Understanding the Roles of Stabilizers and Reductants on Soluble Pt Nanoparticle Catalysts for Highly Efficient Hydrogenation of Benzoic Acid under Mild Condition

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S.1. Synthesis of SPtNP catalysts:

For the synthesis of SPtNP catalysts, in a round bottle, Dihydrogen hexachloroplatinate (IV) hexahydrate (H_2PtCl_6, 41 mg, 0.1 mmol) and polyvinylpyrrolidone (PVP, 11.1 mg, 0.1 mmol) were added to 20 mL deionized water and stirred for 30 minutes in the ice-water bath. A fresh aqueous sodium borohydride ($NaBH_4$) solution (0.16 M, 5.0 mL) was added to the mixture under vigorous stirring. The resulting solution immediately became black. After stirring for 2 h, a solution of SPtNP catalyst was obtained. The molar ratio of Pt to PVP varied in the range of 1/1 to 1/100. The SPtNP catalyst solution was dialyzed and washed with deionized water and then directly used for the BA conversion.

Similarly, other SMNP catalysts of Ru, Pd, and Au were synthesized with a molar ratio of metal to PVP of 1/10. The precursors of Ru, Pd, and Au were $RuCl_3{\cdot}xH_2O$, $H_2PdCl_4{\cdot}H_2O$, and $AuCl_3{\cdot}HCl{\cdot}4H_2O$, respectively.

In addition, other reduction reagents, including ethanol, formaldehyde, and hydrazine hydrate, were also used for the synthesis of SPtNP catalysts. The desired amount of H_2PtCl_6 (41 mg, 0.1 mmol) and PVP (111 mg, 1 mmol) were dissolved in water (20 mL) and stirred for 30 minutes in ice-water bath. Then, hydrazine hydrate (0.25 mL) was added quickly under vigorous stirring. After stirring for 2 h, a solution of SPtNP catalysts was obtained. In addition, other reduction formaldehyde was also used by the similar method. The reduction temperature was 80 ^{o}C when formaldehyde was used as reductant. When ethanol was used as reductant, desired amount of H_2PtCl_6 (41 mg, 0.1 mmol) and PVP (111 mg, 1 mmol) were dispersed in ethanol (25 mL). The mixture was heated to 120^{o}C for 3 h under argon affording a dark-brown solution. The SPtNP catalyst solution was dialyzed and washed with deionized water and then directly used for the BA conversion.

S.2. Characterization of SPtNP catalysts:

The prepared metal SPtNP catalysts were characterized by transmission electron microscopy (TEM). The TEM images were taken on a Hitachi 9000 NAR transmission electron microscope operating at 200 kV. Samples for TEM analyses were prepared by placing a droplet of the dispersed SPtNP catalyst solution onto a carbon-coated copper grid. The size distributions of the SPtNP catalysts were determined by randomly measuring more than 300 particles on the images.

X-ray photoelectron spectra (XPS) were performed on a Kratos XASM800 X-ray photoelectron spectrometer with a mono Al K_a source (hv = 1486.7 eV) operated at 15 mA and 12 kV and a hemispherical electron analyzer connected to an eight-channel detector. The survey spectrum and the high-resolution spectrum were scanned with pass energies of 20 eV. During the acquisition of a spectrum, charge neutralization was applied to compensate for the insulating problem of the sample. CASAXPS software was used for the data processing. Binding energies were referenced to C(1s) (at 284.7 eV).

X-ray diffraction (XRD) measurements for the fresh catalysts were recorded on a DX-1000 transmission X-ray powder diffraction system using Cu $K_{\alpha1}$ radiation (λ = 1.5406 Å), operated at 30 kV and 100 mA. The 2θ range angles were scanned from 15 to 80°, with sweep speed of 3°C/rain and 0.06°C/s.

S.3. Hydrogenation of BA:

The hydrogenations of BA were carried out in water. The 50 mL fresh SPtNP catalyst solution (0.1 mmol) and 0.240 g BA (2.0 mmol) were placed into a 100 mL round bottle with a branch pipe and piston. The reactor was purged with 1 atm H_2 (99.999%) several times and then heated to the desired reaction temperatures with vigorous stirring. The final reaction mixtures were extracted by diethyl ether, and then the catalysts were collected for recycling. The products were analyzed by a Fuli 9790-II-GC equipped with an FID detector and an AT.SE-54 column (30 m, 0.25 mm).

S.4. Results

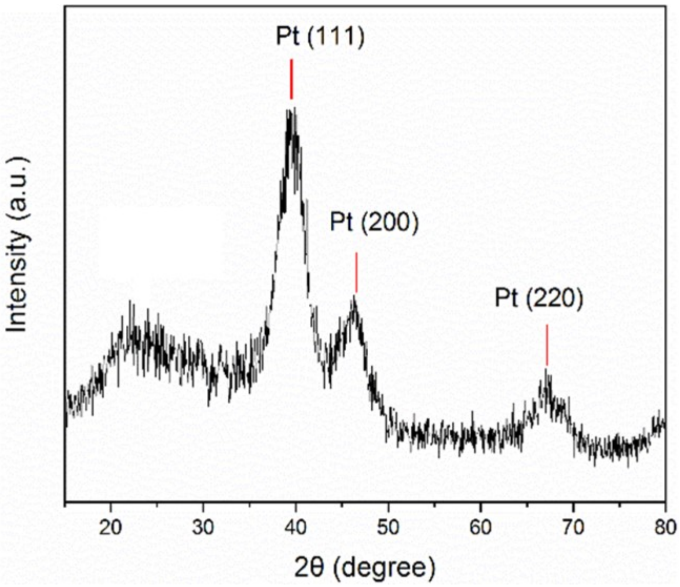

Figure S1. XRD pattern of freshly prepared SPtNP catalyst (Pt : PVP = 1 : 10 in mole) after dialyzing.

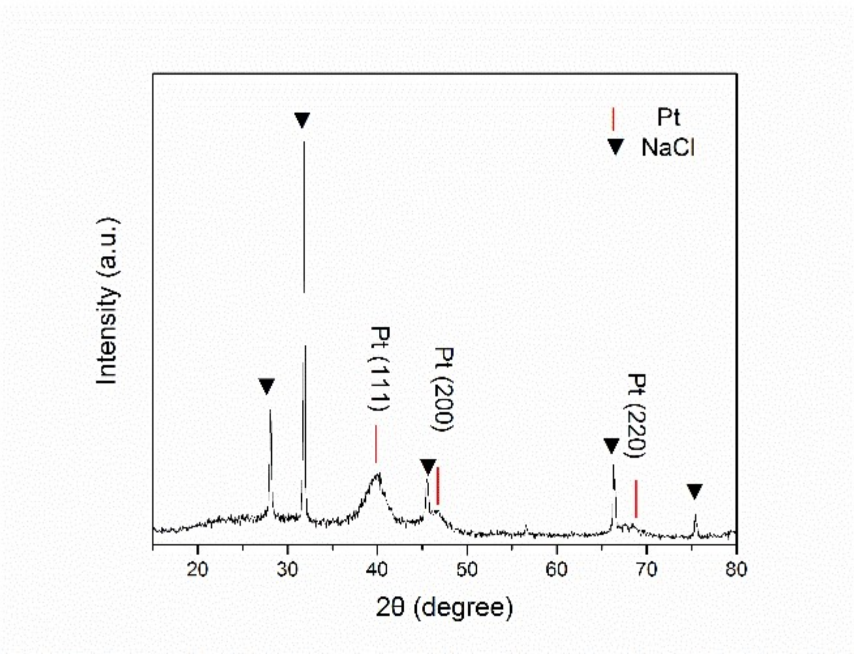

Figure S2. XRD pattern of freshly prepared SPtNP catalyst (Pt : PVP = 1 : 10 in mole) before dialyzing.

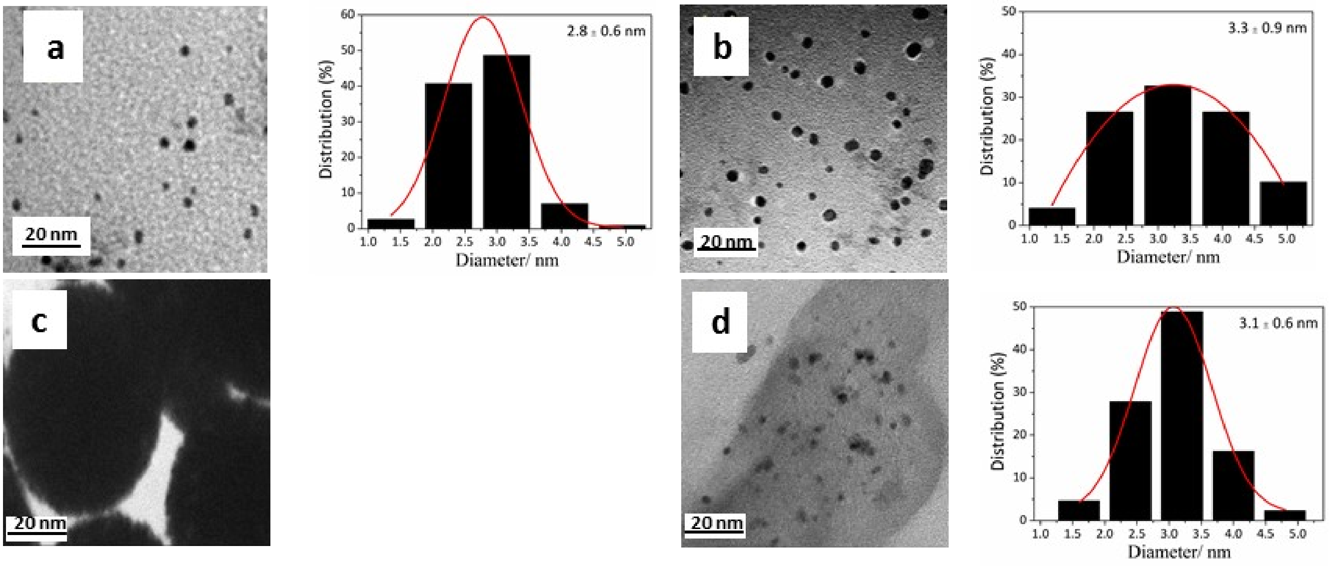

Figure S3; SPtNP catalysts reduced by (a) formaldehyde, (b) ethanol, (c) hydrazine hydrate, and (d) Pt/C.

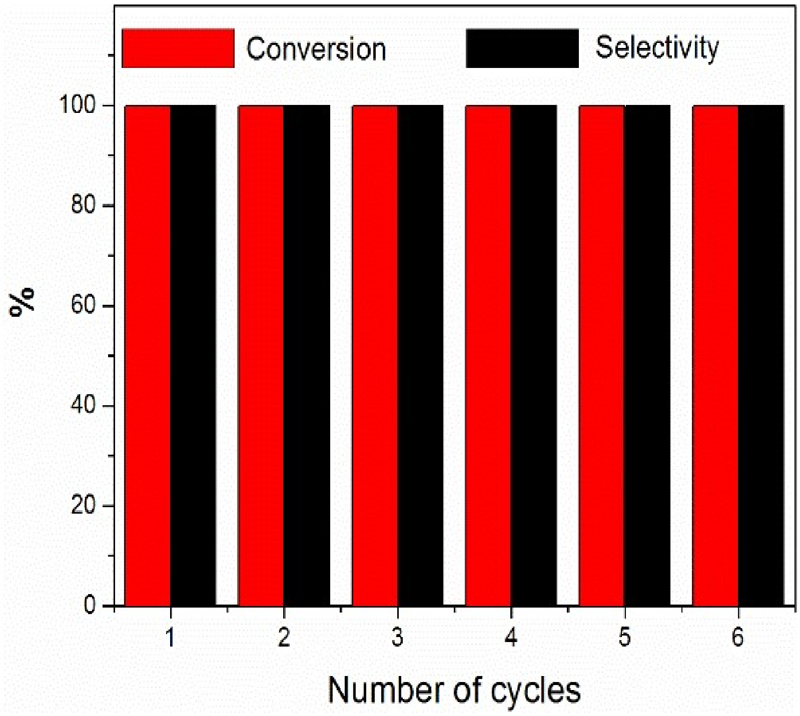

Figure S4. Recycling of the SPtNP catalyst in the hydrogenation of BA to CCA (0.1 mmol SPtNP catalyst, 2.0 mmol BA in H_2O, 30°C, 1 atm H_2, 3 h).

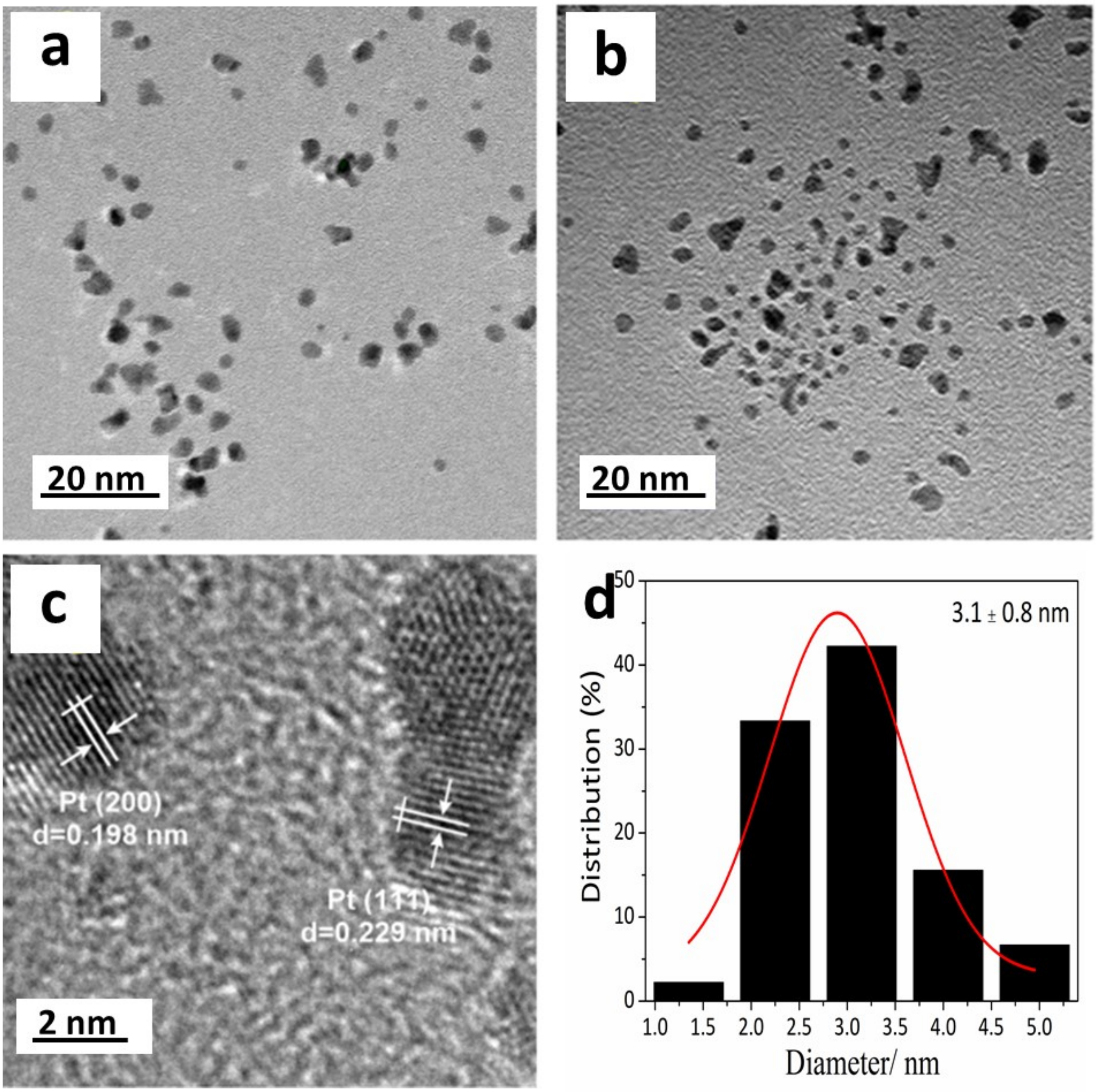

Figure S5: TEM images (a and c) of freshly prepared SPtNP catalyst (Pt : PVP = 1 : 10 in mole) and HRTEM image (b) and particle size distribution (d) of SPtNP catalyst after 5 recycles.

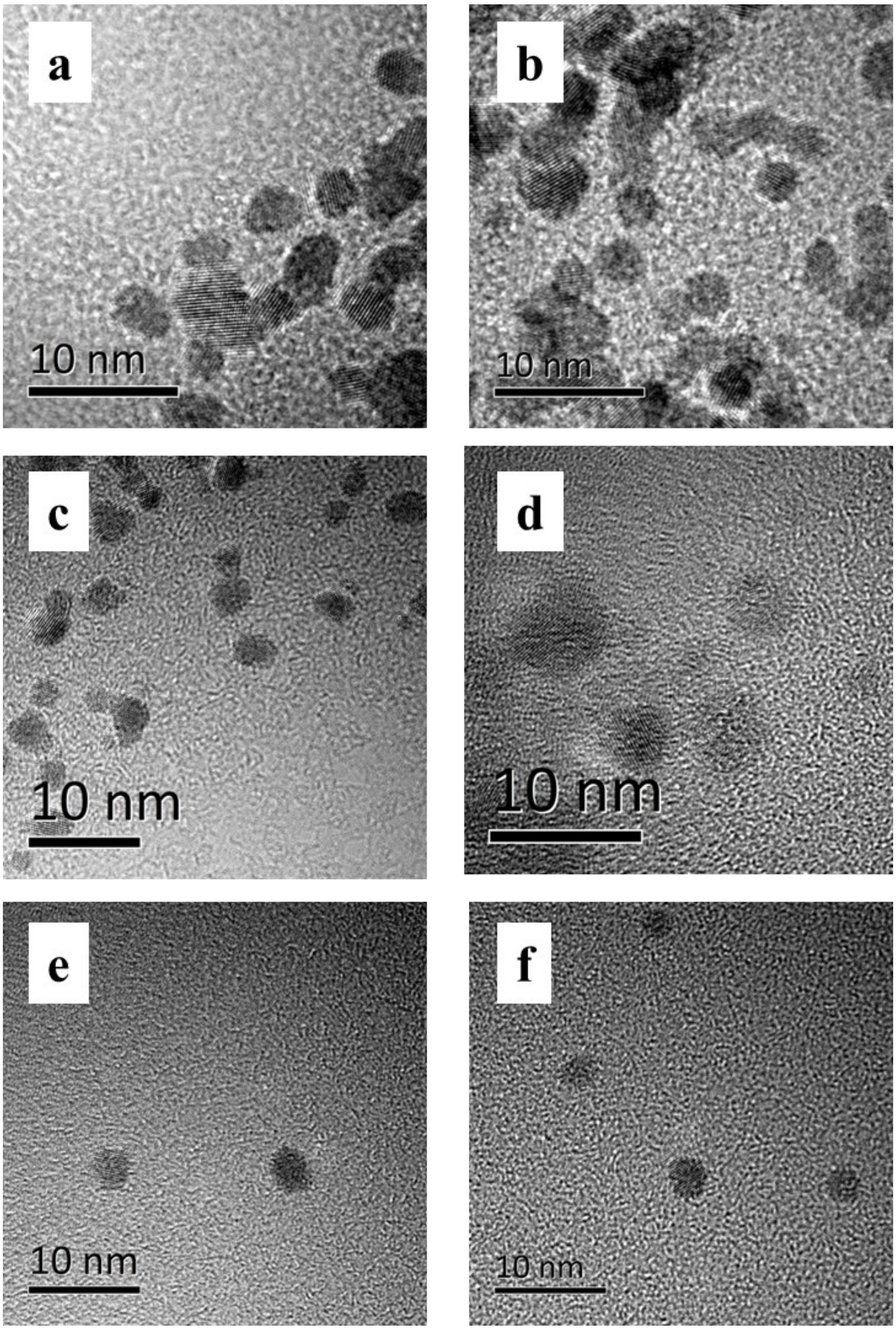

Figure S6: HRTEM images of freshly prepared SPtNP catalysts with molar ratio of Pt to PVP (a) 1 : 1; (b) 1 : 5; (c) 1 : 10; (d) 1 : 20; (e) 1 : 50; (f) 1 : 100.

Table S1. Hydrogenation of benzoic acid by different SMNP catalysts.[a]

Entry	Catalysts	C (%)[b]	S (%)[c]
1	PVP	0.1	100
2	Au, PVP	0.2	100
3	Pd, PVP	1.0	100
4	Ru, PVP	0.6	100
5	Pt, PVP	100	100

[a] Reaction conditions: 5 mol% metal relative to BA, 30 °C, 1 atm H_2, 3 h; [b] BA conversions; [c] selectivities of CCA.

As shown in Table S1, under 30°C and 1 atm H_2 for 3 h, soluble AuNP catalyst exhibits negligible activity for the hydrogenation of BA to CCA (Table S1, entry 2), similar to that in the absence of MNPs (Table S1, entry 1). The BA conversion is only 1.0% on soluble PdNP catalyst (Table S1, entry 3) and 0.6% on soluble RuNP catalyst (Table S1, entry 4), with the MNPs aggregating after reaction, which shows that SPtNPs have a unique catalytic effect for this reaction.

Table S2. Hydrogenation of benzoic acid under different conditions.[a]

Entry	T (°C)	t (h)	C (%)[b]	S (%)[c]
1	10	3	31.5	100
2	20	3	66.1	100
3	30	0.5	16.5	100
4	30	1	36.1	100
5	30	2	68.3	100
6	30	3	100	100

[a] Reaction conditions: 5 mol% metal relative to BA, 1 atm H_2,; [b] BA conversions; [c] selectivities of CCA.

Lower reaction temperature led to lower BA conversion, at 10°C, the BA conversion is only 31.5%. Clearly, the activation temperature is 30°C (Table S2). And as shown in Table S2, with prolonging the reaction time from 0.5 h to 1 h, 2 h and 3 h at 30°C, the BA conversion increased from 16.5% to 36.1%, 68.3% and 100%, respectively. The BA conversion is directly proportional to the time.

Table S3. The results of the hydrogenation of BA by different catalysts are in the previous literatures.

Catalysts	Solvent	T (°C)	P (atm)	t (h)	C (%)	S (%)	References
NiZrB-PEG(800)	water	150	40	4	93.5	93.6	1
NiPdB-PEG(800)	water	150	50	5	97.6	100	2
NiZrB/Al_2O_3(K_2CO_3)	cyclohexane	150	50	4	99.9	95.3	3
Ni/mSiO_2-AE	cyclohexane	150	50	3	98.9	99.1	4
Ru/MC-i	water	120	40	2	96.7	99.8	5
Ni/CSC-b	water	200	30	8	54.2	100	6
Pd/MCN	water	110	25	2.5	100	100	7
RuPd/CN	water	100	50	2	100	100	8
Rh-PVP	water	150	10	1	48	96	9
$Ni_2Mg_{0.5}Al_1$-MMO	cyclohexane	150	50	3	98	97	10
Ni/Al_2O_3-NS	cyclohexane	150	10	2.5	98	100	11
Pd/800N-AC	water	110	25	2	65.9	100	12
PdAu/MHSS	CH_2Cl_2	100	10	1	22	99	13
Ru/MCM-41	water	50	60	2	100	100	14
Pt/C	/	50	100	3	3.4	100	15
Rh/C	/	50	100	3	99.1	100	15
Rh/N−C-700	water	55	10	1	76	100	16
Pt nanowires($AlCl_3$)	HOAc	70	10	24	98.4	100	17
Ru/C-TiO_2	water	70	25	3	100	100	18
Ru@GCS-700	water	80	50	4	98.5	95.7	19
Pd@UiO-66-2OH	water	85	10	8	100	100	20
Pd/CN	water	85	1	24	100	100	21
RuPd/CN	water	85	1	6	67	100	8
Ir/γ-Al_2O_3	water	85	1	0.5	52	100	22

References

1. G. Y. Bai, X. Wen, Z. Zhao, F. Li, H. X. Dong and M. Qiu, *Ind. Eng. Chem. Res.*, 2013, **52**, 2266;
2. G. Bai, Z. Zhao, H. Dong, L. Niu, Y. Wang and Q. Chen, *ChemCatChem*, 2014, **6**, 655;
3. X. Wen, Y. Y. Cao, X. L. Qiao, L. B. Niu, L. Huo and G. Y. Bai, *Catal. Sci. Technol.*, 2015, **5**, 3281;
4. H. L. Zhang, X. J. Gao, Y. Y. Ma, X. Han, L. B. Niu and G. Y. Bai, *Catal. Sci. Technol.*, 2017, **7**, 5993;
5. Z. L. Jiang, G. J. Lan, X. Y. Liu, H. D. Tang and Y. Li, *Catal. Sci. Technol.*, 2016, **6**, 7259;
6. X. H. Lua, Y. Shen, J. He, R. Jing, P. P. Tao, A. Hua, R. F. Nie, D. Zhou and Q. H. Xia, *Mol. Catal.*, 2018, **444**, 53;
7. H. Z. Jiang, X. L. Yu, R. F. Nie, X. H. Lu, D. Zhou and Q. H. Xia, Appl. Catal. A-Gen., 2016, 520, 73;
8. M. Tang, S. Mao, M. Li, Z. Wei, F. Xu, H. Li and Y. Wang, *ACS Catal.*, 2015, **5**, 3100;
9. C. Chaudhari, H. Imatome, Y. Nishida, K. Sato and K. Nagaoka, *Catal. Commun.*, 2019, **126**, 55;
10. H. L. Zhang, J. Dong, X. L. Qiao, J. R. Qin, H. F. Sun, A. Q. Wang, L. B. Niu and G. Y. Bai, *J. Catal.*, 2019, **372**, 258;
11. W. J. Lian, B. Chen, B. Y. Xu, S. Zhang, Z. Wan, D. Zhao, N. Zhang and C. Chen, *Ind. Eng. Chem. Res.* 2019, **58**, 2846;
12. R. F. Nie, H. Z. Jiang, X. H. Lu, D. Zhou and Q. H. Xia, *Catal. Sci. Technol.*, 2016, **6**, 1913;
13. X. Yang, L. Du, S. Liao, Y. Li and H. Song, *Catal. Commun.*, 2012, **17**, 29;
14. H. W. Lin, C. H. Yen and C. S. Tan, *Green Chem.*, 2012, **14**, 682;
15. H. J. Wang and F. Y. Zhao, *Int. J. Mol. Sci.*, 2007, **8**, 628;
16. Y. L. Cao, M. H. Tang, M. M. Li, J. Deng, F. Xu, L. Xie, and Y. Wang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 9894;
17. Z. Guo, L. Hu, H. H. Yu, X. Cao and H. Gu, *RSC Adv.*, 2012, **2**, 3477;
18. H. F. Zhang, G. Q. Li, R. F. Nie, X. H. Lu and Q. H. Xia, *J. Mater. Sci.*, 2019, **54**, 7529;
19. J. J. Shi, M. S. Zhao, Y. Y. Wang, J. Fu, X. Y. Lu and Z. Y. Hou, *J. Mater. Chem. A*, 2016, **4**, 5842;
20. X. Xu, M. H. Tang, M. M. Li, H. R. Li and Y. Wang, *ACS Catal.*, 2014, **4**, 3132;
21. M. H. Tang, S. J. Mao, X. F. Li, C. H. Chen, M. M. Li and Y. Wang, *Green Chem.*, 2017, **19**, 1766;
22. D. Chen, W. Yang, L. Jiao, L. Li, S. H. Yu and H. L. Jiang, *Adv. Mater.*, 2020, 2000041.