Combining ultrasound and microwaves in chemical processes

María Jesús Morán Plata
Department of Drug Science and Technology, University of Turin
mariajesus.moranplata@unito.it
Tutor: Katia Martina (UniTO)

The actual environmental concern and the desire of facing the current planetary emergency has opened a door for an extensive number of green research procedures. Conventional protocols are replaced with new efficient processes where safer chemicals, solvent free conditions, natural abundant solvents and alternative energy sources are used to achieve sustainability and scalability. In particular, the fine chemicals and pharmaceuticals industries are in search of simple, environmentally friendly and inexpensive synthetic routes as alternative of using risky conditions and hazardous compounds in which also high E factor are pursued. One of the most direct way to pursue Green Chemistry principles is the use of truly efficient catalytic reactions. The efforts focused on the development of selective catalysts that are able to suppress the undesired noble metals such as Pd and Pt, has awakened an enormous interest in the topic of 3d metals (Fe, Co, Ni and Cu) as "perfect" candidates. In particular, during the last years, copper (Cu) heterogeneous catalysis has gained more and more attention due to important advantages: compared to other transition-metal, copper catalysts are inexpensive, readily available and can be easily handled.

Being part of important building blocks in organic synthesis, the selective reduction of aromatic nitrocompounds represents a fundamental procedure in organic synthesis and many synthetic routes have been described *via* the catalytic hydrogenation. Herein, we report a mechanochemical reduction of aromatic nitro compounds in a stainless steel jar with formate salts without catalyst addition.[1] In addiction, a new efficient and hydride free Cu-catalysed procedure for the selective reduction of nitroarenes[2] to anilines and azocompounds has also been developed, using glycerol as an excellent "sacrificial" hydrogen source. US has been shown to play an important role in the process *via* its ability to enhance copper nanoparticles (CuNPs) dispersion, favour mechanical depassivation and increase catalytic active surface area, while MW irradiation shortened the reaction time from some hours to a few minutes. Moreover, since recovery and reuse of catalysts is an important factor for sustainable process management, heterogeneous copper supported catalysts has been studied. Copper nanoparticles supported over celite proved to be an ideal material for the transfer hydrogenation reaction of nitrobenzene in continuous flow, as well as a new solid supported copper catalyst based on an efficient grafting of β-CD onto the inorganic silica surface in Cu(II)-catalysed alkyne azide reactions in the absence of a reducing agent.[3]

Figure 1: a) Selective copper-catalyzed reduction of aromatic nitro compounds and alkynes under microwave and ultrasound irradiation; b) Highly efficient nitrobenzene and alkyl/aryl azide reduction in stainless steel jars without catalyst addition; c) Sonochemically promoted preparation of silica-anchored cyclodextrin derivatives for efficient copper catalysis.

(1) Martina, K.; Baricco, F.; Tagliapietra, S.; Moran, M. J.; Cravotto, G.; Cintas, P. Highly efficient nitrobenzene and alkyl/aryl azide reduction in stainless steel jars without catalyst addition. *New J. Chem.* **2018**, *42* (23), 18881–18888.

(2) Submitted: Moran, M.J.; Martina, K.; Stefanidis, G. D.; Jordens, J.; Van Gerven, T.; Goovaerts, V.; Manzoli, M.; Groffils, C.; Cravotto, G. Glycerol: an optimal hydrogen source for microwave-promoted Cu-catalysed transfer hydrogenation of nitrobenzene to aniline. *Front. Chem.* **2019**.

(3) Martina, K.; Calsolaro, F.; Zuliani, A.; Berlier, G.; Chávez-Rivas, F.; Moran, M. J.; Luque, R.; Cravotto, G. Sonochemically-promoted preparation of silica-anchored cyclodextrin derivatives for efficient copper catalysis. *Molecules* **2019**, *24* (13), 2490.