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Sonochemical deposition of platinum nanoparticles on polymer beads and their transfer on the pore surface of a silica matrix

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ABSTRACT

This study reported the sonochemical deposition of platinum on the surface of polystyrene beads (PSBs) and the transfer of obtained Pt nanoparticles into a porous silica matrix using the PSB as a sacrificial template. Platinum nanoparticle deposition was ensured by the sonochemical reduction of Pt(IV) at room temperature in latex solutions containing polystyrene beads in the presence of formic acid under Ar or under Ar/CO atmosphere without any additives. After ultrasonic treatments for few hours, well dispersed Pt nanoparticles within the range of 3–5 nm deposited on PSB were obtained in both studied conditions. Samples were then mixed with TEOS, dried, and heated at 450 °C to ensure the PSB removal from the silica matrix. TEM and SEM results clearly show that final silica pore size is within the same order of magnitude than initial PSB. Finally, platinum decorated silica matrix with chosen pore sizes was successfully prepared.

1. Introduction

Noble metal nanoparticles have been widely studied, especially for their unique size-dependent properties [1]. Several metals have drawn the attention like gold, palladium, or platinum, which can be found in many applications such as catalytic converters, water–gas-shift reaction, or large scale chemical synthesis [2–4]. In catalysis, noble metal nanoparticles (NPs) can be used alone or deposited on different supports in order to facilitate their use, to be stabilized toward the aggregation or to enhance their catalytic activity [1,5–6]. Various supports can be considered from silicon or metal oxides to carbon black as well as polymeric materials. For latter thermosensitive supports, the conventional impregnation/hydrogen reduction method is not applicable. To date, several alternative synthetic routes have been considered for such kind of supports: electrodeposition [7], preformed metal particle sorption on polystyrene beads (PSBs) [8], and chemical reduction including electroless deposition [9–11]. Other techniques can also be considered for the synthesis of nanomaterials. Sonochemistry for instance was successfully applied for the preparation of noble metal particles with or without surfactants or additives [8,12–14]. In fact, when submitted into a liquid, power ultrasound induces the nucleation, growth, and violent collapse of cavitation bubbles. This phenomenon known as acoustic cavitation produces a non-equilibrium plasma inside the cavitation bubbles which is responsible for in situ radical formation [15]. In pure water, homolytic split of H_2O molecules leads to the formation of H_2 within the bubble and H_2O_2 at the bubble–liquid interface due to the mutual recombination of H atoms and OH° radicals, respectively [16]. Local heating within the solution surrounding the bubble during its collapse can accelerate the chemical processes with non-volatile species [17]. Recently, it was reported that platinum(IV) could be reduced under ultrasonic irradiation in formic acid media and also in pure water under Ar/CO atmosphere [18]. In homogenous solutions, the sonochemical reactions could be achieved within few hours at room temperature. The strength of this process relies in the fact that the platinum reduction could be envisaged in a large array of experimental conditions and in presence of various supports, especially thermal sensitive materials.

In the current paper, the platinum deposition on polystyrene beads was investigated under two different experimental conditions namely within formic acid media and also in presence of Ar/CO gas mixture in latex solutions containing PSB. Obtained materials were then characterized and used as a template for the preparation of controlled porous silica with platinum decorated pores.

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2. Materials and methods

2.1. Reagents

The preparation of the PS latex was done as previously reported [19]. It was based on the emulsion polymerization of styrene (99.0%, Aldrich) using potassium persulfate (KPS) (99.0%, Sigma Aldrich), sodium metabisulfite (SMBS) (97.0%, Sigma Aldrich) as redox initiating system and sodium dodecyl benzene sulfonate (SDBS) (Aldrich) as surfactant. The molar composition of the reaction mixture was styrene: water: KPS: SMBS: SDBS = 1: 50: 5×10^{-3}: 3.2×10^{-3}: 6.5×10^{-4}. The polymerization was performed in a round-bottom flask under inert atmosphere and gentle magnetic stirring at 65 °C for 1 h, 72 °C for 2 h, and then 90 °C for 2.5 h. This protocol gives a stable acidic latex suspension (pH = 2.3) with a number average molecular weight of ~30,000 g mol^{-1} and 8 wt% PS in the latex suspension. The resulting PSB exhibits diameters ranging from 50 to 100 nm.

Formic acid (98%), $H_2PtCl_6{\cdot}6H_2O$ (99.9% Pt) were purchased from Aldrich and Strem. Deionized water (Milli-Q 18.2 MΩ cm at 25 °C) was used to prepare all aqueous solutions. Ar/CO gas mixture with 10% of CO and Ar of 99.999% purity were provided by Air Liquide. TEOS ($Si(OC_2H_5)_4$) (99%, Aldrich) was used as silica precursor.

2.2. Ultrasonic irradiation

Ultrasonic treatments were carried out within a tightly closed thermostated glass reactor equipped with a 1 cm^2 titanium horn and piezoelectric transducer supplied by a 20 kHz generator (750 W Sonics). In all experiments, the solution volume was 50 mL insuring that the sonotrode was reproducibly immersed below the surface of the sonicated liquid. All kinetics were studied at a steady temperature of 20 ± 1 °C in the sonicated liquid reached after 30 min of sonication. Prior sonication, Ar or Ar/CO gas mixture was bubbled through formic acid or initially pure water, respectively, for 15–20 min at a 100 mL min^{-1} rate and maintained during the ultrasonic treatment. The irradiation intensity, I (W cm^{-2}) as well as the absorbed acoustic power, P_{ac} (W mL^{-1}), were assessed by calorimetric method and checked by chemical probe with measurement of the hydrogen peroxide formation rate during water sonolysis in pure argon [20]. In our conditions, I and P_{ac} values were equal to 18 W cm^{-2} and 0.35 W mL^{-1}, respectively, with a H_2O_2 formation rate of 0.07 μmol min^{-1}.

2.3. Platinum(IV) reduction kinetic

Platinum(IV) concentration in solution was measured by following the 260 nm absorption peak with a GBC UV/Vis 920 spectrophotometer [21]. Aliquots were centrifuged at 15,000 rpm and diluted 10 times in pure water prior spectra recording within 1 cm wide quartz Suprasil precision cells. Total platinum concentrations in solution were determined by ICP-OES analyses performed on a Spectro Arcos ICP-OES spectrometer by following 6 platinum emission lines. Solution samples were filtered on 0.2 μm PTFE membrane and diluted 20 times in nitric acid (0.3 M) prior analysis. ICP calibration curves were achieved for Pt concentrations from 0 to 15 ppm using SCP Science platinum standard solutions.

2.4. Sample characterizations

SEM analyses were performed on a FEI QUANTA 200 ESEM FEG device. For TEM observations, obtained samples were dispersed in absolute ethanol. One drop was then deposited on carbon coated copper grid prior analysis using a modified Jeol 200 CX TEM. Sample carbon weight percentages were assessed after heat treatment by analyzing the solid phase with a LECO CS230 device calibrated with appropriate carbon standards.

3. Results and discussion

3.1. Platinum(IV) reduction kinetic in presence of PSB

In all experiments, the equivalent of 4.5 mg of platinum (5.10^{-4} M) was injected within 50 mL of a mixture made of polystyrene beads (0.25 g of PSB) and water or formic acid (1 M). As shown in Fig. 1, Pt(IV) reduction kinetics were investigated in presence of PSB suspension diluted within pure water under Ar/CO atmosphere and also in formic acid medium under argon. Solution aliquots were taken at different time and assessed by ICP-AES and UV–Vis spectroscopy. This procedure ensures the complete determination of platinum ions in the medium, and thus, the percentage of synthesized platinum nanoparticles can be estimated.

Results confirm the reduction of Pt(IV) ions is a two-step mechanism with the sequent reduction of Pt(IV) to Pt(II) and finally to platinum metal as already reported within the literature [13]. In our previous study [18], it was stated that under ultrasonic irradi-

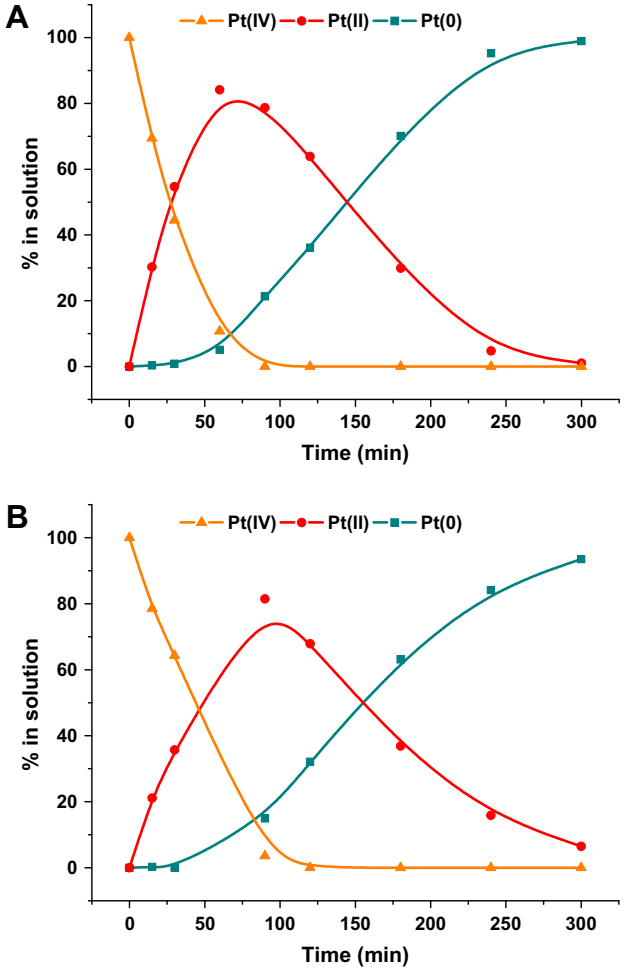

Fig. 1. Platinum(IV) and (II) concentration evolution in solution and the estimated percentage of Pt(0) obtained during ultrasonic irradiation of latex suspension diluted (A) in HCOOH 1 M under Ar atmosphere (B) in water under Ar/CO atmosphere. Temperature was kept at 20 ± 1 °C and P_{ac} = 0.35 W mL^{-1}. Initial platinum(IV) concentration was around 0.5 mM and an equivalent of 250 mg of PSB was introduced before platinum injection.

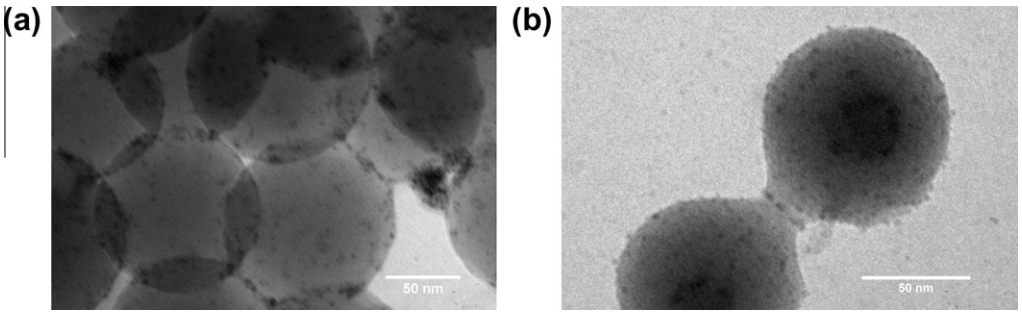

Fig. 2. TEM images of platinum NPs deposited on PSB under ultrasonic irradiation of latex suspension diluted (a) in 1 M HCOOH under Ar or (b) within pure water under Ar/CO atmosphere. Temperature was kept at 20 ± 1 °C and P_{ac} = 0.35 W mL^{-1}.

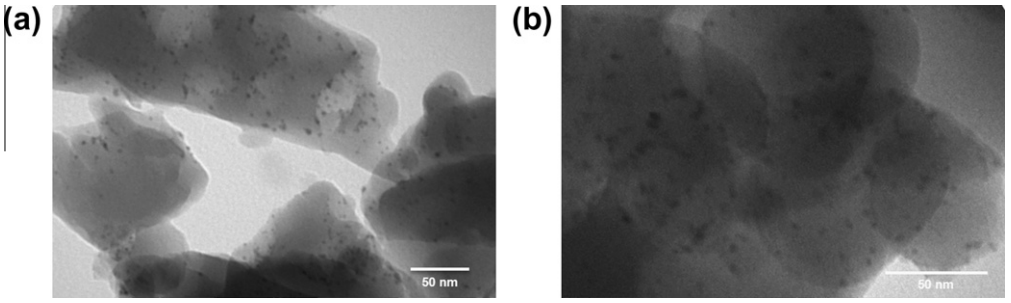

Fig. 3. TEM images of samples obtained after TEOS addition and heat treatment at 450 °C. Platinum NPs were deposited on PSB under ultrasonic irradiation of latex suspension diluted (a) in 1 M HCOOH under Ar and (b) within pure water under Ar/CO atmosphere.

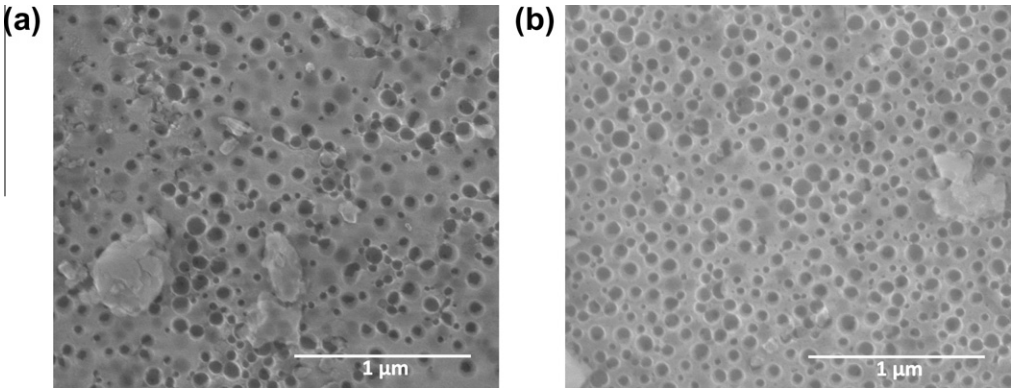

Fig. 4. SEM images of samples obtained after TEOS addition and heat treatment at 450 °C. Platinum NPs were deposited on PSB under ultrasonic irradiation of latex suspension diluted (a) in 1 M HCOOH under Ar and (b) within pure water under Ar/CO atmosphere.

ation, the formation of Pt(0) involved both common reduction by formic acid, as observed under silent conditions, but also by in situ formed hydrogen under ultrasonic irradiation. Indeed, the reduction of platinum ions during the sonolysis of pure water under Ar atmosphere could be confirmed even at low ultrasonic frequency. However, the reaction rate appeared to be very low and after 4 h of sonolysis, around 15% of initial Pt(IV) remained unreduced with almost no formation of Pt(0) [18]. In HCOOH case, after around 90 min all initial Pt(IV) is reduced into Pt(II) and Pt(0). Complete reduction to platinum metal can be achieved with longer irradiation time, namely after 5 h, in formic acid medium. Control experiments carried out under homogeneous conditions showed that HCOOH in the absence of ultrasound is a weak reducing agent however can lead to the formation of platinum nanoparticles with significant lower reaction rates compared to experiments under ultrasonic irradiation.

As shown in Fig. 1B, similar results were also obtained in initially pure water under Ar/CO atmosphere, and platinum reduction kinetics were finally within the same order of magnitude. In presence of Ar/CO gas mixture, platinum ions are reduced by in situ formed hydrogen but also by CO due to the local heating in the vicinity of the cavitating bubbles as reported elsewhere [18]. In the same way, we previously stated that addition of 10% of CO in the gas phase totally inhibits the formation of H_2O_2 in solution under ultrasonic irradiation and prevents accumulation of oxidative species in the medium. It was also observed that contrary to HCOOH, the reduction of platinum ions under silent conditions in the presence of Ar/CO leads to the slow formation of platinum carbonyl which appeared to be unstable under ultrasonic irradiation. Finally, we observed that addition of 10% of CO in the gas phase totally inhibits the formation of H_2O_2 in solution under ultrasonic irradiation and prevents accumulation of oxidative species in the

medium. Thus, it can be stated that HCOOH and CO exhibit very similar behaviors under ultrasonic irradiation explaining the analogous reduction kinetics observed in Fig. 1B. As a matter of fact, both reagents act as reducing agents but also as OH° scavengers, preventing back oxidation of Pt(II) ions. Moreover, the ability of HCOOH and CO to reduce platinum ions at room temperature is enhanced due to the local heating in the liquid shell surround the bubble during its collapse.

It should be noted that in absence of PSB, the formation of Pt NPs was completed within 2 h. However, in the studied case, more time is needed certainly due to remaining chemicals within the latex suspension. As a matter of fact, PSB are obtained by an emulsion polymerization process as previously described and traces of potassium persulfate, sodium metabisulfite, sodium benzene sulfonate, and a small amount of styrene could remain within the solution. Noteworthy, for the deposition of platinum under ultrasonic irradiation, the initial latex suspension is diluted, and the final concentrations of these remaining chemicals are several orders of magnitude lower than that of formic acid. Thus, those compounds can hinder the Pt reduction kinetic without necessarily changing the global mechanism under ultrasonic irradiation in presence of formic acid or carbon monoxide.

3.2. Platinum nanoparticle deposition on PSB and transfer within silica matrix

After 2 h of ultrasonic treatment, samples were analyzed by TEM as shown in Fig. 2. In both formic acid medium and in pure water under Ar/CO atmosphere, platinum nanoparticles within the range of few nanometers are deposited at the surface of the polystyrene spheres. Noteworthy, the sample prepared under Ar/CO atmosphere exhibits less particle aggregation than the sample obtained in presence of HCOOH. This result is in a full agreement with experiments carried out in homogenous system without supported materials and constitutes a further evidence that the overall reduction mechanism is the same than the one stated previously [18]. Noteworthy, even if HCOOH can thermally reduce platinum ions, ultrasonic irradiation in our case contributes to the reduction of platinum ions at room temperature, ensures a good dispersion of the platinum nanoparticles on the support, and finally prevents the formation of micrometric aggregates observed by thermal heating [22].

After deposition of platinum on PSB substrate, the suspension was mixed with TEOS (approximately 1:1 volume ratio between latex particle and resulting silica) under mechanical stirring. Solution acidity due to latex suspension synthesis route was enough to ensure TEOS hydrolysis. In order to form the silica matrix and to remove PSB, the mixture was then dried under air at room temperature before being heated at 450 °C during 2 h with two previous steps at 250 and 350 °C. Less than 1 wt% of carbon was detected within obtained samples after heat treatment. TEM analyses of the final products in Fig. 3 clearly show that for both Ar/CO and HCOOH conditions, platinum nanoparticles could be transferred into the silica matrix. On SEM images in Fig. 4, it can be pointed out that silica pore sizes are within the range of 50–100 nm and are in a good agreement with initial PSB sizes. Noteworthy, even after 450 °C heat treatment, Pt NPs remain very similar in term of size and dispersion within the silica matrix in comparison with samples obtained just after noble metal deposition on polystyrene spheres. Last but not least, homogeneous nanoparticle dispersion obtained by sonochemical reduction of platinum in the presence of Ar/CO can be of great importance in order to avoid subsequent aggregation processes and possible catalytic activity loss due to this phenomenon.

4. Conclusion

This study stated that platinum deposition on thermal sensitive materials can be performed under low frequency ultrasonic irradiation in both formic acid medium and also in pure water under Ar/CO atmosphere at room temperature. After few hours, platinum nanoparticles obtained on the polystyrene surface are within the range of 3–5 nm and exhibit a good dispersion, especially when noble metal reduction was performed under Ar/CO atmosphere. By mixing Pt/PSB with TEOS and then heating the sample at 450 °C, platinum decorated silica matrix with chosen pore sizes were successfully prepared. Finally, this procedure demonstrated at the same time, the ability of the sonochemical reduction process to ensure noble metal deposition on thermal sensitive materials as well as the transfer of platinum nanoparticles into silica matrix using sacrificial polymer porogen.

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