Supporting information

to

In situ study of the evolution of NiFe nanocatalysts in reductive and oxidative environments upon thermal treatments

François Robert^{a,b}, Pierre Lecante^c, Jean-Sébastien Girardon^d, Robert Wojcieszak^d, Éric Marceau^d*, Valérie Briois^e, Catherine Amiens^{a,b}*, and Karine Philippot^{a,b}*

a. CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F- 31077 Toulouse Cedex 4, France.

b. Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France.

c. CNRS, CEMES (Centre d'Elaboration des Matériaux et d'Etudes Structurales), 29 Rue Jeanne Marvig, BP 4347, F-31055 Toulouse Cedex 4, France.

d. Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

e. Synchrotron SOLEIL, CNRS-UR1, L'Orme des Merisiers, BP48, Saint-Aubin, F-91192 Gif-sur Yvette, France

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1. TEM images of NPs before and after deposition onto silica, in inert conditions or in air.



Fig. SI 1 : a) TEM image and size histogram of the Ni2Fe1 NPs before deposition onto silica ; b) TEM image of Ni2Fe1-S (dark field mode, red arrows showing typical NPs); c) TEM image of Ni2Fe1-S-Ox (red arrows showing typical NPs)



Fig. SI 2 : a) TEM image and size histogram of the Ni1Fe1 NPs before deposition onto silica ; b) TEM image of Ni1Fe1-S (red arrows showing typical NPs); c) and d) TEM image of Ni1Fe1-S-Ox in bright and dark field respectively



Fig. SI 3 : a) TEM image and size histogram of the Ni1Fe9 NPs before deposition onto silica ; b) TEM image of Ni1Fe9-S (red arrows showing some typical isolated NPs); c) TEM image of Ni1Fe9-S-Ox (red arrows showing some typical isolated NPs)

2. XAS spectra of the initial state of the nanomaterials



Fig. SI 4 : XANES spectra of a) at Fe K-edge and b) at Ni K-edge for Ni2Fe1-S-Ox, Ni1Fe1-S-Ox and Ni1Fe9-S-Ox in comparison with reference data from maghemite (γ -Fe₂O₃), hematite (α -Fe₂O₃), magnetite (Fe₃O₄), fcc Ni and NiO.



Fig SI 5 : EXAFS k3-weighted oscillations (solid black line) and results of k3 $\chi(k)$ EXAFS fitting (red dotted line) in R-space (top panel) and k space (bottom panel) for Ni2Fe1-S-Ox at Fe (left) and Ni (right) K edges. Data collected at 30°C.



Fig SI 6 : EXAFS k3-weighted oscillations (solid black line) and results of k3 $\chi(k)$ EXAFS fitting (red dotted line) in R-space (top panel) and k space (bottom panel) for Ni1Fe1-S-Ox at Fe (left) and Ni (right) K edges. Data collected at 30°C.

3. Evolution of the XAS spectra of Ni1Fe1-S-Ox under reducing atmosphere as a function of the temperature



Figure SI 7 : Superposition of the XAS spectra recorded at Ni K-edge (colour scale from blue : 30°C to red : 530°C; for the sake of clarity only one spectrum over four is drawn).



Figure SI 8 : Superposition of the XAS spectra recorded at Fe K-edge (colour scale from blue : 30°C to red : 530°C; for the sake of clarity only one spectrum over four is drawn).

4. Evolution of the XAS spectra of Ni1Fe9-S-Ox under reducing atmosphere during the temperature ramp



Figure SI 9 : Superposition of the XAS spectra recorded at Ni K-edge (colour scale from blue : 30°C to red : 530°C; for the sake of clarity only one spectrum over four is drawn).



Figure SI 10 : Superposition of the XAS spectra recorded at Fe K-edge (colour scale from blue : 30°C to red : 530°C; for the sake of clarity only one spectrum over four is drawn).

5. MCR-ALS analysis



Fig. SI 11 : At Ni K-edge: a) XANES spectra of the two components used to fit the data and b) TF of the EXAFS of the second components used to fit the XAS spectra, compared to NiO, fcc Ni and Fe in a polytetrahedral atomic packing.

Concerning the second spectral component, the position of the main peak in the FT of the EXAFS (Fig SI 11b) is close to the one in fcc Ni for the two Ni-rich samples. Concerning the Fe-rich one, it is significantly shorter. Comparison was made with the FT of the EXAFS data collected from Fe NPs in a polytetrahedral environment, as this atomic packing is not known for Ni, and it led to a better agreement than the fcc structure. Still, it is difficult to conclude on the local environment around Ni in this component. However, it is clear from the position of the edge (XANES spectrum, Fig SI 11a) that is corresponds to zerovalent Ni.



Fig. SI 12 : At Fe K-edge. XANES spectra of a), b) respectively the first and second components in comparison with maghemite (Fe_2O_3) and Mohr's salt ($FeSO_4$. $SO_4(NH_4)_2$); c) the third component and d) FT of its EXAFS data in comparison with polytetrahedral and fcc Fe

Concerning the third spectral component, its XANES spectrum (Fig SI 12c) is closer to the one of fcc Fe for the two Ni-rich samples which is confirmed by position of the main peak in the FT of the EXAFS (Fig SI 12 d), close to the one in fcc Fe. Concerning the Fe-rich one, its XANES spectrum resembles none of the references (Fig SI 12c). The position of the main peak in the FT of the EXAFS is slightly shifted to lower r values (Fig SI 12 d) than in the fcc reference. Comparison was made with the FT of the EXAFS data collected from Fe NPs in a polytetrahedral environment and it led to a better agreement than the fcc structure (or bcc, not shown on the image for clarity). Still, it is difficult to conclude on the local environment around Fe in this component. However, it is clear from the position of the edge that is corresponds to zerovalent Fe.





Fig. SI 13 : MCR-ALS analysis of the reduction of a) Ni2Fe1-S-Ox, b) Ni1Fe1-S-Ox and c) Ni1Fe9-S-Ox as a function of time. Temperature is reported in the right vertical axis.

c. Evolution of Ni2Fe1-S-Ox under He



Fig. SI 14 : MCR-ALS analysis during thermal treatment of Ni2Fe1-S-Ox under He as a function of temperature.



6. Study of the reoxidation of the nanomaterials (XAS and TEM data)

Fig SI 15: Comparison of the XAS spectra of NiFe-S-Ox nanomaterials at the Fe (top panel) and Ni (bottom panel) K-edges. Thin solid line: as produced nanomaterials (initial state); dotted line: after reduction under H_2 (5% in He), dashed line: after re-oxidation for a minimum of 7h in air; thick solid lines : reference spectra.



Fig SI 16 : EXAFS k3-weighted oscillations (solid black line) and results of k3 $\chi(k)$ EXAFS fitting (red dotted line) in R-space (top panel) and k space (bottom panel) for Ni2Fe1-S-Ox after reoxidation at Fe (left) and Ni (right) K edges. Spectra recorded at r.t.



Fig SI 17 : EXAFS k3-weighted oscillations (solid black line) and results of k3 $\chi(k)$ EXAFS fitting (red dotted line) in R-space (top panel) and k space (bottom panel) for Ni1Fe1-S-Ox after reoxidation at Fe (left) and Ni (right) K edges. Spectra recorded at r.t.



Fig. SI 18 : TEM images after TPR of a) Ni2Fe1 NPs (dark field), b) Ni1Fe1-S-Ox (dark field) and c)Ni1Fe9-S-Ox (bright field, red circle showing a typical NP)