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## **Supporting Information**

## Heterogeneous Catalytic Hydrogenation of *N*-Benzyl Nicotinamide: A Comparative Study with Nicotinamide Adenine Dinucleotide

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Catalyst	Т	H <sub>2</sub> Pressure	Conversion	Yield	Selectivity	TOF	Ref.
	(°C)	(atm)	(%)	(%)	(%)	(/h)	
Pt/Al <sub>2</sub> O <sub>3</sub>	20	1.0	-	50	-	13	1
Pt/SiO <sub>2</sub>	37	10	80	23	20	1,600	2
Pt/C	37	10	80	28	25	1,123	2
Pt/MgO	37	10	50	12	17	990	2
Pt/TiO <sub>2</sub>	37	1.0	100	63	63	20	3
Sn-Pt/SiO <sub>2</sub>	22	8.9	100	88	90	514	4
Ni-TiO <sub>2</sub> /POP-Rh	37	4.9	100	-	91	16	5
NRase-Au/Pt NPs	20-25	0.9	20	20	>99	-	6

Table S1. Reports on 1,4-NADH Production from NAD<sup>+</sup> Hydrogenation Using Heterogeneous Catalysts

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Catalyst type Sacrificial reductant	Catalyst -	Reductant/ Electron mediator NaBH4	Conversion (%) -	Yield (%) 36	Selectivity (%)	TOF (/h) -	TON or TTON	Ref.
Molecular catalyst	CoCl(DMG)₂(py)	20 atm H <sub>2</sub>	-	57		0.285	5.7	8
Molecular catalyst	[Cp*Rh(bpy)H]	Formate	-	-	> 95 %	8	-	9
Photocatalyst	[lr(dFsppy)₃]	TEOA/ [Cp*Rh(bpy)] <sup>2+</sup>	64	64	> 99 %	7	6	10
Photocatalyst electrode	N-doped carbon nanodots	TEOA/ [Cp*Rh(bpy)] <sup>2+</sup>		100	> 99 %	33	15	11
Photocatalyst electrode	CoMoS	H <sub>2</sub> O	37	35	94	-	-	12
Supported metal catalyst	Pt/SiO <sub>2</sub>	H <sub>2</sub>	96	31	34	81	119	This work

## Table S2. Reports on 1,4-BNAH production from BNA<sup>+</sup> reduction.

Turnover Frequency (TOF), TOF (h<sup>-1</sup>) = 1,4-BNAH (mol)/catalyst (mol)/ t(h)

Turnover Number (TON), TON = 1,4-BNAH (mol)/catalyst (mol)



Fig. S1. The performance of light-driven regeneration of 1,4-NADH and 1,4-BNAH using N-doped carbon nanodots (N-CDs) as photocatalyst electrode, Rhodium-based complex,  $[Cp*Rh(Bpy)(H_2O)]^{2+}$ , as electron mediator (M), and triethanolamine (TEOA) for reductant. Determined by UV-Vis spectroscopic analysis after 5 min of reaction. TOF: turnover frequency; reaction conditions: N-CDs (0.10 mg mL<sup>-1</sup>), M (25 µmol L<sup>-1</sup>), and NAD<sup>+</sup> or BNA<sup>+</sup> (2 mmol L<sup>-1</sup>) in a TEOA buffer (500 mmol L<sup>-1</sup>, pH 7.5)<sup>(11)</sup>.



Fig. S2-1. Calibration curves for BNA<sup>+</sup> and 1.4-BNAH, respectively. The mobile phase consisted of a 1:1 (v/v) mixture of methanol and 100 mmol L<sup>-1</sup> potassium phosphate buffer (pH 7).



Fig. S2-2. Calibration curves for NAD<sup>+</sup> and 1,4-NADH, respectively. The mobile phase consisted of a 1:9 (v/v) mixture of methanol and 100 mmol L<sup>-1</sup> potassium phosphate buffer (pH 7).



Fig. S3-1. The mobile phase consisted of a 1:1 (v/v) mixture of methanol and 100 mmol  $L^{-1}$  potassium phosphate buffer (pH 7) for BNA<sup>+</sup>, and 1,4-BNAH. BNA<sup>+</sup> hydrogenation condition: BNA<sup>+</sup> (0.8 mmol  $L^{-1}$ ) was reacted in 20 mL of Tris-HCl buffer (0.1 mol  $L^{-1}$ , pH 8.8) using the Pt/SiO<sub>2</sub> catalyst (0.5 wt%, 10 mg) at 20°C under 1 atm of H<sub>2</sub>.



Fig. S3-2. The mobile phase consisted of a 1:9 (v/v) mixture of methanol and 100 mmol L<sup>-1</sup> potassium phosphate buffer (pH 7) for NAD<sup>+</sup>, and 1,4-NADH. NAD<sup>+</sup> hydrogenation condition: NAD<sup>+</sup> (1.5 mmol L<sup>-1</sup>) was reacted in 20 mL of Tris-HCl buffer (0.1 mol L<sup>-1</sup>, pH 8.8) with the Pt/SiO<sub>2</sub> catalyst (0.5 wt%, 10 mg) at 20°C under 1 atm of H<sub>2</sub>.



Fig. S4. Reaction solutions from left to right: 5, 10, 15, 30, and 60 mins.  $BNA^+$  (1.7 mmol  $L^{-1}$ ) was reacted in Tris-HCl buffer (0.1 mol  $L^{-1}$ , pH 8.8) using the 4wt% Pt/SiO<sub>2</sub> catalyst at 20°C under 1 atm of H<sub>2</sub>.



Fig. S5. A comparison of the yield ratios of 1,4-BNAH and 1,6-BNAH was conducted for the hydrogenation of BNA<sup>+</sup> using the Pt/SiO<sub>2</sub>. The reaction conditions were as follows: BNA<sup>+</sup> (1.7 mmol L<sup>-1</sup>) was reacted with the Pt/SiO<sub>2</sub> (4 wt%, 20 mg) in 80 mL of Tris-HCl Buffer (0.1 mol L<sup>-1</sup>, pH 8.8) at 20°C under 1 atm of H<sub>2</sub> for 45 min. For comparison, the BNA<sup>+</sup> hydrogenation using a Co complex (CoCl(DMG)<sub>2</sub>(py)) <sup>8</sup> and the chemical reduction using NaBH<sub>4</sub> <sup>7</sup>. The yields of 1,4-BNAH and 1,6-BNAH were determined by NMR.



Fig. S6.  $H_2$ -TPR measurement of 4, 1, and 0.5 wt% Pt/SiO<sub>2</sub>. Measurement conditions: The flow gas was 5%  $H_2$ /Ar at a flow rate of 30 mL min<sup>-1</sup>. Prior to the measurement, the sample was pre-treated at -30°C for 30 min. The temperature was then ramped from -30 to 250°C at a rate of 10°C min<sup>-1</sup>.

Table S3. Pt reduction degree of	f 4, 1	1, and 0.5 v	vt% Pt/	′SiO <sub>2</sub> by	/ H <sub>2</sub> -TPR	measurement
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	Catalyst	Pt amount	Total H <sub>2</sub> consumption	Pt reduction degree
	(g)	(mmol)	(mmol)	(%)
4 wt% Pt/SiO <sub>2</sub>	0.05	0.01	0.021	98
1 wt% Pt/SiO <sub>2</sub>	0.05	0.0026	0.0052	99
0.5 wt% Pt/SiO <sub>2</sub>	0.05	0.0013	0.0026	99

Assumption for estimation of metal reduction degrees: Pt is reduced near 293 K (PtO<sub>2</sub> +  $2H_2 \rightarrow$  Pt +  $2H_2O$ ).



Fig. S7. Time course of the BNA<sup>+</sup> hydrogenation (1.5 mmol L<sup>-1</sup>) in 20 mL of 0.1 mol L<sup>-1</sup> Tris-HCl buffer (pH 8.8) using H<sub>2</sub> pretreated Pt/SiO<sub>2</sub> catalysts, 4 wt% (5 mg), 1 wt% (20 mg), and 0.5 wt% (40 mg) at 20 °C under 1 atm H<sub>2</sub>.



Fig. S8. Comparison of the 1,4-BNAH production rate per Pt amount. Reaction conditions:  $BNA^+$  (1.5 mmol  $L^{-1}$ ) in 20 mL of 0.1 mol  $L^{-1}$  Tris-HCl buffer (pH 8.8) using H<sub>2</sub> pretreated Pt/SiO<sub>2</sub> catalysts. Blue bars: 4 wt% Pt/SiO<sub>2</sub> (5 and 10 mg); Gray bars: 1 wt% Pt/SiO<sub>2</sub> (10 mg); Orange bars: 0.5 wt% Pt/SiO<sub>2</sub> (40, 10, and 5 mg). All reactions were performed at 20 °C under 1 atm H<sub>2</sub>.

Table S4. CO pulse measurement of 4, 1, and 0.5 wt% Pt/SiO<sub>2</sub>

	Catalyst	CO adsorbed	Dispersion	Metal surface area		Pt Particle size
	(g)	(cm <sup>3</sup> g <sup>-1</sup> )	(%)	(m <sup>2</sup> g-catalyst <sup>-1</sup> )	(m g-Pt <sup>-1</sup> )	(nm)
4 wt% Pt/SiO <sub>2</sub>	0.10	1.3	29	2.9	71	3.9
1 wt% Pt/SiO <sub>2</sub>	0.10	0.44	38	1.0	95	2.9
0.5 wt% Pt/SiO <sub>2</sub>	0.10	0.24	41	0.51	101	2.8

The metal dispersion was calculated as the ratio of surface metal atoms (amount of CO adsorbed) to the total number of metal atoms introduced. These values were calculated based on the assumption that CO adsorbs on the Pt surface with a 1:1 stoichiometry and that the Pt particles are spherical. The metal dispersion was calculated by dividing the number of surface metal atoms by the total number of metal atoms introduced into the catalyst. The metal surface area and average metal particle size was calculated by using a Pt atomic weight of 195.08 g mol<sup>-1</sup>, a density of 21.45 g cm<sup>-3</sup>, and a metal cross-sectional area of 0.08 m<sup>2</sup> atom<sup>-1</sup>.



Fig. S9. Comparison of the 1,4-BNAH production rate per Pt surface active site. Reaction conditions:  $BNA^+$  (1.5 mmol  $L^{-1}$ ) in 20 mL of 0.1 mol  $L^{-1}$  Tris-HCl buffer (pH 8.8) using H<sub>2</sub> pretreated Pt/SiO<sub>2</sub> catalysts. Blue bars: 4 wt% Pt/SiO<sub>2</sub> (5 and 10 mg); Gray bars: 1 wt% Pt/SiO<sub>2</sub> (10 mg); Orange bars: 0.5 wt% Pt/SiO<sub>2</sub> (40, 10, and 5 mg). All reactions were performed at 20 °C under 1 atm H<sub>2</sub>.



Fig. S10-1. XRD patterns of  $H_2$ -pretreated  $Pt/SiO_2$  catalysts with Pt loadings of 4, 1, and 0.5 wt%.



Fig. S10-2. XRD patterns of  $H_2$ -pretreated Pt/SiO<sub>2</sub> catalysts (Pt loadings of 4, 1and 0.5wt%: black) and SiO<sub>2</sub> (blue). In the 2 $\theta$  = 35–50°, the 4, 1 and 0.5wt% Pt/SiO<sub>2</sub> catalysts were measured at scan rates of 0.5, 0.2 and 0.1°min<sup>-1</sup>, respectively. The orange XRD patterns on the right shows the difference profiles obtained by subtracting the SiO<sub>2</sub> pattern from each Pt/SiO<sub>2</sub> pattern.

	Pt particle size (nm)				
	Calculated from CO pulse measurement	Calculated from XRD patterns			
4wt% Pt/SiO <sub>2</sub>	3.9	3.7			
1wt% Pt/SiO <sub>2</sub>	2.9	2.8			
0.5wt% Pt/SiO <sub>2</sub>	2.8	2.6			

Table S5. Comparison of the Pt particle sizes determined by CO pulse measurements and from XRD patterns. The particlesizes derived from the XRD patterns were calculated using the Scherrer equation.



Fig. S11-1. Comparison of 1,4-BNAH production using  $BNA^+$  under different  $Pt/SiO_2$  catalyst loading amount. Reaction conditions:  $BNA^+$  (1.8 mmol L<sup>-1</sup>) in 20 mL of 0.1 mol L<sup>-1</sup> Tris–HCl buffer (pH 8.8) with 0.5 wt% H<sub>2</sub> pretreated  $Pt/SiO_2$  catalysts at loadings of 5, 10, and 40 mg. For the 5 mg catalyst, a 20 min reaction resulted in 18% conversion and a 3.8% yield and for the 40 mg catalyst, a 5 min reaction produced 26% conversion and a 6.9% yield.



Fig. S11-2. Comparison of 1,4-NADH production using Pt/SiO2 catalyst loadings. Reaction conditions: NAD+ (1.8 mmol L<sup>-1</sup>) in20 mL of 0.1 mol L<sup>-1</sup> Tris–HCl buffer (pH 8.8) using a 0.5 wt% H2-pretreated Pt/SiO2 catalyst at loadings of 5, 10, and 40 mg.For the 5 mg catalyst, a 30 min reaction resulted in 8.5% conversion and 0.7% yield; and for the 40 mg catalyst, a 3 minreactionproduced6.7%conversionand0.6%0.6%



Fig. S12-1. Comparison of 1,4-BNAH Production Rate under different Initial BNA<sup>+</sup> concentrations. Reaction conditions: BNA<sup>+</sup> (1.8, 1.0, or 0.4 mmol L<sup>-1</sup>) in 20 mL of 0.1 mol L<sup>-1</sup> Tris–HCl buffer (pH 8.8) using a 0.5 wt% H<sub>2</sub> pretreated Pt/SiO<sub>2</sub> catalyst (10 mg). For the 1.0 mmol L<sup>-1</sup> solution, a 6.5 min reaction yielded 25% conversion and 3.7% yield; for the 0.4 mmol L<sup>-1</sup> solution, a 9.5 min reaction resulted in 26% conversion and 2.8% yield.



Fig. S12-2. Comparison of 1,4-NADH production rate under Different Initial NAD<sup>+</sup> Concentrations. Reaction conditions: NAD<sup>+</sup> (1.8, 0.8, or 0.3 mmol L<sup>-1</sup>) in 20 mL of 0.1 mol L<sup>-1</sup> Tris-HCl buffer (pH 8.8) using a 0.5 wt% H<sub>2</sub>-pretreated Pt/SiO<sub>2</sub> catalyst (10 mg). For the 0.8 mmol L<sup>-1</sup> solution, a 15-min reaction yielded 11% conversion and 1.5% yield; for the 0.3 mmol L<sup>-1</sup> solution, a 5-min reaction resulted in 10% conversion and 1.0% yield.



Fig. S13-1. Comparison of 1,4-BNAH under different  $H_2$  pressure conditions. Reaction Conditions: A 1.8 mmol L<sup>-1</sup> BNA<sup>+</sup> solution (20 mL) in 0.1 mol L<sup>-1</sup> Tris–HCl buffer (pH 8.8) was reacted using a 0.5 wt%  $H_2$ -pretreated Pt/SiO<sub>2</sub> catalyst (10 mg) at 20 °C under  $H_2$  pressures of 1, 2, and 4 bar. At 2 bar, a 7-min reaction resulted in 25% conversion and 4.8% yield; similarly, at 4 bar, a 3-min reaction resulted in 17% conversion and 4.7% yield.



Fig. S13-2. Comparison of 1,4-NADH production under different  $H_2$  pressure conditions: Reaction Conditions: A 1.8 mmol L<sup>-1</sup> NAD<sup>+</sup> solution (20 mL) in 0.1 mol L<sup>-1</sup> Tris–HCl buffer (pH 8.8) was reacted using a 0.5 wt%  $H_2$ -pretreated Pt/SiO<sub>2</sub> catalyst (10 mg) at 20 °C under  $H_2$  pressures of 1, 2, and 4 bar. At 2 bar, a 10-min reaction yielded 6.8% conversion and 1.1% yield; similarly, at 4 bar, a 4-min reaction resulted in 11% conversion and 0.8% yield.

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