Mechanochemical Catalysis

Products of chemistry are all around us, from drugs to plastics, and organic synthesis is central to improve our daily lives. As these syntheses improved with time, becoming more efficient and more profitable, notably through petrochemistry, the amount of waste has been heightened. A large part of that waste is due to the intensive use of solvents in the current chemistry.[1]

For years solution-based chemistry using solvent has dominated the field for many reasons. Solvents are a good reaction media, allowing reactions between liquids and/or solids dissolving the latter. It is easy to bring energy to a solvent-based system by heating and stirring it. The huge arsenal of solvents known allows to adapt the physical conditions of a reaction, or to purify, extract, clean products. That is why solvents are sometimes thought to be essential for conducting a chemical synthesis. However, even if they are very effective a lot of these solvents are hazardous for the environment and human health. Moreover they usually come from oil which will not be available for long. Some solvents can be replaced by cleaner ones but when it is not possible sustainable alternatives must be found.

According to the principles of green chemistry[2], it is better: to prevent waste than to treat it, to use less hazardous chemicals and processes, to use auxiliary as solvent only when there is no other ways and to use renewable feedstocks among other things. Solvent-based chemistry does obviously not fit with these criteria at all, and in a changing world where the environment needs to be taken care of, a new way of doing chemistry is not only recommended but it is necessary.

Mechanochemistry is based on the use of mechanical energy enabling a reaction to occur.[3] Ball milling, for instance, shakes vials containing solid reagents and balls. (Figure 1) The reason why ball milling can be a sustainable alternative to solution-based chemistry is that the energy provided by grinding and milling process is sufficient to make solids react with each others without the use of solvent. The

absence of solvent induces much more simple of a methodology. What is more, for purification green solvents as acetone or water can be used because the use is limited for extraction and not as a reaction medium. Thus, ball mill reactions are respectful of the principles of green chemistry by reducing the waste and the hazards, being a cleaner, easier and cheaper process.

Metal vials and balls

High speed ball mill

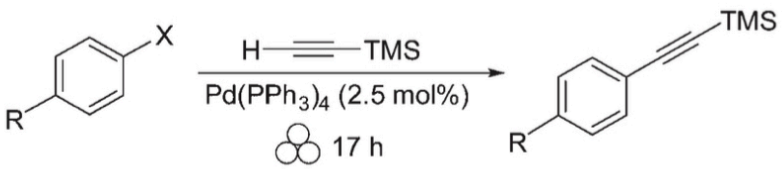
Compartment where the vial is inserted

Figure 1

The interest of ball milling is that the reaction media can also catalyse the reaction[4], that can then happen with a source of proton as simple as water. Indeed, when milling, the balls and the vial are first reducing the particles into small sizes. Getting shaken there are not only providing the energy for the reaction to occur but also create small nanoparticules of metal that work as catalysts.

The Mack group in the University of Cincinnati ran a Sonogashira reaction in solvent-less method using a ball mill. They have found that adding copper balls to the reaction increases the yield and running the synthesis in a copper vial makes it even

more efficient (Figure 2), thus proving that the reaction media is also the catalyst of the reaction.



X	R	% yield without Cu	% yield with Cu balls	% yield with Cu balls and vial
I	H	39	87	88
I	Me	17	46	83
I	Br	43	31	89
I	Cl	37	52	86
I	OMe	58	40	42
Br	CHO	44	85	84
Br	CHO *	46	88	90

* 1,2- disubstituted

Figure 2

In the light of this result, other reactions could be catalyzed by metal nanoparticules. That is why reduction reactions in the ball mill are thought to be able to provide a « greener » process. These really common organic reactions are usually conducted using hard reducing agents like lithium aluminium hydride or sodium borohydride, or rare metal catalyst as palladium, during complex and rigorous processes. Furthermore, these reducing agents leave a stoichiometric amount of waste that could be avoided. A ball milling method consists in introducing solid reagents in a earth abundant metal vial with metal balls, adding water and closing with a cap and an o-ring to prevent any sorts of leakage. This vial is then put into a ball mill and agitated at pre-defined frequency.

According to Y. Shawama's work[5], the use of stainless steel balls and water under ball milling conditions generates dihydrogen gas by splitting the components of water using the metals that comprise stainless steel to transfer an electron. Compared to the traditional electrolysis of water requiring rare metals as catalysts, this is a very sustainable way to obtain H_2 which is a clean source of energy for the future. Furthermore, the creation of dihydrogen could also be a way to make catalyzed hydrogenation on chemical compounds and thus enable reduction of alkynes or carbonyl based compounds.

The reduction reactions could be made possible by the catalysis of nanoparticles of metal created during the milling, and/or by the creation of dihydrogen. Further research has to be made to determine the mechanisms that occurred when doing these reactions inside a ball mill, we already know that it could be a very sustainable way to reduce organic compounds, and therefore a gain of time, money and energy.

References:

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