

## Effect of Transition Metals on Selective Hydrogenation of Cinnamaldehyde over Pt/ZrO<sub>2</sub> Catalysts

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**Abstract:** The effect of transition metals (Cr, Mn, Fe, Co and Ni) on the hydrogenation of cinnamaldehyde over Pt/ZrO<sub>2</sub> catalysts was studied in ethanol at 343K under 2.0MPa H<sub>2</sub> pressure. PtCo/ZrO<sub>2</sub> and PtFe/ZrO<sub>2</sub> catalysts exhibit high selectivity and activity of hydrogenation for C=O (93.8% at 87.3% conversion and 83.6% at 88.6% conversion, respectively), and PtNi/ZrO<sub>2</sub> exhibits high selectivity of hydrogenation for C=C (64.3% at 70.6% conversion). In the presence of trace H<sub>2</sub>O and NaOH, over the PtNi/ZrO<sub>2</sub> (0.4wt%Ni) catalyst the selectivity to hydrocinnamaldehyde reaches 90.6% and the conversion of cinnamaldehyde is 90.5%.

**Keywords:** Hydrogenation, cinnamaldehyde (CMA), cinnamyl alcohol (CMO), phenylpropanol (HCMO), hydrocinnamaldehyde (HCMA).

As all known, research in catalytic selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is of great importance in potential industrial applications and theoretical aspects<sup>1-4</sup>. Cinnamaldehyde, a member of  $\alpha, \beta$ -unsaturated aldehydes, and its semi-hydrogenated products such as cinnamyl alcohol and hydrocinnamaldehyde are important fine chemicals and intermediates especially in perfume industry and medicine manufacture. Many excellent catalysts have been discovered to gain products of selective hydrogenation<sup>5-8</sup> of C=O or C=C. The key factor controlling the selectivity and activity of hydrogenation of cinnamaldehyde yet remains unclear, although it is well known as a general rule that the electronic effects and stereo-hindrances predominate the selectivity and activity. In this paper, we investigate the catalytic properties of Pt/ZrO<sub>2</sub> catalyst modified by transition metal (Cr, Mn, Fe, Co and Ni) on the hydrogenation of cinnamaldehyde.

The monometallic Pt/ZrO<sub>2</sub> catalyst was prepared by conventional impregnation. The sample impregnated was reduced by KBH<sub>4</sub> before use. The content of platinum was 0.3 wt%. The bimetallic PtM/ZrO<sub>2</sub> catalysts (M= Cr, Mn, Fe, Co and Ni) were also prepared by impregnation, *i.e.* platinum might be impregnated after the transition metal was impregnated on ZrO<sub>2</sub>. The preparation process was similar to monometallic Pt catalyst, and the content of M and Pt was 0.1 wt% and 0.3 wt%, respectively.

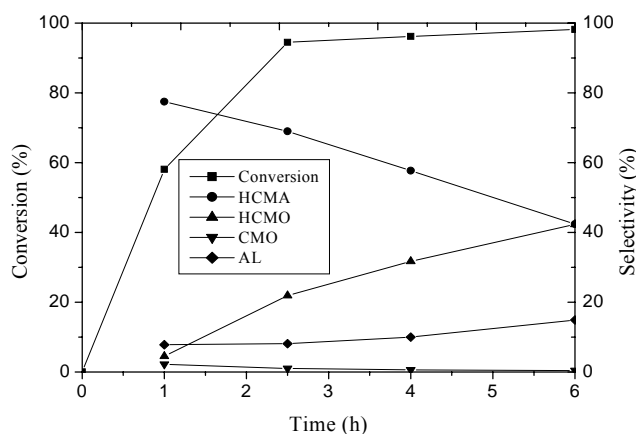
The hydrogenation reaction was carried out in a stainless steel reactor equipped with a hydrogen inlet, a Teflon vessel and a magnet stirrer under 2.0 MPa and 343 K. The

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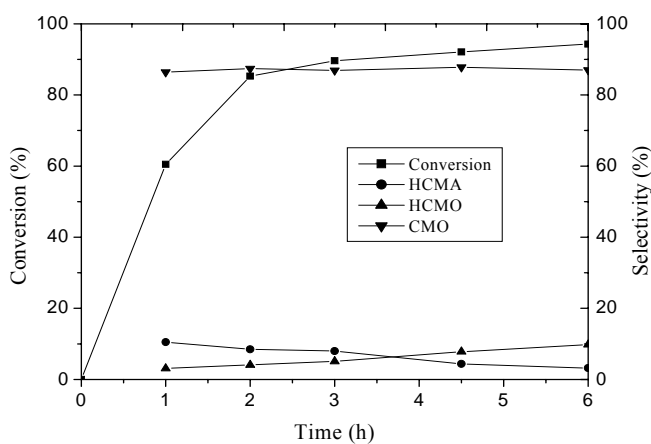
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temperature was maintained by water bath. Reaction products were analyzed with GC. The results were listed in **Table 1**. From **Table 1**, we find that the platinum catalysts modified by transition metal show different catalytic properties. PtFe/ZrO<sub>2</sub> and PtCo/ZrO<sub>2</sub> catalysts show better selectivity of hydrogenation for C=O (83.6% at 88.6% conversion and 93.8% at 87.3% conversion, respectively), but PtNi/ZrO<sub>2</sub> catalyst shows better selectivity of hydrogenation for C=C(64.3% at 70.6% conversion). The influence of contents of transition metals on the selectivity and conversion of the hydrogenation over PtM/ZrO<sub>2</sub>(M=Co,Ni) was also investigated. The most active catalyst was PtNi/ZrO<sub>2</sub>(Ni 0.4 wt%) and PtCo/ZrO<sub>2</sub>(Co 0.15wt%).

**Figure 1** The conversion of CMA and the selectivity to each product as functions of the reaction time for PtNi/ZrO<sub>2</sub> (Ni 0.4 wt%)



**Figure 2** The conversion of CMA and the selectivity to each product as functions of the reaction time for PtCo/ZrO<sub>2</sub> (Co 0.15 wt%)



**Table 1** Results of the hydrogenation of cinnamaldehyde over PtM/ZrO<sub>2</sub> catalysts<sup>a</sup>

Catalyst	Conversion (%)	Selectivity (%)			
		HCMA <sup>b</sup>	HCMO <sup>c</sup>	CMO <sup>d</sup>	others
Pt/ZrO <sub>2</sub>	49.9	25.5	21.7	42.2	10.6
PtCr/ZrO <sub>2</sub>	21.4	46.5	8.0	1.0	44.5
PtMn/ ZrO <sub>2</sub>	55.2	27.4	6.6	52.0	14.0
PtFe/ ZrO <sub>2</sub>	88.6	5.4	10.7	83.6	0.3
PtCo/ ZrO <sub>2</sub>	87.3	2.5	3.7	93.8	0.0
PtNi/ ZrO <sub>2</sub>	70.6	64.3	11.8	7.8	16.1

<sup>a</sup>0.6 g catalyst, 8.0 mmol cinnamaldehyde, and 19.0 mL C<sub>2</sub>H<sub>5</sub>OH were used at 343K under 2.0 MPa. Reaction time is 6 h.

<sup>b</sup>HCMA = hydrocinnamaldehyde.

<sup>c</sup>HCMO = phenylpropanol.

<sup>d</sup>CMO = cinnamyl alcohol.

The conversion of CMA and the selectivity to each product as functions of the reaction time were showed in **Figure 1** and **Figure 2**. From **Figure 1**, we find that the selectivity to HCMA decreases monotonously with the reaction time. The conversion of CMA increases rapidly in 2 hours, levels off then. A little acetal(AL) appears in the reaction system. From **Figure 2**, we find that the selectivity to CMO is always higher than 85%. Acetal disappears. By comparison, the conversion of CMA over PtCo/ZrO<sub>2</sub> (Co 0.15 wt%) is slightly lower than that over PtNi/ZrO<sub>2</sub> (Ni 0.4 wt%) at the same reaction time.

In order to increase the conversion and the selectivity to HCMA, the hydrogenation reaction over PtNi/ZrO<sub>2</sub> catalyst was observed in the presence of trace H<sub>2</sub>O and NaOH. It was found that both the catalytic activity and the selectivity to HCMA were obviously increased. The selectivity to HCMA reached about 90.6% at 90.5% conversion under 1h in the presence of 1mLH<sub>2</sub>O and 1mg NaOH.

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