

Competitive hydrogenation/dehalogenation of halogenoarenes with surfactant-stabilized aqueous suspensions of rhodium and palladium colloids: A major effect of the metal nature

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Abstract

The original palladium colloidal suspensions with an average size of 2.7 nm have been synthesised by reducing Na_2PdCl_4 with sodium borohydride and were stabilized by water soluble *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt. The catalytic hydrogenation and dehalogenation of various halogenoarenes have been investigated with this aqueous suspension of palladium nanoparticles and compared with the well-known rhodium suspension. The influences of the halogen fragment and the experimental conditions have also been studied. It was observed that the kinetics and selectivity of the competitive dehalogenation/hydrogenation depend on the nature of metal colloids and the hydrogen pressure. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The last decade has evidenced an ever-increasing interest in the nanometric size chemical species namely metal nanoparticles and their applications in various areas such as catalysis [1,2]. The development of soluble nanoparticles or colloids as highly active nanocatalysts has been the focus of considerable effort in terms of preparation to prevent agglomeration and to control particle size [3–7]. In this context, various stabilizers have been investigated according to the “organic” or “aqueous” nature of media which generally depends on the nature of the precursor, namely metals salts or organometallic compounds. Our approach is to use ionic surfactants to prepare and stabilize aqueous colloidal suspensions of metallic particles. Previously, we have described the easy synthesis of *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium salts HEA16X with X = Br, Cl, I, CH_3SO_3 , BF_4 [8]. Among these compounds, the chloride salt HEA16Cl has particularly been studied as a protective agent for

rhodium and iridium particles for the hydrogenation of aromatic [9,10], heteroaromatic [11] compounds under mild conditions, and also for platinum colloids for the asymmetric hydrogenation of ethyl pyruvate [12]. In this paper, we report the synthesis and the characterization of the analogous palladium aqueous suspension and the efficient nanoparticles stabilization which depends on the surfactant/Pd ratio. We describe the use of this nanoparticles suspension for the dehalogenation of arylhalides, and more particularly of chlorobenzene. The catalytic hydrodehalogenation of halogenated aromatic wastes has been recognized as an important chemical transformation in organic synthesis as well as in industrial applications [13], as it is considered as an environmentally friendly and cost saving alternative to traditional incineration disposal. In that context, the development of new dechlorination methods to remove toxic aryl halides under aqueous conditions remains a topic of interest. Due to the harmful nature of arylchlorides, a great number of hydrodehalogenation reactions with homogeneous or heterogeneous catalysts have been reported with ruthenium or rhodium and especially with palladium [13,14]. Few reports have described the use of rhodium nanoparticles in a sol–gel matrix [15] or palladium immobilized on MontK10 [16,17]. Recently, Uozomi

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described the hydrodechlorination of chloroarenes with an amphiphilic polystyrene-poly(ethyleneglycol) resin dispersion of palladium nanoparticles under aqueous conditions [18]. Here, we demonstrate the efficient activity of our aqueous palladium suspension in dehalogenation of various arene derivatives and show the influence of the halogen group. Finally we compare rhodium and palladium nanoparticles in the competitive dehalogenation–hydrogenation of the aromatic ring.

2. Experimental

2.1. Starting materials

Rhodium chloride hydrate and sodium tetrachloropalladate II were obtained from Strem Chemicals and Alfa Products, respectively. Sodium borohydride and all halogenoarenes were purchased from Aldrich or Acros and used without further purification. Water was distilled twice before use by conventional method. The surfactant HEA16Cl was prepared as previously reported and was fully characterized [8].

2.2. Analytical procedures

2.2.1. TEM-analysis

The transmission electronic microscopic studies were conducted using a FEI Technai G2 Sphera at 200 kV (cathode LaB6). Samples were prepared by a dropwise addition of the stabilized palladium nanoparticles in water onto a copper sample mesh covered with carbon. The colloidal dispersion was partially removed after 1 min using cellulose before transferring to the microscope. The picture is obtained at X 80.000 with a video GATAN USC1000 (CCD detector 2048X2048) and associated software DIGITAL Micrograph. Measurement of about 970 particles was made with program SCION Image (NIH) and was analyzed with KaleidaGraph program providing the histograms of the nanoparticles size distribution.

2.2.2. Gas chromatography

All analyses were performed using a Carlo Erba GC 6000 with a FID detector equipped with an Alltech AT1 column (30 m, 0.25 mm i.d.). Parameters were as follows: initial temperature, 40 °C; initial time, 10 min; ramp, 10 °C/min; final temperature, 80 °C; final time, 30 min; injector temperature, 220 °C; detector temperature, 250 °C.

2.3. Catalytic tests

2.3.1. Synthesis of the aqueous palladium(0) suspension

The aqueous suspensions of palladium nanoparticles were prepared following our previously described rhodium suspension synthesis [9].

An aqueous solution of surfactant HEA16Cl (544 mg, 1.7×10^{-3} mol L⁻¹ in 40 mL H₂O) was added in a flask containing 16 mg of sodium borohydride (4.2×10^{-4} mol). Then this solution was quickly added under vigorous stirring to an aqueous solution (10 mL) of the precursor Na₂PdCl₄ (50 mg, 1.7×10^{-4} mol) to obtain an aqueous Pd(0) colloidal suspension

(50 mL). The reduction occurs instantaneously and is characterized by a color change from yellow to black. The obtained suspensions are stable for several weeks.

2.3.1.1. General procedure for hydrogenation under atmospheric hydrogen pressure. A 25 mL round bottom flask, charged with 10 mL of aqueous suspension of the appropriated Rh(0) or Pd(0) catalyst and a magnetic stirrer, was connected with a gas burette (500 mL) and a flask to balance the pressure. The flask was closed by a septum, and the system was filled with hydrogen. The halogenoarene compounds ([substrate]/[metal] = 100) was injected through the septum and the mixture was stirred at 1500 min⁻¹. The reaction was monitored by the volume of gas consumed and by gas chromatography. Turnover frequency (TOF) was determined for 100% conversion.

2.3.1.2. General procedure for hydrogenation under hydrogen pressure. The stainless steel autoclave was charged with the previously prepared aqueous suspension of Pd(0) (10 mL) and a magnetic stirrer. The appropriate substrate (3.8×10^{-3} mol, 100 equiv.) was added into the autoclave and dihydrogen was admitted to the system at constant pressure (up to 40 bar). The mixture was stirred until the reaction was finished. Samples for gas chromatographic analysis were removed from time to time. The TOF was determined for 100% conversion.

3. Results and discussion

The aim of the present work was the synthesis of stable palladium nanoparticles and their use in the dehalogenation of various benzene derivatives. Our approach is to use colloidal metallic particles finely dispersed in water and protected by surfactants. In preliminary studies, we have shown the efficiency of the water soluble *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt to stabilize various metal colloids. In a first step, we have optimized the preparation of the aqueous suspension in catalytic reaction conditions. We have compared the stability of the suspension before and after catalysis in the dechlorination of chlorobenzene as standard reaction. Then, the characterization of the best system was realized by microscopy experiments (TEM). Finally, the colloidal suspension was investigated in the catalytic dehalogenation of various aromatic substrates and compared with rhodium suspension which gives complete hydrogenation of the aromatic ring.

3.1. Preparation and characterization of palladium colloids

The catalytically active aqueous suspension was made of palladium(0) colloids prepared by reducing sodium tetrachloropalladate II with sodium borohydride in dilute aqueous solution of chloride surfactant, *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt HEA16Cl. The molecular ratio R = HEA16Cl/Pd was optimized to prevent aggregation and to provide a good stability after catalysis to investigate the potential recycling of the aqueous phase. Specif-

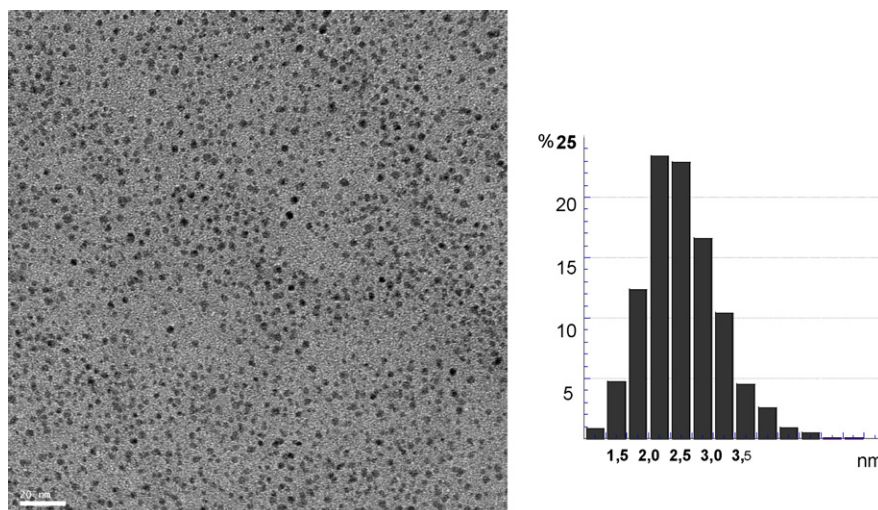


Fig. 1. Transmission electron micrograph (scale bar = 20 nm) and size distribution histogram of Pd/HEA16Cl suspension.

ically, the hydrogenation of chlorobenzene into benzene in standard conditions (20 °C, 1 bar H₂, [substrate]/[Pd] = 100) was studied with different ratios of HEA16Cl/Pd = 2, 3, 5 and 10. The visual stability of the suspension was observed after 3 h of reaction. A molar ratio ≥ 2 was sufficient to maintain stable Pd colloids. Nevertheless, a molar ratio $R < 10$ leads to the precipitation of the suspension after catalysis. To conclude, we have imposed a ratio HEA16Cl/Pd = 10 for the stable and reproducible synthesis of Pd nanoparticles and their use in the dehalogenation of benzene derivatives under aqueous conditions.

This optimized active aqueous suspension was characterized. The histogram of the particle sizes distribution of the Pd/HEA16Cl systems has been determined by transmission electron microscopic observations (Fig. 1). The mean diameter of the Pd nanoparticles, calculated from about 970 particles found in an arbitrary chosen area, corresponds to an average diameter of 2.7 nm with 85% of colloids between 1.50 and 3.50 nm.

3.2. Catalytic performances

First, we have studied the hydrodechlorination of different organic chlorides using Pd/HEA16Cl and hydrogen (1 or 10 bar) in water (Table 1). Hydrodechlorination of chlorobenzene to benzene was complete in about 3 h at atmospheric hydrogen pressure. In the same conditions, functionalized chloride compounds (2-chlorophenol, 4-chloroanisole, 4-chlorotoluene) were slowly transformed into benzene derivatives in less than 24 h. This study was extended to the dechlorination of two polychlorinated species (1,2- and 1,3-dichlorobenzene) and shows complete benzene formation without intermediates. The reaction was also investigated under 10 bar H₂. Surprisingly, we observed that hydrogen pressure was not a crucial parameter to increase the kinetics. This behaviour could be explained by a more favourable partial oxidation of palladium particles by HCl under hydrogen pressure [19]. In all cases, the hydrogenolysis is the major reaction under 1 or 10 bar H₂. Nevertheless, the hydrodechlorination of chlorobenzene performed under 40 bar

Table 1
Hydrogenolysis of a series of aryl chlorides with Pd colloidal suspension^a

Substrate	P_{H_2} (bar)	Product	Conversion ^b (%)	Reaction time (h)
Chlorobenzene	1	Benzene	100	3.2
Chlorobenzene	10	Benzene	100	1.5
Chlorobenzene	40	Benzene/cyclohexane	80/20	22
2-Chlorophenol	1	Phenol	>98	24
2-Chlorophenol	10	Phenol	100	22 ^c
4-Chloroanisole	1	Anisole	100	24
4-Chloroanisole	10	Anisole	100	22
4-Chlorotoluene	1	Toluene	100	6.5
4-Chlorotoluene	10	Toluene	88	5.5
1,2-Dichlorobenzene	1	Benzene	>97	20.5
1,2-Dichlorobenzene	10	Benzene	91	22.8
1,3-Dichlorobenzene	1	Benzene	>97	23
1,3-Dichlorobenzene	10	Benzene	100	18.4

^a Conditions: palladium 3.4×10^{-5} mol, substrate 3.4×10^{-3} mol, HEA16Cl 3.4×10^{-4} mol, substrate/Pd = 100 (molar ratio), water (10 mL), temperature (293 K).

^b Determined by GC analysis.

^c Not optimised.

Table 2
Hydrodehalogenation of halobenzene compounds with colloidal suspension of Pd^a

Substrate	P_{H_2} (bar)	Product	Conversion ^b (%)	Reaction time (h)
Chlorobenzene	1	Benzene	100	3.2
Iodobenzene	1	Benzene	0	7
Bromobenzene	1	Benzene	100	10.3
Bromobenzene	10	Benzene	100	7.3
3-Bromotoluene	1	Toluene	100	24
3-Bromochlorobenzene	1	Chlorobenzene	100	24
3-Bromochlorobenzene	10	Chlorobenzene	100	6.3

^a Conditions: palladium 3.4×10^{-5} mol, substrate 3.4×10^{-3} mol, HEA16Cl 3.4×10^{-4} mol, substrate/Pd = 100 (molar ratio), water (10 mL), temperature (293 K).

^b Determined by GC analysis.

of H₂ shows the simultaneous formation of benzene and cyclohexane with a final ratio of 80/20. The potential recycling process of the suspension was also studied. Successive hydrogenations of chlorobenzene were carried out after simple decantation of the aqueous phase containing palladium nanoparticles in a separating funnel. No loss of activity was observed after two runs. After a third run, the activity significantly decreased with a conversion of 32% due to a surface deactivation with produced HCl but no sedimentation of nanoparticles was observed.

This preliminary investigation shows that the activity was influenced by the nature of the functional groups. Particularly, the kinetics decreases with OH and OMe groups on the aromatic ring and a light destabilization of the catalytic system with the formation of aggregates is observed. This phenomenon could be explained by a presumed interaction between oxygen and palladium. We have already reported similar observation with NH₂ functional group as fragment on aromatic ring in recycling studies of aniline hydrogenation with rhodium nanoparticles [9]. This behaviour was not observed with pure heterogeneous catalysts [20].

In a second step, we have investigated the influence of halide (Table 2). The dehalogenation of chlorobenzene, iodobenzene, bromobenzene was essentially performed at 1 bar of H₂. The reactivity observed in the individual hydrogenolysis processes varied in the following sequence ClBz > BrBz ≫ IBz. Chloro and bromo derivatives proceeded in quantitative yields to the corresponding aromatic products. In the same conditions, no reaction was curiously observed with iodobenzene. To explain this absence of reactivity, we have tested the dehalogenation of chlorobenzene in the presence of iodobenzene. Two reactions have been investigated according to the addition of iodobenzene at the beginning and after 30% of conversion. In both cases, after stirring for 1 h, no hydrogen consumption was detected indicating that iodobenzene had completely inhibited the catalytic

system and stopped the cleavage of the C–Cl bond. Consequently, we could presume that iodobenzene is a poison of palladium nanoparticles in our conditions and justify the absence of reactivity when iodobenzene was alone used as a substrate. Under hydrogen pressure, dehydrobromation was still slower than standard dehydrochlorination (1 bar H₂, 20 °C). Finally, in catalytic conditions, chloride compounds were better tolerated than other halides.

The hydrogenolysis of 3-bromotoluene was complete in 24 h but we observed a small amount of black precipitate at the end of the reaction. The hydrogenation of 3-chlorobromobenzene shows the formation of chlorobenzene as final product with the exclusive hydrogenolysis of the C–Br bond. The same phenomenon is obtained under 10 bar of H₂. The C–Cl bond has never been hydrogenolysed, suggesting the negative effect of the bromide atom on the hydrogenolysis process. We have also observed that the turnover frequency calculated for the hydrogenolysis of the C–Br bond in 3-bromochlorobenzene (TOF = 4 h⁻¹) is 2.5 times higher than the one of bromobenzene (TOF = 10 h⁻¹). This decreased reaction rate for the C–Br bond in the 3-chlorobromobenzene could be explained by electric (negative inductive and positive mesomeric effects) and steric effects induced by the presence of the chloride substituent. Moreover, the cleavage of the C–Br bond (281 kJ mol⁻¹) is less energetically demanding than the C–Cl bond (340.2 kJ mol⁻¹). Similar observations have been reported by Urbano for the liquid-phase hydrodehalogenation of the 4-chlorobromobenzene with supported palladium catalysts [21].

We have previously described the efficient hydrogenation of various benzene compounds in biphasic systems by the analogous Rh/HEA16Cl [8,9]. To complete this study, the hydrodechlorination of chlorobenzene and chlorotoluene has been carried out with the similar aqueous suspension of rhodium nanoparticles under 10 bar of H₂ (Table 3). Interestingly, the

Table 3
Effect of the metal nanoparticle nature on the hydrodechlorination of chlorobenzene derivatives^a

Substrate	Metal	P_{H_2} (bar)	Product	Conversion ^b (%)	Reaction time (h)
Chlorobenzene	Pd	10	Benzene	100	1.5
Chlorobenzene	Rh	10	Cyclohexane	100	1.7
4-Chlorotoluene	Pd	10	Toluene	>90	6
4-Chlorotoluene	Rh	10	Methylcyclohexane	100	7.3

^a Conditions: palladium or rhodium 3.4×10^{-5} mol, substrate 3.4×10^{-3} mol, Pd/HEA16Cl = 10, Rh/HEA16Cl = 2, substrate/metal = 100 (molar ratio), water (10 mL), temperature (293 K).

^b Determined by GC analysis.

aqueous rhodium suspension leads to the cleavage of the C–Cl bond and also to the total hydrogenation of the aromatic ring, whereas the palladium system is only limited to the hydrogenolysis of the C–Cl bond. The partial hydrogenation of the aromatic ring with palladium colloids has just been observed under 40 bar of H₂. Nevertheless, the activity of the reaction decreases with rhodium nanoparticles in comparison with palladium nanoparticles. The kinetic analysis of the dehydrochlorination of chlorobenzene with rhodium system suggests that the dehalogenation and the hydrogenation were carried out in a consecutive process. Finally, according to the preliminary choice of the metal, the reaction will lead to the formation of benzene or cyclohexane derivatives as the final product.

4. Conclusion

The present work reports catalytic activities of an aqueous suspension of nanoparticles in dehydrohalogenation of aryl halides. The colloidal palladium(0) suspension based on the classical approach developed in our laboratory has been optimized for this application. The chloride salt HEA16Cl has been used to efficiently stabilize palladium colloids. In the dehydrohalogenation process, rhodium and palladium nanoparticles have been compared. We have shown that the aqueous palladium suspension was efficient for the cleavage of the C–Cl bond and reusable in two successive runs. Nevertheless, poorly results have been obtained with bromo compounds; in that case, the hydrogenolysis is efficient but the formation of aggregates is observed at the end of the catalysis.

The rhodium nanoparticles were active for the hydrodechlorination. Under hydrogen pressure, the slow hydrogenation of the aromatic ring was also obtained and cyclohexane derivatives were produced as the final products. The hydrogenation of the aromatic ring with palladium system could only be performed under significant hydrogen pressure (>40 bar of H₂).

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