Electronic Supporting Information

$PdCl_2$ immobilized on metal-organic framework CuBTC with the aid of ionic liquids: enhanced catalytic performance in selective oxidation of cyclohexene

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1 Experimental section

1.1 Materials

All reagents were purchased from commercial suppliers and used without further purification. Trimesic acid (99%) and 5, 5-Dimethyl-1-pyrroline N-oxide (97%) (DMPO) were purchased from Meryer Chemical Technology Co., Ltd. The *n*-heptane (98%) was purchased from Aladdin Industrial Corporation. Tert-butyl hydroperoxide (TBHP, 65%), cyclohexene (99%), 2,6-di-tert-butyl-methylpheonl (BHT) were purchased from Sinopharm Chemical Reagent Co., Ltd. Diethyl ether (99.5%), cupric nitrate trihydrate ($Cu(NO_3)_2{\bullet}3H_2O$) (99.5%), acetonitrile (99.5%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Palladium chloride (99.9%) was purchased from Shanghai BoKa Chemical Reagent Co., Ltd. Carboxyl-ionic liquid (99%) was obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

1.2 Catalyst preparation

1.2.1 Synthesis of CuBTC

Metal-organic framework material CuBTC was synthesized under solvothermal condition as reported previously.[1] Typically, 2.5 mmol trimesic acid and 4.5 mmol cupric nitrate trihydrate was dissolved in 15 mL ethanol and deionized water, respectively. And then the solutions were mixed and stirred for 30 min at ambient temperature. Finally, the mixture was transferred to a 50 mL Teflon autoclave and crystallized for 12 h at 393 K. The product was filtered and washed with ethanol and deionized water. The obtained blue solid was further dried under vacuum overnight at 423 K.

1.2.1 Synthesis of $PdCl_2$-ILs/CuBTC

Typically, 0.1334 g (0.70 mmol) 1-carboxyethyl-3-methyl imidazole chloride salt ionic liquids and 0.059 g (0.33 mmol) palladium chloride were dissolved in 20 mL acetonitrile. In this process, the experimental mole ratio of ionic liquids and palladium chloride was slightly more than stoichiometric ratio (2:1) to guarantee complete formation of $PdCl_2$-ILs complex. Subsequently, 0.5 g CuBTC material was added into the above solution, and the obtained mixture was refluxed for 24 h at 343 K. Finally, the solvent was removed by rotary evaporation and washed with diethyl ether to remove the surface excess ILs and $PdCl_2$ until filtrate is colourless. The synthesized catalysts were denoted as $PdCl_2$-ILs/CuBTC. Similarly, 0.5 g SBA-15 or CNTs materials under the identical condition is used to prepare $PdCl_2$-ILs/CNTs and $PdCl_2$-ILs/SBA-15 catalyst, respectively. The method for synthesis of $PdCl_2$-ILs complex is as same as the above procedure in absence of support.

1.3 Characterizations

Powder X-ray diffraction (PXRD) was performed on a Rigaku diffractormeter (D/MAX -IIIA, 3 kW) using Cu Kα radiation. Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on Optima 2000DV (Perkin Elmer, USA). Elemental analysis (EA) was performed on vario EL III. Fourier transform infrared spectra were obtained by using Bruker-Tenson 27 infrared spectrometer. UV-vis spectra were performed on Agilent Cary 5000 spectrophotometer. ^{1}H-NMR spectra were obtained with a Bruker Avance DMX500 spectrometer (CD_3CN as solvent). MS spectra were obtained with Thermo Scientific LTQ Orbitrap XL. X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB250 (Thermo VG) using Al K Alpha source (AlK_α=1486.6eV, P=150W, HV=15kV, I=10mA). Electron paramagnetic resonance (EPR) at X-band was recorded using a Bruker spectrometer (Experimental parameters: Microwave frequency=9.42 GHz, Power=0.212 mW, Modulation frequency=100 kHz, Modulation amplitude=1.00 G).

1.4 Catalytic testing

Aerobic oxidation of cyclohexene was performed in 25 mL two-necked flask reactor equipped with a spherical reflux condenser, magnetic stirrer, and gas inlet. Initially, the solution of *n*-heptane-TBHP was prepared in advance. Specifically, 0.0823 g (0.6 mmol, 10% $n_{\text{cyclohexene}}$) TBHP was dissolved in 10 mL (6.8 g) *n*-heptane and was layered overnight to remove water. During a typical catalytic test, the upper solution of *n*-heptane-TBHP, 6 mmol (0.4894 g) cyclohexene and 50 mg catalyst were added in the reactor. Before reaction, the reactor was firstly flushed with oxygen flow (5 mL/min) for 5 min. Subsequently, the top of reflux condenser was sealed by using a rubber balloon. To avoid any evaporation of the chemicals during the reaction, the coolant water temperature was controlled at 278 K by using cycle refrigerator. The mixture was stirred (800 rpm) and temperature was adjusted to 323-343 K. After the completion of the reaction, the products were separated by centrifugation. The activity and selectivity were determined by Agilent 6890 GC (HP-5 capillary column 25 m, 0.32 mm).

1.5 Theoretical simulation and calculation

The simulated XRD pattern is obtained from Materials Studio Software by using CIF data (CCDC number: 112954) of HKUST-1. Specifically, the reflex modules is employed to calculate the X-ray powder diffraction data. Electrostatic potential surfaces were obtained using the density functional theory (DFT) method through Gaussian 09 program suites. Calculations were performed at the b3lyp/genecp level of theory. Los Alamos National Laboratories 2 Double Zeta basis set and pseudo-potentials (Lanl2dz) were employed for Pd atoms, while 6-31g basis set was used for other atoms (C, H, N, O).

2 Results

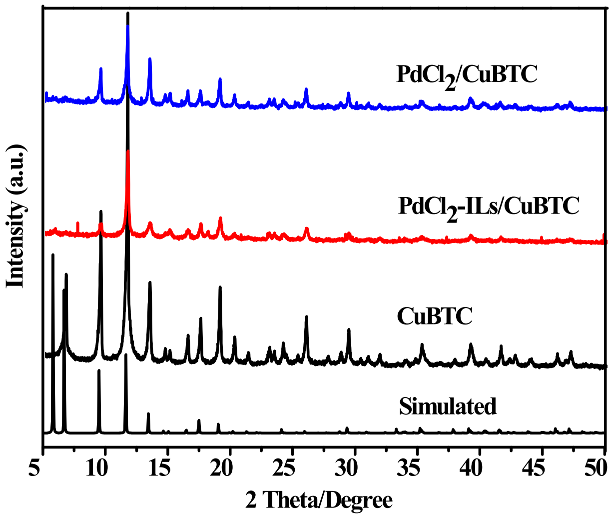


Fig. S1 XRD patterns of all synthesized samples.

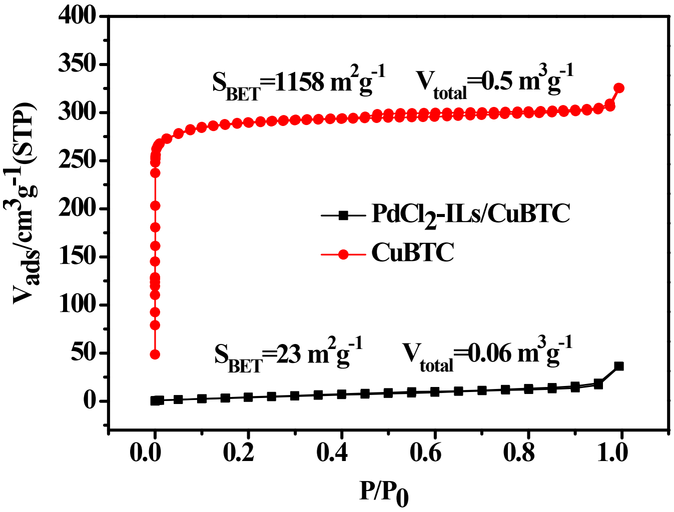


Fig. S2 N_2-physical adsorption and desorption isotherms of all synthesized samples.

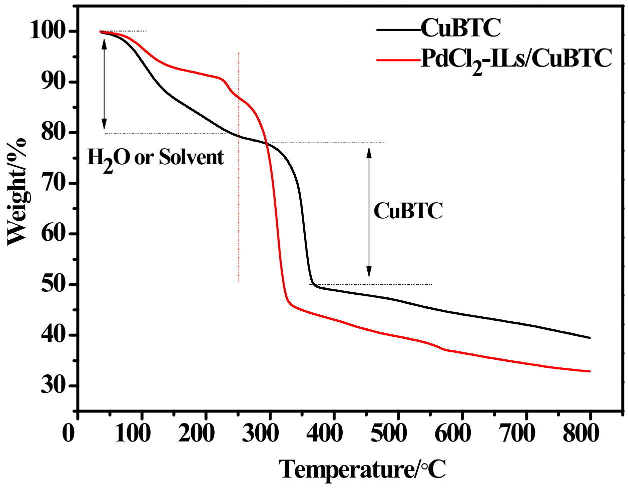


Fig. S3 TG curves of all synthesized samples.

Table. S1 Quantitative analysis of catalyst composition

Samples	ILs[a] (mmol·g^{-1})	Pd (II)[b] (mmol·g^{-1})	ILs/Pd
$PdCl_2$-ILs/CuBTC	1.26	0.40	3.1
$PdCl_2$-ILs/CNTs	1.02	0.44	2.3
$PdCl_2$-ILs/SBA-15	1.13	0.44	2.5
$PdCl_2$/CuBTC	—	0.36	—

[a] Nitrogen content is determined by elemental analysis;

[b] Palladium content is determined by ICP-OES analysis

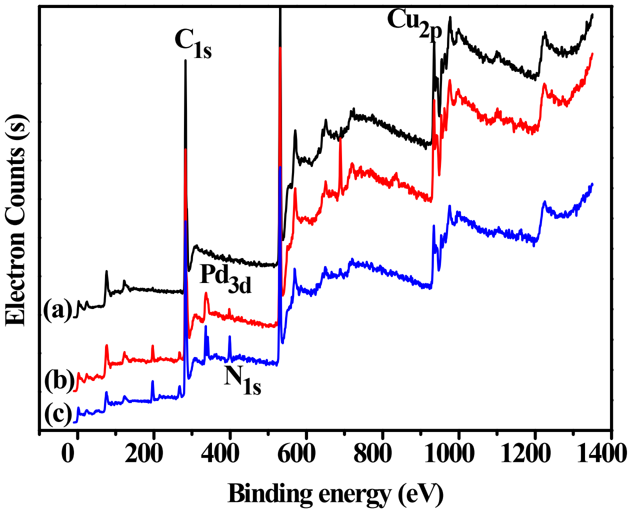


Fig. S4 XPS survey spectra of all synthesized samples.

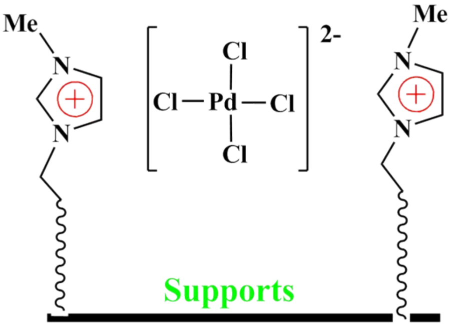


Fig. S5 Structural model of $PdCl_2$-ILs complex immobilized on solid supports.[2-5]

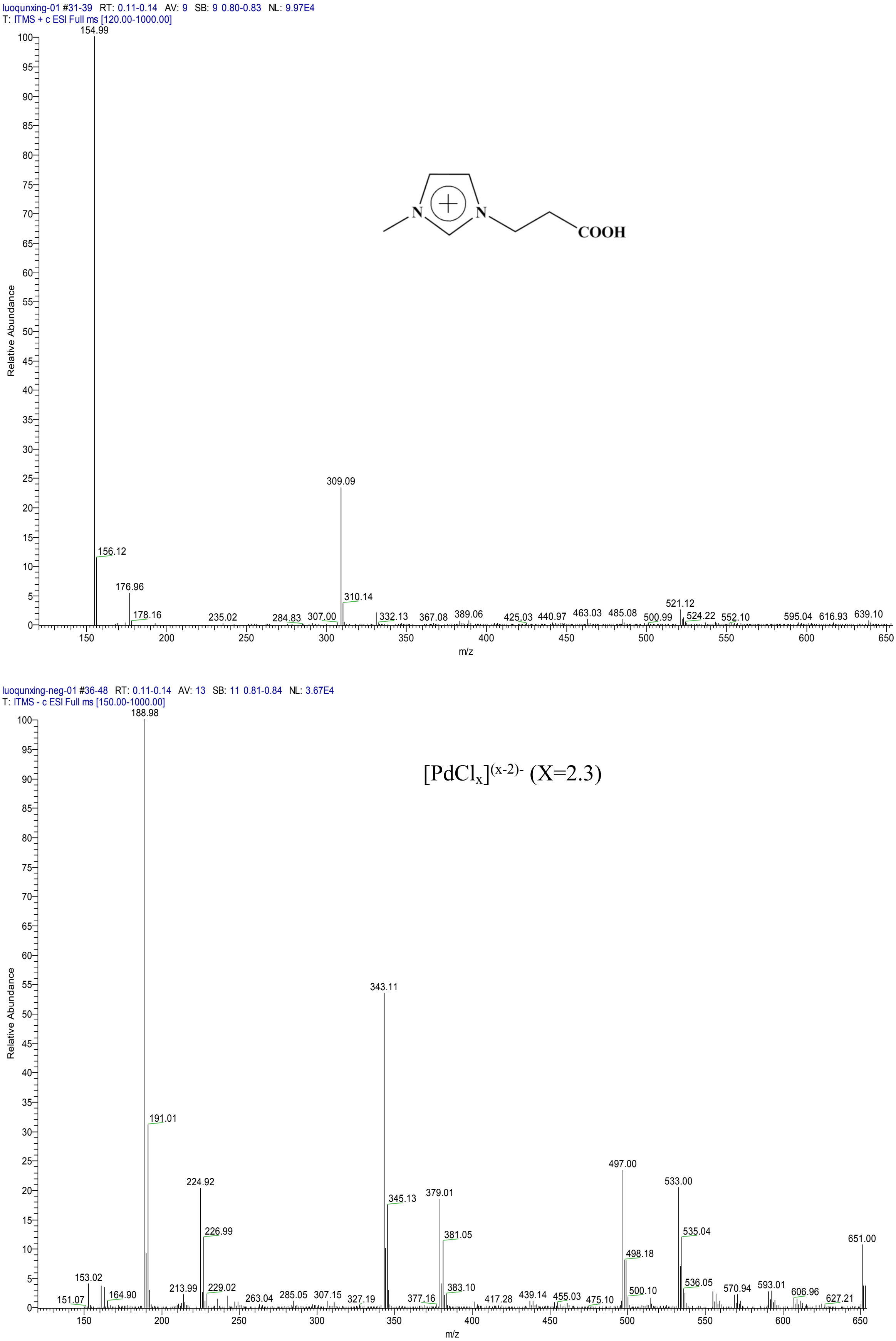


Fig. S6 MS spectra of $PdCl_2$-ILs complex

Table. S2 Catalytic performance of cyclohexene oxidation with different catalysts[a]

Catalysts	Conversion (%)	Selectivity (%)			
		Expo	-OH	=O	-OOBu
ILs[b]	5.9	n.d[e]	t.a[f]	100	n.d
$PdCl_2$[c]	7.8	n.d	t.a	100	t.a
$Cu(NO_3)_2$[d]	14.0	n.d	30.4	69.6	t.a

[a] Reaction condition: 10 mL solution of *n*-heptane-TBHP (n_{TBHP}=0 or 10% $n_{cyclohexene}$), 6 mmol cyclohexene, 333 K.

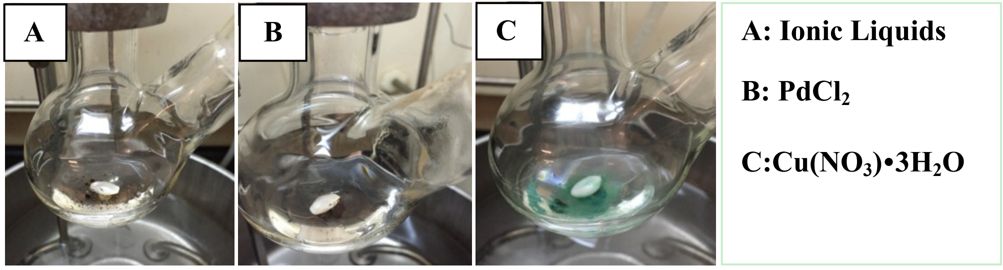
[b]Using same amount of ILs species with $PdCl_2$-ILs/CuBTC catalyst (0.063 mmol, 0.0120 g)

[c]Using same amount of Pd species with $PdCl_2$-ILs/CuBTC catalyst (0.020 mmol, 0.0035 g)

[d]Using same amount of Cu species with $PdCl_2$-ILs/CuBTC catalyst (0.271 mmol, 0.0655 g)

[e]n.d=not detected

[f] t.a= trace amount of cyclohexene oxide cannot be quantified by GC



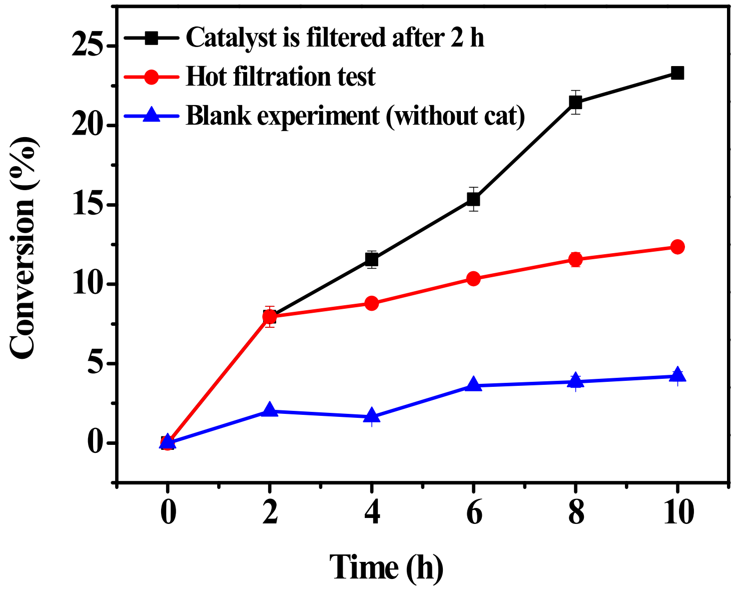


Fig. S7 Hot filtration test for oxidation of cyclohexene with $PdCl_2$-ILs/CuBTC.

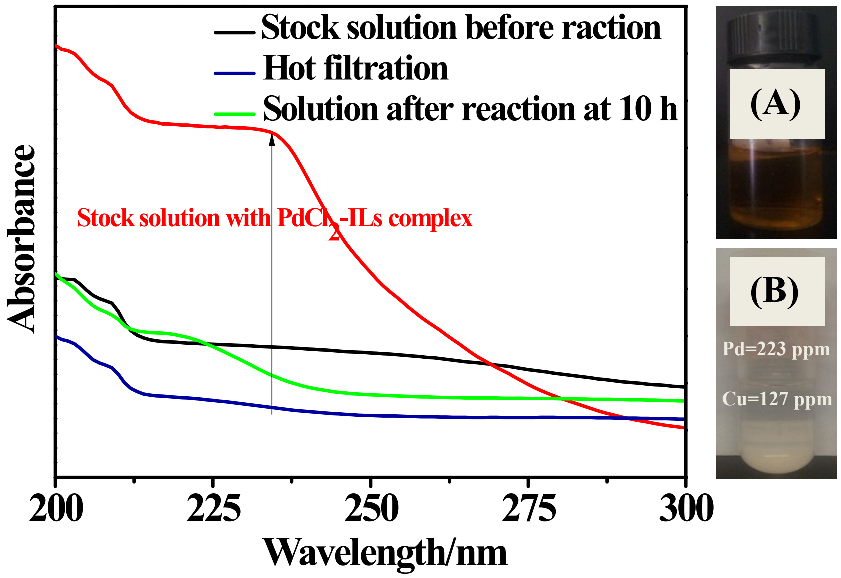


Fig. S8 The leaching test of palladium in reaction solution by Uv-vis and ICP analysis. (A) Stock solution with $PdCl_2$-ILs complex; (B) Solution of reaction after 10 h.

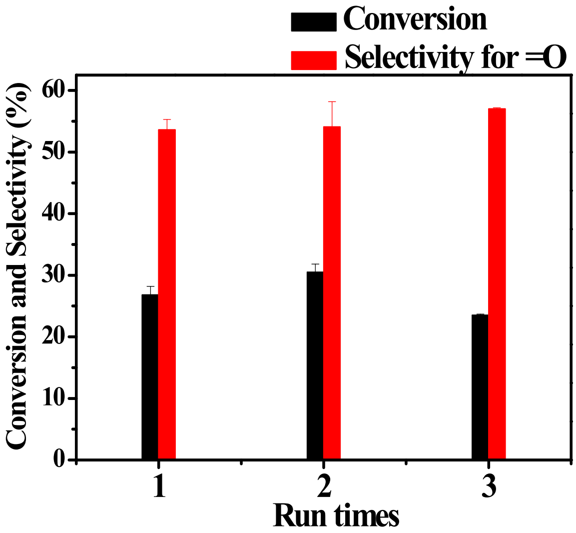


Fig. S9 The recyclability of $PdCl_2$-ILs/CuBTC catalyst in selective oxidation of cyclohexene.

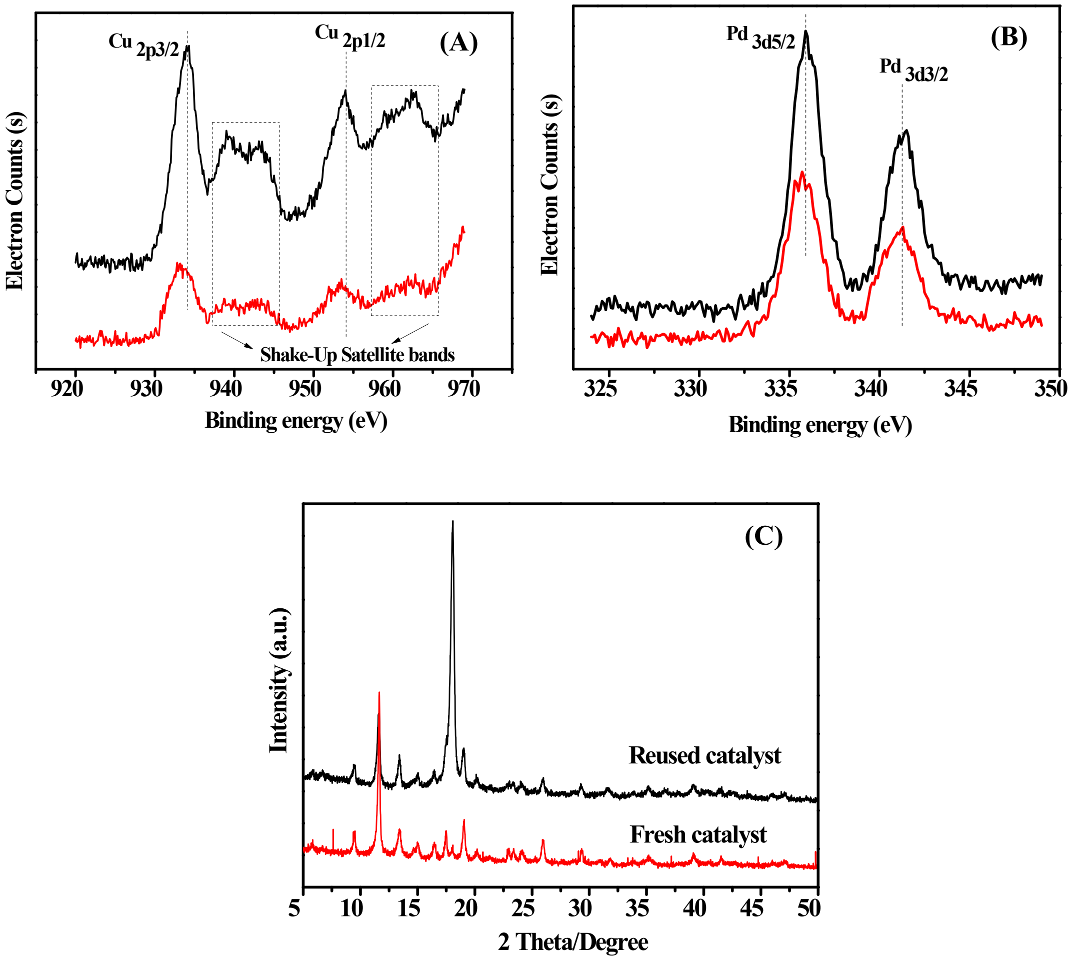


Fig. S10 Characterization of reused catalyst. (A): Cu 2p spectra; (B): Pd 3d spectra; (C): XRD characterization

3 References

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