

# Catalytic behaviors of silica-supported chitin–platinum complex for asymmetric hydrogenation of $\alpha$ -phenylethanol

Guo-Li Yuan, Mao-Ya Yin, Ting-Ting Jiang, Mei-Yu Huang, Ying-Yan Jiang<sup>\*</sup>

*Institute of Chemistry, Chinese Academy of Sciences, Zhongguancun, Beijing 100080, People's Republic of China*

## Abstract

Silica-supported chitin–platinum complex ( $\text{SiO}_2\text{-CT-Pt}$ ) has been prepared and found to be a high stereoselective catalyst for asymmetric hydrogenation of racemic  $\alpha$ -phenylethanol to *R*-(+)-1-cyclohexyl ethanol at 30°C and under an atmospheric hydrogen pressure. The optical selectivity of *R*-(+)-1-cyclohexyl ethanol amounted to 100% when a fitting condition was selected. In this case, the yield and optical selectivity were affected greatly by many factors, such as Pt content in  $\text{SiO}_2\text{-CT-Pt}$  complex, the reaction temperature, the solvent, and the amount of the additive of hydrochloric acid, etc.  $\text{SiO}_2\text{-CT-Pt}$  catalyst also has shown high stability. The optical selectivity for *R*-(+)-1-cyclohexyl ethanol was almost keeping at 100% when the catalyst was reused for many times. Moreover,  $\text{SiO}_2\text{-CT-Pt}$  complex is an economical chiral catalyst. The chitin is an abundant natural biopolymer and the procedure for preparation of the complex is very simple. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Silica-supported chitin–platinum complex; Asymmetric hydrogenation; Optical activity;  $\alpha$ -Phenyl ethanol; *R*-(+)-1-cyclohexyl ethanol

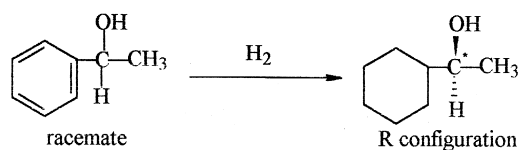
## 1. Introduction

Asymmetric reduction of acetylcyclohexane has been reported as one of the best methods to obtain *R*-(+)-1-cyclohexyl ethanol [1–3]. In these cases, one equivalent chiral reagent was used, such as, (*R,R*)-2,5-dimethylborolane,  $\beta$ -chlorodiiso-2-ethylapopinocampheylborane and titanocene. Another reported method for preparation of *R*-(+)-1-cyclohexyl ethanol was to hydroborate unsaturated alkene, which also need one equivalent of borane [4]. However,

these reagents are all expensive and unstable to be recovered for reuse. So, any one of the methods mentioned above costs too high for preparation of *R*-(+)-1-cyclohexyl ethanol.

It has been reported that a palladium complex of a natural polymer, silk, could catalyze the asymmetric hydrogenation of some unsaturated compounds, especially imines, but the optical yields were not high [5]. In previous papers, natural biopolymer–metal complex, chitin–Pd complex [6], and silica-supported chitin–Pt complex [7] have been found to be able to catalyze the hydrogenation of various compounds under mild condition, but never for asymmetric hydrogenation.

<sup>\*</sup> Corresponding author. Fax: +86-10-6255-9368.



Scheme 1.

Recently, a platinum complex of silica-supported chitin ( $\text{SiO}_2\text{-CT-Pt}$ ) was found to be able to catalyze the racemic  $\alpha$ -phenyl ethanol to *R*-(+)-1-cyclohexyl ethanol at 30°C and under an atmospheric hydrogen pressure (Scheme 1). The enantioselectivity of products reached 100% when fitting condition was selected. At the same time, this catalyst was very stable for reuse.

It has been reported that hydrogenation of  $\alpha$ -phenyl ethanol could obtain 1-cyclohexyl ethanol by Pt catalyst, but the yield was only 20–35% without optical activity [8].

Chitin is an abundant natural biopolymer, which widely dispersed in living organisms. It was manufactured commercially from crustaceans of crabs and lobsters. Furthermore, chitin is a chiral biopolymer. As shown in the structure of chitin (Fig. 1), besides including stereogenic carbon atom in every repeated unit of molecular chain, chitin is shaped in the form of a helix structure [9]. There is no doubt that chirality is the natural character of the helix structure. However, it is difficult to get the specific rotation of chitin, because chitin is insoluble to common solvent. While the chitin was deacetylated into chitosan, the specific rotation could be measured,  $[\alpha]_D^{20} + 250$  (c 0.5, 2%  $\text{CH}_3\text{COOH}$ ) [10]. Thus, it is proved that chitin is an optically active biopolymer, and could coordinate with platinum ions to form a chiral  $\text{SiO}_2\text{-CT-Pt}$  complex for asymmetric hydrogenation.

## 2. Experimental

### 2.1. Materials

Silica (specific surface area: 370  $\text{m}^2/\text{g}$ ) was obtained from Shenyang Chemical Reagent Fac-

tory. Chitin was commercial product. All reagents were of analytical grad and without further purification,  $\alpha$ -phenyl ethanol was got as a racemate.

### 2.2. Preparation of $\text{SiO}_2\text{-CT-Pt}$ complex

The method for preparation of silica-supported chitin ( $\text{SiO}_2\text{-CT}$ ) is following a weight ratio of  $\text{CT}/\text{SiO}_2 = 1:2$ . Chitin weighting 5 and 10 g of silica powder were mixed and ground to 200 mesh for using the next step.

Several samples of  $\text{SiO}_2\text{-CT-Pt}$  complex with different Pt content were prepared by the reaction of a constant amount of  $\text{SiO}_2\text{-CT}$  with various amounts of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in ethanol solution, respectively (shown in Fig. 2). For example, a 25-ml flask, equipped with magnetic stirrer and reflux condenser, was charged with 1 g of  $\text{SiO}_2\text{-CT}$  powder, 0.1 mmol of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (in ethanol solution) and 10 ml ethanol. The mixture was stirred and refluxed under an atmosphere of nitrogen for 4 h. The white powder became dark gray, and the solution became colorless and transparent from yellow. After being filtered, washed with ethanol and dried, about 1 g of dark gray product ( $\text{SiO}_2\text{-CT-Pt}$ ) was obtained. In this case, the content of Pt in the  $\text{SiO}_2\text{-CT-Pt}$  complex was 0.1 mmol/g.

### 2.3. Hydrogenation of $\alpha$ -phenyl ethanol

A 25-ml flask was charged with 0.1 g of catalyst ( $\text{SiO}_2\text{-CT-Pt}$ ), 1 mmol of  $\alpha$ -phenyl ethanol, 5 ml of solvent and 0.2 ml of 0.1 mol/l

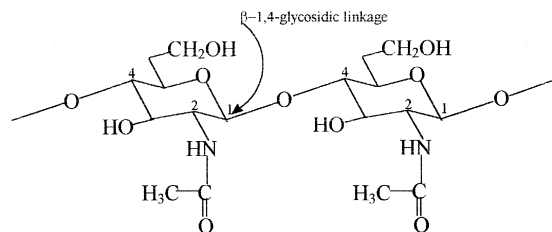


Fig. 1. The structure of chitin.

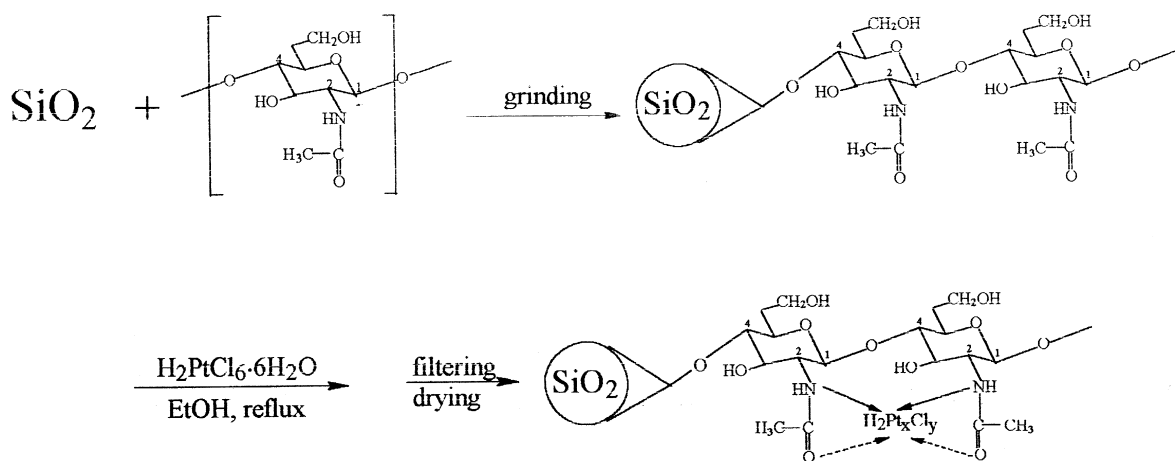


Fig. 2. The procedure for preparation of SiO<sub>2</sub>-CT-Pt complex.

of hydrochloric acid aqueous solution, which was equipped with magnetic stirrer and hydrogenation inlet tube connected to a hydrogen volume measuring burette and a hydrogen storage cylinder. The hydrogenation reaction system was alternatively evacuated and flushed with hydrogen several times, and the hydrogenation was carried out at a definite temperature and under an atmospheric hydrogen pressure for several hours. The reaction mixture was then filtered in order to separate and recover the catalyst for reuse. The composition of hydrogenation products was analyzed by gas chro-

matography and the optical rotation was measured by automatic polarimeter.

### 3. Results and discussion

#### 3.1. Effect of Pt content in SiO<sub>2</sub>-CT-Pt complex

The influence of Pt content in SiO<sub>2</sub>-CT-Pt complex on catalytic activity and stereoselectivity in the hydrogenation of  $\alpha$ -phenyl ethanol is given in Table 1. It is observed that the value of

Table 1

Asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed by SiO<sub>2</sub>-CT-Pt complex with various Pt content in the complex  
Conditions: catalyst, SiO<sub>2</sub>-CT-Pt 0.1 g; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent, ethanol 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution), 0.02 mmol; 30°C, 1 atm H<sub>2</sub>, 24 h.

Pt content in SiO <sub>2</sub> -CT-Pt complex (mmol/g)	Conversion of $\alpha$ -phenyl ethanol (%)	Product, 1-cyclohexyl ethanol			
		Yield (%)	$[\alpha]_D^{20}$ (°)	<i>ee</i> <sup>a</sup> (%)	Abs. <sup>b</sup> config.
0.050	40.2	40.2	+10.8	100	R
0.100	65.0	65.0	+10.8	100	R
0.116	68.4	68.4	+10.2	94.4	R
0.154	70.0	70.0	+8.7	80.6	R
0.193	78.0	78.0	+6.8	63.0	R
0.250	90.2	90.2	+2.0	18.5	R

<sup>a</sup>Enantiomer excess were calculated on basis of reported values for specific rotation of pure enantiomer: (*R*)-(+)-1-cyclohexyl ethanol = +10.6° (c 2.25, CCl<sub>4</sub>) with 97.9% *ee* [4].

<sup>b</sup>The absolute configuration was determined by comparison of optical rotation with literature reference.

conversion of  $\alpha$ -phenyl ethanol is equal to the yield of 1-cyclohexyl ethanol although Pt content in the complex changes, so the selectivity of the catalyst is not influenced by the Pt content in  $\text{SiO}_2\text{-CT-Pt}$  catalyst. However, the yield and the optical yield were affected greatly by the Pt content in the catalyst. The yield of 1-cyclohexyl ethanol is increasing as the content of Pt increasing. On the contrary, the value of *ee* for *R*-(+)-1-cyclohexyl ethanol is decreasing as the Pt content increases, while the Pt content in catalyst exceeds 0.1 mmol/g. Thus, it can be understood that all of Pt active centers are chiral catalytic centers for hydrogenation when the Pt content is below 0.1 mmol/g in  $\text{SiO}_2\text{-CT-Pt}$  complex, but only some of Pt active centers are chiral and the others are achiral when it is beyond 0.1 mmol/g.

### 3.2. Effect of the reaction temperature

Table 2 shows the result of asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed by  $\text{SiO}_2\text{-CT-Pt}$  complex at different temperature. It can be seen that the reaction temperature is a critical condition for optical selectivity. The enantiomer excess of *R*-(+)-1-cyclohexyl ethanol is kept at 100%, while the reaction tempera-

Table 2

Asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed by  $\text{SiO}_2\text{-CT-Pt}$  complex at different temperature

Conditions: catalyst,  $\text{SiO}_2\text{-CT-Pt}$  0.1 g, Pt 0.01 mmol; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent, ethanol 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution), 0.02 mmol; 1 atm  $\text{H}_2$ , 24 h.

Temperature (°C)	Conversion of $\alpha$ -phenyl ethanol (%)	1-Cyclohexyl ethanol	
		Yield (%)	<i>ee</i> for <i>R</i> config. <sup>a</sup> (%)
20	35.5	35.5	100
25	50	50	100
30	65	65	100
40	72.5	72.5	87.5
50	47.5	47.5	12.1
60	30.5	30.5	0
70	15.0	15.0	0

<sup>a</sup>The method for calculation and identification same as Table 1.

Table 3

Asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed by  $\text{SiO}_2\text{-CT-Pt}$  complex in various solvents

Conditions: catalyst,  $\text{SiO}_2\text{-CT-Pt}$  0.1 g, Pt 0.01 mmol; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution), 0.02 mmol; 30°C, 1 atm  $\text{H}_2$ , 24 h.

Solvent	Conversion of $\alpha$ -phenyl ethanol (%)	1-Cyclohexyl ethanol	
		Yield (%)	<i>ee</i> for <i>R</i> config. <sup>a</sup> (%)
Ethanol	65.0	65.0	100
Methanol	32.8	32.8	95
1,2-Dichloroethanol	10.7	10.7	0
Cyclohexane	21	21	44.9
1,4-Dioxane	13.5	13.5	97.8

<sup>a</sup>The method for calculation and identification same as Table 1.

ture is not higher than 30°C, but it changes to 0% while temperature rise to 60°C. It is not difficult to understand that one kind of enantiomers was produced accompanying with another enantiomer at high reaction temperature. In this case, the product, *R*-(+)-1-cyclohexyl ethanol was produced with one equivalent of *S*-(-)-1-cyclohexyl ethanol. Because the pair of enantiomers became equal, the enantiomer excesses of product changed to 0%, and the product became an optically inactive racemate.

At same time, the yield of *R*-(+)-1-cyclohexyl ethanol was also effected by reaction temperature. The highest hydrogenation yield of 1-cyclohexyl ethanol (72.5%) occurs at 40°C, although the optical yield is just 87.5% in this temperature. While the temperature is above 40°C, the partial hydrogen pressure in the reaction flask decreases for the evaporation of solvent as the reaction system is kept at one atmospheric pressure. Thus, the hydrogenation rate is down and low yield occurs.

### 3.3. Effect of solvent

Table 3 shows asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed by  $\text{SiO}_2\text{-CT-Pt}$  complex in various solvents. It is clear that the solvent plays an important role in this catalytic reaction. Ethanol is the optimum-selected sol-

vent in asymmetric hydrogenation of  $\alpha$ -phenyl ethanol to obtain *R*-(+)-1-cyclohexyl ethanol catalyzed by  $\text{SiO}_2$ -CT-Pt complex, and the highest yield reaches 65% with 100% *ee*. However, the catalytic activity and the stereoselectivity are very low in the solvent of 1,2-dichloroethane and 1,4-dioxane.

The effect of an additive on the asymmetric hydrogenation of  $\alpha$ -phenyl ethanol over  $\text{SiO}_2$ -CT-Pt was also studied, and the result is shown in Fig. 3. The catalytic activity of  $\text{SiO}_2$ -CT-Pt was highest when 0.02 mmol hydrochloric acid was added to the reaction system.

### 3.4. Effect of time

Fig. 4 shows that relationship between the reaction time and the catalytic activity and stereoselectivity of the  $\text{SiO}_2$ -CT-Pt catalyst for asymmetric hydrogenation of  $\alpha$ -phenyl ethanol. The stereoselectivity of the catalyst is also not changed with time delay; moreover, the value of *ee* is kept at 100%. This result reflects the optical stability of the catalyst for this reaction. The yield increases slowly over 24 h, increasing of for just 15% in 12 h; thus, the catalytic activity of  $\text{SiO}_2$ -CT-Pt complex is decreases with the time delay.

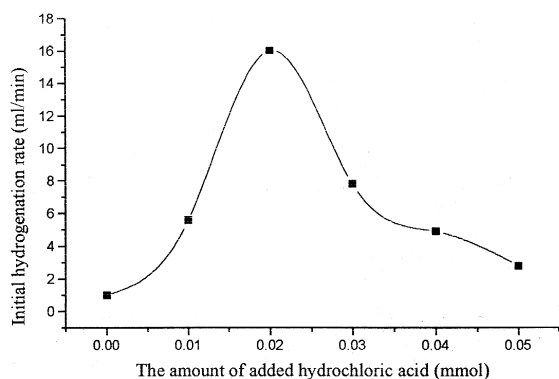


Fig. 3. The relationship between initial hydrogenation rate and the amount of added hydrochloric acid in the reaction solution. Conditions: catalyst,  $\text{SiO}_2$ -CT-Pt 0.1 g, Pt 0.01 mmol; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent, ethanol 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution); 30°C, 1 atm  $\text{H}_2$ , 24 h.

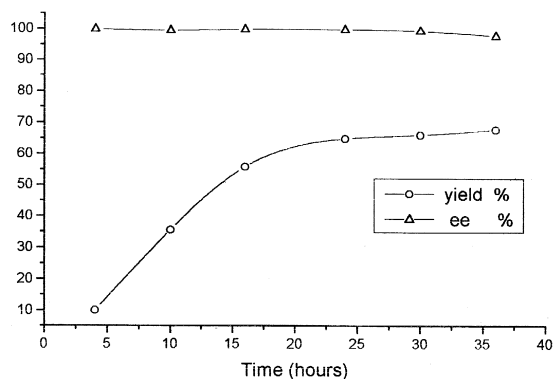


Fig. 4. The relationship between the reaction time and the yield (the yield of 1-cyclohexyl ethanol) and *ee* (enantiomer excess of *R*-(+)-1-cyclohexyl ethanol). Conditions: catalyst,  $\text{SiO}_2$ -CT-Pt 0.1 g, Pt 0.01 mmol; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent, ethanol 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution) 0.02 mmol; 30°C, 1 atm  $\text{H}_2$ , 24 h.

### 3.5. Recovery of the catalyst

Table 4 shows asymmetric hydrogenation of  $\alpha$ -phenyl ethanol over the recovered  $\text{SiO}_2$ -CT-Pt complex. When the catalyst was reused for six times, the yield of 1-cyclohexyl ethanol has almost no remarkable change, and the enantiomer excess of the product was steady or close to 100% in every reaction time by reused catalyst. Hence, the  $\text{SiO}_2$ -CT-Pt catalyst does not

Table 4

Asymmetric hydrogenation of  $\alpha$ -phenyl ethanol catalyzed over recovered  $\text{SiO}_2$ -CT-Pt complex

Conditions: catalyst,  $\text{SiO}_2$ -CT-Pt 0.1 g, Pt 0.01 mmol; substrate,  $\alpha$ -phenyl ethanol 1 mmol; solvent, ethanol 5 ml; additive, hydrochloric acid (in 0.1 mol/l aqueous solution), 0.02 mmol; 30°C, 1 atm  $\text{H}_2$ , 24 h.

Number of times of catalyst reused	Conversion of $\alpha$ -phenyl ethanol (%)	Product, 1-cyclohexyl ethanol	
		Yield (%)	<i>ee</i> <sup>a</sup> for <i>R</i> config. (%)
1	65.0	65.0	100
2	64.8	64.8	99.8
3	61.8	61.8	100
4	63.0	63.0	99.5
5	62.5	62.5	99.0
6	61.6	61.6	98.7

<sup>a</sup>The method for calculation and identification same as Table 1.

only have high catalytic activity and stereoselectivity, but it is also very stable for asymmetric hydrogenation of  $\alpha$ -phenyl ethanol in obtaining *R*-(+)-1-cyclohexyl ethanol.

#### 4. Conclusions

A silica-supported chitin–platinum complex ( $\text{SiO}_2$ –CT–Pt) is prepared by a simple method, the mixture of silica and chitin being ground and coordinated with  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , then filtered and dried for use.

It has been found that  $\text{SiO}_2$ –CT–Pt complex was a chiral catalyst, and it has high catalytic activity and stereoselectivity for asymmetric hydrogenation of  $\alpha$ -phenyl ethanol to *R*-(+)-1-cyclohexyl ethanol with 65% yield and 100% *ee*. Furthermore, the  $\text{SiO}_2$ –CT–Pt catalyst was very stable for reuse above six times, and the catalytic and optical activity was almost not changed. Therefore, the  $\text{SiO}_2$ –CT–Pt complex is an economical and effective catalyst for

asymmetric hydrogenation of  $\alpha$ -phenyl ethanol in obtaining *R*-(+)-1-cyclohexyl ethanol.

#### References

- [1] T. Imai, T. Tamura, A. Yamamuro, T. Sato, T.A. Wollman, R.M. Kennedy, S. Masamune, *J. Am. Chem. Soc.* 108 (1986) 7402.
- [2] H.C. Brown, P.V. Ramachadran, A.V. Teodorovic, S. Swaminathan, *Tetrahedron Lett.* 46 (1991) 6991.
- [3] M.B. Carter, B. Schifft, A. Gutiérrez, S.L. Buchwald, *J. Am. Chem. Soc.* 116 (1994) 11667.
- [4] S. Masamune, B.M. Kim, J.S. Petersen, T. Sato, S.J. Veestra, T. Imai, *J. Am. Chem. Soc.* 107 (1985) 4549.
- [5] S. Akabori, Y. Izumi, Y. Fujii, S. Sakurai, *Nature* 178 (1956) 323.
- [6] X.X. Wang, M.Y. Huang, Y.Y. Jiang, *Markromol. Chem., Macromol. Symp.* 59 (1992) 113.
- [7] M. Zhang, M.Y. Huang, Y.Y. Jiang, 3rd China–Japan Bila. Symp. on Effect. Util. of Carbon Resources, preprints, Guangzhou, China, 1991, P171.
- [8] D.K. Sanders, S.D. Lin, M.A. Vannice, *J. Catal.* 147 (1) (1994) 375.
- [9] S.R. Buxton, S.M. Roberts, *Guide to Organic Stereochemistry*, Addison Wesley Longman, London, 1996.
- [10] H. Takeda, K. Kadowaki, *Agric. Biol. Chem.* 49 (1985) 3151.