

# The effects of tin on the hydrogenation of $\alpha$ -diketones over platinum nanoclusters

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## Abstract

The effect of tin on the hydrogenation of  $\alpha$ -diketones over polymer-stabilized platinum nanoclusters (PVP-Pt) or the corresponding  $\text{Al}_2\text{O}_3$  supported platinum nanoclusters ( $\text{Pt}/\text{Al}_2\text{O}_3$ ) was investigated. It was shown that  $\text{Sn}^{2+}$  has a rate-promoting effect either on the enantioselective hydrogenation of  $\alpha$ -diketones modified with cinchonidine or on the racemic hydrogenation of them. The average rate increases by a factor of more than 2 for the racemic hydrogenation of 3,4-hexanedione over polymer-stabilized platinum nanoclusters in ethanol solution with a  $\text{Sn}^{2+}$  concentration of  $1.6 \times 10^{-4}$  mol/l. The enantioselectivity could also be enhanced by the addition of  $\text{Sn}^{2+}$  in the enantioselective hydrogenation of these compounds. It is believed that the electrophilic nature of  $\text{Sn}^{2+}$  is responsible for the rate promotion. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The effects of tin on platinum catalysts are fascinating. The addition of tin to  $\text{Pt}/\text{Al}_2\text{O}_3$  reforming catalysts results in a higher catalytic activity in aromatization of hydrocarbons [1–8]. Platinum–tin catalysts have been found to exhibit a methanol oxidation rate higher than that of pure platinum [9,10]. The use of tin chloride in  $\text{Pt}/\text{nylon}$  or  $\text{Pt}/\text{C}$  system leads to a large increase in the overall rate of the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes and to a high selectivity towards the formation of the corresponding unsaturated alcohol [11]. Organic tin has considerable promotion effect on the catalytic activity of the enantioselective hydrogenation of ethyl pyruvate over platinum

catalysts with no influence on the enantioselectivity [12]. Comprehensive studies on the platinum–tin surface chemistry had been carried out by Sachtler and co-workers in 1970s [13,14], which provided useful information for understanding the catalytic behaviour of  $\text{Pt-Sn}$  catalyst. For the hydrogenation of  $\text{C}=\text{O}$  group over platinum catalyst upon adding tin ions, it seems feasible that the electrophilic nature of tin ions increases the polarization of the  $\text{C}=\text{O}$  bond and facilitates the attack of the chemisorbed hydrogen [11].

Metal colloids or clusters are of interest in catalysis, from both the theoretical and practical point of view [15–17]. Recently we investigated the enantioselective hydrogenation of  $\alpha$ -ketoesters [18–20] and  $\alpha$ -diketones [21] over polyvinylpyrrolidone-stabilized platinum or iridium nanoclusters. It was shown that the catalyst not only afforded a superior enantioselectivity but also exhibited novel catalytic properties that differ completely from their conventional heterogeneous

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counterparts. Interested by the unusual performances of this type of catalyst and the fascinating effects of tin on the platinum catalysts, we investigated the enantioselective hydrogenation of  $\alpha$ -diketones over platinum nanoclusters modified with tin chloride. Here we present the results.

## 2. Experimental

### 2.1. Materials and instruments

2,3-Butanedione and 3,4-hexanedione were purchased from Acros and used as received. PVP (average MW 40 000) was provided by BASF. Hydrogen ( $H_2$ ) with a purity of 99.999% was supplied by Beijing Gases Factory. Other reagents were purchased from Beijing Chemicals and they were of analytical grade. Polyvinylpyrrolidone-stabilized platinum nanocluster (PVP-Pt) in the form of dark-brown homogeneous dispersions and the corresponding  $Al_2O_3$  supported platinum nanoclusters (Pt/ $Al_2O_3$ ) were prepared and characterized according to the published procedures [18–20]. The mean diameter of platinum particles is 1.5 nm with a standard deviation of 0.38 nm.

The enantioselectivity and catalytic activity were determined by a Bei-Fen SQ-204 gas chromatograph with a Chirasil-DEX CB (Chrompack) capillary column. The enantioselectivity is expressed as e.e. (%) =  $100 \times ([R] - [S]) / ([R] + [S])$ .

### 2.2. Hydrogenation reaction

The hydrogenation reaction was carried out in an 100 ml stainless steel autoclave. Typically, the reaction mixture contained  $1.15 \times 10^{-2}$  mol 2,3-butanedione or 3,4-hexanedione, 10 ml PVP-Pt dispersion (containing  $6.4 \times 10^{-6}$  mol Pt and 10 ml solvent). In the case of  $Al_2O_3$  supported platinum nanoclusters, 0.1 g Pt/ $Al_2O_3$  (containing  $2.8 \times 10^{-6}$  mol Pt) and 10 ml solvent were used. A proper amount of  $SnCl_2$  and/or cinchonidine were added. Hydrogen was charged several times to replace air and the final pressure of hydrogen was 4.0 MPa. The reaction mixture was stirred vigorously at 25°C for a definite period. Then, the reaction was stopped for gas chromatography analysis.

## 3. Results and discussion

In order to investigate the effect of tin ions on the enantioselective hydrogenation of  $\alpha$ -diketones, we introduced  $Sn^{2+}$  to the  $\alpha$ -diketone/cinchonidine/platinum system. Table 1 shows the hydrogenation results.

In both cases that PVP-Pt and Pt/ $Al_2O_3$  were used as catalyst in alcohol solution,  $Sn^{2+}$  at the concentration of  $4.8 \times 10^{-4}$  mol/l can lead to a moderate increase in both enantioselectivity and catalytic activity for the hydrogenation of 2,3-butanedione (Entries 1, 2; 5, 6; 9, 10 and 11, 12). While  $Sn^{2+}$  at this concentration increases the enantioselectivity for the hydrogenation

Table 1  
Effects of tin ions on the enantioselective hydrogenation of  $\alpha$ -diketones<sup>a</sup>

Entry	Catalyst	Solvent	Substrate <sup>b</sup>	$Sn^{2+}$	Average rate <sup>c</sup>	e.e. (%)
1	PVP-Pt	Ethanol	2,3-B	No	61.5	14.7
2	PVP-Pt	Ethanol	2,3-B	Yes	71.9	19.9
3	PVP-Pt	Ethanol	3,4-H	No	28.2	17.1
4	PVP-Pt	Ethanol	3,4-H	Yes	26.8	22.5
5	Pt- $Al_2O_3$	Ethanol	2,3-B	No	53.9	12.1
6	Pt- $Al_2O_3$	Ethanol	2,3-B	Yes	57.4	16.7
7	PVP-Pt	Acetic acid	2,3-B	No	78.7	16.0
8	PVP-Pt	Acetic acid	2,3-B	Yes	54.2	0
9	PVP-Pt	Methanol	2,3-B	No	65.1	13.6
10	PVP-Pt	Methanol	2,3-B	Yes	79.1	17.8
11	PVP-Pt	<i>n</i> -Propyl alcohol	2,3-B	No	60.3	15.3
12	PVP-Pt	<i>n</i> -Propyl alcohol	2,3-B	Yes	73.1	18.7

<sup>a</sup>  $Sn^{2+}$  concentration:  $4.8 \times 10^{-4}$  mol/l; cinchonidine concentration:  $1.7 \times 10^{-3}$  mol/l; reaction time: 20 min for entries 1, 2, 7–12 and 60 min for entries 3–6.

<sup>b</sup> 2,3-B: 2,3-butanedione; 3,4-H: 3,4-hexanedione.

<sup>c</sup> mol 2,3-B (or 3,4-H)/mol Pt min.

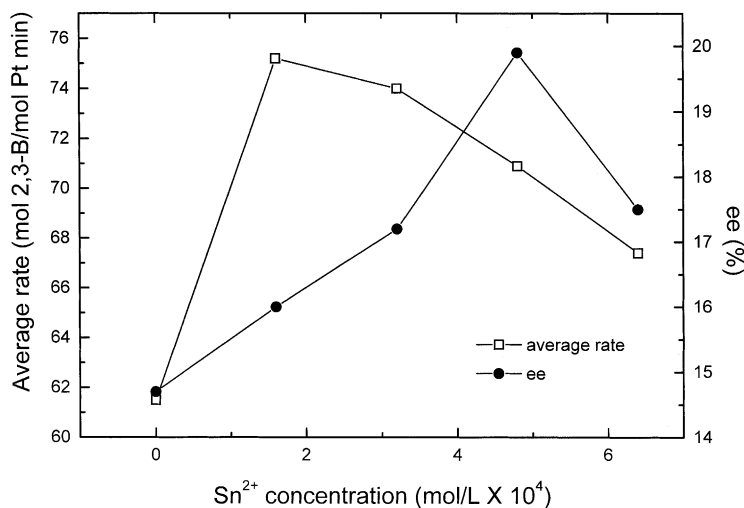


Fig. 1. The relationship between  $\text{Sn}^{2+}$  concentration and enantioselectivity or average rate for the enantioselective hydrogenation of 2,3-butanedione over PVP-Pt (cinchonidine concentration:  $1.7 \times 10^{-3}$  mol/l; reaction time: 20 min).

of 3,4-hexanedione, it also decreases the catalytic activity slightly (Entries 3, 4). For the hydrogenation of 2,3-butanedione over PVP-Pt in acetic acid solution, the use of  $\text{Sn}^{2+}$  leads to a remarkable decrease in activity and no enantiomeric excess is observed (Entries 7, 8). The acetic acid probably fails to act as an inert solvent. It converts tin chloride into the inactive tin acetate.

The effect of tin ions in a more extensive concentration range in ethanol solution is shown in Fig. 1 (for the enantioselective hydrogenation of 2,3-butanedione) and Fig. 2 (for the enantioselective hydrogenation of 3,4-hexanedione). It can be seen that in both cases the catalytic activity reaches its maximum at the  $\text{Sn}^{2+}$  concentration of ca.  $1.6 \times 10^{-4}$  mol/l. Above this optimum concentration the activity decreases

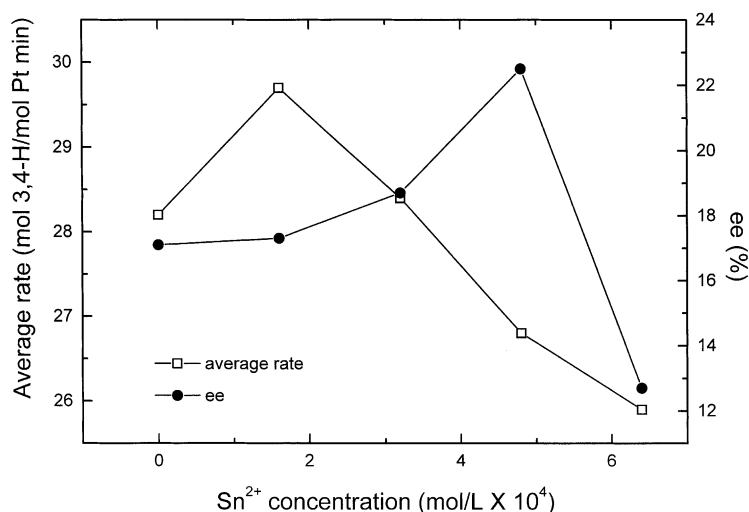


Fig. 2. The relationship between  $\text{Sn}^{2+}$  concentration and enantioselectivity or average rate for the enantioselective hydrogenation of 3,4-hexanedione over PVP-Pt (cinchonidine concentration:  $1.7 \times 10^{-3}$  mol/l; reaction time: 60 min).

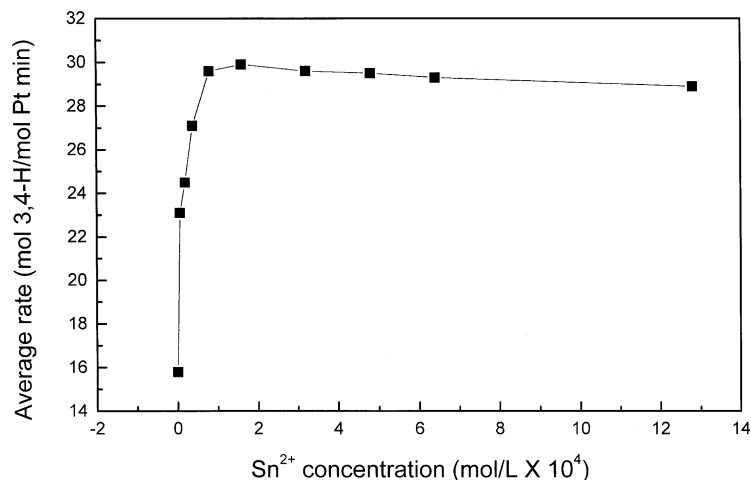


Fig. 3. The relationship between  $\text{Sn}^{2+}$  concentration and average rate for the racemic hydrogenation of 3,4-hexanedione over PVP-Pt (reaction time: 60 min).

with the increase of  $\text{Sn}^{2+}$  concentration. Whereas, the enantioselectivity climbs to its top point at the  $\text{Sn}^{2+}$  concentration of ca.  $4.8 \times 10^{-4}$  mol/l and again decreases above this optimum condition.

It is well known that cinchonidine itself has considerable rate promotion effect on this type of reaction [21–24]. In this work the utilization of tin ions in the  $\alpha$ -diketone/cinchonidine/platinum system leads to an additional rate promotion. This observed phenomenon is in fact the consequence of the combined effects from tin ions and cinchonidine. But how about the net role of  $\text{Sn}^{2+}$  on this type of reaction? We therefore investigated the effect of tin ions on the racemic hydrogenation of 3,4-hexanedione in the absence of cinchonidine. Fig. 3 shows the results.

It is shown that the net promotion effect of  $\text{Sn}^{2+}$  is very similar to that of cinchonidine [21]. The average hydrogenation rate increases sharply with the increase of  $\text{Sn}^{2+}$  concentration and climbs quickly to its maximum in the low  $\text{Sn}^{2+}$  concentration range. In the relative high  $\text{Sn}^{2+}$  concentration range, the average hydrogenation rate decreases very slightly with the increase of  $\text{Sn}^{2+}$  concentration.

Both tin ions and cinchonidine have rate promotion effect on the hydrogenation of  $\alpha$ -diketones, but the promotion mechanism is quite different. The promotion effect of tin ions is due to their electrophilic nature which increases the polarization of the C=O

bond and facilitates the attack of the chemisorbed hydrogen [11]. While the promotion effect of cinchonidine is mainly caused by the alicyclic nitrogen atom in its molecule, which acts as a type of N-base and stabilizes one of the half-hydrogenated transition state in the hydrogenation process [25]. In the case that both tin ions and cinchonidine are used as modifiers in the enantioselective hydrogenation of  $\alpha$ -diketones the observed overall rate-promotion is the result of the combination of the above two factors from tin ions and cinchonidine. In the low  $\text{Sn}^{2+}$  concentration range, the interaction between  $\text{Sn}^{2+}$  and cinchonidine is negligible. The two types of modifier act independently on the hydrogenation reaction and the overall rate increases. However, with the increase of the  $\text{Sn}^{2+}$  concentration in the reaction system, the interaction between  $\text{Sn}^{2+}$  and cinchonidine becomes more and more evident. This interaction consumes tin ions as well as alicyclic N-base in the cinchonidine molecule, both of which are essential for promoting the hydrogenation reaction. Therefore, the overall hydrogenation rate declines in higher  $\text{Sn}^{2+}$  concentration range. This speculation about the interaction between tin ions and cinchonidine in different concentration range has been justified by the UV spectra of cinchonidine solution containing tin ions (Fig. 4).

Remarkable rate promotion effect of tin ions on the regioselective hydrogenation of 2,3-pentanedione over

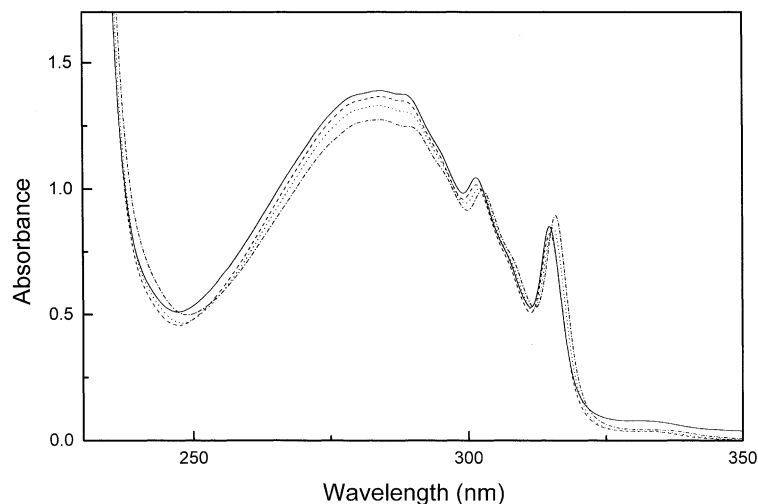


Fig. 4. UV spectra of cinchonidine in ethanol solution containing tin ions (cinchonidine concentration:  $2.5 \times 10^{-4}$  mol/l.  $\text{Sn}^{2+}$  concentration: 0 mol/l (—);  $2.5 \times 10^{-5}$  mol/l (- - -);  $1.0 \times 10^{-4}$  mol/l (· · ·);  $2.5 \times 10^{-4}$  mol/l (- · - · -)).

PVP-Pt has also been reported [26]. It should be noted that only tin ions have great promotion effect on the hydrogenation of  $\alpha$ -diketones. Other metal ions, such as  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc. have little influence on the catalytic activity or remarkably decrease the catalytic activity [26]. Although other metal ions have similar or even stronger electrophilic nature compared with tin ions, other factors must be taken into account for interpreting the observed experimental results, i.e. the different interaction between platinum surface and metal ions [27]. Some metal ions interact with platinum surface so strongly that they hinder the substrates from being effectively adsorbed on the platinum surface.

What makes things more fascinating is that the addition of tin ions in the hydrogenation system also leads to an enantioselectivity improvement. Under optimum condition, a 40% enhancement has been observed. The similar phenomena have also been observed in the enantioselective hydrogenation of  $\alpha$ -ketoesters over the same types of catalysts upon adding rare earth ions [28]. Although the role of metal ions in the enantioselectivity improvement is not clear at present, it may be feasible that the presence of metal ions can (i) change the surface coverage of hydrogen and substrate, (ii) alternate the mode of adsorption of the reactants and (iii) change the mechanism of hydrogenation [12]. Study on the exact modification mechanism of metal ions on

the enantioselectivity improvement is now in progress in our laboratory.

In summary, we have investigated the effect of tin ions on the hydrogenation of  $\alpha$ -diketones. Remarkable rate promotion in the racemic hydrogenation and moderate rate promotion as well as enantioselectivity improvement in the enantioselective hydrogenation have been observed. The rate alteration is attributed to the electrophilic property of  $\text{Sn}^{2+}$  and the interaction between  $\text{Sn}^{2+}$  and cinchonidine.

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