Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Metal Functionalized Carbon Nanotubes for Biomass Conversion: Base-Free Highly efficient and Recyclable Catalysts for Aerobic Oxidation of 5-Hydroxymethylfurfural

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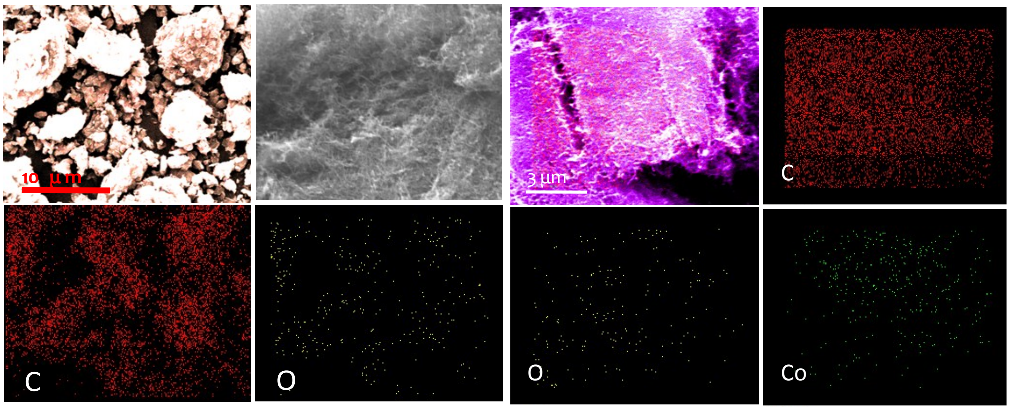
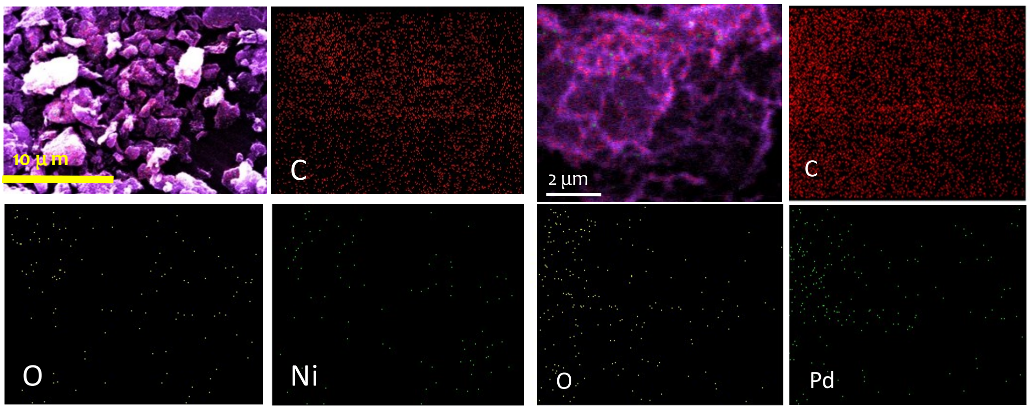




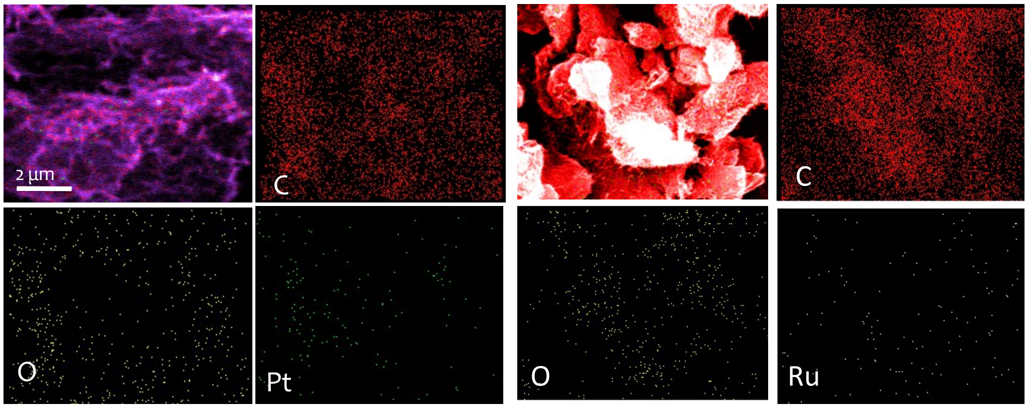
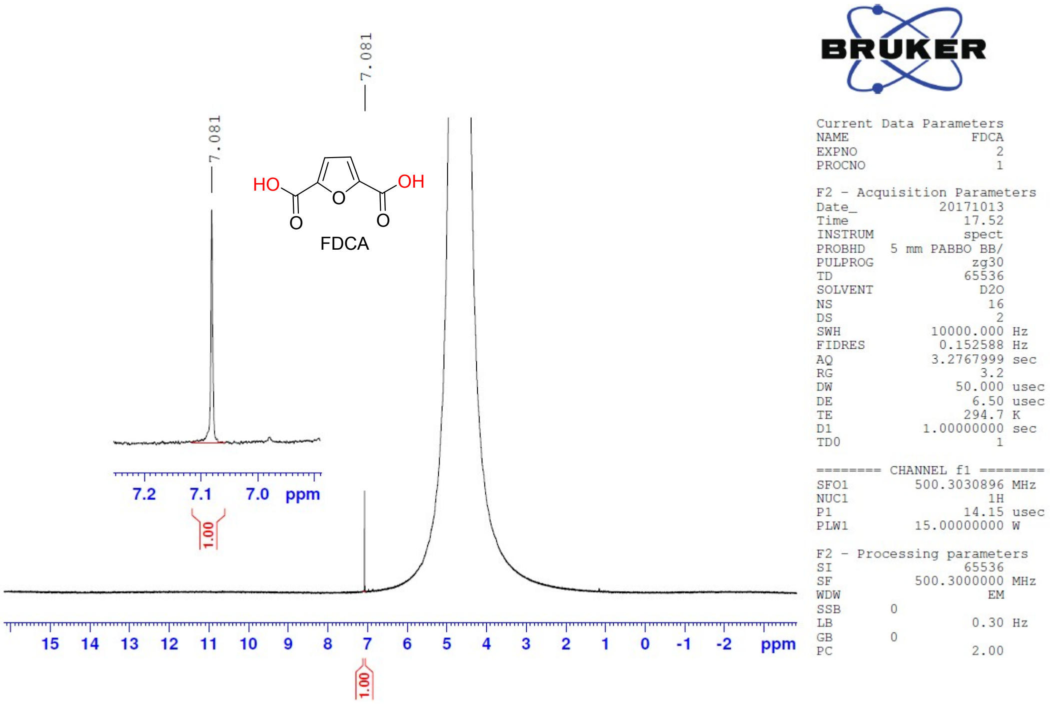


Figure S1. EDX mapping of (a) Functionalized CNT (b) Co/CNT (c) Ni/CNT (d) Pd/CNT (e) Pt/CNT, and (f) Ru/CNT

NMR spectra

FDCA

NMR- Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) are carried on a Bruker spectrometer operating at 500 MHz in D_2O (10%) for locking. ^{1}H NMR (500 MHz, D_2O, 298K): 7.08 (2H, s, furan-H); 13C NMR: 163.40, 148.32, 117.92 ppm[1]



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DS                     2
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AQ             3.2767999 sec
RG                   3.2
DW                50.000 usec
DE                  6.50 usec
TE                 294.7 K
D1            1.00000000 sec
TD0                    1

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NUC1                  1H
P1                 14.15 usec
PLW1         15.00000000 W

F2 - Processing parameters
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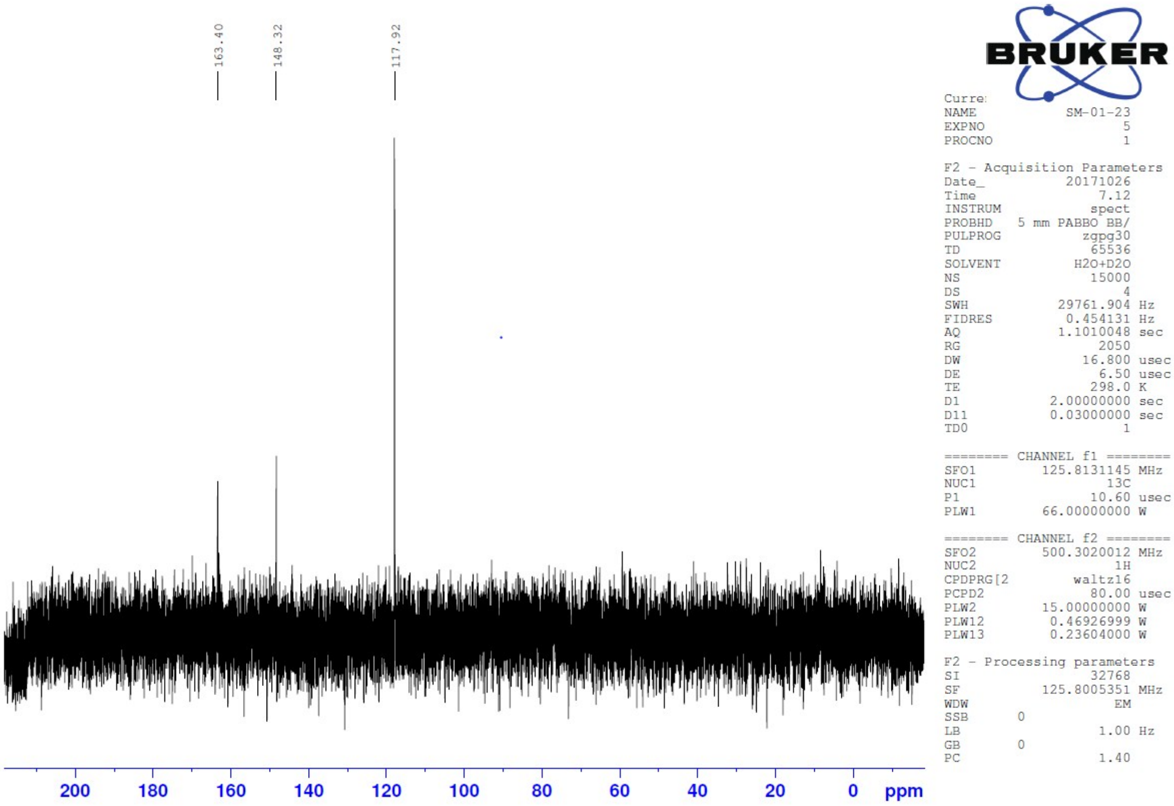
Figure S2. 1H-NMR spectrum of purified FDCA



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CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        15.00000000 W
PLW12        0.46926999 W
PLW13        0.23604000 W

F2 - Processing parameters
SI                32768
SF          125.8005351 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
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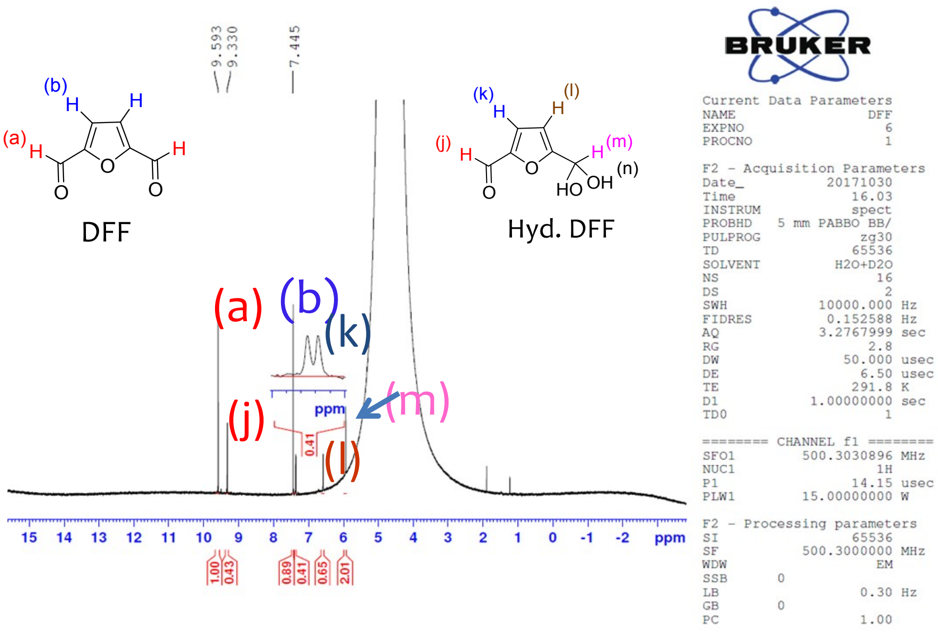
Figure S3. ^{13}C-NMR of purified FDCA.

DFF

^{1}H NMR (500 MHz, D_2O, 298K): 9.5 (2H, s, CHO), 7.4 (2H, s, Furan-H); ^{13}C NMR: 179.40, 154.6, 119.35 ppm[2]



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PROCNO                    1

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PULPROG                zg30
TD                    65536
SOLVENT             H2O+D2O
NS                       16
DS                        2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                      2.8
DW                50.000 usec
DE                  6.50 usec
TE                 291.8 K
D1            1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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NUC1                     1H
P1                 14.15 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                    65536
SF           500.3000000 MHz
WDW                      EM
SSB      0
LB                  0.30 Hz
GB       0
PC                     1.00
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Figure S4. 1H-NMR spectrum of DFF and hydrated DFF.

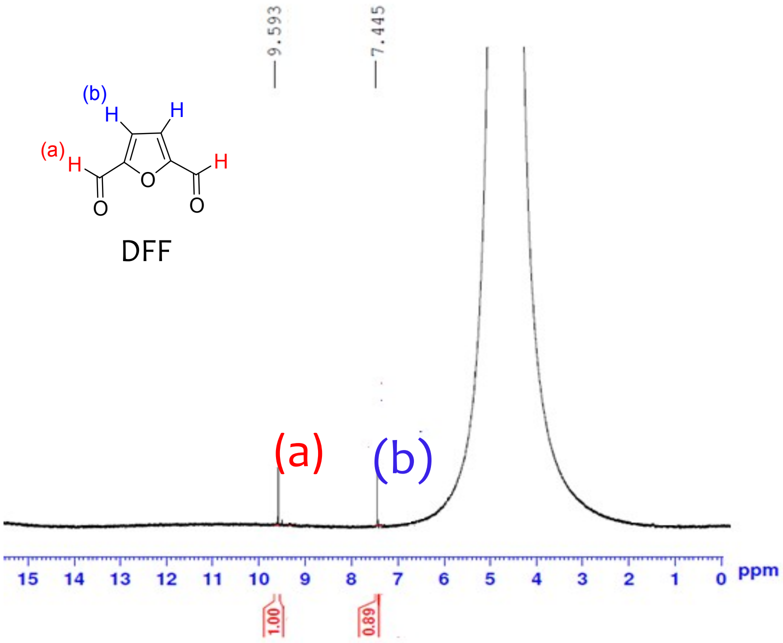
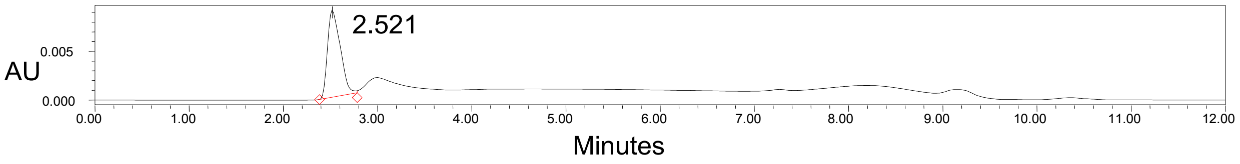


Figure S5. 1H-NMR spectrum of purified DFF.

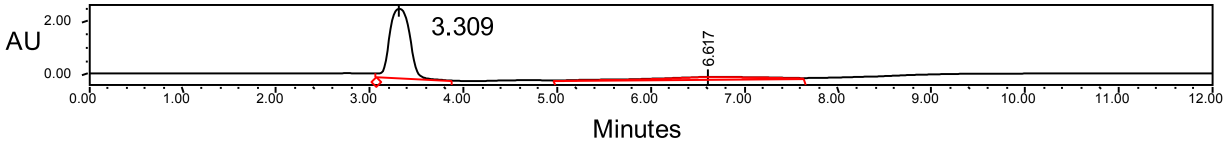
HPLC chromatogram

S.N.	Parameters	Values
1.	Temperature	40° C
2.	Flow rate	1 ml/min
3.	Detection (Wave length)	284 nm
4.	Solvent ratio	5:95 :: Acetonitrile:H_2O
5.	Injection volume	20 µl
6.	Reverse phased C18 Column 5.0 µm, 100 Å (Waters)	(4.6mm * 250 mm) Column



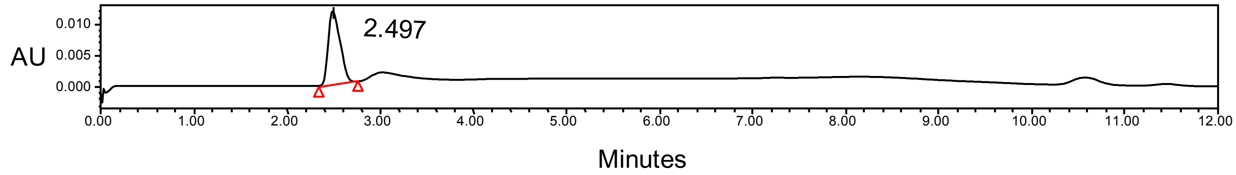
E.No.	Name	Retention Time	% Area
1	FDCA	2.52	97.6
2.	FFCA	3.0	1.4
3.	DFF	8.30	1.0

Figure S6. HPLC chromatogram of FDCA at optimized reaction condition.



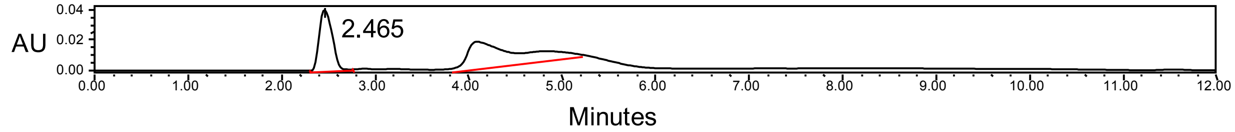
	Name	Retention Time	% Area
1	FFCA	3.309	86.82
2	HMF	6.617	13.18

Figure S7. HPLC chromatogram of FFCA in the presence of functionalized CNT.



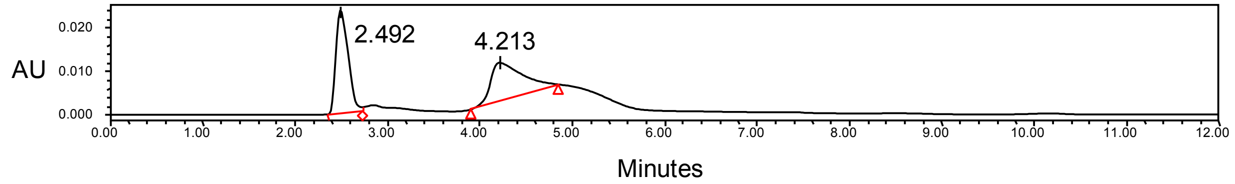
E.No.	Name	Retention Time	% Area
1	FDCA	2.49	97.8
2.	FFCA	3.0	1.3
3.	Unknown	10.9	0.9

Figure S8. HPLC chromatogram of FDCA over Pt/CNT catalyst.



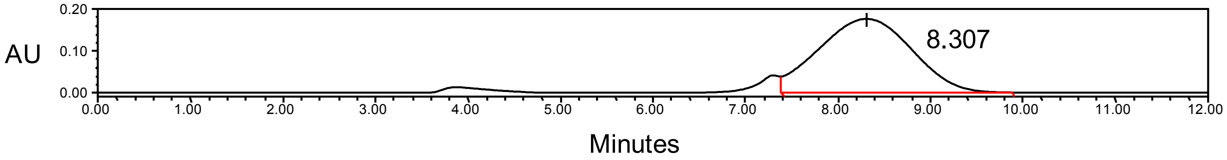
E.No.	Name	Retention Time	% Area
1	FDCA	2.46	95.6
2.	FFCA	3.9	2.4
3.	Unknown	5.9	2.0

Figure S 9. HPLC chromatogram of FDCA over Pd/CNT catalyst.



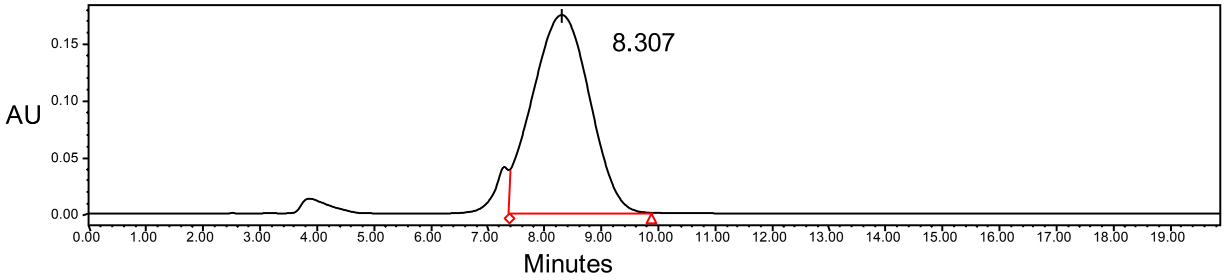
E.No.	Name	Retention Time	% Area
1	FDCA	2.49	92.8
2.	FFCA	4.2	6.1
3.	Unknown	5.6	1.1

Figure S10. HPLC chromatogram of FDCA over Ru/CNT catalyst.



E.No.	Name	Retention Time	% Area
1	FFCA	3.9	1.1
2.	HMF	7.3	2.5
3.	DFF	8.30	96.4

Figure S11. HPLC chromatogram of DFF over Ni/CNT catalyst.



E.No.	Name	Retention Time	% Area
1	FFCA	3.9	3.1
2.	HMF	7.3	4.5
3.	DFF	8.30	92.4

Figure S12. HPLC chromatogram of DFF over Co/CNT catalyst.

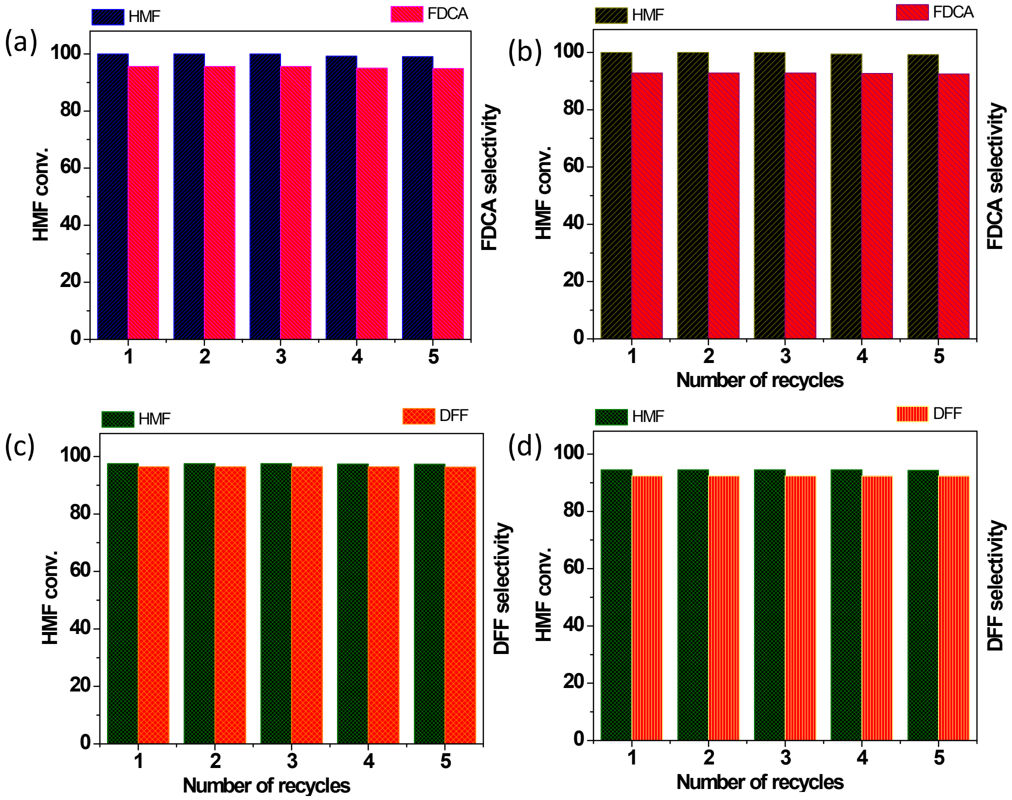


Figure S13. Recyclability of catalysts (a) Pd/CNT (b) Ru/CNT (c) Co/CNT, and Ni/CNT.

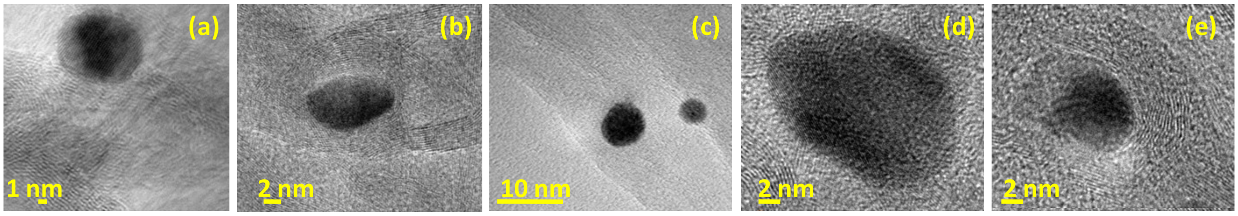


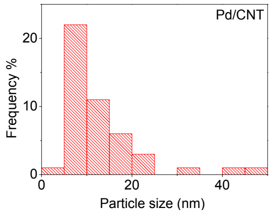
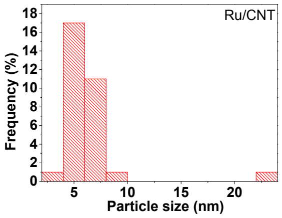
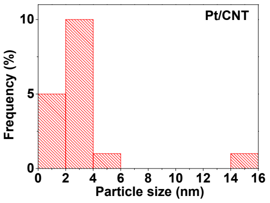
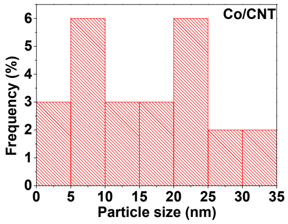
Figure S14.TEM images of recycled (a) Pd/CNT, (b) Ru/CNT, (c) Pt/CNT, (dj) Co/CNT, and (e) Ni/CNT after 5 cycles.

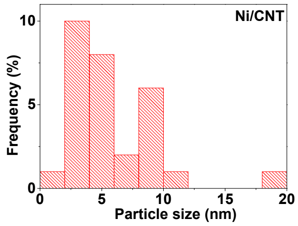
Table S1. Literature review.

Catalysts	Condition (solvent ,Temp ,Pressure)	FDCA Yield (%)	DFF Yield (%)	DOI
(5%) Pt/C	Alkaline water, 100°C, 40 bar	99	-	[3]
Au –Pd (0.96%)/ CNT NPs	Water, 100°C, 1 MPa pressure O_2 bar	96	-	[4]
(3 %)Pt /C	Neutral /acidic condition, , 21.2°C	86 (Selectivity)	-	[5]
Pt/C, Pd/C and Au/C	NaOH, 22°C, 690 kPa O_2	79	-	[6]
Au/TiO_2	Methanol, 130°C, 4 bar O_2	-	-	[7]
Co/Mn/ Br	H2O/HCl, 180°C, 30 bar	90	-	[8]
Ru (OH)2/ La_SO_3	ionic liquid , 100°C, 30 bar	48	-	[9]
(4%) Ru/$MnCo_2O_4$	Water, 120°C, 2.4 MPa	99.1	0	[10]
(5%) Ru/C $Mg(OH)_2$	Water, 110°C, 1.0 MPa O_2	97.3	-	[11]
(5%)Pt/C	Water (20 ml), 50°C, 10 bar O_2	80	-	[12]
Pd modified Au on Carbon	60°C, 3 MPa O_2	>99	-	[13]
Pd/ C@ Fe_2O_3	H2O, 80°C, O_2 bubbling (20 ml/min)	86.7	-	[14]
Pt/ non- reducible support	140°C, 1 bar	96 in presence of (Pt-Al_2O_3 , TiO_2)	-	[15]
K-10 clay-Mo	toluene ,110°C (O_2 flow)	-	-	[16]
Au-Cu NPs	NaOH, 60°C, 60°C	99	-	[17]
Au-CeO_2	Water ,NaOH, 65°C, 10 bar O_2	>99	-	[18]
Pd/HT	Water, 110°C, O_2 bubbling (100 ml/min)	92.4	-	[19]

Au/C	water, Na_2CO_3 (0.4 mmol), 90°C, 10 bar O_2	75	-	[20]
$Ni_{0.90}Pd_{.10}$/ $Mg(OH)_2$	water ,$Na_2CO_{3,}$ 100°C	83	-	[21]
Titania NPs in aqueousmedium	H_2O, 70°C, 1 atm O_2	23	88	[22]
Au-Pd alloy NPs	Water, 90°C, atm O_2	99	-	[23]
CeCP @Pt	H_20, 70°C,atp	96.2	-	[24]
Au Nano cluster	H_20, 60°C, 0.3 M Pa O_2	>99	-	[25]
(5%)Pt/CNT	$H_20,O_{2,}$ (0.5 Mpa), 368 K	96		[26]

Table S2. Average particle size and histograms of catalysts.

Catalysts	Average particle size (nm)	Histograms
Pd/CNT	12.4	
Ru/CNT	6.4	
Pt/CNT	3.4	
Co/CNT	15.2	

Ni/CNT	5.9	

References

1. J. Ma, Y. Pang, M. Wang, J. Xu, H. Ma, X. Nie, *Journal of Materials Chemistry*, **2012**, 22, 3457-3461.
2. J. Chen, J. Zhong, Y. Guo, L. Chen, *RSC Advances*, **2015**, 5, 5933-5940.
3. H. A. Rass, N. Essayem, M. Besson, *Green Chemistry*, **2013**, 15, 2240-2251.
4. X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, *ACS catalysis*, **2014**, 4, 2175-2185.
5. S. E. Davis, A. D. Benavidez, R. W. Gosselink, J. H. Bitter, K. P. De Jong, A. K. Datye, R. J. Davis, *Journal of Molecular Catalysis A: Chemical*, **2014**, 388, 123-132.
6. S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye, R. J. Davis, *Catalysis Today*, **2011**, 160, 55-60.
7. E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen, C. H. Christensen, *ChemSusChem: Chemistry & Sustainability Energy & Materials*, **2008**, 1, 75-78.
8. X. Zuo, P. Venkitasubramanian, D. H. Busch, B. Subramaniam, *ACS Sustainable Chemistry & Engineering*, **2016**, 4, 3659-3668.
9. T. Ståhlberg, E. Eyjólfsdóttir, Y. Y. Gorbanev, I. Sádaba, A. Riisager, *Catal Lett*, **2012**, 142, 1089-1097.
10. J. J. Morrison, J. M. Wasikiewic, J. M. Koelewijn, L. Abu-Sen, H. Lan, A. Horn, S. G. Yeates.
11. W. Partenheimer, V. V. Grushin, *Adv Synth Catal*, **2001**, 343, 102-111.
12. K. R. Vuyyuru, P. Strasser, *Catalysis Today*, **2012**, 195, 144-154.
13. A. Villa, M. Schiavoni, S. Campisi, G. M. Veith, L. Prati, *ChemSusChem*, **2013**, 6, 609-612.
14. B. Liu, Y. Ren, Z. Zhang, *Green Chemistry*, **2015**, 17, 1610-1617.
15. R. Sahu, P. L. Dhepe, *Reaction Kinetics, Mechanisms and Catalysis*, **2014**, 112, 173-187.
16. Z. Zhang, B. Liu, K. Lv, J. Sun, K. Deng, *Green Chemistry*, **2014**, 16, 2762-2770.
17. T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J. A. Lopez-Sanchez, M. Sankar, Q. He, C. J. Kiely, *Green chemistry*, **2011**, 13, 2091-2099.
18. O. Casanova, S. Iborra, A. Corma, *ChemSusChem: Chemistry & Sustainability Energy & Materials*, **2009**, 2, 1138-1144.
19. Y. Wang, K. Yu, D. Lei, W. Si, Y. Feng, L.-L. Lou, S. Liu, *ACS Sustainable Chemistry & Engineering*, **2016**, 4, 4752-4761.
20. B. Donoeva, N. Masoud, P. E. De Jongh, *ACS catalysis*, **2017**, 7, 4581-4591.
21. K. Gupta, R. K. Rai, S. K. Singh, *Inorganic Chemistry Frontiers*, **2017**, 4, 871-880.
22. D. Gupta, K. K. Pant, B. Saha, *Molecular Catalysis*, **2017**, 435, 182-188.
23. Q. Wang, W. Hou, S. Li, J. Xie, J. Li, Y. Zhou, J. Wang, *Green Chemistry*, **2017**, 19, 3820-3830.
24. W. Gong, K. Zheng, P. Ji, *RSC Advances*, **2017**, 7, 34776-34782.
25. J. Cai, H. Ma, J. Zhang, Q. Song, Z. Du, Y. Huang, J. Xu, *Chemistry–A European Journal*, **2013**, 19, 14215-14223.
26. C. Zhou, W. Deng, X. Wan, Q. Zhang, Y. Yang, Y. Wang, *ChemCatChem*, **2015**, 7, 2853-2863.