

Supporting Information

Pt nanoparticle supported on nanocrystalline CeO₂: Highly selective catalyst for up-gradation of phenolic derivatives present in bio-oil

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Figure S1

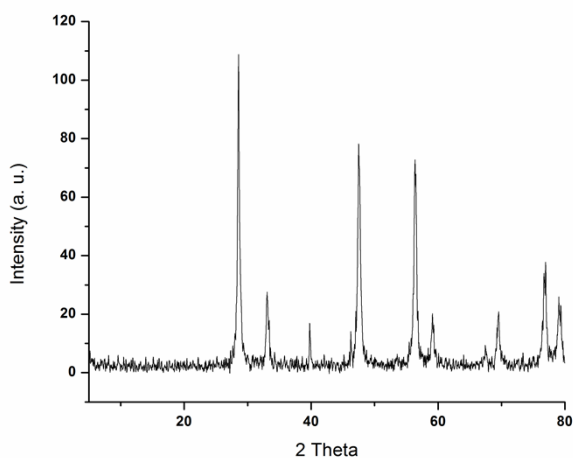


Figure S1. XRD spectra (with a scan rate of 0.1°/min) of 2%Pt-CeO₂ catalyst.

Figure S2

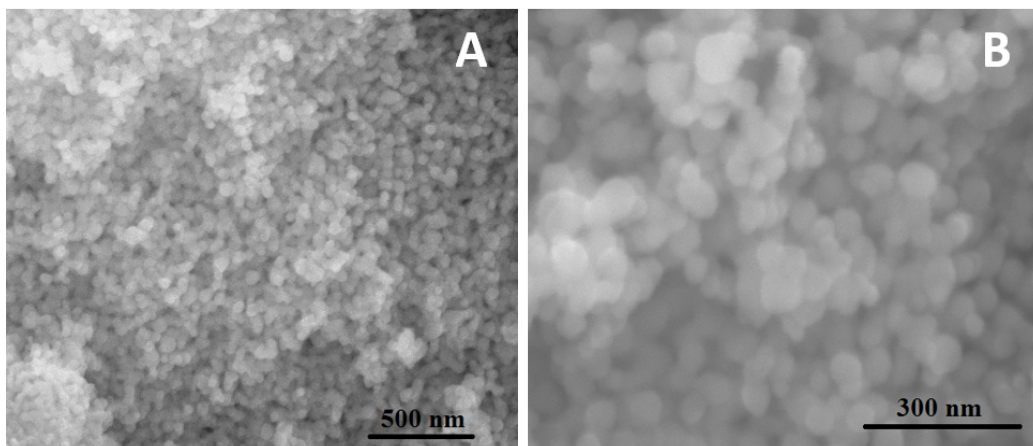


Figure S2. SEM images of 2%Pt-CeO₂ samples showing homogeneously distributed CeO₂ crystallites of size between 15-30 nm.

Figure S3

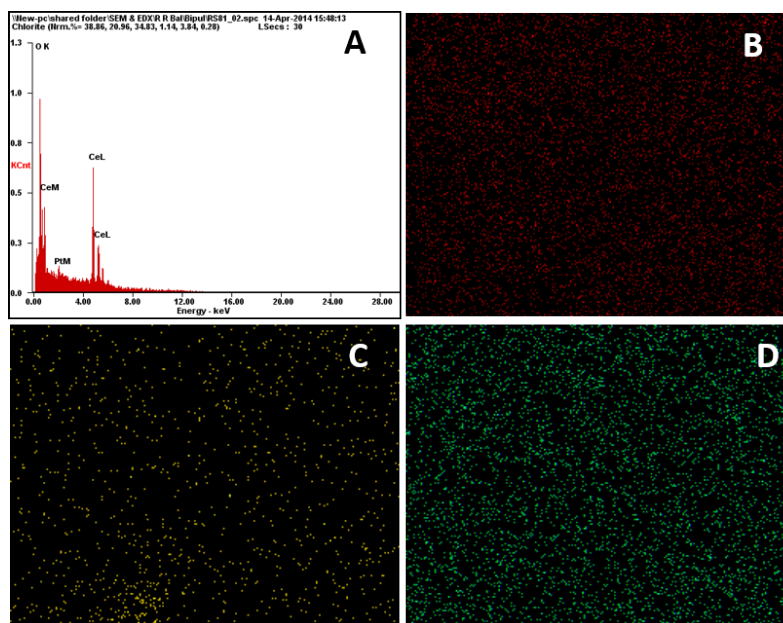


Figure S3. EDAX (A) and elemental mapping (B-D) of as prepared 2%Pt-CeO₂ catalyst; where B, C and D corresponds to the elemental mapping of O, Pt and Ce respectively.

Figure S4

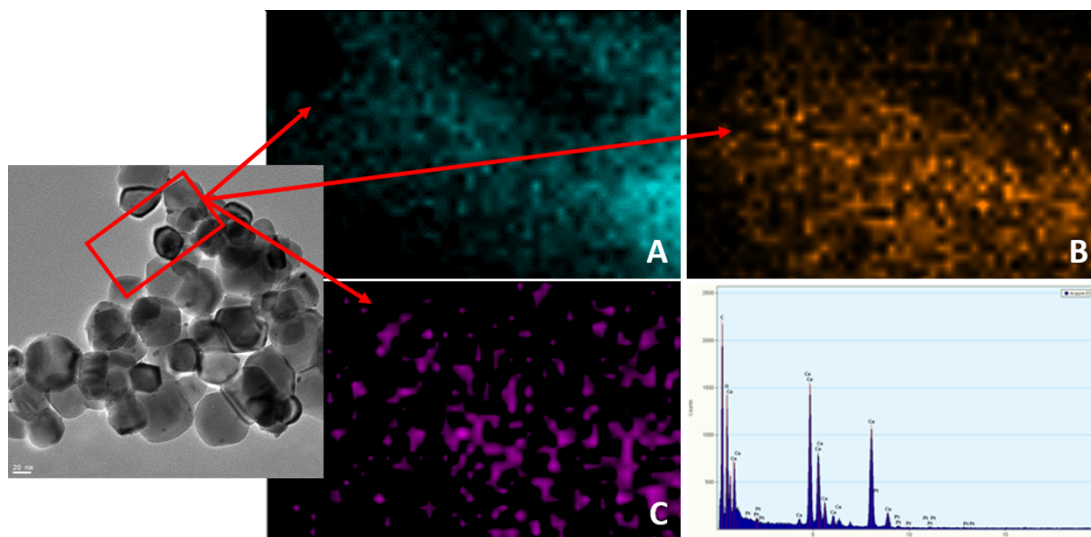


Figure S4. Elemental mapping (A-C) and EDAX (D) analysed by HR-TEM of prepared 2%Pt-CeO₂ catalyst; where A, B and C corresponds to the elemental mapping of Ce, O and Pt respectively. (Inset: quantitative percentage of the element of the catalyst).

Figure S5

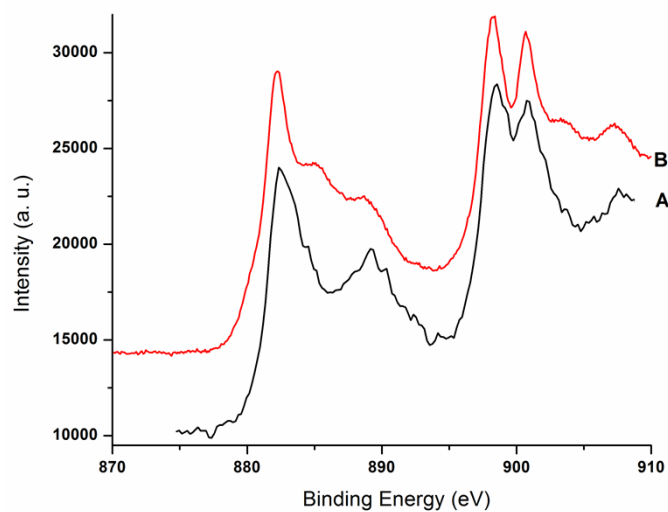
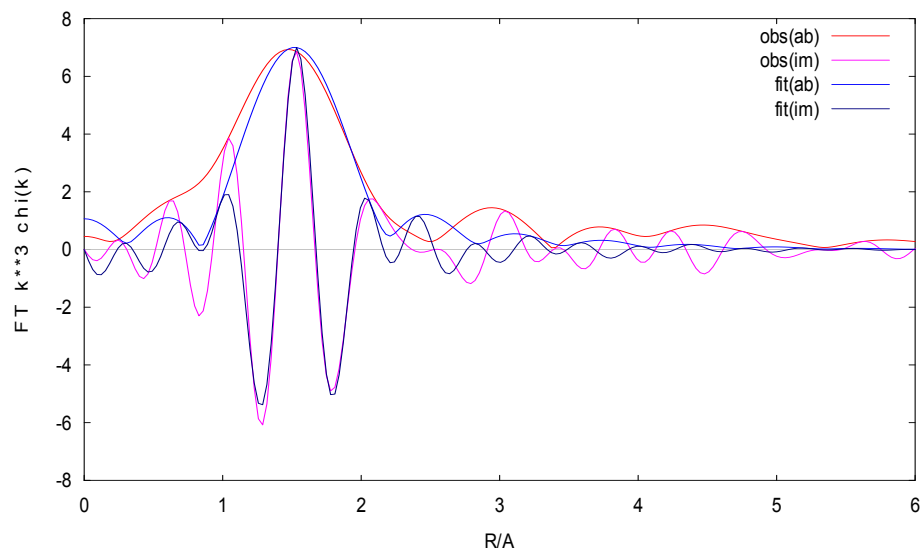


Figure S5. X-ray photoelectron spectra of Ce 3d in (A) fresh and (B) used Pt-CeO₂ catalyst.

Figure S6

(A) Fresh Catalyst



(B) Spent Catalyst

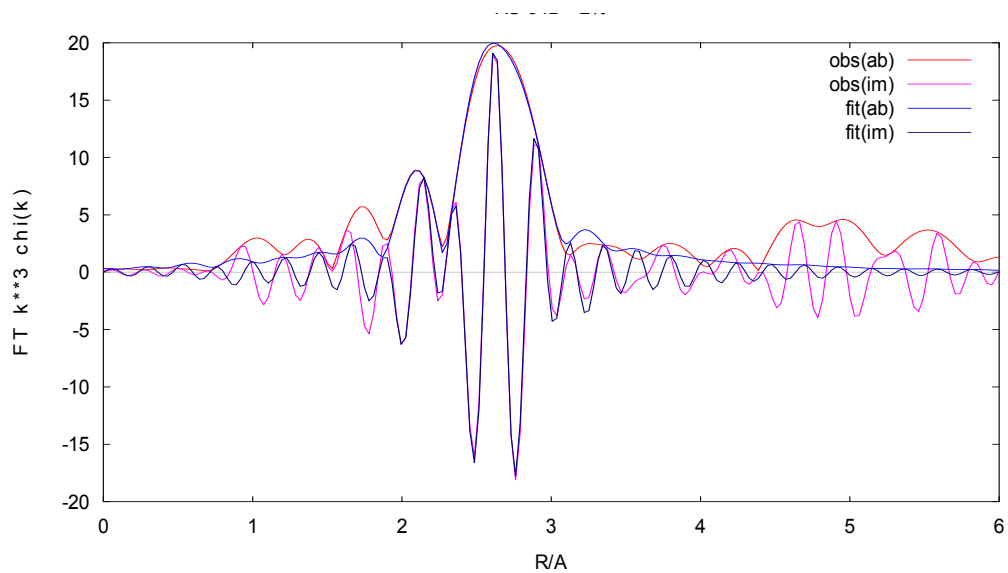


Figure S6. k_3 -weighted Fourier transform of Pt-K edge EXAFS for the fresh (A) and spent (B) 2%Pt-CeO₂ catalyst.

Figure S7

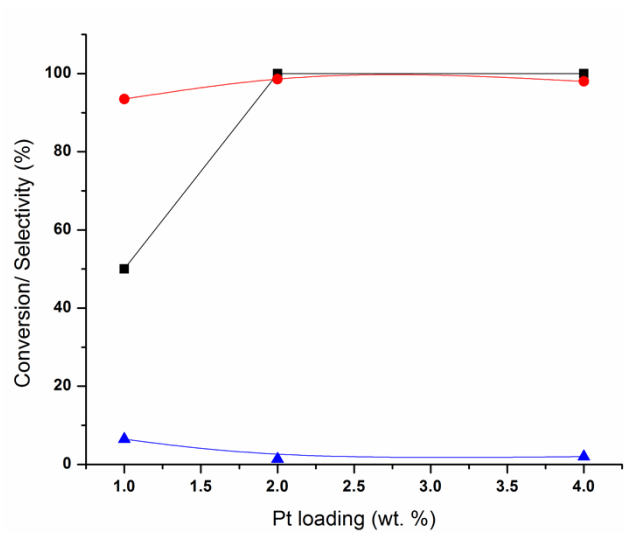


Figure S7. Influence of Pt loading as a function of phenol conversion [■]; cyclohexanol [●] and cyclohexanone [▲] selectivity.

Figure S8

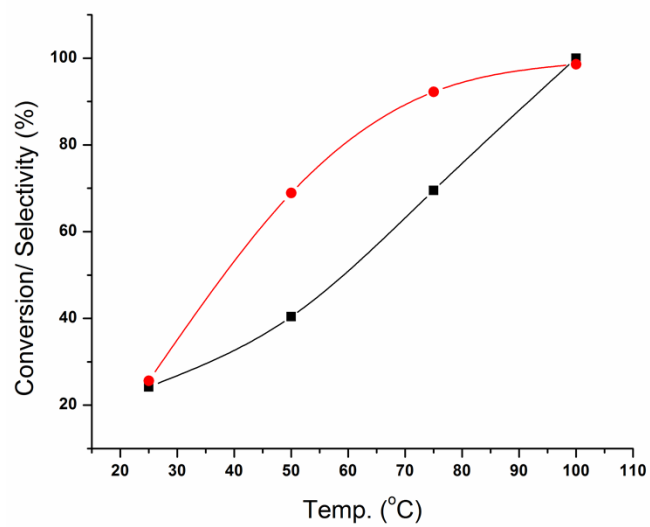


Figure S8. Influence of reaction temperature as a function of phenol conversion [■] and cyclohexanol [●] selectivity.

Figure S9

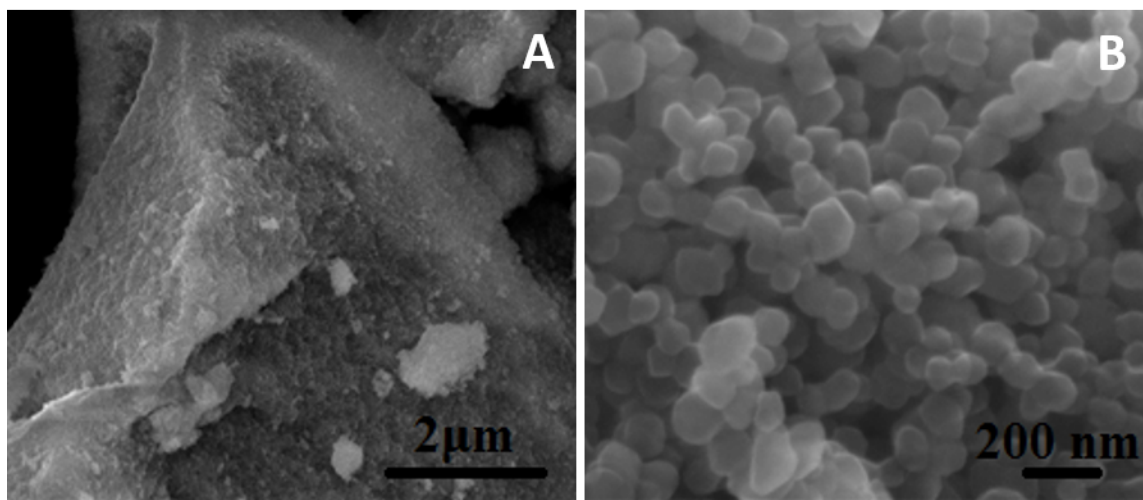


Figure S9. SEM images of commercially CeO₂ nanoparticle showing CeO₂ crystallites of size between 60-140 nm.

Figure S10

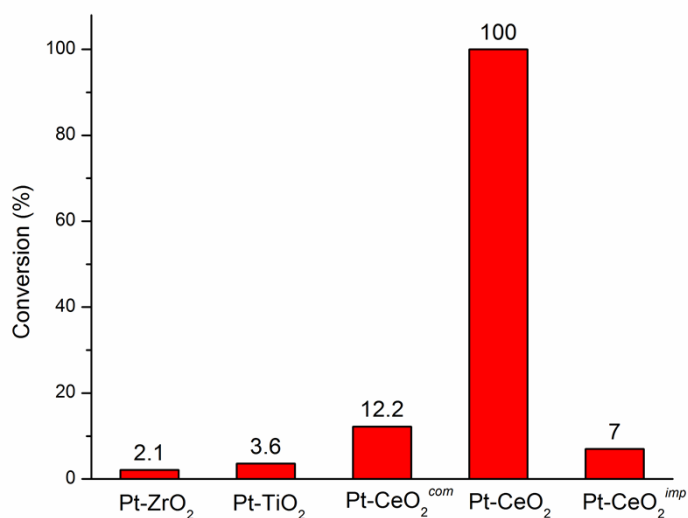


Figure S10. Activity of the different supported Pt catalyst in hydrogenation of phenol.

Pt supported on ZrO₂, TiO₂ shows negligible activity, whereas Pt supported on commercial CeO₂ nanopowder shows enhancement of activity during hydrogenation of phenol. The result clearly indicates that the CeO₂ is a better support for hydrogenation. When we used CeO₂ prepared by our method, the activity took more than 8 fold increase and give 100% phenol conversion, confirming smaller CeO₂ as well as Pt has vital role for phenol dehydrogenation. The Pt-CeO₂ catalyst prepared by impregnation method has also shows nominal activity. Based on the result we believe CeO₂ is the better support for hydrogenating reaction. We also found that Pt nanoparticle supported on commercial CeO₂ showed little activity. So we believe

that Pt nanoparticle (1-5 nm), CeO₂ nanoparticle (15-30nm) and the synergistic effect between Pt nanoparticles and CeO₂ nanoparticles play the key role for this high activity.

Turn over frequency (TOF):

TOF and TON is calculated using the following equation

$$TON = \frac{\text{Moles of desired product formed}}{\text{Number of active center}}$$

$$TOF = \frac{\text{Turn over number (TON)}}{\text{Time of reaction}}$$

Detail calculation of TOF for the entry in Table 1 as follows

Entry	Catalyst	Metal loading (%)	Active metal (mol)	Conversion (mole %)	Conversion (mol)	TON	Time (h)	TOF (h ⁻¹)
1	CeO ₂	0	0	0	0	-	3	-
2	2%Ni- CeO ₂	2	3.40716E-05	24	0.0024	70.44	3	23.48
3	2%Re- CeO ₂	2	1.07527E-05	20	0.002	186	3	62
4	2%Pd- CeO ₂	2	1.88679E-05	61	0.0061	323.3	3	107.76
5	2%Rh- CeO ₂	2	1.94363E-05	24	0.0024	123.48	3	41.16
6	2%Pt- CeO ₂	2	1.02564E-05	100	0.01	975	3	325
7	2%Pt- CeO ₂	2	1.02564E-05	100	0.01	975	1.5	650
8	2%Pt- CeO ₂	2	1.02564E-05	12	0.0012	117	3	39
9	2%Pt- CeO ₂	2	1.02564E-05	98	0.0098	955.5	3	318.5
10	2%Pt- CeO ₂ ^{imp}	2	1.02564E-05	67.6	0.00676	659.1	3	219.7
11	5%Pd-C*	5	9.39673E-06	26	0.0026	276.692	3	92.23
12	Pd-AlCl ₃ *	5	4.69836E-06	78	0.000078	16.60152	12	1.38
13	Pd@mpg-C ₃ N ₄ *	5	1.17459E-05	99	0.000495	42.14232	4	10.53558
14	Pd NP _s *	100	9.39673E-05	99	0.00198	21.07116	16	1.316948
15	10%Pd@C*	10	4.69836E-05	100	0.001	21.284	20	1.0642

*TOF and TON calculation of the entry 11-15 is done on the basis of the data available in the cited reference 2b, 7a, 18, 18a and 18b of the manuscript.