From Spent Lithium-Ion Batteries to an Heterogeneous Co-Ni Catalyst for the Reductive Upgrading of Biomass-derived furanics

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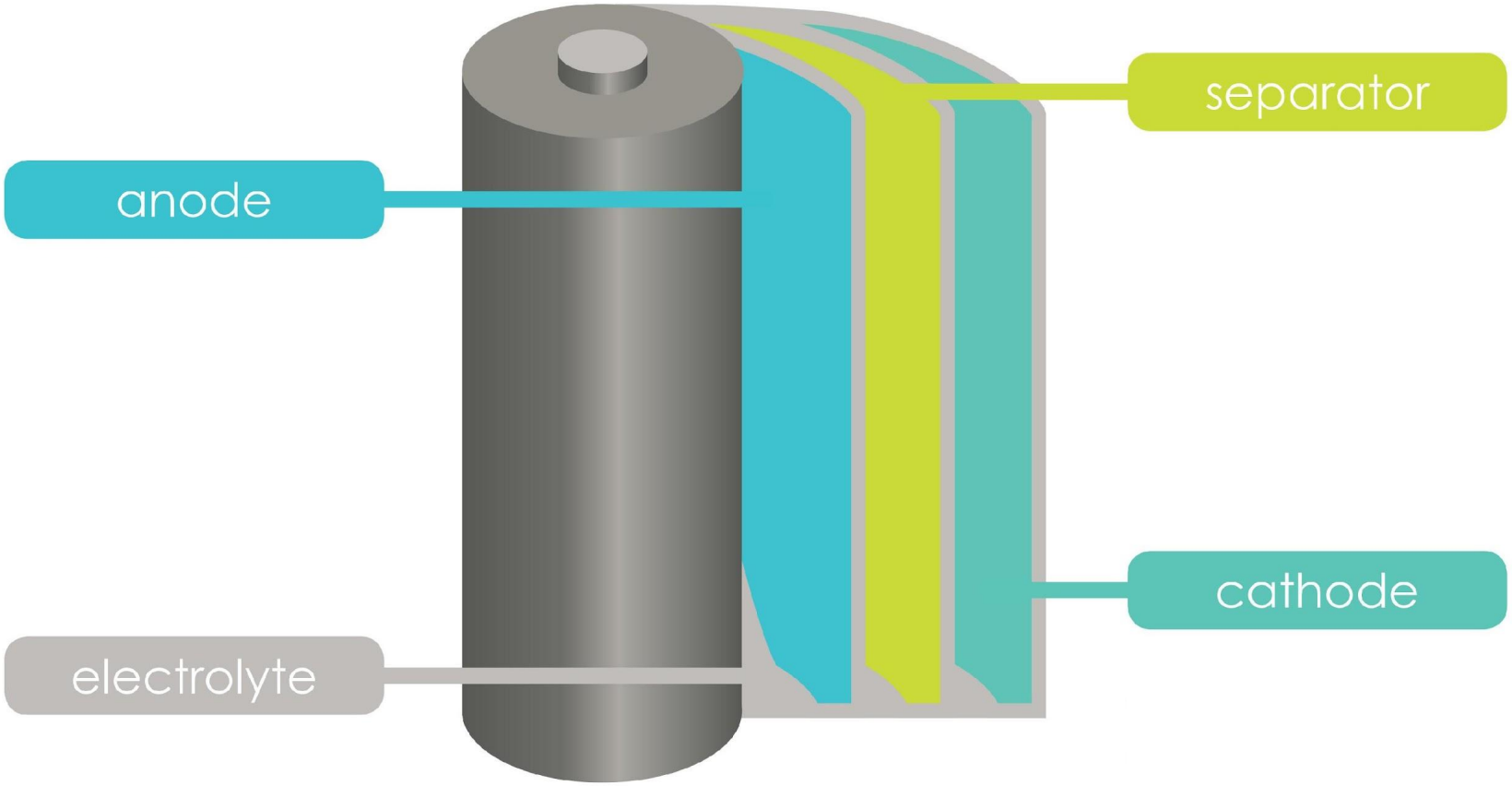
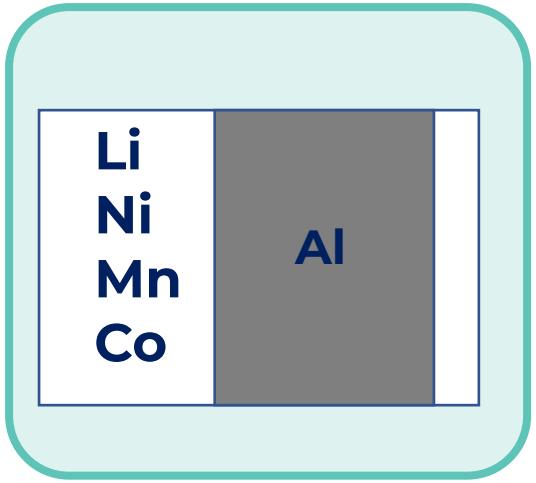
in 2019

53.6 Mt

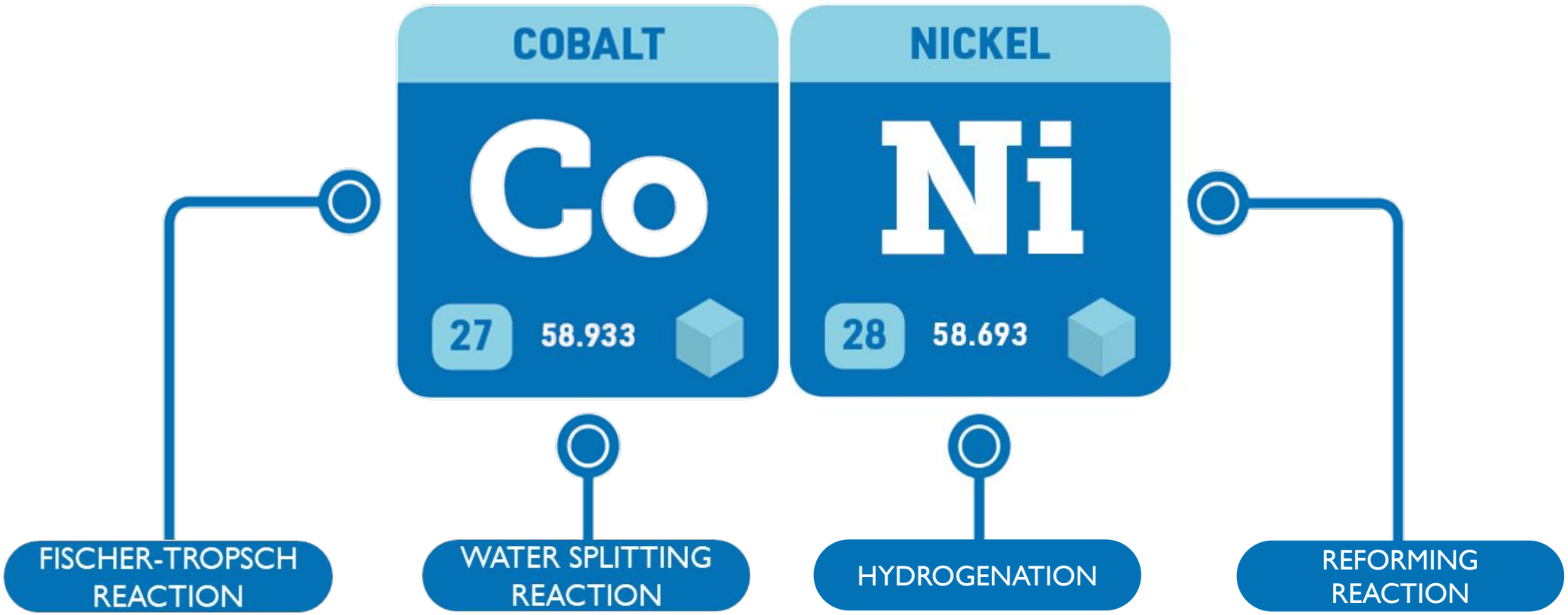
e-waste arising from the disposal of electrical and electronic equipments with an average of 7.3 kg per capita

Li-ion Battery (LIB)





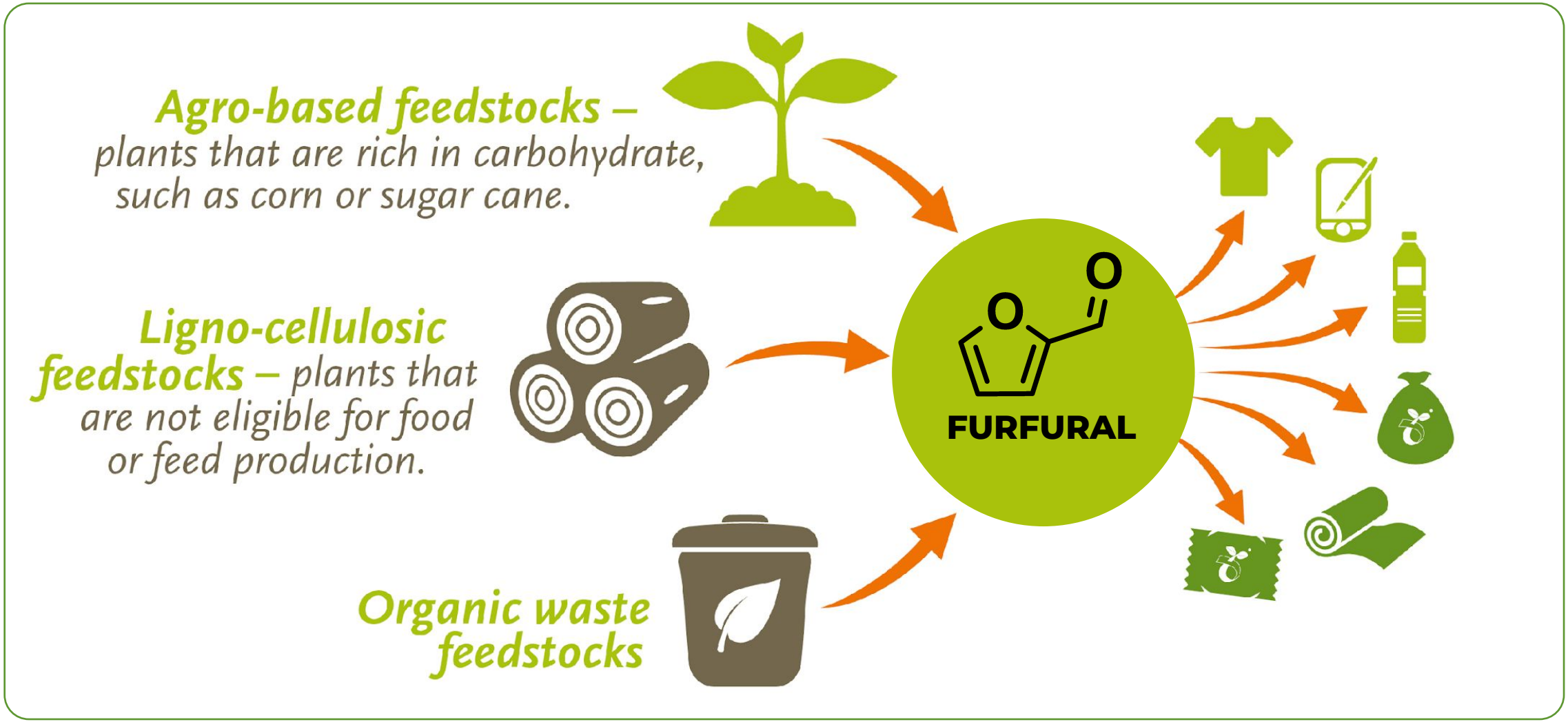
Co- and Ni-based catalysts



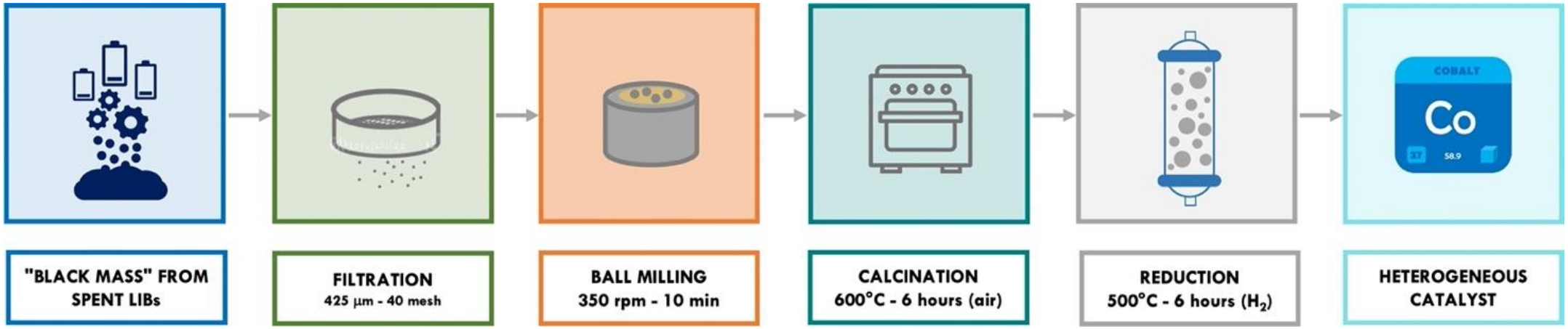
F. Mauriello, E. Paone, R. Pietropaolo, A.M. Balu, R. Luque. ACS Sustain. Chem. Eng., 2018, 6(7), 9269-9276.
F. Mauriello, H. Ariga-Miwa, E. Paone, R. Pietropaolo, S.Takakusagi, K. Asakura. Catal. Today. 2020, 357, 511-517.

...and many others!

FURFURAL: a platform molecule for biobased industry



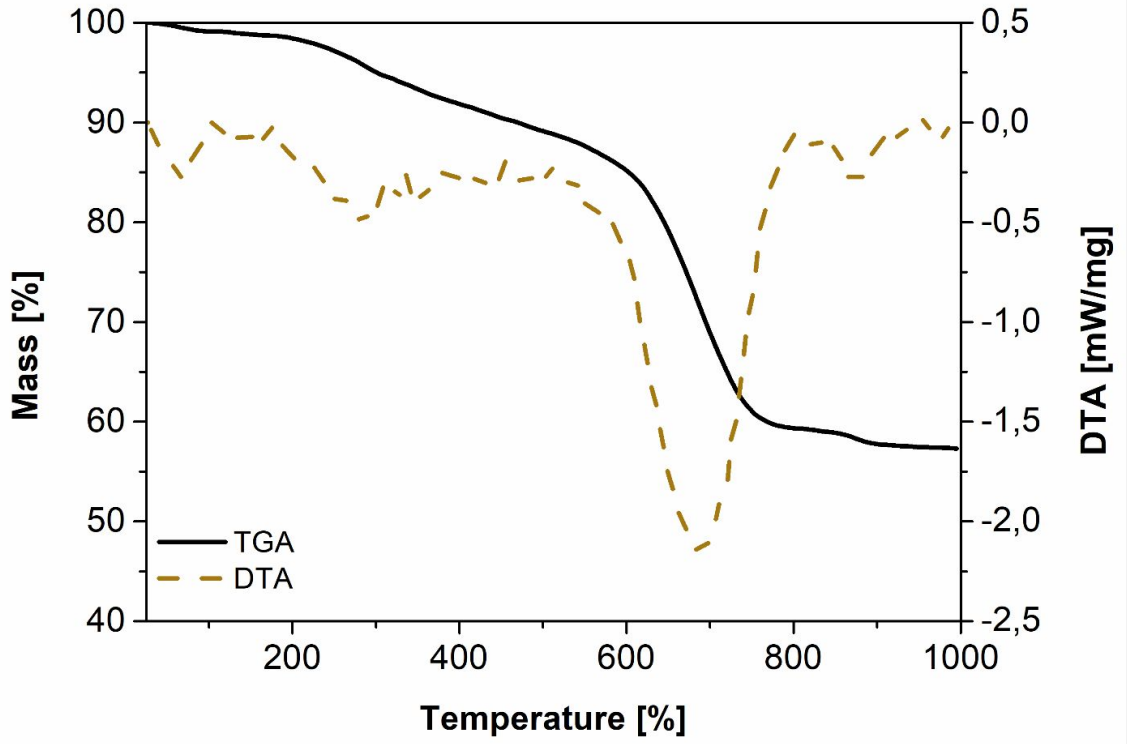
FROM LIBs to HETEROGENEOUS Co-based CATALYST



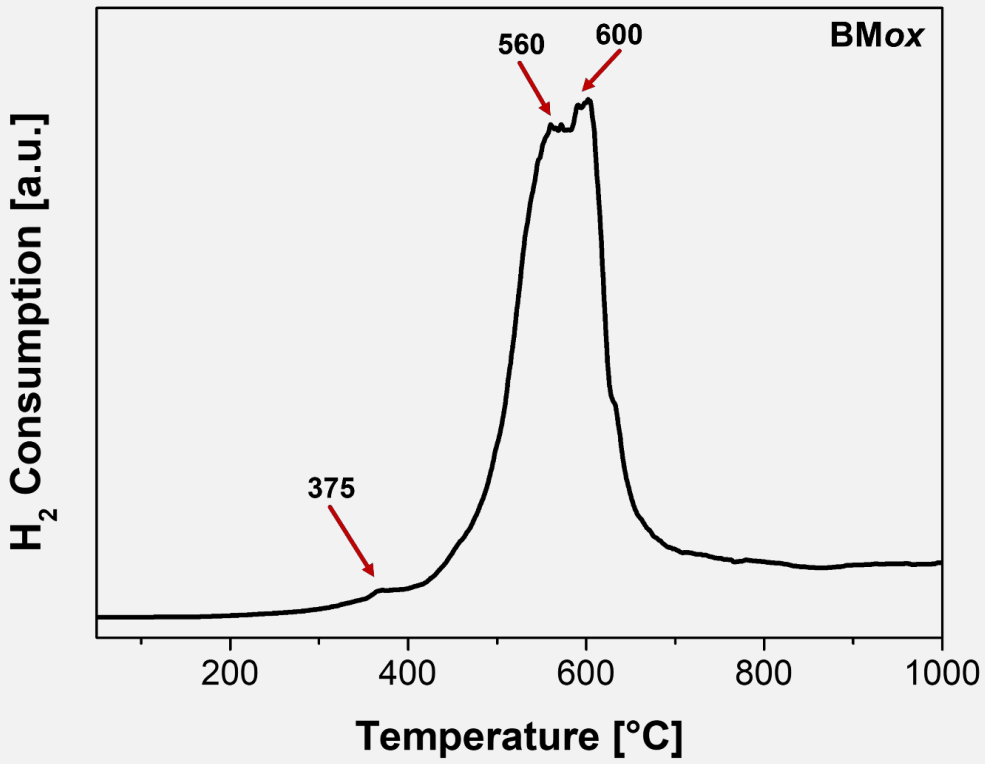
After a first **ball milling process (350 rpm for 10 min)**, the milled sample was filterd by using a sieve screen mesh (425 µm - 40 mesh) and **calcined under atmosphere conditions at 550°C for 6 hours**. Before catalytic tests, BM was finally **reduced at 500 °C for 6 hours under H_2 flow (1 mL/min)**

PHISICO-CHEMICAL CHARACTERIZATION (i)

TGA

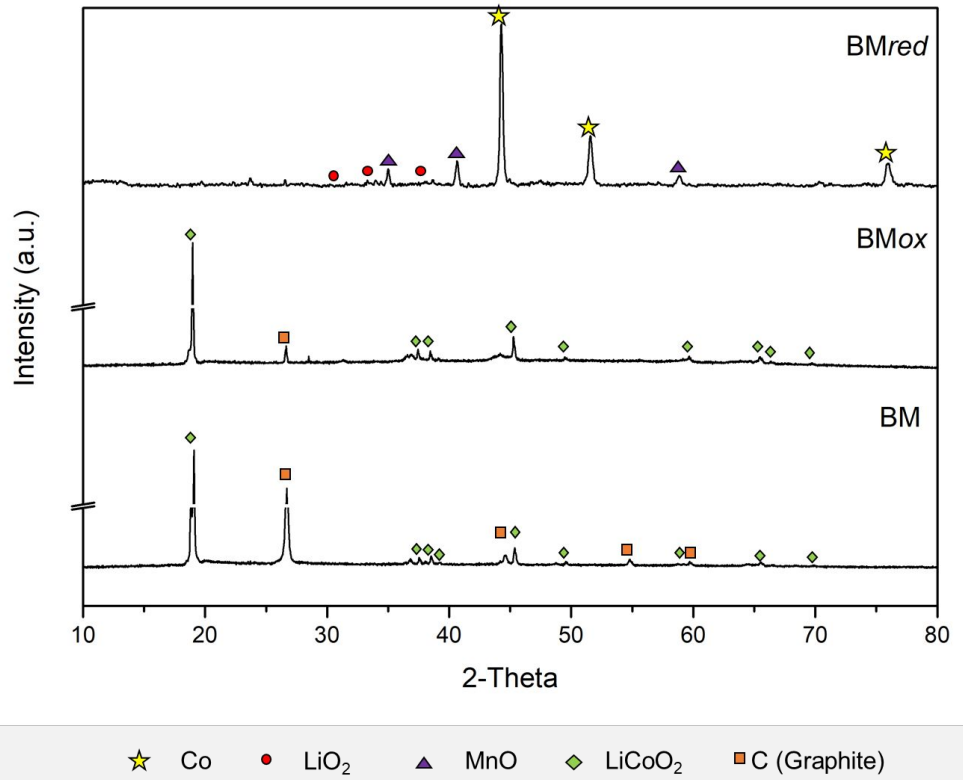


H_2-TPR



PHISICO-CHEMICAL CHARACTERIZATION (ii)

XRD



$$2LiMeO_2 + 2C + 2O_2 \rightarrow 2LiMeO_2 + 2CO_2$$

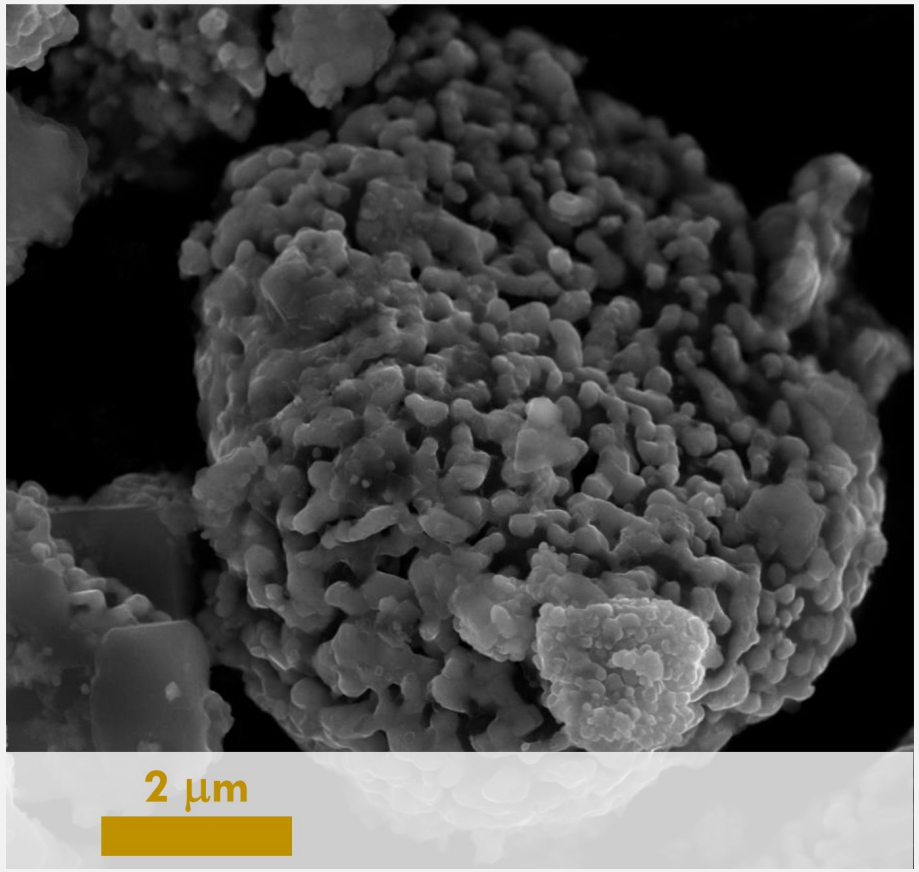
[Me: Co, Ni, Mn] (BM oxidation)

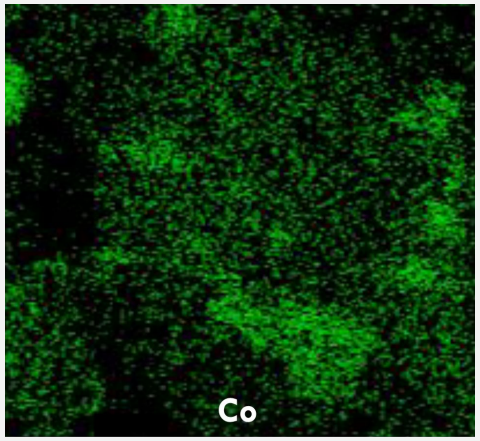
$$2LiMeO_2 + 3H_2 \rightarrow Li_2O + 2Me + 3H_2O$$

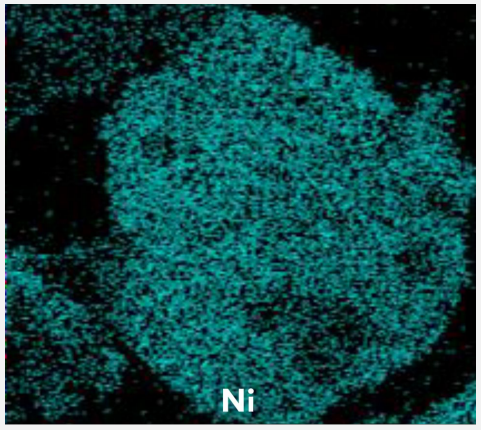
[Me: Co, Ni] (BM reduction)

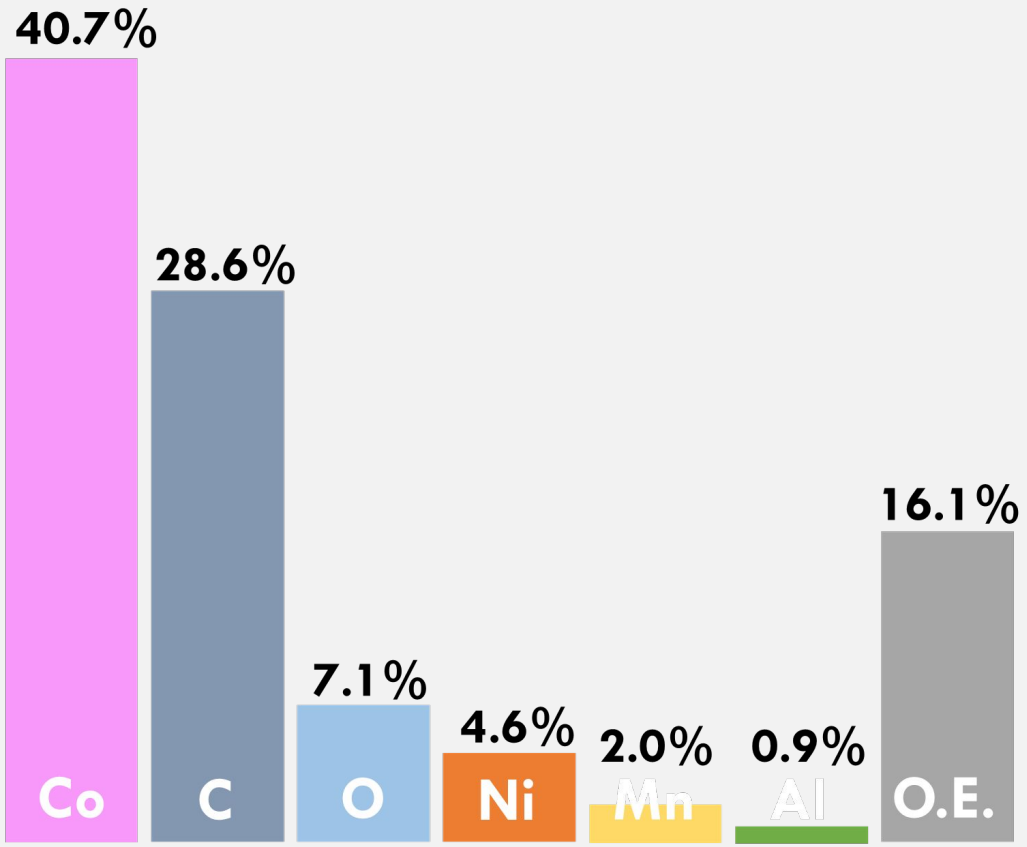
PHISICO-CHEMICAL CHARACTERIZATION (iii)

SEM-EDX

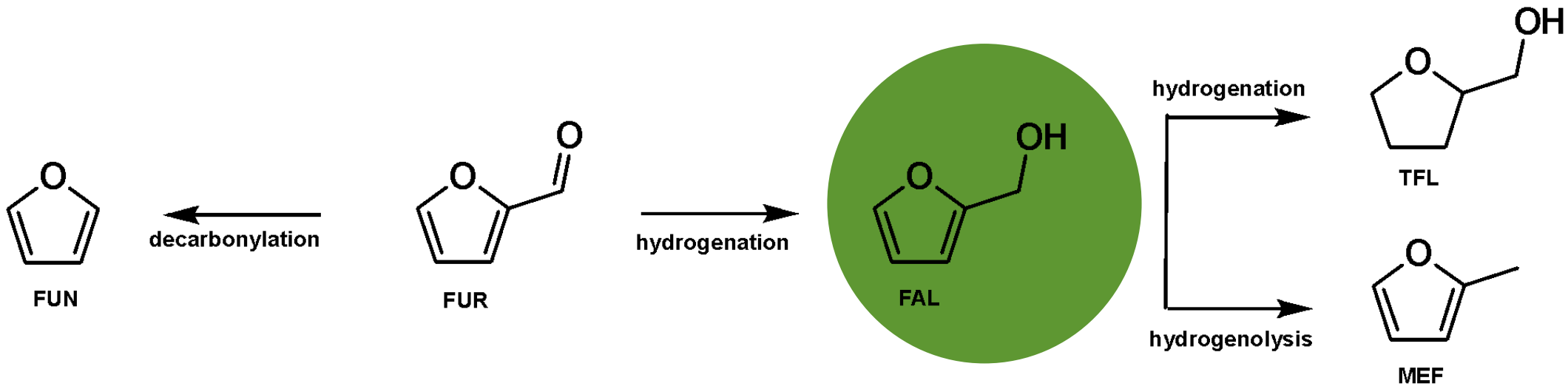








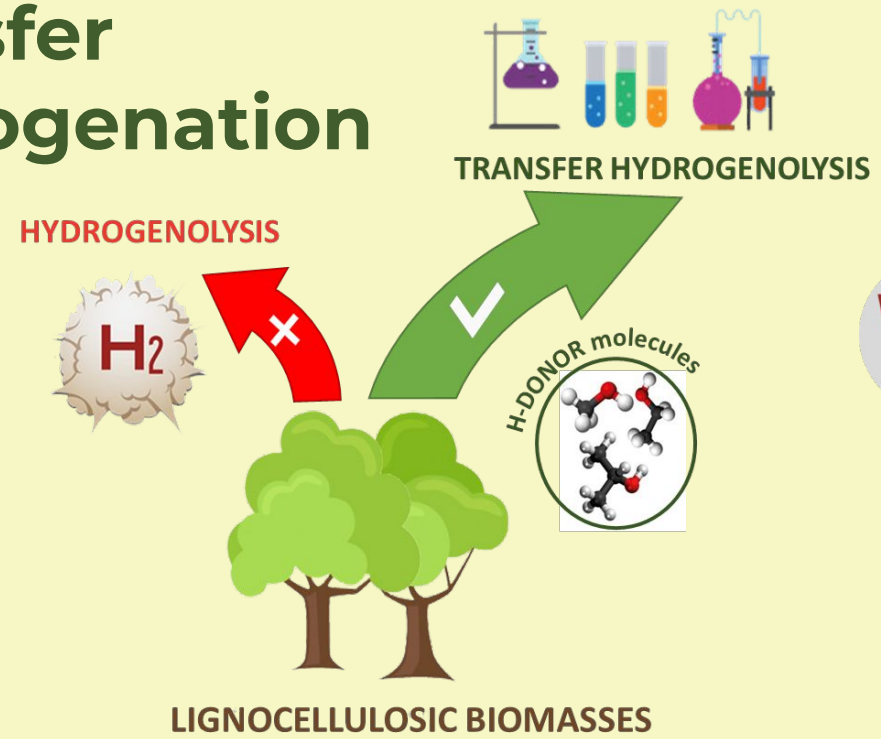
From Furfural to Furfuryl Alcohol



Furfuryl alcohol *is also the chemical substrate in the production of tetrahydrofurfuryl alcohol, levulinic acid, pentane diols and precursor molecules for many materials and pharmaceutical intermediates*

From Furfural to Furfuryl Alcohol

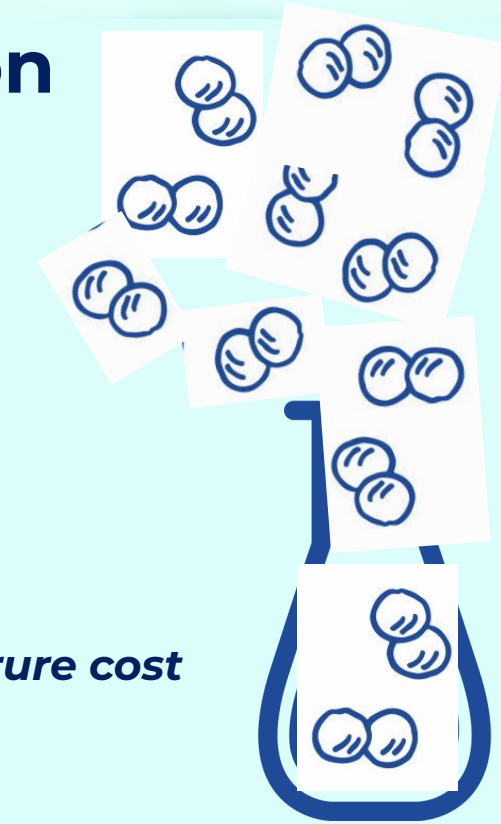
Transfer hydrogenation



C. Espro, B. Gumina, T. Szumelda, E. Paone, F. Mauriello. Catalysts, 2018, 8(8), 313.

VS

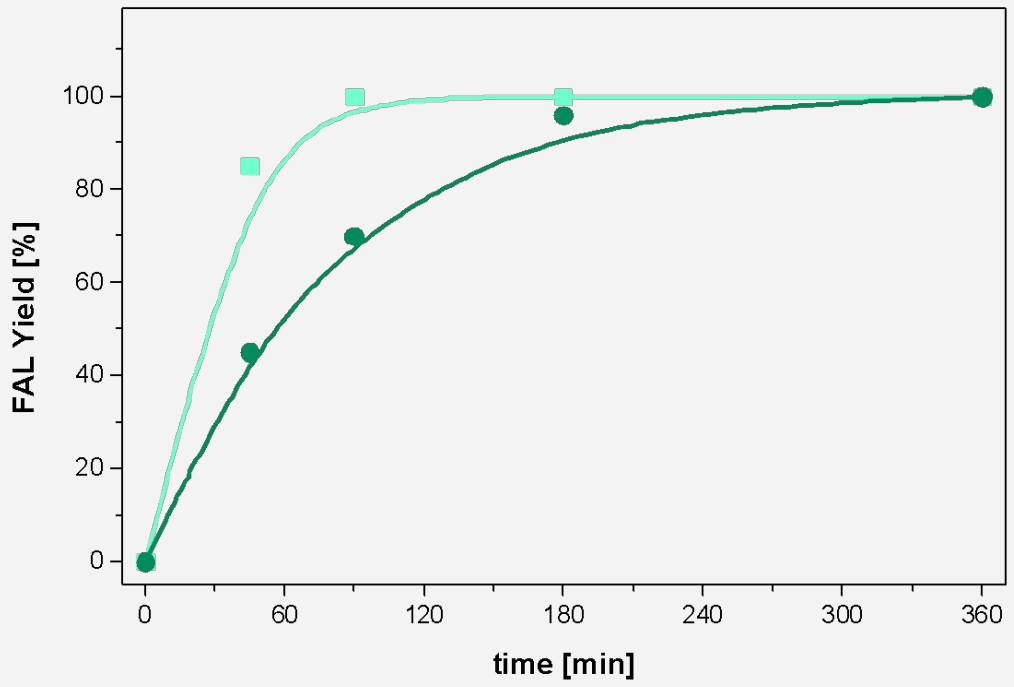
Hydrogenation reactions



- *pure selective*
- *explosive*
- *high safety and infrastrure cost*

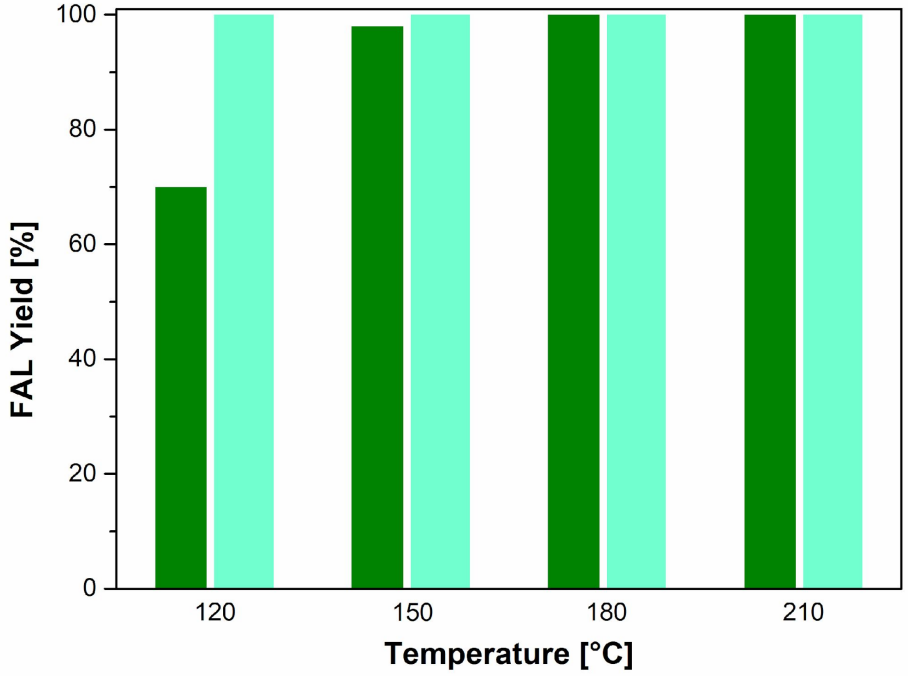
CATALYTIC TESTS: hydrogenation of furfural

A TIME EFFECT



Reaction conditions: *120 °C, 0.25 g catalyst; 40 mL solution of furfural (0.1 M); solvent, 2-propanol; H_2 or N_2 pressure, 10 bar; stirring, 500 rpm; FAL, furfuryl alcohol.*

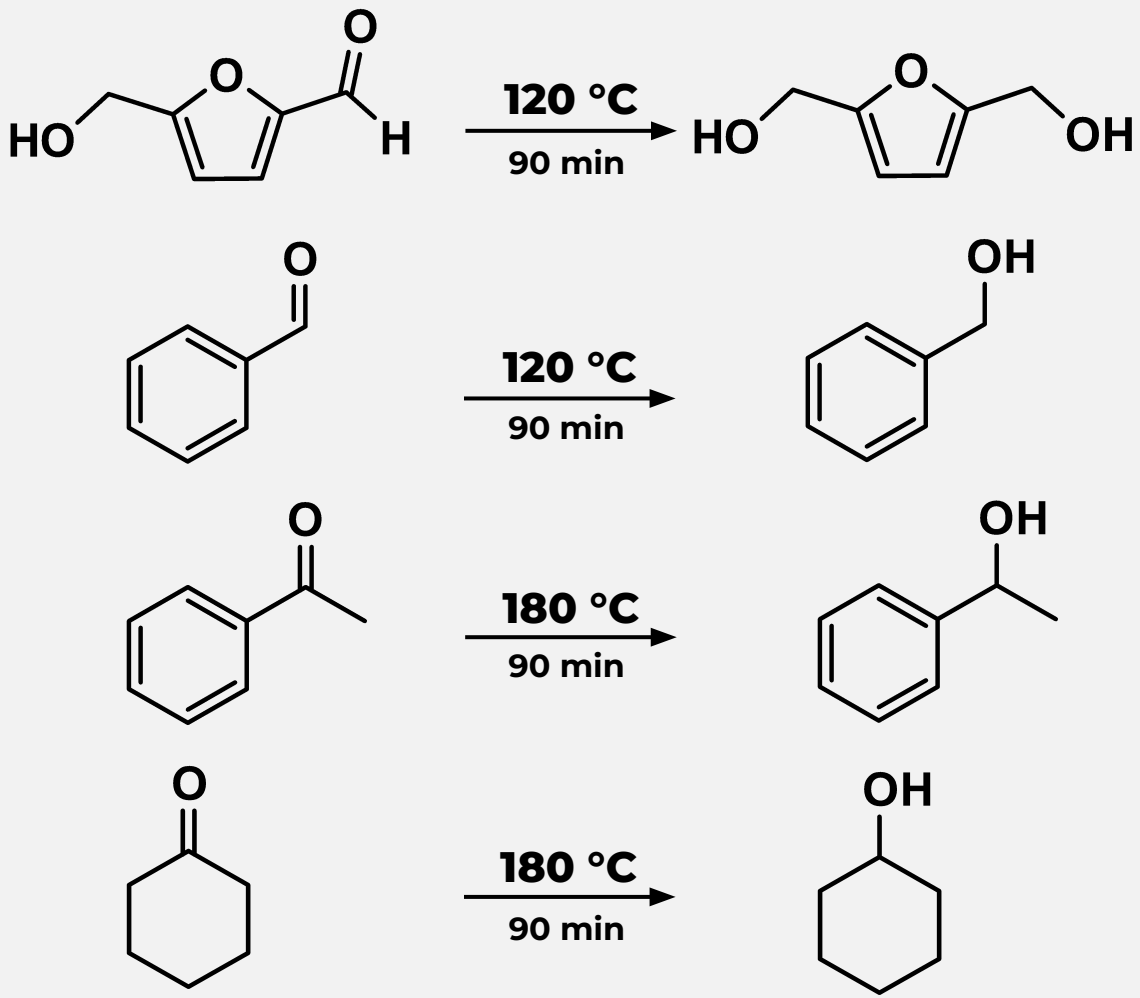
B TEMPERATURE EFFECT

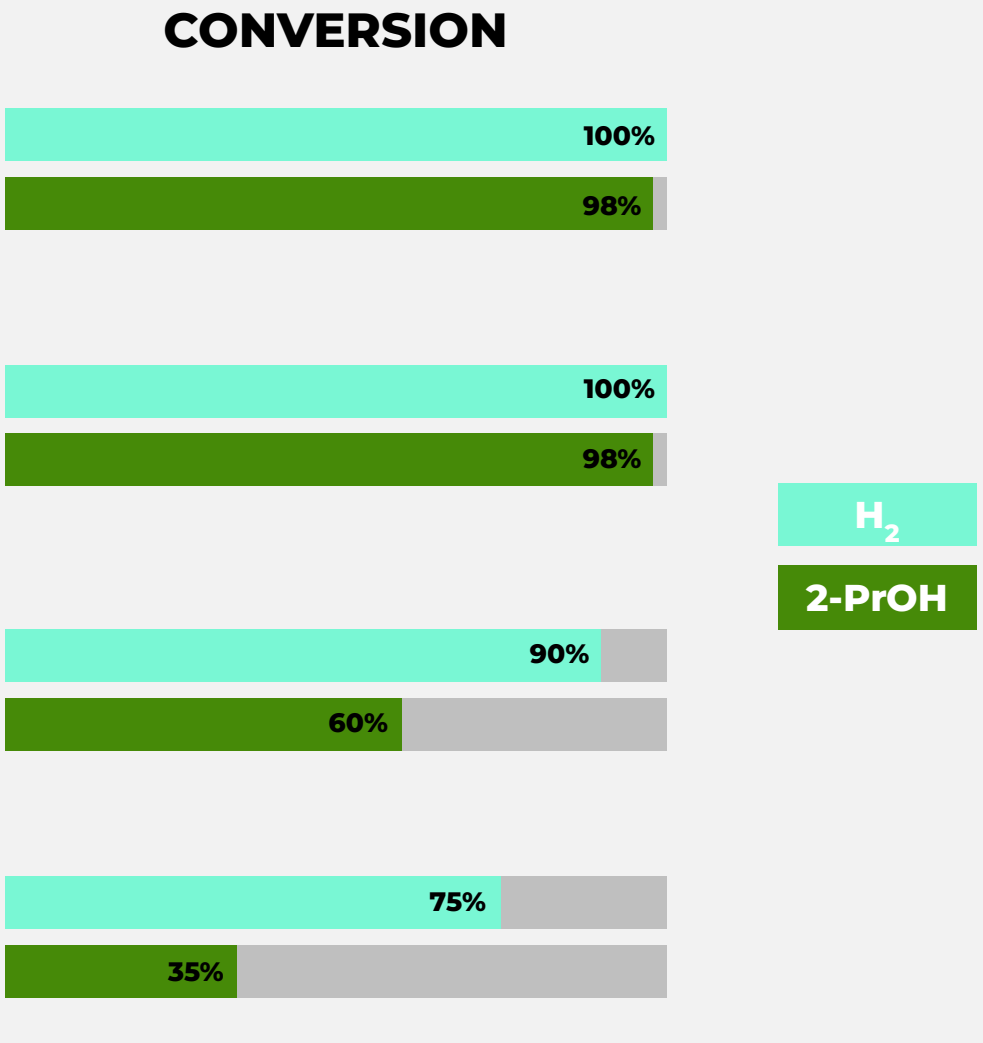


Reaction conditions: *90 min, 0.25 g catalyst; 40 mL solution of furfural (0.1 M); solvent, 2-propanol; H_2 or N_2 pressure, 10 bar; stirring, 500 rpm; FAL, furfuryl alcohol.*

H-source: **H_2** ***Hydrogenation conditions*** **2-PrOH** ***Transfer Hydrogenation conditions (CTH)***

CATALYTIC TESTS: extending the substrate scope





CONCLUSIONS

1. SPENT LITHIUM-COBALT BATTERIES WERE EFFICIENTLY USED AS **HETEROGENEOUS Co-Ni CATALYST** FOR THE REDUCTIVE UPGRADING OF LIGNOCELLULOSIC DERIVED MOLECULES

2. PHYCO-CHEMICAL CHARACTERIZATION CLEARLY INDICATE THAT, AFTER A THERMAL PRETREATMENT, **METALLIC Co AND Ni SPECIES** ARE PRESENT

3. BM CATALYST IS ABLE TO PROMOTE THE **SELECTIVE HYDROGENATION OF FURFURAL IN FURFURYL ALCOHOL** UNDER BOTH HYDROGENATION AND CTH CONDITIONS

4. BM CAN BE SUCCESSFULLY ADOPTED AS HETEROGENEOUS Co-Ni BASED SYSTEM FOR THE **HYDROGENATION OF OTHERS CARBONYL COMPOUNDS**

ACKNOWLEDGMENT

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