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Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Tandem dehalogenation-hydrogenation reaction of halogenoarenes as model substrates of endocrine disruptors in water: Rhodium nanoparticles in suspension vs. on silica support

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ARTICLE INFO

Article history: Received 4 October 2010 Received in revised form 20 December 2010 Accepted 3 January 2011 Available online 8 January 2011

Keywords: Nanoparticles Hydrogenation Dehalogenation Halogenoarenes Endocrine disrupting compounds

1. Introduction

Endocrine disrupting compounds (EDCs) from domestic, agricultural or industrial sources have been widely released into the aquatic environment [1]. These substances could alter endocrine functions and adversely disrupt growth, development and reproduction through interactions with the endocrine system [2,3]. Due to their persistence in aquatic environment and potential adverse health effects, the removal and the degradation of EDCs from aqueous effluents have been an object of public concern. Among the numerous EDCs, the four major classes that have recently received scientific and public interest as the most potential disruptors are polyaromatic compounds, alkylphenols, organic oxygenated compounds such as dioxins, phthalates and pesticides (Fig. 1). The common feature of these compounds is the presence of one or more aromatic rings in their structure, which could sometimes be halogenated.

Since conventional wastewater treatments are inefficient for the remediation of EDCs and particularly in the case of high concentrations, numerous efforts have been devoted to the development

ABSTRACT

This paper focuses on the removal of mono- and poly-halogenated arenes, as model substrates of endocrine disrupting compounds from aqueous effluents. The efficiency of catalysts based on metallic nanoparticles in the tandem dehalogenation–hydrogenation reaction as a pre-treatment for the remediation of organic halogenated pollutants was studied. Two catalytic systems – aqueous colloidal Rh⁰ dispersions and SiO₂-supported Rh⁰ nanoparticles – were easily prepared under mild conditions and were compared in the hydrodehalogenation reaction of the model substrates. Interesting results in terms of catalytic activity were obtained, particularly with Rh⁰@SiO₂ catalyst, which proved to be more stable and efficient under the reaction conditions.

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of appropriate methods that could be integrated into treatment facilities to avoid the release of EDCs into natural waters. Among them, advanced oxidation processes are relevant techniques for the removal of some EDCs [3,4] but have proved to be difficult in the case of some refractory compounds. In that context, the pretreatment of aqueous effluents to modify the chemical structure of these recalcitrant chemicals could be a promising alternative. For that purpose, the reductive hydrodehalogenation reaction [5], which involves the reductive cleavage of a C-X bond, represents a viable, low cost and environment friendly method [6]. This reaction has appeared in the environmental field as a potential technique to eliminate organic chlorinated compounds, competing with oxidation processes. In the case of halogenoarenes compounds, the tandem dehalogenation-hydrogenation reaction seems promising for the detoxification of these hazardous compounds into less harmful products.

In that context, noble metal nanoparticles are considered as robust, high surface area heterogeneous catalysts [7,8], which are particularly pertinent for the hydrogenation of arene derivatives [9,10] and also efficient in the hydrodehalogenation reactions [11]. A few examples of the tandem dehalogenation–hydrogenation reactions have already been reported with Rh⁰ nanoparticles in aqueous solution [12] or on support [13]. Indeed, the deposit of metallic nanospecies on inorganic supports has emerged as a powerful means for the development of new, highly active and easily recyclable catalysts [14,15]. The colloidal suspensions

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Fig. 1. Some endocrine disrupting compounds.

of zerovalent rhodium nanoparticles (Rh⁰@HEA16Cl), presenting sizes around 3.0 nm, were easily prepared by a bottom-up approach based on the chemical reduction of an aqueous solution of RhCl₃·3H₂O in the presence of *N*,*N*-dimethyl-*N*cetyl-*N*-(2-hydroxyethyl)ammonium chloride HEA16Cl salt as protective agent [16]. The silica-supported rhodium⁰ nanoparticles (Rh⁰@SiO₂), having sizes around 5.0 nm, were obtained by a simple impregnation of the inorganic support by the previously described aqueous colloidal suspensions without any particular treatment [17,18]. In this paper, we compare the catalytic performances of rhodium⁰ nanoparticles in aqueous suspension or supported on silica towards the tandem dehalogenation/hydrogenation reaction of various halogenoarenes (Cl, Br), which were chosen as model substrates for endocrine disruptors.

2. Experimental

2.1. General

RhCl₃·3H₂O was obtained from Strem Chemicals. All the organic compounds were purchased from Acros Organics or Sigma–Aldrich–Fluka and used without further purification. The silica Si80 was obtained from Merck and presents the following characteristics: mean diameter: $80 \,\mu$ m, pore diameter 5.4 nm, specific area $490 \, \text{m}^2 \, \text{g}^{-1}$, pore volume $0.77 \, \text{cm}^3 \, \text{g}^{-1}$ and internal porosity 58%. Water was distilled twice before use by conventional method. The hydroxyethylammonium chloride salt HEA16Cl, which was used as a protective agent for the Rh⁰ nanoparticles in aqueous solution, was synthesized as previously described in the literature and fully characterized [19,20]. All gas chromatography analyses of catalytic reactions were performed using a Carlo Erba GC 6000 with a FID detector equipped with a Factor Four column (30 m, 0.25 mm i.d.).

2.2. Preparation and characterization of rhodium catalyst

2.2.1. Preparation of Rh⁰@HEA16Cl aqueous colloidal suspension

The aqueous colloidal suspension was prepared following the previously reported method [16,21].

Sodium borohydride (18 mg, 0.48 mmol) was added to an aqueous solution of ammonium surfactant HEA16Cl (133 mg, 0.38 mmol in 40 mL H₂O). Then, this solution was quickly added under vigorous magnetic stirring to an aqueous solution of the precursor RhCl₃·3H₂O (50 mg, 0.19 mmol in 10 mL H₂O). The initial red solution darkened instantaneously. The obtained suspensions are acidic (pH = 2.4) and are stable for several weeks. They have been

previously characterized by transmission electron microscopy (TEM) [16,17,21], showing that the particles are well-dispersed on the grid with an average diameter of 2.1 nm.

2.2.2. Preparation of $Rh^0 @ SiO_2$ catalyst by a wet impregnation method

The Rh⁰@SiO₂ catalyst was prepared according to a procedure developed in the laboratory [17,18] and based on the simple impregnation of the inorganic support by the previously described Rh⁰@HEA16Cl colloidal suspension [16,21]. Silica (18.5 g) was vigorously stirred in 40 mL of deionized water for 2 h. Furthermore. 50 mL of Rh⁰@HEA16Cl $(1.9 \times 10^{-4} \text{ mol of Rh})$ was added under vigorous stirring and the system was kept under stirring for 2 h. The coloration of the aqueous phase turned from black to colourless, evidencing the adsorption of the rhodium⁰ nanoparticles on the silica surface. The catalyst was recovered by filtration, then washed several times with distilled water and dried at 60 °C overnight. The rhodium loading of the materials, which was evaluated by ICP-AES, was of 0.08 ± 0.01 wt% and near the theoretical value (0.1 wt%). Previous TEM analyses [17] have evidenced well-dispersed Rh⁰ particles with an average size of 5 nm, which is limited by the pore diameter.

2.3. Hydrogenation procedure

Catalytic hydrogenations were carried out at room temperature and at atmospheric hydrogen pressure or under hydrogen pressure according to the catalytic results. The conversions and the identification of the obtained products were monitored by gas chromatography analysis. Turnover frequency (TOF) was determined for 100% conversion.

2.3.1. Hydrogenation under atmospheric pressure

A 25 mL round bottomed flask, charged with $Rh^0@HEA16CI$ (10 mL) or $Rh^0@SiO_2$ (1 g in 10 mL of distilled water) and the substrate ([substrate]/[metal] = 100), are connected to a gas burette and a flask to balance pressure. Then the system is filled with hydrogen and the mixture is magnetically stirred.

2.3.2. Hydrogenation under hydrogen pressure

A stainless steel autoclave was charged with the catalyst – $Rh^0@HEA16Cl(10 mL)$ or $Rh^0@SiO_2(1 g in 10 mL of distilled water)$. The substrate (100 eq.) was then added and dihydrogen was admitted to the system at constant pressure. Then the reaction was stirred until completion.



^a Rh (3.8×10^{-5} mol), HEA16Cl (7.6×10^{-5} mol), substrate (3.8×10^{-3} mol), H₂O (10 mL), room temperature.

^b Rh⁰@SiO₂ (1 g, 0.08 wt%, 7.8×10^{-6} mol), substrate (9.6×10^{-4} mol), H₂O (10 mL), room temperature.

^c Determined by gas chromatography.

^d Turnover frequency defined as the number of mole of hydrogen per mole of rhodium per hour for 100% conversion.

3. Results and discussion

In the drive towards the remediation of organic chlorinated pollutants from natural environment and industrial sites, the tandem dehalogenation–hydrogenation reaction seems to be a promising means to transform endocrine disruptors in less harmful products. In these preliminary studies, we have chosen halogenated (Br, Cl) anisoles as model substrates, which are also considered as a family of endocrine disruptors, for this tandem reaction. The use of metallic nanoparticles as catalysts for this reaction seems to be relevant, considering their outstanding activity in the hydrogenation of aromatic derivatives.

3.1. Hydrogenation of chloroanisoles isomers – comparison of $Rh^0@HEA16Cl$ and $Rh^0@SiO_2$

First, we studied the hydrogenation of the different regioisomers of chloroanisole using the suspension and supported nanocatalysts $(Rh^0@HEA16Cl or Rh^0@SiO_2)$ at room temperature under hydrogen pressure (1 or 5 bar) in water (Table 1). The turnover frequencies (TOFs) were calculated considering an optimized reaction time for complete conversion of the substrate and based on the introduced amount of metal and not on the exposed surface metal and thus may be underestimated. As previously reported by Janiak et al. [22] the catalytic activity results not only from the exposed surface metal atoms since the surface can restructure, atoms can shift positions during heterogeneous processes and partial aggregation could occur during catalysis, modifying the fraction of surface atoms. These changes in the surface render the determination of the number of surface atoms difficult.

The reaction leads to the formation of two products: the expected methoxycyclohexane and also significant quantities (20–60%) of cyclohexanone. The methoxycyclohexane was obtained from the tandem dehalogenation-hydrogenation reactions. The cyclohexanone has already been observed in acidic media via the formation of a hemiacetal during the hydrogenation of anisole with aqueous colloidal Rh⁰ suspensions [23]. In the present work, the neutralisation of the reaction media, as already described in the literature [24,25], was not carried out in order not to modify the ionic force. In contrast, no cyclohexanone was observed in the hydrogenation of anisole with the Rh⁰@SiO₂. In this case, the formation of cyclohexanone during the hydrogenation of chloroanisole isomers could be explained by the release of HCl in the reaction media during the dehalogenation, which constitutes the first step of the tandem dehalogenation–hydrogenation reaction, as shown in Fig. 2.

The chloroanisole regioisomers were totally dehalogenated and hydrogenated at atmospheric pressure with TOFs ranging from 34 to $75 h^{-1}$, depending on the halogen position and the nature of the catalyst (suspension vs. support). The formation of cyclohexanone, ranging from 24 to 52%, is much higher with 2-and 4-chloroanisoles. No real influence of the pressure was observed concerning the ratio of obtained cyclohexanone. Finally, the Rh⁰@SiO₂ catalyst seems to be more active than the aqueous Rh⁰colloidal suspension with higher TOFs and a 35–40% ratio of cyclohexanone for the three isomers. The increase in pressure up to 5 bar H₂ leads to higher TOFs up to $375 h^{-1}$ for Rh⁰@SiO₂ catalyst with quite the same ratio of cyclohexanone.

The hydrogenation of di- or tri-chloroanisoles isomers was also investigated in water under 5 bar H_2 and at room temperature to study the influence of the polysubstitution on the aromatic rings towards the tandem dehalogenation–hydrogenation reaction. The results are gathered in Table 2.

The reaction leads to the formation of the same products than those previously observed with monochlorinated compounds: the expected methoxycyclohexane and also cyclohexanone. The



Fig. 2. Mechanism of the formation of cyclohexanone during the chloroanisoles hydrogenation.

| | Rh ⁰ @HEA16Cl ^a | | | | Rh ⁰ @SiO ₂ ^b | | | |
|------------------------|---------------------------------------|----|--------------|------------------------|--|----|--------------|------------------------|
| | Ratio ^c (%) | | <i>t</i> (h) | Conv. ^c (%) | Ratio ^c (%) | | <i>t</i> (h) | Conv. ^c (%) |
| | OCH ₃ | | | | OCH3 | | | |
| CI CI | 75 | 15 | 4 | 90 ^d | 88 | 12 | 1 | 100 |
| OCH ₃ Cl | 65 | 23 | 4 | 88 ^d | 86 | 14 | 1 | 100 |
| | 71 | 19 | 4 | 90 ^d | 86 | 14 | 1 | 100 |

 Table 2

 Hydrogenation of di- or trichloroanisoles

^a Rh (3.8×10^{-5} mol), HEA16Cl (7.6×10^{-5} mol), substrate (3.8×10^{-3} mol), H₂O (10 mL), 5 bar H₂, room temperature.

^b Rh⁰@SiO₂ (1 g, 0.08 wt%, 7.8 × 10⁻⁶ mol), substrate (7.8 × 10⁻⁴ mol), H₂O (10 mL), 5 bar H₂, room temperature.

^c Determined by gas chromatography.

^d No increase in the conversion is observed after 5 h.

conversions of the Rh@HEA16Cl colloidal suspension in the hydrogenation of di-or tri-chlorinated anisoles are lower than those observed with monochlorinated compounds, with a 90% conversion after 4h. Moreover, the conversion did not increase significantly with longer times (after 5 h). This could be explained by a chlorine poisoning effect of the particle surface, leading to a deactivation of the catalyst, as already observed in the literature [26,27]. The Rh@SiO₂ catalyst showed similar kinetic activities with polychlorinated substrates than with monochlorinated ones, with TOFs ranging around $300 h^{-1}$. This result is quite different to the literature as usually the increase in chlorine substituents leads to a significant decrease of the catalytic activity [28]. Moreover, smaller quantities of cyclohexanone, around 10-15% were formed, compared to those obtained with monochlorinated substrates (30-40%). The higher chlorine content in the reaction media has an influence on the selectivity of the reaction, decreasing the cyclohexanone ratio. The effect of the chlorines was

demonstrated by the addition of 960 μ l of HCl 1 N (corresponding to one equivalent of formed HCl during the dehalogenation of dichlorinated compounds) in the hydrogenation of *o*-chloroanisole with the Rh@SiO₂ system. In this case, the reaction leads to the formation of methoxycyclohexane (82%) and cyclohexanone (18%), thus modifying the selectivity observed in Table 1 (36% cyclohexanone).

3.2. Hydrogenation of bromoanisoles at 1 bar H_2 – comparison of $Rh^0@HEA16Cl$ and $Rh^0@SiO_2$

The dehalogenation/hydrogenation reaction was also investigated with bromoanisole regioisomers at atmospheric pressure and room temperature with the aqueous Rh^0 colloidal suspension or the SiO₂-supported catalyst. The results are summarized in Table 3.



^a Rh (3.8 × 10⁻⁵ mol), HEA16Cl (7.6 × 10⁻⁵ mol), substrate (3.8 × 10⁻³ mol), H₂O (10 mL), 1 bar H₂, room temperature.

^b $Rh^0@SiO_2$ (1 g, 0.08 wt%, 7.8 × 10⁻⁶ mol), substrate (9.6 × 10⁻⁴ mol), H_2O (10 mL), 1 bar H_2 , room temperature.

^c Determined by gas chromatography.

First, contrary to the results obtained with chloroanisoles, conversions were not complete after 24h whatever the bromide position. As already described in the literature [28], the lower reactivity of bromoaromatics can be attributed to the lower electron affinity of Br (3.364 eV) compared to Cl (3.615 eV) that translates into a less effective activation of the bromo-reactant through surface σ -complex formation. Indeed, in the presence of Rh⁰@HEA16Cl catalyst, only 45% conversion was achieved with the formation of three products: anisole, methoxycyclohexane and cyclohexanone. Moreover, the aqueous suspension was slightly destabilized after catalysis due to Br⁻ formation. To check the detrimental effect of the Br⁻ ions on the stability and the activity of Rh⁰@HEA16Cl, the hydrogenation of 2-chloroanisole was carried out in the presence of HBr and showed the particle aggregation and a decrease in conversion rate. The supported catalyst seems to be more active with 87-95% conversion in 24h with the formation of the three products. Moreover, the deposit of metallic nanoparticles on silica increases the stability of the catalytic system. This difference could be explained by the nature of the halogen. The release of HBr significantly increases the ionic strength of the media and could modify the charged double layer organization around the particles and thus destabilize the aqueous suspensions. As for, in the case of the supported catalyst, rhodium⁰ particles are adsorbed at the surface of silica preventing aggregation in solution and providing better catalytic activities.

4. Conclusions

We have demonstrated the possibility to efficiently use Rh⁰ nanocatalyst (in suspension or on support) for the tandem dehalogenation-hydrogenation reaction of halogenoanisoles as model substrates of endocrine disrupting compounds. These compounds and their analogous halogenophenol derivatives are abundant industrial or agricultural components, coming from pesticides, herbicides, solvent manufacturing or paint industry [29]. Their disposal has become a major environmental concern due to their high toxicity, their persistence and their bioaccumulation in aquatic organisms and efficient catalytic methods are needed to eliminate poorly biodegradable chloroaromatic compounds from industrial effluents or polluted groundwater. In that context, the hydrodechlorination process in aqueous solution has potential application in the remediation of contaminated industrial wastewater and our described Rh⁰ nanoparticle approach is promising, leading to the formation of relatively non-toxic saturated compound and added value cyclohexanone in liquid phase. Both catalytic systems described here exhibited quite good catalytic activities. However, the aggregation of the nanospecies was sometimes observed. In that case, the deposit of the metallic nanospecies on silica is an interesting alternative, increasing the stability and leading to complete tandem dehalogenation-hydrogenation reaction with good TOFs. As already described, the methodology developed for the deposit of metallic nanospecies on silica has been extended to other inorganic supports, such as TiO_2 anatase [30], which is known for its higher photocatalytic activity than rutile [31]. Further developments are ongoing concerning the remediation of EDCs from aqueous effluents, combining tandem dehalogenation–hydrogenation reaction and photocatalytic activity using metallic nanoparticles doped-TiO₂ materials.

Acknowledgements

This work was financially supported by the Région Bretagne (PhD fellowship for C. Hubert) and the Université Européenne de Bretagne.

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