Improvement in the enantioselective hydrogenation of methyl pyruvate over platinum clusters by addition of rare earth cations

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The modification of some rare earth metal cations to polymer-stabilized Pt colloidal clusters leads to significant increase in both the ee and the activity in the homogeneous enantioselective hydrogenation of methyl pyruvate to (R)-(+)-methyl lactate. Compared to ee (72.5%) in the absence of rare earth cations, the highest ee (88.0%) in ethanol solvent is obtained by adding a suitable amount of Yb^{3+} into the Pt colloidal cluster catalyst. The modification effect of rare earth cations is also effective in other alcohol and water solvents.

KEY WORDS: methyl pyruvate; colloidal platinum clusters; rare earth cations; enantioselective hydrogenation

1. Introduction

As a model of enantioselective catalysis, the hydrogenation of α-keto esters (*e.g.*, ethyl pyruvate) over cinchona-modified Pt catalysts, originally reported by Orito *et al.* [1], is of great scientific interest [2]. Meanwhile, nanoscopic metal colloidal clusters, because of their substantial difference from metal atoms and bulk metal, have also received intense renewed attraction especially in catalysis [3]. However, their application in the enantioselective hydrogenation of methyl pyruvate is less studied. Bönnemann obtained 80% enantioselectivity (ee) in the enantioselective hydrogenation of ethyl pyruvate over the protonated dihydrocinchonidine-stabilized Pt colloidal clusters [4]. Employing polyvinylpyrrolidone (PVP)-stabilized Pt colloidal clusters (designated as PVP-Pt) as catalyst, we observed that cinchonidine (CD)-modified PVP-Pt clusters were highly selective for (R)-(+)-methyl lactate [5].

It is well known that additives such as metal cations can markedly improve the catalytic properties of supported catalysts [6]. Most of the commercial catalysts related to promoters. The modification effect of additives on the enantioselective hydrogenation of α-keto esters has been rarely reported and has been mainly related to rate enhancement [7]. Margitfalvi *et al.* [8] recently reported that the addition of different achiral tertiary amines caused significant promotion in both the ee and the activity of CD-modified Pt/Al_2O_3 in the enantioselective hydrogenation of ethyl pyruvate. We also observed that the incorporation of some metal cations (*e.g.*, Fe^{3+}, Co^{2+}, Ni^{2+}) caused remarkable increase not only in the selectivity but also in the activity of PVP-Pt clusters in selective hydrogenation of unsaturated aldehydes [9] and chloronitrobenzenes [10]. However, the modification effect of metal cations has so far been strictly confined to the chemoselective reactions since Adams' pioneering work reported 3/4 century ago. In the present study, a significant improvement of both the ee and the activity in the enantioselective hydrogenation of methyl pyruvate over CD-modified PVP-Pt was observed in our group when employing rare earth metal cations as modifiers. To our best knowledge, this is the first time that the addition of suitable metal cations has been shown to significantly enhance both the ee and the activity of a metal cluster catalyst in asymmetric catalysis. Here, we report our preliminary results.

2. Experimental

PVP-stabilized colloidal platinum clusters were prepared according to a reported method [11]. The average diameter of as-prepared PVP-Pt is 1.5 ± 0.38 nm.

Hydrogenation of methyl pyruvate (MP) was conducted in a 100 ml stainless autoclave. The reaction solution contained 1.05×10^{-2} mol MP, 1 ml n-butanol (as an internal standard for gas chromatography), certain amount of CD, 9.0 ml PVP-Pt dispersion (containing 6.4×10^{-6} mol Pt, 6.4×10^{-5} mol PVP in terms of monomeric units) and metal cation. H_2 was charged several times to replace air and the final H_2 pressure was kept at 4.0 MPa at 298 K. After 0.5 h the resultant products were analyzed by gas chromatography with a 25 m × 0.25 mm capillary column (CP-Chirasil-Dex CB, Chrompack Co.).

3. Results

We observed that the ee value in the present study was different from that in our earlier studies for the same catalysts and under the same experimental conditions. A com-

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Table 1
Enantioselective hydrogenation of MP over CD-modified PVP-Pt clusters in the presence of rare earth metal cations.[a]

Cation	Concentration of CD (10^{-4} M)	Conversion of MP (%)	ee[b] (%)
–	6.8	65.9	69.5
Cu^{2+}	6.8	39.8	78.5
Zn^{2+} [c]	6.8	49.3	79.0
Nd^{3+}	6.8	69.0	80.2
Ce^{3+}	6.8	70.1	78.6
–	3.4	45.7	72.5
La^{3+}	3.4	63.5	80.1
Ce^{3+}	3.4	48.2	82.3
Pr^{3+}	3.4	66.7	84.4
Nd^{3+}	3.4	55.7	83.8
Eu^{3+}	3.4	55.8	85.7
Yb^{3+}	3.4	53.3	88.5

[a] Solvent: ethanol. The molar ratio of M^{n+} to Pt = 1 : 20.
[b] The enantioselectivity for (R)-(+)-methyl pyruvate.
[c] The molar ratio of Zn^{2+} to Pt = 1 : 10.

parison has been made between the old batch of MP (purchased three years ago from Acros) and the new batch of MP (used currently). The new batch of MP exhibited ee values that were slightly lower than those in our earlier studies. The fluctuation of ee values resulting from different origins or batches of substrate has also been reported by other researchers [2,12,13]. As shown in table 1, when using PVP-Pt colloidal clusters as catalyst with [CD] = 6.8×10^{-4} M, 65.9% conversion of MP with *ca.* 69.5% ee for (R)-(+)-methyl lactate (ML) was observed in ethanol medium. However, upon introducing a small amount of Cu^{2+} or Zn^{2+} into the system, the ee for (R)-ML increased to *ca.* 79.5% with a decrease in the activity to different extent. Both ee value and catalytic activity were increased when using rare earth cations as modifiers. The introduction of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+} and Yb^{3+} obviously enhanced both the conversion of MP and the ee value (table 1), especially at [CD] = 3.4×10^{-4} M. With the presence of Pr^{3+}, the conversion of MP increased ~50%, while the ee increased to 84.4% compared to 72.5% in its absence. The highest ee (88.5%) was obtained by employing Yb^{3+} as a promoter. It was notable that the increase of ee resulting from the introduction of rare earth cations grew greater with the sequence of atomic number, whereas the rate enhancement was diverse.

Figure 1 shows the influence of the concentration of metal cations to CD-modified PVP-Pt at [CD] = 6.8×10^{-4} M. When a little Nd^{3+} was added to the system, both the ee and the conversion of MP were clearly enhanced. As $[Nd^{3+}] = 3.2 \times 10^{-5}$ M (Nd^{3+}/Pt molar ratio of 1 : 20), the ee reached a maximum value ($ee_{max} = 79.6\%$) while the maximum conversion (78.5%) achieved at $[Nd^{3+}] = 6.4 \times 10^{-5}$ M (Nd^{3+}/Pt molar ratio of 1 : 10). The ee and conversion of MP then gradually decreased with the increasing concentration of $[Nd^{3+}]$. This indicated that the modification effect of metal cations is strongly concentration dependent.

The effect of CD with the presence and absence of Nd^{3+} was investigated and it is shown in figure 2. The addition of CD in the presence of Nd^{3+} not only induced enantioselectivity but also considerably promoted the reaction rate, namely it performed a ligand acceleration effect. At ee_{max}, the concentration of CD in the presence of Nd^{3+} is five times that in the absence of Nd^{3+}. In addition, white precipitates were observed in mixed concentrated ethanol solution of Nd^{3+} and CD. This may be attributed to the interaction between Nd^{3+} and CD.

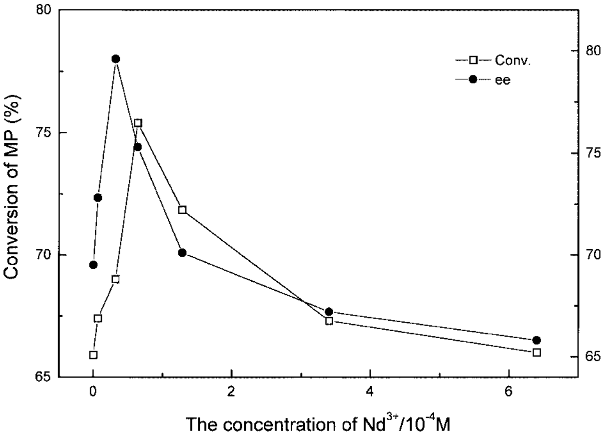

Figure 1. Influence of the concentration of Nd^{3+} on the enantioselective hydrogenation of methyl pyruvate over CD-modified PVP-Pt clusters. [CD] = 6.8×10^{-4} M.

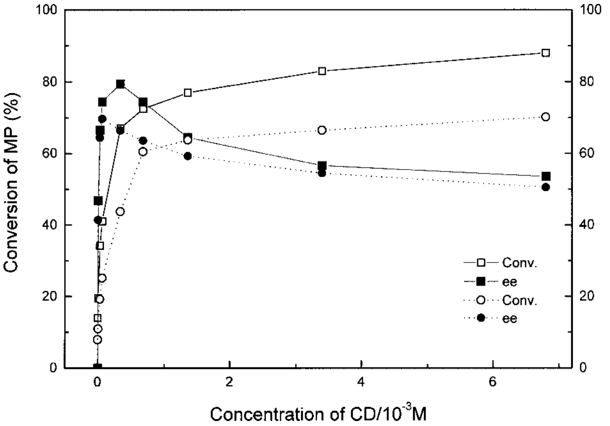

Figure 2. Influence of the concentration of cinchonidine on the enantioselective hydrogenation of methyl pyruvate over CD-modified PVP-Pt clusters with Nd^{3+} (—) and without Nd^{3+} (···). $[Nd^{3+}] = 6.4 \times 10^{-5}$ M.

The influence of solvents in the presence of Nd^{3+} was examined too, and it is shown in table 2. Taking the solubility of metal cations and PVP into account, only alcohols and water were employed as solvents. Consequently, metal cations showed a positive effect in all selected solvents. This takes the advantage over the solvent dependence in Margitfalvi's work [10], in which toluene is the exclusive solvent for the modification of achiral tertiary amines to CD-modified Pt/Al_2O_3. The conversion of MP increased with the polarity of solvents, whereas the ee value was disordered. If only the ROH solvents were taken into account, a maximum conversion of MP was obtained in *n*-propanol medium ($\varepsilon = 20.1$). The effect of solvent is rather complicated, especially with the presence of metal cations.

Table 2
Influence of solvents on the enantioselective hydrogenation of MP over CD-modified PVP-Pt clusters in the presence of Nd^{3+}.[a]

Solvent	Dielectric constant, ε	Conversion of MP[c] (%)	ee[b,c] (%)
Water	78.54	84.5 (72.1)	66.3 (61.8)
Methanol	32.63	51.8 (45.5)	76.7 (67.0)
Ethanol	24.30	74.0 (65.9)	75.5 (69.5)
1-propanol	20.1	76.5 (63.0)	76.5 (69.8)
1-butanol	17.1	72.0 (61.8)	74.5 (68.2)
1-pentanol	13.9	65.3 (57.8)	75.7 (70.5)
1-hexanol	13.3	56.2 (50.5)	73.2 (70.8)

[a] The molar ratio of Nd^{3+} to Pt was 1 : 10; [CD] $= 6.8 \times 10^{-4}$ M.
[b] The enantioselectivity for (R)-(+)-methyl lactate.
[c] The data in parentheses stand for the results without Nd^{3+}.

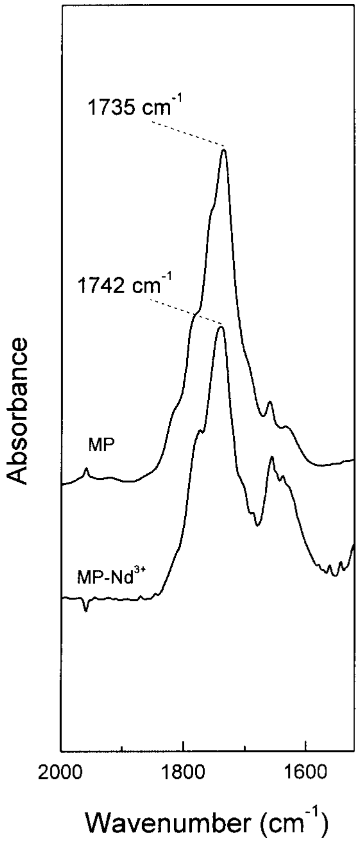

Figure 3. IR spectra of MP and MP-Nd^{3+}. [Nd^{3+}] = 0.144 M. MP as solvent.

IR spectra of MP and MP-Nd^{3+} (figure 3) clearly showed that the incorporation of Nd^{3+} activated the methyl pyruvate substrate, thereby it was suggested that the absorption model of substrate MP on the Pt surface was changed to some extent. The precise mechanism for this unusual modification of metal cations on the PVP-Pt performance still remains unclear and further investigation is in progress.

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