comparison of the sizes, standard deviations and coefficients of variation (% size dispersion) obtained in the standard reactor and liquid cell with OAm ligands.

It appears that at the early stage of growth, the contrast in the particles is weak, and no lattice fringes are noticed. This suggests that at the beginning of the nucleation and growth process, the particles are disordered. Lattice fringes are seen in a few NPs starting from 70 s. After about 100 s, lattice fringes are observed in most of them. Some particles are not favorably oriented relative to the electron beam, and therefore, no fringes appear. The easiness for the

particles to rearrange their internal structure is increased by the electron beam that induces atom displacements by non-thermal effects [86][104][112].

The rotation of the particles is the proof that they are not epitaxially oriented on graphene oxide, which can be explained by the presence of the OAm ligands on the surface of the NPs and the movement in the liquid phase. A similar behavior was observed for pure Pt NPs.

It was shown (section 3.4.1) that the growth of monometallic Pt NPs in TEM liquid cells occurs by addition of atoms and by coalescence. However, different power laws have been found for the growth rate, which gave rise to some contradictions in the interpretation. In the case of pure Pt, Zheng et al. [70] observed that the growth rate followed a power law with time with a **1/3** exponent, which was explained by the **diffusion-limited** Lifshitz–Slyozov–Wagner (LSW) growth model for Ostwald ripening [113]. The same exponent was also observed in the case of pure Ag NPs [91]. For other studies of Ag NPs, a 1/8 exponent was observed at high beam current, while at low beam current, the exponent was 1/2 [90]. According to the LSW growth model, the **1/2** exponent corresponds to the case where the growth kinetics is limited by the rate of surface reduction of the precursor (**reaction-limited** growth) [114]. However, as noticed by Woehl et al. [91], the **LSW model is not valid when coalescence occurs**. The coalescence is treated by the model of coagulation developed by Smoluchowski [115]. Application of this model explained for example the evolution of the size distribution observed in the case of Ag [91].

The absence of coalescence of Pt-Pd nanoalloys during the growth is different from the mechanism observed in the case of pure Pt particles ([70],[72] and section 3.4.1), where nucleation and coalescence occurred simultaneously. In the present case of Pt-Pd, we can thus make use of the LSW model. Moreover, the beam current is rather weak compared to that from experiments for pure Pt [70] and corresponds to the low current range in the study of pure Ag, which showed a 1/2 exponent [90]. Experimentally a 1/2 exponent was found, so we can conclude that the growth is in accordance to a surface-reaction limited growth described by the LSW model.

The fact that no dynamic coalescence occurs is possibly due to the presence of Pd at the surface and Pt at the subsurface, which modifies the electronic properties at the surface (see section 1.4.2 and further in calculated structures in Chapter 4). For other nanoalloys, e.g. Pt-Fe, coalescence was still observed with up to 30% oleylamine [93]. Similar experiments of pure Pd could unfortunately not be done, to support this hypothesis. Also an influence of the graphene oxide windows on the nucleation and diffusion process cannot be excluded, although the particles were certainly not strongly bound to the windows.

54

3.5.3 Conclusions on Pt-Pd(OAm) nanoalloys

The growth of Pt-Pd nanoalloys with OAm ligands was studied in situ in real time by HRTEM in a graphene oxide liquid cell, using the electron beam as reducing agent. The nucleation ended after 70 s. Later on, the particles grow slowly by addition of monomers and little or no coalescence occurs. The growth rate measured from the early stage of nucleation until their final size followed a power law as a function of time with an exponent of 1/2. This is in agreement with the LSW model in the case where the growth is limited by surface reaction. At the beginning, the NPs are not well structured, and later on, they rearrange their internal structure to form faceted crystals that are comparable to the ones prepared in a standard reactor. Taking into account that in a collection of growing NPs the density increased with time without coalescence, the LSW model is the best appropriated to describe the Pt-Pd kinetics of growth. [116]

3.6 Growth of a Pt layer on a Pd nanosphere

The aim was then to study the growth of a thin Pt layer on a pre-synthesized Pd core. There is an increased interest in these types of structures to limit the quantity of Pt and to optimize catalytic performance (section 1.4.1). However only few have succeeded to deposit Pt homogeneously at the surface, because of its high cohesive energy.

In this part, the 5nm spherical Pd nanoparticles, synthesized with OAm ligands (synthesis described in section 2.1.1) are used as the core. Generally, a drop of crystallized Pd nanoparticles is mixed with a drop of a 0.05 M Pt(acac)₂ solution. The ratio of Pd/Pt in the liquid cells is not well controlled, since the Pd tends to agglomerate. This causes local variations in Pd concentrations in the liquid cells (with variable volume), so that it cannot be compared from one liquid cell to another.

To slow down the reduction rate, n-octylsilane ligands is added (as in section 3.4.2) to make atomic resolution imaging more feasible.

3.6.1 Observations with a JEOL 3010 at 300kV

The successive images of a liquid cell with a Pd(OAm) core in a $0.05M Pt(acac)_2$ solution with 4 molar equivalent octylsilane (so 4 times more ligands than Pt) can be seen in Figure 3.17. At the magnification of 500K, the corresponding beam current was $2.10^5 A/m^2$. The growth started at about 6 min of observation (Figure 3.17) at one side of the particle. However, the lattice fringes visible after 6.5 min of growth are somewhat expanded compared to the Pd

core. Due to the limited lattice parameter difference between Pt and Pd, this cannot be ascribed to the growth of a Pt layer. Moreover, it can be seen after 8 min that the original core (the area with dark contrast) has shrunken in size. The measured lattice parameter of the less contrasted phase is 0.26 nm, in epitaxy with the 0.20 nm of (200) Pd lattice planes.

These fringes around the core were attributed to the formation of a PdO phase. The interpretation is not unambiguous, because of the different reactive (unknown) species present. Nevertheless, the measured lattice parameter fits well with 0.267 nm of (002) or 0.265 nm of (101) of tetragonal PdO [117]. Although somewhat contradictory with the reducing power of the electron beam, it is known that also oxidizing species can arise from irradiation process (section 3.3 and [99]). Moreover, a comparable PdO formation was previously observed in standard TEM on a Pd foil [118]. Indeed after removal of a contaminant layer by a strong electron beam, a PdO layer was formed, epitaxially oriented on Pd.

The Pd particles, observed without Pt-precursor in the liquid cell, did not show any beam induced changes. So the presence of Pt(acac)₂ seemed to play a key role in this phenomenon. It can be seen in Figure 3.17 at 8.5 to 10.5 min, that a small particle of Pt is incorporated at the side, with an increase in contrast at the bottom, so the exact composition at the surface is probably more complex.



Figure 3.17 : In situ growth of a Pt layer on a Pd(OAm) pre-synthesized NP (conditions 0.05M Pt(acac)₂, 4 eq octylsilane and 2.10^5 A/m² at 500K magnification) showing PdO formation.

Homogeneous nucleation of pure Pt NPs was always present under these conditions (Figure 3.18 a-b). Heterogeneous nucleation only on top of the Pd seed is expected for a lower supersaturation, obtained by a lower Pt concentration, a higher number of seeds or a slower reduction process (e.g. [84], [35]). A limit of the graphene oxide liquid cell is that the solution dries out in 20-30 min (under electron beam irradiation). It was not possible to image the growth for a slower reduction by decreasing the intensity. Also, decreasing the precursor concentration did not give any observable changes at the Pd seed surface (Figure 3.18 c).



Figure 3.18 : In situ growth of a Pt layer on a Pd(OAm) pre-synthesized NP after about 15 min of observation (a) same particle as in Figure 3.17 (b) other example in the same conditions (c) lower concentration 0.001M Pt(acac)₂, 1 eq octylsilane and 5.10^5 A/m² at 500K magnification.

3.6.2 Observations with a JEOL-ARM 200F at 200kV

Following results are obtained in collaboration with C. Ricolleau and D. Alloyeau at the *Matériaux et phénomènes quantiques (MPQ) laboratory, Université Paris Diderot.*

Similar experiments were conducted with an aberration-corrected JEOL-ARM 200 F, with a cold field emission gun (c-FEG), operating at 200kV. With this SUPER TEM, a remarkable resolution was obtained in the liquid cell.

It is demonstrated in Figure 3.19 (a-b) that again frequent homogeneous nucleation of pure Pt NPs occurred (for 0.05M Pt(acac)₂ and 5 eq octylsilane), instead of the nucleation on the Pd seeds. The Pd cores rotated, characteristic for the movements in the liquid phase, but no PdO like phase was formed.



Figure 3.19 : In situ growth study of (a-b) homogeneous nucleation (conditions 0.05M Pt(acac)₂, 5 eq octylsilane and 2.10^5 A/m², 600 K) (c-d) relatively heterogeneous nucleation on the Pd(OAm) core (conditions 0.05M Pt(acac)₂, 0.5 eq octylsilane and 4.10^5 A/m², 800K).

When the concentration of octylsilane ligands was decreased, the heterogeneous nucleation of Pt on the Pd core was observed (Figure 3.19 (c-d)). Less pure Pt particles were formed aside, or they stayed very small.

The particle equivalent diameter increased from 7.2 nm to 8.4 nm as can be seen with atomic resolution in Figure 3.20. All measured lattice parameters fit well with Pt and/or Pd and no PdO formation was observed. Due to the defective nature of the Pd seed and its rotation, it was unfortunately not possible to determine preferential facets for the deposition.





3.6.3 Conclusions on the growth of a Pt layer on a Pd nanosphere

It was shown to be challenging to deposit a homogeneous layer of Pt on a Pd core. Homogeneous nucleation of pure Pt, induced by the strong electron beam and octylsilane ligands, seemed to be more favorable than heterogeneous nucleation. The formation of a PdO-like phase was observed at 300kV, but not at 200kV. When the concentration of octylsilane ligands was decreased, the growth of Pt on the Pd core was imaged with atomic resolution. However the core was too defective to follow precisely the deposition.

3.7 Growth of a Pt layer on Pd nanocubes

It was shown in section 2.2.1 that successive amounts of Pt could be deposited on Pd cubes by sequential reduction, with a resulting concave shape. Similar synthesis was now studied in a liquid cell, under electron beam irradiation. The pure Pd nanocubes, synthesized in a standard reactor were used as the starting point. Concentrations in the liquid cell were similar as the second/third addition of Pt(acac)₂ in the standard synthesis. 75µl of as synthesized Pd cubes in DMSO (not washed) was diluted with 1,2-dichlorobenzene (1:2, since DMSO is strongly contaminating) and 10µl with Pt(acac)₂ was added, with a final 0.3 molar Pt/Pd equivalent and a 3mM concentration of Pt precursor.

3.7.1 Observations in the liquid cell

Figure 3.21 shows the evolution with time of a Pd nanocube in the 3mM Pt(acac)₂ solution. The irradiation conditions correspond to 3. 10^5 A/m² at 800K magnification. At around 3 min of observation, the contrast at the upper left corner increased drastically, and the shape became a little more concave compared to the original shape. Around 6 min of observation, some more growth is initiated both at the corners and the sides. Then, at 9 min, a homogeneous nucleation of small Pt nanoparticles next to the Pd cubes was noticed. Some particles were close to the Pd surface and were probably incorporated in the structure, since they disappeared after a certain time (e.g. black particle at the arrow of 8.7 min).


Figure 3.21 : Evolution with time of a Pd nanocube in a 3mM Pt(acac)₂ solution in a liquid cell under electron beam irradiation (3. 10^5 A/m^2 at a magnification of 800K).

After 10 min of observation, the interpretation became more complex, since a PdO-like phase again appeared at the sides (see zoom 1 in Figure 3.22) and frequent coalescence with homogeneously nucleated Pt particles occurred.



Figure 3.22 : HRTEM magnification of area 1 in Figure 3.21, showing a thin semi-epitaxial layer (as seen on the inset FFT) with expanded lattice parameter, attributed to PdO.

However after 20 min, a clear concave side was formed, with a lattice spacing on the edges of 0.22 nm, consistent with Pt and/or Pd (111) fringes (zoom 2, Figure 3.23).



Figure 3.23 : HRTEM magnification of area 2 in Figure 3.21, showing continuous lattice planes with 0.22 nm spacing, up to the surface of the concave shape. Some PdO-like component with 0.26 nm lattice spacing was formed on top.

The size evolution is represented in Figure 3.24, but no large increase in size could be demonstrated. After 20 min, the shape has changed and the particle slightly rotated, so that comparison with the original shape became less accurate.



Figure 3.24 : Limited size evolution of a Pd cube in Pt(acac)₂ liquid, shown by the white dotted line (images extracted from Figure 3.21).

3.7.2 Interpretation of the shape changes

At the start of growth at 2.8 min, the Pd side seemed to have formed a concave shape, at the same time of the increase in contrast at the corner. Since no size increase can be noticed (Figure 3.24), it suggests that the growth starts at the corner sides, together with a **galvanic replacement reaction** at the (100) Pd side. This type of galvanic replacement was reported for systems containing I^- ions together with Pt(acac)₂-precursors and originates from the formation of $[PdI_4]^{2^-}$ compounds together with the reduction of Pt(acac)₂ [41].

Compared to the standard synthesis, the concave shape seems to return quite fast to a more cubic shape (e.g. at the side around 4.3 min in Figure 3.21). This restructuring could be induced by the electron beam. [72][104][105]. The concave side formed at the end of the

observations would generally not be created by beam effects and more probably would result from the stated mechanisms.

PdO formation and shape changes hinder the accurate measurement of the size evolution. What can be noticed is that although some small Pt particles were incorporated, the size did not increase too much. The limited increase in size is consistent with the low concentration of Pt. If all Pt would be deposit equally at the sides, 3-4 layers of Pt (0.8 nm) would be deposited. However it is clear that homogeneous nucleation of Pt NPs from the solution lowers this maximal layer thickness. Moreover, an exclusive galvanic replacement reaction, as suggested above, would also keep the size constant.

3.7.3 Conclusions on Pt layer on a Pd nanocube

The evolution of Pd cubes immersed in a Pt-containing solution was imaged in-situ in a graphene oxide liquid cell. Although changes were subtle and influenced by electron beam effects, concave sides were formed, as observed in a standard synthesis. The almost constant size, and the simultaneous increase in contrast at the corners together with the concave side formation, supports the mechanism of iodide-assisted galvanic replacement reaction, as was observed by others [41][119][120]. Once again, homogeneous nucleation of small Pt NPs and PdO formation, initiated by the strong electron beam, could not be avoided.

3.8 General conclusions on the liquid TEM studies

Nucleation and growth of different Pt and Pt-Pd nanoparticles were studied in-situ by liquid TEM, with the use of a graphene oxide liquid cell. Reduction of the metal precursors was initiated directly by the electron beam. Nucleation and growth were imaged, up to final NP structures that were comparable with the structures synthesized using a chemical reducing agent in a conventional synthesis.

It was demonstrated that the stabilizing ligands play an important role, also in the liquid cell. They stabilize certain sizes or prevent coalescence and form intermediate precursor complexes that influence the nucleation. Moreover, the ligands prevented the particles from being strongly bound to the graphene oxide surface.

Moreover, it was shown that the growth of small homogeneous Pt-Pd nanoalloys, stabilized with oleylamine ligands, does not follow the same growth mechanism as pure Pt, for which frequent coalescence was observed. Their growth rate was found to be compatible with a

Lifshitz–Slyozov–Wagner (LSW) mechanism in the limiting case of a reaction limited process, without coalescence.

Next, we also studied the growth of a thin Pt layer on different Pd seeds. As such, the nucleation and growth of a very thin shell of Pt on a spherical (but defective) Pd core was imaged with atomic resolution. In addition, similar concave Pd@Pt core-shell nanocubes as synthesized in section 2.2.1 were prepared in situ. The limited size increase and concave sides were attributed to the iodide-assisted galvanic replacement reaction.

Another more general result is the optimization of the use of the graphene oxide liquid cell, with great potential in further studies. The nucleation and first growth stages can as such be imaged with very high resolution. For these small particles, the structure is generally observed when the growth is finished, which shows the advantage of this type of cell. The use of graphene liquid cells can be complementary with micro-fabricated liquid cells, since a disadvantage of the graphene liquid cell is that it dries out after about 20 min of observation, preventing the study of larger nanoparticles.

Further studies on electron beam effects in organic media need to be done. A frequently observed phenomenon was the formation of an epitaxial Pd-compound, which was attributed to PdO, but could be a more complex compound including C, S, Si, O and Pt. It shows that some precaution is necessary to distinguish real growth phenomena and beam induced artefacts.

In conclusion, the results gave insights in the nucleation and growth mechanism of Pt-Pd NPs in solution and explained differences in obtained structure. It is important to further study the nucleation and growth mechanisms in colloidal nanoparticle systems, to limit the empirical optimization of the synthesis route. Information on the crystal growth obtained by liquid TEM can be a guide for the synthesis of a specific size, shape and composition, to be able to optimize all their related properties.

Chapter 4 Theoretical structure of Pt-Pd nanoalloys

In previous chapters it was shown that the chemical structure of Pt-Pd nanoalloys can be controlled with solution synthesis. Many studies of Pt-Pd nanoalloys have determined the Pd surface segregation, due to the lower surface energy of Pd compared to Pt. Despite, no real consensus has been reached on the extent of this phenomena and the influence of the environment, because of limitations in the experimental techniques (section 1.4).

Simulations can provide supplementary information and understanding at the atomic level that is not yet accessible with experimental techniques. Nevertheless, existing theoretical studies often focused on equilibrium structures of very small particles ('clusters'), specific compositions and/or low temperatures. In most applications of Pt-Pd nanoalloys in catalysis, the sizes vary from 1 to 5 nm. Density Functional Theory (DFT) calculations of transition metals in this size domain are still very time-consuming. Moreover, since their applications in catalysis are often at high temperatures (or at least above OK which is normal in DFT), it is of interest to study the equilibrium structure at different temperatures.

Hence to be able to cover the application domain of catalytic Pt-Pd NPs, Monte Carlo simulations based on a semi-empirical tight binding potential were carried out. The presented results are comparable to the 3 nm small homogeneous Pt-Pd nanoalloys, as prepared in the standard reactor (section 2.1) or in the graphene oxide liquid cell (section 3.5) and for which the structure will be linked to reactivity further on (section 5.3 and section 6.3.1).

First, previous theoretical studies of Pt-Pd NPs are presented. Then, the energetic model and the simulation method are described. The results show a Pd surface segregation and a Pt subsurface segregation for a wide range of compositions, shapes (truncated octahedra and icosahedra) and different sizes, up to realistic temperatures. Even if this theoretical study focusses on vacuum conditions, it is a first step in the throughout understanding of the chemical arrangement of Pt-Pd nanoalloys in more realistic conditions.

This study was done in collaboration with C. Mottet with a model developed at the department '*Theory and simulation*' of *CINaM*.

4.1 Background and state of the art

Because of their successful applications in catalysis, a lot of theoretical studies on the Pt-Pd nanoalloys have been done in the last ten years. These studies search for the minimum of the energy described by a model of the electronic structure. It is again important to notice that these calculated structures describe an equilibrium. The structures obtained from solution are not necessarily at equilibrium, and the influence of for example defects is mostly not included in these types of calculations.

For the applications in this thesis, it is especially important to **study the equilibrium surface and subsurface composition**, since the catalytic reaction mostly occurs at the surface. It was moreover shown that the growth process in liquid also depends on the surface composition (section 3.5), although the precise surface composition could not be determined by HRTEM in the liquid cell.

The main factors influencing the chemical equilibrium structure and surface segregation in Pt-Pd in vacuum were analyzed:

- The **bulk cohesive energy** of Pt (-5.86 eV) is higher than that of Pd (-3.94eV) [121]. This favors a maximal amount of Pt-Pt bonds, which stimulates the demixing of the two metals.
- A consequence of the bulk cohesive energy is also that Pd has a lower **surface energy** [122], so Pd wants to segregate to the surface. This is because the surface consists of broken bonds and it costs less energy to break bonds in Pd than in Pt. The main driving force of this surface segregation is the difference in surface energy of Pt and Pd.
- A strain effect will promote segregation of the largest atom at the surface. It seems here to have little impact, since the difference in atom size for Pt and Pd is small (covalent radii Pd 1.39Å and Pt 1.36Å [123]).
- Pt-Pd bulk alloy form a solid solution in the whole concentration range [124] with a maximum of the **mixing enthalpy** around equi-concentrations of -40 meV/at. This negative mixing enthalpy supports the formation of Pt-Pd mixed bonds and possibly ordered phases at low temperature, although it is a small effect.
- Charge transfer is of no issue for Pt-Pd because of the similar electronegativity.

One of the first theoretical surface segregation studies for Pt-Pd NPs was done by Rousset et al. [55] by Monte Carlo simulations with the energetics described by a modified tight-binding scheme. They calculated that for the truncated octahedron of different sizes (1.8-4.2 nm) and two different compositions, Pd segregated to the surface. Pd occupied preferentially the corners, edges, (100) and then (111) sites (Figure 4.1 (a)).

Since then, most calculations showed Pd surface segregation with the use of different models. It was observed for extremely small atom clusters (less than 100 atoms) of different shapes, calculated with a global optimization of an empirical potential [125][126][127] and also by subsequent local energy minimization by density functional theory (DFT) calculations [128].

Besides a Pd surface segregation, also an onion-ring structure [129][130][131] was described for icosahedral and decahedral shapes. This structure consists of successive shells of Pd-Pt-Pd-Pt, as shown in Figure 4.1 (b). However these studies were mostly limited to specific compositions to construct a perfect onion-ring structure.



Figure 4.1 : Examples of frequently reported chemical equilibrium structures of Pt-Pd nanoalloys (a) surface segregation of Pd for a truncated octahedron, preferentially to low coordinated sites [55] and (b) onion-ring structure visible in the cross-sections of an icosahedron [130] (dark gray Pd, light gray Pt).

Most of these previous studies use the same empirical potential ('Gupta' potential), although this potential gave a large underestimation of both the surface energy and the surface energy difference. This underestimation of the surface energy (difference) is a general problem encountered also for other atomic potential models as embedded atom methods [132][133].

More recently, other chemical structures have been described. For example, a site specific segregation was demonstrated with a DFT-based method, with chessboard patterned (100) facets [134]. Another DFT calculation showed a 'patchy multishell' with an alternated pattern of Pt and Pd [135].

This overview briefly showed the variety of theoretical models and simulation methods. Our goal was to compare different shapes and compositions, at higher realistic temperatures. This gives insight in the mechanisms and stability of the previously reported structures and some new chemical arrangements were found.

4.2 Simulation method

4.2.1 Energetic model (SMA-TB)

The energetic model used in this work is a semi-empirical many-body potential, derived from the tight binding approximation with a second moment approximation of the density of states (SMA-TB). This can be understood with the following remarks:

- It is known that transition metals as Pd and Pt have high cohesive energy due to a partially filled narrow d-band, where the electrons are relatively localized around the ions. This justifies a **tight-binding approximation**.
- In the second moment approximation, the realistic electron density of states of the dband is replaced by a rectangular one, having the same second-moment. This approximation makes it possible to describe an electron band term with square root dependence with neighboring atoms, and as such include in a relative simple way the many-body interactions.
- This leads to a **semi-empirical potential**, since its analytical expression (square root) is derived from the electronic structure, but there are parameters to be fitted either on experimental or DFT values.

The energy of an atom at site i of type α is as such expressed as the sum of the attractive many-body band energy term and a pairwise Born-Mayer ion-ion repulsive term, as a function of the interatomic distances r_{ii} [136] (Equation 4.1).

$$E_i^{\alpha} = -\sqrt{\sum_{j,r_{ij} < r_{\alpha\beta}^{cut}} \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1\right)}} + \sum_{j,r_{ij} < r_{\alpha\beta}^{cut}} A_{\alpha\beta} e^{-p_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1\right)}$$

Equation 4.1 : SMA-TB potential energy of an atom i of type α as a sum of an attractive band energy term and a pairwise repulsive term.

 r_{ij} represents the interatomic distance between the atom at site i and the neighbor at site j. For a bimetallic system with type α and β , there are three different distances: $r_{\alpha\alpha}$, $r_{\beta\beta}$ and $r_{\alpha\beta}$ (taken as the average). $r_{\alpha\beta}^0$ is the first neighbor distance, and $r_{\alpha\beta}^{cut}$ the cut-off distance of the potential, taken at the fourth neighbor.

The total energy of a binary system of N atoms then writes as the following sum:

$$E_{tot}(\{p_i^{\alpha}\}) = \sum_{i=1}^{N} (p_i^{\alpha} E_i^{\alpha} + p_i^{\beta} E_i^{\beta})$$

Equation 4.2 : Total energy of a binary system as a sum of the energy of the atoms.

The occupation factor p_i^{α} is an occupation factor equal to 1 if the site "i" is occupied by an atom of type " α " or zero if not α .

A polynomial fit between the third and the fourth neighbor helps to avoid discontinuities of the potential at the cut-off and links the potential to zero at the fourth neighbor. The extension of this cut-off distance was found especially important for the simulation of transition metals at higher temperatures [137].

The parameters $\xi_{\alpha\beta}$, $A_{\alpha\beta}$, p and $q_{\alpha\beta}$ are adjusted (Table 4:1) based on the density functional theory (DFT) values of lattice parameters, cohesive energies, surface energies and elastic constants of the pure metals (Table 4:2) and permutation energies of the impurity of one metal in the pure bulk of the other metal for the mixed interactions (Table 4:3). We take into account the fact that Pt-Pd bulk alloy forms a solid solution in all the concentration range with a maximum of the mixing enthalpy equal to -40 meV/at. around the equi-concentration [124].

The DFT calculations have been performed by C. Mottet using the VASP code with the generalized gradient approximation (GGA) [138] and the projector augmented wave (PAW) [139][140] interaction potential between the ions and the electrons[141]. The permutation energies corresponds to the energy difference, when we permute a Pd atom in Pt in a bulk of Pd, which can be linked to the dissolution energy of one impurity of Pt in a bulk of Pd, written 'Pd(Pt)' and vice versa for 'Pt(Pd)'.

Since the SMA potential underestimates the surface energies in an inhomogeneous way, the potential was fit to the values of the surface energy. This adjustment allows to better reproduce the experimental difference in surface energy as compared to older parametrization [137]. It is an important improvement in this study, since the difference in surface energy is the main driving force of segregation in the case of Pt-Pd.

Metal α - β	$p_{lphaeta}$	$q_{\alpha\beta}$	$\xi_{lphaeta}({ m eV})$	$A_{lphaeta}({ m eV})$
Pd-Pd	12.74563	2.08250	1.19723	0.06670
Pt-Pt	11.22000	2.30000	1.91171	0.12857
Pt-Pd	11.98281	2.19125	1.53980	0.09020

Table 4:1: Parameters of the Pt-Pd SMA potential.

Metal	a(Å)	E _{coh} (eV/at.)	γ ⁽¹⁰⁰⁾ (eV/at.)	γ ⁽¹¹¹⁾ (eV/at.)
Pd (DFT)	3.96	-3.71	0.76	0.59
Pt (DFT)	3.98	-5.53	0.91	0.64
Pd (SMA)	3.96	-3.71	0.62	0.50
Pt(SMA)	3.98	-5.53	0.85	0.68
Pd (exp.)	3.89	-3.94	0.94	-
Pt (exp.)	3.92	-5.86	1.19	-

Table 4:2 : Lattice parameters, cohesive energy and surface energies of Pd and Pt. The experimental values of the lattice parameters and cohesive energy are taken from Kittel [121], the surface energies from De Boer et al. [122].

(eV/at)	Pd(Pt)	Pt(Pd)
ΔH^{perm} (DFT)	-1.911	1.601
ΔH ^{perm} (SMA)	-2.077	1.610
ΔH ^{dissol} (exp.)	-0.18	-0.10
ΔH ^{dissol} (DFT)	-0.09	-0.12
ΔH ^{dissol} (SMA)	-0.26	-0.21

Table 4:3 : Permutation and dissolution enthalpy calculated by DFT and SMA potential compared to the experimental values in the two diluted limits of the mixing enthalpies at 300K. [124]

4.2.2 Initial cluster configurations

In the range between 1 and 7 nm, it has been shown that there is a metal-dependent crossover between different most stable shapes [13]. For Pt and Pd, icosahedra would be stable only for very small sizes, with decahedra at intermediate sizes and truncated octahedra (i.e. fcc Wulff equilibrium shape [11]) for sizes larger than 6 nm [13]. Real nanoparticles would however consist of a distribution of these and other non-equilibrium shapes.

Here, we mainly focus on the **truncated octahedron (TOh)**, with a specific amount of atoms to reproduce full shells ('magic numbers'). The different number of atoms used here, was 405 and 1289 representing a NP with a diameter of respectively 2.2 and 3.5 nm. A further notation as Pt_{n-number-atoms}Pd_{m-number-atoms} is used, since it includes information on both composition and size. The atoms at the different sites of the TOh are distinguished by their number of nearest neighbors. Atoms at the vertices have only 6 nearest neighbors, at the edges 7, on the (100) surfaces excluding edges 8 and on (111) surfaces 9.

A comparison with **icosahedra (Ih)** with 147, 309 and 1415 atoms is made (1.7, 2.2 and 3.5 nm). Icosahedra are mainly found for very small sizes. This shape might however be relevant for the nuclei in liquid, which often determine the further growth of the nanocrystals.

A cluster with a random chemical distribution was used as starting structure for the Monte Carlo simulations. It was verified with other input structures (e.g. L1₀ structure) that the initial chemical configuration did not influence the final result.



Figure 4.2 : The two different initial cluster shapes (a) truncated octahedron TOh with (100) and (111) facets and (b) icosahedron Ih with only (111) facets.

4.2.3 Monte Carlo simulation method

The global minimum of the energy potential describes 'the' most stable cluster configuration. However, since we want to consider finite temperature physical properties, we need to take into account that the system is not all the time in the minimum. Hence we attribute statistical weights to all different possible configurations, dependent on their energy and the temperature.

Monte Carlo (MC) simulations were used to optimize the chemical configurations described by the semi-empirical potential towards the equilibrium in a certain amount of macrosteps (here: 2000). The next macrosteps (3000) of the equilibrium MC part are used to make sufficient statistical sampling of all states of the system around equilibrium. Both simulations in the canonical and semi-grand canonical ensemble were made.

In canonical MC (CMC), the number of atoms, composition, temperature and pressure of the system remains constant. The exchange of two atoms of different species is then performed (exchange step), and the total energy of the new system is calculated. The new configuration is accepted for a lowering of the energy. If not, a Boltzmann statistical probability is applied (i.e. Metropolis sampling [142]). This means that for an increase in energy, the new configuration can still be accepted with a probability of $e^{\frac{-\Delta E}{kT}}$ with ΔE the energy difference between configurations before and after the trial, k the Boltzmann constant and T the temperature.

The difference with the semi-grand canonical MC (S-GCMC) is that in this case, the composition of the cluster can be varied, while keeping the difference in chemical potential $\Delta\mu = \mu_{Pd}-\mu_{Pt}$ constant. Also the number of atoms, temperature and pressure remain constant. The energy difference before and after changing the chemical identity of a randomly selected atom (permutation step) is then calculated, with a similar acceptance rate. These simulations are then done for a range of chemical potential differences, large enough to cover the pure Pt to pure Pd domain ($\Delta\mu$ from 0.9 to 2.5 eV), and for two different temperatures (100K and 300K).

Structural relaxation of the system was accomplished by random small lattice displacements, with a magnitude of 0.01 Å. In each macrostep we propose randomly to any atom of the cluster ten atomic displacements for one exchange or permutation, repeated as many times as there are atoms in the cluster.

4.3 Results and discussion

First, the most stable chemical structures at low temperature were calculated, for varying chemical composition, calculated with S-GCMC. This low temperature study shows the preferred segregation tendencies and stable compositions.

The chemical arrangements of both the truncated octahedron as the icosahedron are presented, to illustrate the effect of the shape. Then, the stability with increasing size is shown. Also the effect of a realistic temperature is discussed for a fixed composition, with the use of CMC methods.

4.3.1 Low temperature ordering in TOh

• Representation with segregation isotherm graphs

It was found that at low temperatures (100K), the Pt-Pd nanoalloy shows some ordering of the chemical arrangement. The segregation isotherms of the 405 atoms TOh at 100k have been calculated for different types of sites (see 4 graphs in Figure 4.3).

In this type of graphic representation, the Pd composition of a certain site, 'c-site', can be read of the y-axis, for a varying Pd total concentration on the x-axis. If the composition of a type of site is higher than the average composition, which is represented by the dotted line, preferential segregation of Pd to that specific site occurs. If the composition is lower than average, it can be interpreted as segregation of the other component, in this case Pt. As such, we can have an idea of the preferential sites of Pd atoms with increasing Pd composition.

The different type of sites are divided into surface site i.e. vertex, edge, and facets (upper two graphs), and into concentric shells starting from the surface, subsurface, shell 1, ... up to the central site (lower two graphs). The segregation isotherms are shown for a variable chemical potential difference $\Delta \mu = \mu_{Pd}-\mu_{Pt}$ (left two graphs) or for variable Pd concentration (right two graphs). In the representation of $\Delta \mu$, very stable ordered structures appear as plateaus, and less stable ordered structures as softer shoulders. It means that the particle is 'blocked' at a certain composition that is not influenced by changing the chemical potential difference.

• Remarkable ordered structures and implications on segregation

A first example to illustrate the interpretation of the graphs is the $Pt_{381}Pd_{24}$ structure, shown in the snapshot of Figure 4.3 (a). This structure is represented by a plateau in the surface/total composition at $\Delta\mu\approx1.25$. In this case, the concentration of the vertices (black line of upper row) rises quickly to 100%, which shows the **strong preferential occupation by Pd of the vertices**. In the next ordered structure, $Pt_{321}Pd_{84}$ Figure 4.3 (b), Pd decorates all vertex and **edge** sites. As was previously reported by others [55], we found a surface segregation of Pd from the low coordinated sites to the higher coordinated sites.

When increasing the total Pd concentration, Pd occupies the **(100)** facets together with the **middle of the (111)** facets ($Pt_{273}Pd_{132}$, Figure 4.3 (c)), where Pt atoms form hexagonal rings in the (111) facets. This motif resembles the patchy multishell segregation profile characterized by Barcaro et al. [135] in Pt-Pd TOh of 38 to 201 atoms. This structure corresponds to the small step in the (111) facet segregation curve (blue curve).

So the surface is first filled with Pd atoms up to 55% Pd, to form an **almost perfect core-shell** structure with a pure Pd surface shell and an almost pure Pt core. Indeed, when the surface shell is fully filled with Pd, the core already contains Pd atoms, as can be seen in the cross-sections of Pt₁₇₇Pd₂₂₈ in Figure 4.3 (d). It can be understood with the arrows in the left column graphs, showing that for a fully filled Pd shell (100% at the surface), the composition in the core is about 12% Pd. The specific sites inside the core are also represented in the lower graphs, with a subdivision in concentric shells. At this point, both shell 1 and 2 are filled with about 30% Pd, as is shown by the arrow in the lower graph.

Then shell 1 is completely filled before shell 2. A sort of **onion-shell** structure is formed as such, with the three pure shells near the surface (surface Pd, subsurface Pt, and again shell 1 Pd), as can be seen in $Pt_{136}Pd_{269}$ of Figure 4.3 (e).

It can clearly be seen that the subsurface is the last shell to be populated with Pd. This can equally be described as **segregation of Pt at the subsurface shell**. In the $Pt_{24}Pd_{381}$ nanoalloy the 24 Pt atoms are situated just below the vertices (Figure 4.3 (f)).



Figure 4.3 : (a-f) Snapshots of Pt_nPd_m TOh nanoalloys of 405 atoms (2.2 nm) at 100 K, at chosen compositions (Pt =blue, Pd=grey) and 4 graphs with segregation isotherms as a function of the difference in chemical potential (left column) and as a function of the total Pd concentration in the cluster (right column). The different type of Pd segregation sites are divided into surface sites (upper row) or concentric shells starting from the surface up to the center (lower row).

4.3.2 Low temperature ordering in Ih

Likewise, the segregation isotherms of the 147 atoms Ih at 100k have been calculated, for different types of sites (4 graphs in Figure 4.4).

• Similar segregation tendencies than for TOh

We again observe a Pd surface segregation which starts at the **vertices** (less coordinated sites), then at the **edges** with one Pd atom at the central site in the core. Finally the complete **(111) facets** are filled. Since the 147 atom Ih has no (100) facets and only one atom at the (111) facet, this gives the successive structures of Pt₁₃₄Pd₁₃, Pt₇₄Pd₇₃, Pt₅₀Pd₉₇ in the snapshots of Figure 4.4 (a-c). The subsurface is again the last shell to be populated with Pd, so that there is again **Pt segregation at the subsurface** shell.

• Comparison with TOh and comment on the local stress

The difference between the two cores is that we can get a **more perfect onion-shell** structure, which extents all across the core in the Ih than in the TOh. However this perfect onion-shell structure with the specific Pt₄₃Pd₁₀₄ composition, as reported in previous studies [131][130], exists only in a very narrow range of chemical potential. The central site, initially occupied by a Pd atom, is only in a narrow range replaced by Pt to create this perfect core-shell structure. It transits back to the structure with a Pd atom at the central site (Pt₄₂ Pd₁₀₅, Figure 4.4 (e)), with a greater stability. It is therefore expected that the perfect onion-shell structure is not formed under real conditions. This observation can be explained by the very strong **compressive stress at the center of the Ih** that can be released partially by replacing the Pt atom (slightly bigger) by a Pd one (slightly smaller). The atomic stress, illustrated in Figure 4.5, is obtained by the derivation of the energy as a function of the local deformation around the atom [141].

Again, the remaining Pt atoms occupy the sites at the subsurface, below the vertices ($Pt_{12}Pd_{135}$ Figure 4.4 (f)). This configuration, both observed in the TOh and the Ih, cannot be explained by the misfit of the two elements, as it has been shown for the Cu-Ag system [143]. Here it is the larger atom (Pt) which occupies the more compressed sites, situated below the vertices, as is illustrated by the stress map for the TOh in Figure 4.5. This specific chemical arrangement, which was not described before, is thus the result of the small ordering tendency in Pt-Pd nanoalloys.



Figure 4.4 : (a-f) Snapshots of Pt_nPd_m Ih nanoalloys of 147 atoms (1.5 nm) at 100 K, at chosen compositions (Pt =blue, Pd=grey) and 4 graphs with segregation isotherms as a function of the difference in chemical potential (left column) and as a function of the total Pd concentration in the cluster (right column). The different type of Pd segregation sites are divided into surface sites (upper row) or concentric shells starting from the surface up to the center (lower row).



Figure 4.5 : Atomic stress on each site (from the center up to the surface) of the Pt24Pd381 TOh and Pt₂₉₆Pd₁₃ Ih as compared to the pure systems. The snapshots below show the relative variation of the atomic stress (high= red and low=blue, however both color codes have an order of magnitude difference between the Ih and TOh, as seen on the stress y axis in the graphs).

4.3.3 Effect of the size

In the following, the stability of these chemical arrangements as a function of the cluster size is discussed. In the Figure 4.6 and Figure 4.7 the segregation isotherms at 100 K of TOh and Ih of larger sizes are shown (only as function of $\Delta\mu$).

A similar evolution as described above is illustrated, although the **ordered structures are less pronounced for larger sizes** (i.e. smoother segregation curves). For example, the segregation of the Pd at the vertices or Pt below the vertices in the subsurface can no more be distinguished by a plateau of the global isotherms, as it was the case for smaller sizes.

The surface is again almost pure in Pd before the other shells start to be filled, but there is never a perfect core-shell structure in the TOh because the core begins to contain Pd atoms before complete surface filling. Shell 1 is again filled in Pd before all the other ones and finally the subsurface is the last to be filled with Pd, for all sizes. The remaining shells of NPs with larger sizes are more mixed, slightly enriched with Pt (line below the black dotted 'total' line). From this, it can be seen that whatever the size and the shape, an **alternation (Pd-Pt-Pd)** of pure concentric shells starting from the surface for the three most external shells is predicted at 100K.

For the larger TOh the onion-shell alternated structure extinguishes after about 3 layers. In the larger Ih also shell 2 is enriched in Pt but not completely (an almost 4 layer onion-shell). The concentration in each shell of the core, apart from the ones near the surface, are slightly more inhomogeneous in Ih than in TOh, but not enough to describe an onion-shell structure among the entire core, as was previously noticed for larger icosahedra by F. Calvo [131]. In this study however, this observation was explained by a strain assisted core melting for the strongly compacted Ih. Because of the generalization to the TOh shape presented in this study, for which the strain pattern is not centered in the core, it is clear that the core mixing is the result of the extinction of the surface segregation induced ordering and is not stress related.

Also for larger sizes, there is a systematic Pd segregation at the central site in the Ih structures. On the contrary to the above core mixing, this can be related to the stress release in the core center of the Ih.



Figure 4.6 : Segregation isotherms of TOh Pt-Pd nanoalloys of 405 and 1289 atoms at 100 K as a function of the difference in chemical potential for surface and core sites (left column) and for each concentric shell in the core (right column).



Figure 4.7 : Segregation isotherms of Ih Pt-Pd nanoalloys of 147, 309 and 1415 atoms at 100 K as a function of the difference in chemical potential for surface and core sites (left column) and for each concentric shell in the core (right column).

4.3.4 Effect of the temperature

As a few but still rare theoretical studies [130][131][132][133][134][144], the thermal stability of the surface segregation and onion-shell structure was studied for both shapes. This part is especially important to relate to the catalytic tests, that are performed at higher temperatures around 500K (Chapter 6). In that purpose, canonical Monte Carlo simulations on chosen nanoalloys with fixed composition and varying temperature, up to 900K were done. The occupation probability of Pd on each site was computed by averaging all values of the equilibrium CMC part (after elimination of the first 2000 steps).

The concentrations in Pd of the different surface sites and shells, as a function of the temperature, are plotted in Figure 4.8 for different TOh and in Figure 4.9 for Ih shapes. Note that for illustration purpose not all have the same total Pd concentration. All sites become more mixed at higher temperature, and the ordered structures mostly disappear. However there is a difference in the extent of the attenuation.

• Small attenuation of Pd surface and Pt subsurface segregation

It can be seen in the curves and snapshots of Figure 4.8 and Figure 4.9 that especially the (111) and (100) surface sites become mixed at higher temperatures, while the edges and vertices stay very rich in Pd.

For the TOh, the mixing of the (111) facets starts at lower temperature than the (100) facets. For example, at T=100 K the surface of the 1289 atom TOh with 42% Pd (snapshots Figure 4.8) is almost completely red, which means fully occupied by Pd atoms. However, at 500 K the (111) facets become orange and a ring in contact with the edge of the (111) facet becomes yellow. So there is an increased probability to find Pt atoms at the surface at higher temperature, although it was rather considered as a core-shell structure at low temperature.

At 500K the surface contains up to 20% Pt atoms for this 1289 atom TOh. The probability to find Pt atoms at the (111) facets at high temperature depends however also on the composition of the cluster. When the total percentage of Pd is higher than 50%, the surface remains almost pure in Pd, as is the case for the smaller 405 atom TOh with 66% Pd (Figure 4.8).

On the other hand, the Pt subsurface segregation is maintained in the whole subsurface shell up to high temperature, although also attenuated. Pt subsurface segregation was more stable below (100) facets in the TOh, since it is coupled with the Pd surface segregation that was more stable on (100) facets.

The Pd surface segregation was found a bit more stable on (111) facets of the Ih than on (111) facets of the TOh. This can be seen in the snapshots at 900K of the 405 atom TOh and the 309 atom Ih, both with 66% Pd. So in general, the Pd surface is slightly better maintained for the Ih than the TOh, although the Pd surface and Pt subsurface segregation effects remain stable for both shapes up to high temperature.

• Large attenuation of the onion-shell structure in the core

Starting with an onion-shell TOh structure of three shells Pd-Pt-Pd at low temperature, only the Pd surface segregation and the Pt subsurface segregation are maintained at 500 K and up to 900 K. For the lh structure the conclusion is rather similar. As can be noticed in Figure 4.9, the nearly perfect onion-shell structure, which is stable at 100 K in the whole core of the 147 and 309 atoms lh, does not persist at 500 K and above. So the **onion-shell at higher temperature concerns mainly the surface and subsurface and the remaining core is disordered.** This disordered core was previously shown in the study of lh structures by F. Calvo [131]. However in that study it was not identified that the Pd surface and Pt subsurface segregation can remain stable up to 500 K and above, for both shapes.

These results thus show that even if there is a strong Pd surface segregation, the Pt atoms stay near or even at the surface at higher temperature. The Pt-Pd nanoalloys are therefore likely to behave different than pure Pd. This would not be the case for several Pd surface layers or for a more mixed subsurface at higher temperatures.



Figure 4.8 : Caloric curves of Pt-Pd TOh of 405 and 1289 atoms with 66% and 42% Pd as a function of the temperature. Snapshots of the clusters at different temperatures with a color code relative to the occupation probability: red (100% occupied by Pd atoms) to blue (100% occupied by Pt atoms) going through green which is equally occupied by Pd or Pt atoms.



Figure 4.9 : Caloric curves of Pt-Pd Ih of 147, 309 and 1415 atoms with 71%, 66% and 60% Pd as a function of the temperature. Snapshots of the clusters at different temperatures with a color code relative to the occupation probability: red=100% Pd to blue=100% Pt.

4.4 Comment on the effect of the environment

Since the energy differences causing the segregation in vacuum are only weak, one can understand that the environment can have a large influence on the stability of these equilibrium configurations. Some calculations in this area were already done, however mostly limited to DFT calculations on small 'slabs'.

• Small gas molecules adsorbed on alloyed Pt-Pd

For example, even if the Pt subsurface was thermodynamically preferred in vacuum, it was shown by DFT calculation on small slabs that the presence of adsorbed O or OH can pull Pt from the subsurface to the surface. Then, the most stable configuration was found to be a 25% up to 50% Pt mixed surface. [35]

DFT calculations of 38-atom TOh with 16% Pd or Pt were used to calculate the energetic difference of discrete chemical structures when adsorbing one CO or H₂ molecule [145] [146]. As such, Pd-CO bonds would be weakened by the presence of neighboring surface Pt atoms, whereas the opposite was shown for Pt-CO bonds. The results gave a first indication of the possible inversion of the Pt_{core} -Pd_{shell} structure towards a Pt shell. The effect was however quantitatively modest compared to other alloys [146]. These types of calculations are still limited to small sizes and very specific chemical arrangements.

• Comparing adsorption energies of ligands on pure Pt and Pd

The use of pure Pt or Pd (slabs, NPs or extended surfaces) does not take into account the possible change in electronic configuration by alloying. However, we can still extract information from the difference in adsorption energy of a ligand or small molecule on pure Pd and Pt.

It was for example calculated by V. Oison and C. Mottet that a silane ligand binds more strongly to a pure Pt than a Pd nanoparticle. They found an energy difference ~0.25 eV between adsorption on Pt and Pd. This is in the same order of magnitude than the difference in surface energy, which is the main driving force of segregation in this system (unpublished results). As such, it would thus be possible to reverse the segregation to a Pt shell, with the aid of the ligands used in the colloidal synthesis.

A perspective to this work would thus be to take into account the possible gas and/or ligand adsorption at the surface of the nanoalloy to simulate realistic experimental conditions. However it is clearly still challenging to take into account realistic conditions and sizes together with the effect of alloying.

4.5 Comment on core-shell Pd@Pt NPs

Trying to make Pd@Pt core-shell alloys clearly goes against the thermodynamic equilibrium state. However, it was shown that such structures can be made by the colloidal method. It means that these structures are metastable and insight in the stability is therefore necessary. Another type of calculation such as Molecular Dynamics can give insights into the kinetics.

For example, an energy barrier of 1.07 eV was calculated to replace a Pd atom of a (100) surface by a Pt ad-atom [35], with an overall energy gain of 0.45eV. The addition of a Pt surface on top of a Pd core would thus evolve to a Pt subsurface, or at least to a more homogeneous chemical distribution at the surface. However bulk diffusion would have a much higher energy barrier of 3.36-3.66 eV [147], limiting the further diffusion to the core, especially for bigger particles. This means that thicker shells would be less affected.

4.6 Conclusion on the theoretical study

Structure and chemical arrangement of small Pt-Pd nanoalloys with the icosahedral and truncated octahedral symmetry were studied using Monte Carlo simulations, with a tight binding interatomic potential fitted to density-functional theory calculations. The presented structures are related to the 3nm homogeneous Pt-Pd nanoalloys prepared with oleylamine ligands.

The results show a strong Pd surface segregation, from the lowest (corners and edges) to the highest coordinated sites ((100) and (111) surface sites). Also the enrichment in Pt at the subsurface can have important implications in crystal growth and catalysis, due to a modification of the electronic structure at the Pd segregated surface.

Pd segregation results from the significant lower cohesive energy of Pd as compared to Pt and the weak ordering tendency leads to the Pt subsurface segregation and onion-shell structure. The very weak size mismatch does not prevent the bigger atoms (Pt) to occupy subsurface sites, which are slightly in compression whereas the smaller ones (Pd) occupy the central site of the icosahedra where the compression is an order of magnitude higher.

Onion-shell chemical configuration, as described previously by others [129][130][131] only for Ih, concerns both TOh and Ih symmetries and is initiated from the Pd surface segregation. It is amplified in the icosahedral symmetry and small sizes but when considering larger sizes, the oscillating segregation profile occurs near the surface on about three to four shells at 100 K whatever the structure. The remaining core is disordered.

Also new chemically ordered structures were presented, which have not been characterized to our knowledge. One of them showed hexagonal rings at the limit of the (111) facets, where Pt atoms remains before the completion of the surface shell with Pd. Another one displays subsurface Pt atoms located below the vertices in the Pd-rich clusters. For the main application of Pt-Pd, we should be careful with low temperature simulations, as was shown that most of the ordered structures were lost at higher temperatures. Also the ordered structures seem to be less pronounced for larger sizes, concerned in this work.

It is however of great importance in this study that the observed segregation patterns subsist when increasing the temperature. The Pd surface can become more mixed at higher temperature for concentrations rich in Pt. The onion-shell structure is damped but the Pd surface segregation and Pt subsurface segregation are preserved at higher temperature.

All this chemical mixing of Pd and Pt species at the vicinity of cluster surface are susceptible to bring important consequences for the catalytic properties of such systems, especially for the structures that are stable up to higher temperatures (surface segregated Pd, subsurface segregated Pt and Pt located at certain sites of the (111) Pd facets).

It is clear that theoretical calculations can give important insights to details in the structure that are not yet accessible in current experimental characterization techniques, but have an influence on the catalytic performance. Further insights can be obtained by including realistic environments, such as stabilizing ligands or adsorbed molecules of the catalytic reaction.

Chapter 5 Structure of Pt-Pd nanoalloys in gas environment

Environmental transmission electron microscopy (ETEM) can give insight into the structure of nanoparticles directly in the gas phase. With this in situ technique, different nanoparticles were investigated: small homogeneous Pt-Pd nanoalloys, pure Pd nanocubes and Pd@Pt core-shell NPs (as synthesized in Chapter 2). They were supported on the carbon windows of the environmental cell and exposed to H_2 and O_2 gas at room temperature.

5.1 Instrument and sample preparation

Electron microscopes normally need a high vacuum environment to minimize the scattering of electrons. However, the development of the environmental TEM (ETEM) allowed the introduction of different gasses directly at the level of the sample, during microscopy observations. Two approaches were developed. The first approach uses a closed environmental cell (E-cell) with thin electron-transparent windows and the second approach is based on a differential pumping system in the TEM column (DP-ETEM), with direct injection of gas at the level of the sample.

The instrument used in this work is a prototype of an E-cell sample holder, designed by a collaboration between JEOL and CINaM, described in reference [148] and put in operation in the year 2002. The E-cell is closed by 20 nm thick amorphous carbon windows and is inserted in a standard high resolution electron microscope (JEOL 3010-300kV) (Figure 5.1). The carbon windows are home-made by evaporation of carbon on a cellulose polymer, which is then deposited on a copper disc with 7 holes of 150 μ m in diameter. The polymer is dissolved in acetone before use. Then, the sample is deposited on the carbon windows and the reactor is precisely closed.



Figure 5.1: E-cell sample holder that was used for in situ TEM observations in a gas environment

The different NPs were in situ observed at room temperature, under a measured pressure of around 1 mbar of pure H_2 and O_2 . The pressure in the cell was estimated with a pressure gauge at the gas outlet. However, there is a pressure drop between the E-cell and the gauge, so that the pressure in the cell will be higher than indicated. The maximal pressure allowed by the constructor in the E-cell is 10 mbar.

A major issue in environmental microscopy is the contamination, since the electron beam can crack organic contaminants, which are then re-deposited as carbon fragments (Figure 5.2). Sometimes, the NPs move under influence of the gas flow. Because of the contamination and the carbon windows, resolution is often limited.



Figure 5.2 : Example of contamination and particle agglomeration that hinders relatively fast the further imaging during environmental microscopy (a) first image (b) after 5 min of imaging in H_2 at beam current of 10^4 A/m^2 for a magnification of 150K.

5.2 State of the art

• Adsorbate-induced shape changes

It was explained in section 1.3.1 that gas adsorbates can induce a shape change of the nanoparticle. Environmental TEM is an ideal technique to image directly this effect. Several metal NPs were previously studied with the E-cell in CINaM. For example, a set of cubic Pt nanoparticles were observed during oxidation-reduction cycles (Figure 5.3) [149]. It was shown that H₂ gas stimulated a rearrangement towards a Wulff shape of the fcc crystal, with dominant (111) facets (Figure 5.3 (b)). Oxygen adsorption on the other hand stabilized the more open (100) facets of cubic Pt. This shape change was reversible (Figure 5.3 (c)) [149].



Figure 5.3 : Illustration of the reversible morphology changes of a pure Pt cubic nanoparticle observed by ETEM (a) particle mainly limited by (100) facets, truncated by (111) facets at the corners, observed in O_2 (b) increase of the (111) facets under H_2 gas (c) again extend of the (100) facets under O_2 which shows the reversibility of the structural changes.(from reference [149]).

Other fcc metals showed a similar response. Under H_2 atmosphere, a pure Au particle was observed to have a truncated octahedral shape, while under O_2 it showed a rounding of the surface [150]. The development of higher index facets at the expense of (111) facets leads to an overall rounding of the particle shape.

It should be mentioned that, if there is a shape change, it is more easily imaged for larger particles. They can be observed at lower magnification, so with a lower electron dose. However large particles need also a larger mass transport to change their shape. The surface mobility is increased by the electron beam but can be a limiting factor and beam damage effects have to be avoided.

• Adsorbate-induced surface segregation in nanoalloys

Next, it was shown in section 1.3.2 that the presence of gas adsorbates can induce a surface segregation in nanoalloys. Also several metal nanoalloys were previously studied with this technique. It was for example shown that Pd segregated to the surface of the Pd-Au NP, under a CO+O₂ reaction mixture [31]. Others have studied Pt-Co nanoalloys by ETEM and observed the reversible migration of Co to the surface under oxygen gas exposure [151]. Up to now, no ETEM study of the Pt-Pd nanoalloys was described, and the number of ETEM studies of nanoalloys is still limited.

• Recent developments

Since the installation of the first DP-ETEMs in the USA and Denmark, and the E-cell prototype in Marseille, a number of new DP-ETEM or E-cells were installed in France (Paris, Lyon and Strasbourg) and in the rest of Europe and the world. Recent design improvements of both the microscope and E-cells make it now possible to study the nanoparticles up very high pressures (1 bar), with 'nanoreactors' resulting from the microelectromechanical system (MEMS) technology [152]. New powerful spherical aberration corrected (Cs-corrected) ETEM with differential pumping can maintain very high resolution. It was for example possible to image the CO molecules, adsorbed at the surface of a gold nanoparticle [153].

A real challenge is to couple the reactivity in a catalytic reaction to the observed dynamic structural changes. For example, a CO/air mixture at room temperature would have an even stronger rounding effect on Pt than pure O_2 [154]. However at higher temperatures, in a regime where the Pt particle is expected to be active for the CO oxidation, the particle would again become faceted in CO/air [154]. Some studies tried to couple the observations directly with the measurement of the products of the catalytic reaction ('operando'). A recent operando ETEM study associated the periodic faceting of Pt to the oscillating behavior in the CO oxidation reaction [155].

Some examples of other recent studies include detection of a hydrogen-induced phase transitions a Pd nanocubes [156], or facet-dependent graphene oxidation on platinum NPs [157]. From all these studies, it is clear that ETEM is an interesting tool for the study of structure-dependent catalytic reactivity in near-realistic conditions.

5.3 ETEM observations

5.3.1 Small homogeneous Pt-Pd nanoalloys

A collection of small Pt-Pd (1:1) nanoalloys synthesized with OAm ligands (section 2.1), was dropped on one of the carbon windows of the E-cell.

• Influence of the gas environment on the 2D organization

An overview of the 2D arrangement with regular interparticle spacing of the Pt-Pd nanoalloys is shown in Figure 5.4. They were exposed respectively to H_2 and O_2 pressures of around 0.1 mbar. At low magnification (x100.000), no change in the self-organization was observed as long as ligands are present on the surface of the particles. When the ligands were removed due to electron irradiation, the particles rapidly coalesced. A suggestion for further studies on the organization under gas environment is to make use of the UV-ozone technique to remove the ligands prior to observation (section 2.1.2). This was not done here, because of the fragile carbon windows. However it should be possible for another type of E-cell with Si₃N₄ windows.



Figure 5.4 : ETEM observations of oxidation-reduction gas cycles on the 2D organization of Pt-Pd NPs with OAm ligands (a-c) after reduction in H₂ (b-d) in 0.1 mbar O₂: no effect was noticed.

• Adsorption-induced shape changes

The behavior of individual clusters during gas exposure was then studied at higher magnifications (Figure 5.5). The alloyed Pt-Pd particles in H_2 were mostly limited by (100) and (111) facets as shown in Figure 5.5 (a), although unambiguous indexation could not be done because of the limited resolution and the small sizes. During oxygen exposure, the particles seemed to change their shape, with and overall rounding as result (Figure 5.5 (b)). The suggested shape changes are drawn by white lines in Figure 5.5 (c-d).

Such rounding in pure O₂ was observed by other techniques for pure Pt and pure Pd. Environmental GIXRD attributed the rounding in O₂ atmospheres to the formation of (112) facets for pure Pd NPs [24] and to different high index facets for pure Pt NPs [23]. Also, ab initio calculations of the oxygen adsorption on pure Pd [27] and Pt [28] nanoparticles showed that low energy (111) surfaces dominate at UHV conditions. However (110) and other higher index surfaces have higher oxygen adsorption energies. Oxygen adsorption then takes preferentially place at more open (110) and high index surfaces (of the (11n) type), thereby reducing the difference in surface free energy, resulting in an overall rounding [27][28].



Figure 5.5 : Effect of the oxidation-reduction gas cycles on the shape of alloyed Pt-Pd NPs: (a) after reduction in H_2 (b) in 0.1 mbar O_2 (c-d) same images but with white lines as suggestion of the facets that are rounded under influence of O_2

• Adsorption-induced surface segregation

No segregation or core shell formation was observed in any of the particles, even after a long exposure or in a strong electron beam leading to the coalescence of the clusters.

It was shown by the theoretical calculations in Chapter 4 for vacuum conditions that Pd preferentially segregated to the surface due to the lower surface energy. However, the Pt subsurface segregation prevents the formation of a thick Pd surface layer. Only a thick Pd shell would be possible to observe in our TEM, which would show a lower electronic contrast.

Previously, Pd was found preferentially at the surface after H_2 exposure [56][58] or O_2 exposure [57]. Since Pd binds more strongly to both H_2 and O_2 (Table 1:2 p.17), in all cases, Pd would stay at the surface with little changes in the chemical structure.

It is however not excluded that, considering the limited resolution, some small changes might occur, notably in the first few surface layers.

5.3.2 Pd nanocubes

Then, the pure Pd cubes, as synthesized in section 2.2 with PVP/KI stabilizers, were observed during oxidation-reduction cycles in pressures of around 1 mbar O_2 or H_2 . The particles were washed 3 times by centrifuge-redispersion in acetone/ethanol, which could remove large part of the PVP/KI stabilizers (FTIR study Figure 2.17).

The nanocubes were observed in standard bright field (Figure 5.6) or weak beam dark field imaging (Figure 5.7). Different features can become visible in both imaging modes.

• Adsorption-induced shape changes

In hydrogen gas (Figure 5.6 (a) and Figure 5.7 (a-b)), not much shape changes were detected compared to the as-synthesized structure. The formation of the hydride phase was previously studied for similar Pd cubes, with an expansion of the lattice parameter, but with no reported influence on the cubic shape [156]. Because of limited resolution, this lattice expansion could not be imaged. A schematic illustration of this cube with mainly (100) facets and small truncated (110) facets and (111) corners can be seen in Figure 5.6 (b).

During oxygen gas exposure, some shape changes were noticed. Dark lines appeared in the bright field image in Figure 5.6 (c) or bright lines in the dark field image in Figure 5.7 (d). These modifications can be the result of the **extension of more open (110) faces under O₂**, as illustrated schematically in Figure 5.6 (d).
This transformation corresponds to the increase of the anisotropy ratio $\gamma(001)/\gamma(110)$ to about 0.8, as compared to 0.7 before gas exposure. This change is coherent with previous ETEM studies of fcc crystals [148][149][150] showing the formation of higher index facets of in pure O₂.

It is not completely clear from the images whether the (111) facets at the corners are modified. On Figure 5.7 (c) the faceting of the corners is suggested. It can be seen on the illustrations of Figure 5.6 that this can be a result of the projection of the larger (110) facets at the corners, so this observation would again supports the observation of enlarged (110) facets.

Similar experiments were performed in previous works with pure Pt nanocubes, prepared by wet chemistry with other organic stabilizers [149] (Figure 5.3). For these Pt nanocubes, a clear shape change was observed, with a change of $\gamma(001)/\gamma(111)$ from 0.8 (cubic shape) in oxygen to $\gamma(001)/\gamma(111) = 1.12$ (closer to Wulff equilibrium shape) in hydrogen.



Figure 5.6 : ETEM observations of a Pd cubes under (a) 3 mbar H_2 with limited effect on the shape and (c) under 1 mbar O_2 with extension of the (110) facets as presented in the model (b-d).



Figure 5.7 : ETEM observations of another Pd cube under (a-b) 3 mbar H₂ with limited effect on the shape and (c) under 1 mbar O₂ with extension of the (110) facets, better visible in the dark field images (d) of the same particle. The faceting of the corner is indicated with an arrow.

5.3.3 Cubic core-shell Pd@Pt nanoalloys

Finally, the Pd@Pt_{0.4eqL} cubes, as prepared in section 2.2, were observed in similar conditions, in pure H_2 and pure O_2 . Again 3 centrifuge-redispersion cycles removed most of the PVP polymer before deposition on the carbon window.

• Adsorption-induced shape changes

The Pd@Pt_{0.4eqL} cubes have concave shapes in pure H_2 , as seen in Figure 5.8 (a-b), with no noticeable difference with the as-synthesized shape (Figure 2.12 (d-f) p. 31).

In pure O_2 , they are much rounded at the corners (Figure 5.8 (c-f)). Also for $Pd@Pt_{0.4eqL}$ nanocubes, the **(110) facets** are extended compared to the same samples in H₂, visible by the dark lines. The same explanations as described for the rounding of the small homogeneous Pt-Pd NPs by higher index facets and the preferential adsorption of O_2 on more open facets of (110) can be made.

• Adsorption-induced surface segregation

It is reported that hydrogen adsorption-desorption cycles can convert Pd@Pt core-shell structures into a solid solution [158]. In our case, only little Pt was deposited, preferentially at the corners, which is not easily resolved by TEM. Moreover, the contrast difference due to the shape changes could not be separated from possible chemical restructuring, so unfortunately this experiment could not resolve adsorption-induced chemical restructuring.



Figure 5.8 : ETEM observations of two different series (right and left) of Pd@Pt_{0.4eqL} under (a-b) 1 mbar H_2 with limited effect on the shape and (c-f) under 1 mbar O_2 with a visible rounding of the sharp corners and extension of the (110) facets.

Another series of $Pd@Pt_{0.4eqL}$ under H_2 and O_2 can be seen in Figure 5.9. One of the particles was observed at high resolution in O_2 , after rotation of the particle. The (111) lattice fringes became clearly visible throughout the whole particle up to the surface. Thus, the observed effects were not due to the oxidation of the particles under O_2 (further discussed in the next section).



Figure 5.9 : similar ETEM observations of a series of Pd@Pt_{0.4eqL} under (a) 1 mbar H₂ with limited effect on the shape and (b) under 1 mbar O₂ with a visible rounding of the sharp corners and extension of the (110) facets. One of the particles rotated while imaging in O₂, and 0.22 nm (111) lattice spacing became clearly visible for the whole particle up to the surface.

5.3.4 Beam effects

As was the case for liquid TEM, the ionization power of the electron beam can create reactive species in the gas phase. Oxidation of a thin shell on a small Pt NP surface under ETEM observations was reported already at room temperature (normally only at 800-1000°C) [159]. It was attributed to activated oxygen gas species, under conditions of strong current densities $>> 0.1 \text{ A/cm}^2$ and $P_{O_2}> 0.013$ mbar. For lower current densities, the competing effect of reduction/desorption of oxygen by the electron beam eliminates this surface layer.

For our conditions of 1 mbar O_2 and current densities around 1-2 A/cm² (at 300K), it is possible that the surface oxidation at room temperature occurs. Some particles showed the formation of a lower contrasted area around the cube, with lattice fringes that are compatible with PdO (Figure 5.10). It is not clear why some particles showed this behavior and others not. Differences in polymer coverage could be at the origin.



Figure 5.10 : Oxide formation sometimes observed for the Pd and Pd@Pt nanocubes (a) formation of a shell layer with lower contrast (b) fringes of 0.26-0.27 nm which are compatible with PdO.

5.4 Conclusion on the ETEM observations

The effect of H_2 and O_2 gas adsorption on Pt-Pd NPs was in situ observed by transmission electron microscopy with an environmental E-cell.

 H_2 was shown to have limited effect on the as-synthesized particle morphology. On the contrast, O_2 induced some shape changes. Small homogeneous Pt-Pd NPs were rounded in O_2 atmospheres. This is compatible with the formation of more open, higher index facets. Pd and Pd@Pt nanocubes also developed more open (110) facets in an O_2 environment. For Pd@Pt nanocubes, the Pt enriched corners are stable in pure H_2 , but they get rounded in pure O_2 .

No adsorption-induced surface segregation could be observed during the oxidation-reduction gas cycles. Although the resolution was limited, it is in agreement with the results from other in situ technique such as XPS [29][30], that show a stable Pd surface segregation. Although this Pd surface layer was observed by other techniques, it is too thin to be observed by TEM.

With environmental TEM one can study the changes in morphology and chemical structure of the NPs under gas environments, to try to understand the catalytic mechanisms. During the catalytic CO oxidation reaction described in the next chapter, it will be shown that the rate limiting step of the reaction is the adsorption of O_2 , which is hindered by a strong CO adsorption. Comparison of the presented ETEM results with the CO oxidation reaction is therefore limited.

Chapter 6 Reactivity of Pt-Pd nanoalloys for the CO oxidation reaction

In previous chapters, it was shown that a thorough control over the nanoalloy structure can be attained with the colloidal preparation method. This makes it interesting to use these nanoparticles as model catalysts. In this chapter, the catalytic reactivity is associated to the observed nanoparticle characteristics. The test reaction that is used is the CO oxidation reaction, which is studied by gas phase chromatography.

6.1 Background, principles and state of the art

The CO oxidation reaction has a long history in surface science studies. In this way, clean welldetermined single crystal surfaces and model catalysts of supported nanoparticles were prepared in ultrahigh vacuum (UHV) chambers and studied by in situ techniques. It was demonstrated by Engel and Ertl [160] that the reaction mechanisms on Pt group metals followed a Langmuir-Hinshelwood mechanism (Equation 6.1). Accordingly, O_2 chemisorbs dissociatively at the surface $(O_2 \rightarrow 2O_{ads})$ and CO chemisorbs molecularly $(CO \rightarrow CO_{ads})$, whereafter they react on the surface to form CO_2 molecules $(CO_{ads} + O_{ads} \rightarrow CO_2)$ that desorb relatively fast. According to this Langmuir-Hinshelwood mechanism, the rate of the reaction is a function of the coverage θ_{CO} and θ_O (Equation 6.1). The Langmuir-Hinshelwood rate constant can be derived from the Arrhenius theory with activation energy E_{LH} .

$$Rate_{LH} = k_{LH}\theta_{CO}\theta_{O} = v_{LH}e^{\left(\frac{-E_{LH}}{kT}\right)}\theta_{CO}\theta_{O}$$

Equation 6.1: General Langmuir-Hinshelwood expression for the rate of the bimolecular CO oxidation reaction, with k_{LH} the LH rate constant, θ the coverage. The rate constant can be derived from the Arrhenius theory with v_{LH} a prefactor, E_{LH} the energy barrier, k the Boltzmann constant and T the temperature.

Later this mechanism was confirmed for the high pressure regime [161]. In most conditions at atmospheric pressure, the rate-limiting step is the O_2 adsorption and dissociation step, which is inhibited by a strong CO adsorption. In this case, the reaction rate can be approximately described as a function of the desorption energy of CO ($E_{CO,des}$) (Equation 6.2). Then, the rate has a first order dependence on the O_2 partial pressure and a negative first order dependence on the CO partial pressure.

$$Rate_{high \,\theta_{CO}} = ve^{\left(\frac{-E_{CO,des}}{kT}\right)} \frac{P_{O_2}}{P_{CO}}$$

Equation 6.2 : Limiting case of strongly bound CO of the Langmuir-Hinshelwood equation, with the $E_{CO,des}$ the CO desorption energy and P_{O_2} and P_{CO} the partial pressures.

Practically, the conversion rate can be measured as a function of the temperature, and as such be plotted in an Arrhenius diagram (In rate vs. 1/T). The **apparent activation energy E**_a of the reaction can then be determined by the slope ($-E_a/R$) of a linear regression of this diagram (Equation 6.3). At low temperature, this E_a of the CO oxidation on Pt metals is reported ~110 kJ/mol, close to the CO desorption energy, as described in Equation 6.2 [161]. However these plots do not take into account changes in concentration of adsorbed reactants over the temperature range (exothermic adsorption) and assume that the orders of the reaction are constant, although this might not be the case.

$$\ln rate = \ln A - \left(\frac{E_a}{R}\right) \frac{1}{T}$$

Equation 6.3 : Arrhenius equation used to determine the apparent activation energy E_a , with R the gas constant and A a frequency factor.

For surfaces and well defined particles the **Turn-Over Frequency (TOF)** can be calculated, which is defined as the number of CO_2 molecules formed, per surface metal atom, per second. The CO oxidation reaction was first claimed to be structure-insensitive, which means that the TOF is independent of the size and type of exposed facets [160][162]. However it was later found to be dependent on the particle size at low pressures [163], for high O_{ads} coverages.

The CO oxidation reaction is one of the few reactions for which the reaction mechanism is so well documented. Hence, it is often used as test reaction and particularly interesting for the comparison of the controlled structures, obtained with colloidal methods. To compare literature results, the **mole fraction of CO**, $\mathbf{x}_{cO}=P_{CO}/(P_{CO}+P_{O_2})$ has certainly to be taken into account, since the rate depends on these partial pressures (Equation 6.2). Other experimental parameters that are important for the comparison of results are the support, the loading and reactor specific parameters.

• CO oxidation on colloidally prepared pure Pt and Pd NPs with different shapes

The structure-activity relationship of the CO oxidation reaction was already studied with pure Pt or Pd nanoparticles, prepared by colloidal methods. The catalytic activity showed an important dependence on the shape with different facets, studied at high pressures (structure-sensitivity). It was not possible before to investigate such dependence by wetimpregnation methods or physical deposition, because it was not possible by these preparation methods to obtain a single shape and a small size distribution. Table 6:1 gives a literature overview of the CO oxidation on different shapes of pure Pt and Pd NPs, prepared with different stabilizers. It is clear that the measurement conditions are not the same, which makes it difficult to compare the studies with each other. Murray's group found that Pt octahedra were much more active than similar size Pt nanocubes, both prepared with oleylamine and oleic acid [164]. The difference in reactivity was however only noticed for very O₂-rich environments (x_{CO} =0.02). Likewise Pd octahedra were demonstrated to be more reactive than Pd nanocubes [165], even for x_{CO} =0.5, however the different shapes were prepared with different stabilizers. Xia's group showed a strong size dependence of the reactivity of Pd nanocubes [51]. They reported that the TOF was higher for smaller sizes.

The implication of the stabilizers in the heterogeneous gas phase stays questionable. There are some studies on the benefits of different ligands in the CO oxidation, notably in the protection against oxidation or coalescence [166]. However, most researchers report the loss of activity due to the blocking of the active sites. Therefore one has tried to remove the stabilizers at maximum prior to the catalytic experiment, although the frequently reported deposition-redispersion is often not sufficient to remove all stabilizers. Nevertheless, the activation energy was reported independent of the stabilization type/coverage (e.g. 113-117 kJ/mol for Pt cubes on SiO₂ wafer [167])

Pt shape	stabilizers	size (nm)	E _a (kJ/mol)	x _{co}	support	loading (wt.%)	ref
cubic	OAm,OA,	9.3	80.9	0.02	AI_2O_3	1	[164]
	Mn ₂ (CO) ₁₀		/	0.5			
			50.8	0.97			
octahedral	OAm,OA,	12.6	80.9	0.02	AI_2O_3	1	[164]
	Mn ₂ (CO) ₁₀		/	0.5			
			50.8	0.97			
cubic	TTAB, HAD,	12.3-9.5	113-117	0.3	SiO ₂ wafer	-	[167]
	HDT or PVP						
spherical	DDA	2.3	-	0.14	γ - Al ₂ O ₃	0.8	[168]
cubic	PVP, AgNO₃	8.9	98.1	0.5	SiO ₂	9.0	[169]
cuboctahedral	PVP, AgNO₃	16.2	79.0	0.5	SiO ₂	8.6	[169]
octahedral	PVP, AgNO₃	18.4	74.0	0.5	SiO ₂	9.1	[169]
Pd shape	stabilizers	size (nm)	E _a (kJ/mol)	X _{CO}	support	loading (wt.%)	ref
cubic	CTAB, AA	20.5	76.5	0.5	fumed SiO ₂	3	[165]
octahedral	PVP, CA	22.4	52.9	0.5	fumed SiO ₂	3	[165]
spherical	P123	3.9	42.6	0.5	fumed SiO ₂	3	[165]
cubic	AA, PVP, KBr	6, 10, 18	-	0.05	ZnO wires	2	[51]

Table 6:1 : Different literature results of the CO oxidation on controlled shapes of pure Pt and Pd nanoparticles, prepared by colloidal methods.

• CO oxidation on Pt-Pd nanoalloys prepared by wet-impregnation

The number of studies on the CO oxidation on Pt-Pd nanoalloys, prepared by colloidal methods is still limited. Most studies on the increased activity of colloidally prepared Pt-Pd nanoalloys focus on electrochemical reactions (as described in section 1.4.1) and only some on other heterogeneous gas phase reactions (hydrogenation [38], PROX [40]).

However Pt-Pd nanoalloys are well known in car exhaust catalysts, with the CO oxidation as one of the main reactions. The preparation in these studies was done by wet-impregnation (see Table 6:2). Comparison of our results (colloidal Pt-Pd) presented in this chapter, with these nanoparticles, prepared by wet-impregnation, should be done with care. A major difference is that no stabilizers block the active surface sites, although other contaminants can be present (e.g. Cl or S). In addition, the wet impregnation gives no control over the shape, with often large size dispersion. Moreover, the studies in Table 6:2 often combined different reactions (e.g. oxidation of hydrocarbons), which gives other testing conditions.

Although they had limited control over the structure with this preparation method, they still tried to study the benefits of combining both metals in a specific way. First studies of Pt-Pd in car catalysts, claimed that Pd_{core}@Pt_{shell}, prepared by sequential impregnation, showed an improved reactivity compared to co-impregnation alloy or Pd@Pt [170]. Since then, other studies have showed similar results (e.g. [171]), although the real structure, distribution and surface sites are often not further specified. Others have focused on the homogeneous alloy structure by co-impregnation. They aimed to determine the most active mol% ratio (e.g. [172], [173], [174]). It was clear from these studies that alloying has a beneficial effect on particle aging and stability, but there was no consensus on an electronic effect, because of the limited control over the structure.

Pt-Pd	chemical	size	Ea	x _{co}	support	loading	ref
preparation	structure	(nm)	(kJ/mol)			(wt.%)	
sequential	core-shell	-	-	-	MIL-101	1.8% Pd	[171]
impregnation						3.2% Pt	
sequential	core-shell	2	_	0.17-0.21	-	2-6	[170]
impregnation							
co-impregnation	random	2-3.5	56.4	0.67	γ-Al ₂ O ₃	1	[173]
0,25,50,75,100%Pt	alloyed		average				
co-impregnation	-	3-4	-	0.02	Boehmite on	0.1	[172]
0,20,80,100%Pt				(+xylene)	monolite		

Table 6:2 : Different literature results on the CO oxidation on Pt-Pd nanoalloys, prepared by wet impregnation.

6.2 Experimental technique and optimization

The activity for the CO oxidation reaction was evaluated in a fixed-bed quartz tubular reactor (inner diameter 3 mm, length 20 cm) at atmospheric pressure for a variable oven temperature. A thermocouple placed near the reactor bed was used to estimate the catalyst temperature (see setup Figure 6.1). Typically, 20 mg of catalyst powder was loaded into this quartz reactor, after cleaning with aqua regia and drying.

Two individually controlled mass flow meters gave the opportunity to vary the entry fraction of CO (Linde, 3.7 purity, 9% mixture with N₂ 5.5) and O₂ (Linde 5.6). O₂ could vary between 0.1 and 5.9 ml/min and CO/N₂ between 10 and 200 ml/min. A separate entry of pure N₂ (Air liquid, 2.2) without flow meter could place the oven under controlled atmosphere and was necessary to evacuate CO gas before opening the system to load a sample.

A gas chromatograph equipped with a thermal conductivity detector (TCD) and two columns (Porapak Q 1/8" 2m 80/100 and Molecular sieve 1/8" 2m 13x 60/80) was used to analyze the reaction products (Figure 6.1). At the oven outlet, automatic sample injection was done and the gas sample was mixed with the helium carrier gas. Identification of the reaction products by chromatography is based on the difference in retention time of the compounds passing through specially coated columns. A peak was then detected by the TCD, when the helium carrier gas (Linde, 5.0) differs in thermal conductivity from the sample+helium passed through the columns.



Figure 6.1 : Overview of the setup: (left) flow meters and the oven containing the sample, (right) the gas phase chromatograph and an example of a spectrum with the different peaks (CO₂, O₂, N₂ and CO) detected as a function of the time.

Complete automatic sampling while heating the sample continuously was found to be inaccurate. The temperature needs to be at least 60 min constant (for 22.3 ml/min) before steady state flow is reached (see Figure 6.2). So manual temperature increments (at rates of 0.3-0.5°C/min) with a successive ramp of 60 min were done, to measure one point of the conversion curve. Heating the oven at higher rates can create an important temperature overshoot, which means longer waiting time for steady state conditions.



Figure 6.2 : Illustration of the waiting time after temperature increment to reach steady state conditions for a flow of 22.3 ml/min.

The steady state production of CO_2 could be evaluated for different mole fraction of CO, $x_{CO}=P_{CO}/(P_{CO}+P_{O_2})$ (Table 6:3). It was verified that the response of the chromatograph was in accordance with the CO/O_2 ratio change for an empty reactor. For a same total gas flow rate, a linear increase of x_{CO} was obtained, with a small deviation of less than 10%, related to the limited accuracy of the flow meters (Figure 6.3). Note that again some precaution has to be taken to wait long enough after changing the flow rates (e.g. 100 min for 22.3 ml/min). Since the range of the flowmeters is limited, and the waiting time for stabilization depends on the flow rate, the practical range for x_{CO} with current setup is 0.2-1. Thus very rich O_2 environments could not be tested.

x _{co}	Flow O ₂	Flow CO+N ₂	Flow CO	P_{02}/P_{CO}
	(ml/min)	(ml/min)	(ml/min)	
0.2	5.9	16.4	1.48	4.0
0.3	3.9	18.4	1.66	2.3
0.4	2.7	19.6	1.76	1.5
0.5	1.8	20.5	1.85	1.0
0.6	1.3	21.0	1.89	0.7

Table 6:3 : The variable O_2 and CO flow rates for a constant total flow rate of 22.3 ml/min, with associated x_{co} or P_{O_2}/P_{co} ratios.

Low flow rates were chosen, so that the reaction would not be limited by diffusion, which alters the conversion rates. However due to the exothermic nature of the CO oxidation reaction, local temperature rises in the catalyst bed can occur. In this way, the reaction is so fast, that it becomes diffusion limited. To avoid this, conversions were kept below 10% when determining the activation energy, to stay in the kinetically controlled regime. Above 10% of conversion, 100% conversion was attained for only a small temperature increase.



Figure 6.3 : Linear response of the ratio (peak surface area CO/(CO+O₂)) detected by the chromatograph, when changing the ratio x_{co} by the flow meters, for a constant flow rate of 22.3 ml/min.

For the classical wet impregnation, most of the catalytic tests are done after conditioning of the surface to the reduced state in H_2 at high temperature. However for our study of colloidal particles, we do not want to expose them to these severe conditions, which may alter the targeted structure. So it has to be kept in mind that the surface might not be completely clean and activated. However, it was aimed to obtain reproducible conditions.

The oven was always put under pure N_2 to ensure similar starting conditions, since the reaction rates were found to be very dependent on the starting oxygen level [61]. This practically means that very high oxygen levels (also for example left in the tubes from previous experiments) can induce reactivity at much lower temperatures than expected. Due to the exothermic reaction, it can even attain 100% conversion, at a temperature showing little activity for well controlled conditions.

During several experiments, problems arose from powder that was blown out of the reactor in the oven and to the gaskets (Viton O-rings). Frequent cleaning should be done, and pumping of the system should be done with precaution. No decrease in activity was observed for the duration of the experiments. The longest test for 100% conversion was performed for 20h, with no noticeable decrease.

6.3 Evaluation of the CO conversion

6.3.1 Reactivity of small Pt, Pd and Pt-Pd nanoalloys

First, the small nanoparticles as described in section 2.1 were tested. Pure Pt, pure Pd and Pt-Pd (1:1) alloys deposited on SiO_2 were compared. For each experiment, 17 mg of sample (with estimated loading of 3-4 wt.% based on mixing parameters) was cleaned by 20 min UV-ozone at room temperature. The samples were loaded in the reactor under N₂ flow for 1h at 140°C.

The CO conversion yield, calculated as the area of the CO₂ peak divided by the maximal area of the CO₂ peak (when no CO peak is left = 100% conversion) is measured for increasing temperatures. Three successive temperature ramps were done for one sample, first for x_{CO} =0.2, then x_{CO} =0.4 and then again x_{CO} =0.2. As the reaction proceeds, it can have a 'cleaning effect' of the surface and activate the NPs. This is especially true for these samples prepared with organic stabilizers, for which the active sites might be blocked by contaminants. Also, UV-ozone can leave carbon fragments on the surface from the decomposition. Therefore, the same condition for x_{CO} =0.2 was repeated to study this effect.

The conversion for increasing temperature for both x_{CO} =0.2 experiments is plotted in Figure 6.4. The Pt-Pd sample was found slightly more active than pure Pt, and much more active than pure Pd. The pure Pt and Pd samples showed little difference after the first reaction. They are active in a range expected for Pt and Pd NPs of 3-5 nm, around 200°C. For the Pt-Pd alloy, the sample became more active after the first ramp, which is shown by the arrows in Figure 6.4. Likewise, the light-off temperature (at 50% conversion) decreased by 10°C (Table 6:4). It was shown that the oleylamine ligands were removed between 220°C-360°C in Ar (TGA p. 28) which are temperatures higher than the range we used here, but these temperatures could be much different for reactive CO+O₂ environments. Also, the alloyed structures could rearrange their chemical structure under reaction conditions (section 1.4.2), resulting in a more active sample for the second ramp. In this case, it is expected that Pt segregates (more) to the surface, due to higher adsorption energy of CO (146 kJ/mol for Pt(111) [64] versus 134 kJ/mol for Pd(111) [63]). It is however challenging to separate both effects of higher ligand removal during reaction and reaction-induced surface segregation.

Then **for higher CO partial pressures**, x_{co} =0.4, the activity decreased for all samples, indicated by an increase of the 2% conversion temperature (Table 6:4). For pure Pt and Pd, it can be seen clearly in Figure 6.5, with an increase of the light-off temperature T_{50%} with about 15°C. This is consistent with strongly bound CO molecules that block the O₂ adsorption sites with, according to Equation 6.2, a positive order of the reaction in O₂ and a negative order in CO. The light-off temperature (T_{50%}) of the alloy Pt-Pd for x_{co}=0.4 is again much lower than for both pure elements. Also for x_{CO} =0.2 the $T_{50\%}$ of the alloy was generally lower than the pure metals. Due to the strong exothermic reaction, it was not possible to measure very accurately $T_{50\%}$.



Figure 6.4 : CO conversion as a function of temperature for small Pt, Pt-Pd and Pd nanoparticles for the first and third measurement under same conditions (reaction gas composition x_{co}=0.2, flow rate 22.3 ml/min). The arrows indicate a small activation of Pt-Pd NPs.



Figure 6.5 : CO conversion as a function of temperature for small Pt, Pt-Pd and Pd nanoparticles for the second measurement (reaction gas x_{co} =0.4, flow rate 22.3 ml/min).

sample	x _{co} =0.2	x _{co} =0.4	x _{co} =0.2	x _{co} =0.2	x _{co} =0.4	x _{co} =0.2
	T _{2%}	T _{2%}	T _{2%}	T _{50%}	T _{50%}	T _{50%}
Pt	168±1	188±2	168±1	200±3	218±1	198±2
Pt-Pd	177±2	185±1	170±5	198±4	190±2	189±1
Pd	196±1	203±2	189±1	203±4	215±3	202±2

Table 6:4 Temperatures for 2% conversion and 50% conversion for the three successive measurements on Pt, Pt-Pd and Pd nanoparticles.

In conclusion, these measurements showed a higher activity of alloyed Pt-Pd than both the pure elements. This could possibly be explained by **an electronic ligand effect, due to a mixed Pt-Pd surface**. However, it should be mentioned that the Pd NPs were somewhat larger (5 nm instead of 3-4 nm for Pt and Pt-Pd, Table 6:7). A **size effect** is expected for Pd in this size range [163]. Particles even more related in structure, with similar preparation (ligands) would be necessary to exclude this size effect.

6.3.2 Reactivity of cubic core-shell Pd@Pt nanoalloys

• Reactivity of 0 to 2.2 equivalent layers of Pt on Pd cubes

Then, the reactivity of the cubic Pd NPs with 0 to 2.2 equivalent shell layers of Pt was tested. Their synthesis with PVP/KI stabilizers was described in section 2.2. Characteristics of the different samples can be found in Table 6:5. All samples were exposed to UV-ozone cleaning for 2h and loaded under N_2 flow for 1h at 160°C.

sample name	equivalent atomic layers on 14.6 nm cube	estimated total metal loading (wt.%) on SiO ₂
Pure Pd	0	2.3
Pd@Pt _{0.2eqL}	0.2	2.4
Pd@Pt _{0.4eqL}	0.4	2.5
Pd@Pt _{0.5eqL}	0.5	2.6
Pd@Pt _{1.6eqL}	1.6	2.9
Pd@Pt _{2.2eqL}	2.2	3.1

Table 6:5 Sample characteristics for reactivity tests of cubic Pd@Pt nanoparticles.

The CO conversion in the kinetically controlled regime of the different samples for x_{CO} =0.4 are shown in Figure 6.6. For comparison, the sample with small Pt NPs prepared with OAm ligands is also added. It was unfortunately not possible to synthesize pure Pt cubes with our method, since irregular shape and sizes were obtained. The measurements can be divided into three

main groups, from low to higher reactivity (marked with arrows in Figure 6.6). The temperature of 5% conversion for all the samples can be compared in Table 6:6.

First, the conversion of the cubic pure Pd NPs and $Pd@Pt_{0.2eqL}$ (group 1) was much lower than the samples with more Pt. The temperature of 5% conversion is above 300°C as can be seen in Table 6:6. This high temperature can be explained by the large NPs sizes, especially compared to previous small Pd particles [51]. Moreover, it is thought that Pd is very sensible to sulfur poisoning, more than Pt [175] or the Pt-Pd alloy [176], although this was also contested [177]. Very similar activity was found for 20 nm cubic Pd/SiO₂ under similar measurement conditions with no sulfur present [165]. It was found that it is in the range where the SiO₂ or the empty reactor started to show some activity. This means that the activity of group 1 is very low.

Then, with increasing coverage of Pt, a significant superior performance was obtained. The temperature of 5% conversion decreased by 80°C for Pd@Pt_{0.4eqL} (group 3). As seen in Table 6:6, increasing the Pt coverage does not improve anymore the conversion efficiency (group 2). $T_{5\%}$ seemed even to increase about 25°C for higher coverages.



Figure 6.6 : CO conversion as a function of temperature for cubic Pd and Pd@Pt nanoparticles for the second measurement (reaction gas $x_{co}=0.4$, flow rate 22.3 ml/min).

(°C)	Pure Pd	Pd@Pt _{0.2eqL}	Pd@Pt _{0.4eqL}	Pd@Pt _{0.5eqL}	Pd@Pt _{1.6eqL}	Pd@Pt _{2.2eqL}	Pt(OAm)
T _{5%}	308±4	302±4	224±2	258±4	250±3	254±2	206±2

Table 6:6 Temperatures (°C) for 5% CO conversion of the cubic Pd and Pd@Pt nanoparticles.

So the highest activity was obtained with 0.4 equivalent Pt layers (group 1) corresponding to only 0.2 wt.% Pt. Unfortunately, it was not possible to make pure Pt nanocubes with similar size and shape, with the same PVP/KI stabilizers/solvent. However, the activity of Pd@Pt $_{0.4eqL}$ was comparable with the activity of pure Pt in the case of small particles prepared with oleylamine ligands. Also, when converting the results of Murray's group for 9.3 nm pure Pt nanocubes [164], it was clear that the conversion was exponentially with a rapid rise at 250°C, which is represented by the dashed straight line in Figure 6.6.

So from these results, a **maximum in the activity** was found for a quantity equivalent to 0.4 monolayers of Pt on the 14.6 nm Pd cubes. It shows that **only a small quantity of Pt is able to increase drastically the reactivity of the Pd nanocubes, possibly even at a higher level than pure Pt nanocubes**.

• Comparison with other Pd@Pt core-shell NPs in literature

Similar studies of Pt layers on Pd cores with other test reactions were presented by different groups. They are compared here, in order to get insight in the mechanisms that can cause this maximal activity.

A first example is a study of the catalytic activity of <u>Pd@Pt nanocubes for the ORR</u>, which has shown a maximal specific activity for 2-3 atomic layers of Pt, epitaxially grown on 18 nm Pd cubes [35]. The increase of the activity has been explained by a decrease of the stability of OH species, which has been shown from DFT calculations to be the rate limiting step in the ORR reaction [178]. The decrease of the adsorption energy of OH would be due to a modification of the electronic structure (downshift of the d-band center) of the surface Pt atoms due to the presence of the Pd core, through both the strain and ligand effect (as discussed in section 1.2.2).

- The **compressive strain** of the Pt shell would arise due to the misfit between Pt and Pd lattices. This misfit of the atomic radius is moderate (1.4%), but the strain effect can be increased by the small size and roughness of the particles, as was shown by EXAFS [179].
- The **ligand effect** was first described by Nørskov and coworkers [18] for metal alloys. It is due to the modification of the electronic structure of Pt atoms by the presence of Pd atoms as nearest neighbors.

The decrease of the activity for more atomic layers of Pt on the Pd cubes, was then explained by a decrease of the ligand effect for thicker layers [35].

Then, in the case of <u>p-CNB hydrogenation on Pd@Pt core shell octahedra [</u>38], a maximum of activity was observed for 1 monolayer of Pt. A decrease of the activity for more Pt layers (up to 4) showed that the **ligand and strain effect was largest for the first layer**.

In the case of <u>methanol electro-oxidation on Pd@Pt cubes [48]</u>, an increase in activity relative to pure Pt was observed for Pt shells of 2.5 nm. This layer is quite thick (12-13 atomic layers) so that the ligand and strain effect should be weak. However since the Pt layer was very rough, it could also be explained by the strain (EXAFS study [179]) and ligand effect (more mixed bonds for rough layer).

• Possible interpretation of the structure-activity relationship

These studies showed that it is important to take into account the whole structure (size, shape, roughness) and not only the amount of deposited Pt layers. It is clear that it stays difficult to study the structure-activity relationship for an exact number of layers. Even the atomic structure of smooth Pd@Pt nanocubes prepared by the group of Xia [35], studied in detail by aberration corrected STEM [66], showed a mixing of Pd and Pt, especially for the first 2 deposited Pt layers. Also in our study, only little Pt was deposited (less than 2.2 equivalent monolayers), which suggests that it should be interpreted mostly as a Pt-Pd alloy at the surface. For this type of structure, the ligand effect will be important.

What is important to notice is that in the operating conditions of the CO oxidation, the high CO coverage blocks the sites for the dissociation of oxygen. It means that the reaction rate can be increased by decreasing the adsorption energy of CO. This can be done by the electronic effects (downshift of the d-band center) induced by the ligand and compressive strain effects. A decrease of the CO bond strength on the surface of the Pd@Pt particles can thus explain the increase in reactivity by increasing the Pt layer thickness [19]. Again, the ligand and strain effects are shielded for higher Pt layers, which can be the cause of a decrease of the activity. It should be mentioned that the maximal activity was observed for 0.4 equivalent layers, however this is only an average thickness because of the preferentially deposition at the corners and the presence of some larger bars that were not taken into account in the calculation of the equivalent layer thickness.

• Activation after consecutive measurements

For the two consecutive measurements of $x_{CO}=0.2$, the **Pd@Pt_{0.4eqL} sample showed an increase in activity**, while other samples showed no activation (Figure 6.7). This could be related to the fact that it was the only sample that attained 100% conversion for the first measurement. However, it was already the most active sample in the first measurement, with 10% conversion at 220°C, while other samples showed very little activity, so its highest activity was only little related to this activation process. No deactivation was noticed either, since especially polymers as PVP are believed to decompose at higher temperatures into carbon fragments. These can easily block the active surface sites and thus deactivate the catalyst [180].



Figure 6.7: Activation of the Pd@Pt _{0.4eqL} after 3 consecutive measurements (arrows) and similar activity after 3 consecutive measurements of Pd@Pt _{2.2eqL}.

• Turnover frequency

Then, the number of active sites was estimated, in order to compare the Pd@Pt with conversion rates in literature. The turnover frequency (TOF) was calculated in units of mmol produced CO₂, per mmol surface metal sites, per second of reaction time (s⁻¹). It was estimated based on the size and shape observed in TEM, with the estimation of 8% of the Pd atoms at the surface, and with 0.004 mmol in one sample of 20 mg. The conversion was multiplied by the number of CO mmol/s (from the flow meter) to get the number of produced CO₂ mmol/s. For all samples, it was assumed that the number of atoms at the surface does not change, since the shape is more or less retained for the different samples.

The TOF values at 240°C are given in Table 6:8 further on. The most active sample, $Pd@Pt_{0.4eqL}$, showed a TOF of 3.8 s^{-1} at 240°C (although it can be even higher since this is the value for 100% conversion). For the curves of Pt cubes of Murray's group given in [164], we recalculated a TOF of 0.04 s⁻¹ (compensated for x_{co} =0.4) which is two times lower than the Pd@Pt $_{0.5-2.2eqL}$. A TOF of 1 s⁻¹ at 240°C was reported for Pt(100) [181] or 0.4 s⁻¹ for Pt/SiO₂ by wet-impregnation [162] (x_{co} =0.66). Although comparison is limited because of the low pressures used in these later studies, it shows that we are in the high range of TOF values.

6.4 Apparent activation energy

6.4.1 Arrhenius plot of small Pt-Pd nanoalloys

The apparent activation energy, found as the slope of the Arrhenius plots (Figure 6.80 and values in Table 6:7) did not vary much for the three different measurement conditions (variation of x_{CO}). The lowest apparent activation energy was found for pure Pt, than Pt-Pd and the highest for Pd. The apparent activation energy of Pd was clearly higher than the ones of Pt and Pt-Pd. However, the E_a of Pd is also much higher than values normally reported. It is not clear what is at the origin of this discrepancy. Although the measurement error can be quite large, it is supposed to be at very maximum 15kJ/mol (for 10% error in measured CO₂ area and 5°C error in temperature). Moreover, a measurement error does not explain the systematic large E_a, for three consecutive measurements. The R² of the fitting is high, in average 0.997.

Sample	used temperature	E _a (kJ/mol)	order O ₂	order CO	v_a	size (nm)
	range (°C)	(averaged)				
Pt	168-216	109±7	0.9	-0.7	2.10 ¹²	3.7 ± 1.5
Pt-Pd	163-187	128±6	1.3	-0.6	4.10 ¹³	3.2 ± 0.8
Pd	191-211	182±2	1.5	-0.7/-1	4.10 ¹⁸	5.0 ± 1.0

Table 6:7 Apparent activation energy E_a and reaction orders determined for the small Pt, Pt-Pd and Pd NPs.



Figure 6.8: Arrhenius plots of the Pt, Pt-Pd and Pd nanoparticles with linear regression.

6.4.2 Arrhenius plot of cubic core-shell Pd@Pt nanoalloys

The apparent activation energies (E_a) for the cubic core-shell Pd@Pt nanoalloys, obtained from the Arrhenius plots (Figure 6.9) are listed in Table 6:8. The variation of the gas composition (in a limited range of x_{CO} =0.2-0.4) had again no influence on the apparent activation energy.

The values are close to typical values obtained for colloidal pure Pt NPs (Table 6:1 [164][167][169]). Two values, for $Pd@Pt_{0.4eqL}$ and $Pd@Pt_{2.2eqL}$ are somewhat higher than expected. These values of around 150-160 kJ/mol were found for two consecutive measurements for different x_{co} (Figure 6.10).

Sample	used temperature	Ea (kJ/mol)	TOF at 240°C	order O_2	order CO	v_a
	range (C)	10 $x_{CO} = 0.4$	(\$)			
Pd pure	250-330	108	-			
Pd@Pt _{0.2egL}	268-345	118	-	1.7	-1.1	1.10 ⁹
Pd@Pt _{0.4eqL}	165-228	145	3.8	1.6	-0.8	1.10^{16}
Pd@Pt _{0.5eqL}	202-275	131	0.07			
Pd@Pt _{1.6eqL}	202-258	119	0.1			
Pd@Pt 2.2eqL	190-258	156	0.07	1.7	-1.1	1.10 ¹⁵

Table 6:8 : Apparent activation energy E_a, TOF and reaction orders determined for the cubic Pd and Pd@Pt NPs.







Figure 6.10 : Determination of the apparent activation energy E_a from the Arrhenius plots for different gas compositions ($x_{co}=0.4$ and $x_{co}=0.2$) for Pd@Pt nanoparticles.

6.4.3 Compensation effect

For all observations, a linear correlation between the apparent activation energy E_a and the pre-exponential factor In A was observed (Figure 6.11). This phenomenon is known as the compensation effect [182][183]. It means that in the Arrhenius expression, a high E_a (which normally means a low reaction rate) is compensated by a high coefficient In A.

$$Ln A = mE_a + cst$$

Equation 6.4 : Compensation equation showing a linear correlation between the parameters of the Arrhenius equation.

There are numerous possible explanations for this effect and it still seems a matter of discussion. For example a change in kinetic regimes or a combination of two reactions on different active sites was reported to be at the origin [182]. The scope of this work was not to determine precise reaction mechanisms, but it shows that true understanding of the observed reaction rates may be more complicated than the factors given in previous chapters.



Figure 6.11 : Compensation plot of the parameters of the Arrhenius equation In A versus E_a for all measurements showing the linear dependence.

6.5 Preliminary kinetic analysis

It was then aimed to determine the orders of the reaction, to get insight in the kinetics. The measured surface areas of CO_2 (without transformation to conversion yield) can be described by Equation 6.5, with x and y the orders of the reaction in O_2 and CO.

Surface area
$$CO_2$$
 peak $\approx v_a e^{\left(\frac{-E_a}{RT}\right)} P_{O_2} {}^x P_{CO} {}^y$

Equation 6.5 : Determination of the reaction orders x and y by fitting the measured CO_2 surface areas for different P_{O_2} and P_{CO}

The second and third surface area measurements (x_{CO} =0.4 and 0.2), in the low conversion regime were used. P_{O_2} and P_{CO} were calculated as the partial pressure (flow rate/total flow rate) times the atmospheric pressure. The average of the two measurements of E_a was used. Then, a least square fitting with variable v_a , x and y of this equation could reasonably describe the measurements (Figure 6.12 and Figure 6.13). The orders and prefactor v_a as determined by this fitting can be found in Table 6:7 for small Pt, Pd and Pt-Pd nanoalloys and in Table 6:8 for Pd@Pt nanocubes. The reaction was described as first order in O₂ (x=1), and negative first order in CO (y=-1), which is close to the values generally found.

An order in O_2 of 0.9 was found for small Pt, while slightly higher order in O_2 were found for small Pd and Pt-Pd, which would mean that the rate is more sensible to O_2 pressures. Orders in CO between -0.6-0.7 are consistent with similar values reported for Pt NPs with different shapes [164].

Somewhat higher reaction orders in O_2 were found for Pd@Pt nanocubes compared to the small particles, around 1.7 (values given in Table 6:8). The positive correlation on the reaction rate clearly shows the increase in reactivity for higher O_2 flows. A close to negative first order in CO was consistent with the Langmuir-Hinshelwood equation for the limiting case of strongly bound CO.

A variation in the prefactor v_a could indicate differences in loading (amount of active sites) or packing in the reactor (probability of molecule to hit the surface).

It is clear that the determination by this least square fitting of only two measurement conditions (which are dependent on each other), is not the best way to determine reaction orders. Unfortunately, the O_2 and CO flow could not be varied independently for a constant flow rate (since CO is mixed with the N_2 carrier gas). To determine x and y independently, a third carrier gas supply would be needed. This would make better kinetic measurements possible.



Figure 6.12 : Determination of the orders in O_2 and CO by a least square fitting of the rate function (CO₂ surface area) for small Pt, Pt-Pd and Pd nanoparticles for x_{co} =0.2 and 0.4 (second and third measurement).



Figure 6.13 : Determination of the orders in O_2 and CO by a least square fitting of the rate function (CO₂ surface area) for Pd@Pt nanocubes for x_{co} =0.2 and 0.4 (second and third measurement).

6.6 Structure after reaction

For the small Pt, Pd and Pt-Pd nanoalloys, prepared with OAm ligands, TEM images before and after catalysis show little structural changes such as excessive sintering or specific interactions with the support. Some of the particles seemed to increase in size compared to the average, but these larger particles were also found in the as prepared sample and might be the result of the agglomeration during deposition (Figure 6.14.).



Figure 6.14 : The small (a) Pt (b) Pt-Pd (c) Pd nanoparticles prepared with OAm ligands after deposition on SiO₂, 20 min UV-ozone and 3 cycles of CO oxidation up to 210°C.

Unlike the small particles, the larger cubic core-shells changed drastically their structure during the measurements. It can be seen on Figure 6.15 that the cubic shape is not maintained and some sintering to even larger particles occurred. Also the hollow structures (Figure 2.14) shown for larger Pt depositions, seemed to have disappeared. This is not surprising, because of the higher temperatures (>250°C) and the long reaction times (>24h). The structural deformation for PVP capped Pt cubes in air was found to be initiated around 250°C (and in N_2 around 200°C) [184]. According to Murray's group, the presence of CO+air promotes the deformation of Pt nanocrystals at high temperature. Also extended reaction time causes the NPs to lose their original shape [164].



Figure 6.15 : TEM images of the $Pd@Pt_{1.6eqL}/SiO_2$ (a) before and (b) after the reaction up to 258°C and 7% conversion.

6.7 Conclusions on the reactivity studies

The reactivity of different small homogeneous Pt-Pd and core-shell nanoalloys for the CO oxidation was investigated by gas phase chromatography. The potential and limits of the available equipment was presented, as well as major issues when testing colloidal NPs in heterogeneous gas phase reactions.

First, the reactivity of small pure Pt, pure Pd and Pt-Pd nanoparticles deposited on SiO₂ was presented. An improved reactivity of Pt-Pd nanoalloys compared to the pure components was noticed. This could possibly be attributed to an electronic effect due to the mixed Pt-Pd surface. Further optimization of the structure is however necessary to exclude other effects, such as a size effect, which might play a role in the decreased activity of pure Pd NPs.

The CO oxidation test reaction was then used to investigate the effect of a more controlled alloyed structure, Pd@Pt core-shell nanocubes, with increasing amount of Pt at the surface. A notably improved activity was found for the addition of only small quantities of Pt, with a maximal reactivity for 0.4 equivalent atomic layers of Pt, and a decrease for higher Pt

deposition. This value should not be taken too strict, since it is a calculation neglecting the preferential deposition at the corners and the presence of larger bars. However, similar behavior of the reactivity was reported in literature for other reactions, such as the ORR.

This improved activity can be interpreted in terms of decrease of the CO adsorption energy. Indeed, a strong adsorption of CO hinders the O_2 adsorption and dissociation. This effect is explained in terms of compressive strain and proximity of Pd atoms in the epitaxial Pt layer on Pd cubes (ligand effect). This can result in a change of the electronic structure of the Pt and consequently, a decrease of CO adsorption energy.

Analysis of the apparent activation energy and reaction kinetics at atmospheric pressure was not straightforward. The high apparent activation energies found are possibly related with contaminations of stabilizers and solvents. It was also shown that possibly more complex mechanisms occurred that are at the origin of the observed compensation effect.

It was shown that colloidal methods can provide new insights in limiting factors and reaction mechanisms, in order to improve the reactivity. The colloidal method is known for its control in structure (chemical structure, size and shape). Previous studies that report on colloidal NPs for heterogeneous CO oxidation have mainly focused on controlling the size and shape. Here, we show that colloidal preparation methods are also interesting for the investigation of the effect of alloying.

Chapter 7 Conclusions

7.1 Achieved results

The colloidal synthesis of nanoparticles consists of the decomposition of a metal precursor in a solvent, in the presence of stabilizers. Two types of Pt-Pd nanoalloys were prepared by reduction of Pt(acac)₂ and Pd(acac)₂ in the presence of two different stabilizers (oleylamine, PVP/KI). In this way, small homogeneously alloyed and cubic core-shell Pt-Pd nanoparticles were synthesized. They were characterized by a well-defined size, shape and composition. Their nucleation and growth in solution, theoretical structure, dynamic behavior in gas and their reactivity were subsequently investigated.

7.1.1 Small homogeneous Pt-Pd nanoalloys

In the presence of oleylamine ligands, 50-50 mol% Pt-Pd nanoparticles were synthesized from solution with a homogeneous size of 3.2 ± 0.8 nm. They were mostly monocrystalline, with some twinned structures and had a near-spherical shape. They were self-organized in 2D arrangements on flat surfaces, with regular interparticle distance. Compared to monometallic Pt, the alloys were more homogeneous in size and shape. The elongated structures, present for pure Pt, were not observed for Pt-Pd nanoalloys.

• In situ liquid TEM study of the nucleation and growth in solution

In order to control the structure and therefore the reactivity of nanoalloys prepared from solution, it is important to study their nucleation and growth mechanism. This was done with an original in situ TEM study in the liquid phase, in which the nucleation and growth is initiated by electron beam irradiation. Between two layers of graphene oxide, the crystal growth of Pt-Pd stabilized by oleylamine ligands was observed. It was significantly different from the growth of pure Pt. In contrast to the frequent coalescence that was commonly found for pure Pt with OAm ligands [70][72], Pt-Pd nanoalloys grew separately without coalescence until their final size. The cluster size increased as a function of the time, as t^{1/2}, which is consistent with a growth mechanism by monomer addition in a reaction limited process. Furthermore, the use of a graphene liquid cell makes it possible to observe the internal structure (lattice spacings) of the particles during their growth.

• Preparation of model catalysts and reactivity for the CO oxidation

Then, the pure Pt, Pd and Pt-Pd NPs were deposited on SiO_2 powder with little disturbance of their structure. The ligands were removed by UV-ozone, to expose the catalytic active sites before testing of their reactivity. The chosen test reaction was the CO oxidation reaction,

followed by gas phase chromatography. An improved reactivity of Pt-Pd nanoalloys compared to the pure components was noticed, especially for conditions with higher CO concentrations.

• Theoretical structure at realistic temperatures

Because of limitations in current characterization techniques to determine precisely the chemical structure, these particles were compared with theoretical equilibrium Pt-Pd nanoalloys. Using Monte Carlo simulations, with a tight binding semi-empirical interatomic potential, fitted to density-functional theory calculations, the stability of the Pd surface and Pt subsurface configuration was shown. This chemical arrangement was independent of the shape, since it was demonstrated for icosahedra and truncated octahedra. Pd surface segregation, which is strongest for the least coordinated sites, results from the lower cohesive energy of Pd as compared to Pt. The weak ordering tendency in the alloy leads to the Pt subsurface segregation. For lower temperatures, even an onion-shell structure with several symmetric layers up to the core was found. At higher temperatures, only the Pd surface and Pt subsurface are maintained. These observations can be related to a different crystal growth in solution and catalytic properties of alloyed versus pure nanoparticles. This can be understood, since this configuration represents both the influence of Pd at the surface and an electronic effect of the Pt subsurface on Pd.

• In situ environmental TEM study of the structure in gas environment

Finally, the influence of oxidizing and reducing gasses (around 1 mbar) on these small Pt-Pd nanoalloys was studied in situ with a HRTEM with environmental E-cell. Although resolution was limited, small shape changes were noticed that are consistent with previous studies of the pure components (i.e. more rounded shape in O₂). However measurements in presence of CO gas would be necessary to relate to the reactivity study. This was not possible due to contamination limitations and limited resolution.

7.1.2 Cubic core-shell Pd@Pt nanoalloys

Then, Pd@Pt core-shell structures have been obtained by growing successive amounts of Pt on Pd cubes. The Pt layer grows epitaxially on the Pd cubes, but is more concentrated at the corners, which induces sharp corners.

• In situ liquid TEM study of the nucleation and growth of a Pt layer

Similar synthesis was studied in a liquid cell, under electron beam irradiation, to get insight in the formation of the concave shape. The pure Pd nanocubes, pre-synthesized in a standard

reactor were immersed in a Pt(acac)₂ containing solution. Some changes occurred but the size increase was limited. The simultaneous increase in contrast at the corners together with the formation of concave sides was attributed to an iodide-assisted galvanic replacement reaction. Unfortunately, electron beam effects could not be avoided in this study.

• In situ environmental TEM study

By ETEM it has been observed that under 1 mbar of hydrogen, the Pd@Pt particles (prepared in a standard reactor) keep the cubic shape and under 1 mbar of oxygen, (110) facets and rounded corners appear at the edges of the cube. This was consistent with similar previous studies on the pure metals. ETEM studies did not show adsorbate-induced surface segregation.

• Preparation of model catalysts and reactivity for the CO oxidation

Next, the reactivity of the Pd@Pt core-shell cubes has been studied for the CO oxidation reaction as a function of the thickness of the Pt ad-layer. For these studies the particles were deposited on SiO₂ powder and the PVP polymer is removed by UV-ozone. A maximal reactivity has been found for an equivalent thickness of 0.4 atomic Pt layers. For this thickness the core-shell particles are more active than pure Pd cubes or similar Pt cubes reported in literature. This behavior is explained by a decrease of the adsorption energy of CO, due a compressive strain, induced by the misfit between the two metal bulk lattices and by a ligand effect due to the modification of the electronic structure of Pt atoms in contact with Pd atoms. A similar qualitative evolution as a function of thickness of the Pt layer was already observed in electrocatalysis and was also explained by the decrease of the strength of adsorbed species.

7.1.3 General progress in the research field

• Use of graphene oxide liquid cells in TEM

The obtained results of this thesis show the importance of the recent evolutions of in situ TEM for the development and application of controlled nanostructures, synthesized through colloidal methods. The several in situ growth studies, demonstrated in this thesis, encourage the further use of graphene oxide liquid cells as straightforward encapsulation technique. It was shown that the particles obtained in situ in the liquid cell can be compared with particles prepared with a reducing agent in a standard reactor. From this, conclusions on nucleation (effect of the ligands, heterogeneous vs. homogeneous nucleation), growth mode (e.g. reaction limited) or growth mechanism (e.g. galvanic replacement) were made. However it was also shown that the beam damage effects need to be considered.

• Colloidal nanoparticles as model catalysts

It was also shown in this thesis that the colloidal preparation of nanoparticles is an excellent technique to produce model catalysts, because of their homogeneous and controlled structure, especially for nanoalloys. The CO oxidation reaction is a relatively simple test reaction. It was possible to interpret some of the structure-reactivity relationships. The results suggest that bimetallic Pt-Pd can show synergetic properties in catalysis, explained by the formation of mixed bonds and the strain effects.

7.2 Research outlook

New approaches for the development of promising catalysts were demonstrated in this thesis. Finally, several concrete future developments and more general future research directions are discussed.

7.2.1 Possible future research topics

A parameter that was not explored, but would be highly interesting, is the effect of the **support**. As the particles can easily be deposited on different supports and do not change their structure. This is another advantage of the wet chemical synthesis. It would be interesting to deposit them on a reducible support (e.g. CeO₂), which makes them more active in the low temperature regime. As such, the particles can be studied at a lower temperature and possibly avoid high temperature structural changes.

Some small improvements on the gas chromatography setup could be done. A recalibration of the O_2 flowmeter to reach the very oxygen rich regime could be considered (to have more information on the structure-sensitivity of the reaction), as well as a third flow meter to add H_2 , for the study of the PROX reaction. This reaction has gained interest to remove poisoning CO from fuel cells H_2 streams.

Also the deposition on flat surfaces was initiated and can be further used as model catalyst to study the effect of the **organization and particle spacing** on the catalytic properties, e.g. by Molecular Beam Relaxation Spectrometry (MBRS). It is anticipated that regular organization of nanoparticles can promote the catalytic reaction. However, when using high vacuum techniques, the in situ cleaning of the particles should be considered.

Further optimization of the colloidal particles could be done, notably in terms of cleaning of contaminants. Especially the use of the DMSO solvent (used for the synthesis of cubic NPs)
could be replaced by a similar non-sulfur containing solvent for example NMP (however highly toxic). To avoid agglomeration, the particles could be deposited first on the support and then extensively cleaned with ethanol/acetone. However this could possibly dissolve the particles again, since they are only weakly interacting with the support.

7.2.2 Outlook for in situ electron microscopy methods

New developments in electron microscopy are promising to get further insight in structure of NPs in liquid and gas environments. Tomography, a method which makes 3D reconstructions will find its application in these type of in situ studies, both in liquid and gas (e.g. Park et al., July 2015 [185]). As such, a better insight in the influence of the walls of the liquid cell on the nucleation (heterogeneous vs homogeneous) might be obtained. Higher time and spatial resolution of new state of the art microscopes will certainly improve the quantitative measurements. As was stated before, also the development of new type of microfluidic liquid flow cells, in which two liquids can react with each other (e.g. precursor and reducing agent containing liquid) will greatly improve insights in the role of the reducing agent [106][95]. The questions that remain are the exact components of the environment present under electron beam irradiation and the implications of the electron beam on the structural changes.

It is clear that transmission electron microscopes are more and more used and have their unique place as investigation technique of catalytic nanoparticles (review Su et al., April 2015, [186]). Graphene (oxide) liquid cell is an excellent tool to investigate the nucleation of NPs starting from small atom clusters, to attain maximal resolution.

7.2.3 Outlook for catalytic colloidal nanoparticles

What is currently blocking the use of colloidal nanoparticles in real applications is the lack of reproducible and high-throughput synthesis. A reduction of the organic solvents or even a conversion to water based synthesis methods should be done to enable 'green' production methods. The deposition and cleaning stays an additional step (and cost) in the preparation. It is thus a challenge to develop particles that are much more active, to be economically beneficial for their use in real applications. Also long term stability issues need to be addressed. Multimetallic nanoalloys will further improve the reactivity and stability. It was for example calculated that the addition of Au would stabilize the Pd_xAu_{140-x}@Pt core-shell structure (July 2015, [187]). New types of catalytic nanoparticles will aid the development of new technologies for clean energy (e.g. artificial photosynthesis, fuel cells), sensors, imaging techniques, environmental pollution limitation and many more.

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List of Figures

Figure 1.1: Successive steps of the colloidal synthesis method for the preparation of a supported model catalyst
Figure 1.2: Simplified representation of the stabilization of a nanoparticle with (a) oleylamine ligands and (b) PVP polymer. (from reference [3] and [4])
Figure 1.3 : Equilibrium shapes of NPs by minimization of the surface free energy (a) truncated octahedron (b) decahedron (c) icosahedron, with red (100) and blue (111) facets
Figure 1.4: Frequently observed shapes of nanoparticles of fcc metals prepared by colloidal methods, showing the importance of the initial seed on the further shape evolution. Color code as green= (100), yellow=(111) and purple (110) facets. The parameter R is defined as the ratio between the growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ direction. (extracted from [13])
Figure 1.5 : Different chemical structures of a bimetallic nanoparticle: (a) homogeneously mixed (b) ordered (c) core@shell (d) onion-shell (e) Janus segregated structures. (from reference [16])9
Figure 1.6: Sche matic illustration of the variation in binding strength of an a dsorbant due to the interaction of the a dsorbate valence states and the d-bands of the transition metal. The filling of the antibonding states that we aken the interaction is related to the position of the d-band center compared to the Fermi level.[19]
Figure 1.7 : Illustration of the rounding of the faceted corners by high index surfaces that a ppear with the introduction of O_2 . (from reference [23])11
Figure 1.8: Statistical distribution of the shape of Au NPs on CeO_2 support, as a function of the partial pressures of P_{CO} and P_{O2} measured by ETEM. (extracted from [25])
Figure 1.9: Evolution of the atomic fractions of both elements in Rh-Pt (1:1) nanoalloys in presence of different gases at 300°C, measured by in situ ambient pressure XPS. (from [29])
Figure 1.10 : Au@Pd core-shell formation in AuPd nanoalloys in O ₂ observed by ETEM. (from [30]) 13
Figure 1.11 : Evolution of the atomic fractions of both elements at the surface in Pt-Pd nanoalloys in presence of different gases at 300°C, measured by insitu ambient pressure XPS. (from [29]) 17
Figure 2.1: Illustration of the method to keep the three neck flask under continuous argon atmosphere (a) under argon flow, the condenser and temperature probe can be put into place (b) dosing of the reactor with a balloon to compensate pressure differences while heating
Figure 2.2 : TEM images of the NPs with OAm ligands, organized on a carbon grid and corresponding size histogram below of (a) pure Pt with a verage size of 3.7 ± 1.5 nm (b) Pt-Pd (1:1) nanoalloy with a verage size of 3.2 ± 0.8 nm (c) pure Pd with a verage size of 5.0 ± 1.0 nm. The FFTs in inset illustrate the organization due to the ligands
Figure 2.3 : Representative HRTEM images of the small nanoparticles prepared with OAm ligands (a) monocrystalline elongated pure Pt (b) poorly crystallized pure Pd (c) Pt-Pd with defective, single crystal and twin structure
Figure 2.4 : Variation of the interparticle spacing of Pt-Pd NPs, due to a difference in density of NPs on the TEM grid, with a superposition of multiple 'layers' for very high concentration (left) or a less regular interparticle distance for lower concentrations (right)
Figure 2.5: Pt-Pd NPs on Al_2O_3 thin films (a) as prepared (b) after O_2 plasma cleaning during 1 min (c) and 5 min (d) after cleaning by acetic a cid (e) after UV-ozone cleaning during 20 min and (f) after Ar plasma cleaning during 30 s. The calculated FFT in the insets represents the corresponding evolution of the order (visible circle) or coales cence (diffuse circle)

Figure 2.6 : The FTIR spectra of Pt-Pd NPs deposited on KBr flat substrates and treated to remove the oleylamine ligands by the different techniques. (a) Ar plasma (d) Acetic acid are not efficient, while (b) 1 min O ₂ plasma and (c) 20 min UV-ozone decreased the OAm characteristic peaks below reference level
Figure 2.7: Importance of different steps in the deposition: (a) agglomeration when not using ultrasound mixing (b) agglomeration when not removing the non-deposited particles by a heptane wash. When using both steps, a homogenous deposition can be obtained as in (c) with an example on SiO ₂ powder
Figure 2.8: Importance of the centrifuge-redispersion step before the deposition of Pt-Pd NPs on MgO powder: TEM image of the density after (a) 1 time centrifuge-redispersion with 2h ultrasound mixing (b) 5 times (c) 6 times
Figure 2.9 : TGA of OAm-capped Pd NPs on MgO powder under Ar flow
Figure 2.10 : Ill ustration of the sequential reduction method used to prepare Pd@Pt core -shell NPs
Figure 2.11 : TEM images of the Pd seeds obtained in presence of PVP and KI in DMSO solvent (a-b) collection of cubes (40-60%), bars (40-20%) and other shapes (20%) (c) Magnified Pd cube with visible truncations and (d) high crystallinity demonstrated by the SAED pattern of the fcc crystals30
Figure 2.12 : TEM images of Pd seeds with successive cove rage of Pt, with a ddition of (a -c) 0.1 molarequivalent (d-f) 0.2 molar equivalent (g-i) 0.5 molar equivalent
Figure 2.13 : HRTEM image of the corner of a Pd seeds covered with a bout 2 equivalent layers of Pt (0.5 eq Pt/Pd precursor), with the creation of higher index surfaces
Figure 2.14 : TEM images of the etching of the Pd cores when depositing larger amounts of Pt (here: 0.5 eq Pt/Pd precursor), creating irregular structures
Figure 2.15 : TEM images of the Pd@Pt nanoparticles (a) relatively homogeneously dispersed on SiO_2 powder (b) with some local agglomeration of the particles
Figure 2.16 : TEM images demonstrating the minimal effect of UV-Ozone on the morphology: (a) $Pd@Pt_{2.2eqL}$ after 1h UVO on a carbon grid and (b) pure Pd cubes on SiO ₂ after 2h UVO
Figure 2.17 : The FTIR spectra of Pd@Pt _{0.2eqL} NPs deposited on KBr flat substrates. A decrease of the characteristic PVP peaks was observed after UV-ozone treatment. However only a combination of extensive washing (3x) and successive UV-ozone treatment can completely bring these peaks below reference level
Figure 3.1: Illustration of the reduction of metal precursors under electron beam irradiation with subsequent formation of nanoparticles, stabilized by ligands
Figure 3.2 : Method to make the graphene oxide liquid cell
Figure 3.3: Typical view of a liquid zone (containing pre-synthesized NPs) in TEM (a) with wrinkled graphene oxide over the holey circular zone and (b) irregular local contrast
Figure 3.4 : TEM images of nucleation and growth of pure Pt NPs with OAm ligands, by reduction of the electron beam, in a graphene oxide liquid cell. Nucleation starts fast and then the particles grow both by monomer attachment and frequent coalescence (beam current 4.10^4 A/m ² at a magnification of 300K)
Figure 3.5 : Pt(OAm) particle density in the liquid cell, in a fixed frame of 230 nm ² as a function of the time. The increase in particle density by nucleation up to 5 min is limited due to the competition with coalescence during the whole time interval
Figure 3.6 : TEM images of the coalesœnœ event of two pure Pt NPs, along the <111> direction 46

Figure 3.7 : TEM image of the final Pt NPs synthesized with OAm ligands in a graphene oxide liquid cell, after electron beam exposure for about 12 min and with corresponding particle diameter histogram
Figure 3.8 : TEM images of nucleation and growth of pure Pt NPs with OS ligands, by reduction of the electron beam, in a graphene oxide liquid cell. Nucleation only starts a fter 10 min irradiation, then the particles grow by both monomer attachment and coalescence (beam current 1.10 ⁴ A/m ² at a magnification of 300K)
Figure 3.9 : TEM images of coalescence events of pure Pt NPs with OS ligands. The particles can come very close without coales cence
Figure 3.10 : TEM image of the final Pt NPs synthesized with OS ligands in a graphene oxide liquid cell (from other series), after electron beam exposure for a bout 20 min and with corresponding particle diameter histogram
Figure 3.11 : Pt(OS) particle density in the liquid cell, in a fixed frame of 650 nm ² , as a function of the time. Nucleation starts only at a bout 10 min of irradiation and continues for another 10 min, with some coalescence events
Figure 3.12 : (a–g) In situ nudeation and growth of Pt-Pd NPs in the liquid cell with time, by reduction of the electron beam. The density of particles is stable after approximately 70 s of irradiation. The inset of (g) shows a faceted cluster, mostly limited by (111) and (100) facets (beam current 1.5. 10^4 A/m^2 at a magnification of 300K)
Figure 3.13 : (a) Density of clusters in the liquid as a function of the irradiation time during the nucleation and growth process of Pt-Pd NPs. (b) Cluster diameter as a function of the irradiation time during nucleation and growth process, for one isolated duster with $t^{\frac{1}{2}}$ exponential fit
Figure 3.14 : Structure and morphology evolution with time of the same Pt-Pd NP in the liquid œll between 50 and 180 s as they rotate in the solution
Figure 3.15 : Shape and crystal structure of Pt-Pd nanoalloys in liquid after longer time of observation. Both single crystals and twins are visible
Figure 3.16 : Size distribution of Pt-Pd nanoalloys with OAm ligands in the liquid cell (10min)
Figure 3.17 : In situ growth of a Pt layer on a Pd(OAm) pre-synthesized NP (conditions 0.05M Pt(a ca c) ₂ , 4 eq octylsilane and 2.10^5 A/m ² at 500K magnification) showing PdO formation56
Figure 3.18 : In situ growth of a Pt layer on a Pd (OAm) pre-synthesized NP after a bout 15 min of observation (a) same particle as in Figure 3.17 (b) other example in the same conditions (c) lower concentration 0.001M Pt(a ca c) ₂ , $1 eq$ octylsilane and 5.10^5 A/m ² at 500K magnification57
Figure 3.19 : In situ growth study of (a-b) homogeneous nucleation (conditions 0.05M Pt(a cac) ₂ , 5 eq octyl silane and 2.10^5 A/m ² , 600 K) (c-d) relatively heterogeneous nucleation on the Pd(OAm) core (conditions 0.05M Pt(acac) ₂ , 0.5 eq octyl silane and 4.10^5 A/m ² , 800K)
Figure 3.20 : Zoom of the in situ growth of a Pt layer on a Pd(OAm) pre-synthesized NP (conditions $0.05M$ Pt(acac) ₂ , 0.5 eq octylsilane and 4.10^5 A/m ² at 800K magnification): example of a more heterogeneous nucleation of Pt on the Pd seed, imaged at a tomic resolution
Figure 3.21 : Evolution with time of a Pd nanocube in a $3mM Pt(a cac)_2$ solution in a liquid cell under electron beam irradiation (3. $10^5 A/m^2$ at 800K magnification)
Figure 3.22 : HRTEM magnification of a rea 1 in Figure 3.21, showing a thin semi-epitaxial layer (as seen on the inset FFT) with expanded lattice parameter, attributed to PdO
Figure 3.23 : HRTEM magnification of a rea 2 in Figure 3.21, showing continuous lattice planes with 0.22 nm spacing, up to the surface of the concave shape. Some PdO-like component with 0.26 nm lattice spacing was formed on top
Figure 3.24 : Limited size evolution of a Pd cube in Pt(acac) ₂ liquid, shown by the white dotted line (images extracted from Figure 3.21)

Figure 4.1: Examples of frequently reported chemical equilibrium structures of Pt-Pd nanoal loys (a) surface segregation of Pd for a truncated octahedron, preferentially to low coordinated sites [54] and (b) onion-ring structure visible in the cross-sections of an icosahedron [128] (dark gray Pd, light gray Pt)
Figure 4.2 : The two different initial cluster shapes (a) truncated octahedron TOh with (100) and (111) facets and (b) icosahedron Ih with only (111) facets
Figure 4.3: (a-f) Snapshots of Pt_nPd_m TOh nanoalloys of 405 atoms (2.2 nm) at 100 K, at chosen compositions (Pt = blue, Pd=grey) and 4 graphs with segregation isotherms as a function of the difference in chemical potential (left column) and as a function of the total Pd concentration in the cluster (right column). The different type of Pd segregation sites are divided into surface sites (upper row) or concentric shells starting from the surface up to the center (lower row)
Figure 4.4: (a-f) Snapshots of Pt_nPd_m Ih nanoalloys of 147 atoms (1.5 nm) at 100 K, at chosen compositions (Pt = blue, Pd=grey) and 4 graphs with segregation isotherms as a function of the difference in chemical potential (left column) and as a function of the total Pd concentration in the cluster (right column). The different type of Pd segregation sites are divided into surface sites (upper row) or concentric shells starting from the surface up to the center (lower row)
Figure 4.5: Atomic stress on each site (from the center up to the surface) of the Pt24Pd381 TOh and $Pt_{296}Pd_{13}$ I h as compared to the pure systems. The snapshots below show the relative variation of the atomic stress (high= red and low=blue, however both color codes have an order of magnitude difference between the I h and TOh, as seen on the stress yaxis in the graphs)
Figure 4.6 : Segregation isotherms of TOh Pt-Pd nanoalloys of 405 and 1289 atoms at 100 K as a function of the difference in chemical potential for surface and core sites (left column) and for each concentric shell in the core (right column)
Figure 4.7: Segregation isotherms of Ih Pt-Pd nanoalloys of 147, 309 and 1415 atoms at 100 K as a function of the difference in chemical potential for surface and core sites (left column) and for each concentric shell in the core (right column)
Figure 4.8 : Caloric curves of Pt-Pd TOh of 405 and 1289 atoms with 66% and 42% Pd as a function of the temperature. Snapshots of the clusters at different temperatures with a color code relative to the occupation probability: red (100% occupied by Pd atoms) to blue (100% occupied by Pt atoms) going through green which is equally occupied by Pd or Pt atoms
Figure 4.9: Caloric curves of Pt-Pd Ih of 147, 309 and 1415 atoms with 71%, 66% and 60% Pd as a function of the temperature. Snapshots of the clusters at different temperatures with a color code relative to the occupation probability: red=100% Pd to blue=100% Pt
Figure 5.1 : E-cell sample holder that was used for insitu TEM observations in a gas environment 91
Figure 5.2 : Example of contamination and particle agglomeration that hinders relatively fast the further imaging during environmental microscopy (a) first image (b) after 5 min of imaging in H_2 at beam current of 10^4 A/m^2 for a magnification of 150K
Figure 5.3: Illustration of the reversible morphology changes of a pure Pt cubic nanoparticle observed by ETEM (a) particle mainly limited by (100) facets, truncated by (111) facets at the corners, observed in O_2 (b) increase of the (111) facets under H_2 gas (c) again extend of the (100) facets under O_2 which shows the reversibility of the structural changes.(from reference [147])92
Figure 5.4 : ETEM observations of oxidation-reduction gas cycles on the 2D organization of Pt-Pd NPs with OAm ligands (a-c) after reduction in H_2 (b-d) in 0.1 mbar O_2 : no effect was noticed
Figure 5.5 : Effect of the oxidation -reduction gas cycles on the shape of alloyed Pt-Pd NPs :
Figure 5.6: ETEM observations of a Pd cubes under (a) 3 mbar H_2 with limited effect on the shape and (c) under 1 mbar O_2 with extension of the (110) facets as presented in the model (b-d)

Figure 5.7 : ETEM observations of another Pd cube under (a-b) 3 mbar H ₂ with limited effect on the shape and (c) under 1 mbar O ₂ with extension of the (110) facets, better visible in the dark field images (d) of the same particle. The faceting of the comer is indicated with an arrow
Figure 5.8 : ETEM observations of two different series (right and left) of Pd@Pt _{0.4eqL} under (a-b) 1 mbar H_2 with limited effect on the shape and (c-f) under 1 mbar O_2 with a visible rounding of the shape corners and extension of the (110) facets
Figure 5.9: similar ETEM observations of a series of Pd@Pt _{0.4eqL} under (a) 1 mbar H ₂ with limited effect on the shape and (b) under 1 mbar O ₂ with a visible rounding of the sharp corners and extension of the (110) facets. One of the particles rotated while imaging in O ₂ , and 0.22 nm (111) lattice spacing became dearly visible for the whole particle up to the surface
Figure 5.10 : Oxide formation sometimes observed for the Pd and Pd@Pt nanocubes (a) formation of a shell layer with lower contrast (b) fringes of 0.26-0.27 nm which are compatible with PdO
Figure 6.1 : Overview of the setup: (left) flow meters and the oven containing the sample, (right) the gas phase chromatograph and an example of a spectrum with the different peaks (CO_2 , O_2 , N_2 and CO) detected as a function of the time
Figure 6.2 : Illustration of the waiting time after temperature increment to reach steady state conditions for a flow of 22.3 ml/min
Figure 6.3 : Linear response of the ratio (peak surface area $CO/(CO+O_2)$) detected by the chromatograph, when changing the ratio x_{CO} by the flow meters, for a constant flow rate of 22.3 ml/min
Figure 6.4 : CO conversion as a function of temperature for small Pt, Pt-Pd and Pd nanoparticles for the first and third measurement under same conditions (reaction gas composition x _{co} =0.2, flow rate 22.3 ml/min). The arrows indicate a small activation of Pt-Pd NPs
Figure 6.5 : CO conversion as a function of temperature for small Pt, Pt-Pd and Pd nanoparticles for the second measurement (reaction gas x_{co} =0.4, flow rate 22.3 ml/min)113
Figure 6.6 : CO conversion as a function of temperature for cubic Pd and Pd@Pt nanoparticles for the second measurement (reaction gas x_{co} =0.4, flow rate 22.3 ml/min)
Figure 6.7 : Activation of the Pd@Pt _{0.4eqL} after 3 consecutive measure ments (arrows) and simil a r activity after 3 consecutive measure ments of Pd@Pt _{2.2eqL}
Figure 6.8 : Arrhenius plots of the Pt, Pt-Pd and Pd nanoparticles with linear regression
Figure 6.9 : Arrhenius plots with linear regressions of the cubic Pd and Pd@Pt NPs
Figure 6.10 : Determination of the apparent activation energy E_a from the Arrhenius plots for different gas compositions (x_{co} =0.4 and x_{co} =0.2) for Pd@Pt nanopartides121
Figure 6.11 : Compensation plot of the parameters of the Arrhenius equation ln A vers us E_a for all measurements showing the linear dependence122
Figure 6.12 : Determination of the orders in O_2 and CO by a least square fitting of the rate function (CO_2 surface area) for small Pt, Pt-Pd and Pd nanoparticles for x_{CO} =0.2 and 0.4 (second and third measurement)
Figure 6.13 : Determination of the orders in O_2 and CO by a least square fitting of the rate function (CO ₂ surface area) for Pd@Pt nanocubes for x_{CO} =0.2 and 0.4 (second and third measurement)
Figure 6.14 : The small(a) Pt (b) Pt-Pd (c) Pd nanoparticles prepared with OAm ligands after deposition on SiO ₂ , 20 min UV-ozone and 3 cydes of CO oxidation up to 210°C
Figure 6.15 : TEM images of the Pd@Pt _{1.6eql} /SiO ₂ (a) before and (b) after the reaction up to 258°C and 7% conversion

List of Tables

Table 1:1: Overview of some of the reported Pt-Pd nanoalloy structures (alloyed or core-shell) showing an increased activity in electrochemical reactions (red=Pd, blue=Pt)
Table 1:2 : Estimations of the adsorption energies of O_2 , H_2 and CO on Pt and Pd surfaces17
Table 2:1: EDX analysis for different quantities of Pt added to the solution of Pd cubes
Table 3:1: Comparison of the sizes, standard deviations and coefficients of variation obtained in the standard reactor and liquid cell with OAm ligands
Table 4:1 : Parameters of the Pt-Pd SMA potential71
Table 4:2 : Lattice parameters, cohesive energy and surface energies of Pd and Pt. Theexperimental values of the lattice parameters and cohesive energy are taken from Kittel [119],the surface energies from De Boer et al. [120].71
Table 4:3 : Permutation and dissolution enthalpy calculated by DFT and SMA potential compared to the experimental values in the two diluted limits of the mixing enthalpies at 300K. [122]
Table 6:1 : Different literature results of the CO oxidation on controlled shapes of pure Pt and Pd nanoparticles, prepared by colloidal methods
Table 6:2 : Different literature results on the CO oxidation on Pt-Pd nanoalloys, prepared by wet impregnation
Table 6:3 : The variable O_2 and CO flow rates for a constant total flow rate of 22.3 ml/min, with associated x_{CO} or P_{O2}/P_{CO} ratios
Table 6:4 Temperatures for 2% conversion and 50% conversion for the three successivemeasurements on Pt, Pt-Pd and Pd nanoparticles114
Table 6:5 Sample characteristics for reactivity tests of cubic Pd@Pt nanopartides
Table 6:6 Temperatures (°C) for 5% CO $\cos v$ ersion of the cubic Pd and Pd@Pt nanopartides 115
Table 6:7 Apparent a ctivation energy E_{a} and reaction orders determined for the small Pt, Pt-Pd and Pd NPs
Table 6:8 Apparent a ctivation energy E _a , TOF and reaction orders determined for the cubic Pd and Pd@Pt NPs 120

List of Equations

$\label{eq:constraint} Equation \ 4.1: SMA-TB \ potential \ energy \ of \ an \ atom \ i \ of \ type \ \alpha \ as \ a \ sum of \ an \ attractive \ band \ energy \ term \ and \ a \ pairwise \ repulsive \ term \$
Equation 4.2 : Total energy of a binary system as a sum of the energy of the atoms
Equation 6.1: General Langmuir-Hinshelwood expression for the rate of the bimolecular CO oxidation reaction, with kLH the LH rate constant, θ the coverage. The rate constant can be derived from the Arrhenius theory with vLH a prefactor, ELH the energy barrier, k the Boltzmann constant and T the temperature
Equation 6.2: Limiting case of strongly bound CO of the Langmuir-Hinshelwood equation, with the $E_{CO,des}$ the CO desorption energy and <i>PO2</i> and <i>PCO</i> the partial pressures
Equation 6.3 : Arrhenius equation used to determine the apparent activation energy E_a , with R the gas constant and A a frequency factor
Equation 6.4: Compensation equation showing a linear correlation between the parameters of the Arrhenius equation
Equation 6.5 : Determination of the reaction orders x and y by fitting the measured CO $_2$ surface areas for different $PO2$ and PCO

List of Abbreviations and symbols

c-FEG	Cold Field Emission Gun			
CMC	Canonical Monte Carlo simulation			
Cs	Spherical aberration corrector			
C _v	Coefficient of variation			
DFT	Density Functional Theory			
DP-ETEM	differentially pumped ETEM			
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy			
Eo	Reduction Potential			
Ea	Apparent Activation Energy			
E-cell	environmental cell			
EDX	Energy Dispersive X-ray Spectroscopy			
EELS	Electron Energy Loss Spectroscopy			
ETEM	environmental transmission electron microscopy			
EXAFS	Extended X-ray Absorption Fine Structure Analysis			
FAO	Formic Acid Electro-Oxidation			
FCC	Face-Centered Cubic (lattice)			
FFT	Fast Fourier Transform			
FTIR	Fourier Transform Infrared Spectroscopy			
GISAXS	Grazing Incidence Small Angle X-ray Scattering			
GIXRD	Grazing incidence X-ray diffraction			
HRTEM	High resolution transmission electron microscopy			
Ih	Icosahedron			
k	Boltzmann constant			
LEIS	Low energy ion scattering			
MC	Monte Carlo (simulations)			
MEMS	Microelectromechanical System			
NP(s)	nanoparticle(s)			
ORR	Oxygen Reduction Reaction			
PROX	Preferential Oxidation (of CO in excess H ₂)			
rpm	Revolutions per minute			
SAED	Selected Area Electron Diffraction			
S-GCMC	Semi-grand Canonical Monte Carlo Simulation			
SMA-TB	Second Moment Approximation Tight Binding (potential)			
Т	temperature			
t	time			
TEM	Transmission Electron Microscopy			
TOF	Turnover Frequency			
TOh	Truncated Octahedron			
UHV	Ultra-High Vacuum			
VASP	Vienna Ab initio simulation package			
wt.%	Weight percent			
XPS	X-ray photo-Electron Spectroscopy			
γ	Surface energy			
σ	Standard deviation			

List of Chemical Abbreviations

Chemicals used in this work are marked in bold.

AA	Ascorbicacid	HQ OH OH
C15	Pentadecane	
СА	Citricacid	
DCB	1,2-Dichlorobenzene	
DDA	Dodecylamine	······································
DMSO	Dimethylsulfoxide	H3C CH3
HDA	Hexadecylamine	NH ₂
HDT	Hexadecylthiol	
MB	Morpholine borane	H, BH ₃
OA	Oleicacid	Сн
OAm	Oleylamine	NH ₂
OS	n-octylsilane	~~~~
P123	Triblock Pluronic copolymer	
Pd(acac)₂	Palladium(II)acetylacetonate	
Pt(acac)₂	Platinum(II)acetylacetonate	
PVP	Poly(vinylpyrrolidone)	
ТТАВ	Tetradecyltrimethylammonium Bromide	N ⁺ Br
p-CNB	Penta-Chloronitrobenzene	

The catalytic properties of metal nanoparticles can be improved by the alloying effect. Nanoalloys homogeneous in size, shape and chemical composition can be prepared with the colloidal synthesis method, with an ordered, random or core-shell chemical structure.

Nucleation and growth of colloidal Pt-Pd nanoalloys were studied by transmission electron microscopy (TEM), in standard conditions and in situ with the aid of a graphene oxide liquid cell. The growth kinetics of homogeneous Pt-Pd nanoalloys corresponds to the direct incorporation of the monomers in solution. It was compatible with a process limited by the surface reaction, without coalescence (Lifshitz-Slyozov-Wagner mechanism). On the contrary, coalescence occurs during the growth of pure Pt nanoparticles.

The theoretical structure of Pt-Pd nanoalloys is determined by Monte Carlo simulations. The most stable structure corresponds to a Pd surface and Pt subsurface layer, which is stable up to high temperatures. These calculations show that electronic effects, resulting from the alloying effect, are possible at the surface.

The effect of adsorption of oxidizing or reducing gasses on the shape of pure Pd nanocubes and coreshell Pd@Pt nanocubes is studied in situ by TEM with an environmental cell. The observed changes in a few mbar of oxygen are due to the development of higher index facets.

The CO oxidation reaction is used to compare the reactivity of homogeneous Pt-Pd nanoalloys and core-shell Pd@Pt nanocubes with increasing coverage of Pt at the surface. A maximal reactivity is attained for a low coverage. The effect is interpreted by a decrease in adsorption energy of CO, due to electronic effects originating from the lattice mismatch between Pt and Pd and the mixed Pt-Pd bonds.

Keywords: nanoalloys, core-shell structure, in situ TEM (in gas and liquid), model catalyst, Pt-Pd, colloidal synthesis

Les propriétés catalytiques des nanoparticules métalliques peuvent être améliorées par effet d'alliages. La synthèse en solution par voie colloïdale permet de préparer des nanoalliages homogènes en taille, en forme et en composition chimique, de structure ordonnée, désordonnée ou cœur-coquille.

La nucléation et la croissance des nanoalliages de Pt-Pd sont étudiées ici par microscopie électronique en transmission (MET), en condition standards, puis in situ dans une cellule liquide formée par des feuilles d'oxyde de graphène. La cinétique de croissance des nanoalliages de structure homogène de Pt-Pd correspond à l'incorporation directe des monomères en solution, compatible avec un processus limité par la réaction de surface, sans phénomène de coalescence (mécanisme de Lifshitz-Slyozov-Wagner). Par contre, la coalescence intervient au cours de la croissance des nanoparticules de Pt pur.

La structure théorique à l'équilibre de nanoalliages de Pt-Pd est déterminée par des simulations Monte Carlo. La structure la plus probable correspond à une surface riche en Pd et à une sous couche atomique riche en Pt, stable à des températures élevées. Ces simulations montrent que des effets électroniques résultant de l'effet d'alliage, sont possibles à la surface.

L'effet de l'adsorption de gaz oxydants ou réducteurs sur la forme de nanocubes de Pd et de nanocubes cœur-coquilles de Pd@Pt, est étudié in situ par microscopie environnementale sous pression de quelques mbar, dans un porte objet environnemental. On observe des changements de formes sous oxygène, dus au développement de facettes d'indices plus élevés.

La réaction d'oxydation du CO est utilisée pour comparer la réactivité des nanoalliages de Pt-Pd et des nanocubes cœurs-coquilles de Pd@Pt en fonction du recouvrement de Pt à la surface. La réactivité maximale pour un faible recouvrement est interprétée par une baisse de l'énergie d'adsorption du CO liée au désaccord paramétrique entre le Pt et le Pd et à la modification de la structure électronique du Pt lié au Pd.

Mots-clés: nanoalliages, structure cœur-coquille, MET in situ (en milieu gazeux et liquide), Pt-Pd, catalyseur modèle, synthèse colloïdale