

IMPROVING RENEWABLE ENERGY PRODUCTION USING MECHANOCHEMISTRY AS A METHOD OF SOLID-STATE SYNTHESIS

Introduction

In recent years, the renewable energy sector has been seeking to improve the efficiency of clean energy production, with an emphasis in the field of catalysis. Specifically, researchers have prioritized the study of solid catalysts, which exhibit promising qualities in renewable energy. This is due to the many advantages these catalysts hold compared to liquid catalysts, such as the lack of a reaction mixture and the ability to easily separate the catalyst and the product. These advantages are crucial to improving the efficiency and eco-friendliness of catalytic reactions, as the separation of catalyst and product allows for catalyst recycling and the elimination of a reaction mixture helps reduce waste [1]. These benefits have made solid catalysts an ideal candidate for the synthesis of many organic compounds and high-quality hydrocarbons, indicating their relevance in both organic chemistry research and industrial production settings [1]. Due to their value within the renewable energy sector, solid-state synthesis has become a popular topic of research within materials science, as new methods of synthesis are regularly developed and tested within the production pipeline.

One common issue with synthesis that is faced by the pharmaceutical industry is solvent waste. 85% percent of the chemicals used for pharmaceutical production are solvents, indicating that the elimination of a reaction solvent could have a revolutionary effect on the waste produced in industrial production [2]. One method of solid-state synthesis that accomplishes this is mechanochemistry. It has slowly been gaining traction within the organic chemistry and materials science fields over the past several years, as it is a valuable tool for synthesizing catalysts in an eco-friendly. It utilizes the mechanical energy produced by processes like grinding, milling, and extrusion of reagents to encourage reactions to occur [3][4]. Thanks to its eco-friendly attributes, mechanochemistry has become an area of interest for improving the efficiency, cost, and environmental effects of solid catalyst synthesis. This paper will cover a background of solid-state synthesis techniques as well as several recent innovations in the field of mechanochemistry, focusing on its impact in materials science and industrial production.

Applications of solid catalysts and established synthesis techniques

One established method of solid catalyst synthesis is known as solution combustion synthesis (SCS). First proposed in 1988 by J.J. Kingsley and K.C. Patil, this technique is derived from the discovery of self-propagating, high temperature combustion syntheses in the 1960s by Alexander Merzhanov et al. [5][6]. This method uses a saturated aqueous solution of a metal salt and an organic reducing agent to produce a metal oxide catalyst. These reactants are ignited to induce a combustion reaction, resulting in the desired nanocrystalline metal oxide. Catalysts developed through solution combustion synthesis reactions are valuable due to their unique structure the imperfections in the crystalline structure can actually improve catalytic activity by serving as active centers. Prior to the development of the SCS method for synthesizing catalysts, methods such as sol-gel, impregnation, and deposition-precipitation were used, but were highly inefficient due to their high cost and long separation and thermal stages [6].

SCS derived catalysts have found use in energy and industrial production. According to a 2012 paper by University of Oxford professor Sergio Gonzalez-Cortes and his peers, these catalysts can be used for a myriad of reactions, including the

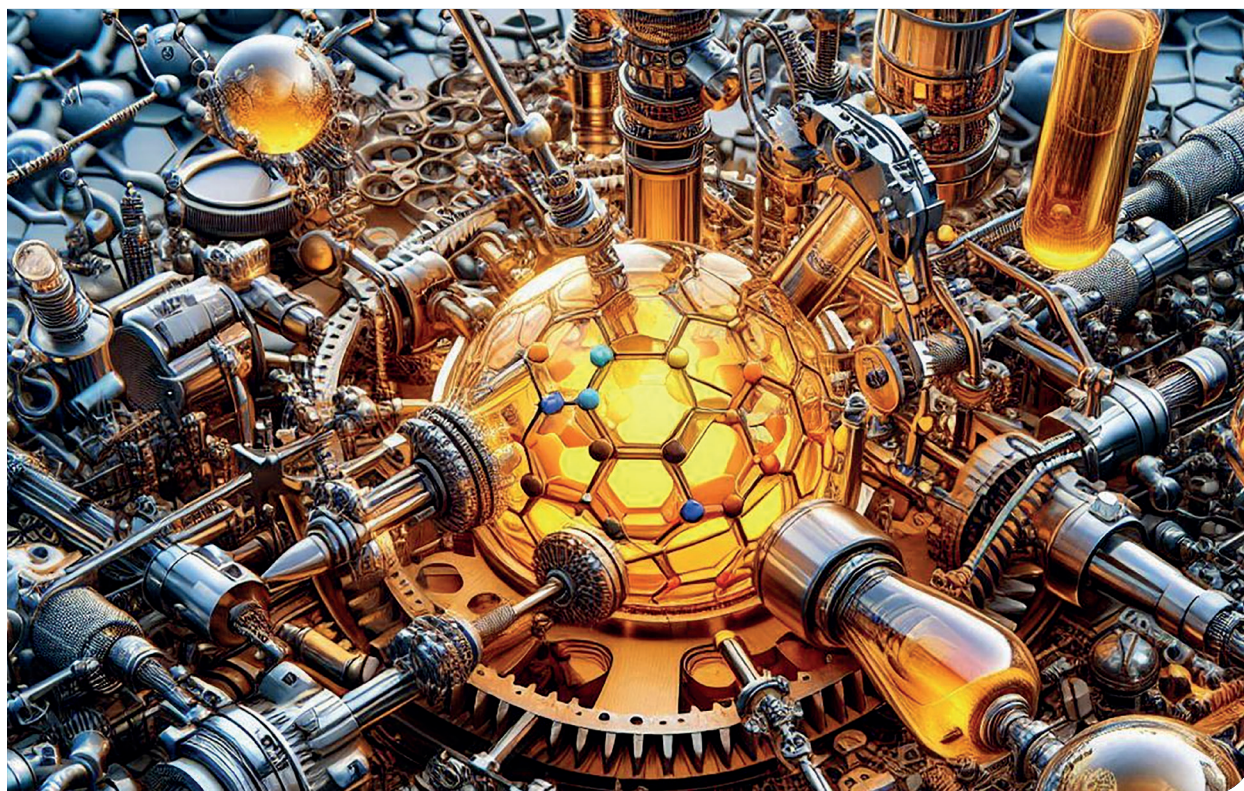


Table 1: Aspects of the different types of catalyst preparation methods used in Lau's study [7].

Ni-MgAl ₂ O ₄ (cop)	Co-precipitation	0.17:1:2	–	–	–	6.09
Ni-MgAl ₂ O ₄ (solid)	Solid state reaction	0.2:1:2	–	–	–	9.77
Ni/MgAl ₂ O ₄ ^{solid}	wet-impregnation	–	Solid state synthesis	1:2	6wt%	5.51
Ni/MgAl ₂ O ₄ ^{cop}	wet-impregnation	–	Co-precipitation	1:2	6wt%	3.86

^a ICP refers to inductively coupled plasma.

hydrogenation of CO₂ into methanol, the oxidation of ethanol into acetic acid, hydrogen production reactions, and more [6].

Additionally, solid catalysts hold further value in the clean energy sector by reducing greenhouse gas emissions [7]. These emissions pose a significant threat to the environment, as the atmosphere's CO₂ level has risen by 35% in the past 200 years, and rapid deforestation is eliminating the earth's ability to absorb that excess carbon [8]. To reduce the quantity of greenhouse gases emitted by industrial plants, researchers have tested many strategies, such as the reforming of methane with excess CO₂. The general process for reforming methane, a dangerous greenhouse gas, uses an oxidizing agent to break methane down into carbon monoxide and hydrogen. This can be accomplished through several methods, such as steam reforming, dry reforming, and partial reforming, which all produce different ratios of hydrogen [9].

To improve the efficiency of methane reformation, solid catalysts have been introduced using multiple methods. One 2014 study by Lau et al. investigated the performance of MgAl₂O₄ mixed oxide supported Ni catalysts for methane reforming when prepared using methods like solid state synthesis, co-precipitation, and wet impregnation. The study examined several characteristics of the differently prepared catalysts, such as the reduction of Ni²⁺ ions in each of the catalysts, metallic surface area, dispersion, particle size, and weight percent of Ni impregnated on the support. The results of the study are shown in Table 1. The study concluded that catalytic activity was most prominent in wet impregnation catalysts with a support prepared by solid state synthesis. The second highest level of activity was found in solid state prepared catalysts, and the catalysts with both supports and

catalysts prepared by co-precipitation were found to have the least amount of activity [7].

The drawbacks of many of the established methods for synthesizing solid catalysts are the conditions under which the reactions must occur. Methods such as SCS have high reaction temperatures due to their reliance on thermochemistry to facilitate reactions [10]. Although the methods examined in Lau's study were carried out at room temperature, they have their own drawbacks, such as deterioration, which prompted the use of a support [7]. Thus, due to the simplicity of its applications, mechanochemistry has become a popular alternative to these prior methods.

Mechanochemistry as a new method of synthesis

Mechanochemical synthesis holds many advantages over established routes of solid catalyst synthesis, most significantly the mild reaction conditions required, unlike in thermochemical routes of synthesis [10]. Ultimately, mechanochemistry's advantages lie in its simplicity. It has been used by humans going back to prehistory, where striking rocks or sticks together created mechanical energy that induced fire.

Mechanochemistry has recently reemerged as a topic of interest in materials science due to its versatility in catalyst production. The International Union of Pure and Applied Chemistry (IUPAC) named it one of 10 emerging innovations in the field of chemistry with the potential to make the planet more sustainable, as its potential in organic synthesis has garnered significant recognition in the past several

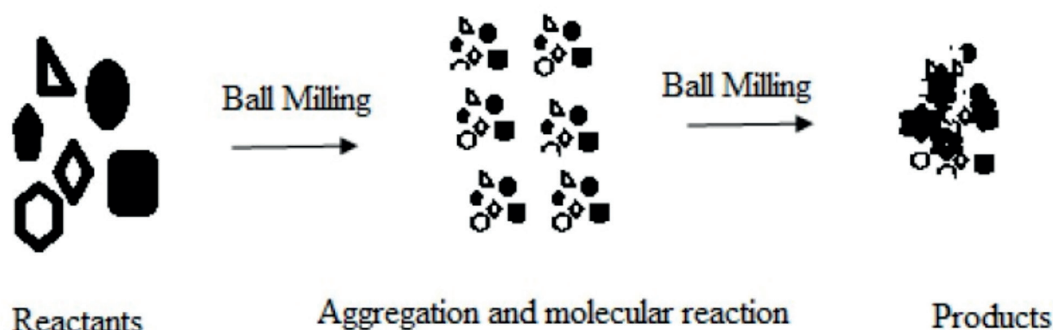


Figure 1: Process of ball milling multiple reactants [13].

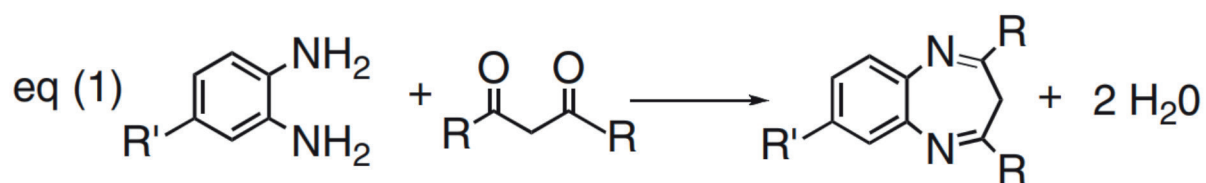


Figure 2: Ball milling diamines and 1,2- or 1,3-dicarbonyls together induced a reaction forming benzodiazepine [14].

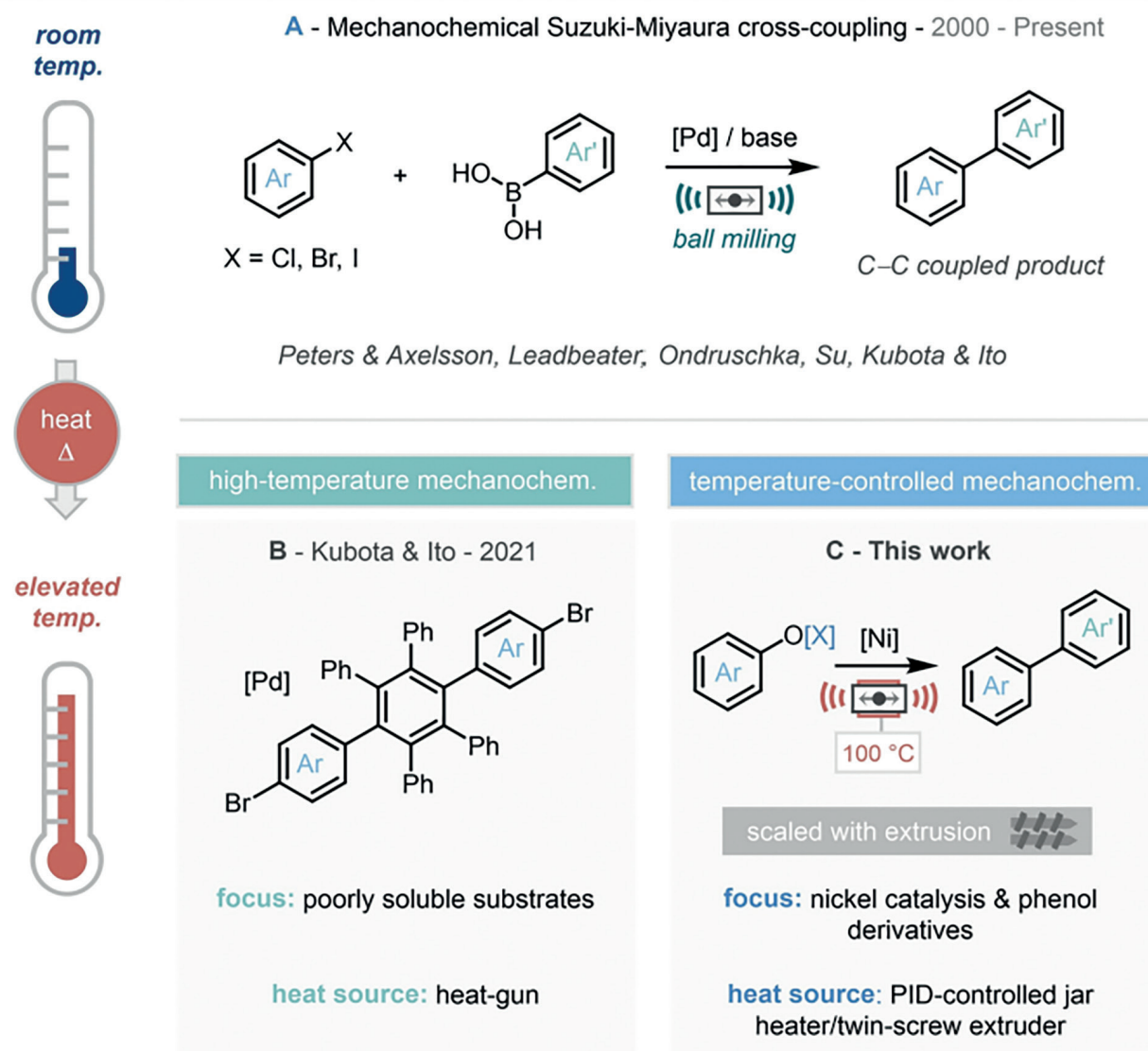


Figure 3: Different types of mechanochemical techniques and their applications in the Bolt et al. study [16].

years [3]. Many studies have investigated how existing mechanochemical methods, especially ball milling, can be used to synthesize supported catalysts. While ball milling method is typically used to grind materials into fine particles, its use in the synthesis of organic molecules extends beyond physical changes. Ball milling is especially useful in increasing the reactivity of compounds [11]. In one study, Carlier et al. ball milled diamines and 1,2- or 1,3-dicarbonyls together, resulting in a reaction occurring to form benzodiazepine, as shown in Figures 1 and 2 [12].

Although many studies of mechanochemical behavior utilize ball milling techniques to induce chemical reactions, there are other techniques that exist within mechanochemistry. A slightly more advanced method that has been gaining traction recently is screw extrusion. It is a process in which a rotating screw is used to push reagents through an extrusion head of a specified size, again encouraging chemical reactions to take place [15]. Unlike ball milling, screw extrusion can

operate under the conditions of flow chemistry, which creates more opportunities for using mechanochemistry at the industrial level. In flow chemistry, reactions are carried out continuously rather than in batches, which has been shown to increase productivity and output and minimize risk within industrial applications [3]. It is certainly another valuable tool for improving future industrial sustainability, as it was also listed by the IUPAC as a promising new technology alongside mechanochemistry. Thus, the implementation of screw extrusions continuously in a flow setup holds a myriad of benefits for synthesizing effective catalytic products on a larger scale [3].

Although there are some difficulties that may be faced when trying to effectively scale up continuous screw extrusion to an industrial size, studies have been conducted in this vein. A British research group, Bolt et al., used both ball milling and screw extrusion to induce a Suzuki-Miyaura coupling reaction between an aryl pseudo-halide and a boronic acid/ester. The

screw extrusion method was used at a large scale and was shown to be able to produce 200 times the output of the small-scale reaction they first studied. Figure 3 indicates the different types and categories of mechanochemical methods the researchers studied, while Figure 4 shows the yield of the products when scaled up with 100 mmol of sulfonate starting product used. The figure indicates the percent yield of the coupling reaction, the leftover starting reagent, and a byproduct of the reaction, displaying the three states the reaction went through before its completion [16].

In summary, two of the most promising current applications of mechanochemistry are ball milling, for its simplicity and reactivity in neutral reaction conditions, and screw extrusion, for its potential in industrial production and green science. However, many other mechanochemistry methods are under investigation by researchers, such as pan-milling, manual grinding, ultrasonication-induced mechanochemistry, and hydrodynamics. The different attributes and applications of some of these methods are summarized in Table 2 below [17]. Despite the multitude of studied mechanochemical methods, catalysis production in industrial settings has been the major focus of this research, which this paper will investigate in the following sections.

Applications of mechanochemistry in industrial catalyst synthesis

The synthesis of TiO_2 , a common photocatalyst in industrial production, was studied by Billik et al. In the experiment, they discovered that ball milling $\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$ and Na_2CO_3 produced TiO_2 that, in comparison to TiO_2 synthesized using other methods, was much more photochemically active. Additionally, they learned that ball milling TiO_2 with different sources of nitrogen induced the doping of nitrogen into substitutional sites, promoting catalytic activity [18].

When they increased the duration of the ball milling process, Billik et al. also found that a phase transformation would occur. Phase transformations comprise one of the two main routes mechanochemical reactions can take: bottom-up strategies (chemical reactions prompted by mechanical energy) and top-down strategies (phase transformations). Zielinski et al. formed $\alpha\text{-Al}_2\text{O}_3$ from $\gamma\text{-Al}_2\text{O}_3$ after 12 hours of ball milling. This process is valuable because $\alpha\text{-Al}_2\text{O}_3$ has a high surface area and is a very valuable catalyst for the Fischer-Tropsch synthesis, as it is very thermodynamically stable unlike $\gamma\text{-Al}_2\text{O}_3$ [18]. Ball milling can be an extremely efficient and effective mechanochemical method for inducing both chemical reactions and phase transformations at room temperature, helping to optimize the thermodynamic and physical properties of catalysts [18].

Applications of mechanochemistry in synthesizing porous materials

Mechanochemistry is also uniquely suited for manufacturing porous materials. It can be used for nanostructuring, forming uniform pore sizes without the use of solvents, providing an economical mode of synthesis [19]. Zhang et al., for example, used mechanochemical methods to produce mesoporous Al_2O_3 . They ball milled aluminum isopropoxide with soft templates such as pluronic P123, polyethylene glycol, Pluronic F127, or cetyltrimethyl ammonium bromide, which were removed in a later step. Then the researchers washed the resulting material with ethanol and dried it under a vacuum. The resulting Al_2O_3 product had a surface area of $644 \text{ m}^2\text{g}^{-1}$, which is considered very high, and an even pore size of 4.2 nm [19]. This showcases the value of mechanochemical methods within the materials science field, as mesoporous metal oxides such as the ones produced in this study not only have potential in catalysis, but also other material science-related fields such as battery technology [20].

Mechanocatalysis as a pathway for molecular synthesis

Mechanochemical synthesis routes do not always rely on mechanochemistry techniques alone. The implementation of a catalyst in addition to mechanical techniques has also been studied by researchers. While methods like ball milling alone can be used to produce ammonia from nitrogen and water, as in a study done by Cui and Chen, the same reaction can also be done with the presence of a metallic catalyst [21]. In Cui and Chen's study, the iron present in the milling containers was used as the catalyst, while another study by Tricker et al. used

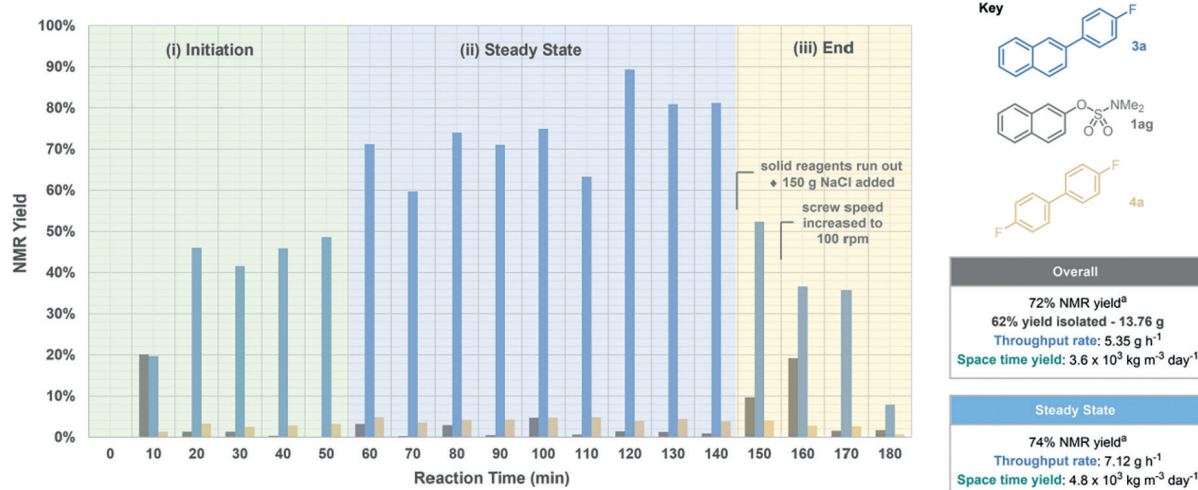
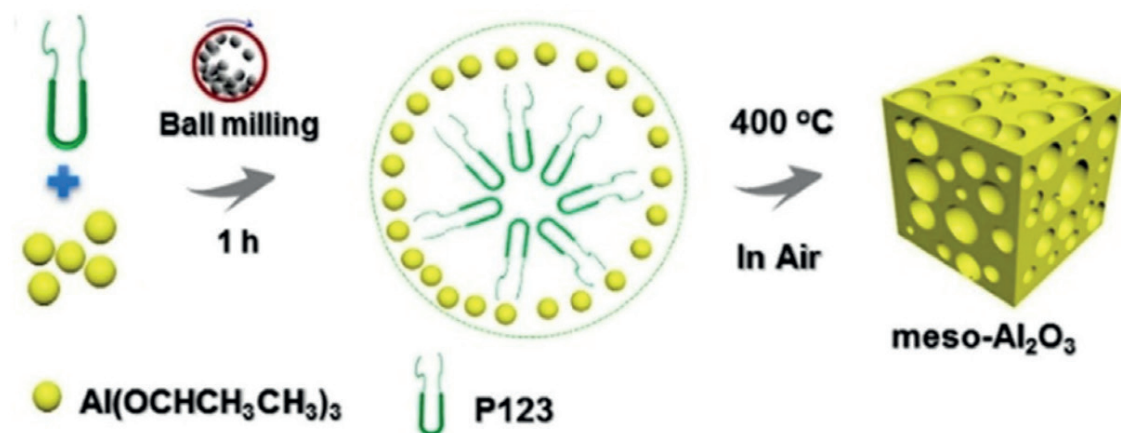


Figure 4: Percent yield of different molecules in the product of the scale-up screw extrusion reaction [16].

Table 2: Comparison of several mechanochemical techniques [17].

Methods	Force	Reaction phase	Product Size	Reactant	Function	Productivity	Loading	Features
Manual grinding	Impact and friction	Solid	1–30 μm	Inorganics, Polymer	<ul style="list-style-type: none"> Grafting and coupling Initiation and acceleration of synthesis reaction 	Milligram to gram scale	<10 wt%	Manual operation, high randomness, suitable for lab-scale exploratory experiment
Ball-milling	Impact or shearing or friction	Solid	500 nm to 1 μm for inorganics, 50–500 μm for polymer	Inorganics, Polymeric composites	<ul style="list-style-type: none"> Filler dispersion Grafting and coupling Induced catalysis Crushing and peeling of inorganics 	Kilogram scale	\approx 40 wt%	Suitable for scalable reactions, difficult to pulverize polymers, suitable for inorganics, batch production
Pan-milling	3D Shearing and pressure	Solid	500 nm to 50 μm	Polymer and Polymeric composites	<ul style="list-style-type: none"> Superfine crushing of polymer Compositing Grafting and coupling Decross-linking 	Kilogram scale	Up to 80 wt%	Continuous industrial production, suitable for polymer and polymeric composites
Ultrasonication	Tension and pressure	Liquid	\leq 1 μm	Nanomaterials, Polymer solutions	<ul style="list-style-type: none"> Dispersion and peeling Initiation of oxidation and radical 	Gram scale	\leq 10 wt%	Suitable for liquid phase dispersion, synthesis reactions, lab-scale sample preparation
Hydrodynamics	Tension and pressure	Liquid	–	Fluids	<ul style="list-style-type: none"> Initiation of oxidation and radical 	0–20 L min^{-1}	–	Suitable for liquid phase reactions and oxidation reactions involving oxygen

Figure 5: Synthesis of meso- Al_2O_3 catalyst with ball milling [19].

the addition of titanium metal to catalyze the same reaction [21][22]. In the latter study, titanium powder was milled in a specifically designed mill that allowed N_2 and H_2 gas to flow through. This resulted in the formation of TiN alongside ammonia [22].

The use of a catalyst, whether it be a separate addition to the process or within the vessel itself, demonstrates the versatility of mechanochemistry and the future possibilities for the field. Mechanochemistry is just one example of how combining different techniques can further improve the process of molecular synthesis.

Conclusion

Mechanochemistry is currently one of the most promising and interesting areas of innovation in organic chemistry and materials science. Its simplicity and effectiveness have allowed a wide range of study in the area of solid-state synthesis, lauded for its focus on decreasing waste on an industrial scale. It utilizes a new set of laboratory techniques

that distinguishes it from other methods of synthesis, such as flow setups, and materials like milling jars [23]. Future studies of mechanochemistry should focus on the scalability of these methods, such as ball milling, as its ability to function without a solvent or unique temperature conditions lends itself to increased production volumes. While certain mechanochemical techniques like screw extrusion have been scaled up, this is still an area ripe for expansion through research, as applying these techniques to various industrial production pathways could greatly improve the environmental friendliness of large-scale production.

References

- Zhang et al. "Eco-friendly solid-state synthesis of Na-promoted Mn-Fe/ZrO₂ catalyst for Fischer-Tropsch synthesis" *Fuel*, Volume 363 (2024)
- James et al. "Mechanochemistry: Opportunities for new and cleaner synthesis" *Chem. Soc. Rev.*, Volume 41 (2012)
- Gomollon-Bel "Ten Chemical Changes That Will Change

Our World" *Chemistry International* (2019)

- Friscic et al. "Mechanochemistry for Synthesis" *Angewandte Chemie* (2020)
- Kingsley et al. "A novel combustion process for the synthesis of fine particle α -alumina and related oxide materials" *Material Letters*, Volume 6 (1988)
- Gonzalez-Cortes et al. "Fundamentals, properties and applications of solid catalysts prepared by solution combustion synthesis (SCS)" *Applied Catalysis A: General*, Volume 452 (2013)
- Lau et al. "Carbon dioxide reforming of methane by solid state synthesis supported catalysts" *International Journal of Hydrogen Energy*, Volume 39 (2014)
- Gossop "Low carbon cities: An introduction to the special issue" *Cities*, Volume 28 (2011)
- Manan et al. "CeO₂-Based Heterogeneous Catalysts in Dry Reforming Methane and Steam Reforming Methane: A Short Review" *Catalysts*, Volume 12 (2022)
- Cuccu et al. "Mechanochemistry: New Tools to Navigate the Uncharted Territory of "Impossible" Reactions" *ChemSusChem*, Volume 15 (2022)
- Sadykov et al. "Advanced Materials for Solid Oxide Fuel Cells and Membrane Catalytic Reactors" *Advanced Nanomaterials for Catalysis and Energy* (2019)
- Chaudhuri et al. "Green synthetic approaches for medium ring-sized heterocycles of biological and pharmaceutical interest" *Advances in Green and Sustainable Chemistry*, Volume 2 (2021)
- El-Sayed et al. "Ball Milling Promoted N-Heterocycles Synthesis" *Molecules*, Volume 23 (2018)
- Carlier et al. "Use of co-grinding as a solvent-free solid state method to synthesize dibenzophenazines" *Tetrahedron Letters*, Volume 52 (2011)
- Yan et al. "Screw extrusion process used in the polymer modified asphalt field: A review" *Journal of Cleaner Production*, Volume 448 (2024)
- Bolt et al. "Temperature-Controlled Mechanochemistry for the Nickel-Catalyzed Suzuki-Miyaura-Type Coupling of Aryl Sulfamates via Ball Milling and Twin-Screw Extrusion" *Angewandte Chemie*, Volume 61 (2022)
- Liu et al. "A Review on Mechanochemistry: Approaching Advanced Energy Materials with Greener Force" *Advanced Materials*, Volume 34 (2022)
- Yang et al. "Mechanochemical Synthesis of Solid Catalysts and Application in Catalytic Reaction" *ChemCatChem*, Volume 16 (2024)
- Amrute et al. "Mechanochemical Synthesis of Catalytic Materials" *Chemistry – A European Journal*, Volume 27 (2021)
- Zhang et al. "Mechanochemical Nonhydrolytic Sol-Gel-Strategy for the Production of Mesoporous Multimetallic Oxides" *Chemistry of Materials*, Volume 31 (2019)
- Cuccu et al. "Ammonia Synthesis by Mechanochemistry" *ChemCatChem* (2023)
- Tricker et al. "Mechanocatalytic Ammonia Synthesis over TiN in Transient Microenvironments" *ACS Energy Letters* (2020)
- Do and Friscic "Mechanochemistry: A Force of Synthesis" *ACS Central Science*, Volume 3 (2017)

About the Authors

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 28 years. He is an elected Fellow by his peers at IChemE, AOCS, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute and The Royal Society of Chemistry. An ASTM Eagle award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants handbook", details of which are available at ASTM's Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available (<https://bit.ly/3u2e6GY>).

He earned his doctorate in Chemical Engineering from The Pennsylvania State University and is a Fellow from The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK. Dr. Shah was recently granted the honourific of "Eminent engineer" with Tau beta Pi, the largest engineering society in the USA. He is on the Advisory board of directors at Farmingdale university (Mechanical Technology), Auburn Univ (Tribology), SUNY, Farmingdale, (Engineering Management) and State university of NY, Stony Brook (Chemical engineering/ Material Science and engineering). An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical engineering, Raj also has over 650 publications and has been active in the energy industry for over 3 decades.

More information on Raj can be found at <https://bit.ly/3QvfaLX>

Contact: rshah@koehlerinstrument.com

Ms. Cameron Corter and Mr. Beau Eng

are part of a thriving internship program at Koehler Instrument company in Holtsville, and are student of Chemical Engineering at Stony Brook University, Long Island, NY, where Dr. Shah chairs the external advisory board of directors.



Cameron Corter



Beau Eng

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company • Holtsville, NY11742 USA • Email: rshah@koehlerinstrument.com

• Web: www.koehlerinstrument.com

