

# Supplementary Materials: Chlorodifluoromethane Hydrodechlorination on Carbon-Supported Pd-Pt Catalysts. Beneficial Effect of Catalyst Oxidation

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**Table S1.** CHClF<sub>2</sub> hydrodechlorination on Pd-Pt/(acac)/Norit1600 catalysts precalcined at 320 °C for 1 h. TOFs, selectivities and apparent energies of activation.

Catalyst <sup>a,b</sup>	Reaction temperature °C	TOF <sup>c</sup> s <sup>-1</sup>	Product selectivity, %				Activation energy, kJ/mol
			CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	CH <sub>2</sub> F <sub>2</sub>	
Pd100(acac) H/Pd = 0.123	272	1.06 × 10 <sup>-3</sup>	26.7	-	-	73.3	97.3 ± 1.9
	262	7.15 × 10 <sup>-4</sup>	23.2	-	-	76.8	
	252	4.7 × 10 <sup>-4</sup>	20.6	-	-	79.4	
Pd80Pt20(acac) H/(Pd+Pt) = 0.191	271	1.41 × 10 <sup>-3</sup>	32.8	3.6	-	63.6	97.8 ± 5.2
	262	1.02 × 10 <sup>-3</sup>	24.7	5.2	-	70.1	
	251	6.2 × 10 <sup>-4</sup>	24.9	6.0	-	69.1	
Pd60Pt40(acac) H/(Pd+Pt) = 0.252	271	1.95 × 10 <sup>-3</sup>	43.0	9.5	-	47.5	91.1 ± 8.8
	262	1.30 × 10 <sup>-3</sup>	40.8	9.3	-	48.9	
	251	9.0 × 10 <sup>-4</sup>	36.6	14.8	-	48.6	
Pd40Pt60(acac) H/(Pd+Pt) = 0.331	271	1.64 × 10 <sup>-3</sup>	44.2	13.5	-	42.3	76.6 ± 4.3
	263	1.25 × 10 <sup>-3</sup>	40.9	14.6	-	44.5	
	252	8.7 × 10 <sup>-4</sup>	36.5	14.9	-	48.6	
Pt100(acac) H/Pt = 0.465	271	6.0 × 10 <sup>-4</sup>	58.4	14.9	14.0	12.7	103.6 ± 2.7
	262	4.0 × 10 <sup>-4</sup>	60.2	20.7	4.0	19.1	
	251	2.5 × 10 <sup>-4</sup>	74.0	9.4	-	16.6	

<sup>a</sup> For the catalyst designation, see Methods (subsection 3.1); <sup>b</sup> Metal dispersion data (from H<sub>2</sub> chemisorption) located below catalyst designation; <sup>c</sup> GHSV 5760 h<sup>-1</sup>, catalyst weight 0.20 g.

**Table S2.** CHClF<sub>2</sub> hydrodechlorination on Pd-Pt/(acac)/Norit1600 catalysts precalcined at 350 °C for 1 h. TOFs, selectivities and apparent energies of activation.

Catalyst <sup>a,b</sup>	Reaction temperature °C	TOF <sup>c</sup> s <sup>-1</sup>	Product selectivity, %				Activation energy, kJ/mol
			CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	CH <sub>2</sub> F <sub>2</sub>	
Pd100(acac) H/Pd = 0.161	272	2.30 × 10 <sup>-3</sup>	29.5	-	-	70.5	102.3 ± 1.5
	261	1.46 × 10 <sup>-3</sup>	25.0	-	-	75.0	
	251	9.25 × 10 <sup>-4</sup>	20.6	-	-	79.4	
Pd80Pt20(acac) H/(Pd+Pt) = 0.223	272	2.30 × 10 <sup>-3</sup>	38.0	4.2	-	57.8	98.8 ± 2.8
	261	1.50 × 10 <sup>-3</sup>	33.7	4.0	-	62.3	
	251	9.6 × 10 <sup>-4</sup>	30.0	4.0	-	66.0	
Pd60Pt40(acac) H/(Pd+Pt) = 0.243	272	2.32 × 10 <sup>-3</sup>	43.6	7.9	-	48.5	97.7 ± 4.8
	261	1.61 × 10 <sup>-3</sup>	39.4	8.5	-	52.1	
	251	1.02 × 10 <sup>-3</sup>	35.0	8.5	-	56.5	
Pd40Pt60(acac) H/(Pd+Pt) = 0.321	272	2.25 × 10 <sup>-3</sup>	47.2	13.2	-	39.6	92.9 ± 1.3
	262	1.55 × 10 <sup>-3</sup>	41.5	14.9	-	43.6	
	251	9.9 × 10 <sup>-4</sup>	38.4	15.6	-	46.0	
Pt100(acac) H/Pt = 0.348	272	7.5 × 10 <sup>-4</sup>	52.8	13.8	22.0	11.4	107.5 ± 0.4
	262	4.8 × 10 <sup>-4</sup>	60.2	20.6	-	19.2	
	251	2.9 × 10 <sup>-4</sup>	66.3	18.7	-	15.0	

<sup>a</sup> For the catalyst designation, see Methods (subsection 3.1); <sup>b</sup> Metal dispersion data (from H<sub>2</sub> chemisorption) located below catalyst designation; <sup>c</sup> GHSV 5760 h<sup>-1</sup>, catalyst weight 0.20 g.

**Table S3.** CHClF<sub>2</sub> hydrodechlorination on Pd-Pt/(acac)/Nortit1600 catalysts precalcined at 400 °C for 15 min. TOFs, selectivities and apparent energies of activation.

Catalyst <sup>a,b</sup>	Reaction temperature °C	TOF <sup>c</sup> s <sup>-1</sup>	Product selectivity <sup>c</sup> , %				Activation energy, kJ/mol
			CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	CH <sub>2</sub> F <sub>2</sub>	
Pd100(acac) H/Pd = 0.105	272	2.63 × 10 <sup>-3</sup>	33.7	-	-	66.3	98.5 ± 3.7
	262	1.80 × 10 <sup>-3</sup>	30.1	-	-	69.9	
	252	1.15 × 10 <sup>-3</sup>	24.4	-	-	75.6	
Pd80Pt20(acac) H/(Pd+Pt) = 0.198	272	2.50 × 10 <sup>-3</sup>	37.5	4.0	-	58.5	92.6 ± 8.3
	262	1.60 × 10 <sup>-3</sup>	33.2	4.0	-	62.8	
	251	1.1 × 10 <sup>-4</sup>	28.9	3.9	-	67.2	
Pd60Pt40(acac) H/(Pd+Pt) = 0.212 0.229	272	2.52 × 10 <sup>-3</sup>	42.6	7.8	-	49.5	94.4 ± 6.4
	261	1.72 × 10 <sup>-3</sup>	38.4	8.4	-	53.2	
	251	1.09 × 10 <sup>-3</sup>	34.0	8.5	-	57.5	
Pd40Pt60(acac) H/(Pd+Pt) = 0.317	272	2.10 × 10 <sup>-3</sup>	44.2	14.0	-	41.8	88.3 ± 2.8
	262	1.43 × 10 <sup>-3</sup>	40.5	14.9	-	44.6	
	252	1.0 × 10 <sup>-4</sup>	36.4	15.7	-	47.9	
Pt100(acac) H/Pt = 0.273	271	9.2 × 10 <sup>-4</sup>	53.1	13.8	21.5	11.5	97.9 ± 12.8
	262	5.8 × 10 <sup>-4</sup>	60.4	19.2	-	20.4	
	251	4.0 × 10 <sup>-4</sup>	70.2	19.3	-	10.5	

<sup>a</sup> For the catalyst designation, see Methods (subsection 3.1); <sup>b</sup> Metal dispersion data (from H<sub>2</sub> chemisorption) located below catalyst designation; <sup>c</sup> GHSV 5760 h<sup>-1</sup>, catalyst weight 0.20 g.

**Table S4.** CHClF<sub>2</sub> hydrodechlorination on Pd-Pt/Norit catalysts prepared from palladium and platinum chlorides. TOFs, selectivities and apparent energies of activation.

Catalyst <sup>a,b</sup>	Reaction temperature °C	TOF <sup>c</sup> s <sup>-1</sup>	Product selectivity <sup>c</sup> , %				Activation energy, kJ/mol
			CH <sub>4</sub>	CH <sub>3</sub> F	CHF <sub>3</sub>	CH <sub>2</sub> F <sub>2</sub>	
Supported on Norit1600, after calcination at 400 °C (0.25 h), and reduction at 400 °C (3 h)							
Pd100(Cl) H/Pd = 0.266	271	2.80 × 10 <sup>-3</sup>	36.8	1.2	-	62.0	95.9 ± 1.3
	261	1.90 × 10 <sup>-3</sup>	33.6	1.2	-	65.2	
	252	1.30 × 10 <sup>-3</sup>	30.1	-	-	69.9	
Pd60Pt40(Cl) H/(Pd+Pt) = 0.277 0.287	271	2.80 × 10 <sup>-3</sup>	53.4	5.6	-	41.0	91.1 ± 1.4
	261	1.90 × 10 <sup>-3</sup>	50.9	5.9	-	43.2	
	252	1.35 × 10 <sup>-3</sup>	47.4	6.3	-	46.2	
Pt100(Cl) H/Pt = 0.62	271	1.0 × 10 <sup>-3</sup>	70.9	12.9	0.3	15.8	97.0 ± 4.4
	261	6.9 × 10 <sup>-4</sup>	68.7	12.7	-	18.5	
	252	4.6 × 10 <sup>-4</sup>	66.9	13.5	-	19.6	
Supported on Norit1800, after reduction at 400 °C for 3 h							
3 wt.% Pd H/Pd = 0.215	272	2.90 × 10 <sup>-3</sup>	34.8	-	-	65.2	86.4 ± 9.1
	261	2.10 × 10 <sup>-3</sup>	31.0	-	-	69.0	
	251	1.35 × 10 <sup>-3</sup>	25.7	-	-	74.3	

<sup>a</sup> For the catalyst designation, see Methods (subsection 3.1); <sup>b</sup> Metal dispersion data (from H<sub>2</sub> chemisorption) located below catalyst designation; <sup>c</sup> GHSV 5760 h<sup>-1</sup>, catalyst weight 0.20 g.

#### SET S1. Characteristics of 3 wt.% Pd/Norit1800 catalyst.

Taken from M. Bonarowska, B. Burda, W. Juszczak J. Pielaszek, Z. Kowalczyk, Z. Karpiński, Appl. Catal. B 35 (2001) 13-20.

Support: Norit RO 08 activated by helium pretreatment at 1800 °C.

Preparation: ex-PdCl<sub>2,aq</sub> acidified with HCl, incipient wetness

Metal dispersion after reduction at 400 °C: H/Pd = 0.20; CO/Pd = 0.21 (previous data); H/Pd = 0.215 (recent measurement).

Pd crystallite size (from XRD line broadening): ~3 nm.

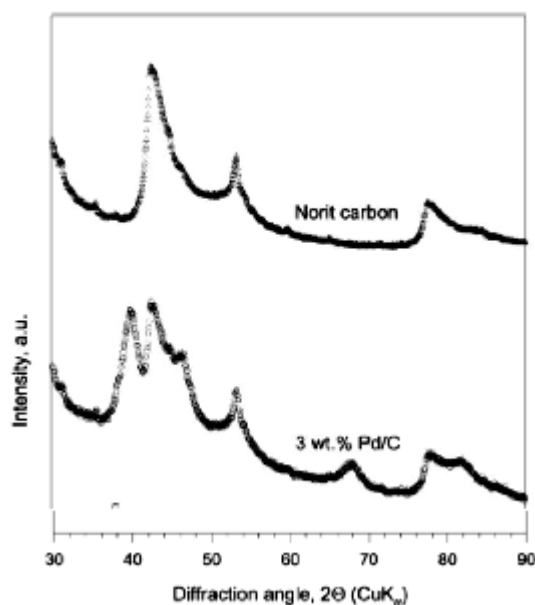


Figure S1: XRD profiles from Norit1800 and 3 wt.% Pd/Norit1800 catalysts.

adapted from Bonarowska et al., cited above.

#### Characteristics based on determination of N<sub>2</sub> adsorption isotherm.

BET surface area 85.2 m<sup>2</sup>/g  
 $T_{\text{plot}}$  micropore volume = 0.0010 cm<sup>3</sup>/g  
 BJH pore volume (adsorption) 0.2082 cm<sup>3</sup>/g  
 BJH pore volume (desorption) 0.2065 cm<sup>3</sup>/g.

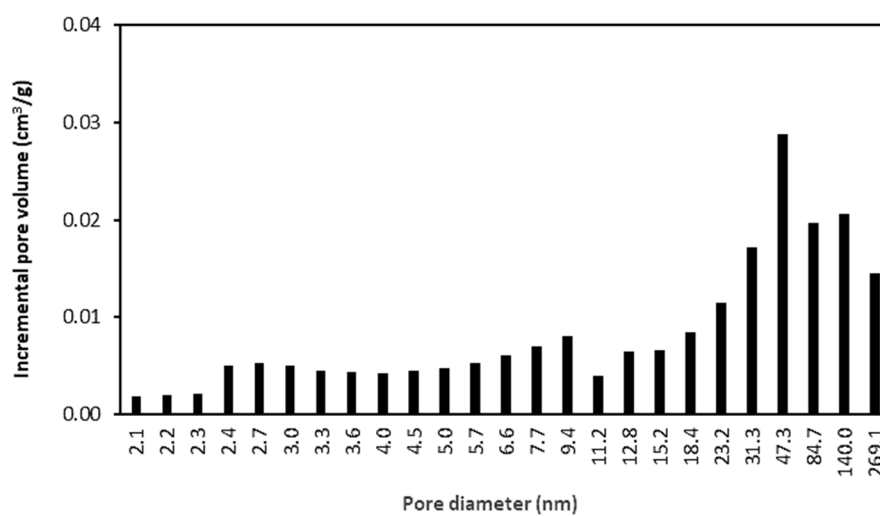
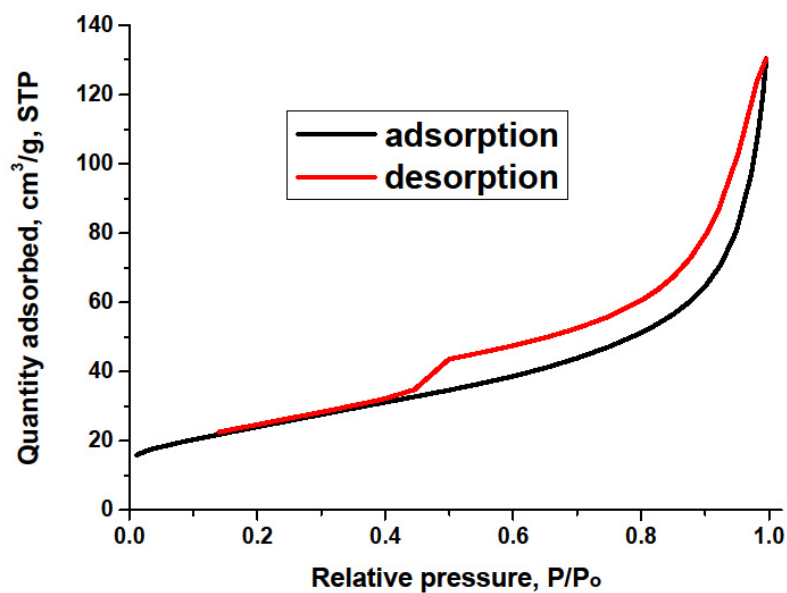


Figure S2: N<sub>2</sub> adsorption-desorption isotherms of N<sub>2</sub> on Norit1800 carbon (top) and pore size distribution in Norit1800 activated carbon (bottom).