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Selective Hydrogenation of Unsaturated Aldehydes over Pt Nanoparticles Promoted by Cooperation of Steric and Electronic Effects

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Selective hydrogenation of α,β -unsaturated aldehydes to unsaturated alcohols can reach high selectivity and activity at room temperature using Pt nanoparticles immobilized on nonporous Al₂O₃ support stability by aspartic acid. Aspartic acid molecules had significant steric effect for C=C hydrogenation and could modify the electronic state of metal particles.

Producing chemicals using feedstocks from natural resources has attracted much attention because the feedstocks can be obtained sustainably. Many aldehydes can be obtained from biomass or biomass derivatives, such as furfural cinnamaldehyde, crotonaldehyde, and 5hydroxymethylfurfural. Selective hydrogenation of α , β unsaturated aldehydes can produce unsaturated alcohols which are widely used in flavor, perfume and pharmaceutical industries, etc.¹⁻¹³ However, it is a challenge to develop effective catalysts for this kind of transformation because hydrogenation of the C=C double bond is thermodynamically more favourable than the C=O group,¹⁴⁻²¹ especially at room temperature.²²⁻²⁶ Tang and his co-workers reported that MIL-101(Fe)@Pt@MIL-101(Fe) can catalyse the selective hydrogenation of unsaturated aldehydes at room temperature, however, the synthesis procedure of the catalyst was complex.²² Amine-capped platinum-cobalt nanocrystals were also used to catalyse the selective hydrogenation of unsaturated aldehydes under mild conditions, however, the stability of the catalyst were not checked.²⁴ Development of simple, efficient, recyclable heterogeneous metal catalysts for

selective hydrogenation of unsaturated aldehydes at room temperature is highly desirable.

Improving the performance of heterogeneous metal catalysts by the steric and electronic effects using inorganic and organic modifiers has been studied widely.²⁷⁻³³ For ethylenediamine-coated example, ultrathin platinum nanowires exhibited excellent performance for the selective hydrogenation of nitroaromatics to N-hydroxylanilines.²⁷ Polyvinyl pyrrolidone has been used as electronic and geometric modifier of palladium nanoparticles.²⁸ Phosphine oxide ligands also affect the performance of gold nanoparticles for the chemoselective hydrogenation of substituted aldehydes.²⁹⁻³⁰ Self-assembled monolayers (SAMs) have also been used to modify catalysts that thiol molecules covalently bind to the metal through a sulfur attachment group producing ordered and stable monolayer films.³¹⁻³²

Herein, we develop an active, selective, and stable catalyst for the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols by immobilizing Pt nanoparticles on commercial non-porous Al₂O₃ (n-Al₂O₃ hereafter) support using aspartic acid (1a hereafter). The reaction could proceed effectively at room temperature and the selectivity to unsaturated alcohols was >90% for different substrates. The TOF value can reach 3746. The non-porous Al₂O₃ exhibited better performance than mesoporous Al₂O₃. The catalyst can be recycled at least 5 times without notable loss of activity. Detailed study indicated that aspartic acid and the non-porous property of the support played key roles for the excellent performance of the catalyst.

The catalysts prepared using n-Al₂O₃ as support without and with 1a-1c as modifier are denoted as Pt/n-Al₂O₃, Pt-1a/n-Al₂O₃, Pt-1b/n-Al₂O₃ and Pt-1c/n-Al₂O₃ respectively. Pd-1a/n-Al₂O₃, Ni-1a/n-Al₂O₃, Au-1a/n-Al₂O₃, and Ru-1a/n-Al₂O₃ have similar meanings, i.e., the Pt was replaced by the corresponding metals. The catalysts prepared using mesoporous $Al_2O_3^{34}$ as the support without and with aspartic acid as the modifier are named as Pt/mesoporous-Al₂O₃ and Pt-1a/mesoporous-Al₂O₃, respectively.

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⁺ Footnotes relating to the title and/or authors should appear here.

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The performance of the catalysts for selective hydrogenation of cinnamaldehyde (2a) is first discussed because cinnamyl alcohol (3a) is an important perfume and organic synthesis intermediate.³⁵⁻³⁸ The activity of the Pt/mesoporous-Al₂O₃ was higher than Pt/n-Al₂O₃, while the selectivity of cinnamyl alcohol was higher over Pt/n-Al₂O₃ than that over Pt/mesoporous-Al₂O₃ (Table 1, entries 1-2). Both the conversion of cinnamaldehyde and the selectivity of cinnamyl alcohol were improved greatly when aspartic acid was used as the modifier and n-Al₂O₃ as the support (Table 1, entries 3-5), while the effect of aspartic acid on the catalytic performance of Pt-1a/mesoporous-Al₂O₃ was much smaller (Table 1, entries 6-8).

We also performed the reaction using Pd-1a/Al₂O₃, Au-1a/n-Al₂O₃, Ru-1a/n-Al₂O₃ and Ni-1a/n-Al₂O₃ catalysts for the reaction. The conversion of cinnamaldehyde was only 20% over Pd-1a/n-Al₂O₃ and no cinnamyl alcohol was generated (Table S2, entry 7). Au-1a/n-Al₂O₃, Ru-1a/n-Al₂O₃ and Ni-1a/n-Al₂O₃ exhibited no activity for the hydrogenation of cinnamaldehyde (Table S2, entries 8-10). The effect of succinic acid (1b) and ethanediamine (1c) were also checked. The conversion of cinnamaldehyde was 56% and the selectivity of cinnamic alcohol was 41% over Pt-1b/Al₂O₃ (Table S2, entry 11). These results indicate that the functional group -COOH can't increase the selectivity of the reaction. The conversion of cinnamaldehyde was 49% and the selectivity of cinnamic alcohol was 65% over Pt-1c/Al₂O₃ (Table S2, entry 12). It makes clear that only -NH₂ group also can't improve the performance of the catalyst. Aspartic acid also improved the performance of Pt/SiO₂. The conversion of cinnamaldehyde and the selectivity of cinnamyl alcohol over Pt/SiO2 was 39 % and 75 %, respectively (Table S2, entry 13). The conversion of cinnamaldehyde increased to 72 % and the selectivity of cinnamyl alcohol increased to 90% over Pt-1a/SiO₂ (Table S2, entry 14). Aspartic acid just improved the selectivity of Pt/C, while the activity of Pt-1a/C was lower than Pt/C (Table S2, entries 15 and 16).

Table 1 The performances of different catalysts for the hydrogenation of cinnamaldehyde a

	2a 3a		3a'		3a''	
Entry	Catalyst	t	Conversi	Selectivity (%) ^c		
		(h)	on(%) ^b	3a	3a'	3a"
1	Pt/n-Al ₂ O ₃	2	50	46	40	14
2	Pt/mesoporous-Al ₂ O ₃	1	53	38	49	13
3	Pt- 1a/ n-Al ₂ O ₃	1	45	93	4	3
4	Pt- 1a/ n-Al ₂ O ₃	2	76	94	3	3
5	Pt- 1a/ n-Al ₂ O ₃	3	99	91	3	6
6	Pt-1a/mesoporous-Al ₂ O ₃	1	56	38	48	14
7	Pt-1a/mesoporous-Al ₂ O ₃	2	98	19	49	32
8	Pt- 1a /mesoporous-Al ₂ O ₃	3	99	12	48	40

^a Reaction conditions: cinnamaldehyde 1 mmol, P_{H2} = 10 atm, catalyst 30 mg, methanol 0.5 mL, water 0.1 mL, 30 °C. ^b Conversion of **3a** was determined by GC. ^c Selectivity was determined by GC using n-decane as the internal standard.

It has been reported that size of metal particles could influence the selectivity to cinnamyl alcohol.³⁹⁻⁴¹ The Pt-1a/n-Al₂O₃, $Pt/n-Al_2O_3$, Pt-1a/mesoporous-Al₂O₃, and Pt/mesoporous-Al₂O₃ were characterized using transmission electron microscopy (TEM). Figures 1a, 1b and 1e show that size of Pt particles in the Pt-1a/n-Al₂O₃ was about 4 nm. Figure 1c demonstrates that the Pt particles were larger and obvious aggregation was observed in the Pt/n-Al₂O₃ catalyst. This indicates that aspartic acid was necessary for the uniform dispersion of the Pt nanocatalysts. In EDS mapping of the Pt-1a/n-Al₂O₃ catalyst, Pt, O, N and Al were detected, suggesting that aspartic acid was introduced into the catalyst (Figure 1f-1i). The surface active metal atoms in Pt-1a/n-Al₂O₃ and Pt/n- $\mathrm{Al_2O_3}$ were determined by chemisorption method^{42} in this work were 9.69% and 2.12%, respectively. Figures S2a and S2b show the nanostructure of $\mathsf{Pt}\text{-}\mathbf{1a}/\mathsf{mesoporous}\text{-}\mathsf{Al}_2\mathsf{O}_3$ and Pt/mesoporous-Al₂O₃. The size of Pt particle in the Pt-1a/mesoporous-Al₂O₃ was also about 4 nm, and obvious aggregation of Pt particles was observed in Pt/mesoporous-Al₂O₃.



Figure 1 TEM (a, e) and HRTEM (b) images of Pt-1a/n-Al₂O₃, TEM image of Pt/n-Al₂O₃ (c), TEM image Pt-1a/n-Al₂O₃ after recycled five times (d), EDS images of Pt-1a/n-Al₂O₃ (f-i).

Although the sizes of Pt particles in Pt-**1a**/n-Al₂O₃ and Pt-**1a**/mesoporous-Al₂O₃ were similar, the selectivity to the desired product over Pt-**1a**/n-Al₂O₃ was much higher than that over Pt-**1a**/mesoporous-Al₂O₃ (Table 1, entries 5 and 7). The contents of Pt in Pt-**1a**/n-Al₂O₃ and Pt-**1a**/mesoporous-Al₂O₃ - were 0.68% and 2.53%, respectively, as determined by ICP. - The surface active metal atoms in Pt-**1a**/n-Al₂O₃ and Pt-**1a**/mesoporous-Al₂O₃ were 9.69% and 8.02 %, respectively. The TOF value of Pt-**1a**/n-Al₂O₃ was 3746 h⁻¹ and was also much higher than 1571 h⁻¹ of Pt-**1a**/mesoporous-Al₂O₃. The TOF value was calculated based on the surface active metal atoms of the Pt and the data of entries 4 and 7 in table 1.

XPS characterization was carried out to identify the surface electronic states of the catalysts. Figure S3a shows the Al2p peak together with the Pt4f. The Al2p peak at 74.8 eV was a typical binding energy of the Al^{3+} state in Al_2O_3 .⁴³ The Pt4f spectra (Figure S3a) for the Pt/n-Al₂O₃ could be resolved into two spin-orbit pairs with 4f7/2 binding energies of 74.5 eV and 75.9 eV, and with 4f5/2 binding energies of 71.4 eV and 72.7

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eV, respectively. The peaks at 75.9 eV (Pt 4f7/2) and 72.7 eV (Pt 4f5/2) are attributed to the oxidation state of Pt(II). The peaks of 74.5 eV and 71.4 eV are attributed to reduced metallic Pt(0). The Pt4f spectrum shifted to lower binding energy direction for Pt-1a/n-Al₂O₃ in comparison with Pt/n-Al₂O₃. It was obvious that the modification of aspartic acid resulted in enrichment of electrons on the metal surfaces, which is favourable to activation of the electrophilic C=O group by enhancing its adsorption, leading to higher activity and selectivity to the unsaturated alcohols. To be more accurate, the Pt4d spectra were also analysed because the Pt4f signal was overlapped with Al2p signal. The Pt4d5/2 spectra show the indicative peaks of elemental Pt and oxidized Pt at 314.6 eV and 317.6 eV for Pt/n-Al₂O₃, respectively, and they also shifted to lower binding energy direction for Pt-1a/n-Al₂O₃ which were 314.3 eV and 317.2 eV, respectively (Figure S3b). The results further indicate the electron enrichment on the Pt surface because of the modification of aspartic acid.

The extended X-ray absorption fine structure (EXAFS) was also used to study the catalysts. The EXAFS spectra (Figure S4) show that Pt-**1a**/n-Al₂O₃ exhibited a distinct Pt-N peak.²⁷ The length Pt-Al bond changed from 2.50 Å in Pt/n-Al₂O₃ to 2.42 Å in Pt-**1a**/n-Al₂O₃.⁴⁴⁻⁴⁵ This indicates that Pt particles contacted more tightly on the support in Pt-**1a**/n-Al₂O₃. This is understandable because aspartic acid interacts strongly with both the support and Pt particles by hydrogen bonding and coordination, respectively, which enhances the interaction between the support and the Pt particles at the Pt/support interface.

The temperature-programmed reduction (TPR) characterization showed that only one single major reduction peak could be observed for the Pt/n-Al₂O₃ and Pt-**1a**/n-Al₂O₃ catalysts (Figure S5). The peak was observed at relatively higher temperature for the Pt-**1a**/n-Al₂O₃ than that for the Pt/n-Al₂O₃, indicating that the interaction between the Pt particles and the support was stronger in Pt-**1a**/n-Al₂O₃ because of the modification of aspartic acid. The results from TPR and EXAFS techniques are consistent.

As discussed above, Pt-1a/n-Al₂O₃ was much more active and selective than Pt/n-Al₂O₃ and Pt-1a/mesoporous-Al₂O₃ for the reaction. On the basis of the results above, we can discuss the reasons for the interesting phenomenon. The better activity of Pt-1a/n-Al₂O₃ than Pt/n-Al₂O₃ resulted mainly from the uniform dispersion of Pt particles in the former (Figures 1a and 1c). The much higher selectivity of Pt-1a/n-Al₂O₃ than Pt/n-Al₂O₃ is attributed to the difference in steric hindrance, as shown schematically in Figures 2a and 2b. There existed a layer of aspartic acid on the Pt particles. Thus, steric hindrance is much more significant for hydrogenation of C=C than C=O because C=O group can approaches the Pt particles when the reactant molecule is perpendicular to the surface of the Pt particles, as shown in Figure 2a. However, both C=C and C=O can contact the Pt particles on Pt/n-Al₂O₃ easily, and thus the selectivity was low. The better selectivity of Pt-1a/n-Al₂O₃ than Pt-1a/mesoporous-Al₂O₃ can be discussed by comparing Figures 2a and 2c. When the reactant molecules pass the Pt particles in the mesopores, the C=C groups are forced to

contact with the Pt particles, resulting in hydrogenation C=C groups. The lower activity of Pt-**1a**/mesoporous-Al₂O₃ than Pt-**1a**/n-Al₂O₃ originated mainly from the poorer mass transfer in the mesopores than the non-porous support.



Figure 2 Possible adsorption mode of $Pt-1a/n-Al_2O_3$ (a), $Pt/n-Al_2O_3$ (b) and $Pt-1a/mesoporous-Al_2O_3$ (c).

The reusability of the $Pt-1a/n-Al_2O_3$ was studied. After the reaction, the catalyst was easily separated through centrifuging. It was used for the next run after washing and drying. The catalyst could be reused at least five times without notable loss of activity (Figure S8). The TEM characterization of the catalyst after reused five times (Figure 1d) indicated that the morphology of the catalyst did not change considerably.

Considering the excellent performance of Pt-**1a**/n-Al₂O₃, we studied the selective hydrogenation of other α , β -unsaturated aldehydes to the corresponding unsaturated alcohols, and the results are presented in Table 2. It can be known that Pt-**1a**/n-Al₂O₃ could promote the hydrogenation of a series of substrates with moderate condition to high conversion and excellent selectivity towards the corresponding unsaturated alcohols. Citral is a mixture of two isomers: 50% neral (cisisomer) and 50% geranial (trans-isomer). The selectivity of the corresponding product all can reach above 95% for these two isomers. Interestingly, the double bond geometry can survive after the hydrogenation of carbonyl group.

In conclusion, Pt-1a/n-Al₂O₃ was a very active, selective, and stable catalyst for the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols. The Pt nanoparticles could be immobilized stability on the support because aspartic acid interacts strongly with both the support and the Pt nanoparticles. The Pt nanocatalysts on the non-porous support are much more active and selective for this kind of reaction. The aspartic acid and the non-porous property of the support played key roles for the unusual catalytic performance of the catalysts. Aspartic acid molecules adsorbed Pt particles had significant steric effect for the C=C bond hydrogenation and could modify electronic state of the metal particles, which improved the selectivity of the reaction. We believe that the route to combine non-porous supports and modifiers can also be used to design highly selective nanocatalysts for some other reactions.

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Table 2 Hydrogenation α,β -unsaturated aldehydes over Pt-**1a**/n-Al₂O₃^{*a*, *b*, *c*}



^{*a*} Reaction conditions: aldehyde 1 mmol, $P_{H2} = 10$ atm, catalyst 30 mg, methanol 0.5 mL, water 0.1ml, 30 °C, 3 h. ^{*b*} Conversion was determined by GC. ^{*c*} Selectivity was determined by GC using n-decane as the internal standard.

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Conflicts of interest

There are no conflicts to declare.

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