



Cyclodextrin-based systems for the stabilization of metallic(0) nanoparticles and their versatile applications in catalysis



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ABSTRACT

In order to better respond to environmental standards, the development of metal nanoparticles using green approaches has exponentially grown for the last decade. Cyclodextrins, which are cyclic oligosaccharides composed of 6(α), 7(β) or 8(γ) glucopyranose units, have appeared to be interesting candidates for the synthesis of metal nanoparticles. Indeed, through the ability to form inclusion complexes or supramolecular adducts with organic molecules or metal precursors, cyclodextrins can be successfully employed to stabilize size-controlled zerovalent metallic nanoparticles active for hydrogenation reactions carried out in aqueous or gas-phase media. In this summary of our works, we report that cyclodextrins could be used in various forms and environments: (i) in free form, (ii) in complexed form with appropriate guests molecules, (iii) in combination with polymer matrices, (iv) in thermosensitive hydrogels and (v) immobilized onto porous carbons supports. All these studies highlight the fact that cyclodextrins can be seen as multi-task agents for nanocatalysis.

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1. Introduction

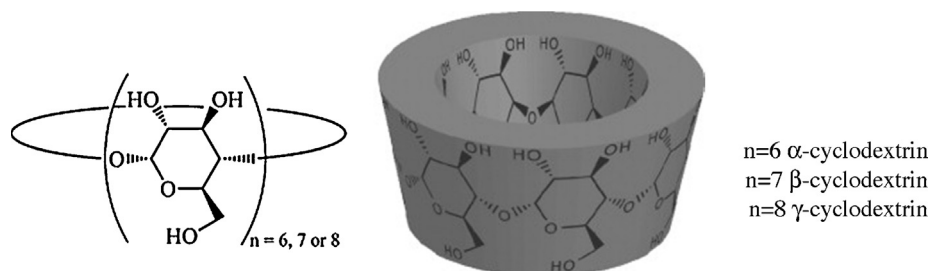
Transition-metal nanoparticles (NPs) have attracted a growing interest both in academic and industrial communities in the last decades due to their unique physical properties and their potential applications in biomedical [1], optical [2] and electronic [3] areas as well as in catalysis [4]. Much effort has therefore been focused on the NPs synthesis for catalytic applications by judicious choices (solvent, stabilizing and reducing agents, metal precursors) in order to investigate correlations between synthesis, structure and reactivity. In addition, the efficiency of colloidal metallic particles in catalysis is closely related to the stability issue of the catalytic system in the course of the reaction. The choice of the capping agent is critical as it controls both the size and shape of the particles, but also the dispersion of the metal species, while providing long-term stability during the catalytic process. Moreover, the development of green synthetic approaches, such as aqueous suspensions of nanoparticles, leads researchers to

introduce ecofriendly capping agents, such as ammonium salts, water soluble phosphanes, dendrimers, polymers or cyclic oligosaccharides. In this context, cyclodextrins (CDs), which are nontoxic cyclic oligosaccharides consisting of six (α -CD), seven (β -CD) or eight (γ -CD) α -1,4-linked D-glucopyranose units, have appeared to be interesting candidates in the noble metal nanoparticle synthesis (Scheme 1) [5].

The specific coupling of the glucose monomers gives rise to a rigid conical cylinder whose inner surface is hydrophobic and the outer surface hydrophilic. Through host–guest interactions, the internal cavity can form inclusion complex with a large number of organic molecules of appropriate size and shape [5,6]. This complexation property has long been utilized in pharmaceutical, food, cosmetic or textile industries and has found applications in the field of chemical sensing, environmental remediation and catalysis [7–9].

The first example of CD stabilized metal NPs for catalysis was reported by Komiyama in 1983, involving non functionalized CDs, called native CDs [10]. The authors reported that the refluxing of an aqueous solution of rhodium (III) and α -CD or β -CD in the presence of ethanol gave a colloidal suspension of rhodium particles that could effectively catalyze the hydrogenation of olefins. In another

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Scheme 1. Cyclodextrins structure.

approach, Kaifer and coworkers have extensively described that *per*-6-thio- β -CD can effectively stabilize platinum [11], palladium [11–13], silver [14] and gold [15,16] nanoparticles through multiple sulfur bonds between the metal core and the oligosaccharide. Interestingly, it has been found that *per*-6-thio- β -CDs-stabilized palladium NPs were effective catalysts for the hydrogenation of C=C or C=N double bonds [11] and C–C coupling reactions [12]. The efficiency of the nanocatalyst is not only reduced on its stability but also on its capacity to be closed to the substrate in liquid or gas phase in order to convert it.

Our continuous interest in the use of chemically modified cyclodextrins in catalysis [17–22] has led us to envisage the use of cyclodextrins as stabilizers of aqueous suspensions of noble metal nanoparticles for hydrogenation reactions carried out in aqueous or gas phase conditions. On the basis of our contributions in this field since 2006, we describe that cyclodextrins could be used in various forms and environments: (i) in free form, (ii) in complexed form with guest molecules, (iii) in combination with polymer matrices, (iv) in thermosensitive hydrogels and (v) to immobilize the particles onto porous carbon supports.

More precisely, we showed that (i) methylated CDs can be used as metallic NPs capping agents for the hydrogenation of alkenes and arenes in aqueous biphasic conditions. An optimization of the NPs synthesis parameters has afforded to get smaller particles size with less cyclodextrin amounts. We will report also that catalytically active metallic nanoparticles can be obtained using (ii) inclusion complexes formed between cyclodextrins and ammonium salts or diphosphine ligands or (iii) water soluble polymers (in which cyclodextrins are used as co-additives or grafted covalently onto the polymer backbones). Then we will describe that (iv) a supramolecular-based hydrogel with α -cyclodextrin has recently proved to be an excellent candidate to lead to stable metallic nanoparticles active in thermoregulated aqueous-phase hydrogenation. Finally, we will extend the applications of cyclodextrins to the preparation of supported heterogeneous catalysts, thus showing that (v) preformed cyclodextrin stabilized metallic NPs can be easily immobilized onto a porous carbon support and successfully used in gas-phase hydrogenation reactions.

2. Free cyclodextrins as metallic(0) NPs protective agents

As it has been reported by the group of Kaifer, cyclodextrin-based colloidal suspensions have proven to be stable and active catalysts in hydrogenation or C–C coupling reactions [12,13,23,24]. In some cases, the cyclodextrins have shown a dual role as NPs stabilizer but also as mass transfer agent. The first studies

dealing with the synthesis of Ru(0) NPs in water using methylated cyclodextrins as protective agents was reported by Monflier and Roucoux [25,26]. These cyclodextrins have the advantage to be highly soluble in water, cheap, non-toxic, commercially available and have the property of being surface active [27]. It is worth noting that, generally, these cyclodextrins are not fully methylated and several degrees of substitution (DS) could be obtained (Table 1). These cyclodextrins are named RaMe-CDs.

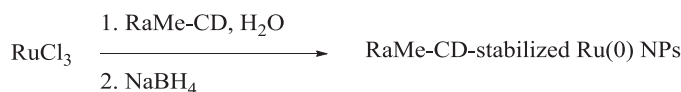
2.1. Classical preparation

Catalytic aqueous suspensions of zerovalent Ru nanoparticles are easily prepared by chemical reduction of ruthenium trichloride with an excess of sodium borohydride in dilute aqueous solution of methylated cyclodextrins (Scheme 2).

In order to get information on the ruthenium nanoparticles stabilized by methylated cyclodextrins, TEM characterization has been performed. As an illustrative example, Fig. 1 shows the TEM picture and corresponding particle size distribution of Ru(0) nanoparticles synthesized by using RaMe- β -CD (1.8) as stabilizer with an optimized ratio of CD to metal of 10 [26]. The ruthenium nanoparticles are organized into non-ordered superstructures with an average particle size of 2.5 nm, with 80% of the metallic species between 2 and 3 nm.

The catalytic activity of ruthenium nanoparticles stabilized by 10 equiv. of RaMe- β -CD has been evaluated in the hydrogenation of various unsaturated substrates such as long-chain alkenes under 1 bar of hydrogen at room temperature (Table 2).

These alkenes were totally hydrogenated in their saturated analogs with TOFs ranging from 12 to 22 h⁻¹. These TOF are modest in comparison to other aqueous nanocatalytic systems but the experimental conditions are less harsh [28]. It is worth noting that the RaMe- α -CD and RaMe- γ -CD-stabilized NPs were active for the decene hydrogenation (entries 1 and 4). However, the catalytic activity decreased with increasing the chain length (C₁₀ > C₁₂ > C₁₄). This phenomenon was already observed in aqueous biphasic organometallic catalysis in the presence of modified cyclodextrins and hydrophobic substrates and this decrease was attributed to a lower solubility of the resulting inclusion complex in water [29,30]. The results obtained with RaMe-CD-stabilized Ru(0) NPs emphasize that the methylated cyclodextrins could play the role of a supramolecular shuttle. The CD/Ru molar ratio has been lowered and it appeared that ratios below 10 were not sufficient to obtain stable and catalytically active colloidal suspensions during the reaction course. These observations can be explained by the dual role of the cyclodextrin. Indeed, CDs are not only steric



Scheme 2. RaMe-CD-stabilized Ru(0) NPs synthesis [25,26].

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