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Cyclodextrins as growth controlling agents for enhancing the catalytic activity of PVP-stabilized Ru(0) nanoparticles[†]

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Cyclodextrins act as growth controllers in the synthesis of PVP-stabilized Ru(0) nanoparticles, leading to enhancement of the catalytic activity in the hydrogenation of furfural.

In recent years, nanoscale metal particles have received a growing interest in a number of fields including catalysis.¹ Owing to the large fraction of metal atoms that are exposed to the surface, the use of metal nanoparticles (NPs) as nanocatalysts allows mild reaction conditions and high catalytic efficiency in a wide range of chemical transformations.¹ However, one of the fundamental issues lies in maintaining the stability of the metallic particles during the course of the reaction. The choice of the capping agent is therefore critical as it controls the size and shape of the particles, but also the dispersion of the metal core, while providing long-term stability. In aqueous media, the use of ammonium salts,² dendrimers,³ water-soluble phosphanes,⁴ polymers⁵ or block copolymers⁶ has already been investigated. In addition, the possibility of using supramolecular assemblies of polymers and surfactants has also been proposed to control the morphology of metallic NPs.7 Thus, it has been reported that the size of silver NPs stabilized by cetyltrimethylammonium bromide (CTAB) can be tuned by adding poly(vinyl alcohol).^{7a} Other researchers have also shown that the use of an amphiphilic triblock copolymer (P123) modified by small amounts of CTAB or tetrabutylammonium bromide (TBAB) led to the formation of shape-controlled gold NPs, starting from HAuCl₄ as the metal precursor.7b This shape effect has been associated with the oriented adsorption of CTAB or TBAB on the surface of the gold nuclei during the growth of the particles.

In the present work, we have explored the possibility of using cyclodextrins (CDs) as new additives in the synthesis of polymerstabilized metallic NPs in colloidal suspensions. Cyclodextrins are



Scheme 1 Hydrogenation of furfural catalyzed by Ru(0) NPs.

cyclic oligosaccharides that are composed of six (α -), seven (β -) or eight (γ -) α -D-glucopyranose units connected by α -(1,4)-linkage. Our idea is to take advantage of the amphiphilic properties of CDs⁸ as well as their ability in stabilizing molecule–metal ion adducts with inorganic metal salts⁹ to control the size of metal clusters. This strategy has been examined in the synthesis of zerovalent ruthenium NPs, starting from ruthenium chloride (RuCl₃, H₂O) and poly(*N*-vinyl-2-pyrrolidone) (PVP) as the metal precursor and the protective polymer, respectively. The activity of these species has been examined in the aqueous hydrogenation of furfural into furfuryl alcohol (Scheme 1), which is considered as a promising chemical intermediate for the synthesis of bio-sourced products.¹⁰

Briefly, the Ru(0) colloidal suspensions are prepared in aqueous media in a one-step procedure by using controlled mixtures of PVP and CD as stabilizers and sodium borohydride as the reducing agent (procedure in ESI†). PVP-K30 (MW = 58 000) has been chosen as the standard polymer, and preliminary studies showed that the minimum molar ratio of the PVP monomer unit to ruthenium required to form stable nanoparticles was 8. Based on this observation, we have studied the effect of different ratios of PVP to CD on the stability of Ru(0) NPs (maintaining the PVP to Ru ratio constant at a value of 8). Synthesis experiments have been conducted with two kinds of cyclodextrins, *i.e.* the native CDs¹¹ and randomly methylated CDs, denoted as RaMe-CDs¹² (Table S1 in ESI†). The so-obtained Ru(0) NPs are visually stable and no sedimentation is observed.

The impact of CDs on the morphology of the PVP-stabilized Ru(0) NPs has been evaluated by Transmission Electron Microscopy (TEM) with a Ru : PVP : CD ratio of 1 : 8 : 2 (Fig. 1). It should be noted that, in the absence of PVP, there is no possibility to stabilize Ru(0) NPs by cyclodextrins by using a ratio of Ru : CD as low as 1 : 2. Indeed, a ratio of 1 : 5 is at least required to protect ruthenium from agglomeration.¹³ For comparison, the picture of the sample stabilized by PVP alone has been included. Thus, we observe that the Ru(0) NPs, with

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Fig. 1 TEM photographs (left) of the PVP-stabilized Ru(0) NPs and their corresponding particle size distributions (right) obtained from the measurement of about 225 particles: without CD (a) and with α -CD (b), γ -CD (c), RaMe- α -CD (d), RaMe- β -CD (e) and RaMe- γ -CD (f) in the Ru : PVP : CD ratio of 1 : 8 : 2.

a relative low-size dispersity, are entrapped in string-like assemblies by the effect of PVP molecules.¹⁴ A mean diameter of 2.95 nm with 64% between 1.5 and 3 nm is obtained. These superstructures do not seem strongly altered by the presence of CDs (Fig. S1 and S2 in ESI†). However, a significant decrease in the particle size is observed by adding native α - and γ -CDs to the PVP (2.53 and 2.51 nm, respectively).

This effect is even greater with the use of methylated CDs, for which smaller Ru nanoparticles ranging from 2.23 to 2.30 nm are obtained. In addition, narrower distributions are clearly achieved. For instance, by using RaMe- γ -CD, we observe that 95% of the particles have a size between 1.5 and 3.0 nm and no particles larger than 4 nm are found.

Here, it is worth emphasizing that the effect of cyclodextrin on the control of the metallic particle size cannot be connected to the formation of supramolecular assemblies occurring between the PVP and the oligosaccharide through molecular recognition or self-assembly phenomenon. Indeed, ¹H and T-ROESY NMR experiments performed on the equimolar mixture of RaMe- β -CD and PVP have not revealed any evidence of the inclusion of PVP (*via* its cyclic amide group) in the hydrophobic cavity. In addition, DOSY analyses have shown that the diffusion coefficient was similar to that of the pure polymer, confirming that their properties were not affected by the presence of RaMe- β -CD.

In contrast, we have found that the aggregation state of CDs was deeply disturbed by the addition of PVP. It should be remembered that, in pure aqueous solutions, CDs (especially native) can self-associate by forming stable and large aggregates of a few hundreds of nanometers.¹⁵ In the presence of PVP, the cyclodextrin aggregates tend to disappear. This effect is particularly prominent in the case of methylated CDs, with aggregates that can be dissociated into small assemblies containing 2 or 3 cyclodextrin units at most, as evidenced by dynamic light scattering measurements (Fig. S3 and S4 in ESI[†]). The presence of high amounts of cyclodextrins in their disaggregated form could be associated with the decrease in size of the metallic NPs. In fact, the disaggregated CDs are supposed to be more reactive than PVP towards Ru(III) species, so that they would be more efficient in controlling the growth of NPs by interacting more strongly with the metal centers. This idea is further supported by an additional synthesis based on a two-step procedure as described below: (i) stabilization for 24 hours under stirring of the Ru(0) NPs using PVP alone as stabilizer (no CD) and (ii) subsequent addition of RaMe-B-CD in a ratio of PVP : CD of 8 : 2 to the previous suspension and stirring for another 24 hours. Notably, we have observed that the size of the so-obtained NPs was very similar to that of the control preparation (without CD), thus confirming that the effect of CDs on the size of Ru(0) NPs occurs very early during the genesis of the metallic NPs. In contrast, the contribution of PVP allows providing long-term protection to the colloidal NPs by producing a stable polymeric layer wrapping the metallic clusters. However as already mentioned, the protective action of PVP can occur only if the polymeric agent is added in a large excess, *i.e.* for ratios of PVP to Ru greater than 8.

The behavior of the Ru(0) NPs protected by mixtures of PVP and CD has been further evaluated in the hydrogenation of furfural (Table 1). Catalytic tests have been performed

				Selectivity (%)	
Entry	CD	PVP : CD	Conversion (%)	FA	THFA
1	/	8:0	30	94	6
2	α-CD	8:2	30	95	5
3	γ-CD	8:2	38	94	6
4	RaMe-α-CD	8:2	34	97	3
5	RaMe-γ-CD	8:2	61	90	10
6	RaMe-β-CD	8:2	53	90	10
7	RaMe-β-CD	8:0.5	37	97	3
8	RaMe-β-CD	8:1	52	93	7
9	RaMe-β-CD	8:4	52	90	10
Reaction	on conditions:	Ru(0) (3.8	\times 10 ⁻⁵ mol), P	VP-K3	0 (3.0 ×
10^{-4}	mol), substrat	e/Ru(0) (mo	ol/mol) = 50,	H ₂ O ((12 mL),
$H_{2}(1.0)$) MPa), stirring	rate (750 rp	m). 30 °C. 1.5 h.		

at 30 °C under a dihydrogen pressure of 1 MPa (detailed procedure in ESI⁺). Note that, under these conditions, control experiments, performed with PVP-stabilized Ru(0) NPs and no CD, have allowed us to show that the ratio of PVP to Ru of 8 was the best compromise between stability and reactivity (Table S2 in ESI[†]). When adding cyclodextrin with a ratio of PVP : CD of 8 : 2, it appears that the efficiency of the cyclodextrins mixed with the PVP depends on the number and modification of the glucose units. When comparing the conversions after 1.5 hours, the reaction run using the control PVP-stabilized Ru(0) gives a low 30% conversion (entry 1) whereas the addition of native γ -CD to PVP leads under the same conditions to an 8% increase (entry 3). However, it is readily apparent that RaMe-y-CD and RaMe-\beta-CD are by far the most efficient promoters of PVP with levels of conversion of 61 and 53%, respectively (entries 5 and 6). These activities are of the same order of magnitude as those reported by Liaw et al. on NiB NP catalysts, but under more severe conditions (T = 80 °C, P(H₂) = 1.8 MPa).¹⁶ Note also that RaMe-α-CD does not appear as a valuable additive since a precipitate is observed at the end of the reaction, probably explaining the moderate activity (entry 4). The product distribution shows in all cases the preferential formation of furfuryl alcohol with selectivity ranging from 90 to 97%.

The above results can be rationalized in terms of size and morphology control of Ru(0) NPs. As previously described, the mean size of the metallic NPs was shown to decrease in the following order: no CD ($\sim 2.9 \text{ nm}$) > native CD ($\sim 2.5 \text{ nm}$) > RaMe-CD (~ 2.3 nm). In line with what is generally observed in nanocatalysis, the decrease in the particle size results in the increase in the number of available surface active sites, and consequently increases the catalytic efficiency. The reusability of the catalytic system prepared from mixtures of PVP and RaMe-CD (β and γ) has also been evaluated. Notably, no significant loss of activity is observed after three consecutive runs. More impressively, TEM examination of the catalytic suspensions recovered after the first run has proved that the particles remain stable against aggregation with practically unchanged particle size distributions: 2.12 and 2.23 nm for RaMe- β -CD and RaMe- γ -CD, respectively (Fig. S5 in ESI^{\dagger}).

Finally the effect of CD on the hydrogenating performances of Ru(0) NPs has also been examined at different PVP : CD ratios by using RaMe- β -CD (entries 6–9). Our results establish that only a small amount of CD (one equiv. per ruthenium) is required to induce a significant increase in activity without causing any decrease in furfuryl alcohol selectivity (entry 8). Moreover, the fact that the conversion can be maintained at high levels with a wide range of PVP : CD ratios, *i.e.* from 8 : 1 to 8 : 4, is a clear indication of the stability of these CD-involving catalytic systems.

In conclusion, we have reported that cyclodextrins could be successfully used as growth controlling agents of polymerstabilized Ru(0) NPs. The most impressive effects were obtained with β - and γ -methylated CDs, allowing the stabilization of catalytically active NPs with a narrow size-distribution centered at around 2.3 nm, while retaining an excellent stability under reaction conditions. We believe that this finding will give new opportunities to expand the scope of aqueous supramolecular assembly studies in the fields of nanochemistry and nanocatalysis.

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