

C. Amiens replied [†] :

The metal loading on the silica support is close to 7% (the exact values can be found in the experimental part of the paper). Some aggregates can be observed in the TEM images both before (Figure SI1-3) and after the reduction /re-oxidation process (Figure SI18). TEM images after re-oxidation do not show a larger extent of aggregation. Still, only a very limited part of the samples could be observed by TEM, so it is difficult to draw any firm conclusion on that point.

Concerning the use of these NiFe nanoparticles in catalysis, so far we have considered two applications: the electro-oxidation of water and the hydrogenation of a sugar, xylose.

For the electro-oxidation of water, unsupported NiFe nanoparticles of different compositions (Ni₂Fe₁, Ni₁Fe₁, Ni₁Fe₉) were used after exposure to air. Characterization results indicate that the structure and chemical state of these air-exposed NiFe NPs are very close to those of the silica-supported NiFe nanoparticles prepared in air, as described in the Faraday Discussion paper. For the electrocatalysis study, these NiFe NPs were dispersed into water, then deposited onto fluorine doped tin oxide electrodes. The results evidenced a higher electrocatalytic activity for the Ni₂Fe₁ composition. ⁱ

The study of the catalytic hydrogenation of D-xylose was performed with the silica-supported NiFe nanomaterials described in this paper. To compare with previous results obtained with NiFe nanocatalysts prepared on silica by deposition-precipitation with urea (DPU),ⁱⁱ the catalytic tests were carried out in the same catalytic set-up, in water, at 80°C and under 20 bar of H₂, with a molar ratio of 10.6 between xylose and the total metal content in the catalysts. The silica-supported catalysts were not exposed to H₂ prior to reaction.

Ni₂Fe₁-S, Ni₁Fe₁-S, Ni₁Fe₉-S and Ni₂Fe₁-SO_x nanomaterials were evaluated as catalysts in comparison to a pure metallic nickel nanomaterial also supported onto silica (Ni-S)ⁱⁱⁱ. The conversion of xylose and yield/selectivity towards xylitol were monitored by HPLC over a period of 7 h.

A freshly prepared Ni₂Fe₁-S nanomaterial was first compared to its oxidized counterpart Ni₂Fe₁S-Ox. The former was extremely active (xylose conversion of 95% after 7 h). The latter displayed a good activity despite a long-term exposure to air (75% conversion after 7 h), as evidenced on Figure 1. This interesting result is attributed to the persistence of a reduced Ni fraction that facilitates the reduction of the surface oxide under H₂ pressure, as observed during temperature-programmed experiments monitored by XAS. It is assumed that the higher hydrogen pressure (20 bar of pure H₂ in catalytic experiments, *versus* 5% H₂ in helium flow - 50 mL.min⁻¹ - at atmospheric pressure for XAS measurements) compensates for the lower temperature (80°C in catalytic experiments, while the onset of reduction was observed at 272°C in XAS measurements). In addition and remarkably, these nanomaterials displayed an excellent selectivity towards xylitol which was even exclusive with the Ni₂Fe₁-S-OX nanomaterial.

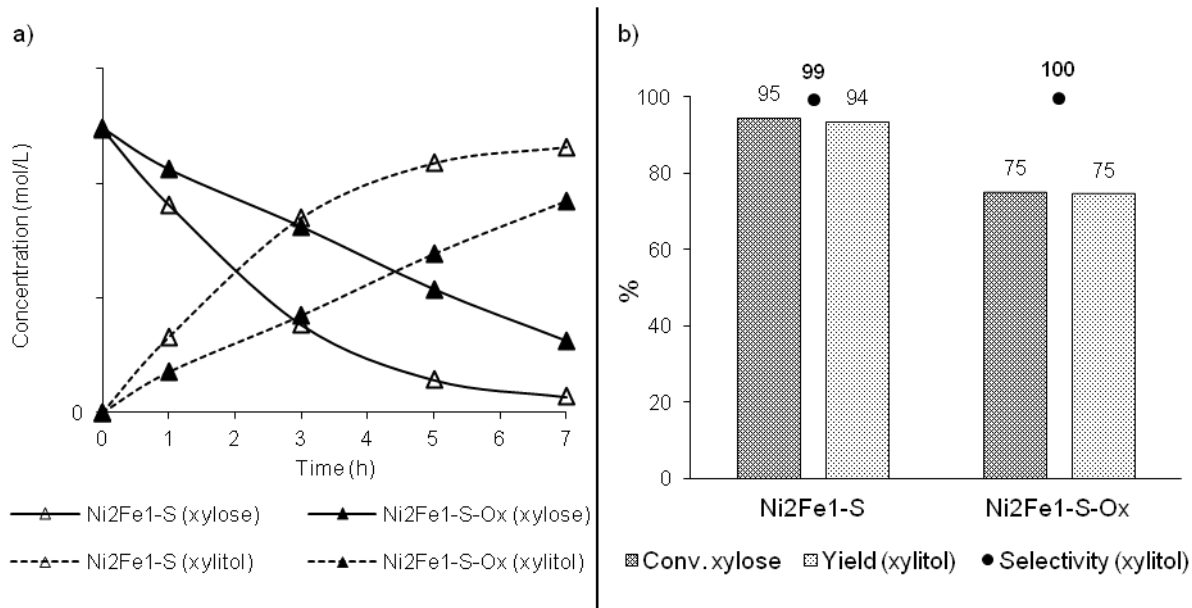


Figure 1: a) Concentration of xylose and xylitol as a function of time for freshly prepared Ni2Fe1-S and Ni2Fe1-S-Ox; b) conversion (conv.) of xylose, yield and selectivity in xylitol.

A handling restricted to freshly prepared catalysts was not possible, and the effect of composition was assayed on a series of 7-months-old Ni2Fe1-S, Ni1Fe1-S and Ni1Fe9-S nanomaterials in comparison to a pure metallic nickel nanomaterial also supported onto silica (Ni-S). The conversion of xylose after 7 h was measured as 73, 44 and 29% for Ni2Fe1-S, Ni1Fe1-S and Ni1Fe9-S, respectively (Figure 2a). These values are higher than the conversion measured for the silica-supported Ni catalyst (Ni-S, 18% of xylose conversion only), thus confirming the synergistic effect between Ni and Fe in the NiFe-S catalysts, previously observed for DPU prepared nanomaterials,ⁱⁱ with a higher performance of the composition Ni2Fe1 as in the electro-oxidation of water (see above). The target polyol, xylitol, was the only hydrogenation product formed on Ni2Fe1-S and Ni1Fe1-S, thus evidencing a selectivity of 100% for the two catalysts (Figure 2b-c). The iron-rich nanomaterial Ni1Fe9-S displayed a poor selectivity towards xylitol (10%), because the ketose isomer of xylose, xylulose, and a polyol isomer, arabitol, were also formed with this catalyst. Metal ions on partially oxidized/incompletely reduced Ni1Fe9-S may have acted as Lewis acidic sites for the isomerization of xylose. In terms of yield (Figure 2c), in the applied reaction conditions the Ni2Fe1-S nanomaterial was thus the most promising catalyst for the hydrogenation of xylose, which confirms the observations made by Sadier and col.ⁱⁱ (when working in the same conditions with NiFe nanocatalysts prepared by DPU on the same silica support). Metal leaching after 7 h of reaction was low. Measurements in solution by ICP gave 1.5 ppm Ni for the monometallic Ni catalyst, and 4.7 ppm Ni and 4.1 ppm Fe for Ni2Fe1-S.

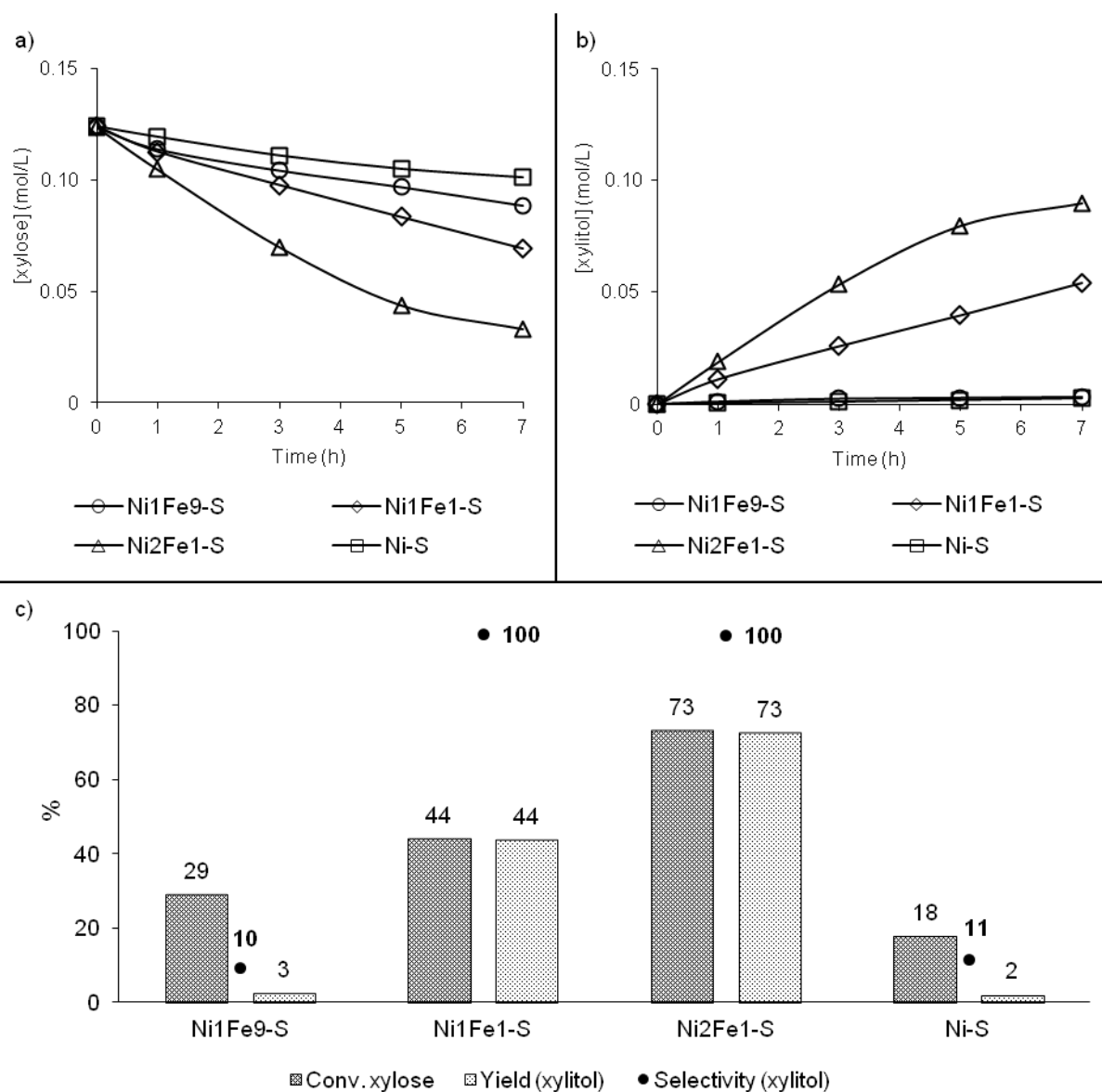


Figure 2: a) concentration of xylose as a function of reaction time for Ni1Fe9-S, Ni1Fe1-S and Ni2Fe1-S (after 7 months of storage of the nanomaterials in the glove-box) in comparison with an 100% Ni nanomaterial Ni-S ; b) concentration of xylitol against time ; c) conversion (conv.) of xylose, yield and selectivity in xylitol.

Altogether, these results emphasize the interest of NiFe nanomaterials prepared by the organometallic route for the catalytic hydrogenation of sugars: the very small size and the chemical composition of the nanoparticles are well controlled, the deposition onto silica can be made easily by a simple impregnation method, and even after purification and storage in air, these nanoscale catalysts display high activity and excellent selectivity in the hydrogenation of xylose.

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ⁱ Synthesis of NiFeOx nanocatalysts from metal-organic precursors for the oxygen evolution reaction. Nguyen Thi Quyen, Francois Robert, Vincent Colliere, Pierre Lecante, Karine Philippot, Jérôme Esvan, Tran Dinh Phong, Catherine Amiens, Dalton Trans, 2022, 11457 – 11466. DOI :10.1039/d2dt01370c.

ⁱⁱ Sadier, A.; Shi, D.; Mamede, A.-S.; Paul, S.; Marceau, E.; Wojcieszak, R. Selective Aqueous Phase Hydrogenation of Xylose to Xylitol over SiO₂-Supported Ni and Ni-Fe Catalysts: Benefits of Promotion by Fe. Applied Catalysis B: Environmental 2021, 298, 120564. <https://doi.org/10.1016/j.apcatb.2021.120564>.

ⁱⁱⁱ F. Robert, PhD dissertation, University Paul-Sabatier, 2022.