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Nanocatalysts: Properties and applications

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Chapter 1

Introduction

1. Nanochemistry

Over the past few decades chemistry has contributed a lot to the knowledge of nanoparticles (NPs).^[1-4] In the beginning of the 20th century, the “*nano-era*” was undergoing tremendous growth due to pioneering contributions from Ostwald, Faraday, Mie, Svedberg and Zsigmondy.^[5, 6] Then the revitalization came in 1980s mainly by the groups of Henglein, Kreibig, Rao and Schimdt.^[3, 7, 8] Since then, significant advances in both experimental and theoretical aspects have led to an explosion of interest in the areas of nanoscience and nanotechnology. This is attracting increasing investments from government and industries from many parts of the world.^[9] Nanomaterials are used in various applications such as catalysis^[10, 11], optical systems^[12, 13], drug delivery^[14, 15] and biological sensors^[16, 17], quantum computers^[18] and industrial lithography.^[19]

Till today the aim of those studies is to understand the changes in the physicochemical properties in nano-structured materials compared with the bulk or with individual atoms. In the nano-scale regime neither quantum chemistry nor classical laws of physics hold.^[20] Nanomaterials have strong chemical bonding and delocalization of electrons that can vary with the size of the system. This effect leads to unique optical, electronic, magnetic, thermal, catalytic and mechanical properties that are completely different than the bulk metal.^[21]

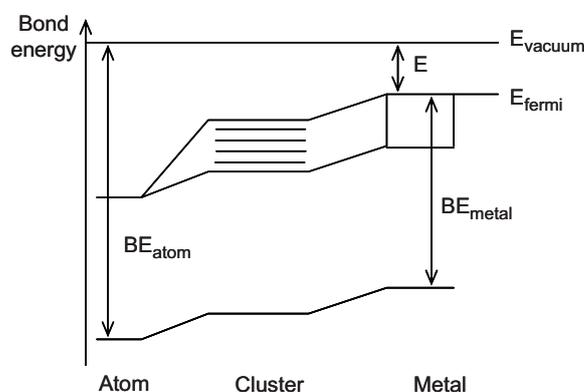


Figure 1. Schematic presentation of energy band structure of atom, cluster and metal.

The electronic energy levels (bond energy, BE) in NPs are not continuous as in the bulk metal, but are discrete, due to the confinement of the electron wave function in the finite physical dimensions of the particle (see figure 1). With increasing cluster size, the gradual development of metallic bands from single atomic orbitals is observed in the

valence band region. Additionally, a well-defined Fermi edge develops in clusters containing several thousands of atoms, which separates occupied and unoccupied electronic states.^[8]

1.1. Synthesis and stabilization of NPs

In general, NPs are composed of metals in their neutral valence state or their oxides, sulphides or selenides.^[22] During the past few decades many methods were developed for preparing NPs with well defined shapes and sizes.^[8] These methods range from chemical to metal vapour synthesis.^[4] In metal vapour synthesis, atomic metal vapour is condensed in a dispersing medium at low temperatures.^[23] In chemical synthesis of NPs in solution, the reducing agent and stabilizing agent are the two major parameters. The most commonly used reducing agents are sodium borohydride^[24, 25], sodium citrate,^[26, 27] hydrotriorganoborates,^[28] hydrogen gas and organic solvents like ethanol and dimethylformamide.^[29] Other reducing methods involved radiolysis^[30], electrolysis^[31], thermolysis^[32], laser ablation^[33] and photolysis.^[34, 35]

NPs must be stabilized by molecules attached at their surface or must be embedded in a solid matrix to avoid aggregation. In the absence of stabilizing agents, two NPs will coagulate mainly due to Van der Waal's forces.^[36] This is avoided by steric and electrostatic stabilization.^[1] These stabilizers are mainly long chain molecules such as polymers^[37], surfactants^[38, 39] and the coordinating ligands.^[40] Alternatively NPs can be grown in confined solid matrices such as zeolites^[41], alumina.^[42]

1.2. Application of NPs in catalysis

Nanocatalysis is a rapidly growing field, which involves the use of NPs as catalysts for a variety of reactions.^[43] The important difference between NPs and bulk solids is, the ratio between the number of surface and bulk atoms.^[4] This property can be exploited in processes where surfaces are important, such as catalysis. For example, a particle, consisting of only 201 atoms has approximately 60% of the atoms at the surface of the particle.^[44] Numerous review articles are published on the use of colloidal and supported transition metal NPs as catalysts for a variety of organic and inorganic reactions.^[10, 45, 46]

One of the first processes using such catalysts is the catalytic reforming in refineries.^[47] Supported catalysts containing Pt and Re NPs were first introduced in industry in the 1960s and 1970s.^[48] Zeolites supported noble and non-noble metal NPs are currently used in hydrogenation, hydrocracking and aromatization processes.^[49-51] More

recently, metal NP-catalysts were successfully employed in automotive catalytic converters.^[52] In homogenous catalysis, as early as 1986, Lewis *et al.* envisaged the participation of Pt NPs in catalytic hydrosilylation reactions.^[53] Since then, noble-metal NPs catalysts appeared in numerous reports and reactions.^[54-57] Part of this thesis deals with the mechanism of nanoparticle catalyzed C-C coupling reactions.

1.3. Application of NPs in optics

Aggregates of a few, up to several thousands of atoms, show very interesting optical properties. This was understood already by Mie, who wrote in 1908^[5, 58]

“Da Goldatome sich sicher optisch anders verhalten als kleine Goldkugeln wäre es daher wahrscheinlich sehr interessant, die Absorption der Lösungen mit allerkleinsten amikroskopischen Teilchen zu untersuchen und gewissermaßen optisch den Vorgang zu verfolgen, wie sich die Goldteilchen aus den Atomen aufbauen.”

—Gustav Mie

One of the unique properties of metal NPs is the surface plasmon resonance (SPR).^[59, 60] In metal NPs, the resonance band is generated by the coherent excitation of conduction band electrons with incident wave. This excitation is called a SPR. The SPR resonance can take place in metal NPs bigger than 5 nm, with visible light. In smaller NPs, SPR is rather damped.^[13] SPR has enabled a vast array of applications, including surface-enhanced spectroscopy, biological and chemical sensing, cancer therapy and lithographic fabrication.^[61, 62] Plasmonic materials can already be found in commercial instruments, such as the BIAcore®, which monitors the thermodynamics and kinetics of biological binding processes using SPR spectroscopy.^[63] Major part of the work presented here, utilizes the SPR of NPs to study the mechanism of NPs formation, measuring their size and determining their shape.

2. Surface plasmon resonances (SPR) in metal NPs

The SPR is the interaction of electrodynamic waves with the surface of the NPs and these interactions are very well described by Maxwell's theory^[64] and a simple semi classical model. These resonances are electromagnetic modes bound to metal-dielectric interfaces, involving charges in the metal and electromagnetic fields in both media. The plasmon maxima (λ_{max}) depend strongly on the exact properties of both the metal (complex dielectric function, corrugations, roughness) and the refractive index of the media.^[58, 65] In

small NPs, the complex dielectric property (ϵ) is a function of the frequency of the incident light as well as particle size.^[66]

2.1. Semi classical model

Many properties of particle plasmons are qualitatively understood by the semi-classical model. Since the diameter of a nanoparticle is on the order of the penetration depth of electromagnetic waves in metals, the excitation light is able to penetrate the particle. The field inside the particle shifts the conduction electrons collectively with respect to the fixed positive charge of the lattice ions. The electrons build up a charge on the surface at one side of the particle. The attraction of this negative charge and the positive charge of the remaining lattice ions on the opposite side results a restoring force (see figure 2). If the frequency of the excitation light field is in resonance with the eigen-frequency of this collective oscillation, even a small exciting field leads to a strong oscillation. The resonance frequency is mainly determined by the strength of the restoring force. This force depends on the separation of the surface charges, i.e. the particle size, and the polarizability or dielectric properties of the medium between and around the charges. The alternating surface charges effectively form an oscillating dipole, which radiates electromagnetic waves. The magnitude of the oscillation depends only on the damping involved due to size confinement effect of NPs.^[67]

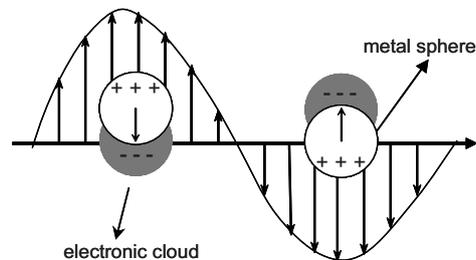


Figure 2. Schematic of visible light interaction with NPs.

2.2. Mie theory and metal NPs

The resonance spectra of dilute dispersions can be calculated using Mie theory. Mie was the first to solve Maxwell's equation for light interacting with small spheres. Assuming that NPs behave as frequency-dependent dielectric media, Mie's solution yields the particle extinction cross-section, C_{ext} . For spherical particles with a frequency

dependent dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$, embedded in a medium of dielectric function ε_m , C_{ext} is given by,

$$C_{ext} = \frac{2\pi}{K^2} \sum (2n+1) \Re(a_n + b_n) \quad (1)$$

where $K = 2\pi(\varepsilon_m/\lambda)^{1/2}$ and \Re is the real part of the Mie scattering coefficients a_n and b_n , which are calculated by:

$$a_n = \frac{m \times \varphi_n(mx) \times \varphi_n'(x) - \varphi_n(x) \times \varphi_n'(mx)}{m \times \varphi_n(mx) \times \xi_n'(x) - \varphi_n'(mx) \times \xi_n(x)} \quad (2)$$

$$b_n = \frac{\varphi_n(mx) \times \varphi_n'(x) - m \times \varphi_n(x) \times \varphi_n'(mx)}{m \times \varphi_n(mx) \times \xi_n'(x) - m \times \varphi_n'(mx) \times \xi_n(x)} \quad (3)$$

with $m = \sqrt{\varepsilon_r} = N_{particle}/N_{medium}$ and the Riccati-Bessel functions φ_n and ξ_n . m is the strong function of frequency of the incident light and the size of the particle.^[68] A detailed description of Mie theory is given in Chapter 3.

2.3. Electronic effects on SPR

The SPR depends strongly on the electron density inside the NPs. The plasmon band shifts upon adding or subtracting electrons to the overall metallic core. NPs in solution are rarely ‘‘naked’’. Their surface is covered with stabilizing molecules or ligands, such as amines, thiols and phosphines. This shell, strongly impacts the plasmon behaviour of NPs. First because it modifies the dielectric constant of the surrounding medium and second, they interact electronically with metal atoms. They also partially reduce or oxidize the NPs.^[66] In standard coordination chemistry, the electron density on the metal centre is not only directed by the ligands donating properties but also by their ability of back donation from the metal.^[69] Interestingly, the same is true for metallic NPs. The association of a metal oxide NP and a noble metal NP results in a red shift of the plasmon peak of the latter.^[70] This can be rationalized considering that the oxide part deprives the NPs from a part of its electron density.

2.4. Size effect of metal NPs on SPR

The influence of NPs size on the SPR is a question that has arisen very early.^[7] Dielectric properties of the material are a strong function of the size of NPs and in turn affect the position and bandwidth of SPR. It is generally accepted that a good approximation to the dielectric function of small particles is easily obtained from the bulk

dielectric function.^[13] In the 19th century, Drude developed a simple model based on the kinetic gas theory for describing the size and frequency dependent dielectric function $\epsilon(\omega)$.^[71] It is mainly the combination of interband term $\epsilon_{IB}(\omega)$, Drude's term $\epsilon_D(\omega)$, and the damping constant γ_0 . Interband term is included due to nonradiative damping. The nonradiative damping is due to a dephasing of the oscillation of individual electrons. In terms of the Drude-Sommerfeld model this is described by scattering events with phonons, lattice ions, other conduction or core electrons, the metal surface and impurities. According to Pauli's exclusion principle, the electrons can only be excited into empty states in the conduction band. These excitations can be divided into inter- and intraband excitations by the origin of the electron either in the d -band or the conduction band. For small particles, the electron surface scattering becomes more important. Since the size of the metal particle is almost equivalent to the mean free path of conduction electrons, it leads to additional collisions of the conduction electrons.^[72]

Many theories have been studied to correlate the size to the SPR position some predicting a blue shift, some a red one; others no shift at all.^[7] In fact, experimental results finally evidenced a blue shift of the SPR on decreasing the NPs size.^[73] In the case of noble metal, the existence of d electrons induces a mutual s - d polarisation. In the same way, the bandwidth grows upon increasing the mean NP's size.^[74]

2.5. Morphology effect on SPR

Since the shape and size of a metallic nanoparticle dictate the spectral signature of its plasmon resonance, the ability to change these two parameters and study the effect on the SPR is an important experimental challenge.^[65] Especially Au, Ag and Cu anisotropic NPs show multiple peaks. The incident light is polarized in different direction due to sharp edges of anisotropic NPs. It is tedious to calculate the Mie absorption spectra of those particles

In the case of nanorods, plasmon absorption splits into two bands corresponding to the oscillation of the free electrons along and perpendicular to the long axis of the rods. With the increased aspect ratio of the rods, the plasmon maxima shift to the higher wavelength. For these objects, the dielectric medium seems to be dependent on the aspect ratio in a non-linear fashion.^[75] For more complicated shapes, other model like dipole-dipole approximation (DDA) is an ideal tool for predicting plasmon properties. Schatz *et al.* evidenced recently that three-tip-star like NPs featured SPR, which are red-shifted (by 130 to 190 nm) compared to the spherical equivalents.^[76] Moreover, DDA showed that the

SPR is mainly determined by the influence of the tips. Triangular nano-plates show four plasmon peaks. These peaks are attributed to the out of-plane quadrupole, in-plane quadrupole, and in-plane dipole plasmon modes. Hexagonal nanoplates show broad plasmon peaks. (in general all these anisotropic particles show broad absorption peaks). Thus, single NP spectroscopy is the best way for better understanding of their SPR properties.^[77]

2.6. Effect of surrounding medium refractive index on SPR

Another major factor is the refractive index (RI) of the medium. Mie theory can predict the variation in SPR with RI of solvent and stabilizer. In some cases, the variation in the λ_{max} of SPR is linearly dependent on the solvent RI. According to the Drude's model, the SPR peak position, λ , is related to the RI of the surrounding medium and eventually dielectric index (ϵ_m) by the relation,

$$\lambda = \lambda_p^2 (\epsilon^\infty + 2\epsilon_m) \quad (4)$$

where λ_p is the bulk plasmon wavelength and ϵ^∞ is the high frequency dielectric constant due to interband transitions. Murray *et al.*^[78] then modified this equation for contribution of RI of the organic stabilizer shell around metal nanoparticle as,

$$\lambda = \lambda_p^2 \left[(\epsilon^\infty + 2\epsilon_m) + 2g(\epsilon_s - \epsilon_m)/3 \right] \quad (5)$$

where ϵ_s is the dielectric constant of the shell layer and g is the core to shell volume ration.

2.7. Surface plasmons and transition metal NPs

Most of the past work focused on Au, Ag and Cu NPs. These metal NPs show the distinct surface plasmon peak. On the other hand, *d*-block metal NPs absorption spectra do not have particular structure, giving broad or at least partly resolved absorption bands in and near the UV region. The continuous absorption is due to damping by the *d-d* interband transitions. This leads to large values of the imaginary part of the refractive index (ϵ'') in the visible part of the spectrum, which causes additional damping of the spectra.^[79]

3. Nanoparticles in solution

Although colloidal chemistry in last few years offered various possibilities of preparing NPs in solution, controlling and measuring their size and shape in a simple way remains a major challenge.^[80] In the literature generally a phenomenological approach is encountered. Attempts are made to deduce a mechanism of formation from the structure of

the product. On “super-saturation, nucleation, growth” a plethora of theories and interpretations is encountered, which must be taken into account to understand how a nanoparticulate system is formed.^[81] This knowledge is of prime importance as only with the mechanistic aspects of particle formation, one can manipulate the process specifically. This is done by variation of the process parameters or by using suitable additive molecules. Morphology mainly depends on the growth mechanism of NPs. In this thesis we focus on NPs formation by reduction of metal salts in solution in the presence of stabilizer.

The metal NPs formation goes through three basic steps explained by Turkevich.^[82] 1) reduction of metal ions to metal atoms, 2) nucleation and 3) growth of NPs. Later one intermediary step was added that is called autocatalysis.^[83] Since the nucleation and the growth cannot be analyzed separately, it is always difficult to understand the evolution of different size and shape of the particles at early stages of their formation. Various reports showed the reducing agent and templating effect of the stabilizer and this can lead to the different shapes of the NPs.^[84, 85, 46, 86] Another major problem is the unavailability of easy and fast measurements of the NPs size. One of the aims of this thesis is to find the optimum and simple solution on these problems. They are explained in further sections.

3.1. Growth mechanisms of metal NPs

In the 1950s, LaMer and co-workers extensively developed their mechanistic scheme for the formation of colloids or clusters in homogeneous, initially supersaturated solutions.^[87] Their mechanism assumes that homogeneous nucleation occurs via a stepwise sequence of bimolecular additions until a nucleus of critical size is obtained. According to the fluctuation theory, the energy barrier to nucleation can only be surmounted in supersaturated solutions, where the probability of such bimolecular encounters is sufficiently high. Further growth on the nucleus is spontaneous but diffusion-limited (i.e., limited by diffusion of precursor to the nuclei surface). Others, however, dispute LaMer’s nucleation mechanism, finding kinetics in gold sol formations that are incompatible with the super saturation hypothesis. In the late 1990’s pioneering work of El-sayed and Murphy gave new insight to the mechanism of nanoparticle formation.^[40, 84, 88] Reduced metal atoms cluster to form seeds (typically less than 1 nm) that act as nucleation centres. Metal ions that colloid with these seeds will be trapped and autocatalysed.^[89] Another hypothesis proposes that two or more metal atoms form an irreversible “seed” of stable metal nuclei (figure 3). The diameter of the “seed” nuclei can be well below 1 nm

depending on the strength of the metal to metal bonds and the difference between the redox potentials of the metal salt and the reducing agent applied.

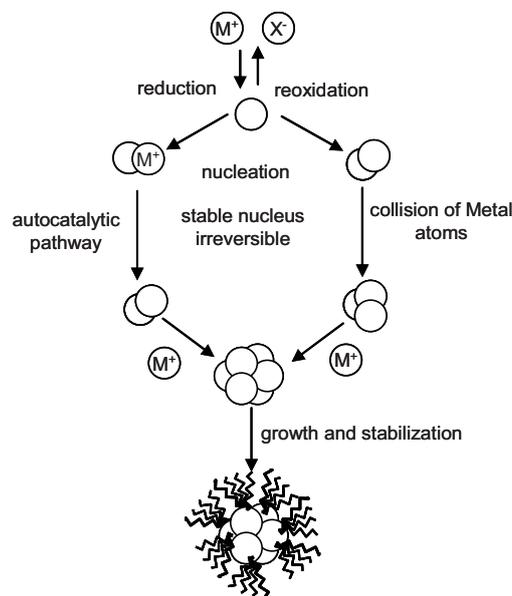


Figure 3. Schematic of the two proposed pathways for the nanoparticle formation.

Watzky *et al.* proposed a mechanism describing growth of Pt and Ir NPs.^[90] They used H_2 as a reducing agent for metal ions and for simultaneous hydrogenation of cyclooctene to the corresponding octane. Then measuring the H_2 uptake they arrived to the detailed kinetic model as shown in figure 4 (top). The kinetic profile of the nanoparticle growth always shows a 's' type curve as shown in figure 4 (bottom). The first induction period shows the reduction followed by nucleation. In the embryonic stage of the nucleation, the metal salt is reduced to give zero valent metal atoms. These atoms can collide with metal ions or other metal atoms to form nuclei. In a subsequent autocatalytic reaction the surface of these nuclei further catalyzes the reduction of metal ions to form small clusters. Once all metal ion precursors are consumed the growth stops. Further growth only occurs by aggregation of small leading to larger clusters. The relative rates of all these processes determine the final size of the NPs.

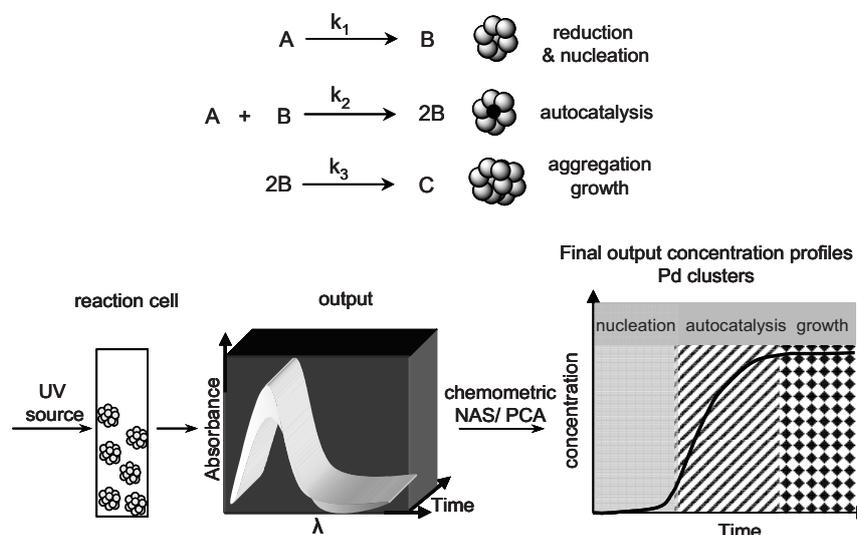


Figure 4. (Top) Three step cluster formation and growth mechanism. A, B, C denote metal ions, seeds and large clusters respectively. (Bottom) shows the schematic diagram of typical cluster growth.

3.1.1 Using chemometrics to interpret nanoparticle growth mechanisms

After understanding the growth mechanism of NPs and their UV-visible properties one has to know the extraction of the required entity from the UV spectra to establish its kinetic profile. Chemometrics is one of the simplest and most effective tools to achieve this. We will discuss some important aspects and some definitions of those tools that are used in this thesis.

Most spectra obtained in *in-situ* spectroscopy consist of the contributions from all compounds in the mixture, e.g. solvent, reactants, catalyst, etc. resulting in severe spectral overlap. Hence, the Net Analyte Signal (NAS) approach can be used to extract information on chemical composition from these spectra.^[91] The NAS concept was introduced and was subsequently applied in several studies by Lorber.^[92] This method reduces calibration efforts. Even with few calibration samples one can assess whether the calibration is feasible at all. The absorbance spectrum of a mixture of spectroscopically active substances ($k = 1, \dots, K$) is measured at J wavelengths. Assume that the analyte of interest k , is one compound in this mixture. All the remaining compounds are called interferents.

Each spectrum represents a vector in the J dimensional space. The length and direction of this vector translates, the spectrum's intensity and shape respectively.

This approach assumes that the conditions under which the Beer–Lambert law is valid are satisfied. \mathbf{R}_k is the matrix composed of spectra with the analyte of interest, formed by the absorbance spectra of samples containing the analyte, while \mathbf{R}_i is the matrix composed by the interferents. The net vector of interested analyte can be divided into two parts. One, parallel and the second, orthogonal to the interferents space represented as \mathbf{r}_k^{\perp} as shown in figure 5. The \mathbf{r}_k^{\perp} component is unique for this particular analyte. In this way each spectrum can be decomposed in a part orthogonal to the interferent's space and a part that lies in the interferent's space. The latter can be described as a linear combination of the interferents. So the procedure for finding the concentration profile of the analyte of interest is as follows:

- 1) Calculate the \mathbf{r}_k^{\perp} vector using different calibration samples. This also called as NAS vector.
- 2) Calculate the vector in the same direction of \mathbf{r}_k^{\perp} from reaction spectra (i.e. the unknown concentration r_{un}) represented as \mathbf{r}_{un}^{nas} .
- 3) The product of this vector and the reaction spectra will give the concentration of the required analyte.

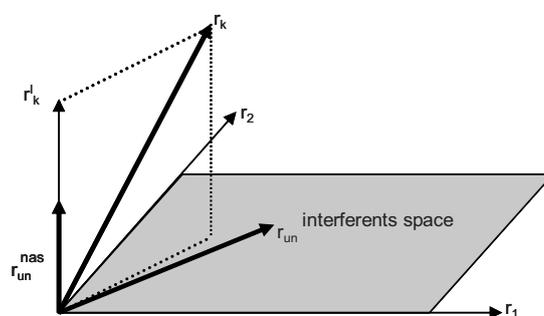


Figure 5. Schematic presentation of the NAS approach.

Using NAS approach and *in-situ* UV-visible spectroscopy one can find the concentration profiles with respect to time. In our case the analyte of interest are the metal nanoclusters. These profiles can then be modelled using the three steps mechanism (as discussed in earlier section). One can obtain different rate constants of intermediary steps. This gives the quantitative information about the cluster growth mechanism.

3.2. Measuring the size of NPs

There are different traditional methods to measure the size of the NPs such as transmission electron microscopy (TEM), X ray diffraction (XRD), dynamic light scattering (DLS), atomic force microscopy (AFM).^[93] All these equipments have advantages and disadvantages. Some of the most important disadvantages are tedious sample preparation; equipment availability and the cost of measurements but most of these instruments give accurate results. On the other hand UV-visible spectroscopy is a simple instrument and can be used effectively for measuring the size of NPs using their SPR properties. It is known that metals like Au, Ag and Cu show a significant shift in the surface plasmon resonance with respect to their size, shape and their surroundings.^[66] The advantage is that this shift is in the visible range.

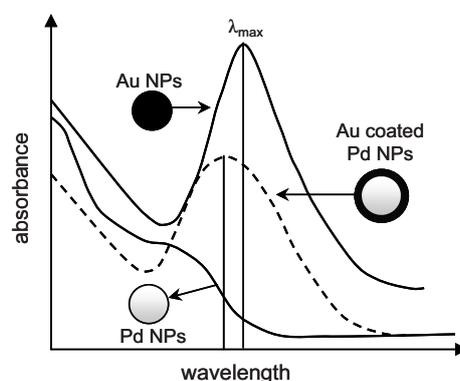


Figure 6. Schematic presentation of measuring Pd NPs size.

However, SPR of the catalytically active transition metal NPs is small and only lies near UV region. Hence to use UV-visible spectroscopy one can prepare multi-metallic NPs.^[94-97] Bimetallic NPs are atomic mixtures of two metal atoms that are generally prepared in solution by co-reduction of two metal salts. The size dependent dielectric properties of these nanoparticle and their SPR become the function of the mole fraction of these metals. The shift in the surface plasmon maxima of bimetallic particles depends on their respective amount. Though in this case one can observe the SPR in the visible range, it does not give any information on the size of the transition metal NPs. Another way to solve this problem is to prepare core/shell NPs by coating these transition metal NPs with Au or Ag (see figure 6)

It is still a challenge to prepare a homogenous shell around the core and control the shell thickness. The SPR in core/shell NPs is the function of size of the core and that of

shell thickness. The dielectric properties are then the composite function of the core and the shell material. They are considered as a homogenous sphere coated with homogeneous layer of uniform thickness and can be generalized as multilayered sphere. In this case, the modified scattering coefficients are given by,

$$a_n = \frac{m_2 \varphi_n(m_2 x) \times \varphi_n^1(m_1 x) - m_1 \varphi_n^1(m_2 x) \times \varphi_n(m_1 x)}{m_2 \xi_n(m_2 x) \times \varphi_n^1(m_1 x) - m_1 \xi_n^1(m_2 x) \times \varphi_n(m_1 x)} \quad (6)$$

$$b_n = \frac{m_2 \varphi_n(m_1 x) \times \varphi_n^1(m_2 x) - m_1 \varphi_n(m_2 x) \times \varphi_n^1(m_1 x)}{m_2 \xi_n^1(m_2 x) \times \varphi_n(m_1 x) - m_1 \xi_n(m_2 x) \times \varphi_n^1(m_1 x)} \quad (7)$$

with core and shell refractive index m_1 and m_2 . These, new scattering coefficients are used in equation 1 to predict the absorption spectra of the core transition metal NPs. The absorption maxima λ_{max} can be correlated to the size of the core nanoparticle.^[68]

3.3. Controlling the shape of NPs

Even though lot of reports managed to obtain NP with uniform size distribution, easier and better morphological control of nanocrystals has become increasingly important, as many of their physical and chemical properties are highly shape dependent.^[98] Nanocrystal shape control for both single- and multiple-material systems, however, remains empirical and challenging.^[99, 100] The formation of a particular shape in the synthesis of metal nanocrystals is often explained in terms of the presence of surfactants or capping agents that can change the order of free energies of different facets through their interactions with the metal surface in a solution-phase synthesis.^[101, 102] This alteration may significantly affect the relative growth rates of different facets and thus lead to different morphologies for the final products.

Some researchers argue that the thermodynamics or physical restrictions imposed by the surface stabilizing agent must be considered and other suggest that the nucleation and kinetics are also important.^[28] Main parameters, that can change the shape of particles, are the concentration of metal precursor, temperature, pH, type of seeds, presence of foreign ions, reducing agent, solvent and stabilizer.^[103] Figure 7 shows the general scheme of controlling the shape of Pd NPs by tuning different factors. In the following section these factors and their general effects on the NP's shape selectivity are discussed in short.^[104]

3.3.1 Type of precursor

Many studies showed that the precursor type and concentration affects the rate of reduction and nucleation which then ultimately decides the final shape of the NPs. Reetz *et al.* obtained spherical Pd NPs using PdCl₂ as a precursor and triangular particles in case of Pd(NO₃)₂.^[105] This effect is generally associated with the anions associated with the metal and the solvation ability of these ionic pairs in solution. Different anions have a specific affinity towards some crystal surface and thus create various shapes of seed. These seeds then results in different shapes of particles. There are many other reports in case of Au, Ag, Cu and Ru NPs.^[106]

3.3.2 Type of reducing agent

The strength of the reducing agent is also an important factor influencing the size and shape of NPs. Xia and co-workers showed that varying citric acid and ethylene glycol concentrations resulted in different shapes of Pd NPs.^[107, 108] Murphy *et al.* and many others showed that stronger reducing agent such as NaBH₄ and weak reducing agent like ascorbic acid results in various shapes of gold NPs.^[84]

3.3.3 Type of stabilizer

Generally the stabilizers are long carbon chain compounds, surfactants and organic ligands. In all these stabilizers their chain length, nature of the associated counter ion, concentration, shape and affinity toward specific crystal surface determines the NP shape. Most of the process use CTAB as a stabilizer in water and PVP in organic solvents, playing both the roles of stabilizer and structure directing agent.^[109-111] The templating effect of the stabilizer decides the final shape of the particles. For example, some stabilizers selectively adsorb on one particular crystal surface and allow the remaining surface to grow, resulting into different shapes of the NPs. Pileni *et al.* showed that different concentrations of stabilizer result in various shapes of Cu NPs.^[38, 112] Chaudret *et al.* showed that indeed, depending on ligand's skeleton and functional groups, the stabilizers can interact more or less with the surface of the particles and then favour or not the growth of the particles in a privileged direction.^[113, 114]

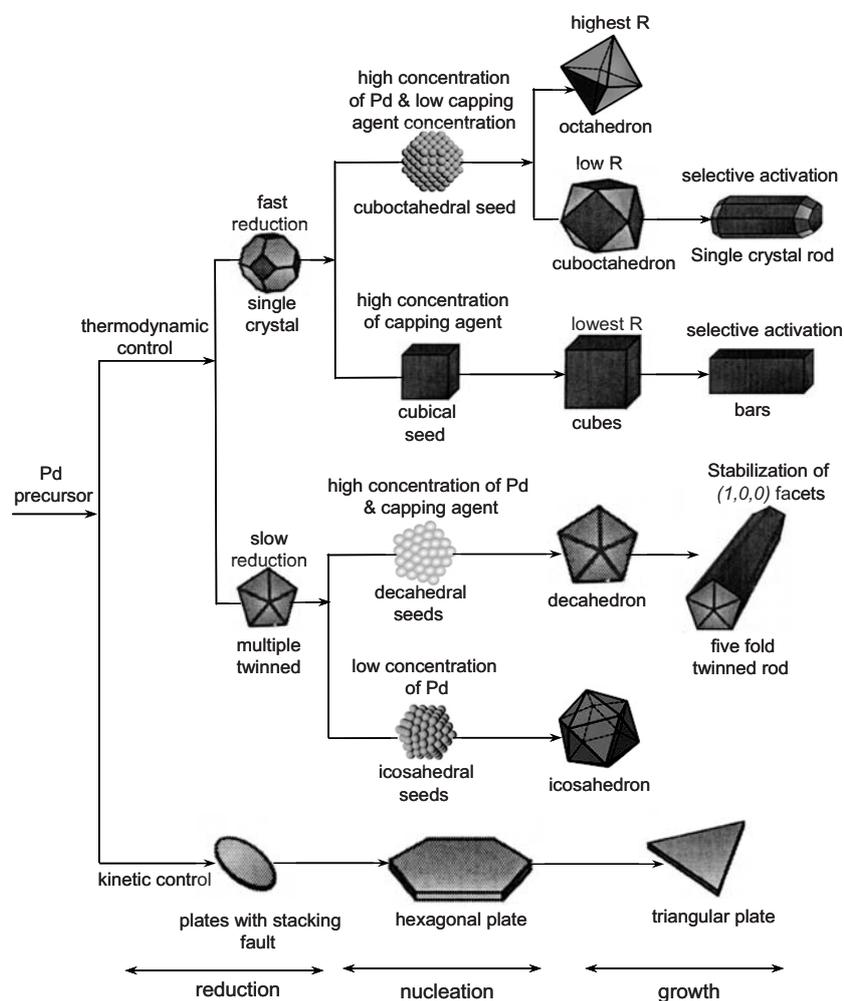


Figure 7. Schematic presentation of shape controlled synthesis of Pd NPs. The parameter R is defined as the ratio between the growth rates along the $(1,0,0)$ and $(1,1,1)$ axes.^[107, 108]

3.3.4 Miscellaneous factors

Other factors such as temperature, pH, solvent or media and presence of foreign ions indirectly affect the shape of the NPs.^[115] They tune selective adsorption of stabilizers on some crystal surface, and allow other surfaces to grow.^[116] One can alter the reduction kinetics by changing the pH. Some solvents themselves act as a reducing agent or they have better co-ordination ability, which can change the shape of the particles.^[117] In all these cases the most important factor is the shape, size and crystal structure of the NPs seeds.^[118, 119]

3.4. Self assembled NPs

Amphiphilic surfactant molecules assemble into various organized structures including one-dimensional spherical micelles, two-dimensional sheet-like mesophases, and three-dimensional cubic and hexagonal matrices.^[120] The stability of the phases depends on the surfactant concentration, solution composition, solution ionic strength, and temperature.^[121] One can obtain different phases as shown in the figure 8, by tuning these factors.

These surfactant systems are used as a stabilizer and as a soft crystal template for synthesizing different shapes of NPs. Surfactant mesophases used as templates for synthesizing mesostructured organic-inorganic composites. These templated materials have found applications in biological separations^[122], as catalysts and catalyst supports.^[123-126] Currently, two different approaches have been described to guide the location of NPs into membranes.^[127] (a) *In situ* formation of NPs within a specific compartment, either within interior, or directly within its membrane and (b) the incorporation of NPs after the formation of a structure.

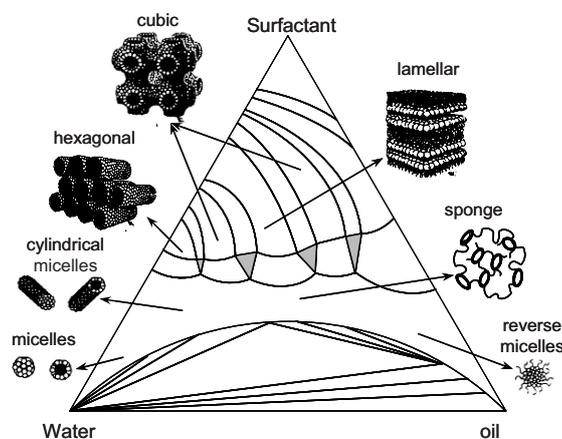


Figure 8. Phase diagram showing the different surfactant self-assembled structures.

In the former approach, usually metal salts are either solubilized within the compartment or the hydrophobic membrane. Then subsequent chemical reduction yields the final metal NPs within this compartment or membrane, where the initial metal-salt species were present. The main disadvantage of this process is the reduced stability of the membrane, which leads to a reduced control of the individual growth of the NPs. In the

second approach, preformed NPs of a specific size with a defined shell structure are incorporated into structures; combining the lyotropic phase with nanoparticles directly. In this case, the interfacial interaction between the membrane and the nanoparticle can be tuned much more efficiently, enabling to guide the location of the nanoparticle within a specific compartment of the structure. We will discuss incorporating NPs in different soft crystals especially randomly connected bilayer sponge (L_3) phases.

3.4.1 Incorporating NPs in liquid soft crystals

A lamellar phase is a periodic packing of alternating water layers separated by a membrane consisting of both surfactant and co-surfactant molecules. In oil-swollen lamellar systems, the two leafs of the bilayer are separated by the oil as shown in the figure 8. The thickness of the layers is of the order of almost twice the length of the main amphiphilic molecule. However, this length can increase due to the addition of a non-polar solvent. The thickness also depends on the temperature of the sample. Wang *et al.* showed that hydrophilic and hydrophobic NPs can be directed in water and oil layer respectively without disturbing the overall structure of the lamellar phase.^[128] In other reports Fabre *et al.*^[129] and Menager *et al.*^[130] described a lyotropic lamellar phase incorporated with oil or water-stabilized magnetic NPs.

When a lamellar phase is subjected to perturbation, lamellae can curve into closed shell structures called vesicles. A vesicle is a hollow aggregate with a shell made from one or more amphiphilic bilayers. A vesicle formed from a single bilayer is a unilamellar vesicle, while one with a shell of several bilayers is known as a multilamellar vesicle (or sometimes an onion vesicle). Many different examples such as the incorporation of Au, Ag, CdS, SiO₂, or iron-oxide or titanium oxide NPs into vesicles made from lipid-molecules have been described.^[131]

In the hexagonal phase, the amphiphilic molecules are packed as long cylinder like aggregates, with large shape anisotropy (see figure 8). The diameter of the cylinders is of the order of twice the length of the main amphiphilic molecule of the mixture, and the typical lengths are at least fifty times larger than the diameter. Self-assembly of ordered nanostructures is an attractive synthetic concept. Fabre *et al.* and Eiser *et al.* have shown that different metal NPs such as Ag, Au, and Pd are successfully incorporated inside the cylindrical soft crystals.^[132] This method can be used successfully to form self-assembled nanotubes.^[133]

Another interesting structure is the bicontinuous cubic structure. Luzzati reported the first structure in 1966.^[134] In the bicontinuous structure both oily and aqueous phase are continuous throughout the sample. At least three kinds of cubic phase were observed and they are called as Ia3d, Pn3m and Im3m. Hyde *et al.* then described these structural transformations in detail.^[135] These structures are important for developing controlled release formulations of biologically active agents in the field of drug delivery and in food technology for the encapsulation of enzymes^[136, 137] but incorporation of NPs in this phase is not reported yet.

3.4.2 NPs and bicontinuous sponge phases (L_3)

The flow bi-refractive bicontinuous sponge phase (L_3) is isotropic in nature and observed in very dilute surfactant solutions. In the last ten years, it has received a lot of attention.^[138] This phase exists in water or oil rich corners but in very narrow range of co-surfactant concentrations. According to the most popular view, the L_3 phase is a three dimensional, random and multiply connected bilayer of surfactant and co-surfactant; dividing the space into two sub-spaces filled with solvent. The two monolayers building the membrane are expected to be symmetric and free of defects such as holes and edges, which are energetically unfavourable. This sophisticated structure was also evidenced by several images of freeze fracture electron microscopy.^[139]

The disordered L_3 phase forms due to the existence of the swollen lamellar phase (L_α).^[140] The swollen lamellar phase has bilayers of constant thickness and low bending rigidity ($k \sim K_B T$). The thermal undulations in this phase, lead to connections in bilayer, resulting into a sponge like structure. These two phases of a local bilayer structure are characterized by an average number of bilayer connections per unit volume, called as topological factor α . In the lamellar phase the lack of connection leads to $\alpha = 1$; while in the dilute L_3 phase the degree of connection between the solvent cells was reported to be $\alpha = 1.57 \pm 1$. The interfacial curvature of the continuous surfactant membrane is expressed in terms of two parameters, the mean and the Gaussian curvature. L_3 phase exists when co-surfactant molecules permeate into the bilayer and stabilizes the negative curvature of bilayer ($C_0 < 0$). This then makes the Gaussian curvature modulus of the bilayer positive ($K > 0$), and the L_3 phase becomes energetically more favourable.

Some reports also studied the effect of polymers, temperature, foreign ions, pH and external shear stress. In the presence of polymers, the sponge phase transforms to a new phase, which exhibits a reverse sponge-like structure (L_5).^[141] Moreover, exposed to an

external shear stress that is sufficiently high to tear off all the membrane passages, sponge phase turns to bi-refrangent lamellar phase.^[142] Temperature is another important factor. Above a critical temperature the L_3 phase transforms to more ordered phases and above critical solution temperature, the phase separation occurs. Recently, L_3 phase was used as a template to prepare inorganic materials with uniform porosity.^[143, 144] These materials can be used as supports for various separation processes or for catalytically active materials. Part of this thesis discusses the stability of the sponge phase in the presence of the various NPs, which then can be applied, for catalysis.

3.5. Nanocatalysts and their separation

The contribution of soluble transition-metal complexes as selective homogeneous catalysts for a number of chemical transformations under mild reaction conditions has increased significantly during the last decades.^[145] The tedious separation of the catalyst from the reaction products is a major drawback of these processes.^[146] Individual solutions have been developed for catalyst separation and recovery. In most cases, the development of materials combining the advantages of classical homogeneous and heterogeneous catalysts has remained an elusive goal.^[147, 148] The field of synthesizing well defined homogeneous catalyst that can be separated easily is the centre of many investigations into green chemistry.^[149-151] Molecular-weight enlargement^[152-155] and immobilization of transition-metal complexes^[151, 156-159] are effective solutions. Catalysts separation with filtration methods offers the possibility to still operate the catalyst under homogeneous reaction conditions, hence maintaining the intrinsically high selectivity, activity and low energy consumption while avoiding mass-transfer limitations.^[160] Selective retention of macromolecular catalysts is possible by membrane filtration. The development of new compatible and robust membranes and reactors for using ultra- or nano-filtration membranes, for separating the high-molecular-weight catalysts from low-molecular-weight reactants are in progress. This is an alternative to heterogeneous immobilisation of homogeneous catalysts.^[161]

Many important homogeneous catalysts are used in industry in biphasic systems or by fixation on supports, the bridge between these two approaches is now being built through the use of NPs, whose activity is very high under mild conditions because of their very large surface area.^[162] A heterogeneous catalyst such as supported NPs simply releases its active species into solutions to be useful.^[163] The first years of the 21st century have seen an exponential growth in the number of publications in the nanoparticle field for

improving catalyst activities, selectivity, understanding the catalytic mechanisms. Various methods and separation technologies were used to understand the nature of true catalytic species. In the following section we will study the separation of homogeneous catalysts for understanding the mechanism of C-C coupling reaction and later, for efficient separation of the catalyst in homogeneously catalyzed reactions.

3.5.1 NPs separation for understanding the mechanism of nanoparticles catalyzed C-C coupling reactions

Aromatic C-C bond coupling reactions have recently emerged as exceedingly important methodologies for the preparation of complex organic molecules in pharmaceutical industries. Commonly used coupling reactions are Heck, Suzuki, Sonogashira and Stille reactions.^[164] In most of these reactions Pd is foremost important metal used as the catalyst. There are many claims of heterogeneous catalysis by supported palladium, but under more rigorous testing, it is often found that the true active species are from leached metal.^[165] Reactions, especially, which are carried above 120 °C, the leaching of metal atoms and/or ions is a key issue. There has been much scientific argument regarding the actual catalytic species. Bradley and co-workers and El-Sayed showed that nanocatalysis is heterogeneous in nature and that low coordination sites at the surface takes part in catalysis.^[43, 166] Conversely, Amatore, Arai, de Vries, Du-pont, Biffis and Reetz suggested a homogeneous mechanism in which the NPs act as “reservoirs” of active Pd atoms or ions.^[167] At the same time typically for hydrogenation reactions soluble metal precursors often form metal nanoparticle and then act as a true catalytic species.^[168] Many reports used various reaction tests such as hot filtration/split test, solid poisoning, polymer encapsulated Pd^{II} complex and Collman test.^[169] In Chapter 5, part A we demonstrate a novel separation technique using ceramic membrane for studying the nature of the actual active species in Pd nanoparticle catalyzed Suzuki and Heck reactions.

3.5.2 Easy separation of homogeneous catalyst using membranes

In recent years, the application of membrane technology in homogeneous catalyst recycling has received widespread attention. Homogeneous catalysts are frequently used in highly selective organic transformations. Catalysts separation using membrane is an attractive approach to achieve this goal.^[170] Membrane separation technique is already being used in different important reaction, such as metathesis, Kharasch addition, and asymmetric hydrogenation reactions.^[171] This approach will create catalytic processes that

possess a high selectivity and activity, minimizing the need for processing of the product stream, efficient use of the generally expensive homogeneous catalysts.

In the field of membrane filtration a distinction is made between different kinds of membrane processes on the basis of the size of the particles to be retained, that is, micro-filtration, ultra-filtration, nano-filtration and reverse osmosis. Ultra filtration (UF) and nano-filtration (NF) are the two types of filtration techniques used a lot in the catalytic applications and are defined to retain macromolecules with dimensions between 8-800 nm and 0.5-8 nm, respectively.^[172] Usually, the molecular weight cut off (MWCO) is used as the quantitative criterion for the retention characteristics of a membrane and the retention factor (R) is defined by the ratio of the concentration of a component in permeate and retentate. However, for actual separation processes the pore-size distribution (which exists in all UF and NF membranes), charge effects, hydrophilicity, hydrophobicity, and polarity (of the solvent) can also greatly influence the permeability of the membrane. Mainly used continuous membrane reactors are dead-end-filtration and cross flow filtration.^[170, 173]

As for the membrane material itself, two types of membranes are frequently used: organic (polymer) membranes and inorganic (ceramic) membranes.^[149] The most widely applied commercial organic membrane is the MPF series of Koch Int. with (MWCO range of 400–700 Da), STARMEM series from MET (polyimidebased), with MWCOs in the range of 200–400 Da. Ceramic membranes are much less common and have pore sizes between 0.5 and 0.8 μm and consist of several support layers of α - and γ - alumina, while the selective top layer at the outer wall of the tube is made of amorphous silica.^[174] Chapter 5, part B of this thesis deals with the use of ceramic membranes for Ru based catalyst separation for industrially important transfer hydrogenation reactions.

4. Motivation of this work

The motivation for the work presented in this thesis comes from different objectives that we wanted to achieve mainly in the area of metal NPs and their applications in the catalysis. Today nanochemistry is advancing fast but still there are some unsolved questions and we tried to answer some of these questions.

Many studies showed different methods for preparing various metal NPs in solution with uniform size distribution. Scientists are trying to study the major factors that decide the size and shape of NPs. One of the aims of this work is to study the effect of different factors such as different stabilizing agents and metal precursors on the nanoparticle formation process by describing an appropriate kinetic model, using *in-situ* UV-visible spectroscopy.

After studying the nanoparticle formation process, we were enthusiastic about searching easy and simple methods for measuring the size of metal NPs especially catalytically active noble metal NPs. Using our experience in *in-situ* UV-visible spectroscopy and innumerable literature on optical properties of NPs, we came up with an idea of coating Pd NPs with a gold layer. Then combining plasmon properties of NPs and Mie theory for their visible light scattering we decided to find the size of Pd NPs. While coating Pd NPs with gold we came across a very interesting observation: we obtained different shapes of the gold NPs. Gold is emerging as a competitive candidate for catalysis, and its catalytic properties depend on the shape of NPs. So we went ahead and studied in detail the factors that affect the gold NPs shape.

At this moment we knew three important things in NP's chemistry. 1st the detail kinetic model for nanoparticle formation, 2nd, an easy method to obtain their size and the 3rd, unknown factor that decides the shape of the gold NPs. Then we were interested in trapping these NPs in surfactant self assembly system. One of the bilayer phases is called sponge phase and it is used as a template for making porous silica supports. These supports are used for various metal NPs for heterogeneous catalysis and so we investigated the stability of sponge phase in presence of NPs.

Finally, it is always interesting to search for an application of our knowledge about NP's. Since our group is very active in nanocatalysis, we wanted to strengthen our knowledge further in this particular field. NPs are used in different reactions as a catalyst and we were especially interested in C-C coupling reactions. Pd NPs are very active for this reaction but one of the most important issues is the nature of the true catalytic species. We used the new ceramic membrane for separating Pd NPs from active species. Further

for showing the new application of this membrane in separation of homogeneous catalyst we prepared special membrane cup. We investigated novel idea of “cat in a cup” for separating a dendritic Ru catalyst in transfer hydrogenation of acetophenone.

5. Outline

Chapter 2 “*In Situ UV-visible spectroscopy: A simple method for understanding nanoparticles’ formation and measuring their size in solution*” **A)** This section of the chapter gives an easy solution for predicting the growth mechanism of NPs. Here we analyze the Pd nanoparticle formation reaction using *in-situ* UV-visible spectroscopy. We used different Pd precursors such as PdCl₂, Pd(OAc)₂, and Pd(NO₃)₂ and various tetra-*n*-octylammonium carboxylates as reducing and stabilizing agents. All reactions are followed with respect to time using UV-visible spectroscopy. Then we analyzed the data using chemometric techniques called as Net analyte signal (NAS) method and principle component analysis (PCA). The extracted profiles of Pd NPs formation are fitted using three step kinetic model.

Section B This section describes application of Mie theory for measuring the size of Pd metal NPs using their surface plasmon resonance properties. Here, Pd/Au core/shell particles are prepared and a computer model is developed using extended Mie theory for core/shell particles, which is then used to predict the size of Pd NPs. The application of this model for Pd/Au homogeneous NPs is also demonstrated.

Chapter 3 “*Growing anisotropic gold nanoparticles in organic media*” demonstrates the effect of Au precursor aging, solvent reduction nature and reducing/stabilizing agent concentration on the shape selectivity of the Au NPs.

Chapter 4 “*Stable ‘soap and water’ sponges doped with metal NPs*” shows the stability of surfactant bilayer sponge phase in presence of Au, Pd and Ag NPs in organic and aqueous layer. We studied its stability using small angle X-ray (SAXS) scattering and rheological behaviour under applied external stress.

Chapter 5 “*Detailed mechanistic studies of Pd nanoparticle-catalyzed cross-coupling reactions*” we studied the application of the ceramic membranes for separating the true catalytic species from Pd NPs. By doing this we were able to study the actual mechanism of Pd nanoparticle catalyzed Heck and Suzuki reactions.

Chapter 6 “*‘Cat-in-a-cup’: Facile separation of nanocatalysts using ceramic membranes*” describes other application of these ceramic membranes for catalyst separation. We developed a new “*Cat-in-a-cup*” approach for Ru based homogeneous catalyst separation in transfer hydrogenation of acetophenone.

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