Scanning different Ni-noble metal (Pt, Pd, Ru) bimetallic nanoparticles supported on carbon nanofibers for one-pot cellobiose conversion

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Products analysis by GC:

The reaction products were silylated and analyzed by Gas chromatography (GC, Perkin Elmer Instruments, Clarus®580) equipped with a autosampler, a splitter injection port and flame ionization detector (FID). Separation of the products (0.5 µL of sample, split ratio of 1:11) was performed on an Elite-5 column (Crossbond 5% diphenil-95% dimetyl polioxane, 250 µm×30 m) and using helium (10 mL/min, 99,9992%, Air Liquid) as carrier gas. Oven temperature program is initially held at 40ºC for 2.5 min, ramped to 330 ºC at 10 ºC /min, and kept at 330 ºC for 1 min, while injection and detection temperatures were fixed at 275 ºC and 330 ºC, respectively.

In short, the derivatization procedure is as follows: sample aliquots (3mL) were first evaporated to dryness under vacuum (75ºC) and then converted to their trimethylsilylether counterparts using an overstoichiometric proportion (1mL per 10 mg of solid rescued) of commercial sylilation agent (HMDS:TMCS:Pyridine, 3:1:9, Sylon™ HTP, Superlco). The reaction proceeds at 60ºC for 30 min under sonication. Before the injection, pyridine is exchanged for toluene and the sample is filtered over a 0.45 µm PTFE filter. This methodology was similarly applied for the analytical standards used in the quantification.

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In order to determine all those volatile compounds (i.e., EG, HMF) which could be lost during sample drying, an aliquot of the filtered sample and diluted in methanol (1:4) are also directly injected.

Products distribution during the hydrolysis test:

Table S1. Cellobiose conversion and itemized products yields during the hydrolysis tests

Time (h)	Cellobiose conversion	$Y_{PRODUCTS}$ (mass %)				
		Glucose	Fructose	HMF	Levulinic acid	Others*
0	21.40	13.25	1.26	1.00	0.50	5.39
0.5	42.66	14.67	2.11	1.46	0.64	23.77
1	56.68	23.69	3.72	3.00	0.98	25.28
1.5	71.02	27.24	3.96	4.12	0.91	34.79
2	72.73	26.35	3.04	3.99	0.60	38.75
2.5	77.24	28.92	5.09	5.18	1.22	36.84
3	84.24	26.70	5.56	5.71	1.23	45.05

*Determined as the difference between the cellobiose conversion and the sum of quantified products.

Hydrogen-temperature programmed reduction (TPR-H_2) results:

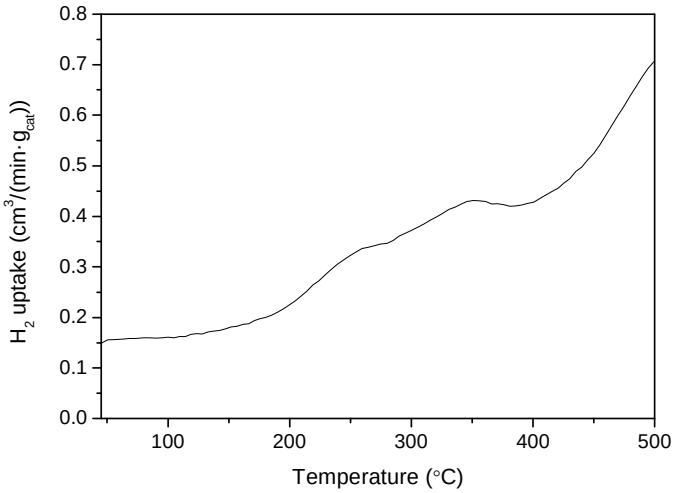
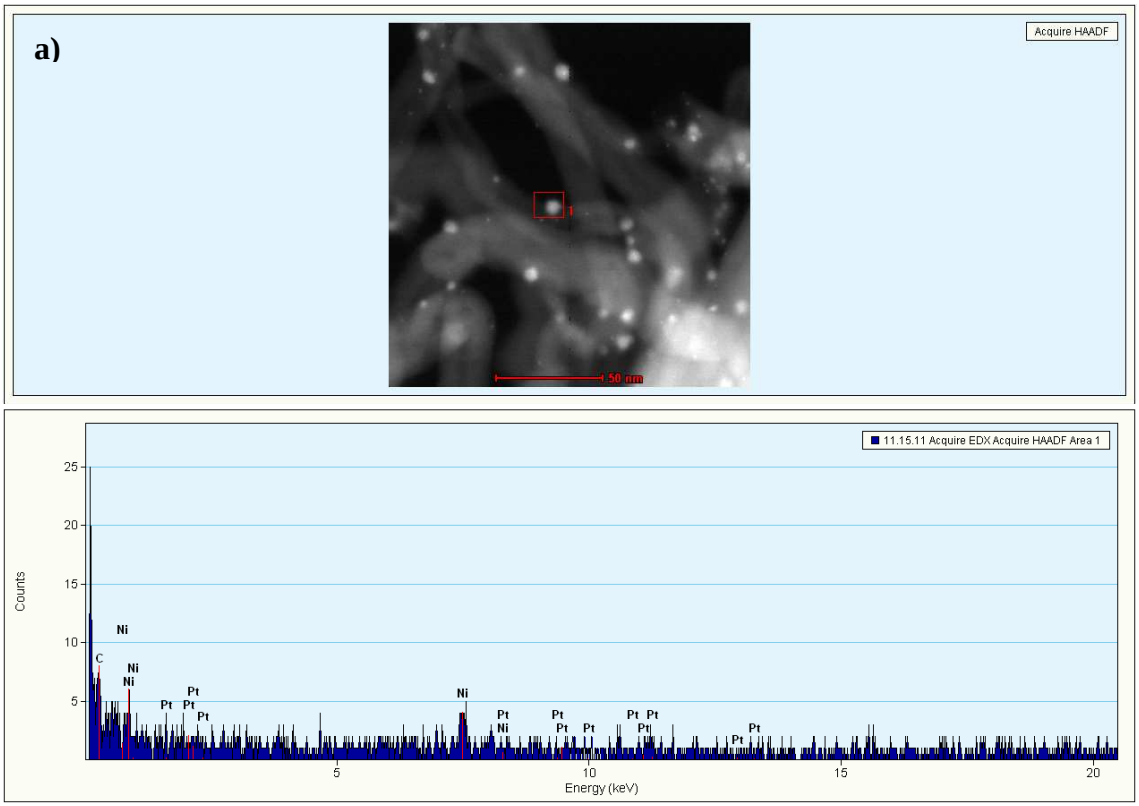


Fig. S1 TPR-H_2 signal correspondent to the CNF gasification.


a)
Acquire HAADF
50 nm
11.15.11 Acquire EDX Acquire HAADF Area 1
Counts
Energy (keV)
C
Ni
Pt
b)
Acquire HAADF
20 nm
12.13.54 Acquire EDX Acquire HAADF Area 1
Counts
Energy (keV)
C
Ni
Pd

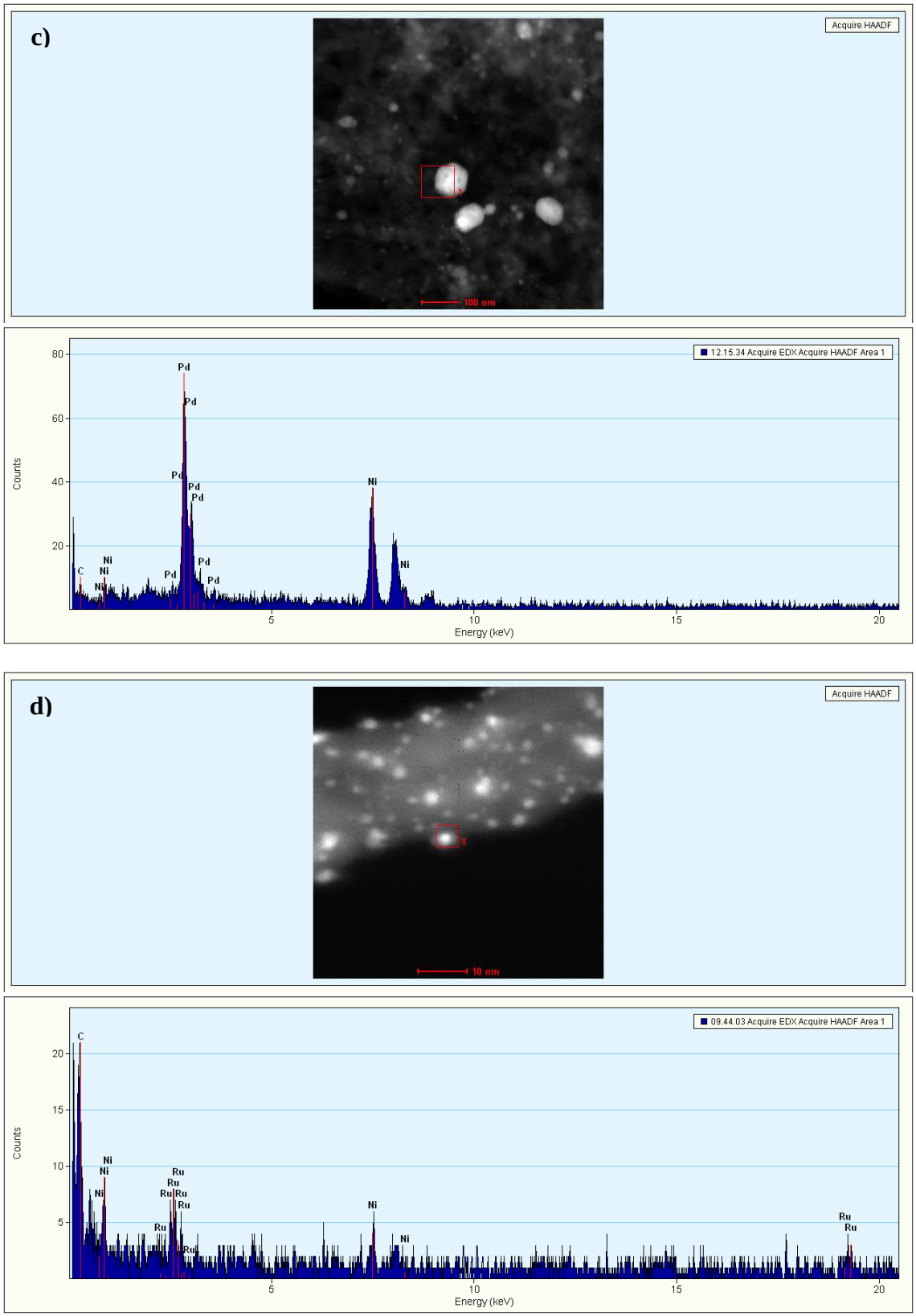
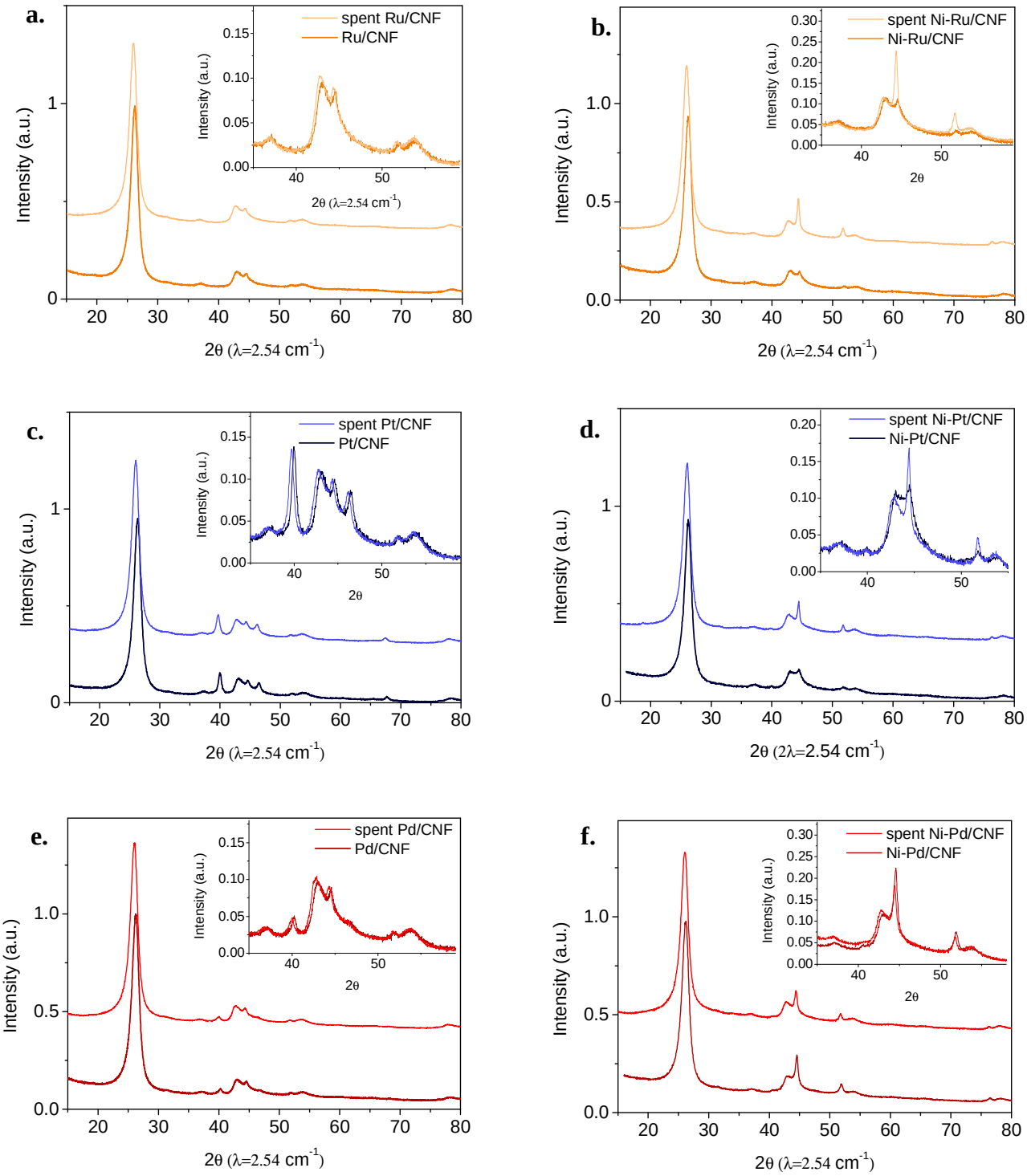


Figure S2 Chemical composition of individual bimetallic nanoparticles determined by EDX analysis: a) Ni-Pt/CNF, b) y c) Ni-Pd/CNF, d) Ni-Ru/CNF.

Catalysts durability

XRD diffractograms of the post-mortem catalysts did not show important morphological changes after reaction tests.



g.

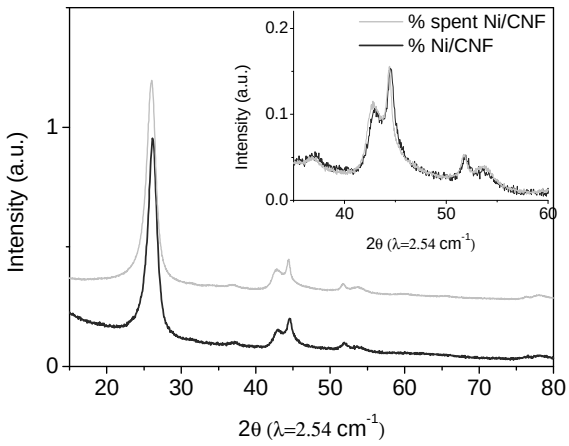


Figure S3. Comparison between XRD signal of fresh and spent catalysts before and after the reaction: a) Ru/CNF, b) Ni-Ru/CNF, c) Pt/CNF, d) Ni-Pt/CNF, e) Pd/CNF, f) Ni-Pd/CNF and g) Ni/CNF.