Effect of oxygen functionalities on the hydrous hydrazine decomposition over carbonaceous materials

Silvio Bellomi[a], Ilaria Barlocco[a], Simone Tumiati[b], Patrizia Fumagalli[b], Nikolaos Dimitratos[c,d], Alberto Roldan[e]*, Alberto Villa [a]*

[a] Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, I-20133, Milano, Italy.

[b] Dipartimento di Scienze della Terra Ardito Desio, Università degli Studi di Milano, via Mangiagalli 34, Milano I-20133, Italy

[c] Dipartimento di Chimica Industriale "Toso Montanari", Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, Bologna 40126, Italy

[d] Center for Chemical Catalysis-C3, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, Bologna 40136, Italy

[e] Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, CF10 3AT, Cardiff, United Kingdom.

* alberto.villa@unimi.it

* RoldanMartinezA@cardiff.ac.uk

Supporting Information

HR C1s model

For the C1s region, seven main peaks were considered[1]: the most intense peak at binding energy (BE) of 284.5 eV us assigned to C in sp^2 bonding configuration, appeared in combination with a satellite at BE of 291.0 eV, relative to the π-π* shaking signals. Peaks at BE of about 286.3-286.4, 287.8-287.9 and 288.8-288.9 eV are assigned to C-O, C=O and O=C-O moieties respectively. A signal related to the presence of CO_3 groups at BE of 289.6 is also identified.

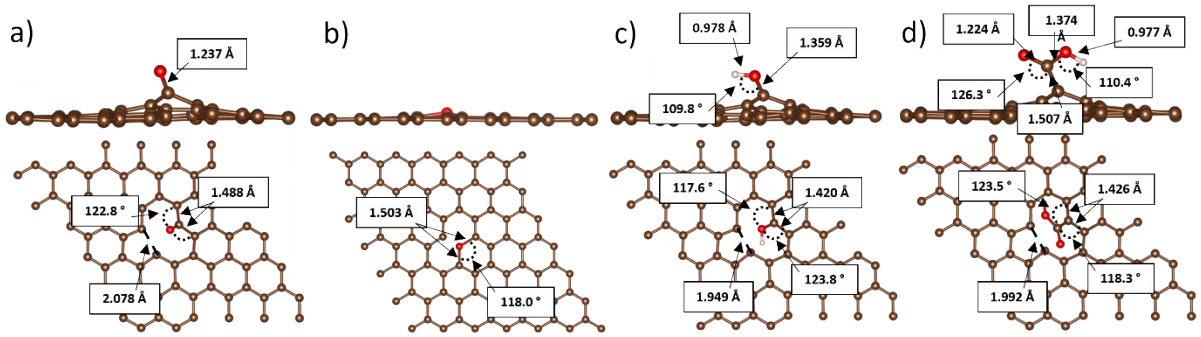

Figure S1 *:* Top and side view of the optimized functionalized graphitic surfaces: a) C=O, b) C-O-C, c) C-OH and d) COOH. Carbon atom is labelled brown, oxygen in red and hydrogen in white. Insets are bond distances and angles.

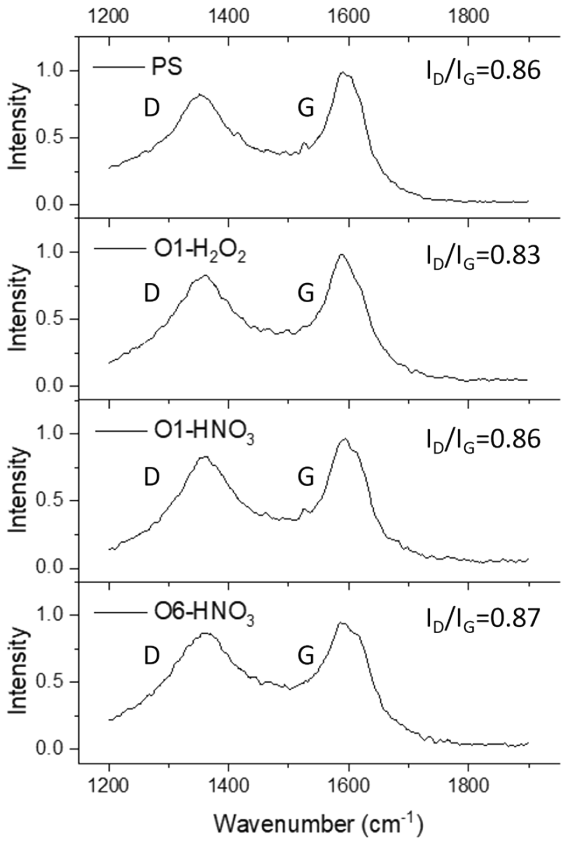

Figure S2 Raman spectra comparison of the fresh catalysts. The D band (≈1350 cm^{-1}), symmetry-forbidden, is enhanced by the presence of intrinsic defects (sp^3), whereas the G band (≈1350 cm^{-1}), symmetry-allowed, is representative of an ideal graphitic behaviour (sp^2).[2] Inset are bands labels and the I_D/I_G ratio, a widely employed descriptor for the defectivity quantification of carbonaceous materials.

Table S1 Trends of conversion at 150' and H_2 selectivity, oxygen content (O/C ratio) as obtained from the XPS survey analysis and graphitization degree quantification (I_D/I_G) from Raman.

Sample	**Conversion 150' / %**	**H_2 selectivity / %**	**O/C ratio**	**I_D/I_G**
CNFs	45	89	0.122	0.86
O1-H_2O_2	52	35	0.141	0.83
O1-HNO_3	65	14	0.157	0.86
O6-HNO_3	89	8	0.181	0.87

Table S2 Summary of the XPS high resolution analysis of the O1s spectral region of the fresh materials

Sample	C-O-C / BE. (At%)	C-OH / B.E. (At%)	C=O / BE. (At%)	COOH / B.E. (At%)	H_2O / BE. (At%)
CNFs	532.9 (19.5)	533.4 (14.3)	531.4 (26.7)	532.3 (32.3)	535.0 (7.3)
O1-H_2O_2	533.2 (23.1)	533.1 (18.2)	531.1 (24.5)	532.1 (29.3)	535.1 (7.9)
O1-HNO_3	532.9 (14.8)	533.8 (11.6)	531.5 (28.6)	532.8 (37.9)	535.0 (7.2)
O6-HNO_3	533.1 (7.4)	534.0 (4.4)	531.3 (37.7)	532.8 (44.4)	535.0 (6.2)

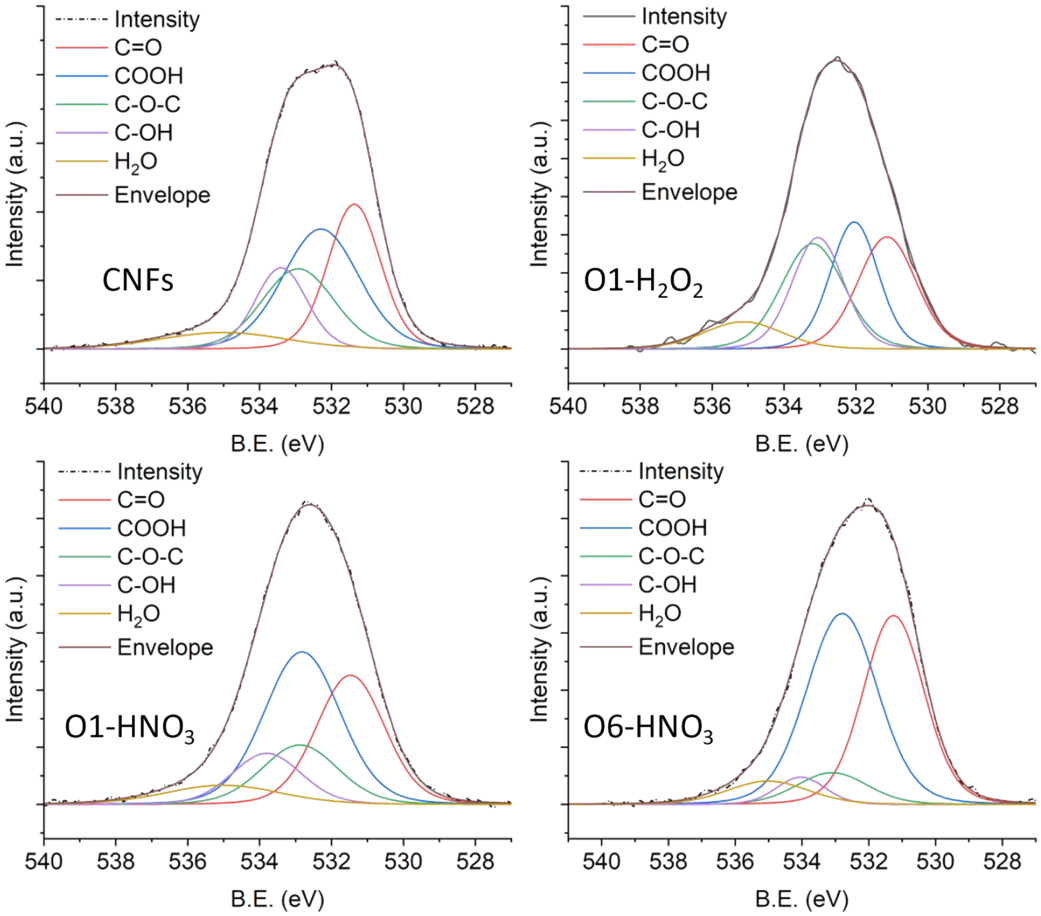

Figure S3 HR analysis of the O1s region for the fresh catalysts.

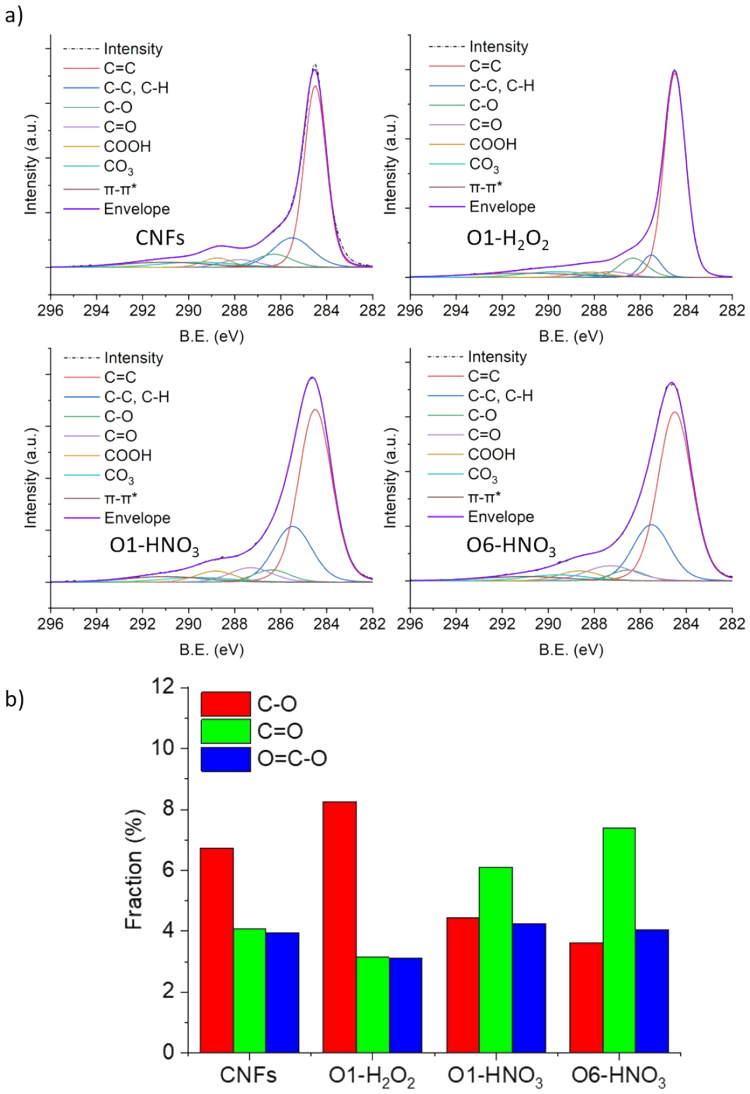

Figure S4 HR analysis of the C1s region: a) fitting and b) speciation of the oxygen-containing functional groups for the different catalyst.

Table S3 Summary of the XPS high resolution analysis of the C1s core level for the fresh materials.

Sample	C=C / BE. (At. %)	C-C,C-H / B.E. (At. %)	C-O / B.E. (At. %)	C=O / BE. (At. %)	O=C-O / BE. (At. %)	π-π* / BE. (At. %)	CO_3 / BE. (At. %)
CNFs	284.5 (56.7)	285.5 (16.3)	286.3 (6.7)	287.8 (4.1)	288.8 (4.0)	291.0 (6.5)	289.6 (5.8)
O1-H_2O_2	284.5 (66.1)	285.5 (6.6)	286.3 (8.3)	287.3 (3.1)	288.2 (3.1)	291.0 (7.1)	289.6 (5.8)
O1-HNO_3	284.5 (56.5)	285.5 (20.9)	286.4 (4.4)	287.3 (6.1)	288.8 (4.3)	291.0 (4.4)	289.6 (3.4)
O6-HNO_3	284.5 (55.8)	285.5 (21.0)	286.5 (3.6)	287.3 (7.4)	288.6 (4.1)	291.0 (3.8)	289.6 (3.8)

Table S4 Summary of the XPS high resolution analysis of the O1s spectral region of the spent materials.

Sample	C-O-C / BE. (At%)	C-OH / B.E. (At%)	C=O / BE. (At%)	COOH / B.E. (At%)	H_2O / BE. (At%)
CNFs	532.1 (3.2)	533.6 (21.7)	531.6 (29.5)	532.6 (38.6)	535.2 (7.0)
O1-H_2O_2 spent	533.2 (15.4)	534.0 (24.1)	531.5 (25.6)	532.5 (24.7)	535.0 (10.3)
O1-HNO_3 spent	532.4 (4.3)	533.7 (12.2)	531.1 (35.9)	532.2 (36.5)	535.0 (11.1)
O6-HNO_3 spent	533.1 (3.1)	534.1 (6.9)	531.3 (39.2)	532.6 (43.0)	535.3 (7.8)

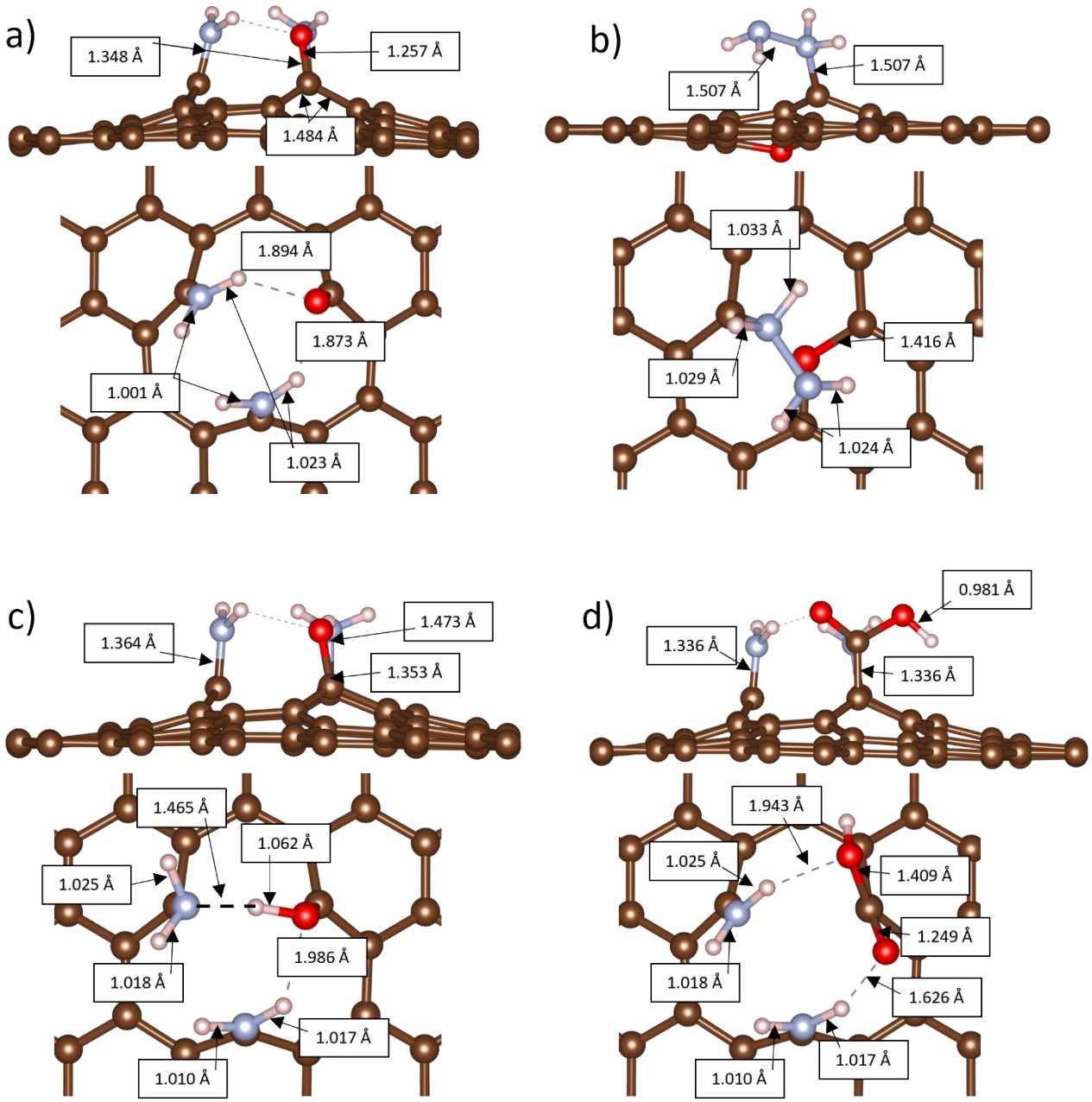

Figure S5 . Top and side view of the most favourable adsorption configurations upon interaction with N_2H_4: a) C=O, b) C-O-C, c) C-OH and d) COOH. The carbon atom is labelled brown, oxygen in red and hydrogen in white. Inset are bond lengths and angles.

Table S5 Adsorption energies (E_{ads}), zero-point corrections (E_{ZPE}) and entropic thermal contribution (TS, obtained at 323 K) used for the adsorption Gibbs free energies calculations.

Structure	**E_{ads} / eV**	**E_{ZPE} / eV**	**TS / eV**
C=O	-1.32	0.35	-0.42
C-O-C	-1.56	0.36	-0.42

C-OH	-0.78	0.38	-0.42
COOH	-1.33	0.41	-0.42

References

1 R. Arrigo, M. Hävecker, S. Wrabetz, R. Blume, M. Lerch, J. McGregor, E. P. J. Parrott, J. A. Zeitler, L. F. Gladden, A. Knop-Gericke, R. Schlögl and D. S. Su, *J. Am. Chem. Soc.*, 2010, **132**, 9616–9630.

2 F. Tuinstra and J. L. Koenig, *J. Chem. Phys.*, 1970, **53**, 1126–1130.