Contents lists available at SciVerse ScienceDirect



# Catalysis Communications



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

### Short Communication

# Amphiphilic tannin-stabilized Rh nanopartciles: A highly active and reusable catalyst in biphasic aqueous–organic system

## Hui Mao<sup>a</sup>, Xuepin Liao<sup>a, b,\*</sup>, Bi shi<sup>a, b,\*</sup>

<sup>a</sup> Department of Biomass chemical and Engineering, Sichuan University, Chengdu, 610065, PR China

<sup>b</sup> National Engineering Laboratory of Clean Technology for Leather Manufacture, Sichuan University, Chengdu, 610065, PR China

#### ARTICLE INFO

Article history: Received 19 May 2011 Received in revised form 5 September 2011 Accepted 30 September 2011 Available online 7 October 2011

Keywords: Plant tannins Amphiphilic nature Aqueous-organic Biphasic hydrogenation Activity and reusability

#### 1. Introduction

Over the past several decades, the researches in biphasic catalysis have focused on the development of more environmentally benign systems [1,2]. Among them, aqueous–organic biphasic system is one of the most attractive choices since water is nontoxic and nonflammable, and is immiscible with most organic molecules and solvents. Compared with organic-organic biphasic system, aqueous-organic biphasic system is much preferred from the perspective of green chemistry. However, this system usually suffers a persisting problem of low reactivity owing to the poor interfacial interactions between the hydrophilic catalysts and the hydrophobic substrates [3]. To solve this problem, cosolvents, phase transfer agents or surfactants have been applied in the reaction systems to decrease the interfacial resistance [4-7], but the acceleration of reaction rate is quite limited and the separation of catalysts from the products is often complicated as well. Up to now, the finding of new strategies that combine high activity with excellent reusability is still an attractive challenge in aqueous-organic biphasic catalysis. More recently [8,9], Kania et al. reported that the use of carbon materials as mass transfer additives can effectively reduce the masstransfer limitation in biphasic system. Those findings promoted us to explore new materials with unique interface properties to enhance the activity of biphasic catalysis.

In this communication, we provided a novel and facile strategy for the synthesis of Rh nanoparticles, which were highly active and

## ABSTRACT

A series of Rh nanoparticles were prepared by using plant tannins as stabilizers. The as-prepared plant tanninstabilized Rh nanoparticles were subsequently characterized by TEM, DES, FTIR and XPS. Due to the amphiphilic nature of plant tannins, the plant tannin-stabilized Rh nanoparticles were highly active in aqueous–organic biphasic hydrogenation of styrene. Furthermore, the as-prepared Rh catalyst can be reused 5 times without significant loss of catalytic activity, thus exhibiting a remarkable reusability.

Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.

reusable in aqueous-organic biphasic hydrogenation. The basic principle of our strategy is to utilize amphiphilic plant tannins as the stabilizers to improve the hydrophilic/hydrophobic properties of Rh nanoparticles. Plant tannin is a kind of environmentally benign and water-soluble amphiphilic polyphenol, which has a large number of hydrophilic phenolic hydroxyls on its hydrophobic macromolecular backbone [10]. According to our previous work [11], the phenolic hydroxyls of plant tannins are able to chelate with metal species with empty atomic orbits, like noble metal ions. Consequently, the abundant phenolic hydroxyls of plant tannins should be able to constrain Rh nanoparticles into aqueous phase by attaching the phenolic hydroxyls onto the surface of Rh nanoparticles via chelating interaction while the aromatic backbone of plant tannin is able to provide steric hindrance to prevent Rh nanoparticles from aggregating. More importantly, those aromatic backbones of plant tannins are capable of forming hydrophobic bonds with the organic phase, which increases the possibility of hydrophobic substrate to be catalyzed on the catalytic species.

To confirm our proposed strategy, black wattle tannin (BWT), a typical kind of condensed tannin, was employed as the stabilizer to prepared BWT-stabilized Rh nanoparticles (BWT-Rh) catalysts. The molecular structure of BWT is shown in Fig. 1. Indeed, black wattle tannin is a mixture of poly-prodelphinidin with average molecular weight of 1250. It can be seen that BWT consists of flavan-3-ols, and a large number of multiple phenolic hydroxyls are located at its Brings, which provide BWT enough water-solubility. In addition, the macromolecular backbone of BWT mainly contains aromatic rings, which can interact with the hydrophobic substrate and/or solvent by hydrophobic interactions. By changing the concentration of BWT,

<sup>\*</sup> Corresponding authors at: Department of Biomass chemical and Engineering, Sichuan University, Chengdu, 610065, PR China. Tel.: +86 28 85400382; fax: +86 28 85400356. *E-mail addresses*: xpliao@scu.edu.cn (X. Liao), shibi@scu.edu.cn (B. shi).

<sup>1566-7367/\$ -</sup> see front matter. Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2011.09.038



Fig. 1. The molecular structure of black wattle tannin (BWT).

a series of BWT-Rh catalysts with different particle size were synthesized, which were further characterized by TEM, EDS, FTIR and XPS. To evaluate the catalytic properties of BWT-Rh catalysts, aqueous–organic biphasic hydrogenation of styrene was carried out. Moreover, the reusability of the catalyst was also conducted.

#### 2. Experimental

#### 2.1. Materials

RhCl<sub>3</sub>, NaBH<sub>4</sub>, and other chemicals were all analytical reagents and purchased from Sigma-Aldrich Cooperation, which were used as received without further purification. Black wattle tannin (BWT), a kind of typical condensed tannin, was provided by the plant of forest product in Guangxi province (China).

#### 2.2. Preparation of BWT<sub>x</sub>-Rh catalyst

5.0 mL of RhCl<sub>3</sub> solution (2.5  $\mu$ mol Rh<sup>3+</sup>) was added into 3.0 mL of BWT solution at different concentrations. After magnetic stirring for 20.0 min, 2.0 mL of NaBH<sub>4</sub> solution (12.5  $\mu$ mol) was drop-wise added into the aforementioned mixture within 2.0 h. Finally, a series of BWT<sub>x</sub>-Rh were prepared, where *x* is the concentration of BWT varying from 1.5 to 6.0 g/L, and the concentration of Rh is fixed at 0.25 mmol/L.

#### 2.3. Characterization of BWT<sub>1.5</sub>-Rh catalyst

The particle size and EDS mapping of the catalyst were analyzed by Transmission Electron Microscopy (TEM, Tecnai G<sup>2</sup>F20 S-TWIN, U.S.). The chemical valence of the catalyst was determined using Xray Photoelectron Spectroscopy (XPS, Kratos XSAM-800, UK). Fourier Transform Infrared Spectroscopy (FTIR, PerkinElmer, USA) analyses of samples were carried out by using compressed film of KBr pellet and sample powder prepared by drying the catalyst.



Fig. 2. TEM image and the corresponding particle size distribution of BWT<sub>1.5</sub>-Rh, BWT<sub>3.0</sub>-Rh and BWT<sub>6.0</sub>-Rh. HAADF-STEM image and EDS mapping images of BWT<sub>3.0</sub>-Rh.

10.0 mL of BWT-Rh (containing 2.5  $\mu$ mol Rh) was added into a stainless steel reactor, and then 15.0 mL of ethyl acetate containing 5.0 mmol of styrene was added. After the reactor was flushed three times with H<sub>2</sub>, the catalytic hydrogenation was conducted under 1.0 MPa of H<sub>2</sub> and 303 K, of which the resultant products were analyzed using GC–MS and GC. The organic phase was removed to recover the BWT-Rh catalyst. The activities of BWT-Rh catalyst to other substrates were also investigated, which includes quinoline, cyclohexene and nitrobenzene.

#### 3. Results and discussion

#### 3.1. Characterization of the catalyst

The synthesis procedures for the preparation of tannin-stabilized Rh nanoparticles are quite simple. First, a predetermined quantity of RhCl<sub>3</sub> solution is added into black wattle tannin (BWT, a typical plant tannin) solution at different concentrations, and then the Rh<sup>3+</sup> are reduced by NaBH<sub>4</sub> to yield water-soluble BWT-stabilized Rh nanoparticles (BWT-Rh). Herein, a series of BWT<sub>x</sub>-Rh are prepared, where *x* is the concentration of BWT varying from 1.5 to 6.0 mg/L, and the concentration of Rh is fixed at 0.25 mmol/L. TEM results in Fig. 2 show that BWT-Rh nanoparticles with different particle size are successfully synthesized by varying the concentration of BWT, and smaller particle size is found to be predominated in those samples with higher content of BWT. EDS mapping analyses of a distinct BWT<sub>1.5</sub>-Rh nanoparticle reveal that the mapping image of Rh has similar shape to that of O (Fig. 2e and f), which suggests that the Rh nanoparticle is indeed stabilized by the supramolecular shell of BWT because only BWT consists of O element.



Fig. 3. FTIR spectra of BWT and BWT<sub>1.5</sub>-Rh.

The FTIR spectra of BWT and BWT<sub>1.5</sub>-Rh are shown in Fig. 3. In Fig. 3a, the peak at 3400  $\text{cm}^{-1}$  can be attributed to the stretching vibration of phenolic hydroxyls (O–H bond), and its broad range is due to the formation of hydrogen bonds with water molecules. Peaks in the vicinity of 1614–1458 cm<sup>-1</sup>indicate the presence of aromatic rings of BWT [12,13]. In Fig. 3b, the hydroxyl peak in FTIR spectrum of BWT is narrowed after reacting with Rh nanoparticle. Moreover, the peaks that belong to the aromatic rings of BWT also become weak. These changes confirm the stabilization interactions of phenolic hydroxyls of BWT with the Rh nanoparticles [14], which are consistent with the results of the EDS mapping analyses in Fig. 2d-f. Subsequently, the XPS analysis of the BWT-Rh catalyst was carried out, and the corresponding results are shown in Fig. 4a. It is observed that the Rh 3d XPS spectrum of BWT<sub>1.5</sub>-Rh consists of Rh 3d 5/2 and Rh 3d 3/2 peaks resulting from the spin-orbital splitting. The first peak of Rh 3d 5/2 located at 307.14 eV is attributed to the elemental Rh while the second peak of Rh 3d 5/2 located at 308.38 eV confirms the existing of trivalent state of Rh [15]. Based on the integration calculation, the content of elemental Rh in the BWT<sub>15</sub>-Rh is about 21.92%. As a consequence, those BWT-Rh nanoparticles observed in Fig. 2a-c are Rh (0) nanoparticles and/or Rh(0)-Rh(III) hybrid nanoparticles.

#### 3.2. Aqueous–organic biphasic hydrogenation of hydrophobic substrate

To show that the BWT-Rh catalyst can exhibit high activity and stability in aqueous–organic biphasic hydrogenation of hydrophobic substrate, styrene was employed as a probe substrate. Ethyl acetate, a commonly used organic solvent, was used as the organic phase to constitute biphasic system with aqueous phase. Fig. 5 illustrates the schematic diagram for aqueous–organic biphasic hydrogenation of styrene using BWT-Rh as the catalyst. Before the reaction, the hydrophobic styrene and hydrophilic BWT-Rh strongly partition into ethyl



Fig. 4. XPS 3d spectrum of BWT<sub>1.5</sub>-Rh catalyst.



Fig. 5. The schematic diagram of aqueous–organic biphasic hydrogenation of styrene using BWT-Rh catalyst.

#### Table 1

Biphasic hydrogenation activity of styrene using different BWT-Rh catalysts\*.

Parameter	BWT <sub>1.5</sub> -Rh		BWT <sub>3.0</sub> -	WT <sub>6.0</sub> -
	1-run	5-run	Rh	Rh
TOF (mol•mol <sup>-1</sup> •h <sup>-1</sup> ) Conversion yield (%) TON[substrate]/[Rh]	11,820 98.5 1970	11,712 97.6 9760	9924 82.7 1654	2760 23 460

\* Catalyst/substrate, 2.5 µmol/5.0 mmol; organic solvent, ethyl acetate; pressure, 1.0 MPa; temperature, 303 K; reaction time, 10 min.

acetate phase and aqueous phase, respectively. Upon the reaction to proceed, the aqueous and organic phases were mixed together by vigorous stirring, which allows the styrene to contact with BWT-Rh and the activated atomic H dissociated over Rh nanoparticles to yield the product of ethylbenzene (confirmed by GC–MS) [16].

Table 1 summarizes the turnover frequencies (TOFs) and conversion yield for biphasic hydrogenation of styrene. As for BWT<sub>1.5</sub>-Rh, its average TOF in 1-run is as high as  $11820 \text{ mol}^{-1} \cdot h^{-1}$ , and the conversion yield reaches 98.5% in 10.0 min. Based on CG-MS analvsis, ethylbenzene was the only detected product, and no other products derived from the reduction of aromatic rings were detected even the reaction time was prolonged for 2.0 h. These results suggested that our catalyst can be used for the highly active and selective hydrogenation of styrene to ethylbenzene. We believe that the strengthened hydrophobic properties of Rh nanoparticles and the decreased interfacial resistance in aqueous-organic phases should be the mainly reasons responsible for the highly activity. As for the catalytic selectivity of the BWT<sub>15</sub>-Rh catalyst, it is quite difficult to give specific explanations but one can still reason that the relative mild reaction conditions may be responsible for the total inhibition of aromatic ring reduction because the reduction of aromatic ring often requires much higher temperature and/or pressure. For comparison, a mixture of BWT and RhCl<sub>3</sub> was also used as the catalyst (denoted as BWT<sub>1.5</sub>-Rh<sup>3+</sup> complexes) for the biphasic hydrogenation of styrene, in which the concentration of BWT and Rh were fixed at 1.5 g/L and 0.25 mmol/L, respectively. Compared with the BWT<sub>1.5</sub>-Rh catalyst, the BWT<sub>1.5</sub>-Rh<sup>3+</sup> complexes exhibited much lower catalytic activity. For example, the conversion yield of styrene was only 9.0% when the reaction was conducted using BWT<sub>1.5</sub>-Rh<sup>3+</sup> complexes at 303 K and 1.0 MPa H<sub>2</sub> for 10.0 min whileit was high up to 98.5 for the BWT1.5-Rh.

In addition, the used BWT<sub>1.5</sub>-Rh can be easily recovered by simple decantation, and reused 5 times without significant loss of catalytic activity. In the 5-run, the average TOF of BWT<sub>1.5</sub>-Rh is still 99.1% of the 1-run, and the final conversion yield also reaches 97.6%. The detailed reusability results of the BWT<sub>1.5</sub>-Rh catalyst are present in supporting information 1. Due to its excellent reusability, the turnover number (TON) of BWT<sub>1.5</sub>-Rh is high up to 9760. The FTIR spectrum of the used BWT<sub>1.5</sub>-Rh catalyst shows no obvious changes as compared with that of fresh catalyst, which suggest that the mainly functional groups of BWT were still unchanged. Thus, it can be concluded that BWT was stable enough during the catalytic reaction. According to the XPS analysis (Fig. 4b), the content of elemental Rh in the BWT<sub>1.5</sub>-Rh catalyst is increased from 21.92% to 70.07%, which suggested that the trivalent Rh in the BWT<sub>1.5</sub>-Rh catalyst was further reduced during the hydrogenation reaction.

It is interesting that the hydrogenation activity to styrene is decreased to 9924 mol•mol<sup>-1</sup>• $h^{-1}$  when BWT<sub>3.0</sub>-Rh was used as the catalyst, and this value is drastically reduced to 2760 mol•mol<sup>-1</sup>•h<sup>-1</sup> when BWT<sub>6.0</sub>-Rh was employed. TEM images in Fig. 1 clearly show that BWT<sub>6.0</sub>-Rh has the smallest Rh nanoparticles while its activity is actually the lowest. To specifically explain this phenomenon is difficult, but one can still speculate that the BWT molecules stabilized on the surface of Rh nanoparticles should provide steric hindrance to restrict the styrene to access the active sites of Rh nanoparticles [17,18]. As has been proved by the aforementioned EDS mappings, supramolecular shells of BWT are indeed formed around the Rh nanoparticles. Thus, it can be reasoned that much denser supramolecular shells of BWT would be constructed around the Rh nanoparticles in the BWT<sub>6.0</sub>-Rh catalyst because the hydrogen bonds and/or hydrophobic interactions will be strengthened among BWT molecules when the concentration of BWT is increased [19]. These results suggest that the increase of BWT content in BWT-Rh catalyst can substantially restrict the access of substrate to the active sites of the catalyst, which is potential used for the size-based selective hydrogenation.

The activities of BWT<sub>1.5</sub>-Rh catalyst to other substrates were also investigated. Due to that the hydrogenation of cyclic olefin and nitro bond were much difficult than that of double carbon bond, we therefore carried out these biphasic hydrogenation reactions under higher  $H_2$  pressure and reaction temperature. As shown in Table 2, the BWT<sub>1.5</sub>-Rh catalyst still exhibited high activity for the biphasic

Table 2
Biphasic hydrogenation activity of BWT <sub>1.5</sub> -Rh to other substrates <sup>*</sup> .

Substrate	Product	H <sub>2</sub> (MPa)	T (K)	t (min)	Conversion (%)
		2	353	30	94.0
$\bigcirc$		2	333	60	24.6
NO <sub>2</sub>	NH <sub>2</sub>	2	323	30	98.4

\* Catalyst/quinoline, 5 µmol/0.5 mmol; catalyst/cyclohexene, 2.5 µmol/2.5 mmol; catalyst/nitrobenzene, 50 µmol/2.5 mmol; organic solvent, ethyl acetate;

hydrogenation of quinoline, cyclohexene and nitrobenzene, thus demonstrating its comprehensive application in biphasic hydrogenation to other unsaturated compounds.

#### 4. Conclusions

In summary, we have developed a facile strategy for the synthesis of Rh nanoparticles using plant tannin as the stabilizer. Furthermore, the particle size of the Rh nanoparticles can be controlled by changing the amount used plant tannin. Due to the amphiphilic nature of the plant tannins, the as-prepared plant tannin-stabilized Rh nanoparticles were highly active in aqueous-organic biphasic hydrogenation of styrene. Additionally, the catalysts can be reused 5 times without significant loss of activity.

#### Acknowledgements

We acknowledge the financial support provided by (KPNSFC, 20536030), (NNSFC, 20776090) and (FANEDD, 200762). We also give thanks to Test Centre of Sichuan University for the help of TEM tests.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.09.038.

#### References

- [1] K.X. Li, Y.H. Wang, J.Y. Jiang, Z.L. Jin, Catalysis Communications 35 (2000) 3523.
- H. Azoui, K. Baczko, S. Cassel, C. Larpent, Green Chemistry 10 (2008) 1197. [2]
- K.H. Shaughnessy, Chemical Reviews 109 (2009) 643. [3]
- P. Purwanto, H. Delmas, Catalysis Today 24 (1995) 135. [4]
- [5] E. Paetzold, G. Oehme, Journal of Molecular Catalysis A: Chemical 152 (2000) 69.
- M Baur M Frank J Schatz F Schildbach Tetrahedron 57 (2001) 6985
- F. Hapiot, L. Leclercq, N. Azaroual, S. Fourmentin, S. Tilloy, E. Monflier, Current Or-[7] ganic Synthesis 15 (2008) 162.
- [8] N. Kania, N. Gokulakrishnan, B. Leger, S. Fourmentin, E. Monflier, A. Ponchel, Journal of Catalysis 278 (2011) 208.
- [9] N. Gokulakrishnan, N. Kania, B. Leger, C. Lancelot, D. Grosso, E. Monflier, A. Ponchel, Carbon 49 (2011) 1290.
- [10] S. Quideau, D. Deffieux, C. Douat-Casassus, L. Pouysegu, Angewandte Chemie International Edition 50 (2011) 586.
- X. Huang, H. Wu, X.P. Liao, B. Shi, Catalysis Communications 11 (2010) 487. [11]
- C.W. Oo, M.J. Kassim, A. Pizzi, Industrial Crops and Products 30 (2009) 152. Y. Nakano, K. Takeshita, T. Tsutsumi, Water Research 35 (2001) 496. [12]
- [13]
- [14] X. Huang, Y.P. Wang, X.P. Liao, B. Shi, Green Chemistry 12 (2010) 395. [15] Y. Wang, Z. Song, D. Ma, H.Y. Luo, D.B. Liang, X.H. Bao, Journal of Molecular Catalysis A: Chemical 149 (1999) 51.
- [16] M. Pozzo, D. Alfe, International Journal of Hydrogen Energy 34 (2009) 1922.
- [17] N. Sakulchaicharoen, D.M. O'Carroll, J.E. Herrera, Journal of Contaminant Hydrology 118 (2010) 117.
- [18] Y.H. Wang, J.K. Lee, Journal of Molecular Catalysis A: Chemical 263 (2007) 163.
- [19] J.H. Huang, Y.F. Liu, X.G. Wang, Journal of Hazardous Materials 160 (2008) 382.