Supplementary Information

Synthesis of Pt_3Zn_1 and Pt_1Zn_1 Intermetallic Nanocatalysts for Dehydrogenation of Ethane

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Text S1. Calculation of expected ZnO weight gain.

Given the surface area of Silicycle SiO_2 is 96.1 m^2/g (Table 1), and the ZnO growth rate of 1.8 Å/cycle, we can calculate the expected ZnO mass gain for one cycle. Assuming the ZnO density is 5.61 g/cm^3, the expected ZnO mass gain can be estimated using the following equation (1):

$$W = (h \cdot A_{substrate})\rho_{ZnO} \times 100\% \quad ...eqn(1)$$

Where W is the expected weight gain, A is the surface area of the substrate, ρ is the density of ZnO, and h is the growth rate of ZnO ALD. The expected weight gain is calculated to be ~9.7 wt%.

Text S2. Determination of conversion, selectivity and TOF

The C_2H_6 conversion is calculated by:

$$conversion\ \% = \frac{[C_2H_6]_{inlet} - [C_2H_6]_{outlet}}{[C_2H_6]_{inlet}} \times 100\ \%$$

Where $[C_2H_6]_{inlet}$, $[C_2H_6]_{outlet}$ are the inlet and outlet concentration of ethane in the reactor (mol/ml), respectively;

The C_2H_4 selectivity is determined by:

$$selectivity\ \% = \frac{2[C_2H_4]}{2[C_2H_4] + [CH_4]} \times 100\ \%$$

Where $[C_2H_4]$, $[CH_4]$ are concentrations of ethylene and methane (mol/ml), respectively.

C_2H_4 TOF (s^{-1}) is given by:

$$C_2H_4\ TOF = \frac{q[C_2H_4]}{N_{Pt} \times Pt\%}$$

Where q is the volumetric flow rate (ml/min), N_{Pt} is the amount of Pt in the catalyst tested (mol), $Pt\%$ is Pt dispersion (%).

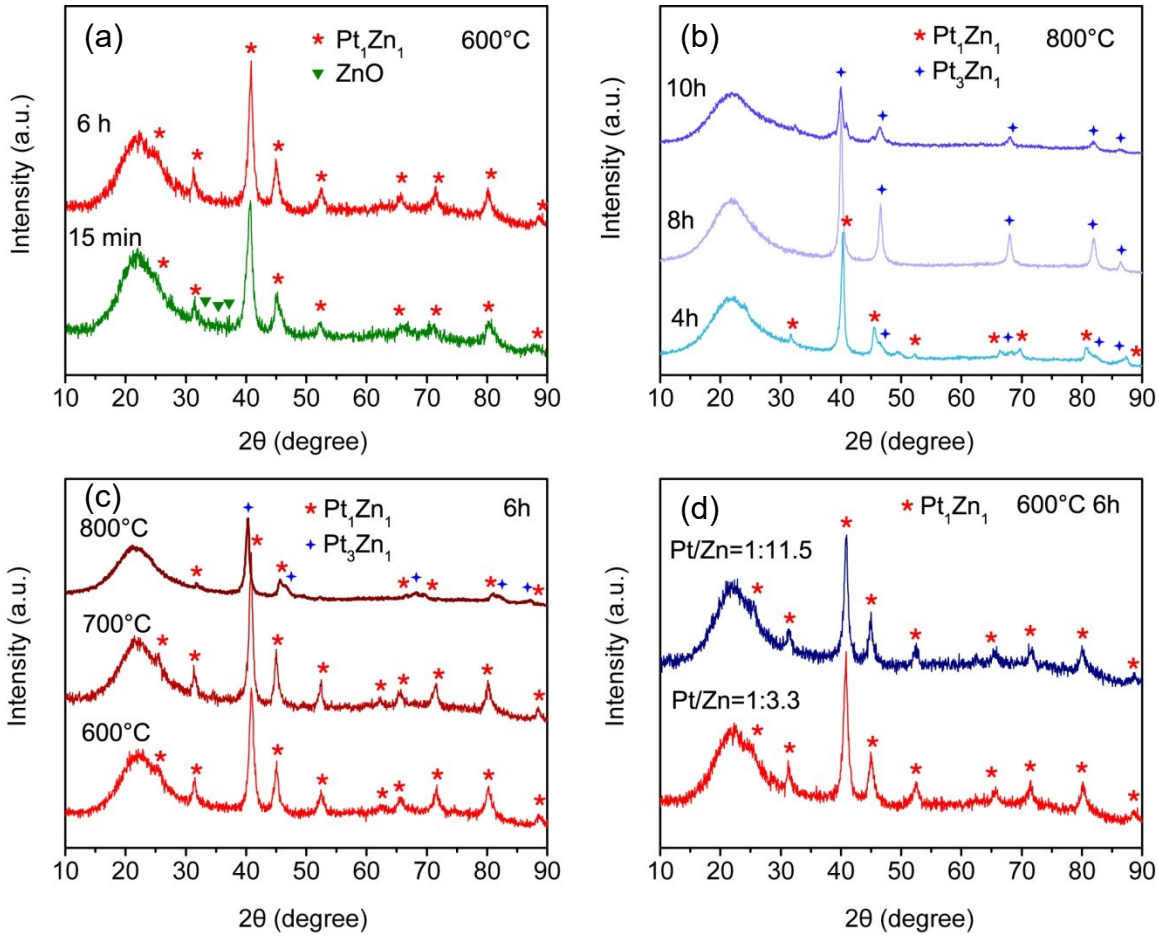

Figure S1. XRD patterns of $Pt/ZnO/SiO_2$ after hydrogen reduction using various temperature, time and initial Pt: Zn ratio: (a) reduced at 600 °C, (b) reduced at 800 °C, (c) reduced for 6 h, and (d) reduced at 600 °C for 6 h with different Pt:Zn initial ratio.

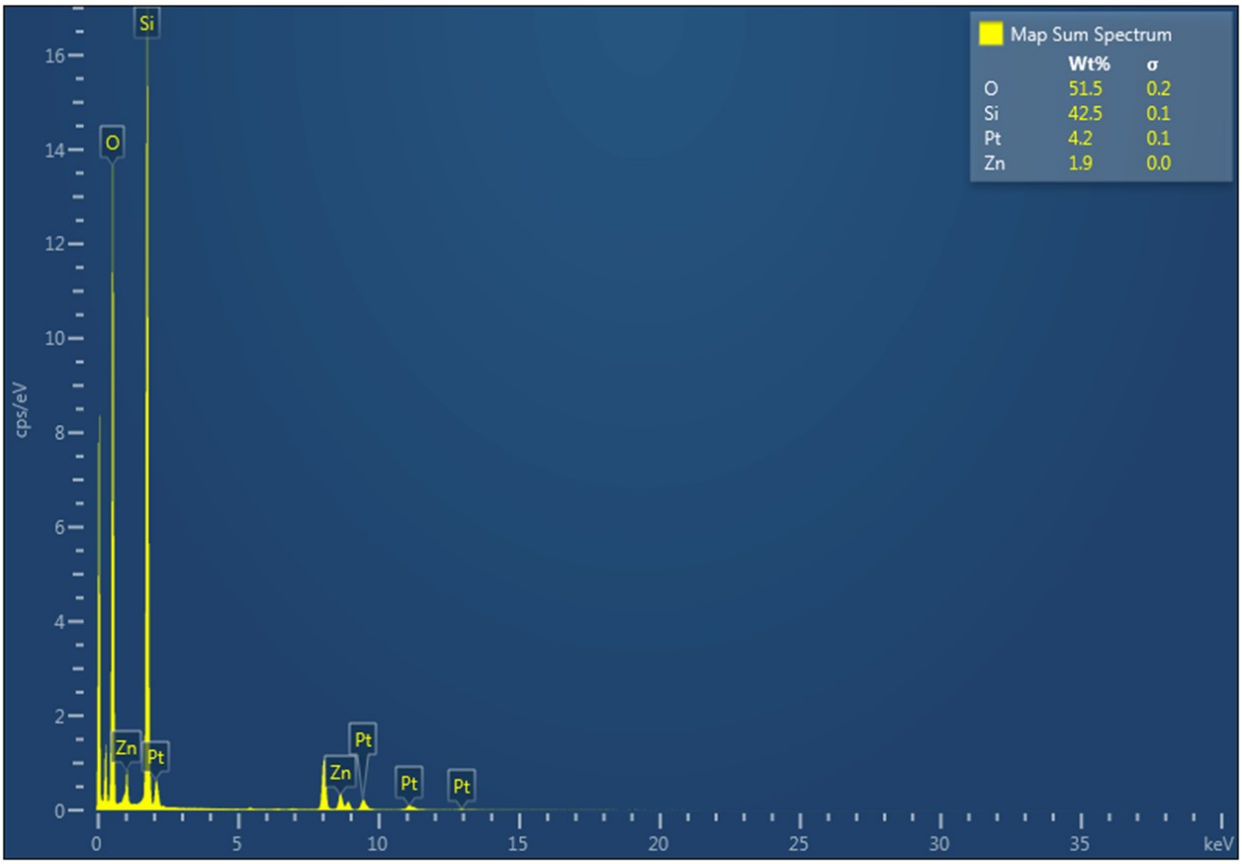

Figure S2. EDX spectrum of Pt_1Zn_1/SiO_2.

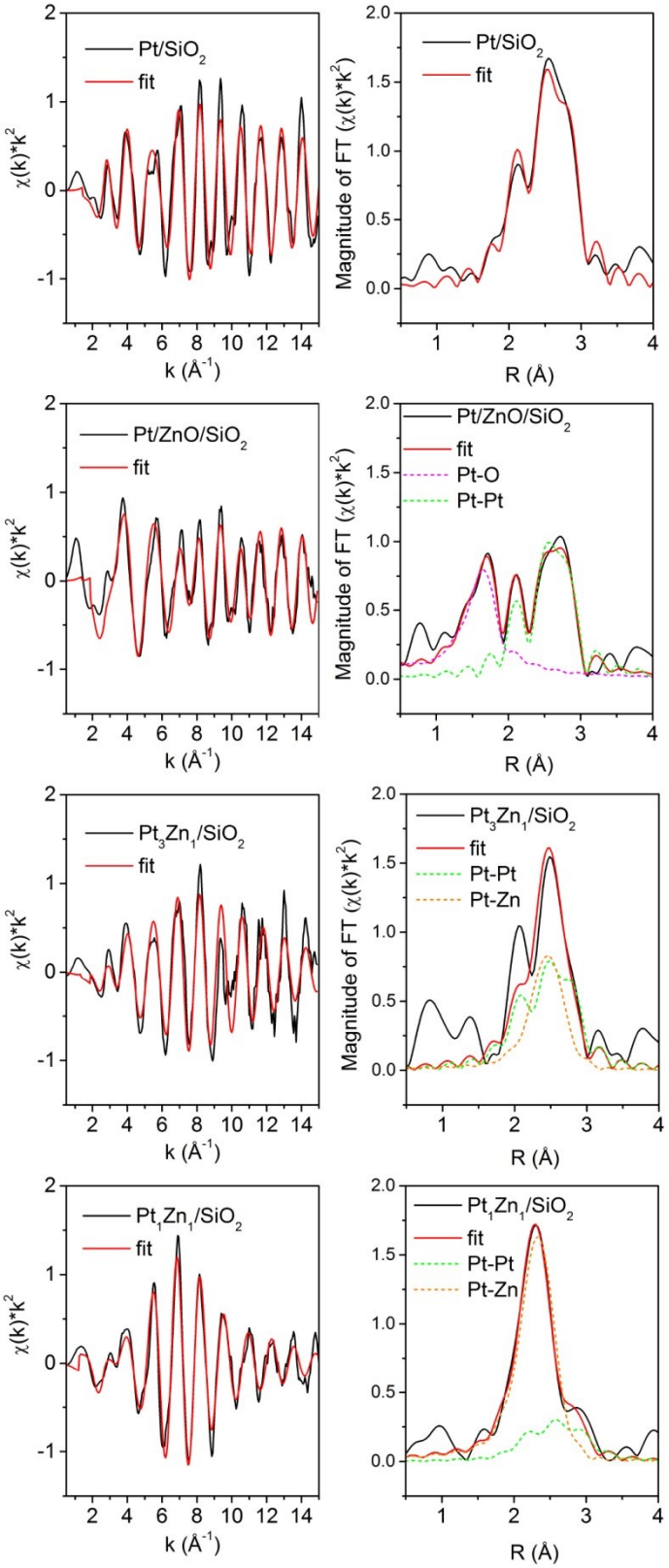

Figure S3. Pt L_3 EXAFS fittings of Pt/SiO_2, $Pt/ZnO/SiO_2$, Pt_3Zn_1/SiO_2, and Pt_1Zn_1/SiO_2. $k = 3.0–14.0$ Å^{-1} and $r = 1.3–3$ Å.

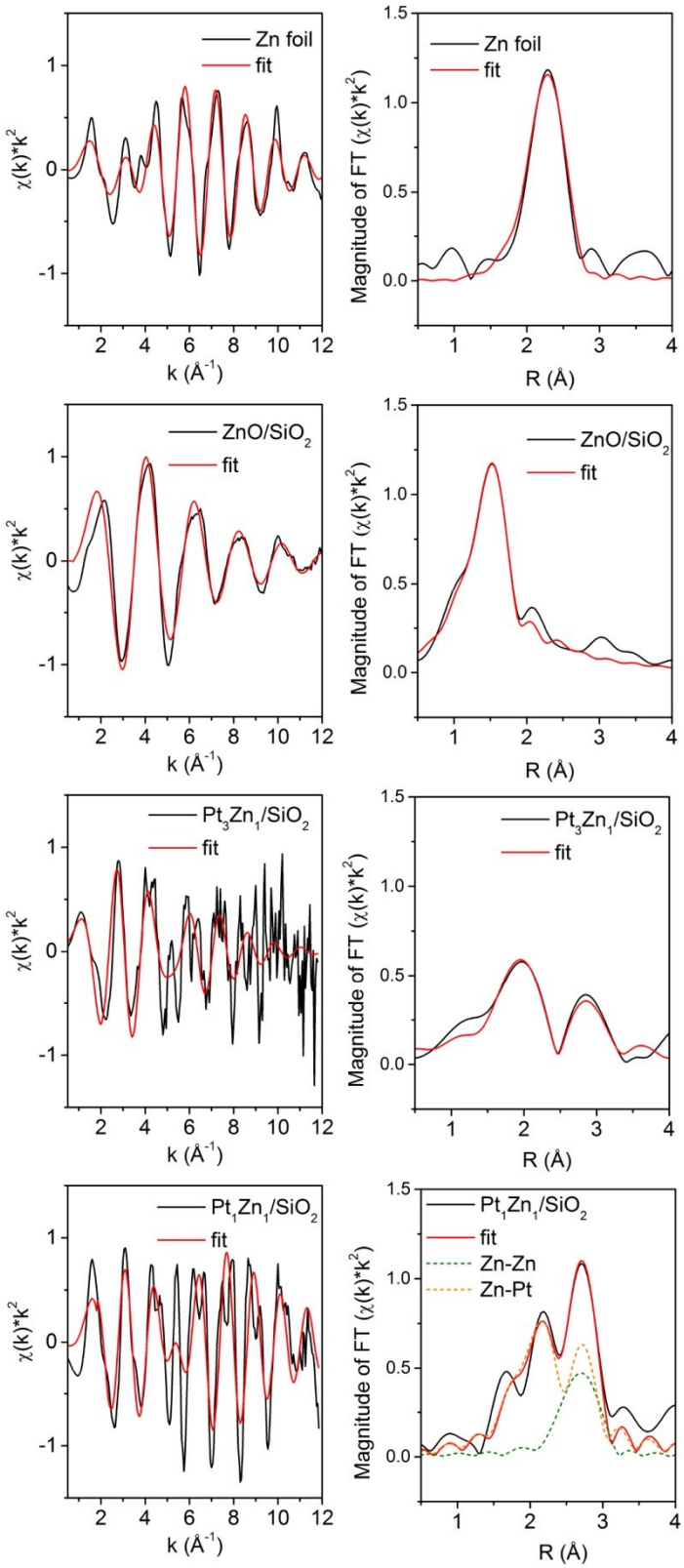

Figure S4. Zn K EXAFS fittings of Zn, ZnO/SiO_2, Pt_3Zn_1/SiO_2, and Pt_1Zn_1/SiO_2. $k = 3.0–12.0$ Å^{-1} and $r = 1.3–3$ Å.

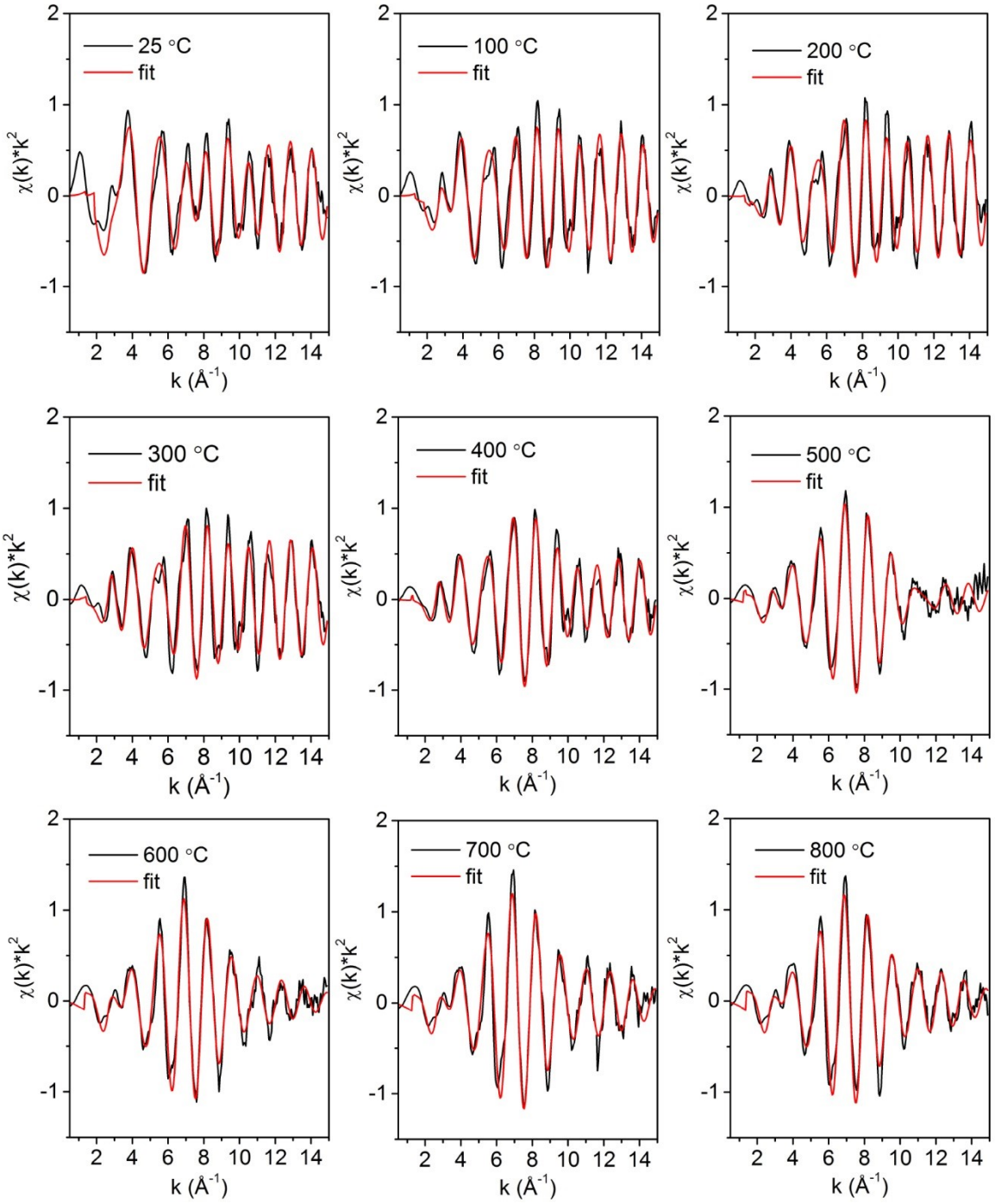

Figure S5. Pt L_3 edge EXAFS k-space fittings of $Pt/ZnO/SiO_2$ during hydrogen reduction. $k = 3.0–14.0$ Å^{-1} and $r = 1.3–3$ Å.

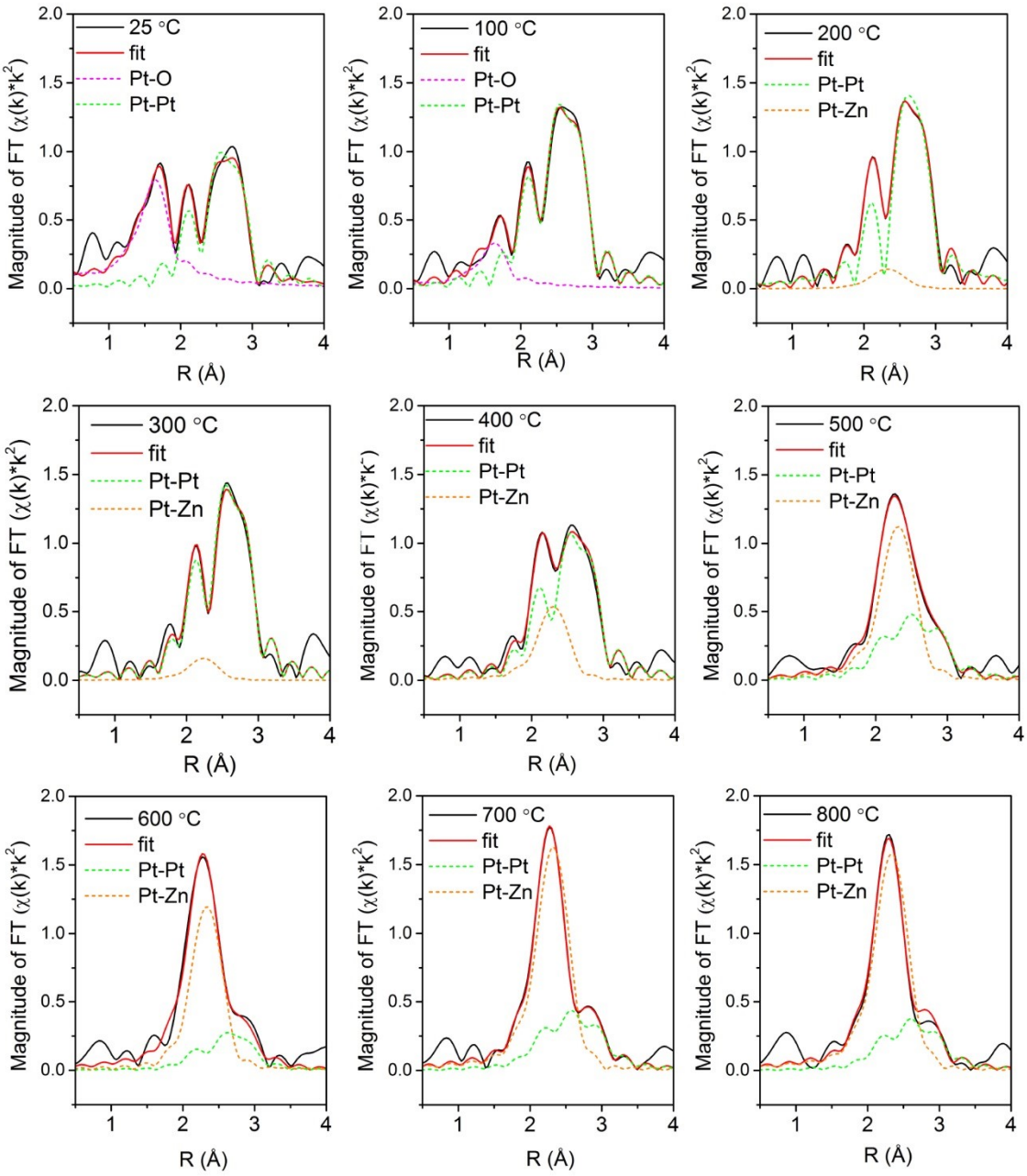

Figure S6. Pt L_3 edge EXAFS FT fittings of Pt/ZnO/SiO_2 during hydrogen reduction. k = 3.0–14.0 Å^{-1} and r = 1.3–3 Å.

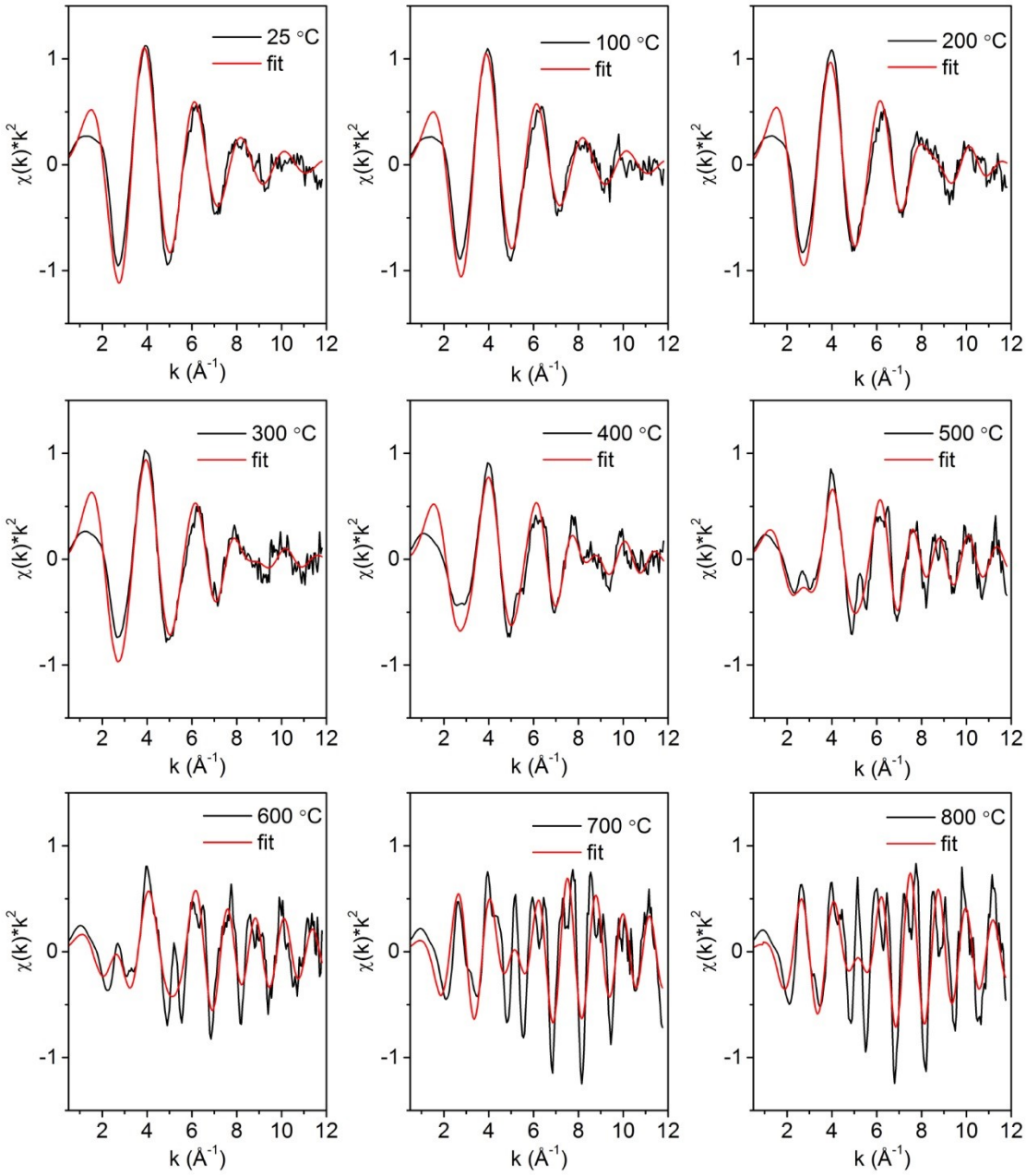

Figure S7. Zn K edge EXAFS k-space fittings of Pt/ZnO/SiO_2 during hydrogen reduction. k = 3.0–12.0 Å^{-1} and r = 1.3–3 Å.

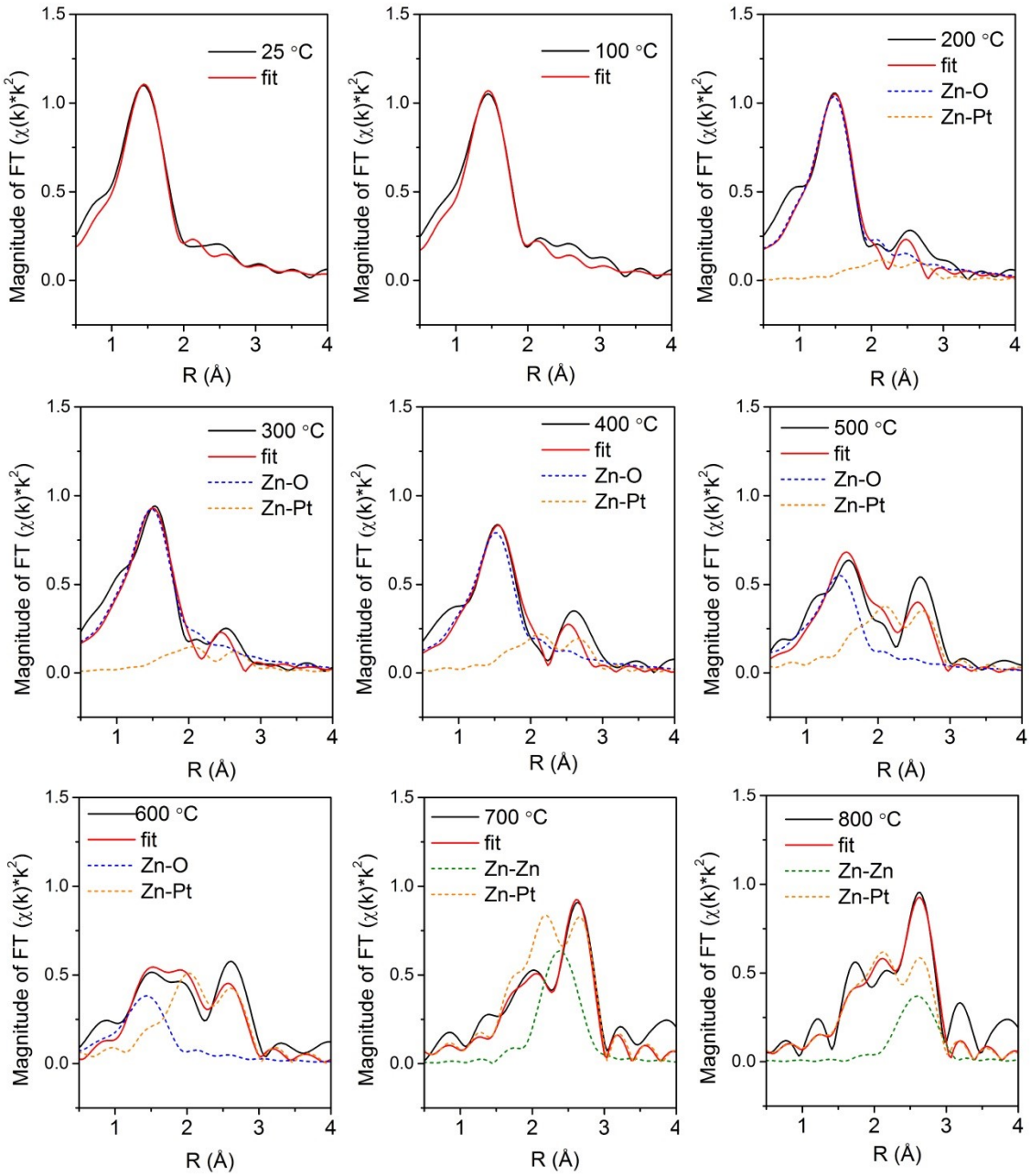

Figure S8. Zn K edge EXAFS FT fittings of Pt/ZnO/SiO_2 during hydrogen reduction. k = 3.0–12.0 Å^{-1} and r = 1.3–3 Å.

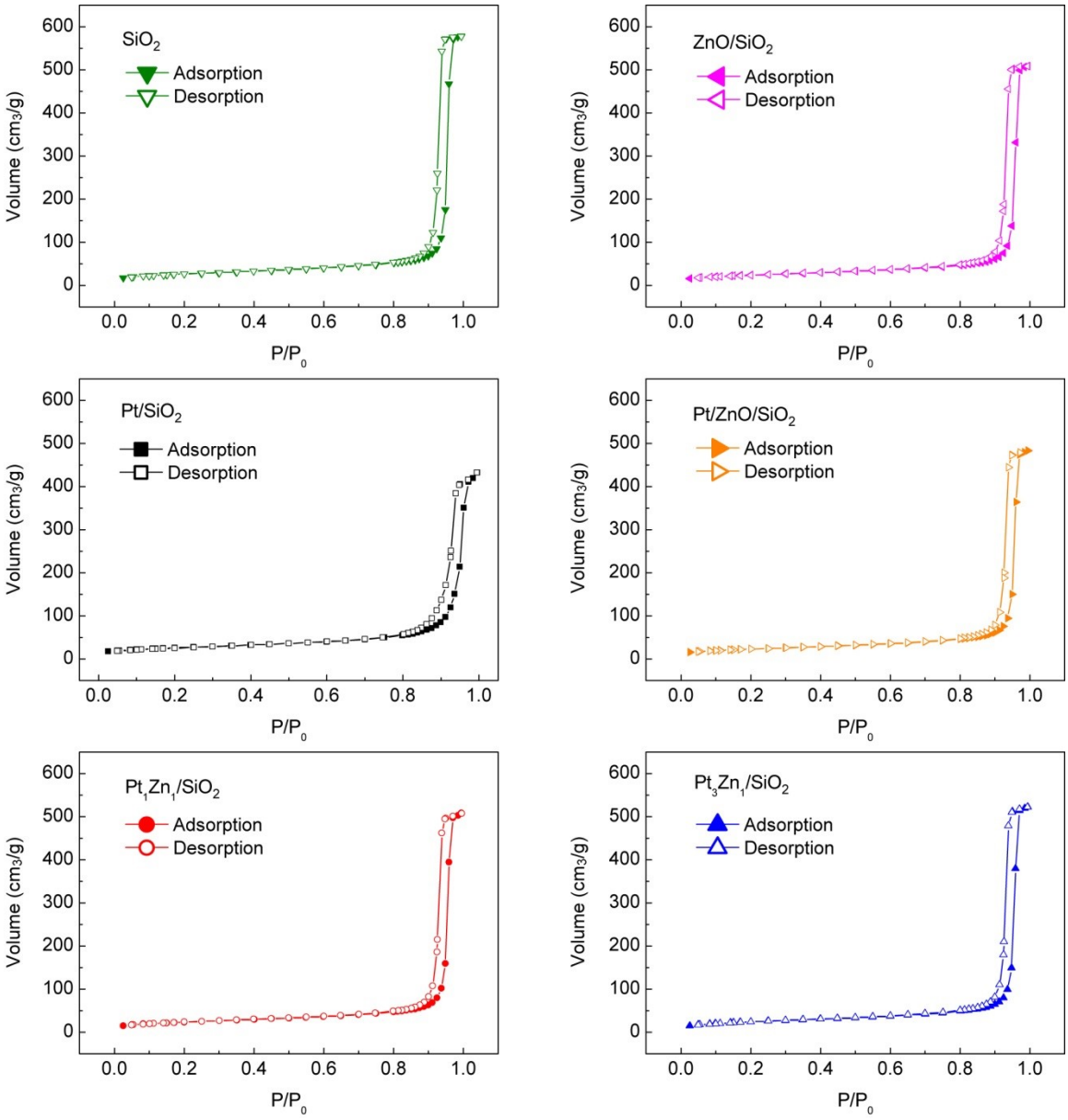

Figure S9. Nitrogen adsorption-desorption isotherms used to determine surface area, pore volume and pore diameter

Table S1. Unit cell parameters determined from XRD patterns

Sample	Space Group	*a*	*b*	*c*	α=β=γ /°	R_{Pt-Pt} /Å	R_{Pt-Zn} /Å
Pt/SiO_2	Fm3m	3.92	3.92	3.92	90	2.77	N.A.
Pt_3Zn_1/SiO_2	Pm-3m	3.89	3.89	3.90	90	2.75	2.75
Pt_1Zn_1/SiO_2	P4/mmm	4.03	4.03	3.49	90	2.84	2.66

Table S2. Pt L_3 edge EXAFS fittings for first scattering shell

Sample	Scatterer	CN[a]	R /Å	σ^2 /Å^2
Pt foil	Pt-Pt	*12*	2.77	0.005
Pt/SiO_2	Pt-Pt	10.5	2.76	0.006
Pt_3Zn_1/SiO_2	Pt-Pt	6.1	2.73	0.007
	Pt-Zn	3.0	2.73	0.007
Pt_1Zn_1/SiO_2	Pt-Pt	3.1	2.85	0.008
	Pt-Zn	6.8	2.65	0.008

[a]CN – coordination number

Table S3. Zn K edge EXAFS fittings for first scattering shell

Sample	Scatterer	CN[a]	R /Å	σ^2 /Å^2
ZnO/SiO_2	Zn-O	*4*	1.96	0.006
Zn foil	Zn-Zn	*6*	2.64	0.012
Pt_3Zn_1/SiO_2	Zn-Pt	9.6	2.73	0.021
Pt_1Zn_1/SiO_2	Zn-Pt	6.8	2.65	0.010
	Zn-Zn	3.4	2.92	0.010

[a]CN – coordination number

Table S4. Pt L_3 edge EXAFS fittings of $Pt/ZnO/SiO_2$ for the first scattering shell during reduction in hydrogen. *k*=3-14. *r*=1.3-3.

Reduction Temperature /°C	Scatterer	CN[a]	R /Å	σ^2 /Å^2	ΔE	Assigned Phases
25	Pt-O	2.3	2.01	0.005	13.5	PtO_2+Pt
	Pt-Pt	4.6	2.76	0.004	7.4	
100	Pt-O	0.8	2.01	0.003	12.5	PtO_2+Pt
	Pt-Pt	7.6	2.76	0.005	6.7	
200	Pt-Pt	7.8	2.76	0.005	7.8	Pt+Pt_1Zn_1
	Pt-Zn	0.1	2.60	0.011	12.5	
300	Pt-Pt	8.2	2.76	0.006	7.8	Pt+Pt_1Zn_1
	Pt-Zn	0.4	2.56	0.006	5.8	
400	Pt-Pt	6.8	2.76	0.006	7.5	Pt+Pt_1Zn_1
	Pt-Zn	1.5	2.62	0.006	6.5	
500	Pt-Pt	4.9	2.78	0.009	5.5	Pt+Pt_1Zn_1
	Pt-Zn	4.7	2.64	0.008	6.1	
600	Pt-Pt	4.4	2.83	0.009	7.1	Pt_1Zn_1
	Pt-Zn	5.7	2.64	0.008	6.8	
700	Pt-Pt	4.4	2.84	0.008	7.4	Pt_1Zn_1
	Pt-Zn	5.6	2.64	0.007	6.1	
800	Pt-Pt	3.6	2.85	0.008	8.3	Pt_1Zn_1
	Pt-Zn	6.2	2.65	0.008	7.2	

[a]CN – coordination number

Table S5. Zn K edge EXAFS fittings of $Pt/ZnO/SiO_2$ for the first scattering shell during reduction in hydrogen. *k*=3-12. *r*=1.3-3.

Reduction Temperature /°C	Scatterer	CN[a]	R /Å	σ^2 /Å^2	E	Assigned Phases
25	Zn-O	3.4	1.94	0.008	-3.3	ZnO
100	Zn-O	3.2	1.94	0.008	-3.1	ZnO
200	Zn-O	3.0	1.96	0.008	-2.3	ZnO_x
	Zn-Pt	0.7	2.60	0.008	-3.6	Pt_1Zn_1
300	Zn-O	3.5	1.97	0.012	-1.4	ZnO_x
	Zn-Pt	1.2	2.57	0.012	-4.5	Pt_1Zn_1
400	Zn-O	2.5	1.99	0.009	0.2	ZnO_x+Pt_1Zn_1
	Zn-Pt	1.5	2.61	0.009	-3.9	
500	Zn-O	1.8	1.96	0.009	-3.9	ZnO_x+Pt_1Zn_1
	Zn-Pt	2.8	2.60	0.009	-7.9	
600	Zn-O	1.2	1.95	0.008	-4.8	ZnO_x+Pt_1Zn_1
	Zn-Pt	3.3	2.59	0.008	-9.6	
700	Zn-Zn	1.9	2.79	0.007	-11.8	Pt_1Zn_1
	Zn-Pt	5.1	2.65	0.007	-7.3	
800	Zn-Zn	1.6	2.94	0.009	3.4	Pt_1Zn_1
	Zn-Pt	4.9	2.63	0.009	-9.2	

[a]CN – coordination number

Table S6. BET surface area, average pore size and pore volume of different samples.

Sample	S_{BET} (m^2/g)	D[a] (Å)	Pore volume (cm^3/g)	dispersion	monolayer uptake (μmol H_2/g_{cat})
SiO_2	96.1	276	0.95	-	
ZnO/SiO_2	85.4	308	0.83	-	
Pt/SiO_2	93.0	277.2	0.69	17.8%	18.2
$Pt/ZnO/SiO_2$	82.8	277	0.79	-	
Pt_1Zn_1/SiO_2	85.3	276	0.83	9.9%	10.9
P_3tZn_1/SiO_2	87.6	276.8	0.85	2.7%	3.2

[a]average pore diameter

Table.S7 Comparison of DHE performance over Pt-based catalysts

catalyst	T (°C)	WHSV (h^{-1})[a]	Feed (%)	Conv (%)	Sel (%)	C_2H_4 TOF (s^{-1})	ref
Pt_1Zn_1/SiO_2	550	7.2	C_2H_6/He= 18/72	24.5	100	0.56	This work
Pt_1Zn_1/SiO_2 [b]	600	N/A	$C_2H_6/H_2/He/N_2$= 2.5/1/46.7/49.8	~9	100	0.4	[1]
Pt_3Sn/Mg(Al)O	600	257	C_2H_6/H_2/He= 20/25/55	6	93	6	[2]
ALD-Pt/γ-Al_2O_3	600	N/A	C_2H_6/He= 1.6/98.4	50	N/A	0.1	[3]

[a]weight hourly space velocity of ethane

[b]The Pt_1Zn_1/SiO_2 was prepared by sequential IWI of ZnO and IWI of Pt on SiO_2

Table.S8 Comparison of ODHE performance over Pt-based catalysts

catalyst	T (°C)	WHSV (h^{-1})[a]	Feed (%)	Conv (%)	Sel (%)	C_2H_4 TOF (s^{-1})	ref
Pt_1Zn_1/SiO_2	550	90	$C_2H_6/O_2/He$= 22.3/2.7/76	13	90	2.79	This work
ALD/Pt/Al_2O_3	600	1.5	$C_2H_6/O_2/He/N_2$= 9/4.3/62.5/6.7	41.8	64.9	0.3	4
PtSn/Al_2O_3	700	5.3	$C_2H_6/O_2/H_2$= 57.1/28.6/14.3	11	90	1.5	5

[a]weight hourly space velocity of ethane

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