

Supporting Information for

Oxygen Surface Groups of Activated Carbon Steer the Chemoselective Hydrogenation of Substituted Nitroarenes over Nickel Nanoparticles

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Experimental details

1.1 Preparation of catalysts

The AC_{OX} support was prepared by treating activated carbon (denoted as AC, Norit, S_{BET} = 638 m²/g) with concentrated nitric acid solution (33 wt%) at 80 °C for 24 h. After that, the material was washed by deionized water several times until neutral filtrate was obtained, and then dried at 120 °C for 12h.

The Ni/AC_{OX} catalyst was prepared by incipient wet impregnation of the AC_{OX} support with an aqueous solution of nickel nitrate (0.2527 g nickel nitrate dissolved in 1.3 g deionized water was used for impregnating 1g AC_{OX}), and then dried at room temperature overnight and at 120 °C for 5h. Before characterization and reactivity test, the Ni/AC_{OX} catalyst was reduced in a tube-furnace reactor, which was ramped from 20 °C to 350 °C at a rate of 10 °C/min under 10%H₂/He (20mL/min) and held at 350 °C for 30min. Then, H₂ was switched off and He was introduced continuously until the reactor was cooled down to room temperature. Finally 5%O₂/He was switched into the reactor for 10 min to passivate the Ni catalyst.

Other supported Ni catalysts, including using different supports and different nickel precursors, were prepared with a similar procedure to the above Ni/AC_{OX}.

1.2 Characterization methods

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer equipped with a Cu-K α radiation source with a scanning angle (2θ) of 10° to 80°, operated at 40 kV and 40 mA.

N₂ adsorption-desorption was performed on a Quadrasorb SI instrument. Before the measurement, the sample was pretreated at 120 °C for 2 h and at 250 °C for 3 h in vacuum to remove adsorbed hydrates and carbonates. The specific surface area was calculated using a Brunauer–Emmett–Teller (BET) method in the range of P/P₀ from 0.05 to 0.30.

Temperature-programmed desorption (TPD) was conducted on an Auto Chem II 2910 automatic catalyst characterization system equipped with a mass spectra detector. Firstly, a catalyst sample was loaded into a U-shape quartz reactor and pretreated at 150 °C in He for 0.5 h to remove adsorbed

hydrates and carbonates. Then, after cooling down to room temperature, the sample was heated to 900 °C in He at a ramping rate of 10 °C min⁻¹.

Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100F microscope operated at 200 kV. Before microscopy examination, the sample was ultrasonically dispersed in ethanol for 5-10 min and then a drop of the solution was put on a copper TEM grid coated with a thin holey carbon film.

X-ray photoelectron spectroscopy (XPS) spectra were obtained on a Thermo ESCALAB 250 X-ray photoelectron spectrometer equipped with Al K α excitation source and with C as internal standard (C1s = 284.6 eV).

Ni leaching in solution was determined by inductively coupled plasma spectroscopy (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

1.3 Reaction tests

The chemoselective hydrogenation of nitroarenes was performed in an autoclave equipped with a temperature and pressure control. A mixture solution in a total volume of 5 ml, including nitroarene substrate as reactant, toluene as solvent and O-xylene as internal standard, was put into the autoclave. Then, the reactor was sealed and purged with 10 bar of hydrogen for five times. Afterwards, the autoclave was pressurized with H₂ up to 3 bar (for hydrogenation of nitroarenes to anilines) or 20 bar (for hydrogenation of α,β -unsaturated nitroarenes to oximes) and heated to the desired reaction temperature in a water bath, and the reaction was initiated with stirring using a magnetic stirring bar. After finishing the reaction, the product was analyzed by a gas chromatograph equipped with a FID detector.

Pretreatment procedure: After reduction at 350 °C, the powder catalyst, 5 ml toluene and magnetic bar were putted into the autoclave. And then the autoclave was charged with 1 MPa hydrogen and sealed. Finally the reactor was heated at 40 °C for 1 h in the wash bath to remove the surface O of the catalyst. Subsequently, toluene was poured out and a total volume of 5 ml solution including 3-nitrostyrene, toluene and internal standard O-xylene, was put into the autoclave to start the reaction test.

Table S1. Chemoselective hydrogenation of 3-nitrostyrene over different supported Ni catalysts.

Catalyst	Time (min)	Con. (%)	Sel. (%)
Ni/AC _{OX}	190	97.9	97.1
Ni/AC	190	27.4	95.2
Ni/SiO ₂	190	0.0	0.0
Ni/Al ₂ O ₃	190	0.0	0.0
Raney Ni ^[a]	155	76.8	62.5
AC	360	-	-

Reaction conditions: T=40 °C, P=3 bar, 0.1g catalyst; 5 ml reaction mixture: 0.5 mmol 3-nitrostyrene, toluene as solvent, and o-xylene as internal standard. [a] 50 °C, 15 mg Raney Ni.

Table S2. Chemoselective hydrogenation of 3-nitrostyrene over 5%Ni/AC_{OX} catalysts prepared by different Ni precursors.

Catalyst	Ni Precursor	Time (min)	Con. (%)	Sel. (%)
Ni/AC _{OX}	Ni(NO ₃) ₂	190	97.9	97.1
Ni/AC _{OX}	Ni(CH ₃ COO) ₂	190	62.6	99.7
Ni/AC _{OX}	NiSO ₄	190	0.0	0.0
Ni/AC _{OX}	NiCl ₂	190	3.3	90.0

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

Table S3. XRF analysis of 5%Ni/AC_{OX} catalyst prepared by NiSO₄ precursor.

Catalyst	Ni Precursor	Element and content (wt%)				
		C	Na	Ni	Si	S
Ni/AC _{OX}	NiSO ₄	91.7	0.4	5.2	0.6	2.0

Table S4. Recycling results for chemoselective hydrogenation of 3-nitrostyrene over 5% Ni/AC_{OX} catalyst.

Catalyst	Recycling time	Time (min)	Con. (%)	Sel. (%)
Ni/AC _{OX}	0	190	97.9	97.1
Ni/AC _{OX}	1	100	94.7	94.9
Ni/AC _{OX}	2	195	92.4	95.4
Ni/AC _{OX}	3	420	85.6	97.6

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

Table S5. 3-nitrostyrene adsorption on Ni/AC_{OX} and Ni/AC catalysts.

Catalyst	Adsorption amount ($\mu\text{mol/g}$)	
	Before wash	After wash
Ni/AC	410	185
Ni/AC _{OX}	470	215

Table S6. Control experiments with styrene and nitrobenzene as the substrates over Ni/AC_{OX} catalyst.

Condition	Feeding (mmol)		TOF(mmol converted $\text{h}^{-1}\text{mol Ni}^{-1}$)	
	Styrene	Nitrobenzene	Styrene	Nitrobenzene
Non-competitive condition	0	0.5	0	827
	0.5	0	3398	0
Competitive condition	0.25	0.25	101	1382

Reaction condition: T = 40 °C, P = 3 bar, 5 ml toluene, and mesitylene was used as internal standard.

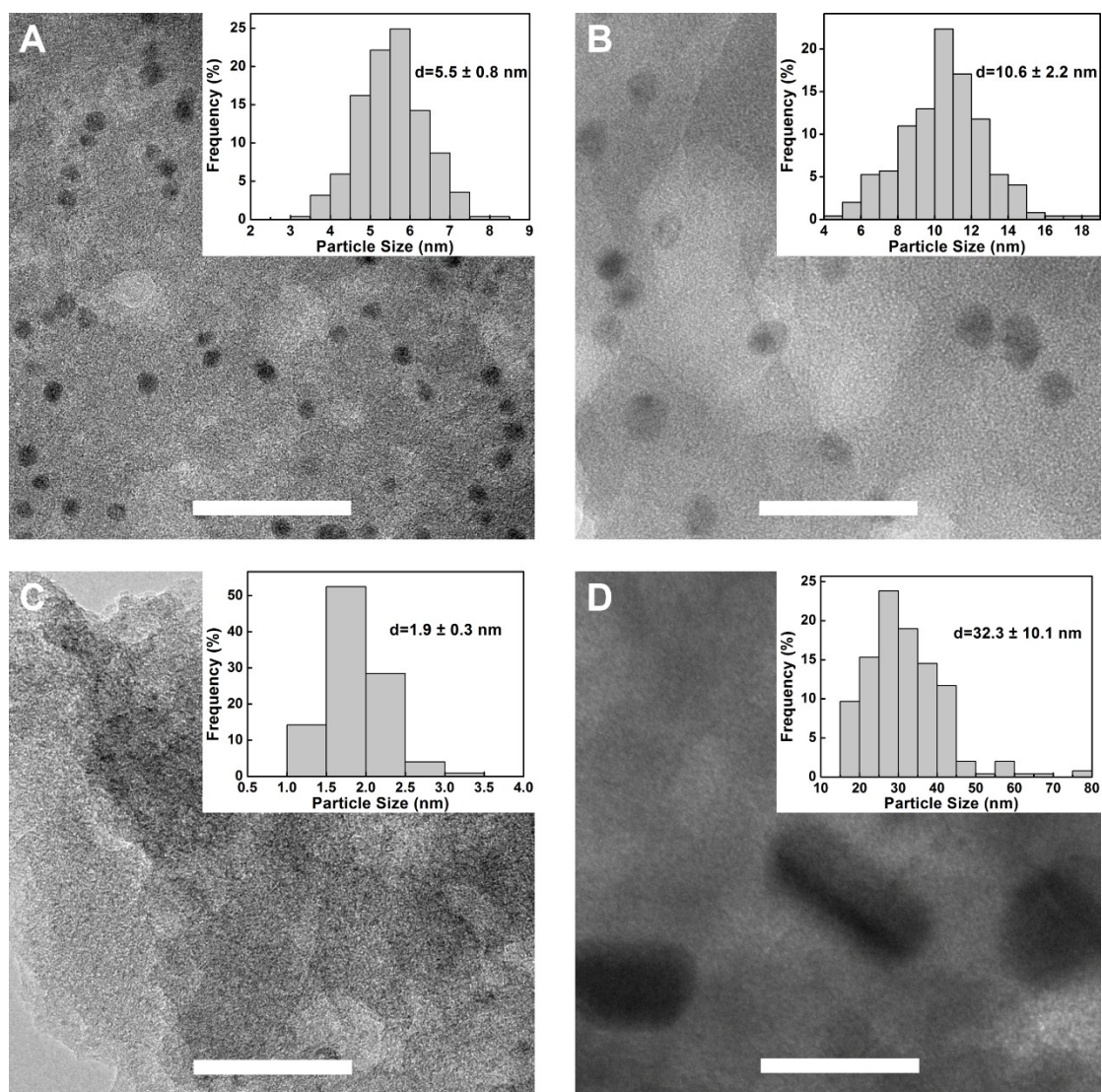


Figure S1. HRTEM images and size distributions of Ni/AC_{Ox} catalysts which were prepared with different Ni precursors. (A): Ni(NO₃)₂; (B): Ni(CH₃COO)₂; (C) NiSO₄ and (D) NiCl₂. Scale bar, 50 nm.

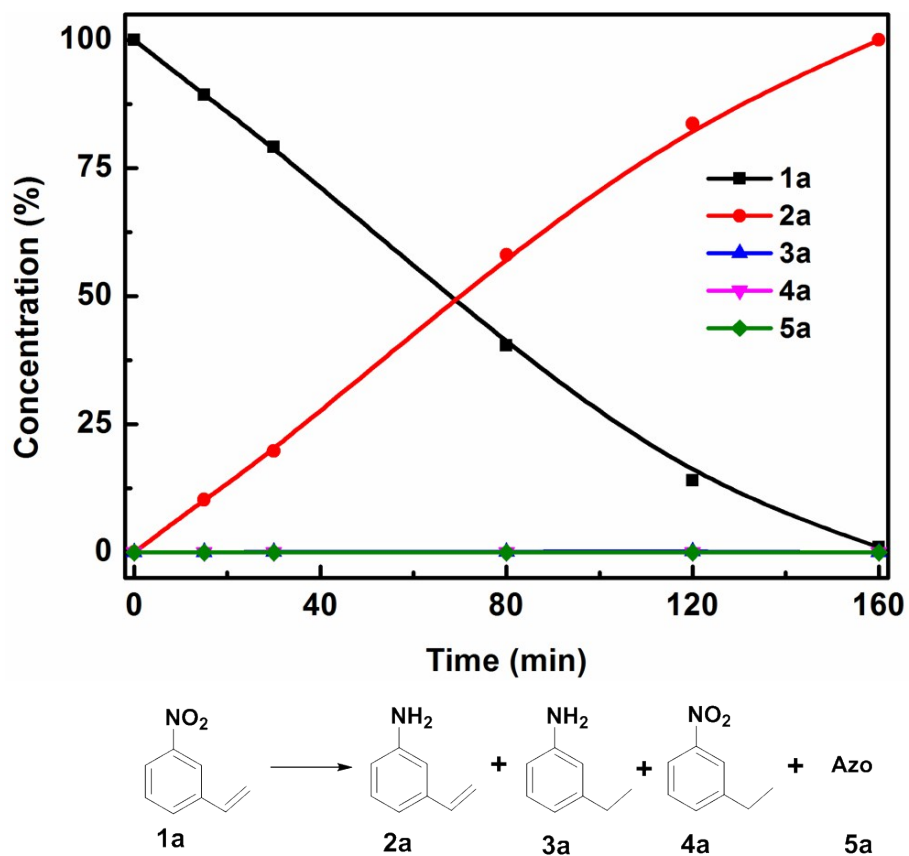


Figure S2. Kinetic curve for the 3-nitrostyrene hydrogenation over Ni/ACOX catalyst. Prior to reaction, the catalyst was pre-reduced with 1MPa H₂ in toluene at 40 °C for 1h. Reaction conditions: T = 40 °C, P = 3 bar, 0.1 g catalyst; 5 ml reaction mixture: 0.5 mmol 3-nitrostyrene, toluene as solvent, and o-xylene as internal standard.

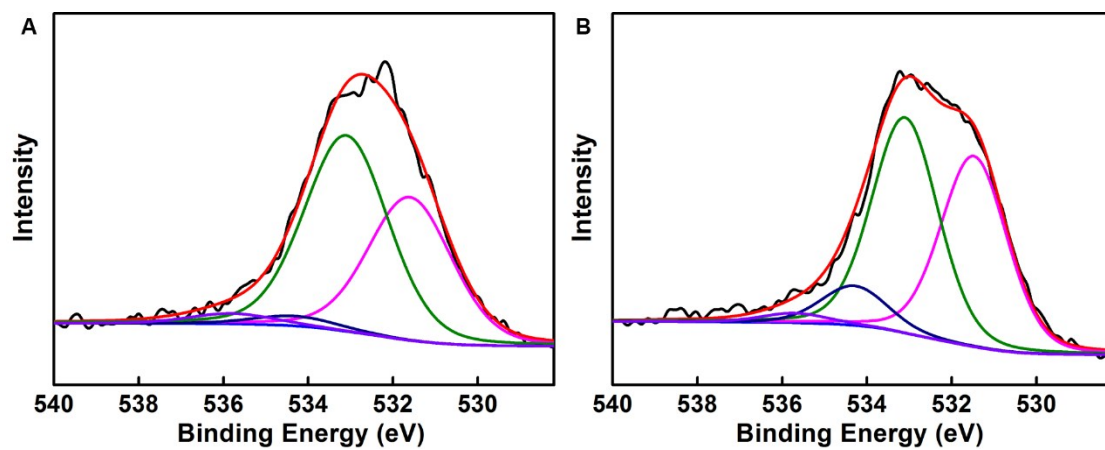


Figure S3. O 1s XPS spectra of (A) AC and (B) AC_{ox} supports.

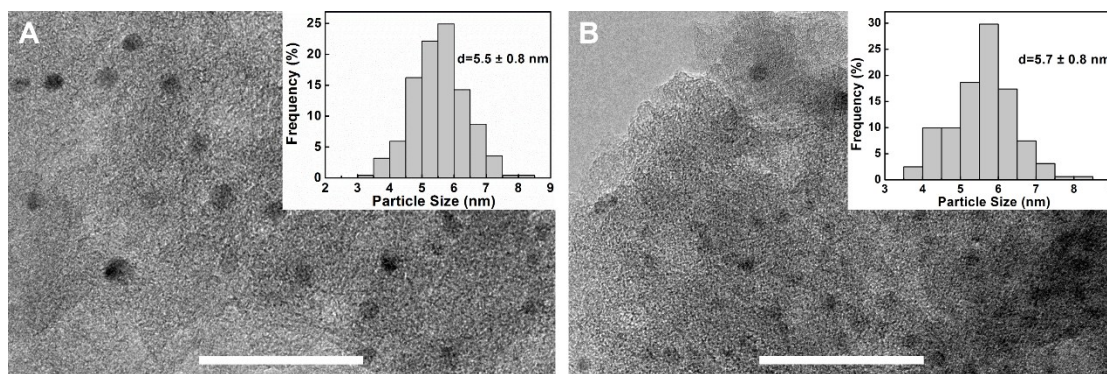
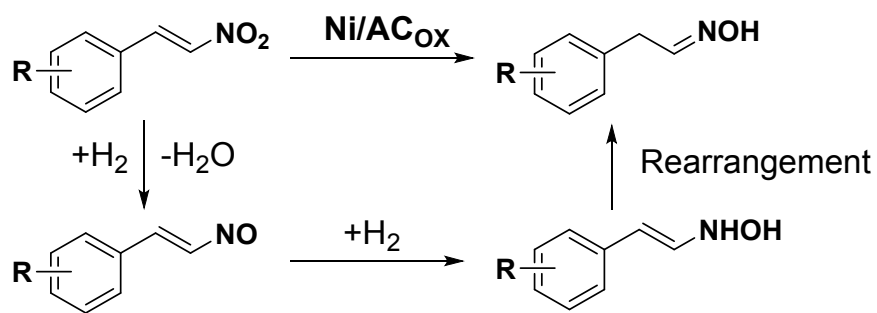


Figure S4. HRTEM images and size distributions of (A) fresh and (B) used Ni/AC_{OX} catalysts. Scale bar, 50 nm.



Scheme S1. Proposed reaction mechanism for hydrogenation of α,β -unsaturated nitroarenes to produce oximes.