Electronic Supplementary Material

Zinc modification of Ni-Ti as efficient $Ni_xZn_yTi_1$ catalysts with both geometric and electronic improvements for hydrogenation of nitroaromatics

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Figure S1-S6, Table S1-S2

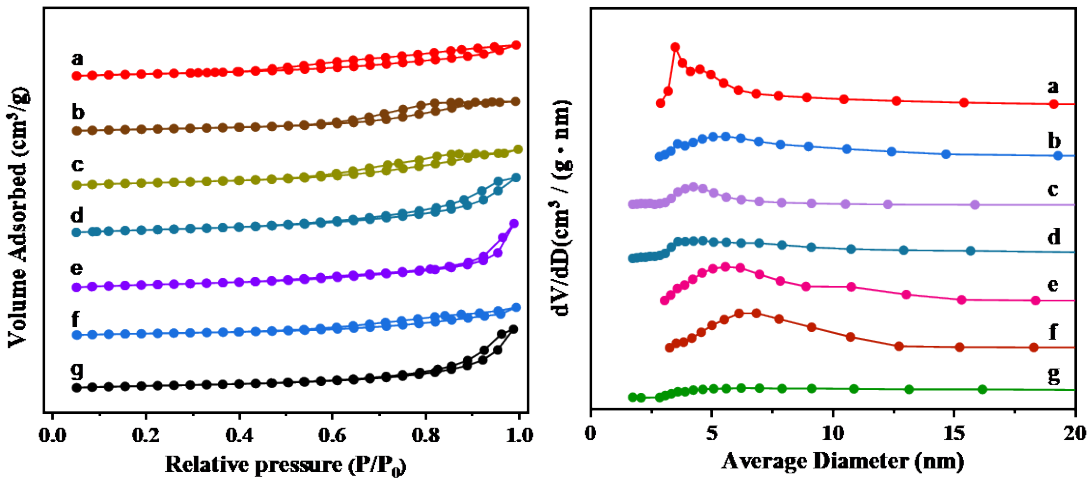

Figure S1 N_2 adsorption-desorption isotherms and pore size distributions of the reduced samples: (a) Ni_1Ti_1, (b) $Ni_{0.8}Zn_{0.2}Ti_1$, (c) $Ni_{0.67}Zn_{0.33}Ti_1$, (d) $Ni_{0.5}Zn_{0.5}Ti_1$, (e) $Ni_{0.33}Zn_{0.67}Ti_1$, (f) $Ni_{0.2}Zn_{0.8}Ti_1$, (g) Zn_1Ti_1

The nitrogen adsorption-desorption isotherms and pore size distribution of the reduced $Ni_xZn_yTi_1$ samples are shown in **Figure S1**. Most of the samples exhibit a mixed isotherm of type II (the latter half rises sharply without plateau) and type IV (the adsorption value is lower when the P/P_0 is low), which indicates that all the prepared $Ni_xZn_yTi_1$ catalysts have typical mesoporous structure. Among them, **Figure S1c** and **d** show obvious steps at high P/P_0, which accords with the type IV isotherm. Moreover, the position and slope of the hysteresis loop of the samples are different, indicating that the pore structure of the catalysts alters with the change of Zn content. This is mainly due to the texture properties improvement of the catalysts because of the interaction between Ni, Zn and TiO_x species during the reduction process.

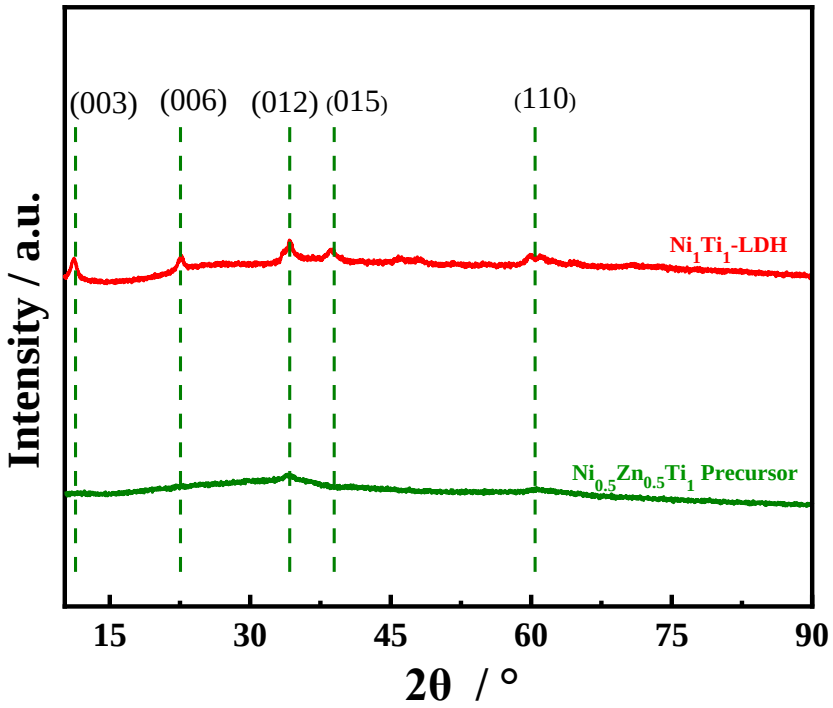

Figure S2 XRD patterns of Ni_1Ti_1 and $Ni_{0.5}Zn_{0.5}Ti_1$ precursors.

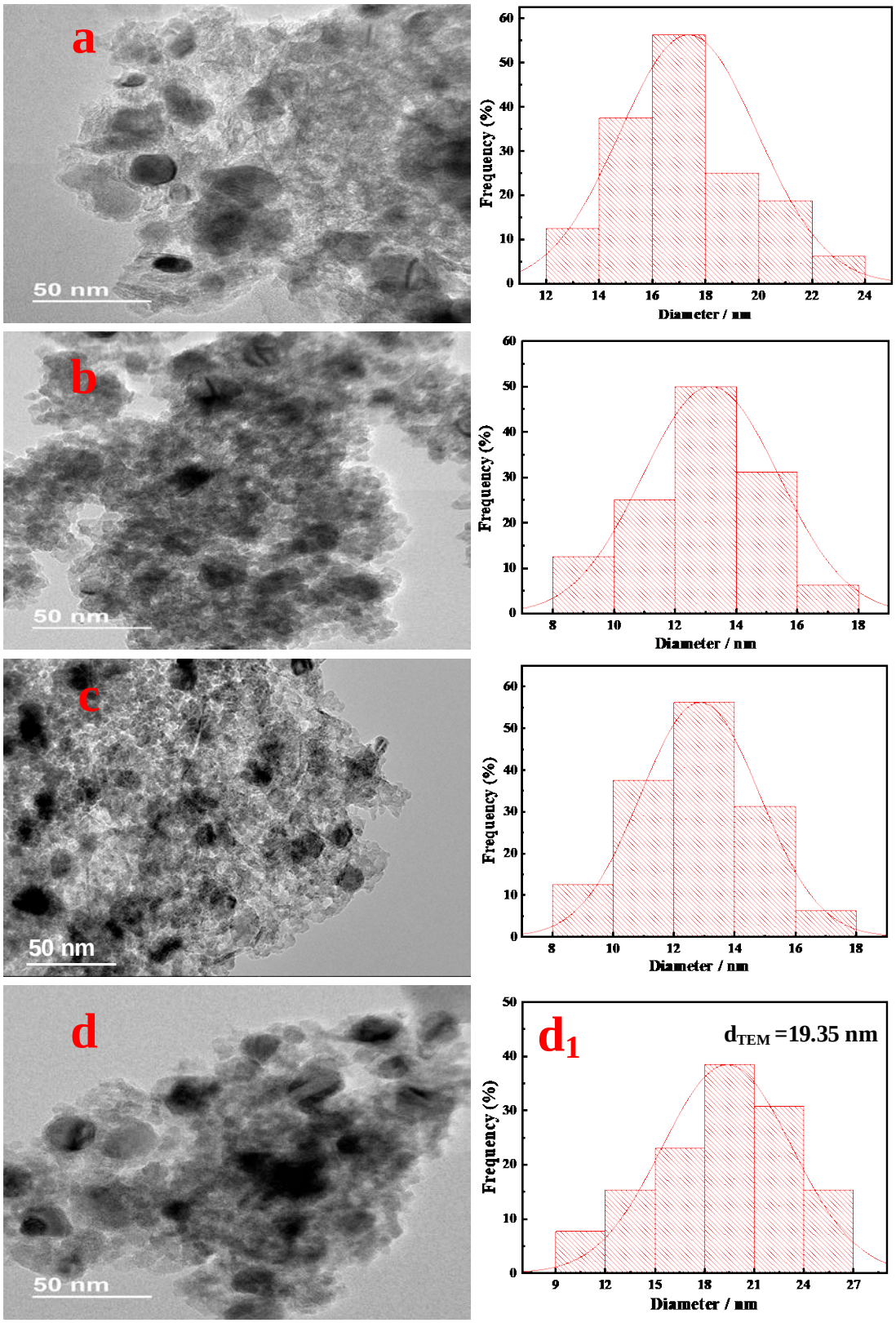

Figure S3 TEM images of (a) Ni_1Ti_1, (b) $Ni_{0.33}Zn_{0.67}Ti_1$, (c) $Ni_{0.5}Zn_{0.5}Ti_1$, and (d) $Ni_{0.67}Zn_{0.33}Ti_1$.

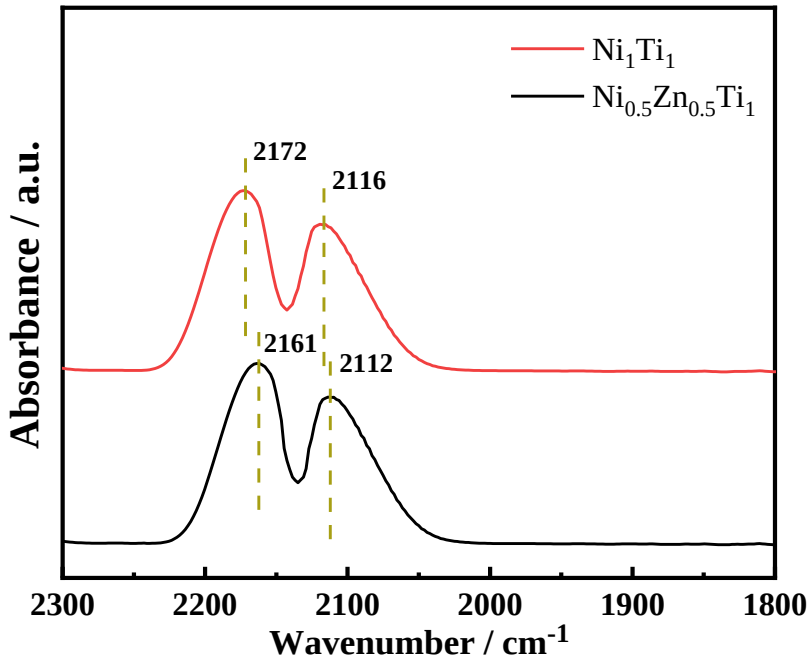

Figure S4 *In situ* Fourier-transformed infrared spectra of CO adsorption over Ni_1Ti_1 and $Ni_{0.5}Zn_{0.5}Ti_1$.

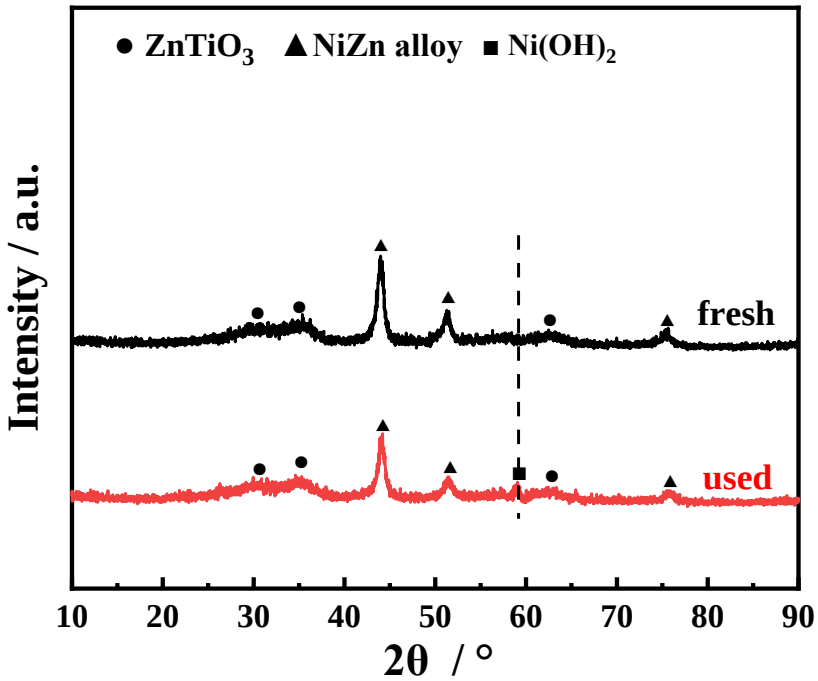

Figure S5 XRD patterns of fresh $Ni_{0.5}Zn_{0.5}Ti_1$ and the fourth run of $Ni_{0.5}Zn_{0.5}Ti_1$.

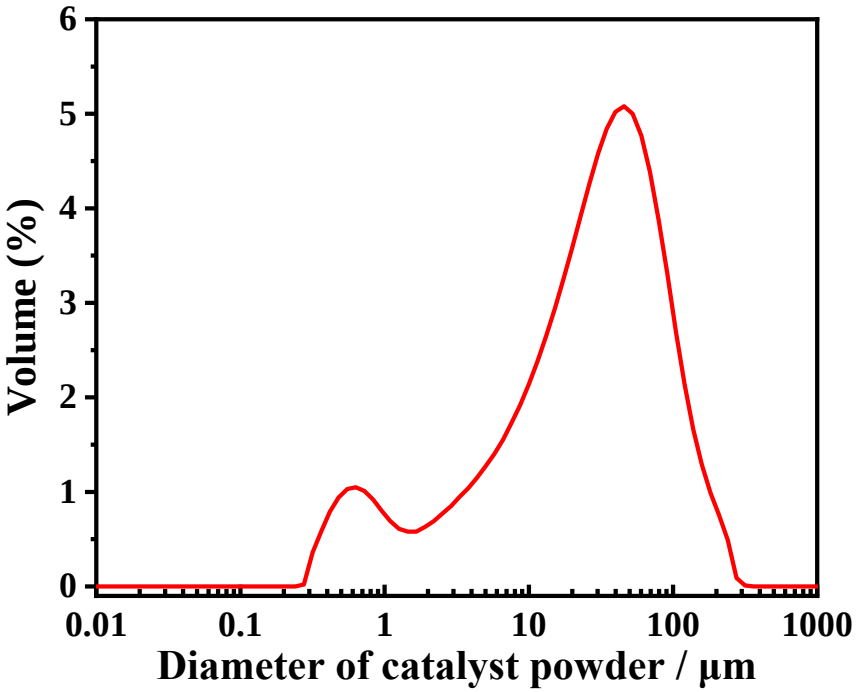

Figure S6 Particle size distribution of $Ni_{0.5}Zn_{0.5}Ti_1$ powder.

Table S1 Apparent reaction rate constant *k* for 1-nitronaphthalene hydrogenation over Ni_1Ti_1 and $Ni_{0.5}Zn_{0.5}Ti_1$ at different temperatures.

T / °C	*k* / mol·L^{-1}·h^{-1}		Correlation coefficient (R^2)	
	Ni_1Ti_1	$Ni_{0.5}Zn_{0.5}Ti_1$	Ni_1Ti_1	$Ni_{0.5}Zn_{0.5}Ti_1$
40	--	0.0145	--	0.997
50	0.0059	0.0233	0.999	0.999
60	0.0126	0.0385	0.999	0.999
70	0.0231	0.0595	0.999	0.998
80	0.0383	--	0.999	--

Table S2 The comparison of the catalytic performance of the present work and the literatures

Samples	Reaction conditions	Substrate	Con./Sel.	Ref.
CoO_x@NC-800	H_2O,110 °C, 300 min 5 MPa	nitrobenzene	100/>99	[1]
CoO_x@NCNTs	EtOH,110 °C, 150 min 3 MPa	nitrobenzene	>99/98	[2]
10Ni-Zn/AC-350	DMF, 90 °C, 300 min 0.6 MPa	1-nitronaphthalene	100/96.82	[3]
20Ni/N-AC-900	DMF, 100 °C, 300 min 0.6 MPa	1,5-dinitronaphthalene	100/18.59	[4]
$Ni_{0.5}Zn_{0.5}Ti_1$	DMF, 80 °C, 300 min 0.6 MPa	1-nitronaphthalene	100/>99.9	This work

References

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