

Effective Catalytic Hydrogenation of Fatty Acids Methyl Esters by Aqueous Rhodium(0) Nanoparticles Stabilized by Cyclodextrin-Based Polymers

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The first example of metal nanoparticles stabilized in aqueous medium for the catalytic hydrogenation of methyl linoleate is reported. Contrary to classical rhodium stabilizers such as PVP, PVA or HEA16Cl, cyclodextrin-based polycarboxylates prove to be efficient stabilizers for rhodium nanoparticles which show high catalytic activities under mild experimental conditions. This activity enhancement clearly demonstrates the beneficial effect of both the grafting of the β -cyclodextrin onto the polymer backbone and the amount of grafted β -cyclodextrin per polymer chain.

1. Introduction

Concurrently to the industrial uses of Fatty Acid Methyl Esters (FAMES) such as personal care products, plastics, and household commodities (Gill and Valivety 1997), production of biodiesel has undoubtedly become the most developed area (Verziu et al. 2008). Control of the oxidative stability of fatty esters is crucial for the quality of the resulting biodiesel (Carvalho et al. 2011). Indeed, linoleic acid (*cis*-9, *cis*-12-octadecadienoic acid C_{18:2}) methyl ester is susceptible of autoxidative degradation resulting in undesired byproducts such as polymers that prevent fuel to be in line with regulatory standards (Moser et al. 2007). Moreover, a total saturation of the FAME dramatically increases the viscosity and the melting point (Moser et al. 2007). To circumvent the issue, the formation of monounsaturated esters is greatly expected as their presence improves the stability towards oxidation. The selective hydrogenation to mono-unsaturated products (*cis/trans*-9-octadecadienoic acid methyl esters or *cis/trans*-12-octadecadienoic acid methyl esters) has therefore received an increasing interest in heterogeneous catalysis (Figure 1).

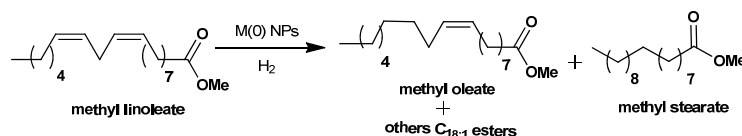


Figure 1. Catalytic hydrogenation of methyl linoleate

Several studies dealing with the metal dispersions and loadings (McArdle et al. 2011), the support (Mäki-Arvela et al. 2008), the solvent (Carvalho et al. 2011), the temperature (Bernas et al. 2009), the presence of additives such as amines (Nohair et al. 2005) or alkanethiols (Kahsar et al. 2013) have been performed to convert C_{18:2} with a minimal amount of saturated compounds. Surprisingly, in spite of their unique physicochemical properties, only few solvent-dispersed nanoheterogeneous catalysts are described for the conversion of vegetable oils. To the best of our knowledge, no metal nanoparticles (NPs) stabilized in aqueous medium has been reported so far for the FAMES hydrogenation. Rh(0)-NPs are recognized to be efficient catalysts

for the hydrogenation of olefin (Callis et al. 2007) and aromatic compounds in water (Schulz et al. 2002). However, they must be stabilized to avoid aggregation and to facilitate recyclability. For instance, polymers bearing carboxylate groups are effective metal NPs stabilizers (Yan et al. 2011). Cyclodextrins (CDs) also proved to be interesting partners in nanocatalysis to stabilize metal nanoparticles for liquid phase hydrogenation of arenes (Nowicki et al. 2006) or biosourced substrates such as furfural (Herbois et al. 2012) in addition to their supramolecular properties (Hubert et al. 2009). In a previous paper, we used a hydrophilic polymer containing carboxylate and β -CD moieties for the stabilization of Rh(0) colloids (Noel et al. 2012). The resulting colloidal suspensions proved to be active and recyclable in hydrogenation of arenes and olefins. In this context, the study has been extended to the hydrogenation of methyl linoleate using Rh-NPs stabilized in water by several CD-based polycarboxylates having varying contents of CDs.

2. Experimental

2.1 General

Rhodium chloride was purchased from Strem Chemicals. β -CD was a gift from Roquette Frères. Lithium hydride, dimethylformamide, sodium borohydride, poly(vinylpyrrolidone) average M_w 58.000, poly(vinyl alcohol) 88% hydrolyzed M_w 20.000-30.000, were purchased by Acros Chemicals and sodium hydroxide, methyl linoleate min 99 % GC, poly(methyl vinyl ether-alt-maleic anhydride) M_w 216.000 were purchased by Sigma Aldrich.

2.2 TEM analysis

Transmission Electron Microscopy (TEM) was performed on a Tecnai microscope (200 kV). A drop of a colloidal suspension was deposited on a carbon coated copper grid. The size distribution was estimated after the measurement of 200 particles with the program SCION Image.

2.3 NMR analysis

NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei. D_2O (99.92 % isotopic purity) were purchased from Euristop.

2.4 Synthesis section

Poly(mono-(β -cyclodextrin-2-yl)-maleate-co-maleate-alt-methylvinylether)

7.26 g β -CD (6.40 mmol) previously dried at 110 °C under vacuum were solubilized in 190 mL anhydrous DMF under inert atmosphere. 51.2 mg LiH (6.44 mmol) were added on the previous solution and the resulting mixture was stirred overnight at room temperature under inert atmosphere. 2 g poly(vinylmethylether-alt-maleic anhydride) (12.8 mmol) were solubilized in 90 mL of DMF. The polymer solution was then added on the previous suspension and the resulting mixture was stirred overnight. DMF is evaporated and a deep purple solid was obtained. The solid was then dissolved in 150 mL distilled water and subjected to ultrafiltration with a 30 kDa cellulose membrane with water (2 L), a saturated NaCl solution (750 mL) and again with water (1 L, six times). The CD-grafted polymers were isolated by freeze-drying. The substitution degree corresponding to the number of CD residues per maleic anhydride unit was determined by ^1H NMR spectroscopy. A substitution degree of $X = 0.24$ was calculated from the ratio of integrations of the peak at $\delta = 4.9$ ppm (assigned to the H_1 anomeric protons signal of the CD) to that at $\delta = 1.8$ ppm (assigned to the CH_2 of methyl vinyl ether units).

Colloidal suspension synthesis

The colloidal suspensions were prepared at ambient temperature and open air. The desired polymer (6.7×10^{-4} mol of carboxylic acid function) was solubilized in 7 mL of water. Drops of NaOH 1N solution and additional amounts of water were added to get 8.3 mL polymer solution with a pH value of 5. The resulting solution was stirred during 1 h and RhCl_3 dissolved in 1.7 mL was added. NaBH_4 (2.0×10^{-4} mol), dissolved in 0.7 mL water, was then added quickly to the previous solution under vigorous stirring. The reduction instantaneously occurred and was visualized by a color change from red to black/brown. The surfactant HEA16Cl and the corresponding colloidal suspension were prepared as previously described (Schulz et al. 2002). The PVP and PVA-stabilized Rh(0) nanoparticles were also synthesized according a previous procedure (Herbois et al. 2012).

2.5 General procedure for hydrogenation reaction and catalyst recycling

The stainless steel autoclave was charged the desired Rh(0) colloidal suspension. 150 equiv. methyl linoleate were solubilized in 10 mL heptane and the resulting solution was added into the autoclave. The latter was pressurized under hydrogen at constant pressure up to 1.0 MPa. The mixture was heated to 303

K and stirred at 1500 rpm. The reaction was monitored by analyzing aliquots of the reaction mixture using a Shimadzu GC-17A gas chromatograph, equipped with a methyl silicone capillary column (30 m × 0.32 mm) and a flame ionization detector. For the recycling procedure, after complete substrate conversion, the products were extracted by liquid-liquid extraction and decantation with heptane until complete elimination of organic products from the aqueous phase. After heptane removal under vacuum, the colloidal suspension was reused for another hydrogenation.

3. Results and discussion

3.1 Colloidal suspension synthesis and characterization

Three polymers having several degrees of substitution X (0, 0.24 and 0.46) have been used for the preparation of the Rh-NPs at different pH values. The two polymers where β -CD was grafted were synthesized according to a literature procedure (Volet and Amiel 2009). Rh-NPs were synthesized by chemical reduction of rhodium trichloride metallic salt with an excess sodium borohydride in the presence of polyCOONa- g - β -CD(X) in aqueous medium at different pH values.

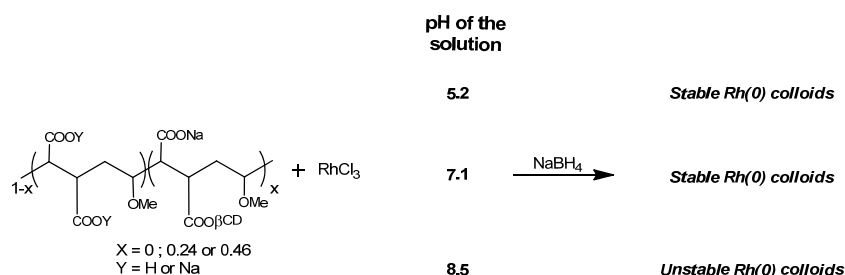


Figure 2. PolyCOONa- g - β -CD(X) based Rh(0) NPs synthesis

The pH of the rhodium trichloride solution in the presence of polymers has been set to three different values. The first value (5.2) corresponded to the mixture of metal salt and polymers. For the others values, an alkaline solution was added. After sodium borohydride addition, whatever the degree of substitution (X), visually stable Rh(0)-NPs were obtained for initial pH values of 5.2 and 7.1 at which the polymer was in its carboxylate form (COO^-). When the pH was set to 8.5, metal sedimentation was observed resulting in a colloids agglomeration. Note that nanoparticles syntheses for pH values lower or equal to 4 have not been achieved because, in these conditions, the polymer is mainly in its carboxylic acid form (COOH). Rh(0) colloidal suspensions have been characterized by Transmission Electron Microscopy in order to evaluate the influence of the CD amount on the size and dispersion of Rh(0)-NPs. The results related to the colloidal suspensions prepared at pH 5.2 are summarized in Figure 3.

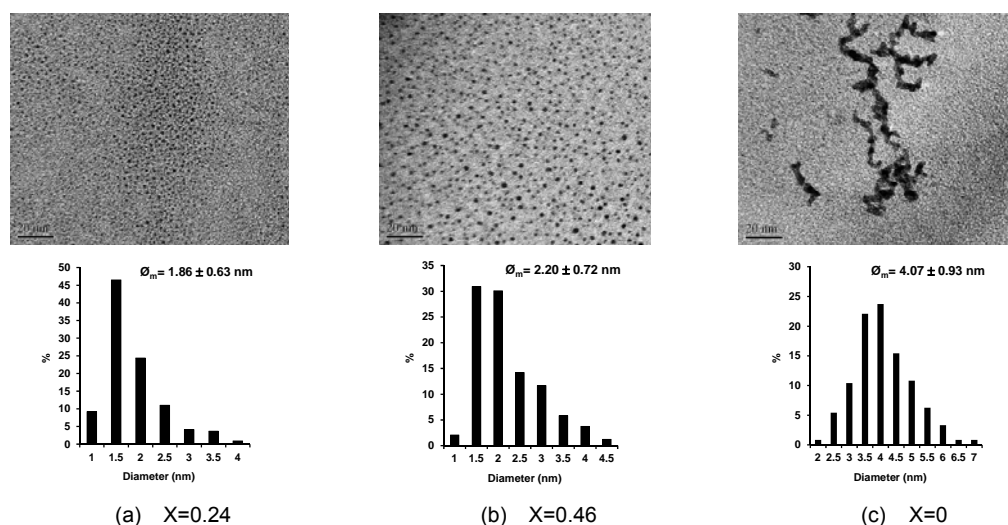


Figure 3. TEM images of polyCOONa- g - β -CD(X) Rh(0) NPs prepared at pH = 5.2

It should be noted that, whatever the polymer, no aggregates were observed. Moreover, this study clearly showed the beneficial effect of the grafting of CDs onto the polymer chain. Indeed, for polymer without CD, the Rh(0)-NPs were organized into non-ordered superstructures with a mean diameter around 4 nm (Figure 3c). In the presence of CD, for $X=0.24$ and $X=0.46$, homogeneous dispersions of Rh(0) colloids were observed with mean diameters of 1.86 nm and 2.20 nm for $X=0.24$ and $X=0.46$, respectively (Figure 3a and 3b). These results were in agreement with our previous works (Noel et al. 2012). To assess the influence of the pH on the dispersion and size of Rh(0)-NPs, TEM characterization of polyCOONa-*g*- β -CD(0.46) Rh(0)-NPs prepared at initial pH of 7.2 has also been realized. The images are given in Figure 4.

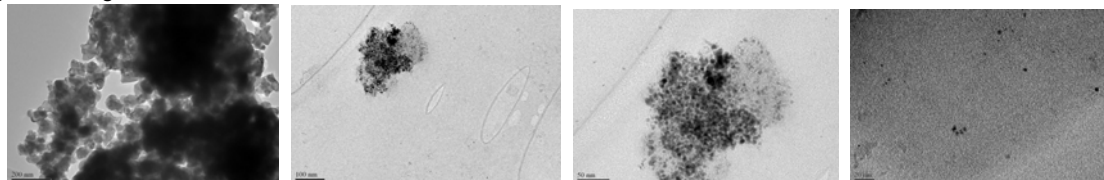


Figure 4. TEM images of polyCOONa-*g*- β -CD($X=0.46$) Rh(0) NPs prepared at pH = 7.1

This study highlighted that, for an initial pH of 7.2, a heterogeneous colloidal suspension of Rh(0)-NPs was obtained along with clear metal aggregates and also well dispersed Rh(0)-NPs. These results showed that the stabilisation strongly depended upon the pH of the solution and that high pH values were deleterious for the Rh(0)-NPs stabilisation. To ensure a good stabilisation of the Rh(0)-NPs at the nanometre scale, a pH of 5.2 was chosen for the following catalytic study.

3.2 Methyl linoleate hydrogenation

Table 1: Hydrogenation of methyl linoleate by CD-polymer stabilized Rh(0)-NPs^a

Catalytic system	Stability	Conversion (%)	C _{18:1} selectivity	C _{18:0} selectivity	C ₁₈ -alcohols selectivity
X=0	yes	23	39	22	39
X=0.24	yes	48	79	19	2
X=0.46	yes	93	57	41	1
X=0+ β -CD ^b	Stable emulsion	88	32	65	3
X=0+ β -CD ^c	Stable emulsion	98	41	56	3

^a Conditions: 30 °C, 10 bar H₂, FAME/Rh molar ratio = 150, "COO"/Rh = 100, 10 min, 1500 rpm.

^b the free CD amount corresponds to a substitution degree of 0.24.

^c the free CD amount corresponds to a substitution degree of 0.46.

Considering the above characterization, the catalytic properties of polyCOONa-*g*- β -CD-stabilized Rh(0)-NPs prepared at pH 5.2 were evaluated in aqueous hydrogenation of methyl linoleate at 30 °C under 10 bar H₂ pressure (Table1). According to these catalytic results, all the prepared nanocatalysts were active and stable in methyl linoleate hydrogenation with no metal sedimentation. Nevertheless, for colloids synthesized using a physical mixture of polyCOONa-*g*- β -CD ($X=0$) and free β -CD, stable emulsions have been obtained once the reaction was complete, leading to a difficult catalyst recovery. The catalytic activity increased with the amount of grafted CDs. It is worth noting that, in absence of CD, an important amount of C18-alcohols was obtained (39 % selectivity). This amount dropped to 1-3 % for Rh colloids containing grafted or free β -CD. The oligosaccharides seemed to prevent the reduction of the ester function into the corresponding alcohols. Unfortunately, the selectivity towards the monounsaturated esters did not exceed 60% for methyl linoleate conversions close to 100 %. The catalytic efficiency of the Rh(0) colloids stabilized by CD-grafted polycarboxylates can be easily correlated with the TEM images previously obtained. Indeed, well-dispersed Rh-NPs afforded good catalytic activities.

Comparison with classical Rh(0)-NPs stabilizers

The catalytic performance of the Rh(0)-NPs stabilized by CD-based polycarboxylate polymers was compared to those obtained with Rh(0)-NPs stabilized by classical stabilizers such as PVP (Gacem and Diao 2013), PVA (Jaine and Mucalo 2012) or HEA16Cl (Roucoux et al. 2003) (Table 2). Polymers containing carboxylate moieties provided stable Rh(0) colloids during the catalytic hydrogenation. Others hydrophilic polymers such as polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVA), which are known to stabilize Rh-NPs, did not prevent particles aggregation and further sedimentation during the methyl

linoleate hydrogenation. The same behaviour was observed for Rh(0) colloids stabilized by an ammonium-based surfactant (HEA16Cl). These results clearly showed that CD-based polycarboxylate polymers were very efficient Rh(0)-NPs stabilizers.

Table 2: Rh(0)-NPs-catalyzed hydrogenation of methyl linoleate^a

Catalytic system	Stability	Conversion (%)	C _{18:1} selectivity	C _{18:0} selectivity	C ₁₈ -alcohols selectivity
X=0	yes	23	39	22	39
X=0.24	yes	48	79	19	2
X=0.46	yes	93	57	41	1
PVP	sedimentation	0	-	-	-
PVA	sedimentation	0	-	-	-
HEA16Cl	sedimentation	4	97	3	0

^a Conditions: 30°C, 10 bar, FAME/Rh molar ratio= 150, "COO"/Rh = 100, 10 min, 1500 rpm.

Recyclability

The recyclability of the catalytic system was checked by re-use of the aqueous catalytic suspension in successive runs of methyl linoleate hydrogenation using Rh-NPs stabilized by polyCOONa-*g*- β -CD (X=0.46) (Figure 5). The catalytic runs were performed over 20 min for complete conversion irrespective of the C_{18:1} selectivity. Saturated C_{18:0} were mainly obtained in that case. The goal of this series of tests was to evaluate the robustness of the catalytic system.

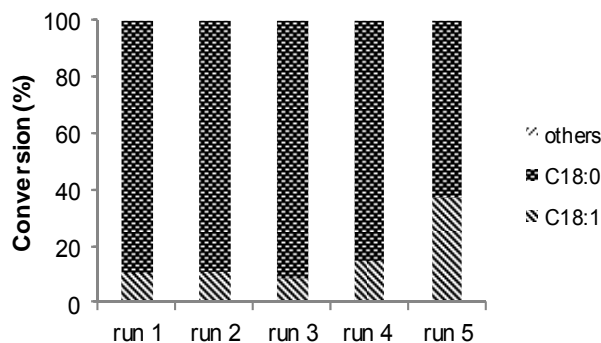


Figure 5. Recycling of polyCOONa-*g*- β CD(X=0.46)-stabilized Rh(0) NPs

The catalytic aqueous phase could be efficiently used in four consecutive runs. The fifth run showed a selectivity decrease towards the total hydrogenated product.

Confirmation of the heterogeneous nature of the nanocatalysts

Thiolated compounds are known to slow down the catalytic activity of metal nanoparticles. We used a hydrophobic thiol (1-adamantanethiol) able to form an inclusion complex with the CD cavity (Rekharsky and Inoue 1998). With 0.5 or 0.05 equivalents 1-adamantanethiol per CD cavity, no conversion was noticed justifying that conversion of methyl linoleate exclusively resulted from Rh-NPs and not from molecular species.

4. Conclusions

In this article, we reported the first use of Rh(0) nanoparticles stabilized in water by CD-based polymers for the hydrogenation of methyl linoleate. We highlighted the beneficial effect of grafted CDs onto the polymeric backbone by a catalytic activity enhancement and an easy recovery of the catalyst. Increasing the CD amount on the polymer chain undoubtedly increased the methyl linoleate conversion. Moreover, the grafting of CDs onto the polymer chain also avoided the formation of stable emulsions once the catalytic test was complete. Accordingly, the Rh-NPs could be recycled. C_{18:1} esters were mainly obtained using this catalytic system. The inhibitive effect of 1-adamantanethiol emphasized that the conversion occurred onto the Rh-NPs surface and not through molecular species.

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