

Asymmetric hydrogenation of ketones catalyzed by a silica-supported chitosan–palladium complex

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Abstract

A silica-supported chitosan–palladium complex has been found to catalyze the asymmetric hydrogenation of some ketones to corresponding chiral alcohols, such as acetophenone to (*R*)-1-phenyl ethanol, propiophenone to (*R*)-1-phenyl-1-propanol, 3-methyl-2-butanone to (*R*)-3-methyl-2-butanol, and 4-methyl-2-pentanone to (*R*)-4-methyl-2-pentanol at room temperature and under 1 atm H₂. The optical yield was greatly affected by N:Pd mole ratio in the complex and a little change in the structure of ketone. The optical yields of (*R*)-1-phenylethanol and (*R*)-3-methyl-2-butanol could be obtained in 99 and 100%, respectively. This chiral natural polymer–palladium complex catalyst was very easy to prepare, and could be reused without appreciable change in optical catalytic activity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Asymmetric hydrogenation; Ketones; Chitosan–palladium complex

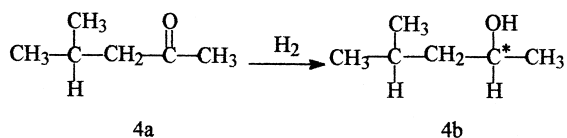
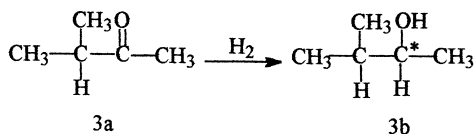
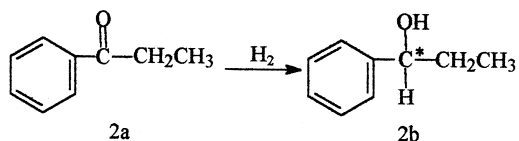
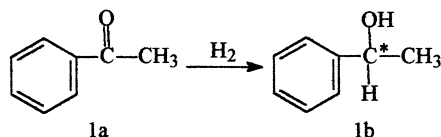
1. Introduction

Chitosan is a natural biopolymer. It can be easily obtained from chitin which is widely dispersed in living organisms, such as crustaceans of crab, lobster etc. In the previous papers [1–3], a silica-supported chitosan–palladium complex (abbreviated as SiO₂–CS–Pd) has been found to catalyze the hydrogenation of nitrobenzene, hexene-1, acrylic acid, chloronitrobenzene and phenol to aniline, hexane, propionic acid, chloroaniline and cyclohexone in high yield at 30–70°C and under atmospheric pressure. Chitosan is an optically active polymer, [α]_D²⁰ + 250°(c 0.5, 2% CH₃COOH) [4], and the amino groups in chitosan may coordinate with palladium ions to form a chiral polymer–palladium complex. However, such a complex has not been used as chiral catalyst for asymmetric hydrogenation in the previous papers [1–3].

Recently, the SiO₂–CS–Pd complex has been found to catalyze the asymmetric hydrogenation of some ketones to corresponding chiral alcohols, such as acetophenone (**1a**) to (*R*)-1-phenylethanol (**1b**), propiophenone (**2a**) to (*R*)-1-phenyl-1-propanol (**2b**), 3-methyl-2-butanone (**3a**) to (*R*)-3-methyl-2-butanol (**3b**), and 4-methyl-2-pentanone (**4a**) to (*R*)-4-methyl-2-pentanol (**4b**) at room temperature

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and under 1 atm H_2 . The influence of N:Pd mole ratio in SiO_2 -CS-Pd complex on the optical yields of chiral alcohols was researched, and the stability of the complex catalyst was determined by the method of reusing.



2. Experimental

2.1. Preparation of silica-supported chitosan (SiO_2 -CS)

Ten grams of chitosan and 570 ml of 1.5% acetic aqueous solution were placed in a 1000-ml three-necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel. After dissolving chitosan with stirring at $50^\circ C$, 100 g of silica (prepared by precipitation method; surface area: $90\text{ m}^2/\text{g}$) was added to the solution. The mixture was stirred, then 4 N sodium hydroxide aqueous solution was added dropwise to cause chitosan to deposit on the surface of silica. Chitosan could be deposited completely on the surface of silica by adjusting the pH value of the solution to 13. The product was filtered and washed with water until the pH value of the filtrate became 8, then dried by infra-red ray to obtain 109.8 g of fine white particles, SiO_2 -CS. The nitrogen content was determined to be 0.79 wt.% by elemental analysis.

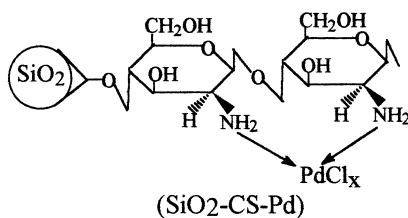
2.2. Preparation of silica-supported chitosan–palladium complex ($\text{SiO}_2\text{-CS-Pd}$)

Several samples of the $\text{SiO}_2\text{-CS-Pd}$ complex with different Pd content were prepared. They have following N:Pd mole ratio in $\text{SiO}_2\text{-CS-Pd}$ complex.

Pd content in $\text{SiO}_2\text{-CS-Pd}$ (mmol/g)	N:Pd mole ratio in $\text{SiO}_2\text{-CS-Pd}$
0.12	4.7
0.18	3.1
0.24	2.3
0.30	1.9

For example, in order to obtain a sample with N:Pd mole ratio of 3.1, 1 g of $\text{SiO}_2\text{-CS}$ (N, 0.79 wt.%), 0.12 mmol of $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ and 10 ml of ethanol were placed in a flask equipped with magnetic stirrer and a reflux condenser. The mixture was stirred and refluxed for 6 h to cause solid particles to become dark grey, and the solution to become colorless and transparent. The product was filtered, washed with ethanol and dried to obtain about 1 g of dark grey powder ($\text{SiO}_2\text{-CS-Pd}$).

Table 1 shows the X-ray photoelectron spectroscopy (XPS) data for $\text{SiO}_2\text{-CS-Pd}$, $\text{SiO}_2\text{-CS}$ and PdCl_2 . It can be seen that the binding energies of Si_{2p} and O_{1s} in $\text{SiO}_2\text{-CS-Pd}$ are similar to those in $\text{SiO}_2\text{-CS}$, and Cl_{2p} binding energy of $\text{SiO}_2\text{-CS-Pd}$ is similar to that of PdCl_2 . However, the difference of N_{1s} binding energies between $\text{SiO}_2\text{-CS-Pd}$ and $\text{SiO}_2\text{-CS}$ is 1.0 eV, and the difference of $\text{Pd}_{3d 5/2}$ binding energies between $\text{SiO}_2\text{-CS-Pd}$ and PdCl_2 is 2.0 eV. These results show that coordination bonds are formed between two nitrogen atoms and a palladium atom in the complex as follows:



2.3. Hydrogenation of ketones

0.1 g of catalyst ($\text{SiO}_2\text{-CS-Pd}$), 0.1 g of ketone and 5 ml of solvent (ethanol) were placed in a 25-ml flask equipped with magnetic stirrer and a hydrogen inlet tube which was connected to a hydrogen volume measuring burette and a hydrogen storage cylinder. The hydrogenation reaction

Table 1
X-ray photoelectron spectroscopy (XPS) data for $\text{SiO}_2\text{-CS-Pd}$, $\text{SiO}_2\text{-CS}$ and PdCl_2

XPS peak	Binding energy (eV)		
	$\text{SiO}_2\text{-CS-Pd}$	$\text{SiO}_2\text{-CS}$	PdCl_2
$\text{Pd}_{3d 5/2}$	336.6	–	338.6
N_{1s}	400.7	401.7	–
$\text{Si}_{2p 3/2}$	285.6	285.5	–
O_{1s}	104.1	104.1	–
Cl_{2p}	109.7	–	109.8

system was alternately evacuated and flushed with hydrogen for several times, and hydrogenation was carried out at 30°C and under 1 atm H₂ for 8 h. Then the reaction mixture was filtered in order to separate and recover the catalyst. Sometimes, the recovered catalyst was reused. The composition of the hydrogenation products was analyzed by GC, and the optical rotation was measured by polarimeter.

3. Results and discussion

Table 2 shows the results of asymmetric hydrogenation of aromatic ketones, acetophenone and propiophenone by SiO₂–CS–Pd complex catalyst. It can be seen that the yields and optical yields of 1-phenylethanol and 1-phenyl-1-propanol are greatly affected by N:Pd mole ratio in SiO₂–CS–Pd complex. In the case of hydrogenation of acetophenone, the optical yield of (*R*)-1-phenyl ethanol reached 98.1 and 99.1% at the N:Pd mole ratio of 3.1 and 2.3, respectively. In the case of the hydrogenation of propiophenone, the optical yields of (*R*)-1-phenyl-1-propanol were relatively low at the same N:Pd mole ratio. These results show that the structures of acetophenone and propiophenone are different only a little, but the results of asymmetric hydrogenation are different considerably by such a polymeric catalyst, SiO₂–CS–Pd.

Table 3 shows the results of the asymmetric hydrogenation of aliphatic ketones, 3-methyl-2-butanone and 4-methyl-2-pentanone by SiO₂–CS–Pd complex catalyst. The yields of alcohols were all obtained near 100%, so did not show them in the table. It can be seen that in the case of the hydrogenation of 3-methyl-2-butanone, the optical yield of (*R*)-3-methyl-2-butanol amounts to 100% at the N:Pd mole ratio of 4.7, 3.1 or 2.3, and the optical yield is not changed (at N:Pd, 2.3) or changed a little (at N:Pd, 3.1) when the complex catalyst is reused. This is a very important result for the practical application. In the case of the hydrogenation of 4-methyl-2-pentanone, the optical yields of (*R*)-4-methyl-2-pentanol are relatively low. These results also show that the structures of 3-methyl-2-butanone and 4-methyl-2-pentanone are very similar, but the results of the hydrogenation of both are fairly different.

It has been reported that the asymmetric hydrogenation of **1a** to **1b** and **2a** to **2b** could be catalyzed by a chiral Rh complex of hydroxyalkylferrocenyl phosphine under 50 atm, but the optical yields were

Table 2
Asymmetric hydrogenation of aromatic ketones catalyzed by SiO₂–CS–Pd complex

Ketone	N:Pd mol ratio in SiO ₂ –CS–Pd	Alcohol produced			
		Yield (%)	[α] _D ²⁰ (deg)	Optical yield ^a (%)	Absolute configuration ^b
Acetophenone	4.7	13.2	+44.7	85.1	<i>R</i>
	3.1	37.7	+51.5	98.1	<i>R</i>
	2.3	41.7	+52.0	99.1	<i>R</i>
	1.9	73.9	+21.2	40.4	<i>R</i>
Propiophenone	4.7	29.3	+38.5	81.9	<i>R</i>
	3.1	49.2	+21.1	44.9	<i>R</i>
	1.9	93.9	+9.4	20.0	<i>R</i>

Catalyst, SiO₂–CS–Pd, 0.1 g; ketone, 0.1 g; solvent, 5 ml ethanol, 30°C, 1 atm H₂, 8 h.

^aOptical yields were calculated on the basis of reported values for the specific rotation of pure enantiomer: (*S*)-1-phenyl-1-ethanol, [α]_D²⁰-52.5°(c 2.27, CH₂Cl₂) [6]; (*S*)-1-phenyl-1-propanol, [α]_D²⁰-47.03°(Me₂CO) [6].

^bDetermined by the sign of optical rotation.

Table 3
Asymmetric hydrogenation of aliphatic ketones catalyzed by SiO₂–CS–Pd complex

Ketone	N:Pd mole ratio in SiO ₂ –CS–Pd	Number of used times of catalyst	Alcohol produced	
			Optical yield ^a (%)	Absolute configuration ^b
3-Methyl-2-butanone	4.7	1	100	<i>R</i>
		2	81.6	<i>R</i>
		3	77.3	<i>R</i>
	3.1	1	100	<i>R</i>
		2	99.1	<i>R</i>
		1	100	<i>R</i>
2.3	1	100	<i>R</i>	
	2	100	<i>R</i>	
	3	100	<i>R</i>	
4-Methyl-2-pentanone	4.7	1	67.8	<i>R</i>
	2.3	2	53.0	<i>R</i>
	1.9	3	34.7	<i>R</i>

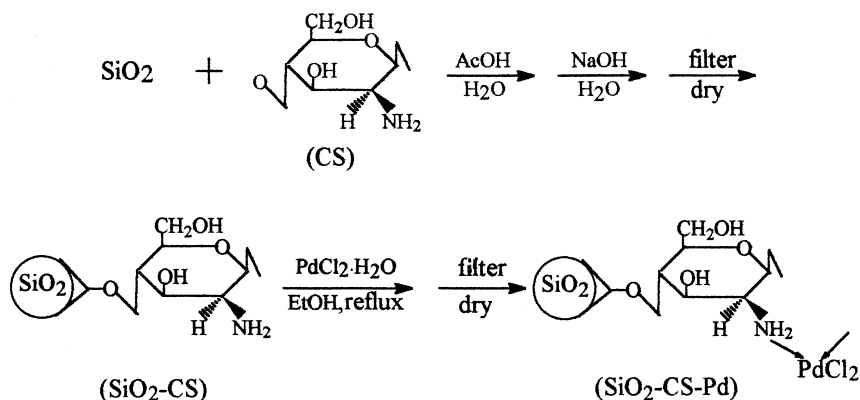
Catalyst, SiO₂–CS–Pd, 0.1 g; ketone, 0.1 g, solvent, 5 ml ethanol; 30°C, 1 atm H₂, 8 h.

^aOptical yields were calculated on the basis of reported values for the specific rotation of pure enantiomer: (R)-3-methyl-2-butanol, [α]_D +5.3°(neat) [7]; (S)-4-methyl-2-pentanol, [α]_D-20.5°(neat) [7].

^bDetermined by the sign of optical rotation.

not so high, only 43, and 30% [5]. Obviously, such a homogeneous Rh complex catalyst is difficult to prepare and unstable. **1b** and **2b** could also be obtained by asymmetric reduction of **1a** and **2a** with a reagent prepared from (*S*)-(-)-2-amino-3-methyl-1, 1-diphenylbutan-1-ol and borane in high optical yields [6]. This reagent could also be used for asymmetric reduction of **3a** to **3b** and **4a** to **4b** in 60 and 61% optical yields. Anyway, such a reduction method using reagent is not economical.

A bio-polymer, chitosan (CS) is a very abundant and cheap material for preparing chiral polymer ligand. In order to obtain an effective ligand, the chitosan was dissolved in dilute acetic acid aqueous solution and mixed with fine silica particles, then the acid was neutralized to deposit chitosan on the surface of silica particles to obtain a polymer ligand, SiO₂–CS. The SiO₂–CS–Pd complex was obtained by the reaction of SiO₂–CS with PdCl₂·2H₂O in ethanol solution. The scheme of preparation of SiO₂–CS–Pd complex may be shown as follows:



The preparation method is very simple, so such a chiral polymer–Pd complex, SiO₂–CS–Pd, can be obtained only in one or two days.

Above experimental results indicated that the $\text{SiO}_2\text{-CS-Pd}$ complex could catalyze the asymmetric hydrogenation of some ketones at room temperature and under 1 atm H_2 . The optical yield was very sensitive to N:Pd mole ratio in the complex and a little change in the structure of ketone.

The optical yields of (*R*)-1-phenylethanol and (*R*)-3-methyl-2-butanol could be obtained in 99 and 100%, respectively. This chiral bio-polymer-palladium complex catalyst was very easy to prepare, and could be reused without appreciable change in the optical catalytic activity.

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