Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

An effective approach for modifying carbonaceous materials with niobium single sites to improve their catalytic properties

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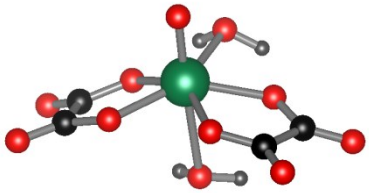
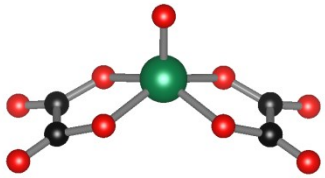
Figure S1. Studied reactions to propose the most stable interaction model of the niobium complex with carbonaceous materials.

Table S1: Energetic variations[(a)] for the studied reactions[(b)].

A.

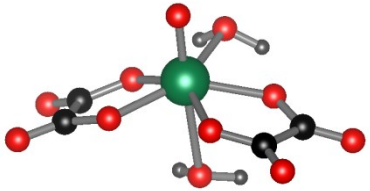


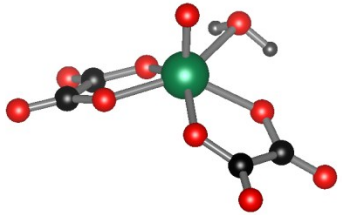
$[NbO(ox)_2(H_2O)_2]^-$ →  + $2H_2O$

$[NbO(ox)_2]^-$

ΔG^{total} = -7.8 kcal mol^{-1}

B.

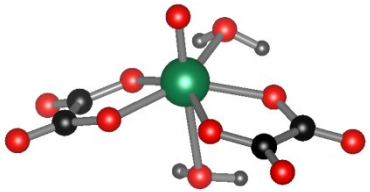


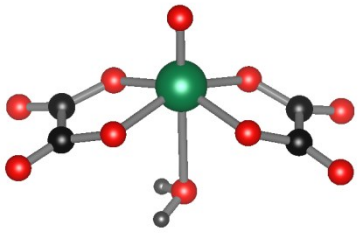
$[NbO(ox)_2(H_2O)_2]^-$ →  + H_2O

$[NbO(ox)_2(H_2O_{equatorial})]^-$

ΔG^{total} = -4.2 kcal mol^{-1}

C.



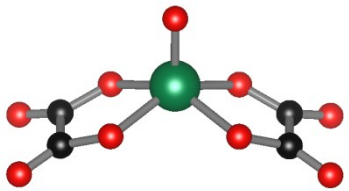
$[NbO(ox)_2(H_2O)_2]^-$ →  + H_2O

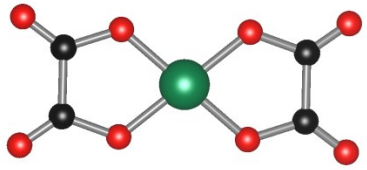
$[NbO(ox)_2(H_2O_{axial})]^-$

ΔG^{total} = -3.0 kcal mol^{-1}

Figure S1 continues in the next page.

D.

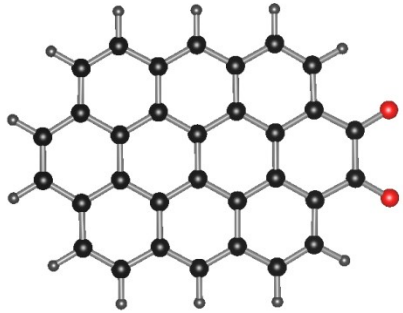


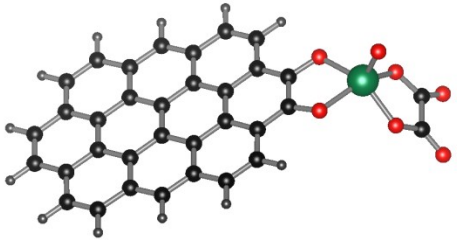
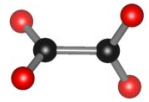
$[NbO(ox)_2]^-$ + H_3O^+ →  + H_2O + OH^-

$[Nb(ox)_2]^+$

$\Delta G^{total} = 122.2$ kcal mol^{-1}

E.

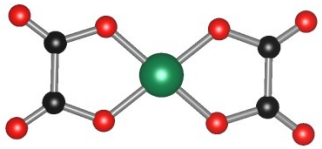


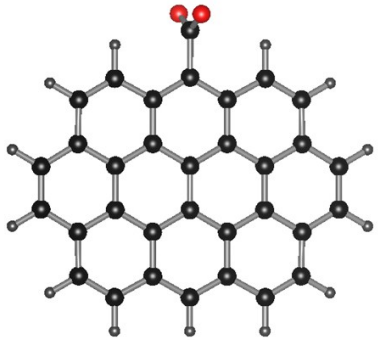
$[NbO(ox)_2]^-$ + $[Graphene\text{-}O_2]^{2-}$ →  + 

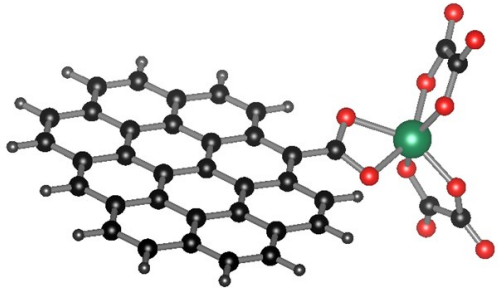
$\{[NbO(ox)]\text{-}[Graphene\text{-}O_2]\}^-$ + Oxalate (ox^{2-})

$\Delta G^{total} = 4.2$ kcal mol^{-1}

F.





$[Nb(ox)_2]^+$ + $[Graphene\text{-}COO]^-$ → 

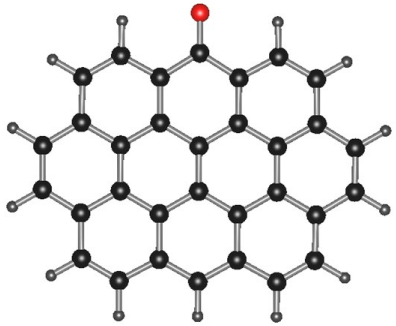
$[Nb(ox)_2]$-$[Graphene\text{-}COO]$

$\Delta G^{total} = -75.8$ kcal mol^{-1}

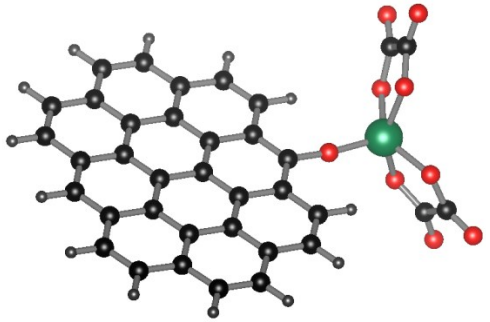
Figure S1 continues in the next page.

G.

+



→

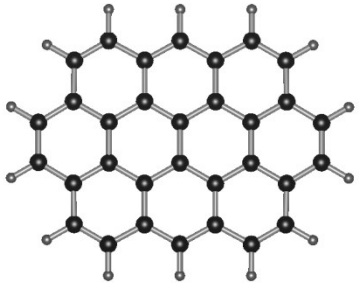


ΔG^{total} = -78.4 kcal mol^{-1}

$[Nb(ox)_2]^+$ $[Graphene\text{-}O]^-$ $[Nb(ox)_2]$-[Graphene-O]

H.

+



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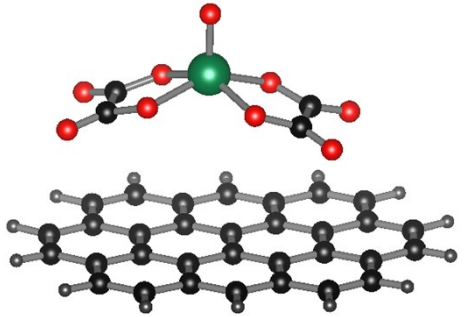
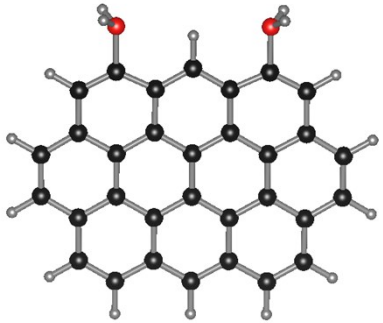


ΔG^{total} = 39.7 kcal mol^{-1}

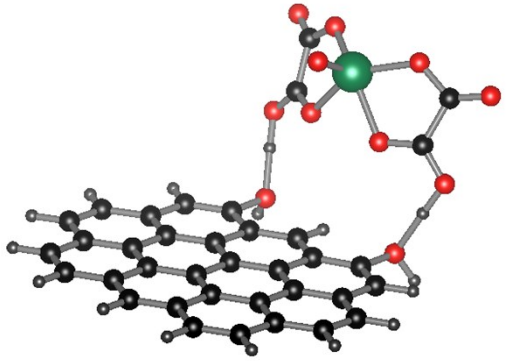
$[NbO(ox)_2]^-$ Graphene $[NbO(ox)_2]\cdots$Graphene

I.

+



→

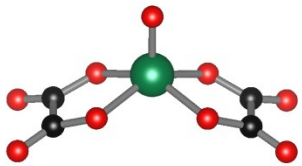


ΔG^{total} = -108.7 kcal mol^{-1}

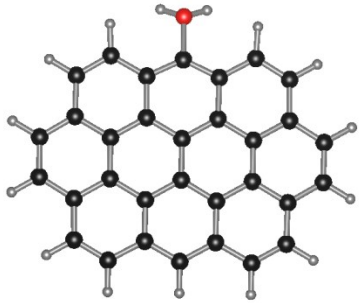
$[NbO(ox)_2]^-$ $[Graphene\text{-}(H_2O)_2]^+$ $\{[NbO(ox)]\text{-}[Graphene\text{-}(H_2O)_2]\}^+$

Figure S1 continues in the next page.

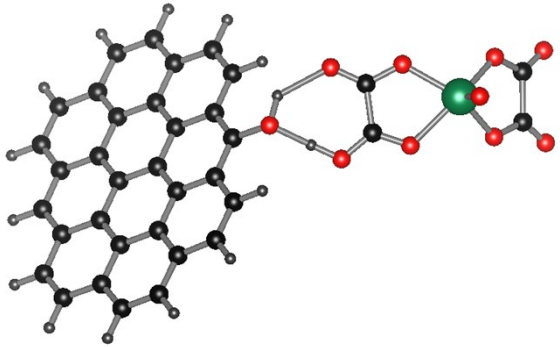
J.



$[NbO(ox)_2]^-$ +



$[Graphene\text{-}H_2O]^+$ →

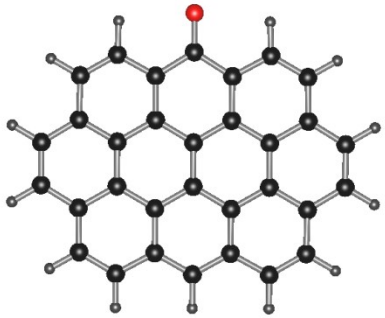


$[NbO(ox)]\text{-}[Graphene\text{-}(H_2O)]$

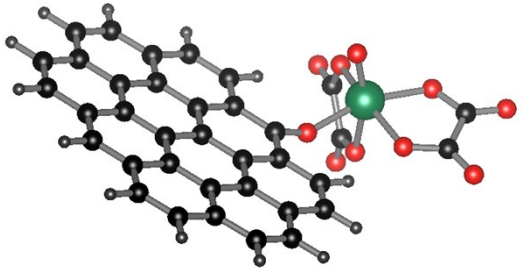
$\Delta G^{total} = 2.1$ kcal mol^{-1}

K.

$[NbO(ox)_2]^-$ +



$[Graphene\text{-}O]^-$ →

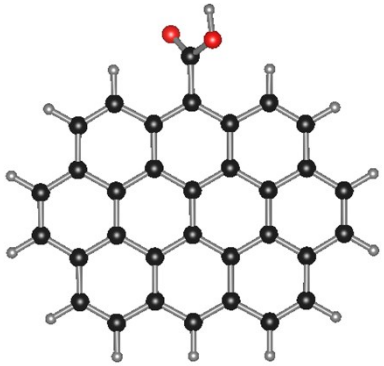


$\{[NbO(ox)_2]\text{-}[Graphene\text{-}O]\}^{2-}$

$\Delta G^{total} = 15.7$ kcal mol^{-1}

L.

$[NbO(ox)_2]^-$ +



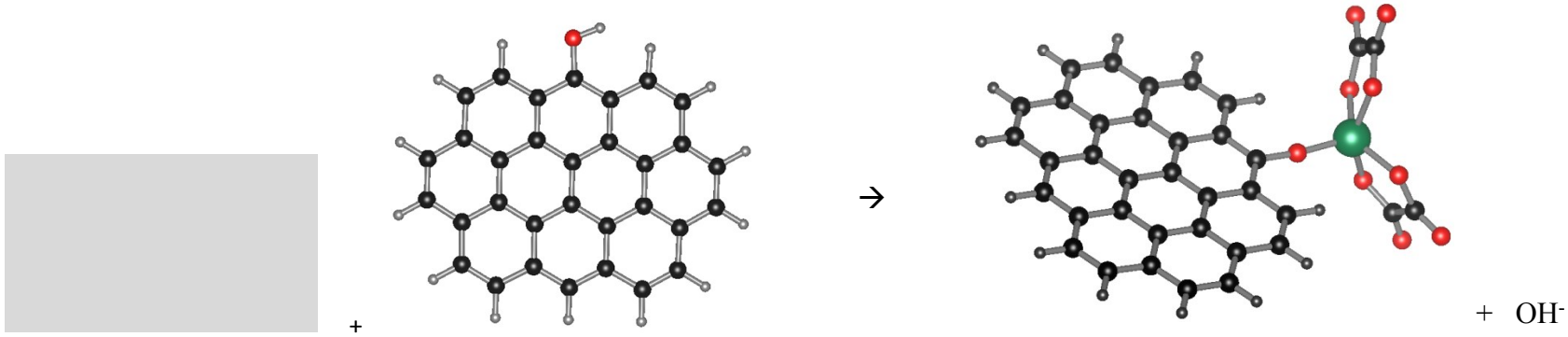
Graphene-COOH →

$[Nb(ox)_2]\text{-}[Graphene\text{-}COO]$ + OH^-

$\Delta G^{total} = 72.0$ kcal mol^{-1}

Figure S1 continues in the next page.

M.



N.

Figure S1 continues in the next page.

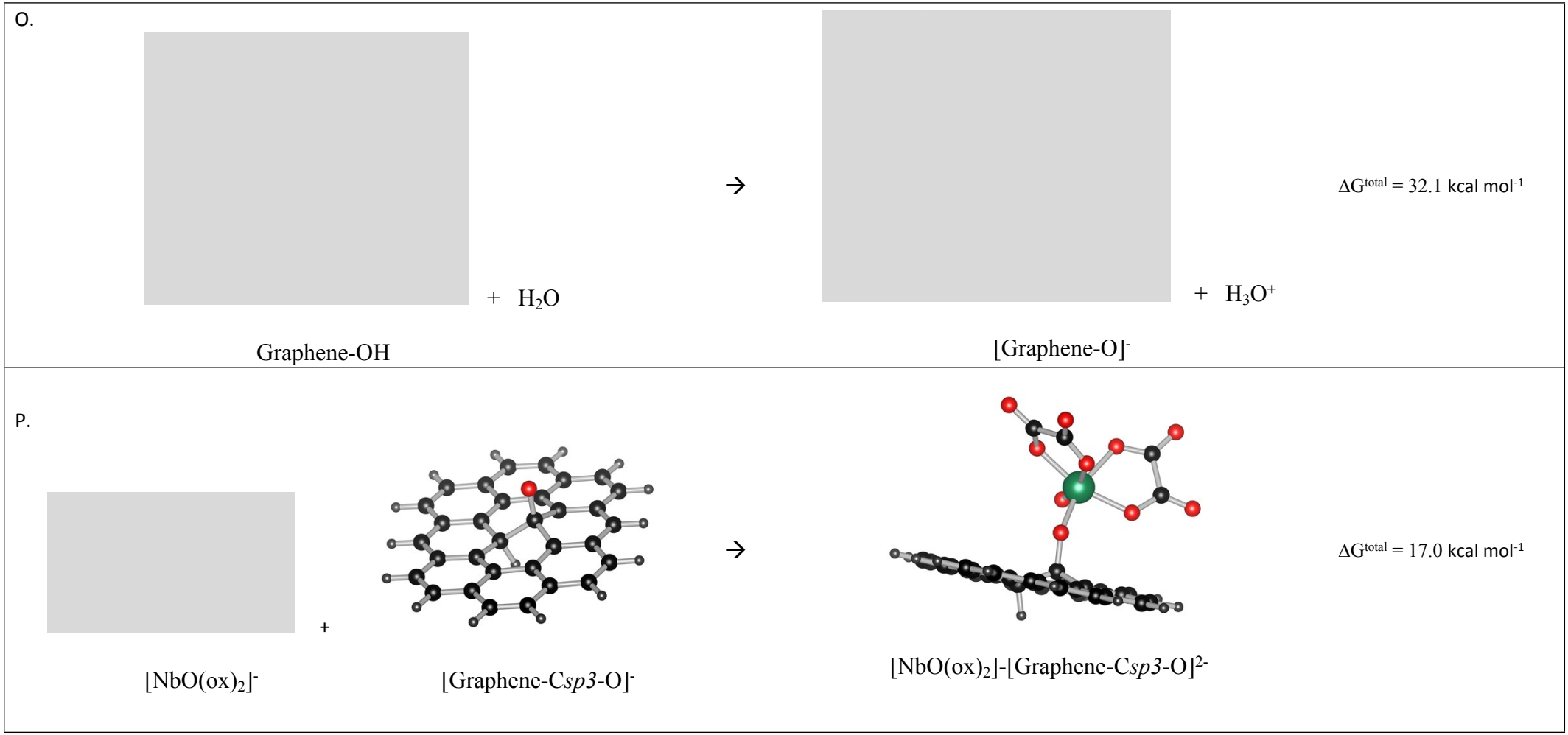


Figure S1. Studied reactions to propose the most stable interaction model of the niobium complex with carbonaceous materials. C (black), Nb (green), H (grey), O (red).

Table S1: Energetic variations[(a)] for the studied reactions[(b)].

Reaction	ΔE^{ele}	ΔG^{term}	ΔG^{solv}	ΔG^{total}
A	14.0	-23.6	1.8	-7.8
B	5.2	-10.8	1.4	-4.2
C	7.4	-13.3	2.9	-3.0
D	200.8	-14.4	-64.1	122.2
E	60.6	3.2	-59.6	4.2
F	-233.0	17.1	140.1	-75.8
G	-222.4	14.5	129.5	-78.4
H	15.0	12.6	12.1	39.7
I	-168.5	15.2	44.6	-108.7
J	-86.1	13.1	75.1	2.1
K	40.4	13.5	-38.2	15.7
L	125.5	0.2	-53.7	72.0
M	129.3	-0.9	-52.4	76.0
N	157.8	-2.5	-129.7	25.6
O	150.9	-1.0	-117.8	32.1
P	33.5	14.0	-30.5	17.0

(a)Values in kcal mol^{-1} estimated at 298.15 K. (b)The reactions are sketched in Figure S1.