Catalytically active nanoparticles stabilized by host–guest inclusion complexes in water†

Claudie Hubert,[a] Audrey Denicourt-Nowicki,[a] Alain Roucoux,[a] David Landy,[b] Bastien Leger,[c] Gregory Crowyn[c] and Eric Monflier*[c]

Received (in Cambridge, UK) 22nd October 2008, Accepted 3rd December 2008
First published as an Advance Article on the web 14th January 2009
DOI: 10.1039/b818786j

Hydrogenation of arene derivatives can be successfully performed in water by using ruthenium(0) nanoparticles stabilized by 1 : 1 inclusion complexes formed between methylated cyclodextrins and an ammonium salt bearing a long alkyl chain.

The synthesis of well-controlled nanometric size metal species has received a great deal of interest over the past few years due to their physical and chemical properties.[1] Based on their high surface specific area and their small size providing numerous potential active sites, their use in catalysis is associated to the development of fine chemistry in an economical and environmental context.[2] Several methods have been developed for the preparation of metal nanoparticles according to the "organic" or "aqueous" reaction media and the nature of the metal precursor or protecting agents.[3]

In this context, we have explored the possibility to stabilize catalytically active metallic nanoparticles (NPs) in water by inclusion complexes formed between β-cyclodextrin (CD) derivatives and organic compounds as guests. In fact, a careful examination of the literature indicate that CD inclusion compounds can be adsorbed on metallic NPs. For instance, the strong affinity of ferrocene derivatives for the β-CD has been used to modify the surface of CD capped NPs.[4] Thus, Kaifer *et al.* showed that hydrophilic β-CD capped NPs can be solubilized in chloroform by adding cationic ferrocene moieties that have long aliphatic chains.[5] Flocculation of gold NPs has also been achieved by the same group using a dimeric ferrocene guest.[6] Similar work was also performed by Reinhoudt and co-workers. They probed the influence of multivalency and cooperativity on the assembly of network aggregates from β-CD-capped gold NPs and various adamantyl-containing guest molecules.[7] Highly photo-responsive monolayer-protected gold NPs can also be achieved by self-assembling of an inclusion complex between α-CD and an azobenzene-terminated alkanethiol on the surface of the gold NPs.[8] Finally, the self assembly of gold NPs produced by sputter deposition onto microcrystal faces of a α-CD–dodecanethiol inclusion compound has been recently reported by Jara *et al.*[9] Surprisingly, no study has been performed to evaluate the potential of inclusion complexes as stabilizer agents of catalytically active metallic NPS.

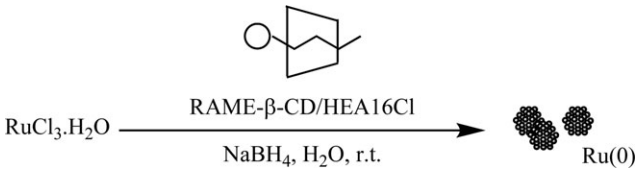
In this paper, we report the preparation of ruthenium(0) NPs stabilized by inclusion complexes formed between the chloride salt of *N*,*N*-dimethyl,*N*-hexadecyl,*N*-(2-hydroxyethyl)-ammonium (HEA16Cl) and randomly methylated cyclodextrins (RAME-β-CD)‡ and the ability of these stabilized Ru(0) NPs to perform hydrogenation of various aromatic derivatives. Our attention was focused on inclusion complexes formed between CD and ammonium salts bearing a long alkyl chain as it is well known that these compounds can strongly interact with β-CD derivatives.[10] Furthermore, we have demonstrated that these compounds and methylated CDs could be used separately to stabilize metal NPs in water.[11]

First, 1D and 2D NMR spectroscopic studies have been performed to prove the formation of inclusion complexes between the HEA16Cl surfactant and RAME-β-CD in aqueous medium. For comparison, the interactions between HEA16Cl and native β-CD were also examined. The existence of inclusion processes and the stoichiometry of the inclusion complexes were provided by the continuous variation technique (Job's method).[12] Indeed, the ^{1}H NMR spectra of aqueous solutions containing variable ratios of CD and HEA16Cl exhibited chemical shift variations for the HEA16Cl protons and for most of the CD protons (see ESI†). Furthermore, all Job's plots derived from the corresponding ^{1}H NMR spectra show a maximum at $r = 0.5$ and symmetrical shapes, indicating that the stoichiometry of inclusion complexes is 1 : 1 (see ESI†). The formation of inclusion complexes was definitively proved by two-dimensional T-ROESY experiments. Indeed, strong dipolar contacts were observed between the alkyl chain protons of the HEA16Cl and protons situated inside the hydrophobic CD cavity (see ESI†). The association constant of each inclusion complex was evaluated at 298 K from UV-Vis spectroscopic data. The association constant for the β-CD/HEA16Cl inclusion complex (K_a = 181 000 M^{-1}) was found to be higher than that of the RAME-β-CD/HEA16Cl inclusion complex (K_a = 97 000 M^{-1}), indicating that methylation of the CD decreases the recognition ability of the CD (see ESI†).

As the above results provided evidences of the formation of very stable inclusion complex between HEA16Cl and

[a] *Ecole Nationale Supérieure de Chimie de Rennes, Equipe Chimie Organique et Supramoléculaire, UMR CNRS 6226 Sciences Chimiques de Rennes, Avenue du Gal Leclerc, 35700 Rennes, France*
[b] *Université du Littoral, LSOE, EA 2599145 Avenue Maurice Schumann, 59140 Dunkerque, France*
[c] *Université d'Artois, Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Rue Jean Souvraz, SP 18, 62307 Lens Cédex, France. E-mail: eric.monflier@univ-artois.fr; Fax: (+33)3-2179-1755*

† Electronic supplementary information (ESI) available: Experimental details, ^{1}H and T-ROESY NMR spectra of inclusion complexes, determination of association constants, procedure for the nanoparticle synthesis and catalytic experiments. See DOI: 10.1039/b818786j



Scheme 1 Chemical preparation of RAME-β-CD/HEA16Cl inclusion complex stabilized Ru(0) NPs

RAME-β-CD, the possibility to stabilize ruthenium NPs with this inclusion complex was investigated (Scheme 1).

Adapted from procedures previously reported for the synthesis of HEA16Cl[11a] or RAME-β-CD[11b] stabilized ruthenium(0) NPs, NPs stabilized by the inclusion complex were synthesized in two steps. First, an aqueous solution containing a stoichiometric amount of RAME-β-CD and HEA16Cl was prepared and maintained under vigorous stirring during 15 min at room temperature. Then sodium borohydride (2.5 eq.) was added to the above solution and the resulting solution was immediately added to a ruthenium trichloride salt solution (RAME-β-CD : Ru = 1 : 1). The solution was stirred overnight before catalytic experiments.

The obtained colloidal suspensions are stable without visual agglomeration during several weeks. Compared to usual catalytic systems composed of only RAME-β-CD or HEA16Cl, efficient NPs stability is clearly observed. Indeed, control experiments performed by using only RAME-β-CD or HEA16Cl as stabilizer indicate that colloidal suspensions are unstable for a [HEA16Cl] : [Ru] ratio of 1 : 1 and for a [RAME-β-CD] : [Ru] ratio of 2 : 1 or less. The particle size of the RAME-β-CD/HEA16Cl-stabilized Ru(0) NPs has been determined by transmission electron microscopy (Fig. 1).

These particles are monodispersed in size with an average diameter of about 4 nm. In comparison with HEA16Cl or RAME-β-CD stabilized Ru(0) colloids, NPs stabilized by inclusion complex have larger dimension. Indeed, the average size for HEA16Cl or RAME-β-CD stabilized Ru(0) NPs were found to be 3 and 2.5 nm, respectively. Fig. 1 shows also that NPs stabilized by inclusion complexes are organized in superstructures which are similar to those observed with RAME-β-CD-stabilized Ru(0) NPs.

The catalytic properties of Ru(0) NPs stabilized by inclusion complex were evaluated in the hydrogenation reaction of aromatic compounds by using a stabilizer to ruthenium ratio of 2 : 1 (RAME-β-CD–HEA16Cl–Ru = 1 : 1 : 1). For comparison, catalytic experiments with HEA16Cl stabilized Ru(0) NPs were also performed in the same conditions. It should be noted that experiments with the RAME-β-CD stabilized Ru(0) NPs cannot be performed in these experimental conditions as the catalytic system was found unstable. Indeed, stable RAME-β-CD stabilized Ru(0) NPs can only be obtained for a RAME-β-CD : Ru ratio higher than 3 : 1.[11c] The catalytic results are summarized in Table 1.

Whatever the substrate, the best catalytic activities have been obtained with RAME-β-CD/HEA16Cl stabilized Ru(0) NPs. In the case of anisole, the conversion performed with inclusion complex stabilized Ru(0) NPs is three times higher than that obtained with the HEA16Cl stabilized Ru(0) NPs (compare entry 2 with 1). In the case of toluene, an increase by a factor of 4.5 was observed (compare entry 4 with 3). In the same way, a complete conversion of styrene into ethylbenzene required a shorter reaction time in the case of supramolecular complex stabilization than in the case of surfactant stabilization (compare entry 7 with 5). Interestingly, hydrogenation of the aromatic ring was also observed for longer reaction times in the case of inclusion complex stabilized Ru(0) NPs. Indeed, 29% of the ethylbenzene was hydrogenated into ethylcyclohexane after 7 h reaction time *vs.* 1% with the HEA16Cl/Ru(0) catalytic system (compare entry 8 with 6). Finally, it should be noted that the colloidal suspensions were stable at the end of the catalytic reaction, demonstrating that the RAME-β-CD/HEA16Cl complex is a very efficient stabilizing agent.

The difference of catalytic behaviour between the HEA16Cl/Ru(0) catalytic system and the RAME-β-CD/HEA16Cl/Ru(0) catalytic system could be explained by the fact that the organization of the protective agents around the nanoparticle is greatly different. As previously characterized by Chen[13] and El Sayed[14] with ammonium salts stabilized Cu and Ni NPs or Au nanorods, HEA16Cl stabilized ruthenium NPs in aqueous solution are protected by a surfactant double-layer as schematically represented in Fig. 2(a).

In the case of ruthenium NPs stabilized by inclusion complex, we assume that the RAME-β-CD/HEA16Cl inclusion complex is adsorbed onto the surface metallic species, as schematically displayed in Fig. 2(b). According to the literature and the well-known adsorption of chloride anion to electron deficient metal surfaces,[15] the polar head of the surfactant is directed towards the metallic surface and the RAME-β-CD interacting with the alkyl chain of the surfactant is located close to the bulk aqueous phase. This adsorption mode is preferred to an adsorption of the RAME-β-CD on the

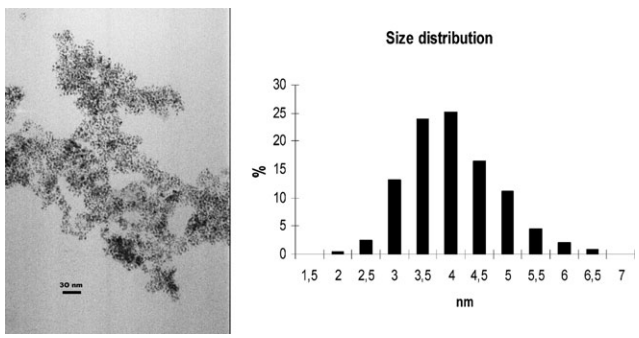


Fig. 1 TEM micrograph and size distribution of RAME-β-CD/HEA16Cl stabilized Ru(0) NPs

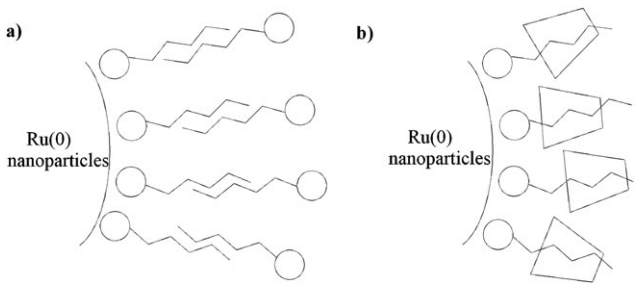


Fig. 2 Model proposed for the stabilization of (a) HEA16Cl/Ru NPs and (b) RAME-β-CD/HEA16Cl/Ru NPs

Table 1 Hydrogenation of aromatic compounds with Ru(0) NPs[a]

Entry	Stabilizer	*t*/h	Substrate	TOF[b]/h^{-1}	Product[c] (%)
1	HEA16Cl	24	Anisole	3.4	Methoxycyclohexane (27)
2	RAME-β-CD/HEA16Cl	24	Anisole	10.2	Methoxycyclohexane (82)
3	HEA16Cl	24	Toluene	2.2	Methylcyclohexane (18)
4	RAME-β-CD/HEA16Cl	24	Toluene	10.1	Methylcyclohexane (81)
5	HEA16Cl	3.2	Styrene	31.2	Ethylbenzene (100)
6	HEA16Cl	7	Styrene	14.3	Ethylbenzene (99), ethylcyclohexane (1)
7	RAME-β-CD/HEA16Cl	1.2	Styrene	83.3	Ethylbenzene (100)
8	RAME-β-CD/HEA16Cl	7	Styrene	26.7	Ethylbenzene (71), ethylcyclohexane (29)

[a] *Reaction conditions*: Ru(0) (3.8×10^{-5} mol), HEA16Cl (7.6×10^{-5} mol) or HEA16Cl (3.8×10^{-5} mol) + RAME-β-CD (3.8×10^{-5} mol), Substrate (mol/mol) = 100, 1 bar H_2, 20 °C, H_2O (10 mL), stirred at 1500 rpm. [b] Based on hydrogen consumption. [c] Determined by GC analysis.

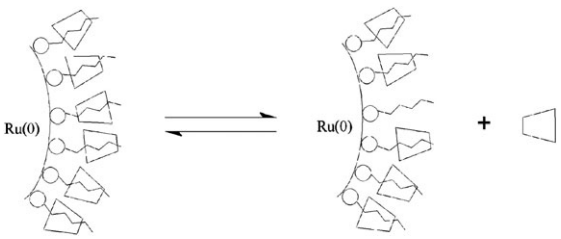


Fig. 3 Dynamic organisation of the stabilizers around the Ru(0) NPs

surface with the polar head of the surfactant directed towards the bulk aqueous phase. Indeed, experiments conducted with RAME-β-CD or HEA16Cl alone have demonstrated that the amount of stabilizing agent required to stabilize metallic NPs is lower in the case of HEA16Cl than in the case of RAME-β-CD, suggesting that interaction of HEA16Cl with metallic NPs is stronger than that of RAME-β-CD. Finally, it should be pointed that the stabilization mode proposed for the RAME-β-CD/HEA16Cl/Ru(0) NPs displays some analogies with that proposed for the HEA16Cl stabilized Ru(0) NPs. Indeed, the metallic NP is always protected by a double layer of stabilizer. The first layer is composed of HEA16Cl and the second layer of RAME-β-CD. Interestingly, this type of stabilization could contribute to greatly improve the mass transfer between the metallic surface of the NPs and the bulk aqueous solution. Indeed, cyclodextrin could exert some control on the HEA16Cl adsorption process, acting as a suitable spacer between the alkyl chains of the surfactants, reducing their intermolecular interactions and, as a consequence, allowing a better diffusion of substrates towards the metallic surface. Furthermore, substrate access to the surface could also be increased by a partial release of cyclodextrin in the bulk aqueous as schematically shown in Fig. 3.

In this case, the steric hindrance around the particle is clearly reduced and some free cyclodextrins are available to solubilize the organic substrate in the aqueous phase.

Taken together, these results demonstrated that catalytically active metallic NPs can be stabilized by a CD inclusion complex in water. These NPs appear more active than the NPs stabilized by classical surfactants. The origin of this better efficiency is probably in connection with a dynamic organization of the protective agents around the NPs. Indeed, it is assumed that the cyclodextrin can interact with the surfactant adsorbed onto the surface but also with organic substrate. Work is currently underway in our laboratories to confirm this hypothesis.

Notes and references

‡ The RAME-β-CD was a native β-CD partially O methylated with statistically 1.8 OH groups modified per glucopyranose unit.

1 G. Schmid, in *Nanoscale Materials in Chemistry*, ed. K. J. Blabunde, Wiley-VCH, New York, 2001.
2 A. Roucoux and K. Philippot, in *The Handbook of Homogeneous Hydrogenation*, eds. J. G. de Vries and C. J. Elsevier, Wiley-VCH, 2007; A. Roucoux, A. Nowicki and K. Philippot, in *Nanoparticles and Catalysis*, ed. D. Astruc, Wiley-VCH, 2007.
3 L. Duran Pachon and G. Rothenberg, *Appl. Organomet. Chem.*, 2008, **22**, 288; D. Astruc, F. Lu and J. R. Aranzaes, *Angew. Chem., Int. Ed.*, 2005, **44**, 7852.
4 J. Liu, W. Ong, E. Roman, M. J. Lynn, R. Xu and A. E. Kaifer, *Langmuir*, 2000, **16**, 3000; J. Liu, J. Alvarez and A. E. Kaifer, *Adv. Mater.*, 2000, **12**, 1381; J. Liu, R. Xu and A. E. Kaifer, *Langmuir*, 1998, **14**, 7337.
5 J. Liu, J. Alvarez, W. Ong, E. Roman and A. E. Kaifer, *J. Am. Chem. Soc.*, 2001, **123**, 11148.
6 J. Liu, S. Mendoza, E. Roman, M. J. Lynn, R. Xu and A. E. Kaifer, *J. Am. Chem. Soc.*, 1999, **121**, 4304.
7 O. Crespo-Biel, A. Jukovic, M. Karlsson, D. N. Reinhoudt and J. Huskens, *Isr. J. Chem.*, 2005, **45**, 353.
8 F. Callari, S. Petralia and S. Sortino, *Chem. Commun.*, 2006, 1009.
9 L. Barrientos, N. Yutronic, F. del Monte, M. C. Guttierez and P. Jara, *New J. Chem.*, 2007, **31**, 1400; S. Rodriquez-Llamazares, P. Jara, N. Yutronic, M. Noyong, J. Bretschneider and U. Simon, *J. Colloid Interface Sci.*, 2007, **316**, 202.
10 B. Tutaj, A. Kasprzyk and J. Czapkiewicz, *J. Inclusion Phenom. Macrocycl. Chem.*, 2003, **47**, 133.
11 A. Nowicki, V. Le Boulaire and A. Roucoux, *Adv. Synth. Catal.*, 2007, **349**, 2326; A. Nowicki, Y. Zhang, B. Léger, J.-P. Rolland, H. Bricout, E. Monflier and A. Roucoux, *Chem. Commun.*, 2006, 296; A. Nowicki, A. Ponchel, E. Monflier and A. Roucoux, *Dalton Trans.*, 2007, 5714.
12 V. M. S. Gil and N. C. Oliveira, *J. Chem. Educ.*, 1990, **67**, 473.
13 S. H. Wu and D. H. Chen, *J. Colloid Interface Sci.*, 2004, **273**, 165; S. H. Wu and D. H. Chen, *Chem. Lett.*, 2004, **33**, 406.
14 B. Nikoobakth and M. A. El-Sayed, *Langmuir*, 2001, **17**, 6368.
15 J. D. Aiken, III, Y. Lin and R. G. Finke, *J. Mol. Catal. A: Chem.*, 1996, **114**, 29; S. Bucher, J. Horms, H. Modrow, R. Brinkmann, N. Waldofner, H. Bonnemann, L. Beuermann, S. Krischok, W. Maus-Friedrichs and V. Kempter, *Surf. Sci.*, 2002, **497**, 321; J. Schulz, S. Levigne, A. Roucoux and H. Patin, *Adv. Synth. Catal.*, 2002, **344**, 266; A. Roucoux, J. Schulz and H. Patin, *Adv. Synth. Catal.*, 2003, **345**, 222.

