

Supplementary information

Nanoceria-modified platinum supported on hierarchical zeolites for selective alcohol oxidation

Marisa Ketkaew,^a Duangkamon Suttipat,^a Pinit Kidkhunthod^b,

Thongthai Witoon^c and Chularat Wattanakit^{a*}

^aDepartment of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, 21210, Thailand

^bSynchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang District, Nakhon Ratchasima, 30000 Thailand

^cDepartment of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

*Corresponding author: E-mail Chularat.w@vistec.ac.th

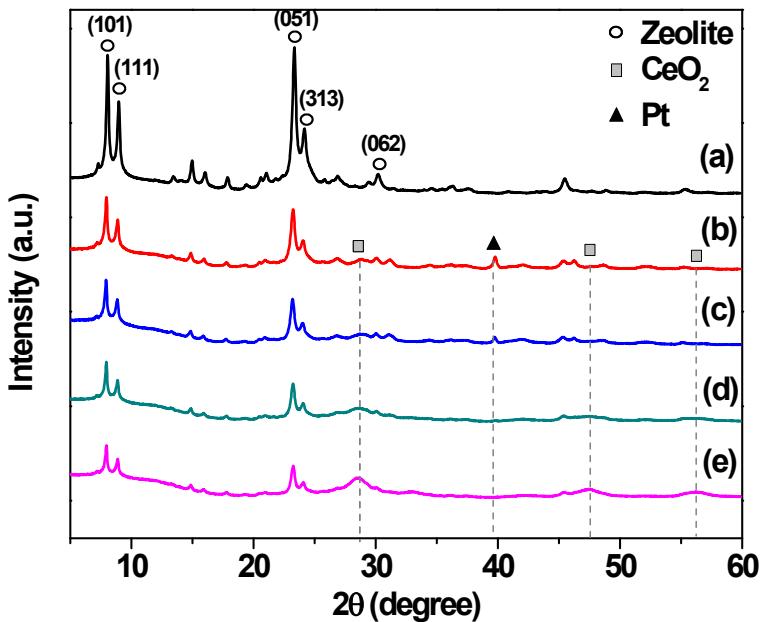


Fig. S1 XRD patterns of Pt/ CeO_2 supported on hierarchical zeolites obtained using different CeO_2 loading: (a) Silicalite1-HIE; (b) 1Pt/5 CeO_2 -Silicalite1-HIE; (c) 1Pt/10 CeO_2 -Silicalite1-HIE; (d) 1Pt/20 CeO_2 -Silicalite1-HIE; (e) 1Pt/30 CeO_2 -Silicalite1-HIE.

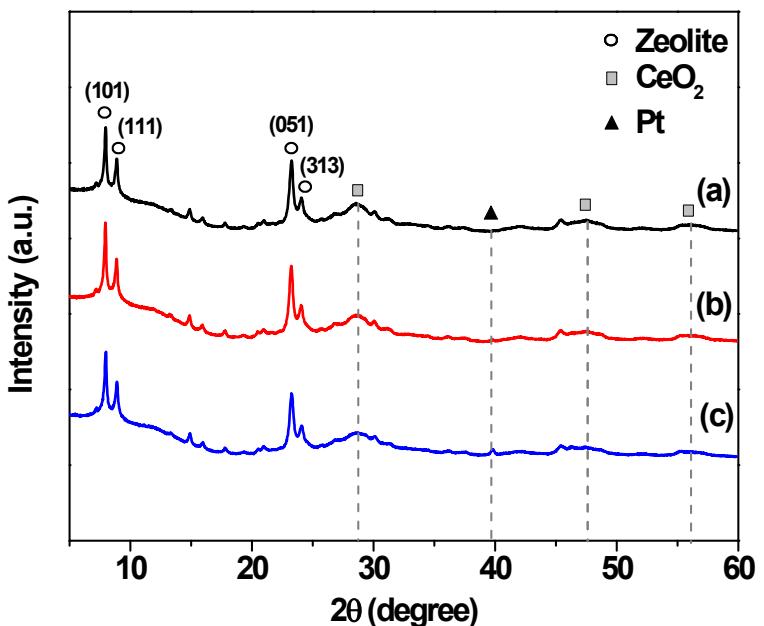


Fig. S2 XRD patterns of Pt/ CeO_2 supported on hierarchical zeolites obtained using different Pt loading: (a) 0.5Pt/20 CeO_2 -Silicalite1-HIE; (b) 1Pt/20 CeO_2 -Silicalite1-HIE; (c) 2Pt/20 CeO_2 -Silicalite1-HIE.

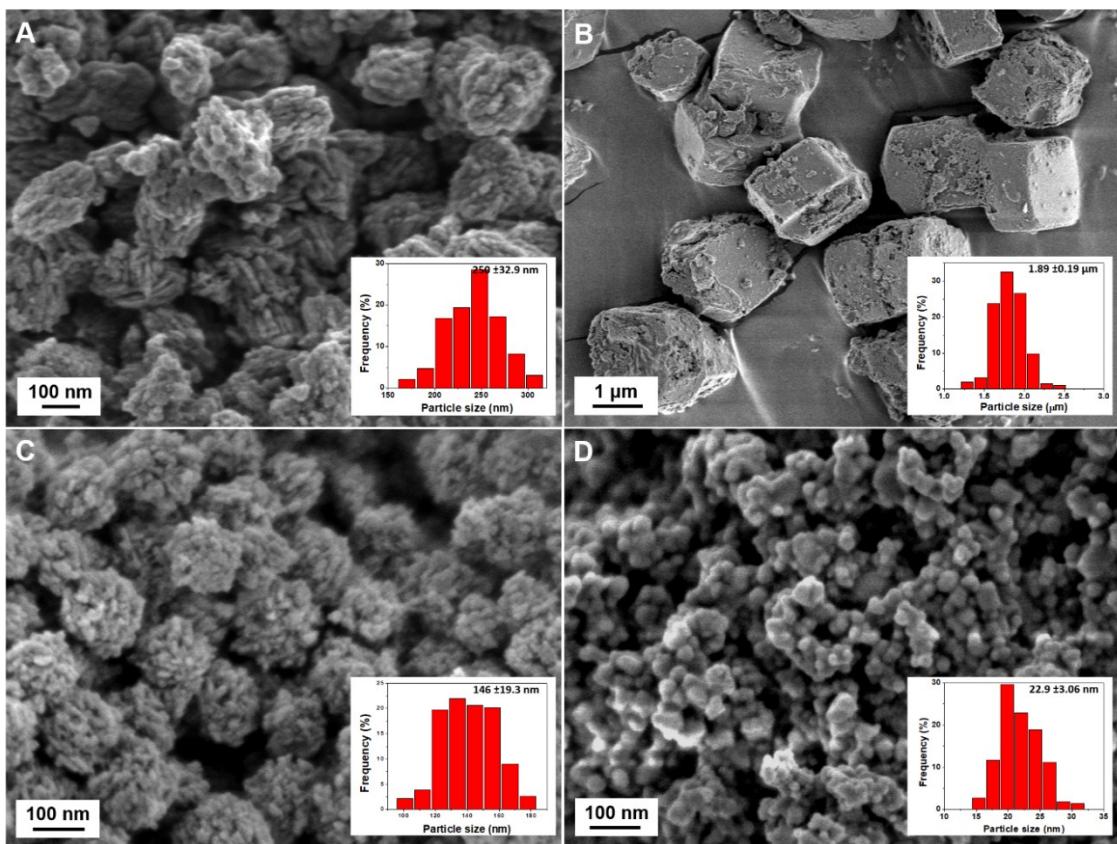


Fig. S3 SEM images of (A) 1Pt/20CeO₂-Silicalite1-HIE; (B) 1Pt/20CeO₂-Silicalite1-CON; (C) 1Pt/20CeO₂-ZSM5-HIE; (D) 1Pt/CeO₂.

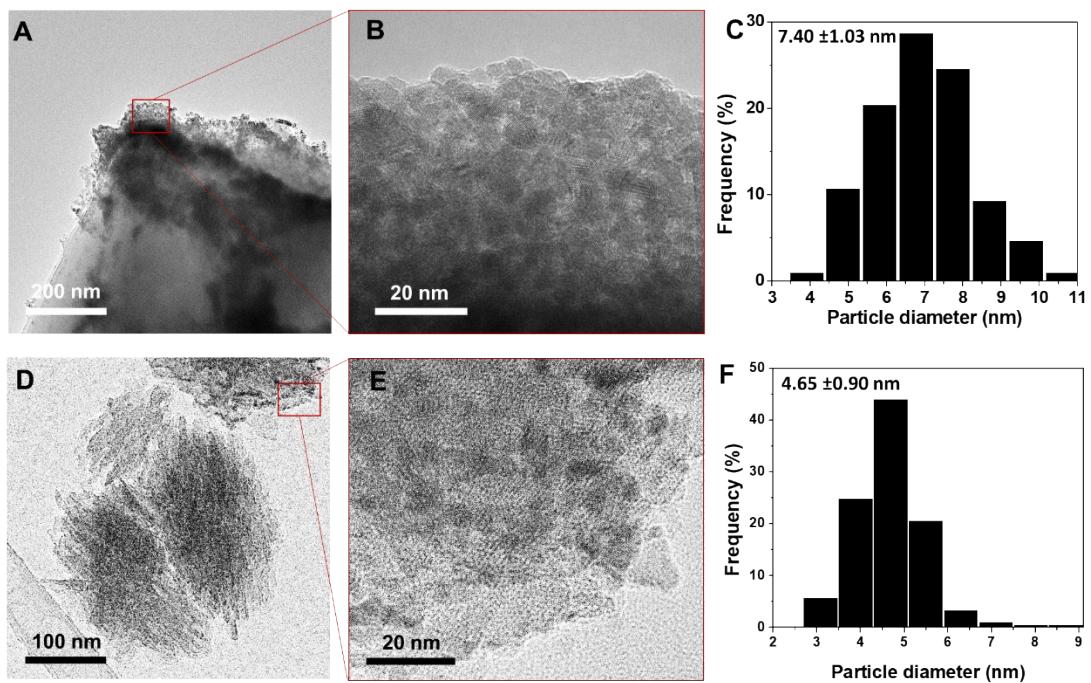


Fig. S4 TEM images and the particle size distribution of (A-C) 1Pt/20CeO₂-Silicalite1-CON; (D-F) 1Pt/20CeO₂-Silicalite1-HIE.

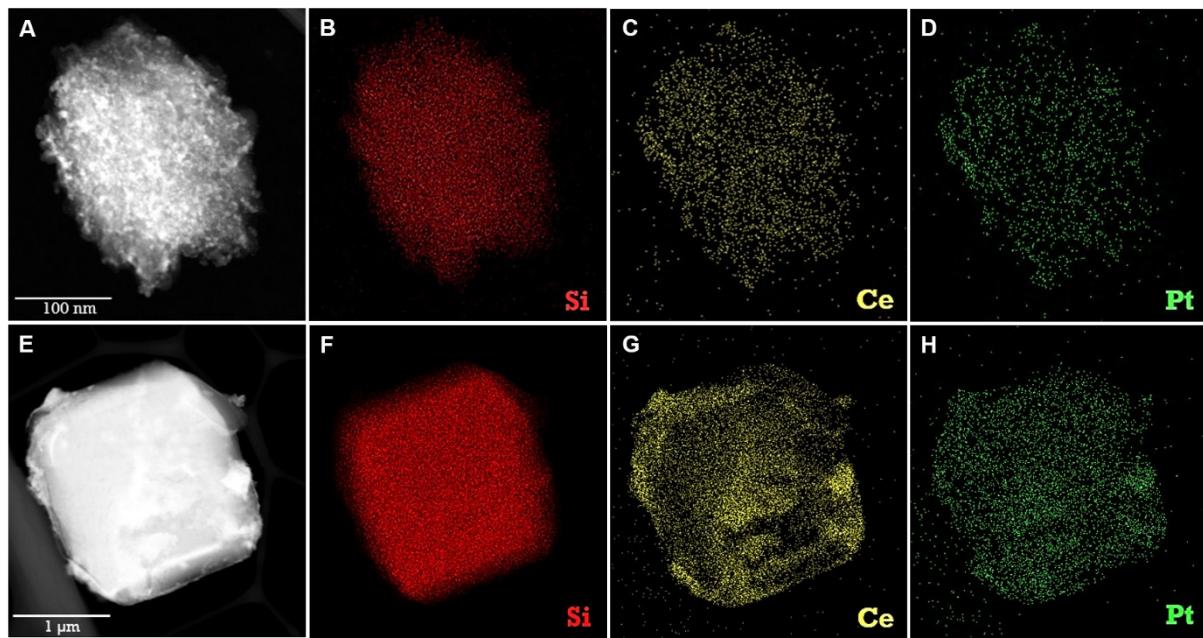


Fig. S5 TEM-EDX images of (A-D) 1Pt/20CeO₂-Silicalite1-HIE; (E-H) 1Pt/20CeO₂-Silicalite1-CON.

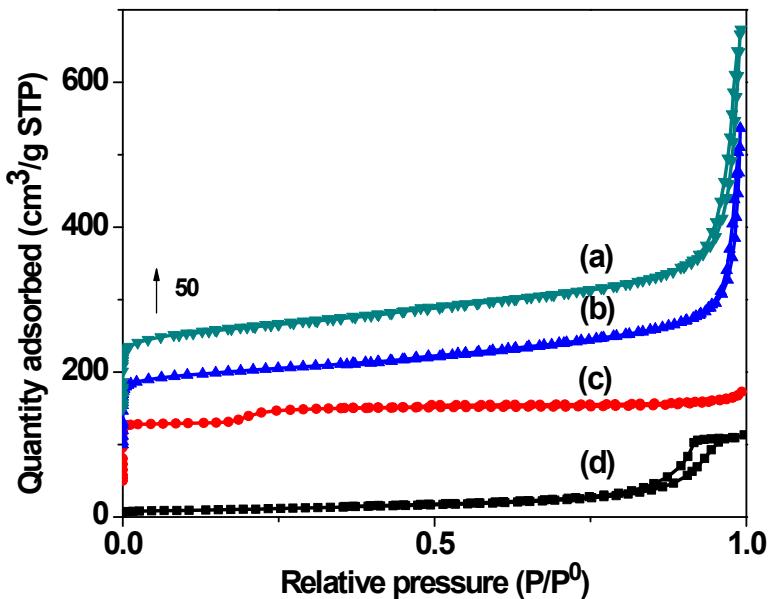


Fig. S6 N₂ adsorption/desorption isotherms of (a) 1Pt/20CeO₂-ZSM5-HIE; (b) 1Pt/20CeO₂-Silicalite1-HIE; (c) 1Pt/20CeO₂-Silicalite1-CON; (d) 1Pt/CeO₂.

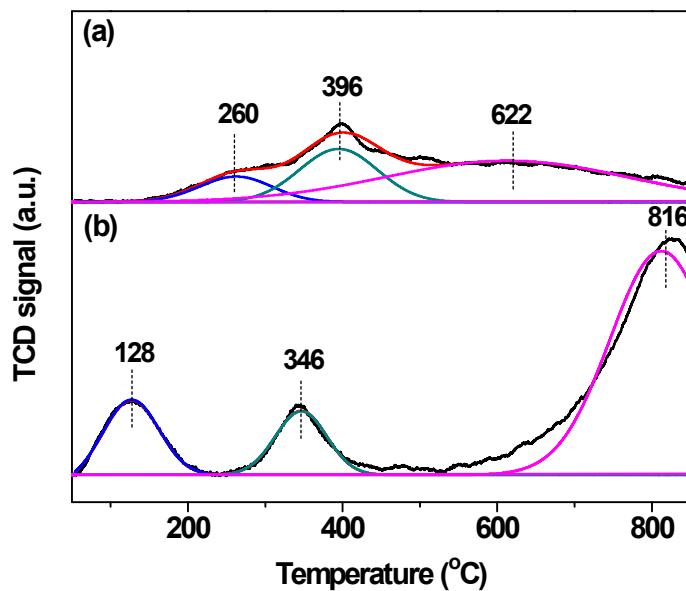


Fig. S7 H₂-Temperature programmed reduction (H₂-TPR) profiles of (a) 1Pt/20CeO₂-ZSM5-HIE and (b) 1Pt/CeO₂.

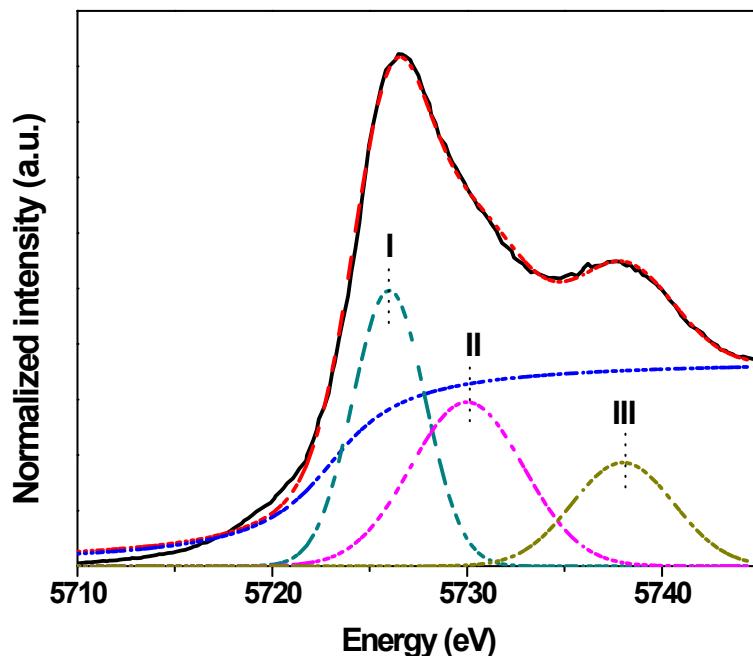


Fig. S8 Fitting curves of XANES spectra of the Ce L₃ edge for 1Pt/20CeO₂-ZSM5-HIE.

Table S1 Textural properties

Catalyst	Si/Al ratio ^a	Pt dispersion ^b (%)	Particle size ^b (nm)	S _{BET} ^c (m ² g ⁻¹)	S _{ext} ^d (m ² g ⁻¹)	S _{micro} ^e (m ² g ⁻¹)	V _{total} ^f (cm ³ g ⁻¹)	V _{micro} ^g (cm ³ g ⁻¹)	V _{ext} ^h (cm ³ g ⁻¹)
1Pt/20CeO ₂ -ZSM5-HIE	110.2	37.89	2.99	404.86	225.48	179.38	0.80	0.003	0.80
1Pt/20CeO ₂ -Silicalite1-HIE	∞	29.57	3.83	375.69	164.35	211.34	0.66	0.03	0.63
1Pt/20CeO ₂ -Silicalite1-CON	∞	17.65	6.41	331.45	13.98	317.47	0.19	0.15	0.04
1Pt/CeO ₂	-	-	1.74	38.58	6.03	32.55	0.17	0.16	0.02

^a Si/Al determined by wavelength dispersive x-ray fluorescence.^b Pt dispersion and average particle size were determined by H₂-pulse method.^c S_{BET}: Specific surface area (m²g⁻¹) determined by BET method.^d S_{ext}: External surface area (m²g⁻¹).^e S_{micro}: micropore surface area (m²g⁻¹), determined by t-plot method.^f V_{total}: total pore volume (cm³g⁻¹) obtained at P/P₀=0.90.^g V_{micro}: micropore volume (cm³g⁻¹), determined by t-plot method.^h V_{ext}: external pore volume (cm³g⁻¹), V_{ext}=V_{total}-V_{micro}.**Table S2** Quantitative analysis of Ce oxidation obtained from XANES for fresh and spent catalysts^{1, 2}.

Catalysts	I ^I	I ^{II}	I ^{III}	%Ce ³⁺
1Pt/20CeO ₂ -ZSM5-HIE-Fresh	5.79	5.353	3.044	65.5
1Pt/20CeO ₂ -ZSM5-HIE-Spent	7.904	4.132	3.197	71.2
1Pt/20CeO ₂ -Silicalite1-HIE-Fresh	5.166	6.156	3.175	61.9
1Pt/20CeO ₂ -Silicalite1-HIE-Spent	5.451	5.66	3.309	62.2
1Pt/20CeO ₂ -Silicalite1-CON-Fresh	0.69	5.853	7.714	8.2
1Pt/20CeO ₂ -Silicalite1-CON-Spent	0.225	4.132	4.458	4.8
1Pt/CeO ₂ -Fresh	1.642	5.651	9.683	14.5
1Pt/CeO ₂ -Spent	1.426	1.898	5.815	19.7

* Fittings of the experimental XANES spectra of the Ce L₃ edge of the synthesized samples.** The estimation of Ce³⁺ concentration in the sample is calculated as follows:%Ce³⁺ = I^I/(I^I+I^{II}+I^{III}), where I^I, I^{II} and I^{III} are the intensities of the different peaks.

References

1. N. Qiu, J. Zhang, Z. Wu, T. Hu and P. Liu, *Crystal Growth & Design*, 2011, **12**, 629-634.
2. S. Phokha, S. Pinitsoontorn and S. Maensiri, *Nano-Micro Letters*, 2013, **5**, 223-233.