

Supporting Information for

Effects of Multiple Platinum Species to Catalytic Reactivity Distinguished by Electron Microscopy and X-ray Absorption Spectroscopy Techniques

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Table S1. Testing conditions of Arrhenius plots (r_w) for **Pt-CZL** samples.

CZL			0.5Pt-CZL		
21,000 mL g ⁻¹ h ⁻¹			57,000 mL g ⁻¹ h ⁻¹		
	Conv.(%)	$r_w(\mu\text{mol}_{\text{CH}_4} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1})$		Conv.(%)	$r_w(\mu\text{mol}_{\text{CH}_4} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1})$
425 °C	6.6	0.18	425 °C	7.3	0.52
450 °C	11.8	0.32	450 °C	12.2	0.87
475 °C	20.9	0.56	475 °C	20.6	1.47

1Pt-CZL			2Pt-CZL		
100,000 mL g ⁻¹ h ⁻¹			120,000 mL g ⁻¹ h ⁻¹		
	Conv.(%)	$r_w(\mu\text{mol}_{\text{CH}_4} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1})$		Conv.(%)	$r_w(\mu\text{mol}_{\text{CH}_4} \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1})$
425 °C	9.7	1.24	425 °C	8.0	1.19
450 °C	15.1	1.93	450 °C	11.6	1.73
475 °C	22.5	2.87	475 °C	19.1	2.65

Table S2 Testing conditions for CO plus chemisorption.

Sample	1Pt-CZL				
Reduction T (°C)	180	220	300	400	450
Dispersion(%)	12	13	22	39	30
Sample	0.5Pt-CZL	1Pt-CZL	2Pt-CZL		
Reduction T (°C)	400	400	400		
Dispersion (%)	36	39	23		

Table S3. Calculation on the efficiencies of different platinum species for **Pt-CZL** samples.

	Atom	Cluster	Particle	
Occupation(O)	$(CN_{\text{Pt-O}} - CN_{\text{Pt-O-Pt}})/8$	$CN_{\text{Pt-O-Pt}}/8$	$CN_{\text{Pt-Pt}}/12$	
Fraction (f)	$O_{\text{atom}}/(O_{\text{atom}} + O_{\text{cluster}} + O_{\text{particle}})$	$O_{\text{cluster}}/(O_{\text{atom}} + O_{\text{cluster}} + O_{\text{particle}})$	$O_{\text{particle}}/(O_{\text{atom}} + O_{\text{cluster}} + O_{\text{particle}})$	
Pt dispersions (d)	$f_{\text{atom}} \times 100\% + f_{\text{cluster}} \times (1/D_{\text{cluster}}) \times 100\% + f_{\text{particle}} \times (1/D_{\text{particle}}) \times 100\%$			
TOF	r_{Pt}/d	$f_{\text{atom},0.5\text{Pt-CZL}} \times E_{\text{atom}} + f_{\text{cluster},0.5\text{Pt-CZL}} \times E_{\text{cluster}} + f_{\text{particle},0.5\text{Pt-CZL}} \times E_{\text{particle}} = \text{TOF}_{0.5\text{Pt-CZL}}$		
Efficiency (E)	$f_{\text{atom},1\text{Pt-CZL}} \times E_{\text{atom}} + f_{\text{cluster},1\text{Pt-CZL}} \times E_{\text{cluster}} + f_{\text{particle},1\text{Pt-CZL}} \times E_{\text{particle}} = \text{TOF}_{1\text{Pt-CZL}}$			
	$f_{\text{atom},2\text{Pt-CZL}} \times E_{\text{atom}} + f_{\text{cluster},2\text{Pt-CZL}} \times E_{\text{cluster}} + f_{\text{particle},2\text{Pt-CZL}} \times E_{\text{particle}} = \text{TOF}_{2\text{Pt-CZL}}$			

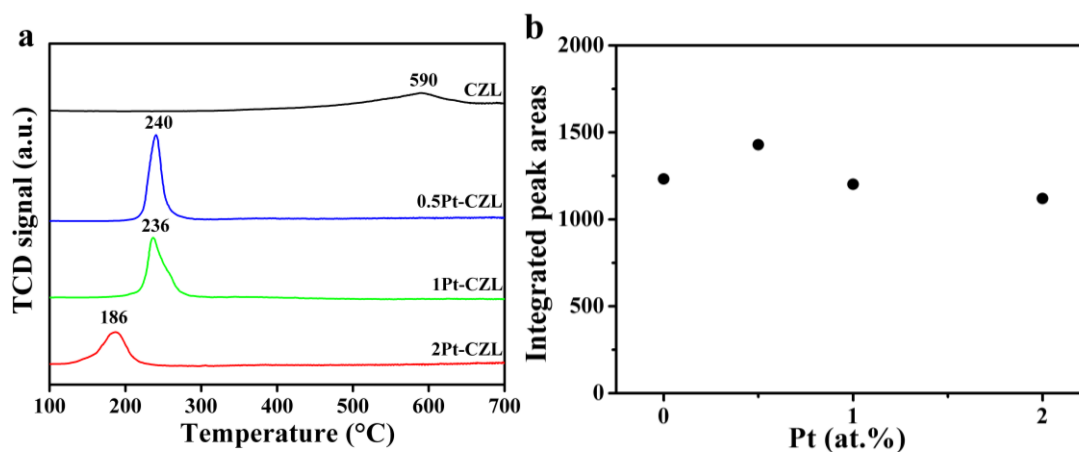


Figure S1. (a) H₂-TPR profiles and (b) integrated peak areas as function of platinum concentrations for Pt-CZL samples.

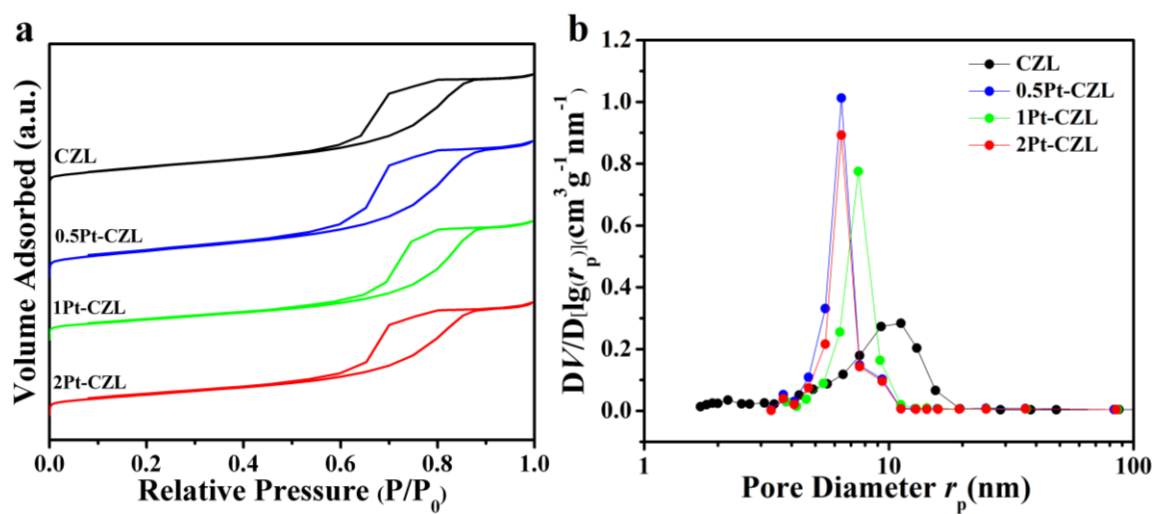


Figure S2. Nitrogen adsorption measurements of **Pt-CZL** samples:(a) adsorption-desorption isotherm, (b) BJH pore size distribution.

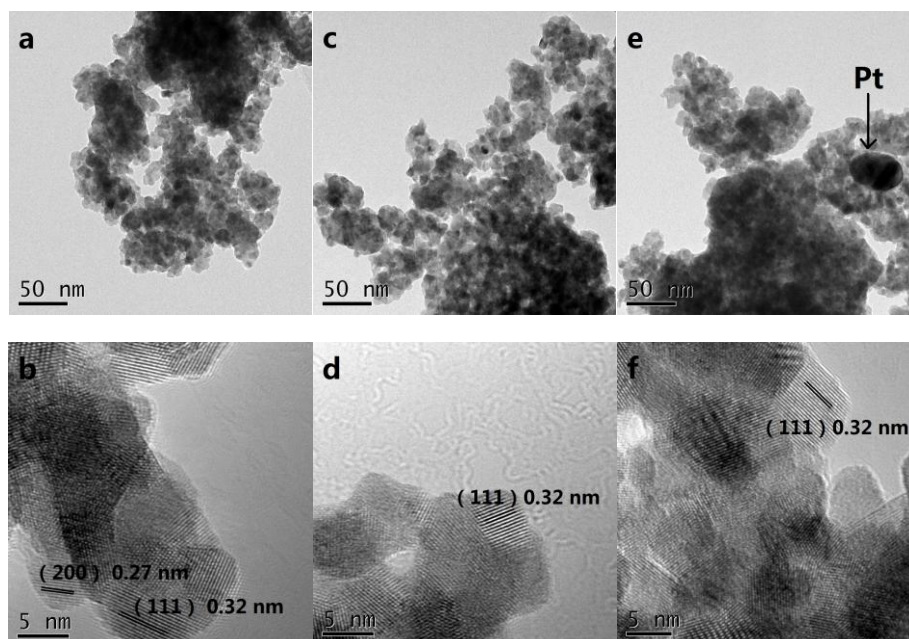


Figure S3. TEM (a, c, e) and HRTEM (b, d, f) images of used **Pt-CZL** samples: (a, b) **0.5Pt-CZL**; (c, d) **1Pt-CZL**; (e, f) **2Pt-CZL**.

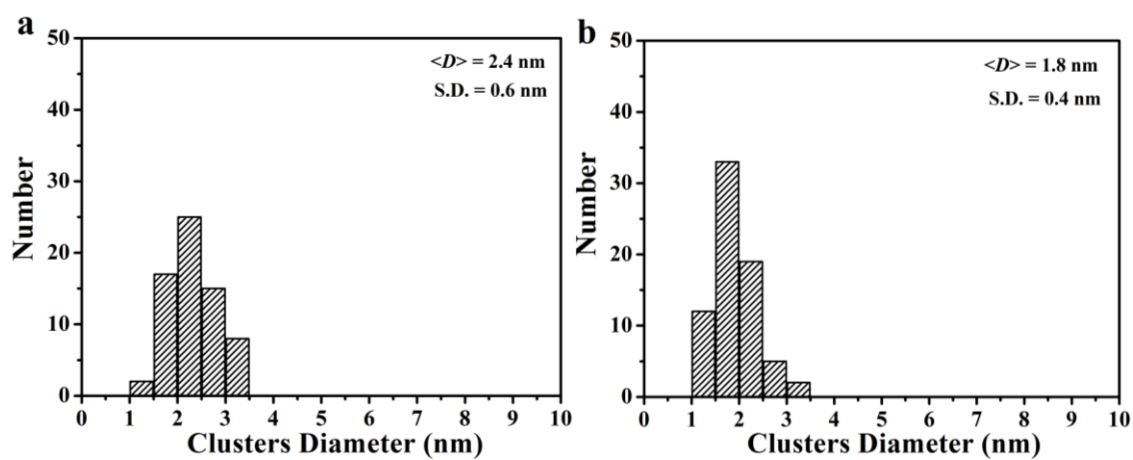


Figure S4. Diameter histograms on platinum clusters of fresh **Pt-CZL** samples on the basis of HAADF-STEM data: (a) **0.5Pt-CZL**; (b) **1Pt-CZL**.

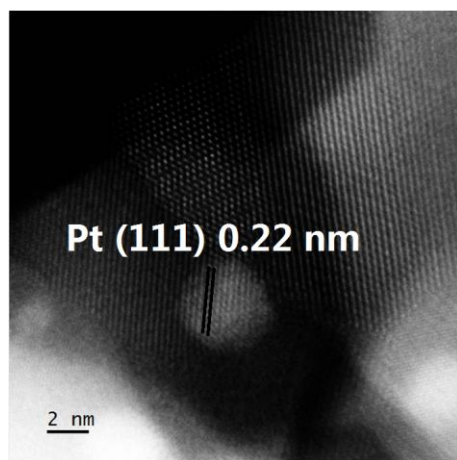


Figure S5. Aberration-corrected HAADF-STEM images of fresh **1Pt-CZL** samples, indicating the presence of ~ 4 nm Pt metallic crystal.

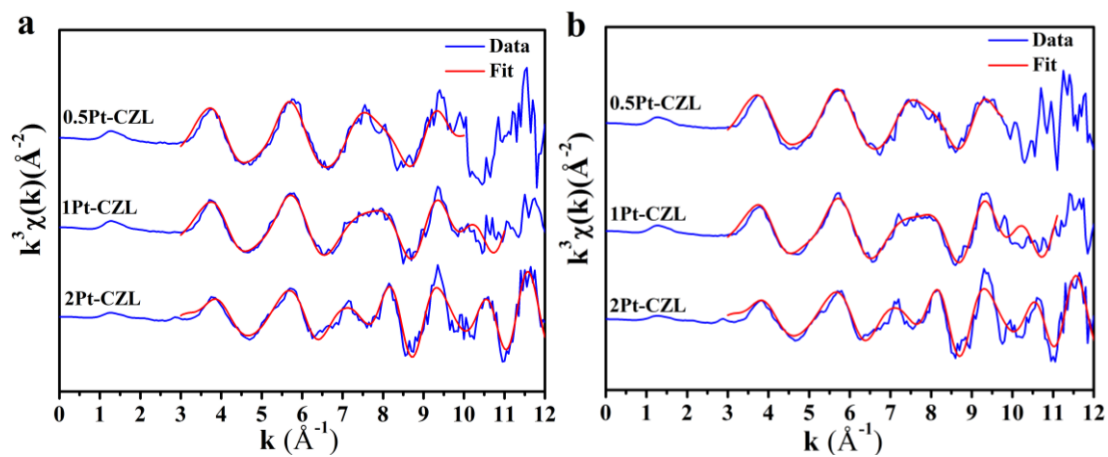


Figure S6. k^3 -weighted EXAFS data in k -space of **Pt-CZL** samples: (a) fresh;(b) used.

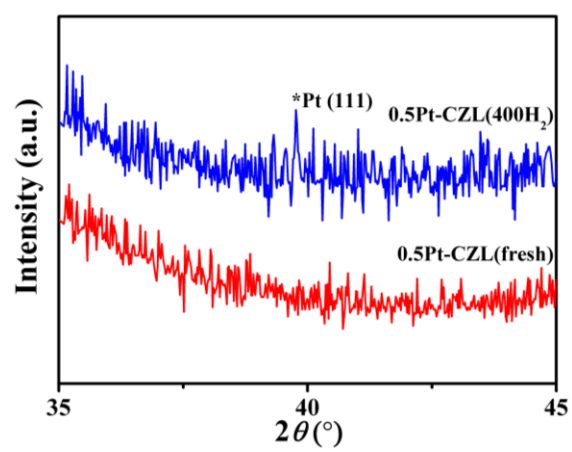


Figure S7. XRD patterns of **0.5Pt-CZL** samples after hydrogen reduction. **0.5Pt-CZL (400H₂):** Sample **0.5Pt-CZL** after reduction at 400 °C in 5%H₂/He.