

Molecular Mechanics Study on Asymmetry Catalysis

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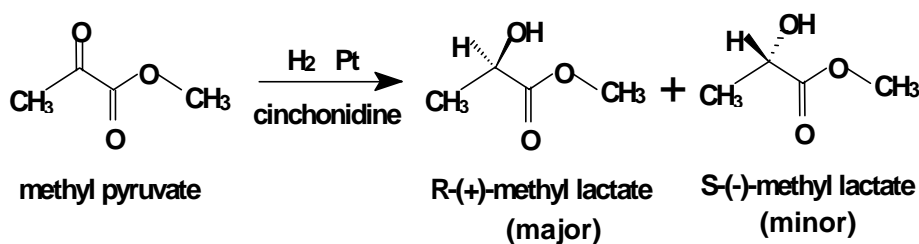
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Abstract: A ground state model about an asymmetry hydrogenation of methyl pyruvate over Pt-nanocluster catalyst with a modifier cinchonidine has been built. The role of the modifier in the catalytic process is explained .

Keywords: molecular mechanics, asymmetry catalysis, methyl pyruvate, Pt-cluster catalyst, modifier.

The asymmetry catalysis is an important chemical reaction widely used in biology, pharmacy and agriculture. It is preferred to enantioselective hydrogenation of methyl pyruvate (MP) over supported platinum nanoclusters.

Scheme 1. The reaction of the hydrogenation of methyl pyruvate



Cinchonidine (CD) is a modifier, a co-catalyst to the reaction. Without the modifier, there would be no enantioselectivity to the hydrogenation of pyruvate. In order to obtain better understanding of the mechanism of the reaction, especially the role of the modifier, the present study by molecular modeling has been performed and the results are reported here.

The model in the present study consisting of CD, MP and Pt surface or Pt cluster differs from the 1:1 interaction model in the early study¹, where the real interaction from the metal surface was not considered in calculation.

The Pt clusters are built in fcc structure regularly arranged according to the $10n^2+2$ (n is the layer number) packing rule. The $10n^2+2$ cluster model is a regular icosahedron

and possesses two kinds of faces, the smaller one in a triangle shape with $(n+1)(n+2)/2$ atoms and the larger one in a square shape with $(n+1)^2$ atoms. In the present simulation, the Universal Force Field 1.02 (UFF) ² was applied and validated by examining the conformational structure of cinchonidine (CD) calculated with the observed.

The adsorption energy for individual MP was found to be 8~10 kcal/mol higher than that with CD together on a 4×4 nm Pt surface (100). Using the optimized geometry of CD on the Pt, we examined the stable configurations when MP is involved in turn with two kinds of configurations, which have been recognized in literature ^{1,3-7} as the precursors that lead to the R-methyl lactate or S-methyl lactate upon hydrogenation. It shows that the energy difference (ΔE) between the two configurations is 1.53 kcal/mol in favor of R-methyl lactate. This is comparable to the early AM1 study obtaining the energy difference 1.4 kcal/mol ⁵.

The results show that in the case of the modifier CD exists, the adsorption probability of MP on the Pt surface increases and the reaction possesses an enantioselectivity to the hydrogenation of pyruvate. The modifier, therefore, plays a role of molecular identification.

Next attempt is focused on a possibility if in the limited area the modifier and the reactant adsorbed on the cluster could have the same recognition behavior. Firstly, the energies of CD adsorbed on the larger or on the smaller face of the 3-layer to 6-layer clusters were examined. It shows that CD is generally more stable on the larger face except for $n=5$ (as shown in **Table 1**). So the following simulations are focused on the case that CD is fixed on the larger face.

As the limitation of the speed of our workstation, the examination was performed through a series of clusters from 1.6 nm to 3.3 nm in particle size. Obtained results show that even for the smaller sizes the recognition works, however, with relatively lower efficiency (compared to the results on much larger Pt surface above), and that the effective recognition can be put into two cases. In one case, CD is in the same face with MP; in the other, CD and MP are in the adjacent faces.

It shows that only when the layer of the cluster increases to 5, *i.e.* 561 Pt atoms (2.7 nm in particle size) can both of the molecules be fully anchored on the same face which is quadrangle, such as the corresponding 36-atom-face (**Figure 1A**). The energy difference ΔE is 0.73 kcal/mol and favorable for the precursor to R-methyl lactate. While the number of layers of the cluster is up to 6, including 923 Pt atoms (3.3 nm in particle size), the energy difference ΔE is 0.90 kcal/mol, it obeys the same trends as well as in the larger face.

Table 1 Energy of CD in different plane in Pt cluster

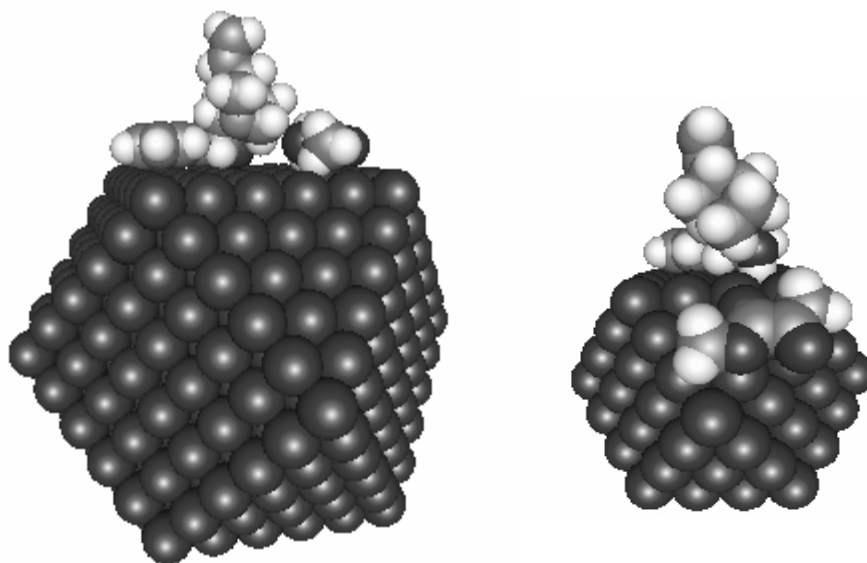
Number of layers in Pt cluster	in smaller face		in larger face		ΔE Kcal/mol
	Number of atoms	E Kcal/mol	Number of atoms	E Kcal/mol	
3	10	79.2719	16	78.1218	1.1501
4	15	79.3102	25	78.3204	0.9898
5	21	78.3908	36	78.4049	- 0.0141
6	28	78.7564	49	78.0635	0.6929

When the two molecules are located in the adjacent faces, the recognition works until the size of the cluster decreases to 3-layer one (147 atoms, 1.6 nm in particle size). **Figure 1B** shows that CD and MP are adsorbed parallel to the adjacent faces of a 3-layer

Figure 1 The modeling of CD and MP on Pt cluster with various size.

A: 5-layer, 561 atoms, 2.7 nm

B: 3-layer, 147 atom, 1.6 nm



Pt particle. In this case, the formation of R-product is energetically more favorable than that of S-product ($\Delta E = 1.0$ kcal/mol). In the other clusters, or in the other case, the same performance was not found in our calculation.

Although this recognition behavior works for generally larger Pt surface, or in larger cluster, the possibility has also been validated of the recognition even working for the limited surface of the smaller Pt cluster, such as 1.6 nm in particle size. It thus supports the experiments that the enantiodifferentiation is well performed for the smaller clusters.

Acknowledgments:

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