MECHANOCHEMISTRY: A GREEN SOLUTION IN CHEMICAL SYNTHESIS

[1]Adeoye I.O.*, [1]Onawumi O.O.E. and [2]Onawumi A.S.

[1]Department of Pure and Applied Chemistry,
[2]Department of Mechanical Engineering,
Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria

*Author for correspondence: adeoyeid@gmail.com,
(+234) 803 7008 413; 805 1008 368

ABSTRACT
Efforts to encourage economic, environmentally and user friendly synthetic method has continued to gain general support of researchers and general society in recent time. Mechanochemistry is a key way that has proved to be safety conscious and hazard minimizing and control production/reaction methods. Mechanochemical synthesis can be described as an application of green chemistry which has as its aim the usage of chemical products and processes in such a way that it eliminates the use or generation of hazardous substances from its design, manufacture and use. This paper attempts to review the emerging principles and potentials of mechanochemistry as a green way to synthesis and cleaner production of chemical products without the use of which are toxic and are potentially harmful to human health and environment. Based on this work, researchers are encouraged to intensify efforts on improving mechanochemical based manufacturing technique.

Key words: mechanochemistry, manufacturing process, chemical reactions, solvents.

Introduction

The need for the use of solvent as a media in synthesis and for chemical reactions to take place is well known. Mechanochemistry was first proposed by Ostward in 1919 as an energy source for chemical reaction (Oswald 1919). Generally done in the absence of reagents, it involve the activation of local reaction sites by the mechanical energy caused by the stress, shear deformation, friction and other mechanical agitation as well as the high concentration and closest contact among reacting species resulting from lack of salvation. The applications of mechnochemistry phenomena have come a long way in the areas of material science and metallurgy (Baláž, 2000). It is primarily applied to processes relating to materials such as ferroelectrics, miniral fertilizers, semiconductors and superconductors ceramics cements alloys etc (Fernandez-Bertran 1999). It is generally accepted as the interface between mechanical and chemical engineering disciplines. As a branch of solid state chemistry, mechanochemistry enquire into processes in solids as a result of application of mechanical energy. Majority of solvents in use are volatile organic solvents which have been found to have a deleterious effect on the user and the environment. In recent times, researchers are turning increasing attention to the use of alternative reaction media that circumvent the problems associated with the use of many of the traditional volatile organic solvents. The concept of mechanochemistry has been applied in many fields, such as organic synthesis, catalyst synthesis, coordination chemistry, nanochemistry, drug production (in the improvement in solubility and bioavailability of drugs), waste treatment, materials engineering, extractive metallurgy, coal ashes utilization, crystal engineering, coal industry, building industry, and agriculture in solubility increase of fertilizers.(Baláž 2008; Baláž *et .al* 2009; Zyryanovv 2008; Wieczorek-Ciurowa K 2007; Guo *et. al* 2010; Ivanov et al 2000; Avvakumov 2002; Todres 2006).Environmentally being solvents (i.e. water and supercritical CO_2) or those with negligible vapour pressure like ionic liquids are becoming more popular in the choice of solvents for synthesis.

It has also been suggested that the best solvent in reactions and synthesis is to use no solvent at all. In the light of this what should come to mind in initiating a reaction or synthesis is whether the reaction is possible by mechanochemical means and without the use of a solvent. It has been found long ago that reactions are possible without the use of solvents and in some cases faster and more convenient than solvent based methods.

The idea of mechanochemical phenomena in producing chemical reactions and forming new products is not new, it has been utilized since time immemorial for example, in making fires by rubbing pieces of wood against each other thereby creating friction and hence heat allowing the wood to undergo combustion at high temperature. Another example is the use of flint and steel during which a spark (a small particle of pyrophoric metal) spontaneously combusts in air starting fire instantly.

Mechanochemistry can therefore be defined as the chemical and physicochemical transformation of substances during the aggregation caused by mechanical energy. It is the coupling of mechanical and chemical phenomena on a molecular scale and includes mechanical breakage chemical behaviour of mechanically stressed solids (Drezler,2009). This paper therefore attempts to review aspects of the emerging principles and potentials of mechanochemistry as a green way to synthesis and cleaner production of chemical products without the use of which are toxic and are potentially harmful to human health and environment.

Materials and Methods

Mechanochemical Devices

These are the devices employed to provide mechanical activation energy for reaction to take place and proceed to products. It could be grinding or milling devices.

Grinding

The simplest reaction using mechanochemical method is by the use of a pestle and mortar and is suitable when a prolonged reaction time is required. This promotes grinding to a fine powder (triturating) and mixing. During grinding, there is an increase in the surface area of the molecules of the reactants, dislocation of the crystal lattices, formation of defects and the kinetic energy supplied can easily lead to an increase in the rate and number of collisions of crystalline solid of the reactants leading to products (Baláž 2002). Grinding can be likened to a sort of stirring as it provides mass transfer. Toda and coworkers have employed this method to investigate some solvent free organic reactions (Toda 1993, 1995).The use of mortar and pestle for grinding reactants together for reaction to take place is one way forward in mechanochemistry but has its obvious limitations. A new version of pestle and mortar known as Mortar Grinder 100 equipped with rotary speed of 90rpm is available commercially from Retsch GmbH and Co KG.

Milling

Milling has an advantage over grinding, in that that it supplies greater power and of course it allows systematic study of the reaction phases involved. The two commercially available mills are the shaker (or mixer vibrant or "SPEX") and the planetary mills. Shaker mills are the most commonly used for laboratory investigations. The shaker mills employ the hard balls in a rapid side to side motion impacting the side of the vessel and its reactants. Planetary mills on the other hand involves a circular motion mimicking the back and forth movement of the planet. Planetary mills have larger capacities than shaker mills but they have lower impact energy than the shaker mills. There a lot of parameters associated with ball milling. The grinding speed affects the kinetics i.e. the faster the milling speed the faster the reaction. Kaupp (2009) explained the mechanism of reactions this way: for an intercrystalline reaction between crystal A and B to give product C, the reactants first undergoes phase rebuilding in which there will be long range and directional migrations of molecules of A to cleavages presented in the crystalline structure of B and vice versa. The distortion in structure that results will give rise to a new mixed A-B-C phase which on continued grinding results in the growing of crystals of C which is the product.

Solvent free reactions using Mechanochemistry

Mokhtari (2007) have reported a facile, environmentally friendly and clean synthesis of phenylhydrazones, and 2,4-dinitrophenylhydrazones from carbonyl compounds in a ball-mill with a 100% yield. Carlier *et .al* (2007) used ball milling method in the synthesis of dibenzophenazines (fig 1).

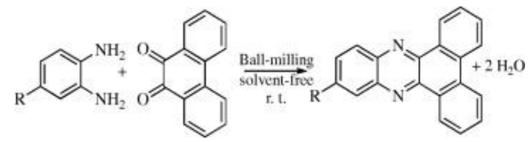

Fig 1: Synthesis of dibenzophenazines (Carlier *et .al* 2007)

The self-aldol reaction of valeraldehyde to 2-propyl-3-hydroxyl-heptanal is catalyzed by fresh aluminum surface created during high-energy ball milling.(Heintz et al 2006)

Mechanochemical processing is a novel and cost effective method of producing a wide range of nanopowders. It involves the use of a high energy ball mill to initiate chemical reactions and structural changes. The book "High energy ball milling: Mechanochemical processing of nanopowders" reviews the latest techniques in mechanochemistry and how they can be applied to the synthesis and processing of various high-tech materials (Klimakow et al 2010; Sopicka-Lizer 2010). PbS nanocrystals using surfactant assisted mechanochemical synthesis have been prepared by co-milling of lead acetate $(CH_3COO)_2Pb3H_2O$ and sodium sulfide $Na_2S_9H_2O$ (Balaz *et. al* 2011). The theoretical background behind the solid drug mechanochemical activation by cogrinding as it has affect drug solubility and drug bioavailability has been reviewed (Garnovskii *et al* 1999).

Mechanochemical methods of synthesis have also been extended to the synthesis of a wide range of metal complexes (Garay *et al*, 2007). For example, the complex $[Ni(phenanthroline)_3]^{2+}$ was reported to form in only two minutes by manually grinding nickel nitrate with phenanthroline, and even relatively inert metal salts such as platinum(II) chloride will react with phosphines in a ball mill.(Wang *et al*, 2009). Solventless grinding of $[Pd(\mu\text{-}LH)Cl_2]_2$ (LH = 3,5-bis(diphenylphosphino) benzoic acid) and ferric nitrate yielded an insoluble networked Pd–phosphine complex $[LPdCl_2Fe_{2/3}]_\infty$ in which Fe atom bonds to the carboxylate group of LH. The networked complex has been characterized by using FT-IR, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), and BET surface area analysis (Kolotilov *et. al* 2004). A mechanochemical synthesis of Mn(II), Co(II) and Ni(II) tris(pyrazolylborates) (Tp^-) has been developed(23), which enabled preparation of metal complexes of the type TpMCl and TpMCl · Hpz type (Hpz is the substituted pyrazole generated by hydrolysis of the corresponding Tp^- ligand). Ternary Potassium metal chlorides have also been synthesized by mechanochemical method (Roland *et. al* 2009). A mechanochemical reaction of BaO and TiO_2 using zirconium oxide vial and zirconium oxide balls as the milling medium leads to the gradual formation of barium titanate $BaTiO_3$ (Mitic *et.al* 2005).

A patented method has been described for building a mechanosynthesis tool intended to be used for the molecularly precise fabrication of physical structures—as for example, diamond structures (US Patent 2010). A mixture of metallic calcium and calcium oxide has been prepared by mechanochemical as a degradation agent for chlorinated contaminants in fly ash(Mitoma *et. al* 2011).Metal organic framework has also been synthesized by mechanosynthesis.

Conclusion

Mechanochemistry as a tool could further be advanced to provide the solution to scientists and researchers continuous exposure to hazard and chemicals which form the bulk of the solvent used in chemical reactions in most laboratories today. Production processes would become safer, non-offensive and economical with the adoption of mechanochemical methods.

The possibility of reactions and synthesis taking place without the use of solvents opens up a new area to explore more in future for a cleaner, more efficient and economical way to practice chemistry.

Acknowledgement

The authors acknowledge Pure and Applied Chemistry and Mechanical Engineering Departments of LAUTECH. Nigeria for support.

References

Avvakumov E, Senna M, and Kosova N, (2002). Soft mechanochemical synthesis: a basis for new chemical technologies Kluwer Academic Publishers.

Balaz P, and Dutkova E. (2009). Fine milling in applied mechanochemistry [J]. Minerals Engineering, 22: 681−694.

Baláž P. (2008). Mechanochemistry in Nanoscience and Minerals Engineering. Springer. p. 167. ISBN 3540748547.

Baláž P. (2002). Extractive Metallurgy of Activated Mineral, Elsevier, Amstadam, 200, 270.

Baláž P., Pourghahramani P., Achimovičová M., Dutková E., Kováč J, Šatka A., and Jiang J. (2011) Mechanochemical synthesis and reactivity of PbS nanocrystals Journal of Crystal Growth, Volume 332, Issue 1, 1 Pages 1-6.

Carlier L., Michel B., Alain C., Guy C. (2007). Use of co-grinding as a solvent free solid state method to synthesize dibenzophenazines Tet Lett 52 4686-468.

Drezler E. (2009). Mechanochemistry mechanosynthesis and Molecular Machinery Metamodern Trajectory of Modern Technology for http://metamodern.com/2009/04/14/mechanochemistry-mechanosynthesis-and-molecular-machinery.

Fernandez-Bertran J. F., (1999). Pure and Applied Chemistry. 71, 581..

Garay A.L., Pichon A. and James S. L, (2007). Solvent-free synthesis of metal complex Chem Soc Rev 36 846-855.

Garnovskii A. D. and Kharisov B. I(1999). Chapter 4 - Mechanosynthesis of Coordination Compounds.Direct Synthesis of Coordination and Organomettallic Compounds Elsevier S.A Pages 199-217

Guo X, Dong X, Duan G,and Peng M. (2010)A review of mechanochemistry applications in waste management [J]. Waste Management, 30: 4−10.

Heintz A. S., Gonzales J. E., Fink M. J., Mitchell B. S. (2009) Catalyzed self-aldol reaction of valeraldehyde via a mechanochemical method Journal of Molecular Catalysis A: Chemical, Volume 304, Issues 1-2, 1 Pages 117-120.

Ivanov E. and Suryanarayana C. (2000). Materials and process design through mechanochemical routes Journal of

Materials Synthesis and Processing, 8: 235−244.

Kaupp G. (2009). Mechanochemistry: the varied applications of mechanical bond-breaking CrystEngComm, 11, 388-403

Klimakow M, Klobes P, Thunemann A. F, Rademann K, and Emmerling F. (2010) Mechanochemical Synthesis of Metal−Organic Frameworks: A Fast and Facile Approach toward Quantitative Yields and High Specific Surface Areas Chemistry of Materials Volume: 22, Issue: 18, 5216-5221

Kolotilov S. V, Addison A. A, Trofimenko S, Dougherty W, and Pavlishchuk V. V. (2004) Efficient mechanochemical synthesis of tris(pyrazolylborate) complexes of manganese(II), cobalt(II) and nickel(II) Inorganic Chemistry Communications, Volume 7, Issue 4, April Pages 485-488.

Mitic V. V. and Varela J. A. (2005). Mechanochemical synthesis of barium titanate. Journal of the European Ceramic Society, 25 1985–1989.

Mitoma, H., M., Naoyoshi E., Alina M. S., Mitsunori K., and Cristian S. (2011). Mechanochemical degradation of chlorinated contaminants in fly ash with a calcium-based degradation reagent Chemosphere, Volume 83, Issue 10, Pages 1326-1330.

Mokhtari J., Naimi-Jamal M. R., Hamzehali H., and Dekamin M. G. (2007). Simple and Efficient Method for Quantitative Solvent-Free Synthesis of Phenylhydrazones and 2,4-Dinitrophenylhydrazones 11th International Conference on Organic Chemstry

Ostwald W. (1919). Handbuch der allgemeine Chemie. B. I,. Academische Verlagsgesellschaft, p. 70.

Roland H. P., Michael F., Claudia W., Borislav B., and Ferdi S. (2009). Mechanochemical Synthesis of Ternary Potassium Transition Metal Chlorides. Journal of Inorganic and General Chemistry Vol 635(2) 265-270.

Sopicka-Lizer M. (2010). High Energy ball milling: Mechanochemical processing of nanopowders Oxford : Woodhead Publishing ; Boca Raton : CRC Press p445.

Todres,Z.,V. (2006) Organic mechanochemistry and its practical applications CRC/Taylor& Francis.

Toda F.(1995) Acc Chem Res 98, 480-486.

Toda F. Synlett(1993) 303-312.

US Patent Publication (2010) *Publication No.* US 7687146 B1 *published on* 30-Mar-*Application No.*US 11/56567*filed* (Source: USPTO).

Wang X, He L, He Y, Zhang J, Su C(2009) Solvent-free synthesis of a Pd(II) coordination networked complex as reusable catalyst based on 3,5-bis(diphenylphosphino)benzoic acid Inorganica Chimica Acta, Volume 362, Issue 10, 1, Pages 3513-3518

Wieczorek-Ciurowa K, Gamrat K. (2007). Some aspects of mechanochemical reactions [J]. Materials Science-Poland, 25(1): 219−232.

Zyryanovv V. (2008). Mechanochemical synthesis of complex oxides [J].Russian Chemical Reviews, 77(2): 105−135.