Supplementary Information

Pt-Ni single atom alloy: Maximized synergistic effect for NO reduction with CO

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Supplementary Figures and Tables

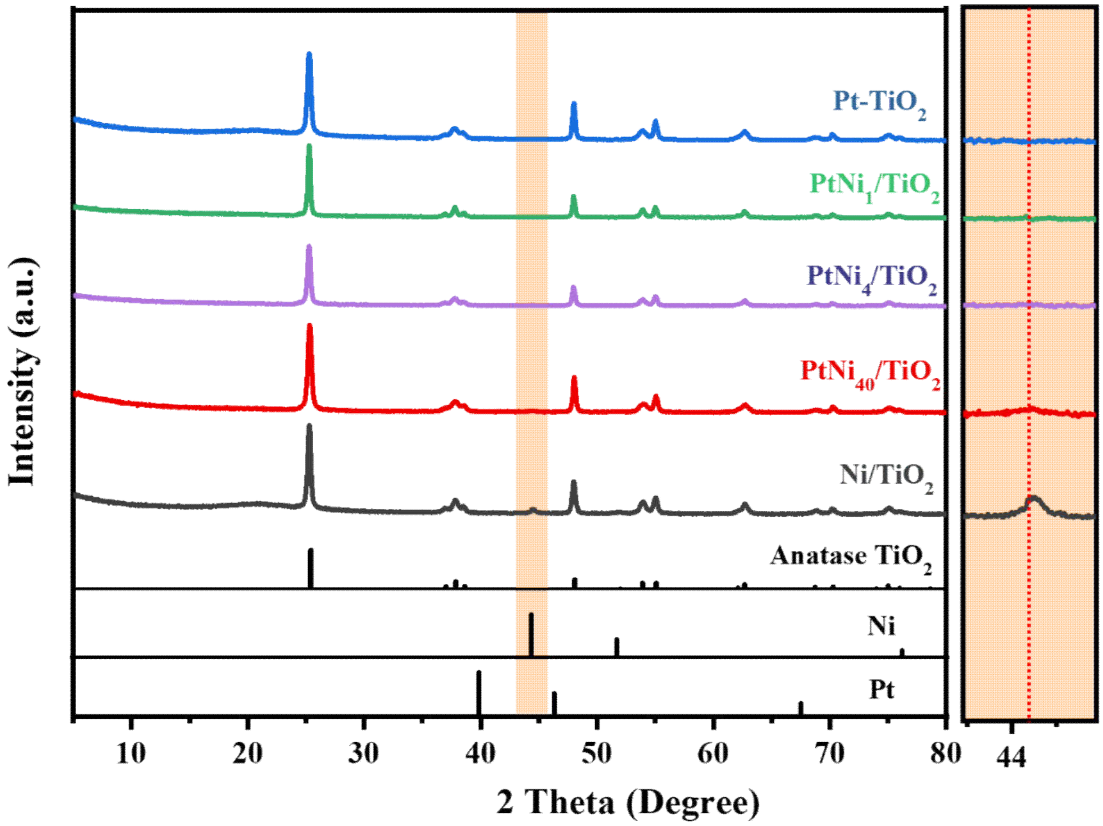

Figure S1. XRD patterns of $PtNi_x/TiO_2$ catalysts with various Pt/Ni ratios.

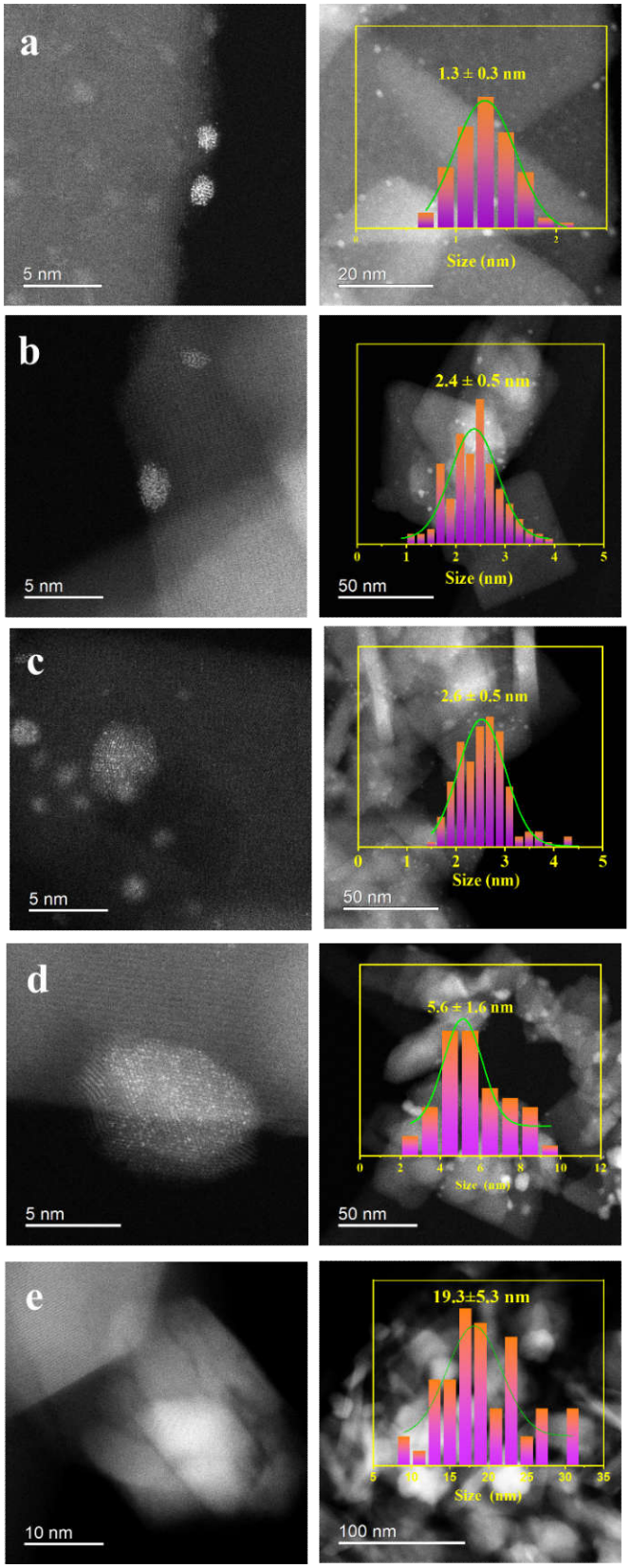

Figure S2. Aberration-corrected HAADF-STEM images taken from different areas and particle size distributions of the (a) Pt/TiO_2, (b) $PtNi_1/TiO_2$, (c) $PtNi_4/TiO_2$, (d) $PtNi_{40}/TiO_2$ and (e) Ni/TiO_2, respectively.

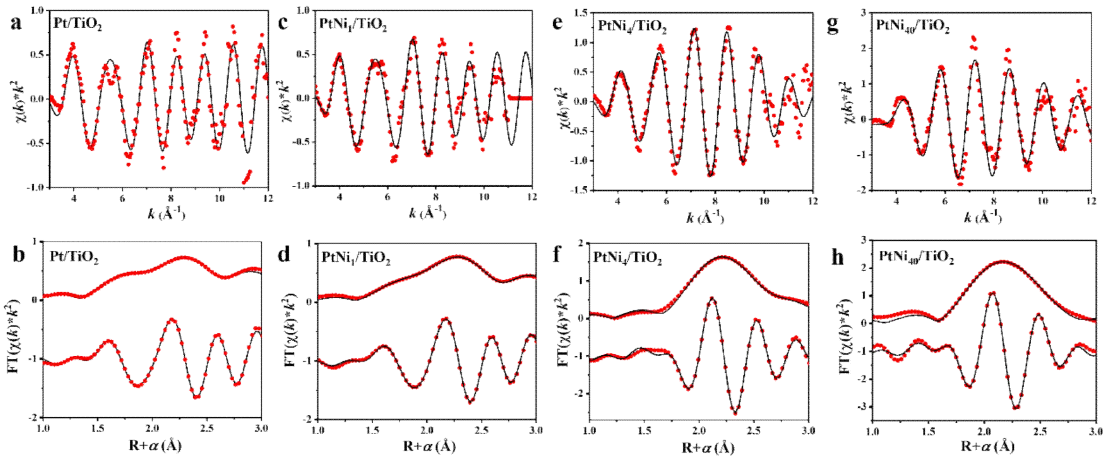

Figure S3. Pt L_3-edge EXAFS (points) and the curvefit (line) for Pt/TiO_2 (a,b), $PtNi_1/TiO_2$ (c, d), $PtNi_4/TiO_2$ (e, f) , $PtNi_{40}/TiO_2$ (g, h) shown in k^3 weighted k-space and R-space (FT magnitude and imaginary component) respectively.

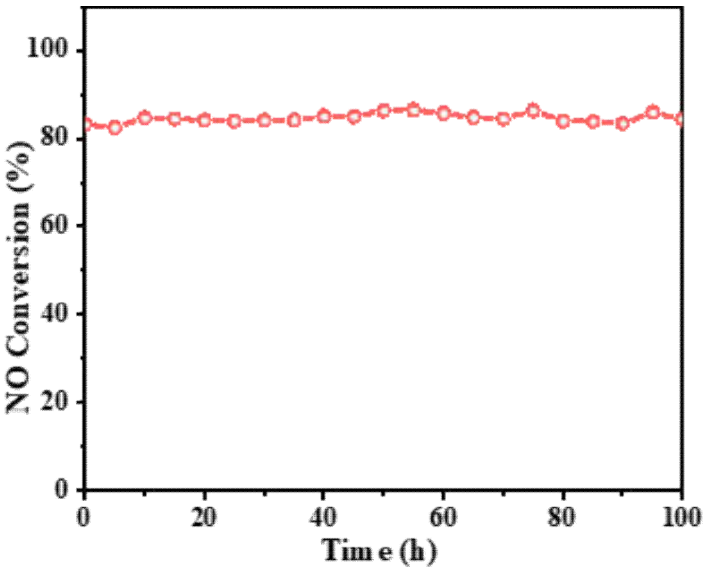

Figure S4. Stability test of $PtNi_{40}/TiO_2$ SAA catalyst at 250 °C. Reaction conditions: 30mg catalyst, 0.2% CO, 0.2% NO, He balance; total flow rate: 33.3mL/min.

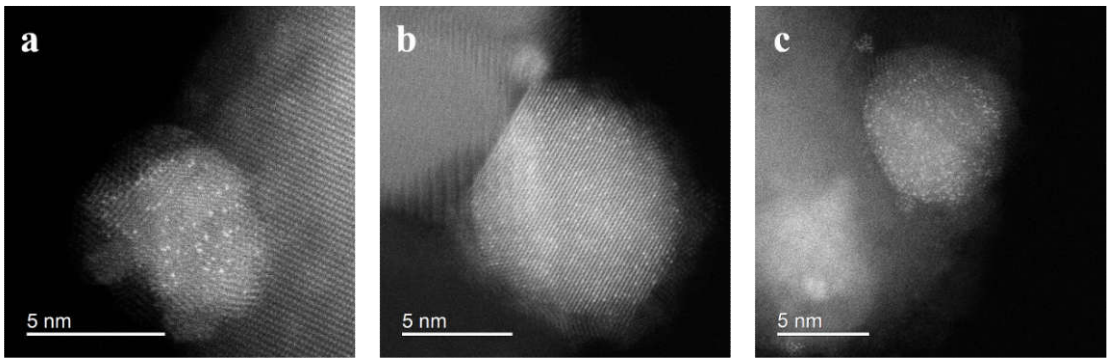

Figure S5. Aberration-corrected HAADF-STEM images of $PtNi_{40}/TiO_2$ SAA catalyst after 100-h reaction.

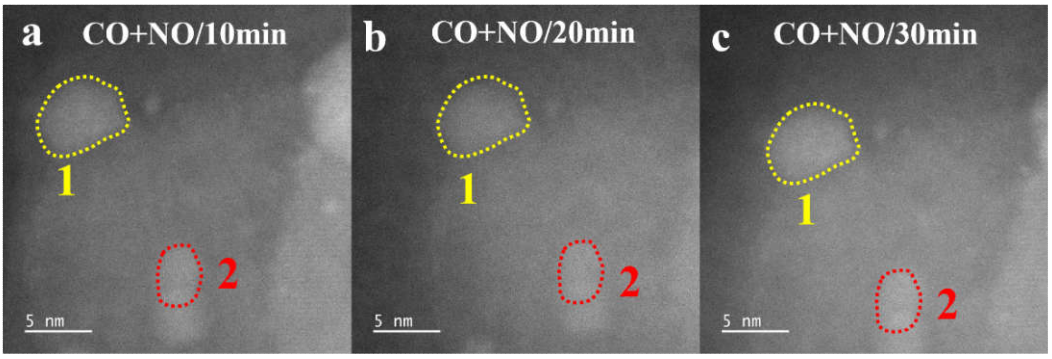

Figure S6. *in situ* observation of $PtNi_{40}/TiO_2$ by ETEM in 2 mbar CO + NO (molar ratio 1:1) atmosphere at 400 °C.

After exposure to 2 mbar atmosphere of CO and NO (1:1 molar ratio) at 400 °C for 30 min, both particles 1 and 2 (circled in yellow and red, respectively) maintained their original morphology without observable reconstruction or shape change. This demonstrates the high structural stability of the $PtNi_{40}/TiO_2$ catalyst under reaction conditions.

Table S1. The physico-chemical properties of different catalysts

Samples	Metal loading[a] (wt%)		BET surface area (m^2/g)	$Pt^{4+} \rightarrow Pt^0$		$Ni^{2+} \rightarrow Ni^0$	
	Pt	Ni		Reduction temperature (°C)[b]	H_2 consumption (μmol/g)	Reduction temperature (°C)[b]	H_2 consumption (μmol/g)
Pt/TiO_2	0.48	-	50.0	59	252	-	-
$PtNi_1/TiO_2$	0.50	0.16	48.6	100	206	319	33
$PtNi_4/TiO_2$	0.51	0.58	46.0	114	230	323	139
$PtNi_{40}/TiO_2$	0.49	6.0	45.7	94	200	348	677
Ni/TiO_2	-	6.0	42.8	-	-	410	1273
TiO_2	-	-	50.9	-	-	-	-

[a]: Determined by ICP-OES

[b]: Determined by H_2-TPR

Table S2. The best-fitted results of the EXAFS data at the Pt L_3-edge of different samples [a].

Samples	Path	R(Å)	CN[a]	ΔE_0 (eV)	σ^2 (Å^2)	R factor (%)
Pt foil[b]	Pt - Pt	2.76+/-0.00	12	7.7+/-0.5	0.004+/-0.000	0.2
Pt/TiO_2	Pt - Cl	2.26+/-0.01	0.8+/-0.1	6.8+/-1.0	0.004+/-0.001	0.3
	Pt - Pt	2.74+/-0.01	6.2+/-0.8		0.004+/-0.001	
$PtNi_1/TiO_2$	Pt - Cl	2.29+/-0.01	0.9+/-0.1	8.5+/-0.9	0.006+/-0.001	0.3
	Pt - Pt	2.75+/-0.01	7.2+/-0.9		0.006+/-0.001	
$PtNi_4/TiO_2$	Pt - Ni	2.57+/-0.02	3.9+/-1.2	5.5+/-2.0	0.005+/-0.002	0.6
	Pt - Pt	2.67+/-0.03	4.8+/-1.8		0.005+/-0.002	
$PtNi_{40}/TiO_2$[c]	Pt - Ni	2.54+/-0.00	9.3+/-1.0	6.0+/-1.3	0.007+/-0.001	1.0

[a]CN is the coordination number (error: ± 20%) for the absorber-backscatterer pair; R is the average absorber-backscatterer distance (error: ±1%); σ^2 is the Debye−Waller factor; ΔE_0 is the inner potential correction. S_0^2 was fixed as 0.78. Data ranges: $3.0 \leq k \leq 10.0$ Å^{-1}, $1.2 \leq R \leq 3.0$ Å. [b]The CN for Pt-Pt was fixed as 12 based on Pt foil crystal structure (Pt mp-126). [c]Data ranges: $3.0 \leq k \leq 11.3$ Å^{-1}, $1.2 \leq R \leq 3.0$ Å.

Table S3. The dispersion of Pt species and the TOF of different catalysts.

Samples	Pt dispersion (%)[a]	TOF (h^{-1})
Pt/TiO_2	47.6	35.7
$PtNi_1/TiO_2$	37.3	73.8
$PtNi_4/TiO_2$	60.4	81.6
$PtNi_{40}/TiO_2$	75.6	127.2
$0.1PtNi_{40}/TiO_2$	84.1	129.5
$PtNi_{80}/TiO_2$	66.8	129.0
$PtNi_{160}/TiO_2$	61.4	133.8

[a]: Determined by H_2-O_2 titration.

Table S4. Activation energy (E_a) and reaction energy (ΔE) for NO adsorption, the dissociation of adsorbed NO, and the formation of N_2 and CO_2 reaction on Pt_1/Ni and Pt surface.

Reactions	**Ea (eV)**	
	Pt_1Ni (111)	**Pt (111)**
NO(g) → NO*	/	/
NO* → N*+O*	1.37	2.08
N*+N* → N_2*	1.63	2.06
CO*+O* → CO_2*	1.04	1.02