

# Enantioselective hydrogenation of methyl pyruvate over polymer-stabilized and supported iridium clusters

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## Abstract

The enantioselective hydrogenation of methyl pyruvate was studied over finely dispersed polyvinylpyrrolidone-stabilized iridium (PVP-Ir) and the corresponding alumina-supported iridium cluster ( $\text{Al}_2\text{O}_3$ -Ir) modified with cinchonidine. It was found that the modifier, apart from inducing enantioselectivity, has a considerable rate-promoting effect on this reaction with the average rate increased by a factor of 2–3.5 over both the two kinds of catalysts. Favorable reaction parameters were 283 K, 4.0 MPa and alcohols or acetic acid as solvents. Similar to what had been reported in Pt/cinchona system, the highest value of the enantiomeric excess (34.1%) was obtained in acetic acid, accompanied by a marked enhancement of the reaction rate. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Iridium; Methyl pyruvate; Cinchonidine; Enantioselective hydrogenation; Rate-promoting effect

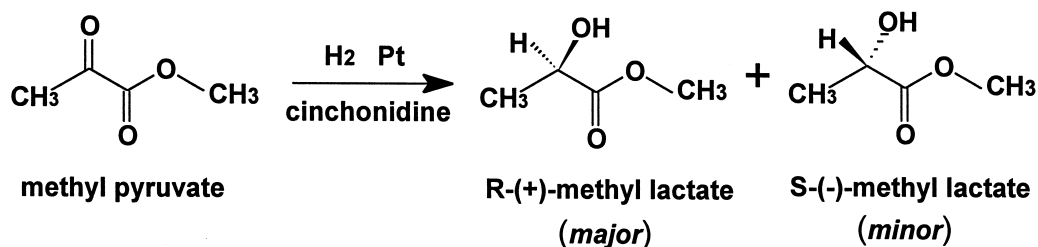
## 1. Introduction

$\alpha$ -Hydroxyesters are important chiral intermediates for the synthesis of biological active compounds [1]. In 1978, Orito et al. designed the Pt/cinchona system that catalyze the asymmetric hydrogenation of  $\alpha$ -ketoesters (e.g., methyl pyruvate, Scheme 1) with enantiomeric excess (e.e.) approaching 90% [2–5]. Since then it has been widely investigated by Blaser et al. [6–8], Baiker et al. [9–11], Wells et al. [12,13], Augustine et al. [14,15]. It is found that when cinchonidine (Scheme 2) is chosen as the modi-

fier, *R*-(+)-lactate is formed in enantiomeric excess, while the use of its diastereoisomer cinchonine yields *S*-(-)-lactate as the major enantiomer. A fascinating character of the modifier is its effectiveness in trace quantity, of course, dependent on the solvent used. For example, the ratio of modifier to  $\text{Pt}_{\text{surf}}$  can be as low as 1 in ethanol [16], 0.5 in toluene [16] and less than 0.1 in acetic acid [17,18] where the lowest modifier reactant ratio amounts to 1:130000. Several mechanisms [12,19–23] have been proposed which predicts the sense of the observed enantioselectivity and which interprets the significantly enhanced rates that always attend this enantioselective hydrogenation over Pt.

However, as has been reported so far, the reaction is almost enzymic in its specificity

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Scheme 1. The asymmetric hydrogenation of methyl pyruvate.

because good enantioselectivity can only be obtained with very specific combinations of metal, modifier and substrate [6]. Although some new efficient modifiers have been synthesized recently [24–26], little progress is made in exploring the substitute for Pt. Utilization of other platinum metals such as Ru, Rh, Pd normally leads to inferior and irreproducible enantioselectivities [6,27]. Based on the researches of H/D exchange in 10,11-dihydrocinchonidine adsorbed on platinum metals [28], Wells et al. for the first time discovered that reproducible enantioselectivities could also be registered over a series of Ir catalysts [27], e.g., the highest e.e. was 39% when catalyzed by a calcium carbonate supported Ir under 10 bar, 298 K and in ethanol.

A most remarkable feature of the Pt/cinchona is that the modifier not only induces enantioselectivity, but also causes a distinct increase in the reaction rate, which is defined as the

ligand-accelerated catalysis [29,30]. This is quite different, however, in Wells' Ir/cinchona system [27]: the change in activity upon the modification is substantially less pronounced and, in some cases, it is even more active for racemic hydrogenation than for enantioselective hydrogenation.

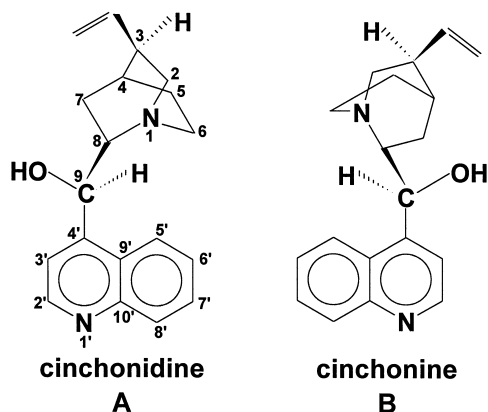
Catalytic activity and enantioselectivity are greatly influenced by the reaction parameters. The previous work related to the effect of pressure, temperature, and solvent is briefly summarized as follows.

### 1.1. Hydrogen pressure

Reactions are generally run under a pressure above 10 bar and most studies showed a first-order rate dependence for the Pt/cinchona system, which is also the same for the Ir/cinchona as hydrogen pressure varies from 4.1 to 10 bar [27]. Enantioselectivity is moderately influenced by hydrogen pressure, but falls sharply below 10 bar [6,8].

### 1.2. Reaction temperature

It is interesting that enantioselectivity as well as activity strongly decreases above 318 K for both Pt/cinchona and Ir/cinchona systems [12–14,27]. This is probably caused by the thermal desorption of the modifier from the metal surface, as confirmed by Augustine et al. with UV analysis [14]. However, a change in the manner of alkaloid adsorption should also be possible, inferred from the strong increase in the angle between the aromatic ring plane and the



Scheme 2. The naturally occurring alkaloids.

metal surface plane above 200 K by NEXAFS measurements of pyridine chemisorption on Pt (111) [31].

### 1.3. Solvent

As concerns the Pt/cinchona system, the commonly chosen solvents are toluene, ethanol and acetic acid. Baiker et al. [32] correlated the enantioselectivity and activity with the solvent polarity and found that both of them decreased linearly with increasing dielectric constant of the solvents. Nevertheless, it is hard to generalize the solvent effect because one can always find several exceptions. A most typical one is acetic acid, a moderately polar solvent in which e.e. as high as 95% can be achieved along with a notable augmentation of the reaction rate [17]. Augustine et al. [14] selected methyl acetate as the standard solvent because of its minimal interaction with Pt. Wells et al. [27] described for the Ir/cinchona that enantioselectivity and activity collapsed in the sequence of ethanol, dodecanol, toluene and dichloromethane, contrary to the above report on Pt/cinchona system in view of the solvent polarity [32]. Regrettably, acetic acid was not adopted in their work. Solvent affects the adsorption of modifier on the surface of the catalysts [6], besides, they can interact with the substrates [10,33] or even change the conformation of the modifiers [33], thus increasing the complexity of solvent effect.

To our knowledge, the title reaction is mostly carried out over conventional supported Pt or Ir catalysts. Nanoscopic noble metal clusters or colloids have aroused much interest in recent years not only because of the large area of the particles with rather few metal atoms but also because of their unique functions as compared to bulk metal or metal atoms. Among the numerous researches, their application in catalysis is one of the most attractive fields. A great variety of organic reactions such as hydrogenation of various alkenes [34–37], selective hydrogenation of cinnamaldehyde [38–40] and *o*-chloronitrobenzene [41,42], hydration of

acrylonitrile [43,44] and photochemical evolution of hydrogen [45] have successfully been carried out with colloidal nanoclusters. Using polyvinylpyrrolidone-stabilized platinum colloidal clusters (PVP-Pt) as the catalysts and cinchonidine as the modifier, we achieved the highest enantioselectivity (97.6%) ever reported in the heterogeneous hydrogenation of methyl pyruvate and also observed their different catalytic properties from the conventional supported ones [46]. This, as well as Wells' work on Ir/cinchona, prompted us to examine the performance of iridium clusters (both in solution and on carrier) in this reaction, which may bring about some new information as regard to the nanocluster catalysis.

## 2. Experimental

### 2.1. Materials and instruments

Poly (*N*-vinyl-2-pyrrolidone) (PVP) ( $M_w = 40,000$  Fluka), methyl pyruvate (Acros), cinchonidine (Acros) were used as received. Other reagents were supplied by Beijing Chemicals with a level of analytical grade.

Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR instrument. Specimens were prepared by placing a drop of the colloid dispersion upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameter was determined from the enlarged photographs and the size distribution histogram was obtained on the basis of the measurement of about 250 particles.

### 2.2. Preparation of the colloidal clusters (PVP-Ir)

The polyvinylpyrrolidone-stabilized iridium colloidal clusters (designated as PVP-Ir) were prepared by the alcohol/water reduction method as literature [47]. For example, chloroiridic acid ( $H_2IrCl_6 \cdot nH_2O$ , 0.210 mmol) was dissolved in

a mixture of *n*-propanol (270 ml) and distilled water (30 ml) containing PVP (0.232 g, 2.08 mmol) and heated under reflux for 3 h. A dark brown sol resulted, which was then evaporated to dryness by a Rotavap and redispersed in ethanol prior to use. Another sol that was to be supported on alumina (see below) was synthesized in the same way except employing ethanol as the reducing agent.

### 2.3. Preparation of the supported cluster ( $Al_2O_3$ -Ir)

In a 100-ml beaker, 3.6 g  $Al_2O_3$  (specific surface area  $16.8 \text{ m}^2 \text{ g}^{-1}$ ) was stirred with the required amount of PVP-Ir sol for 40 h at room temperature. After filtration, the supported Ir was washed with ethanol and water and then dried at ambient temperature under vacuum for 15 h. The content of iridium was 0.26% by weight as determined by atomic absorption spectroscopy (AAS). Elemental analysis showed the content of nitrogen to be out of detection level, which indicated that the stabilizing polymer PVP, was thoroughly washed off.

### 2.4. Hydrogenation of methyl pyruvate

Enantioselective hydrogenation of methyl pyruvate was conducted in a 100-ml stainless autoclave under the following standard conditions.

(a) For hydrogenation over PVP-Ir: 1.0 ml methyl pyruvate; 1.0 ml *n*-butanol (as the internal standard); 6.0 ml PVP-Ir (containing 0.014 mmol Ir, 0.139 mmol PVP and 6.0 ml ethanol); 4.3 mg cinchonidine; temperature 283–323 K; hydrogen pressure 1.0–8.0 MPa.

(b) For hydrogenation over  $Al_2O_3$ -Ir: 1.0 ml methyl pyruvate; 7.0 ml solvent; 0.2 g  $Al_2O_3$ -Ir (containing  $2.7 \times 10^{-3}$  mmol Ir); 2.0 mg cinchonidine; temperature 298 K; hydrogen pressure 4.0 MPa.

The reaction was stopped after 4 h (a) or 2 h (b) and the conversion analyzed by gas chromatography (column: PEG 20 M, 2 m, 120°C).

Activity was sometimes expressed as the average reaction rate ( $\text{mmol h}^{-1} \text{ g}_{\text{Ir}}^{-1}$ ) derived from the conversion; Enantiomeric excess-e.e.(%) =  $100 \times ([R] - [S]) / ([R] + [S])$  was determined by gas chromatography on a modified  $\beta$ -cyclodextrin column (20 m, 70°C).

## 3. Results and discussion

### 3.1. TEM characterization of the iridium clusters

It can be seen from the TEM photographs (Fig. 1) that the two colloidal clusters synthesized are in small size (1.1 nm and 1.4 nm, respectively) and with narrow size distribution (0.43 nm and 0.35 nm, respectively).

### 3.2. Rate-promoting effect of the modifier

From the earlier studies on the Pt/cinchona system, it can be concluded that the rate increase in the presence of the modifier is caused not only by the base catalysis of the carbonyl reduction (modifier acts as an alicyclic N base by the quinuclidine N) [48,49], but also by the special substrate–modifier interaction that occurs between the quinuclidine N of the modifier and the keto group of the substrate [21,22,33]. Here in the hydrogenation of methyl pyruvate over PVP-Ir, this phenomenon is again observed: the addition of the modifier elevated the average rate by a factor of 2–3.3 (Table 1), which argues with the results over Wells' supported Ir catalysts [27]. Interestingly, the rate acceleration has also been detected when employing PVP-Pt (by a factor of 6.8, ethyl pyruvate) as catalyst, and even over PVP-Rh (by a factor of 6.9, methyl pyruvate) which affords racemic hydrogenation products [50]. As a result, the modifier has an extensive rate-promoting effect in the asymmetric hydrogenation of  $\alpha$ -ketoesters, not limited to Pt or the extent of enantiodifferentiation.

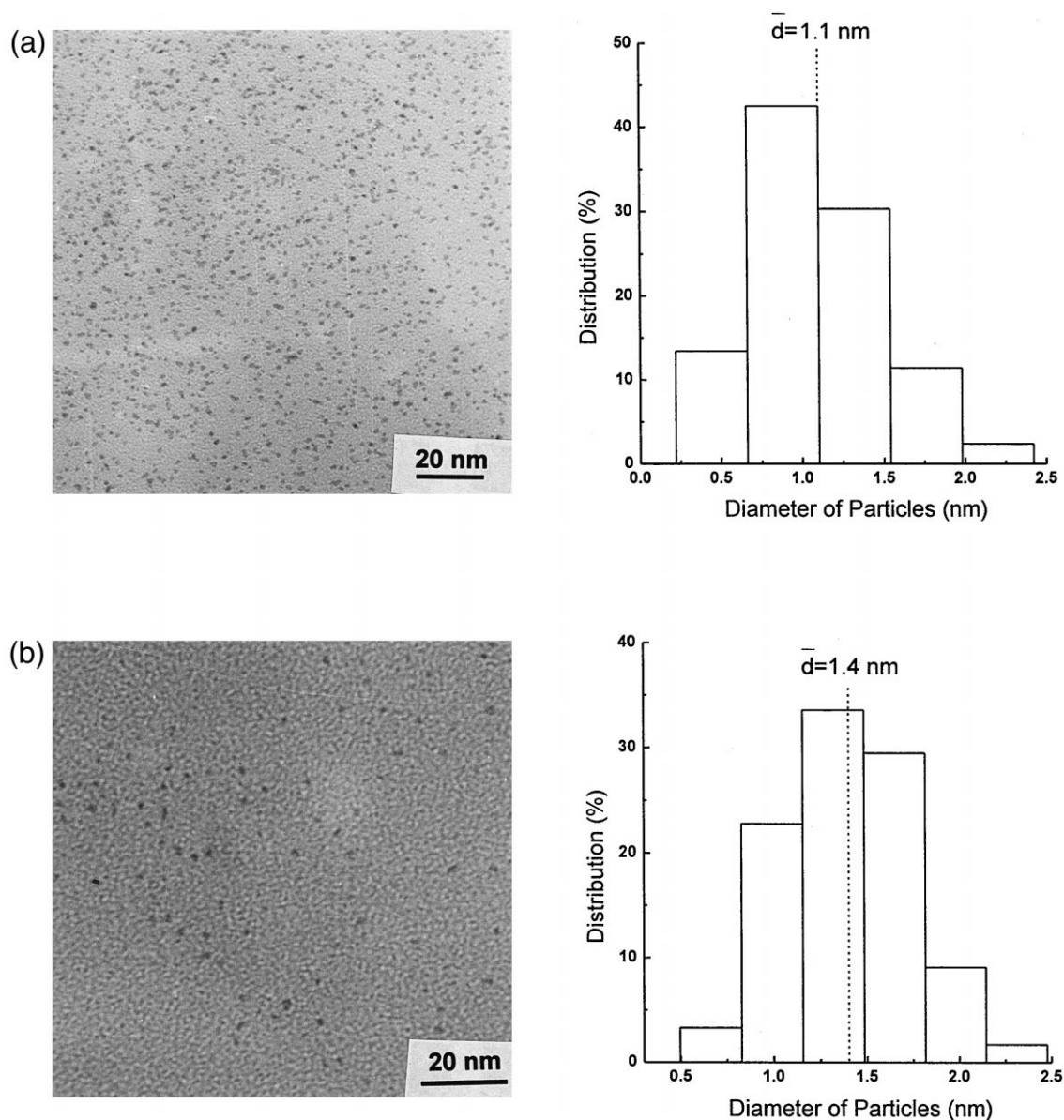


Fig. 1. TEM photographs (left) with the histogram plot of the particle size distribution (right) of the PVP-Ir colloidal clusters; (A) *n*-propanol, (B) ethanol as the reducing agent.

### 3.3. Reaction temperature

The temperature dependence of the reaction over PVP-Ir shows that lower temperature is better for enantioselectivity. An e.e. near 30% can be got at 283 K, then it decreases gradually and is less than 10% above 313 K (Fig. 2). However, the activity keeps rising with 100%

conversion of methyl pyruvate at 323 K, which differs from the drastic loss of activity exhibited by the conventional supported Pt and Ir when temperature is elevated to 318 K [12,13,27]. It seems contradictory when combining the effect of temperature on activity with that on enantioselectivity because the decreasing e.e. with ascending temperature can be attributed to the

Table 1  
Role of cinchonidine (CD) in the enantioselective hydrogenation of methyl pyruvate over PVP-Ir colloidal cluster<sup>a</sup>

Addition of CD	Hydrogen pressure (MPa)	Average rate (mmol h <sup>-1</sup> g <sub>Ir</sub> <sup>-1</sup> )	e.e. <sup>b</sup> (%)
Yes	4.0	777.5	23.1
No	4.0	370.6	0
Yes	2.0	838.3	17.0
No	2.0	252.0	0

<sup>a</sup>Reaction temperature 298 K.

<sup>b</sup>*R*-methyl lactate in excess.

desorption of cinchonidine or the change of its adsorption mode on the Ir surface, while the increasing reaction rate is less possible to happen according to the ligand accelerating effect displayed by the modifier (adsorbed on Ir via quinoline ring, see below). This remains unclear for the time being and merits further study.

### 3.4. Hydrogen pressure

It can be seen from Fig. 3 that the e.e. obtained over PVP-Ir reaches a plateau at 4.0

MPa and decreases somewhat with the further increase of the pressure. This agrees with Wells' work in Pt/cinchona system that enantioselectivity exhibits a weak maximum at 50 bar (69%) and drops a little (60%) when the pressure is 110 bar [13]. The ascending e.e. can be rationalized in terms of the rise in the solution hydrogen concentration ( $[H_2]$ ) which has been proved in Blackmond et al.'s kinetic study [51,52] to have a positive effect on the formation of the [*R*] isomer, yet the descending e.e. above 4.0 MPa seems intriguing. In our opinion, the e.e. reduction (both in Wells' and ours) might be ascribed to the competitive adsorption of hydrogen that to some extent hinders the access of the substrate and the modifier to the metal surface, especially in the case of PVP-Ir as catalyst. As far as we know, the stabilizing polymer PVP has a weakly shielding effect on the reaction since it can coordinate with the metal by the carbonyl group on polymer chains [53], thus obscuring the efficient adsorption of the substrate and modifier. However, the adsorption of hydrogen is much less influenced on account of its much smaller size as compared to methyl

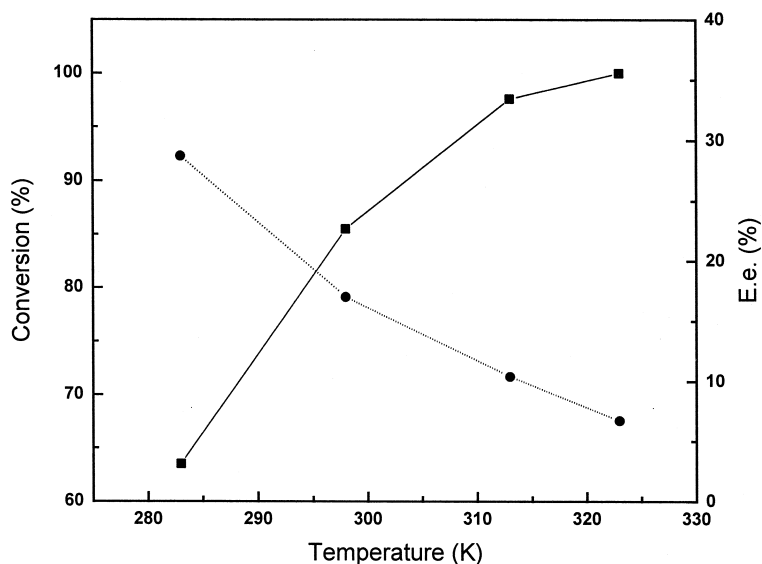


Fig. 2. Effect of temperature on the enantioselective hydrogenation of methyl pyruvate over PVP-Ir colloidal cluster (Hydrogen pressure = 2.0 MPa; ■ Conversion; ● e.e.).

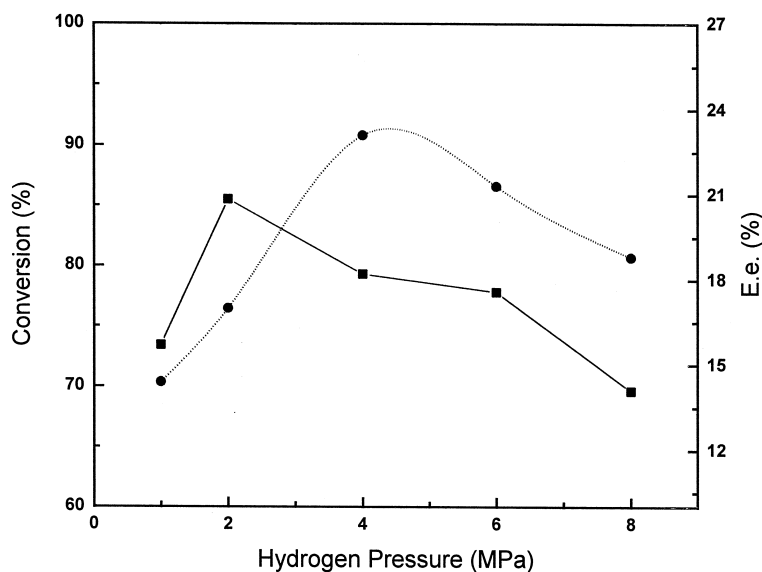


Fig. 3. Effect of hydrogen pressure on the enantioselective hydrogenation of methyl pyruvate over PVP-Ir colloidal cluster (Temperature = 298 K; ■ Conversion; ● e.e.).

pyruvate and cinchonidine. Therefore, the Ir surface is more superior to be occupied by hydrogen at higher pressure, which is probably not advantageous to the enantiodifferentiation as the reason above. To our surprise, the conver-

sion of methyl pyruvate collapses from 85.5% to 69.6% in the range of 2.0 to 8.0 MPa. This is unexpected since higher pressure is beneficial to the activity over conventional supported Pt and Ir catalyst. However, by characterizing with

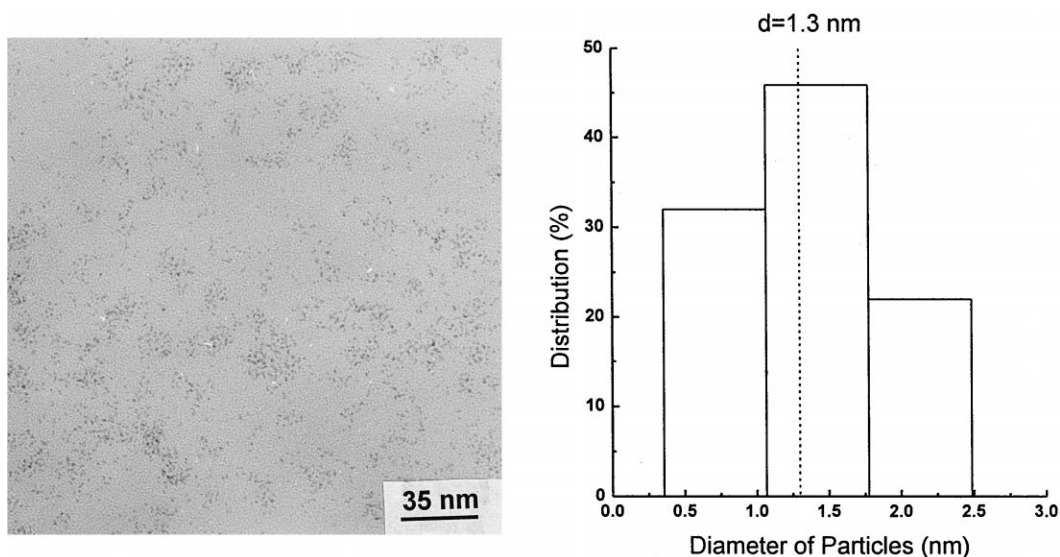


Fig. 4. TEM photograph (left) with the histogram plot of the particle size distribution (right) of the PVP-Ir colloidal cluster that underwent hydrogenation at 8.0 MPa.

TEM photograph (Fig. 4), the reaction solution that underwent hydrogenation at 8.0 MPa, we found some agglomeration in the colloid (compare Fig. 1A Fig. 4). As a result, the activity decrease can be attributable to the diminution of the surface atoms which play an essential role in the reaction.

### 3.5. Solvent

Considering the limited solubility of PVP in apolar or moderately polar solvents and also the fact that the dry PVP-Ir (PVP:Ir = 10) cannot be easily redispersed in acetic acid,<sup>1</sup> we studied the solvent effect by using the Al<sub>2</sub>O<sub>3</sub>-Ir derived from the immobilization of PVP-Ir. It should be noted that the metal particle size and the size distribution remain unchanged after the immobilization [35,37,54]. Hydrogenation of methyl pyruvate was carried out in solvents of different polarity (Table 2) with the dielectric constant ranging from 2 (cyclohexane) to 80 (H<sub>2</sub>O). Unlike the experience over conventional heterogeneous Pt that activity and enantioselectivity are generally better in apolar solvents than in polar ones [32], there is no close relationship between the performance of the Al<sub>2</sub>O<sub>3</sub>-Ir cluster and the solvent polarity, as is shown in Table 2. Alcohols such as *n*-butanol, ethanol and methanol are suitable solvents for the reaction in which e.e. approximate to 20%. A modest e.e. is obtained in tetrahydrofuran (THF), however, the activity is extremely low in comparison with that in the other solvents. This is in line with our results over Al<sub>2</sub>O<sub>3</sub>-Pt cluster prepared in a similar method that the reaction rate in THF is the slowest among the solvents investigated [50], whereas it should be noted that in the previous work good activity (100% conver-

Table 2

Effect of solvent on the enantioselective hydrogenation of methyl pyruvate over Al<sub>2</sub>O<sub>3</sub>-Ir cluster

Solvent	Dielectric constant	Conversion (%)	E.e. (%)
Cyclohexane	2.02	60.2	16.0
Toluene	2.38	35.9	11.4
Ethyl acetate	6.02	16.5	11.0
Acetic acid	6.15	90.8	34.1
Tetrahydrofuran	7.6	5.9	14.3
Dichloromethane	9.08	27.0	16.8
<i>n</i> -Butanol	17.1	41.3	17.4
Ethanol	24.3	46.4	18.1
Ethanol <sup>a</sup>	24.3	13.2	0
Methanol	33.6	23.9	16.7
H <sub>2</sub> O	80.4	43.4	12.0

<sup>a</sup>Without cinchonidine.

sion of ethyl pyruvate) as well as high enantioselectivity is afforded in THF [32], which further complicates the solvent effect. As we have expected, the supported Ir cluster behaves best in the presence of acetic acid: the reaction tends to be complete with enantioselectivity as good as 34.1%, comparable to Wells' best results in Ir/cinchona system. The mechanism of this promoting effect in acetic acid has thoroughly been studied by molecular modeling and quantum chemical calculations for Pt/cinchona system [20,21]. In our work we propose the same case on cinchonidine modified Ir that the favorable interaction between the protonated N-base alkaloid modifier and the activated carbonyl compound substrate is responsible for the improvement of activity and enantioselectivity. In addition, it should be pointed out that the modifier promotes the activity obviously also on the supported Ir cluster in solvent ethanol (see Table 2, the average rate increases by a factor of 3.5), as is mentioned above over PVP-Ir.

Summarizing the preliminary studies, we can make a conclusion that the PVP-Ir colloidal cluster and its supported analogue indeed exhibit quite different catalytic properties from the conventional heterogeneous Pt or Ir in the enantioselective hydrogenation of methyl pyruvate. Nevertheless, we have not achieved an e.e. higher than 39% (Wells' best value) in our

<sup>1</sup> The dry PVP-Pt (PVP:Pt = 10) prepared similarly is readily dissolved in acetic acid. Based on these facts, we propose a stronger interaction between PVP and Ir. The detailed investigation is being undertaken in our group by using IR and some other methods.



system—on one hand, the limited solubility of the dry PVP-Ir in acetic acid confines its better function as presented by PVP-Pt [46]; on the other, the reaction condition for the supported Ir cluster has the potential to be further optimized. Besides these, our experiments have offered us more evidence on the inferior catalytic behavior of Ir to Pt in this reaction on the basis of Wells' work, which may arise from the different interaction mode between the modifier and the metals.

In a recent review [55], Baiker dissected the modifier into three important functional parts: (1) the aromatic ring (quinoline) which serves as the anchoring part and is assumed to be adsorbed on the platinum surface via the  $\pi$ -bonding system; (2) the chiral C-8 and C-9 which functions as the stereogenic center determining the chirality of the products; (3) the tertiary quinuclidine N which is directly involved in the interaction with the substrate  $\alpha$ -ketoesters. According to Wells' Deuterium tracer study [28], Rh and Pd are ineffective as the catalysts because the former leads to the hydrogenolysis of the quinuclidine moiety and the latter induces a deep hydrogenation of the quinoline ring of the modifier. For Pt and Ir, these side reactions are less likely to take place. Experiments revealed that the exchange of H for D occurred in the quinoline ring of 10,11-dihydrocinchonidine over both of them, indicating the parallel adsorption of the aromatic system on the metal surface. The difference between the two metals lies in the extent of exchange, that is, exchange is observed at all six positions of quinoline ring system over Pt but only at 2-, 6-, and 8-positions (Scheme 2) over Ir. So it seems that Pt interacts more efficiently with the modifier than Ir does, which maybe provide us an explanation concerning the much poorer enantioselectivity recorded over Ir as compared to Pt. All in all, the choice of a metal catalyst for this asymmetric hydrogenation is very critical and it is difficult to find an alternative for Pt that not only accommodates the modifier effectively but also causes no essential destruction to

it under the reaction conditions. A deeper research on the metals including bimetallic catalysts is being conducted in our laboratory.

## Acknowledgements

Financial support of the national Natural Foundation of China (Grants No. 29774037 and 29873058) and the fund of the Chinese Academy of Sciences (Grant No. KJ952-J1-508) were gratefully acknowledged.

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