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Supplementary data

Hydrogenolysis process for lignosulfonate depolymerization using synergistic catalysts of noble metal and metal chloride

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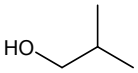
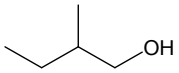
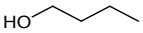
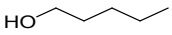
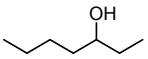
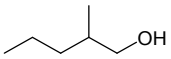
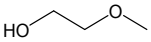
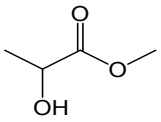
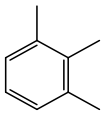
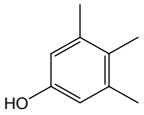
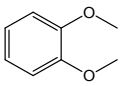
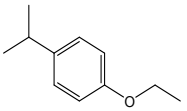
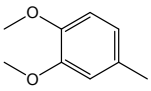
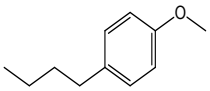
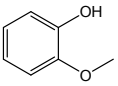
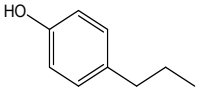
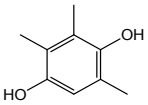
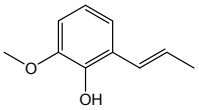
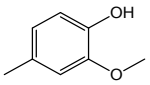
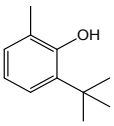
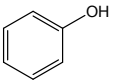
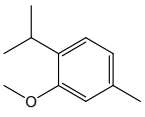
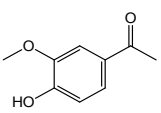
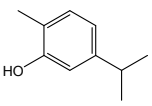
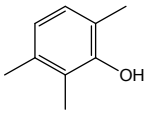
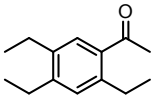
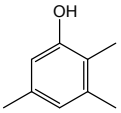
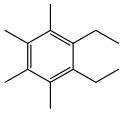
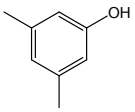
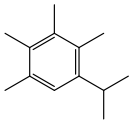
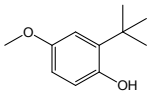
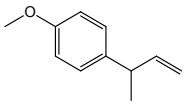
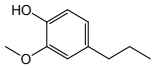
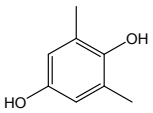
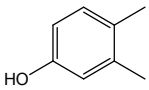
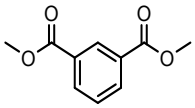
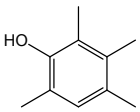
Table S1 The main composed elements of sodium lignosulfonate.

Elements	Content (%)
C	42.65
H	5.05
O[a]	40.40
N	0.18
S	5.07
Na	6.65

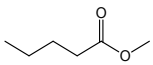
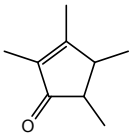
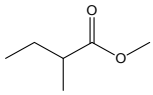
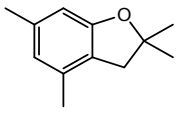
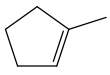
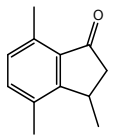
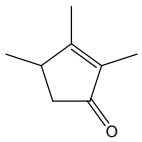
[a] The oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, H, N, S, Na and O.

Table S2 The main components of the volatile products.

RT (min)	Compound	Structure	RT (min)	Compound	Structure
		Aliphatic alcohols			
3.63	1-Propanol, 2-methyl-		5.08	1-Butanol,2-methyl-	
4.25	1-Butanol		5.67	1-Pentanol	
4.51	3-Heptanol		6.38	1-Pentanol,2-methyl-	
4.72	Ethanol, 2-methoxy-		6.83	Propanoic acid,2-hydroxy-,methyl ester	
		Monomers			
5.60	Benzene,1,2,3-trimethyl-		16.91	Phenol,3,4,5-trimethyl-	
11.83	Benzene,1,2-dimethoxy-		17.29	p-Isopropylphenetole	
12.71	3,4-dimethoxytoluene		17.39	Benzene,1-butyl-4-methoxy-	
13.43	Phenol, 2-methoxy-		17.49	Phenol, 4-propyl-	
14.05	1,4-Benzenediol, 2,3,5-trimethyl-		17.92	Phenol,2-methoxy-6-(1-propenyl)-	
14.37	Phenol,2-methoxy-4-methyl-		18.66	Phenol,2-(1,1-dimethylethyl)-6-methyl-	
14.99	Phenol		18.77	Benzene,2-methoxy-4-methyl-1-(1-methylethyl)-	
15.12	Ethanone,1-(4-hydroxy-3-methoxyphenyl)-		18.93	Phenol,2-methyl-5-(1-methylethyl)-	

15.36	Phenol,2,3,6-trimethyl-		19.51	Ethanone,1-(2,4,5-triethylphenyl)-	
15.44	Phenol, 2,3,5-trimethyl-		19.96	Benzene,1,2-diethyl-3,4,5,6-tetramethyl-	
15.77	Phenol, 3,5-dimethyl-		20.12	Benzene,1,2,3,4-tetramethyl-5-(1-methylethyl)-	
15.83	3-tert-Butyl-4-hydroxyanisole		20.22	Benzene,1-methoxy-4-(1-methyl-2-propenyl)-	
16.00	Phenol,2-methoxy-4-propyl-		20.30	1,4-Benzenediol,2,6-dimethyl-	
16.50	Phenol, 3,4-dimethyl-		21.37	1,3-Benzenedicarb-oxylicacid,dimethyl ester	
16.82	Phenol,2,3,4,6-tetramethyl-				

Other volatile products

3.46	Pentanoic acid,methyl ester		9.34	2-Cyclopenten-1-one,2,3,4,5-tetramethyl-	
4.12	Butanoic acid,2-methyl-,methyl ester		20.62	Benzofuran, 2,3-dihydro-2,2,4,6-tetramethyl-	
7.02	Cyclopentene, 1-methyl-		21.35	1H-Inden-1-one, 2,3-dihydro-3,4,7-trimethyl-	
9.16	2-Cyclopenten-1-one,2,3,4-trimethyl-				

Condition: 0.5 g sodium lignosulfonate, 0.1 g 5% wt Pt/C, 1 mmol $CrCl_3$, 40 ml methanol, 3 MPa H_2, 280 °C, 5h; Analysis condition: GC-MS capillary column: HP-INNOWAX, 30 m × 0.25 mm × 0.25 um.

Table S3 Surface properties of the different catalysts.

Catalysts	Surface area[a] (m^2g^{-1})	Total pore volume[b] (cm^3g^{-1})	Pore diameter[b] (nm)
Pd/C	1023.89	0.45	3.79
Ni/C	910.81	0.46	3.83
Ru/C	1189.62	0.22	3.80
Pt/C	1239.76	0.65	3.82

[a] MultiPoint Brunauer, Emmett &Teller (BET) method.

[b] Barrett, Joyner & Halenda (BJH) method.

Table S4 The main composed elements of the oligomers.[a]

Elements	Content (%)
C	44.67
H	5.75
O[b]	47.98
N	0.25
S	0.58
Na	0.77

[a] Reaction condition: 0.5 g lignosulfonate, 0.1 g Pt/C, 1 mmol $CrCl_3$, 3 MPa H_2, 5 h, 280 °C.

[b] The oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, H, N, S, Na and O.

Table S5 The sulfur content of the lignosulfonate and the residues with different catalysts.

Component	Lignosulfonate[a]	Residues[b]		
		No catalyst	$CrCl_3$	Pt/C+ $CrCl_3$
S (weight)	5.07%	2.47%	0.83%	0.66%

[a] Measured by a vario EL III element analyzer;

[b] Measured by EDS.

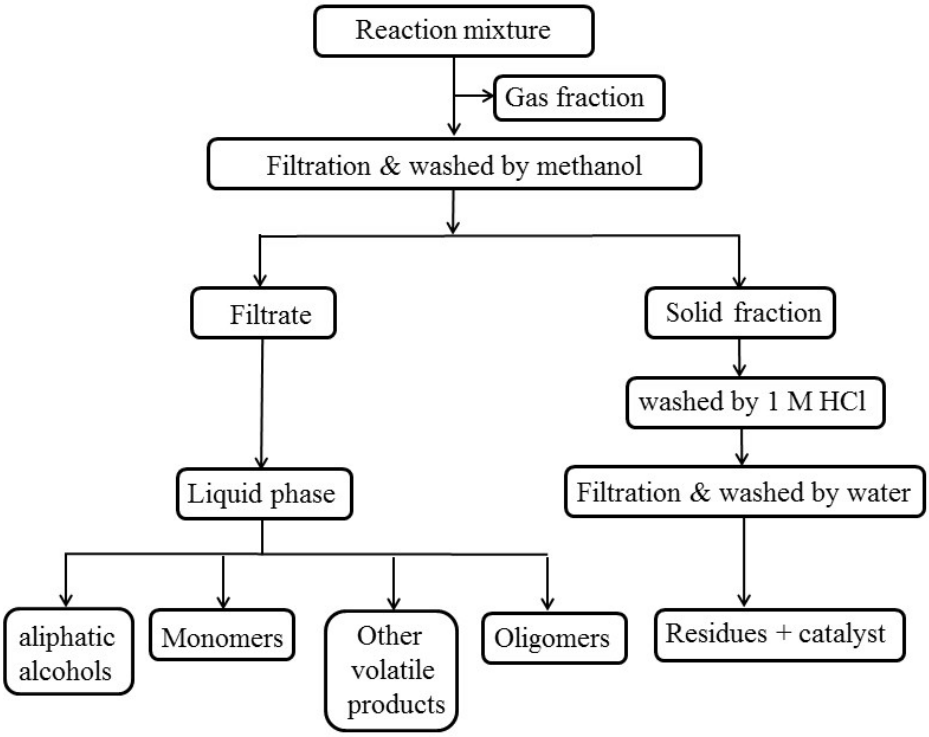


Fig. S1 Separation procedure for the hydrogenolysis products.

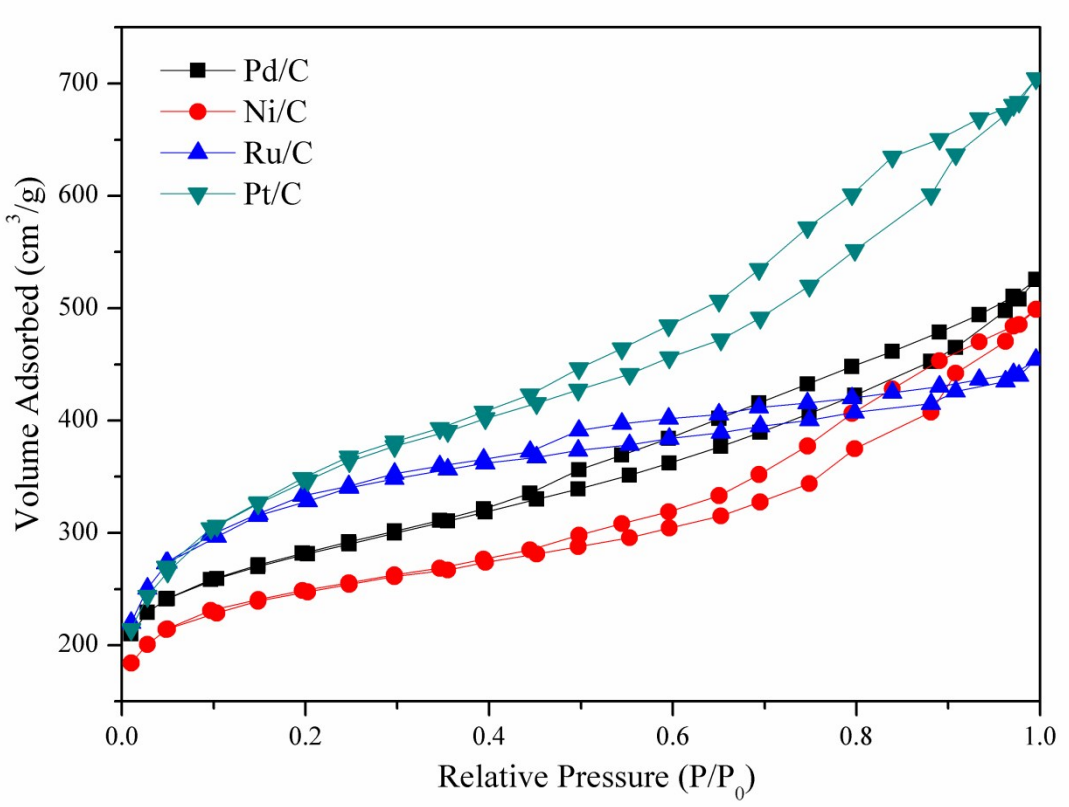


Fig. S2 The N_2 adsorption-desorption isotherms of Pd/C, Ni/C, Ru/C and Pt/C.

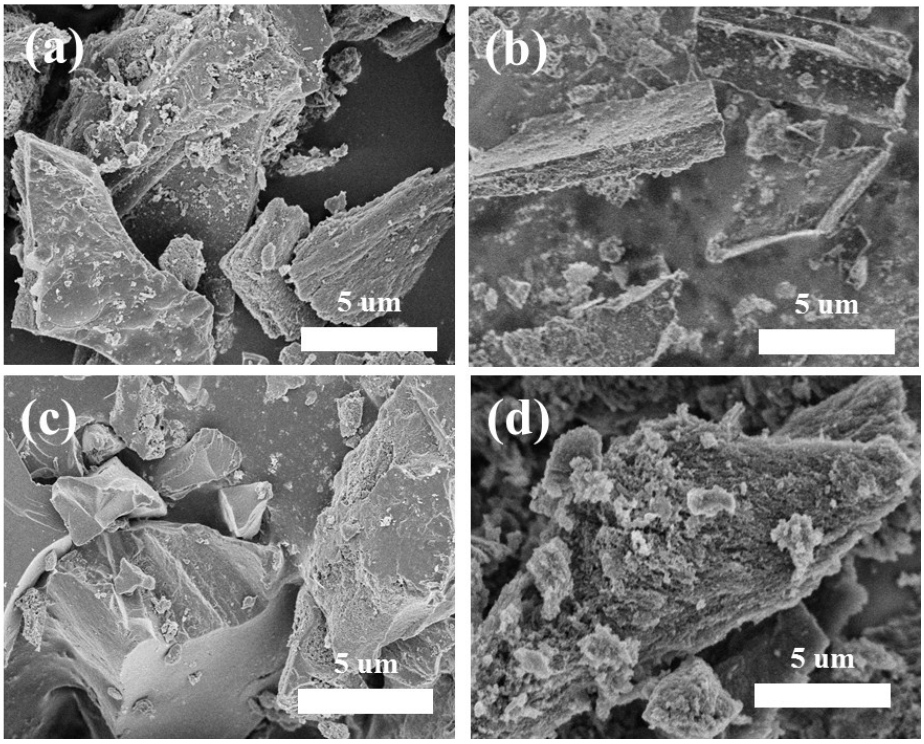


Fig. S3 SEM images of the fresh (a) Pd/C, (b) Ni/C, (c) Ru/C and (d) Pt/C.

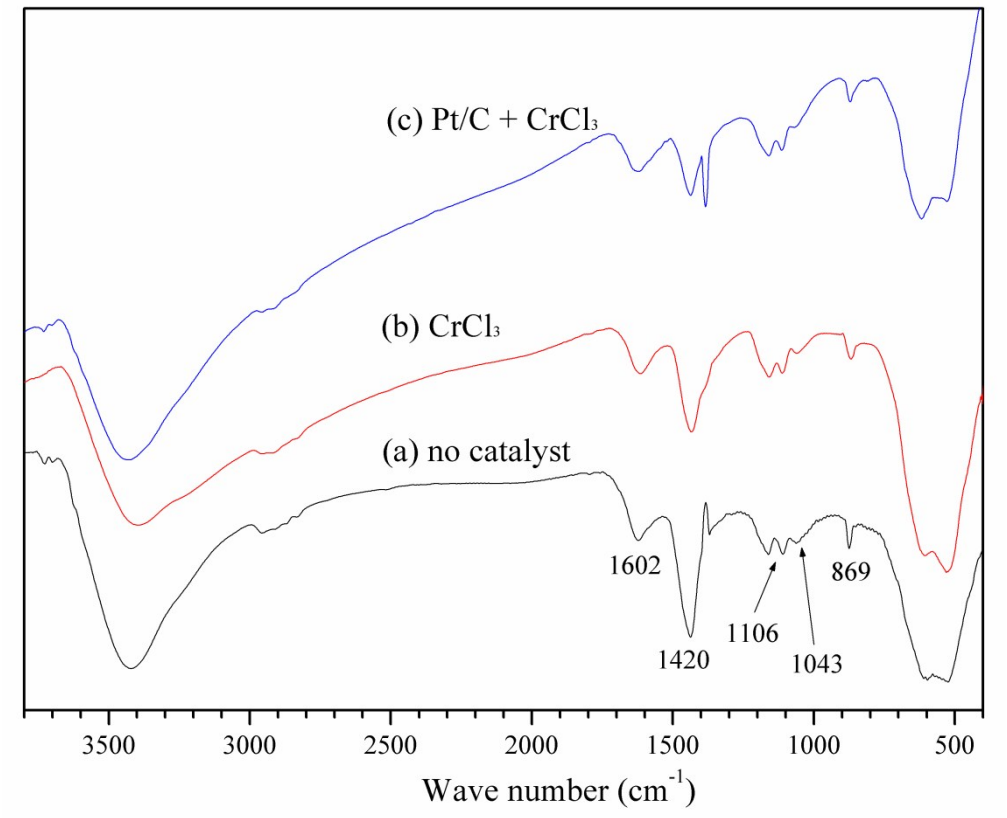


Fig. S4 FT-IR analysis of the residues with different catalysts

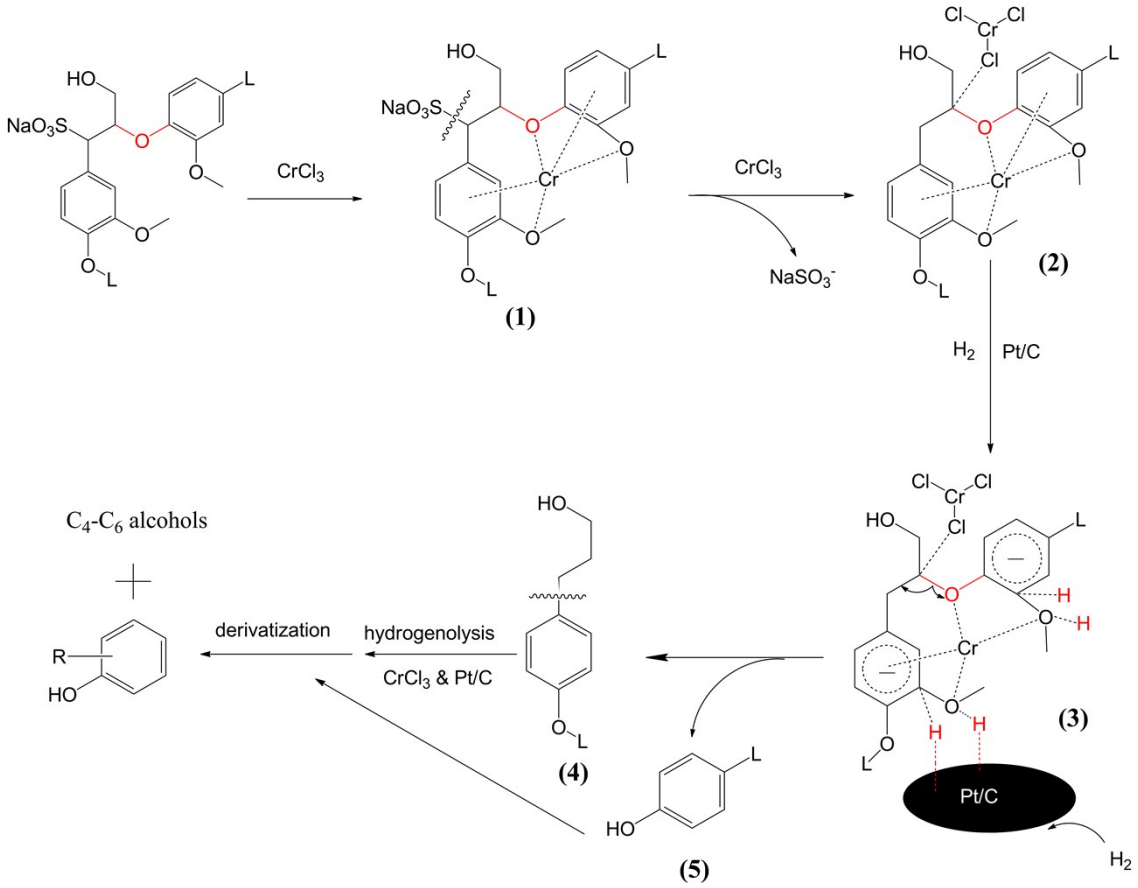


Fig. S5 Proposed catalytic mechanism of synergistic catalysis.

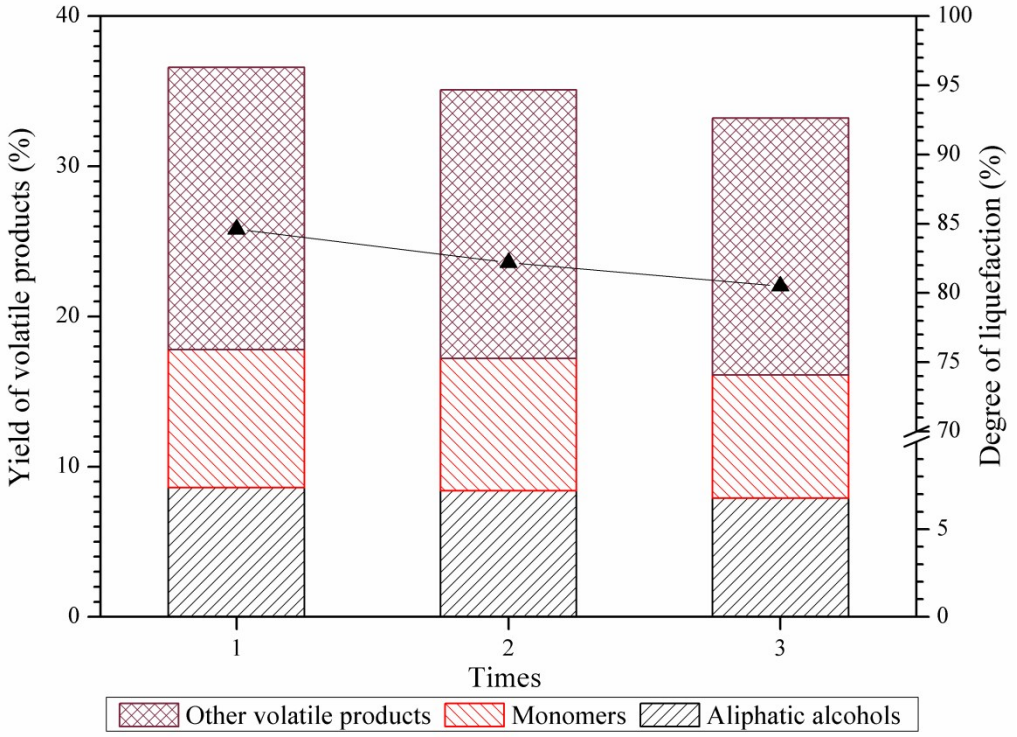
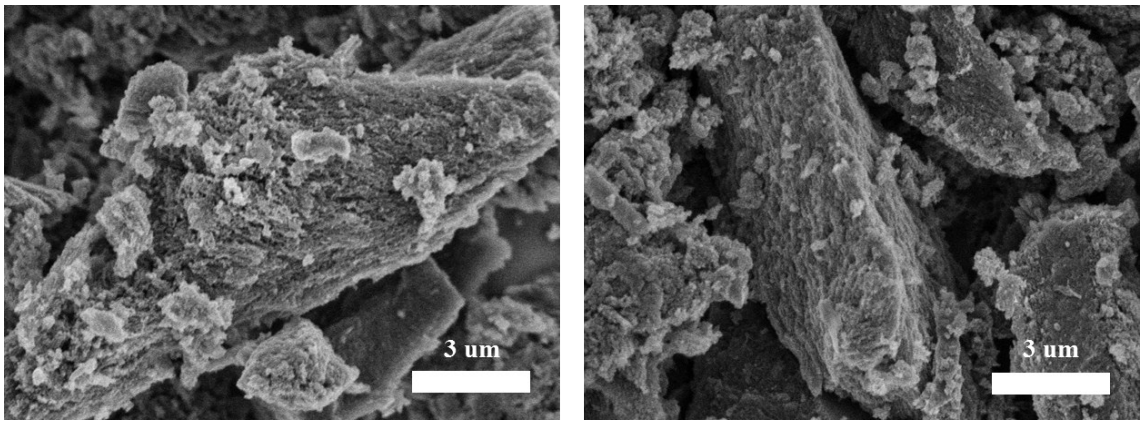
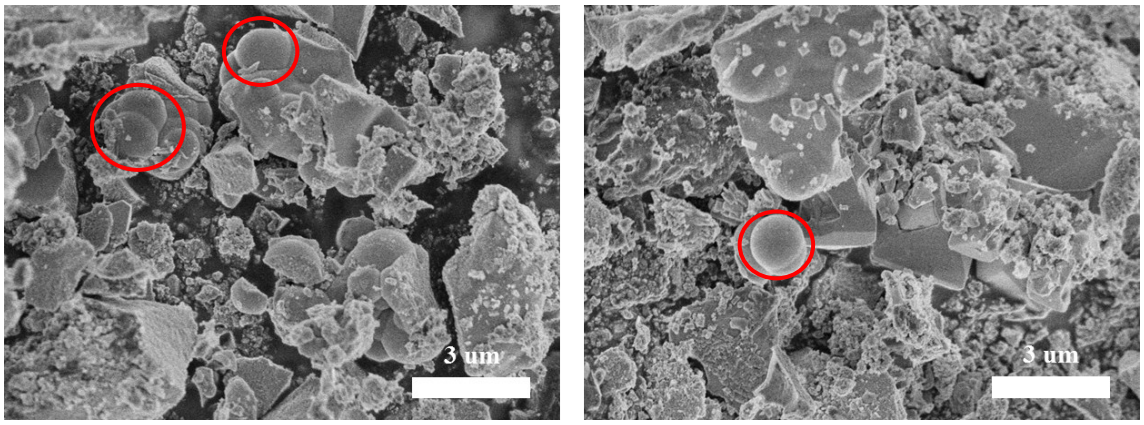


Fig. S6 The recyclability of Pt/C catalyst

Conditions: 0.1 g 5 wt% Pt/C, 1 mmol $CrCl_3$, 280 °C, 3 MPa H_2, 5 h.



(a) fresh Pt/C



(b) recovered Pt/C after 3 runs

Fig. S7 SEM images of (a) fresh Pt/C and (b) recovered Pt/C after 3 runs.

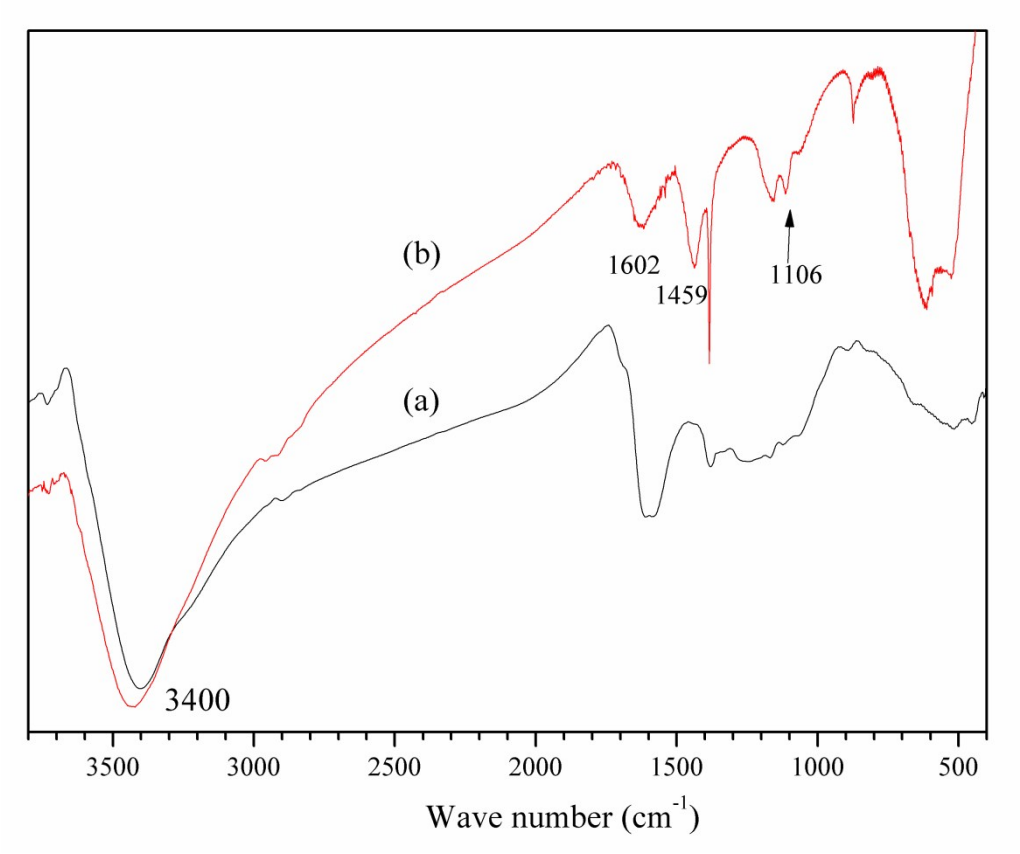
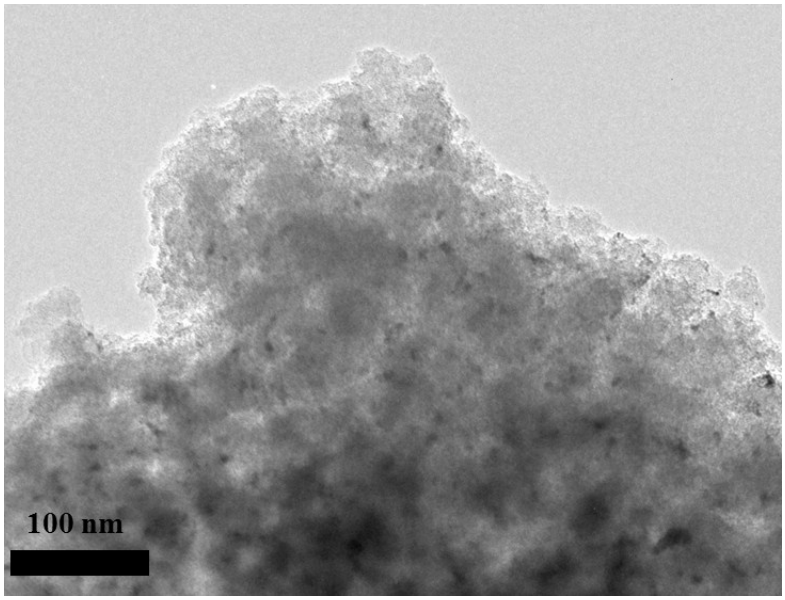
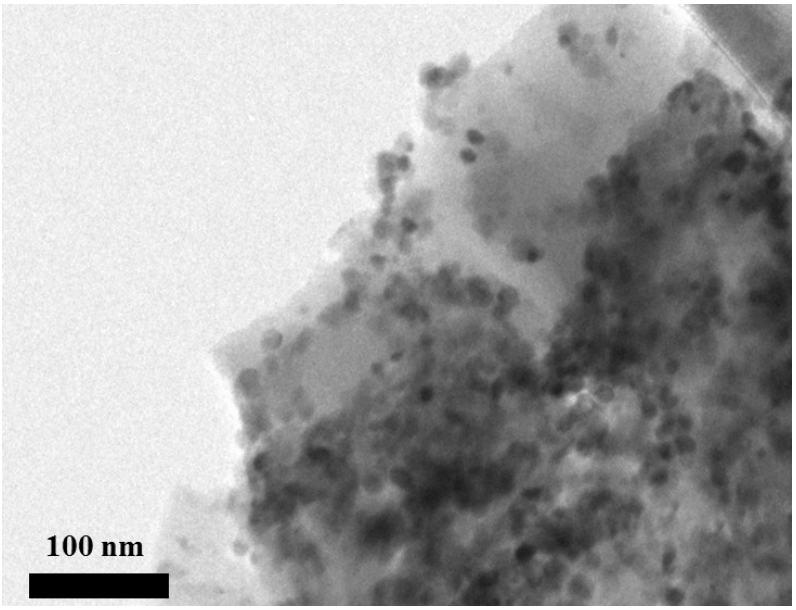


Fig. S8 FT-IR spectrum of (a) fresh catalyst and (b) recovered catalyst after 3 runs



(a) fresh Pt/C



(b) recovered Pt/C after 3 runs

Fig. S9 TEM images of (a) fresh Pt/C and (b) recovered Pt/C after 3 runs.