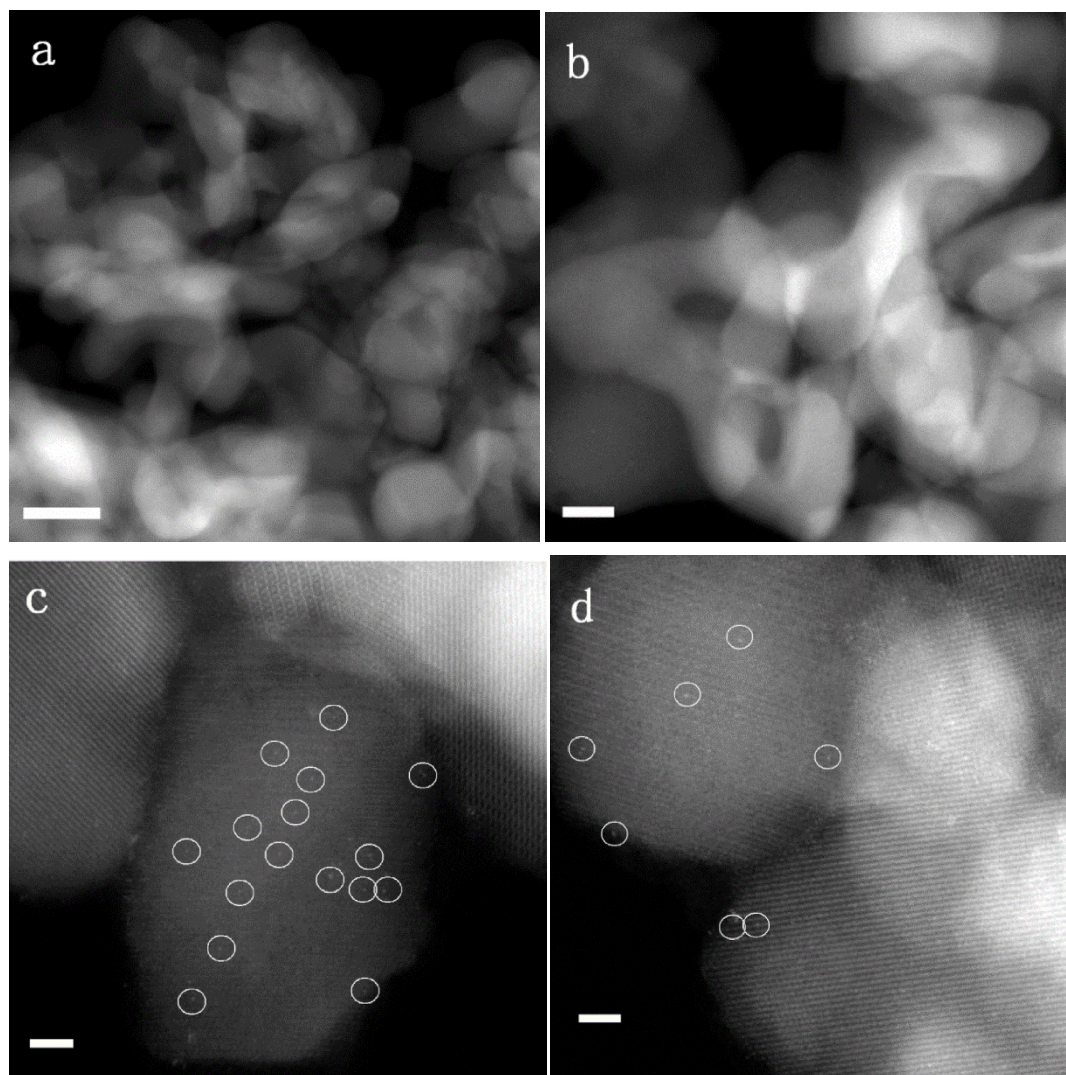
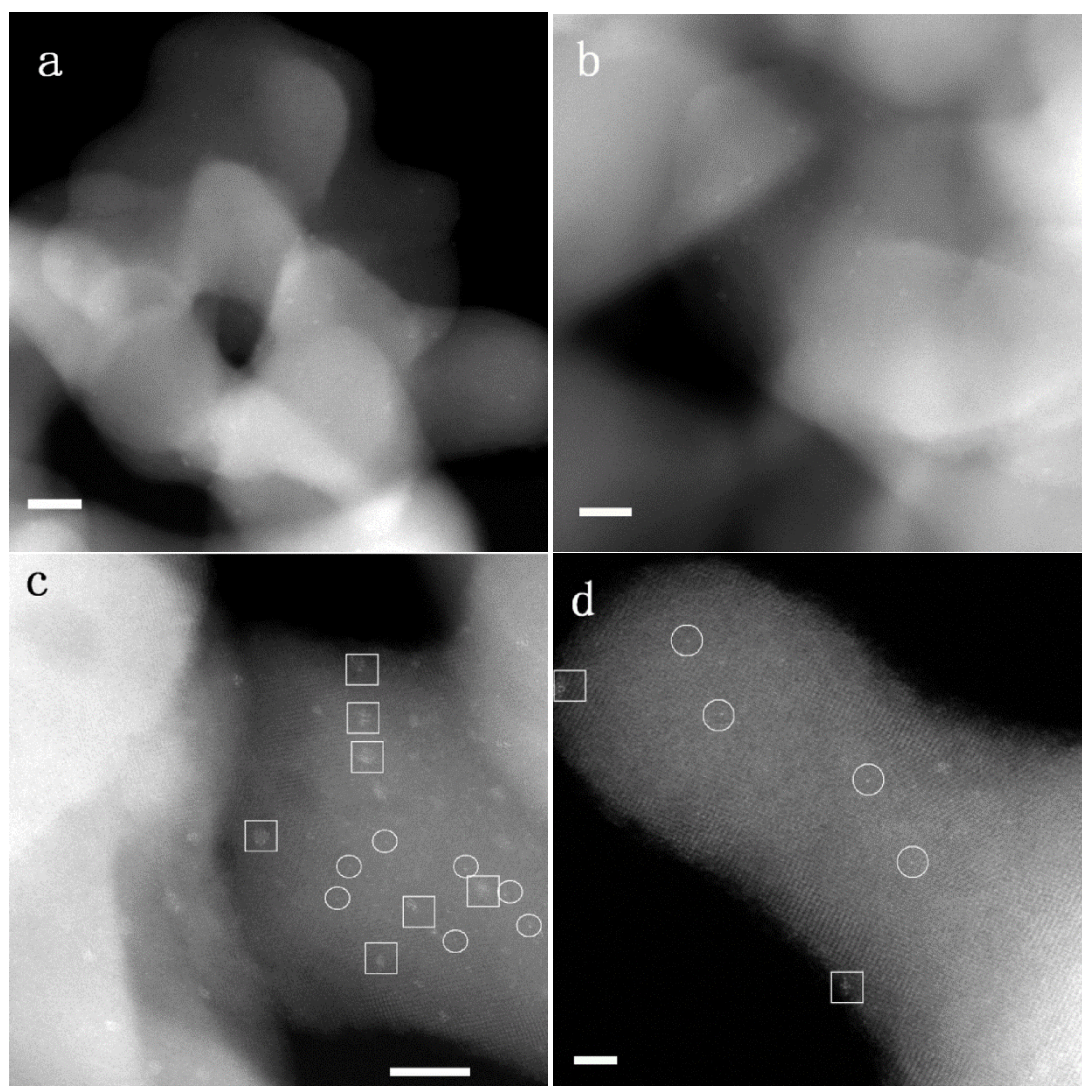
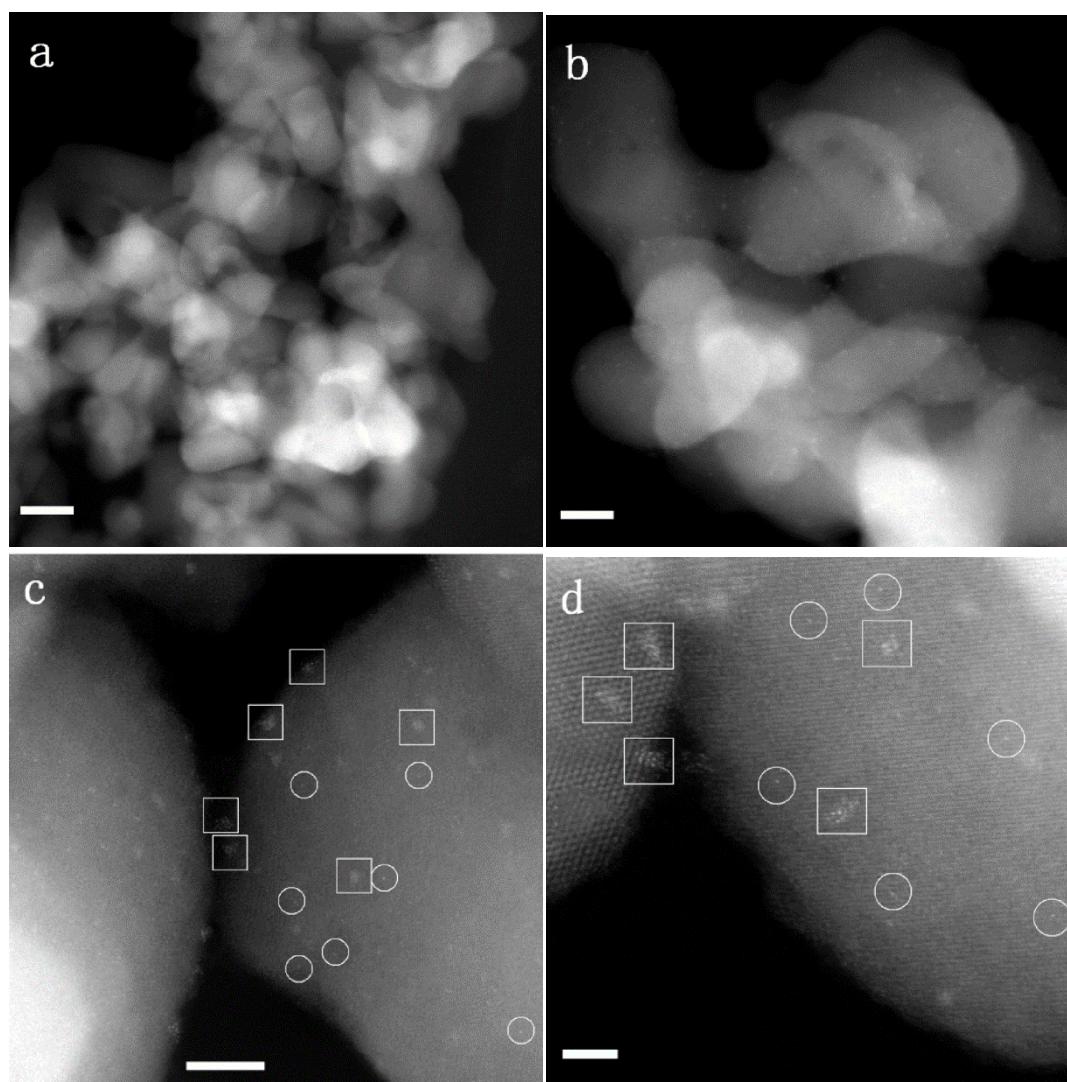




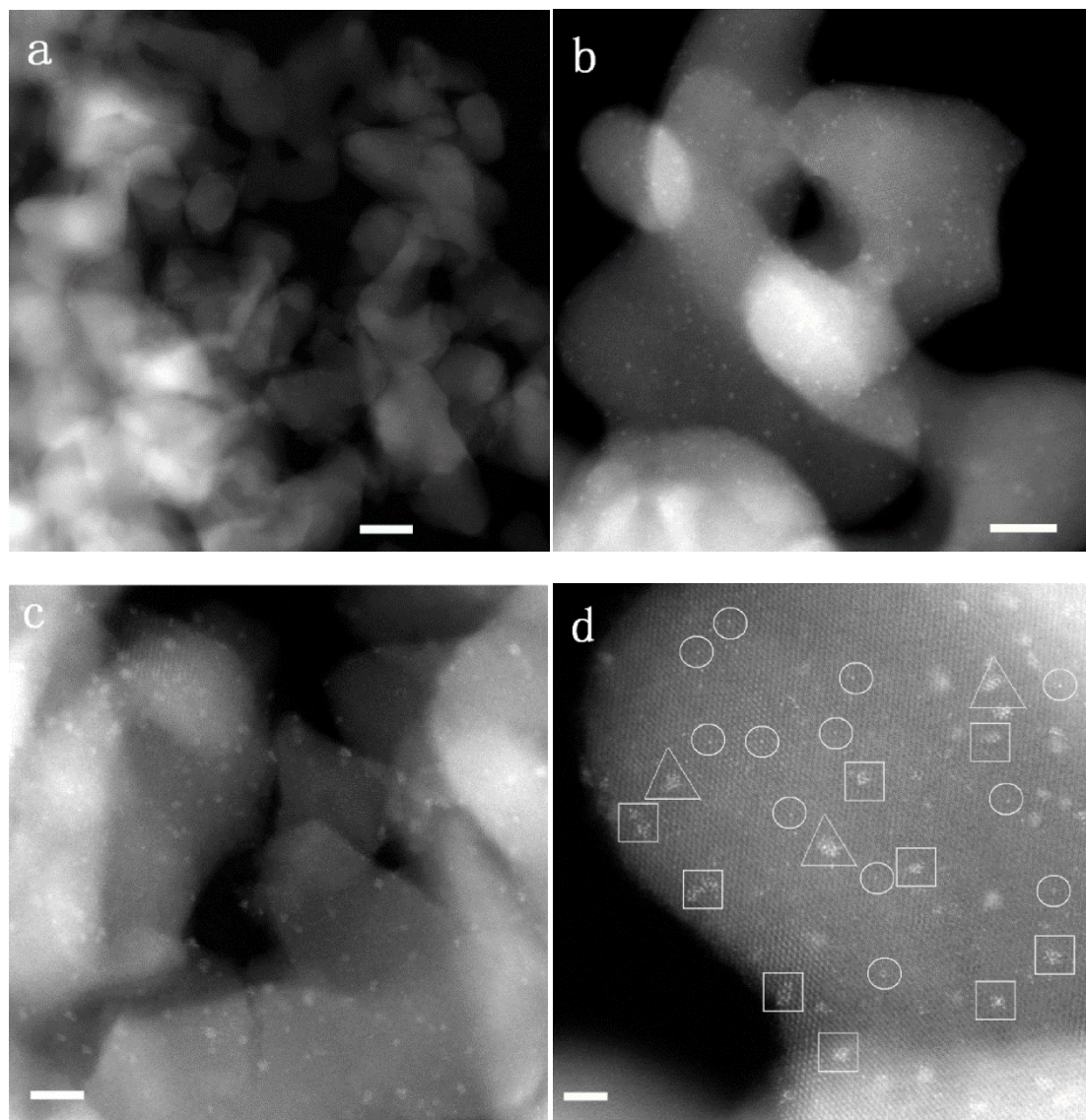
Supplementary Figure 1 HAADF-STEM images of 0.08%Pt/FeO_x-R200 single-atom catalyst with different magnifications. Scale bar: a, 20 nm; b, 10 nm; c, 2 nm; d, 2 nm. The low magnification images demonstrate that there are no large or small particles in the catalyst. The high magnification images clearly reveal the presence of isolated Pt single atoms (indicated by the white circles).



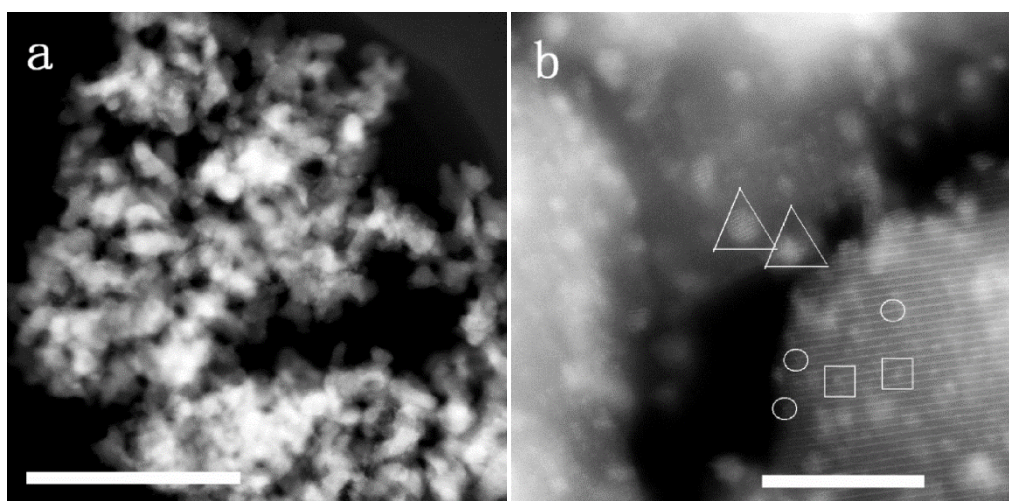
Supplementary Figure 2 HAADF-STEM images of 0.08%Pt/FeO_x-R250 catalyst with different magnifications. Scale bar: a, 10 nm; b, 5 nm; c, 5 nm; d, 2 nm. The low magnification images reveal the presence of very small clusters and the absence of large particles. The high magnification images show the co-presence of 2D rafts (squares) and single atoms (circles).



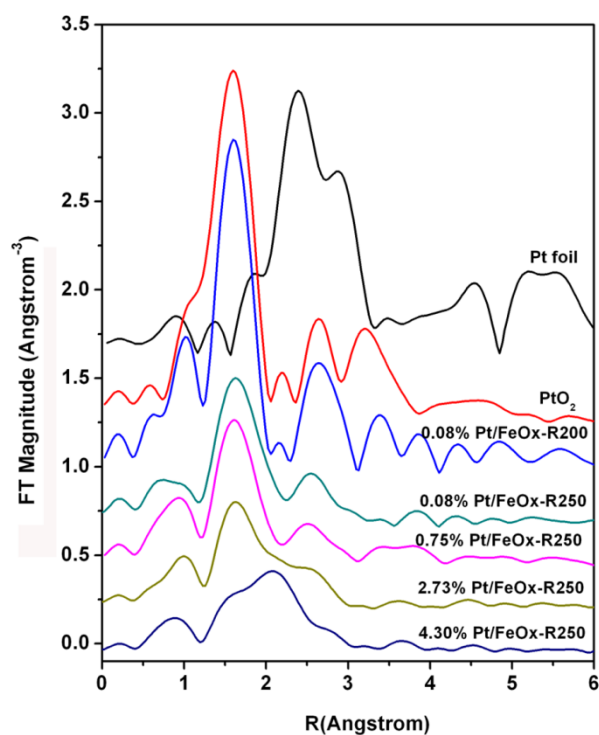
Supplementary Figure 3 HAADF-STEM images of 0.31%Pt/FeO_x-R250 catalyst with different magnifications. Scale bar: a, 20 nm; b, 10 nm; c, 5 nm; d, 2 nm. The low magnification images reveal the presence of small clusters and the absence of large particles. The high magnification images show the co-presence of 2D rafts (squares) and single atoms (circles).



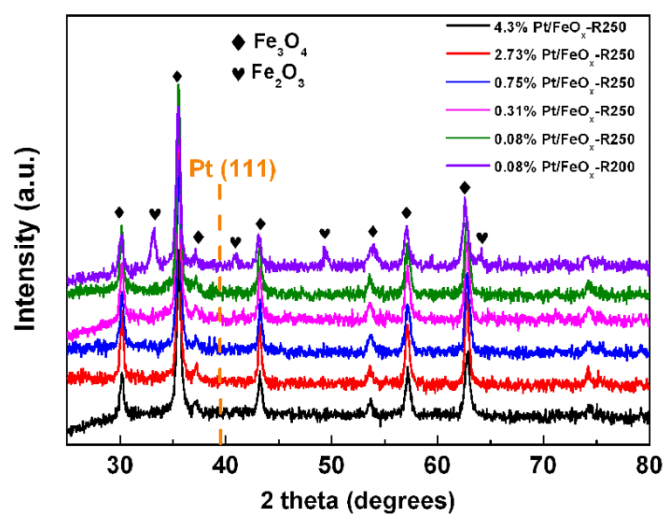
Supplementary Figure 4 HAADF-STEM images of 0.75%Pt/FeO_x-R250 catalyst with different magnifications. Scale bar: a, 20 nm; b, 10 nm; c, 5 nm; d, 2 nm. The low magnification images reveal the presence of highly populated small clusters and the absence of large particles. The high magnification images show the presence of small 3D particles (triangles), 2D rafts (squares) and single atoms (circles).



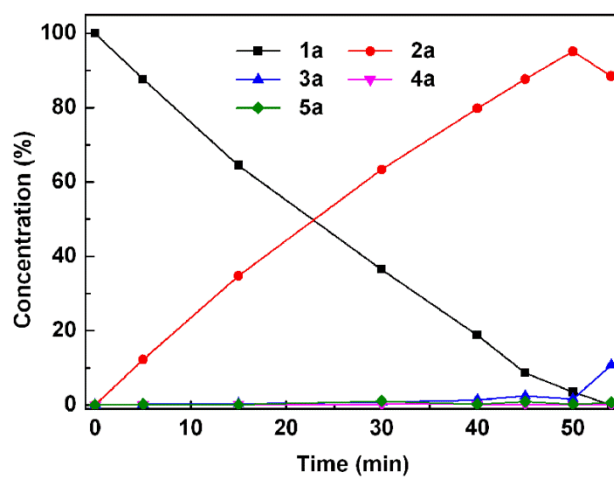
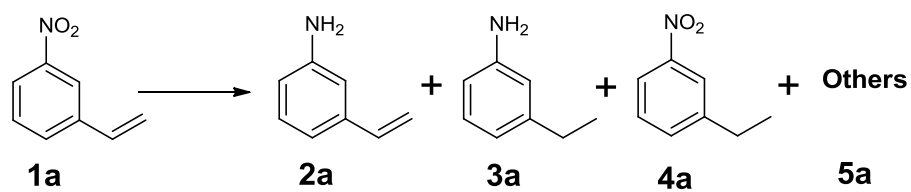
Supplementary Figure 5 HAADF-STEM images of 4.30%Pt/FeO_x-R250 catalyst with different magnifications. Scale bar: a, 200 nm; b, 10 nm. The low magnification images reveal the presence of highly populated small clusters and the absence of large particles. The high magnification images show the co-presence of small 3D particles (triangles), 2D rafts (squares) and single atoms (circles).



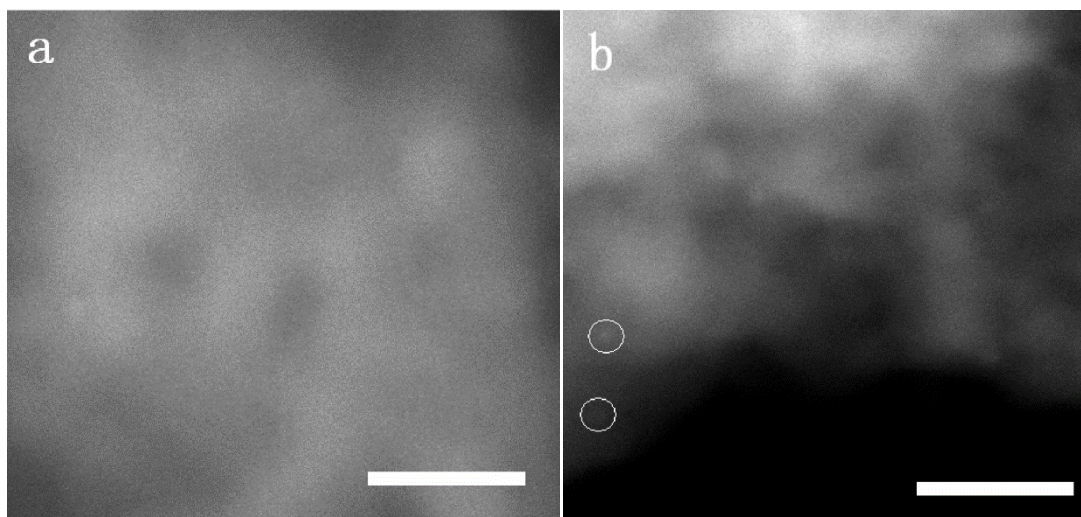
Supplementary Figure 6 The Fourier transform of k^2 -weighted extended X-ray absorption fine structure spectra of the Pt/FeO_x samples with different Pt loadings. No phase correction was made. The first main peak is due to Pt-O bonding. It is clear that Pt-Pt metallic bond is absent in either 0.08%Pt/FeO_x-R200 or 0.08%Pt/FeO_x-R250.



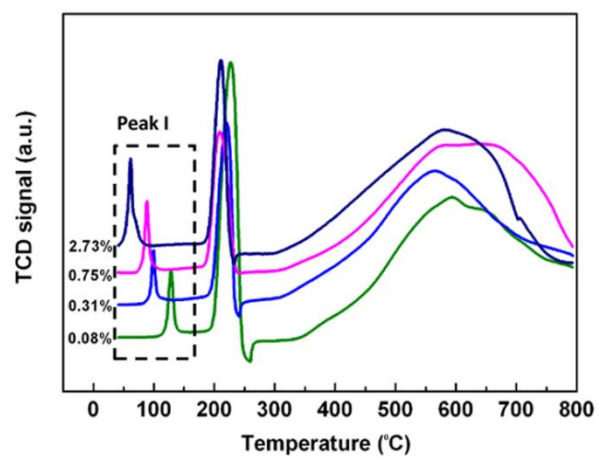
Supplementary Figure 7 XRD patterns of different Pt/FeO_x catalysts. It is clear that both Fe₂O₃ and Fe₃O₄ phases are present in the 0.08%Pt/FeO_x-R200 sample, while only Fe₃O₄ phase is detected in the other samples. No any Pt phase is detected in all the samples.



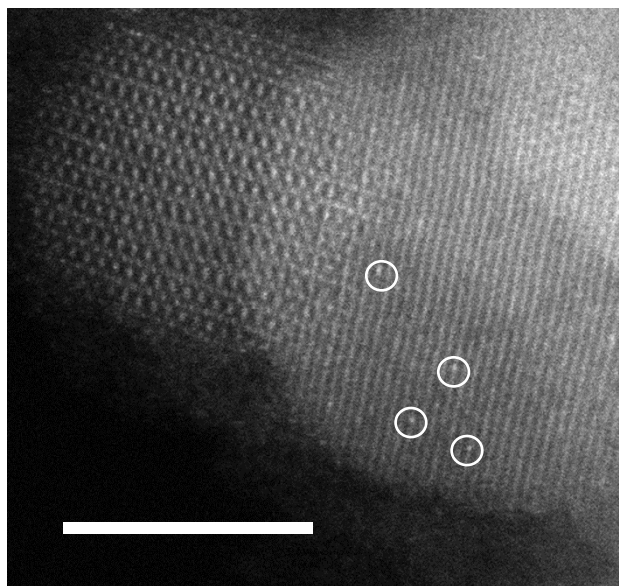
Supplementary Figure 8 The concentration change of reactant and products during the reduction of 3-nitrostyrene over 0.08%Pt/FeO_x-R250 catalyst.



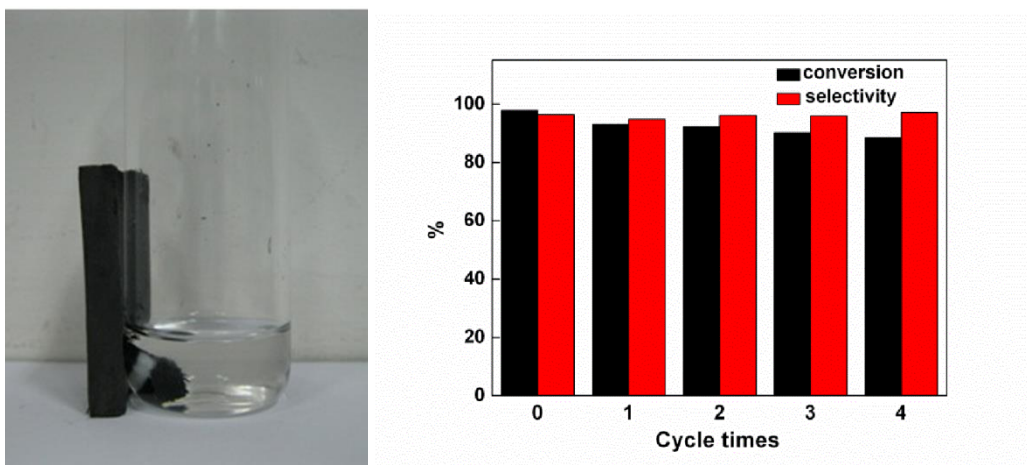
Supplementary Figure 9 HAADF-STEM images of 0.08%Pt/Al₂O₃-R250. Scale bar: a, 10 nm; b, 10 nm. The bright dots in circles indicates very small particles.



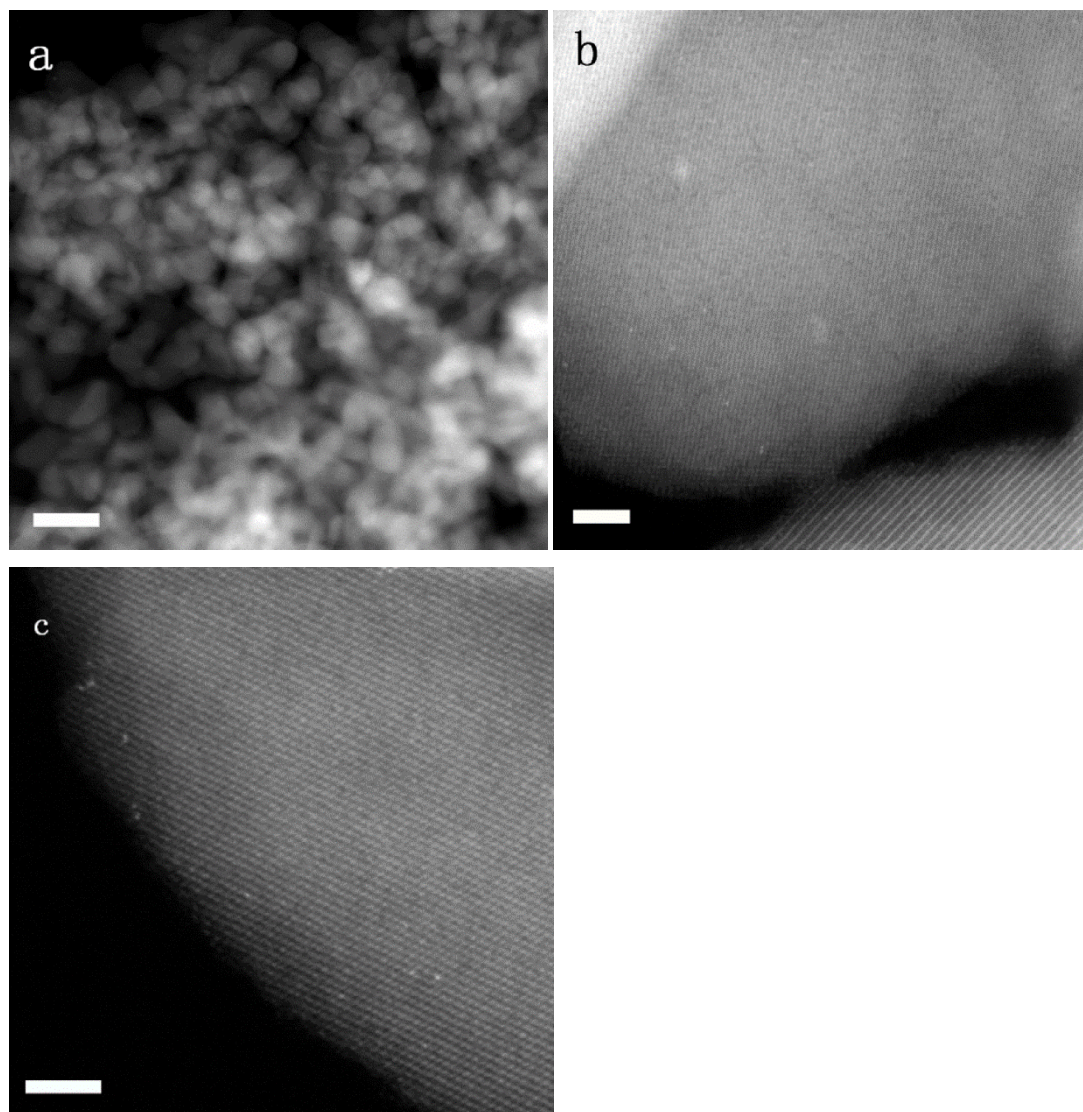
Supplementary Figure 10 H₂-TPR profiles of different Pt loading catalysts. The peak I is not only due to the reduction of Pt(IV) but also of Fe(III) via the spillover of H₂.



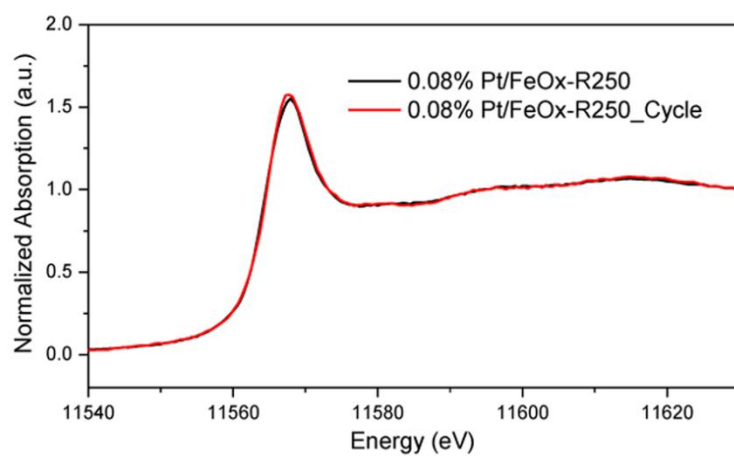
Supplementary Figure 11 HAADF-STEM image of Ir₁/FeO_x-R250. Scale bar: 5 nm. The white spots in circles indicate the single atoms of Ir.



Supplementary Figure 12 Recycling test of the 0.08%Pt/FeO_x-R250 catalyst. (left) Magnetic separation of the catalyst from the reaction medium; (right) The conversion of 3-nitrostyrene and the selectivity of 3-aminostyrene during five recycling runs.



Supplementary Figure 13 HAADF-STEM images of 0.08%Pt/FeO_x-R250 catalyst after 5 recycle experiments. Scale bar: a, 50 nm; b, 2 nm; c, 2 nm. It is clear that both the single-atom and pseudo-single-atom structures of Pt remain unchanged after the reaction.



Supplementary Figure 14 XANES spectra of 0.08%Pt/FeO_x-R250 catalyst before and after 5 recycle experiments. It indicates that the oxidation state of Pt remains unchanged after the reaction.

Supplementary Table 1. The residual Na content in the catalysts detected by ICP.

Catalyst	Na (wt%)
0.08%Pt/FeO _x -R250	0.40
0.31%Pt/FeO _x -R250	0.49
0.75%Pt/FeO _x -R250	0.13
2.73%Pt/FeO _x -R250	0.07
4.30%Pt/FeO _x -R250	0.74

Supplementary Table 2. H₂-TPR data analysis of Pt/FeO_x catalysts

Pt loading (wt%)	Theoretical H ₂ consumption required for Pt ⁴⁺ (μmol/g cat)	Actual H ₂ consumption for Peak I (μmol/g cat)	molar ratio (Fe ³⁺ → Fe ²⁺)/ (Pt ⁴⁺ → Pt ⁰) for peak I
0.08	8.2	135.7	62.2
0.31	31.8	144.1	14.1
0.75	76.9	224.8	7.7
2.73	279.9	324.3	0.6

Supplementary Table 3. Chemoselective hydrogenation of 3-nitrostyrene over different FeO_x-supported metal catalysts

Catalyst	Time(min)	Conv.(%)	Sel.(%)
0.2%Ir/FeO _x	240	98.4	98.7
0.17%Pd/FeO _x	28	88.5	16.0
0.17%Rh/FeO _x	95	2.1	66.1
0.17%Au/FeO _x	190	-	-

Reaction condition: 0.1g catalyst, T = 40 °C, P = 3 bar, 5 ml reaction mixture: 0.5 mmol 3-nitrostyrene, toluene as solvent, o-xylene as the internal standard.

Supplementary Table 4. Control experiments with styrene and nitrobenzene as the substrates over 0.08%Pt/FeO_x catalysts.

Catalyst	TOF(mol _{converted} h ⁻¹ mol _{Pt} ⁻¹)			
	Nitrobenzene ^a	Styrene ^a	Nitrobenzene ^b	Styrene ^b
0.08%Pt/FeO _x -R200	2414	1453	2510	117
0.08%Pt/FeO _x -R250	2175	2377	2538	139

Reaction condition: T = 40 °C, P = 3 bar, 5 ml toluene, mesitylene was used as internal standard. Substrates: [a] 0.5 mmol nitrobenzene or styrene; [b] competitive reaction: 0.25 mmol nitrobenzene and 0.25 mmol Styrene.

Supplementary Table 5. Comparison of differently pretreated catalysts

Catalyst	Time (min)	Conv. (%)	Sel. (%)
0.08%Pt/ FeO _x -R250 ^[a]	88	88.4	98.2
0.08%Pt/ FeO _x -R250 ^[b]	50	96.5	98.6
0.08%Pt/ FeO _x -R250 ^[c]	50	95.2	97.6

Reaction conditions: T = 40 °C, P = 3 bar, Pt/Substrate = 0.08%; 5 mL reaction mixture: 0.5 mmol 3-nitrostyrene, toluene as solvent, o-xylene as internal standard. ^[a] catalyst stored at ambient conditions was directly used without any pretreatment; ^[b] prior to the test, the catalyst was pretreated at 40 °C for 1 h in autoclave charged with 5 mL toluene and 1 MPa H₂; ^[c] The freshly reduced catalyst was directly transferred into the autoclave without exposure to air.