Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Highly stable Pd^{2+} species anchoring on ethylenediamine-grafted-MIL-101(Cr) as a robust oxidation catalyst

Materials

Terephthalic acid (98%), Chromium(III) nitrate ($Cr(NO_3)_3.9H_2O$, 99%), ethylenediamine (99%), palladium(II) acetate ($Pd(OAc)_2$, 98%), phenylacetylene (98%), iodobenzene (98%) and nitrobenzene (99%) were obtained commercially from Sigma-Aldrich. *N,N*-dimethylformamide (DMF, 99.8%), methanol (99.8%), ethanol (99.5%), acetone (99.5%), acetonitrile (99.8%), potassium carbonate (K_2CO_3, 99%), sodium carbonate (Na_2CO_3, 99%), 30% H_2O_2 solution and diethyl ether (99%) were provided by Carlo. Styrene (99%, Merck) was purified by extracting twice with 10% sodium hydroxide (NaOH, 98%) solution, washed three times with distilled water and dried over calcium hydride (Merck, 95%). Toluene (99.5%), dichloromethane (99.8%) and *n*-hexane (95%) were dried and stored under molecular sieve 4A.

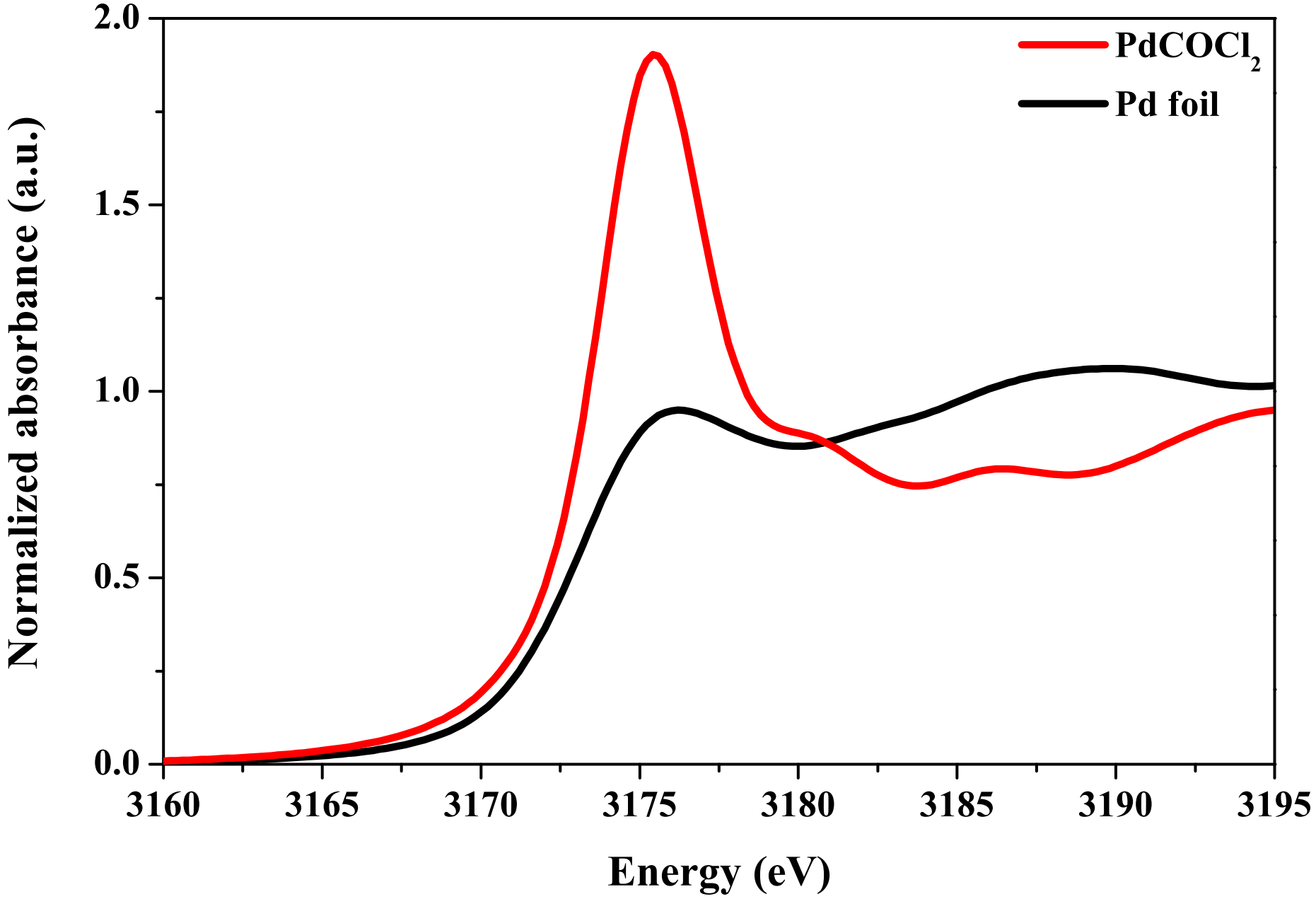

Fig. S1 Pd L_3-edge XANES spectra of Pd foil and $PdCOCl_2$ standards, recorded at room temperature.

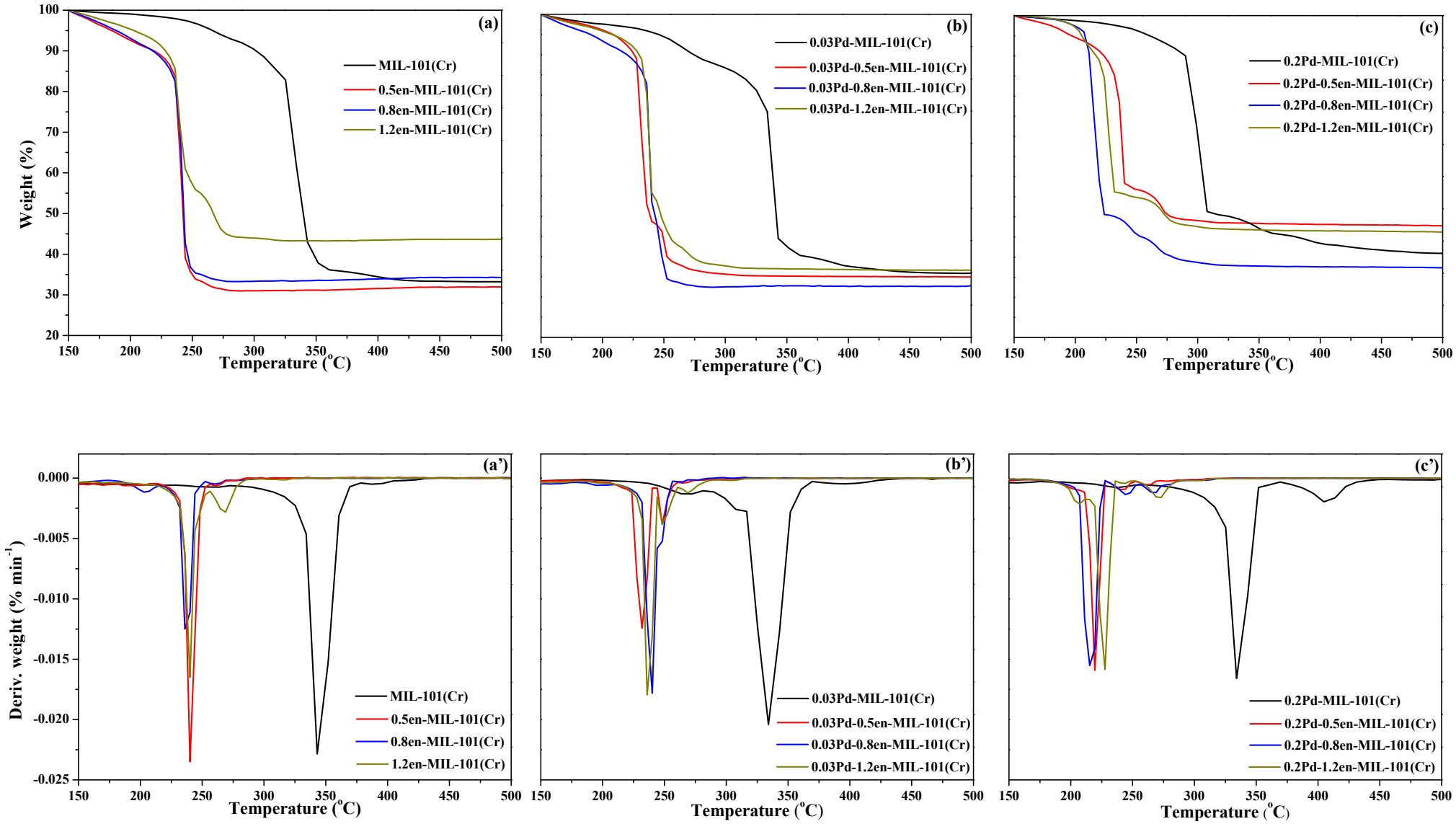

Fig. S2 TGA and DTG thermogram of MIL-101(Cr) when (a, a′) grafted with ethylenediamine and introduced (b, b′) 0.03 wt%Pd and (c, c′) 0.2 wt%Pd over ethylenediamine-grafted samples

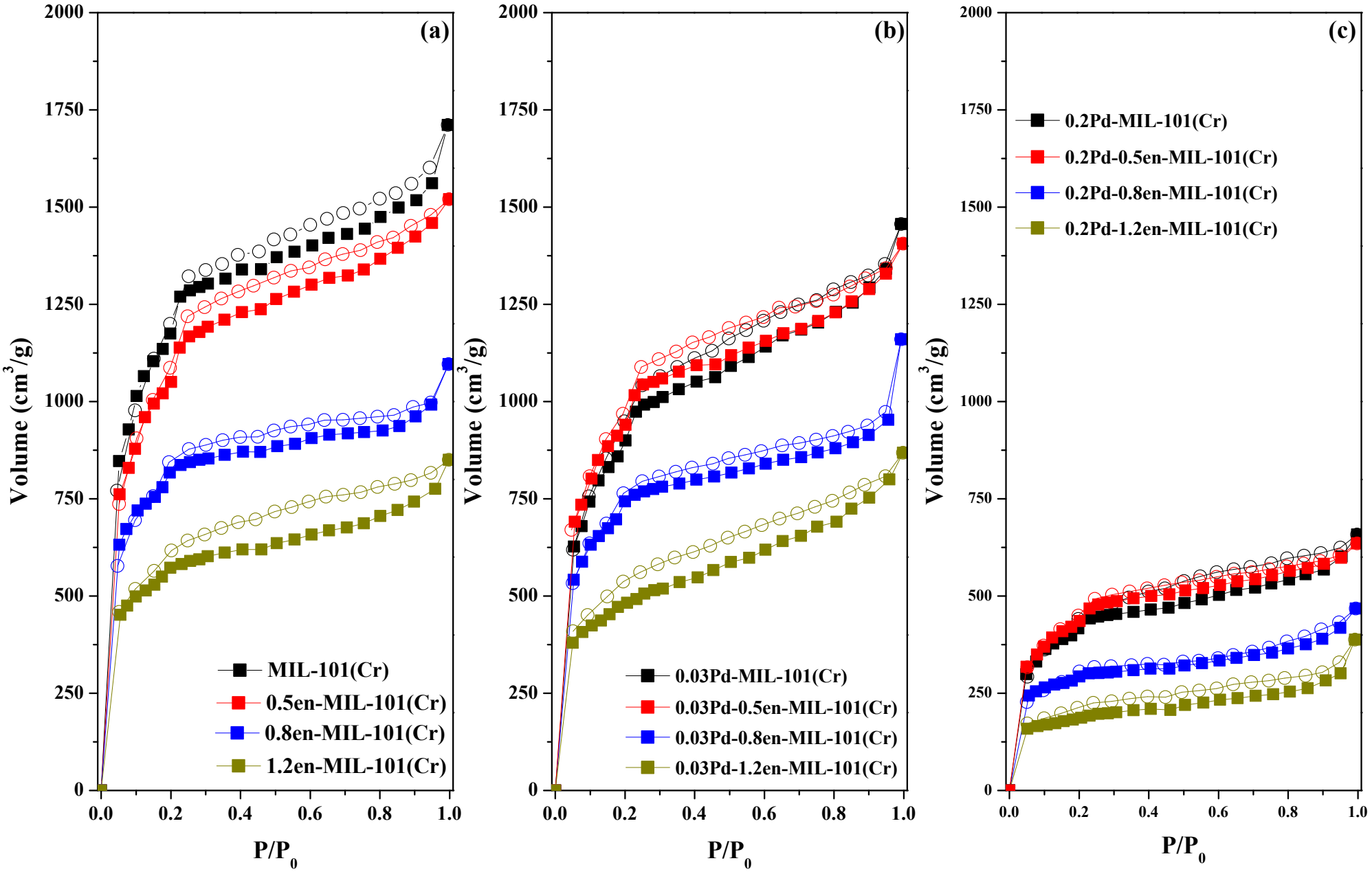

Fig. S3 N_2 adsorption isotherm of (a) ethylenediamine-grafted MIL-101(Cr) with (b) 0.03 wt%Pd and (c) 0.2 wt%Pd loadings.

Determination of ethylenediamine (en) in MIL-101(Cr) samples

The amount of ethylenediamine can be determined by the total N content from CHN analysis. However, in addition to ethylenediamine, this N content also consists of the nitrate counter anion and remained DMF, which cannot directly be measurable.

From N 1S XPS spectra (Fig. 2), the mol fraction from those N species can be calculated through integrated of each peak.

Table S1 mol fraction and ethylenediamine content in MIL-101(Cr), en-MIL-101(Cr), Pd-en-MIL-101(Cr) and Pd-MIL-101(Cr) samples

Entry	Samples	Mol fraction[a] (%)			Total N content[b] (wt%)	NO_3^- content (wt%)	en content	
		DMF	NO_3^-	en			(wt%)	(mmol/g)
1	MIL-101(Cr)	47	53	-	1.9	1.00	-	-
2	0.5en-MIL-101(Cr)	-	49	51	3.2	1.57	1.63	0.58
3	0.8en-MIL-101(Cr)	-	49	51	4.0	1.97	2.04	0.73
4	1.2en-MIL-101(Cr)	-	39	61	5.3	2.06	3.23	1.15
5	0.03Pd-0.5en-MIL-101(Cr)	-	46	54	2.5	1.15	1.35	0.48
6	0.03Pd-0.8en-MIL-101(Cr)	-	-	-	3.4	1.73[c]	1.67[c]	0.60[c]
7	0.03Pd-1.2en-MIL-101(Cr)	-	43	57	4.6	1.96	2.62	0.94
8	0.2Pd-0.5en-MIL-101(Cr)	-	-	-	2.1	1.13[c]	0.97[c]	0.35[c]
9	0.2Pd-0.8en-MIL-101(Cr)	-	-	-	2.2	1.00[c]	1.20[c]	0.43[c]
10	0.2Pd-1.2en-MIL-101(Cr)	-	42	58	3.3	1.40	1.91	0.68
11	0.03Pd-MIL-101(Cr)	55	45	-	1.6	0.72	-	-
12	0.2Pd-MIL-101(Cr)	-	-	-	1.3	-	-	-

[a]Calculated from integrated peak of N 1S XPS spectra, [b]CHN analysis and [c]Estimated content

Calculation of ethylenediamine content

From XPS result, we can calculate ethylenediamine content as follow;
For example, 1.2en-MIL-101(Cr)

From XPS analysis			
N %mol of nitrate	=	39 %	
N %mol of ethylenediamine	=	61 %	
From CHN analysis			
Total N content	=	5.3	wt%
	=	5.3	g/100 g_{sample}
N content of nitrate	=	(5.3 x 39) / 100	g/100 g_{sample}
	=	2.1	g/100 g_{sample}
N content of ethylenediamine	=	(5.3 x 61) / 100	g/100 g_{sample}
	=	3.23	g/100 g_{sample}
mmol of ethylenediamine	=	(3.2 x 1000) / (14 x 2)	mmol/100g_{sample}
	=	115	mmol/100g_{sample}
	=	1.15	mmol/g_{sample}

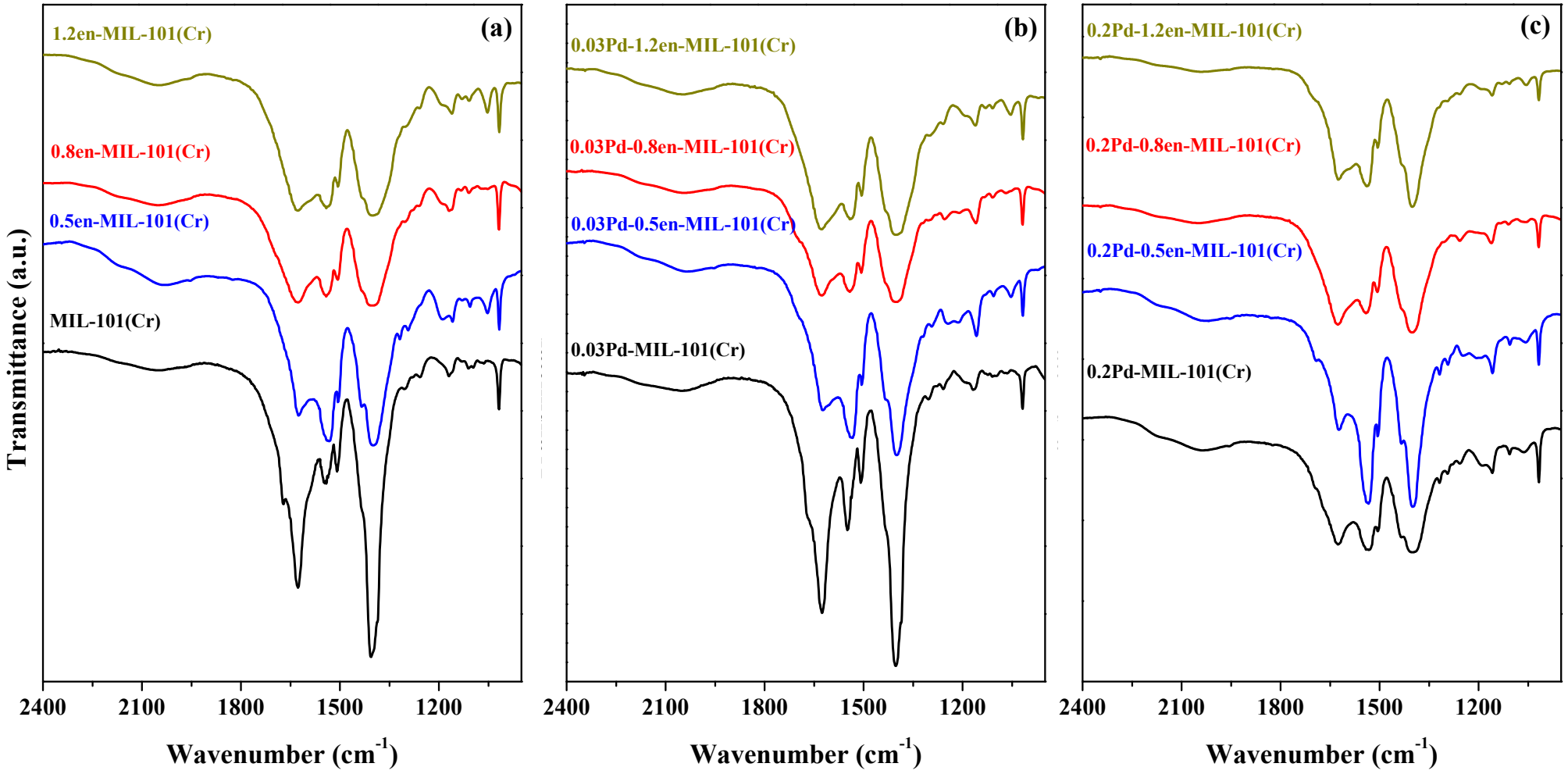

Fig. S4 FTIR spectra of (a) ethylenediamine-grafted MIL-101(Cr) with (b) 0.03 wt%Pd and (c) 0.2 wt%Pd loadings.

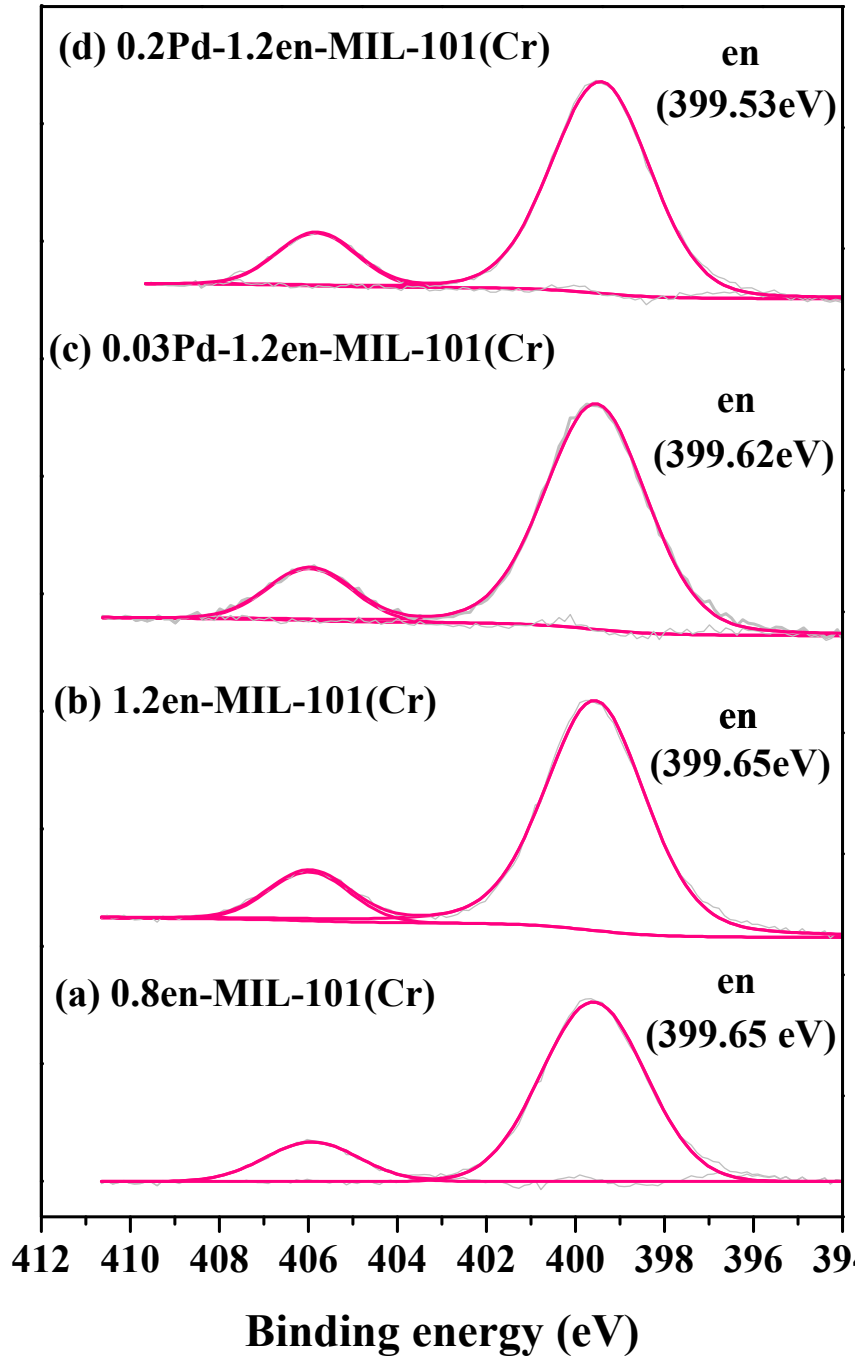

Fig. S5 High-resolution N 1s XPS spectra of (a) 0.8en-MIL-101(Cr), (b) 1.2en-MIL-101(Cr), (c) 0.03Pd-1.2en-MIL-101(Cr) and (d) 0.2Pd-1.2en-MIL-101(Cr) samples.

Table S2 Absorption edge energy of all samples under *in situ* reduction from 30 ˚C to 150 ˚C

	Temp (˚C)	Absorption edge energy (eV)					
		0.03Pd-1.2en-MIL-101(Cr)	0.03Pd-MIL-101(Cr)	0.03Pd-SiO_2	0.2Pd-0.8en-MIL-101(Cr)	0.2Pd-MIL-101(Cr)	0.2Pd-SiO_2
Activation	150	3174.2	3174.1	3173.3	3174.2	3173.6	3173.7
Reduction under H_2	30	3174.2	3173.1	3173.4	3174.2	3173.5	3173.6
	70	3174.2	3173.2	3173.3	3174.2	3173.3	3173.4
	110	3174.2	3173.1	3173.5	3174.2	3173.4	3173.5
	150	3174.2	3173.0	3173.1	3174.2	3173.4	3173.5
Holding in H_2 at 150 ˚C	150 (20min)	3174.2	3173.2	3173.4	3174.2	3173.2	3173.4
	150 (40min)	3174.2	3173.2	3173.4	3174.2	3173.3	3173.5
	150 (60min)	3174.2	3173.2	3173.3	3174.2	3173.3	3173.5

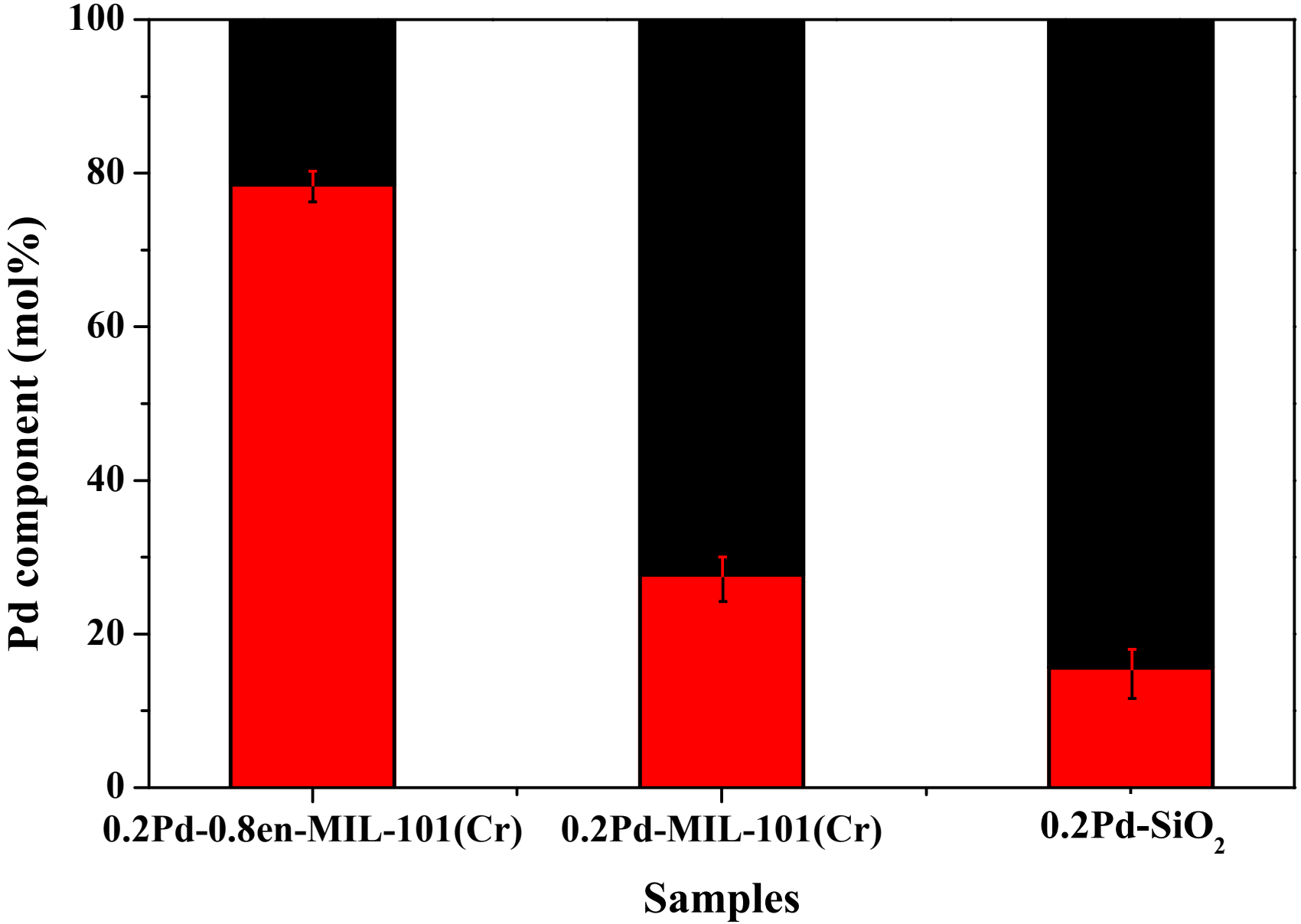

Fig. S6 Pd component from Pd L_3-edge XANES linear combination fitting of 0.2Pd-0.8en-MIL-101(Cr), 0.2Pd-MIL-101(Cr) and 0.2Pd-SiO_2 upon in situ reduction at 150 ˚C under 10%H_2/N_2.

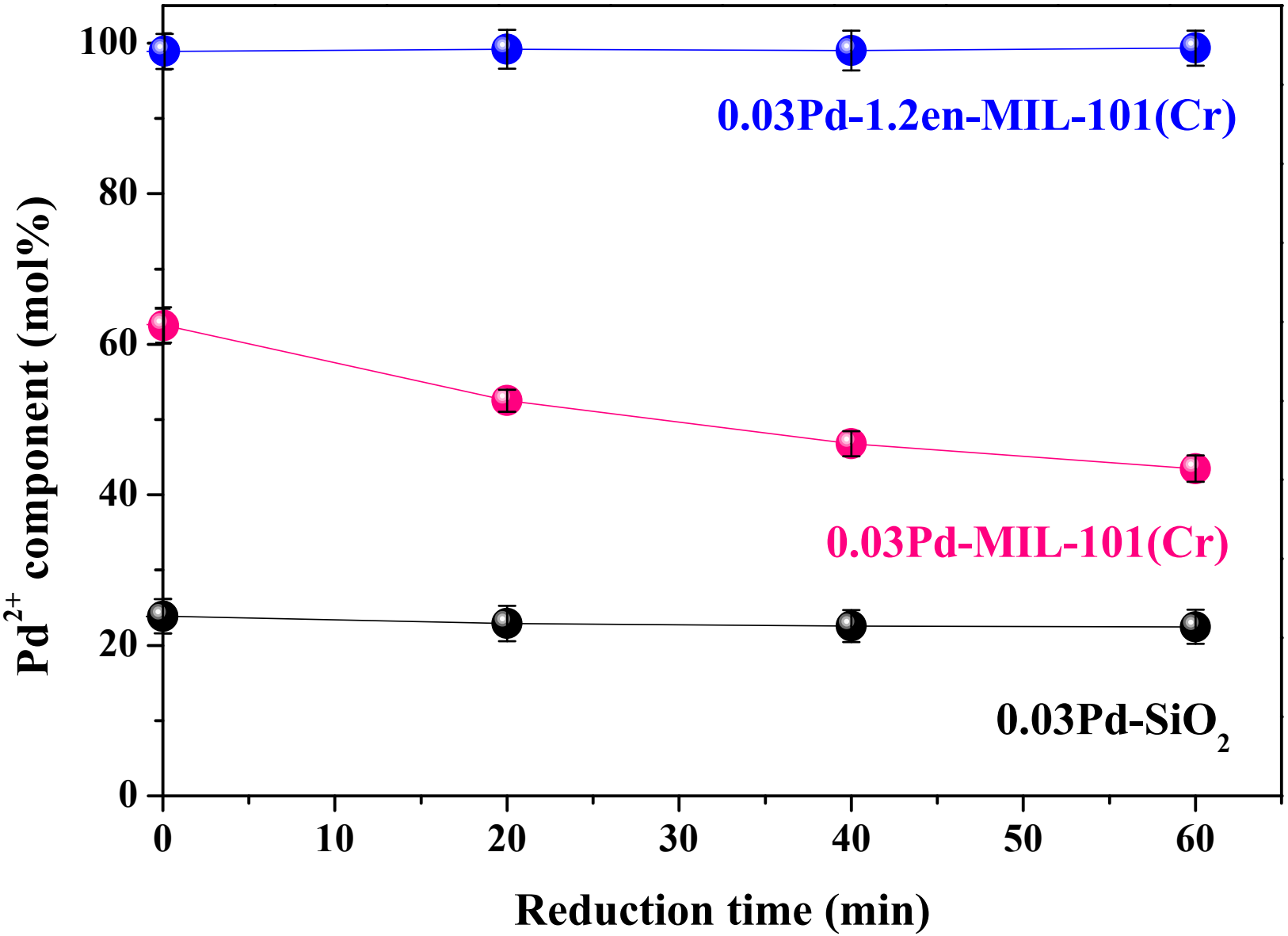

Fig. S7 Pd^{2+} component from Pd L_3-edge XANES linear combination fitting of 0.03Pd-1.2en-MIL-101(Cr), 0.03Pd-MIL-101(Cr) and 0.03Pd-SiO_2 upon in situ reduction at 150˚C during 0 – 60 min under 10%H_2 in N_2 .

Table S3 R-factor of 0.03 wt%Pd loaded over 1.2en-MIL-101(Cr), MIL-101(Cr) and SiO_2 samples and 0.2 wt%Pd loaded over 0.8en-MIL-101(Cr), MIL-101(Cr) and SiO_2 samples after linear combination fitting.

	Temperature (˚C)	R factor *					
		0.03Pd-1.2en-MIL-101(Cr)	0.03Pd-MIL-101(Cr)	0.03Pd-SiO_2	0.2Pd-0.8en-MIL-101(Cr)	0.2Pd-MIL-101(Cr)	0.2Pd-SiO_2
Activation	150	0.045	0.007	0.050	0.046	0.035	0.037
Reduction under 10%H_2/N_2	30	0.045	0.009	0.043	0.037	0.048	0.053
	70	0.045	0.027	0.044	0.026	0.045	0.054
	110	0.031	0.040	0.044	0.028	0.046	0.051
	150	0.038	0.014	0.045	0.030	0.044	0.057
Hold at 150˚C	150 (20 min)	0.043	0.021	0.036	0.034	0.051	0.051
	150 (40 min)	0.045	0.023	0.041	0.027	0.059	0.057
	150 (60 min)	0.034	0.007	0.050	0.046	0.034	0.037

* $R = \frac{\sum(data - fit)^2}{\sum(data)^2}$

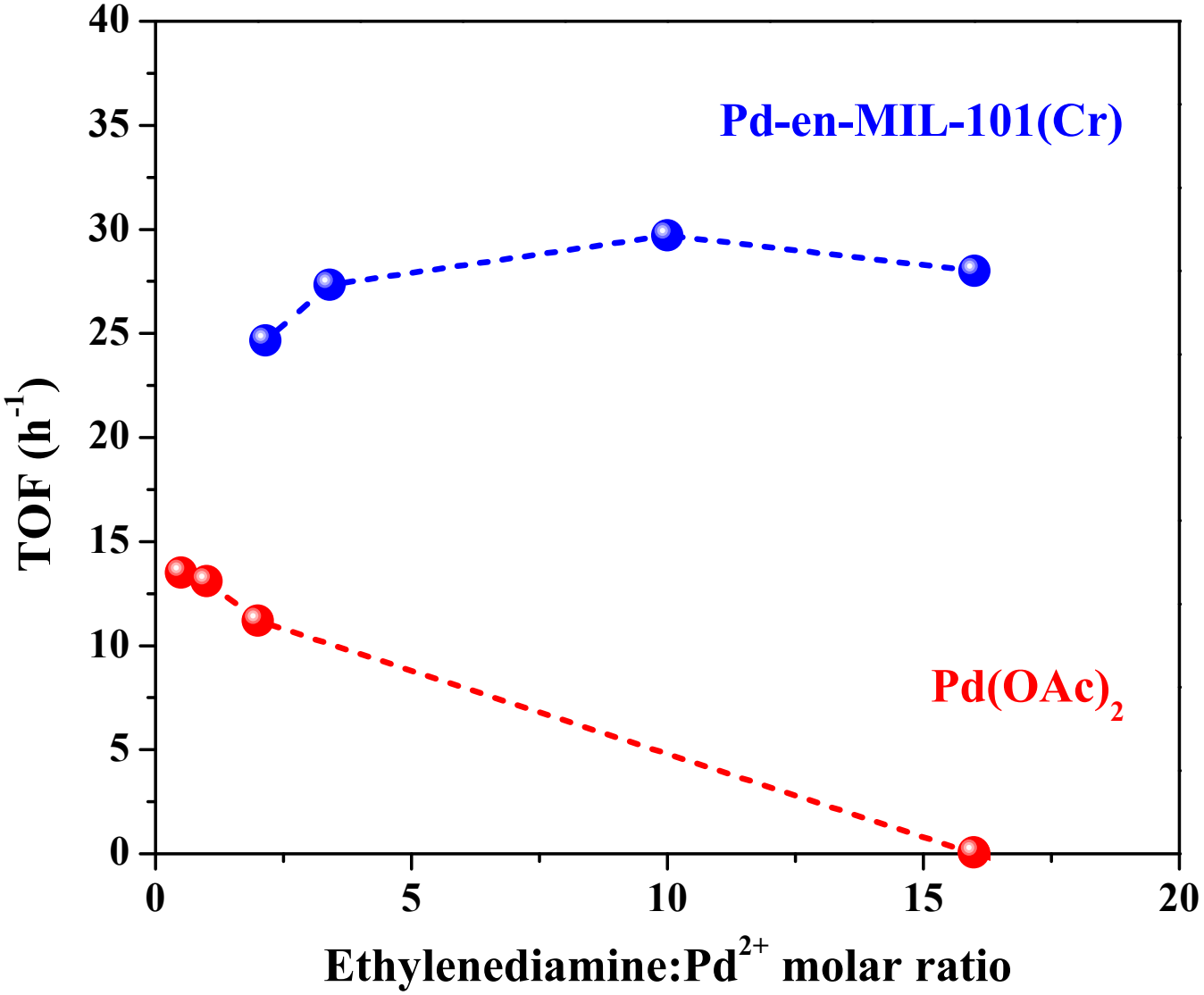

Fig. S8 Effect of ethylenediamine on Pd^{2+} activity of Pd-en-MIL-101(Cr) and $Pd(OAc)_2$.