The synthesis of monodisperse colloidal core@shell spheres and hollow particles

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This work is dedicated to ANA LAURA
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"Was willst du denn jetzt noch wissen?"

fragt der Türhüter,

"du bist unersättlich."

"Alle streben doch nach dem Gesetz,"
sagt der Mann,

"wieso kommt es, daß in den vielen Jahren niemand außer mir Einlaß verlangt hat?"

Der Türhüter erkennt, daß der Mann schon an seinem Ende ist, und, um sein vergebendes Gehör noch zu erreichen, brüllt er ihn an:

"Hier konnte niemand sonst Einlaß erhalten, denn dieser Eingang war nur für dich bestimmt. Ich gehe jetzt und schließe ihn."

Kafka F [1]
Part I

Motivation
Motivation

Nano-structured materials in the colloidal domain are expanding the scientific horizon towards limits, which were desired, but not achievable only a few decades ago. The advances in this field are progressing rapidly, but there are still some important restrictions. One of them is the variety of materials that can be used. Silica has been, by far, the most employed material in the preparation of nano-structured materials. The use of other oxides is desirable, but has been impeded for many applications by, for instance, the structural changes occurring at relative low temperatures. These changes often destroy the interesting properties of these materials.

The spatial distribution of the different constituents in nano-structured materials plays also a key role in the properties they have. The utility of some of them is due rather to their spatial ordering than to their chemical composition. One particularly interesting order of matter is present in composite materials with a core@shell structure and with a narrow particle size distribution (monodisperse) centered in the upper colloidal region (i.e.: 100 nm to 1 μm). These particles as a subgroup of nano-structured materials, face similar restrictions. Most core@shell particles in the upper colloidal region have, so far, a core made of either silica or a polymer; the same materials and a few oxides (e.g.: TiO₂) can be found in the shell. Also, these materials show severe limitations due to structural modifications occurring as soon as temperature is raised a few hundred degrees above room temperature.

Another unusual order of matter is present in colloidal hollow particles with a narrow distribution in size in the upper colloidal region. These particles have many real and potential applications due to the presence of a relatively big void in their interior. The limitations in the synthesis of such particles originate in the fact, that most of them are prepared from core@shell particles by removal of the cores. Hence, the composition of hollow particles have been limited by the parent materials.

The aim of this work was the development of new types of core@shell and hollow particles with a particle size distribution in the upper colloidal domain and with material compositions beyond the usual ones. Very specific procedures for a given material combination are a serious drawback, since this would require development work for any new target system. Therefore, emphasis was placed in the development of generic pathways which are suitable for the production of many different materials combination after slight adaptation. Since thermally stable structures are created in a number of applications, a target material for the shell was required with high temperature stability. Therefore, the work was focussed on zirconia -and to some extent carbon- as the shell material.
Part II

State of the Art
"Cuando descubrí que tanto las matemáticas como la historia, la física y todas las demás disciplinas del saber humano tienen autores, con nombres y apellidos, me sentí estafado. De pequeño, en la escuela me lo enseñaron todo sin mencionarme ni un científico de los que trabajaron en cada campo (quizá sólo Newton y Galileo, por lo de la manzana y lo del juicio), de modo que entendía el saber como algo absoluto, objetivo e independiente de las personas. No se podía estar en desacuerdo o entenderlo de otra manera; era así y punto."

"De mayor aprendí a relativizar el conocimiento y a verlo simplemente como la explicación más plausible, pero no la única, que podemos dar a la realidad. Me di cuenta de que el saber no existe al margen de las personas, sino que se va construyendo a lo largo de la historia gracias a las aportaciones de todos."

Cassany D. [2]
Chapter 1

Monodisperse colloidal particles

1.1 Colloidal domain & colloidal particles

The term *colloid* was coined by Graham in 1861. In his work titled *Liquid Diffusion Applied to Analysis* he describes two classes of matter: crystalloids and colloids. The former are substances that diffuse through a membrane separating an aqueous solution from water. The latter can not diffuse through. For instance: salts and sugar belong to the first class; albumin, gum arabic, gelatin, among others, belong to the latter [3]. Nowadays the term *colloid* is used in a broader sense to designate those particles having a characteristic length between 1 nm and 1 μm (Figure 1.1).

![Colloidal Domain Diagram](image)

**Figure 1.1:** The colloidal domain.

The *colloidal science* studies *colloidal particles*, which have a characteristic length between 1 nm and
1 µm. The Colloidal Domain has somewhat diffuse limits and is in the focus of several disciplines such as chemistry, biology, physics, material science, among others [4]. For instance, proteins, virus, quantum dots and monodisperse silica spheres are all colloidal systems approached from different scientific disciplines.

Particles can be characterized by a shape and there are many ways of doing this. As a first approximation many particles can be considered as spheres. This approximation is valid for particles with a high degree of symmetry, like for instance the particles which will be considered in this work. The spherical shape is convenient, because it is characterized by a single parameter. Other shapes can be considered in case of less symmetrical particles, but at the price of introducing more parameters for their description.

Once the shape of the particle has been stated, the term particle size becomes meaningful. Normally, a system containing more than a few particles is considered. Hence a statistical description of the systems is an appropriate way to obtain the structural parameters. In general, any experimental quantity for a system containing many particles is an average quantity \( \langle \phi \rangle \) and can be represented by the Equation 1.1:

\[
\phi = \frac{1}{N} \sum_{i=1}^{n} ((\text{Weighting factor})_i (\text{Quantity being averaged})_i)
\]

The most used weighting factor is the number fraction of the Quantity being averaged in each class \( i \). This can be represented by:

\[
f_{n,i} = \frac{n_i}{\sum_{i=1}^{n} n_i}
\]

The Quantity being averaged can be measured itself or any other property mathematically related to it. For instance, in the case of spheres, the diameter – or equivalently the radius - is used to define the size of the particles. Thus, the diameter \( (\text{d}) \) or the surface \( (\pi \text{d}^2) \) or volume \( (\frac{\pi}{6} \text{d}^3) \) can be measured.

The value of \( \phi \) can also be obtained, if the distribution function for \( \phi \) is experimentally attainable. The normal or Gaussian distribution function is probably the most familiar, but there are many other useful and well known examples. The distribution function is mathematically related to its \( \phi \). So, if the distribution function is known, the \( \phi \) can be known.

Why is that information about \( \phi \) important? In general, different experimental approaches give different averages for what nominally might be called the same quantity. This has to be considered when comparing a value for \( \phi \) obtained in different ways. It is important to mention that these differences arise from the way chosen to measure \( \phi \), but have nothing to do with the experimental conditions employed in the measurements. For example, it can be proven that the surface average diameter is always larger than the direct average of the diameters [4].

Distribution functions can be classified in several ways. The modality indicates how many maxima the curve has. Thus, if it has one maximum, it is said to be monomodal, if it has two bimodal and more polymodal. The dispersion is related to the broadness of the maximum in the distribution. One sharp distribution is said to be monodisperse while a broad one to be polydisperse. This last classification has no clear boundary, though often used in the literature to characterize systems of particles. Moreover, monodisperse particles should be in the strict sense a group of particles having all exactly the same size. Nevertheless, this term is often used to designate a sharp monomodal distribution of particles.
1.2 COLLOIDAL core@shell & @shell PARTICLES

Some distribution functions can be associated to physicochemical processes [4]. The mechanical subdivision of larger chunks is likely to produce particles with diameters whose distribution is the log-normal. Processes determined by a large number of purely random factors are likely to show a normal distribution.

Summing up, in this section the colloidal domain was introduced. Furthermore, a few words were spent on the concepts of the shape and size of the particles. Though a philosophical treatment is beyond the scope of this work, some care should be taken when comparing the mean particle sizes obtained by different experimental procedures. The importance of this will be stressed in the next Section, where it will be shown how important it can be to know an exact and precise value for the mean particle size.

1.2 Colloidal core@shell & @shell particles

1.2.1 core@shell

Before the explanation of why the core@shell particles are attracting scientists’ interest a definition of core@shell and a nomenclature for those particles will be presented. Then will follow a description of the historical development of this kind of particles. Finally a few words about the classification will be mentioned.

A core@shell particle can be defined as a particle formed by a core of a material A covered with a shell of a material B. A nomenclature has been adopted from the metal-doped Buckminsterfullerenes [5]: core@shell. In case of the particle having n shells, the particle can be designated by core@shell,@shell,... @shell. If the core or one shell is composed of 2, 3 or m phases, then all components are separated by a colon and separated from the core or other shells by @. For example, core@A,B means a core@shell particle with a core of one substance and one shell composed of substances A and B.

How thick shall the shell be to consider the whole as core@shell particle? Particles covered with a molecular protecting group or capping-agent are normally not considered as core@shell particles, though the presence of this species can modify the properties of the whole particles, and the shell can contain hundreds of atoms. For instance, the preparation of nanometer-sized gold particles can be done by using a polymer as stabilizer. Due to the relatively important size of the polymeric shell formed around the gold particle, the polymer could be considered to form a shell around a gold core [6]. Contrastingly, a few atomic monolayers are in some cases enough to consider the particle as core@shell [7].

A brief history of the core@shell particles can be found elsewhere [5]. Already in the 1920s encapsulated particles were known. About 30 years later a theoretical study about the interaction of electromagnetic waves extended the use of Mie’s theory to the core@shell particles. Though in the 1960s some experimental studies on these systems were done, other 30 years had to be waited till the 1980s, when more detailed studies began.
1.2.2 @shell

A hollow particle in the colloidal domain can be considered as core@shell particle with a solid shell and a liquid or gaseous core. The solid shell can be either rigid or flexible depending on the material from which it is formed. Moreover, the shell is often porous or permeable, what permits a mass exchange between the interior and exterior of the particle. In the interior of the particle there is a void, which is usually filled with either a gas or a liquid. These substances are readily adsorbed when the material is in contact with the atmosphere. The key point is that the filling should be easily removed by mild physical procedures (e.g.: increase in temperature, vacuuming), which do not imply changes in strong atomic bonds (e.g.: covalent, ionic). The removal of the substance in the internal void leading to an empty hollow particle is possible, but only under vacuum. It is this solid shell which defines the hollow particle and not the liquid or gaseous substance, which circumstantially fills its interior.

For hollow colloidal particles a nomenclature similar to the one used for core@shell particles can be used. The difference is that nothing is written in the position corresponding to the material of the core: @shell. The presence of several concentric shells can be designated by @shell1,@shell2,…@shellN. Furthermore, if a composite shell is present, the two or more components should be written separated by colons. For example, @shell1@AB,…,N@shell3 is the name for a hollow particle containing 3 shells, the second shell having N phases.

1.3 Particle’s structure

1.3.1 Colloidal particles

The structure of a particle can be classified in several ways. Here two of them will be discussed.

From the point of view of the crystallographic order, particles can be said to be monocristalline, polycristalline or amorphous. In a monocristalline particle the constituents have a certain ordering, characterized by a symmetry, in the space enclosed by the boundaries of the particle. When a particle has several domains, where a certain ordering exists inside each of them, and a boundary formed by a mismatch in the ordering of the constituents separate the domains from each other, the particle is said to be polycristalline. When the ordering of the constituents of the particles is such, that no periodicity is present, the material is said to be amorphous.

For particles with sizes in the lower part of the colloidal domain, care should be taken in the interpretation of X-ray diffraction patterns for the determination of the crystallinity of the particles. With this technique only crystalline domains having a size bigger than a critical size -which depends on the constituents- can be detected. The reason is that there have to be enough lattice planes present for the X-ray beam to positively interfere and build the diffraction pattern. Characteristically, as a crystalline domains increases in size, firstly no reflection is seen and then a broad reflection appears, which sharpens as the size of the domains further grows. Hence, for instance, a polycristalline micrometer-sized particle could show no reflection in a diffractogram, if the domains are small enough. Amorphous particles show a broad scattering signal due to the interaction of the X-ray with the electrons in the atoms. The
maximum of the scattered signal correlates with interatomic distances. For instance, amorphous silica exposed to CuKα1 radiation shows a maximum at about 22° 2θ, which roughly correspond to the average Si-O distance.

A second way to characterize the particles is by their porosity as either porous or non-porous. As a first approach, it is possible to say that the presence or absence of cavities, channels and interstices determines whether a particle is or is not porous, respectively. In general, the porosity is in all cases associated to a given method used for its determination, which must be stated together with some additional experimental information [8, 9].

The pores in the particles can be further classified as micropores (d < 2 nm), mesopores (2 nm < d < 50 nm) and macropores (50 nm < d) [8, 9]. This classification is independent from the former one based on the crystallinity. Hence, for instance, a TS-1 zeolite (MFI Structure) is a microporous material where both constituting atoms and pores show a crystalline structure; as another example, SBA-15 is siliceous material with amorphous walls and crystal-like pore/wall periodicity.

1.3.2 Core@shell & @shell

Core@shell and @shell particles can be classified following similar criteria as were mentioned in Chapter 1.3.1 for monodisperse colloidal particles. But in the case of core@shell the classification has to be applied to both the core and the shell. Hence, combining different structural properties a wide range of particles can be prepared.

1.4 Why are colloidal particles interesting?

1.4.1 Colloidal particles

Particles in the colloidal domain show the interesting feature that for a given chemical composition, the change in size may affect both the properties of the particles themselves and the properties of the system containing them. The properties of colloidal particles are sometimes different from those corresponding to the bulk material and to the constituting atoms or molecules [4, 10]. The change in the properties with respect to the bulk ones appear in the lower colloidal region, when the particles reduce their size [11, 12]. One example is the change in the fusion point of gold, which rapidly decreases with the particle size below 20 nm [13, 14, 15, 16, 17].

The change in the particle size can also affect the properties of the whole colloidal system -not of isolated particles. The viscosity or aggregation behavior of a material system containing colloidal particles can be changed by changing the size of the dispersed phase. Another important property is the specific surface area of the material, which strongly grows as particles reduce their size below 10 nm. Related to this is the energy of the system, which increases as the particles size decreases, because the creation of a surface is always a thermodynamically unfavorable process.

Some properties can strongly vary with the particle size in some interval of the spatial domain. The catalytic activity of gold, for instance, strongly depends on the particle size. Particles below a critical
value show activity and the activity increases as particle size decreases. Particles with a difference in size of a few nanometers can show an appreciably different activity.

Moreover, colloidal systems normally contain many particles, which show a distribution of particle sizes. If the distribution stretches along a spatial interval where a change of a property with particle size occurs, then the observed property for the system is an averaged property. Hence some care should be taken when relating a property of a system of particles to the mean particle size.

In sum, colloidal particles can show a change in their properties and the properties of the system they form due to change in size, by keeping an invariable chemical composition.

1.4.2 Core@shell particles

The presence of a shell around a core can change the chemical and physical properties of the particle. Hence, the formation of a shell can be considered as a way to change the properties of the material in the core. One particle can, for instance, be protected [18] or its chemical properties can be changed [19] by covering with another substance. The formation of core@shell particles can also be used to create templates [20, 21] or supports [22, 23] with wide range of scientific and technological applications.

1.4.3 @shell particles

Hollow particles offer a confined space varying in size from a few nanometers to tens of micrometers, wherein processes can be made or materials can be stored. The confinement of a process is a tool that can be used to couple reactions in time and space, which is expected to increase the efficiency of chemical conversions on scales ranging form the laboratory bench to industrial plants [24]. Hollow particles can also be used as colloidal containers to store a substance, whose release can be triggered a posteriori.

An increasing demand of hollow spheres in the mass market, where huge quantities at low prices are required, increases the interest in new manufacturing processes [25].

1.5 Applications

1.5.1 Monodisperse colloidal particles

Colloidal particles find their place in a huge number of applications nowadays [4, 26]. Just to mention some big areas, colloidal particles can be found to play a crucial role in photography, paints, chromatography, data storage and handling, sensors, catalysis and preparation of nanocomposites, among others.

One key point in the usefulness of the colloidal particles relates to the change of their properties with particles size. This introduces an important variable to modify the properties of a material systems by modifying a characteristic length, but not a chemical composition. In photography, for example, the size of the silver halide particles used in the film and its distribution are photographically relevant [27].
1.5.2 Monodisperse core@shell particles

The applicability of core@shell particles reaches wide and diverse technological and scientific fields. Here some interesting examples will be shown.

In chromatography, superficially porous silica microspheres can be used for high-performance liquid chromatography (HPLC) of macromolecules. The presence of a porous shell around an impervious core improves the mass-transfer kinetic properties compared to conventional totally porous particles of the same size, which permits more rapid separation of macromolecules. For instance, proteins and synthetic polymers have been separated with columns filled with the core@shell material [28, 29].

In material science, core@shell particles have been used as hard templates to prepare monodisperse particles with diverse compositions [30, 31]. Hence a wide range of new monodisperse particles with one or more components can be prepared. In some cases there are no other known pathways to obtain monodisperse particles.

In photovoltaics core@shell particles have been proposed as potential alternative to thin-films in the fabrication of solar cells [32]. The advantage of using core@shell particles resides in the protection created by the shell. Nanoparticles tend to decrease their surface energy by reducing their specific surface area with a consequent growth of the particles. The formation of a shell can avoid the further growth of the nanoparticles. Moreover, the shell modifies the dispersibility of the particles in certain solvents. This can be used for the preparation of composite materials by embedding core@shell particles in a polymeric matrix.

1.5.3 Monodisperse @shell particles

In nature, chemical conversions often take place in a confined environment. Human beings have developed a wide range of nanoreactors, for instance, from synthetic and biological building blocks, which can be linked by both covalent and non-covalent bonds. These self-assembled nanoreactors can be considered as the simplest mimics of a cell and contain a cavity in which a chemical reaction can take place [24].

Another application for @shell is their use as colloidal carriers [33, 34]. These carriers can be used to transport a substance and to liberate it only when a certain environment is present. For such applications a shell with a trigger-mechanism should be available, for instance, for determined pH-values.

In material science, hollow spheres can be used to prepare, for instance, foams for biomedical ultrasonic imaging and underwater hydrophones [35]. The use of hollow spheres may provide materials with a higher signal-to-noise ratio.
1.6 Syntheses

1.6.1 Monodisperse particles in the colloidal domain

Pathways to obtain monodisperse colloidal particles have been known for a long time. The gold sols prepared by Faraday about 150 years ago, which can still nowadays be seen, could be mentioned as one example [36]. In this Section a broad overview of some well established pathways to obtain monodisperse colloidal particles will be presented.

The methods for preparation of colloidal particles are customarily classified into Dispersion Methods and Condensation methods [26]. In the former milling, grinding, attrition, repeated quenching, lithography, aerosol synthesis or other methods of comminution are employed until the material reaches the desired level of fineness. Stabilizing agents have to be used to prevent agglomeration. In the latter, the particles are grown from atoms, ions, molecules or clusters until the desired size is reached. Here, again, stabilizers must be used. Other more modern names for those methods are Top-down and Bottom-up approaches, respectively [37]. Lithographic techniques and other top-down approaches, though being important techniques, will remain out of focus in this work. The bottom-up approaches allow in general to obtain more monodisperse particles, which are the particles in the focus of this work [38].

The bottom-up methods can be further classified in confined methods and non-confined methods. To the former group belong, for instance, the synthesis inside of micelles or in porous materials. The confinement can determine an upper limit to the size the growing particles might achieve. In non-confined media the particles have in principle no steric hindrance to grow, the limitation being somewhere else, for instance in the amount of precursor present in the reacting medium.

In the following, synthetic pathways leading to chemically different kinds of monodisperse particles will be presented. One of the prerequisites for a successful bottom-up synthesis of monodisperse particles in the colloidal domain is that the growth of the particles stops before the size of the particles crosses the upper limit of this domain. The required conditions for the preparation of such particles can only be provided experimentally [39]. Another prerequisite is the use of substances with a clearly specified purity and the strict following of the experimental procedure, this all with the most care in working in a clean way. The presence of impurities which can act as modifiers are in many cases known to modify the shape of monodisperse particles or even hinder their formation. Slight changes in temperature, concentration, reaction time, among others, can drastically change the obtained product [39].

Metals

Colloidal dispersions of metals are generally prepared by the reduction of metal salts in dilute solutions or the thermal decomposition of organometallic compounds. The reacting medium contains a metal precursor, a reducing agent (or an electrode), a protecting agent and a solvent [38, 40, 41].

Metal precursor are mostly salts and organometallic compounds. These are reduced by using many different reducing agents (e.g.: CaH$_2$Na$_2$O$_7$, B$_2$H$_6$, Alcohol with α-H, H$_2$, NR$_4$(Et$_4$H), h- generated radicals, CO, Carboxylic acid and Carboxylates, Aldehydes, Silanes, Tetraakis(hydroxy-methyl)phosphonium chloride (THPC), N$_2$H$_4$, NH$_2$OH). Low-valent organometallic complexes can be decomposed by heat,
1.6. SYNTHESSES

light and ultrasound to form metallic particles with narrow size distribution. The main classes of protective groups are both N, P, O and S electron-donor and ionic species. They can either be added to the reacting medium (e.g.: polymers, block copolymers, phosphanes, amines, thioureas, carboxylic acids) or be the solvent itself (e.g.: THF, alcohols) [38, 40, 41, 42, 43].

Besides the temperature and pressure, the metal precursor, the reducing agent (or electrochemical variables), the protecting agent and a solvent can have an influence in both the final particle size distribution and the morphology of the synthesized particles. It is clear then that care should be taken in the selection and maintenance of the required experimental condition during the synthesis.

Non-metals

Non-metallic colloidal particles play a major role in many technological and scientific applications. Since this field is very wide, this Section will be restricted to the synthetic pathways to Silver Halides, Semiconductors, Sulfur, Organic Polymers and Oxides. This pathways’s clustering is most probably related to the different scientific fields, where syntheses were developed.

Silver Halides Silver halides can be prepared in several ways, but all methods have in common that nucleation and growth of the particles are separated [44]. The particles can be prepared with cubic, octahedral or other shapes, but rarely spherical. These photosensitive particles are useful in photography, where the monodispersity in size is advantageous.

Semiconductors The bottom-up pathways to obtain monodisperse particles of semiconductor materials can be divided into two groups according to the order of magnitude in size of the final particles. Colloidal particles in the lower colloidal size range are normally obtained differently than those particles with sizes in the middle and upper colloidal regions.

Semiconductor colloidal particles in the lower colloidal domain can be prepared by thermolysis of organometallic precursors in dry coordinating solvents at high temperatures (ca. 423-723 K) in the presence of protecting or capping agents [45]. Organometallic precursors for II-VI semiconductors (ME where M = Zn, Cd, Hg; E = S, Se, Te) are generally metal alkyls (dimethyl cadmium, diethylcadmium, diethylzinc, dibenzylmercury). Chalcogenide precursors are often organophosphine chalcogenides (R₃PE) or bistrimethylsilylchalcogenides (TMS₂E; TMS = trimethylsilyl). For III-V semiconductors, InCl(C₂O₄) is typically employed as metallic precursor and TMS₂E (where E = P, As) as group V atoms. Oxygen and water have to be excluded from the syntheses, because they are mostly very reactive against the organometallic precursors. The solvents usually used to obtain II-VI and III-V semiconductors are mixtures of long-chain alkylphosphines (R₃P), alkylphosphine oxides (R₃PO), alkylphosphites ((RO)₃P), alkylphosphates ((RO)₂PO), pyridines, alkylamines and furanes.

The mean size of the particles can be controlled experimentally. The slow growth by Ostwald ripening during days [45] permits the selection of sizes by the control of the aging time.

Semiconductor colloidal particles in the middle and upper regions of the colloidal domain can be prepared by both reactions in high-boiling point solvents and homogeneous precipitation in water [45]. The polyol-method can be often used to prepare crystalline particles due to the high temperatures of the
synthesis [46]. Metal acetates of Zn, Cd and Hg have been used as metallic precursors and thiourea as sulfur source for the preparation of metallic sulfides [47]. In aqueous solution a salt containing metal (e.g.: Zn, Cd, Pb) is used as metallic precursor. The non-metallic atoms are provided either by (a) passing $H_2S$ through the solution, (b) by thermally decomposing thiourea, thioacetanilid or selenourea in the solution or (c) by addition of a $Na_2S$ or a $H_2S$ solution to the liquid containing the cation [48, 49, 50, 51].

**Organic Polymers** Polymeric particles in the colloidal domain can be prepared by following two main routes [52]. In the first one either natural or synthetic polymers are given a spherical shape by coacervation, solvent evaporation in emulsion, or spray-drying, among others. Despite being bottom-up pathways, these procedures yield particles broadly distributed in size. The second group includes those pathways, where spherical particles form by Heterogenous Polymerization. Among these methods are Emulsion Polymerization, Suspension Polymerization, Dispersion Polymerization, Precipitation Polymerization (Figure 1.2), which are also a bottom-up methods, but these ones yielding more monodisperse particles.

![Polymerization pathways](image)

Figure 1.2: Polymerization pathways related to the order of magnitude of the obtainable particles. Adapted from ref. [52].

In the case of particles prepared by Heterogenous Polymerization, the properties of the particles mainly depend on the monomers used, but emulsifiers and initiators play likewise an important role. Emulsifiers have been used to prepare a variety of polymer lattices with a high degree of monodispersity and with a mean size which can be varied within wide limits [53]. Initiators are required to start the polymerization leading to the monodisperse particles. Emulsifiers are often weakly bonded to the structure of the particle, and their release can modify in an undetermined way both the composition of the dispersive medium and the surface of the particles in the colloidal system. Initiators are normally tightly bonded to the structure of the particle and have an influence on the surface structure of the particles. The problem created by the emulsifiers has been overcome by the development of a soap-free emulsion polymerization and by the use of polymerizable emulsifiers.
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A great number of monomers has been used to prepare colloidal dispersions of monodisperse spherical particles [52]. Mostly vinyl-monomers have been used, but more recently aniline and pyrrole have been polymerized in this form as well. In the former case, the vinyl-moiety of the monomers is involved in the formation of the polymer. The rest of the monomer influences the properties of the material. By judiciously choosing the monomer, polymeric particles with a wide range of properties can be prepared. Moreover, further modification of the polymeric particle is possible, if monomers with reactive groups are chosen [54].

Most of the polymer latices are prepared by emulsion polymerization [52]. This process can be considered to occur in two stages: firstly a nucleation and then a growth stage [53]. The monomer is emulsified in water with a suitable emulsifier to obtain a stable oil-in-water emulsion. Then the initiator is added and the polymerization is started. In a first stage nuclei with a fairly broad particle size distribution are formed and then follows the growth, which sharpens the particle size distribution.

Dispersions of monodisperse latices can also be prepared by growth from a seed-dispersion [52, 53]. Most commercial processes involve the use of seed-dispersion, which are semicontinuously fed with monomers, initiators and surfactants [55]. The sole purpose of the use of a pre-seed solution is control of the particle size. In the laboratory, batch syntheses are common practice, and though producing latices with broader particle size distribution, they are considerably easier to operate.

Oxides Among the oxides, monodisperse silica spheres are probably the scientifically and technologically most important. Monodisperse oxidic particles of elements different than silicon have been prepared with a diversity of morphologies [56, 48]. In contrast, only few examples of monodisperse, oxidic spheres have been reported [57, 49, 58].

Oxidic colloidal particles are commonly prepared by reaction in a liquid medium. Precursors for the elements forming the oxide are organometallic compounds (e.g.: alkoxides, acetates) or inorganic salts. The reaction medium is normally a mixture of water and an organic solvent. Catalysts are often used.

The reaction in the liquid medium can be considered as constant competition between hydrolysis and condensation reactions, which can lead to oxidic, colloidal particles. As materials with a wide range of morphologies can also be obtained by the sol-gel method, it is important to find the pathway providing monodisperse particles.

The monodisperse silica spheres are well studied colloidal particles. Since the first publication [59], much work has been done with this model colloid. In the synthesis alkoxides are dissolved in water-alcohol mixtures, where hydrolysis and condensation takes place. The alcohol is a co-solvent, which facilitates the hydrolysis of the alkoxide by making with this water-immiscible precursor a homogeneous solution in water-alcohol as solvent [60]. A basic catalyst (e.g.: NH₃) is added to favor both the hydrolysis of the precursors and condensation of the reacting silicon-containing species.

The mechanism of formation of the silica spheres is under debate [56]. Matter of debate is whether there is an initial nucleation followed by a diffusional growth, or there is an initial formation of clusters or small particles which subsequently aggregate into uniform, larger particles.
1.6.2 Core@shell particles

The reported syntheses for monodisperse core@shell particles can be divided into four groups, according to the method used for the creation of the shell. The first group includes syntheses where monodisperse particles used as templates are directly coated with atomic or molecular precursors [61, 62, 63, 64, 65, 66]. The second class resembles deposition-precipitation methods known for the formation of catalysts, where a surface controlled precipitation is used to directly form on the template [67]. The third method comprises syntheses using core@shell particles as templates, where a non-porous core is surrounded by a porous shell [20]. Thus particles of the type template@template,A can be obtained. The last class of syntheses resembles Langmuir-Blodgett techniques, in that the shells are formed by alternately depositing monolayers of polyelectrolytes and/or nanoparticles [68].

There are more methods to produce core@shell particles than those discussed in the following. However, those methods typically yield polydisperse particles instead of monodisperse, which are the topic of this work. Those methods yielding monodisperse particles above the colloidal domain, like for instance membrane emulsification, are also out of the focus of the work [69].

1.6.3 @shell particles

The reported syntheses for monodisperse hollows spheres can be divided into two groups, according to the method used for the creation of the shell.

The first group includes syntheses, where the core of a core@shell particle is removed by a either a chemical or a thermal treatment. Principally core@shell particles with either a siliceous or a polymeric core have been used. Aqueous solutions of NaOH and HF can remove silica at room temperature. Organic polymers can be removed with a solvents or by thermal treatment [70, 71, 72, 73, 74].

A second group considers the synthesis through a mechanism analogous to the Kirkendall Effect [75, 76, 61]. Hollow nanostructures form because of the difference in diffusion rates between two components in a diffusion couple. This process provides a general route to the synthesis of hollow particles with wide chemical compositions.

There are more methods to produce hollow spheres than those discussed before. However, these methods, such as spray-drying and dripping, emulsion and suspension techniques typically yield either polydisperse hollow spheres instead of monodisperse spheres which are the topic of this work or particles outside of the colloidal region [77, 78, 79]. Moreover, monodisperse hollow particles prepared by photolithographic methods are beyond the scope of this work [80].
Chapter 2

Monodisperse core@shell as binary exotemplates

Monodisperse colloidal particles with a homogeneous composition, with a core@shell structure and a hollow structure were introduced in the first three Chapters. In this and the coming Chapters of the introduction the focus of interest will be put on some applications of those particles. Here, the use of monodisperse core@shell particles as exotemplate to prepare either composite particles, hollow composite particles, core@shell particles and hollow particles will be presented.

2.1 Templating

Templates can be classified in two group according to whether the template is completely surrounded or not by another material phase. Molecular or supramolecular units added to a synthesis mixture can be occluded in the growing solid and form a composite material. In this case, the template is called an endotemplate. Alternatively, when the template contains a pore structure that can be filled with the precursor for a solid material, the template is called an exotemplate.

2.1.1 Historical development

The historical development of the use of templates and structure directing agents (SDA) (molecules which favor a structure, but not necessarily acts as template in the sense of a 1:1 replication) will be presented from two points of view. Ordered porous materials and monodisperse core@shell particles will be considered.
Ordered Porous Materials

Syntheses for zeolites have been developed in the 1930s using alkali and alkaline-earth cations. In the 1960s the synthesis of zeolites was revolutionized with the introduction of short-chained quaternary alkylammonium ions [81]. But it was in the early 1980s that the words template and templating started to appear in the zeolite-community in connection with organic SDA capable of forming micropores with sizes up to 1.2 – 1.3 nm [82].

Ordered porous materials with pore sizes in the range of 2 – 10 nm have been synthesized by extending the alkyl-chain-length of the quaternary ammonium ions to 10-20 carbon atoms [83, 84]. By changing the type and increasing the size of the SDA, mesoporous silica with periodic, 5 to 30 nanometer-sized pores could be created a few years later [85, 86]. Since the end of the 1990s colloidal crystals have been used as exotemplate to prepare ordered, macroporous solids [87, 88]. Here, instead of molecules, monodisperse colloidal particles have been used to form periodic arrays of macropores in oxidic structures.

In the late 1990s ordered mesoporous materials of silica were used as templates to prepare ordered mesoporous carbons [89, 90, 91]. Hence, the material obtained by using a molecular SDA became itself a template to prepare mesoporous structures of materials which can not be prepared by following the same way that had been used so far for silica.

The use of ordered mesoporous materials was taken one step further in 2002, when ordered mesoporous carbon materials were used as templates to obtain again a mesoporous silica. Three consecutive replications were done to prove the potential of the replication in the preparation of ordered composite and porous materials [92].

Summing up, the templating has made possible the preparation of ordered porous solids over several length scales without major gaps.

Monodisperse core@shell particles

The preparation of core@shell particles belongs to another field that has been using the templating concept. Similar to the ordered porous materials, the preparation of core@shell particles started in the first half of the 20th century. In the following, a chronological description of its development will be presented.

The encapsulation of particles leading to core@shell systems is known since the 1920s, but only 30 years later appeared the first paper dealing with a theoretical study considering this kind of system, namely the expansion of Mie’s theory of the diffraction of electromagnetic plane waves to core@shell particles [5]. In the late 1950s a general method for covering particles with silica was patented [18], but not until the middle 1960s was the synthesis of metallic core@shell particles for optical studies reported. In this work colloidal gold particles were covered with a layer of silver. In the late 1980s more detailed investigations about the synthesis of core@shell particles started. In the 1990s the Layer-by-Layer self-assembly of polyelectrolytes and nanoparticles applied on monodisperse spheres made possible the preparation of monodisperse core@shell particles [93], having its conceptual origin in what nowadays is known as the
2.2 APPLICATIONS

Langmuir-Blodgett technique [94]. Nevertheless, it seems that the scientists had been mostly interested in the studies of the application of such particles [56, 48] and less in the development of new materials on the basis of such particles as templates.

This changed in the last years of the 1990s: templating starts to be considered in synthetic pathways for core@shell particles. Monodisperse silica spheres were used as endotemplate, but this time a SDA was incorporated in the shell to build SiO$_2$@SiO$_2$ Organic. After a thermal treatment the particles converted to SiO$_2$(non-porous)@SiO$_2$(porous) [95]. The idea of covering particles with a homogeneous composite shell containing a SDA triggered the synthesis of new kinds of particles that can serve as hard templates to prepare monodisperse carbon particles [20, 21].

2.1.2 Binary Exotemplate

The use of exotemplates can be broadened by introducing binary exotemplates that will be described in the following.

Most exotemplates so far used are made of one substance. Templated synthesis of ordered porous materials takes place in most cases by using either silica, or carbon, or a polymer [82]. Core@shell particles have been prepared mainly with these materials in the upper colloidal region, where the variety of materials is much more restricted than in the lower colloidal region.

Exotemplates formed by more than one substance expand the potential pathways for the preparation of either composite or porous materials. Exotemplates with two solid components will be called binary exotemplates.

In particular, the use of core@shell particles as binary exotemplates opens new pathways for the synthesis of monodisperse porous and/or composite particles. Hence, materials can be shaped into forms otherwise difficult to prepare, if known at all.

2.2 Applications

The use of binary exotemplates in the synthesis of monodisperse colloidal particles is a new idea.

Exotemplates made of the same substance have already been used in the synthesis of monodisperse colloidal particles [20, 21]. Following this pathway it is possible to prepare carbonaceous particles monodisperse in size.

An endotemplate and an exotemplate have been combinedly used in the synthesis of monodisperse core@shell particles [95, 96]. The common strategy followed in the latter cases is the deposition of a composite layer containing the SDA and the precursor for an inorganic compound onto monodisperse spherical particles. The difference in those pathways is that one uses the same SDA in the core and the shell and the other different ones in both places.
In Chapter 6 the use of binary exotemplates will be presented. This made possible the formation of different composite core@shell and hollow particles, all of them monodisperse in size [31].

2.3 Templating with \(A(\text{non-porous})@B(\text{porous})\)

In this work \(A(\text{non-porous})@B(\text{porous})\) particles will be used as binary exotemplates. The binary exotemplate which is going to be used was developed during this thesis. A thorough description of these particles will be given in Chapter 4. Briefly, they are \(SiO_2@ZrO_2\) particles with a non-porous, amorphous core and a porous, crystalline shell.

To show how the templating works, the porous structure of the binary exotemplate will be first filled with furfuryl alcohol (FA). This monomer will be then polymerized in the porous structure of the shell and finally carbonized. The filling with the monomer, the polymerization and the carbonization will be seen in Chapter 6.

2.3.1 Polymerization of furfuryl alcohol

There is little known about the chemistry of FA in the formation of composite materials. Contrastingly, the polymerization in solution has been widely studied [97, 98]. FA starts its polymerization with condensation reactions between \(OH\) groups and either an H1 atom of a furan ring (head-to-tail structure 2) or another \(OH\) group (head-to-head structure 3) (Figure 2.1 & 2.2) catalyzed under acid conditions irrespective of the nature and strength. Oligomers containing two types of bridges, namely methylene and dimethyleneoxide, can be prepared. However, under strongly acidic conditions 3 tends to lose formaldehyde and reverts to 2. This latter tendency and a kinetic favorable head-to-tail condensation results in macromolecular structures in which methylene bridges are in general much more frequent than the dimethyleneoxide ones.

![Figure 2.1: Furfuryl alcohol with the numbering of its hydrogen atoms.](image)

As the polymerization continues, two major side events take place, which lead to a change in color and the cross-linking in the polymer. The change in color -the material becomes firstly grey and finally black- is ascribed to the abstraction of hydrogen from the methylene groups, which leads to the formation of highly delocalized carbenium ions. The more conjugated carbenium ions are formed in the polymer, the stronger the absorption of the chromophores in the visible region of the electromagnetic spectrum [99].
If the only reaction in the polymerization would be the condensation, the polymer should be colorless, because the 2,5-dialkylsubstituted furans absorbs radiation with $\lambda < 250$ nm [98].

The second event is the branching and eventually the cross-linking of the polymer. This process has been attributed to a Diels-Alder reaction between a furan ring (diene) in one molecule and a conjugated dihydrofuranic sequence (dienophile) in another oligomer [99]. The former are part of the monomers linked by a condensation reaction. The latter belongs to the chromophores which develop after the abstraction of hydrogen from the methylene groups in the linear oligomers.

### 2.3.2 Carbonization of poly(furfuryl alcohol)

Poly(furfuryl alcohol) (PFA) has long been known as a good carbogenic precursor for the preparation of microporous carbons [100, 101]. A few years ago the first ordered mesoporous carbons -containing also micropores- were synthesized by a templating route using PFA as precursor of the carbon [102].

The carbonization of PFA is a rather complex process, where several chemical reactions are involved [103]. From the chemical point of view, four processes -which can overlap- are known to be involved. Firstly, the furan rings disappear between 623 and 773 K. One way this can happen is by an opening of the ring leading to vinylene 4,5 and unsaturated carbonyl 4,5 groups (Figure 2.3). Those unsaturated carbonyls are known to present a keto-enol equilibrium. Secondly, the amount of saturated ketones decreases at 473 K, increases at 573 K and abruptly disappears between 573 and 632 K. Thirdly, the amount of methylene groups fluctuates in the temperature range 573-673 K, and decreases by further increase of the temperature. Finally, the aromatic rings start to form at temperatures around 632 K. This is considered to occur by both a reaction between dienes and unsaturated carbonyl and a dehydration between two unsaturated carbonyl groups (Figure 2.4).

The pore structure of the final carbon depends on thermal treatment used during the carbonization [104, 105, 106]. Considering the many irreversible reactions happening during the carbonization, these results should be expected. The micropores in the carbon are usually considered to be slit-shaped. It has been experimentally observed that (a) the surface area of the material goes through a maximum at intermediate temperatures for the carbonization, (b) at higher temperatures the maximum of the
Figure 2.3: Reaction causing ring-opening in furanes (top) and keto-enol equilibrium of the products (right).

Figure 2.4: Reactions between a diene and an enol group (top) and two enol groups (bottom) leading to unsaturated ring formation.
micropores size distribution shifts towards smaller values, (c) the higher the temperature and the longer the sample remains at the final temperature, the narrower becomes the pore size distribution, (d) carbon obtained at about 673 K is heavily distorted on an atomic scale and possesses a relatively open structure which could be considered as an assembly of carbonaceous, polymeric-like chains, (e) carbons obtained at 1073 K contain curved and defective graphene sheets, and (f) carbons made at 1473 K have crystalline, nanometer-sized domains of graphene.

2.4 Conclusion

Core@shell particles containing a few different substances can in principle be used for the preparation of many other materials via the templating route. This pathway is particularly interesting in those cases where particles with a controlled shape and pore structure are controlled, for which no direct synthetic route is known.

As proof of concept, furfuryl alcohol is an adequate monomer to be used in the filling of and in the polymerization in the pore structure of the template. Furthermore, this polymer is a good carbonogenic material, which can straightforwardly be converted into carbon inside of the particle used as template.
Chapter 3

Morphology in Crystalline Structures

"On the basis of an analysis of everyday experience and practice, criteria of legitimate assertions of existence and truth are offered. [...] these criteria can be extended to the scientific theoretical level to support a selective and moderate version of scientific realism according to which entities like the electromagnetic and gravitational fields, but not crystalline spheres [...] can legitimately be asserted to exist."

Glins M. [107]

This last Chapter of the introduction shows a structure which differs completely from the previous ones. Originally, core@shell particles with a ZrSiO$_4$ shell were looked for. Instead, spherical and spheroidal crystalline particles were serendipitously found and thus the conditions for the occurrence of spherical crystals will be discussed.

3.1 The Polyhedra

Nowadays, it is widely accepted that the equilibrium shapes of crystals can be described as polyhedra, where either thermodynamic or kinetic factors determine the final shape of a crystalline particle [108]. In the former case, the equilibrium shape is determined by the minimization of

\[ \sum_{i=1}^{n} \Delta G_{s,i} A_i \]  (3.1)

where \( \Delta G_{s,i} \) is the interfacial free enthalpy change per unit area of the face \( i \) and \( A_i \) the surface area of the face \( i \). When \( \Delta A_i \) for the interface required by different morphologies become very small, the
habit of a particle is determined by kinetic rather than thermodynamic effects. The overwhelming empirical evidence collected during almost a century since Wulff’s publication of the theory of crystalline habitus [109] together with the fact that interfacial energies are not usually accessible experimentally but estimated [108] might have played an important role in the solidification of the idea that a crystal’s habitus has to be a polyhedron.

Despite the fact that there is a widely accepted opinion on crystals being polyhedra, is it realistic to think about a crystal without edges?

3.2 The Edgeless Phase

3.2.1 Formation of a new phase

A new phase can be created from a homogeneous system in two different ways: (a) by nucleation and growth and (b) by spinodal decomposition [108, 110]. From the synthetic point of view this is very important, because materials with different properties can be prepared by following one way or the other. The manner of leading a system through one way or the other can schematically be shown with the phase diagram for the binary system Li$_2$O-SiO$_2$ (Figure 3.1).

If the system is brought from the homogeneous liquid melt above the liquidus line into the region located between the miscibility and spinodal lines, the melt tends to separate into two glassy phases. For instance, if brought to the point a, the composition of the two glassy phases is given by composition at the points b and c. As a result of the nucleation occurring under these conditions, usually one phase forms droplets and the other a matrix in which the droplets are immersed.
3.2 \textit{THE EDGELESS PHASE}

On the other side, if the system is brought from the liquid melt into a region below the spinodal line, the system undergoes a spinodal decomposition. Hence, habitually two interconnected, worm-like, glassy structures form. The presence of a worm-like structure in a material is a good indication that it has been prepared by a spinodal decomposition \cite{110}.

A drawback for such an approach to predict the conditions to which a melt should be brought in order to obtain a material with a desired structure is the insufficient knowledge about what happens below the immiscibility line for most material systems. Moreover, it is known that the position of the bell-shaped miscibility line is markedly affected by the addition of a third component \cite{110}, so that if the phase diagram is known for a binary mixture, the influence of impurities should be also explored experimentally.

3.2.2 Crystallization of spherical phases in a matrix: Devitrification

After the phase separation leading to two amorphous phases - either spherical domains in a likewise amorphous matrix or two interconnected, worm-like structures- crystallization can start in each of both phases \cite{111}. From now on the interest will be focused on systems with spherical domains embedded in a matrix of another material.

The composition of the two phases will not be that of pure substances, if the phase separation is a consequence of a nucleation and a further growth. The phase will be richer in one of the components, but the other will typically be present. The composition of each phase is determined by the temperature and the location of the miscibility line in the phase diagram. Hence there can be either a partial crystallization leading to a further phase separation or a complete crystallization of one phase \cite{110}.

In case of a complete crystallization of the spherical phase, a distortion of the crystalline structure might be expected, because the phase is not a pure substance but a phase rich in one substance. If an isomorphous replacement of cations takes place during crystallization, a change in the averaged unit cell of the crystal is expected. But a signal attributable to one defined crystalline phase should be seen by X-ray diffraction, if the crystalline domains are sufficiently big.

One nice example of the crystallization of spherical phases is offered by fluorosilicate-glasses \cite{111}. Amorphous spherical domains are present after the phase separation. There is experimental evidence that crystallization usually starts inside of both phases, but not from the interface between them \cite{110}. The crystal grows in the spherical domain till it reaches the phase boundary. Then crystallization stops.

It is difficult to know in those cases reported in the literature, whether the crystal structure retains the smooth interphase present after the phase separation and before the crystallization started, or a rough interface forms at a length scale bigger than a few nanometers \cite{111, 112}. In other cases the crystals formed from the spherical amorphous phases show clearly edges or a surface roughness.

3.2.3 Usefulness of Devitrification

The crystallization of a two-phase glass has been initially investigated by researchers working in the preparation of glasses. This devitrification was considered a problem in the glass preparation. In order
to avoid it, the study of the nucleation and growth of crystals in glasses shifted into the focus of the investigations [111, 112], to be able to predict the occurrence of nucleation and to avoid it.

But later the crystallization in glasses became a pathway to obtain materials which received the name glass-ceramics. They are actually materials with important uses. Among these materials are the Corning-glasses which have a small thermal expansion coefficient, bio-ceramics for medical applications and photo-sensitive glasses and ceramics [111, 112].

One application that seems to not be considered so far for this process is the preparation of spherical crystals. The amorphous, spherical domains embedded in a likewise amorphous matrix can be considered to be on the way leading to spherical crystals.

### 3.2.4 Spherical crystals

It was said that the crystallization can start inside the amorphous, spherical domain. The success in the preparation of spherical crystals depends on the shaping of the interphase.

One possible scenario is the kinetic arrest of the crystallization at the boundary of the spherical phase. If the crystallization is frozen as soon as the crystalline-amorphous boundary reaches the composition boundary, it is plausible to think that the spherical shape can be frozen in the vitreous matrix. An argument for this statement could be based on the high viscosity of the amorphous matrix.

Another possible scenario is the presence of very small differences in the surface energies for all imaginable crystalline planes of the crystal. As the formation of a surface is considered to be always a non-favorable process, the crystalline particle could reduce its surface by taking a spherical shape. This could also happen, if crystalline particles with any shape would be embedded in a vitreous matrix and the material would be heated up. Hence the crystals could melt inside of the matrix and acquire the spherical shape.

### 3.3 Conclusion

The formation of spherical crystals seems to be plausible based on what is known from the investigations developed by scientist working in the preparation of glasses and glass-ceramics. Moreover, the presence of perfectly spherical crystals can be observed in some published studies [113]. Nevertheless, the existence of crystals with an unusual habitus does not seem to attract a high level of attention.
Part III

Results and Discussions
Chapter 4

$\text{SiO}_2 @ \text{ZrO}_2$

Can one prepare monodisperse core@shell spheres with a non-porous core of silica and a porous shell of zirconium oxide? Can silica and zirconium oxide react to form zircon ($\text{ZrSiO}_4$)? In this chapter an investigation conducted to find out answers to those questions will be presented. The synthetic procedure to obtain the core@shell particles will be given at first. Then follows the characterization of the material at both intermediate stages and at the end of the synthetic pathway. Finally, a study of the thermal behavior of the core@shell spheres is undertaken.

4.1 Synthesis

The synthesis of the material, the characterization of which will be seen in Section 4.2, has four steps (Table 4.1). In the first one, monodisperse siliceous spheres are prepared following the well established Stöber process [59]. The synthesis starts by mixing 64 g of ethanol (LiChrosolv, Merck) and 22 g of an aqueous solution of $\text{NH}_3$ (Acros Organics, 28 – 30 %) in a 500 ml flask with one neck. The flask is sealed with a septum and the solution is heated under stirring to 303 K. Then 4.2 ml of tetraethoxysilane (TEOS) are rapidly injected into the solution. The system is left to react under stirring for 60 minutes over which a colloidal suspension containing monodisperse siliceous particles forms. Then the liquid phase of the colloid is exchanged for ethanol. This is done by centrifugation (5000 rpm, 5 min.), removing the liquid phase, and re-dispersing the solid in water (100 ml). This step is repeated three times, and then additionally three times by re-dispersing the solid in 100 ml of ethanol, except after the last centrifugation, where silica spheres are dispersed in 100 g ethanol (step 1).

In the second step, the monodisperse silica particles dispersed in 100 g ethanol are poured in a 500 ml single neck flask. Again, the flask is sealed with a septum and heated under stirring to 303 K. Afterwards, 0.5 ml of an aqueous solution of 0.43 g Lutensol AO5, a nonionic amphiphilic surfactant, in 11 g $\text{H}_2\text{O}$ are added. One hour later follows the addition of 1.8 ml of zirconium butoxide (80 w/w in butanol, Aldrich) and the reaction is allowed to proceed overnight at 303 K. Then, the liquid phase of the colloid is exchanged again, this time for water by centrifuging and re-dispersing the solid four times in $\text{H}_2\text{O}$ (100 ml) (step 2).
Table 4.1: Description of the samples obtained at different stages of the synthesis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Silica sphere (endotemplate)</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>Silica core and amorphous shell with zirconium hydroxide</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>Silica core and amorphous shell with zirconium hydroxide, aged 3 days at 293 K</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>Silica core and zirconium oxide shell after calcination at 1173 K</td>
<td>4</td>
</tr>
</tbody>
</table>

Third, the particles are aged in water at 293 K for three days. It should be noted here that this step has an important influence on the structure of the shell (step 3).

Finally, the removal of the organic material and the crystallization of the hydrated zirconia present in the shell into the oxide are achieved during a calcination step under air by heating with a rate of 2 K min\(^{-1}\) to 1173 K (step 4).

### 4.2 Characterization

In this section, the characterization of the material synthesized in Section 4.1 will be presented. At first, a morphological study is done by Transmission Electron Microscopy (TEM), which can provide information about the homogeneity of the coverage surrounding the siliceous core. Then the pore structure of the material is explored by Nitrogen Sorption, which also gives the specific surface area of the material. Thereafter, information about the presence of crystalline and amorphous phases is sought by X-ray diffraction. At last, we will get a picture about the core@shell particles that is completed with the results of the analysis of the silicon present in the material by Nuclear Magnetic Resonance.

#### 4.2.1 TEM

The morphology and crystallinity of the different material phases present in the core@shell particles can be explored by Transmission Electron Microscopy.

The sphericity of the core@shell particles and their monodisperse distribution in size can be seen in the TEM-images. In the foreground of Figure 4.1 we can see several black circles corresponding to core@shell particles. In the background we catch a sight of the sample holder. The dark grey zones correspond to the carbon-film, on which the particles are supported, and the light grey ones to the holes etched therein. In the upper left corner there is a magnified picture of one core@shell particle. The particle in
4.2 CHARACTERIZATION

Figure 4.1: Morphology of secondary core@shell particles after step 4. Scale bar 2 μm and 100 nm (inset).

This picture shows two regions: the shell and the core. A morphological characterization of the different phases present in a composite material can be done, provided there is a good contrast between them. The roughness of the external surface of the shell can be appreciated. This is due to the presence of nanometer-sized primary particles. The shell surrounds a siliceous core, which appears as a black circle.

The shell comprises nanometer-sized crystalline particles, which are also monodisperse in size. While the core@shell spheres are monodisperse in size with a maximum in the upper colloidal region (ca. 100 nm to 1 μm), the nanocrystalline particles have a mean size of around 5 nm. The nanocrystals are two orders of magnitude smaller than the core@shell spheres. In TEM-images of the shell with high magnifications the lattice fringes of the crystalline structure in those nanocrystals can be appreciated.

The cores shrink somewhat during the thermal treatment at the last step of the synthesis and the shells keep a perfectly spherical shape. The shrinkage of the core can be seen in the TEM-images (Figure 4.3 Inset), where the core lost the spherical shape it had as endotemplate in the first step of the synthesis. A gap seems to form between the surface of the condensed core and inner surface of the spherical shell.

Summing up, core@shell particles were synthesized, which are monodisperse in size. While the shells contain nanometer-sized particles and keep their perfectly spherical shape after calcination, the cores shrink, losing the spherical form they had before the thermal treatment.
Figure 4.2: Morphology of particles in the shell of the core@shell particles after step 4.

Figure 4.3: Nitrogen sorption isotherm of the exotemplate a and the core@shell after 4th step.
4.2 CHARACTERIZATION

4.2.2 Nitrogen sorption

The information obtained by TEM can be complemented by an analysis by nitrogen sorption. This technique informs about the presence of pore structures in the micro \((d < 2 \text{ nm})\), meso \((2 \text{ nm} < d < 50 \text{ nm})\) and lower macropore ranges \((50 \text{ nm} < d < 200 \text{ nm})\) [114]. Furthermore, the specific surface area of the material can be estimated by the BET-method [115].

Information about the pore structure in the core@shell particles is extractable from the shape and position of the isotherm. A view of the nitrogen sorption isotherms of both the monodisperse siliceous spheres (a) and the core@shell particles (b) can be taken in Figure 4.3. At the bottom of the Figure, the endotemplate presents an isotherm of type II [8], which is typical for non-porous particles bigger than several hundreds of nanometers (a). At low relative pressures there is a small up-take of nitrogen. Then a relative flat curve follows, which represents a low adsorption during the formation of a multilayer with \(N_2\) on the surface of the material as the relative pressure increases. Finally, an increase in the up-take is seen due to the condensation of nitrogen at junctions between spheres when the relative pressure approaches unity. At the middle of the Figure 4.3, a sorption isotherm of type IV (b) corresponding to the core@shell particles can be seen. There is, unlike in the case of the template, an important up-take of nitrogen at low relative pressures, which indicates the presence of micropores. These micropores were absent in the endotemplate. As the relative pressure increases, there is an increasing up-take of nitrogen. This suggests capillary condensation of the gas molecules in big micropores and in small mesopores. The adsorption in the mesopores continues till high relative pressures, where the condensation in the space among the core@shell particles becomes evident by the steeper increment of the adsorbed volume of nitrogen. The desorption branch meets the adsorption branch at relative pressures slightly higher than 0.42 and both branches form a hysteresis. This suggests the presence of mesopores bigger than 4 nm in the core@shell particles.

It is legitimate to ask whether the microporous structure developed in the siliceous core or arose with the shell during the synthesis. It is for this reason, that monodisperse silica spheres without a shell were thermally treated like the core@shell particles in the fourth step of the synthesis (cf. Table 4.1). These particles were analyzed by Nitrogen Sorption and the isotherm (not shown) indicates that no pore structure developed. This result strongly supports the assessment that the porosity forms with the shell, but is not a definitive proof. The formation of a microporous structure in the core in the core@shell particles can not be fully excluded, although it is highly probable and will be corroborated by results discussed in the following.

Another important piece of information can be obtained from those sorption isotherms for the endotemplate and for the core@shell spheres: the specific surface area of the particles. On one side, the exotemplates show a low value, \(5 \text{ m}^2\text{g}^{-1}\), which is expected for spherical siliceous particles with a diameter between 500-1000 nm and a density somewhere between 1.5 – 2.0 g.cm\(^{-3}\). On the other side, the core@shell particles have a specific surface area of 160 \(\text{m}^2\text{g}^{-1}\). In Chapter 5 it will be shown that these particles lose a big portion of their mass after the extraction of the siliceous core. If we neglect the contribution from the solid core to the surface area and attribute the 160 \(\text{m}^2\text{g}^{-1}\) calculated for the core@shell particles only to the shell, the shell alone thus would have a specific surface area close to 300 \(\text{m}^2\text{g}^{-1}\). This important increase in the specific surface area after the formation of the shell together with the observations from the TEM-images validate the presence of small particles in the shell.
A distribution for the pore sizes can be obtained from the sorption isotherm by NLDFT. This analysis indicates the presence of both micropores and mesopores. The latter have a bimodal distribution with maxima at about 3.0 nm and at 5.2 nm. Additionally, the TEM-images (Figure 4.3 Inset) show the presence of large cavities, much bigger than the pores determined by sorption analysis. Before calcination, both the core and the shell are spherical and concentric. It is likely that the different thermal behaviors during calcination lead to a dissimilar expansion and/or contraction of core and shell, which results in the formation of voids between the core and the shell. However, the gap may also be caused by removal of organic material which is also introduced prior to the zirconium butoxide.

In sum, the core@shell spheres have a microporous and mesoporous structure and a high specific surface area, which is attributed to the presence of a pore structure in the shell.

4.2.3 XRD

The amorphous and crystalline phases present in the core@shell particles can be explored by X-ray diffraction (XRD). Amorphous phases scatter X-rays, which form a broad signal. The position of its maximum in the diffractogram correlates with the interatomic distance in the matter, for example, in the case of silica with the average length of the bond Si-O. Crystalline phases with a periodicity in the atomic range diffract X-rays in such a way, that Bragg reflections appear in the diffractogram. In the latter case, two valuable pieces of information can be obtained. Firstly, the symmetry and size of the unit cell in the crystal, which is obtained from the number and location of the reflections in the 2θ axis. Secondly, the size of the crystalline domains, if they are smaller than about 100 nm. This information is contained in the reflections’s broadness and can be extracted with Scherrer’s equation [116].

The core@shell spheres contain very small crystals of tetragonal ZrO$_2$ (Figure 4.4). The reflection with a maximum at about 30° 2θ is assigned to (111) planes of tetragonal ZrO$_2$. The broadness of this reflection indicates the presence of very small crystalline domains. From the analysis of that reflection using Scherrer’s equation a mean crystalline domain size of about 5 nm is obtained. In principle, one single particle can contain one or more crystalline domains. If the ZrO$_2$ particles in the core@shell spheres are considered to be as big as the crystalline domains, the material in the shell would have a specific surface area of ca. 300 m$^2$g$^{-1}$ (cf. Section 5.10). This value is very close to the result estimated for the shell from the sorption isotherm in Section 4.2.2. So, there is sound evidence supporting the statement that the nanocrystals seen by TEM in the shell are monocrystals of ZrO$_2$.

The presence of an amorphous siliceous core can be inferred from the broad signal at lower 2θ, which is attributed to SiO$_4$-tetrahedra typically present in amorphous silica. The siliceous endotemplates thus remain amorphous, though a loss of sphericity, which could be possibly attributed to condensation of residual bonds, occurred.

In short, the material synthesized in Section 4.1 contains core@shell particles with an amorphous core and a crystalline shell. The shell has micropores and mesopores and the core is non-porous.
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![Figure 4.4: XRD of the core@shell particles after step 4.](image)

![Figure 4.5: $^{29}$Si MAS NMR of the exotemplate (a) and the core@shell particles after step 4 (b).](image)

4.2.4 NMR

Information about the atomic environments for elements having a permanent nuclear magnetic moment different than zero can be obtained by Nuclear Magnetic Resonance Spectroscopy (NMR). This information about the environment can complement the results obtained by diffraction methods (e.g.: X-ray diffraction), specially for materials which exhibit no long-range order or which consist of powders and are not available as single crystals of adequate size and perfection. In solids, the random motion characteristic of liquids is strongly constrained causing large line broadenings. Therefore, several techniques for narrowing the resonance lines in solid-state spectra were introduced in the early 1970’s: magic-angle sample spinning (MAS), high-power dipolar decoupling and multiple pulse sequences. In addition, the cross-polarization (CP) technique was developed to overcome the problem of low sensitivity of nuclei with low natural abundance (e.g.: $^{13}$C and $^{29}$Si) [117]. In this Chapter $^{29}$Si MAS NMR is used to follow changes in the environment of silicon atoms (e.g.: due to condensation or reaction of silica with zirconium oxide).

The silica present in the core@shell particles condenses during the thermal treatment of the synthesis. This phenomenon can be appreciated by $^{29}$Si MAS NMR (Figure 4.5). Before the thermal treatment, the endotemplates (a) show signals, which can be attributed to predominantly $Q^3$ (102 ppm) and $Q^4$ (111 ppm) silicon atoms. After the aging and the high temperature treatment, the two signals merge into one centered at 109 ppm, which can be assigned to $Q^4$ species (b). This can be attributed to an almost complete condensation of the silica, which is in fact expected after treatment at 1171 K.
Silica and zirconium oxide seem to not react under the thermal treatment employed during the synthesis of the core@shell spheres. Nevertheless, it is difficult to make a sound statement, because the broad signal in the spectrum may hide chemical changes under its final shape.

Thus, the core@shell particles contain silica, which has a higher degree of condensation than the siliceous spheres used as templates, and no bulk reaction seems to occur between both oxides.

4.3 Effect of temperature on structure: \( \text{SiO}_2@\text{ZrO}_2 \) to \( \text{SiO}_2@\text{ZrSiO}_4 \)\?

The plausible transformation of \( \text{ZrO}_2 \) in the shell into \( \text{ZrSiO}_4 \) triggered this study about the thermal behavior of the core@shell spheres. \( \text{ZrSiO}_4 \) has extraordinary thermal, mechanical and chemical stabilities, which would be extremely interesting in, for instance, the form of either nanometer-sized crystals or a shell in a core@shell particle. The presence of mainly \( \text{Q}^4 \) species after the synthesis of the core@shell particles (cf. Section 4.2.4) shows that only a highly condensed silica is present. A further thermal treatment at higher temperatures could produce \( \text{ZrSiO}_4 \) [118].

4.3.1 Thermal treatment

In the following the thermal treatment of the material is described. Monodisperse core@shell spheres are brought into a crucible of \( \text{Al}_2\text{O}_3 \), which is then placed in an oven. The thermal treatment follows under either air or argon. Under air, samples were treated up to 1673 \( K \); under Ar between 1673 \( K \) and 1973 \( K \). The heating program is:

\[
30 - T_{\text{final}} \ (2 \ \text{K min}^{-1}); \text{cooling down in oven}
\]

with \( T_{\text{final}} = 1313, 1373, 1473, 1573, 1673, 1773 \) and 1973 \( K \).

4.3.2 Characterization

Thermally treated core@shell spheres for the different \( T_{\text{final}} \) were characterized by XRD. This technique can directly show whether the desired transformation takes place.

X-ray diffraction

The growth of nano-sized crystals and the change of crystalline phases to see whether \( \text{SiZrO}_4 \) formed or not can be followed by XRD. The crystalline domains of \( \text{ZrO}_2 \) grow as temperature increases, but remain small up to 1473 \( K \). This can be seen in figure 4.6. The as made core@shell particles show a broad
4.3  EFFECT OF TEMPERATURE ON STRUCTURE: $\text{SiO}_2@\text{ZRO}_2$ TO $\text{SiO}_2@\text{ZRSIO}_4$?

Figure 4.6: Influence of final temperature on primary particle size.

(111) reflection at about $30^\circ \theta$ (bottom). Between 1313 and 1473 K a contraction of this reflection is seen. If the temperature is further increased, not only the crystalline domains grow, but also a phase transformation occurs (Figure 4.7). Crystalline domains gradually change from the tetragonal to the monoclinic phase of ZrO$_2$. But the phase transformation is not completed and both crystalline phases -tetragonal and monoclinic- are present up to 1673 K. And this remains so, even if the sample is kept at that temperature for 5 hours (Figure 4.8). But in the latter case another crystallization starts. The amorphous silica present in the core@shell particles crystallizes to cristobalite.

Figure 4.7: Influence of final temperature on primary particle crystalline phase.

The reaction of tetragonal ZrO$_2$ and SiO$_2$ could lead to the formation of ZrSiO$_4$ [118]. The idea of getting core@shell particles with a zircon shell was tempting. The treatments up to 1673 K did not show any formation of this phase. Therefore, treatments at higher temperatures were accomplished. Under an Ar atmosphere, samples were heated with the same rate up to 1773 K and 1973 K (Figure 4.9). Unfortunately both phases of ZrO$_2$ remained, and the SiO$_2$ crystallized at the highest temperature.

It is interesting to mention that the crystallization of SiO$_2$ is slowed down in this material system.
By heating up at 2 K min\(^{-1}\), silica remains amorphous up to 1773 K and crystallizes between 1773 and 1973 K. In contrast, monodisperse siliceous spheres used for preparing those core@shell particles start to crystallize between 1373 and 1673 K.

4.3.3 Conclusion

Starting from the core@shell particles, silica and zirconium oxide do not react to form ZrSiO\(_4\). Instead, a growth of crystalline domains of the transition-metal oxide and a phase change leading to a mixture of the tetragonal and monoclinic structures are seen as temperature rises. Noteworthy is a delay in the crystallization of silica, which takes place at a temperature between 1773 and 1973 K.
4.4 SiO$_2$@TiO$_2$

TiO$_2$ is an interesting material for catalysis and solar cells, among other applications. As this metal is in the same group with zirconium, a similar chemical behavior is expected, which could be exploited for the synthesis of monodisperse core@shell spheres. In fact, it was possible to prepare monodisperse core@shell particles with a siliceous core and a shell containing TiO$_2$.

Monodisperse SiO$_2$@TiO$_2$ spheres can be prepared by following a similar pathway like in the case of SiO$_2$@ZrO$_2$. In Figure 4.10 it is possible to see TEM-images of core@shell spheres in bright-field and dark-field modi. In the latter case the presence of spherical particles with a shell having a different structure than the core can be appreciated. Moreover, it is possible to see that the core@shell particles have a narrow particle size distribution. However, many of the shells seem to be fused, and such materials therefore require more development work.

![TEM image of SiO$_2$@TiO$_2$ particles](image)

Figure 4.10: TEM-image of SiO$_2$@TiO$_2$ particles in bright-field (left) and dark-field (right) modi. Scale bar 2 $\mu$m (top) and 200 nm (bottom).

In Figure 4.11 the nitrogen sorption isotherm shows the presence of the mesopores in a similar way as in the case of monodisperse SiO$_2$@ZrO$_2$ spheres (cf. Figure 4.3). The hysteresis indicates the presence of mesopores in the core@shell particles, which, as was already seen for SiO$_2$@ZrO$_2$, can be attributed to the shell in the SiO$_2$@TiO$_2$ particles. The monodisperse silica spheres used as endotemplates in the synthesis of the core@shell particles are non-porous.

An optimization of the synthesis and an adequate characterization of the material remain an open task, though the preliminary results are promising.
4.5 Conclusion

Monodisperse core@shell spheres with a non-porous core of silica and a porous shell of zirconium oxide can be prepared. The siliceous cores present a higher condensation than the parent silica spheres used as exotemplates. The shells are composed of monodisperse tetragonal zirconium oxide crystals with a mean size of 4 to 5 nm. Among these crystals a pore structure is present in the shell, which is responsible for the surface area of 160 m$^2$ g$^{-1}$ of the core@shell particles.

Silica and zirconium oxide do not react to form SiO$_2$@ZrSiO$_x$. Thermal treatments done up to 1973 K induce an increase of the crystalline domains of zirconium oxide followed by a partial phase transformation from the tetragonal to the monoclinic structure. A significant delay in the crystallization of the silica is observed.
Chapter 5

Monodisperse spherical @shell

The different behavior of ZrO$_2$ and SiO$_2$ in aqueous NaOH can be used to selectively extract the siliceous core from the core@shell spheres presented in Chapter 4. On one side, silica has a low solubility in water at a pH = 1-9, but it rapidly increases above pH = 9 [119]. On the other, ZrO$_2$ is known to be very resistant to an alkaline NaOH solution [120]. The removal of the core provides monodisperse hollow spheres (secondary particles) made of likewise monodisperse nanocrystals of ZrO$_2$ (primary particles).

Interestingly silicon remains in the hollow spheres - not as silica anymore - after the extraction of the core. Its presence, puzzling at the beginning, seems to play a crucial role in the properties of the @ZrO$_2$.

5.1 Removal of the siliceous core

Silica is removed from the core@shell particles by a treatment with sodium hydroxide solution (1N). The procedure is described in the following. Firstly, about 1.5 g of the sample is kept for 16 h at 303 K in 50 g of the alkaline solution. Afterwards, the alkaline solution is changed for a fresh one and the extraction is continued at 333 K for 6 to 8 hours. In order to completely remove the sodium hydroxide solution from the particles, the colloidal dispersion is suction filtered, washed five times with $H_2O$, three times with ethanol and finally once with ethyl tertiary-butyl ether (50 ml in each wash) (step 5).

In the following the characterization of the material at different stages of the alkaline treatment will be presented.

5.1.1 TEM

The removal of the siliceous core can clearly be followed by TEM thanks to the favorable contrast between the spheres with and without the silica inside. So, the sample can straightforwardly be prepared for the analysis by deposition of particles onto the sample holder. A time consuming preparation of the sample, requiring first a dispersion of the particle in a polymeric matrix and then thin cuts, can be avoided.
Particles at different stages during the alkaline treatment were analyzed by TEM. For this, samples were periodically extracted and thoroughly washed. The core@shell particles before the extraction can be seen in Figure 5.1a. The spherical shells are made of nanometer-sized ZrO₂, which can be appreciated as small dots. The surface of the shell is rough towards the outside and smooth towards the inside. The core lost the sphericity this material had before the synthesis, most probably due to the condensation of the polymeric silica. After 17 h of alkaline treatment the silica core is partially dissolved in some particles and completely removed in the rest (Figure 5.1b). No changes are seen for the shell, which retains its spherical structure. All siliceous cores disappeared after 22 hours of treatment and left behind well defined hollow spheres. The particles extracted for 42 hours (Figure 5.1c) are representative for particles extracted between 22 and 65 hours.

It is noteworthy that the hollow spheres show an extraordinary chemical stability in the alkaline medium. This stability is expected for the individual ZrO₂ crystals, but not for the secondary particles formed by those nanocrystals.

The primary and secondary structures of hollow spheres can be appreciated in the four images in Figure 5.2. The upper-left image introduces the secondary structure of the hollow spheres. Most of the particles are well defined spheres, which can be ground in an agate mortar without being destroyed. However, some of them do not resist the mechanical stress and break, as seen on the left and on the right of this first image. It is interesting to see how the remaining broken pieces hint at the sphericity of the original particles. This suggest the presence of strongly bonded primary particles (ZrO₂). The upper-right and lower-left images show the roughness of the external surface and the perfectly defined circular section of the hollow spheres. Moreover, the primary particles forming the shell show a fairly monodisperse distribution in size. The lower-right image gives a view into the atomic structure of the nanocrystals present in the shell. Crystalline planes therein can be appreciated.

Briefly, the siliceous core can be removed from the core@shell spheres, providing monodisperse hollow spheres.

5.1.2 Nitrogen sorption

In addition to the characterization by TEM, the dissolution of the siliceous core can be followed by Nitrogen Sorption experiments. This analytical tool makes possible both the examination of the pore structure and the changes in the specific surface area in the core@shell spheres, the intermediate materials and the @shell. The change in the specific surface area can arise from either the formation or disappearance of pores as well as from the removal of a portion of the spheres contributing little to surface area and much to mass.

If the only consequence of alkaline treatment on the core@shell spheres would be the removal of the siliceous core, how would this be reflected in the results of the analysis by Nitrogen Sorption? As already discussed in Chapter 4, the monodisperse silica spheres used as exotemplate are not porous. If the non-porosity of the endotemplate after the formation of the core@shell particles is assumed, the dissolution of the core should only reduce the amount of mass of the core@shell particles, without changing the
Figure 5.1: Dissolution of siliceous core at (a) 0 h, (b) 17 h, and (c) 42 h.
pore structure of the shell. This reduction in mass would stretch the isotherm along the ordinate in the graph representing the sorption isotherms. At the same time, the specific surface area of the spheres should increase, not because new pores have formed, but due to the loss of the non-porous fraction of the particles. This expected behavior is seen in Figure 5.3, but something else happens.

Apart from the displacement and stretching of the isotherm, the hysteresis present in the core@shell spheres vanishes during the alkaline treatment. The broad hysteresis has its closure at \( P/P_0 \sim 0.45 \). The location of the closing point complicates the interpretation of the isotherm: there could be either mesopores with narrow windows desorbing \( N_2 \) at those relative pressures or spontaneous desorption of the condensate in the pore structure of the particles due to the meniscus’s instability at this point [121]. The calculation of the pore size distribution in the core@shell particles by NLDFT (cf. Sections A.1.1 and 4.2.2) yields a trimodal distribution with maxima at 1.6 nm, 3.0 nm and 5.2 nm. When compared to the particle size of \( \text{ZrO}_2 \) estimated from the TEM-images, the biggest mesopores seem to be too big for a shell formed by randomly ordered nanocrystals. Are the biggest mesopores located in the shell?

The disappearance of the hysteresis from the isotherm coincides with the complete removal of the silica cores, as seen by TEM, and there is an experimental study supporting the absence of pores in the core (cf. Section 4.2.2). The pores should be somewhere else. Where?

The hysteresis in the isotherm might arise from the condensation of nitrogen in the space between the core and the shell. In Chapter 4 the presence of a space between the core and the shell arising as a consequence of the thermal treatment during the synthesis was mentioned. The closure of the hysteresis at \( P/P_0 \sim 0.45 \) suggest the presence of pore network effects. So, a plausible explanation is that the nitrogen can condense in that internal space during the adsorption and the release can be delayed during the desorption. The smaller pores from the shell would then produce an "ink-bottle" or "bottle-neck" effect [122, 123].

Figure 5.2: \( \text{ZrO}_2 \) obtained after an alkaline treatment of \( \text{SiO}_2@\text{ZrO}_2 \).
Figure 5.3: Sorption isotherms of monodisperse silica spheres used as template (a), the core@shell particles extracted for 0 h (b), 17 h (c), 23 h (d), 28 h (e), 42 h (f), 51 h (g) and 65 h (f).
The complete dissolution of the core resembles the formation of huge macropores inside the sphere, where nitrogen is incapable of condensing at the measuring conditions. The calculation of the pore size distribution in the hollow spheres by NLDFT shows a bimodal distribution -instead of a trimodal one-, where the biggest mesopores vanished and the two other maxima corresponding to smaller pores remained unchanged. Moreover, the TEM-images suggest no changes in the structure of the shell. So, the experimental information supports the view that the shells contain micro and small mesopores while the bigger mesopores are located between the core and the shell. But the calculation with NLDFT seems to underestimate the mean size for the pores located between the core and the shell when compared with the TEM-images. This is due to the fact that all nitrogen in the gap is desorbed at the point of the meniscus instability, and a more appropriate size distribution for these pores would be obtained from the adsorption branch.

In conclusion, we can say so far that the core@shell particles contain a non-porous siliceous core and a porous shell. The pore structure of the shell has a distribution with two maxima: one corresponding to micropores and the other to mesopores with a mean size of 3.0 nm. Between the core and the shell a mesoporous structure forms due to different thermal behaviors of those materials. The removal of the silica leads to formation of well defined hollow spheres, which retain the pore structure of the shell in the core@shell particles.

5.1.3 XRD

Changes in the amorphous and crystalline components in the core@shell spheres are followed by an analysis with XRD from samples taken out periodically during alkaline treatment -like for the TEM-analysis. The obtained results support the image so far established for the core@shell particles and the @shell spheres.

The nanocrystals of \( \text{ZrO}_2 \) remain unchanged during the treatment with \( \text{NaOH} \) solution, as seen in Figure 5.4. The intensity of the signal corresponding to the scattered X-ray by \( \text{SiO}_4 \) units without long-range order reduces, but does not vanish completely. The broad signal centered at \( 30^\circ \ 2\theta \) is attributed to the reflection at the (111) plane from the tetragonal structure of \( \text{ZrO}_2 \). The reflection retains its broadness indicating no change in the crystalline particles in the shell. The alkaline solution reaches the interior of the spheres through the pore structure of the shell and dissolves the silica from the core.

\( \text{SiO}_4 \) units remain in the hollow spheres after the extraction with the alkaline solution. These units remain even after a treatment for several hours more than the time required for the complete extraction of the siliceous core. Why is that signal still there?

5.1.4 EDX & XPS

The possible presence of \( \text{SiO}_4 \) units in the hollow spheres triggered the following study about the elemental composition of both the particles at the outer surface and of the particles as a whole. This study made use of XPS and EDX, respectively. XPS gives information about the atomic composition of the particles to a depth of at most a few nanometers [124]. EDX informs in the case of these particles -which are
Figure 5.4: XRD results obtained for (a) core@shell particles before extraction and the same material extracted for 23 h (b), 42 h (c) and 65 h (d).
smaller than 1 μm- about their bulk composition. The molar ratios Zr/Si calculated from XPS and EDX results are shown in Figure 5.5. Three important pieces of information were obtained. First, the core@shell particles contain Si atoms at the surface, which remain after the treatment with the alkaline solution. To this conclusion we arrive from the finite value for the \((\text{Zr/Si})_{\text{surface}}\) for the material before the extraction and for those samples taken during the extraction. The \((\text{Zr/Si})_{\text{surface}}\) reaches a plateau when no siliceous cores are seen anymore by TEM. Second, for the bulk elemental composition a similar tendency is seen as in case of the superficial elemental composition, but the amount of Si is higher in the beginning. This is seen in the \((\text{Zr/Si})_{\text{bulk}}\), where the value before the treatment is lower in this case. Finally, the elemental surface and bulk composition of the particles converge.

\[
(\text{Zr/Si})_{\text{surface}} - (\text{Zr/Si})_{\text{bulk}} = 2
\]

This indicates the presence of a homogeneous distribution of Zr and Si in the hollow spheres throughout the shell.

![Graph showing molar ratio Zr/Si vs. time of extraction](image)

Figure 5.5: Molar ratio of Zr/Si obtained by EDX (▲) and XPS (○) for samples extracted for different times.

The presence of Na was revealed by the elemental analysis done by EDX (Figure 5.6). Before the alkaline treatment, Na was absent. During the extraction this element was incorporated into the particles. This phenomenon has already been reported for other systems [123] and seems to be due to a strong adsorption of sodium. As already observed for \((\text{Zr/Si})\), \((\text{Na}/\text{Zr})_{\text{bulk}}\) seems to reach a plateau, too. The presence of sodium in the form of residual sodium hydroxide can be excluded on the based of \(^{23}\text{Na}\) NMR analysis (not shown).

A qualitative assessment about the different environments of Zr, Si and Na could be obtained from the XPS results. XPS data show one signal for Si as well as for Na and Zr. However, discrimination of different compounds of the same oxidation state is possible by XPS only in fortunate cases; an overlapping of signals corresponding to different environments is possible. Therefore, this result does not mean that only one defined compound is present in the materials. For the O 1s spectrum both an oxidic species and an oxygen species on the surface can be assigned.
5.1. REMOVAL OF THE SILICEOUS CORE

The study by EDX and XPS added an additional piece of information to understand why the signal corresponding to the $SiO_4$ units observed in XRD remains after the extraction with the alkaline solution. There is a substantial amount of Si homogeneously distributed in the hollow spheres. Nevertheless, the precise location of the Si remains unknown. For that, a study of the environment of Si by $^{29}Si$ MAS NMR was undertaken.

5.1.5 NMR

Provided that the spectra are sufficiently well resolved and the lines are correctly interpreted in terms of $Q^n$ units $(Si(OSi)_n(OH)_{4-n}, n = 0 \rightarrow 4)$, $^{29}Si$ MAS NMR spectroscopy allows very precise determination of the degree of condensation in amorphous silicas. However, for thermally treated silicas usually unresolved asymmetric resonance lines as those in Figure 5.7 are obtained. Obviously, the deconvolution of such a line is less reliable. Furthermore, the ranges of the chemical shift observed for $Q^n$ groups ($n = 0, 1, 2$) in silicates heavily overlap due to the effect of local geometry and/or counterions [126]. Hence, no assignment to specific $Q^n$ group can be given for the $^{29}Si NMR$ line observed for the extracted sample (Figure 5.7c). Nevertheless, the obvious difference in the chemical shift before (Figure 5.7b) and after extraction shows that the degree of condensation of the $SiO_4$ tetrahedra is significantly changed by this treatment from the $Q^2-Q^4$ range to the $Q^0-Q^2$ range.

On the basis of the experimental evidence, it is possible to state that nanometer sized particles of $ZrO_2$, which are clearly identified by their XRD pattern, are either covered or linked by a siliceous compound which is different from silica and contains the $SiO_4$ units. This compound may contain $SiO_4$ tetrahedra having a low degree of condensation, sodium and zirconium. It is not probable, that it is a pure sodium silicate, since that should not be stable under the leaching conditions. Several materials containing those atoms and a $Q^n (n < 2)$ environment for silicon have been reported [127], but the
available experimental evidence is not sufficient to determine more precisely the structure of the material.

Figure 5.7: $^{29}\text{Si MAS NMR}$ of the monodisperse siliceous spheres used as exotemplate (a), the SiO$_2$@ZrO$_2$ (b) and the @ZrO$_2$ (c).

Summing up, the core@shell particles can be treated with an alkaline solution of NaOH to extract their siliceous cores. The shells contain ZrO$_2$ and silicon. The location of this latter element, which has a different environment after the extraction than that characteristic for SiO$_2$, remains unclear. The hollow spheres retain the pore structure of the shell, the sphericity and the monodispersity belonging to the starting material.

5.2 Thermal stability of the hollow spheres

High surface area zirconias are especially interesting in high temperature applications, such as in washcoat materials in automotive exhaust catalysts. It is therefore important to assess the thermal stability of the materials synthesized. The structural changes in the hollow spheres caused by the thermal treatments are followed by TEM, Nitrogen Sorption and XRD.
5.2 Thermal stability of the hollow spheres

5.2.1 Thermal treatment

Samples of hollow spheres were placed in a crucible, which was thereafter heated in an oven. The heating followed in an air atmosphere and the program was:

\[ 30 - T_{\text{final}} \text{ (2K min}^{-1}) \]; cooling down in oven

with \( T_{\text{final}} = 673, 773, 873, 973, 1073, 1173, 1273 \) and 1373 K.

In the following the characterization of those materials will be presented.

5.2.2 TEM & EDX

Changes in the secondary and primary particles after the thermal treatment can be seen in the TEM (Figure 5.8). By a vertical displacement of the eye along the left column we can follow the changes produced for different temperatures. Moving the eyes horizontally from left to right in the Figure a magnification at one temperature can be appreciated. By doing so, we can see that the well defined sphericity of the secondary particles remains unchanged up to 1173 K. Above this temperature the well defined sphericity starts to blur, though the particles are still reminiscent of spheres.

The reason why the sphericity of the secondary particles blurs is the growth of the primary particles. Moving from the bottom to the top of the middle and right columns in Figure 5.8 we can see how the crystalline particles forming the shell grow. As for each hollow sphere the amount of ZrO\(_2\) is constant, a growth in particle size means a reduction in the number of particles forming the shell. The sintering of the primary particles occurs in such a way, that this process does not alter the sphericity up to high temperatures. Such a phenomenon has already been seen, for instance, for TiO\(_2\) [128], but in case of these hollow spheres containing ZrO\(_2\) the primary particles sinter at a temperature hundreds of degrees higher.

The presence of one other phase different than ZrO\(_2\) in the shell can be seen after a treatment above 1173 K by TEM. The ZrO\(_2\) crystals and the other phase were analyzed by TEM and EDX. It was so possible to correlate the observed phases with an elemental composition.

ZrO\(_2\) is never alone, there is always some Si present with the oxide. In Figure 5.9 we see a high-resolution-image of a ZrO\(_2\) crystal. In the middleground of the picture we can see typical ordering for a crystalline phase. This ordered structure is surrounded by an amorphous phase. EDX analysis in the middle of the crystal shows the presence of 0.4 – 1.0 \% Si. It is difficult to assess the location of Si, because the electron beam crosses the sample perpendicularly to the image. Thus, three possible locations are possible: either the crystal is completely covered by an amorphous layer containing silicon, which cannot be seen because it is out of focus, or Si is incorporated in the crystalline structure, or both. The elemental analysis of the amorphous phases surrounding the crystal shows a main presence of Si, but also the presence of Zr. However, due to the spot size for the analysis of circa 10 nm, zirconium would be detected even if the amorphous layer would not contain this element.

Altogether, the hollow spheres show an extraordinary thermal stability. They can be heated up to 1173 K without loosing the sphericity of the secondary particles. The primary particles start to slowly
Figure 5.8: Hollow spheres thermally treated at different temperatures (vertically). Pictures with different magnification (horizontally).
grow above 973 K. When the temperature of the thermal treatment exceeds 1173 K, they become so big that the secondary structure blurs. Moreover, the presence of another material where silicon can be found becomes evident at higher temperatures, when the resolution allows the clear identification of an additional phase. Nevertheless, its exact location and the composition and structure of the silicon containing material stays unknown. It is, however, probable, that a layer of amorphous silica coats the zirconia crystals after high temperature treatment.

### 5.2.3 Nitrogen sorption

The structural changes observed by TEM can be complemented by the results of the Nitrogen Sorption experiments. While TEM extracts information about the morphology of crystalline and amorphous phases, Nitrogen Sorption gives information about the pore structure that might be present. The latter technique is in particular sensitive to changes in the structure of the material, when these changes involve a characteristic length smaller than 10 nm. The curve in Figure 5.10 shows the specific surface area of spherical particles with a density of 6.1 g cm\(^{-3}\) - the density of tetragonal ZrO\(_2\) - as function of the radius. It can be seen how strong the increase of the specific surface area is for spheres with a radius smaller than 20 nm; or, what is the same, how fast the specific surface area reduces by a small increase of the particle sizes in that region.

That sensitivity is useful to analyze the changes in the pore structure of the nanometer-sized ZrO\(_2\). Experimentally it is possible to see that the pore structure of the hollow spheres remains unchanged up to 973 K. This can be seen in the isotherms, which have the same shape and overlap for all the materials thermally treated up to 973 K (Figure 5.11 Inset). By further increase of temperature the measured isotherms are displaced downwards with respect to previous ones. Such a behavior can arise by homogeneous collapse of the pore structure, which is in line with the TEM data.

The homogeneous collapse of the pore structure in the shell manifests itself in the specific surface area, which is calculated from the measured isotherm. The specific surface area for the material without being thermally treated and for materials treated every 100 K from 673 to 1373 K are depicted in Figure 5.11. The specific surface area slightly decreases between room temperature and 673 K. Between
Figure 5.10: Specific surface area of a sample containing spherical particles with a density of 6.1 g cm\(^{-3}\).

Figure 5.11: Specific surface area of hollow spheres thermally treated at different temperatures - Nitrogen sorption isotherms of the materials treated between 673 K and 1173 K (inset)
673 and 973 K the surface area remains more or less constant. Between 973 and 1273 K the specific surface area is reduced, which corresponds to the collapse of the pore structure in the shells. The most significant contribution to the specific surface area of the hollow spheres comes from the pore structure; the external surface area of the particles makes only a small contribution, as already shown (cf. Section 4.2.2). Above 1273 K the specific surface area of the particles equals their external surface area, because the porosity is lost.

In brief, the monodisperse hollow spheres have a high specific surface area due to the pore structure present in the shell. These hollow spheres show a high thermal stability up to 973 K. Above this temperature a homogeneous collapse of the pore structure starts, which ends with a complete loss of the internal surface in the particles.

### 5.2.4 SEM

The morphological characterization initiated by TEM and followed by Nitrogen Sorption can be complemented with the results from the SEM-analysis. In contrast to TEM that supplies in fortunate cases also information about the internal morphology, SEM gives only information on the external morphology of the particles. This is an advantage, because the changes in the secondary structure of the particles can be much better appreciated.

The hollow spheres retain the sphericity of the secondary particle up to 1273 K, though a reduction in size can be seen at this temperature (Figure 5.12). This observation supports the image of a gradual collapse of the pore structure proposed on the basis of the nitrogen sorption data (cf. Section 5.2.3). At 1373 K the sintering of the particles blurs the spherical secondary structure. When removed from the oven a few hard pieces of material can be seen in the crucible.

So the hollow spheres retain their secondary structure up to 1273 K, even though the pore structure at the shell starts to vanish above 973 K. At 1373 K the sintering transforms a collection of spheres into a hard block of material.

### 5.2.5 XRD

The morphological characterization of the hollow spheres done in Sections 5.2.2 to 5.2.4 can be rounded with the structural information provided by XRD. This analytical tool gives information about crystalline and amorphous phases present in the sample.

The ZrO₂ crystals retain a tetragonal structure up to 1273 K (Figure 5.13). At 1373 K the main present phase is the tetragonal, but the reflections corresponding to the monoclinic phase start to appear. The presence of tetragonal zirconia after a treatment at such temperature is unusual [129], but may be due to a stabilization by silicon [130].
CHAPTER 5. MONODISPERSE SPHERICAL SHELL

Figure 5.12: SEM-images of hollow spheres thermally treated at four different temperatures.

Figure 5.13: XRD patterns of samples calcined at 973 K (e), 1073 K (d), 1171 K (c), 1273 K (b) and 1373 K (a).
5.3 CONCLUSION

The growth of the primary crystals seen by TEM (cf. Section 5.2.2) is confirmed by the narrowing of the reflections corresponding to the ZrO$_2$. A quantitative estimation of the particle size can be done by Scherrer’s equation [116]. Table 5.1 shows the mean particle size - calculated from the X-ray diffraction patterns - and the expected specific surface area for spherical particles with those sizes (a$^{\text{Theoretical}}$) and the specific surface area calculated from the sorption data (a). There is an obvious discrepancy between the two values after a treatment at high temperature. However, one should keep in mind, that sorption analyzes particle sizes with respect to their surface area, while XRD determines the sizes of coherently scattering domains. The discrepancy between the values for the specific surface area calculated by both ways may be attributed to the embedment of ZrO$_2$ particles in a siliceous matrix or by the fact that particles are composed of several intergrown domains.

Table 5.1: Particle size calculated after thermal treatments.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$d$ (nm)</th>
<th>$a^{\text{Theoretical}}$ ($m^2g^{-1}$)</th>
<th>$a$ ($m^2g^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>6</td>
<td>164</td>
<td>259</td>
</tr>
<tr>
<td>1073</td>
<td>7</td>
<td>140</td>
<td>127</td>
</tr>
<tr>
<td>1173</td>
<td>14</td>
<td>70</td>
<td>31</td>
</tr>
<tr>
<td>1273</td>
<td>20</td>
<td>50</td>
<td>&lt;5</td>
</tr>
<tr>
<td>1373</td>
<td>35-40</td>
<td>25-28</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

5.3 Conclusion

Monodisperse hollow spheres can be prepared from the core@shell spheres presented in Chapter 4 by an alkaline treatment. The siliceous core is thus completely removed. A small amount of Si remains in the hollow spheres, among the nanocrystalline ZrO$_2$ primary particles, though its location remains unknown. EXAFS and XANES studies are planned for the near future to elucidate the location of the Si in the hollow spheres: by getting information about the surroundings of the Si and Zr, one could in the fortuitous case of having well resolved spectra determine whether the Si is in the ZrO$_2$ nanocrystals, as a silicate among the ZrO$_2$ nanocrystals or in both places. The nanocrystalline ZrO$_2$ retains the tetragonal structure, when heated up to 1373 K. The rapid decrease of the specific surface area of the hollow spheres can be attributed to an increase in the size of the crystals occurring above 973 K. Preliminary catalytic tests in dry reforming and methanol synthesis using these hollow spheres as support have shown promising results.
Chapter 6

$SiO_2@ZrO_2$ as binary exotemplate

The formation of nanostructured composite materials by the combination of different inorganic and/or organic phases is highly promising to generate tailor made systems for applications in catalysis, optoelectronics, sensing, biomaterials, among others [131]. Such hybrid systems can exhibit new properties otherwise not available with only one of the phases or allow the creation of multifunctional integrated systems. Nanocasting employing hard inorganic templates has been shown to be a highly versatile method to produce new porous materials expanding widely the range of compositions available [82].

Spherical core-shell systems with a monodisperse distribution in size centered in the colloidal domain are particularly interesting. These materials are ideal candidates for processes requiring a good mass transfer, for instance to improve the electrolyte diffusion in solar cells [132]. Core-shell spheres with a composite shell are attractive materials for sensing and for selective removal of a component from a mixture. The large pore volume in hollow composite spheres could as well act as a reservoir with a permeable barrier for controlling diffusion.

In this Chapter it will be demonstrated that the binary exotemplate $SiO_2@ZrO_2$ (i.e.: exotemplate with two material phases) opens the path for a versatile and generalized strategy for the synthesis of functional, multicomponent nanoscale systems. The strategy is based on the use of a binary exotemplate, with a spherical core-shell structure ($SiO_2@ZrO_2$) and with a high monodispersity, to synthesize hybrid core-shell spheres, composite hollow spheres and porous hollow spheres. The binary hard template allows the preparation of different materials by replication of one or more of the components. The selective removal of the exotemplate [82] from the hybrid spheres leads to attractive particles, where a new porous structure forms while the spherical morphology remains. The new binary core-shell exotemplate is easily obtained in large amounts as it was described in section 4.

The synthetic strategy by using the binary exotemplate is presented in Figure 6.1. First, a monomer (a precursor molecule for polymers or carbon) is selectively adsorbed in the mesopores of the shell which surrounds the inner core of the exotemplate (a). The impregnation of the monomers is performed in such a way that no organic species remain outside the shell and eventually block the textural porosity between the colloidal spheres. Subsequently, the monomers are thermally polymerized in the confined space of the mesopores (b). In the case of carbogenic polymers, the conversion to carbon by high temperature treatment under either vacuum or an inert atmosphere can be done (c). The composite sphere with either the polymer (b) or the carbon (c) offers a starting point for a stepwise removal of the binary exotemplate.
Figure 6.1: Strategy for preparing core-shell composite spheres, hollow composite spheres and hollow spheres.

This can be done by two pathways, each of them having two steps: one proceeds by removing the exotemplate from the shell to yield new core-shell (nonporous-porous) particles (e) and further continues with the removal of the core to obtain monodisperse hollow particles (f). The other way begins with the extraction of the core to provide a hollow composite sphere (d), it follows the removal of the exotemplate from the shell yielding, again, a hollow sphere (f).

As proof of concept, furfuryl alcohol (FA) was the monomer used for preparing a polymer inside the exotemplate. The polymer was afterwards carbonized to obtain $\text{SiO}_2@\text{ZrO}_2, C_1$, because it is known that the obtained carbonaceous material resists the treatments required to stepwise remove the template [89, 90], being adequate for the proof of concept for the binary exotemplating.

### 6.1 Synthesis of $\text{SiO}_2@\text{ZrO}_2, C$

The synthesis of the $\text{SiO}_2@\text{ZrO}_2, C$ occurs in four steps. First, the materials adsorbed and condensed in the exotemplate (e.g.: $\text{H}_2\text{O}$) are evacuated to obtain an empty porous material. The evacuation proceeds at 473 K under vacuum overnight in a Schlenk flask. The exotemplate does not suffer any changes after a thermal treatment at that temperature. Before continuing with the next step, the Schlenk flask is flooded with dry Ar. It is not clear, whether working under dry conditions up to this point is absolutely necessary. However in previous studies on the replications of pore systems this was found to be beneficial and therefore this pretreatment has been adopted without change.

In the second step the pore structure in $\text{SiO}_2@\text{ZrO}_2$ is filled with FA and $\text{H}_2\text{C}_2\text{O}_4$ -a polymerization catalyst- by an incipient wetness method. About one gram of the pretreated exotemplate is placed in a polypropylene (PP) bottle with a wide mouth. A solution of the monomer and the catalyst in methylterbuthyl-ether (MTBE) and absolute ethanol is drop-wise added to the solid. The volume of the pore structure (0.065 cm$^3$g$^{-1}$ in this case) is extracted from the nitrogen sorption isotherm measured for $\text{SiO}_2@\text{ZrO}_2$ and the density of FA in the pores was assumed to be 1.2 g cm$^{-3}$. As the amount of catalyst
required to obtain a ratio FA/catalyst ≈ 30 is very small, the solid catalyst had to be dissolved in absolute ethanol prior to the preparation of the solution containing the monomer and the catalyst. The volume of alcoholic solution containing the required amount of catalyst is ca. 1/3 of the volume FA. When added to the porous solid, the solution containing the monomer and the catalyst is readily absorbed by the particles, but part of the solution remains outside. This slight excess of liquid conveys to the particles the ability to stick together without forming heterogeneous aggregates visible by naked eye. The wet solid in the PP bottle is forcefully pressed by hand with a spatula against the internal wall for about 10 minutes. After closing the bottle with the cap, the PP bottle is vigorously hit against the working bench, also by hand. Then it is rotated and hit again. This follows for some minutes. The whole process of pressing and hitting is repeated two more times. After hitting the bottle for the last time, it is left on the working bench for an interval between 15 minutes and 1 hour.

Then the bottle containing the sample is opened and placed into a Schlenk Flask, which is then closed with a rubber stopper, and the sample is subjected to freeze-vacuum-thaw cycles [133, 134, 135] using liquid N$_2$ in order to remove air and to facilitate the diffusion of FA into the pores. The closed Schlenk is immersed in liquid nitrogen till the upper border of the PP bottle remains a few centimeters below the level of cooling solid. After a few minutes at 77 K, after the monomer has frozen, the pressure inside the Schlenk is reduced to 1.10$^{-1}$ Pa by opening the connection to the vacuum line. The system remains under these conditions for 15 minutes. This should remove the air trapped in the pore structure and favor the filling of the pores with the monomer and catalyst. Before removing the Schlenk from the cooling bath, the connection to the vacuum line is closed. The precursors in the Schlenk then thaws at room temperature for about 15 minutes. So finishes the first cycle of the freeze-thaw technique, which is repeated two more times.

In the third step, the monomer inside of the pore structure is polymerized. For this, the closed Schlenk with the sample under vacuum is placed in an oven at 308 K (1 h) to facilitate diffusion and then opened. The PP flask is removed from the Schlenk and placed open under air in an oven at 363 K overnight.

Finally the polymer in the composite sphere is carbonized by a thermal treatment under vacuum. The composite is transferred from the oven to a crucible, which is placed in a glass tube with one opening, which is connected to a trap immersed in liquid nitrogen. The trap is connected by a flexible tube to the vacuum pump. The thermal treatment in the tube-oven is as follows:

293-623 K (5 K min$^{-1}$); 623 K (3 h); 623-1023 K (7.5 K min$^{-1}$); 1023 K (2 h);
1023-293 K (40 K min$^{-1}$);

This procedure provides monodisperse composite spheres SiO$_2$@ZrO$_2$,C in sufficient amount for proper characterization, which is presented in the next section.

6.2 Characterization of SiO$_2$@ZrO$_2$,C

In this section the characterization of the SiO$_2$@ZrO$_2$,C particles, the synthesis of which was presented in the previous section, will be discussed. The characterization begins with TEM to obtain structural information from the spheres. This is complemented with line scan by EDX, which provides the
elemental composition of the spheres in a plane cutting them in two. The characterization is completed by studying the changes in the pore structure and specific surface area by nitrogen sorption.

### 6.2.1 Transmission Electron Microscopy

The characterization of SiO$_2$@ZrO$_2$, C starts by looking at the TEM-images, where we come upon well defined monodisperse spheres (Figure 6.2). The carbon is homogeneously distributed in the exotemplate. This is best seen by comparing the exotemplate with and without the carbon (cf. Section 4.2.1). In the latter case, due to the projection of the three dimensional particle onto a plane, the spheres show a dark ring corresponding to the shell and brighter concentric circle. The circles show a homogeneous distribution of dark dots corresponding to the nanometer-sized ZrO$_2$ particles against a light gray background. In the former case, the contrast between the projected ring and the concentric circle is reduced. The dots corresponding to the nanocrystals can not be distinguished at low magnification anymore and both the ring and the circle now have slightly different homogeneously grey colors. The general impression we get is that of filled pore structures.

![TEM-images of composite core-shell spheres (left) and magnification of one sphere (right).](image)

A composite shell can be observed with TEM at high magnification. The presence of fringes corresponding to the crystalline ZrO$_2$ oxide contrasts with the amorphous material among them. The amorphous carbon extends in case of using a volume of FA twice the pore volume of the exotemplate at most a few nanometers beyond the ZrO$_2$ particles (Figure 6.3). The absence of lighter spots in the particles at high-resolution suggests a homogeneous filling of the pore structure. Nanometer-sized voids caused by an incomplete filling of the pore structure should be visible if present, despite the fact that the picture is a projection in 2-dimensions of a 3-dimensional body.

To summarize the TEM-results, it can be said that it is possible to completely polymerize the monomer inside the pore structure and avoid its outwards diffusion to form either a rough surface or even polymere outside. For some applications, the presence of polymer outside might hinder the mass transfer in the textural pore structure and might lead to preferential diffusion pathways. Furthermore, when the polymer is only present in the exotemplate, there is a homogeneous distribution of voids among the spheres. In case of randomly packed monodispersed spheres with a small dispersion in size, a free space of 41% was calculated [136]. In mixtures of bidisperse spheres the fraction of the interparticle voids is always smaller reaching a theoretical minimum of 17.5%.
Figure 6.3: TEM-image of composite core-shell spheres showing the fringes corresponding to the nanocrystals.

6.2.2 EDX (TEM)

A line scan by EDX in the TEM gives an elemental analysis of a slice from a region in the spherical particles contained between two parallel planes separated by about 10 nm. So, the presence of carbon in the exotemplate, besides silicon and zirconium, can be confirmed. Figure 6.4 shows the total counts detected for C, O, Si and Zr in each analyzed point, where counts for all elements were collected for 36 ± 2 seconds. This result qualitatively indicates the expected variation of the elemental composition in the sphere. At the borders of the particle we find all four elements: C, O, Si and Zr. When moving to the middle of the sphere, the amounts of O and Si increase with respect to C and Zr, because we get information from a much bigger portion of the siliceous core. The presence of Si in the shell was explained in Chapter 5.

In short, the elements C, O, Si and Zr are present in the material in the way expected for SiO$_2$@ZrO$_2$,C.

6.2.3 Nitrogen Sorption

The filling of the pore structure of the template with carbon can be appreciated by comparing the nitrogen sorption isotherms of the template and of the composite (Figure 6.5). A full characterization of the template (a) has been presented in Chapter 4. This material has a type IV isotherm, characteristic for mesoporous materials. The capillary condensation indicated by the steep increase of the adsorbed volume at P/P$_0$ below 0.5 and the pronounced hysteresis loop reflects the interparticle mesoporosity of
the shell and the voids present between shell and silica core. The filling of the pore structure in the shell with carbon yields the material $SiO_2@ZrO_2, C$ (c). The latter isotherm clearly evidences the filling of the mesopores, with the reduction of the slope of the adsorption branch and the loss of the hysteresis. The isotherm seems to change to an approximate type I after the filling. The non zero slope in the multilayer-region of the isotherm likely indicates the presence of residual mesopores. Indeed, a similar phenomenon has already been seen for polymerization in confined state [137], where only a certain number of polymeric strands -which later are converted to carbon- fit into the pore structure. The amount of mesopores is, however, quite low.

Summing up, the $SiO_2@ZrO_2$ particles were successfully filled with the monomer FA. Its polymerization in the former pore structure of the exotemplate yielded the composite hybrid spheres $SiO_2@ZrO_2,Poly(FA)$, which after carbonization of the polymer resulted in $SiO_2@ZrO_2,C$. The absence of carbon outside the exotemplate strongly supports the suitability of this method for preparing composite spheres.

### 6.3 Stepwise Removal of Binary Template

The suitability of the binary exotemplate to prepare new types of particles can now be presented, after the successful filling of the pore structure with carbon. From the composite $SiO_2@ZrO_2,C$ two different pathways are possible for a step-wise removal of the inorganic exotemplate (Figure 6.1).
6.3. STEPWISE REMOVAL OF BINARY TEMPLATE

![Graph showing adsorbed volume against ZrO$_2$/SiO$_2$ ratio]

Figure 6.5: Nitrogen sorption isotherm of exotemplate (a) and composite sphere (c).

6.3.1 Pathway 1

This first pathway starts with the extraction of the siliceous cores to obtain composite spherical shells and continues with the removal of the ZrO$_2$ from the composite hollow spheres to yield carbon hollow spheres.

Removal of SiO$_2$

The first step yields hollow composite spheres (Figure 6.1 d). By treating the hybrid core-shell spheres (c) with a solution of NaOH 1N, the siliceous core is removed. A mass transfer across the composite shell allows the inwards diffusion of the alkaline solution and the outwards diffusion of the soluble species containing silicon, which supports the fact that a residual porosity must be present in the shells.

The complete removal of the siliceous core from the hybrid spheres can be seen in TEM-images taken after alkaline treatment. One representative particle can be seen in Figure 6.6. In the outer region of the sphere we find a darker ring corresponding to the shell. This ring surrounds the circle representing the projected region of the spherical void in the particle. In contrast to the composite sphere (cf. Figure 6.2), now it is possible to see again the nano-sized crystals represented by dark spots against a light gray background. Though these images resemble those of the exotemplate after the extraction of the core (cf. Figure 5.1), we should remember that here the pore structure of the shell is filled with carbon. The good contrast between carbon (bright) and zirconia (dark) is likely the reason for the similitude between the TEMs of both kinds of hollow spheres.

The removal of the siliceous core is confirmed by the elemental analysis done by EDX in the form of both a line scan for a single particle and a scan of a big area containing hundreds of spheres. In
Figure 6.6: Composite hollow spheres obtained after the extraction of the $SiO_2$ core.

Figure 6.6 we can see a composite hollow sphere that results from the alkaline treatment with NaOH. On this particles a line scan by EDX was performed at positions in the sphere seen in the TEM-image (Figure 6.7). The elemental composition, represented in the stack-column-bar-graph, shows again the expected qualitative elemental composition for a composite hollow sphere. Carbon is the mayor element present in the material. The ratio $Si/Zr$ is about 1, while the ratio $O/Si$ is twice as high.

![Line-scan-EDX](image)

Figure 6.7: Line-scan-EDX from the particle in Figure 6.6.

Scanning an area containing a high number of particles, it is possible to verify what is observed for the line-scan, but in addition, the element sodium is also seen (Table 6.1). This element has also been found in the EDX and $^{23}$Na-NMR analysis of $SiO_2@ZrO_2$ obtained after the alkaline treatment of $SiO_2@ZrO_2$ (cf. 5.1.4 & 5.1.5). There seems to be a contradiction in the experimental results. A plausible explanation would be a heterogeneous distribution of Na in the composite hollow spheres. The time consuming line-scan can be done in few particles. In order to achieve similar results with both EDX techniques, a large number of planes should be scanned in one particle and this procedure should be repeated for a large number of particles, which is impractical and expensive. Another plausible explanation is that the amount of sodium is below the detection limit of the line scan which is higher than in case of analyzing a much larger area.

The retention of the sphericity of the particles after the alkaline treatment can be seen in the SEM-images (Figure 6.8). A huge amount of monodisperse composite hollow particles can be seen throughout the sample. As seen in TEM, the absence of carbon in the space among the spheres supports again
6.3 **STEPWISE REMOVAL OF BINARY TEMPLATE**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Sodium</th>
<th>Silicon</th>
<th>Zirconium</th>
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<td>50.14</td>
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</tr>
<tr>
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</tr>
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<td>1.17</td>
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<td><strong>Standard deviation</strong></td>
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<td><strong>4.63</strong></td>
<td><strong>0.26</strong></td>
<td><strong>1.46</strong></td>
<td><strong>2.07</strong></td>
</tr>
</tbody>
</table>

The statement that the polymerization occurred only in the pore structure of the exotemplate. In some fortunate cases, where broken spheres appear, a big spherical void is seen instead of a siliceous core (Figure 6.8 Inset).

![Figure 6.8: SEM-image of monodisperse \( \text{@ZrO}_2 \) \( C \) particles. Broken sphere showing hollow core (Inset).](image)

The dissolution of the core from the core-shell composite spheres can be clearly followed by measuring Nitrogen Sorption before and after the alkaline treatment. In Chapter 4 we saw that the \( \text{SiO}_2@\text{ZrO}_2 \) particles contain most probably a non-porous core. So, for the dissolution of the core in composite spheres, an important reduction in the mass of the particles is expected, but without an important lost of surface. How would such a change be reflected in the isotherms? If compared to the isotherm of the material before the alkaline treatment, the isotherm of the composite hollow spheres should appear upwardly displaced and stretched, because a siliceous core providing a relatively important mass and
small surface area is removed from the spheres. In fact, that is what we experimentally observed and no pore structure develops in the spheres (Figure 6.9 d).

![Graph showing nitrogen sorption isotherms](image)

Figure 6.9: Nitrogen sorption isotherms of SiO$_2$@ZrO$_2$ (e), SiO$_2$@C (e) and ZrO$_2$,C (d).

In a word, it is possible to selectively remove the siliceous core from the composite core-shell spheres to yield composite hollow spheres.

**Removal of ZrO$_2$**

The second step of the first pathway consists in treating the composite hollow spheres with a solution of HF. This solution, which is known to dissolve ZrO$_2$ since long [138], generates a pore structure in the shell when removing the inorganic phase.

The complete removal of zirconium and the remaining traces of silicon can be stated on the basis of the EDX mapping of the porous hollow spheres (Table 6.3.1). The presence of oxygen in the sample has two plausible explanations. First, the surfaces in the micro and mesopores present in the material strongly adsorb water from the atmosphere, with which it has been in contact prior to the analysis. Though the material is under high-vacuum during the analysis, the release of the adsorbed water at the working pressure might be slow enough to allow the presence of appreciable amounts of water. Second, each molecule in the carbon precursor contains two molecules of oxygen, which might partially remain in the carbonaceous structure after the carbonization. The presence of oxygen in porous carbon obtained after washing a silica-carbon-composite—prepared using FA as precursor—with HF solution has already
6.3. **STEPWISE REMOVAL OF BINARY TEMPLATE**

Table 6.2: EDX analysis of material after dissolution of exotemplate.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Sodium</th>
<th>Silicon</th>
<th>Zirconium</th>
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<tr>
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<td>8</td>
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<td>Mean value</td>
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</tr>
<tr>
<td>Standard deviation</td>
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<td>3.26</td>
<td>0.00</td>
<td>0.54</td>
<td>0.00</td>
</tr>
</tbody>
</table>

been reported elsewhere [139]. In the absence of a more detailed and careful study, we may say that a combination of both contributions is possible.

In the SEM-images the particles show a shape similar to a red blood cell. This is most probably due to the attraction between the internal wall of the carbon, which has already been observed by others [33]. The image of a carbonaceous material is often that of a hard material, but as can be seen here, the preparation of flexible carbon hollow sphere is also possible. The removal of the rigid structure of the exotemplate yields a softer material capable of bending without breaking (Figure 6.10). The formation of hollow spheres with a thin and flexible wall that tends to deform under the experimental conditions required for a SEM analysis has already been reported somewhere else [33] for the case of a highly cross-linked polymer. This deformation should be avoidable by making a thicker shell. Nonetheless, a successful removal of the exotemplate from the shell is possible.

The hollow carbon spheres show a homogeneous distribution of material. This homogeneity makes it reasonable to assert that there is a homogeneous filling of the carbon in the exotemplate. If there would not be a homogeneous distribution, we would be able to see some holes in the bent hollow spheres. Moreover, in case of a highly heterogeneous filling, no sphere would remain after dissolving the exotemplate from the shell, but only small unconnected polymeric particles previously held in place by the exotemplate.

The formation of a pore structure in the hollow spheres due to the dissolution of ZrO₂ can be proven by nitrogen sorption analysis. Figure 6.11 presents the isotherm for the material after the extraction of the inorganic oxide. When comparing with the isotherm before the extraction (Figure 6.9), a clear development of mesopores is seen. Furthermore, the important upwards displacement and stretching of the isotherm indicates a pronounced reduction of the material’s mass without the corresponding reduction in the specific surface area.

Thus, the stepwise removal of the binary template from the hybrid monodisperse spheres can be accomplished by taking advantage of the different properties of the oxides in SiO₂@ZrO₂. While silica dissolves in strong alkaline solutions, zirconium oxide remains unaltered. After the extraction of silica, the transition metal oxide can be readily extracted with a HF solution. During the stepwise removal
Figure 6.10: SEM image of hollow carbon spheres with a thin shell.

Figure 6.11: Nitrogen sorption isotherm of the hollow carbon spheres. The adsorbed volume should be interpreted with care, because only a very small amount of material (1 mg) was left for this analysis.
6.3  STEPWISE REMOVAL OF BINARY TEMPLATE

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Carbon</th>
<th>Oxygen</th>
<th>Sodium</th>
<th>Silicon</th>
<th>Zirconium</th>
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<tr>
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<td>2.50</td>
<td>0.00</td>
<td>0.90</td>
<td>0.00</td>
</tr>
</tbody>
</table>

different pore structures form. First, monodisperse hollow composite spheres form \( @ZrO_2, C \); finally, monodisperse bent hollow carbon spheres with a pore structure \( @C \).

6.3.2  Pathway 2

The stepwise removal of the exotemplate can be done by inverting the order of extraction of the inorganic phases. Instead of extracting first \( SiO_2 \) and then \( ZrO_2 \), as in pathway 1, in the 2\(^{nd} \) pathway \( ZrO_2 \) is first extracted and then \( SiO_2 \). By changing the order of the removal, it is possible to obtain different kinds of particles. The stepwise removal is not "cumulative".

Removal of \( ZrO_2 \)

The selective removal of the inorganic component from the shell is possible thanks to the strong affinity of zirconium and silica to fluorine. The \( HF \) solution diffuses inwards the composite hybrid first through the composite shell. A fast reaction with zirconium and silicon and the formation of soluble products sweep away only the inorganic material from the shell, if stoichiometric amounts of \( HF \) only sufficient for the dissolution of the shell are used. That means the addition of the amount of \( HF \) necessary to transform only the \( ZrO_2 \) into \( ZrF_6^{2-} \). This selective removal provides core-shell particles with a porous, carbonaceous shell and a non-porous, siliceous core: \( SiO_2@C \).

The retention of the spherical shape in most particles can be seen in the SEM-pictures (Figure 6.12) taken after the acid treatment. Though a few particles seem to have been completely empty (bent spheres), most of them keep their spherical shape. As \( HF \) solution indiscriminately reacts with both inorganic oxides present in the exotemplate, a slight excess has to further attack the siliceous core of the particles.

Naturally, an elemental analysis of the acid-treated material is necessary to sustain the idea of the selective removal of the inorganic component from the shell. The results from a bulk elemental analysis of a vast number of particles done by EDX are presented in Table 6.3.2. There we can clearly see that zirconium was completely removed from the spherical particles. Also sodium, that was present during the pathway 1 after the first step, was washed away with the acid treatment. So a fundamental requirement for selective removal of the binary template from the shell is fulfilled.
Another requirement for a successful removal of only the inorganic component from the shell is the presence of silicon, oxygen and carbon in the remaining particles. The presence of these elements is proven by EDX. If we additionally consider the SEM-images, which show most particles with a spherical shape, and that a complete removal of the exotemplate leads to red-blood-cell-like particles, it is admissible to say that $SiO_2@C$ particles remain after the acid treatment.

What would we expect to see in an analysis by nitrogen sorption after the extraction of the inorganic shell? What happens physically at the shell? We saw that the material $SiO_2@ZrO_2@C$ has a type I isotherm indicating the presence of a non-porous material. The removal of the inorganic component from the shell should produce voids, which, due to the size of the removed nanocrystals, should be mesopores. The presence of mesopores bigger than 4 nm in a material is reflected in the hysteresis formed in the isotherm. The isotherm for $SiO_2@C$ was already presented in Figure 6.9 e. The slight upwards displacement of the isotherm - with respect to the one observed after the dissolution of the core or of the complete exotemplate - suggests a slight decrease in the mass of the particle, which is not accompanied by an important reduction in the specific surface area of the particles. This is only possible if considerable amounts of silica are still present. This result is in complete agreement with the TEM and EDX result and fully supports the notion that mainly the exotemplate from the shell has been removed.

In conclusion, in the first step the $ZrO_2$ and the Si-containing material from the shell could be removed leaving behind $SiO_2@C$ particles.
6.3. **STEPWISE REMOVAL OF BINARY TEMPLATE**

Removal of SiO$_2$

The second step of the second pathway for stepwise removal of the binary exotemplate consists in treating SiO$_2$@C either with NaOH or HF. Both solutions are capable of dissolving the siliceous core. In the following the treatment with an excess of HF is presented.

The complete removal of the remaining exotemplate, namely the core, yields flexible hollow spheres like in the first pathway (cf. Section 6.3.1). In the upper picture in Figure 6.13 we come upon many bent hollow spheres obtained by the acid treatment. Some of them are completely bent in such a way that they form half-spheres and maximize the contact of the internal surface with itself; others are more or less deformed without having a defined shape. In the lower picture we can see two pieces of information indicating the existence of a bent spherical particle. First, the fold of the thin shell marked by the red ellipse. The material forming the hollow particle is flexible, but a small annular void forms at the fold of the particle. Second, the folded particles show a thickness -orange arrows- which is twice the thickness of those particles where the internal surface does not stick to itself -yellow arrows.

An elemental analysis of a big number of particles by EDX shows the expected result: the inorganic exotemplates were completely removed during the acid treatment in this 2nd step and the carbonaceous replicas of the pore structure of the shell were left behind. The remaining bent, hollow spheres contain in average 87.98 % carbon and 11.95 % oxygen. If compared with the hollow particles obtained with the 1st pathway, the material obtained by this 2nd pathway has a slightly higher amount of oxygen (cf. Section 6.11).

An analysis by nitrogen sorption of the resulting material after this 2nd pathway proves the presence of almost identical pore structures in the hollow particles independently of the followed route. In order to make the comparison of the isotherms easier, the isotherm of the material by the 2nd pathway was shifted. This was done by multiplying the values from the latter isotherm by a number $A$, which is the ratio between the adsorbed volume at $P/P_0 = 0.40$ for the latter and former isotherms:

$$A = \frac{V_{0.4}^{Isotherm2}}{V_{0.4}^{Isotherm1}} \quad (6.1)$$

This procedure physically equals the modification of only the density of the particles, without any alteration of the information concerning the pore structure of the material. This is a useful way to compare the pore structures of different materials, at least as a first approach. The @C obtained by the two pathways have the same pore structure and differ at most in their density.

It has to be mentioned here that a value of $A = 0.24$ requires an explanation. Due to the extremely small amount of material used in the measurements of the isotherms, an important error was introduced in the weighting of the samples. This error has an influence on the location of the isotherm. Nevertheless, it is the shape of the isotherms what really matters to prove the successful removal of the binary exotemplate, and therefore the isotherms were considered to contain the necessary information required for this work.

In one word, the inversion in the order of the extraction yields first SiO$_2$@C and then @C. The former differs from the particles obtained after the first step in the pathway 1. The final particles from both pathways have the same pore structure and chemical composition.
Figure 6.13: TEM images of material after treatment with an excess of HF.
Figure 6.14: Comparison of nitrogen sorption isotherms for composite spheres after pathways 1 and 2 ($\Lambda = 0.24$).
6.4 \textit{SiO}_2[@ZrO]_2, Polymer

The strategy shown for FA was extended to produce different core@shell and capsule structures with a wide variety of organic species, which may be integrated in the shell of the binary template, and so far the results seem to converge. For example, organic polymer such as poly(methacrylic acid) (PMAA) and poly(methyl methacrylate) (PMMA) could be introduced into the pores in the shell following a similar selective positioning of monomers inside the mesopores. The vinyl monomers could be subsequently polymerized in the shell to yield organic-inorganic hybrid core@shell spheres. The results confirmed [31] that it is possible to introduce selectively organic precursors within the mesoporous shell of a binary template with core@shell structure and to restrict their polymerization in the confined space of the porous shell. In Figure 6.15 it is possible to see the sorption isotherms of the SiO\textsubscript{2}@ZrO\textsubscript{2}, PMAA before and after the treatment with NaOH 1N. The isotherm before removal of the core demonstrates that the pore system of the shell is blocked by the PMAA. Similarly to SiO\textsubscript{2}@ZrO\textsubscript{2}, C, the removal of the silica produces an upwards displacement of the isotherm. In Figure 6.16 monodisperse hollow spheres with PMAA and PMMA in the shell can be appreciated.

![Figure 6.15: Sorption isotherms of SiO\textsubscript{2}@ZrO\textsubscript{2}, PMAA before (bottom) and after (top) the removal of the siliceous core. Inset: SEM-image of @ZrO\textsubscript{2}, PMAA.](image)

The different chemical behavior of typical carbon precursors and vinyl monomers points to a broad applicability of the proposed procedure for the generation of functional monodisperse core@shell particles.
6.5 Au@SiO$_2$@ZrO$_2$ as precursor for preparation of confined catalysts

Core@shell particles can be used as precursors for synthesizing confined catalysts. The idea of having a particle trapped in monodisperse hollow spheres is relatively new. In 2003 the synthesis of Au, @C and Au, @SiO$_2$ was published (the space between the comma and the @ indicates the presence of a relatively important free space between the gold particle and the shell). In this work the preparation of Au, @ZrO$_2$ and its applications in catalysis as as proof of concept was sought.

So far, two pathways have been followed to create monodisperse hollow spheres loaded with particles. In the first procedure, a hollow sphere is filled with a liquid precursor, which is chemically transformed into a solid particle [140]. In the second, an $A@B@C$ particles is prepared, from which the material $B$ is removed [141].

By following the latter pathway, the possibility to prepare a new type of encapsulated metallic particle became feasible after the development of the SiO$_2$@ZrO$_2$ in this thesis. The already known synthesis of Au@SiO$_2$ was used as the first step of the synthesis [132]. In a second step, the method developed in this thesis for the preparation of SiO$_2$@ZrO$_2$ was used to cover Au@SiO$_2$ with a shell of ZrO$_2$ to prepare Au@SiO$_2$@ZrO$_2$.

The synthesis of Au, @ZrO$_2$ could be realized after the removal of silica with NaOH 1N (Figure 6.17) like in the synthesis of @ZrO$_2$ (cf. Chapter 5). Nevertheless, some optimization is still required, because the reported synthesis for Au@SiO$_2$ had given low yields. Many particles without gold were present in the batch following that pathway. Hence the ratio of particles with and without a gold-core is low. As the coverage with ZrO$_2$ happens on all siliceous particles present in the sample, the obtention of a high yield of spheres with a gold core in the first step of the synthesis and the reproducibility of this step is critical.

Once the majority of the particles contains a gold core inside, enough material will be available to perform catalytic studies. As the shell contains pores smaller than 3.5 nm, the idea is to keep the gold particle inside the hollow spheres and to see whether it is possible to shift the sintering of the metallic particles towards higher temperatures thanks to the encapsulation. If possible, the preparation of this
kind of particles would be valuable in the synthesis of catalyst, which so far show limitations in their use
due to the sintering of the catalyst and, which, of course, can be synthesized following this pathway.

The use of gold shall be seen as a proof of concept for this bottom-up synthetic strategy, which could
be applied to many other metallic catalysts. The benefit of using ZrO₂ lays in its high thermal and
chemical stabilities [142].

6.6 Conclusion

Monodisperse core-shell spheres with a siliceous core and a shell made of nanosized ZrO₂ particles (and
some Si-containing material), SiO₂@ZrO₂, can be used as exotemplate to prepare monodisperse composite
spheres, composite hollow spheres and hollow particles.

Preliminary studies using monomers different than FA (e.g.: methacrylic acid, methyl methacrylate,
sucrose) have shown that the use of monomers with different chemical behaviors can likewise be used to
form monodisperse composite spheres.

Au@SiO₂@ZrO₂ particles have shown to offer an interesting precursor for the synthesis of Au, @ZrO₂
particles. The pathway has proven to be successful, and efforts are now focused towards the increase of
the yield in the first step of the synthesis to get enough particles for a catalytic test.
Chapter 7

Spherical Crystals

The habitus of crystals is normally characterized by polyhedral shapes with a finite number of faces. At the beginning of the 20th century a rational explanation for the polyhedral habit in terms of interfacial free enthalpy change per unit area of the phase \( i \) \( (ΔG_{s, i}) \) was proposed by Wulff: the crystalline shape is determined by the minimization of \( ΣΔG_{s, i}A_i \) [108].

Due to the tendency to minimize the surface energy, all crystals are polyhedral and spherical crystals are normally not known. Even crystals which appear macroscopically round or spheroidal are composed of facets on the microscopic scale. In some cases it is possible to see a high number of facets, which are associated to a great variety of Miller indices, but the number remains finite and the crystals are not perfectly round. Rigorously speaking, an entity such as a spherical crystal can not exist due to the discontinues structure of matter. Nevertheless, this term will be used here to designate those crystals, whose surface atoms can be placed on the surface of an imaginary sphere, because the crystal does not have crystalline edges.

The synthesis of spherical crystals with a boundary, which is smooth till the atomic roughness appears, will be presented in this chapter. As the sample contains spherical crystals intimately mixed with a siliceous matrix, treatments with \( NaOH \) to eliminate the siliceous component will likewise be shown.

7.1 Synthesis of Spherical Crystals

The synthesis of the spherical crystals took place during the thermal treatment of monodisperse core@shell spheres at high temperatures. The heating program was:

\[ 30–T_{final} \text{ (2K min}^{-1}) \text{; cooling down in oven} \]

with \( T_{final} = 1313, 1373, 1473, 1573, 1673, 1773 \text{ and } 1973 \text{ K.} \)

All treatments were done under air except the two at the highest temperature, which were done under \( Ar \).
7.2 Characterization

In this Section the characterization of the thermally treated material by TEM, XRD, HRSEM and Selected Area Diffraction (SAED) will be presented.

7.2.1 TEM

The thermal treatment of SiO$_2$@ZrO$_2$ constitutes a way to obtain spherical domains of ZrO$_2$ (Figure 7.1). The core@shell's transformation during the thermal treatment can be described as the result of the concomitant act of three phenomena. Firstly, there seems to be an inwards diffusion of most nanocrystals from the shell towards the center of the siliceous core (Figure 7.2). This can be concluded when comparing the core@shell particles before and after the thermal treatment. Before, as already seen in Chapter 4, the shell made of nanocrystalline ZrO$_2$ particles covers the siliceous core and the shell contains some Si. The shell and the core in the core@shell particles are clearly separated from each other. Moreover, there are voids between the core and the shell, where N$_2$ condenses during the measurement of the sorption isotherm. After the thermal treatment, we can find spherical crystals of ZrO$_2$ which seem to be embedded in an amorphous matrix. Nevertheless, as the TEM-images are the projected images of a 3-dimensional body, the occurrence of an inwards diffusion should be carefully checked.

![TEM images of spherical crystals at three amplifications.](image)

Figure 7.1: TEM-images of spherical crystals at three amplifications.
Figure 7.2: TEM-image of spherical embedded in the siliceous core.
The second phenomenon is the growth of the spherical domains, which is directly related to the reduction of their number. The growth is in this case a process occurring at constant mass. Therefore, the only way that some domains grow is at the expense of others. After growing, the spherical phases are not in contact with each other, as they apparently were in the material before the treatment, but mostly separated from each other. Moreover, the monodispersity initially possessed by the nanocrystals vanishes or, at best, broadens. Particles of \( \text{ZrO}_2 \) with sizes in the middle and lower region of the colloidal domain can be seen (Figures 7.1 & 7.2).

Finally, the domains acquire a spherical shape while showing a crystal-like atomic order (Figures 7.1 & 7.3). It is possible to magnify the images up to 700,000, to see the roughness of matter due to the presence of atoms, and still appreciate the smooth curvature that can be traced at the boundary of the crystalline structure.

Spherical particles with a crystal-like atomic order can apparently also be obtained from pieces of broken shells. In Figure 7.4 a piece of material that seems to be part of a broken shell can be seen. There \( \text{ZrO}_2 \) domains, all of them being spherical, can be found. We should remember at this point that the shells contain silicon (cf. Chapter 5), which is probably present as silica before the alkaline treatment. Therefore, the \( \text{ZrO}_2 \) crystals at the shell in \( \text{SiO}_2@\text{ZrO}_2 \) seem to be all surrounded by higher or smaller amounts of silica.

The silica present in the core@shell particles seems to play a role in the shaping of the \( \text{ZrO}_2 \) into the spherical form. In Chapter 5 it was shown that - after the extraction of the siliceous core - a thermal treatment of the hollow spheres increases the crystallite size and induces a tetragonal to monoclinic phase transformation, but no spherical domains are formed. Here it is possible to see that in the presence of silica, the \( \text{ZrO}_2 \) crystals can be thermally treated to produce bigger spherical phases. As a first approximation, we can consider that the only difference between the materials before and after the extraction is a change in the chemical nature of the material containing Si. Therefore we might conclude that the silica in the core@shell particles plays a decisive role in the shaping of the domains.

The final temperature of the thermal treatment affects both \( \text{SiO}_2 \) and \( \text{ZrO}_2 \) in \( \text{SiO}_2@\text{ZrO}_2 \). The siliceous cores remain mostly spherical up to 1473 K, forming core@shell particles (Figure 7.1). Above 1473 K the secondary structure of the core@shell particles gets lost. Only in fortunate cases the reminiscence of what was a spherical particle can be seen. For most particles ill-defined contours are observed. The spherical domains containing \( \text{ZrO}_2 \) retain their shape between 1473-1973 K. As the temperature increases, their size grows and their number becomes smaller.

In short, the experimental evidence shows that spherical domains containing \( \text{ZrO}_2 \) with crystalline-like order form between 1473-1973 K. At higher temperatures the amorphous siliceous cores lose their spherical shape and the spherical \( \text{ZrO}_2 \) domains grow in size.

### 7.2.2 XRD

The information obtained by TEM is now complemented by the information provided by XRD. By this technique information about the atomic ordering in the different phases seen by TEM can be collected.
Figure 7.3: TEM-image of spherical crystals at three magnifications.
Figure 7.4: TEM-image of spherical crystals at three magnifications in a piece of broken shell.
In this section, an analysis of the diffractograms obtained for the materials thermally treated between 1313-1973 K will be presented.

The materials obtained after the thermal treatment can be separated in three groups. In the first group are those materials obtained after heating up to 1473 K. There the presence of only one crystalline phase can be seen: ZrO$_2$ in the sample has a tetragonal structure (Figure 7.5). The ZrO$_2$ nanocrystals grow between 1313-1473 K. This can be concluded from the weighted size calculated with Scherrer’s equation using the (111) reflection centred at ca. 30° 2θ for the materials treated at different temperatures.

Figure 7.5: XRD diffraction patterns for thermally treated samples under air (blue) and argon (red). ZrO$_2$ tetragonal (●) and monoclinic (○) and ZrO$_2$ cristobalite (○).

The second group contains those samples treated between 1513–1773 K. Here a new phase of ZrO$_2$ appears: now not only the tetragonal but also the monoclinic phase is present. The change of phase experienced by part of the oxidic crystals occurs without loss of the spherical shape. In the case of ZrO$_2$, this phase transformation requires no atomic diffusion and both phases have very similar structures. This could be a reason why the particles retain their spherical morphology after the change of phase.

Lastly, the material treated up to 1973 K retained both phases for ZrO$_2$ and, additionally, shows the crystallization of SiO$_2$. The crystalline SiO$_2$ present in the sample can be indexed with the cristobalite structure.

It is interesting to remark how delayed the crystallization of the silica occurred. In order to investigate whether this behavior was a consequence of the presence of ZrO$_2$, a portion of the siliceous endotemplate from the same batch used for the preparation of the core@shell sphere- was treated as if it would contain core@shell particles. As the result, we can see that already at 1673 K the silica crystallizes (Figure 7.6). The presence of crystalline and amorphous SiO$_2$ in the material treated up to 1973 K was also seen in TEM images (not shown). The exact temperature at which the crystallization of silica starts lies between 1373 and 1673 K.

In sum, spherical domains seen in Section 7.2.1 seem to be crystals with tetragonal and monoclinic phases, all of them having either a spherical or a spheroidal habitus. Additionally, a delay in the crystallization of SiO$_2$ takes place.
7.3 Removal of the siliceous matrix

In the preceding section it was shown that most spherical crystals were embedded in a siliceous matrix. The EDX-analysis proved that the elemental composition of particles which, according to TEM, seemed to be free of silica contained always Si. In this section the isolation of spherical crystals will be described. For that, the samples containing the spherical crystals were treated with an alkaline solution of sodium hydroxide. First, a brief description of the treatment for the samples containing spherical crystals will be given. Then will follow the characterization of the extracted samples, which was done with TEM, EDX, XRD, Electron Diffraction and HRSEM.

7.3.1 Alkaline Treatment

The materials treated thermally up to 1773 and 1973 K were further treated with a NaOH 1N solution at 333 K in a 60 ml PP bottle with a screw cap. The alkaline treatments were done for 1 and 3 days. The four samples were then carefully washed like after the extraction of the siliceous core from the core@shell spheres (cf. Chapter 5).

7.3.2 TEM & EDX

The characterization of the extracted materials starts with an analysis of the morphology and of the elemental composition of the particles. The morphological study shows three interesting results, which were complemented with EDX locally done in small regions of the sample. Firstly, the non-faceted surfaces remain in most ZrO₂ particles after the alkaline treatment in all analyzed samples. In Figures 7.7 and 7.8 we can see in the upper-left corner a group of particles and, going clockwise, three consecutive magnifications. The last picture in the lower-left corner presents a crystalline surface, the smoothness of which is interrupted only by the roughness of the atomic nature of matter.

Another interesting results is that faceted boundaries were observed only in very few crystals. One example can be seen in Figure 7.9, where one spherical crystal shows a small flat surface. It looks like a
Figure 7.7: TEM-images of the material after treatment up to 1973 K and treated with NaOH 1N for 3 days.

Figure 7.8: TEM-images of the material after treatment up to 1773 K and treated with NaOH 1N for 3 days.
section of the sphere would have been cut off. Moreover, the particle is not completely faceted, but only part of its surface is. This has been equally seen in all samples.

Finally, the silicon containing matrix partially dissolves during the alkaline treatment in solutions of NaOH. The fraction of the silicic acid matrix diminishes for longer times of treatment, leaving bigger amounts of ZrO$_2$ particles free, but the silicon does not completely disappear (Figure 7.10). This behavior contrasts with the behavior of the silicic core in core@shell particles, which dissolves in about one day under similar conditions (cf. Chapter 5).

Moreover, the analysis of the elemental composition of individual ZrO$_2$ particles proves that in all cases each particle apparently free of silica contains about 1 % Si. In the TEM-images with the highest resolution, like for instance in Figure 7.8 (bottom, left), we can see that the crystals are covered with a nanometer-sized layer. This layer could contain the Si in the form of an amorphous mixed oxide with Zr. In Chapter 5 we have similarly seen that the hollow spheres are made of nanometer-sized crystals, which seem to hold together due to the presence of a silicon containing material. Another explanation could be that the spherical domains, leading to an ordered structure, have formed by a phase separation. In such case a phase rich in ZrO$_2$ would form, where Si could be present as a minor component.

### 7.3.3 HRSEM

Additional information about the morphology from the different constituents present in the sample can be obtained with HRSEM. In this mode of studying a material, a higher $\Delta V$ is used for accelerating the electrons directed towards the sample when compared with the other SEM investigations done for this work. For HRSEM $\Delta V = 200kV$ and for SEM 25kV were used. Therefore information from deeper regions in the samples can be obtained with HRSEM.

A comparative study with HRSEM and TEM will be presented. In Figure 7.11 a sample containing the spherical crystals and the silicic matrix is shown from the point of view of both HRSEM (top) and TEM (bottom). While the HRSEM-picture gives a 3D information, the TEM-picture gives information from the 2D projection of the sample. Thus, the presence of spherical and spheroidal particles both on and embedded in the silicon-containing matrix can be seen. The detector receives the electrons emitted by the samples and the emission of the electrons is strongly influenced by the shape of the emitting particles. The position of the detector with respect to the sample influences also the appearance of the image. Thus darker and brighter regions can be appreciated in the pictures, which give the 3D impression to the sample.

Three pieces of information can be obtained from the HRSEM-analysis. First, a broad distribution in the particle sizes can clearly be appreciated in the HRSEM pictures. Particles with sizes covering the whole colloidal domain are seen. Secondly, deviations from the perfect spherical shape become evident. The deviations seem to be more pronounced for the bigger particles. Finally, it remains somewhat unclear, whether the crystalline ZrO$_2$ is completely segregated from the amorphous matrix or only partially segregated from it. From many TEM-images little can be said about the location of a second transition-metal phase; but there are some images, where the location of the second phase inside the matrix is obvious.
Figure 7.9: TEM-images of a crystalline particle with only partially faceted surface.
Figure 7.10: TEM-images of the material after treatment up to 1973 K: (bottom) without alkaline treatment, (middle) treated with NaOH 1N 1 day and (top) treated 3 days.
In short, the presence of spherical and spheroidal domains assumed to be there from the 2D projection of the TEM images shown previously is confirmed by HRSEM.

### 7.3.4 Electron Diffraction

Electron diffraction patterns from single particles obtained with selected area diffraction (SAED) can provide information about the crystallinity of selected regions observed in TEM-images. The performed SAED analysis in no case showed well developed single-crystalline particles of ZrO\(_2\) (Figure 7.12). Instead of getting symmetric diffraction patterns associated with crystalline structure, SAED only shows a few diffraction spots.

The presence of the tetragonal and monoclinic phases of ZrO\(_2\) in the samples treated above 1573 K is known from the XRD-analysis. How can the data from XRD and SAED be understood? The broad reflections in the diffractograms could be attributed to small crystalline domains, which could additionally be distorted by the presence of impurities in their lattices. The SAED results can be attributed to a highly distorted crystalline structure, which does not allow to obtain symmetric diffraction patterns. Hence the spherical particles seems to be neither perfectly crystalline nor amorphous. The material has a degree of ordering between a perfect crystal and an amorphous material.

### 7.4 Conclusion

In conclusion, spherical particles containing mostly ZrO\(_2\) show a crystal-like structure. From the point of view of XRD the particles show typical reflections for a crystalline structure. But from the point of view of SAED the ordering of the atoms seems not to be the expected one for well developed crystal, though the existence of an amorphous structure can be excluded.

The thermal treatment of SiO\(_2\)@ZrO\(_2\) particles could be an interesting way to develop perfectly spherical crystals. The presence of such particle can be seen in some publications [113], nevertheless the fact that crystals with an unusual habitus exist does not seem to attract too much attention.
Figure 7.11: HRSEM (top) and TEM (bottom) of spherical crystals embedded in a siliceous matrix.
Figure 7.12: TEM-image of a spherical crystal-like particle -scale bar 10 nm- (top) and SAED of this particle (bottom).
Part IV

Conclusions
Chapter 8

Conclusions & Outlook

During this Thesis a new type of monodisperse colloidal spheres was developed, which can be used in the preparation of colloidal crystals. First, the synthesis of monodisperse SiO$_2$@ZrO$_2$ and @ZrO$_2$ particles with remarkable structural properties was possible. An alkaline treatment served to remove the silica core from SiO$_2$@ZrO$_2$. Part of the silica seems to react and form an amorphous silicate. The hollow spheres obtained by removing the core have a perfectly spherical shape. This secondary structure is formed by monodisperse, nanometer-sized, tetragonal ZrO$_2$ crystals. The primary particles seem to be covered by an amorphous zirconium-containing silicate, which probably glue the particles with each other.

Those hollow spheres show remarkable structural properties. The specific surface area of 300 m$^2$g$^{-1}$ is consistent with the surface area expected for the primary particles forming the shell. Furthermore, the hollow spheres show only a slight decrease in their specific surface area above room temperature, which remains constant up to about 1000 K. This outstanding thermal stability makes this material an interesting candidate as catalyst support or template, among others.

Second, the preparation of SiO$_2$@TiO$_2$ was possible by following the same pathway which was used for SiO$_2$@ZrO$_2$. Though a preliminary characterization shows that monodisperse core@shell particles can be obtained, an adequate characterization of the material remains a future task. Nevertheless, the particles have doubtless a mesoporous structure in the shell containing TiO$_2$. Core@shell particles with a specific surface area of 140 m$^2$g$^{-1}$ could be prepared, what is slightly smaller than the 160 m$^2$g$^{-1}$ obtained for the particles with a shell containing ZrO$_2$.

Third, the SiO$_2$@ZrO$_2$ can be used as binary exotemplates to synthesize other monodisperse particles. By the selective removal of the different components of the binary exotemplates it was possible to prepare core@shell (SiO$_2$@C), composite hollow spheres (@ZrO$_2$,C) and hollow (@C) particles. This is a new strategy to shape materials into monodisperse spherical particles in the colloidal domain. Except the carbon hollow particles, which showed to have a flexible structure, all other particles were perfectly spherical and can be used for the preparation of colloidal crystals.

Finally, some preliminary experiments showed that this strategy works for polymers made from monomers with wide differences in their chemical properties. Hence it was possible to prepare monodisperse composite particles of the type SiO$_2$@ZrO$_2$,polymer where the polymer was poly(methyl methacrylate) (PMMA) and poly(methacrylic acid) (PMAA). From the TEM-images it is possible to see that the polymerization was confined to the porous structure of the template. Moreover, the nitrogen sorption
isotherms show that the mesopores of the template were completely filled, so that no substantial nitrogen uptake could be seen after the in loci polymerization. This pathway could be used to prepare tailor-made particles, the surface chemistry of which could be controlled by a judicious selection of the monomers.

During this thesis two further projects were developed. The first one was the consequence of a serendipitous discovery when trying to transform $SiO_2@ZrO_2$ into $SiO_2@ZrSiO_4$. It was found that $SiO_2@ZrO_2$ is a good starting material for the preparation of nearly crystalline spheres. Though crystalline spheres have been shown in some previously published articles, it seems that the fact of obtaining crystals without edges and their synthesis has not attracted much attention in the scientific community. Crystals are traditionally considered to be polyhedra with a higher or lower amount of faces, but always with a finite number of faces. Nevertheless, in this work it was proven that the synthesis of spherical particles with a crystal-like ordering of their constituting atoms is possible. The spherical shape of the particles was seen to blur only when the roughness of the individual atoms is achieved.

The second project was the preparation of $Au@ZrO_2$ from $Au@SiO_2@ZrO_2$ by dissolution of the silica from the particles. Although the yields of the $Au@SiO_2$ –which is required in the first step of the synthesis– are low, the pathway has proven to be successful for the preparation of $Au@ZrO_2$. It remains a future task to achieve higher yields of $Au@ZrO_2$, and to subsequently test the material as a catalyst. The aim of the confinement of one gold particle per hollow sphere is to see whether the sintering, which is a problem in catalysis when small particles are used as catalyst and high temperatures are required, can be shifted to higher temperatures.
Part V

Appendix
Appendix A

Characterization

A.1 Nitrogen sorption

The $N_2$ sorption measurements were performed on a Micromeritics ASAP 2010 adsorption unit. Prior to the measurements, the calcined samples were activated under vacuum. The time and temperature of the pretreatment depended on the sample. The measurements were performed at 77 K using a static-volumetric method. The empty volume was determined with helium gas.

A.1.1 Non-local density function theory (NLDFT)

Textural parameters of materials were determined using the NLDFT kernel of the Autosorb software package provided by Quantachrome, applying as model the adsorption of nitrogen on silica at 77 K and using the adsorption branch for the calculation.

A.2 X-ray diffraction (XRD)

The ex-situ measurements were performed on a STOE STADI P transmission X-ray powder diffractometer using CuK$_{\alpha1}$ radiation. It is equipped with a linear position sensitive detector.

The crystallite sizes were calculated using the Scherrer algorithm implemented in the Stoe WinX Pow software package.

A.3 Scanning electron microscopy (SEM)

The pictures were taken using a Hitachi S-3500N scanning electron microscope (SEM) at 25 kV with a working distance of 5 mm. All samples were deposited on Leit-Tab and were covered with a 10 nm thick
layer of gold to improve the image quality.

A.4 High resolution scanning electron microscopy (HRSEM)

The picture was taken using a Hitachi STEM scanning electron microscope at 200 kV and collecting the secondary electrons.

A.5 Energy dispersive X-ray analysis (EDX)

The elemental analyses were performed with an Oxford INCA EDX-System, incorporated into the SEM.

A.6 Transmission electron microscopy (TEM)

The pictures were obtained with a Hitachi H-7500 microscope operated at 100 kV. The solid samples were dry deposited on the sample holder (Lacey-carbon, 400 mesh, 3.05 mm) and analyzed without further treatment.

A.7 X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed with a Kratos HSi spectrometer with a hemispherical analyzer. The monochromatized Al K X-ray source (E = 1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure in the analysis chamber was 4.10−9 Torr. To correct for charging effects, all spectra are referred to C 1s at 285.0 eV.

A.8 Nuclear magnetic resonance (NMR)

Solid-state NMR spectra were measured on a Bruker Avance 500WB spectrometer using a 4-mm MAS probe at spinning rates of at least 10 kHz. The experimental conditions for 29Si MAS NMR were 30 s recycle delay, 2,400 to 2,800 scans, and 2.2 s /4 pulse. Those for 23Na MAS NMR were 4 s recycle delay, 400 scans, and 2.25 s /4 pulse. The chemical shifts are given relative to TMS and 1 M NaCl solution for 29Si and 23Na, respectively. For 23Na, solid NaNO₃ (d = −8 ppm) was used as secondary standard.
Bibliography


[18] Ier RK. Product comprising a skin of dense, hydrated amorphous silica bound upon a core of another solid material and process of making same. *Patent USA*.


