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Modification of Metal Complex on the Stereoselective Hydrogenation of 2,3-Butanedione

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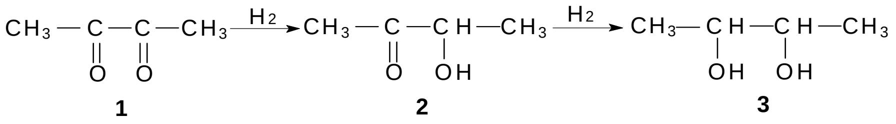
Abstract: The modification of some metal complexes on Pt/Al_2O_3 clusters leads to remarkable increases in both the activity and the selectivity for *meso*-2,3-butanediol in the stereoselective hydrogenation of 2,3-butanedione.

Keywords: Stereoselective hydrogenation, 2,3-butanedione, metal complex, platinum cluster.

Nanoscopic metal clusters, because of their substantial difference from metal atoms and bulk metals in size and structure, have attracted great interest especially in the field of catalysis[1]. It is well known that additives can markedly affect the properties of metal catalysts. The effect of metal ions has been well studied in the field of heterogeneous catalysis[2]. However, the study of metal complex effect is scarce. We have reported that the metal complex can considerably modulate both the activity and the selectivity in the hydrogenation of cinnamaldehyde as well as the hydrogenation of *o*-, *m*-, *p*-chloronitrobenzenes over PVP-Pt clusters[3]. The reported effects have only been confined to chemoselective reactions. Recently, we observed similar effect of metal complexes in the stereoselective hydrogenation of 2,3-butanedione over Pt/Al_2O_3 clusters. As far as we know, this is the first example of modification of the metal complex on stereoselectivity. Herein we report our preliminary results.

The hydrogenation of 2,3-butanedione is a two-step process. **Table 1.** lists the experimental results of the influence of metal complexes, metal ions and ligands on the title reaction. It is obvious that the influence of metal complex is not the sum of those of the metal central ions and the ligands. Taking Co(bpy)Cl_2 for example, Co^{2+} induced very high selectivity for *meso*-**3**, but the activity was decreased greatly; on the other hand, the bipyridine ligand increased the yield of **3** from 68.1% to 80.2% whereas influenced little on the stereoselectivity. When it came to Co(bpy)Cl_2, the yield of **3** could be enhanced to 92.3%, the stereoselectivity for *meso*-**3** was also elevated moderately to 58.5%.



$$\underset{\mathbf{1}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow{H_2} \underset{\mathbf{2}}{CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{H_2} \underset{\mathbf{3}}{CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3}$$

Table 1 The effect of metal complex on the hydrogenation of 2,3-butanedione over a 1.5 nm (σ = 0.38 nm) Pt/Al_2O_3 cluster [a]

Catalytic System	Products (%)			Selectivity for *meso*-**3** (%)
	1	**2**	**3**	
Pt/Al_2O_3	5.7	26.2	68.1	40.6
Pt/ Al_2O_3-$MnCl_2$	0	trace	100	75.0
Pt/ Al_2O_3-$CoCl_2$	10.4	70.9	18.7	95.1
Pt/ Al_2O_3-$NiCl_2$	7.6	65.8	26.6	69.4
Pt/Al_2O_3-3bpy	0	19.8	80.2	43.0
Pt/Al_2O_3-Co(bpy)Cl_2	0	7.7	92.3	58.5
Pt/Al_2O_3-Co(bpy)$_2Cl_2$	0	17.5	82.5	45.5
Pt/Al_2O_3-Co(bpy)$_3Cl_2$	0	67.2	32.8	43.7
Pt/Al_2O_3-2en	0	5.6	94.4	42.9
Pt/Al_2O_3-Ni(en)Cl_2	5.1	52.8	42.1	60.8
Pt/Al_2O_3-Ni(en)$_2Cl_2$	3.3	54.3	42.4	52.2
Pt/Al_2O_3-Ni(en)$_3Cl_2$	0	46.4	53.6	51.6
Pt/Al_2O_3-Mn(en)$_3Cl_2$	0	11.9	88.1	73.3
Pt/Al_2O_3-den	0	10.3	89.7	47.4
Pt/Al_2O_3-Mn(den)Cl_2	0	0	100	85.3
Pt/Al_2O_3-Mn(den)$_2Cl_2$	0	0	100	62.4
Pt/Al_2O_3-Co(den)Cl_2	5.4	31.4	63.2	80.8

[a] metal complex/Pt = 1 (in molar ratio); [b] en : ethylenediamine; bpy : bipyridine; den : diethylenetriamine;
[c] reaction condition : 4.0 MPa H_2, 333 K, 20 h.

With respect to the cobalt bipyridine complexes, different results were obtained at different ratios of bpy : Co^{2+}, the activity was evidently decreased, the stereoselectivity for *meso*-**3** was also decreased slowly with the increase in molar ratio of bpy : Co^{2+}. These results show that the behavior of metal complex is closely related to the number of the ligands coordinated to the central metal ion. Among all the tested metal complexes, the effect of Mn(den)Cl_2 is most pronounced. The addition of Mn(den)Cl_2 not only increased the activity greatly but also induced higher selectivity (85% for *meso*-**3**) than Mn^{2+} did, thus displaying the singular modification effect of the metal complex.

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