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Supplementary Information

Directing the H_2-driven Selective Regeneration of NADH via Sn-doped Pt/SiO_2

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Experimental

Materials

β-Nicotinamide adenine dinucleotide hydrate (NAD^+, ≥ 96.5%), β-nicotinamide adenine dinucleotide reduced disodium salt hydrate (NADH, ≥ 94%), potassium phosphate monobasic (KH_2PO_4, ≥ 99%), potassium phosphate dibasic trihydrate ($K_2HPO_4 \cdot 3H_2O$, ≥ 99%), hexachloroplatinic acid solution (H_2PtCl_6, 8% in water), tin(II) chloride ($SnCl_2$, ≥ 99%), and silicon dioxide (SiO_2, 99.5%) were obtained from Sigma-Aldrich. EnzyChrom^{TM} NAD/NADH assay kit was purchased from Universal Biologicals. All the chemicals were used as received without further purification. The H_2 and N_2 gases of ultrahigh purity (≥ 99.99%) were supplied by BOC.

Catalyst Preparation and Characterisation

Pt-Sn/SiO_2 catalysts were prepared by wet impregnation whereby SiO_2 was co-impregnated with aqueous solutions of H_2PtCl_6 and $SnCl_2$. After impregnation, the mixture was heated to 80 °C until a slurry formed and then dried in static air overnight at 110 °C. The catalysts were calcined in static air at 500 °C for 4 hrs then reduced under 10 % H_2/N_2 at 500 °C for 4 hrs. In all cases, the Pt loading was fixed at 1 wt.% and the amount of Sn added is expressed in terms of nominal atomic percent. For example, Pt90 refers to a catalyst containing 90 at.% Pt and 10 at.% Sn supported on SiO_2. A 1 wt.% Pt/SiO_2 (Pt100) was also prepared by wet impregnation for comparison purposes.

CO chemisorption experiments were performed using a Thermo Scientific TPDRO 1100 at 35 °C. The catalysts (~0.1 g) were re-reduced in 5 % H_2/He (500 °C, 30 min) then flushed with He (500 °C, 30 min) and then cooled to 35 °C under He. Known volumes of CO (equating to ~2.3 μmoles) were pulsed over the catalysts until no further adsorption occurred. Blank experiments using SiO_2 and Sn/SiO_2 were performed and no CO uptake was observed. Transmission electron microscopy (TEM) was used to determine the particle size and morphology. A JEM-2100F was utilised at 200 kV and a minimum of 300 particles were measured to determine average particle sizes and size distributions histograms. STEM/EDX analysis was carried out using JEM-F200 (JOEL) Field Emission Transmission Electron Microscope at 200 kV. Metal loading was analysed by inductive coupled plasma emission spectrometer (ICP-OES, Varian VISTA-MPX). Aqua regia solution (HCl: HNO_3 = 3:1, v/v) was used to dissolve the metals while hydrofluoric acid (HF) was used for the SiO_2 support. The diffraction patterns were studied using X-Ray Diffraction (XRD) using a Rigaku D/max-2500 instrument (Cu Kα, 0.154 nm). Samples were scanned at 0.02° $step^{-1}$ over the range $10° \leq 2\theta° \leq 90°$ and the diffractograms identified against the JCPDS-ICDD database. Surface area and porosity were investigated with N_2 adsorption/desorption using a Micromeritics ASAP 2460 at -196 °C and the BET method was applied to determine the surface area. X-ray photoelectron spectroscopy (XPS) was carried out on a Perkin Elmer PHI 1600 using a monochromatic Al Kα source and a pass energy of 50 eV. ^1H NMR experiments were all performed in D_2O using an Advance III HD 400 Bruker Daltonics NMR at room temperature.

Catalyst Testing

Liquid phase hydrogenation of NAD^+ was carried out in a Parr-5500 Compact Reactor at ambient temperature (22 °C). In a typical reaction, NAD^+ was dissolved in 50 ml of 0.1 M, pH 7 phosphate buffer and then a specific mass of catalyst (0.005-0.020 g) was added, and then the mixture of reactant and catalyst was loaded into the reactor. The reactor was stirred at 900 rpm, flushed 3 times with 5 bar of N_2 then pressurised with 9 bar of H_2, initiating the reaction. Samples were taken using a non-invasive sampling system and the reactant and products were quantified using a combination of UV-Vis spectroscopy (Jenway 6850) and enzymatic assays as described in our previous work.[1] It is noteworthy that we have developed such analytical methods specifically for the experimental quantification of NAD^+/NADH systems allowing the calculation of conversion of NAD^+ (Eq. 1), selectivity (Eq. 2) of 1,4-NADH, 1,2-NADH and 1,6-NADH and material/carbon balance (±2% in this work). In the case of Pt100, other product(s), defined as unknown, can be determined by closing the mass balance. ^1H NMR was also employed in conjunction with the developed analytical method, whereby the reactions using Pt100 and Pt90 were repeated using a higher concentration of NAD^+, to ensure good visibility in the ^1H NMR spectra. Specifically, 6 mM of NAD^+ was dissolved in a 0.1 M, pH 7 phosphate buffer in D_2O and 40 mg of catalyst was used. After ~50 % conversion was achieved (determined by UV-Vis spectroscopy and enzymatic assays), the sample was taken and the ^1H NMR spectra was obtained. All the analyses were conducted on an Advance III HD 400 NMR from Bruker Daltonics (equipped with shielded z-gradient coils for gradient spectroscopy (GRASP)) at room temperature.

The activity of the catalysts was assessed using turnover frequency (TOF), calculated based on the moles of NAD^+ converted (in the initial 5 min of the reaction) over the moles of Pt active sites (determined by CO chemisorption). Conversion and selectivity were determined using the following equations, respectively. Blank tests using SiO_2 and Sn/SiO_2 were performed and both catalysts were inactive for the hydrogenation of NAD^+. Error bars were obtained from triplicate experiments.

$$X_{\mathrm{NAD^+}}\ (\%) = \frac{C_{\mathrm{NAD^+,initial}}\ (\mathrm{mM}) - C_{\mathrm{NAD^+,left}}\ (\mathrm{mM})}{C_{\mathrm{NAD^+,initial}}\ (\mathrm{mM})} \times 100 \tag{1}$$

$$Selectivity_{\mathrm{species}}\ (\%) = \frac{C_{\mathrm{species}}\ (\mathrm{mM})}{C_{\mathrm{NAD^+,reacted}}\ (\mathrm{mM})} \times 100 \tag{2}$$

Characterisation Figure

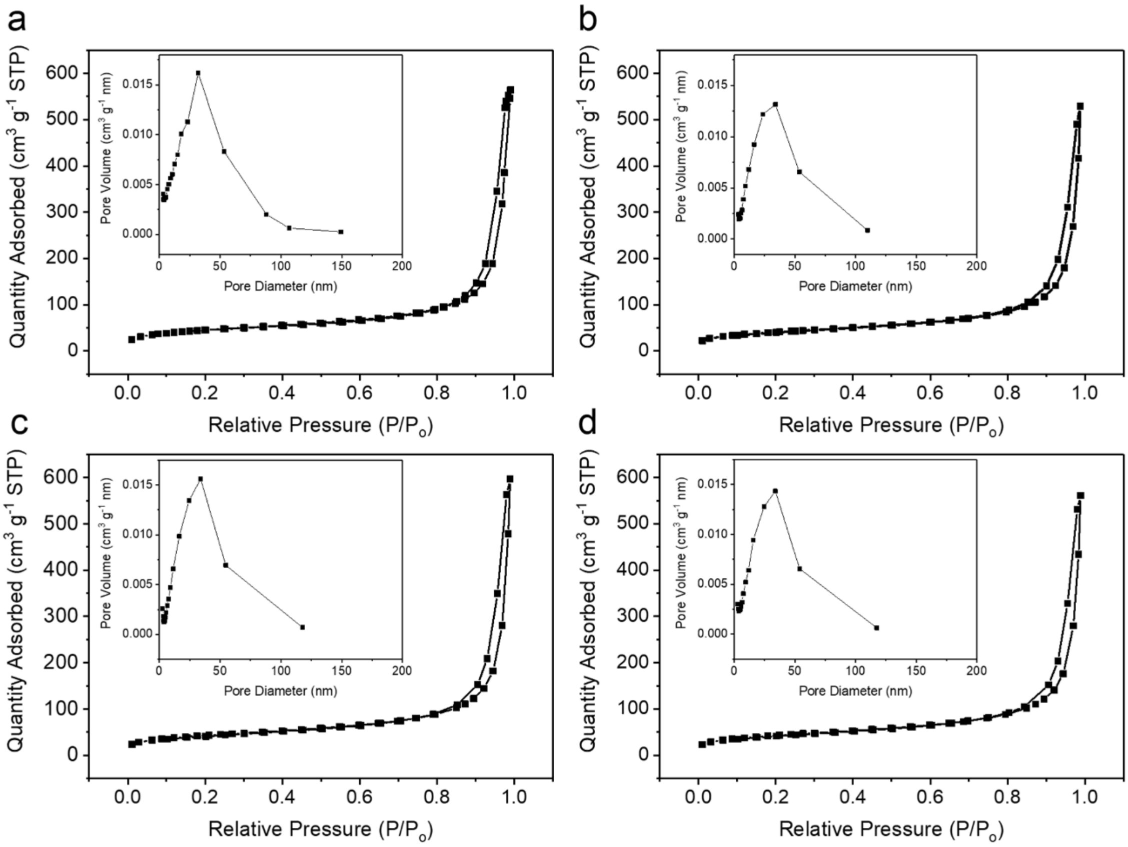

Figure S1: N_2 adsorption/desorption isotherms for (a) Pt100, (b) Pt90, (c) Pt75 and (d) Pt50. Inset: corresponding pore size distributions.

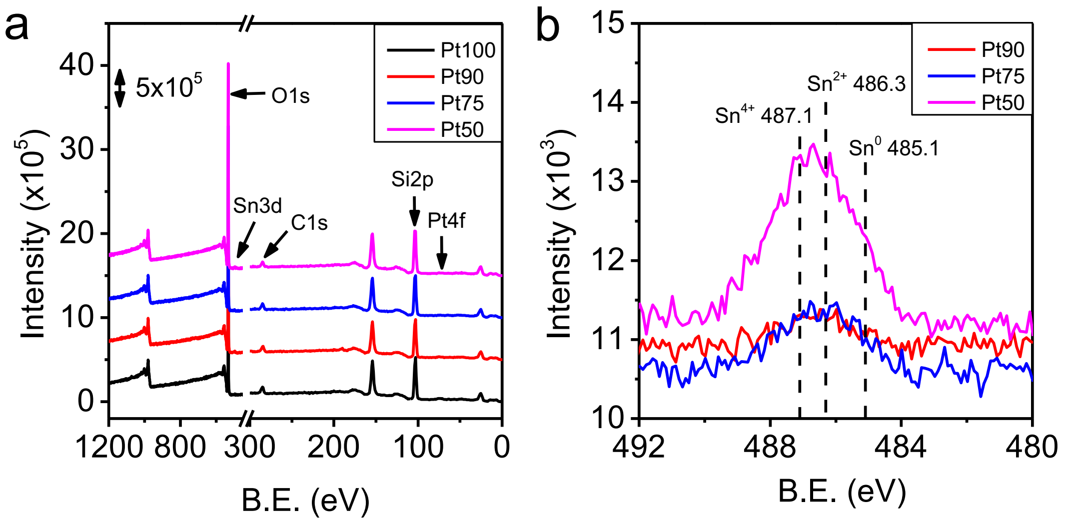

Figure S2: (a) Full XPS scans of catalysts and (b) spectra over the Sn 3d region.

The full scan XP spectra of Pt mono- and bi- metalic catalysts are shown in Figure S2(a). The detailed Sn 3d profiles (Figure S2(b)) have presented a high shift to 486.3 and 487.1 eV, corresponding to the positive charged Sn with valences of +2 and +4. Compared to the metalic Sn^0 state (485.1 eV), it evidenced the electron donation from Sn to Pt.[2] This is consistent with the Pt 4f results shown in the main text, where increasing Sn content lowers the oxidation state of Pt.

References:

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2. H. Rong, Z. Niu, Y. Zhao, H. Cheng, Z. Li, L. Ma, J. Li, S. Wei and Y. Li, *Chem. Eur. J.*, 2015, **21**, 12034-12041.