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Supplementary Material

New insight into catalytic toluene oxidation at Pt-TiO_2 interface: interfacial oxygen species inducing carbon deposition via dehydrogenation

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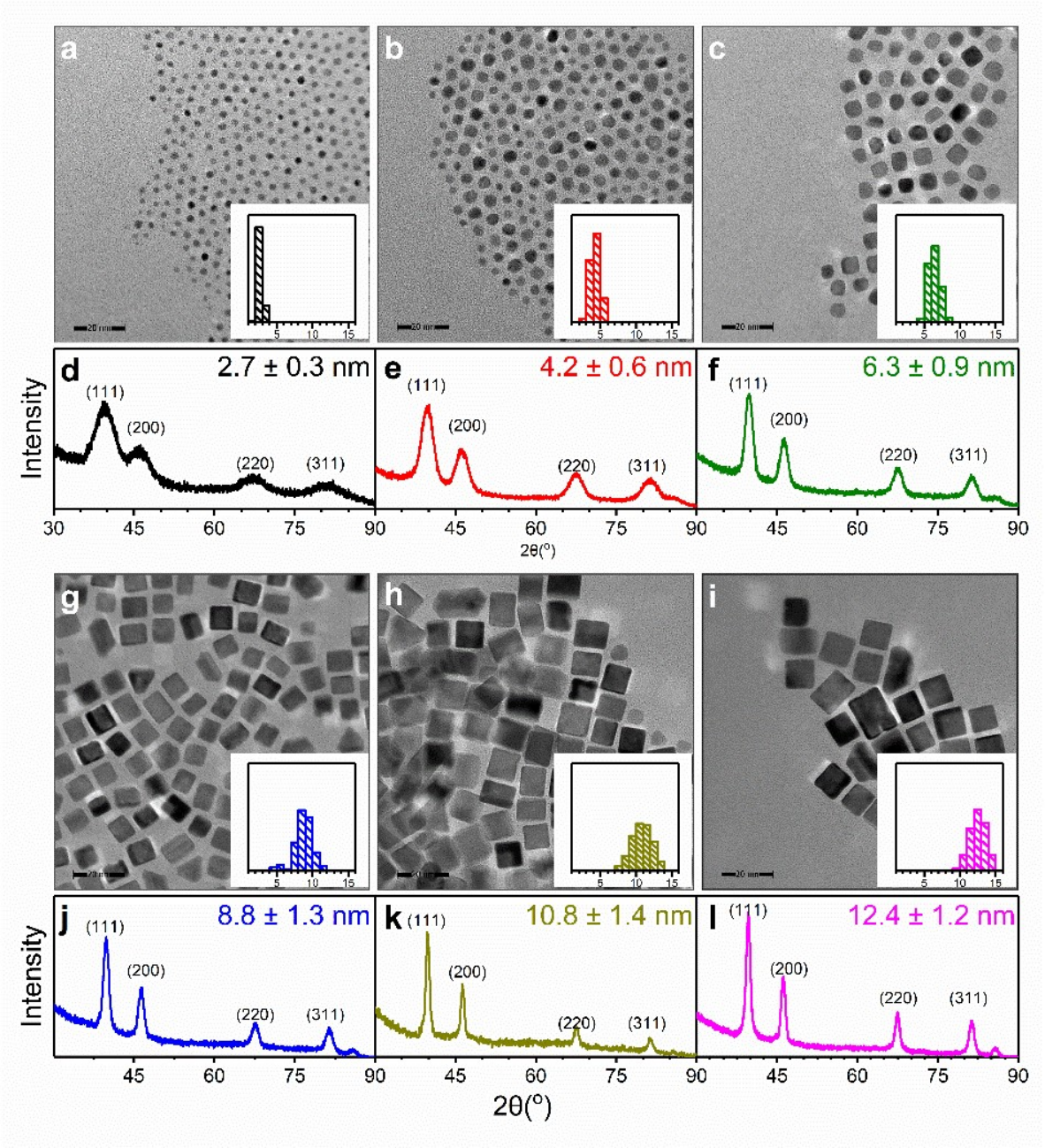

Fig. S1. Representative (a-c) (g-i) TEM images, and (d-f) (j-l) XRD patterns for Pt NPs with different size.

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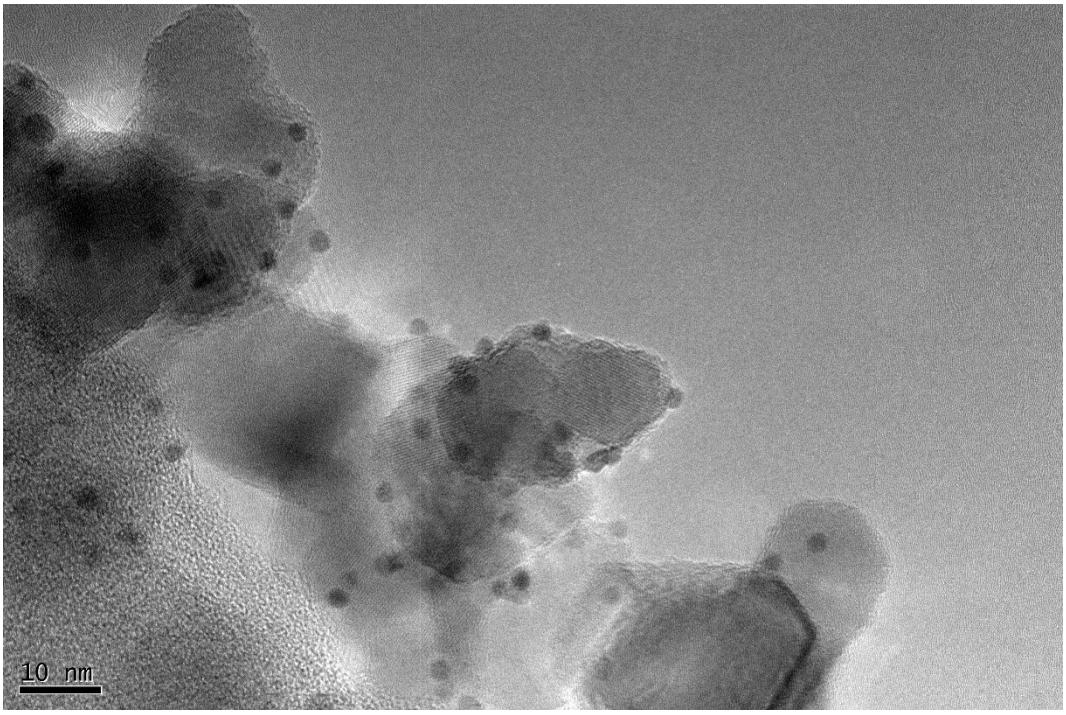

Fig. S2. TEM image of the Pt/TiO_2-2.7 nm.

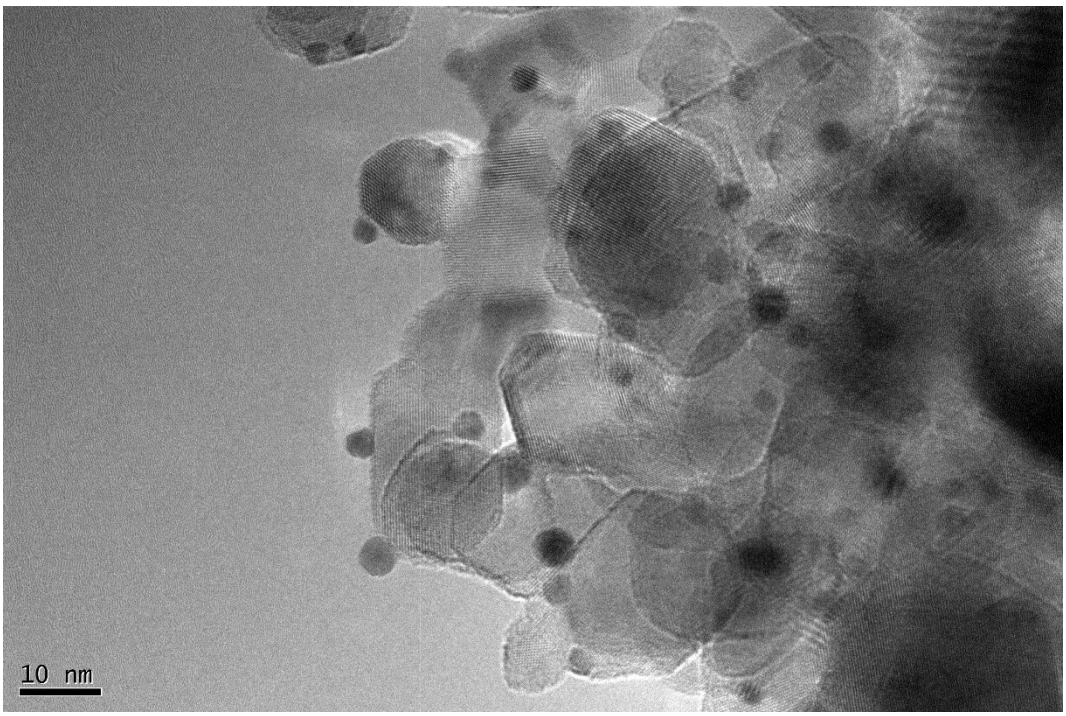

Fig. S3. TEM image of the Pt/TiO_2-4.2 nm.

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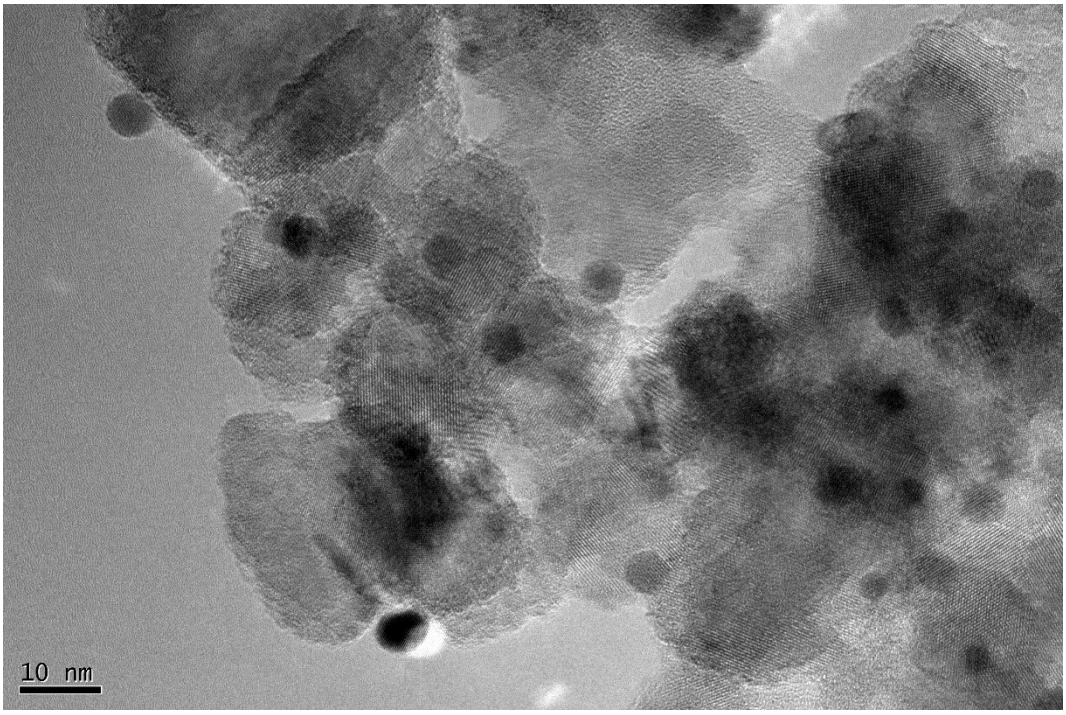

Fig. S4. TEM image of the Pt/TiO_2-6.3 nm.

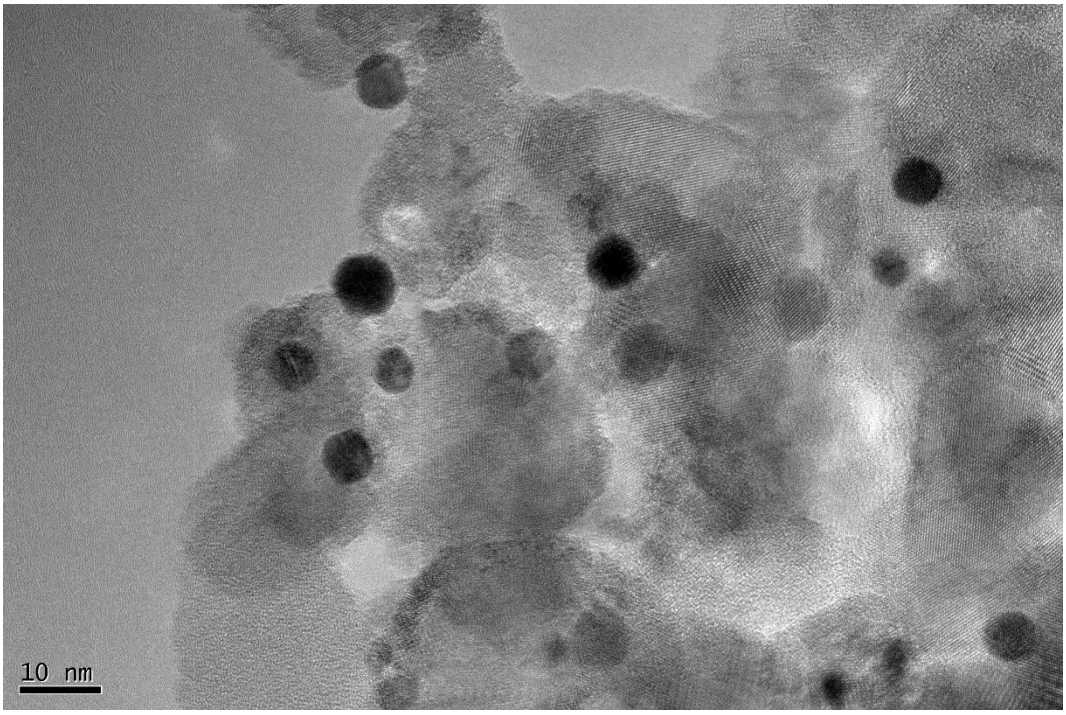

Fig. S5. TEM image of the Pt/TiO_2-8.8 nm.

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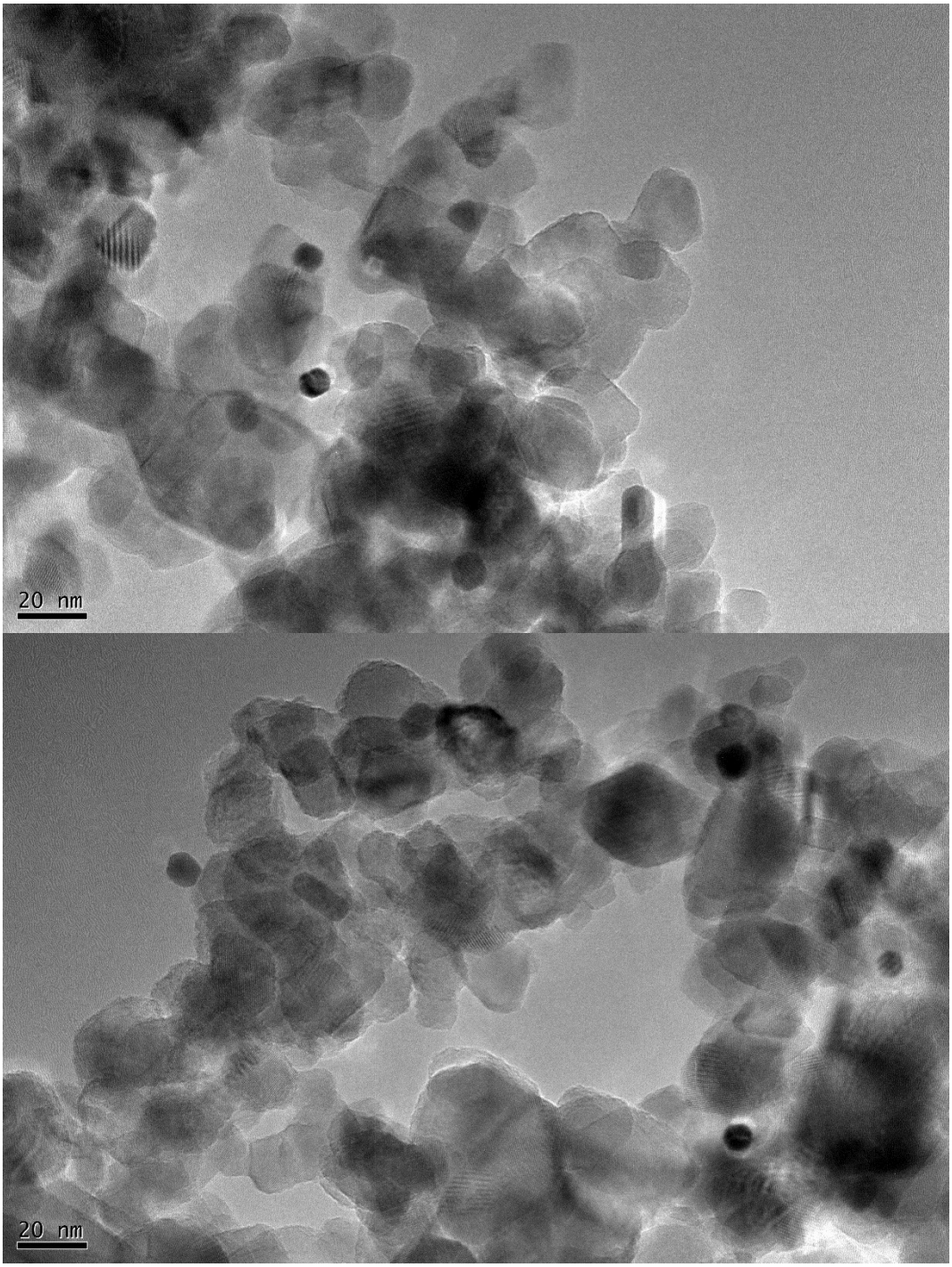

Fig. S6. TEM image of the Pt/TiO_2-10.8 nm.

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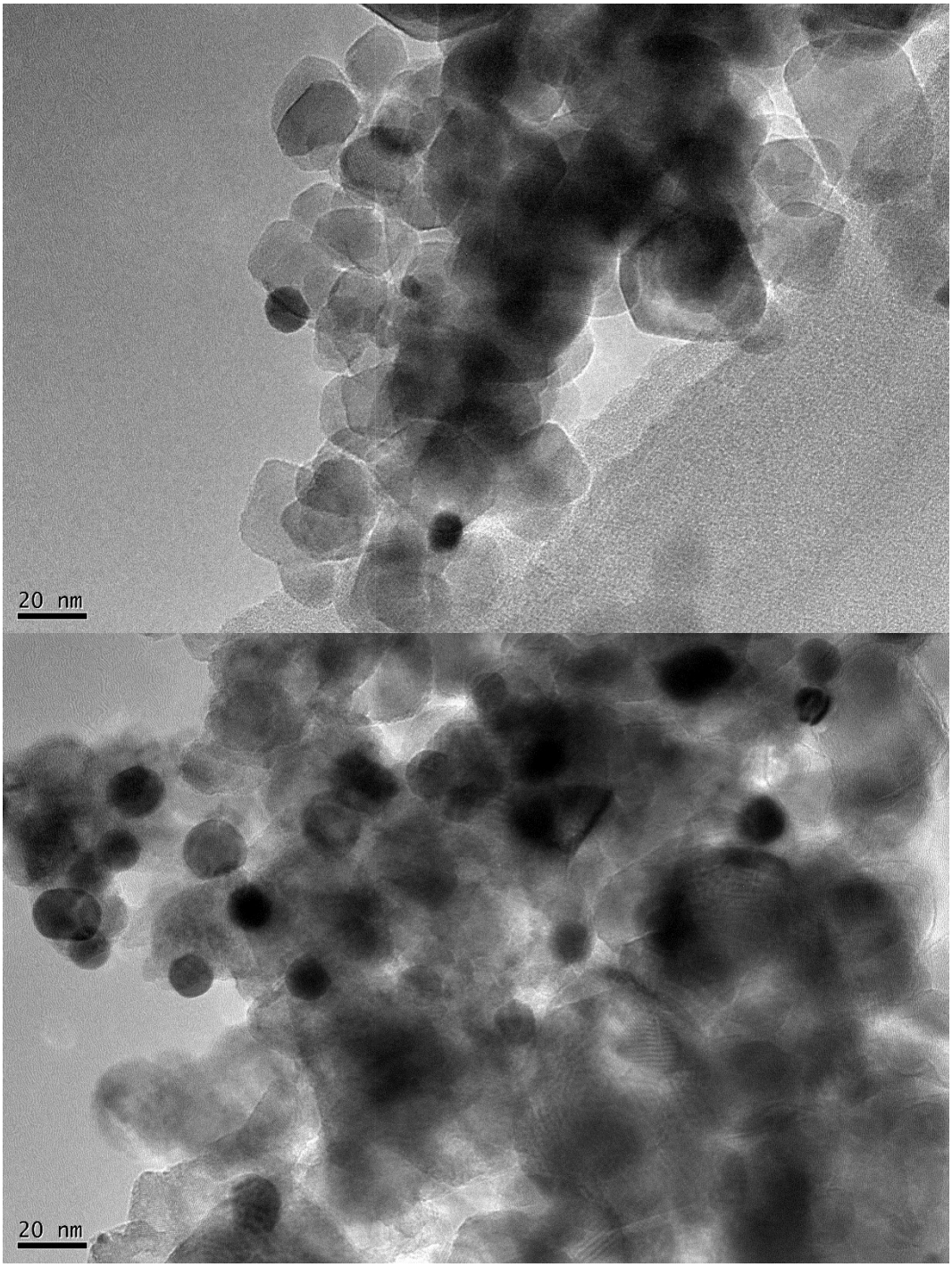

Fig. S7. TEM images of the Pt/TiO_2-12.4 nm.

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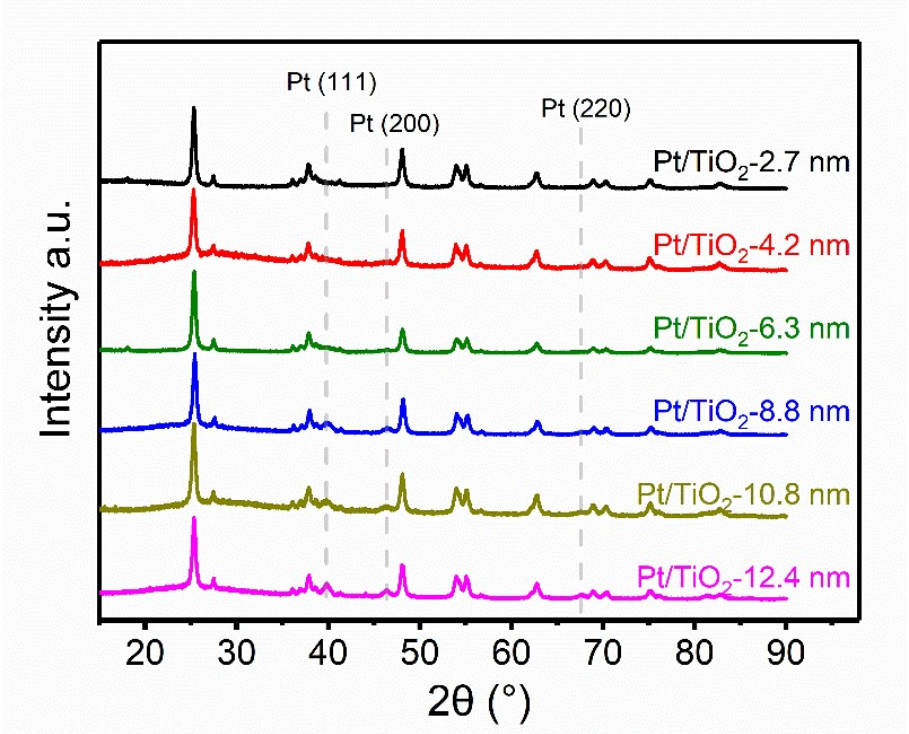

Fig. S8. XRD patterns for Pt/TiO_2 catalysts with different Pt NPs sizes.

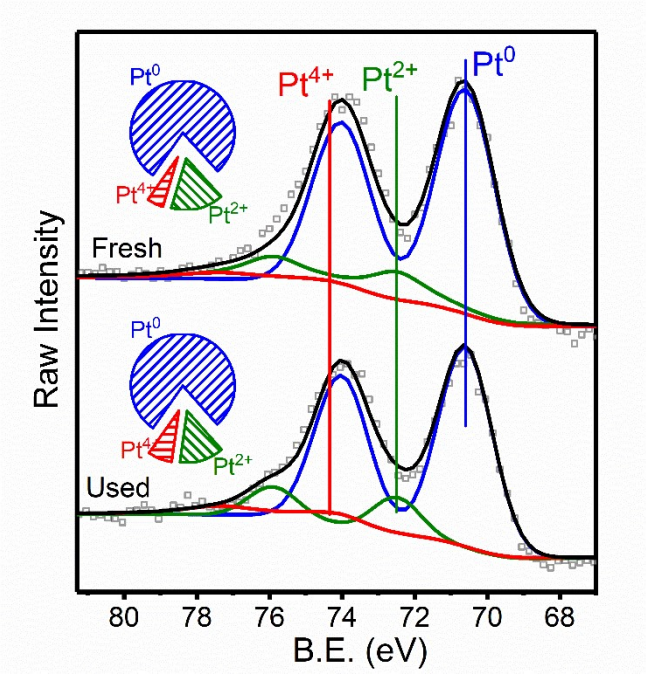

Fig. S9 XPS of Pt 4f for Pt/TiO_2-4.2 nm catalyst. Condition: Pre-treatment in H_2 under 300 °C for 3 h, WHSV = 120,000 mL g_{cat}^{-1} h^{-1} (Fresh); then no-load test in synthetic air only under 160 °C for 3 h, WHSV = 120,000 mL g_{cat}^{-1} h^{-1} (Used).

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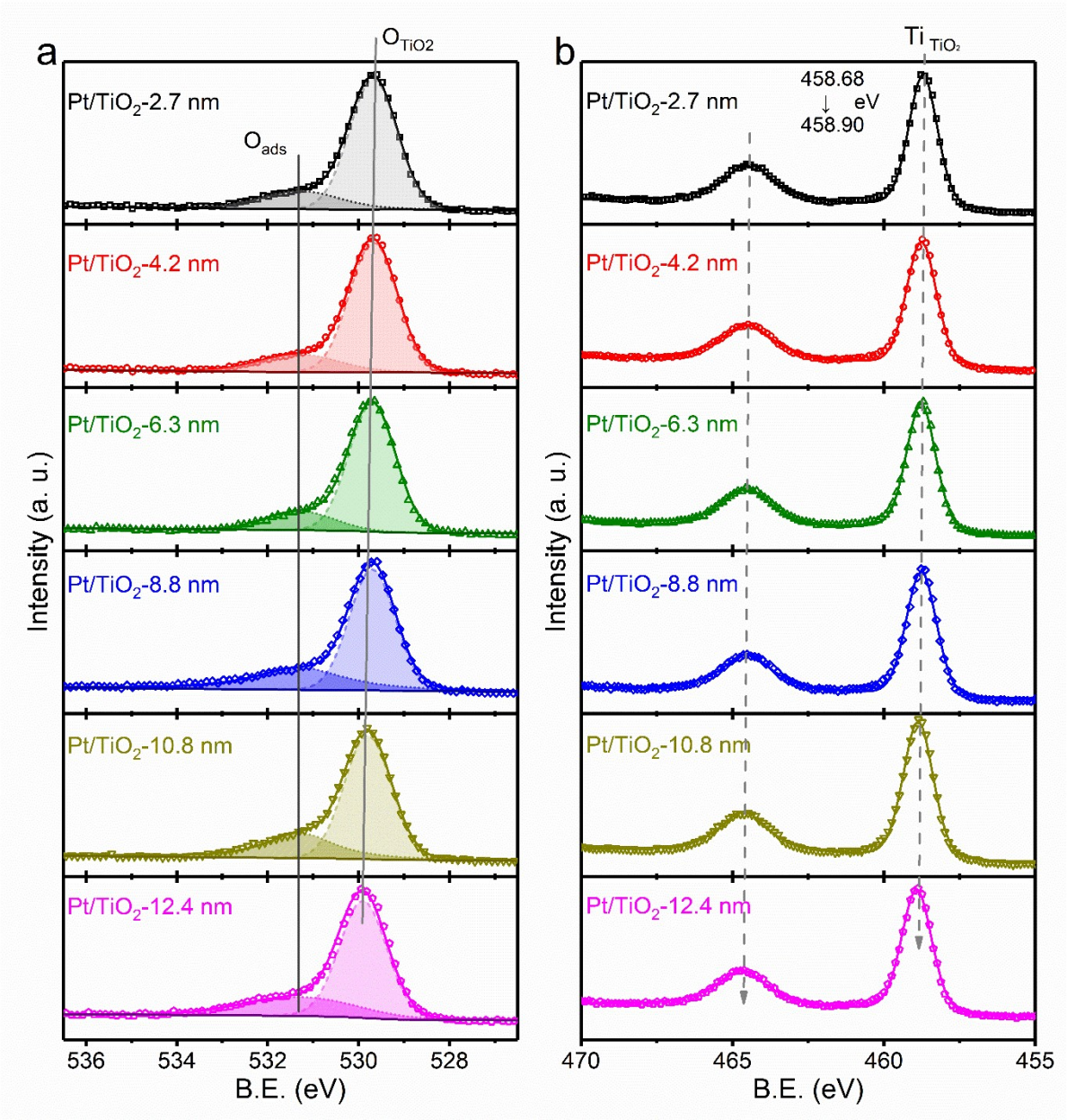

Fig. S10. XPS of (a) O 1s and (b) Ti 2p for catalysts with different Pt NP sizes. Condition: Pre-treatment in H_2 under 300 °C for 3 h, WHSV = 120,000 mL g_{cat}^{-1} h^{-1}.

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Table S1 Elemental analysis[a)] result of Pt/TiO_2-2.6 nm before and after catalytic performance test at stable stage for 140 °C to 150 °C

Name	Weight (mg)		Content (%)		C/N ratio
Pt/TiO_2-2.7 nm - before	4.9240	N: 0.009	C: 1.274	H: 1.989	148.4
Pt/TiO_2-2.7 nm - after	4.4660	N: 0.004	C: 3.220	H: 1.728	726.1

[a)] Elemental analysis was carried out with varioEL III Elementar under CHN mode. The sample was all mixed with ~3 mg combustion-supporting agents for analysis.

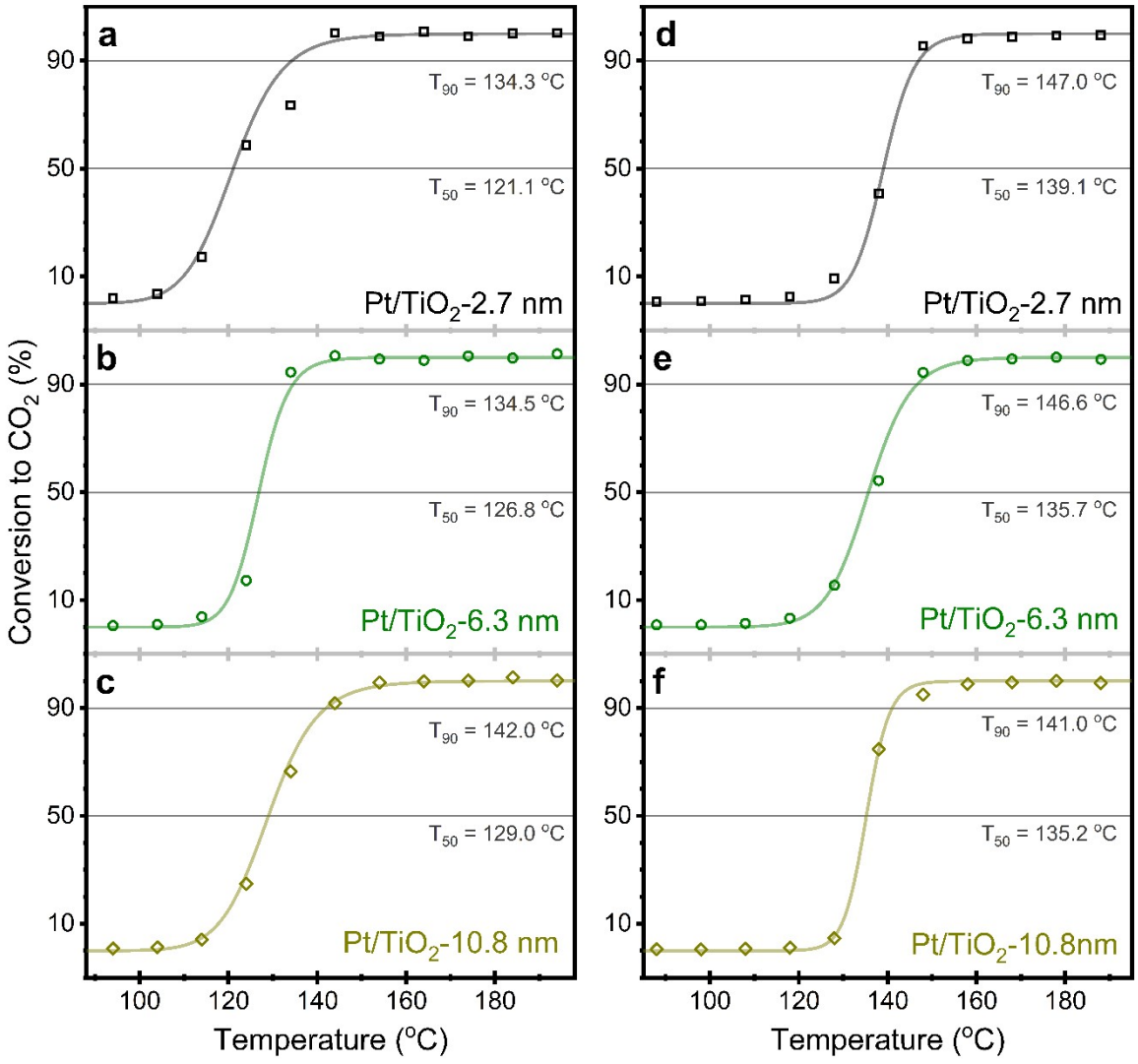

Fig. S11. Toluene light-off curve from 50 °C to 300 °C (1 °C/min) (a-c) without and (d-f) with 5 vol.% water stream. The CO_2 selectivity for all the reactions is higher than 99.5%.

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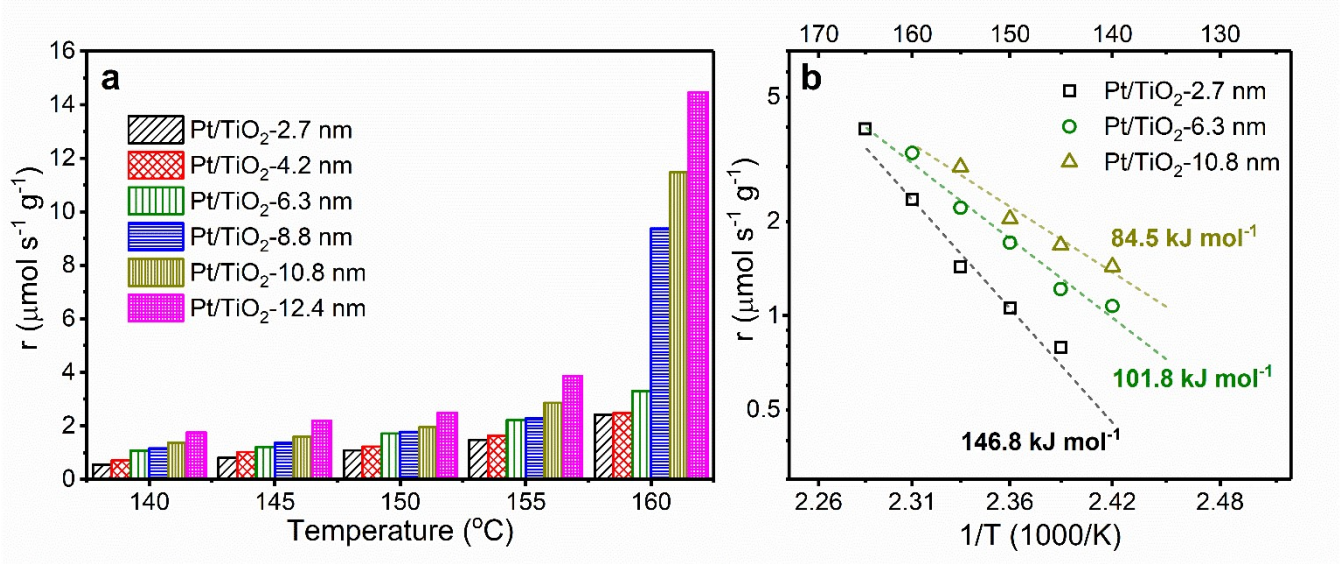

Fig. S12. (d) Reaction rate and (e) Arrhenius plots under steady-state (average of conversion in 150 min after 150 min of stabilization) of Pt/TiO_2 catalysts with different Pt sizes towards the complete oxidation of toluene with 5 vol.% water. The CO_2 selectivity for all the reactions is higher than 99.5%.

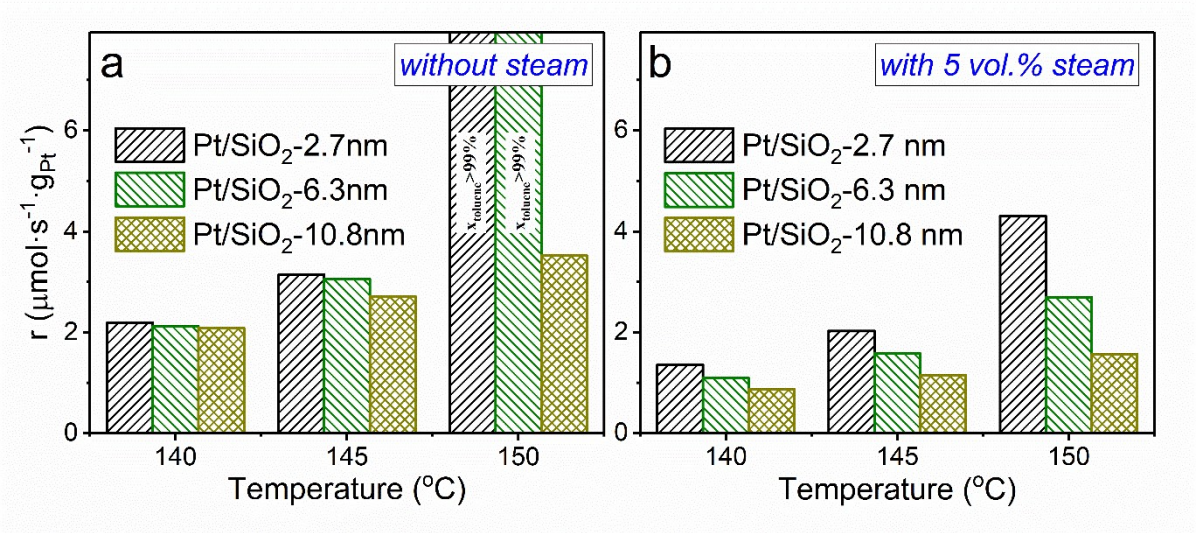

Fig. S13. Conversion and reaction rates (inset) of Pt/SiO_2 with different Pt sizes towards complete oxidation of toluene (a) without and (b) with 5 vol.% steam. The convsion of toluene on Pt/SiO_2-2.7 nm and Pt/SiO_2-6.3 nm is >99 % at 160 °C, thus it is hard to compare their reaction rates under such conditions.

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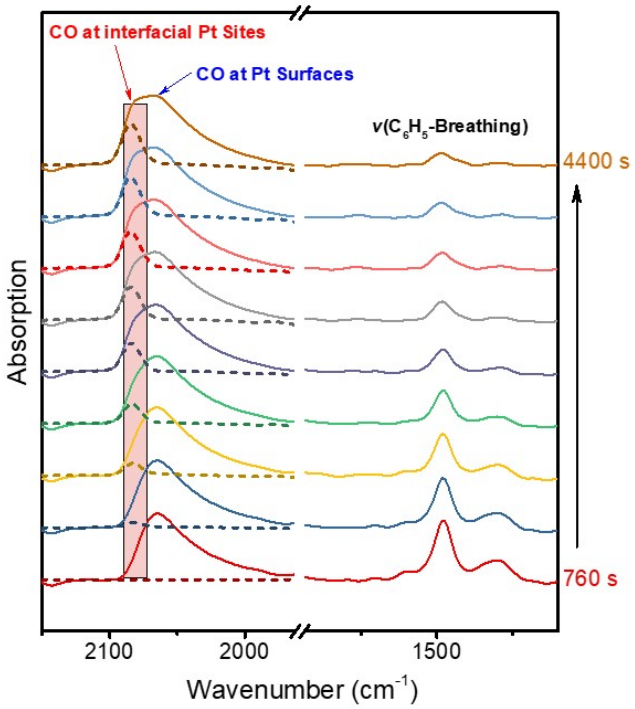

Fig. S14. *In situ* DRIFT spectra of CO adsorption at Pt/TiO_2-4.2 nm. CO adsorption was performed on the same catalyst just after toluene adsorption. The solid lines use the spectra at 0 s as the background, while the dashed lines use the spectra at 760 s as the background.

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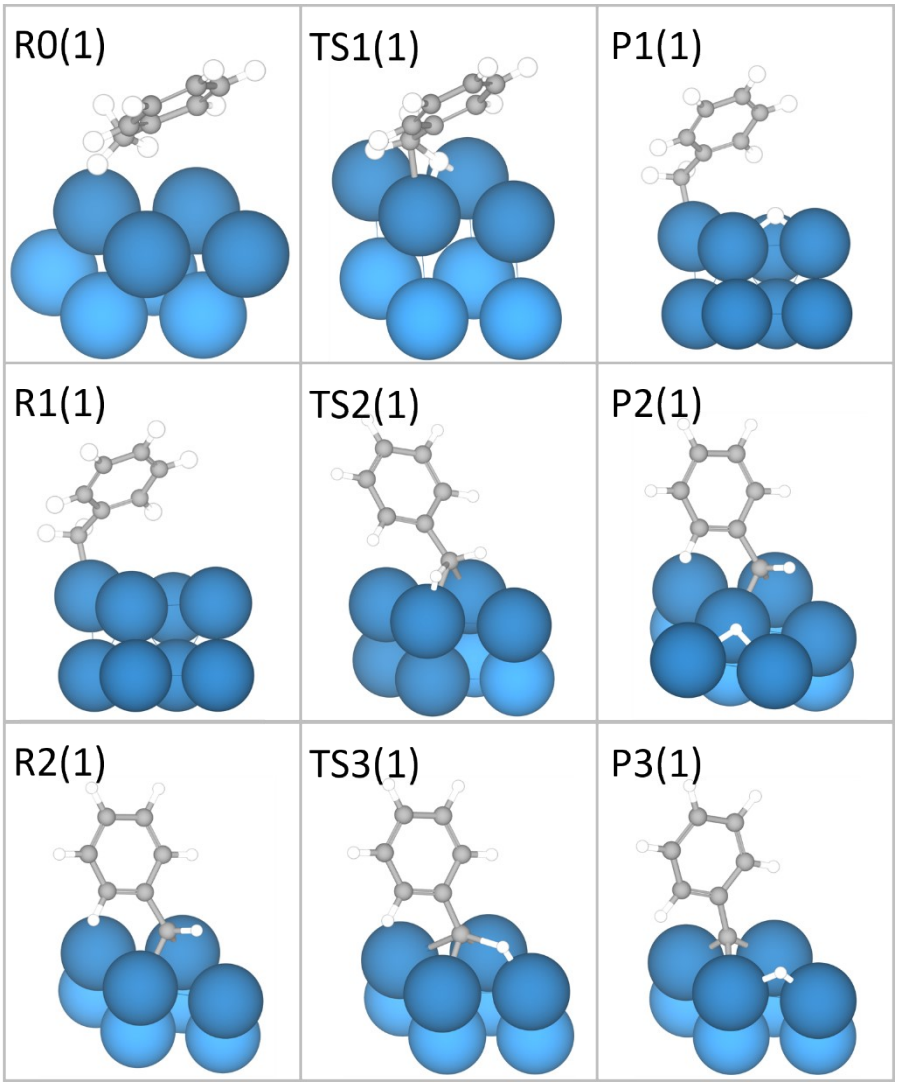

Fig. S15. The optimized structures of reactants, transition states and products for toluene dehydrogenation on Pt surface without OH species.

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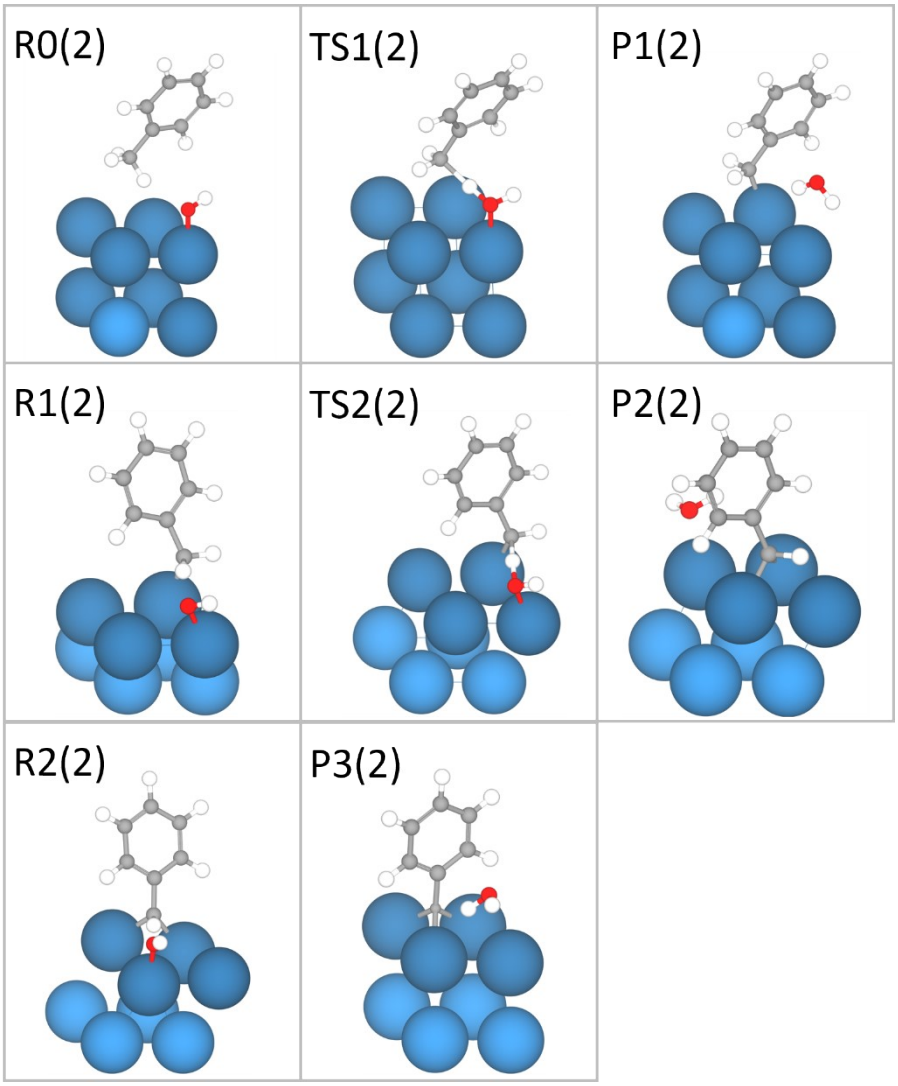

Fig. S16. The optimized structures of reactants, transition states and products for toluene dehydrogenation on Pt surface with an adjacent OH.