Supporting information

Role of the defects in carbon materials in the metal free formic acid dehydrogenation

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The present supplementary information document contains in figure S1the raman spectra of the different samples tested, i.e. pristine graphene, PS-CNFs, LHT-CNFs and graphene oxide, in figure S2 and S3 the deconvolution of C 1s and O1s HR spectra respectively of the different catalyst, in figure S4 the correlation of conversion vs oxygen content considering the different oxygen functionalities disclosed by O1s HR spectra deconvolution. All the different structures, optimized by DFT method forming the pathways on the different defects, are showed from Figure S5 to S20. Table S1 summarises all the different species of C and O obtained from the related XPS-HR spectra.

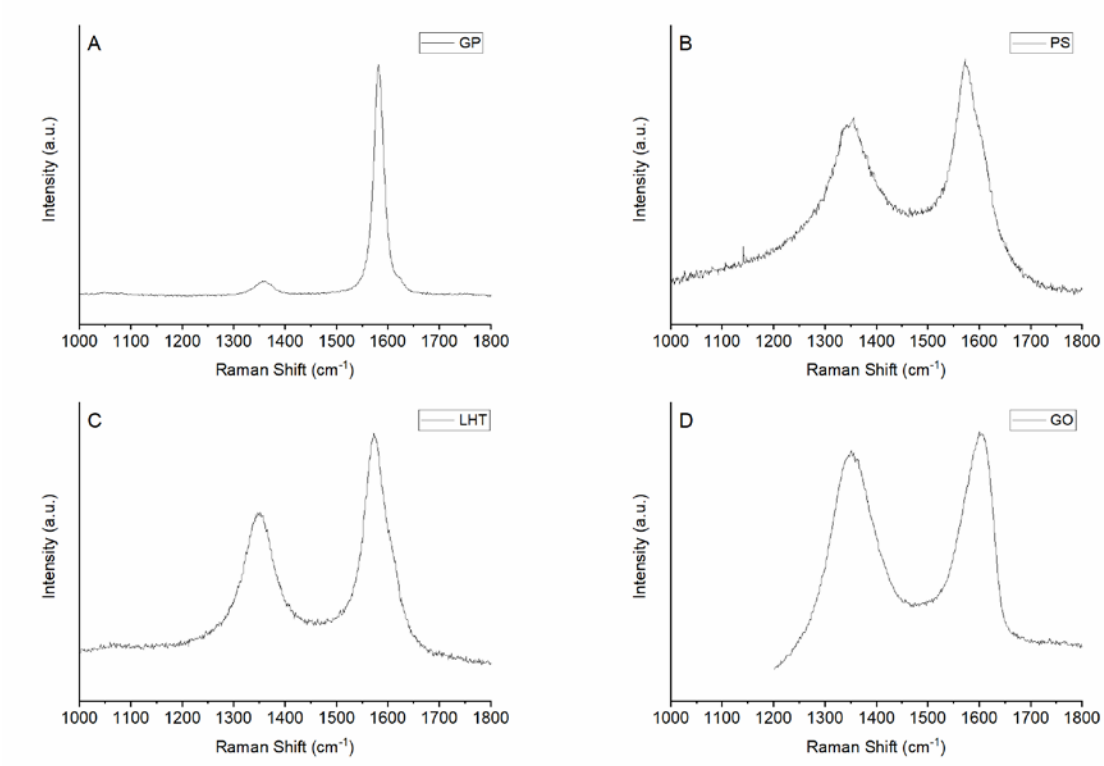

Figure S1: Raman spectra of a) pristine graphene b)PS-CNFs c)LHT-CNFs and d) graphene oxide

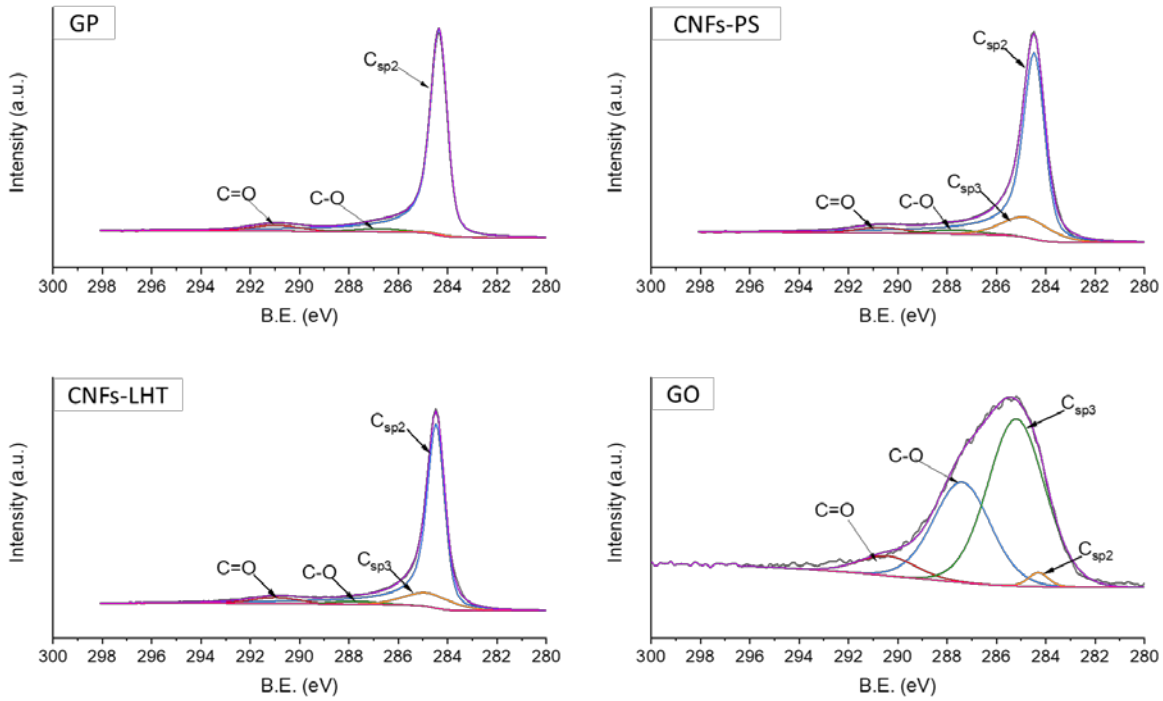

Figure S2: deconvolution of C 1s HR spectra of the different catalyst.

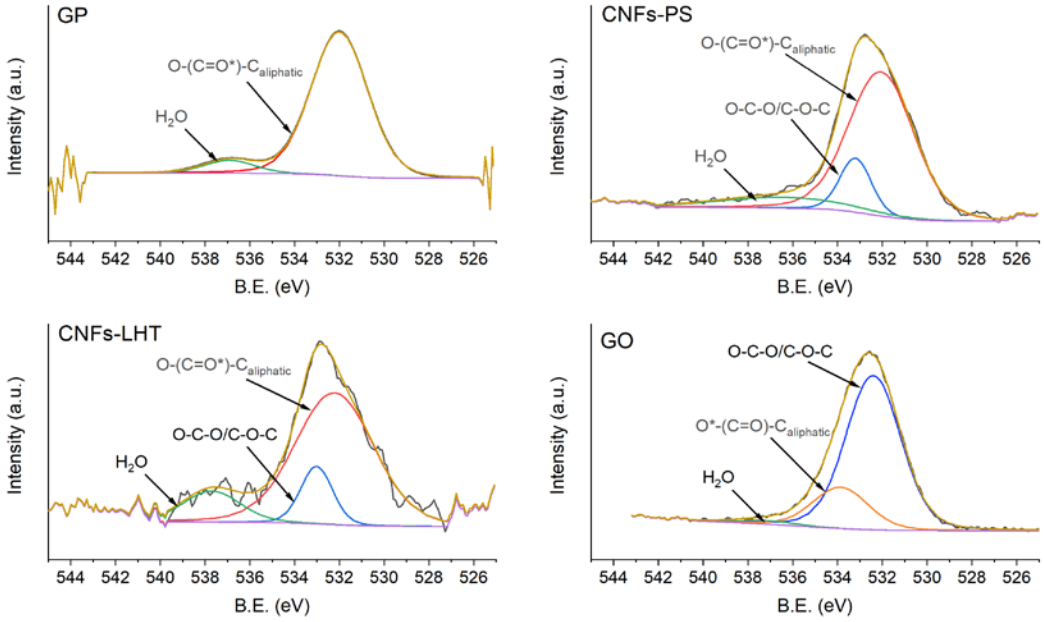

Figure S3: deconvolution of O 1s HR spectra of the different catalyst.

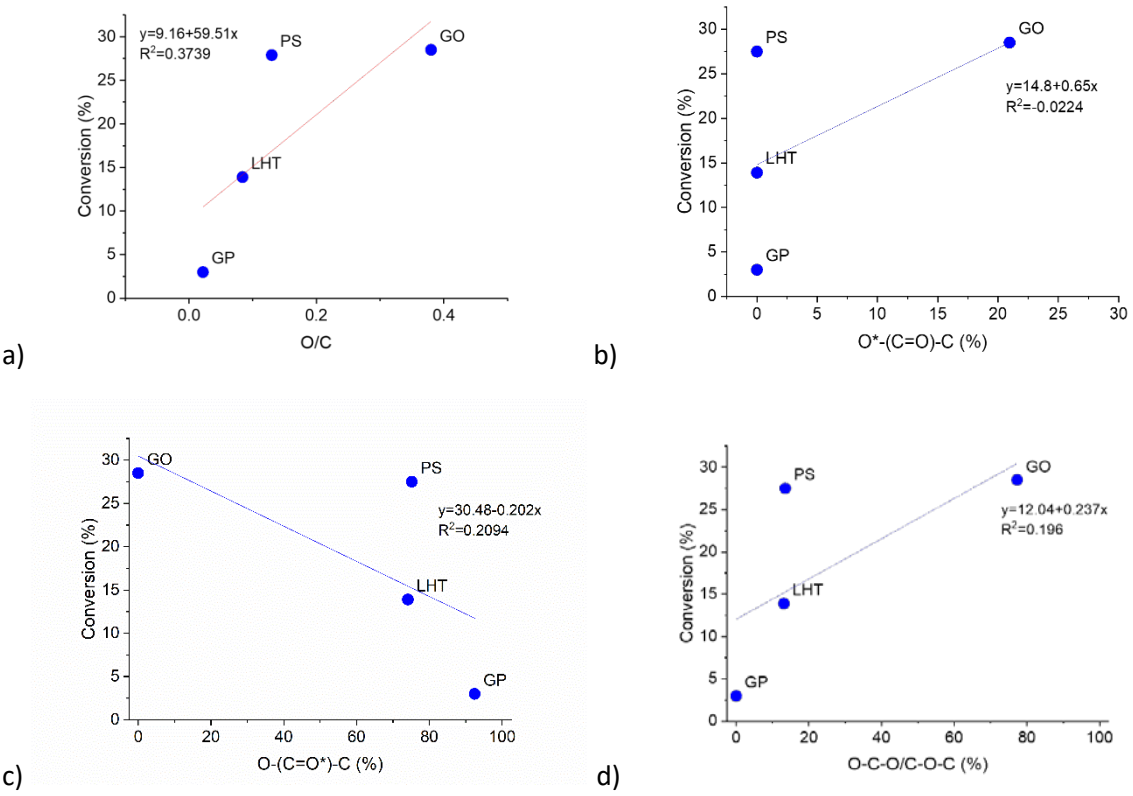

Figure S4: linear correlation of conversion vs: a) O/C b) O*-(C=O)-C c) O-(C=O)*-C d) O-C-O/C-O-C

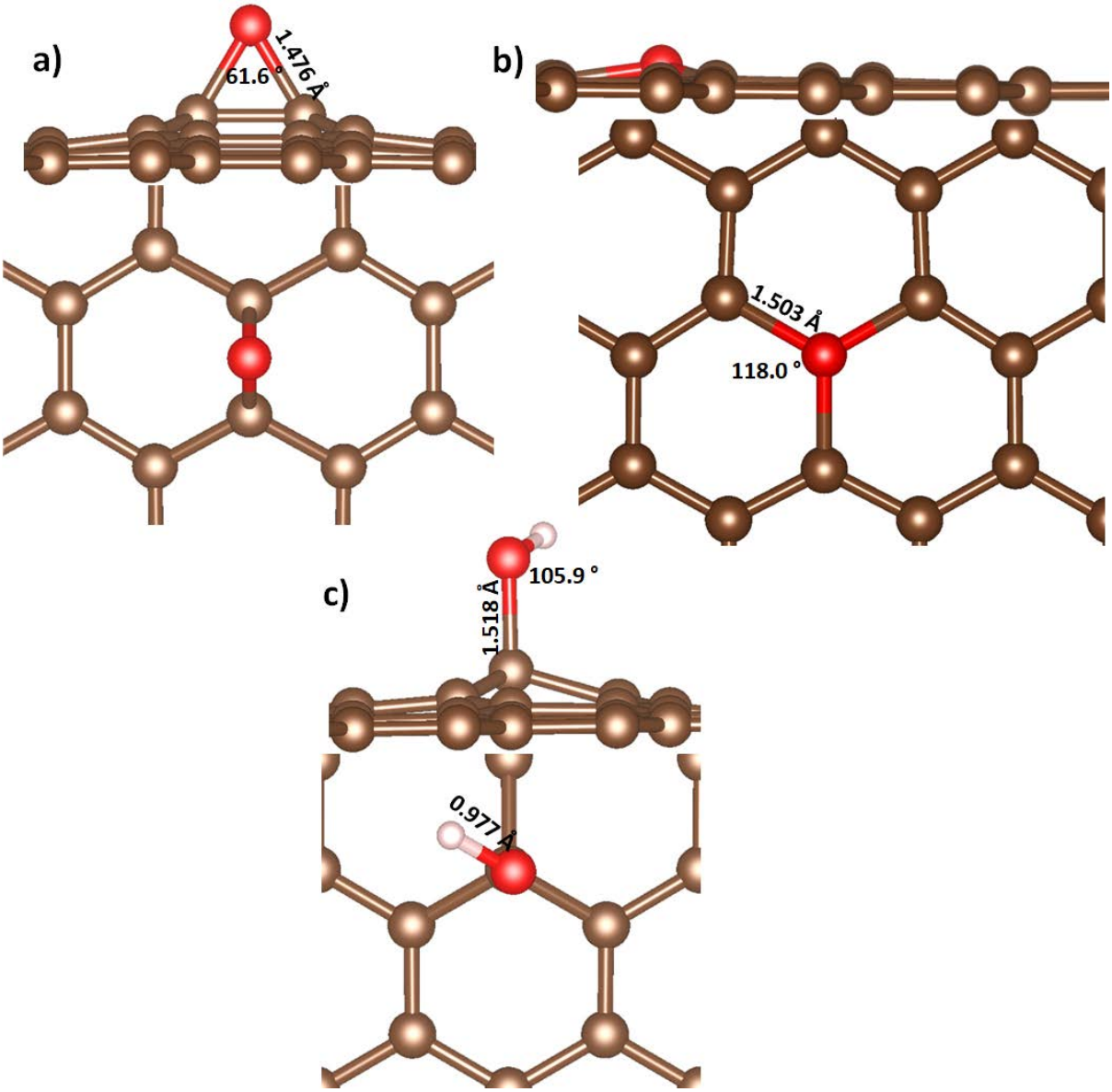

Figure S5: Top and side view of graphene with O-functionalities: a) epoxide b) O incorporated in the surface c) hydroxyl. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red and hydrogen in white.

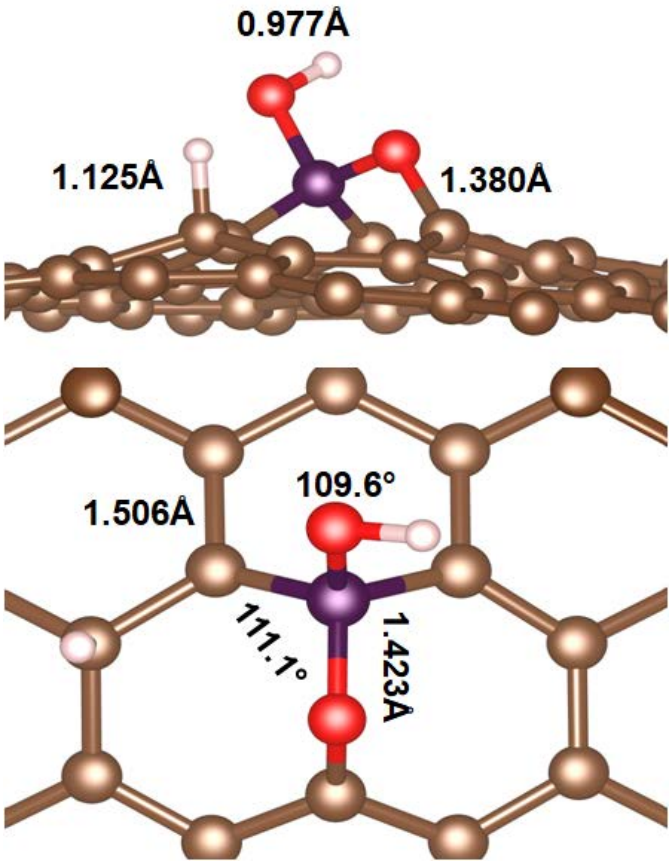

Figure S6: Top and side view of COOH and H adsorbed on SV when C-H bond is broken. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

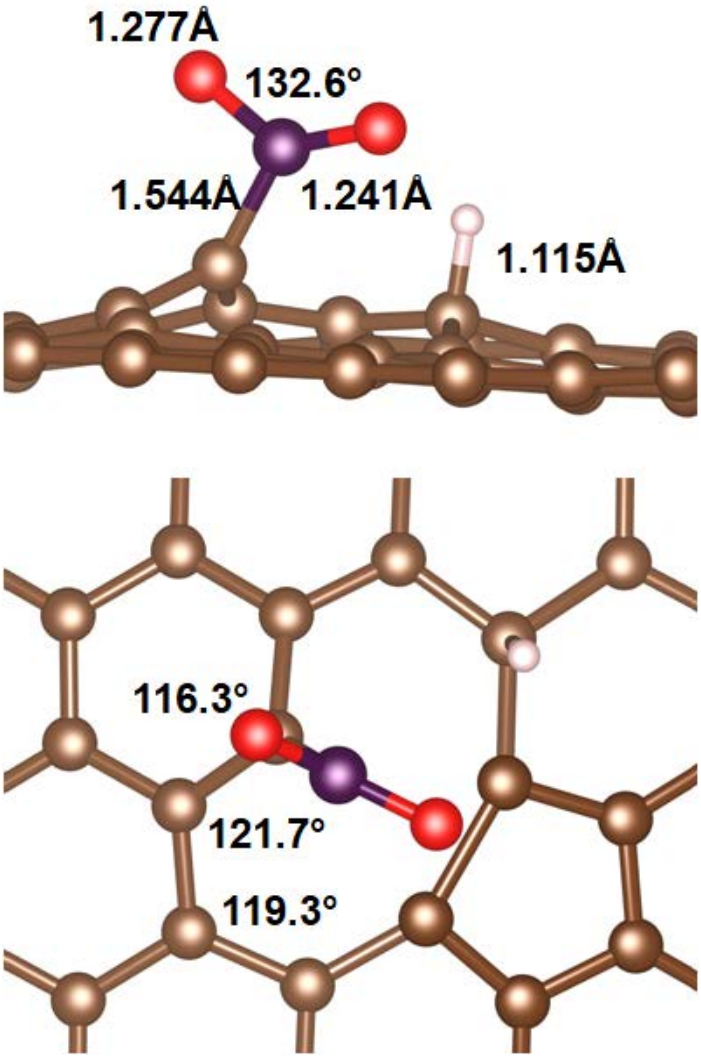

Figure S7: Top and side view of COO and H adsorbed on SV; only one hydrogen is considered in this step because the H adsorbed on the surface migrates in another site. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

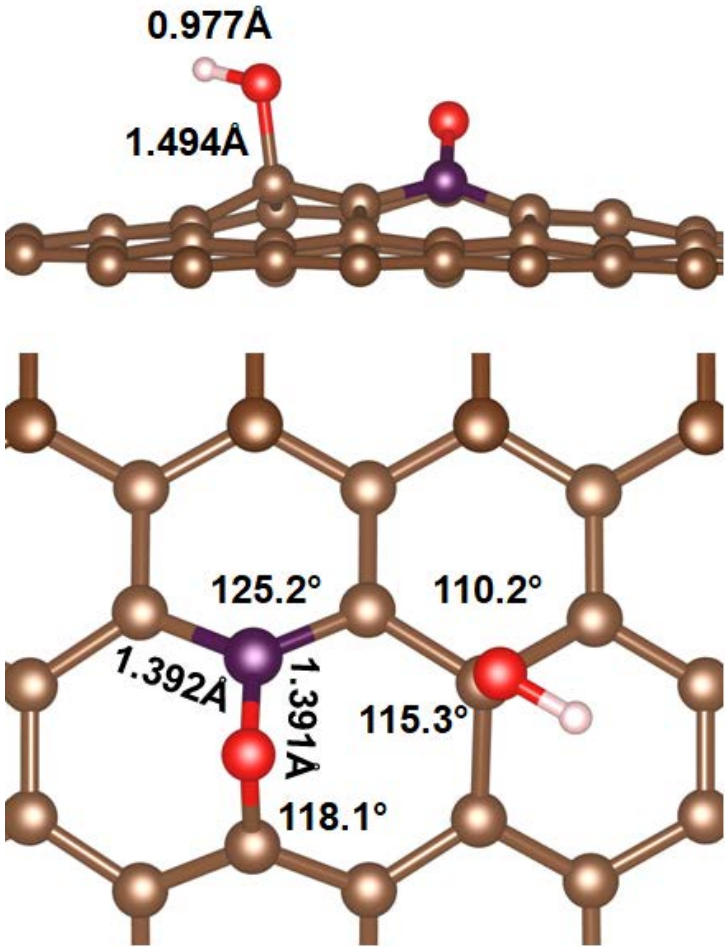

Figure S8: Top and side view of CO and OH adsorbed on SV; only one hydrogen is considered in this step because the H adsorbed on the surface migrates in another site. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

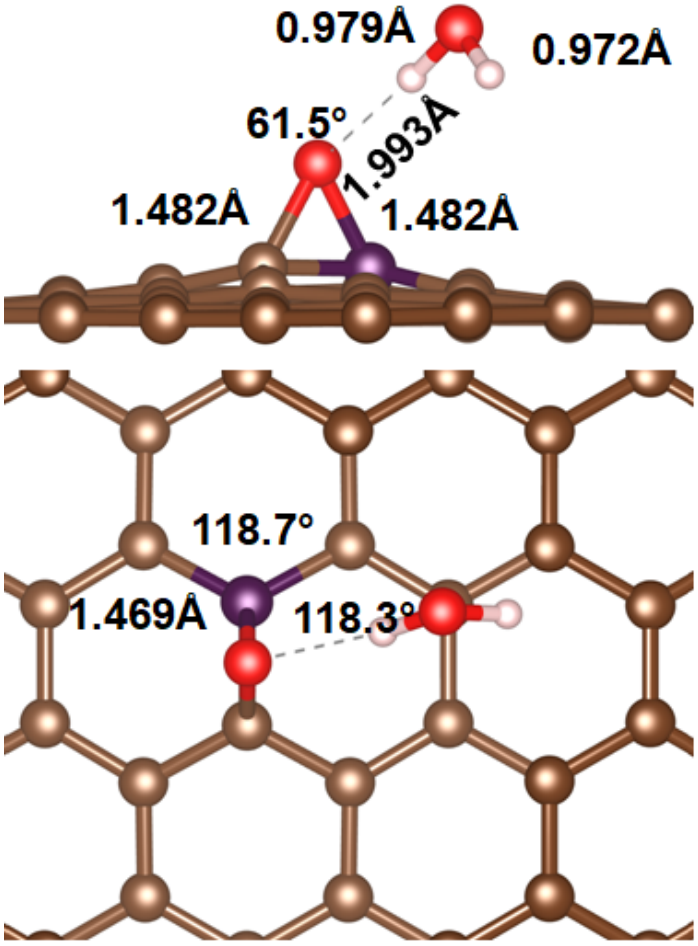

Figure S9: Top and side view of CO and H2O adsorbed on the surface; water is more stable in gas phase than adsorbed. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

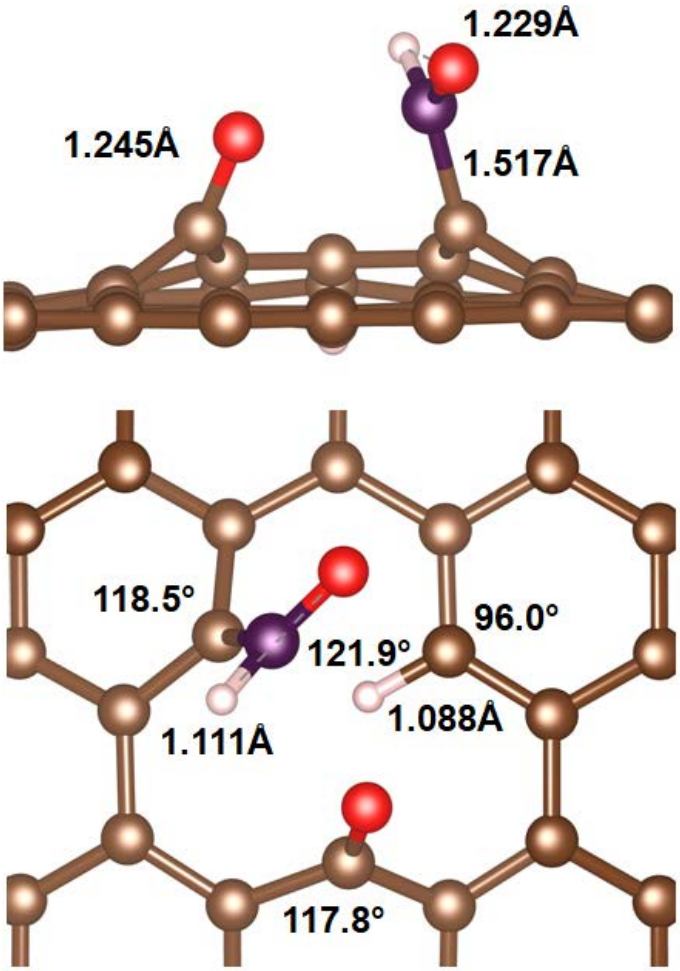

Figure S10: Top and side view of structure obtained taking out the H from the OH group. The carbonyl and the hydroxyl bonds broke. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

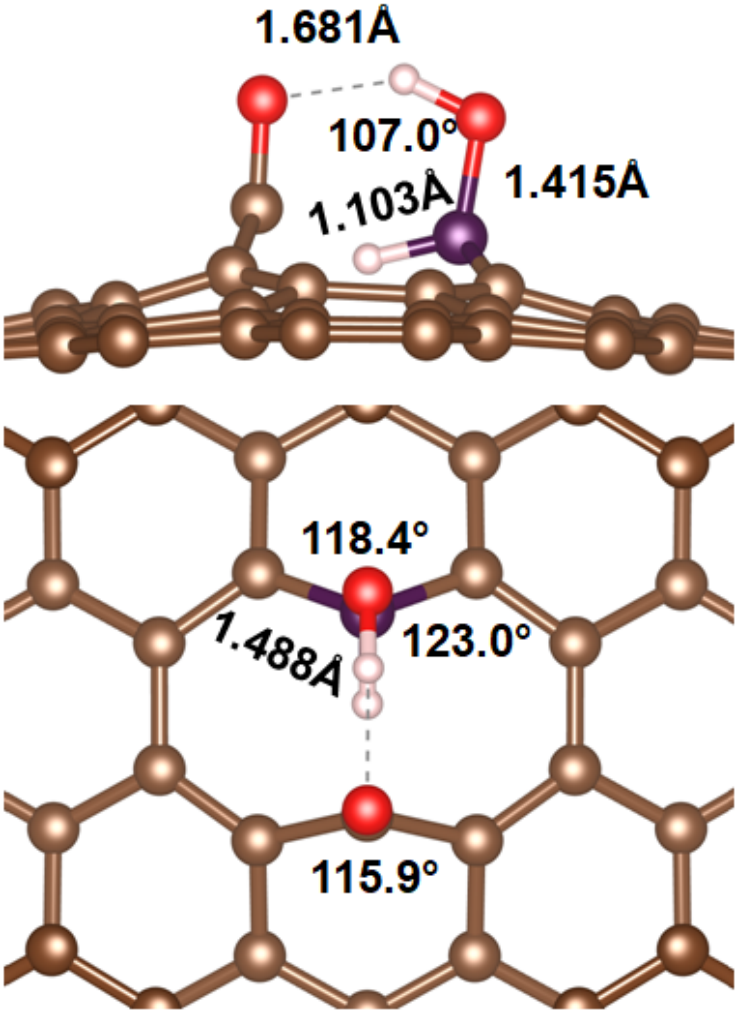

Figure S11: Top and side view of the intermediate structure; breakage of the C-O bond before the O-H one. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

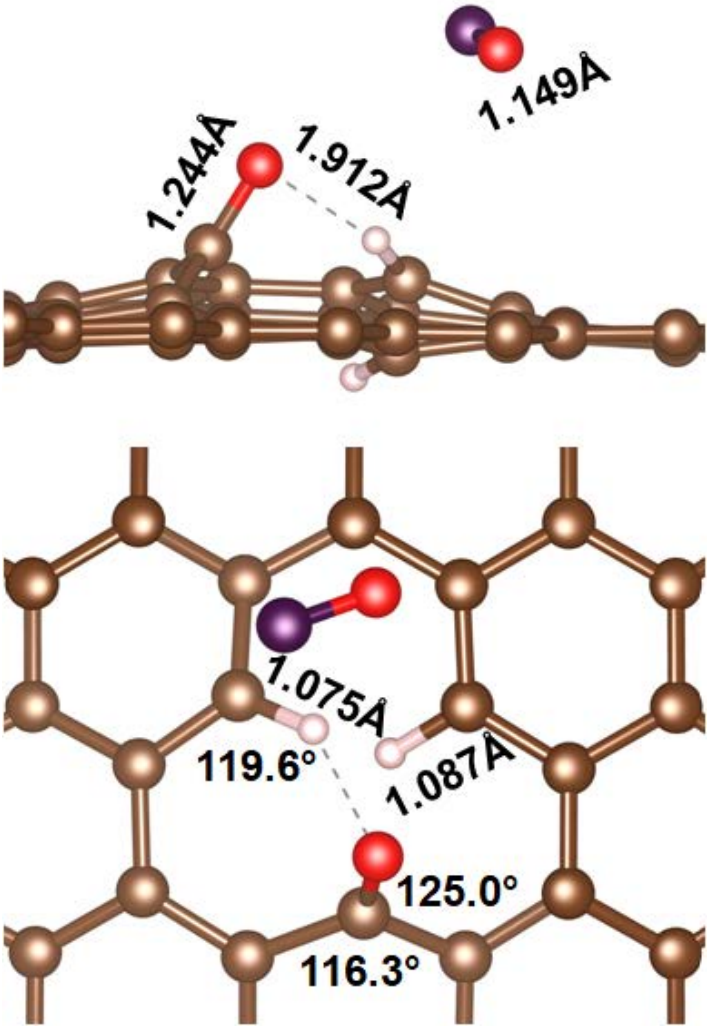

Figure S12: Top and side view of releasing of carbon monoxide from the surface. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

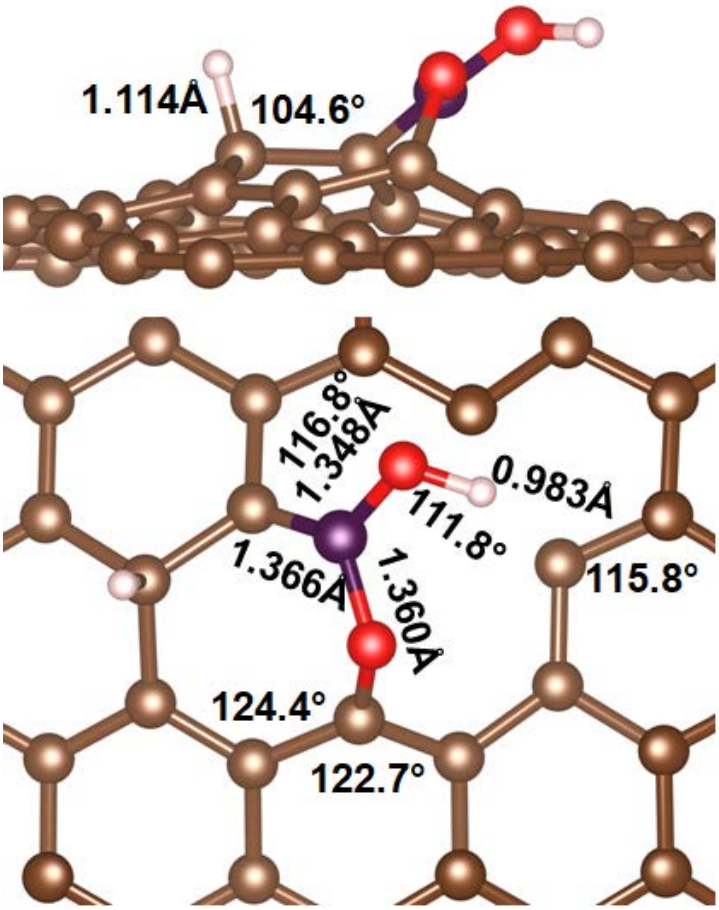

Figure S13: Top and side view of the breakage of C-H bond of FA on Double Vacancy system; COOH and H adsorbed on the surface. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

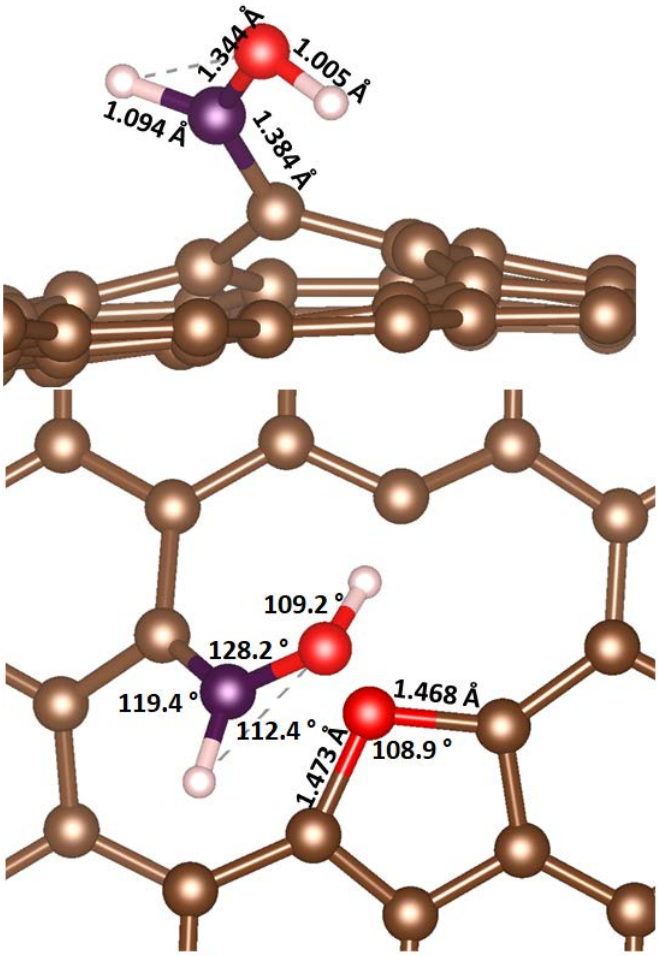

Figure S14: Top and side view of the intermediate structure; breakage of C-O bond. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

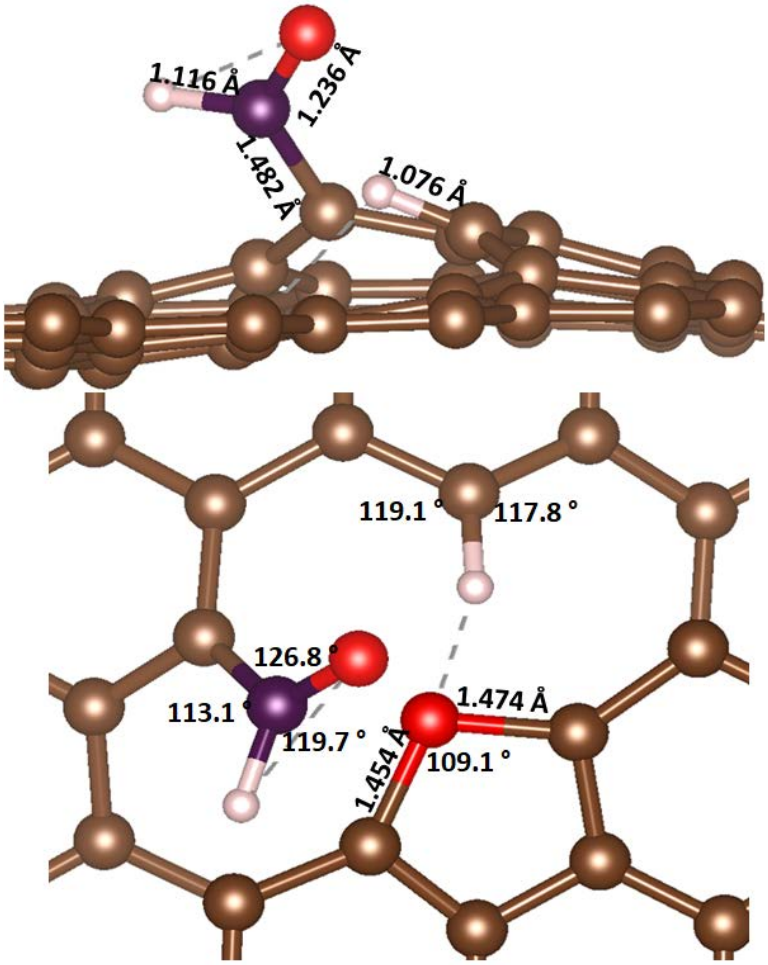

Figure S15: Top and side view of the structure obtained taking out the H from the OH group. The carbonyl and the hydroxyl bonds broke. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

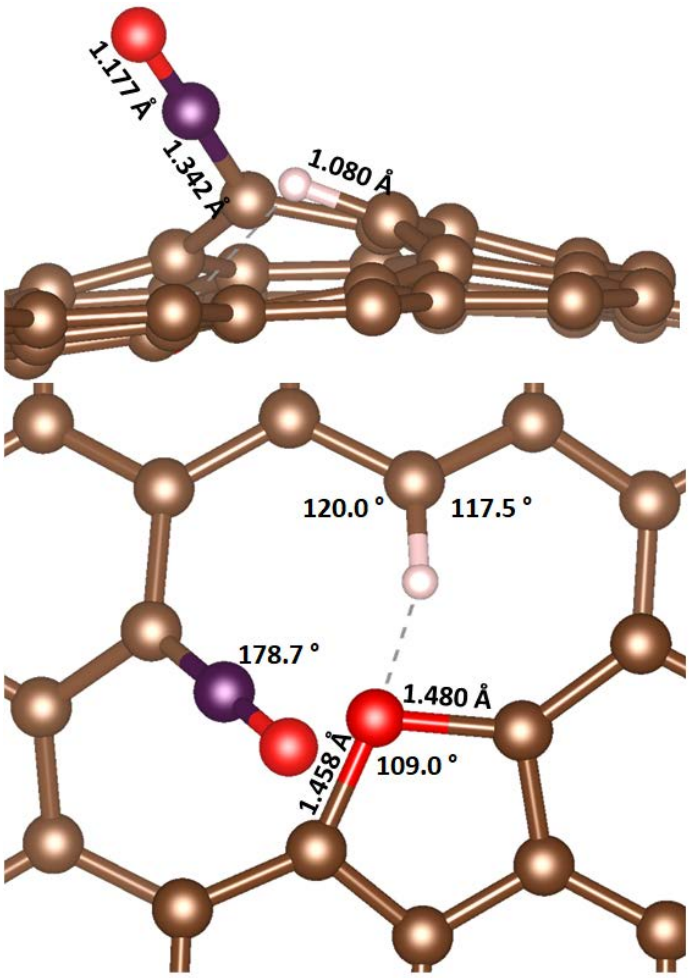

Figure S16: Top and side view of the breakage of the C-H bond. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

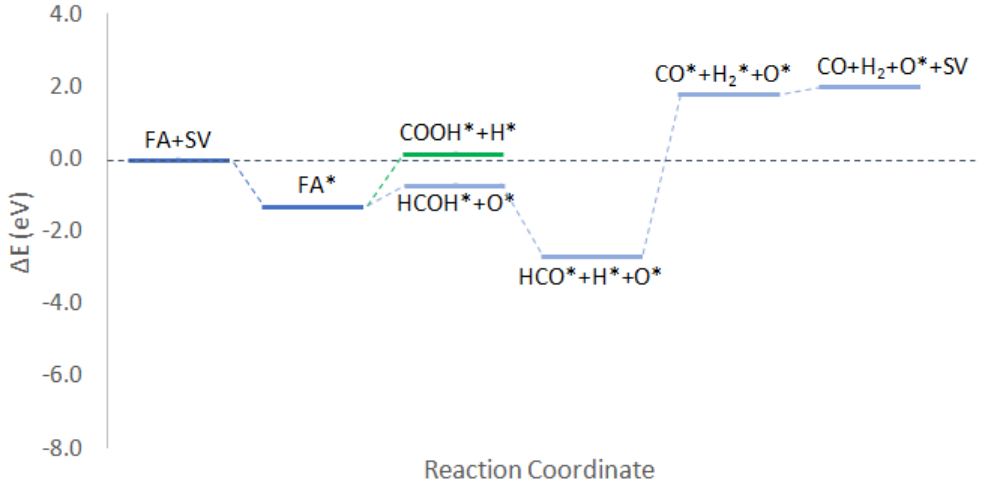

Figure S17: profile for the different pathways of Formic Acid decomposition on DV structure. * indicates adsorbed species.

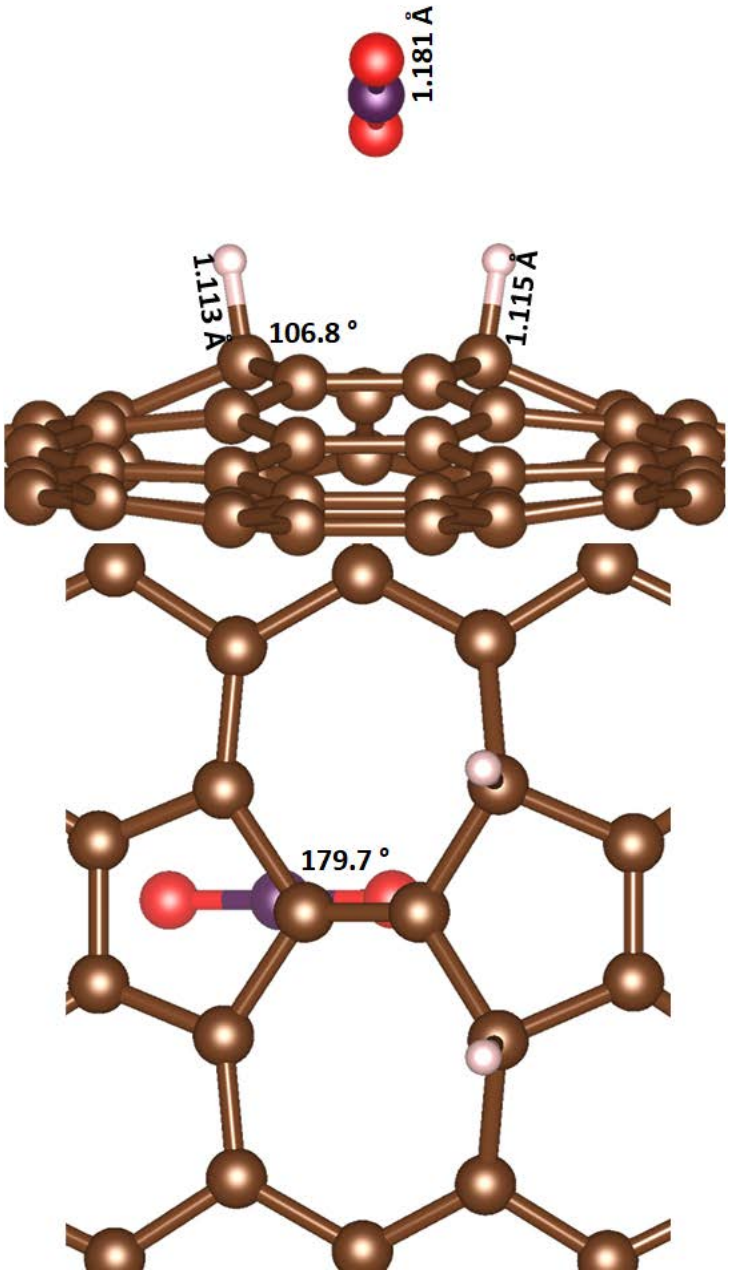

Figure S18: Top and side view of the breakage of the O-H bond. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

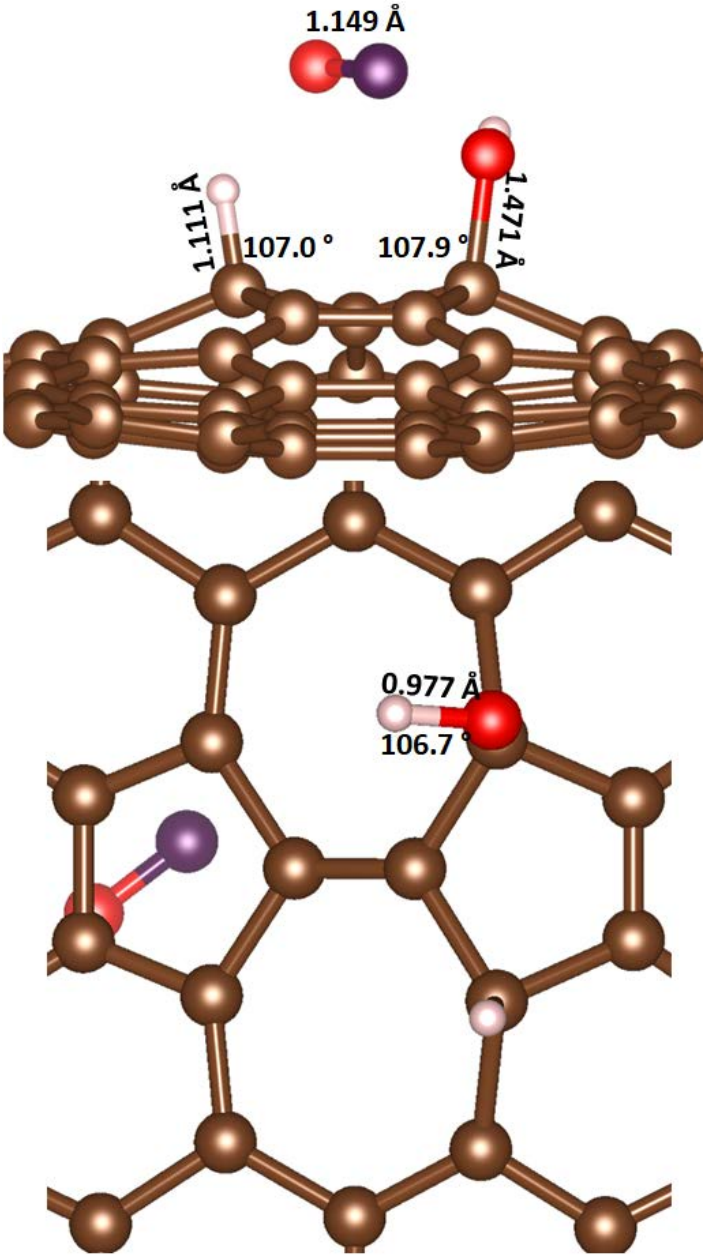

Figure S19: Top and side view of the breakage of C-OH bond. Inset, distances (Å) and angles (°) of interest. Carbon atom is labelled in brown, oxygen in red, hydrogen in white and carbon atom of formic acid in purple.

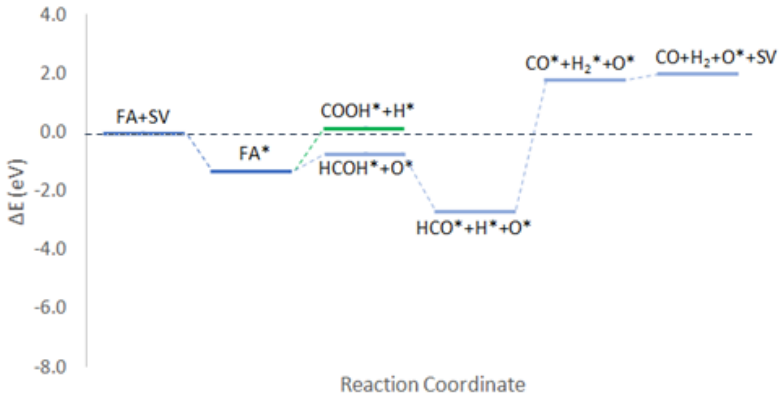

Figure S20: profile for the different pathways of Formic Acid decomposition on SW1 structure. * indicates adsorbed species.

Table S1: atomic % of the different a) O species detected after O 1s HR spectra deconvolution b) C species detected after C 1s HR spectra deconvolution

a)

Sample		O-(C=O*)-$C_{aliphatic}$	O-C-O/C-O-C	O*-(C=O)-$C_{aliphatic}$	H_2O
GP	*B.E. (eV)*	*531.99*	-	-	*536.9*
	At.%	92.48	-	-	7.52
CNFs-PS	*B.E. (eV)*	*532.0*	*533.2*	-	*536.5*
	At.%	75.20	13.53	-	11.28
CNFs-LHT	*B.E. (eV)*	*532.2*	*533.0*	-	*537.6*
	At.%	74.12	13.14	-	12.74
GO	*B.E. (eV)*	-	*532.6*	*533.9*	*537.1*
	At.%	-	77.29	20.95	1.76

b)

Sample		C=C	C-C	C-O	C=O
GP	*B.E. (eV)*				
	At.%				
CNFs-PS	*B.E. (eV)*	*284.4*	*284.9*	*287.2*	*290.0*
	At.%	75.8	18.16	3.7	1.8

CNFs-LHT	*B.E. (eV)*	*284.5*	*284.9*	*287.4*	*290.1*
	At.%	83.8	12.0	2.6	1.6
GO	*B.E. (eV)*	*284.3*	*285.2*	*287.4*	*290.4*
	At.%	1.73	57.14	34.37	6.76