



## Short Communication

# Selective hydrogenation by polymer-encapsulated platinum nanoparticles prepared by an easy single-step sonochemical synthesis

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## ABSTRACT

Polypyrrole-encapsulated platinum nanoparticles (PPy/Pt-NPs) prepared by an easy single-step sonochemical synthesis were used as catalysts for the liquid phase hydrogenation of substituted alkenes in methanol or methanol/water mixtures. Polypyrrole (PPy) coatings on the nanoparticles were able to act as nanoscopic filters for substrates molecules, and consequently substrate selectivity could be controlled in the catalytic processes.

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## 1. Introduction

Metal nanoparticles are attractive for catalysis because their large surface area-to-volume ratio allows effective utilization of expensive metals [1,2]. Moreover, the nanoparticles show unique catalytic properties different from those of bulk metals [3]. However, the naked nanoparticles tend to aggregate, and consequently the excellent catalytic properties would be impaired [4]. To resolve this problem, catalytic nanoparticles have been stabilized by capping with ligands such as polymer [5–7] and dendrimer [8]. Furthermore, these ligands are also able to act as nanoscopic filters for substrates molecules, and consequently substrate selectivity and overall catalytic reactivity can be controlled in the catalytic processes [9–11].

In our previous work, we successfully prepared polypyrrole-encapsulated gold or platinum nanoparticles by one-step sonochemical operation [12,13]. These composite materials could be easily obtained only by ultrasonication to an aqueous solution containing pyrrole monomer, the corresponding metal ion, and stabilizer (Scheme 1).

We envision that polypyrrole-encapsulating catalyst like metal nanoparticles may act as selective gates that control the access of small molecules to the embedded catalysts. Using hydrogenation as a model process, we demonstrate in this communication that polypyrrole-encapsulated platinum nanoparticles (PPy/Pt-NPs)

synthesized by one-step sonochemical operation are highly selective catalysts.

## 2. Experimental

### 2.1. Materials

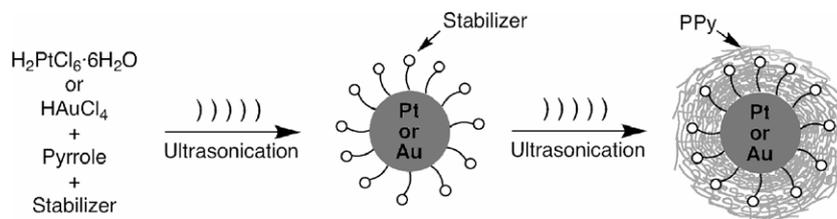
All chemicals were used without further purification. Distilled methanol and deionized water were used as solvents for syntheses of the nanoparticles and hydrogenation reactions.

### 2.2. Sonochemical synthesis of Pt-NPs and PPy/Pt-NPs

Sonochemical synthesis of Pt-NPs and PPy/Pt-NPs and their characterizations were reported in Ref. [13].  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was dissolved in distilled water to make  $0.15 \text{ mmol dm}^{-3}$  solutions in the absence or the presence of 10 mM pyrrole, and SDS (1.25 mM) was added as a stabilizer. The  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution containing SDS was placed in a water bath. Because the local heating produced by the cavitation also depends on the solution temperature, the temperature of the water bath during the sonication was held at  $298 \pm 0.5 \text{ K}$  unless otherwise mentioned. Ultrasonic irradiation was performed with a collimated 20 kHz beam from a ceramic transducer with a titanium amplifying horn (13 mm  $\Phi$ , Branson Sonifier 450D) directly immersed in the solution and operated with an input power of  $22.6 \text{ W cm}^{-2}$ . After the sonication for 4 h, the colloidal suspensions were centrifuged at 2000 rpm for 30 min and separated as sediments. The sediments were rinsed with

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**Scheme 1.** Sonochemical formation of polypyrrole-encapsulated gold or platinum nanoparticles.

deionised water for several times, and dried under vacuum. The average size of Pt-NPs and PPy/Pt-NPs was 34 and 53 nm, respectively. It is well known that SDS plays the role not only as a stabilizer of the nanoparticles but also as a precursor of reducing agent for metal ion reduction in the sonochemical synthesis [14]. Actually, when the sonochemical synthesis was carried out without SDS, the formation rate was quite low and a very small amount of aggregated nanoparticles was obtained after 4 h reaction.

### 2.3. Sonochemical synthesis of poly(1-*n*-butylpyrrole)-encapsulated platinum nanoparticles (PBPY/Pt-NPs)

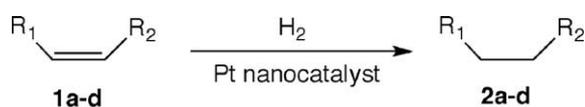
The method to prepare PBPY/Pt-NPs is similar to that to prepare PPy/Pt-NPs. The average size of PBPY/Pt-NPs was found to be 40 nm.

### 2.4. Procedure for hydrogenation reactions

Catalytic hydrogenations were carried out in a 30 mL, 2-neck, round-bottomed flask. Ten milliliters of the catalytic solution and a magnetic bar were placed in the flask. The solutions initially contained either 1.4 mg of Pt-NPs, 3.4 mg of PPy/Pt-NPs, or 3.1 mg of PBPY/Pt-NPs (the amounts of catalyst were chosen to achieve approximately the same quantity of Pt loading in the reactor in the three cases. Pt content in the catalysts was determined by TGA.). The catalytic solutions were bubbled with H<sub>2</sub> for 20 min before adding the substrates. The reactions were carried out by adding 0.1 mmol of substrates by syringe under vigorous stirring conditions at 298 ± 0.5 K. A balloon filled with H<sub>2</sub> (1 atm) was connected to one neck of the flask during the hydrogenation reactions. The reaction products were analyzed by gas chromatography.

## 3. Results and discussion

For a comparison, the naked platinum nanoparticles (Pt-NPs) were also prepared by sonication to H<sub>2</sub>PtCl<sub>6</sub> aqueous solution containing sodium dodecyl sulfate (SDS) as a stabilizer in the absence of pyrrole monomer, and hydrogenation of a series of activated olefins was carried out using Pt-NPs and PPy/Pt-NPs catalysts (Scheme 2). Fig. 1 shows the time-course of the formation of products in the hydrogenation of the corresponding olefins in their methanol solution. In the case of Pt-NPs catalyst, the hydrogenation was completed in 1 h regardless of the structure of substrates (Fig. 1a). In

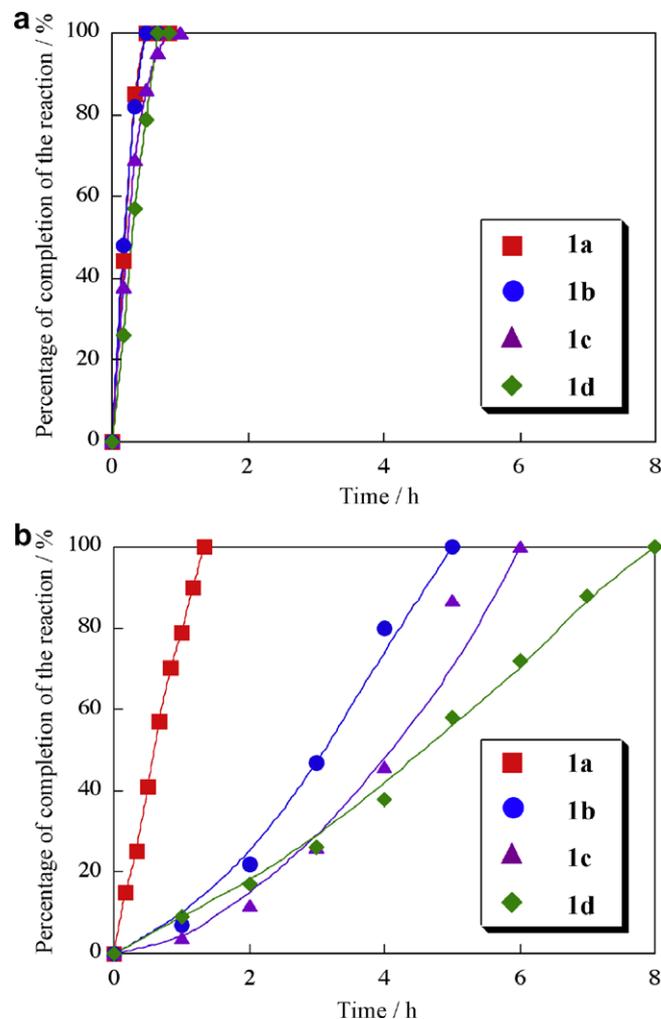


- a:** R<sub>1</sub> = COOMe, R<sub>2</sub> = H  
**b:** R<sub>1</sub> = COOMe, R<sub>2</sub> = COOMe  
**c:** R<sub>1</sub> = COOEt, R<sub>2</sub> = COOEt  
**d:** R<sub>1</sub> = COO*n*-Bu, R<sub>2</sub> = COO*n*-Bu

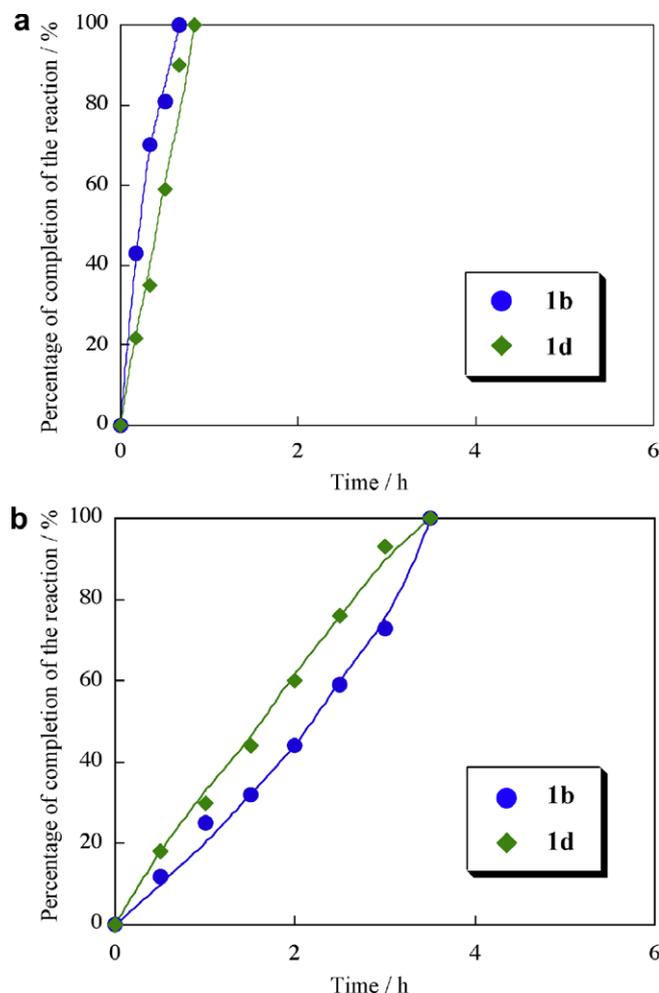
**Scheme 2.** Hydrogenation of a series of activated olefins.

contrast, the presence of the polymer layers decreased the hydrogenation rate for all of the olefins, but hydrogenation rate depended greatly on the size of substrates (Fig. 1b). The rates decreased with an increasing the substrate size. This fact apparently suggested that selectivity was induced by the polymer layer, rather than by the intrinsically nonselective Pt catalyst. Thus PPy layer allows controlled access of substrates to nanoparticles and the substrate selectivity is based on molecular size in methanol solution.

However, when methanol–water mixture (3:2 v/v) was used as a reaction medium instead of methanol solvent, the substrate selectivity did not obey the size of molecular tested in the hydrogenation using PPy/Pt-NPs catalyst as shown in Fig. 2. On “naked”



**Fig. 1.** Percentage of completion of the reaction in the time-course of the hydrogenation of a series of activated olefins using (a) Pt-NPs and (b) PPy/Pt-NPs catalysts in their methanol solution.

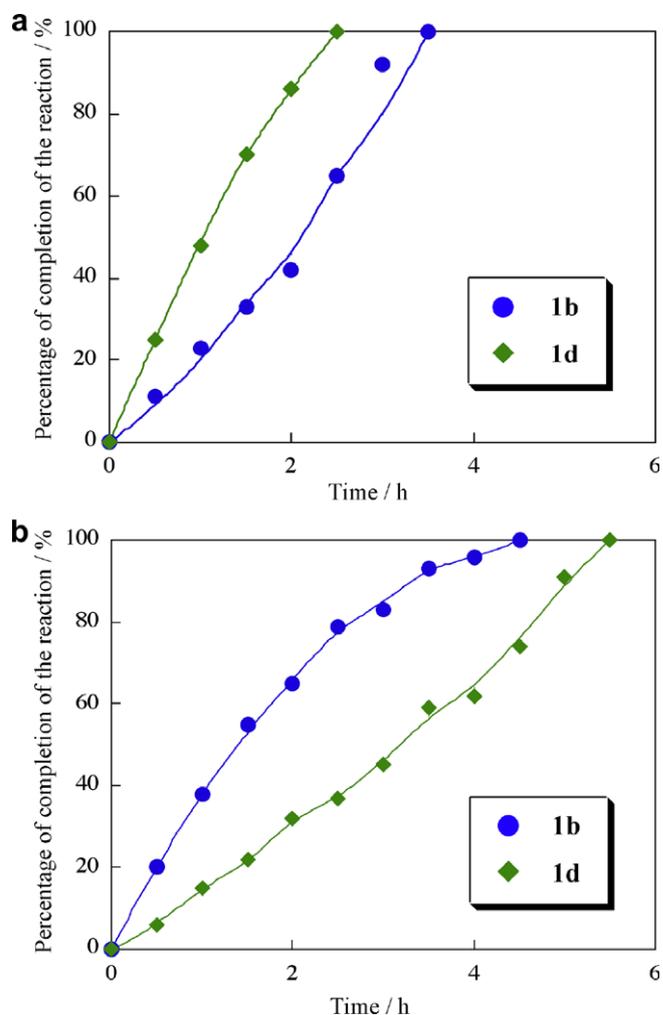


**Fig. 2.** Percentage of completion of the reaction in the time-course of the hydrogenation of the olefins **1b** and **1d** using (a) Pt-NPs and (b) PPy/Pt-NPs catalysts in methanol–water mixture (3:2 v/v).

Pt-NPs, the formation rates for dimethyl succinate (**2b**) and di-*n*-butyl succinate (**2d**) were very close and the hydrogenation of the corresponding olefins **1b** and **1d**, respectively, was completed in 1 h (Fig. 2a). This tendency is quite similar to that in the hydrogenation with Pt-NPs catalyst in methanol solutions. On the other hand, in the case of PPy/Pt-NPs catalyst, the hydrogenation of bigger olefin **1d** was faster than that of smaller olefin **1b** in methanol–water mixture (Fig. 2b). This trend is apparently different from that in the hydrogenation in methanol.

Judging from molecular structures and their solubility in water [15], the hydrophobicity of **1d** is apparently higher than that of **1b**. Therefore, in this case, probably the selectivity was induced by the hydrophobic affinity of substrate molecule with polymer layer, rather than by the substrate size.

To confirm this conjecture, we then sonochemically prepared platinum nanoparticles encapsulated by more hydrophobic polymer such as poly(1-*n*-butylpyrrole), and carried out the hydrogenation in methanol–water mixture using this composite (Fig. 3a). The hydrogenation rate for **1d** was higher on poly(1-*n*-butylpyrrole)-encapsulated platinum nanoparticles (PBPy/Pt-NPs) than PPy/Pt-NPs although the rate for **1b** was little affected by kinds of composites. This can be ascribed to formation of the strong hydrophobic interaction between **1d** and PBPy layer. Thus, in water-containing media, the hydrophobic interaction is a dominant factor for substrate selectivity in the hydrogenation using composite catalysts.



**Fig. 3.** Percentage of completion of the reaction in the time-course of the hydrogenation of the olefins **1b** and **1d** using PBPy/Pt-NPs catalyst in (a) methanol–water mixture (3:2 v/v) and (b) methanol.

Actually, such a hydrophobic interaction did not appear in methanol, and consequently the substrate selectivity obeyed the molecular size even by using PBPy/Pt-NPs catalysts (Fig. 3b).

#### 4. Conclusions

We have demonstrated that polypyrrole-encapsulated platinum nanoparticles (PPy/Pt-NPs) prepared by one-step sonochemical operation were selective catalysts for hydrogenation reactions. This new composite catalyst has many practical advantages and characteristics: (a) the facile synthesis by one-step sonochemical operation; (b) controlling the access of small molecules to the embedded catalysts by the polymer filter; (c) controlling the selectivity in the catalytic reaction by selecting the reaction media. It is hoped that this type of composite catalyst will contribute to the development of nanoreactors with high substrate selectivity as enzymes.

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- [15] The solubility of **1b** and **1d** in water is 80 and 0.5 g dm<sup>-3</sup>, respectively.