# Catalytic transfer hydrogenolysis of lignin derived aromatic ethers promoted by bimetallic Pd/Ni systems

*Francesco Mauriello [1,*], Emilia Paone [1], Rosario Pietropaolo [1] Alina M. Balu[2], and Rafael Luque[2,3,*]*

[1] Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy

[2] Departamento de Quımica Organica, Universidad de Cordoba, Edificio Marie-Curie (C-3), Ctra Nnal IV, Km 396, Cordoba, Spain

[3]Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya str., 117198, Moscow, Russia

# SUPPLEMENTARY INFORMATION

Supporting information contains 10 pages including 3 Figures and 6 Table.

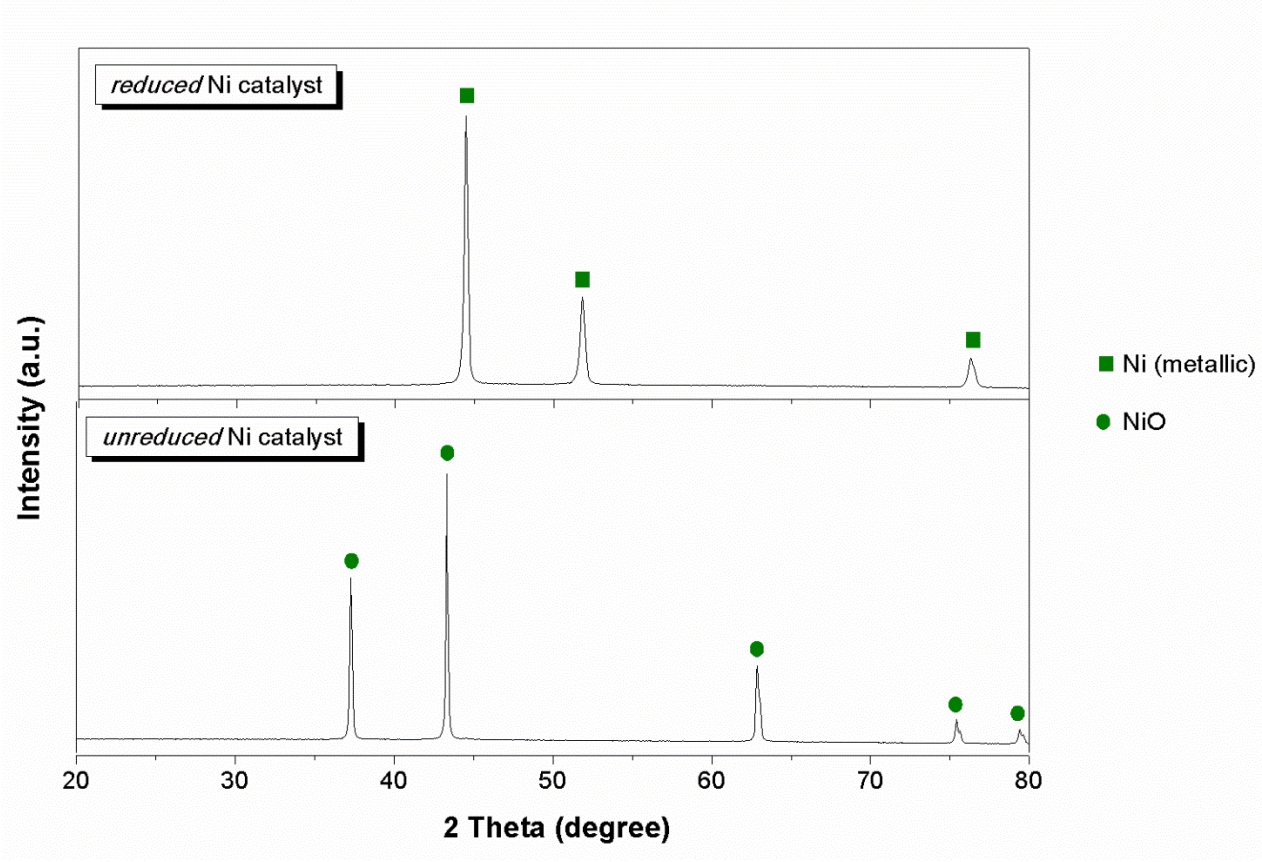


**Figure S1.** XRD of reduced (up) and unreduced (b) Ni catalyst

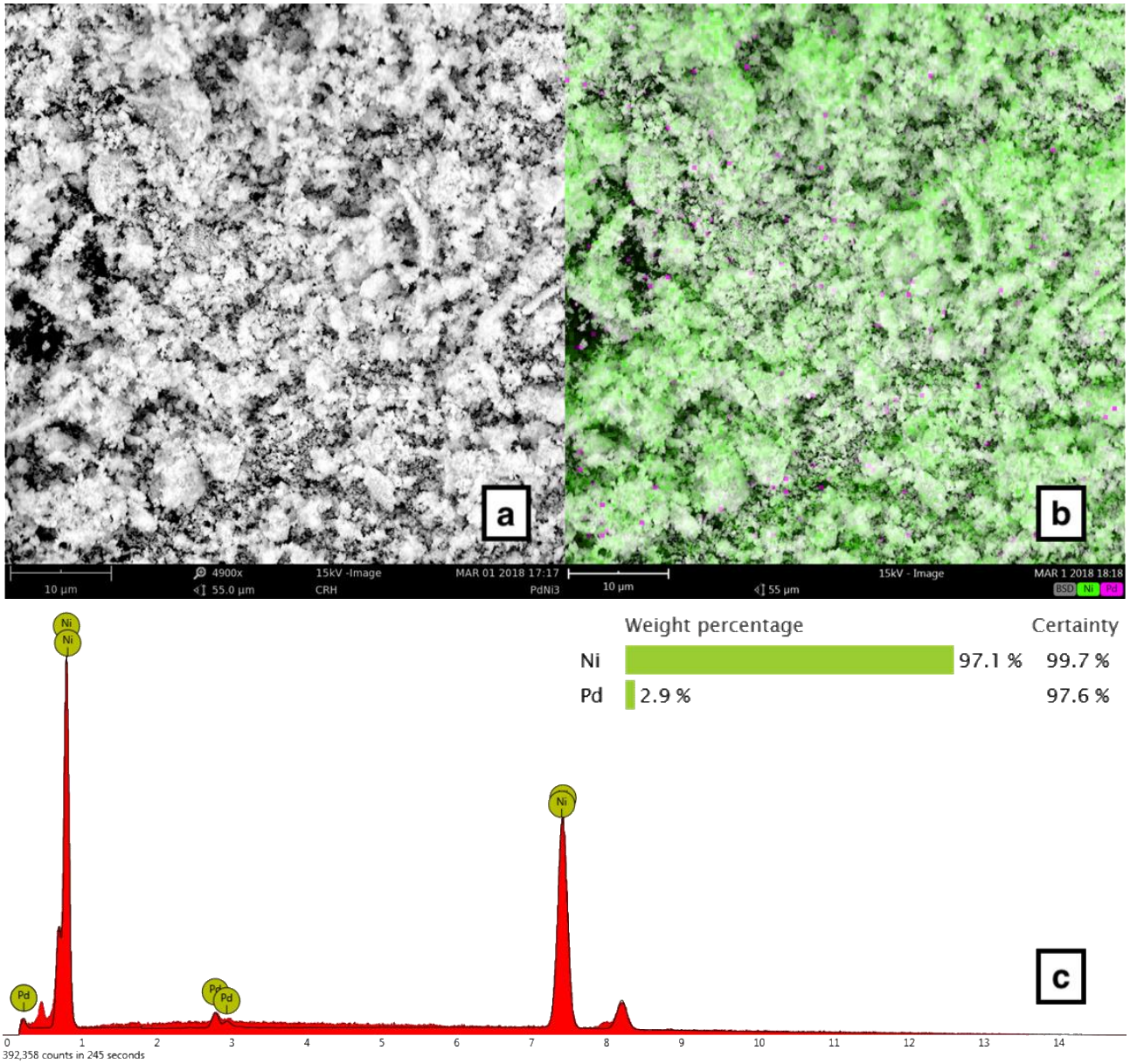


**Figure S2**. SEM-EDX characterization of Pd/Ni catalyst: SEM image (a); EDX maps (b) where green dots refer to nickel atoms and magenta dots refer to palladium atoms; (c) EDX spectra.

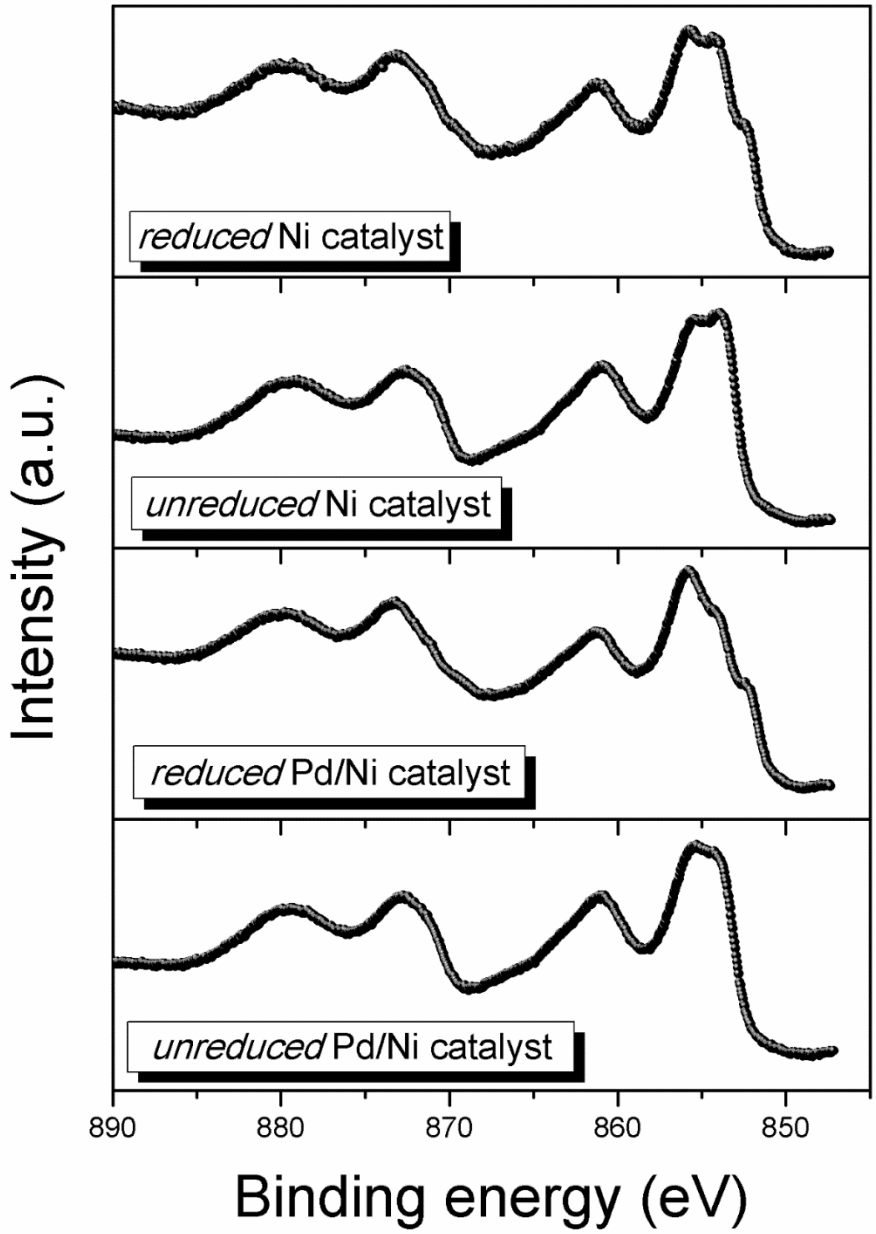


**Figure S3.** XPS Ni $2p_{3/2}$ plots in unreduced and reduced Ni and Pd/Ni catalysts

**Table S1.** Transfer hydrogenolysis of diphenyl ether promoted by Pd-based catalysts

| Catalyst | Temperature [°C] | Time [min] | Conversion [%] | Chemoselectivity [%] | | | | Aromatic Yield [%] |
|---|---|---|---|---|---|---|---|---|
| | | | | BEN | CHX | PHE | CXO | |
| Pd/C | 240 | 90 | <10 | 50 | - | 50 | - | <10 |
| PdO | 240 | 90 | <5 | 50 | - | 50 | - | <5 |
| Pd/C | 210 | 90 | <5 | 50 | - | 50 | - | <5 |
| PdO | 210 | 90 | <2 | 50 | - | 50 | - | <2 |
| Pd/C | 180 | 90 | <1 | - | - | - | - | - |
| PdO | 180 | 90 | - | - | - | - | - | - |

(conditions: catalyst: 0.12 g of Pd/C (5% w.w.), 0.07 g di PdO reduced "in situ"; 60 ml solution of diphenyl ether (4% wt), solvent: 2-propanol; $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CHX: cyclohexane; PHE: phenol; CXO: cyclohexanol.

**Table S2.** Reaction time effect on the transfer hydrogenolysis of diphenyl ether at 180°C promoted by Ni-based catalysts

| Catalyst | Temperature [°C] | Time [min] | Conversion [%] | Chemoselectivity [%] | | | | Aromatic Yield [%] |
|---|---|---|---|---|---|---|---|---|
| | | | | BEN | CHX | PHE | CXO | |
| Pd/Ni | 180 | 30 | 24 | 50 | - | 39 | 11 | 22 |
| Pd/Ni | 180 | 60 | 30 | 50 | - | 38 | 12 | 26 |
| Pd/Ni | 180 | 90 | 39 | 50 | - | 36 | 14 | 34 |
| Pd/Ni | 180 | 180 | 53 | 50 | - | 32 | 18 | 43 |
| Pd/Ni | 180 | 360 | 69 | 49 | <2 | 25 | 25 | 51 |

(Conditions: 0.2 g of catalyst, 60 ml solution of diphenyl ether (4% wt), solvent: 2-propanol; $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CHX: cyclohexane; PHE: phenol; CXO: cyclohexanol)

**Table S3.** Reaction time effect on the transfer hydrogenolysis of diphenyl ether at 240°C promoted by Ni-based catalysts

| Catalyst | Temperature [°C] | Time [min] | Conversion [%] | Chemoselectivity [%] | | | | Aromatic Yield [%] |
|---|---|---|---|---|---|---|---|---|
| | | | | BEN | CHX | PHE | CXO | |
| Pd/Ni | 240 | 30 | 77,9 | 47,4 | 2,6 | 19,1 | 30,9 | 51,8 |
| Pd/Ni | 240 | 60 | 85,3 | 46,4 | 3,6 | 14,2 | 35,8 | 51,7 |
| Pd/Ni | 240 | 90 | 97,3 | 43,9 | 6,1 | 3,8 | 46,2 | 46,4 |
| Pd/Ni | 240 | 180 | 100 | 38,6 | 11,4 | 0,0 | 50,0 | 38,6 |
| Pd/Ni | 240 | 360 | 100 | 18,2 | 31,8 | 0,0 | 50,0 | 18,2 |

(Conditions: 0.2 g of catalyst, 60 ml solution of diphenyl ether (4% wt), solvent: 2-propanol; $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CHX: cyclohexane; PHE: phenol; CXO: cyclohexanol).

**Table S4**. Hydrogenolysis and Transfer hydrogenolysis of DPE promoted by Ni-based catalysts by using water and in water/2-propanol mixture (50% wt) as solvent.

| **Solvent** | **Conversion [%]** | **Chemoselectivity [%]** | | | | **Aromatic Yield [%]** |
|---|---|---|---|---|---|---|
| | | **BEN** | **CHX** | **PHE** | **CXO** | |
| $H_20$ | 0 | - | - | - | - | - |
| $H_20$ | 0 | - | - | - | - | - |
| $H_20$/i-PrOH | 63 | 49 | <2 | 28 | 22 | 45 |
| $H_20$/i-PrOH | 57 | 50 | - | 31 | 20 | 46 |

(Condition: 0.2 g of catalyst, 60 ml solution of diphenyl ether (4% wt), $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CHX: cyclohexane; PHE: phenol; CXO: cyclohexanol).

**Table S5.** Transfer hydrogenation of phenol promoted by Pd/Ni catalyst at 210°C at different reaction times.

| Catalyst | Temperature [°C] | Time [min] | Conversion [%] | Chemoselectivity [%] | | |
|---|---|---|---|---|---|---|
| | | | | BEN | CXL | CXO |
| Pd/Ni | 210 | 30 | 62 | <3 | <3 | 94 |
| Pd/Ni | 210 | 60 | 86 | <3 | <2 | 95 |
| Pd/Ni | 210 | 90 | 98 | <3 | - | 97 |
| Pd/Ni | 210 | 180 | 100 | <3 | - | 97 |
| Pd/Ni | 210 | 360 | 100 | <3 | - | 97 |

(Conditions: 0.2 g of catalyst, 60 ml solution of phenol (4% wt), solvent: 2-propanol; $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CXL: cyclohexanone; CXO: cyclohexanol).

**Table S6.** Hydrogenation of phenol promoted by Pd/Ni catalyst at 210°C at different reaction times

| Catalyst | Temperature [°C] | Time [min] | Conversion [%] | Chemoselectivity [%] | | |
|---|---|---|---|---|---|---|
| | | | | BEN | CXL | CXO |
| Pd/Ni | 210 | 30 | 75,6 | - | <2 | 99 |
| Pd/Ni | 210 | 60 | 100 | - | - | 100 |
| Pd/Ni | 210 | 90 | 100 | - | - | 100 |
| Pd/Ni | 210 | 180 | 100 | - | - | 100 |
| Pd/Ni | 210 | 360 | 100 | - | - | 100 |

(Conditions: 0.2 g of catalyst, 60 ml solution of phenol (4% wt), solvent: 2-propanol; $N_2$ pressure: 10 bar; stirring: 500 rpm; BEN: benzene; CXL: cyclohexanone; CXO: cyclohexanol).