

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

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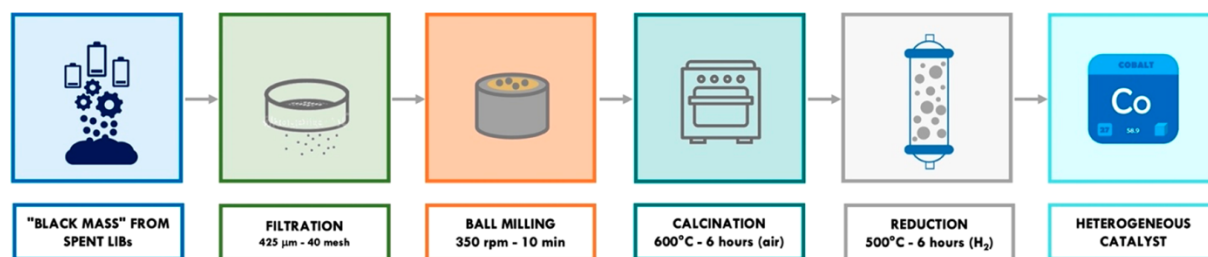
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In 2019, about 2.01 billion metric tons of waste were produced worldwide with 53.6 Mt arising from the disposal of electrical and electronic equipment (e-waste) with an average of 7.3 kg per capita [1]. Lithium-ion batteries (LIBs) are widely used in mobile phones, personal computers, electric vehicles, and solar/wind energy storage devices and already represent an important secondary resource for the recovery of valuable metals such as cobalt, nickel, copper, and lithium.

In this context, a new process for the conversion of the mixture of anodic and cathodic materials arising from mechanical shredding of spent Li-ion batteries (also known as “Black Mass” - BM) into an efficient heterogeneous catalyst for selective reductions has been recently proposed [2]. The method employs a simple calcination of the e-waste material followed by reduction with H<sub>2</sub> at 500 °C (Scheme 1).



Scheme 1. Schematic Representation of Mechano-Thermal Treatment of Spent LIBs “Black mass” for Preparation of Co-Ni Based Heterogeneous catalysts.

The XRD analysis clearly shows that, together with carbon, other chemical elements of BM are arranged in the form of well-defined crystalline states with LiMeO<sub>2</sub> oxides (Me= Co, Li and Mn) being the main phases present. The oxidation process leads to a high decrease in the intensity of peaks at 26.5°, 43.3°, and 54.9° because of the graphitic carbon oxidation to CO<sub>2</sub> while, upon H<sub>2</sub> treatment at 500°C, the formation of metallic Co and Ni as well as Li<sub>2</sub>O is observed.

In the reduced state (BM<sub>red</sub>) the most abundant elements in are Co (39.5%), O (15.1%), Ni (9.7%), and Mn (7.8%) that are uniformly distributed on the surface together with some traces of Al (present in the form of Al<sub>2</sub>O<sub>3</sub>) (Figure 1). At the same time, SEM-EDX images, obtained at higher resolution reveal both the presence of metallic cobalt characterized by rounded shapes as well as the persistence of MnO<sub>2</sub> species in line with XRD and H<sub>2</sub>-TPR analyses.

The so-obtained BM<sub>red</sub> catalyst was then tested in the conversion of furfural both in the presence as well as in the absence of added hydrogen. By using 2-propanol as the H-donor, a significant conversion of furfural into furfuryl alcohol was achieved after 90 min also at temperatures as low as 120 °C with an overall FAL yield of 70%. Within 3 h, FUR was fully converted to FAL without formation of any other products related to undesired side reactions that may arise in CTH processes (e.g., etherification, acetalization, and aldol condensation). The hydrogenation of FUR proceeds faster with a complete conversion into FAL in the presence of H<sub>2</sub> (10 bar) as a reducing agent after 90 min at 120 °C. As expected, the conversion of FUR increases by increasing the reaction temperature in the range from 120 to 210 °C maintaining constant the reaction time of 90 min

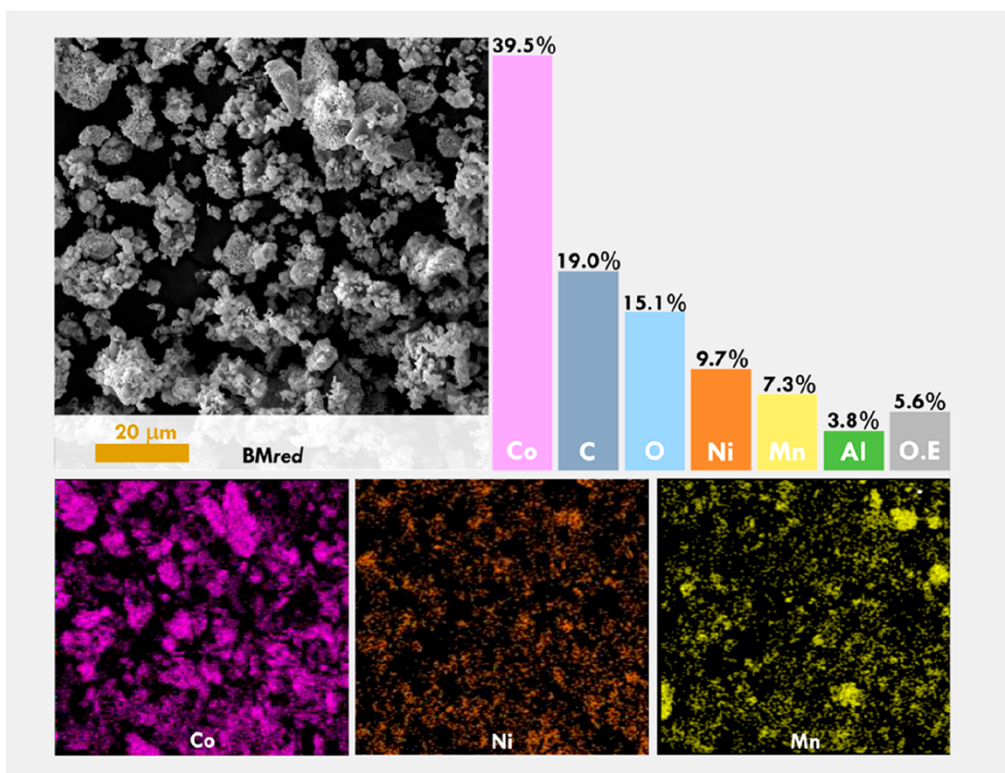


Figure 1. Tropea's red onion plant grown in soil fertilized with AnchoisFert (left), NPK (center) and horse manure (right).

In order to extend the substrate scope, hydrogenations of other aldehydes and ketones were also tested. 5-Hydroxymethylfurfural, benzaldehyde, acetophenone, and cyclohexanone can be converted into the corresponding alcohols by using the BMred catalyst under both hydrogenation and CTH processes. 5-Hydroxymethyl-furfural and acetophenone were converted after 90 min at 120 °C (100% in the presence of H<sub>2</sub>, 98% under CTH conditions), with a selectivity of 100% to 2,5-bis(hydroxymethyl)furan and benzyl alcohol. The use of ketonic derivatives (acetophenone and cyclohexanone) as starting substrates led to lower conversions at similar high selectivities to the corresponding alcohols (>99%). In any case, the results clearly show that BMred can be efficiently used as a heterogeneous catalyst for the reductive upgrading of biomass-derived aldehydes and ketones.

In the present contribution, we demonstrate that black mass derived from spent LIBs, after an opportune oxidative–reductive thermal process, can be directly used as a readily available efficient heterogeneous catalyst thus providing a 2-fold answer to both environmental issues caused by the disposal of end-of-life lithium-based batteries as well as the continuing rise in cobalt (and other noble and non-noble metals) price.

#### References

- [1] Forti *et al* (2020).
- [2] Paone *et al* (2022)

The abstract should be submitted in **word or pdf format** via the website: <https://corfu2022.uest.gr/index.php/en/conference/abstract-submission>. The deadline for abstract submission is **31<sup>st</sup> December 2021**.