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Enantioselective hydrogenation of ethyl pyruvate catalyzed by PVP-stabilized rhodium nanoclusters

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Abstract

The enantioselective hydrogenation of ethyl pyruvate catalyzed by polyvinylpyrrolidone-stabilized rhodium nanocluster (Rh/PVP) modified by cinchonidine and quinine was studied. The results show that cinchonidine and quinine not only can induce the enantioselectivity in the hydrogenation of ethyl pyruvate, but also can greatly accelerate the reaction. Under the optimum conditions, 298 K, 5 MPa of hydrogen pressure and 4.3×10^{-3} mol/l of cinchonidine in tetrahydrofuran, the enantiomeric excess of *R*-(+)-ethyl lactate and turnover frequency (TOF) of ethyl pyruvate reach up to 42.2% e.e. and 941 h^{-1}, respectively. The rate of hydrogenation is faster by a factor of about 50 in the presence of cinchonidine than that without it. Quinine exhibits the similar effect.

Keywords: Enantioselective; Hydrogenation; Cinchonidine; Rhodium; Nanocluster

1. Introduction

Because of the high surface area and high quantum size effect, nanoclusters have generated intense interest over the past decade and have become an important branch in the field of catalysis [1–2]. Nanoclusters not only can be employed as catalysts in quasi-homogeneous catalysis, but also can serve as precursors for heterogeneous catalysis [3]. Among many kinds of transition metal nanocluster catalysts, rhodium catalyst has very high activity and chemiselectivity in hydrogenation of unsaturated and carbonyl compounds [4–9]. However, the results of the enantioselective hydrogenation of α-ketoesters in the presence of cinchonidine indicate that only Pt is effective catalyst (with more than 95% e.e.), and Ir, Rh catalysts have low enantioselectivity [10–14]. In this paper, the application of rhodium nanocluster modified by cinchonidine and quinine to enantioselective hydrogenation of ethyl pyruvate (Scheme 1) is studied. The results show that the modified rhodium nanocluster catalyst is better than the conventional heterogeneous rhodium catalysts (with less than 30% e.e.) in enantioselective hydrogenation of ethyl pyruvate [11].

2. Results and discussion

The polyvinylpyrrolidone stabilized rhodium nanocluster (designated as Rh/PVP) was prepared by reduction in water–alcohol solution according to the literatures [15–16]. The rhodium nanocluster is finely

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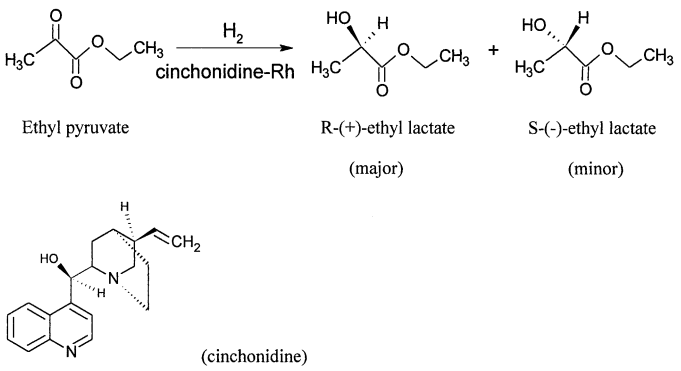

Scheme 1. Enantioselective hydrogenation of ethyl pyruvate.

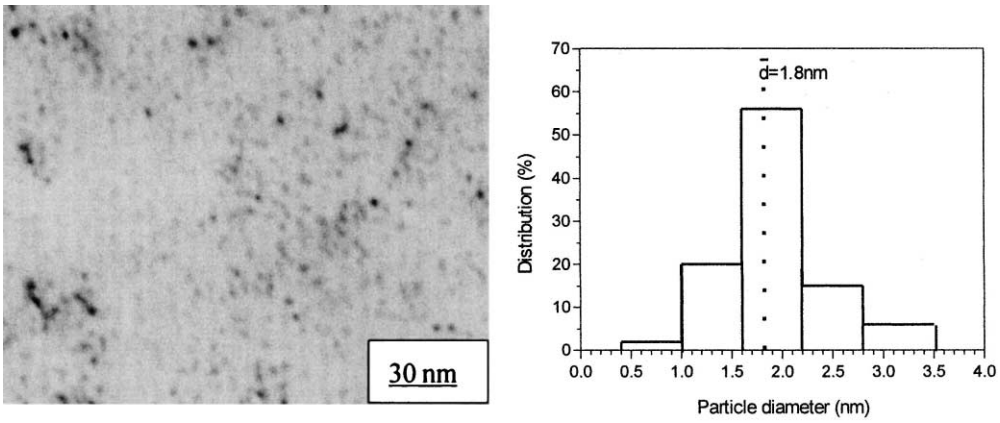

Fig. 1. TEM photograph (left) and the histogram plot of the particle size distribution (right) of the Rh/PVP nanocluster.

dispersed and can be stored in air for a long time without aggregation. The size of rhodium nanocluster was measured by transmission electron microscopy (TEM) (Fig. 1). The average diameter of nanoclusters is about 1.8 nm, as shown in Fig. 1.

As a chiral modifier, cinchonidine not only can induce enantioselectivity with about 42% e.e. for *R*-(+)-ethyl lactate, but also can accelerate the hydrogenation rate of ethyl pyruvate (Fig. 2). These results indicate that the enantioselective hydrogenation of ethyl pyruvate over rhodium nanocluster is a ligand-accelerated catalysis. The average reaction rate can be accelerated by a factor of about 50 (TOF rises from $18\,h^{-1}$ without cinchonidine to $941\,h^{-1}$ when the concentration of cinchonidine is about

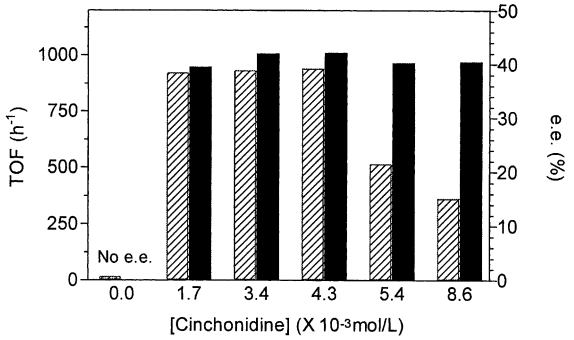

Fig. 2. The effect of cinchonidine concentration on TOF and enantioselectivity.

Table 1
Effect of pyridine, quinoline, alcohol, quinine and cinchonidine on the TOF

Additive	Concentration ($\times 10^{-3}$ mol/l)	TOF (h^{-1})	e.e. (%)	Configuration
No	–	18	0	–
Pyridine	4.3	16	0	–
Quinoline	4.3	20	0	–
Pyridine + quinoline (1:1)	4.3	19	0	–
Iso-propyl alcohol	4.3	21	0	–
Quinine	4.3	900	40.1	(*R*)
Cinchonidine	4.3	941	42.2	(*R*)

4.3×10^{-3} mol/l). However, the high concentration of cinchonidine is unfavorable for reaction rate, as shown in Fig. 2. It is possible that the active sites of Rh catalyst are partly blocked by high concentration cinchonidine owing to its competitive coordination.

In order to specify what functional group(s) in cinchonidine is responsible for the improvement of the catalytic properties, the additive effect of pyridine, quinoline, alcohol and quinine has been investigated. The data listed in Table 1 show that pyridine, quinoline and iso-propyl alcohol can not promote the hydrogenation of ethyl pyruvate, however quinine and cinchonidine exhibit obvious acceleration. The results suggest that the synergistic effect of azabicyclo[2.2.2]octane and hydroxyl group in cinchonidine and quinine molecule may play an important role for accelerating the hydrogenation, while the existence of the two chiral centers in the two modifier is essential for the enantioselectivity of the catalysts. Therefore, cinchonidine and quinine exhibit very similar advantageous effect.

Temperature dependence of the reaction over rhodium nanocluster shows that room temperature is the most suitable for the enantioselective hydrogenation of ethyl pyruvate and then the enantioselectivity drops gradually with temperature increase (Fig. 3). An 42.2% e.e. for *R*-(+)-ethyl lactate can be achieved at 298 K and only 30% e.e. at 318 K. TOF also decreases when the temperature is over 303 K. These phenomena could be due to the desorption of cinchonidine or/and the change of its adsorption mode on the Rh surface.

The effect of hydrogen pressure is shown in Fig. 4. The e.e. values increase initially with increasing H_2 pressure and then reach a platform (42.2% e.e. for *R*-(+)-ethyl pyruvate) when the pressure is higher than 4.0 MPa. The rise of hydrogen concentration in solution could be favorable for improving the enantioselectivity as reported by Blackmond [18–19]. The phenomena are different from Well's report on Pt/cinchonidine system [17] and Liu's result in Ir/cinchonidine system [14]. It is possible that when the coordination equilibrium of hydrogen on the Rh surface has reached, the further rising hydrogen

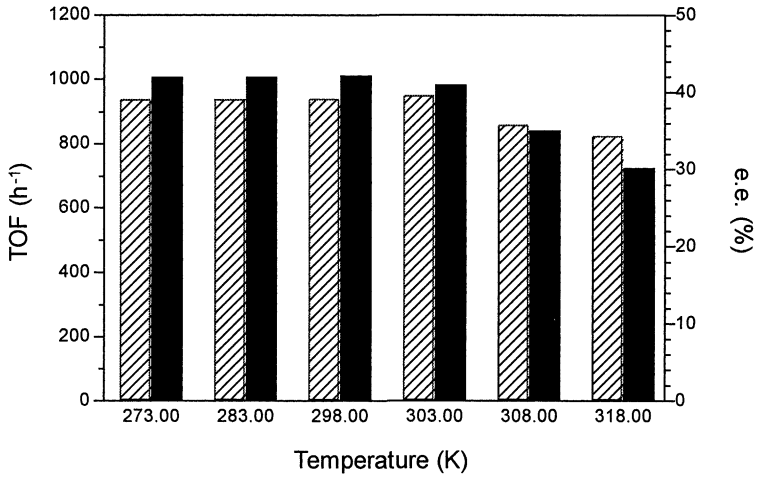

Fig. 3. The effect of temperature on TOF and enantioselectivity.

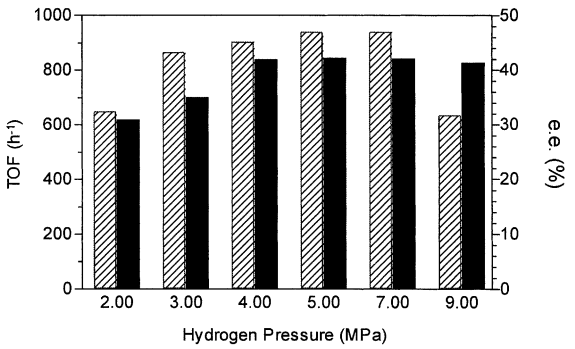

Fig. 4. The effect of hydrogen pressure on TOF and enantioselectivity.

pressure does not obviously influence the enantioselectivity of Rh nanocluster catalyst.

3. Experimental

Ethyl pyruvate, cinchonidine, quinine, polyvinylpyrrolidone (PVP) (MWav. = 10 000) were used as received from Acros without further purification. Hydrogen (99.9%) was purified prior to use. Other regents were used with a level of analytical grade.

Synthesis of the polyvinylpyrrolidone-stabilized rhodium nanoclusters(Rh/PVP): 5.0×10^{-2} mmol of rhodium chloride trihydrate and 55.6 mg of PVP (corresponding to 0.5 mmol of pyrrolidone monomer) were dissolved in a mixture of ethanol and distilled water (70 ml, ethanol:water = 9:1) in a flask. The solution was refluxed at 79°C for 1 h to give a dark brown sol. The sol solution was evaporated to dryness by a Rotavap. The rhodium nanoclusters were redispersed in ethanol (5.0 ml, 9.7 mmol Rh/ml) prior to use.

The TEM measurements were performed with a JEM-100CX. The TEM samples were prepared by dispersing the nanoclusters in ethanol and added onto a copper sample mesh covered with carbon. After the solvent was completely vapoured, the sample was measured by TEM.

Enantioselective hydrogenation of ethyl pyruvate: the hydrogenation was carried out in a 20 ml stainless autoclave with a glass liner and magnetic stirrer. Rh nanocluster in ethanol (0.1 ml), ethyl pyruvate (2.0 mmol), cinchonidine (or other additive) and tetrahydrofuran (2.0 ml) were added into the autoclave. Cinchonidine and quinine were used as chiral modifier. The autoclave was flushed with hydrogen for several times and then hydrogen was added to the desired pressure. The hydrogenation reaction was performed in a quasihomogeneous phase at a constant pressure for a desired period of time. The products were analyzed by gas chromatograph GC960 with FID detector and β-DEX^{TM}120 capillary column (30 m × 0.25 mm, 0.25 μm film) at 80°C.

The enantiomeric excess is obtained as: e.e. (%) = $100 \times (R - S)/(R + S)$.

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