Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

New insights on Fe-N-C catalyst structure from valence-to-core X-ray emission and absorption spectroscopies

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Supporting Information

1. ORCA Input Files Examples

FeN_4C_{10}, pyridinic bulk, Fe^{2+}, charge = 2, multiplicity = 2S + 1 = 1

1.1. Optimization input file

```
! uks bp86 zora zora-def2-tzvp sarc/j ri
! d3bj opt reducedpop cpcm(water)

% pal
   nprocs 10
   end

% basis
   newgto C "ZORA-def2-SVP" end
   newgto H "ZORA-def2-SVP" end
   end

* xyzfile 2 1 coords.xyz
```

1.2 Frequency input file

```
! uks bp86 zora zora-def2-tzvp sarc/j ri
! d3bj freq reducedpop cpcm(water)

% pal
   nprocs 10
   end

% basis
   newgto C "ZORA-def2-SVP" end
   newgto H "ZORA-def2-SVP" end
   end

* xyzfile 2 1 coords.xyz
```

1.3 XES input file

```
! uks bp86 zora zora-def2-tzvp sarc/j ri-somf(1x) ri
! d3bj tightscf reducedpop cpcm(water)

% pal
   nprocs 10
   end

% xes
   coreorb 0,0            # index of the Fe 1s orbital
   orbop 0,1              # use both spin-up and spin-down Fe 1s electrons
   dosoc true             # include spin-orbit coupling
   coreorbsoc 0,1         # index of the Fe 1s orbitals after spin-orbit coupling
   end

% method
   specialgridatoms 26
   specialgridintacc 7
   end

% basis
   newgto C "ZORA-def2-SVP" end
   newgto H "ZORA-def2-SVP" end
   end

* xyzfile 2 1 coords.xyz
```

2. VtC XES: background subtraction

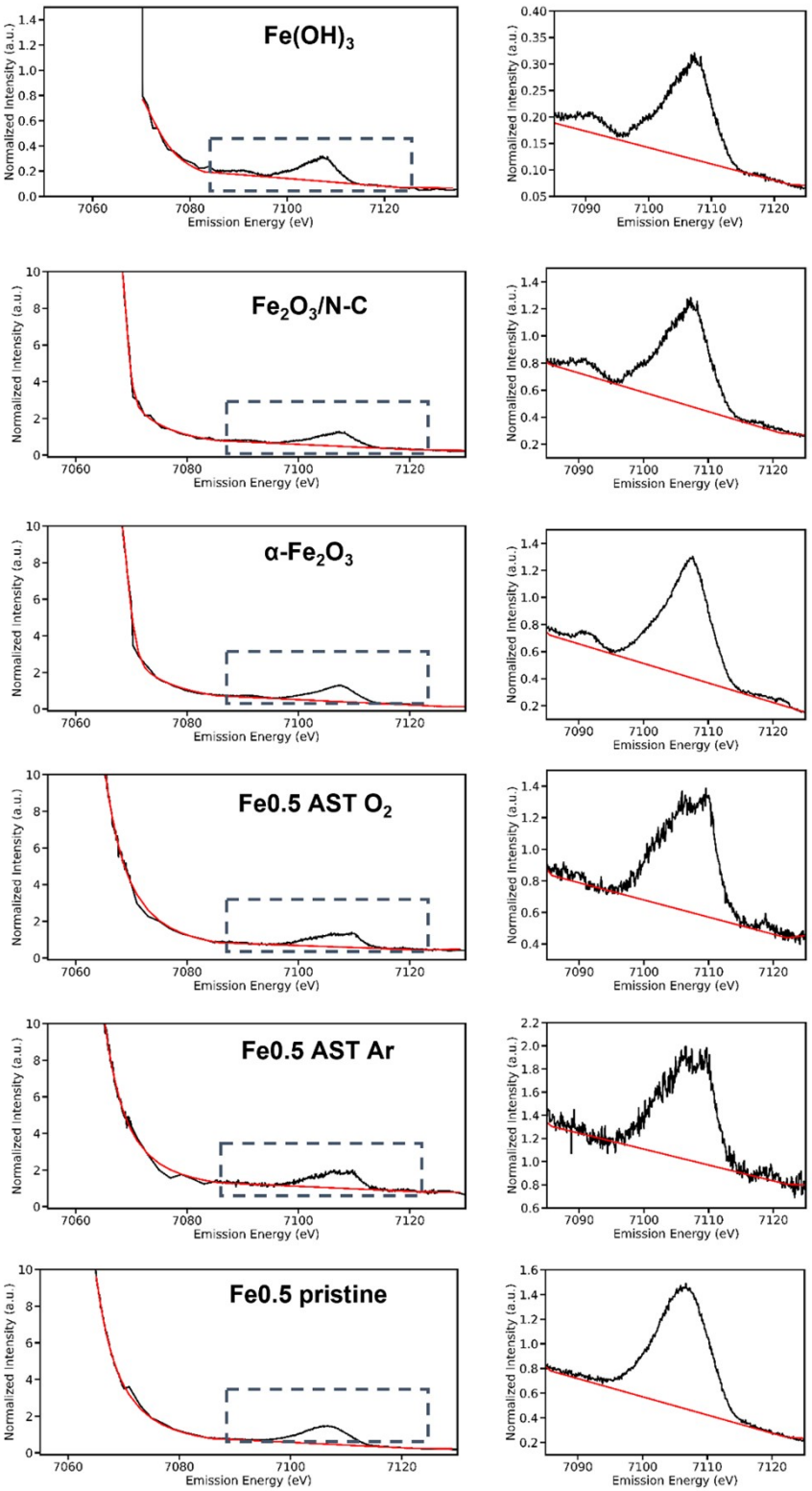

Figure S1. Background fitting for the Kβ emission lines of Fe0.5-based catalyst layers, Fe_2O_3 and $Fe(OH)_3$ powders. The best-fit curve is reported as a red line. The panels on the right show zoomed in the VtC region.

3. Additional spectroscopic data

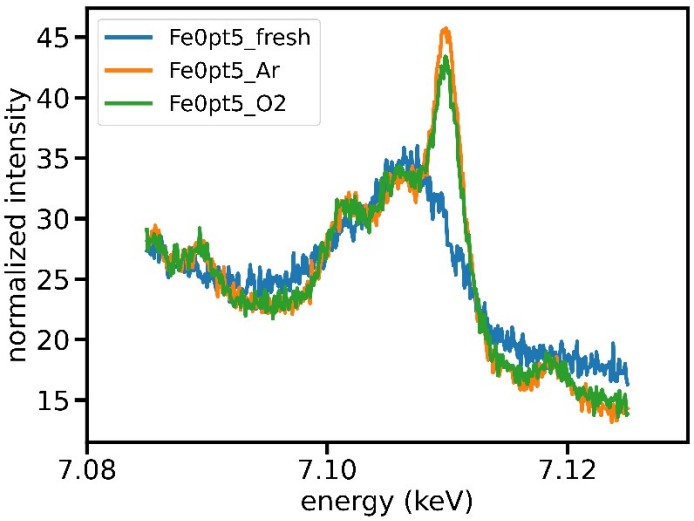

Figure S2. The VtC XES spectra recorded on Fe0.5-based catalyst layers before (fresh) and after the AST tests under Ar and O_2 on the samples presented in Sgarbi et al. [1] The XANES and Kβ XES spectra were presented and discussed in the manuscript mentioned above.

Figure S3 shows XANES and Kβ XES spectra of $Fe(OH)_3$ reference compound plotted together with the spectra of Fe0.5-based CLs. Based on the significant difference in the XANES signature as well as Kβ mainline position of iron hydroxide in comparison to the catalyst' spectra, one should observe the changes in the ASTs samples in case of iron hydroxide formation, which is not the case.

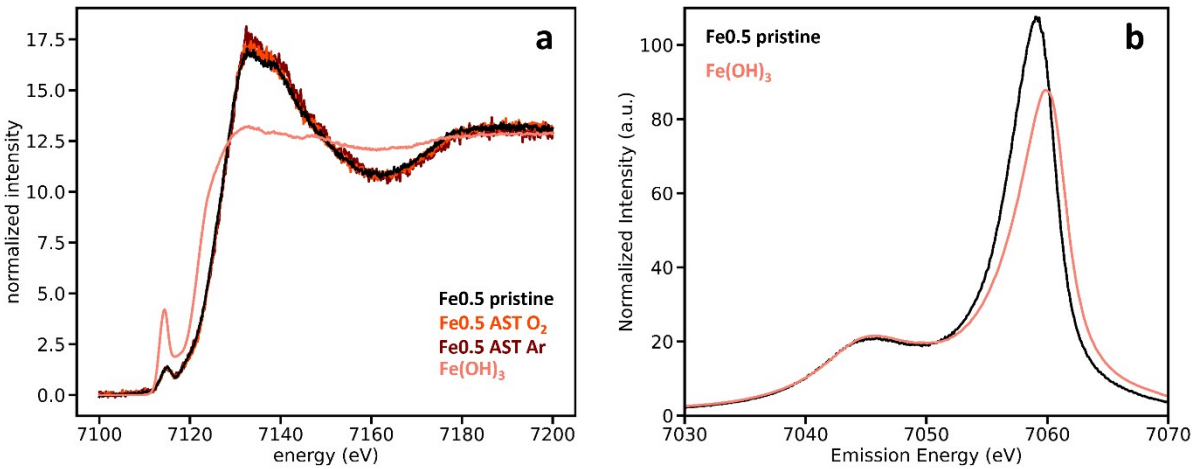

Figure S3. HERFD-XANES and Kβ XES spectra of Fe0.5-based CLs (reproduced from Figure 1 of the main text) and $Fe(OH)_3$ reference sample.

1. Models List

Table S1. Summary of the structural models used in this work. The table includes the overall charge and multiplicity used in the input file, and the calculated Fe Mulliken spin population, the Gibbs free energy (G) for each model, and the relative Gibbs free energy (ΔG) between models sharing the same structure and overall charge, but with different spin multiplicity. Only the XES VtC spectra of the models in bold are discussed.

Structure	Charge	Multiplicity (2S + 1)	Mulliken spin population	Gibbs free energy (Hartree)	Relative Gibbs free energy (kcal/mol)
Fe^{2+} structural models					
"Bulk"-hosted pyridinic models					
FeN_4C_{10}	2	1	−2.19	−6239.746082	11.5
FeN_4C_{10}	**2**	**3**	**2.19**	**−6239.764395**	**0.0**
FeN_4C_{10}	**2**	**5**	**2.27**	**−6239.748238**	**10.1**
$FeN_4C_{10}OH$	1	1	−0.87	−6315.877911	2.4
$FeN_4C_{10}OH$	**1**	**3**	**1.27**	**−6315.881781**	**0.0**
$FeN_4C_{10}OH$	1	5	2.55	−6315.869808	7.5
$FeN_4C_{10}(OH)_2$	**0**	**1**	**0.00**	**−6391.967553**	**13.2**
$FeN_4C_{10}(OH)_2$	**0**	**3**	**0.93**	**−6391.988618**	**0.0**
$FeN_4C_{10}(OH)_2$	0	5	1.60	−6391.965551	14.5
"Edge"-hosted pyridinic models					
FeN_4C_7	0	1	0.00	−5553.973662	15.7
FeN_4C_7	**0**	**3**	**1.56**	**−5553.991806**	**4.4**
FeN_4C_7	**0**	**5**	**2.42**	**−5553.998754**	**0.0**
FeN_4C_7OH	−1	1	−1.21	−5630.093981	2.2
FeN_4C_7OH	**−1**	**3**	**1.39**	**−5630.096232**	**0.8**
FeN_4C_7OH	**−1**	**5**	**2.20**	**−5630.097556**	**0.0**
$FeN_4C_7(OH)_2$	−2	1	−0.95	−5706.168120	3.1
$FeN_4C_7(OH)_2$	**−2**	**3**	**1.27**	**−5706.173054**	**0.0**
$FeN_4C_7(OH)_2$	−2	5	1.36	−5706.168664	2.8
"Bulk"-hosted pyrrolic models					
FeN_4C_{12}	**0**	**1**	**2.16**	**−4637.928764**	**0.0**
FeN_4C_{12}	**0**	**3**	**2.17**	**−4637.928837**	**0.0**
FeN_4C_{12}	0	5	2.31	−4637.927974	0.5
$FeN_4C_{12}OH$	−1	1	0.56	−4714.018953	3.8
$FeN_4C_{12}OH$	−1	3	0.66	−4714.021870	1.9
$FeN_4C_{12}OH$	**−1**	**5**	**2.42**	**−4714.024955**	**0.0**
$FeN_4C_{12}(OH)_2$	−2	1	0.93	−4790.112518	1.8

$FeN_4C_{12}(OH)_2$	**−2**	**3**	**1.13**	**−4790.115450**	**0.0**
$FeN_4C_{12}(OH)_2$	−2	5	1.19	−4790.104393	6.9
Fe^{3+} structural models					
"Bulk"-hosted pyridinic models					
FeN_4C_{10}	3	2	2.19	−6239.571510	1.1
FeN_4C_{10}	**3**	**4**	**2.22**	**−6239.573232**	**0.0**
FeN_4C_{10}	3	6	2.26	−6239.556411	10.6
$FeN_4C_{10}OH$	**2**	**2**	**1.01**	**−6315.70701**	**2.3**
$FeN_4C_{10}OH$	**2**	**4**	**2.30**	**−6315.710754**	**0.0**
$FeN_4C_{10}OH$	2	6	3.96	−6315.696989	8.6
$FeN_4C_{10}(OH)_2$	**1**	**2**	**0.93**	**−6391.831523**	**0.0**
$FeN_4C_{10}(OH)_2$	1	4	1.60	−6391.819413	7.6
$FeN_4C_{10}(OH)_2$	1	6	1.58	−6391.790808	25.5
"Edge"-hosted pyridinic models					
FeN_4C_7	**1**	**2**	**2.40**	**−5553.841287**	**0.0**
FeN_4C_7	**1**	**4**	**2.40**	**−5553.840524**	**0.5**
FeN_4C_7	1	6	2.47	−5553.838598	1.7
FeN_4C_7OH	**0**	**2**	**1.83**	**−5629.953956**	**0.0**
FeN_4C_7OH	**0**	**4**	**1.73**	**−5629.953431**	**0.3**
FeN_4C_7OH	0	6	2.23	−5629.945430	5.4
$FeN_4C_7(OH)_2$	**−1**	**2**	**1.37**	**−5706.035680**	**0.0**
$FeN_4C_7(OH)_2$	**−1**	**4**	**1.37**	**−5706.035597**	**0.1**
$FeN_4C_7(OH)_2$	−1	6	1.48	−5706.022956	8.0
"Bulk"-hosted pyrrolic models					
FeN_4C_{12}	**1**	**2**	**2.14**	**−4637.768152**	**0.0**
FeN_4C_{12}	**1**	**4**	**2.30**	**−4637.764688**	**2.2**
FeN_4C_{12}	1	6	2.55	−4637.746136	13.8
$FeN_4C_{12}OH$	0	2	0.97	−4713.874665	0.5
$FeN_4C_{12}OH$	**0**	**4**	**1.02**	**−4713.875412**	**0.0**
$FeN_4C_{12}OH$	**0**	**6**	**2.65**	**−4713.874223**	**0.7**
$FeN_4C_{12}(OH)_2$	−1	2	−0.91	−4789.977433	1.7
$FeN_4C_{12}(OH)_2$	**−1**	**4**	**1.13**	**−4789.980183**	**0.0**
$FeN_4C_{12}(OH)_2$	−1	6	2.19	−4789.955464	15.5

References

1 R. Sgarbi, K. Kumar, V. A.Saveleva, L. Dubau, R. Chattot, V. Martin, M. Mermoux, P. Bordet, P. Glatzel, E. A. Ticianelli, F. Jaouen and F. Maillard, *Appl. Catal. B Environ.*, 2022, 121366.