

Supporting Information for

Nanocrystalline Pt-CeO₂ as an efficient catalyst for room temperature selective reduction of nitroarenes

Astha Shukla,^a Rajib Kumar Singha,^a Takehiko Sasaki,^b Rajaram Bal*^a

Material:

Ce(NO₃)₃·6H₂O, [Pt(NH₃)₄](NO₃)₂, PVP(Polyvinylpyrrolidone), Commercial CeO₂ were purchased from Sigma-Aldrich. While cetyltrimethylammoniumbromide (CTAB), Na₂CO₃, ethanol, hydrazine, etc. were purchased from Merck KGaA, Darmstadt, Germany. *p*-nitrophenol and other nitro compounds were purchased from Sigma Aldrich with 99.9% purity. Double distilled water was prepared with a BOROSIL® water distillation unit. All the chemicals were used without further purification.

Catalyst characterization:

The surface morphology, particle size, and elementary composition of prepared catalyst was investigated by various characterization techniques such as by XRD, ICP-AES, XPS, SEM, TEM, EXAFS and BET-surface area measurements. Powder X-ray diffraction patterns were recorded on a Rigaku- Geigerflex X-ray diffractometer fitted with a Cu K α radiation as a source. Diffraction patterns in the 5°–80° region were recorded with a 0.04 step size (step time = 4 s). The surface area of the catalyst was analyzed by N₂ adsorption-desorption isotherms at –196°C (BelsorbMax, BEL, Japan). SEM images were taken on a FEI Quanta 200 F, using a tungsten filament doped with lanthanumhexaboride (LaB₆) as an X-ray source, fitted with an ETD detector with high vacuum mode, using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same

spectrophotometer. TEM images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. X-Ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-Alpha X-Ray photoelectron spectrometer and binding energies (± 0.1 eV) were determined with respect to the position of the C 1s peak at 284.8 eV. EXAFS measurements of the Cu K-edge were carried out at the High Energy Accelerator Research Organization (KEK-IMMS-PF). The measurement was made in transition mode and spectra were taken at BL-7C and BL-9C. The electron storage ring was operated at 2.5 GeV and 450 mA, synchrotron radiation from the storage ring was monochromatized by a Si (111) channel cut crystal. The ionized chambers, which were used as detectors for the incident X-ray (I_0) and transmitted X-ray (I), were filled with N_2 gas mixture, respectively. The angle of the monochromators was calibrated with Cu foil. The EXAFS raw data were analyzed with UWXAFS analysis package,¹ including background subtraction program AUTOBK² and curve fitting program FEFFIT.³ The amplitude reducing factor, S_0^2 was fixed at 1.0. The backscattering amplitude and phase shift were calculated theoretically by FEFF 8.4 code.⁴ ATOMS⁵ was used to obtain the FEFF input code for the crystalline materials. Inductively coupled Plasma Atomic Emission Spectroscopic (ICP-AES) analysis was carried out by Inductively Coupled Plasma Atomic Emission Spectrometer; model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA).

Catalytic hydrogenation of *p*-nitrophenol and their nitro derivatives:

Chemoselective reduction experiments were conducted in a batch mode, in a 25ml stainless steel autoclave (Parr reactor, USA) at 25°C. The reactor was equipped with a magnetically driven stirrer, a dip tube and a water cooling system. In a typical experiment, 0.050g catalyst was added to 1gm substrate, dissolved in 10ml solvent contains ethanol and distilled water (2:1mole ratio). Then the system was purged with H_2 four times to remove the air and the system was pressurized with 1.5MPa H_2 with 800 rpm stirring speed. Aliquots (liquid and gas) were withdrawn through the special sample port attached within the reactor. At the end of the reaction, the reaction pressure was released very slowly. The catalyst particles were separated by filtration and the product was identified by GC-MS and was analyzed by Gas Chromatography (Agilent 7890) having HP-5 (length 30m, id.0.28mm,0.25 μ m film thickness) column equipped with flame ionization detector. Conversion was calculated by

[moles of reactant reacted] / [initial moles of reactant used] x 100 and selectivity of products was calculated by [total moles of product formed]/[total moles of reactant converted] x100 by drawing a calibration curve using authentic samples. At the end of the reaction, solid catalyst was isolated by means of filtration and washed with acetone, dried at ambient temperature for the further use.

1. E. A. Stern, M. Newvill, B. Ravel, Y. Yacoby and D. Haskel, *Phys. B*, 1995, **117**, 208.
2. M. Newvill, P. Livins, Y. Yacoby, E. A. Stern and J. Rehr, *J. Phys. Rev. B: Condens. Matter*, 1993, **47**, 14126.
3. A. L. Ankudinov, B. Ravel, J. J. Rehr and S. D. Conradson, *Phys. Rev. B: Condens. Matter*, 1998, **58**, 7565.
4. A. L. Ankudinov, A. I. Nesvizhskii and J. Rehr, *J. Phys. Rev. B: Condens. Matter*, 2003, **67**, 115120.
5. R. Ravel, *J. Synchrotron Radiat.*, 2001, **8**, 314.

Figure S1

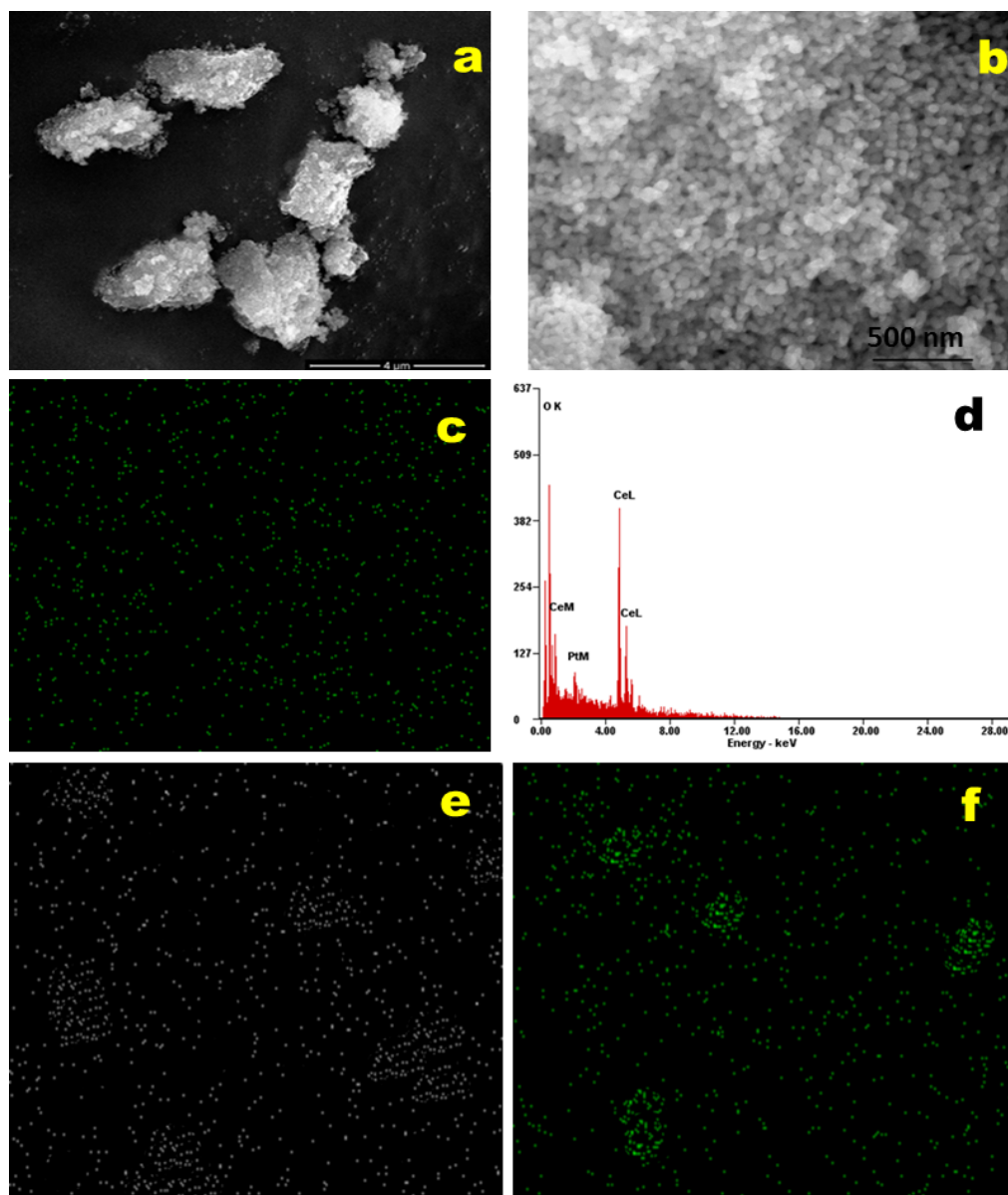


Fig.S1 SEM image of (a) commercial Pt-CeO₂, (b) 0.9% Pt-CeO₂ (c) Elemental mapping of Pt of prepared 0.9% Pt-CeO₂ (d) EDX pattern of 0.9%Pt-CeO₂ catalyst, (e) Elemental mapping of Pt of 1%Pt-CeO₂^{Imp} and (f) Elemental mapping of Pt of 1%Pt-CeO₂^{CoPre}.

Figure S2

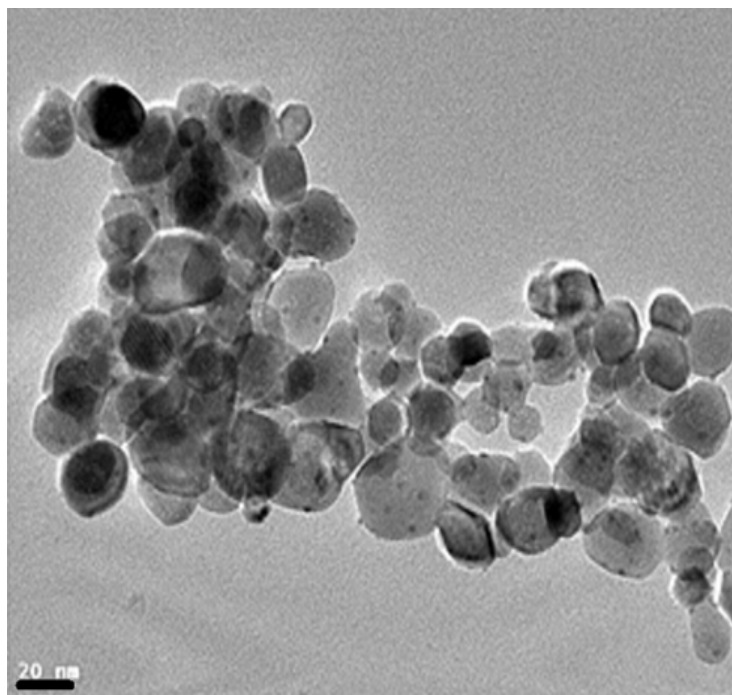


Fig. S2 TEM image of spent catalyst after 5 reuses.

Figure S3

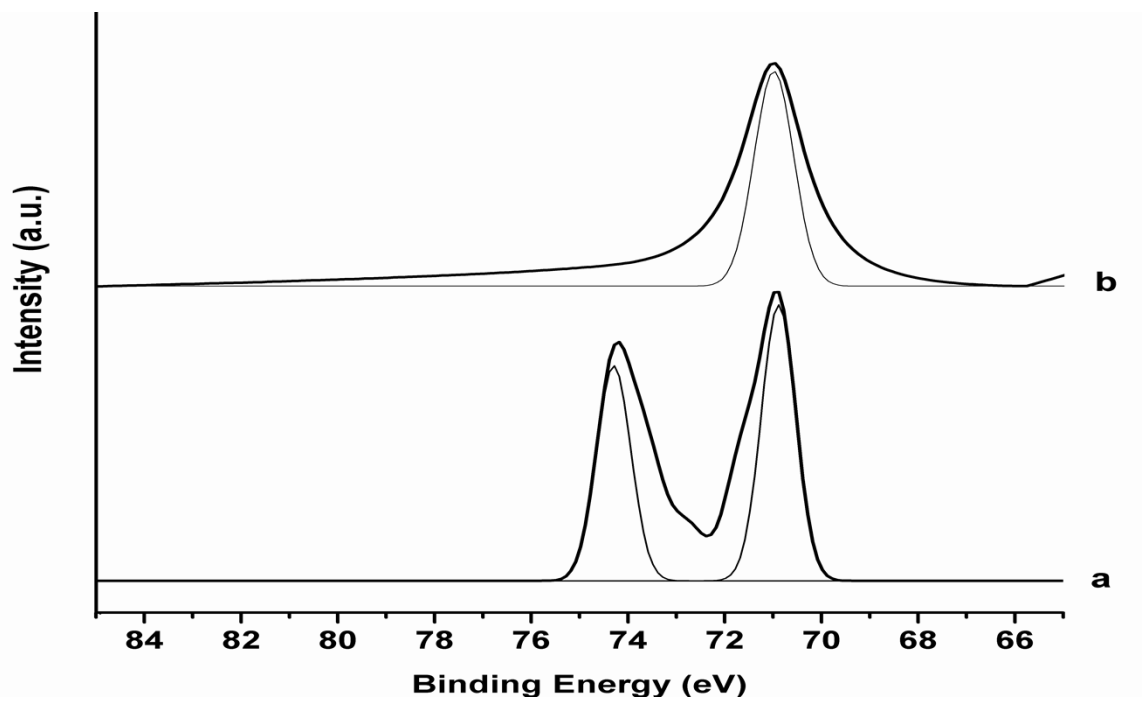


Fig. S3 XPS pattern of Pt4f core levels of 0.9%Pt-CeO₂ catalyst a) fresh catalyst b) spent catalyst.

Figure S4

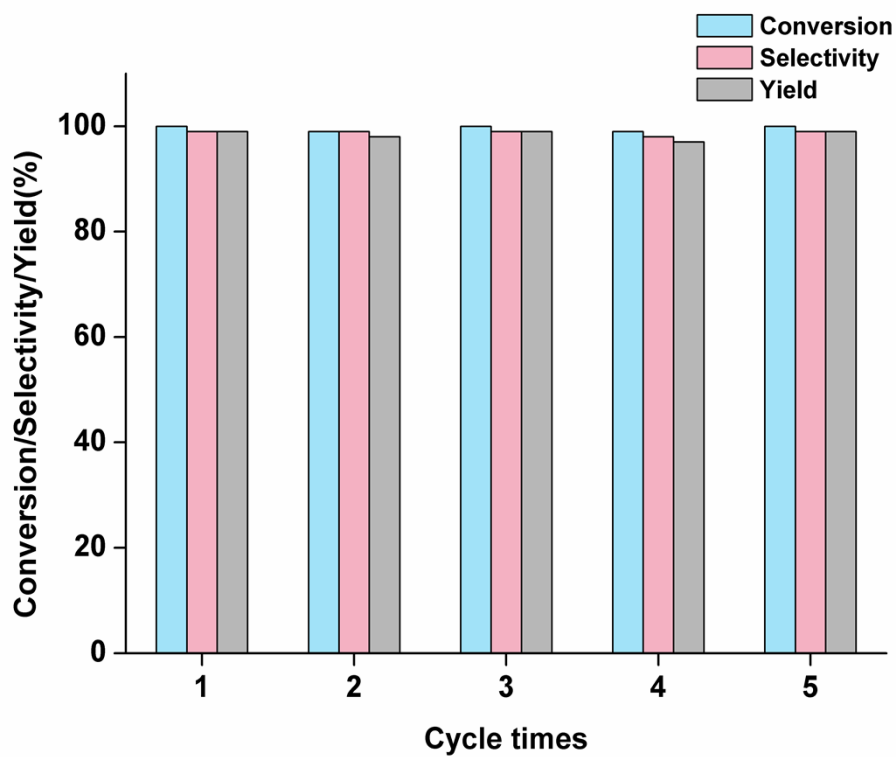
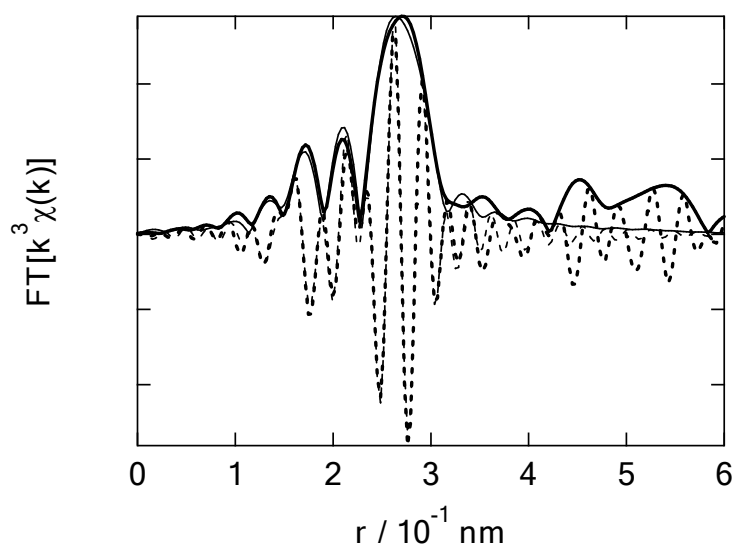


Fig. S4 Recyclability tests of chemoselective reduction of *p*-nitrophenol to *p*-aminophenol.

Figure S5 EXAFS spectra

(a) Fresh catalyst



(b) Spent catalyst

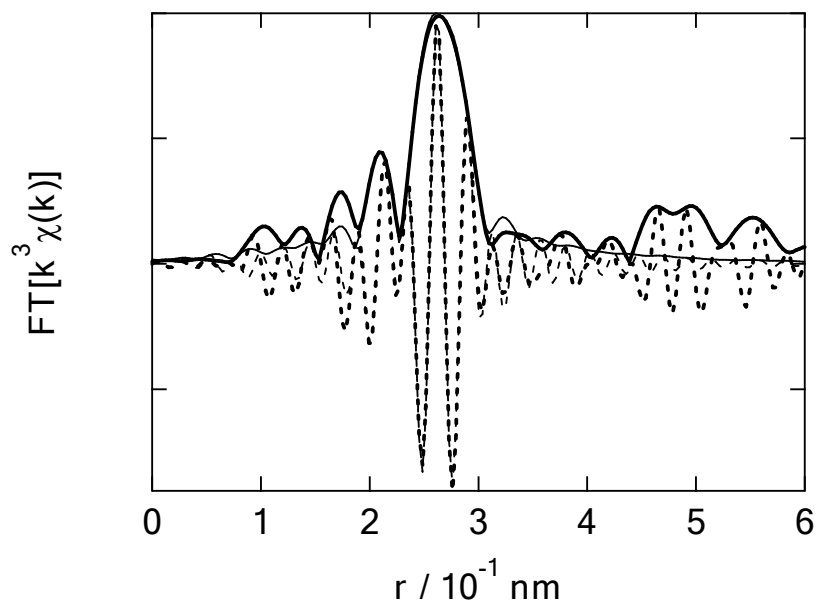


Table1 Activities of different catalyst on *p*-nitrophenol hydrogenation to *p*-aminophenol.

Entry	Catalyst	Catalyst loading (wt%)	Time (h)	C _{PNP} (%)	Selectivity(%)		Y _{PAP} (%)
					PAP	Others	
1	CeO ₂ ^{Com.}	-	6	-	-	-	-
2	PtCeO ₂ ^{Imp.}	1	6	-	-	-	-
3	PtCeO ₂ ^{CoPre.}	1	6	-	-	-	-
4	Pt-ZnO	1	6	12	75	25	9
5	Pt-TiO ₂	1	6	15	82	18	12.3
6	Pt-CeO ₂ ^{NCo.}	1	6	45	95	5	42.8
7	Pt-CeO ₂	0.5	6	50	99	1	49.5

8	Pt- CeO ₂	0.9	6	100	99	1	99
9	Pt- CeO ₂	1.9	6	95	90	10	85.5
10	Pt-CeO ₂	2.8	6	90	85	15	76.5
11	Pt- CeO ₂ ^{NSP}	0.9	5	100	99	1	99
12	Pt- CeO ₂ ^{HAP}	0.9	3	100	99	1	99
13	PtCeO ₂ ^r	0.9	6	100	99	1	99
14	PtCeO ₂ ^d	1	6	-	-	-	-

Reaction conditions: Substrate (*p*-nitrophenol) = 1gm; solvent (ethanol+ water) = 2:1; 25°C; time = 6h ; H₂ = 1.5MPa; Catalyst used is 5wt %, C_{PNP}(%):conversion of PNP based on FID – GC result = moles of PNP reacted/initial moles of PNP used] × 100; S(%): selectivity of product calculated by total moles of product formed/total moles of PAP converted ×100; Y_{PAP}: yield of PAP= conversion × selectivity/100; Com. = commercial; Imp.=impregnation method on comm. CeO₂ powder; NCo. = nanoparticles by post synthesis over commercial CeO₂; CoPre. = co-precipitation method; NSP = 4-nitrosophenol; HAP = 4-(hydroxyamino) phenol; ^d Pt loading on CeO₂ support prepared by different method; PAP:*p*-aminophenol; Others: nitroso or hydroxyamino phenol; ^r Catalyst after 5 reuses.

Table 2 Reactivities of the nitro- compounds over 0.9%Pt-CeO₂.

Entry	Substrate	Product	C _R . (%)	Selectivity(%)		Y _P (%)
				S _a	Others	
1	Nitrobenzene	Aniline	100	98	2	98
2	<i>p</i> -Nitro phenol	<i>p</i> -Amino phenol	100	99	1	99
3	<i>p</i> -Nitro benzaldehyde	<i>p</i> -Amino benzaldehyde	100	99	1	99
4	<i>p</i> -Nitro benzoic acid	<i>p</i> -Amino benzoic acid	100	99	1	99
5	<i>m</i> -Chloro nitrobenzene	<i>m</i> -Chloro aminobenzene	100	99	1	99
6	<i>p</i> -Dinitro benzene	<i>p</i> -Diamino benzene	100	98	2	98

7	<i>p</i> -Nitro toluene	<i>p</i> -Amino toluene	100	98	2	98
8	3-Methoxy nitrobenzene	3-Methoxy aminobenzene	100	98	2	98
9	4-Hydroxy-3-methoxy nitrobenzene	4-Hydroxy-3-methoxy aminobenzene	100	97	3	97

Reaction conditions: Substrates = 1gm; solvent (ethanol + water) = 2:1; catalyst used is 5wt % (0.9%Pt CeO₂); 25°C; time = 6h; H₂ = 1.5MPa; C_R(%): Conversion of reactant; S_a: Selectivity of aminocompounds; Others: nitroso or hydroxyamino compounds; Y_P(%):Yield of product.

Table 3 Comparative table of different reported catalysts (using hazardous chemicals, high temperature, organic solvents etc.)

Entry	Catalysts	Solvent /Temp.	Hydrogen source	Yield (%)	References
1	Au-Al ₂ O ₃ (Al ₂ O ₃ -BT- AuNPs)	H ₂ O, RT	NaBH ₄	95.1	Xin Huang, Xuepin Liao, and Bi Shi, <i>Green Chem.</i> , 2011, 13, 2801–2805
2	SS-Pt (solid supported platinum(0))	PEG400 / 60°C	N ₂ H ₄ .H ₂ O	92	Arun K. Shila, and Pralay Das, <i>Green Chem.</i> , 2013, 15, 3421–3428
3	Pt–Au/TiO ₂	EtOH / 60°C	H ₂	100	Daiping He, Xiangdong Jiao, Ping Jiang, Jian Wang and Bo-Qing Xu, <i>Green Chem.</i> , 2012, 14, 111–116
4	Au/ZrO ₂	EtOH /150°C	H ₂	99.4	Daiping He, Hui Shi, Yu Wu and Bo-Qing Xu, <i>Green Chem.</i> , 2007, 9, 849-851.

5	Zn-Pc Zinc (phthalocyanine with PEG-400)	PEG40 0/ 100°C	N ₂ H ₄ .H ₂ O	99	Upendra Sharma, Neeraj Kumar, Praveen Kumar Verma, Vishal Kumar and Bikram Singh, <i>Green Chem.</i> , 2012, 14, 2289–2293
6	Au-MgO	H ₂ O / RT	NaBH ₄	55-99	Keya Layek, M. Lakshmi Kantam, Masayuki Shirai, Daisuke Nishio-Hamane, Takehiko Sasaki and H. Maheswaran, <i>Green Chem.</i> , 2012, 14, 3164–3174
7	Au-SiO ₂	EtOH/ 140°C	NaBH ₄	95-98	Y. Y. Chen, J. S. Qiu, X. K. Wang and J. H. Xiu, <i>J. Catal.</i> , 2006, 242, 227.
8	Au/Fe(OH) _x	EtOH/ 90°C	H ₂	nd	Lequan Liu, Botao Qiao, Yubo Ma, Juan Zhang and Youquan Deng, <i>Dalton Trans.</i> , 2008, 2542–2548
9	Pt/Cu, Pd/Cu, Pd/Au, Pt/Au, and Au/Cu DENs (bimetallic Nps using dendrimer- encapsulation synthesis route).	H ₂ O/ /H ₂ O	NaBH ₄	92-99	Zachary D. Pozun, Stacia E. Rodenbusch, Emily Keller, Kelly Tran, Wenjie Tang, Keith J. Stevenson, and Graeme Henkelman <i>J. Phys. Chem. C</i> , 2013, 117, 7598–7604.
10	Au-TiO ₂	EtOH /H ₂ O	NaBH ₄	90-96	Ioannis Tamiolakis, Stella Fountoulaki, Nikolaos Vordos, Ioannis N. Lykakis and Gerasimos S. Armatas, <i>J. Mater. Chem. A</i> , 2013, 1, 14311–14319
11	Au/TiO ₂	THF/ 140°C	H ₂	nd	A. Corma and P. Serna, <i>Science</i> , 2006, 313, 332.
12	Au-α-Fe ₂ O ₃	H ₂ O / RT	NaBH ₄	100	Shao-Wen Cao, Jun Fang, Mohammad Mehdi Shahjamali, Zheng Wang, Zhen Yin, Yanhui Yang, Freddy Y. C. Boey, James Barber, Say Chye Joachim Loo and Can Xue, <i>CrystEngComm</i> , 2012, 14, 7229–7235

13	γ -Fe ₂ O ₃ -polymer composites	EtOH / 85°C	N ₂ H ₄ .H ₂ O	74.7	Xianmo Gu, Zhenhua Sun, Shuchang Wu, Wei Qi, Haihua Wang, Xianzhu Xu and Dangsheng Su <i>Chem. Commun.</i> , 2013, 49, 10088—10090.
14	NiPd-colloid	THF / 80-100°C	H ₂	99	Robert Raja, Vladimir B. Golovko, John M. Thomas, Angel Berenguer-Murcia, Wuzong Zhou, Songhai Xie and Brian F. G. Johnson, <i>Chem. Commun.</i> , 2005, 2026–2028.
15	Pt-CeO ₂	EtOH-H ₂ O/ RT	H ₂	98	This work