http://dx.doi.org/10.1595/205651316X691375 *Johnson Matthey Technol. Rev.*, 2016, **60**, (2), 148–150

JOHNSON MATTHEY
TECHNOLOGY REVIEW

www.technology.matthey.com

"Ball Milling Towards Green Synthesis: Applications, Projects, Challenges"

Edited by Brindaban Ranu (University of Jadavpur, India) and Achim Stolle (University of Jena, Germany), RSC Green Chemistry Series, No. 31, Royal Society of Chemistry, Cambridge, UK, 2015, 303 pages, ISBN: 978-1-84973-945-0, £155.00, US$255.00, €193.75

Reviewed by Maria Elena Rivas
Johnson Matthey Technology Centre,
Blounts Court, Sonning Common, Reading RG4 9NH, UK

Email: maria.rivas-velazco@matthey.com

The aim of this book "Ball Milling towards Green Synthesis" is to highlight the importance of ball milling as a potential route to produce organic materials. The book was published by the Royal Society of Chemistry and edited by Brindaban Ranu and Achim Stolle. In this book, applications, projects, advantages and challenges related to ball milling for specific organic syntheses are reviewed. In principle the book should interest researchers working in general mechanochemistry: however in this reviewer's opinion most of the chapters are aimed more at the organic chemist. The book is very well structured for researchers focused on organic synthesis, allowing them to go directly to a specific subject. Also, the book has a very formulaic structure; every chapter systematically describes specific organic syntheses, with experimental procedures, yields and advantages of using ball milling over other techniques. Each chapter describes the ball milling conditions in detail, including specifications of different milling equipment (**Figure 1**), which may be of interest for general research on the technique.

The main reactions described in this book are related to the following processes: carbon–carbon and carbon–heteroatom bond formation, oxidation-reduction, organocatalytic reactions, dehydrogenative coupling, synthesis of peptides and polymeric materials. One key point of the book is that it highlights how ball milling can be used not just for particle size reduction applications but for creating chemical reactions since the energy induced by the mechanical treatment is high enough to induce transformations. In all chapters the authors point out that mechanochemical reactions lead to economic advantages over existing technologies providing the same products.

The content of this book is arranged in ten chapters, which are based on different organic chemistries. Each chapter is divided into several sections related to specific organic syntheses or reactions. All chapters show how successfully the technique can be used to obtain specific organic products, and information is provided about experimental procedures and yields as well as a comparison with conventional routes such as solution chemistry, microwave and ultrasound methods.

Bond-forming Processes

Chapter 1, 'Carbon-Heteroatom Bond Forming Reactions and Heterocycle Synthesis under Ball

Fig. 1. FRITSCH Planetary Mill PULVERISETTE 5 classic line (Image courtesy of FRITSCH GMBH)

Milling' by Brindaban C. Ranu, Tanmay Chatterjee and Nirmalya Mukherjee (Indian Association for the Cultivation of Science, India) covers carbon–heteroatom (C–N, C–O, C–S, C–Cl, C–Br) bond formation and synthesis of heterocycles under ball milling. The authors show examples of the quantitative formation of different organic materials of commercial interest such as imines, azines, hydroquinone and hydrazine. It is pointed out that chemical reactions with fullerenes in solution are difficult to perform. Ball milling gives the opportunity to carry out the synthesis in the solid state. It was found that this method provides better results than performing the reaction in solution.

Chapter 2, 'Carbon–Carbon Bond Forming by Ball Milling' by Katharina Jacob, Robert Schmidt and Achim Stolle (Friedrich-Schiller University Jena, Germany), shows how carbon–carbon bonds can be formed by ball milling to produce compounds such as diphenylacetylene or biphenyl derivatives, which are used in medicine, drug design and electronics. The advantages of this method over conventional routes such as microwave or ultrasound-assisted synthetic routes are highlighted. Shorter reaction times and previously unknown molecular transformations have been reported. Reactions between carbon electrophiles and organometallic nucleophiles, known as cross-coupling reactions, were carried out in different high energy mills, with different milling times, media size and media materials, giving increased selectivity compared to solution based techniques.

Solvent-Free Synthesis

Chapter 3, 'Oxidation and Reduction by Solid Oxidants and Reducing Agents using Ball-Milling' by Giancarlo Cravotto and Emanuela Calcio Gaudino (University of Turin, Italy) deals with several oxidation and reduction reactions in the solid state by application of ball milling, generally under solvent-free conditions. Again the authors emphasise the efficiency and scalability of the ball milling process as well as the absence of solvents and the low energy consumption. The different examples shown in this chapter confirm that technical parameters such as volume, size of the reactor, material and number of milling balls have a clear effect on the final product. Vibration or revolutions, speed and milling time also needed to be optimised in order to improve yields.

Chapter 4, 'Asymmetric Organocatalytic Reactions under Ball Milling' by Elizabeth Machuca and Eusebio Juaristi (Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Mexico) highlights some advantages of the application such as the ability to carry out reactions in the absence of solvent, with an immediate reduction in costs and handling procedures. A very interesting finding is that by-products and potentially toxic wastes are frequently reduced. The shorter heating time, implying energy savings, is once again highlighted, as well as the frequent observation of reduced reaction times.

Chapter 5, 'Cross Dehydrogenative Coupling Reactions by Ball Milling' by Jingbo Yu, Zhijiang Jiang and Weike Su (Zhejiang University of Technology, China) confirms how ball milling can promote cross dehydrogenative coupling (CDC) and asymmetric CDC reactions. This method efficiently provides C–C bonds directly from C–H bonds.

Protection and Synthesis

In Chapters 6, 7, 8 and 9 the authors demonstrated that different processes such as amino acid derivation or protection, peptide synthesis, polymers and cellulose processing could greatly benefit from mechanochemical synthesis. According to the authors it is expected that further studies with ball milling on these areas will lead to significant advances.

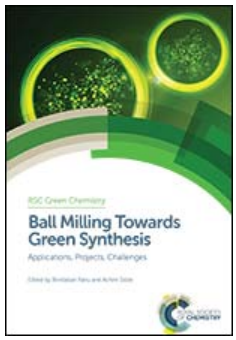
Chapter 7, 'Ball-milling Mechanochemical Synthesis of Coordination Bonds: Discrete Units, Polymers and Porous Materials' by Tomislav Friščić (McGill University, Canada) discusses the importance of the *in situ* analysis of mechanochemical reactions. It is well known that this has been largely limited to temperature and pressure measurements on mechanically induced self-sustaining reactions or monitoring pressure changes in reactions adsorbing or releasing gas, but some progress has been made by the use of penetrating synchrotron X-ray radiation studies.

Technical Implications

Chapter 10, 'Technical Implications of Organic Synthesis in Ball Mills' by Achim Stolle explains that ball mills are characterised by different parameters, regardless of the type of process. This information is of value not just for organic synthesis but for general applications. The author lists a large number of influencing variables including chemical parameters, technological parameters such as the milling media and process parameters such as temperature or pressure. The chemical parameters include all those variables that are directly related to the chemical reactions taking place in the mill.

Summary

In general the book is a summary of the preparation of several organic materials by ball milling. The book would be a very good reference for scientists focused on organic synthesis who are interested in reducing costs and increasing the efficiency of existing reaction processes. Using different examples, the book highlights how mechanochemistry can replace conventional processes for the preparation of organics and green materials for various applications. This book is not a basic text about ball milling or organic synthesis; it is aimed at people with experience in either organic synthesis or ball milling. Several examples confirm that technical parameters such as volume, size of the reactor, material and number of milling balls have a clear effect on the final product. All this is in line with our findings in the field of dry milling for inorganic materials synthesis. An important point described in this book is related to *in situ* analysis. Due to mechanical forces and equipment configuration, *in situ* analysis has been largely limited and milling reactions have been mainly followed by temperature and pressure measurements on mechanically induced self-sustaining reactions or by monitoring pressure changes in reactions adsorbing or releasing gas. Some progress on highly penetrating synchrotron X-ray radiation is reported. Overall the book is a positive review about ball milling for organic materials development.



"Ball Milling Towards Green Synthesis: Applications, Projects, Challenges"

The Reviewer

Maria Elena Rivas obtained a BSc in Chemistry from the Central University of Venezuela, and a PhD in Chemistry (Heterogeneous Catalysis) from the University Complutense of Madrid, Spain. She joined Johnson Matthey in 2012, working in a European Union-funded project (CAtalytic membrane REactors based on New mAterials for C1–C4 valorisation (CARENA)) about catalyst development for membrane reactors. Currently she is working as a Core Scientist in the New Applications group. In this project she is focused on mechanochemistry as an alternative route for the development and improvement of new and current materials.

