Surfactant-free colloidal syntheses
of precious metal nanoparticles
for improved catalysts

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Abstract

Colloidal syntheses of nanomaterials offer multiple benefits to study, understand and optimize un-supported and supported catalysts. In particular, colloidal syntheses are relevant to synthetize (precious) metal nanoparticles. By separating the synthesis of the active phase nanoparticles from supporting steps, a deeper knowledge and a rational control on supported catalyst properties is gained. The effect of nanoparticle size, shape, composition, nature of support or metal loading on a support can be studied in more systematic ways. The fundamental knowledge gained paves the way for catalyst optimization by tuning the catalyst activity, selectivity, and stability. However, a major drawback is that most colloidal syntheses require the use of additives or surfactants, which are detrimental to most catalytic reactions since they typically block catalyst active sites. Surfactant removal typically adds complexity, can introduce a lack of reproducibility, is energy consuming, generates waste, and prevents the full exploitation of the many benefits of colloidal syntheses for catalysis. Several surfactant-free strategies to obtain stable colloidal nanoparticles are here reviewed. A focus is given to laser synthesis and processing of colloids (LSPC), solution plasma process (SPP), N,N-dimethylformamide (DMF), polyols, and recently reported mono-alcohols based syntheses. The relevance of these synthetic approaches for catalysis is detailed with a focus on heterogeneous catalysis and electro-catalysis.

Keywords

Contents

Introduction

Catalysis is a key scientific area of fundamental and applied research. With 80-90 % of the products from the chemical industry requiring a catalyst at some stage of their production, the design of catalysts is at the forefront of shaping societies and addressing environmental challenges.[1-3] Catalysts facilitate a thermodynamically allowed reaction and are not consumed during the reaction. With a catalyst, chemical reactions can be performed with lower energy requirement (e.g. lower temperature), faster and in most cases with less waste generated than for a non-catalyzed reaction. Catalysts can take diverse forms and be used in different ways. They can be in the same phase as the reactants they will contribute to convert to product(s) (*homogeneous* catalysis), in a different phase (*heterogeneous* catalysis), largely designed or inspired by nature (*bio*-catalysis), relying on solar energy (*photo*-catalysis) or electron transfer (*electro*-catalysis). Naturally, there can be overlap between these different types of catalysts but in all cases, catalysts are expected to show common features to be considered performant, i.e. catalytically active, selective and stable. Ideally, catalysts can be easily separated from the products of the reaction catalyzed and can be simply recovered. For practical consideration, in particular scaling up to industrial requirements, it should be added that their production methods must be sustainable and cost efficient. This means that in a broad meaning, catalyst design and life-cycle - considering production, processing, implementation and recovery - must maximize the use of resources and catalysts should be produced in simple and safe ways.

In particular, *heterogeneous* catalysts are popular. For heterogeneous catalysis, a catalytic active phase, typically in the form of metal particles, is stabilized on a support material. The facility to recover the catalysts immobilized on a support, e.g. by simple processes such as filtration, is a major argument for scaling up. This recovery is especially important for the widely used family of precious metal catalysts made of expensive and critical resources such as gold (Au), silver (Ag), platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh) or iridium (Ir). Such catalysts are relevant for a range of applications such as chemical production,[4] energy conversion,[5] sensing,[6] water remediation,[7] to name only a few examples. In contrast to most homogeneous and biocatalysts, heterogeneous catalysts, including electrocatalysts, are easily operated under various and possibly extreme environments such as high pressure or temperature. This gives a degree of freedom to optimize the screening of optimal catalytic conditions and to investigate the fundamental aspects of catalytic processes.[8] Precious metal particle catalysts are

relatively simple to produce and a satisfying control over the catalyst properties such as activity and stability is typically achieved. However, there is room for improvement.

With the recent breakthroughs in nanotechnology, the design of nanomaterials, both as catalysts and catalyst supports, has become a rewarding area of research. In particular, nanoparticles (NPs) are popular catalysts for several reasons.[9] (i) The use of resources can be optimized down to the atomic scale with NPs. This is especially relevant in light of the high price and scarcity of precious metals. It is therefore a rewarding strategy to develop precious metal nanomaterials. (ii) A wide variety of compositions, shapes, sizes can be obtained to modulate the resulting catalytic properties (activity, selectivity, stability, etc.).[8, 10] From a research and development (R&D) perspective, this allows to best tune the materials to address specific needs or meet desired requirements and performances expected for a given reaction. This also allows studying fundamental effects to elucidate synthesis-structure-properties relationships for such materials. (iii) Several synthetic protocols are well documented to obtain in a relatively simple way various nanomaterials in most modern research laboratories.[11-15] (iv) The production methods of precious metal NPs are increasingly developed to respect most of the principles of environment-friendly and s*ustainable chemistry* that are increasingly driving both academic and industrial research.[16] These latest developments are likely to facilitate bridging the gap between academia and industry.

The purpose of this review is not to cover all synthetic approaches of precious metal NPs to develop new catalysts. For a broad overview on the different strategies to prepare supported catalysts, we encourage the readers to refer to previous reviews.[17, 18] Out of all the possible methods to prepare nanomaterials, it can be argued that colloidal *wet-chemical* syntheses, where the catalysis are produced in liquid phase, remains a very popular method, especially in academic research. The colloidal production of nanomaterials is indeed a routine approach in many laboratories over the world.[8, 11, 14, 15] The field of catalysis certainly already largely benefited, and still benefits, from colloidal syntheses of nanomaterials, as it has been extensively highlighted in recent work.[2, 8, 10, 19, 20] A deeper insight into size, shape, composition, support effects, degradation has been gained over the years[2, 9, 21] and recent overviews are available.[8] Unfortunately, colloidal syntheses are not always optimized for catalyst design. *Per se*, some specificities of colloidal syntheses, such as the typical and widespread use of surfactants, are not compatible with the development of catalysts. This usually results in a poor transfer of the knowledge gained in academic research using colloidal syntheses to larger scale with therefore limited direct relevance to industry.

Introduction

This review proposes a definition to *surfactant-free* syntheses, highlights established and emerging *surfactant-free* colloidal syntheses that offer several benefits over more conventional colloidal strategies to develop precious metal NPs, with direct relevance to study and optimize precious metal catalysts. In a first section (I) the benefits but also the limits of common colloidal syntheses are detailed. In particular, the need for surfactants or stabilizers can be a severe drawback to develop optimal NP catalysts. In a second section (II), a definition of *surfactant-free* syntheses is proposed, and the most common *surfactant-free* colloidal syntheses are presented. They can be narrowed down to (i) laser synthesis and processing of colloids (LSPC), (ii) solution plasma process (SPP), and promising syntheses using (iii) N,N-dimethylformamide (DMF), (iv) polyols, or (v) mono-alcohols as solvents and reducing agents. Emerging trends and new opportunities in *surfactant-free* syntheses of catalysts are detailed and discussed; opportunities to bridge the gap between fundamental research and larger scale applications using colloids are highlighted.[12, 22] In a third section (III), examples where *surfactant-free* alcohol-based syntheses were successfully used for catalysis research are detailed. It is demonstrated how *surfactant-free* NPs can be used as an ideal platform for fundamental research on supported catalysts with examples from both heterogeneous catalysis and electrocatalysis. In particular, the opportunities to disentangle the effects of catalyst synthesis, particle size, particle composition, metal loading, nature of support effects and functionalization are highlighted.[23] A focus is given to precious metals due to their relevance for a wide range of (electro)catalytic reactions in energy conversion (oxygen reduction reaction ORR;[24] oxygen evolution reaction, OER[25]; oxidations of small organic molecules,[26] etc.), sensing[27] and chemical synthesis (e.g. hydrogenation,[22] oxidation[28] or coupling reactions[29]).

I.   State-of-the-art syntheses of heterogeneous catalysts

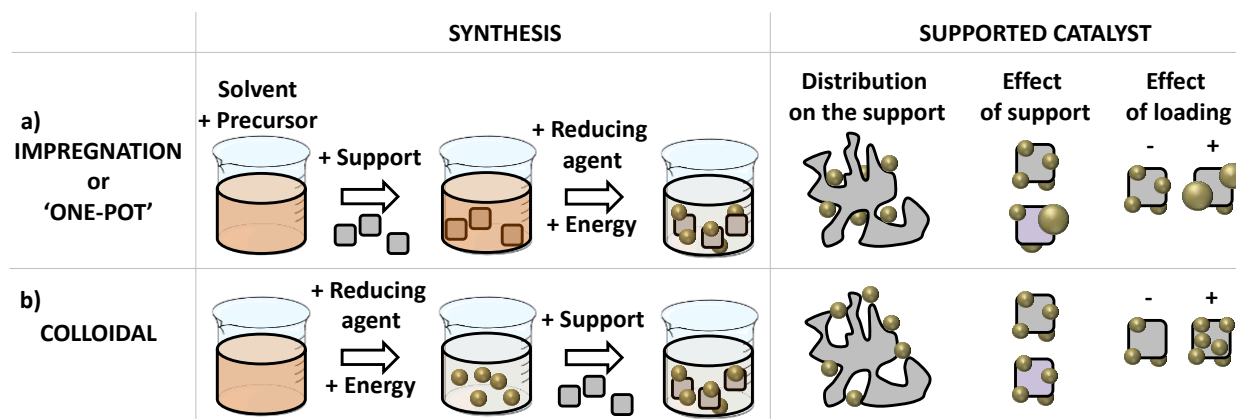## I.1. State-of-the-art: impregnation-calcination

As a starting point, it must be kept in mind that the state-of-the-art method to produce the several tons of heterogeneous nanocatalysts needed today is largely based on impregnation-calcination or incipient-wetness methods.[4, 8, 17] In simple terms, a precursor is impregnated or deposited on a support and further treated, to form nanocatalysts typically by reduction, as illustrated in **Figure 1a**. The method is cost efficient and well developed but not necessarily suited for research/rational catalyst design. A major first drawback in this approach is that several properties of the catalyst are entangled. For example, controlling metal loading, which in turn will affect interparticle distance, may require to reiterate cycles of impregnation-calcination, leading to a change in NPs size *as well*. Typically, larger NP sizes are obtained at higher loadings.[30] Also, the size of NPs obtained by impregnation-calcination is typically larger, with also large size distribution, compared to alternative approaches such as colloidal syntheses detailed below.[22] This relatively poor control over NP properties impairs a fine tuning and so detailed studies of the catalyst. It must be stressed that the same drawbacks come with the use of commercial catalysts in fundamental studies where only the range of supports, particle sizes, or loadings available from commercial suppliers can be investigated. This limited ability to tune the properties of the supported catalysts impairs any true systematic investigations where only one parameter should be tuned independently of the others, e.g. size independent of support, or loading independent of size.

Secondly, catalysts are formed directly on a support. Therefore the knowledge gained from developing a catalyst with a given size and metal loading, size and/or shape is often support-dependent.[22, 31] This means that the synthetic protocol needs to be re-optimized for any new support which can be resource and time consuming. Thirdly, the support material typically has a large surface area. Examples of supports are oxide materials such as alumina,[32] titanium dioxide,[33] silica,[34] or a conductive support (typically carbon) for electrocatalysis,[35] a (semi)conductor for photocatalysis.[36] Such supports are often porous and a drawback of impregnation-calcination is to possibly lead to the formation of nanomaterials in pores of the support that might not be accessible during catalysis,[37] leading to an under-utilization of the (precious) metals. Recent demonstration shows that careful control of the nanoconfinement of the catalyst in porous materials could be beneficial,[38] but in most cases it comes as a drawback.

The above challenges typically lead to under-utilization of the precious metal resources which is a severe limitation both in terms of resources management and general cost.[39] More generally, any synthesis of

catalysts *directly on a support,* often referred to as *one-pot* syntheses for colloidal approaches, may be subject to similar practical drawbacks.[40] There is therefore a need to develop alternative synthetic strategies.

	SYNTHESIS			SUPPORTED CATALYST		
a) IMPREGNATION or 'ONE-POT'	Solvent + Precursor	+ Support	+ Reducing agent + Energy	Distribution on the support	Effect of support	Effect of loading - +
b) COLLOIDAL	+ Reducing agent + Energy	+ Support				- +

Figure 1. Illustration of 'one-pot' synthesis *vs.* colloidal syntheses and possible effects to take into account when studying the influence of support, size or loading. Independent control over properties such as size and loading is more simply achieved by colloidal syntheses.

I.2. A first step beyond state-of-the-art: colloidal syntheses

To overcome the challenges related to the impregnation-calcination approach, the field of catalysis greatly benefited from the development of colloidal syntheses.[19, 41] Interestingly, it has often been scientists with an interest in (electro)catalysis who developed some of the most popular colloidal syntheses of NPs to date. Since 1857 and the first report by Michael Faraday on the possibility to obtain simple and stable gold colloids from molecular precursors in liquid phase,[42] the synthesis of NPs went a long way and other examples are the Turkevich-Frens[43] and the Brust-Schiffrin syntheses.[44] To date, almost every scientific fields refined colloidal syntheses to their specific needs.[45] The production of colloidal metal NPs by so-called wet-chemical methods in aqueous or organic solvents, is very popular and abundantly documented.[8, 11] Its popularity comes from the simplicity of the equipment needed, largely inherited from more traditional organic and inorganic syntheses.[46] Colloidal syntheses can be performed in common

solvents, using simple equipment such as reflux set-up or autoclaves,[47] with minimal hazard and with minimal prior knowledge.

With the increasing availability of modern characterization tools and established synthetic protocols, it has never been easier to explore the potential of colloidal mono- or multi-metallic NP for catalysis.[48] Nevertheless, *easy* does not always mean *simple*. It is a well-acknowledged fact within the academic community that reproducibility of nanomaterial synthesis procedures is a common challenge and can be ascribed to subtle influences of parameters such as different glassware cleaning procedures, different grade of chemicals, different lab conditions, different storage conditions of chemicals, different methods to induce the synthesis, to heat or cool down reaction media, etc.[14, 49-52] On top of this, different testing conditions and the lack of world-used benchmarks for catalytic properties assessment makes it challenging to sometimes compare the *true* benefits of different catalysts compared to another.[53] A large amount of literature covers these challenges and the increase of awareness on good practice will hopefully contribute to fill this gap.[47, 49, 53, 54] Importantly, the need to study well-defined materials is key. In that respect, the use of colloidal syntheses allows to investigate in systematic and controlled ways the effects of size, shape, supports or loading as illustrated in **Figure 1b**.

Understanding the interplay of the NP synthesis method, resulting size and shape, NP dispersion and loading on a support (interparticle distance), support pre-treatments and different catalytic properties assessment protocols, is a prime importance to propose strategies to optimize catalyst activity, selectivity and stability and ultimately mitigate NPs loss or deactivation mechanism(s). Colloidal syntheses are a powerful approach to produce catalysts[2, 22, 47] because the optimization of the catalysts such as size, structure and composition, can be achieved independently of the nature of the support.[23] After synthesis, a supporting step leads to a uniform and well-defined supported catalyst. This general approach illustrated in **Figure 1b** has led to significant insights into the size effects, proximity effects, shape effects but also composition effect in catalysis detailed in **section III**. The opportunities to perform systematic studies lead to breakthrough in our way of thinking about catalysis, slowly allowing moving catalysis away from a *black art* based on trials and errors to a more controlled area of research.[17, 18, 55] Nevertheless, challenges remain, especially to implement systematic studies in practical terms.

I.3. Colloidal syntheses: limitations

The literature on colloidal syntheses will often stress the need for *stabilizers / additives / capping agents / polymers / ligands / surfactants* to stabilize the NPs formed.[56, 57] It is often reported that without such

stabilizers, no NPs are formed or the NPs agglomerate with detrimental effects for further applications, for instance in catalysis.[51] To name only one of such additives among the many possible options, poly(N-vinyl-2-pyrrolidone) (PVP) is widely used in colloidal synthesis and its use has been reviewed by Koczkur *et al.*[58] Recent reviews certainly cover the benefits of *ligands* in the chemical synthesis of nanomaterials.[59, 60] As an illustrative examples, a detailed review includes a discussion on the nature of *ligands* used, from small molecules, polymer to biomolecules, for a wide range of applications beyond catalysis.[61] It is worth pointing out that out of 626 references in this review, the section dedicated to catalysis only comprises 20 references (3.2 % of the citations). This example indirectly highlights the specific challenges of using *ligands* for catalysis. In few instances, however, these *ligands* can bring positive features. The use of *ligands* can bring functionality to active NPs,[62] for instance in catalysis with improved selectivity[63, 64] or stability,[65] and this topic has recently been reviewed by Lu *et al.*[66] However, the authors acknowledge that first considering, and ultimately elucidating the positive aspects of *ligands*, is a relatively recently emerging topic and there is not yet a rational understanding of *stabilizer / ligand* selection, whether to control NP synthesis nor to optimize application in catalysis.

*Additive*s used to control NP nucleation and growth during NP synthesis, lead to unique materials shape and morphology, provide unique re-dispersion properties and even control self-assembly into macrostructrures.[67] The complex interplay between the *capped* NPs and the surface of support material can favor suitable interactions for improved catalysts.[68, 69] Therefore, the benefits of carefully selected and designed *ligands* cannot be neglected. Nevertheless, the use of *surfactants* generally brings drawbacks for the catalytic activity and catalyst preparation. (i) Certainly, different additives allow exploring different NP structures and provide some degree of fundamental understanding for various syntheses and reactions.[70] However, the rational choice of the right *surfactant* and the right amount of it to achieve a given output (being NP size/shape or catalytic activity or selectivity) is still waiting ''a shift from qualitative exploration to quantitative investigation''.[64] This can be explained for instance by different interactions of different additives with different metals. (ii) Furthermore, most surfactants can play different roles during the synthesis which can complicate a full and detailed understanding and control on NP formation and later on applications. This is for instance the case of citrate in the Turkevich-Frens synthesis[56] or PVP,[71] playing the role of stabilizers *and* reducing agents. (iii) Ligands compete with substrates for the access to the active site of the NPs. They can also induce different (negative) interaction with support materials. This overall impairs an optimal catalyst design, e.g. by preventing to reach high NP loadings on supports. (iv) As a consequence, it is generally agreed that surfactants need to be removed for improved catalysis.[72-74] The related steps to remove the surfactants can themselves be detrimental to

the structure of the catalysts, as detailed below. (v) Most surfactants show some degree of toxicity.[75] Additives are typically derived from fossil fuels. In order to develop sustainable approaches to catalyst design, avoiding these additives would be beneficial.[16] In all aspects, to understand the effect(s) of additives or develop *clean* NPs, *surfactant-free* NPs are much needed, as illustrated in **Figure 2**.
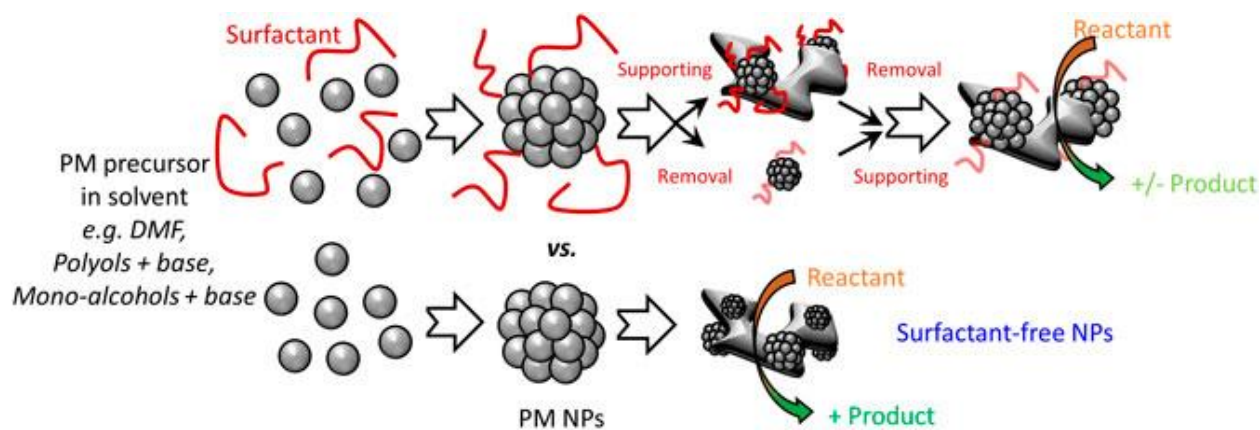
Figure 2. Schematic representation of some colloidal syntheses of precious metal (PM) NPs and illustration of the benefits of surfactant-free approaches to develop supported catalysts with controlled NP size and loading. Adapted and reproduced with permission from [76].
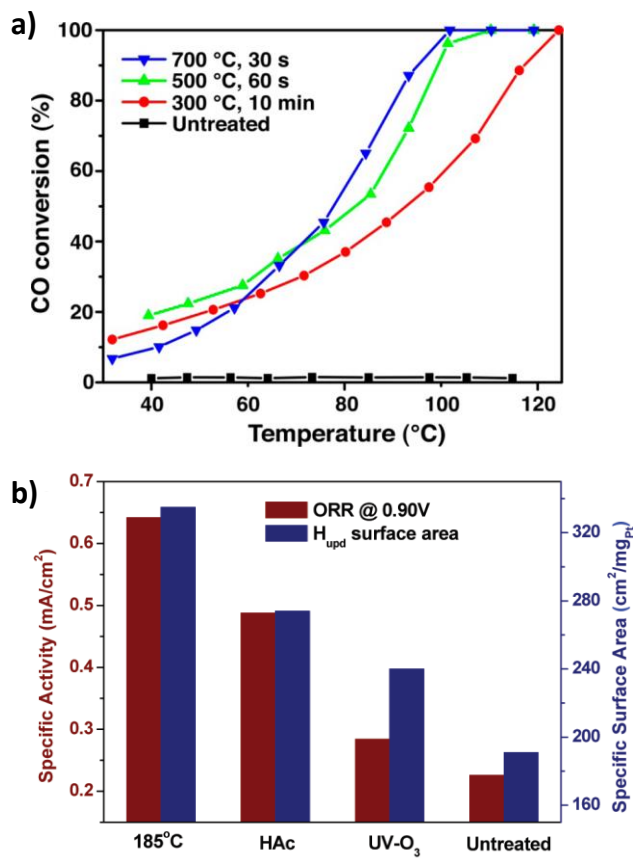
I.4. Surfactant removal

A first approach to develop *surfactant-free* NPs is to remove the surfactants.[77] Surfactant-removal from nanomaterial surfaces is not a trivial task, as pointed out in several reviews: ''one of the major challenges in catalysis is the removal of surface capping molecules''[10] since ''the removal of ligands after deposition of the colloidal metal NPs is rarely studied in detail, even though it is crucial to obtain active catalysts and deserves more attention''.[17] As a consequence, purification and *cleaning* of nanomaterials is still an intense area of research.[78] Surfactant removal strategies have been covered in various reviews and reports.[60, 63, 64, 66, 73, 77, 79, 80] In general, the benefits of surfactant removal are improved catalytic properties as illustrated in **Figure 3**. However, often this is achieved at the detrimental cost of losing some of the initial features of the as-prepared catalysts such as size, shape or composition. The strong need for efficient surfactant removal strategies has been in particular illustrated for thermal heterogeneous catalysis and electrocatalysis. A simple cleaning method is the washing of the NPs,[81] typically performed

using strongly reacting chemicals[82] or a solvent with a strong affinity with the surfactant to remove.[64] Washing offers the benefits to be simple to perform but generates waste. Washing is suitable to remove weakly binding capping agents[63] but usually not enough to remove all surfactants[72] and this calls for further decomposition of the protecting *organic layer*.

Alternative removal approaches include heat,[83, 84] light/ozone[85] or electrochemical treatments,[86] chemical etching,[87] steam treatment,[88] to name only a few of the methods covered in a recent opinion paper.[77] High temperature treatments are generally not recommended[63] because they can modify colloidal NP size/morphology/composition. Too reactive atmospheres are not recommended either because they can induce reactions at the outer surface of colloidal NPs. Low temperature treatments are preferable to ensure that the structure of the as-synthesized NPs are not changed during the process. Examples for short high temperature treatments illustrate the possibility to remove surfactants while conserving even the original shape of the NPs.[84] Electrochemical approaches are usually limited to pre-treatments of the catalysts before catalytic testing, and they are difficult to scale up or to perform on a complete batch of catalyst. To improve surfactant removal, hybrid strategies can be to substitute capping agents with smaller molecules to remove the later more efficiently.[64]

Figure 3. Influence of surfactant removal (a) for CO conversion as a function of temperature for Pd NPs supported on CeO$_2$. Different heat treatments as indicated were performed for surfactant-removal. Reprinted with permission from [84] .Copyright 2022 American Chemical Society. (b) Influence of surfactant removal by different strategies (heat treatment, chemical method and ozone treatment) for the ORR catalyzed by Pt NPs. Reprinted with permission from [72]. Copyright 2022 American Chemical Society.

For a vast majority of catalytic reactions, the use of surfactant remains a severe drawback continuously stressed over the years.[64, 89] In a review from 2019, Losch *et al.* stated that ''the removal of the ligand shell offers hence a vast pool of possible treatments. It remains nevertheless a delicate choice rather guided by trial and error and necessitating an additional characterization step of the material prior its use in catalysis''.[8] The common challenges with surfactant removal strategies can be summarized as: (i) limited efficiency, (ii) impairing reproducibility, (iii) poor scalability. Colloidal synthesis usually poorly transfer to large scale, and to a large extend this is linked to the extra costs and complexity related to the removal of

the surfactants. In addition, multiplying intermediate steps also come with a time and energy cost (e.g. extra characterization of the material after surfactant removal) as well as reproducibility issues calling for improved alternatives.[49, 64]

II. Colloidal surfactant-free syntheses

Colloidal *surfactant-free* syntheses are ideal model systems to understand the effect(s) of additives in NP synthesis. *Surfactant-free* NPs are also a much-needed reference material to understand the effect of additives and ligands in catalysis and/or the effect of surfactant-removal, as schematized in **Figure 4**. *Surfactant-free* NPs are therefore relevant to perform studies leading to a more rational design of catalysts and they are ultimately directly relevant as-prepared to develop catalysts that are more active. Two challenges however raise along with these desirable achievements. The first is a conceptual challenge to define a *surfactant-free* synthesis. The second is a practical challenge, since most syntheses reported to date stress the need for surfactants to stabilize colloidal NPs.
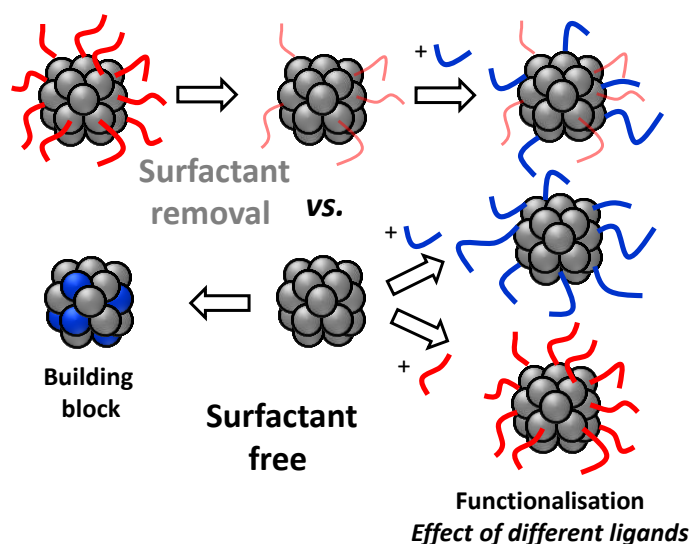
Figure 4. Schematic representation of surfactant removal and comparison with surfactant-free synthesis with possible further use of surfactant-free NPs.

II.1. Surfactant-free syntheses: scope and background

Definition

To the best of our knowledge, the last (and maybe only) review on the broad topic of surfactant-free methods (not specific to a given synthesis approach) to produce NPs is from 2013 by Kawasaki.[90] In 2014, a review by Niu *et al.* addressed various methods to remove surfactants.[64] The first proposed definition of *surface-clean / unprotected / naked / bare / capping agent-free / ligand-free / surfactant-free* NPs was probably given by Niu *et al.* as NPs ''free of formidable long-chain organics'' and ''stabilized by small molecules which are easy to be displaced by reactants during catalytic reactions''.[64] From these statements, it is clear that the term *surfactant-free* is not necessarily well-defined, as there is no clear terminology on how many atoms are required to define a ''long-chain organic''. For thermodynamic reasons, a pure metal NP in a liquid will not be stable, so any colloidal dispersion made of NPs *will be stabilized* in some way. It is commonly agreed that such *unprotected* NPs are stabilized by interactions with the solvent and/or ions present in the solvent.[90] In this respect, the concept of *weakly ligated ligand* developed by Finke and co-workers is close enough to *surfactant-free* NPs.[91]

In practical terms, the definition implicitly suggests that *without additives*, or ''in the absence of usual protective agents'',[92] the formation of stable colloidal dispersion can still be achieved. *Surfactant-free* colloids then refers best to colloidal dispersions obtained in solvents without substances added on purpose to only play a stabilizing role. At the same time, this conveys the idea that the solvent itself, as used, or after degradation and typically oxidation during synthesis, must play the multiple roles of reaction medium, reducing agent and/or stabilizer.[71] In order to clarify the concept of *unprotected* NPs, we propose a more restrictive definition that encompasses all the previous. The wording *stabilizer-free* would be misleading since colloidal NPs must be stabilized somehow in solution. The word *surfactant-free* seems more appropriate, since it conveys the idea that the focus in on the synthesis on not the resulting NPs (although the two are linked). It is considered here that a synthesis is *surfactant-free* if no species with a molar mass greater than 100 g mol^{-1} is added to the synthesis (other than the metal salt to reduce).[20, 76] This means that only qualify syntheses with relatively simple chemicals, typically short carbon length molecules, so ''small' molecules, solvents and reducing agents.

Towards surfactant-free syntheses

On the experimental aspects, interest has been given to the opportunities provided by *almost* surfactant-free syntheses of nanomaterials from an early stage.[93] In 1987,[94] using acetone, ethanol and other simple organic solvents under high temperature and vacuum conditions, ''living'' Pd NPs ca. 8 nm in size were obtained. The colloids will convert to films upon solvent evaporation and so were not yet stable colloids. Although not developed for catalysis, the reduction of Pt(dba)$_2$, Pt$_2$(dba)$_3$ (where dba is dibenzylideneacetone) in toluene or tetrahydrofuran (THF) in presence of CO leads to CO and *solvent protected* Pt NPs.[95] These as-prepared NPs reported by Chaudret and co-workers in the 90s were however not stable enough for further use.[96] The pioneer work from Tang in 2000,[97] using alkaline polyols solutions, showed that surfactant-free syntheses of NPs in the range 1-2 nm were possible and surprisingly simple for metals as diverse as Pt, Rh or Ru.[97] In 2004 the benefits of the approach of using surfactant-free colloids to develop supported catalyst was well established using the selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline as model reaction.[98] The authors noted that ''The catalytic activity for the reaction of interest over the present Ru/SnO$_2$ nanocomposite catalyst is six times higher than the PVP–Ru nanoclusters having the same Ru metal NPs and is much higher than the most effective Ru metal catalyst'' reported at the time. This can be inferred to the absence of surfactant and the ability to investigate independently the effect of SnO$_2$ support. In a nutshell, this result highlights not only the possibility to develop surfactant-free colloids, but also the direct relevance for a range of studies to better understand catalytic systems.

The review from Kawasaki in 2013 gives a comprehensive starting point of different solvents used that were at the time considered suitable to develop surfactant-free NPs.[90] However, most of them have a molar mass greater than 100 g mol^{-1}. Examples of such solvents are diethylene glycol diethyl ether, e.g. for Au NPs;[99] benzyl alcohol, e.g. for Pt NPs[100] and more widely for metal oxides[46, 101] such as Co,[102] or Cu oxides;[103] methyl isobutyl ketone (MIBK), e.g. for Pd synthesis;[104] 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES)[105] or tetrakis(hydroxymethyl)phosphonium chloride (THPC)[106] for Au NPs or N-formylpiperidine reported for PtNi NPs.[107]

Scope

In the present review, a focus is given to solvents with a molar mass less than 100 g mol^{-1}. Furthermore, a choice has to be made to cover the different options to develop surfactant-free syntheses and strategies. The use of gas phase synthesis, such as plasma synthesis[108, 109] or flame pyrolysis,[110] is not discussed, instead we focus on colloidal syntheses of NPs in liquid phase. A major drawback of most gas phase and *physical* syntheses, is the aggregation of the nanomaterials and typically the need to rapidly support the

materials. The use of templates, such as other NPs,[111] electrochemistry or matrixes,[9, 112, 113] is here disregarded. Methods such as photo- and sono-chemistry are also suitable approaches but not detailed here.[90] Syntheses in high temperature, high pressure, supercritical conditions can be considered surfactant-free but often do not lead to stable colloids and are also excluded.[114] Following the definition proposed above for surfactant-free syntheses, the use of ions such as citrate,[115, 116] oxalate,[117] ascorbic acid,[118] most ionic liquids[119] as well as anions such as amino-acids or enzymes[120] is ruled out. However species such as acetate[121-123] or sulfate / phosphate,[124] formaldehyde or formic acid,[125] could be used but are also not considered further here to keep the focus on syntheses where the solvent is playing the triple role of reaction medium, reducing agent and stabilizer.

Kawasaki concluded his review on surfactant-free NPs by identifying three areas of development for the field of surfactant-free NPs:[90] (i) better control on the synthesis (e.g. size), (ii) better understanding of the role of small ions and solvents, (iii) better implementation of surfactant-free NPs beyond academia, so at larger scale. The goal of the present review is to give an overview of the recent advances and opportunities brought by surfactant-free syntheses of colloidal NPs, especially for the field of catalysis. We focus here on the most common and generally applicable methods, in particular approaches reported or significantly developed after 2013.

II.2. Laser Synthesis and Processing of Colloids (LSPC)

Laser synthesis has proven to be extremely useful to produce NPs. Since this approach has been extensively covered and reviewed recently,[6, 12, 126] we encourage the reader to refer to the mentioned literature. In particular, the approach is suitable to obtain surfactant-free NPs.[1, 127] We focus our discussion on the main features of the techniques and recent achievements.

The approach uses a laser directed on a solid material source, typically a plate of metal placed in a liquid (solvent). In liquid phase, plasma formation and cavitation phenomena lead to the nucleation of NPs from solid material. The synthesis can be very fast (seconds to minutes) and generally applicable to a wide range of materials such as oxide, ignoble and noble metals, depending on the target material used. The method is suitable to develop complex structures shape and composition such as alloys and bi-metallic NPs, **Figure 5**. The method has been shown to be scalable[12] and compatible with flow system with production rate of 4 g of NPs per hour.[128]
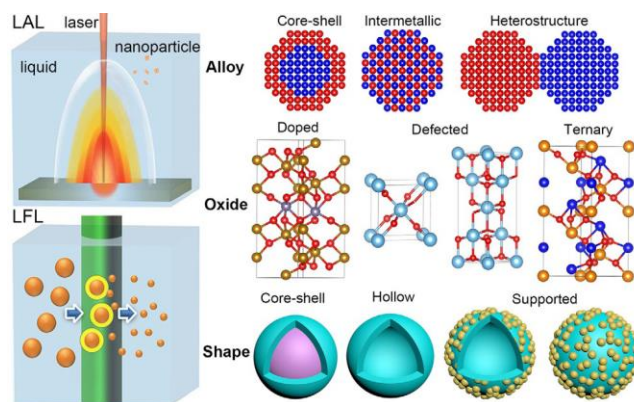
Figure 5. Schematic illustration of laser ablation (LAL) in liquids and laser fragmentation in liquids (LFL) processes and the obtainable possible structure. Copyright 2022 Wiley. Used with permission from Zhang *et al.* ChemNanoMat 2017, 3,512 –533.[127]

LSPC is probably the cleanest approach to produce surfactant-free NPs. The NPs are electrostatically stabilized with a negative zeta potential.[127] As recently detailed by Barcikowski and co-workers,[1] even a small amount of impurities can play an important role in the stabilization of catalysts. In this respect, LSCP can be performed in non-organic media and ensure a higher purity than alternative approaches. This accounts for the fact that *pure* and surfactant-free NPs produced by LSPC have been widely explored for biological and bio-medical applications.[12] Recent illustrative examples of applications of the NPs in

catalysis include Pt_xY for the ORR,[129] PdAu for glucose oxidation,[130] or Pt NPs for the ORR towards fuel cell development,[131] or Au NPs for the CO_2 electro-reduction.[132]
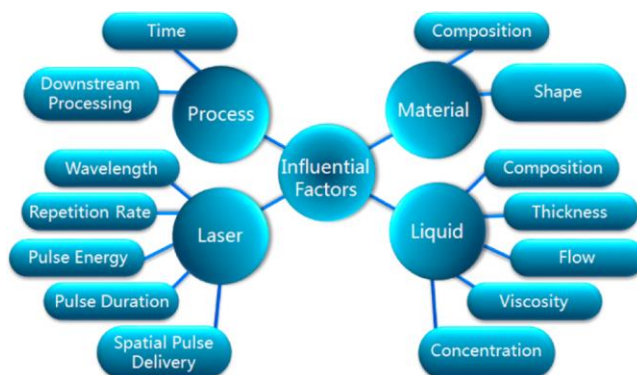
Figure 6. Influencing factors responsible for determining the purity, productivity, shape, size, charge, crystal phase, stability, and dispersion of NPs synthesized by LSPC. Reprinted with permission from Zhang *et al.* Chem. Rev. 2017, 117, 3990–4103. Copyright 2022 American Chemical Society.[12]

The size range typically obtained is 2-100 nm. A main drawback is therefore the relative large size and size distribution (bi-modal distributions are often observed) of the material obtained, as opposed to other surfactant-free methods detailed below. Narrowing down the size distribution comes at the expense of filtration and/or centrifugation steps[133] or careful optimization of many synthesis parameters illustrated in **Figure 6**, such as anions concentrations, presence of support materials or post treatments, e.g. with oxidative conditions or proper laser pulse sequence. The free surface of the NPs can also lead to further reaction upon extended storage.[134]

II.3 Solution plasma process (SPP)

Plasma induced synthesis is maybe less popular than other methods but presents several advantages. It is an approach more common for gas phase synthesis[109] but has been reported in liquid phase as solution plasma process (SPP),[135] suitable to obtain nanomaterials.[136] Interested readers can refer to reviews and perspective produced in recent years.[137] In its principles, plasma synthesis is similar to LSPC. However, in SPP the plasma is not generated by a laser but by an electrode. The main difference is that there is no target material. The production of NPs is fast compared to other wet chemical methods (minutes *vs.* hours) and size control relatively easy to achieve e.g. by tuning pH,[138] precursor concentration,[139] stirring,[140] temperature[140] or reduction current.[139, 140] The stabilization mechanism of the NPs is through

electrostatic charge. A benefit of this approach is to typically lead to smaller NPs compared to LSPC with reported cluster sizes around 1.3 nm for Au,[141] 2 nm for Pt,[142] 2 nm or Ag.[143] Many different set up modules have been explored to generate the plasma outside and inside the solution.[144]

Mun *et al.* compared in details the literature for NPs obtained from wet-chemical methods and solution plasma process.[144] If a reducing agent, a precursor and stabilizers are typically needed in other wet-chemical methods, sometimes none of these are needed in SPP. In some cases, indeed, the electrode itself is the source of the NPs rather than a precursor being reduced. Shape control was even reported by tuning the gas bubbles formed in liquid elelctrolyte[145] or precursor concentration.[139] The approach has been shown to be suitable to obtain surfactant-free NPs as diverse as Ni[146], Au,[138, 141] Pt,[113, 142] Pd,[113] Rh[113] or even TiO_2 nanorods.[147]

For this approach, as per other discussed methods in this review, it is surprising that the advantages of the colloidal NPs were seldom exploited for catalysis.[148] Silver NPs were obtained and demonstrated as suitable catalysts for the ORR. The colloids obtained using a He-H_2 (5%-1%) in N_2 plasma jet at atmospheric pressure with a size around 17 nm were stable as colloids for months. The formation of the plasma generates short live-time reactive species like hydroxyl radicals[144] that contributes to the reduction of the metal precursor and stabilization of the NPs with possible high yields.[113, 149] Another example for catalytic applications is the work by Cyganowski and co-workers who produced first Au NPs ca. 7 nm in diameter, and further cross-lined the NPs in a polymer matrix to develop an hydrogel. The resulting material shows catalytic activity for 4-nitrophenol decomposition completely reduced to 4-aminophenol.[150] The drawbacks of this approach are similar to the LSPC method: It requires relatively advanced equipment and a fine-tuning of several parameters to achieve the right material size, shape or composition.

II.4. N,N-dimethylformamide (DMF) synthesis

N,N-dimethylformamide (DMF)[151] is a suitable solvent and reducing agent for the synthesis of various NPs.[90, 152] In its surfactant-free version, various quantum dots, clusters and NPs of Au,[153-155] Ag,[156] Pt,[157, 158] Pd,[159, 160] Ir,[161, 162] Rh,[163] Cu,[164, 165] F_2O_3[166] and bi-metallic such as PdCu[167] or PtNi[168, 169]can also be obtained, see **Table 1**. DMF acts as solvent, reducing agent and stabilizer.[29, 161] The colloids are typically stable for months in DMF,[157] or even after re-dispersion in various solvents,[155] including aqueous solutions.[153, 165] DMF protection is partially lost at high temperature which makes such DMF-stabilized clusters ideal for heterogeneous catalysts by un-supported NPs. In particular the group of Obora largely contributed to explore the benefits of this method, see **Figure 7**.[29]

The colloids are obtained by reducing a metal precursor in DMF under reflux conditions (typically 140 °C) and in air. Alternatively an autoclave can be used and water added.[170] It is proposed that stabilization occurs via the interaction of the amide groups of DMF[157] and experimental evidence by Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) confirm the presence of DMF on the NP surface. Size control can be challenging owing to the generally already small size of the clusters obtained, see **Table 1**. In N,N- dimethylacetamide (DMA), Ag NPs are similarly obtained with a size control 4-10 nm as the time of reaction increases,[156] which is smaller than for the case of DMF for the same Ag precursors. For Pt NPs, a detailed study on the influence of reaction time, temperature, amount of added water, metal precursor salt used were carried by Gumeci and co-workers.[170] Cubic or truncated octahedral NPs were obtained by tuning the reaction conditions using an autoclave synthesis. In that study, the addition of water was found to lead to carbamic acid as a by-product of DMF oxidation that plays the role of shaping agent.
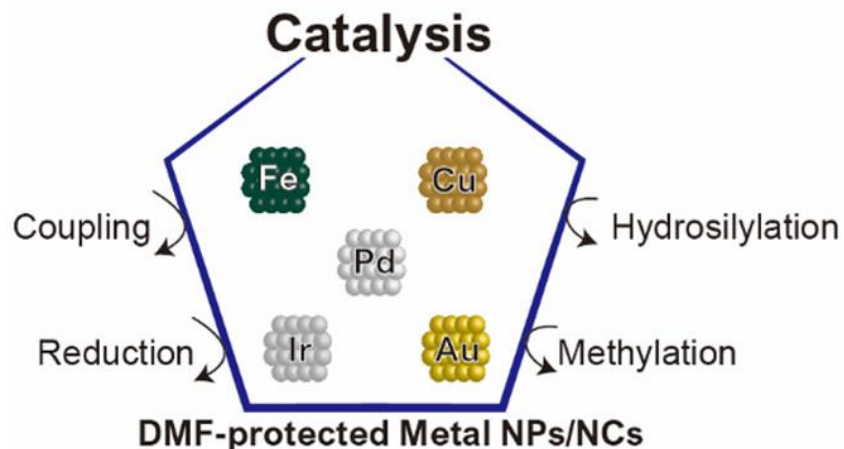
Figure 7. Illustration of some DMF-stabilized NPs for catalysis. Reprinted with permission from [29]. Copyright 2022 American Chemical Society.

The NPs obtained by DMF synthesis have been intensively studied for their optical properties[163, 167] such as fluoresecence[157, 158] or plasmon resonance.[156] For instance, surfactant-free Au NPs produced by the DMF synthesis were used as a platform to evaluate the effect of various ligand functionalization on optical properties.[153] The same batch of Au NPs was used and functionalized by ligand exchange with: thioctic acid, 11-mercaptoundecanoic acid, 1-dodecanethiol, dodecylamine, PVP, triphenylphosphine, poly(amido) amine, thiocholine bromide in order to tune the NP optical properties. The effect of adding PVP during synthesis was also investigated. The amount of PVP had a strong influence to modulate the emission wavelengths. No changes in the absorption wavelengths of the NPs was observed for different PVP concentrations used during synthesis, while the fluorescence emission wavelength changed relative to PVP concentrations. The authors concluded that the ligand-concentration-effect is a cross-linking effect: PVP provided a cross-linking environment for gold cluster agglomeration.

DMF-protected NPs experienced a regain of interest for catalytic reactions in the last years. In particular, the resulting NPs can be used unsupported and yet easily recovered and re-used. Au NPs were used for the reduction of 4-nitrophenol to 4 amino-phenol.[154] The catalytic activity was influenced by the nature of the DMF layer absorbed on the NP surface which was changing over time or heat-treatment. Compared to thiol-protected Au NPs, the DMF-protected NPs did not show a higher catalytic activity. Au clusters where demonstrated for Ullmann homo-coupling of aryl iodides.[171] By controlling the reaction time and temperature different sized were obtained: 1.0, 2.5 and 5.5 nm. The catalytic activity decreased in the order: $Au_{2.5nm} > Au_{1.0nm} > Au_{5.0nm}$. This illustrates that Au surface atoms do not have the same activity for the homocoupling considered, depending on the NP size and so the atomic environment which illustrates the complex interplay of structure-properties at the nanoscale.

Pt NPs obtained by DMF synthesis were used for detection of Fe^{III} in aqueous solution[172] but scarcely considered for catalysts, probably due to the non-metallic nature of the clusters.[158] In contrast, Pd has been largely investigated. Pd NPs were used for cross-coupling reactions of hydrosilane/disilane.[160] A displacement of the DMF by N-dimethylacetamide (DMAc) was observed to lead to higher activity due to easier access of the reactant to the catalyst surface. Pd NPs were also used for the Suzuki–Miyaura cross coupling and Mizoroki–Heck reactions,[159, 173] showing turnover numbers up to 4.5×10^5 and 6.0×10^8, respectively, and being recycled at least five times without loss of activity in Suzuki–Miyaura cross-coupling reaction. Recently the influence of the precursor used for the reaction was investigated and

despite a larger size obtained using acetate-based Pd complexes versus chloride-based complexes, the catalyst obtained using $Pd(OAc)_2$ were about ca. 100 times more active.[173] Pd NPs were also suitable for the Migita-Kosugi-Stille cross-coupling reactions,[174] and the Sonogashira–Hagihara and Mizoroki–Heck coupling polymerizations,[175] with results similar to those achieved with conventional $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ catalysts for these last reactions. The solvent stabilized NPs potentially mitigate one challenge of the Pd homogeneous catalysis for polymerization that is the likely ligand incorporation into the growing polymer. Equally the Larock indole synthesis was investigated for the reaction of substituted 2-iodoanilines with alkynes to give 2,3-disubstituted indoles.[176] Good recyclability was shown by simple recovery by extraction with hexane–ethyl acetate/DMF since Pd NPs have a strong affinity for the DMF phase.

The relatively good recyclability of the catalysts produced by DMF synthesis was also shown with other catalyst such as Fe_2O_3 NPs used for alkene hydrosilylation with good recyclability over 5 cycles.[166] Together with the high turnover typically observed, this explains why further metals were then investigated. Cu NPs were investigated for the Ullmann-type cross-coupling of aryl halides with phenols[164] and Sonogashira–Hagihara coupling leading to improved catalytic performances using low amount of catalyst (0.01 mol.%) yet achieving relatively high turnover number of 4.0×10^3.[177] More recently, Ir nanoclusters were shown to catalyze the β-methylation of alcohols via hydrogen auto-transfer with a turnover number up to 3.1×10^5.[161]

Table 1. Examples of surfactant-free colloidal syntheses in DMF. Typically, the atmosphere is not controlled, and the synthesis performed under reflux conditions.

Ref	Date	Solvent	Size	Metal	Precursor	Conditions	Support	Use
[153]	2008	DMF	< 20 atoms	Au	$HAuCl_4$ (1 mM)	140 °C - 4 h	-	Ligand exchange for optical properties
[155]	2010	DMF	< 20 atoms	Au	$HAuCl_4$ (1 mM)	140 °C - 6 h	-	Optical properties Thermal properties
[157]	2010	DMF	4-6 atoms	Pt	H_2PtCl_6 (1mM)	140 °C - 8 h	-	Optical properties
[156]	2011	DMA DMF	4-10 nm	Ag	$AgNO_3$ (1-10 mM)	RT, dark 30 min-24 h	-	Optical properties
[159]	2011	DMF	1-1.5 nm	Pd	$PdCl_2$ (1 mM)	140 °C - 6 h	-	Suzuki–Miyaura cross-coupling Mizoroki–Heck reactions
[154]	2012	DMF	< 20 atoms	Au	$HAuCl_4$ (1 mM)	140 °C - 6 h	-	4-nitrophenol to 4 amino-phenol
[158]	2012	DMF	< 2 nm	Pt	H_2PtCl_6 (1mM)	140 °C - 2-8 h	-	Optical properties
[164]	2012	DMF	ca. 2 nm	Cu	$CuCl_2$ (0.1 mM)	140 °C - 8 h	-	Ullmann-type cross-coupling of aryl halides with phenols
[178]	2012	DMF	9-17 nm	Pt_xNi_{1-x} $_{1<x<0}$ $PtCo_3$ $PtCu_3$, $PtFe_3$	Pt^{II} (pdate) (30 mM) Ni^{II}(pdate) (10 mM) $Co(acac)_2$, $Co(acac)_3$ $Cu(acac)_2$, $Fe(acac)_3$	200 °C autoclave 4-24 h	carbon	ORR
[169]	2012	DMF	ca. 9 nm	$Pt_{0.46}Ni_{0.54}$	$Pt(acac)_2$, K_2PtCl_6 (2 mM) $Ni(acac)_2$, $Ni(ac)_2$ (6 mM)	120 °C autoclave 16-42 h	carbon	ORR
[168]	2013	DMF	11 nm 12 nm 13 nm	$Pt_{1.5}Ni$ PtNi $PtNi_{1.5}$	$[Pt(acac)_2])$ $[Ni(acac)_2]$	120 °C autoclave 42 h	carbon	ORR
[174]	2013	DMF	1-1.5 nm	Pd	$PdCl_2$ (1 mM)	140 °C - 8-10 h	-	Migita-Kosugi-Stille cross-coupling reactions
[171]	2014	DMF	1.0 nm 2.5 nm 5.5 nm	Au	$HAuCl_4$ (1 mM)	140 °C - 6 h 150 °C - 2 h 150 °C – 8 h	-	Ullmann homocoupling reaction of aryl iodides
[170]	2014	DMF + H_2O (0-30 %)	< 10 nm	Pt	$Pt(acac)_2$ (41 mM) K_2PtCl_4, K_2PtCl_6 $PtBr_2$	120-200 °C autoclave	-	Shape control study
[167]	2015	DMF	< 2.5 nm	Pd_xCu_{1-x} $_{0<x<1}$	$PdCl_2$ (0.1 mM) $CuCl_2$ (0.1 mM)	140 °C 16 h	-	Optical properties
[179]	2015	DMF	13 nm	$Pt_xNi_yCo_z$	$Pt(acac)_2$ $Ni(acac)_2$ $Co(acac)_2$	130-200 °C autoclave 42 h	-	ORR
[161]	2017	DMF	1-1.5 nm	Ir	$IrCl_3$ (1 mM)	140 °C 10 h	-	methylations of alcohols and anilines
[165]	2017	DMF	ca. 3 nm	Cu	$Cu(NO_3)_2$ (0.1 M)	140 °C 9 h	-	Optical properties Interaction with bovine serum albumine
[177]	2017	DMF	2-7 nm	Cu	$CuCl_2$ (0.1 mM)	140 °C 8 h	-	Sonogashira–Hagihara cross coupling
[175]	2017	DMF	1-1.5 nm	Pd	$PdCl_2$ (1 mM)	140 °C 6 h	-	Sonogashira–Hagihara, Mizoroki–Heck coupling polymerizations
[166]	2018	DMF	2-5 nm	Fe_2O_3	$Fe(acac)_3$ (1 mM)	140 °C 8 h	-	hydrosilylation of alkenes

176	2018	DMF	1-1.5 nm	Pd	PdCl$_2$ (1 mM)	140 °C 6 h	-	Larock indole synthesis
162	2018	DMF	< 1 nm	Ir	IrCl$_3$ (1 mM)	140 °C 10 h	-	Optical properties Cr(IV) quantification
160	2019	DMF	ca. 2 nm	Pd	PdCl$_2$ (1 mM)	140 °C 10 h	-	Cross coupling reaction of hydrosilanes/disilanes Silylation of aryl halides and hexamhetyldisilane
163	2019	DMF	2 nm	Rh	RhCl$_3$ (1 mM)	140 °C 8 h	-	Optical properties
173	2020	DMF	3-5 nm 1-2 nm	Pd	Pd(OAc)$_2$ (0.2 mM) PdCl$_2$ (1 mM)	140 °C 8 h	-	Suzuki–Miyaura cross-coupling
180	2021	DMF	1-5 nm	Ir	IrCl$_3$ (1 mM)	140 °C 10 h	-	cross β-alkylation of linear alcohols

ac: acetate; acac: acetylacetonate; pdate: 2,4-pentanedioanate.
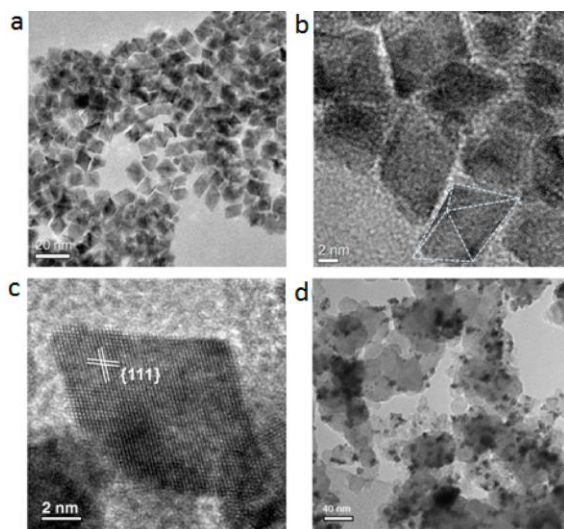
Figure 8. (a, b) TEM and (c) HRTEM images of octahedral PtNi NPs after 42 h obtained by DMF synthesis. (d) TEM image of octahedral PtNi NPs supported on commercial carbon (Vulcan XC-72). Reprinted with permission from [169]. Copyright 2022 American Chemical Society.

Another good example of the benefits of the DMF approach is the synthesis of PtNi or PtNiCo catalysts for the ORR reported by Tessema and co-workers[178] and Strasser and co-workers.[169, 179] Transmission electron microscopy (TEM) and high-resolution TEM micrographs are reported in **Figure 8**. The NPs lead to an unprecedented 9-15 fold mass based activity gained over the state-of-the-art Pt electro catalyst. Strasser *et al.* used different precursors to control the NP shape while the surface composition was tuned by the reaction time.[169] The most performant catalysts were obtained with 40 at.% of Pt at the surface of the NPs. The synthesis was performed at 120 °C in an autoclave for ca. 16 to 42 hours in order to favor a slow growth mechanism and minimize the size of the NPs to around 9 nm. The authors further use the same synthesis approach to prepare $Pt_{1.5}Ni$, PtNi and $PtNi_{1.5}$ catalysts in order to study phase segregation for the ORR, following morphological and compositional evolution before and after catalysis.[168] It was shown in opposition to expected theoretical work that the octahedral NPs feature a Pt-rich frame along their edges and corners, and their Ni atoms are preferentially segregated in their <111> facets. The authors noted that Pt only or Ni only NPs were challenging to obtain. This was further observed by Tessema *et al*. who used higher temperature of 200 °C in their study in order to tune the composition of Pt_xNi_{1-x} NPs and obtained cubic and cuboctahedral Pt_3Ni and octahedral and truncated octahedral PtNi.[178] While Cr precursor did not lead to efficient reduction, $PtCo_3$, $PtCu_3$ and $PtFe_3$ NPs where successfully obtained.

DMF synthesis clearly led to new insights into heterogeneous and electrocatalysis. In particular, unsupported heterogeneous catalysis has been well documented. Given that the materials can also be supported, this opens the room to (re)investigate other reactions, such as electrocatalytic processes, with supported catalysts. However, the synthesis suffers from some limitations. DMF can interact relatively strongly with metal surfaces.[181] DMF itself is a relatively non-eco-friendly solvent[182] with a high boiling point. Possibilities to scale up the reaction remain scarce with a preferred metal concentration in the synthesis around 1 mM. A closer look at the reaction conditions stresses the need for relativity high temperature and very long time of synthesis (> 3 hours). This makes its use slightly more energy intensive than alternatives detailed in the next section.
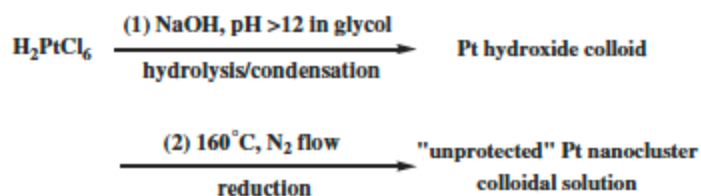
II.5. Surfactant-free polyol synthesis

Background

The polyol synthesis is an extremely popular method for the synthesis of various nanomaterials and metal NPs in particular.[183] First developed by Fievet and co-workers,[184] the method has been the subject of comprehensive reviews.[11, 183] In simple terms and most cases, the method consists in mixing a polyol such as ethylene glycol (EG) or glycerol, and a metal precursor under alkaline conditions. Upon heating up the reaction mixture, nucleation occurs and relatively small size NPs are obtained. A very large amount of literature stresses the *need* for surfactants in this approach among which PVP is a very popular choice.[58, 65] Very often, a support is also directly added during the synthesis.[185, 186]

In the context of the present review, it must be stressed than since 2000 and the pioneer work of Wang *et al.*,[92, 97] it is actually well established that there is *no need* for surfactants in the synthesis of precious metal NPs by the polyol method, see **Figure 9**. Conveniently, the approach is not very sensitive to the concentration of metal: a size 1-2 nm is obtained for Pt NPs regardless of the concentration of precursor (0.4 mM − 51 mM). This finding had two consequences: (i) New studies of catalysts with improved properties could be performed[187] and (ii) a new understanding of the stabilization and formation mechanisms of NPs could be gained.[35, 188-190] Surfactant-free metal NPs such as Pt,[97, 188] Ru,[97, 188, 191] Rh,[97] Ir,[65, 192, 193] Co,[194] Os,[195] Cu,[196] Ni,[197] Ag[198] and alloys such as PtRu,[187, 188, 199, 200] PtFe,[201] PtSn,[202-204] PtNi,[205, 206] PtCu,[205, 206] PtAu,[206] PtMn,[206] PtCo,[206] PtZn,[206] PtRh,[195, 207] Ru@Pt[208, 209] Pt@Ru[209], PtIr,[210, 211] PtSnO$_x$[210] PtPd,[212] PtW,[212] IrCu[213] were obtained and demonstrated in applications ranging from chemical synthesis,[194, 195, 209, 214] oxygen reduction reaction (ORR),[215] oxygen evolution reaction (OER),[193] electro-oxidation of methanol (MOR),[187, 201] ethanol (EOR),[202] ammonia (AOR),[210, 211] and applications in batteries,[216] photocatalysis,[217] sensing,[218] as well as various chemical reactions including hydrogenations,[98, 213, 219] CO,[220] methane[221] or glycerol[206] oxidation. From the literature survey performed and summarized in **Table S1** in the Supporting Information, it can be observed that while surfactant-free polyol syntheses are not as popular as syntheses using surfactants, several research studies already exploited the unique features of this approach along the years. Furthermore, it is observed that the number of reports on the synthesis of Pd,[210, 222] Ag[198] or Au[192, 195] is limited and requires surfactants. This is due to the fact that for the related metal precursors with high redox potentials, surfactants are typically needed to prevent NP agglomeration, due to the fast reduction that can be performed at room

temperature in alkaline polyols. Although, the highly viscous solvent glycerol is a suitable solvent for surfactant-free room temperature synthesis of Au NPs.[223]

$$H_2PtCl_6 \xrightarrow[\text{hydrolysis/condensation}]{\text{(1) NaOH, pH >12 in glycol}} \text{Pt hydroxide colloid}$$

$$\xrightarrow[\text{reduction}]{\text{(2) 160°C, N}_2 \text{ flow}} \text{"unprotected" Pt nanocluster colloidal solution}$$

Figure 9. Procedure of alkaline ethylene glycol method for the chemical preparation of metal nanoclusters stabilized by EG and ions. Reprinted from Wang, Y.; Wang, X. D. Solvent and Simple Ion-Stabilized Metal Nanoclusters: Chemical Synthesis and Application, *Metal Nanoclusters in Catalysis and Materials Science: the Issue of Size Control* 2008, 327-340, Copyright 2022, with permission from Elsevier.[92]

The direct one-pot synthetic approach on a support was extensively used for the surfactant-free polyol synthesis.[224] This is in part because polyols are typically viscous solvents, therefore flocculation of the colloids typically proceeds with an acid ''wash'' to collect the NPs. This washing can be tedious and using a support facilitates further washing steps.[23] A main drawback of combining synthesis *and* supporting step is the challenge to achieve high metal loadings on the support, especially on carbon supports since the negatively charged NPs are repulsed by the negatively charge carbon surface under the alkaline synthesis conditions.[185] It has been shown for instance that direct synthesis on carbon supports is going against size control: smaller sizes require a high level of NaOH, which negatively charges the support surface, resulting in repulsive interactions and a loss of NPs that are not efficiently supported.[185] Generally speaking, the high pH required for the synthesis influence the properties of the support and the NPs.[225] This highlights the benefits of colloidal approaches where the synthesis of the materials and the supporting steps can be separated.

In what is probably the latest review of the surfactant-free polyol approach in 2008,[92] it was already stressed that ''For the purpose of studying the intrinsic properties of metal NPs and employing the metal nanoclusters as nanosized building blocks for assembling some important functional systems conveniently, *unprotected* metal nanoclusters with sufficient stability are desirable''. It was quickly obvious that different challenges needed to be addressed: (i) controlled synthesis with desired composition, shape, size; (ii) use the surfactant-free NPs to advance our understanding of structure-

property relationships for catalysis; (iii) optimize the immobilization of the catalysts on relevant supports. In this review, we therefore give a more detailed focus to work in these directions reported after this date and achievements using surfactant-free NPs obtained using the polyol synthesis.

Methods

Surfactant-free polyol syntheses can be induced at room temperature using ambient light,[226, 227] UV light,[228] by thermal treatment using oil bath syntheses approaches[229] or microwave synthesis.[47] More rarely γ-rays were also used.[230] Different polyols can be considered such as di-ethylene glycol,[231] tri-ethylene glycol, propylene glycol-1,2, and butylene glycol-1,4.[232] A major benefit of these solvents is to show suitable dielectric properties leading to good compatibility with microwave absorption which facilitates the use of microwave reactors.[233] Polyols also have a high temperature boiling point which allows performing the syntheses across a wide temperature range. NaOH (alternatively KOH[234]) is a safer chemical than NaBH$_4$ often used to reduce metal precursors[71] and the method using a relatively safe solvent and reducing agent such as ethylene glycol is relatively *green*.[182] The surfactant-free NPs thus obtained typically show very long term colloidal stability for several months.[97, 188, 235] This is explained by the high viscosity of the solvent and precious metal NP surface functionalization with OH/OH$^-$ and CO species.[188, 189] The mechanism of the polyol synthesis itself is still subject to debate and the formation of glycolic acid / glycolate form by ethylene glycol oxidation while the metal precursor is reduced is not excluded to contribute to the stabilization.[187] Interestingly, carbon dots were reported to facilitate the reduction of metal to NPs.[236] Such carbon dots were reported in polyol synthesis and their role in the formation of NPs is still unclear. It was also reported that anions present in the solution and the type of precursor used could influence the size of the NPs.[237, 238]

Conveniently, the colloidal dispersions of surfactant-free NPs can be re-dispersed in various solvents such as alcohols, ketone (acetone, cyclohexanone, cyclopentanone), THF, acetonitrile, DMF, di-methyl sulfoxide (DMSO).[92] Further attractive features of the synthesis are its scalability: up to 10 g Pt NPs were obtained in a batch reaction.[239] Size control typically in the range 1-6 nm can be simply achieved by adding water to the polyol,[115, 240-242] controlling the 'pH'[187, 211, 242, 243] or alloying.[210, 212] The synthesis proceeds by the formation of metal hydroxide or oxide in alkaline conditions reduced at high temperature.[92] It is often stated that pH control in the alkaline range is key to enable the synthesis to occurs and to achieve size control, but recent results points towards the NaOH/Pt molar ratio as a better descriptor.[35, 244] Conveniently the C-O stretch vibration easily identified by FTIR can be related to the size of the NPs and provides a fast tool to evaluate the relative size of the NPs. This greatly facilities the optimization of the

synthesis by rapid screening alleviating access to more time consuming electron microscopy based facilities.[188]

The polyol synthesis is relatively simpler than the surfactant-free approaches detailed above, see also **Table S1**. Simpler equipment compared to LSPC and SPP is needed and shorter times of synthesis are typically required as compared to DMF-synthesis. Due to the popularity of surfactant-free polyol-based syntheses and the lack of a recent review on this synthesis, a range of different applications of NPs obtained by this method are illustrated further in **Section III**.

II.6. Surfactant-free mono-alcohol synthesis

One of the bottlenecks of the polyol-based syntheses is that they use viscous solvents and are performed are relatively high temperature (> 100 °C). Mono-alcohols such as methanol or ethanol and mixtures with water have long been shown to be suitable reducing agents and solvents for NP synthesis at lower (< 100 °C) temperature.[245] However, surfactants and/or a support are almost always required to prevent NP agglomeration,[246, 247] although some reports suggest that nanomaterials can be obtained without surfactants. For instance, UV-vis induced synthesis of PdPt@Pt NPs in water/methanol mixture was reported to develop electrocatalysts for the MOR.[248] In the quest to simplify catalysts production, we recently reported a surfactant-free synthesis of precious metal NPs in alkaline mono-alcohols. We found that mono-alcohols can be used in alkaline conditions to synthesize stable surfactant-free monometallic and bimetallic NPs made of Pt, Ir, Ru.[22] New insights into the reaction mechanism and the formation of the NPs can be expected using this new synthesis.[249] We showed for instance a strong effect of the cations on the stabilization mechanism of surfactant-free Pt NPs colloids.[234] While the influence of the nature of the base is rarely investigated for other syntheses, we observed that Pt NPs colloids stability decrease with the nature of the cation used in the base in the order Li^+ > Na^+ > K^+ / Cs^+. This was attributed to a decreasing interaction with the Pt NP negatively charged surface. We also showed that the solvent from the synthesis can be recycled several times. In our latest development, the synthesis could be performed at room temperature[52, 250, 251] and a strong influence of the reducing properties of the solvent was shown.[252] Pt has been the most studied materials and size controlled achieved by using alcohol/water mixtures. To date, size control remains more challenging for Ir NPs[253, 254] or Os NPs,[254, 255] as summarized in **Table 2**. In the case of Ir and Os NPs, actually no base is needed to obtain NPs,[255, 256] but the activity and probably the yield of the synthesis are improved using alkaline conditions.

The NPs obtained offer several advantages: the synthesis can be performed at low temperature (e.g. 70-80 °C *vs.* > 140 °C for DMF or polyol synthesis) avoiding possible phase segregation possibly happening in high temperature treatment of alloys.[187] The synthesis can be induced in different ways, oil bath synthesis, UV-vis microwave synthesis, see **Table 2**, and is compatible with flow systems.[257] The colloids are stable in various solvents, including aqueous solutions,[234] and in solvents that are very simple to remove e.g. by simple evaporation[258] while no further flocculation steps are needed. This important simplification of the preparation of the NPs leads to supported Pt catalysts showing higher activity than industrial catalysts for the hydrogenation of butanone even at relatively high metal loading of 10 wt.% on Al_2O_3.[22] The NPs produced turned out to be ideal template to investigate proximity/loading effect in catalysis.[258, 259] One

drawback of the synthesis is to require relatively low concentration of precursor in the case of Pt (2.5 mM)[22] but was shown to lead to small size Ir NPs even at high precursor concentration of 100 mM.[254] The related Ir NPs were shown to be up to ten time more active than the state-of-the-art for the OER.[22, 259] It is expected that the high activity of the catalyst obtained will help to discriminate in more depth NP size or support effects.

While this mono-alcohol approach is challenging for Au and Pd based nanomaterials, recent results show that a fine control over precursor and based concentration in water-alcohols mixtures could lead to the room temperature synthesis of stable surfactant-free NPs in a surprisingly simple manner.[260] The related nanomaterials are directly relevant for catalysis.

Table 2. Examples of use of mono-alcohol surfactant-free colloidal synthesis.

Ref	Date	Solvent	Base	Diameter / nm	Metal	Precursor	Conditions	Support (loading)	Use
22	2018	Methanol Ethanol H_2O	NaOH (50 mM)	2-5 1-2 1-2	Pt Ir Ru	H_2PtCl_6 $IrCl_3$ $RuCl_3$ (2.5 mM)	15-30 min Reflux MW	-	OER Butanone Hydrogenation
257	2019	Methanol H_2O	NaOH (10-250 mm)	2-3	Pt	H_2PtCl_6 (0.5-2.5 mM)	UV MW	-	Synthesis study
234	2019	Methanol H_2O	LiOH, NaOH KOH, CsOH (10-50 mM)	2-3	Pt	H_2PtCl_6 (0.5-2.5 mM)	45 min Reflux MW	-	Synthesis study
258	2019	Methanol	NaOH (44 mM)	1.6	Ir	$IrCl_3$ (4 mM)	30 min Reflux MW	-	OER
253	2020	Methanol Ethanol H_2O	NaOH (0-250 mM)	2.5 1.0-1.7	Pt Ir	H_2PtCl_6 $IrCl_3$, H_2IrCl_6, Na_2IrCl_6 (2 mM)	UV 2 h	-	Synthesis study
252	2020	Methanol Ethanol H_2O	NaOH (10-50 mM)	2	Pt	H_2PtCl_6 (0.5-2.5 mM)	Oil bath MW	-	Synthesis study
52	2020	Methanol H_2O	LiOH (25 mM)	2-3	Pt	Aged H_2PtCl_6 (2.5 mM)	RT seconds minutes	-	Synthesis study MOR
261	2021	Commercial spirits	NaOH (10-50 mM)	2-5	Pt	H_2PtCl_6 (0.5-2.5 mM)	30-60 min Reflux MW	-	MOR
259	2021	Methanol Ethanol EG	NaOH (44 mM)	2	Ir	$IrCl_3$ (4 mM)	30 min Reflux MW	Carbon (10, 30, 50, 70 wt.%)	OER
256	2022	Ethanol	-	2	Ir	$IrCl_3$ (4 mM)	30 min Reflux MW	Carbon (10, 30, 50, 70 wt.%)	OER

254	2022	Methanol Ethanol H_2O	NaOH (0-1 M)	2	Ir Os	$IrCl_3$ $OsCl_3$ (100 mM)	60-85 °C hours to weeks	-	Synthesis study
255	2022	Methanol Ethanol H_2O	NaOH (0-1 M)	1-2	Os	$OsCl_3$, H_2OsCl_6 (2.5-100 mM)	85-90 °C 6 hours	-	Synthesis study
260	2022	Methanol Ethanol H_2O	LiOH, NaOH	5-30 3-4	Au Pd	$HAuCl_4$ $PdCl_2$ (0.5 mM)	RT hours	-	Synthesis study EOR

II.7. Discussion

Size control. One of the main challenges with surfactant-free syntheses is to develop strategies to achieve size control, which is more classically performed by tuning the amount of surfactant in the synthesis. A detail study of the influence of THF/alcohol mixture is reported for Ru NPs obtained from a Ru(1,5-cyclooctadiene)(1,3,5-cyclooctatriene) precursor.[262] It was found that tuning the solvent is a suitable approach to control the size of the surfactant-free NPs obtained. However, the use of home-synthesized precursors hinders further application of the synthesis at larger scale. This explains why relatively simpler precursors such as halide-based complexes such as H_2PtCl_6 or $IrCl_3$ are typically preferred, see **Table 3**. In the case of Pt NPs, size control can be achieved by controlling the amount of water[115, 240-242] or the amount of base in the polyol synthesis,[35, 244] or the solvent in the mono-alcohol synthesis.[22, 252] The degree of size controlled achieved in DMF synthesis is moderate given that the NP formed tend to be small. LSCP leads to relatively broad size NPs and size-exclusion treatments can be required.[133]

Shape control. Shape control is probably the most challenging achievement in surfactant-free syntheses. It is an important area of research since shape will correlate with crystallographic structures, which can severely influence catalytic properties. Interested readers can refer to recent dedicated reviews.[263] Shape control is generally challenging with surfactant-free approaches but reports show that a certain degree of shape control is possible. This is typically achieved adding small-molecules (molar mass < 100 g mol^{-1}) and/or gas molecules.[64, 123] Halogen ions have also been reported as shape controlling agents.[264] In the polyol synthesis, such shape control was achieved for instance by using EG/DMSO, to obtain branched Pd nanowires.[265] Pt NPs shape was controlled from spheres to tetrahedral and octahedra using an increased amount of $AgNO_3$ to slow down the reaction, alter the growth rate and lead to shaped NPs.[266] Shape control can also be achieved due to side reaction of the solvent itself, as is the case for PtNi nanocrystals obtained in DMF.[168, 178] A mixture of Pt and Ir treated at 130 °C in ethylene glycol were used a precursor to study the effect of different high temperature and pressure treatments to obtain for instance nanorods with diameter 1-6 nm as suitable catalysts for the MOR and ammonia detection.[267] There is certainly still room for improvements to achieve a certain degree of shape control with surfactant-free syntheses and rationalize such shape control.

Simpler syntheses. In order to develop simpler and ultimately cost efficient syntheses, a recent trend is the development of syntheses at room temperature and light.[52, 227] Without using a support such syntheses at room temperature can be challenging to obtain stable colloids,[250] but it is possible by a careful

choice of reactants.[227] In this regard, the role of water suggested and observed to exhibit a possible catalytic effect in the synthesis is still to be clarified.[227, 247] It was indeed shown experimentally that in the absence of water, the polyol synthesis could not proceed.[121] Along the line of the importance of water as a simple solvent for NP synthesis, some syntheses are performed in water *only*. Light induces hydrolysis of H_2PtCl_6 in water was reported to lead to Pt_4 clusters leading to colloids stable for months.[268] Water, as simple and safe solvent, has also been reported as a suitable reaction media for RuO_2 NP synthesis used as electrode material for supercapacitor[269] or for the HER,[270] as well as for Pt NPs investigated for the ORR.[271] The synthesis then typically proceeds at temperature over 80 °C for several hours. A reducing agent is technically needed to obtain NPs from a precursor containing metal atoms in an oxidized state. The fact that NPs can be obtained what seems to be *water only*, might actually be related to impurities playing the role of reducing in agent(s) in these syntheses. Impurities or even ''dust'' are known to have an influence in a range of syntheses[272, 273] and are anticipated to have an important or maybe more pronounced role in the case of surfactant-free approaches. The role(s) of impurities must therefore be carefully kept in mind.[1]

Table 3. Overview of pros and cons of different colloidal syntheses of nano-catalysts with a focus on surfactant-free approaches.

Synthesis	Disadvantages	Post-treatments	Pros / Cons			
			Size control	Composition control	Shape control	Scalability
Colloids with surfactant	Surfactant-removal	Surfactant-removal	YES	YES	YES	Challenging
One-pot syntheses	Support dependent	Washings	YES/NO	YES	YES/NO	YES/NO
Surfactant-free colloids						
LSPC	Large size distribution Equipment	Size selection	YES	YES	Can be challenging	YES
Plasma	Equipment	(Size selection)	YES	YES	-	YES
DMF	High temperature	Washings	YES	YES	YES/NO	NO
Polyol	High viscosity	Washings	YES	YES	YES/NO	YES/NO
Mono-alcohol	-	Less Washings	YES	YES	-	YES

Comparison

LSPC, SPP, DMF, polyol and mono-alcohols syntheses offer multiple advantages over commercial catalysts, catalysts prepared by impregnation-calcination, one-pot syntheses or syntheses using surfactants. An overview of the features of each synthesis is proposed in **Table 3**. However, there is room for improvement. LSPC and SPP require careful optimization of many possible parameters or at least hand on experiment of some specific devices such as laser or plasma generating devices. This certainly offers opportunities to finely tune the NPs properties but can also give rise to a relatively complex optimization. Syntheses in DMF, polyols or mono-alcohols remain more intuitive with *a priori* fewer parameters to tune in order to control the NP properties. Nevertheless, DMF synthesis requires relatively long synthesis time and high temperature, see **Table 1**.

The polyol synthesis is generally performed faster in few hours or even few minutes in a microwave reactor. However, some authors report challenges to use the polyol synthesis e.g. for electrochemical testing.[274] This goes against our experience[35, 215] but highlights the need for simpler and more straightforward methods, in particular circumventing washings steps. Washing steps performed to flocculate the NPs obtained by the polyol synthesis do not exclude a loss of some NPs and generate large amounts of waste. For instance, the mixture water-EG resulting from washing the NPs with an acid cannot be re-used for future syntheses.[187, 194] Similar to the case related to ligand removal detailed in **section I**, these washing steps can bring irreproducibility in the process. The above challenges are alleviated in mono-alcohols syntheses performed at lower temperature since no washings steps in acid to flocculate the NPs are needed.[22] The low boiling point solvents can be evaporated and actually recovered for later syntheses, e.g. during a supporting steps of the NPs.[22]

Scaling up the production of colloids to allow their market penetration comes to balance fundamental understanding of the formation mechanism and suitable strategies for large scale production.[275, 276] The careful synthesis of NPs and selection among various strategies take a stronger meaning in the case of precious metal heavily use in the energy conversion sector, typically at high precious metal loadings.[70, 277] Given the high cost and scarcity of precious metals,[278] any even minor improvement in the production of NPs can have significant economic and ecologic impact. Typical drawbacks and challenges in scaling up nanomaterials syntheses are the need for high temperature, vacuum, inert atmosphere, post-treatment of the materials or recycling of the excess of waste/surfactant. In that respect, sustainable processes designed to optimize the production of scalability of NPs are expected to play a key role in future

technologies, especially to facilitate crossing the gap between academia and industry.[41, 279] By avoiding the use of surfactants, less chemicals are needed and extensive washing steps are avoided.

Conceptually, surfactant-free syntheses have the potential to bring the lab-scale findings on how to more rationally design catalysts a step closer to larger scale applications. However, a final consideration is the cost of production of the catalyst that must be balanced by improved performances (e.g., activity, stability, selectivity). For instance, halide-based complexes are often cheaper and therefore preferred precursors compared to halide-free metal precursors, see **Table 1** and **Table S1**. However, the presence of a halide such as chloride can ultimately lead to contaminations in catalysis. Although the presence of residual chloride at lab scale does not seem to be a critical point, it might come as a limitation at larger scale. Another major drawback to date in surfactant-free syntheses is the need for high boiling point and viscous solvents (e.g. DMC or polyols) requiring intensive washing steps and/or high temperature to perform the synthesis. In particular flow systems are envisioned as a key component of the production of large scale production of nanomaterials.[280] Low viscosity solvents such as mono-alcohols are promising candidate in order to avoid high pressure systems.[275] In light of these considerations, it is anticipated that surfactant-free mono-alcohols syntheses will play an increasing role not only for fundamental but also applied research.

III. Surfactant-free colloidal nanoparticles: reference materials and building blocks

As conceptually illustrated in **Figure 4**, surfactant-free syntheses of precious metal NPs are ideal to advance rational catalyst design. For instance, to compare the effect(s) of surfactants or ligands on a catalytic reaction, if standard colloidal synthesis approaches are used, surfactant/ligand removal is often required. As discussed above, this leads to several methodical limitations and the interpretation of the results can be challenging. In contrast, using a surfactant-free synthetic strategy, the NPs can serve as *building blocks* and *reference materials.* One can use the same colloidal stock dispersion to compare "bare" particles to differently functionalized ones, e.g. to assess the effect of ligand functionalization.

Since LSPC,[1] SPP,[137] or DMF based syntheses[29] have been reviewed recently, here catalytic studies using surfactant-free NPs obtained by the polyols and mono-alcohols syntheses are detailed. Rather than summarizing different reactions where surfactant-free NPs were successfully used and for which an account is given in **Table S1** and **Table 2**, we present an overview of the common strategy to investigate and optimize the influence of a given parameter affecting the properties of a catalyst. We previously dubbed this approach *toolbox approach* to highlight its variability.[23, 215, 281]

III.1. The surfactant-free toolbox approach

A major benefit of surfactant-free NPs is to allow parametric studies that will not be possible using commercial catalysts and materials prepared by impregnation-calcination or surfactant-based colloidal methods. The concept in these studies is to go *beyond active site* design and to evaluate in a systematic way not only the influence of the NP composition but also the influence of particle size, support, loading, washing steps, supporting steps, etc.

An illustrative example of this concept is reported in **Figure 10**. The purpose of the related study was to investigate the effect of adding a support at different stages of a catalyst preparation.[282] Qi *et al.* highlighted the benefits of a surfactant-free colloidal approach leading to catalysts with higher mass activity for the ORR and MOR due to smaller size NPs obtained: 1.7-2.5 nm for the colloids (support added last) *vs.* 2.1-3.5 nm by impregnation (support added first). The study also showed a clear effect of different

carbon supports. Two different support types were used with different acid group functionalization and different hydrophobicity. For the carbon support with a larger amount of micropores, attempts to reach higher metal loadings (up to 40 wt.%) with a higher concentration of precursor led to more significant particle size increase from 1.3 up to 3.6 nm. In contrast, in the colloidal approach, the size of the NPs remained between 1.7 and 2.9 nm, i.e. size control could be more finely tuned. A similar strategy was used in a comparison of an aqueous-based synthesis and an impregnation reduction method in order to identify an optimized synthesis strategy of PtSn NPs for the EOR.[283] Ir NPs prepared by the polyol synthesis also show better activity than Ir NPs prepared by deposition-precipitation for formaldehyde oxidation at room temperature.[28]
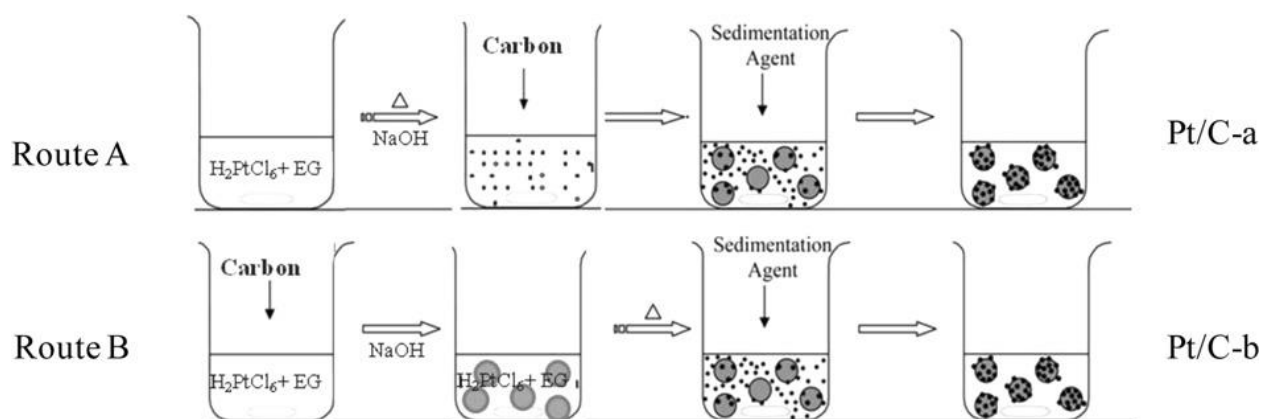
Figure 10. Graphical representation of the preparing process of different Pt NPs supported on carbon. Reprinted from Qi *et al.*, Preparation of Pt/C via a polyol process – Investigation on carbon support adding sequence, *Int. J. Hydrog. Energy* 2011, 36, 17, 10490-10501, Copyright 2022, with permission from Elsevier.[282]

This *toolbox approach* has been formalized, advanced, expanded and improved further over the years.[23, 215, 281] A specific account of the results related to Pt NP optimization for the ORR is detailed as an illustrative example in reference [281]. In **Figure 11**, a scheme of the approach is shown when using the surfactant-free EG synthesis used in several prior studies for rational catalyst design.[47, 284] Using low boiling point solvents, the approach is similar, but no washing step is required. It starts with the synthesis of one or more batches of surfactant-free colloidal NPs with specific properties such as composition or size. These batches serve as stock dispersions. In the surfactant-free EG synthesis, the NPs need to be washed to

remove the EG. Then the NPs can be either directly supported or for example functionalized with specific molecules in a phase transfer. In the supporting step, the NP to support ratio and thus the resulting metal loading is a variable parameter. Before the (electro-)catalytic testing, typically a catalyst ink needs to be prepared, which results in additional parameters that can be varied and investigated.
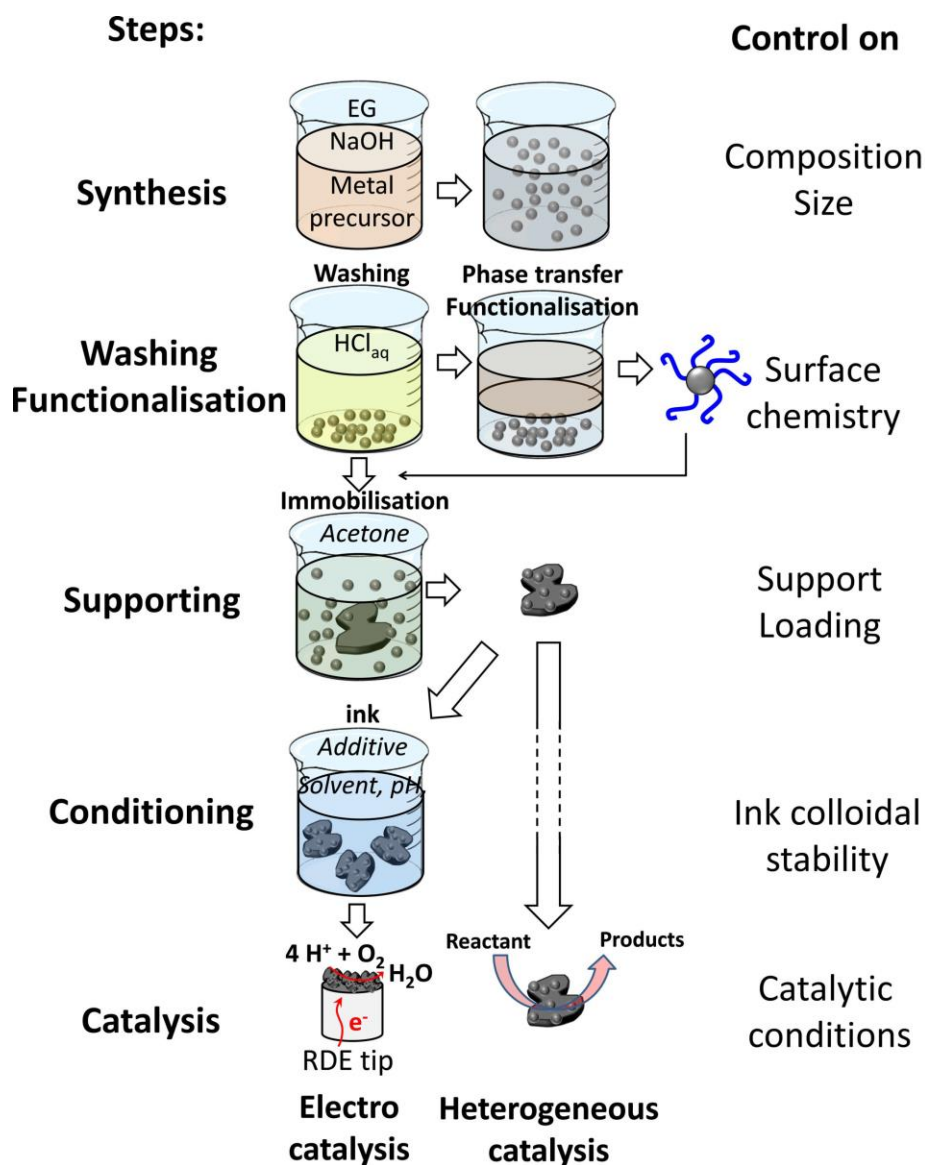
Figure 11. Schematic representation of a toolbox approach to surfactant-free NPs based on the EG synthesis for parametric studies. Example of Pt NPs for the ORR. Copyright 2022 Wiley. Used with permission from Quinson *et al.* ChemCatChem 2021, 13, 7, 1692-1705.[23]

III.2. Synthesis related effects

The first aspect of catalyst design comes with the choice of the synthesis method. The seemingly *same* metal NPs, e.g. Pt NPs 2 nm in size, obtained by different synthetic approaches are known to possibly lead to different catalytic properties. This is due to the experimental nature of catalyst syntheses and limitations in a full characterization of catalyst materials.[272] The cross comparison of different synthetic strategies to develop a similar / same catalyst, however, is not common.[235, 274] Such studies typically hardly bring fundamental insights, since any different step in the syntheses or any different chemical used, or their different concentrations, or even different lab consumables in some cases, can lead to a different outcomes. Nevertheless, it is important to stress that seemingly unimportant experimental parameters can have a strong effect on the catalyst properties, such as the recently observed cation effect in mono-alcohols syntheses,[234] or the influence of the gas atmosphere during synthesis.[285] For instance, using N_2 atmosphere for the NP synthesis, more active catalysts for the ORR and MOR than Pt and PtRu obtained in air are reported.[285] In order to compare the benefits of *similar* catalysts prepared in different ways, extra care must then be given to not only document synthetic procedures but also washings and supporting steps as extensively as possible. In this respect, actual footages of the way the experiments are performed can be of great help to improve reproducibility.[47]

A recent report compares the difference of catalytic activity for NPs obtained by the polyol process and the mono-alcohol synthesis. It must however be kept in mind that not only the solvent but also synthesis temperature and duration of synthesis as a well as precursor concentrations are different. Bizzotto *et al.* observed that Ir NPs prepared in mono-alcohols led to higher mass activities for the OER, as illustrated in **Table 4**.[259] Similar results were obtained for Pt NPs for butanone hydrogenation[22] and illustrate the strong influence of a given colloidal synthetic approach in catalyst preparation.

Table 4. Mass activity for the OER in acid for 2 nm Ir NP catalysts with metal loadings of 10, 30, 50, 70 wt.% prepared in different solvents, as indicated. Reprinted from ', Bizzotto *et al.*, Surfactant-free colloidal strategies for highly dispersed and active supported IrO$_2$ catalysts: Synthesis and performance evaluation for the oxygen evolution reaction, *J. Catal*. 2022*, 401, 54-62, Copyright 2022, with permission from Elsevier.[286]

Ir Loading [%]	Mass activity [A g$_{Ir}^{-1}$]		
	ethylene glycol	methanol	ethanol
10	168 ± 16	348 ± 11	388 ± 14
30	201 ± 11	304 ± 6	456 ± 21
50	185 ± 24	342 ± 30	405 ± 36
70	197 ± 15	212 ± 24	415 ± 2

Another aspect of catalyst preparation that is challenging to document is the storage conditions. It is common to use a batch of colloidal NPs for a same study over extended period of time. However, it is established that long term storage of colloidal NPs can lead to changes affecting the NPs properties.[238] In this respect, the polyol synthesis brings new opportunities. The surface of the NPs is stabilized by CO of OH/OH$^-$ moieties and phase transfer in organic or aqueous solvents makes it possible to tune which species are the major stabilizers.[190] Removing the solvent and storing the NPs as powders is then possible. The dry powders of surfactant-free NPs can be redispersed without any change in the NP size and the NPs recover their original catalytic activity.[190] This example highlight the probably overlooked potential of surfactant-free NPs leading to stable NPs without agglomeration not only in solution but also as solid powders.

III.2. Size effects

One essential parameter in heterogeneous catalytic reactions is the size of the active NPs that typically determines the active surface area of the catalyst. Decreasing the NP size leads to an increase in surface area per mass and thus to an increase in mass normalized reaction rate. However, changing the particle size can also change the specific, i.e., the surface area normalized reaction rate. In this case, one can speak of an intrinsic particle size effect that typically is related to structure sensitive reactions. Catalysts

prepared from surfactant-free NPs are very suitable to investigate size effects. The control of the obtained particle size typically is significantly better in colloidal methods than in standard syntheses where the particles are formed on the support. As illustrated in **Figure 12**, the control over the particle size can be maintained upon immobilizing them on a support material.

Size effects have been extensively and conversely studied for the electrocatalytic properties of Pt using mainly commercial or ill-comparable catalysts.[287-289] For example, for the ORR contradicting results have been obtained, which has led to intense discussions if there is an intrinsic particle size effect, or if the influence is merely an influence of surface area.[288-290] Using the surfactant-free polyol synthesis of Pt a substantially better control of the particle size in the range 1-4 nm could be obtained, which was utilized to study the ORR.[35, 291] As the particle size decreases, controlled by tuning the NaOH/Pt molar ratio in the synthesis, the mass activity of the NPs increased but the intrinsic/specific activity decreased.[35] In the investigated size range, however, the influence on the specific activity was substantially lower than previously reported. Furthermore, using the same synthesis it could be shown that the stability of the NP decreases with decreasing size.[292]

In another study, NPs from 1-3 nm in diameter were compared supported on Fe-based supports for CO oxidation properties.[242] The NP size influenced the chemical states of Pt species and the strength of metal–support interactions. Metal–support interactions in the Pt/Fe_2O_3 catalysts played a role in adjusting the redox properties of the catalysts, to optimize the activation of CO and O_2. A further example, is a series of Pt NPs with size 1.3, 1.5, 1.7, 1.9, 2.1 and 2.3 nm supported on ZSM-5 obtained by controlling the amount of precursor concentration and amount of water.[241] This example illustrate the rather fine size control achievable even without surfactants. The NPs with 1.9 nm diameter exhibit the highest activity due to a balance between Pt dispersion and presence of Pt^0 in the catalyst. The catalysts high activity, stability, and selectivity thus obtained is relevant for volatile organic compounds (VOCs) removal. In another study, surfactant-free NPs were further functionalized with PVP and entrapped in a matrix (SBA-15). The catalytic activity for ethylene hydrogenation of the NPs obtained this way with a relatively small size was compared to larger size NPs produced by other synthetic methods.[293] The authors stressed that the ability to ''synthesize monodisperse particles by solution phase reduction allowed the study of intrinsic activity and selectivity of particle size rather than ensemble (particle size) averaged values of these kinetic phenomena''.[293] Using Pt NPs in the range of 1-4 nm synthesized and supported on γ-Al_2O_3, it was shown that CO oxidation occurs via two mechanisms in parallel.[294] One is the generally accepted Pt catalyzed Langmuir–Hinshelwood mechanism.[295] The second is the Boudouard reaction that occurs between

adjacent CO adsorbates on Pt. The latter mechanism becomes more relevant as particle size increases. This suitability of the polyol synthesis to obtain size controlled and relatively small size deviation was recently exploited to study Pt NPs for plastic recycling by hydrogenolysis, where smaller size NPs are more active.[296]

An example using a different metal, is Ru NPs prepared by investigating the effect of pH, temperature and precursor concentration.[160] It was found that pH was the main factor influencing size control: with a pH increase the NP size decreases. The catalytic activity for the liquid phase hydrogenation of methyl-N-boc-pyrrole-2-carboxylate in ethanol solution at 25 °C and H_2 pressure of 5 bar, was shown to be optimal for a NP size of 1.6 nm.[191] However, if similar sized NPs were obtained by another synthesis route, e.g. with PVP, the activity was significantly decreased. These results illustrating the benefits of the surfactant-free approach leading to size-controlled NPs without blocking surface sites.
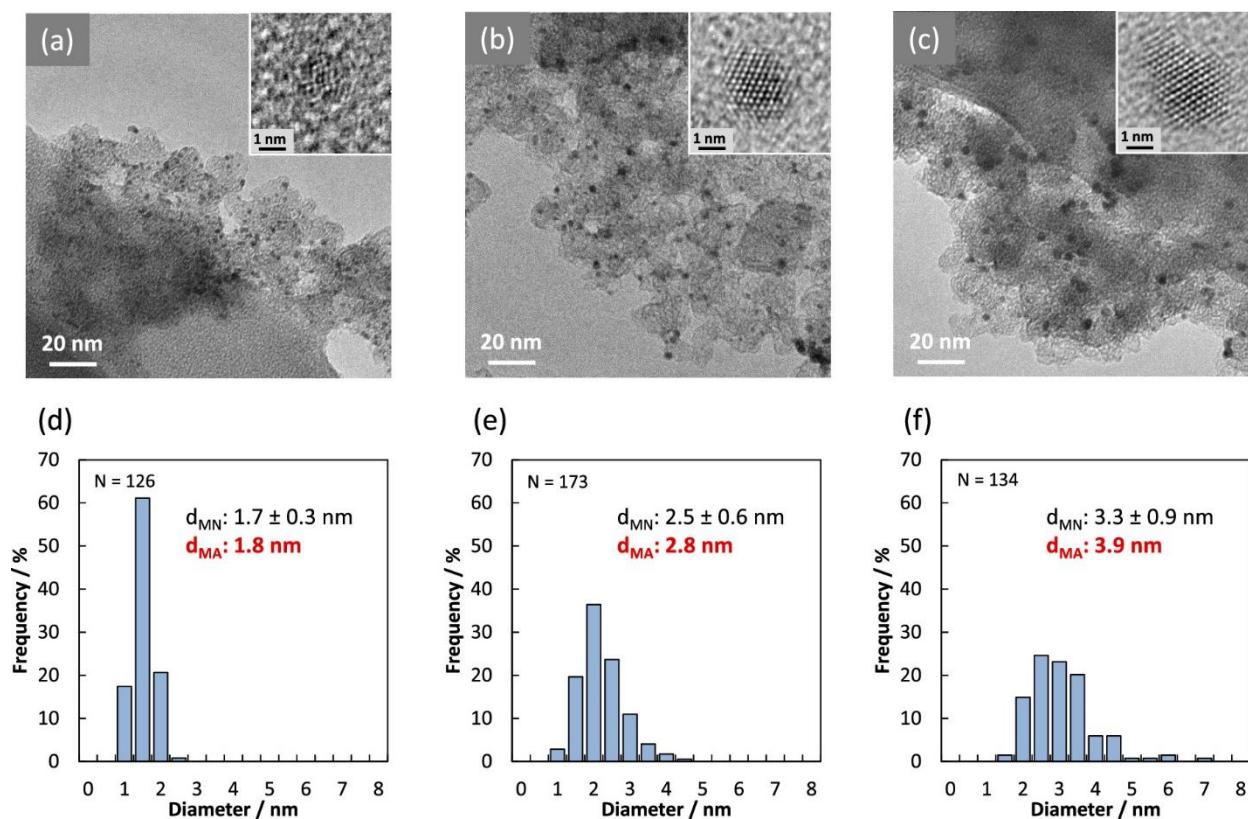
Figure 12. (a-c) TEM micrographs of 30 wt.% Pt/Vulcan catalysts and (d–f) respective particle size distributions for NP prepared with different sizes by the polyol synthesis. N, dMN, and dMA stand for the

number of analyzed Pt NPs, mean number diameter, and mean area diameter, respectively. Reprinted with permission from [291]. Copyright 2022 American Chemical Society.

III.3. Loading and interparticle distance effects

Discussing loading effects, one has to distinguish between loading in the meaning of the amount of catalyst used in a measurement, and in the meaning of metal to support ratio. Here we concentrate on the latter. Metal loadings can strongly affect the properties of the catalysts.[132, 297] As comparative studies typically are performed with a fixed amount of active metal, different metal-to-support ratios of the catalysts lead to different absolute amounts/volumes of supported catalyst. This can have substantial impacts in the utilization of the catalyst and volume utilization in a reactor, possibly affecting mass transport phenomena (e.g. for the same mass of metal, a supported catalyst with high metal loading occupies a smaller volume). In the case of electrocatalysis, different metal loadings typically lead to different thicknesses of catalyst layers on the electrode, as illustrated in **Figure 13**.[298] In addition to the required optimization of the ionic conductance of the catalyst layer, mass transport related phenomena can affect the catalytic properties, especially at high reaction rates.[298, 299] On a more fundamental level, the metal loading also changes the interparticle distance which can alter the oxophilicity of the catalyst and alter the electric double layer resulting in different (electro)catalytic properties.[24, 300] In addition, the metal loading can influence the metal support interaction discussed in the next section.[301] To establish and differentiate these effects experimentally, typically very sophisticated preparation methods such as the preparation of size-selected clusters are required.[24, 302, 303]
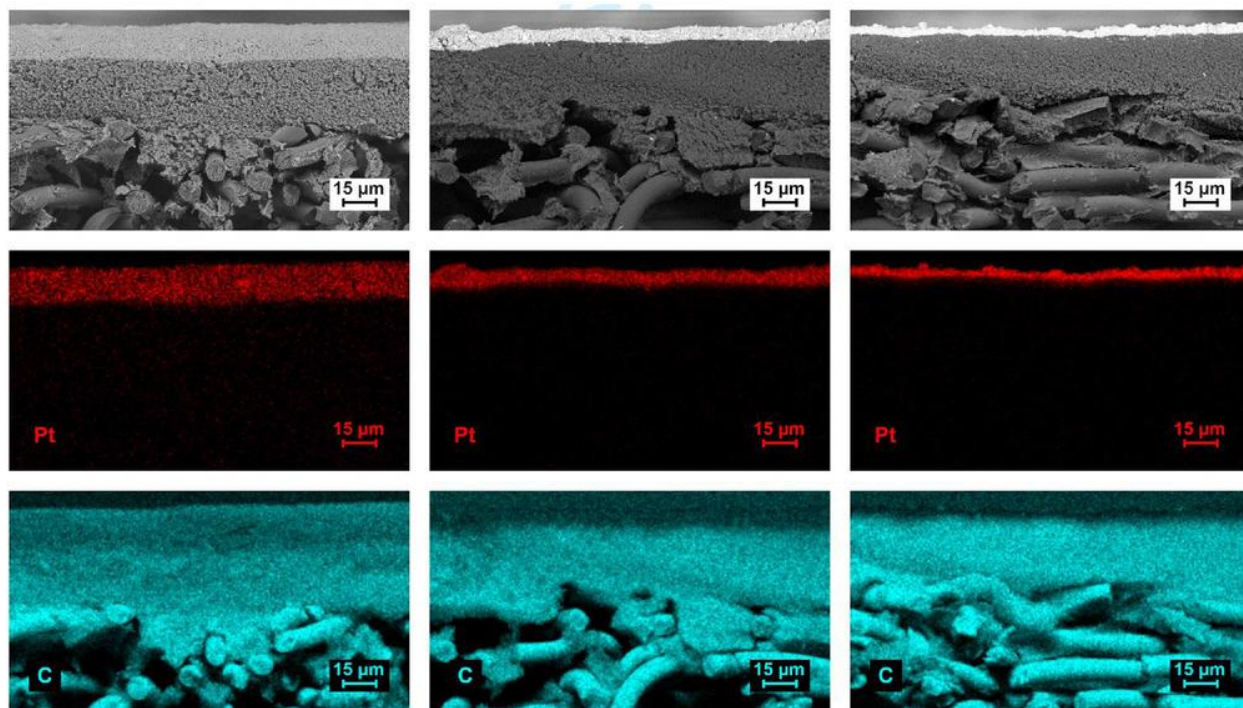
Figure 13. Comparison of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy data on cross-sections of three gas diffusion electrodes prepared with different Pt/C catalysts. (Left) HISPEC 20 wt.%, (middle) TKK 46 wt.%, and (right) HISPEC 70 wt.%. Due to the different metal loading on the carbon support in the Pt/C catalysts, the fixed Pt loading on the GDL (208 ug$_{Pt}$ cm^{-2}) leads to different thicknesses of the catalyst film. Reprinted from Nösberger *et al.* The gas diffusion electrode setup as a testing platform for evaluating fuel cell catalysts: A comparative RDE-GDE study, *Eletrochem. Sci. Adv.* 2022, DOI: 10.1002/elsa.202100190, Copyright 2022, with permission from Elsevier.[298]

However, surfactant-free NP syntheses allow similar control of the catalyst properties. Using the toolbox approach, it was shown that high metal loadings, meaning short interparticle distances, can lead to improve mass activity and stability of Pt NPs for the ORR. The flexibility of the approach allowed to establish that particle size and interparticle distance effects are entangled, see **Figure 14**.[35, 291, 303] It can be seen that at large interparticle distance, i.e., isolated NPs, the specific ORR activity decreases with decreasing particle size; similar to what was reported based on commercial catalysts.[289] In addition, the specific ORR activity increases with decreasing interparticle size; an effect more pronounced for smaller NPs. Therefore, both effects could only be distinguished with the help of a synthesis allowing independent control of NP size and metal loading. The analysis of the electrochemically active surface area (ECSA) as

function of the interparticle distance thereby serves to identify the synthetic limitations, i.e., particle agglomeration during synthesis. The particle proximity effect was also investigated using Ir NPs prepared by the mono-alcohol synthesis for the OER leading to similar conclusions.[258, 259] However, for the OER the effects mainly lead to a difference in oxide formation and not the catalytic activity as the active phase of Ir is IrO_2.
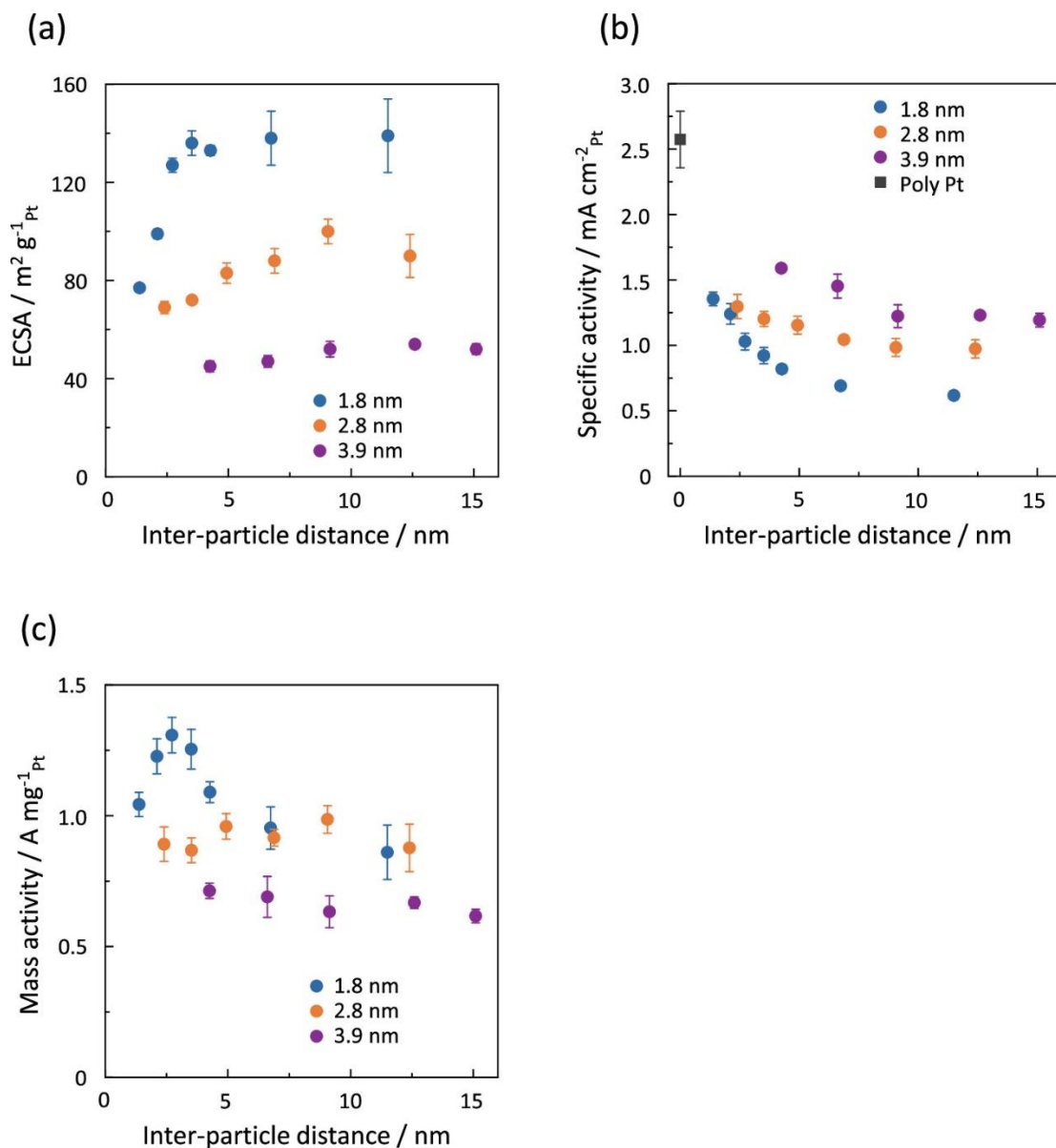
Figure 14. ECSA (a), ORR specific activity (SA) at 0.9 V_{RHE} (b) and ORR mass activity (MA) at 0.9 V_{RHE} (c) of the Pt/Vulcan catalysts with various Pt loadings and Pt NP sizes determined from the RDE measurements. Reprinted with permission from [291].Copyright 2022 American Chemical Society.

Inspired by the concept of *particle proximity effects* detailed above, the surfactant-free colloidal synthesis approach also allows the design of more complex catalysts consisting of different monometallic NPs, which are dubbed nanocomposite catalysts. For example, using the surfactant-free polyol synthesis [Pt + Ir] nanocomposites were recently studied and compared to Pt_xIr_y NPs.[304] The addition of Ir to Pt, either in the form of alloyed NPs or in form of nanocomposite results in a decrease in ORR activity as compared to Pt benchmark, while the OER activity increases. The increase in OER activity is related to an increase in stability upon applying accelerated degradation tests (ADTs). Interestingly, the nanocomposite thereby also showed slightly increased stability compared to Pt_xIr_y NPs. However, in both systems the Ir to Pt ratio decreased upon applying the ADT, indicating challenges for the long-term stability. Nevertheless, the concept of nanocomposites prepared by surfactant-free colloidal NPs allows for a careful optimization of the parameters and is therefore promising to develop further for catalysis. It was also shown using oleylamine-protected Au NPs and surfactant-free Pt that a similar effect of improved activity and stability for the ORR was possible when the surfactants can be removed by a mild treatment.[305] Pt-Au alloy nanoparticles can also be formed *in situ* from co-deposited Pt and Au NPs, towards improved catalysts for formic aid oxidation.[306] This allows including NPs into nanocomposites where a colloidal surfactant-free synthesis is not yet established. It furthermore means that the combination of protected (inactive) and unprotected (active) NPs could ultimately be a "new knob" to tune catalyst properties to promote in the particle proximity effect as a new concept in catalyst design.

III.4. Support effects

Supported heterogeneous catalysts and electrocatalysts are made of an active phase material supported on another material. The support material can play different roles and it is key to investigate its influence, to control and improve catalytic activity and stability.[307] The effects of various supports for various reactions were clarified using surfactant-free colloidal NPs, where conveniently a same batch of colloidal NPs can be supported on different materials.

For instance, Pt NPs on Ti-based supports were used for chloroform degradation and hydrogen evolution.[217] Highly dispersed Pt NPs in well-organized mesoporous bi-crystalline TiO_2 frameworks were obtained. The catalytic efficiency was improved as compared to commercial TiO_2. Surfactant-free Pt NPs were also use to guide support design with TiO_2 based for the ORR.[308] Upon electrochemical testing, the size of the Pt NPs increased from initially around 1.6 nm to a size of 2-2.5 nm and it was shown that the mass activity increased with the design of more conductive $TiO_xC_yN_z$ supports. A range of different supports such as $TiO_2@C$,[309] ordered mesoporous carbon,[310] nitrogen-doped carbon nano-horns,[311] FTO-rGO[312] (where FTO is fluorine-doped Tin Oxide and GO is graphene oxide) were reported to be promising alternatives to standard amorphous carbon supports. Pt-WO_3 on carbon,[313] Pt on carbon nanofiber (CNF) and carbon black[314] were also explored for the MOR. A last illustrative example of support-effect studies is with PtRu on highly ordered meso-porous carbon mesoporous carbon[199], nitrogen-doped carbon nano-horn,[200] carbon[187] achieving higher activity than commercial catalysts.

Surfactant-free Pt NPs were used to show for the first time that o-chloroaniline formation was suppressed using γ-Fe_2O_3 supports for complete conversion of o-chloronitrobenzene (CNB).[315] A catalyst prepared by incipient wetness was also compared in this study and showed lower activity. Hydrogenation of o- and m-CNB, with selectivity superior to 99.4% and complete conversion was achieved over Pt/Fe_3O_4 catalyst.[316] Pt was used on γ-Fe_2O_3 and other FeO_x for selective solvent-less hydrogenation of o-CNB to o-chloroaniline; 99.9% selectivity at 99.95% conversion was achieved and γ-Fe_2O_3 was found to be the best catalyst support.[317] Selective hydrogenation of o-CNB to ochloroaniline was performed with Pt/Al_2O_3[32] without using any solvent and 88.5% selectivity to o-chloroaniline at 98.2% conversion of o-CNB was achieved and 99.8% selectivity to o-chloroaniline at 100% conversion using Sn^{4+}. Ru on SnO_2 was investigated for the same reaction, the high activity observed was attributed to the absence of surfactant and possible contribution from NH_2 groups in o-CAN interacting with Sn^{4+} or Sn^{2+} species at the surface of SnO_2.[98]

Effects of FeO_x supports with different properties were investigated for Pt mediated CO oxidation.[242, 318] Surface hydroxides on FeO_x could participate in the catalytic process, reacting with CO adsorbed on Pt^0 sites and recovered in the co-presence of water gas and oxygen. The properties of the FeO_x support not only affect the oxidation state of supported Pt NPs, but also provide new active sites with the possibility to generate synergies or detrimental effects between the support and the catalytic metal known as strong-metal support interactions (SIMS).[319] Pt NPs of different sizes in the range of 1-4 nm were deposited onto FeO_x and investigated using CO oxidation as a model reaction.[320] Evidence for a Mars van

Krevelen mechanism was found that occurs at the interface between FeO_x support and the Pt NPs. This reaction pathways occurs in parallel to the purely Pt induced Langmuir–Hinshelwood mechanism. As the particle size increases the relevance of the Mars van Krevelen mechanism decreases as the ratio of metal surface to metal-FeO_x interface decreases. Surfactant-free NPs were also supported on zeolites for removal of VOCs.[321] Effect of for α-Al_2O_3, γ-Al_2O_3 and CeO_2–TiO_2 for the AOR by Pt was screened. Superior performance of Pt/CeO_2–TiO_2 was related to a synergy between Pt and the support providing adsorbed and lattice oxygen species for selective NH_3 oxidation to NO.[322] Equally, Ru NPs deposited on rutile and anatase TiO_2 and γ-Al_2O_3 were used to investigate the effect of the support in HCl oxidation.[33] Stable catalysts made of Rh showing high activity were obtained on Υ-Al_2O_3 for the partial oxidation of methane.[221]

Co on CNF was used to achieve excellent activity and regioselectivity for the 1-octene hydroformylation. The higher activity observed was attributed to the better dispersion of the NPs on the support as compared to a commercial catalyst.[194] Effect of Co(OH)$_2$ as support of Pt NPs for the chemoselective hydrogenation of halonitrobenzenes (chloro-, bromo- and iodo-), above 99.6% selectivity to haloanilines was achieved at complete conversion irrespective of the substrates used.[323] These results illustrate that the development of non-precious-metal catalyst can also benefit from surfactant-free NPs.

In electrochemistry as well, the effect of nature of carbon support was invesgiated.[215, 297, 324-327] For instance, out of two common carbon supports commercially available to develop electrocatlaysts, Vulcan XC72R and Ketjenblack EC-300J, the second led to more stable catalysts.[324]

III.5. Support treatment effects

Beyond studying the effect of different supports, the *toolbox* approach also allows to study the effects of different treatments performed on a support in order to tune further the support properties. Surfactant-free NPs were successfully used as catalysts for such studies. For the CO oxidation, Pt/Al_2O_3 with different heat treatments were investigated.[328] The Al_2O_3 support acts as an anchor and inhibited the sintering of Pt particles through intimate interaction between Al_2O_3 and Pt. The catalyst pre-treated at 200 °C showed the highest activity by trapping O_2 molecules on Pt sites and producing active oxygen species. The effect of acid treatment of carbon nanotubes (CNTs) was investigated as well.[329] Both dispersion and sintering resistance of Pt NPs were dependent on the amount of oxygen surface groups on CNTs but no influence

on the Pt loading was observed. The Pt NPs supported on the functionalized CNTs by oxidation treatment gave superior catalytic activity for the phenylacetylene hydrogenation, conversion and selectivity to styrene are 99% and 88%, respectively. This is attributed the higher dispersion of the Pt NPs. Another example of use of surfactant-free NPs is for Pt on CNT to assess the effect of different support treatment (acid treatment or use of polymer) on the resulting activity for the ORR and MOR.[330] It was shown that using polymer polystyrene sulfonate to disperse the CNTs was beneficial to achieve a better dispersion of the supporting material and ultimately a better dispersion of the NPs on the support. This leads to high activity for the ORR and MOR.

For electrocatalytic reactions, it was observed that the film quality of supported catalysts on carbon electrodes from so-called *catalyst inks* was pH-dependent.[327] *Optimized* film properties are essential for reactant transport. It was shown that alkaline inks should be preferred to enable homogenous catalyst films. Alkaline inks favor a more homogenous dispersion and drying of the ink, leading to improved mass transport in the films and so higher mass activities recorded. The optimization of the ink pH was not relevant for commercial catalysts that typically are alkaline without adding base. The washing step of the surfactant-free polyol synthesis, however, renders the ink pH more acidic. The results stress once more the importance of a systematic approach with a careful evaluation of the different factors that may influence the obtained results.[20] NPs obtained by the polyol synthesis were also used to study the optimal amount of ionomer required in catalyst inks.[326] Using the mono-alcohol syntheses, it was also shown that the activity for the OER of Ir NPs prepared in ethylene glycol, methanol or ethanol, was improved using ethanol-based syntheses, see **Table 4**.[259] This is more related to the stability of the carbon support in ethanol than an effect of the solvent on the synthesis of the NPs. These results stress the careful need for optimization of the NPs at all stages of the supported catalyst preparation, from synthesis all the way to characterization including supporting steps, as illustrated in **Figure 11**.

III.6. Composition and structural effects

Controlling NP composition enable to tune further the properties of nano-catalysts.[48] A range of bi- and multi- metallic NPs can be obtained by surfactant-free colloidal syntheses, as summarized in **Table S1**. Illustrative examples are PtIr, PtPd and PtSnO$_x$ catalytsts investigated for the AOR.[210] PtPd based catalysts showed a decreased onset potential *vs.* pure Pt NPs but poor stability. Pt$_7$(SnOx)$_3$ showed similar current density to Pt but improved stability. This is attributed to possible weakening of adsorption of poisonous

N_{ads} intermediates.[210] Higher catalytic activity, stability and activity recovery of PtIr NPs *vs.* Pt NPs is attributed to the electronic effect generated between Pt and Ir atoms in alloy.[211] Pt, Ru, PtRu alloy, Ru@Pt, and Pt@Ru NPs and mixture of Pt and Ru NPs onto CNTs have been investigated for the selective hydrogenation of phenylacetylene.[209] The NPs where prepared from the same precursors and the results highlight the versatility of colloidal approaches to produce complex structures. The benefits of core-shell structure (*vs.* mixture of identical metal) were demonstrated. Pt, Cu, Ni as well as PtSn, PtNi, PtCu, PtMn, PtFe, PtCo, PtZn, PtAu catalysts were produced and screened for their catalytic properties e.g. for glycerol oxdiation.[331] The method of synthesis used was also investigated: conventional thermal heating *vs.* microwave.[205] Pt_9Ni_1 catalyst obtained using a microwave synthesis showed the most promising performances for glycerol oxidation whereas Pt_9Sn_1 showed promising activity for the EOR.[206] IrCu NPs were shown to be suitable catalysts[213] showing an Ir rich surface favorable for hydrogenation of crotonaldehyde with >40% yield to crotyl alcohol in the vapor phase after supporting on mesoporous Co_3O_4. Other comparative study include various bi- and tri- metallic (PtRuW and PtRuMo) alloys with the respective decreasing activity for the EOR: $Pt_1Sn_1/C > Pt_1Ru_1/C > Pt_1W_1/C > Pt_1Pd_1/C > Pt/C$.[212] This was attributed to $-OH_{ad}$ species forming more easily on the surface of Sn-containing catalysts.

Surfactant-free Pt NPs used as building block to develop PtCu catalysts on carbon for *p*-CNB hydrogenation.[332] Seed-mediated grown is a suitable strategy to develop complex nanostructures.[333] Surfactant-free Pt NPs were obtained by the polyol synthesis served as building block for instance for nanowire design[334] or Pt@Sn NPs.[335] Beyond a building block to achieve given catalytic properties, unprotected NPs were also used to develop supported catalysts where zeolitic imidazolate frameworks were built around Pt NPs to stabilize them. The resulting structure obtained was demonstrated as suitable catalyst for hydrogenation of 1-hexene and ciscyclooctene.[336]

For Ru@Pt NPs, a careful control of the pH when developing the shell was showed to be key to best tune the properties of the NP outer surface for the MOR.[208] As the pH increases the outer surface get enriched in Pt. The catalyst obtained lead to 10 times more activity for the MOR for the alloyed shell compared to 5 times higher activity for a rich shell compared to the pure Pt catalysts also obtained by the polyol synthesis. In the synthesis of $Pt_{0.7}Ir_{0.3}$ NPs increasing the pH from 7 to 8.5 lead to formation of a bimodal distribution suggesting that with smaller size at lower pH, less alloying occurs[180] and NP surface expressed different oxidation states: oxidation state 0 at lower pH *vs.* mixed valence at higher pH. The NPs prepared at lower pH showed better activity than Pt NPs or the IrPt prepared at higher pH for the AOR. PtRu NPs were obtained by various methods: co-precipitation, step precipitation starting with Pt of Ru using

different pH to achieve different size and composition.[337] A pH increase leads to size increase in a co-reduction approach. This was however not so marked for steps reduction method. In Pt_7Sn_3 synthesis, the pH was found to control the size of the NPs but also the structure of the alloy obtained.[338] At high NaOH concentration, partial alloying and bi phase Pt/SnO_x structures were obtained while at low NaOH concentration disordered NPs were formed. Bi-phase Pt (6.5 nm)/SnO_x expressed the best catalytic activity for EOR followed by 5 nm disordered alloy Pt_7Sn_3 nano-catalyst. The higher activity for the EOR was attributed to a size effect favoring interaction with ethanol rather than a composition effect.[339]

As a last example, Pt, Rh and PtRh with PVP were produce adding PVP during NPs formation or after NP formation.[207] With presence of PVP during synthesis more Rh atoms were found on the surface of the RhPt NPs. With different surface structures, PVP-RhPt and PVP-added-RhPt show different catalytic activities for the hydrogenation of *o*-CNB. The results give inside into the selection of polymer as a potential way to tune catalytic performance of bimetallic nano-catalysts.

III.7. Improved electron transfer

Surfactant-free NPs can be rationally selected when efficient electron transfer is necessary. This account for the vast literature on electrocatalysis illustrated in **Table S1** but also other applications. Surfactant-free Pt NPs were used as electron relay for enzyme-mediated immunsensor.[340] Pt NPs were used to cover transparent conductive oxide to develop dye-sensitized solar cells where a ''clean surface was needed and so the addition of additives non desirable''.[36] Ru NPs were used to develop improved carbon[216] or carbon free Li-O_2[341] battery support electrode materials, leading to promising specific capacity of 750 mA h g^{-1} and good stability. The superior performances are attributed to the improved conductivity and interfacial contact between the supporting materials and improved ORR and OER activity from the Ru NPs. Ni NPs where formed in alkaline EG in presence of hydrazine and further deposited on GO for glucose sensing.[197] Pt NPs were co-immobilized with enzymes such as glucose oxidase on SiO_2 NPs to favor electron transfer and developed more performing sensors.[34] These examples illustrate the large potential of applications of surfactant-free NPs.

III.8. Effects of surfactants, their removal or absence, towards ligand effects

Surfactant-free NPs are ideal control materials to investigate the effects of surfactants on catalysis, see illustration in **Figure 4**. The benefits of polyol and mono-alcohols syntheses is to be surfactant-free but these syntheses in most cases can also accommodate the presence of surfactants. The influence of various additives on the resulting catalytic properties can then be established. Furthermore, surfactant-free colloidal NP syntheses offer a range of options to functionalize the same batch of NPs with different ligands, i.e. molecules that are not necessarily stabilizing the colloids but would bring catalytic functionality, here referred to as *ligand* by analogy with homogeneous catalysis.

Surfactant and their removal

The pioneer work by Wang *et al.* reported a ligand functionalization by phase exchange of surfactant-free NPs by PVP or triphenylphosphine.[97] It was shown that minimal amount of PVP (compared to previous approaches were PVP was used directly during the synthesis) is required to ensure sufficient protection, e.g. only Pt/PVP ratio of 5. Certainly, these results pave the way to further optimization of resources to NP design by minimizing the amount of chemicals needed to achieve stable NP colloids. Pt NPs then protected by low amount of alkylamine, alkylthiol, PVP, polyvinyl alcohol, or triphenylphosphine showed an increase by 0.5–0.8 eV in the Pt 4f binding energies relative to those of bulk Pt.[342]

Pt NPs served for instance as building block for further functionalization with PVP to investigate the effect of surfactant removal,[343] or to compare Pt NPs *vs.* PVP-protected Pt and AuPt structures.[344] The surfactant-free NPs typically show better activity than the PVP protected NPs., e.g. for the MOR and ORR.[344] Pt NPs were protected by oleylamine,[69] as reference material to stress the benefits of NiPt allowing CO oxidation on different supports such as MgO or Al_2O_3.

A same mother batch of NPs[220] was used and functionalized with three ligands: oleylamine, trimethyl tetradecyl ammonium bromide and PVP. The Pt NPs were immobilized on porous silica (SBA-15) for the ethylene hydrogenation and CO oxidation PVP- and trimethyl tetradecyl ammonium - protected Pt NP expressed mass-normalized reaction rates decreasing with increasing pretreatment temperature, attributed to the partial coverage of the Pt surface with decomposition products from the organic capping agent. Amine capping exhibited a detrimental influence on the catalytic properties as severe deactivation was observed for ethylene hydrogenation and low activity for and CO oxidation, respectively. This highlights the strong influence of the amine groups poisoning Pt surfaces. Further examples are functionalization of Pt NPs with amine and thiol compounds to elucidate the respective binding.[345] The

results stressed the need to consider the effects and properties of capping agents on the catalytic properties.

Pt NPs with 5 different capping agents were investigated and the effect on electrochemical properties (ORR) for each capping agent evaluated.[80] The protected NPs lead to better sensitivity and stability compared to surfactant-free NPs and this was related to the ligand preventing agglomeration of the NPs. Although PVP strongly prevents electron transfer in electrocatalysis, it was reported that small amount of PVP could be beneficial compared to surfactant-free Ir NPs.[65] This was attributed to the PVP stabilizing the NPs on the electrode.

Ligand effects

Functionalization of NP with ligands is to affect the overall catalytic activity and/or selectivity as well as stability. Indeed, ligands are expected to alter the properties of the NPs (e.g. outer surface redox properties or shape), alter the metal-support interaction, but also alter the reaction mechanism for instance by promoting different ligand-reactant interactions.

Activity. For instance, surfactant-free Pt nanocrystals were modified with triphenylphosphine, octadecylamine, PVP, polyvinyl alcohol, and dodecanethiol, to assess the effect of protective agents on the catalytic property of Pt nanocrystals for the hydrogenation of *p*-CNB.[346] In this case, interactions between nanocrystals and protective agents impact the catalytic performance. Electron donating ligands bring the surface atoms into an electron-rich state, changing the adsorption and the reactivity of reactant, intermediates and products. The coordinated Pt atoms oxidized by dodecanethiol generate cationic Pt species that improve the hydrogenation rate and selectivity to *p*-chloroaniline by polarizing the N=O bond in the -NO$_2$ group.

Pt NPs protected with dodecylamine were also deposited on various supports (Υ-Al$_2$O$_3$, SiO$_2$, MgO). It was found that the ligands modify the metal-support interactions and prevent the oxidation of the NPs occurring during deposition. In the case of SiO$_2$, the ligand protected NPs actually showed a higher activity than the surfactant-free NPs for octadiene hydrogenation at low temperature < 100 °C.[68] The ligand was suggested to keep the NPs in a reduced state. However, for Al$_2$O$_3$ and MgO the activity decreased with an increase in ligand amount. At higher temperature for CO oxidation, spillover was observed for all supports and surfactant-free NPs showed better activity. The same concept can certainly be applied to bi-metallic NPs. An examples is the hydrogenation of acetylene to ethylene in ethylene-rich streams on Pt and PtSn NPs.[203] Dodecylamine (DDA)-capped Pt and PtSn NPs were compared with surfactant-free NPs. The most

selective catalyst was found to be the DDA-capped PtSn catalyst. Rh NPs with ligand such as phenyl acetylene and 9-ethnylphenanthrene for hydrogen detection.[27] PtSn NPs were functionalized with different ligands such as dodecanethiol ($C_{12}H_{25}SH$), capric acid($C_9H_{19}COOH,$) and oleic acid ($C_{17}H_{33}COOH,$),[204] to achieve better NP dispersion and improved gas sensing properties for H_2 oxidation.[62]

Selectivity. Beyond tuning activity, ligands have also been shown to be very useful in manipulating selectivity.[347] An example is the so-called N-H effect.[348] As the amino group donates electrons to the catalytic metal, the N-H bond is strongly polarized with the H-substituent acting like a proton. It can interact with the oxygen of a keto group and in this way enhance the activation of the reactant significantly. This improved activation can overcompensate the loss of activity caused by blocking of the catalytic surface through ligand binding. It could be shown that the transfer of the N-H ligand acceleration effect allows enhancing the hydrogenation activity of Pt NPs while increasing simultaneously the selectivity.[349] This finding was further supported by computational and kinetic studies.[350, 351] On the same type of reaction but using different ligands (N-heterocyclic carbenes), an improved selectivity was shown at the expensive of activity. The ligands applied in the latter study do not exhibit a N-H bond that would allow for an N-H effect. As a result, the above mentioned N-H ligand acceleration effect cannot proceed.

Ligand-reactant interactions. Another important opportunity provided by ligand functionalization is the ability to utilize ligand-reactant interactions.[352] This knob to design catalysts allows not only chemo- but also stereo- selective conversions to be performed with supported ligand-functionalized NPs. In particular, using surfactant-free NPs as building blocks, Kunz *et al.* worked towards this goal.[349, 353, 354] An example is the hydrogenation of ketones for which various ligands were tested to explore the possibility to transfer a chiral information from a surface bound ligand to an adsorbed reactant. In order to systematically investigate these complex systems, an approach was developed to functionalize the surfactant-free NPs in a phase-transfer reaction with hydrophilic ligands such as amino acids.[355] In this way the NP synthesis, the surface functionalization with ligands, and the supporting of thus functionalized NPs can be separated into individual steps, while the particle size is maintained. This allows for systematic studies on the effect of the NP properties (metal and particle size), the ligands, and the support material on the catalytic performance, since all relevant material properties of the catalysts can be varied independently.

Stability. A last opportunity offered by surfactant-free NPs is the development of more stable NPs. In particular, the use of hydrophilic ligands is crucial for the application of supported ligand-functionalized NPs as heterogeneous catalysts. Organic reactants (e.g. ketones) and solvents used for colloidal syntheses are lipophilic. If NPs are functionalized with lipophilic such as those that are used for homogeneous

catalysts (e.g. phosphorus-based or N-heterocyclic carbene ligand) the ligand-sphere interacts strongly with the reaction medium and the NPs become solvent-stabilized colloids. As a result, such particles desorb from the support under reaction conditions acting like a homogeneous catalyst. Furthermore, the probability of ligand desorption from the surface increases with increasing solubility of the ligands, leading to fade off the desired selectivity control by ligands. Hydrophilic ligands such as amino acids are not soluble in organic reaction media. The use of such hydrophilic ligand hence allows suppressing desorption of the ligand-functionalized NPs from the support as well as ligand desorption from the particle surface. Functionalizing surfactant-free NPs with hydrophilic ligands therefore bear several promising outcomes.[355]

Optimized NPs. Taking into account the different influences of ligands, and using a rational design approach for supported NPs functionalized with hydrophilic ligands starting with size controlled surfactant-free NPs, it was found that the stereoselectivity does not vary with particle size, but depends merely on the ligand for a given reactant.[356] This result was surprising as it implies that the mechanism of stereoselectivity control is very similar to homogeneous catalysts determined only be ligand-reactant interactions. Furthermore, for most systems that have been investigated in more detail, one-to-one ligand-reactant interactions dominate the stereoselectivity control as determined from studies on nonlinear effects.[357] Surface science techniques may help in the future to get even more insights into ligand-reactant interactions.[358] Investigations on different ligands and reactants eventually led to systems with enantiomeric excesses of more than 80%, clearly demonstrating the potential of ligand-functionalized NPs to design stereoselective heterogeneous catalysts.[350, 354]

Bi-functional ligands. The use of ligands is not limited to covering NPs, bi-functional ligands (ligands with two binding groups) can be used to build NP networks.[359] Such networks have been shown to exhibit high densities of catalytically active sites. This is particularly useful for hydrogen sensing, as the concept of catalytic hydrogen sensing is based on detecting the heat of reaction of the hydrogen oxidation reaction.[360] The use of a support material increases significantly the heat capacity of the catalytic material, as a supported catalysts consists of typically 90-99 wt.% support material. This reduces any heat induced signal and slows down the response time.[361] In contrast, networks formed with bifunctional ligands exhibit more the 70 wt.% catalytic metal, while the remaining less than 30 wt.% are the ligands that take over the role of a support by keeping the NPs at distance. In this way sintering can be inhibited. Particularly suitable for this purpose are aromatic bifunctional ligands with binding groups that are not part of an aromatic moiety. Such ligands barely undergo side reactions under catalytic conditions.[214]

Conclusion

While the controlled use of ligands in heterogeneous catalysis to tune catalytic properties has already shown great potential, it is still in its infancy. The (de)functionalization of NPs with various ligands or surfactants is nevertheless gaining an increasing interest for catalytic studies. The above-mentioned examples and the concepts behind tuning catalyst properties by using ligands are in many aspects very similar to the mechanistic considerations known from bimetallic catalysis. Maybe to date, suitable building blocks to actually study ligand effects were missing. Surfactant-free NPs are promising building blocks in this regard as illustrated above. It is therefore of great importance that researcher explore this potential further and furthermore aim at developing concepts that can be easily transferred into actual applications.

Conclusions

A surfactant-free colloidal synthesis can be defined as a synthesis where the solvent plays the multiple roles of reaction medium, reducing agent and stabilizer. A synthesis with no species with a molar mass greater than 100 g mol^{-1} used as reactant, excluding metal precursors to be reduced to NPs, can be considered surfactant-free. Various surfactant-free syntheses of precious metal NPs have been reported. In particular, laser-based techniques (LSPC), plasma-based syntheses (SPP) and syntheses in DMF, alkaline polyols or alkaline mono-alcohols are well documented. These syntheses offer a suitable control over surfactant-free NP composition and size. Specifically, the polyols and mono-alcohols based syntheses are relatively straightforward to implement without extended prior knowledge and with relatively simple equipment, performed at relatively low temperature and with typically short reaction time. Despite this abundance of options and the multiple benefits of surfactant-free NPs summarized below, a large majority of research in catalysis still uses surfactants and/or direct deposition of NPs on supports in one-pot syntheses.

Surfactant-free NPs are ideal reference materials to investigate and rationalize the still debated effect of surfactant / ligands in NP synthesis and catalysis.[61, 66, 362] The complex interplay between NPs, surface functionalization, effects of ligand functionalization, the influence of surfactant removal, the exact nature of the resulting metal support interaction etc., call for further understanding of the links between metal surface coordination, shape-controlled synthesis and catalytic properties.[60] To achieve this goal, not only new characterization tools are needed but also model systems among which surfactant-free colloids have a place of choice.

Surfactant-free NPs are ideal materials for systematic parametric studies to optimize supported catalysts beyond the active phase design. Effects related to size, loading, interparticle distances, nature of support, supporting steps, washing steps and supported catalyst preparation in general, can be more systematically studied, understood, and controlled.

Surfactant-free NPs are promising building blocks towards increasingly complex nanocatalysts, including with a degree of shape control, e.g., as seed for seed mediated growth or towards multi-metallic NPs, including alloys and core-shell materials.

Surfactant-free NPs are ideal to develop active catalysts. For instance, by avoiding steps to remove surfactant from the NPs, more reproducibility and higher activity can be achieved. In particular surfactant-

free synthesis are well suited to develop supported and unsupported heterogeneous catalysts and electrocatalysts for which *clean* catalyst surfaces are needed. Surfactant-free nano-catalysts have already been investigated for several catalytic reactions illustrated here but are promising for many more. Finally, surfactant-free NPs are ideal building blocks to be functionalized to study further the effect of ligand-functionalization in heterogeneous catalysis.

With the expected increase of modelling in nanoscience,[363] surfactant-free NPs could also prove to be an ideal model system to bridge the gap between theory and experiments. Surfactant-free NPs are indeed arguably simpler than their more complex surfactant-stabilized counterpart.[364] Furthermore, surfactant-free syntheses bear promising features to cross the gap between academia and industry, e.g. using fewer and safer chemicals, such as cheaper solvent such as water or alkaline mono-alcohols. To conclude, colloidal surfactant-free syntheses of metal NPs are probably under-exploited and overlooked to date synthetic approaches to develop catalysts relevant for fundamental and applied research.

Acknowledgements

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