

Novel and Simple Modification of Metal Cation to Supported Pt Catalysts for Chemoselective Hydrogenation of Cinnamaldehyde

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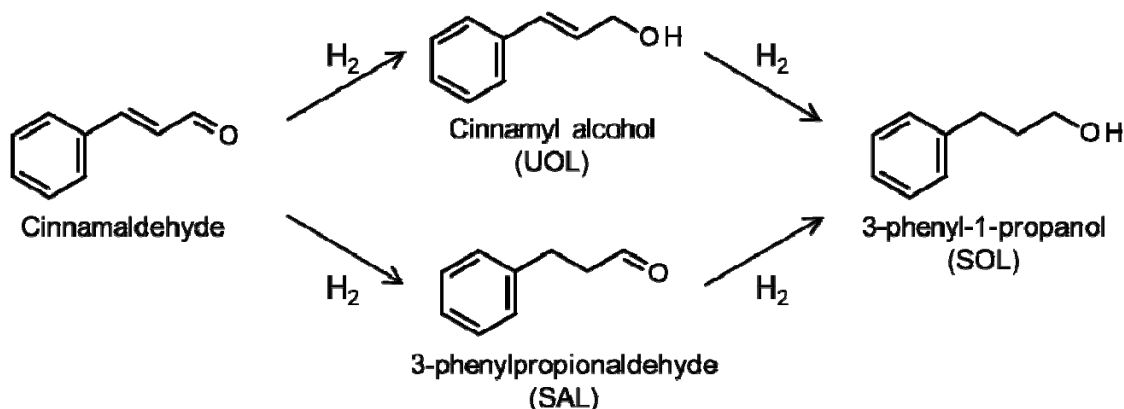
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Highlights

- Co^{2+} in liquid phase can be reduced and deposited over Pt/ SiO_2 catalysts.
- Reductively deposited Co interacted with Pt to form Co-Pt bimetallic sites.
- Formed Co-Pt bimetallic site is effective for chemoselective hydrogenation.

1. Introduction

The selective hydrogenation of unsaturated aldehydes to corresponding unsaturated alcohols (UOL) is an important process for synthesis of perfume, pharmaceutical intermediate and various fine chemicals. Scheme 1 shows the reaction pathway of cinnamaldehyde hydrogenation. Over the conventional hydrogenation catalysts (such as Pt), the hydrogenation of $\text{C}=\text{C}$ bond preferentially proceeds in comparison with that of the $\text{C}=\text{O}$ bond, bringing about the formation of the undesirable compounds (corresponding saturated aldehyde (SAL) and saturated alcohol (SOL)). The bimetallic catalysts, such as the second metal (Co, Fe and Sn) addition to Pt based catalysts, have been widely investigated to improve the selectivity of UOL [1]. In this study, we propose the novel and simple modification method of Co cation to Pt/ SiO_2 catalysts to give the Co-deposited Pt/ SiO_2 catalysts for chemoselective hydrogenation of cinnamaldehyde.



Scheme 1 Reaction pathway of cinnamaldehyde hydrogenation

2. Methods

The Pt/ SiO_2 (4 wt% of Pt loading) catalyst was prepared by an impregnation method. The obtained catalyst precursors were calcined in flowing air at 623 K for 2 h followed by reduction in flowing H_2 at 573 K for 2 h.

The Co-deposited Pt/ SiO_2 catalysts were prepared as follows. The Pt/ SiO_2 (25 mg) and 4 mL of 0.5 mM of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 2-methyl-2-butanol were charged into a stainless steel autoclave, and then 2.0 MPa (gauge) of H_2 or N_2 were charged. The catalyst preparation was carried out at 393 K for 4 h. The amount of deposited Co^{2+} on Co-deposited Pt/ SiO_2 catalysts were measured by adsorption atomic spectrometry.

Table 1 Hydrogenation of cinnamaldehyde over Co-deposited Pt/SiO₂ catalysts prepared under various conditions.

Entry	Catalyst	Co ²⁺ deposition condition		Co deposition ($\mu\text{mol/g-cat.}$)	Conversion (%)	Selectivity of UOL (%)	Yield (%)		
		Temp. (K)	Atmosphere				UOL	SAL	SOL
1	Pt/SiO ₂	-	-	-	14.9	10.1	1.5	12.7	0.7
2	Co-deposited Pt/SiO ₂	393	H ₂ (2 MPa)	77.6	43.4	95.3	41.4	1.2	1.5
3	Co-deposited Pt/SiO ₂	393	N ₂ (2 MPa)	27.1	17.3	40.5	7.0	8.9	1.4

The selective hydrogenation of cinnamaldehyde was carried out in liquid phase. The reaction mixture containing 4 mL of 2-methyl-2-butanol, 25 mg of catalyst, and 0.2 mL of cinnamaldehyde was charged in a stainless steel autoclave. Hydrogen was charged and discharged several times to remove air in the reactor. Subsequently, the autoclave was charged with 2.0 MPa (gauge) of H₂. The hydrogenation reaction was carried out at 393 K for 0.5 h. The products were analyzed by gas chromatography.

3. Results and discussion

Table 1 shows the amount of Co deposition and the catalytic performance of the Co-deposited Pt/SiO₂ catalysts prepared under H₂ and N₂ for hydrogenation of cinnamaldehyde in liquid phase. The amount of Co deposition on the Pt/SiO₂ catalysts under H₂ (entry 2) was larger than that under N₂ (entry 3). Over the SiO₂ (without Pt), the almost same amount of Co deposition (ca. 30 $\mu\text{mol/g-cat.}$) was observed independent of the preparation atmosphere. The Co was suggested to be adsorbed over the Pt/SiO₂ catalysts (probably over the SiO₂ support) prepared under N₂. Not only H₂ but also Pt facilitated the Co deposition over the Pt/SiO₂ catalysts (entry 2), suggesting that the Co species was reduced over the Pt surface. The Co-deposition over Pt/SiO₂ under H₂ atmosphere (entry 2) brought about the significant increase in the conversion and the UOL selectivity up to ca. 43 % and ca. 95 %, respectively, in comparison with the conventional Pt/SiO₂ catalyst (entry 1). The Pt ensembles were well known to accelerate the hydrogenation of C=C bond. Since the C=C hydrogenation was markedly suppressed by the Co deposition on the Pt/SiO₂ under H₂ (entry 2), the reductively deposited Co was suggested to be interact with the surface of Pt particles, bringing about not only the ultra-selective formation of cinnamyl alcohol, but also the enhancement of hydrogenation activity.

4. Conclusions

Co²⁺ cation can be reduced and deposited by H₂ over Pt/SiO₂ catalysts in liquid phase, leading to the formation of the Co-Pt bimetallic catalysts. The formed Co-Pt bimetallic sites is effective for the chemoselective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

References

- [1] P. Maki-Arvela, J. Hajek, T. Salmi, D.Y. Murzin, *Appl. Catal. A: Gen.* 292 (2005) 1–49.

Keywords

Reductive deposition; Co-deposited Pt/SiO₂ catalyst; Chemoselective hydrogenation; Cinnamaldehyde