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# Modification effect of metal cations on the stereoselective hydrogenation of 2,3-butanedione

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The modification of some metal cations to alumina-supported Pt nanoclusters induces 100% selectivity for *meso*-2,3-butanediol in the stereoselective hydrogenation of 2,3-butanedione.

**KEY WORDS:** stereoselective hydrogenation; 2,3-butanedione; Pt cluster; metal cation

## 1. Introduction

Stereoselective hydrogenation of diketones is well documented in both organic synthesis and catalysis [1]. In the middle of the 1980s, Maier et al. studied systematically the chemical reduction of $\alpha$- and $\beta$-diketones, which afforded *meso*- and *dl*-isomers as the main products, respectively, in the presence of $LiAlH_4$ [2]. Later, over a conventional supported Pt catalyst (Pt/C), Ishiyama et al. obtained ca. 60% *meso*-diol in the hydrogenation of 2,3-butanedione [3].

It is well known that additives, such as metal ions, can markedly affect the properties of metal catalysts. On the basis of this concept, improvement of catalytic performance has been reported in a number of cases [4]. Recently, it has been found in our laboratory that the introduction of some transition metal cations, e.g., $Co^{2+}$, $Ni^{2+}$ and $Fe^{3+}$, can enhance not only the selectivity but also the activity in the selective hydrogenation of $\alpha,\beta$-unsaturated aldehyde and chloronitrobenzene over polymer-stabilized and the corresponding supported Pt group metal nanoclusters [5]. Since Adams' pioneering work [4a–d] a large number of researches have been carried out for 3/4 century. However, the modification effect of metal cations has so far been strictly limited to chemoselective reactions. In general, it is more challenging to obtain high stereoselectivity as compared to chemoselectivity because of the minimal energy difference between the two isomers. In this paper, we would like to report the effect of metal cations on the stereoselective hydrogenation of 2,3-butanedione over Pt clusters and to the best of our knowledge, this is the first example of the modification effect of metal cations on stereoselectivity. Here, we describe our preliminary results.

## 2. Experimental

The alumina-supported Pt clusters were prepared by the immobilization of polyvinylpyrrolidone-stabilized Pt clusters [6] synthesized via the alcohol–water reduction method [7]. TEM observation showed that the average diameters of the two as-prepared clusters were 1.5 and 3.3 nm, respectively. The contents of Pt were ca. 0.5%, as determined by atomic absorption spectroscopy (AAS).

Hydrogenation of 2,3-butanedione was carried out in a 100 ml stainless autoclave. Typically, 1.0 ml 2,3-butanedione, 19.0 ml ethanol, 0.2 g catalyst (containing 1.0 mg Pt) and metal salt were used. The reaction mixture was stirred vigorously for 20 h under 4.0 MPa and 333 K. Then the products were analyzed by gas chromatography.

## 3. Results and discussion

The hydrogenation of 2,3-butanedione (**1**) consists of two steps (scheme 1). Step I is much easier to proceed than II due to the stronger adsorption ability of $\alpha$-diketone on the Pt surface through the two conjugated carbonyl groups [8]. According to quantum chemical calculations, the energy difference between *meso*- and *dl*-2,3-butanediol (**3**) is only about 5.2 kJ/mol in favor of *meso*-**3**. So it is very difficult to achieve high stereoselectivity in view of thermodynamics.

$$CH_3COCOCH_3 \xrightarrow[I]{H_2} CH_3\overset{*}{C}H(OH)COCH_3$$

$$\xrightarrow[II]{H_2} CH_3\overset{*}{C}H(OH)\overset{*}{C}H(OH)CH_3$$

Scheme 1.

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First, we studied the modification of some transition metal cations to the 1.5 nm Pt cluster. As shown in table 1, the reaction of **1** gave 68.1% yield of the diol without metal cations, the stereoselectivity being 40.6% for *meso*-**3** (59.4% for *dl*-**3**). This is quite different from the result over the conventional supported Pt catalyst [3] and that with chemical reduction [2] where *meso*-**3** was yielded preferably. The unusual behavior of the cluster might partly be ascribed to the metal–support interaction, as described in [9]. Upon introducing $Fe^{3+}$, $Co^{2+}$ and $Zn^{2+}$ into the reaction system, the selectivity for *meso*-**3** was considerably enhanced despite the decrease of activity. It is noteworthy that $Mn^{2+}$, apart from inducing a moderate increase in the stereoselectivity, could also improve the chemical yield of **3** to some extent. Surprisingly, the addition of $Cu^{2+}$ almost inhibits the reaction. Under otherwise identical conditions, the hydrogenation of **2** modified by $Co^{2+}$ led to 82% selectivity for *meso*-**3**, which could be raised to 100% with the increase of $Co^{2+}$ concentration. This indicates that the stereoselectivity is determined predominantly in step II.

Table 1
Stereoselective hydrogenation of **1** and **2** over a 1.5 nm $Pt/Al_2O_3$ cluster modified with metal cations.[a]

| Reactant | Cation | Products[b] (%) | | | Selecivity for *meso*-**3** |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | (%) |
| **1** | – | 5.7 | 26.2 | 68.1 | 40.6 |
| **1** | $Cr^{3+}$ | 0 | 15.1 | 63.2 | 44.5 |
| **1** | $Mn^{2+}$ | 0 | 17.0 | 83.0 | 70.9 |
| **1** | $Fe^{3+}$ | 11.9 | 43.4 | 19.1 | 98.8 |
| **1** | $Co^{2+}$ | 10.4 | 70.9 | 18.7 | 95.1 |
| **1** | $Ni^{2+}$ | 7.6 | 65.8 | 26.6 | 69.4 |
| **1** | $Cu^{2+}$ | 94.9 | trace | 0 | – |
| **1** | $Zn^{2+}$ | 24.2 | 66.8 | 9.0 | 89.0 |
| **2** | – | – | 0 | 100 | 44.2 |
| **2** | $Co^{2+}$ | – | 58.6 | 41.4 | 82.0 |
| **2**[c] | $Co^{2+}$ | – | 88.5 | 11.5 | 100 |

[a] $MCl_x$ as the metal salt with cation/Pt = 1 unless otherwise mentioned.
[b] The formation of hemiketals between ethanol and **1**, **2** as the by-products in the case of $Cr^{3+}$, $Fe^{3+}$ and $Cu^{2+}$, as determined by GC-MS analysis.
[c] $Co^{2+}/Pt = 5$.

The relationship between the amount of $Co^{2+}$ and the stereoselectivity as well as yield of **3** was investigated over the 3.3 nm Pt cluster. As shown in figure 1, the sense of the stereoselectivity was obviously switched from *dl* (39.2% for *meso*-**3** in the absence of ions) to *meso* (72.2%) upon adding a trace of $Co^{2+}$, corresponding to a $Co^{2+}/\mathbf{1}$ molar ratio as low as 1/22000. When the $Co^{2+}/(Co^{2+} + Pt)$ molar ratio amounted to 0.35 ($Co^{2+}/\mathbf{1} = 1/4400$), the selectivity could reach ca. 100%. However, the yield of **3** was lowered to ca. 15%, as in the case for the 1.5 nm cluster. Besides, the time-resolved stereoselectivity was also surveyed. The nearly constant value revealed that the stereoselectivity was not controlled by the kinetic effects.

The "fate" of metal ions at the end of the reaction could be classified into three categories. (1) $Cu^{2+}$ was totally reduced to $Cu^0$, as verified by AAS. We believe that the further deposition of metal copper onto Pt surface was responsible for the deactivation of the catalyst (table 1). (2) Chemical analysis showed that all $Fe^{3+}$ was reduced to $Fe^{2+}$ but not to $Fe^0$ [5b]. (3) $Mn^{2+}$ and $Zn^{2+}$ remained as ions during the reaction owing to their far lower redox potentials than that of $H_2$. As for $Co^{2+}$ whose redox potential is a little higher than that of $H_2$ under the reaction conditions (4.0 MPa and 333 K), we monitored the pH change of the reaction mixture containing only $Co^{2+}$, Pt cluster and ethanol, in view of the fact that the corresponding amount of $H^+$ would be released if $Co^{2+}$ was reduced by $H_2$. Fortunately, the pH value of the solution kept unchanged. In addition, a blank experiment with **1**, $Co^{2+}$, support $Al_2O_3$ and ethanol showed no conversion of **1**. Based on these supporting facts, we take it for granted that cobalt existed in a 2+ oxidation state during the reaction.

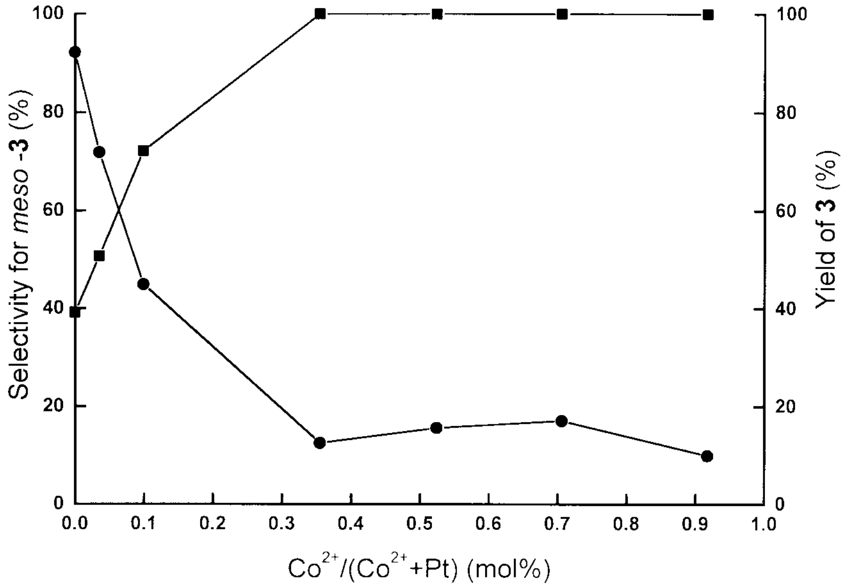

Figure 1. Stereoselectivity for *meso*-**3** (■) and yield of **3** (•) vs. molar percentage of $Co^{2+}$ in the hydrogenation of **1** over a 3.3 nm $Pt/Al_2O_3$ cluster.

By means of UV-Vis spectroscopy, we studied the interaction of Co$^{2+}$ with **1** and **2**. It reveals that the **2**–Co$^{2+}$ interaction is more pronounced than that of **1**–Co$^{2+}$, which is caused by the stronger coordinative ability of the hydroxyl group. Based on these analyses and the experimental facts that the stereocontrol is realized in step II, we present a chelation model in which the intermediate product **2**, through the carbonyl and hydroxyl groups, coordinates with Co$^{2+}$ to form a five-membered cyclic species. Besides, a six-membered one may also be possible with the participation of the surface Pt atom (figure 2). Then according to the former complex, the modification mechanism is shown in figure 3.

When no ions are added, a racemic mixture of **2** is obtained after step I. Taking the $R$ isomer for example (the same case for the $S$ isomer), it has two orientations on the Pt surface, i.e., A and A$'$, which upon hydrogenation would lead to *dl* and *meso*-**3**, respectively. Molecular mechanics calculations of the two selections on the Pt surface show that A is more stable than A$'$ ($\Delta E = 24.1$ kJ/mol) because of the smaller repulsion between the carbonyl and hydroxyl groups as well as between the terminal methyl groups. Thus the surface concentration of A exceeds that of A$'$, which after step II, yields *dl*-**3** in excess. The modification effect of Co$^{2+}$ is exhibited in step II instead of I. It is reasonable to assume that Co$^{2+}$ is much more liable to coordinate with **2** in A$'$ form and at the same time, it is not the steric but the coordination effect that predominates the stabilization of the two orientations. As a result, the precursor to *meso*-**3** is greatly stabilized, which in turn causes the reversal of the sense of stereoselectivity.

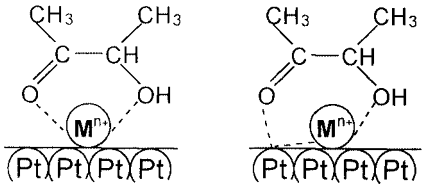

Figure 2. Chelated complexes formed between **2**, Co$^{2+}$ and Pt.

In summary, we have for the first time observed the modification effect of metal cations on the stereoselective hydrogenation of 2,3-butanedione over supported Pt clusters. The selectivity for the *meso*-diol is elevated from ca. 40 to 100% at very low level of the modifier Co$^{2+}$ and depends greatly on the kind of cations introduced. We have also made a primary rationalization of the modification mechanism on the basis of the interaction between metal cation (M$^{n+}$) and the intermediate, hydroxyketone. Nevertheless, the decrease of the activity in most cases (except for Mn$^{2+}$) is still unclear. On the other hand, the interaction of the metal cation with the product diol should not be neglected because it is generally even stronger than that of **2**–M$^{n+}$ mentioned above. Moreover, it is interesting to note that due to a less steric hinderance of the terminal methyl groups, *dl*-**3** is more readily to chelate with metal cations as compared to *meso*-**3** [10], which has also been shown in the UV-Vis analysis. In our opinion, the **3**–M$^{n+}$ interaction may also affect the distribution of the diol as well as the activity. A detailed study including the optimization of the **2**–M$^{n+}$ and **3**–M$^{n+}$ interactions on a Pt surface by use of molecular simulation is currently underway in our laboratory.

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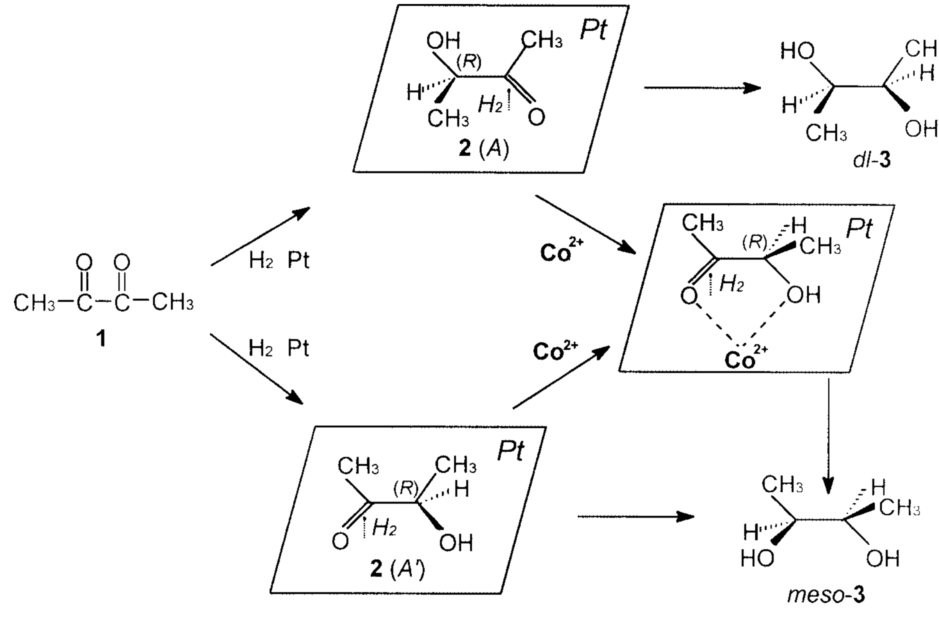

Figure 3. Possible steric courses in the stereoselective hydrogenation of **1** to **3** (A and A$'$ are the two stable selections on the Pt surface optimized by molecular mechanics).

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