

Supporting Information

Catalytically Active Gauze-Supported Porous Nickel

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Experimental methods

Materials

Reagent grade dimethyl sulfone and acetamide were purchased from Alfa Aesar. Anhydrous NiCl_2 was purchased from ChemLab. ZnCl_2 was obtained from Acros Organics. Copper gauze (purity > 99.99 %, nominal aperture: 0.14 mm, wire diameter: 0.115 mm) was purchased from Goodfellow. Nickel wire (purity > 99.98 %, 2 mm diameter) and rod (purity > 99.99 %, 5 mm diameter) were purchased from Chempur. Raney[®]2800 and all other chemicals were purchased from Sigma-Aldrich.

Electrochemical experiments

All electrochemical depositions and electrochemical leaching experiments were performed with a potentiostat (EG&G 273) with reference to Ni/Ni^{2+} . The Ni-Zn alloy precursor was electrodeposited on copper gauze from an acetamide- DMSO_2 eutectic electrolyte containing 0.2 M NiCl_2 and 1.0 M ZnCl_2 . The preparation of the electrolyte, electrodeposition and electrochemical leaching were carried out in a glove box. Typically, the eutectic mixture used for electrodeposition of nickel-zinc alloys was prepared by heating and stirring of a mixture of acetamide (12.0 g, 0.740 mole fraction) and DMSO_2 (4.8 g, 0.187 mole fraction) at 110 °C until a colorless melt was formed. After that, anhydrous NiCl_2 (0.436 g, 0.012 mole fraction) and ZnCl_2 (2.29 g, 0.060 mole fraction) were added to the mixture and stirred well. The electrodeposition was carried out inside a 3-neck flat bottomed electrochemical cell which was mounted in an aluminium heating block on top of a hotplate with a temperature controller. The nickel rod (counter electrode) and the copper mesh (cathode) were clamped and placed on both side necks of the cell while the nickel wire (reference electrode) was placed in the other neck. Approximately 2.3 cm^2 of the mesh was submerged into the electrolyte and this provided an effective deposition area of approximately 6.7 cm^2 . The electrodeposition of nickel-zinc alloy was initiated by supplying 15 C/cm^2 of charge to the electrochemical system at a potential of -1.5 V vs. Ni/Ni^{2+} . The electrochemical leaching of the alloy was carried out in the same setup. The stripping of zinc was carried out at a potential of 0 V vs. Ni/Ni^{2+} until the potentiostat showed a value of zero current. After leaching, the gauze-supported nickel-zinc alloy was rinsed with an excessive amount of water and stored in ethanol.

Chemical leaching

The gauze supported nickel-zinc alloy was also activated by selective removal of zinc in sodium hydroxide (6.0 M, 20 mL) at 90 °C for 3 hours. After alkaline leaching, the catalysts were rinsed with an excessive amount of water and stored in ethanol.

Catalytic testing

The catalytic activities of the gauze-supported porous nickel catalysts were evaluated in the hydrogenation of acetophenone. The weighing and transfer of the catalysts to the reactor were done in a nitrogen protective atmosphere to avoid air oxidation of the catalysts. The catalyst was placed inside a stainless steel catalyst basket which was mounted on a stirring rod (see



illustration). Typically, a 100-mL Parr autoclave was charged with absolute ethanol (60 mL) and acetophenone (116 μ L, 1 mmol). The autoclave was purged with nitrogen for three times, followed by hydrogen for another three times. Finally the autoclave was charged with hydrogen (50 bar) and heated rapidly to 80 °C. The reaction was initiated by stirring of the reaction mixture at 900 rpm. Aliquots for GC analysis were taken at regular intervals through a sampling valve. The aliquot samples were analyzed by GC-FID (Agilent 2010 installed with a CB-SIL 60 column). The peaks on the chromatogram were identified by comparison with the retention time of reference compounds and cross-checked by GC-MS (Agilent 6890N installed with 5973Network MS detector and HP-5 column).

Powder XRD diffraction

Powder diffraction patterns of the nickel-zinc alloys were obtained using an X-ray diffractometer (Siemens D5000) under Cu K_{α} radiation ($\lambda = 1.5405 \text{ \AA}$). For recording X-ray patterns, the nickel-zinc alloy was deposited on a copper plate instead of on the gauze.

Elemental analysis

The elemental composition of the nickel-zinc alloy was determined using ICP-OES (Varian 710-ES). Prior to chemical analysis, a small fragment of the sample was cut and dissolved in concentrated HNO_3 (2 mL). The solution was then transferred to a 100 mL volumetric flask, made up to volume with deionized water, and assayed by ICP-OES.

Scanning electron microscopy

The surface morphology and composition of the alloys were determined by scanning electron microscopy (Philips XL 30 FEG).

Surface area measurement

The specific surface area of the catalyst was measured with a nitrogen adsorption apparatus (Micromeritics Tristar 3000). Prior to the measurement, the samples were cut into smaller fragments, dried and degassed under nitrogen flow at 50 °C for 6 hours. Values, e.g. specific surface areas, are referred to the mass of deposited material that remains after the various leaching treatments.

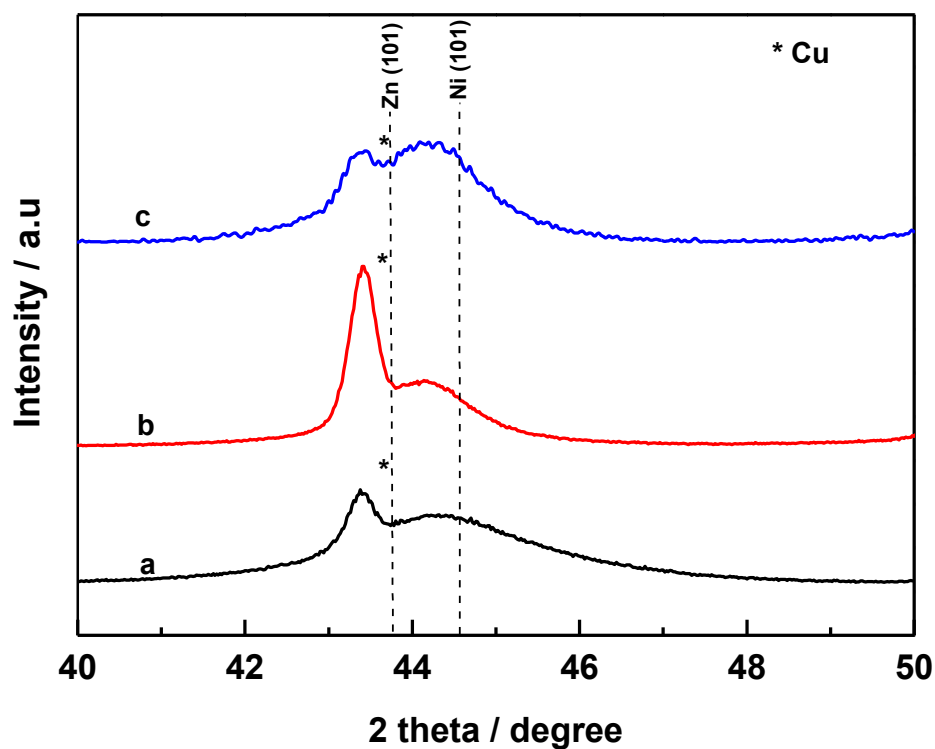


Figure S1. Powder XRD patterns of zinc-nickel alloys on copper plate (a) as-deposited from an acetamide–DMSO₂–NiCl₂–ZnCl₂ quaternary melt (mole fractions: 0.740–0.187–0.061–0.012) at 110 °C and potential of -1.5 V vs. Ni/Ni²⁺, and (b) after alkaline leaching with NaOH (6 M) at 90 °C for 3 hours, and (c) after electrochemical leaching at 0 V vs. Ni/Ni²⁺ until zero current.

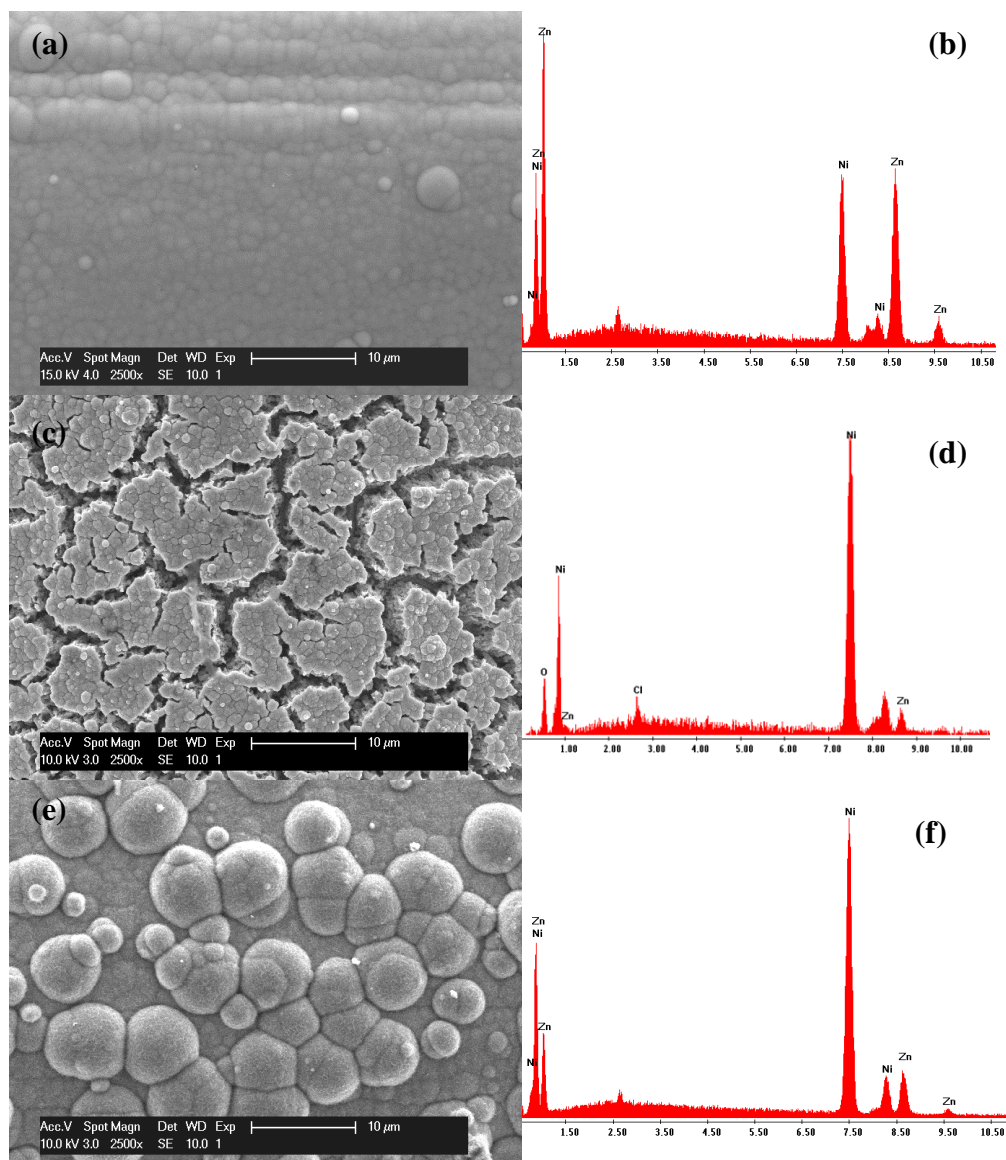
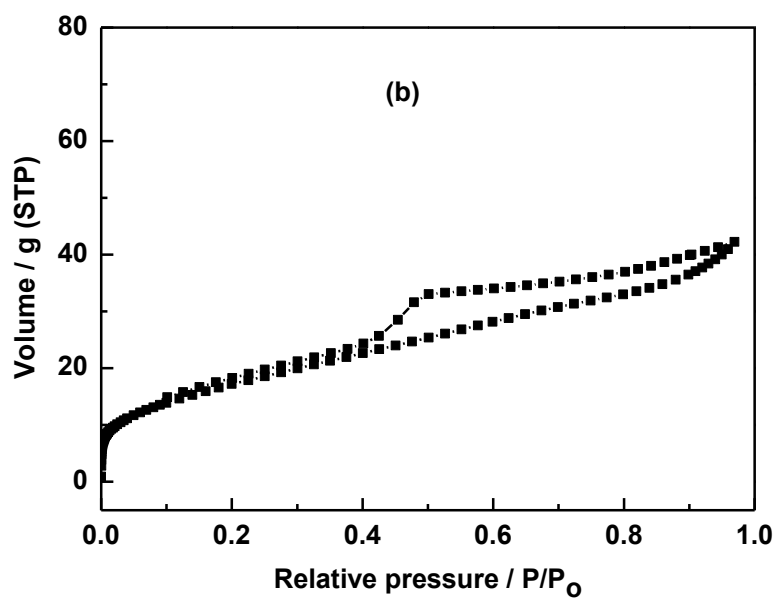
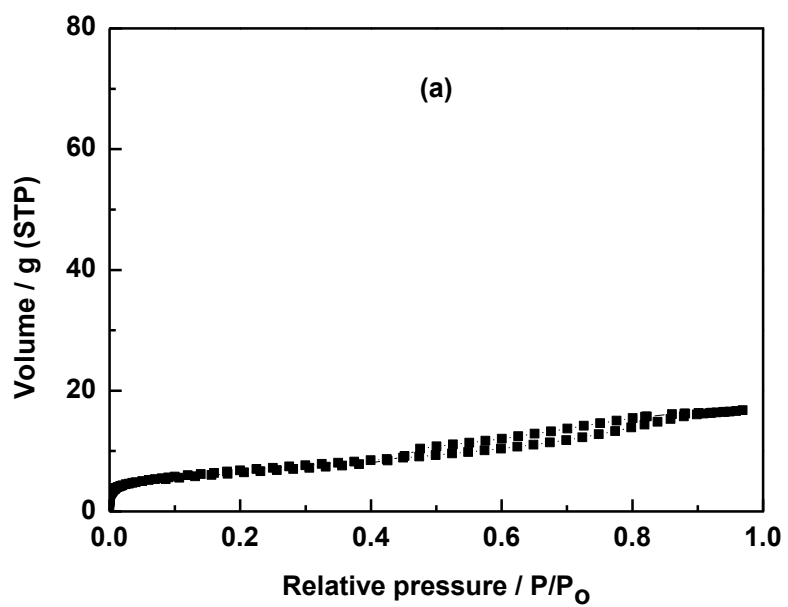


Figure S2. SEM morphology of the zinc-nickel alloys (a) as-deposited from an acetamide–DMSO₂–NiCl₂–ZnCl₂ quaternary melt (mole fractions: 0.740–0.187–0.061–0.012) at -1.50 V vs. Ni/Ni²⁺ and 110 °C, (c) after alkaline leaching in 6.0 M NaOH at 90 °C for 3 hours, and (e) after electrochemical leaching at 0 V vs. Ni/Ni²⁺ in the same electrolyte bath until zero current. The corresponding EDX profiles are in the right hand side. The acceleration voltage was kept at 20 kV during the EDX measurement.



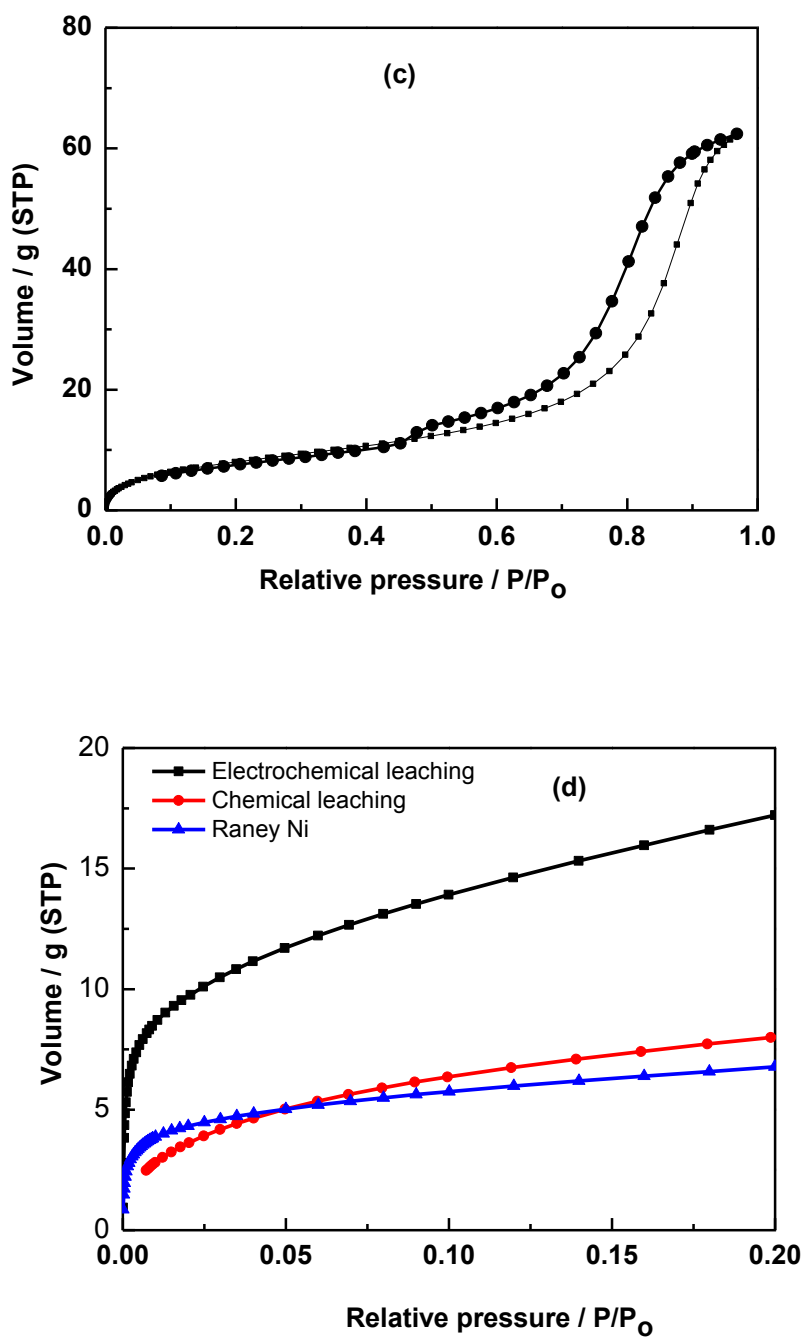


Figure S3. N_2 physisorption texture measurements: adsorption and desorption isotherms recorded at 77 K for (a) alkaline leached alloy (3 h at 90°C in 6 M NaOH), (b) electrochemically leached alloy (at 0 V vs. Ni/Ni^{2+}), (c) commercial Raney Ni catalyst. Panel (d) zooms in on the low-pressure domain of the adsorption isotherms of the three materials, evidencing that the micropore volume increases in the order Raney nickel ~ chemically leached sample < electrochemically leached sample.

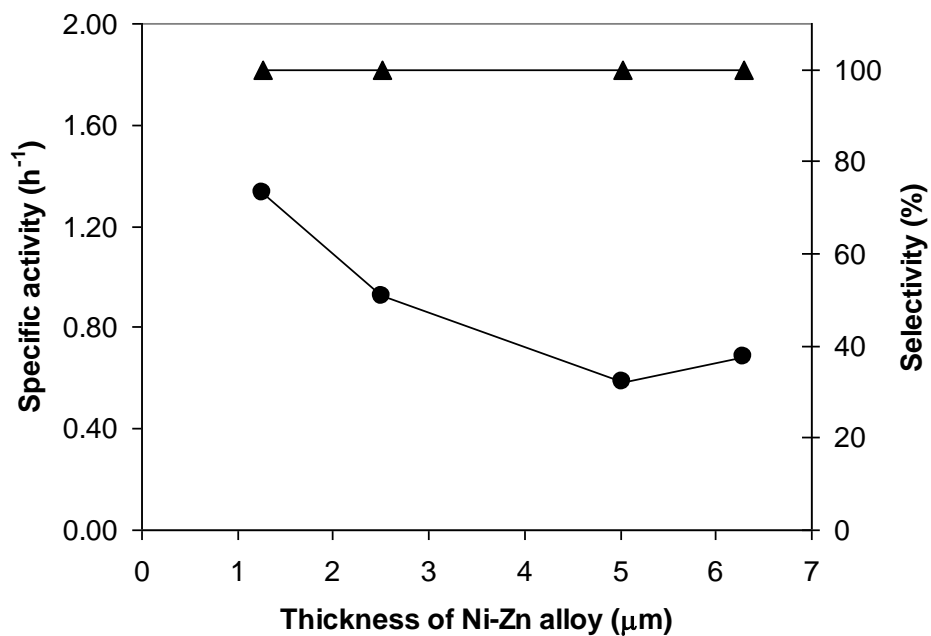


Figure S4. Effect of layer thickness of the nickel-zinc alloy on the (●) specific catalytic activity, and (▲) selectivity towards 1-phenylethanol in hydrogenation of acetophenone.

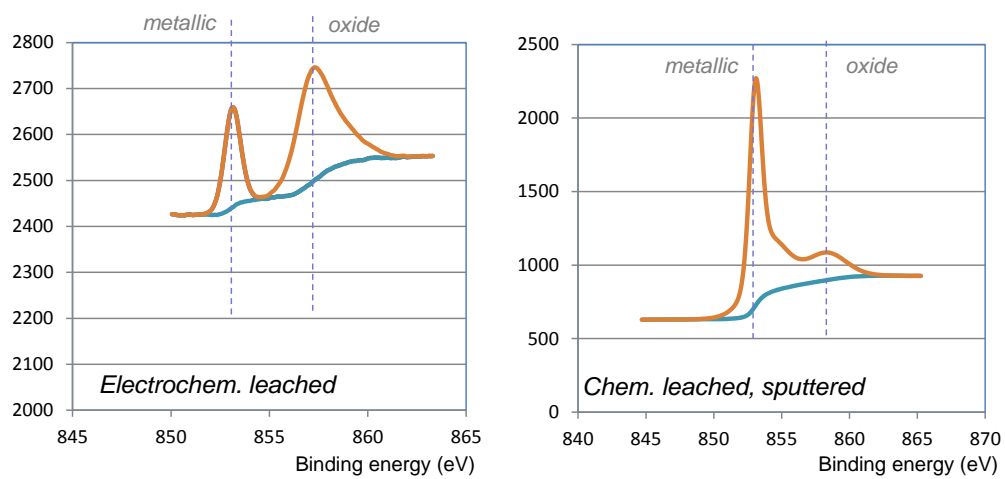


Figure S5. XPS spectra (in the Ni 2p_{3/2} domain) of (left) electrochemically leached catalyst, (right) chemically leached catalyst, after 100 s sputtering treatment.

Table S1. Bulk composition, surface area and catalytic activity of the gauze-supported porous nickel in hydrogenation of acetophenone. The catalysts are prepared from nickel-zinc alloy deposited at -1.5 V vs. Ni/Ni²⁺ followed by chemical or electrochemical removal of zinc. Data are for deposited layers of ~6 μm thickness.

Catalyst	Ni content of the alloy (wt.%, bulk phase)		Specific activity ^[a] (h ⁻¹)	Selectivity (%)	BET surface area (m ² /g _{alloy})
	As- deposited	After leaching			
1 Chemically leached Zn-Ni alloy	33	68 ^[b]	0.68	100	24
2 Electrochemically leached Zn-Ni alloy	33	78 ^[c]	0.33	100	64
3 Raney [®] 2800	—	89 ^[d]	0.62	67	30

[a] Defined as gram of acetophenone converted per gram of alloy; averaged over a period of 10 h.

[b] as studied by EDX: 90 wt.%.

[c] as studied by EDX: 83 wt.%.

[d] This elemental composition (wt. %) is obtained from the manufacturer: 89 % Ni, 9.5 % Al and 0.8 % of Fe.