SUPPORTING INFORMATION

Mesoporous Silica Nanospheres Supported Platinum Nanoparticles (Pt@MSN): One-pot Synthesis and Catalytic Hydrogen Generation

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Chemicals

Cetyltrimethylammonium bromide (≥99.0%), Ammonia solution (28%), TEOS (98%), potassium hexachloroplatinate (VI) (Pt 39.1%), sodium borohydride (≥99.0%) and sodium hydroxide (≥99.0%) were purchased from Sigma Aldrich and were used as received. Ethanol was distilled before use. Deionize water was used as solvent in all the experiments.

Catalyst synthesis

Catalyst was synthesized by following a procedure given in literature, used for palladium.[1] In a typical procedure, 67.5mg (0.0185 mmole) CTAB was dissolved in 30 mL deionized water and suitable amount of liquid ammonia (28 wt %) was added to adjust the pH to 10~12. This solution was heated at 60 ^{o}C for 30 minutes. 1 mL TEOS was dropped into flask with constant stirring, after another stirring of 30 minutes suitable amount of 0.01 M K_2PtCl_6 (VI) was dropped slowly and continued to react for another 2h. After the reaction product was separated via sonication and collected through centrifugation. The product was washed with ethanol and dried at 80 ^{o}C for 10 h. Finally, the powder was calcined in air at 550 ^{o}C for 6 h to remove the organic materials, and then continued to reduce under reducing mixture of 4% H_2 + 96% Ar at 450 ^{o}C for 4h.[1]

Instrumental analysis

The microstructure of the catalysts was determined using TEM (Varian LEO 9220 (200 kV). Functional groups were identified by using BRUKER ALPHA FT-IR. Specific surface area was measured using Quantachrome (NOVA 2000 e) surface area and pore size analyzer. Silica kernel with cylindrical pore morphology and NLDFT (equilibrium mode) were used for the calculation of pore volume and pore size. Powder XRD analysis was carried out on BRUKER D2 PHASER XRD equipped with CuKα radiation (30kV, 10mA) over the range of 10-80°.

Catalytic studies

Catalytic tests were performed by using base-stabilized aqueous solution of $NaBH_4$. All catalytic tests were carried out at a given temperature for two hours under an inert atmosphere. Hydrogen gas, the only gaseous product was measured by gas evolution measurement apparatus (CG-1818, Chemglass, USA). The catalytic activity was accessed in terms of hydrogen generation rate (HGR) and turnover frequencies (TOF) using theoretical metal loading. HGR was recorded as volume of hydrogen gas in liters produced per minute per gram of the metal (L/min/g).

TON and TOF (hr^{-1}) as described by Beller *et al.* [2] were calculated as follows;

$$TON = \frac{V_{observed} - V_{blank}}{V_{m,H_2,25°C} \times n_{catalyst}}$$

Supplementary equation S1

$V_{observed}$: vol. of gas measured from gas burette (ml)

V_{blank}: blank volume (ml)

V_m: molar gas volume (ml/mmol)

$n_{catalyst}$: amount of catalyst (mmol)

Molar gas volume of gas as calculated by Van der Waal's equation as;

$$V_{m,H_2,25°C} = \frac{RT}{\rho} + b - \frac{a}{RT} = 24.49 mmol/mL$$

Supplementary equation S2

Where

R: 8.3145 m^3 Pa.mol^{-1}.K^{-1}

T: 298.15 K

p: 101325 Pa

a: 2.49×10^{-10} Pa·m^3.mol^{-2}

b: 26.7×10^{-6} m^3.mol^{-1}

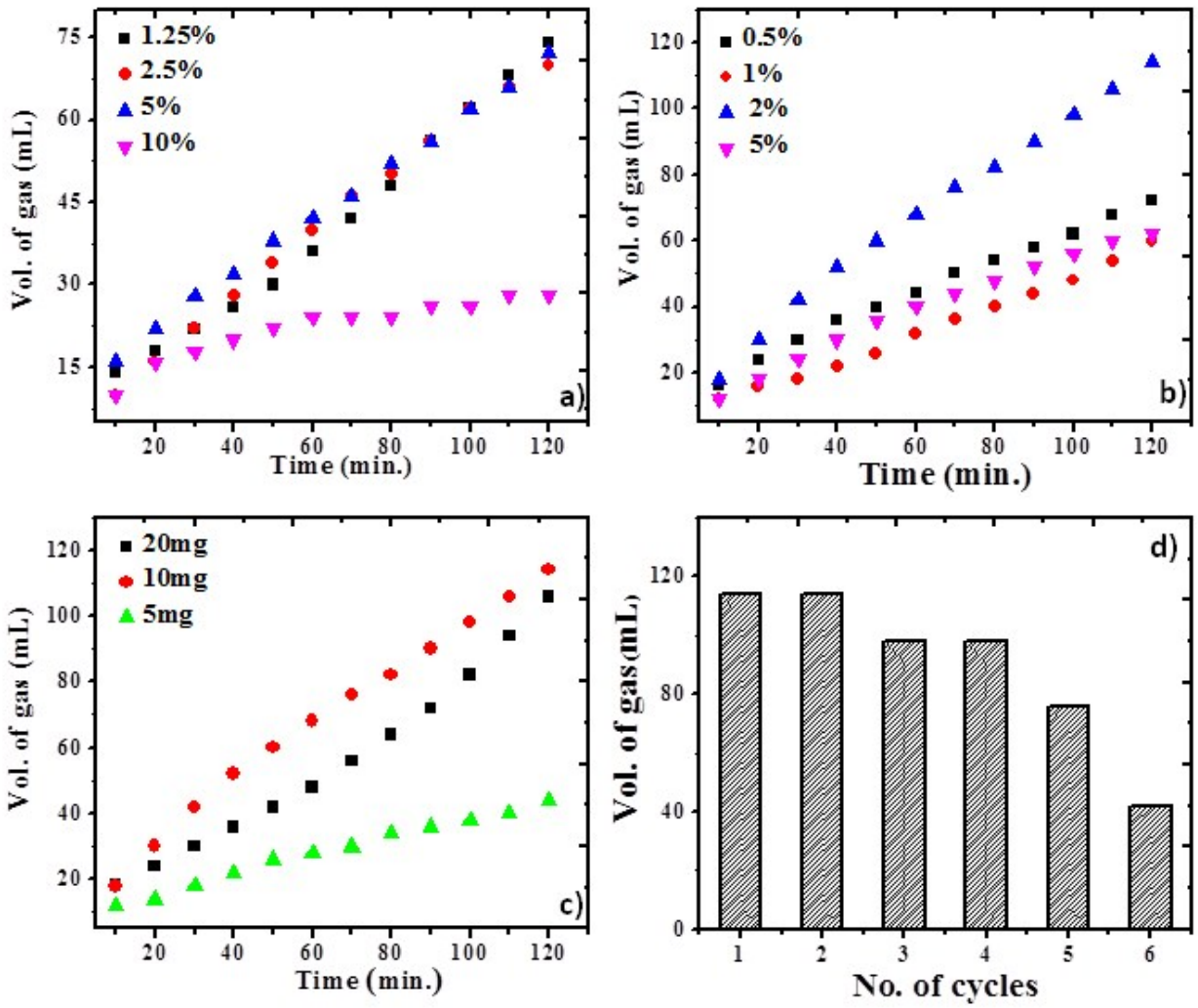

Figure S1. Effect of various parameters on the rate of hydrolysis of $NaBH_4$

a) $NaBH_4$ concentration; **b)** NaOH concentration; **c)** catalyst dose **d**) recycling studies with MI-3

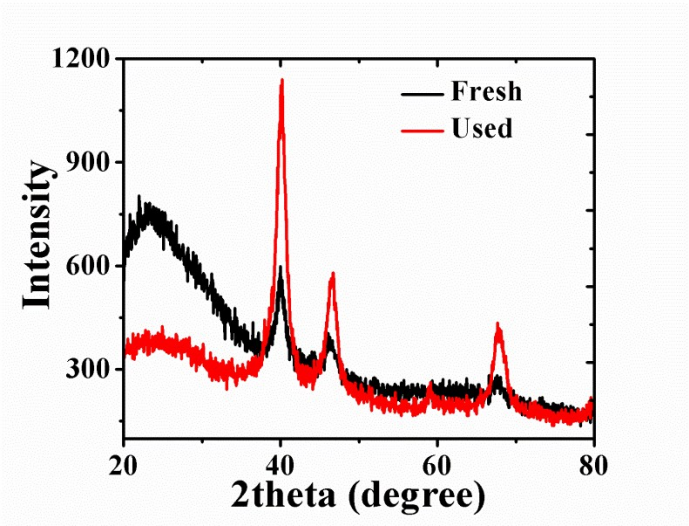

Figure S2 Powder XRD of the fresh and used catalyst (MI-3). Particle sizes: Fresh 14.4 nm, used: 29 nm

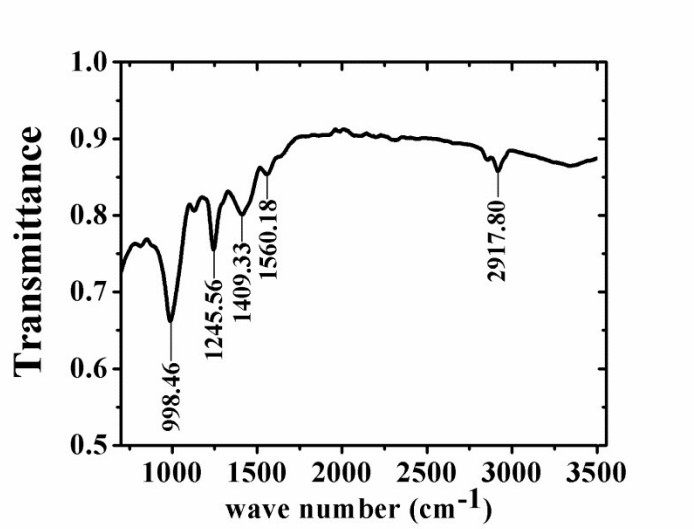

Figure S3 FT-IR of the used catalyst (MI-3) after 5 cycles. Adsorption bands at 1600-1200 cm^{-1} could be attributed to stretching of B-O bond.[3]

Table S1 TOFs and TONs along with the HGR at various metal loading

Entry	Metal loading (%)	TON	TOF (hr^{-1})	HGR ($Lmin^{-1}g^{-1}Pt$)	% Yield
1	MI-1	69.7	34.87	0.445	4.7
2	MI-2	257.14	128.57	0.471	4.7
3	MI-3	416.67	208.33	0.872	12.7

Table S2 TOFs and TONs along with the HGR at variable concentration of $NaBH_4$

Entry	Conc. of $NaBH_4$ (wt.%)	TON	TOF (hr^{-1})	HGR ($Lmin^{-1}g^{-1}Pt$)	% Yield
1	1.25	616.67	308.45	0.582	8.2
2	2.5	583.56	219.78	0.576	7.8
3	5	950.38	475.19	0.872	12.7
4	10	250.71	125.35	0.156	3.1

Table S3 TOFs and TONs along with the HGR at variable concentration of NaOH

Entry	Conc. of NaOH (wt.%)	TON	TOF (hr^{-1})	HGR ($Lmin^{-1}g^{-1}Pt$)	% Yield
1	0.5	600.24	300.12	0.507	8
2	1	500.2	250.1	0.45	6.9
3	2	950.38	475.19	0.872	12.7
4	5	555.15	277.57	0.511	7.1

Table S4 TOFs and TONs along with the HGR at various temperatures

Entry	Temperature (^oC)	TON	TOF (hr^{-1})	HGR ($Lmin^{-1}g^{-1}Pt$)	% Yield
1	25	950.38	475.19	0.872	12.7
2	35	1250.05	625.25	1.13	16.7
3	45	2417.03	1208.82	2.3	32.3
4	55	3418.02	1709.01	3.33	45.7
5	**65**	**5635.58**	**2817.79**	**5.74**	**75.4**
6*	**80**	**22549**	**11274.5**	**19.1**	**30.8**
7‖	80	6821.84	3410.92	6.7	84.9

*$NaBH_4$ (12 wt%, 1mL), NaOH (2 wt%), catalyst (5 µmole Pt), ‖ $NaBH_4$ (5 wt%, 1mL), NaOH (2 wt%), catalyst (5 µmole Pt),

Table S5 TOFs and TONs along with the HGR at various catalyst doses

Entry	Catalyst dose (mg)	TON	TOF (hr^{-1})	HGR ($Lmin^{-1}g^{-1}Pt$)	% Yield
1	5	73.06	36.5	0.598	4.9
2	10	950.38	475.19	0.872	12.7
3	20	416.67	208.33	0.403	11.8

Table S6 TOFs and TONs of Pt@MSN as compared with the others reported in the literature.

Entry	Catalyst	T(°C)	E_a(KJ.mol^{-1})	HGR(L.min^{-1}g^{-1}Pt)	TOF(h^{-1})	Reference
1	Pt@$LiCoO_2$	25°C	70.4	0.05		[19]
2	**Pt@MSN**	**25**	**40.1**	**0.8**	**457.19**	**This paper**
3	Pt@SiO_2	25	-	-	158.6	[17]
4	Pt@Al_2O_3	40		0.2	-	[36]
5	Pt@C	40		0.7		[36]
6	Pt@Si_3N_4	80	-	13.5		[18]
7	Pt@CMK-3	80	-	2.6		[18]
8	**Pt@MSN**	**80**	**40.1**	**19.1**	**11274.5**	**This paper**

References

1. X.-J. Lin, A.-Z. Zhong, Y.-B. Sun, X. Zhang, W.-G. Song, R.-W. Lu, A.-M. Cao and L.-J. Wan, *Chem. Commun.*, 2015, **51**, 7482–7485.
2. M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali and M. Beller, *Nature*, 2013, **495**, 85–89.
3. http://webbook.nist.gov/cgi/cbook.cgi?ID=B6000451&Mask=80#IR-Spec (accessed on January 06, 2016)