Supplementary Material

Promoting effect of Zn in high-loaded Ni-SiO_2 catalysts for selective hydrogen evolution from methylcyclohexane

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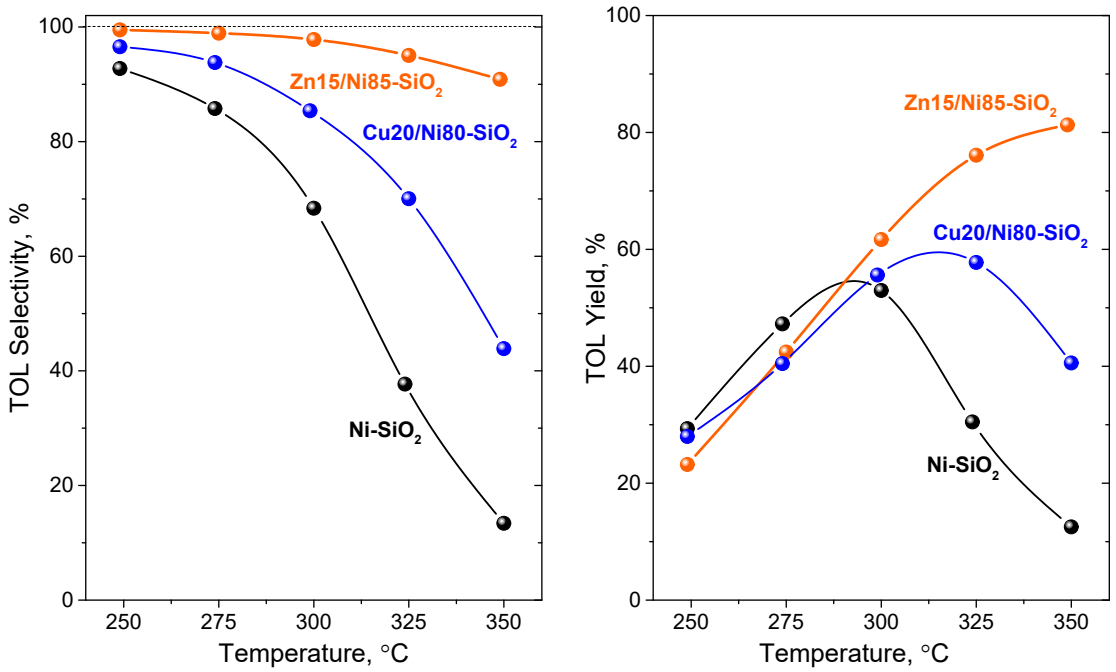

Fig. S1 Comparative catalytic performance of Zn15/Ni85-SiO_2 catalyst, Cu20/Ni80-SiO_2 catalyst (pCu_Ni80Cu20-SiO_2 in ref. [Y.K. Gulyaeva et al. *Catalysts* 10 (2020) 1198]), and Ni-SiO_2 catalyst in methylcyclohexane (MCH) dehydrogenation into toluene (TOL). Reaction conditions: T = 250-350 °C, P = 0.1 MPa, m_{cat} = 0.50 g, equimolar ratio H_2/Ar, gas feed rate of 24 nL h^{-1}, MCH feed rate of 12 mL h^{-1}, WHSV = 18.5 h^{-1}.

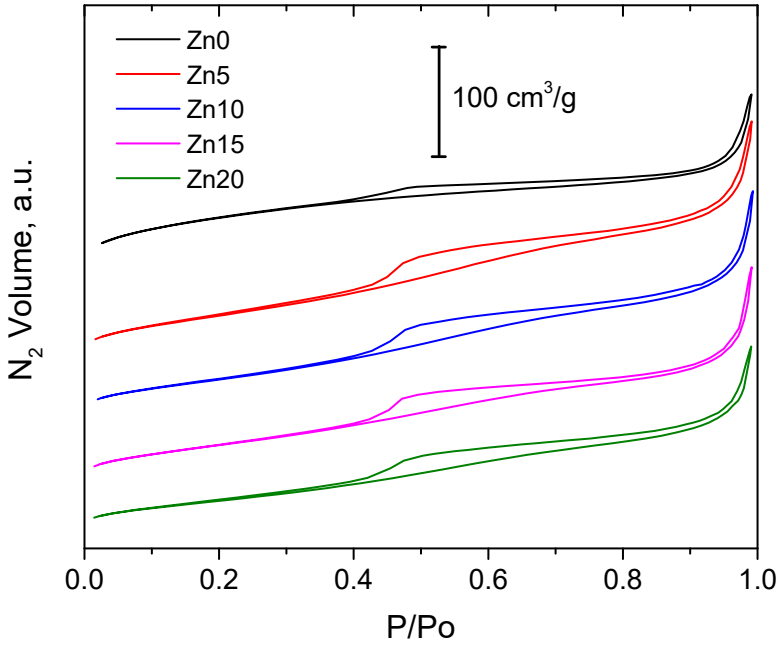

Fig. S2 Physisorption isotherms of N_2 at 77 K for ZnX/Ni(100-X)-SiO_2 catalysts (X = 0, 5, 10, 15, 20 wt%).

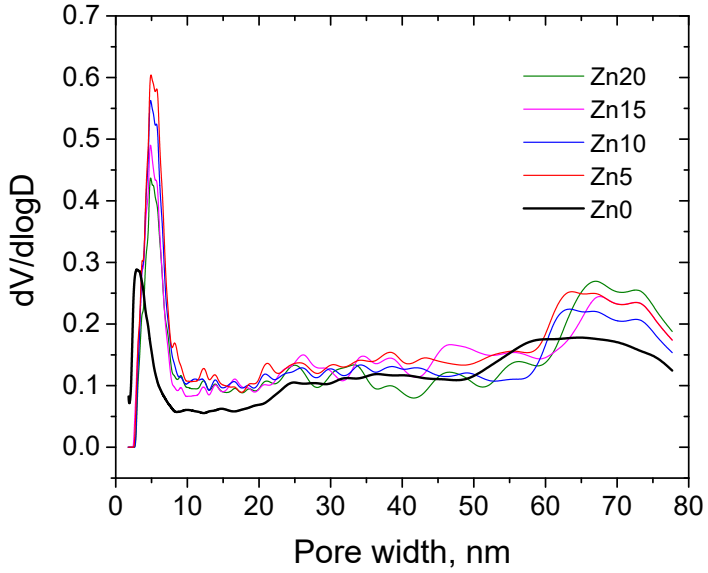

Fig. S3 Pore size distributions of ZnX/Ni(100-X)-SiO_2 catalysts (X = 0, 5, 10, 15, 20 wt%).

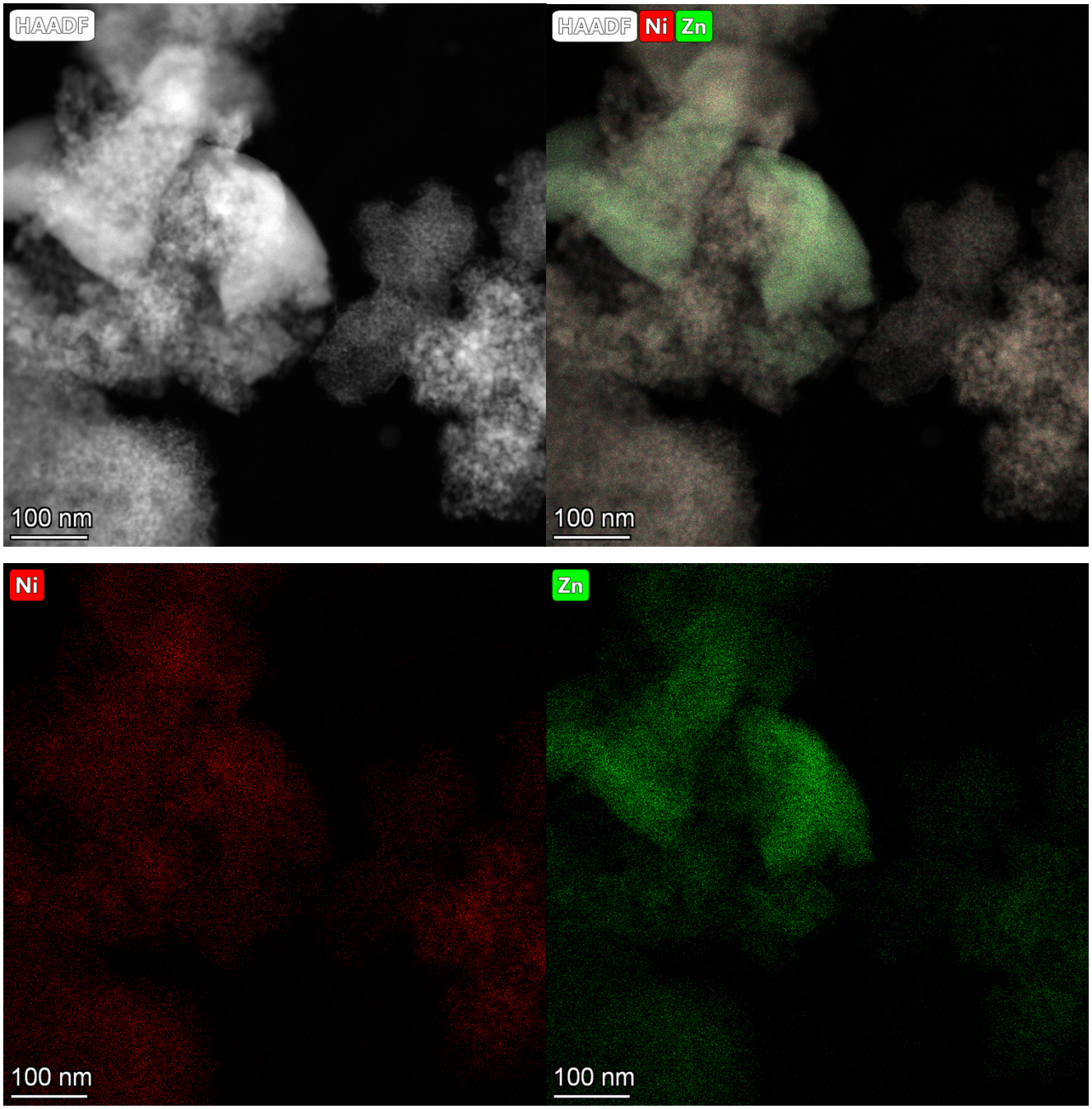

Fig. S4 HRTEM images and EDX mapping (in HAADF STEM mode) of the passivated Zn15/Ni85-SiO_2 catalyst.

Table S1 Liquid phase composition (based on GC analysis) after MCH dehydrogenation over Zn/Ni-SiO_2 catalysts

Chromatographic area, %				
Reaction temperature, °C	**MCH**	**Benzene**	**Toluene**	**Others***
Ni-SiO_2				
250	68.79	0.93	29.51	0.77
275	46.00	4.47	48.39	1.14
300	24.73	15.91	58.11	1.25
325	23.40	33.45	41.96	1.19
350	15.92	52.76	30.11	1.21
Zn5/Ni95-SiO_2				
250	74.28	0.33	25.22	0.17
275	52.27	1.85	45.60	0.28
300	32.34	6.21	60.74	0.71
325	18.64	15.92	64.48	0.96
350	11.77	30.76	56.23	1.24
Zn10/Ni90-SiO_2				
250	76.65	-	23.30	0.05
275	55.19	0.53	44.21	0.07
300	35.37	1.66	62.49	0.48
325	19.45	4.55	75.46	0.54
350	10.02	10.42	78.66	0.90
Zn15/Ni85-SiO_2				
250	76.71	0.07	23.20	0.02
275	57.16	0.33	42.47	0.04
300	37.04	1.07	61.83	0.06
325	20.08	2.89	76.64	0.39
350	10.70	6.10	82.52	0.68
Zn20/Ni80-SiO_2				
250	87.86	-	12.14	-
275	72.24	-	27.76	-
300	53.14	-	46.60	0.26
325	36.54	-	62.74	0.72
350	22.69	-	75.63	1.68

* o-/m-/p-xylenes, 3-methylcyclohexene (based on GC-MS: Agilent 7000B, column ZB-WAX, 30 m × 0.25 mm × 0.25 µm, oven program 50 °C for 3 min then 10 °C/min to 260 °C, electronic ionization energy of 70 eV, the scanning range (m/z) from 40 to 500).

Table S2 Hydrogen evolution rates for MCH dehydrogenation over Zn/Ni-SiO_2 catalysts (T = 250-350 °C, P = 0.1 MPa, m_{cat} = 0.50 g, equimolar ratio H_2/Ar, gas feed rate of 24 nL h^{-1}, MCH feed rate of 12 mL h^{-1}, WHSV = 18.5 h^{-1})

Reaction temperature, °C	**H_2 evolution rate, mmol g_{Ni}^{-1} min^{-1}**	**H_2 evolution rate, mmol g_{cat}^{-1} min^{-1}**
Ni-SiO_2		
250	3.63	2.26
275	4.06	2.53
300	-5.04[a]	-3.14[a]
325	-34.21[a]	-21.31[a]
350	-122.5[a]	-76.32[a]
Zn5/Ni95-SiO_2		
250	3.62	2.17
275	6.37	3.81
300	6.56	3.93
325	1.91	1.14
350	-10.13[a]	-6.07[a]
Zn10/Ni90-SiO_2		
250	3.70	2.12
275	7.15	4.10
300	10.07	5.78
325	11.66	6.69
350	10.85	6.23
Zn15/Ni85-SiO_2		
250	**3.97**	**2.18**
275	**7.27**	**3.98**
300	**10.55**	**5.78**
325	**12.92**	**7.08**
350	**13.42**	**7.36**
Zn20/Ni80-SiO_2		
250	2.11	1.10
275	4.89	2.55
300	8.20	4.27
325	10.85	5.65
350	12.62	6.57

[a] negative hydrogen evolution rates are associated with the partial consumption of H_2 initially supplied to the system.

Table S3 Textural properties of catalysts (after reduction at 400 °C) based on N_2 adsorption-desorption (77 K)

Catalyst coding	SSA (m^2 g^{-1})	V_{Σ} (ml g^{-1})	$V_{\mu pore}$ (ml g^{-1})	$V_{meso-macro}$ (ml g^{-1})	<d> (nm)
Ni-SiO_2	304	0.306	0.041	0.265	4.0
Zn5/Ni95-SiO_2	232	0.376	0.024	0.352	6.5
Zn10/Ni90-SiO_2	201	0.354	0.020	0.334	7.1
Zn15/Ni85-SiO_2	199	0.339	0.020	0.319	6.8
Zn20/Ni80-SiO_2	159	0.288	0.015	0.273	7.2

Table S4 Phase composition and CSD sizes of different phases in Ni-Zn catalysts reduced in situ in the diffractometer chamber

Temperature (°C)	Phase composition	CSD size (nm)
Zn5/Ni95-SiO_2		
30	NiO	2.6
300	NiO	2.7
400	NiO ***Ni***	2.3 *4.2*
450	***Ni*** NiO (trace)	*4.0* nd
500	***Ni***	*4.7*
Zn10/Ni90-SiO_2		
30	NiO	3.3
300	NiO	3.4
400	NiO ***Ni***	2.6 *4.6*
450	***Ni***	*4.6*
Zn15/Ni85-SiO_2		
30	NiO ZnO	3.5 nd
300	NiO ZnO	3.6 nd
400	NiO ***Ni*** ZnO	2.2 *4.7* nd
450	***Ni*** NiO (trace) ZnO	*4.7* nd nd
500	***Ni*** ZnO	*5.3* nd
Zn20/Ni80-SiO_2		
30	NiO (bimodal) ZnO	28.0 / 4.5 nd
300	NiO ZnO	22.0 /4.5 nd
400	NiO ***Ni*** ZnO	5.8 *5.3* nd
450	NiO ***Ni*** ZnO	7.1 *5.6* nd
500	***Ni*** ZnO	*6.6* nd