Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Significant promoting effects of Lewis acidity on Au-Pd systems in the selective oxidation of aromatic hydrocarbons

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Experimental Section

1. Catalyst Preparations

1.1 Synthesis of MIL-101[S1]

MIL-101 was prepared from hydrothermal reaction of $Cr(NO_3)_3·9H_2O$ (2.00 g, 5 mmol), HF (48 wt %, 5 mmol), terephthalic acid (0.823 g, 5 mmol), and 24 ml deionized water at 220 °C for 8 h. The mixture was cooled first to 150 °C in 1 h, and then slowly to room temperature in 12 h. Upon the slow cooling procedure, most of the residual carboxylic acid was in large crystals that can be easily isolated from the solution and MIL-101 powder by using a large pore fritted glass filter (n°2, Schott). The free terephthalic acid was eliminated and the green MIL-101 powder was isolated from the solution using a small pore paper filter (1°, Whatman). The powder was washed thoroughly with deionized water and ethanol, and then soaked in ethanol (95% EtOH with 5% water) at 80 °C for 24 h. The solid was finally dried overnight at 150 °C under vacuum.

1.2 Synthesis of EN-MIL-101[S2]

MIL-101 grafted with ethylenediamine (EN) was prepared according to the following procedures. MIL-101 (0.5 g) dehydrated at 423 K for 12 h was suspended in anhydrous toluene (30 ml). To this suspension, ethylenediamine (0.045 g) was added and the mixture was stirred under reflux for 12 h. The product was recovered by filtration and washed with de-ionized water/ethanol, and then dried at room temperature for 24 h.

1.3 Synthesis of Au/MIL-101

An aqueous solution of $HAuCl_4$ ($1×10^{-3}$ M) was prepared with PVA as a protecting agent (PVA monomer/Au = 10:1, molar ratio). The mixture was vigorously stirred for 0.5 h under a bath of 0 °C. Then, a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/Au = 5:1, molar ratio) was injected rapidly to obtain a dark brown sol. Within a few minutes of sol generation, the MIL-101 was added to the colloidal gold solution under vigorous stirring and kept in contact for 4 h, followed by washing thoroughly with deionized water. The sample was dried under vacuum at 100 °C for 2 h, and then heated at 200 °C in H_2 for 2 h.

1.4 Synthesis of Pd/MIL-101

An aqueous solution of $PdCl_2$ (1×10^{-3} M) was prepared with PVA as a protecting agent (PVA monomer/Pd = 10:1, molar ratio). The mixture was vigorously stirred for 0.5 h under a bath of 0 °C. Then, a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/Pd = 5:1, molar ratio) was injected rapidly to obtain a dark brown sol. Within a few minutes of sol generation, the MIL-101 was added to the colloidal palladium solution under vigorous stirring and kept in contact for 4 h, followed by washing thoroughly with deionized water. The sample was dried under vacuum at 100 °C for 2 h, and then heated at 200 °C in H_2 for 2 h.

1.5 Synthesis of Au-Pd/MIL-101

An aqueous solution of $HAuCl_4$ and $PdCl_2$ (1×10^{-3} M) was prepared with PVA as a protecting agent (PVA monomer/(Au+Pd) = 10:1, molar ratio). The mixture was vigorously stirred for 0.5 h under a bath of 0 °C. Then, a freshly prepared solution of $NaBH_4$ (0.1 M, $NaBH_4$/(Au+Pd) = 5:1, molar ratio) was injected rapidly to obtain a dark brown sol. Within a few minutes of sol generation, the MIL-101 was added to the colloidal solution under vigorous stirring and kept in contact for 4 h, followed by washing thoroughly with deionized water. The sample was dried under vacuum at 100 °C for 2 h, and then heated at 200 °C in H_2 for 2 h.

1.6 Synthesis of Au-Pd/EN-MIL-101

Au-Pd/EN-MIL-101 was prepared according to the reported procedures.[S3] 500 mg of activated EN-MIL-101 was mixed with 25 ml de-ionized water containing 7.95 mg H_2PdCl_4 and 8.62 mg $HAuCl_4$ at pH~3 and 35 °C for 24 h, followed by washing with deionized water. The sample was dried in air, further dried under vacuum 100 °C for 2 h, followed by treating in a stream of H_2 at 200 °C for 3 h to yield Au-Pd/EN-MIL-101.

2. Catalyst Characterization

Powder X-ray diffraction patterns of the samples were obtained on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Kα radiation (40 kV, 30 mA, □□0.1543 nm).

BET surface area and pore size measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 instrument. Before the analysis, the samples were evacuated at 150 °C for 12 h.

The metal contents of the samples were determined quantitatively by atomic absorption spectroscopy (AAS) on a HITACHI Z-2300 instrument.

TEM micrographs were recorded on a FEI Tecnai G^2 fitted with a CCD camera for ease and speed of use. The resolution is around 0.4 nm. Samples were suspended in ethanol and deposited straight away on a copper grid prior to analysis.

XPS (aka ESCA) measurements were performed in a ultra high vacuum (UHV) multipurpose surface analysis system (Specs^{TM} model, Germany) operating at pressures $<10^{-10}$ mbar using a conventional X-Ray source (XR-50, Specs, Mg-Kα, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. The survey and detailed high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon.

The surface acidity was measured in a dynamic mode by means of a pulse chromatographic technique of gas-phase adsorption of PY (sum of Brönsted and Lewis acid sites) and 2,6-dimethylpyridine (DMPY, Brönsted sites) as probe molecules.

DRIFTs characterisation of surface acidity involved the titration of the acid sites with PY. The basic probes were introduced by bubbling a stream of dehydrated and deoxygenated nitrogen through the liquid and into the sample chamber containing the neat (no KBr diluted) catalyst sample. Samples were equilibrated for at least 1 h at each temperature and reactant condition prior to collecting the spectra. Reactant excess was purged from the sample chamber.

3. Catalytic Measurements

3.1 General procedure for the hydrocarbon oxidation

The oxidation reactions was performed in a 20 mL Teflon-lined stainless steel autoclave quipped with a pressure gauge and a magnetic stirrer. The autoclave was connected to an oxygen cylinder, and the reaction pressure was controlled with a precise gas regulator, so that oxygen of fixed pressure could be supplied continuously. Typically, hydrocarbon (47 mmol) and a required amount of catalyst were loaded into the reactor. The autoclave was sealed, cooled to 0 °C by placing it to an ice bath, and purged several times with O_2 to remove the air. Then the reactor was pressurized with O_2 and loaded in an oil bath, which was preheated to the target temperature. After the reaction, the autoclave was cooled to 0 °C in an ice bath. The gaseous products were collected with a gas bag, and subsequently analyzed by a GC equipped with a TCD detector. The GC traces of the gaseous samples indicate that no CO_2 was produced in the oxidation reactions. The solid catalyst was isolated from the solution by centrifugation. The reaction products were quantified and identified by GC-MS and GC analysis (a 0.25 mm × 30 m DB-WAX capillary column). The carbon balance values calculated for all the reaction tests were around 100% (100 ± 3%).

3.2 Recycling of the Au-Pd/MIL-101 catalyst

The recyclability of the Au-Pd/MIL-101 catalyst was tested for toluene oxidation maintaining the same reaction conditions as described above, except using the recovered catalyst. Each time, the catalyst was separated from the reaction mixture by centrifugation at the end of catalytic reaction, thoroughly washed with toluene, and then reused directly as catalyst for the next run. Furthermore, the isolated reaction solution was analyzed for leached metals by atomic absorption spectroscopy (AAS) and metal concentrations were below the detection limits.

3.3 Heterogeneity of the catalyst

To verify whether the catalysis of Au-Pd/MIL-101 is truly heterogeneous, the solid catalyst was hot filtered from the reaction solution after 7 h. The reaction was continued with the filtrate in the absence of solid catalyst for an additional 9 h. The solution in the absence of solid did not exhibit any further reactivity. The results demonstrate that the reaction proceeds on the heterogeneous surface.

Reference

(S1) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science,* 2005, **309**, 2040.

(S2) Y. K. Hwang, D. Y. Hong, J.S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem. Int. Ed.*, 2008, **47**, 4144.

(S3) X. J. Gu, Z. H. Lu, H. L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11822.

Scheme S1. Possible reaction pathways for the production of benzyl benzoate from toluene oxidation.

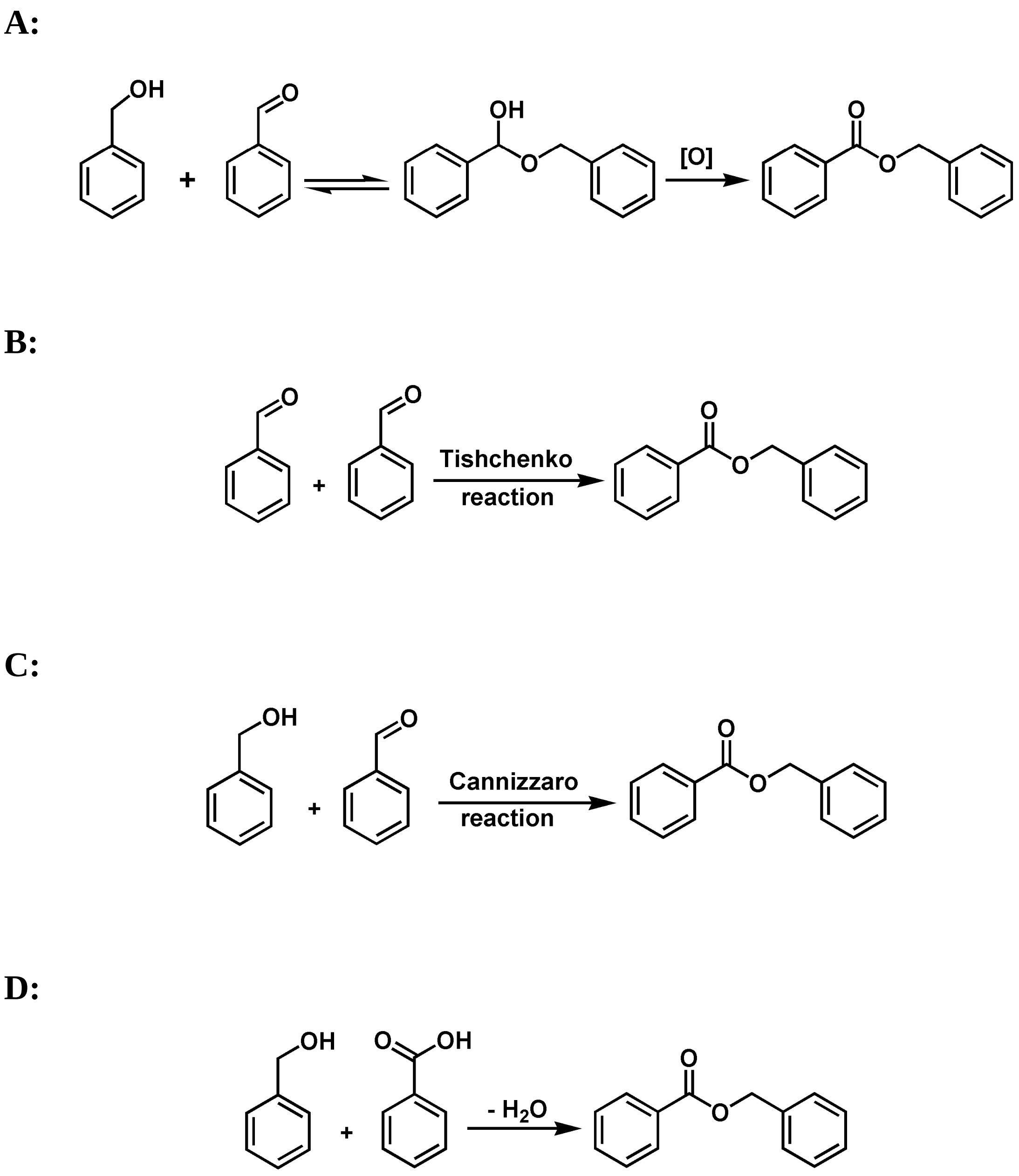


Table S1. Characterization results of 1 wt% Au-Pd/MIL-101 catalysts

Pd-Au molar ratio	BET surface area (m^2 g^{-1})	Langmuir surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
-	3161	4520	1.58
0:1	2535	3689	1.28
1:5	2437	3389	1.22
1:2	2348	3291	1.20
1:1	2253	3210	1.14
1.5:1	2369	3382	1.21
2:1	2302	3298	1.22
4:1	2375	3427	1.23
5:1	2449	3581	1.24
1:0	2325	3295	1.18
1.5:1[a]	2115	3092	1.07

[a] Au-Pd/EN-MIL-101.

Table S2. Surface acidity of various catalytic materials using a chromatographic methodology[a]

Materials	Total acidity (µmol PY/g cat.)	Brönsted acidity (µmol DMPY/g)	Lewis Acidity (PY-DMPY data) (µmol /g cat.)
Parent MIL-101	2020	33	1987
1%Au/MIL-101	1401	51	1350
1% Pd/MIL-101	1523	47	1476
1%Au-Pd/MIL-101	1908	4	1904
1%Au-Pd/EN-MIL-101	<100	-	-

[a] Titrations carried out using the reported chromatographic method (see references 16 and 17 in the main manuscript) using two solutions 1.978 M of PY and DMPY, respectively, in acetonitrile. Flow: 5 mL/min N_2, temperature of titration: 208 ºC.

Table S3. Results of the aerobic oxidation of toluene in the absence of solvent[a]

Entry	Pd:Au molar ratio	Conv. (mol%)	TON	Selectivity to products (mol%)			
				BZ	BZBZ	PhBZ	C-C prod.
1	0:1	2.6	57	16	-	-	84
2	1:5	17.4	383	10	42	3	45
3	1:2	40.7	895	9	72	4	15
4	1:1	52.8	1162	9	81	4	6
5	**1.5:1**	**75.6**	**1663**	**4**	**89**	**4**	**3**
6	2:1	68.5	1507	4	90	3	3
7	4:1	53.5	1177	7	83	4	6
8	5:1	32.5	715	20	72	5	3
9	1:0	1.9	42	100	-	-	-

[a] Reaction conditions: toluene (5 mL), 1 wt%Au-Pd/MIL-101, substrate/metal = 2200, 120 ºC, 1 MPa O_2, 48 h. Products obtained in the reaction; BZ: benzaldehyde; BZBZ: benzylbenzoate; PhBZ: phenyl benzoate; C-C prod.: C-C coupling products from 2 toluene molecules.

Table S4. Studies on the effect of various parameters (temperature and oxygen pressure) in the solventless aerobic oxidation of toluene[a]

Temperature influence in Au-Pd/MIL-101 aerobic oxidation of toluene

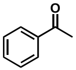
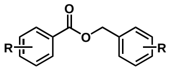
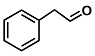
Entry	Temp. (ºC)	Conv. (mol%)	TON	Selectivity to products (mol%)			
				BZ	BZBZ	PhBZ	C-C
1	100	42.2	928	30	64	4	2
2	120	75.6	1663	4	89	4	3
3	140	96.3	2119	2	90	5	3
4[b]	160	98.0	2156	1	89	5	5

Influence of the oxygen pressure in Au-Pd/MIL-101 oxidation of toluene

Entry	PO_2 (MPa)	Conv. (mol%)	TON	Selectivity to products (mol%)			
				BZ	BZBZ	PhBZ	C-C
5	0.6	38.2	840	9	83	5	2
6	0.8	59.6	1311	6	86	5	3

[a] Reaction: toluene (5 mL), 1 wt%Au-Pd/MIL-101, 120 ºC, 1 MPa O_2, 48 h, substrate/metal = 2200, (unless otherwise stated). [b] t = 20 h.

Table S5. Aerobic oxidation of ethylbenzene in the absence of solvent using 1 wt%Au-Pd/MIL-101[a]

Conversion (%)	Product selectivity (%)				TON
				Others	
51.1	51.5	1.6	43.9	3.0	1533

[a] Reaction conditions: ethylbenzene (47 mmol), 1 wt%Au-Pd/MIL-101 (Pd:Au molar ration = 1.5:1), substrate/metal = 3000, 1.0 MP of O_2, 120 °C, 48 h.

Table S6. Liquid phase reaction of benzyl alcohol, benzaldehyde and benzoic acid in toluene at 120 °C without catalysts in the presence of O_2.

Substrate	Time	Toluene (mol)	Benzyl alcohol (mol)	Benz-aldehyde (mol)	Benzoic acid (mol)	Benzyl benzoate (mol)
Benzyl alcohol and Benzaldehyde in toluene	0	0.094420	0.001500	0.001500	0	0
	1	0.09440	0.001481	0.001535	0	0
	5	0.094439	0.001475	0.001506	0	0.000004
	10	0.094452	0.001392	0.001570	0	0.000006
Benzaldehyde in toluene	0	0.09442	0	0.0030	0	0
	1	0.094640	0.000037	0.002743	0	0
	5	0.094280	0.000086	0.002934	0.000120	0
	10	0.094011	0.000137	0.002931	0.000341	0

Reaction conditions: Toluene = 10 ml, T = 120 ºC, P_{O_2} = 1.0 MP.

Table S7. Liquid phase reaction of benzyl alcohol, benzaldehyde and benzoic acid in toluene at 120 °C without catalysts in the presence of He.

Substrate	Time	Toluene	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate
Benzyl alcohol and Benzaldehyde in toluene	0	0.09442	0.0015	0.0015	0	0
	1	0.094396	0.001481	0.001543	0	0
	5	0.094451	0.001467	0.001502	0	0
	10	0.094418	0.001469	0.001532	0.000001	0
Benzaldehyde in toluene	0	0.09442	0	0.0030	0	0
	1	0.094605	0	0.002815	0	0
	5	0.094619	0.000002	0.002798	0.000001	0
	10	0.094587	0.000002	0.002829	0.000002	0
Benzyl alcohol and Benzoic acid in toluene	0	0.09442	0.0015	0	0.0015	0
	1	0.094526	0.001578	0	0.001316	0
	5	0.094663	0.001456	0.000003	0.001298	0
	10	0.094592	0.001485	0.000009	0.001334	0

Reaction conditions: Toluene = 10 ml, T = 120 ºC, P_{He} = 1.0 MP.

Table S8. Liquid phase reaction of benzyl alcohol, benzaldehyde and benzoic acid in toluene at 120 °C with catalysts in the presence of He.

substrate	Time	Toluene	Benzyl alcohol	Benzaldehyde	Benzoic acid	Benzyl benzoate
Benzyl alcohol and Benzaldehyde in toluene	0	0.09442	0.0015	0.0015	0	0
	1	0.094452	0.001447	0.001521	0	0
	5	0.094485	0.001486	0.001449	0	0
	11	0.094398	0.001488	0.001534	0	0
Benzaldehyde in toluene	0	0.09442	0	0.003	0	0
	1	0.094546	0	0.002874	0	0
	5	0.094525	0	0.002895	0	0
	11	0.094645	0	0.002775	0	0
Benzyl alcohol and Benzoic acid in toluene	0	0.09442	0.0015	0	0.0015	0
	1	0.094452	0.001550	0.000011	0.001407	0
	5	0.094506	0.001505	0.000014	0.001395	0
	11	0.094489	0.001476	0.000018	0.001437	0

Reaction conditions: Toluene = 10 ml, T = 120 ºC, P_{He} = 1.0 MP, substrate/metal = 600:1.

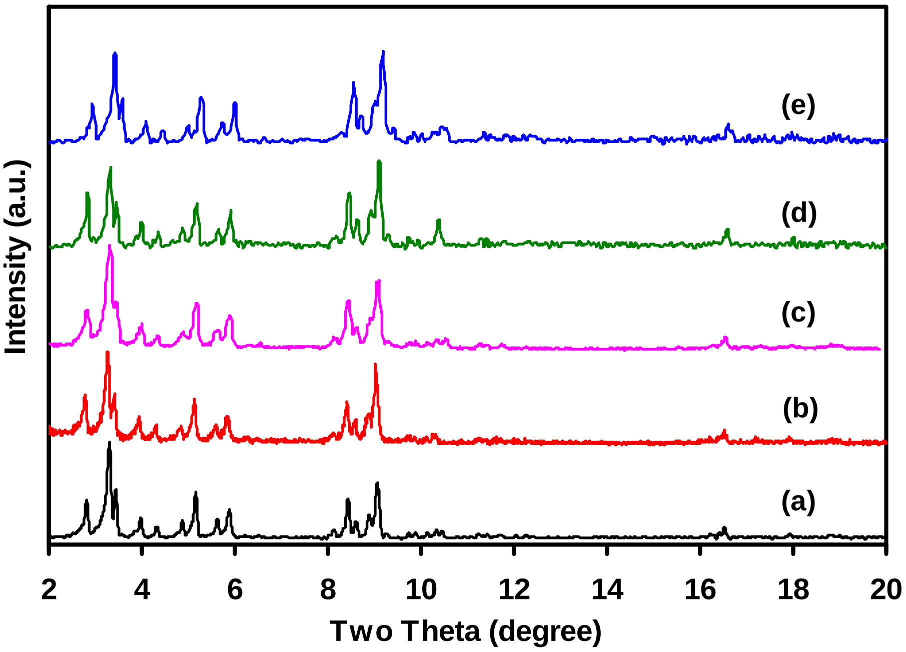


Figure S1. Powder XRD patterns of MIL-101 samples. (a) as-synthesized MIL-101; 1 wt%Au-Pd/MIL-101 (Pd:Au molar ration = 1.5:1) before (b) and after (c) catalytic reaction; (d) EN-MIL-101; (e) Au-Pd/EN-MIL-101.

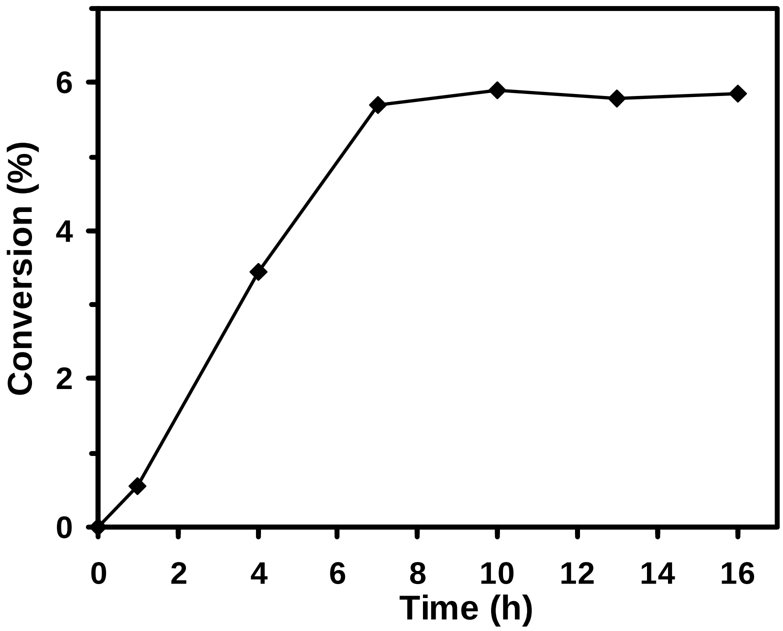


Figure S2. Activity profile for the toluene oxidation. Reaction conditions: toluene (5 ml), 1 wt%Au-Pd/MIL-101, substrate/metal = 6500, O_2 = 1 MP, 120 °C. The solid catalyst was hot filtered from the reaction solution after 7 h and the reaction was continued with the filtrate in the absence of solid catalyst for an additional 9 h. The isolated reaction solution was analyzed for leached metals and levels were below the detection limits.

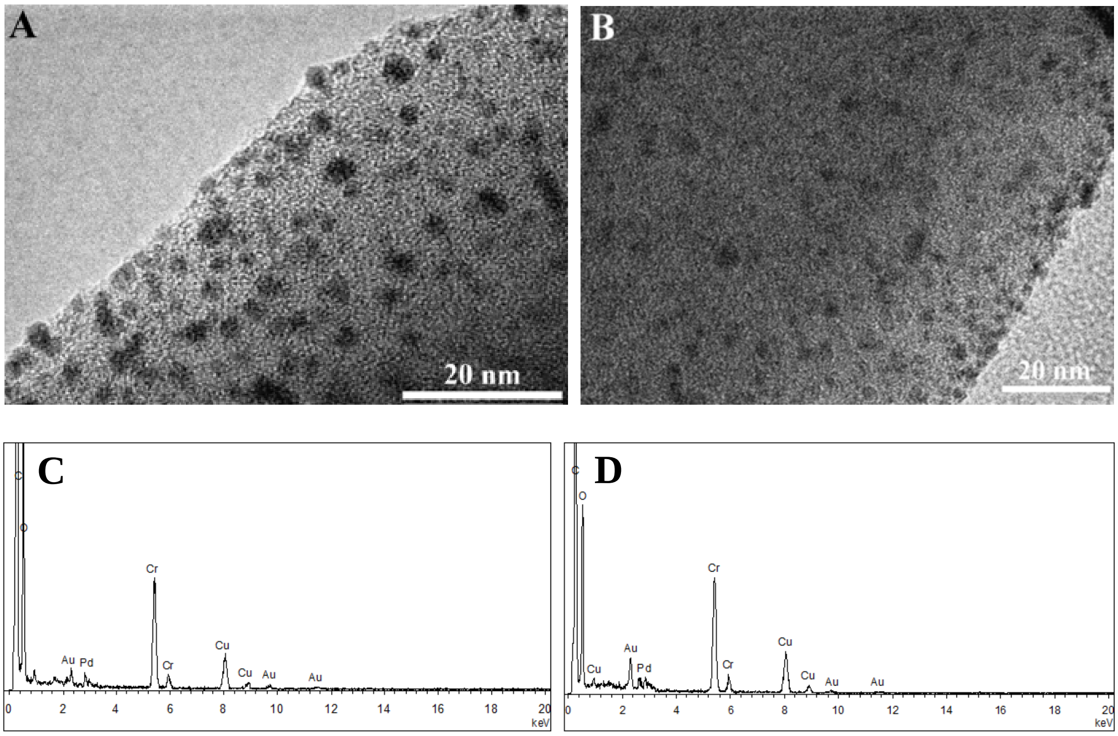


Figure S3. TEM micrographs of the fresh 1 wt%Au-Pd/MIL-101 (A), and the third reused 1 wt%Au-Pd/MIL-101 (B) in the oxidation of toluene; and EDX pattern of the fresh 1 wt%Au-Pd/MIL-101 (C), and the reused 1 wt%Au-Pd/MIL-101 (D).

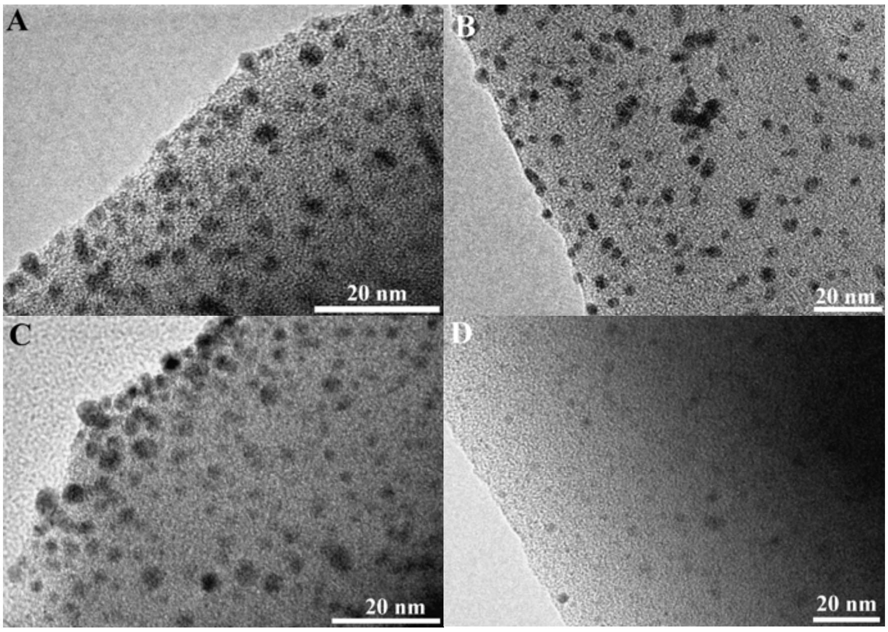


Figure S4. HRTEM micrographs of A) 1wt%Au-Pd/MIL-101; B) 1wt%Au-Pd/C; C) 1wt%Au/MIL-101; D) 1wt%Pd/MIL-101.

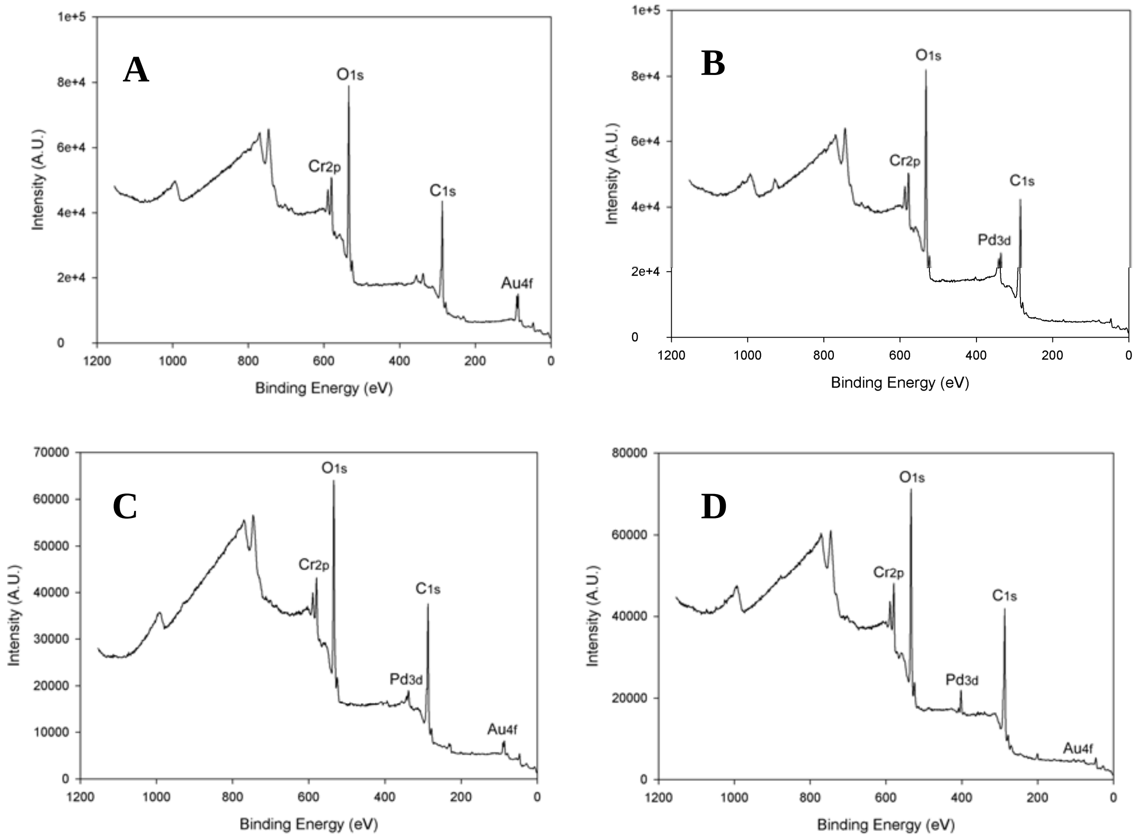
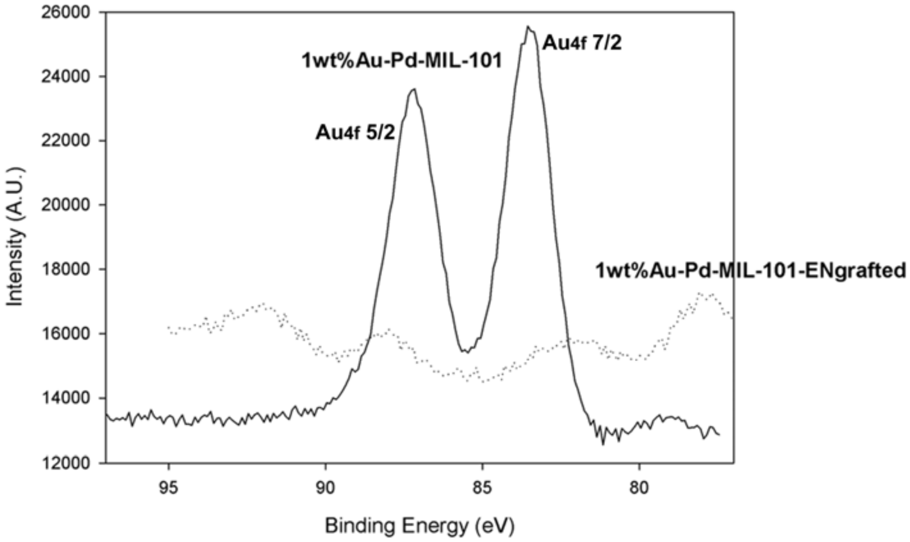


Figure S5 Survey XPS spectra of 1 wt%Au-MIL-101 (A), 1 wt% Pd-MIL-101(B), 1 wt%Au-Pd-MIL-101 (C), and 1 wt%Au-Pd-EN-MIL-101 (D).



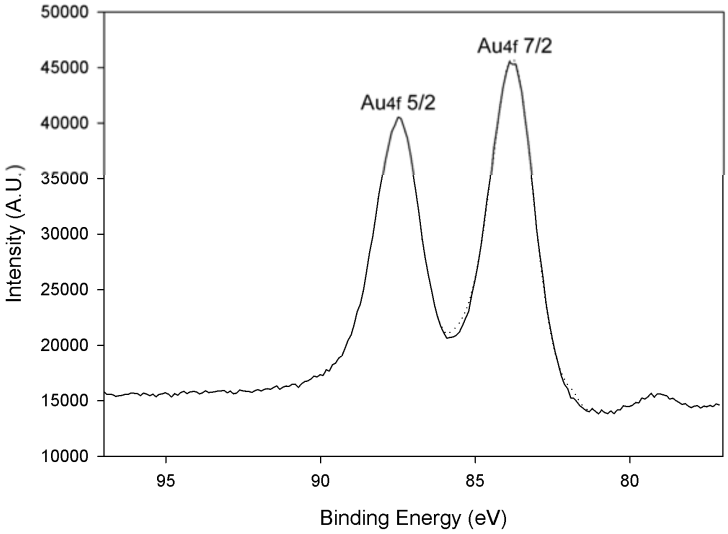


Figure S6 Comparison of Au(4f) XPS spectra for 1 wt%Au-Pd/MIL-101 and 1 wt%Au-Pd/EN-MIL-101 (top), and 1 wt%Au/MIL-101 (bottom). Remarkable differences can be noticed particularly related to the intensity of the bands between the 1 wt%Au-Pd/MIL-101 and 1 wt%Au-Pd/EN-MIL-101 samples.

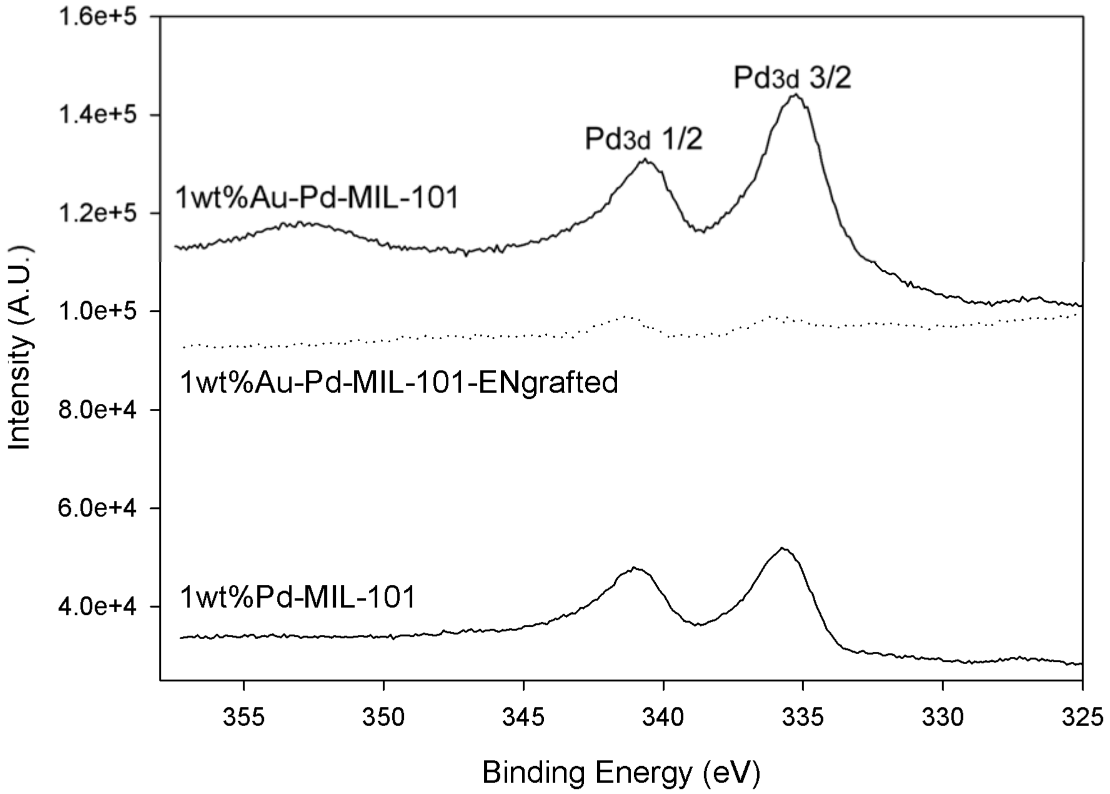


Figure S7 Comparison of Pd(3d) XPS spectra for 1 wt%Au-Pd/MIL-101, 1 wt%Au-Pd/EN-MIL-101, and 1 wt% Pd/MIL-101. Remarkable differences can be noticed particularly related to the intensity of the bands between the 1 wt%Au-Pd/MIL-101 and 1 wt%Au-Pd/EN-MIL-101 samples.

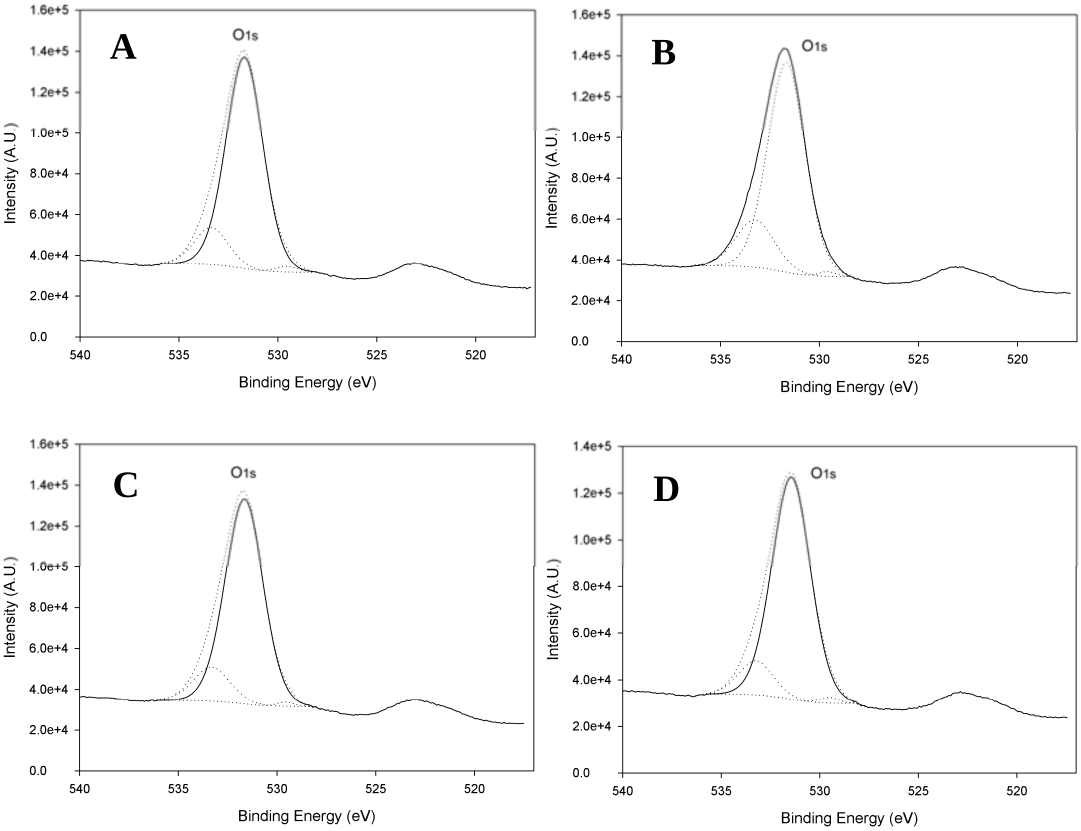


Figure S8 O(1s) spectra of 1 wt%Au/MIL-101 (A), 1 wt% Pd/MIL-101 (B), 1 wt%Au-Pd/MIL-101 (C), and 1 wt%Au-Pd/EN-MIL-101 (D).

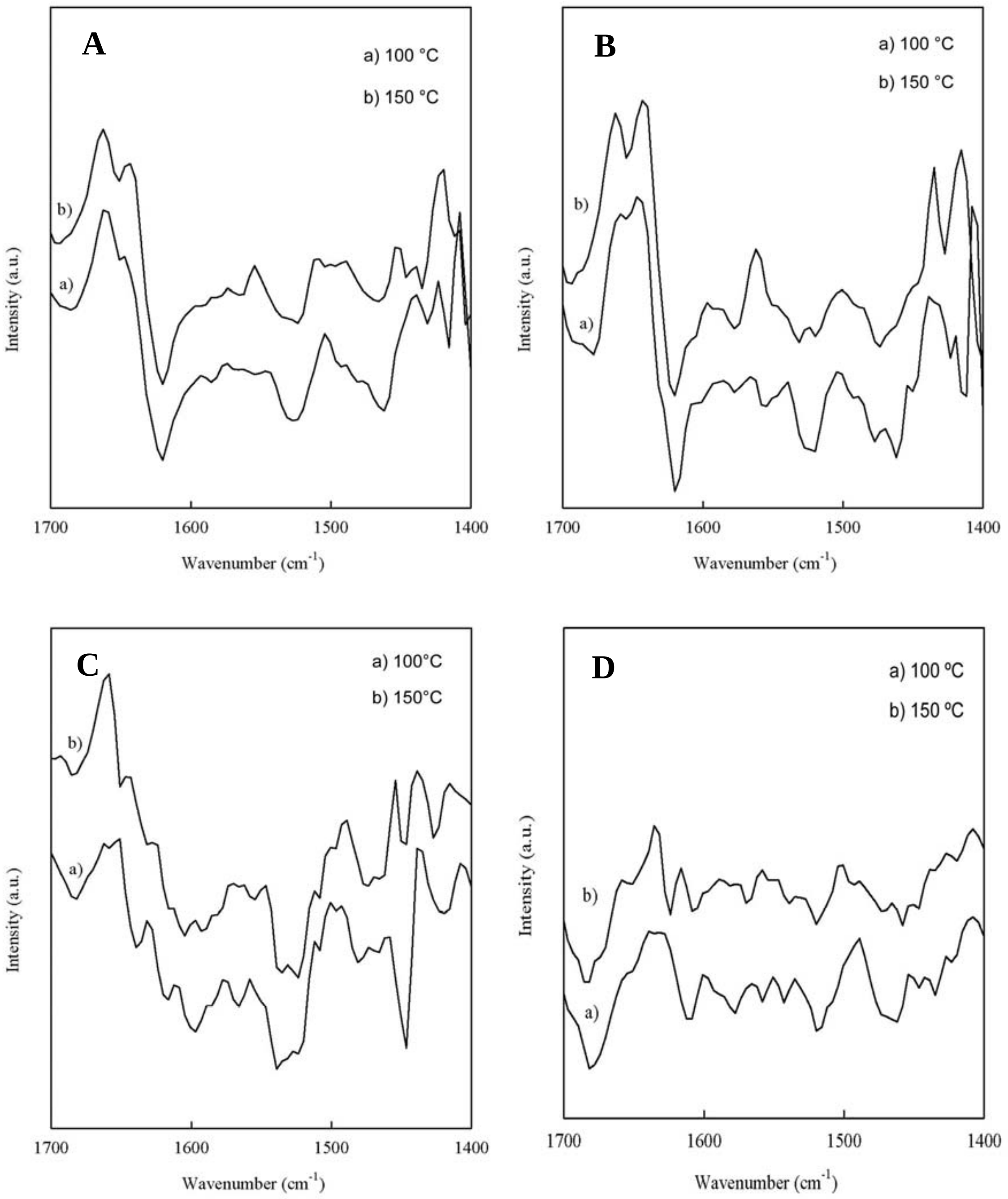


Figure S9 DRIFT spectra of pyridine adsorption for 1 wt%Au/MIL-101 (A), 1 wt% Pd/MIL-101 (B), 1 wt%Au-Pd/EN-MIL-101 (C), and 1 wt%Au-Pd/MIL-101 (D).

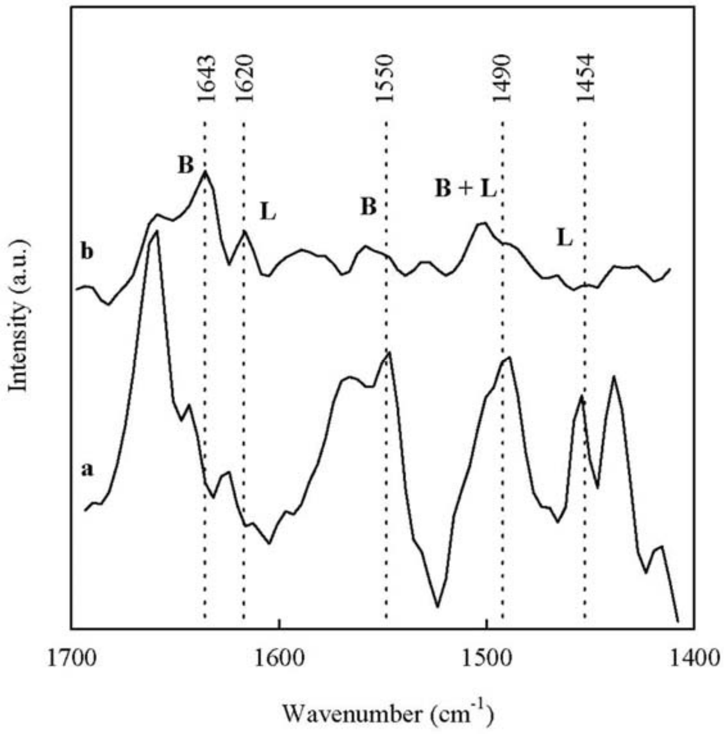


Figure S10 Comparison of DRIFT spectra of pyridine adsorption at 150 °C for 1 wt%Au-Pd/EN-MIL-101 (a), and 1 wt%Au-Pd/MIL-101 (b).