**Electronic Supplementary Information (ESI) for:**

# Double solvent synthesis of ultrafine Pt nanoparticles supported on halloysite nanotubes for chemoselective cinnamaldehyde hydrogenation

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The conversion and selectivity[1] were calculated from Eqs. (1–5), which are:

$$\text{Conversion of CMA} = \text{reacted CMA/CMA (in)} \quad (1)$$

$$\text{Selectivity of CMO} = \text{CMO (in)/reacted CMA} \quad (2)$$

$$\text{Selectivity of HCMA} = \text{HCMA (in)/reacted CMA} \quad (3)$$

$$\text{Selectivity of HCMO} = \text{HCMO (in)/reacted CMA} \quad (4)$$

$$\text{Reaction rate } (h^{-1}) = \frac{nCMA}{nPt} \times \text{conversion/time (h)} \quad (5)$$

where $n_{CMA}$ represents the moles of CMA in the mixture, and $n_{Pt}$ is the moles of Pt used in the reaction.

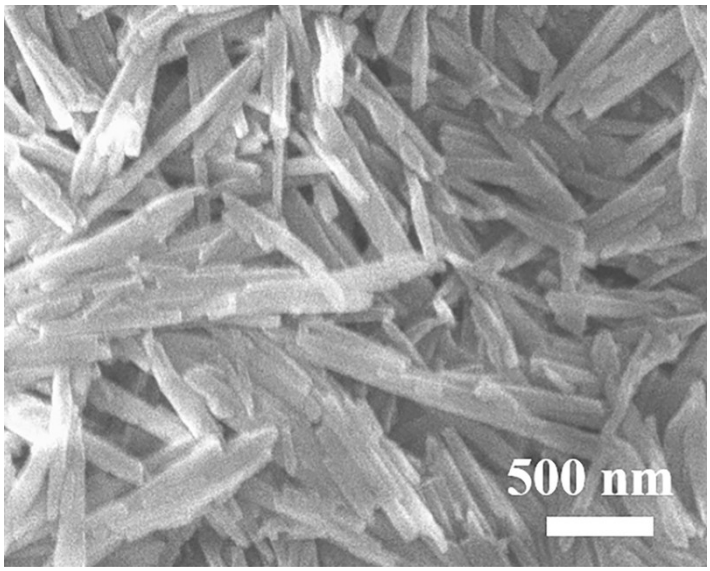


**Fig. S1** SEM image of Pt/HNTs

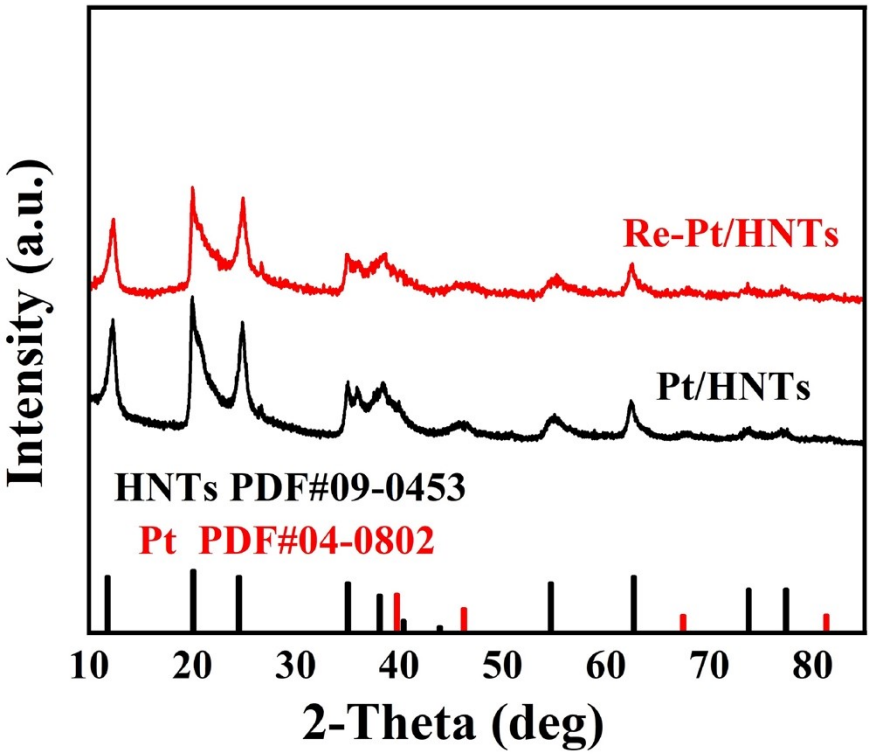


**Fig. S2** The XRD patterns of Pt/HNTs and after four recycle

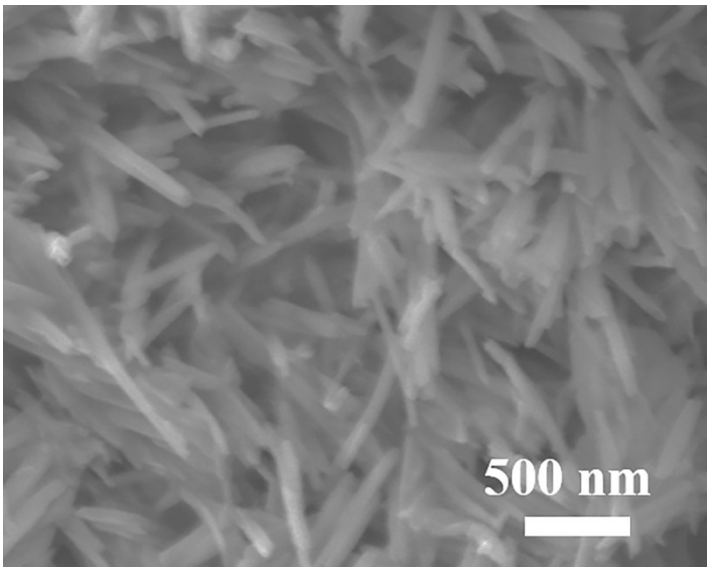


**Fig. S3** SEM image of the recycled Pt/HNTs.

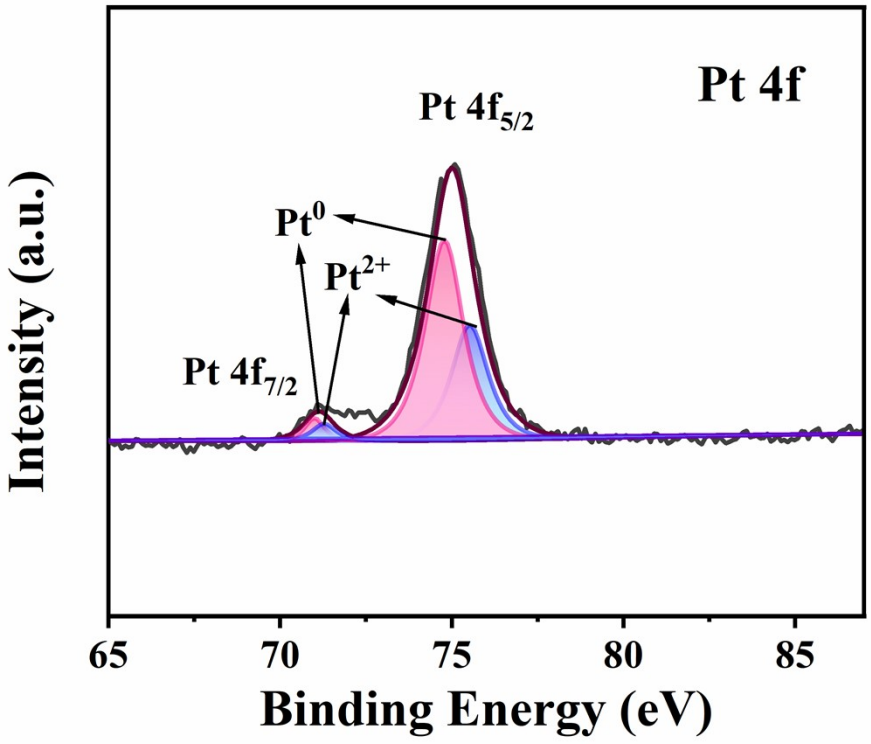


**Fig. S4** XPS spectra of the Pt/HNTs catalysts after the fourth use.

Table S1. Influence of temperature on hydrogenation of CMA over 3.8 wt% Pt/HNTs.

| Temperature (℃) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | CMO | HCMA | HCMO |
| 50 | 32.7 | 81.4 | 9.6 | 9.0 |
| 60 | 51.7 | 87.8 | 8.1 | 4.1 |
| 70 | 69.2 | 88.4 | 6.0 | 5.6 |
| 80 | 94.1 | 95.1 | 2.5 | 2.4 |
| 90 | 93.9 | 85.3 | 5.0 | 9.7 |

Reaction conditions: 5 mmol substrate, reaction time = 2 h, $H_2$ = 2 MPa, 12.5 mL ethanol, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table.

Table S2. Influence of reaction time on hydrogenation of CMA over 3.8 wt% Pt/HNTs.

| Reaction Time (h) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | CMO | HCMA | HCMO |
| 0.5 | 44.4 | 88.5 | 8.1 | 3.4 |
| 1.0 | 61.8 | 89.5 | 6.8 | 3.7 |
| 1.5 | 79.6 | 91.9 | 4.8 | 3.3 |
| 2.0 | 94.1 | 95.1 | 2.5 | 2.4 |
| 2.5 | 91.8 | 75.0 | 4.7 | 20.3 |

Reaction conditions: 5 mmol substrate, temperature = 80 ℃, $H_2$ = 2 MPa, 12.5 mL ethanol, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table.

Table S3. Influence of $H_2$ pressure on hydrogenation of CMA over 3.8 wt% Pt/HNTs.

| $H_2$ (MPa) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | CMO | HCMA | HCMO |
| 0.5 | 46.8 | 86.1 | 10.0 | 3.9 |
| 1.0 | 73.3 | 86.4 | 8.3 | 5.3 |
| 1.5 | 74.1 | 88.0 | 7.2 | 4.8 |
| 2.0 | 94.1 | 95.1 | 2.5 | 2.4 |
| 2.5 | 94.5 | 82.6 | 5.9 | 11.5 |

Reaction conditions: 5 mmol substrate, temperature = 80 ℃, reaction time = 2 h, 12.5 mL ethanol, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table.

Table S4. Effect of percentage metal loading on hydrogenation of CMA.

| Pt (wt%) | Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | CMO | HCMA | HCMO |
| 1.5 | 44.7 | 84.6 | 10.7 | 4.7 |
| 2.3 | 57.3 | 87.3 | 8.4 | 4.3 |
| 3.0 | 63.0 | 87.9 | 7.5 | 4.6 |
| 3.8 | 94.1 | 95.1 | 2.5 | 2.4 |
| 4.6 | 93.0 | 93.0 | 3.7 | 3.3 |

Reaction conditions: 5 mmol substrate, temperature = 80 °C, reaction time = 2 h, $H_2$ = 2 MPa, 12.5 mL ethanol, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table.

Table S5. Influence of solvents on hydrogenation of CMA over 3.8 wt% Pt/HNTs.

| Solvents | Conversion (%) | Selectivity (%) | | | CMO yield (%) |
|---|---|---|---|---|---|
| | | CMO | HCMA | HCMO | |
| Cyclohexane | 45.0 | 68.0 | 18.7 | 13.3 | 30.6 |
| Isopropanol | 56.7 | 78.7 | 11.5 | 9.8 | 44.6 |
| Methanol | 78.8 | 90.9 | 5.7 | 3.4 | 71.7 |
| Ethanol | 94.1 | 95.1 | 2.5 | 2.4 | 89.5 |

Reaction conditions: 5 mmol substrate, temperature = 80 ℃, $H_2$ = 2 MPa, reaction time = 2 h, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table, yield=conversion (%) × selectivity (%).

Table S6. Recycle times on hydrogenation of CMA over 3.8 wt% Pt/HNTs.

| Recycle times | CMA Conversion (%) | Selectivity (%) | | |
|---|---|---|---|---|
| | | CMO | HCMA | HCMO |
| 1 | 94.1 | 95.1 | 2.5 | 2.4 |
| 2 | 92.8 | 95.8 | 1.8 | 2.4 |
| 3 | 91.0 | 95.4 | 2.7 | 1.9 |
| 4 | 89.3 | 94.0 | 3.0 | 3.0 |
| 5 | 87.2 | 91.0 | 5.6 | 3.4 |
| 6 | 81.0 | 87.6 | 7.5 | 4.9 |

Reaction conditions: 5 mmol substrate, temperature = 80 ℃, reaction time = 2 h, $H_2$ = 2 MPa, 12.5 mL ethanol, stirring speed = 800 rpm. Selectivity is reported at the level of conversion in the table.

Table S7. Catalytic results reported recently for hydrogenation of CMA to CMO on supported Pt catalysts.

| Catalyst | Solvents | Pt (wt%) | Tem. (°C) | $P_{H2}$ (MPa) | T (h) | Conv. (%) | Sel. (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Pt/HNTs | ethanol | 3.8 | 80 | 2 | 2 | 94.1 | 95.1 | This work |
| Pt@UiO-66-$NH_2$ | methanol | 10.7 | 25 | 4 | 44 | 98.7 | 91.7 | 2 |
| Pt/$CeO_2$ | ethanol | 3.5 | 70 | 2 | 6 | 81.9 | 27.6 | 3 |
| Pt@$CeO_2$ | ethanol | 2.9 | 70 | 2 | 6 | 63.4 | 69.5 | 3 |
| Pt@Y | isopropanol | 0.6 | 130 | 3 | 13 | 100 | 91.0 | 4 |
| Pt/U-720 | methanol | 2.0 | 50 | 4 | 3 | 90.9 | 89.1 | 5 |
| Pt/MOF-$NH_2$ | isopropanol | 2.9 | 60 | 1 | 3 | 72.3 | 78.9 | 6 |
| Pt@S-1 | isopropanol | 0.22 | 60 | 1 | 4 | 99.8 | 98.7 | 7 |
| Pt/S-1 | isopropanol | 0.17 | 60 | 1 | 4 | 99.9 | 0.1 | 7 |
| Pt@S-1-is | isopropanol | 0.26 | 60 | 1 | 4 | 43.9 | 31.9 | 7 |
| Pt30/$Al_2O_3$ | ethanol | 0.99 | 60 | 2 | 8 | 85.0 | 47.0 | 8 |
| Pt/PCT_1 | ethanol | 1.6 | 80 | 0.2 | 3 | 46.5 | 42.9 | 9 |
| Pt/PCT_2 | ethanol | 1.6 | 80 | 0.2 | 3 | 97.8 | 51.9 | 9 |
| (Pt-enriched cage)@$CeO_2$ core@shell | ethanol | 19.2 | 60 | 1 | 5 | 95.0 | 87.0 | 10 |

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