Supporting information

Particle size effect of SiO_2-supported ZnO catalysts in propane dehydrogenation

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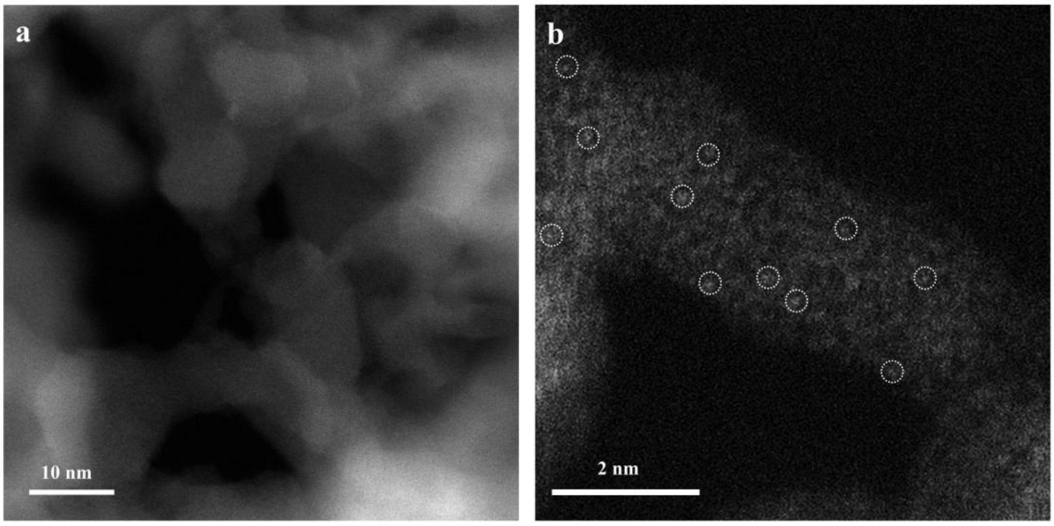

Figure S1. Representative HAADF-STEM images of $1ZnO/SiO_2$ at low and high magnifications.

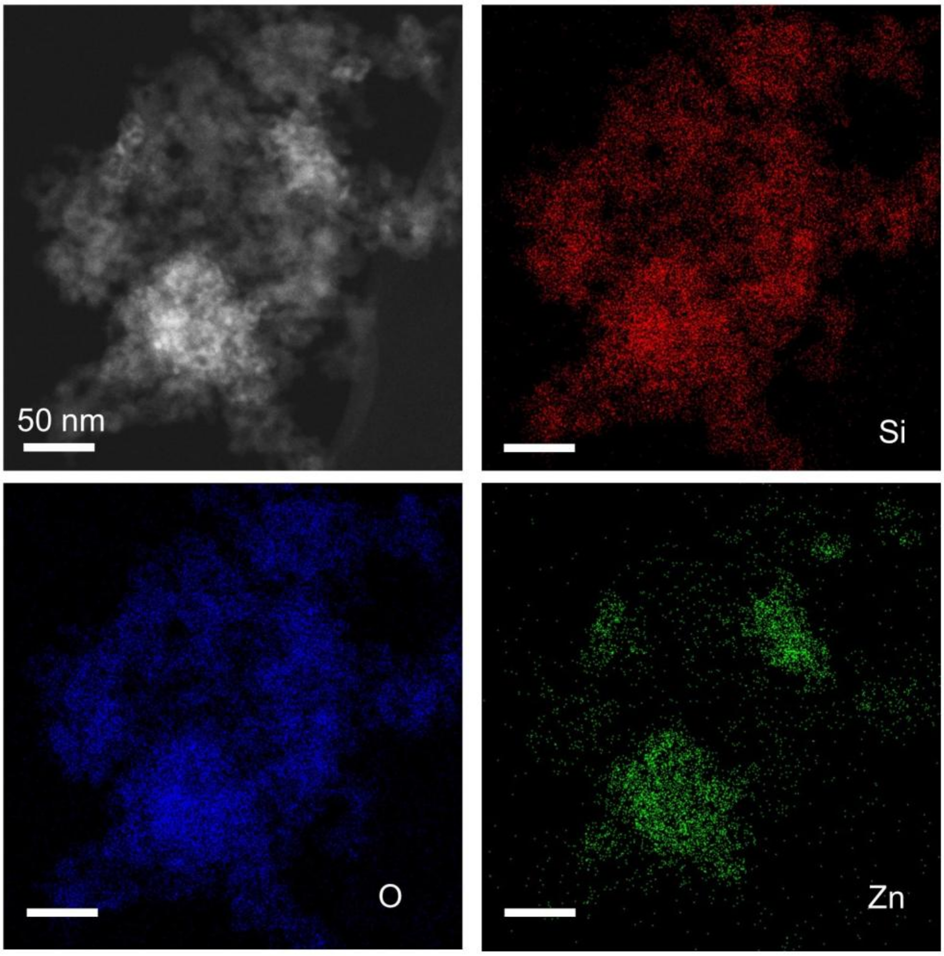

Figure S2. (**a**) A representative HAADF-STEM image of $7ZnO/SiO_2$ and the corresponding EDS mapping of (**b**) Si $K\alpha_1$, (**c**) O $K\alpha_1$, and (**d**) Zn $K\alpha_1$.

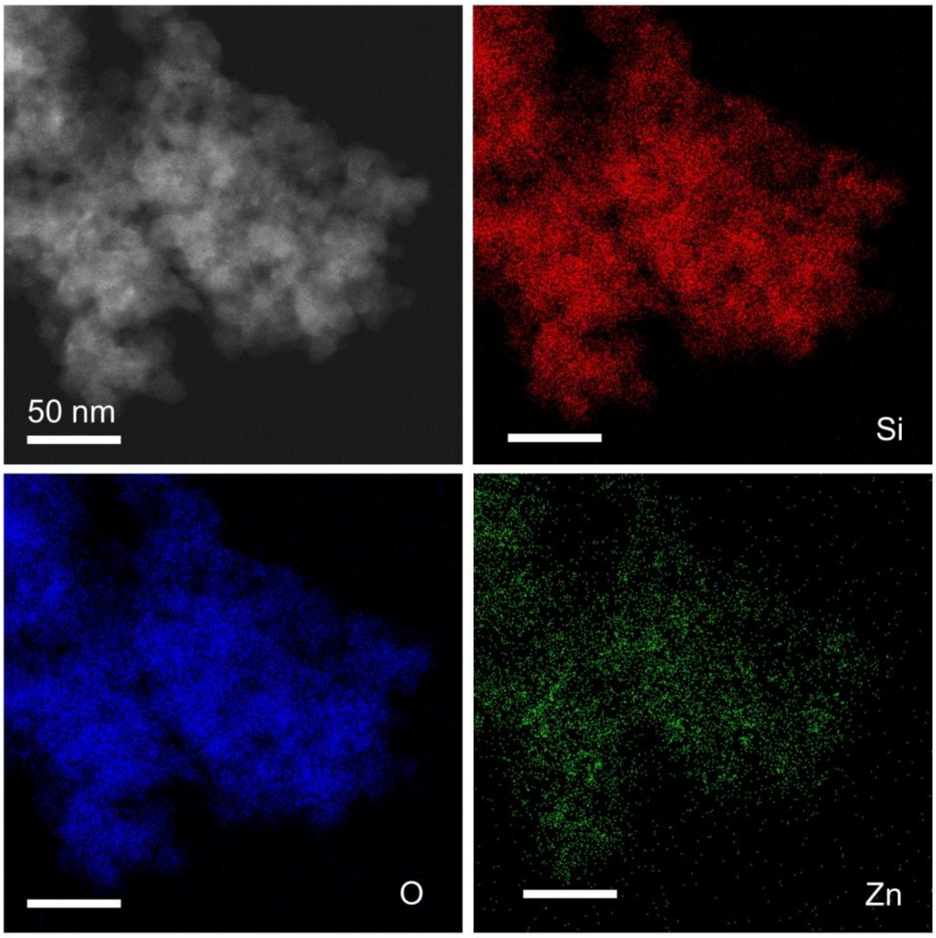

Figure S3. (**a**) A representative HAADF-STEM image of 10ZnO/SiO_2 and the corresponding EDS mapping of (**b**) Si Kα_1, (**c**) O Kα_1, and (**d**) Zn Kα_1.

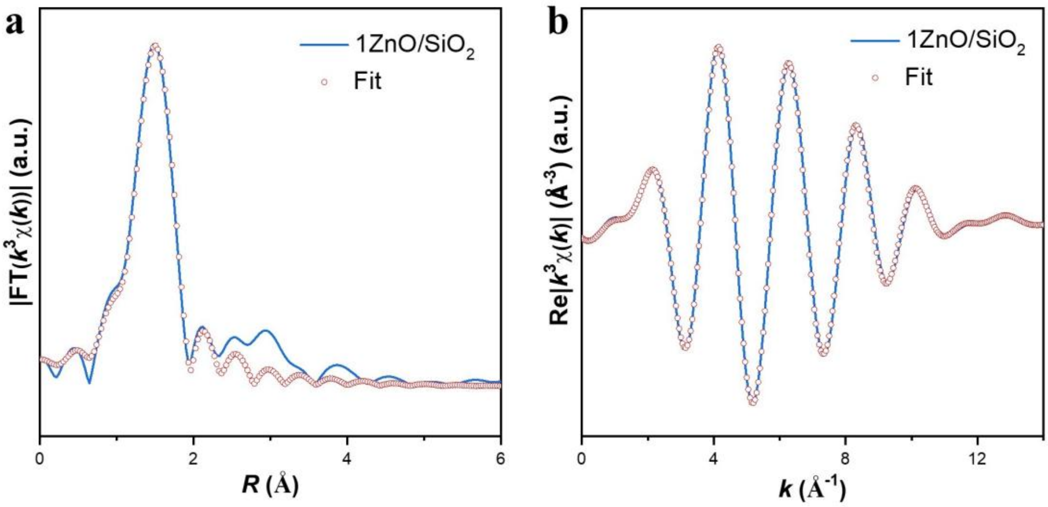

Figure S4. (**a**) The k^3–weighted Fourier transform spectrum and (**b**) the inversely Fourier transforms (FT) *K*-space EXAFS spectrum of the 1ZnO/SiO_2 sample after *ex situ* H_2 reduction at 600 ℃. Least-squares EXAFS fittings in (**a**) and (**b**) are also shown in red dot lines.

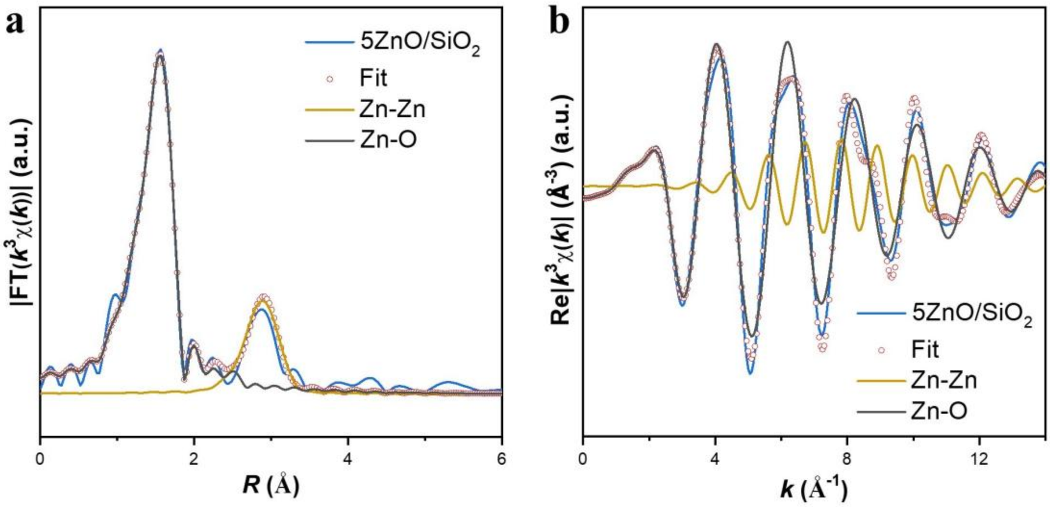

Figure S5. (**a**) The k^3–weighted Fourier transform spectrum and (**b**) the inversely FT *K*-space EXAFS spectrum of the $5ZnO/SiO_2$ sample after *ex situ* H_2 reduction at 600 ℃. Least-squares EXAFS fittings in (**a**) and (**b**) are also shown in red dot lines.

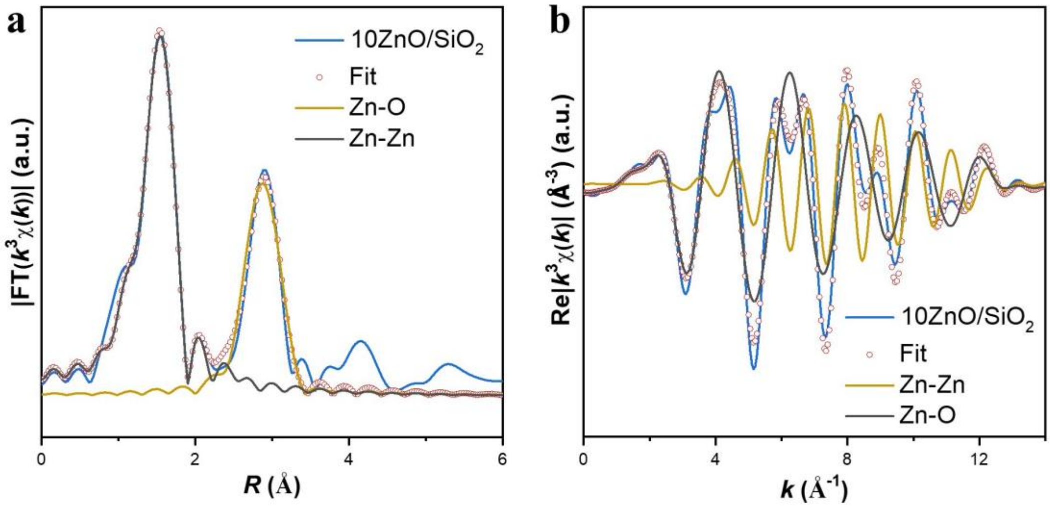

Figure S6. (**a**) The k^3–weighted Fourier transform spectrum and (**b**) the inversely FT *K*-space EXAFS spectrum of the 10ZnO/SiO_2 sample after *ex situ* H_2 reduction at 600 ℃. Least-squares EXAFS fittings in (**a**) and (**b**) are also shown in red dot lines.

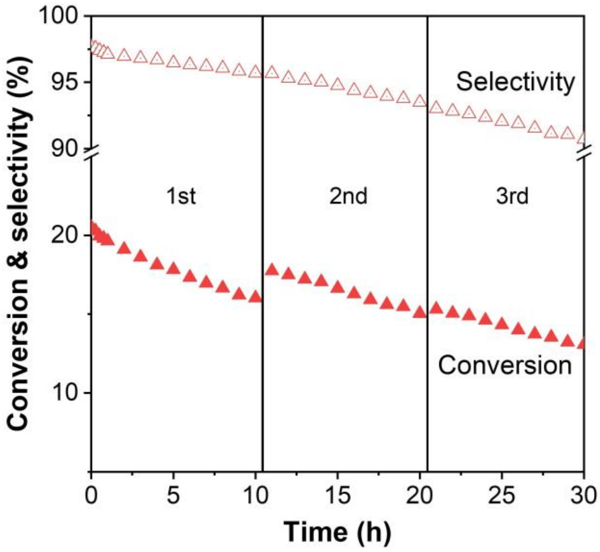

Figure S7. Stability test of the $5ZnO/SiO_2$ catalyst in PDH at 550 ℃ for three successive dehydrogenation cycles with catalyst regeneration in between. Catalyst regeneration was performed by a treatment 10% O_2 in Ar for 0.5 h and a reduction 10% H_2 in Ar for 0.5 h at 550 ℃. Reaction condition: 10% propane, 10% H_2 balanced in Ar; flow rate = 20 mL min^{-1}; pressure = 0.1 MPa.

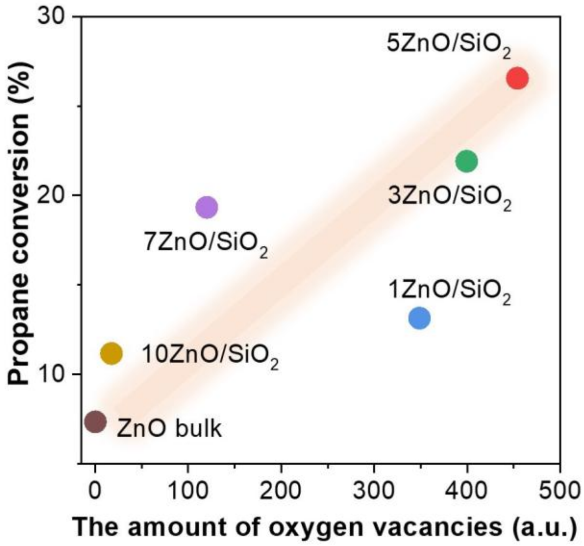

Figure S8. The correlation between the conversion of propane at 600 ℃ and the amount of oxygen vacancies determined by normalized PL spectra based on the Zn content.

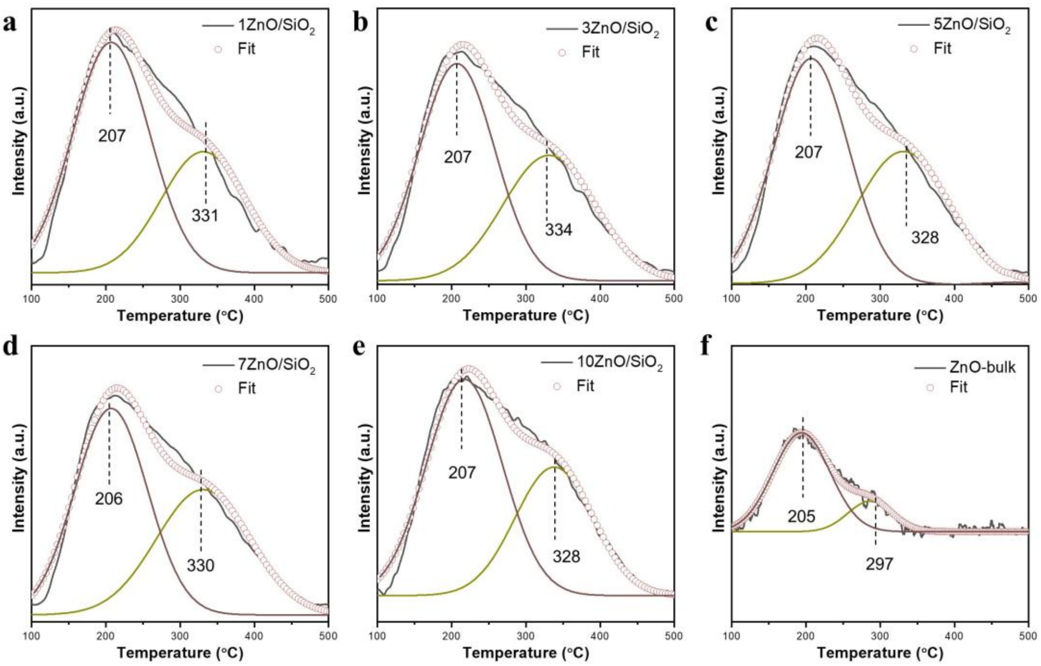

Figure S9. The NH_3-TPD spectra and fittings profiles of ZnO catalysts with different ZnO sizes. (**a**) 1ZnO/SiO_2, (**b**) 3ZnO/SiO_2, (**c**) 5ZnO/SiO_2, (**d**) 7ZnO/SiO_2, (**e**) 10ZnO/SiO_2, and (**f**) ZnO-bulk.

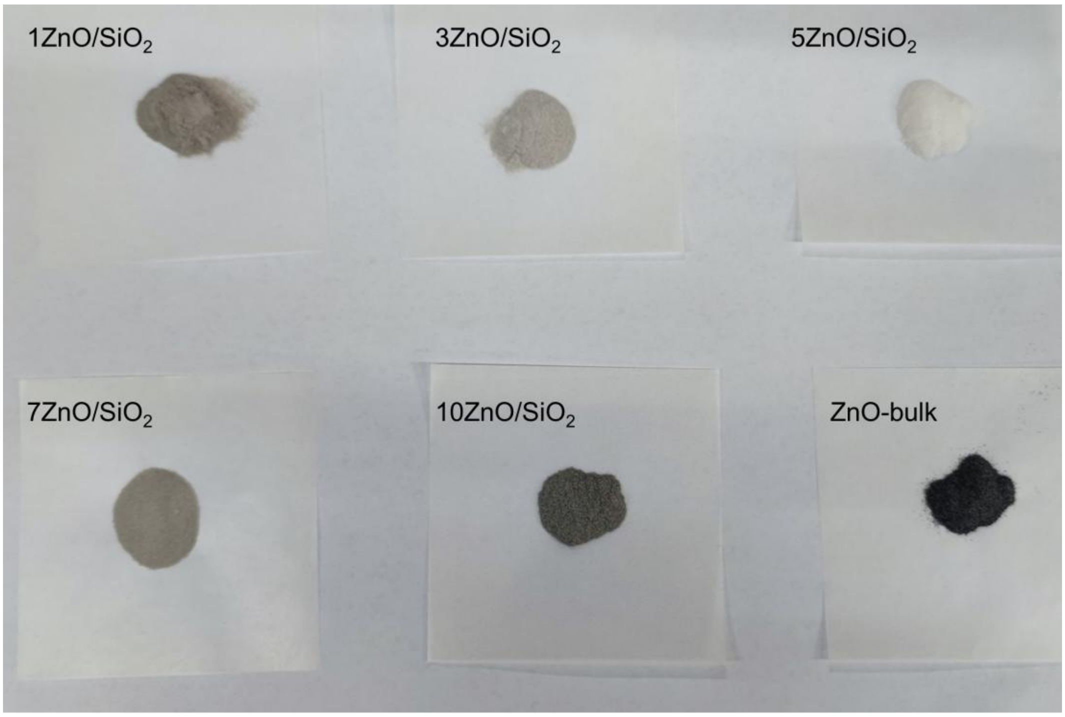

Figure S10. Pictures of used catalysts after 10 h stability test. The different colors indicated the different extent of coke accumulations after the stability test.

Table S1. The EXAFS fitting results of xZnO/SiO_2 catalysts.

Sample	**Path**	**CNs**[a]	**R(Å)**[b]	**σ^2(10^{-3}Å^2)**[c]	**ΔE_0(eV)**[d]
Zn foil	Zn-Zn	6	2.65		
ZnO	Zn-O	4	1.97		
	Zn-Zn	12	3.21		
1ZnO/SiO_2	Zn-O	3.6 ±0.3	1.95 ±0.01	5.9 ±1.4	3.3 ±0.9
5ZnO/SiO_2	Zn-O	3.7 ±0.2	1.96 ±0.01	6.0 ±1.0	1.9 ±0.7
	Zn-Zn	2.1 ±0.5	3.23 ±0.03	9.9 ±0.8	4.4 ±2.1
10ZnO/SiO_2	Zn-O	3.8 ±0.6	1.96 ±0.01	5.5 ±1.7	3.8 ±1.7
	Zn-Zn	5.3 ±0.8	3.22 ±0.02	11.3 ±1.5	6.7 ±2.1

[a]CN is the coordination number for the absorber–backscatterer pair; [b]R is the average absorber−backscatterer distance; [c]σ^2 is the Debye−Waller factor; ΔE_0 is the inner potential correction.

Table S1. Comparison of representative catalysts for catalyzing propane to propylene.

Sample	Temp. (℃)	Components (vol. %)	WHSV (h^{-1})	STY (C_3H_6) g(C_3H_6) h^{-1} g^{-1}	k_d (h^{-1})	Ref.
$5ZnO/SiO_2$	600	$C_3H_8/H_2/Ar$ = 1 : 1 : 8	2.4	**0.58**		This work
	550			**0.41**	0.030	
Zn/Al_2O_3	600	$C_3H_8/H_2/N_2$ =28 : 28 : 44	3.0	0.80	0.178	1
$4Zn/TiZrO_x$	550	$C_3H_8/H_2/N_2$ = 40 : 5 : 55	4.7	1.28	0.539	2
Znβ-10	600	C_3H_8 /N_2 = 5 : 95	0.4	0.18	0.088	3
$50Zn/Al_2O_3$	600	C_3H_8 /N_2 = 1 : 9	2.5	0.38	0.408	4
10%Zn/250HZSM-5	600	C_3H_8 /N_2 = 5 : 95	0.6	0.36	0.055	5
ZnO and ZnO-S-1_3	550	$C_3H_8/H_2/N_2$ = 4 : 2 : 4	3.1	1.11	0.026	6
$Zn_{1.5}Ti_1Al_2$	500	C_3H_8 /N_2 = 5 : 95	2.9	0.73	0.184	7
Cr/Al_2O_3-700	580	C_3H_8/N2 = 1 : 19	0.5	0.09	0.063	8
$7.5Cr/Al_2O_3$	600	C_3H_8/N_2 = 1 : 4	2.2	1.14	0.078	9
10Cr/MCM-41	630	C_3H_8/N_2 = 14 : 86	1.1	0.53	0.100	10
2.5Cr–Ni/Al	550	C_3H_8/ Ar = 1 : 9	1.1	0.42	0.110	11
Pt/Sn-ZSM-5	600	C_3H_8/N_2 = 1.5 : 5	1.8	1.19	0.044	12
K-PtSn@MFI	600	C_3H_8/N_2 = 24 : 76	29.5	0.001	0.013	13
Pt–Sn/SiO_2-1073 K H_2	500	C_3H_8/N_2 = 20 : 80	47.3	12.12	0.013	14
0.3Pt–0.5Zn@S-1	550	C_3H_8/Ar = 19 : 11	6.5	2.76	0.006	15
Pt/ND@G	600	C_3H_8/Ar = 5 : 95	1.6	0.22	0.020	16
$Pt^0Zn^{\delta+}/SiO_2$	550	C_3H_8/Ar = 20 : 80	32	10.52	0.014	17
0.04Pt–0.36Zn–DeBEA	550	C_3H_8/He = 10 : 30	59.1	19.54	0.004	18
15Zn0.1Pt	600	$C_3H_8/H_2/N_2$ = 1 : 1 : 8	3.0	0.94	0.200	1

Here the space time yield of propylene formation [STY(C_3H_6)] was calculated using the following equation:

$$\mathrm{STY}(C_3H_6) = \frac{[C_3H_6] \times M_{C_3H_6}}{m_{cat} \times V_m}$$

Therein, [C_3H_6] is the flow rate of propylene at the outlet of reactor (mL h^{-1}), $M_{C_3H_6}$ is the molar weight of propylene (42 g mol^{-1}). V_m is molar volume (22400 mL mol^{-1}), m_{cat} is catalyst amount (g).

Table S3. Qualitative data of NH_3-TPD measurements of *x*ZnO/SiO_2 with different ZnO size.

Sample	Weak LAS area (a.u.)	Medium LAS area (a.u.)	Total area (a.u.)	Ratio of weak LASs (%)	Ratio of Medium LASs (%)
1ZnO/SiO_2	130	75	205	63.4	36.6
3ZnO/SiO_2	191	134	325	58.8	41.2
5ZnO/SiO_2	216	157	373	57.9	42.1
7ZnO/SiO_2	147	115	262	56.1	43.9
10ZnO/SiO_2	83	75	158	52.5	47.5
ZnO-bulk	5.6	0.6	6.2	90.3	9.7

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