

# Pt/ML (M = Rb, Sr) as highly selective and active catalysts for cinnamaldehyde hydrogenation to cinnamyl alcohol

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**Rubidium and strontium modified L zeolite- supported Pt catalysts were found to be highly active and selective for the hydrogenation of cinnamaldehyde to produce its C=O hydrogenation product, cinnamyl alcohol.**

Allylic alcohols are widely used in the industrial synthesis of perfumes, agro chemicals and pharmaceuticals.<sup>1</sup> Allylic alcohols can be extracted from natural products, but they are most easily obtained by the selective catalytic reduction of  $\alpha,\beta$ -unsaturated aldehydes. Despite having many advantages over homogeneous systems, heterogeneous catalysts are still not widely used in the industrial processing of fine chemicals due to their poor selectivities. The heterogeneous catalysts used for selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes are mainly supported transition metals such as Pt<sup>2</sup>, Ru<sup>3</sup> and Ni<sup>4</sup> promoted by Sn, Fe or Co. The use of zeolites as catalysts and supports in the syntheses of fine chemicals is unusual. Gallezot *et al.*<sup>5</sup> studied the hydrogenation of cinnamaldehyde (UAL) over Pt/Y and Pt/Beta catalysts and concluded that the large Pt particles located in the zeolite channels are responsible for the selective reduction of the carbon–oxygen double bond. Previously, we reported<sup>6</sup> the results of cinnamaldehyde hydrogenation on Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts, where Sn was found to be a useful additive for improving the C=O hydrogenation selectivity of Pt/Al<sub>2</sub>O<sub>3</sub>, albeit with the sacrifice of activity. Here we report the high activity and selectivity of the cinnamaldehyde conversion to cinnamyl alcohol over modified L zeolite-supported Pt catalysts.

Pt/ML catalysts were prepared by incipient wetness impregnation from a water solution of [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>. L zeolites modified by alkali or alkaline earth metal cations such as Li<sup>+</sup>, Na<sup>+</sup>, Rb<sup>+</sup>, Sr<sup>2+</sup> and Mg<sup>2+</sup> were prepared by ion-exchanging KL zeolites two times with an aqueous solution of their nitrates at 373 K for 24 h, followed with drying at 383 K and calcination at 773 K for 4 h. Before reaction, catalysts were reduced in H<sub>2</sub> at 673 K for 2 h followed with passivation in N<sub>2</sub> at 298 K for 30 min. Activity evaluation of cinnamaldehyde hydrogenation was performed in a 100 cm<sup>3</sup> micro-autoclave. Typically, 0.2 g catalyst was suspended in a liquid phase containing 20 cm<sup>3</sup>

isopropanol followed by reduction at 373 K in 5.0 MPa H<sub>2</sub> for 2 h. Cinnamaldehyde (2 g) was then introduced and reaction was started with continuous stirring under 5.0 MPa H<sub>2</sub> pressure at 373 K. Products were separated chromatographically using a 50 m long OV-101 quartz capillary column and analysed by a flame ionisation detector (FID). Only cinnamaldehyde (PhCH=CHCHO, UAL), cinnamyl alcohol (PhCH=CHCH<sub>2</sub>OH, UOL), 3-phenyl propanal (PhCH<sub>2</sub>CH<sub>2</sub>CHO, SAL) and 3-phenylpropan-1-ol (PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, SOL) were detected during the reaction. XRD patterns were recorded on a Rigaku D/MAX-RB spectrometer.

Table 1 lists the selectivities of UOL formation at UAL conversion of 25, 50, 75 and 95%, and their related reaction time, respectively. For unsupported KL, the conversion of UAL is very low (less than 3.5% conversion after reaction for 480 min) and the C=C reduction product SAL is the dominant product. Addition of Pt and Pd onto L zeolites affects the reaction activity of UAL and product distribution drastically. Only 1 mass% of Pt addition to KL enhances the UOL selectivity to 63.2–68.8% at UAL conversion between 25 and 95%. Increased Pt loading enhances both the activity of UAL and the selectivity to UOL simultaneously. In contrast to Pt, the hydrogenation of UAL on Pd/KL catalyst produces mainly saturated aldehyde (SAL) with very high activity. Reaction on Pd/KL (3 mass% Pd loading) at 373 K for only 10 min caused the complete conversion of UAL with an SAL selectivity of 88.8%, indicating that Pd is selective for the activation of the C=C bond, which is in agreement with results on other Pd-based catalysts.<sup>7</sup>

The highest selectivities to UOL were found on Pt/RbL and Pt/SrL catalysts. At a conversion of 25%, the UOL selectivity on Pt/SrL is as high as 98.2%. With the increase of UAL conversion, the UOL selectivity begins to decrease gradually accompanied by the formation of the completely hydrogenated product SOL (Fig. 1). At a UAL conversion of 95%, the UOL selectivities on Pt/RbL and Pt/SrL are still higher than 90%. It is also interesting to note that on both Pt/RbL and Pt/SrL catalysts, the reaction rates of UAL are much higher than those on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>6</sup>

**Table 1** Selectivity to UOL and reaction time at different UAL conversion over L zeolite-supported Pt catalysts<sup>a</sup>

Catalyst	(mass%)	Selectivity to UOL (%)							
		S <sup>25</sup> (%) <sup>b</sup>	t/min <sup>c</sup>	S <sup>50</sup> (%) <sup>b</sup>	t/min <sup>c</sup>	S <sup>75</sup> (%) <sup>b</sup>	t/min <sup>c</sup>	S <sup>95</sup> (%) <sup>b</sup>	t/min <sup>c</sup>
Pt/KL	1.0	63.2	164	68.2	517	69.9	967	68.8	1784
	2.0	66.0	59	76.8	180	78.5	399	77.6	794
	3.0	76.8	58	81.2	159	81.1	312	79.8	610
	4.0	73.2	34	77.0	94	77.6	160	78.1	281
Pt/LiL	3.0	84.4	58	76.4	312	69.6	972	57.4	2100
Pt/NaL	3.0	94.8	8	87.2	27	88.0	73	82.5	208
Pt/RbL	3.0	95.2	18	93.2	46	91.7	95	90.1	217
Pt/MgL	3.0	62.8	70	68.6	314	66.0	757	52.1	1918
Pt/CaL	3.0	52.0	4	66.2	15	77.2	44	70.5	121
Pt/SrL	3.0	98.2	3	95.6	11	94.3	32	92.2	78
Pt/BaL	3.0	70.4	12	74.4	38	73.6	95	65.4	195

<sup>a</sup> Reaction conditions: 373 K, 5.0 MPa. <sup>b</sup> S<sup>x</sup> = selectivity at UAL conversion of x%. <sup>c</sup> T reaction time needed to reach the UAL conversion.

The XRD patterns in Fig. 2 confirm that all of the Pt/L catalysts still possess L-zeolite structures indicating that the processes of catalyst preparation and pretreatment do not destroy the zeolite structures. Characteristic peaks for Pt<sup>8</sup> were found on Pt/KL catalysts with Pt loading at 1–4 mass%, suggesting that rather large Pt particles formed on these catalysts after calcination and reduction. It is difficult to imagine that such large Pt particles exist in the L zeolite channels without destroying the zeolite frameworks. In this

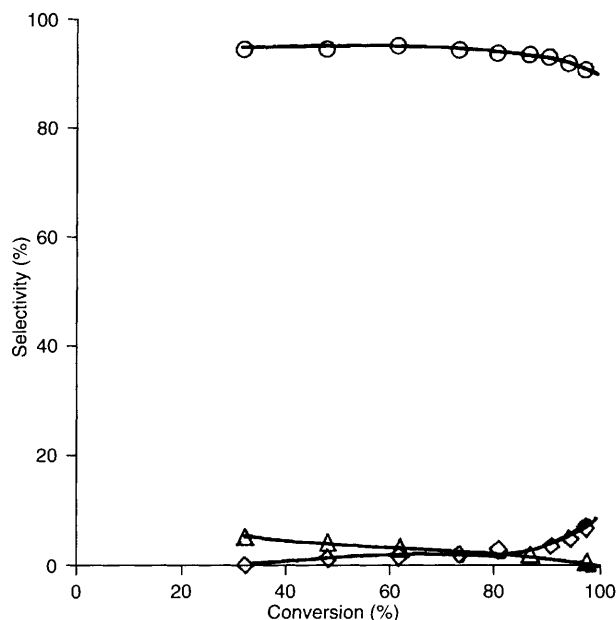


Fig. 1 Selectivity changes of UOL(○), SAL(△) and SOL(◇) vs. conversion of UAL on Pt/SrL (3 mass% Pt loading)

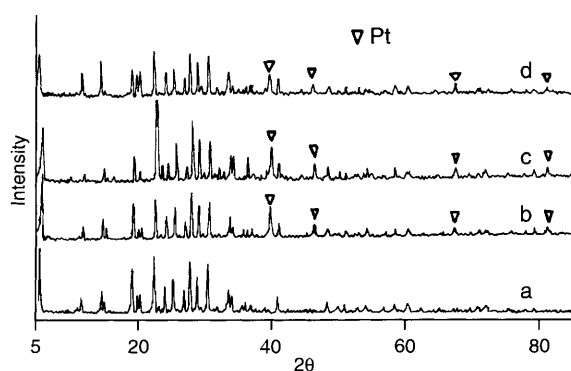


Fig. 2 XRD patterns of (a) KL, (b) Pt/KL, (c) Pt/RbL and (d) Pt/SrL with Pt loading of 3 mass%

case, the large Pt particles may be located on the external surfaces of the L zeolites, while some small particles exist inside the zeolite channels. The results are not in accordance with those reported by Sachtler and co-workers,<sup>9</sup> where Pt in Pt/KL catalysts prepared by the impregnation method exists in the form of Pt<sup>4+</sup> after high-temperature calcination, and as small Pt particles located in the channels of L zeolites after reduction. Comparing the preparation and pretreatment of their catalysts with those of ours, two factors may cause the difference in Pt dispersion between our results and those reported. One is that we used [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> as a precursor for impregnation rather than [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub>. Another important factor is that the metal loadings of our catalysts are much higher than those in the literature (0.5–1.2 mass%).<sup>9</sup>

The results suggest that the selectivity and activity of UAL hydrogenation are controlled by several factors. First, the nature of the metal plays a key role. It is clear that Pt favours C=O hydrogenation while Pd favours the hydrogenation of C=C bonds. Metal morphology also influences the selectivity. Due to the repulsion between the phenyl group of cinnamaldehyde and Pt,<sup>3</sup> UAL is likely to adsorb in an 'end-on' form on large Pt metal particles and thus the UOL selectivity is enhanced. The basicity of L zeolite increases the electron density of Pt, resulting in a lower probability for the activation of the C=C bond and consequently decreases the selectivity to C=C hydrogenation products. Effects of shape-selectivity should also be considered to explain the results on L zeolite-supported catalysts. The channel structures of L zeolites allow UAL molecules to adsorb on Pt particles in zeolites only via the C=O group, resulting in the high UOL selectivity on L zeolite-supported Pt catalysts. Of all the factors discussed, the one which is dominant for controlling the UOL selectivity is still unclear and under further study.

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