ISSN: 0974-5823 Vol. 7 No. 1 January, 2022

International Journal of Mechanical Engineering

The Efficiency of Mechanochemistry in Maintaining Green Synthesis of Metal-organic Framework

Hamza S. Al-Shehri**

Ph.D, Chemistry Division, King Khaled Military Academy, SANG, 11495, Riyadh, Saudi Arabia.

Manoj Shetty

Professor ,Department of Oral Implantology , AB Shetty Memorial Institute of Dental Sciences, Nitte Deemed to be University, Mangalore , India.

Nivya John

Lecturer, Department of Oral Implantology , AB Shetty Memorial Institute of Dental Sciences , Nitte Deemed to be University, Mangalore , India.

Santanu Debnath

Assistant Professor, Brahmananda Keshab Chandra College, 111/2, BT Road, Kolkata- 700108, West Bengal, India.

Tanushree Bose Das

State Aided College Teacher, Sree Chaitanya Mahavidyalay. Ashokenagar, Habra, North 24 Parganas, West Bengal, India.

***Corresponding author**: Hamza S. Al-Shehri

Abstract

Industrialization results in the current global energy and environmental issues that could be solved with the implementation of a metal-organic framework. MOFs provide solutions for emerging environmental problems and act as a boom for facing the challenges. MOFs are required to design and synthesize while manufacturing. Mechanochemistry acts effectively in maintaining the green synthesis of metal-organic frameworks. Mechanochemistry refers to the chemical reaction that takes place at room temperature and is induced by mechanical energy. Mechanochemistry provides various advantages that could be solution-free, energy-saving, low-temperature process, and high productivity. Present studies deal with the synthesis of MOFs that provide information about the synthesis process, characterization of MOFs, and stability strategies. Processing of MOFs production provides various applications that solve the existing environmental issues and the applications are majorly adsorption, separation, clean energy conservation, and fine chemical catalysis. The efficiency of the Mechanochemistry is found to be high to maintain the green synthesis of the metal-organic framework

Keywords: *Mechanochemistry, Industrialization, Chemical reaction, Environmental issues, Metal-organic framework , Green synthesis*

1. Introduction

Here introduce the paper, and put a nomenclature if necessary, in a box with the same font size as the rest of the paper. The paragraphs continue from here and are only separated by headings, subheadings, images and formulae. The section headings are arranged by numbers, bold and 10 pt. Here follows further instructions for authors.

1.1. ***Background of the study***

Demotic environmental awareness was observed at a peak at the beginning of the 21st century which builds pressure on the reduction of emission and energy conservation. Mechanochemistry or green chemical engineering emerges as the alternative and best solution for using hazardous substances [1]. Technical innovation in making eco-friendly products gained tremendous popularity in the market. Green synthesis products are required to be designed in such a way as to deal with market demand, have end-use properties, and fulfill environmental demand for sustainable macro and mesoscale industries. Unusual chemical reactions induced by mechanical energy at room temperature are termed mechanochemistry [28]. Mechanochemistry provides novel materials or products that are versatile and could be applied in multiple platforms. Metal-organic frameworks (MOFs) consist of a regular array of positively charged metallic ions surrounded with organic linker molecules. MOFs are porous materials made up of organic-inorganic hybrid crystals. MOFs gained huge attraction for their application in green chemical engineering due to their diversity in structure, tailor ability function, and unique proportionality. The efficiency of MOFs increases with its property similarly to other inorganic materials it also has control on composition, pore property, function, and morphology [2].

For decades humans get benefits from natural catalysts that underpin life on Earth. Natural catalysts are enzymes that are used for both scientific purposes and applied in industries. Enzymes, while used in industries as industrial catalysts, do not need any solid support and produce a heterogeneous environment that easily separates. Metal-organic frameworks are thus used as solid substrates as they enhance the stability, selectivity, and activity of enzymes. The study is focused on analyzing the efficiency of mechanochemistry in maintaining the green synthesis of the metal-organic framework. A brief introduction of MOFs is provided in the present study along with the application of green chemical engineering. Materials and methods are provided for the synthesis of MOFs [3]. The literature review acknowledged the perspective of mechanochemistry and its role in maintaining the metal-organic framework. MOFs could be synthesized in majorly two ways that include general synthesis and green synthesis which are described in detail in the literature review of the study. The objective of the study is fulfilled with the description of material and methods to obtain accurate and authentic results. Further recommendation fulfills the present knowledge gap.

1.2. Objective

Objectives of the study are as follows:

2. To obtained green synthesis for the Metal-organic frameworks (MOFs)

3. To analyze the efficiency of mechanochemistry in maintaining green synthesis of metal-organic framework

4. To analyze the structural stability and characterization of metal-organic frameworks

5. To analyze the application of the metal-organic framework in adsorption, separation, and fine chemical catalysis

1.3. Significance of the Study

The study is significant in analyzing the efficiency of mechanochemistry and helps to acknowledge the application of mechanochemistry. The role of metal-organic frameworks or MOFs could be understood with the help of this study. The study highlights the green synthesis and general synthesis process for the MOFs which helps in acknowledging the environmental benefits. Metal-organic frameworks have a versatile structure that leads to understanding the stability and its characterization [4]. MOFs gained attraction as it has various applications which are illustrated in the study. Application of MOFs like separation, adsorption, and fine chemical catalysts helps in understanding the brief characteristics of MOFs. MOFs structure helps to understand the complex chemical reactions used in academic sessions. The present study helps in fulfilling the previous knowledge gap by providing in detail the synthesis process and application of MOFs. The methodology of the study provides an authentic and unbiased conclusion which helps readers to understand the outcome of the study [5]. Researchers and scholars can benefit while working on the mechanochemistry of metal-organic frameworks. Future studies based on the topic related to mechanochemistry, green chemistry, MOFs, or the application of MOFs could get help from this study.

2.Literature Review

2.1 Synthesis of Metal-organic Frameworks

Pollution is the biggest problem for the environment and it harms the life of organisms and human health. This problem could be solved with the implementation of green chemistry engineering products. The production of MOFs is a part of green chemistry engineering [6]. Green chemistry engineering is the way of designing and commercialization of products that are used to minimize the generation of pollution. Green chemistry engineering is objected to reducing risk regarding the environment and human health. Rapid development regarding environmental consideration gained the attention of synthesizing metal-organic frameworks. Appropriate synthesis conditions could be gained with the establishment of MOFs synthesis. New MOFs are discovered with the concept of parallelization and miniaturization in the condition of large-scale screening. MOFs are produced for industrial and green sustainability and for that different criteria are being considered [7]. MOFs are produced for choosing safer, cheaper, and for building biocompatible units. MOFs production helps in reducing energy influences and could be used for innocuous reaction media. MOFs are designed in such a manner that they are easily activated and require continuous manufacturing. Synthesis of metal-organic frameworks allows desired compounds to grow and nucleate. The synthesis of Metal-organic frameworks could be classified into two parts: general synthesis and green synthesis [8].

General synthesis of MOFs

Numerous synthetic methodologies are applied and developed to synthesize metal-organic frameworks to date. Coordination bonds are allowed to form, break, and reformed to extensive propagation during crystallization and error correction with MOF synthesis conditions. The most adopted and effective method for the general synthesis of MOFs is the Solvothermal synthesis method. Multi-topic organic ligand metal species are mixed with a high-boiling-point solvent that is DMA, DMF, or DMSO (dimethylformamide, dimethylformamide, or dimethyl sulfoxide) and heated again in the solvothermal synthesis method [9]. Temperature, solvent, reaction time, pH, regent ratio, and other parameters vary systematically and can be optimized. These chemical parameters are obtained to influence not only the obtained structure yet also crystal morphology. Mechanochemical can be established with the alternative methods of MOFs synthesis. Electrochemical, sonochemical, and microwave-assisted synthesis are included in the alternative methods used for the synthesis process. New MOFs can be created and developed with post-synthetic methods that functionalize provided MOFs and these methods are transmetalation and post-synthetic modification [10].

Guest molecules such as solvents and residual starting materials are inevitably found voids of host networks in the process of MOF synthesis. Trapped guest molecules like residual materials and solvents are removed through an activation process which determines surface area and porosity. General synthesis of MOFs process follows the MOF evaluation that routes in mechanochemistry. Design and synthesis of MOF provide structural characterization which leads to property testing, if it is found stable then further processed otherwise strategies are applied to redesign and synthesis [11].

Green Synthesis of MOFs

The mechanochemistry principle aspect researches MOFs that are suitable for environments requiring green synthesis. Green syntheses of MOFs are processed with some key factors like harmless reactants, mild conditions, innocent solvent, and fewer byproducts. HCL and HNO3 are general byproducts obtained with the reaction of protonated ligands and metals salts in an aqueous solution. Thus avoiding such harmful byproducts, metals salts that contain linker salts or benign anions with innocuous metal cation are mostly preferred in green synthesis [12]. High effective efficiency could be achieved with the selection of metal hydroxides and oxides. Mechanochemical synthesis methods are best for the green synthesis of MOFs due to hydroxides being insoluble. Design and utilization of MOFS are highly affected by the selection of organic ligands as it affects the specific functions along with the final topology. Mechanochemistry provides an appropriate selection of metallic salts and provides a direct synthesis of alkoxysilanes. Mechanochemistry provides efficiency in the green synthesis process of metal-organic frameworks [13].

Preparation of MOFs

In the lab, MOFs are generally prepared in milligrams by heating in organic solvents for a few days. Syntheses of industrial MOFs are evaluated and set to provide solutions to the safety, availability, toxicity, and cost of reagents. Green synthesis by mechanochemistry is done to obtain productivity and operability in production materials [14]. MOFs are prepared in small amounts in laboratories while fulfilling the market demand huge production is required. The large variation between the commercialization of MOFs and conditions required for the production of MOFs in the lab creates a high demand for the development of efficiency. Fulfill the demand of MOFs required to be designed with low-cost methods to gain more profits. Scale-up preparation methods include factors that are required for the large-scale production of the metal-organic framework. While producing MOFs demand for the fulfillment of promises made by scale-up approaches faces few challenges. These challenges are the use of organic solvents, accumulation of anion, availability of ligand, shaping, control on particle size, and activation.

The composition, structure, and properties of each MOF create their challenges which make the synthesis process more complicated [15]. Electrochemical, microwave-assisted synthesis, and mechanochemistry is applied to cope up with the present challenges of MOFs. Electrochemical synthesis is used to demonstrate the scale-up synthesis of MOFs with electrochemical processes. Spray drying and flow chemistry permit occurred in microwave-assisted synthesis to enhance the production of MOFs. While mechanochemistry synthesis, heating, or extra solvent is not required and it avoids the activation and post-synthetic washing. Avoiding extra steps in the process of MOF synthesis, mechanochemistry is considered to be the best method to gain efficiency. Therefore, the efficiency of mechanochemistry is observed to be high to maintain the green synthesis of MOFs [16].

2.2 Structural Stability and Characterization of Metal-organic Frameworks

Characterization of MOFs

MOFs production after the designing and synthesis requires structural characterization to test the properties of MOF. The property testing process checks the stability of the metal-organic framework which is later processed for commercialization. Characterization of MOF could be classified into two parts that are structural and morphologic characterization. Absolute structural information about MOFs could be obtained with the data of Rietveld refined of powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction (SXRD). The crystalline and phase purity of the materials could be determined with data of MOF contained in the PXRD pattern [17]. Chemical stability testing of synthesis MOFs in an aqueous solution included additional characterization techniques and protocols. Chemical stability testing is conducted on distinct pH, using SEM (Scanning electron microscopy) to determine particle size and morphology, and TGA (thermogravimetric analysis) for indicating thermal stability of the framework. The aqueous solution in combination with EDS (Energy-dispersive X-ray spectroscopy) was used to check elementary content and composition [18]. NMR (Nuclear magnetic resonance) is a characterization method of MOF that provides a quantified linker ratio for structures that are mixed with linker-based. Characterization methods like NMR and EDS are used for identifying precise structure, composition, and morphology traits that target materials of MOF. Characterization of metal-organic frameworks provides a basic foundation for application exploration and prediction of subsequent characteristics [19].

Stability of MOFs

The stability of MOFs is considered for mechanical, chemical, and thermal stability for production. Production of MOF requires design and synthesis then it processes structural characterization then it goes under testing for its property. Stability testing is an important part of MOF production that checks the properties of the metal-organic framework. Products that fail in the stability test are processed back for resynthesis to enhance the stability [30]. The stability of MOFs is affected by some factors that are metal ions, coordination geometry between ligands and metals, operating environment, hydrophobicity of pore surface, and organic ligands configuration. MOF stabilities could be determined with the coordination bond strength between organic ligands and inorganic nodes. MOFs properties that are required to have high porosity that inescapable decreases mechanical strength in vacuum or resists pressure. A phase transition, amorphizations for structure, or partial collapse consists of mechanical or framework stability [20]. Solvent-exchange methods are applied for gaining mechanical stability for MOFs while avoiding structural collapse. Mechanical stability of MOF includes structural defects, network interpenetration, and framework geometry. Subsets of the metal-organic framework are designed along with a reversibly flexible structure for achieving mechanical stability.

The thermal stability of materials could be measured with the connectivity of coordinated bonds and to determine the strength. While checking the thermal stability of materials it is observed that in most cases coordination bonds are found to be dehydrogenation, carbonization, amorphization, or linker burning. Thermal stability could be obtained or enhanced with the replacement of low valent metallic ions with high valent species such as Al3+, Zr4+, and Ti4+. Stability of materials measured with the testing ability of MOFs that regain structural framework under specific chemical composition [21]. MOFs structure and operating environment are two internal and external factors that could be used to determine the chemical stability of the materials. Materials are found to be either acidic or alkaline imbalance which could be treated with the addition of hydrogen or OH ions. Constructing MOFs with low-valent metal cations and azolate based linkers is the best way to avoid the occurrence of chemical instability. Stability might be mechanical, thermal, or chemical which is required for the processing of materials. Improving the strength of the coordinating bond provides mechanical and thermal stability. Catenation and the addition of hydrophobic functional groups provide chemical stability to the materials. Therefore, materials after property characterization are required to be stable for further processing [27].

2.3 Processing of Metal-organic Framework with Mechanochemistry

Mechanochemistry requires four simple processes in the processing of metal-organic framework. These processes are adsorption, separation, clean energy, and fine chemical catalysis [22]. Processing of MOFs leads to the commercialization of materials and completes the application process. Availability of fossil fuels is decreasing and that leads to the increment of environmental issues emerging due to industrialization and cultivation. Mechanochemistry thus provides a solution to the environmental problem with the application of adsorption. Adsorption-based methods provide several environmental benefits including low energy input, good regeneration of adsorbents, easy operation, and high storage capacity. Mechanochemistry applies adsorption processes for storing hydrogen and methane gas that are termed clean energy [23]. Pollutants removed with the adsorbents like MOFs, treat polluted air, upgrade fuel, and help in treating wastewater. Hence, adsorption is the best way to solve environmental issues. Mechanochemistry in processing involves the application of separation. Separation is one of the most important processes required for the production of MOFs and other materials too [29].

Separation requires high time yet methods are applied to gain high efficiency in the process that could be achieved with the involvement of Mechanochemistry. The separation process includes adsorption gas separation where air, light hydrocarbons, noble gases, and isotopes are being separated. Another separation is based on the separation of liquid mixtures such as linear or branched alkane hydrocarbons. Separation could be done for membranes like gas separation of MOF thin films and oil/water separation [24]. Energy conservation is highly required in mechanochemistry for the green synthesis of MOFs. Production of MOFs could be gained with clean energy accumulation such as hydrogen storage, solar energy conversion, and photodegradation of water contaminants. Energy could be conserved with the implementation of electrical energy storage and conversion [25]. Fine chemical catalysis is used to increase efficiency, reduce waste, and cost and is termed eco-friendly reactants which are essential factors of mechanochemistry. Oxidation and hydrogenation could be used for fine chemical catalysis. Therefore, mechanochemistry provides high efficiency in maintaining the overall process that was implicated after the green synthesis of MOFs [26].

3. Materials and methods

3.1 Materials

Salt

Salts have been used as a metal source and can be classified into various organic acid salts and inorganic acid salts. Nitrates, carbonates, and sulfates are considered as most used inorganic salts whereas acetates, derivatized acetates, and other carboxylates are known organic acid salts. The difference in the salt which has the same metal ions lies in the difference of anti-anions that support the coordination ability and solubility. In the inorganic acid salts, counter anions show a significant effect in the ball milling method. Copper and zinc are the most studied metals in understanding the efficiency of mechanochemistry in the synthesis of the metal-organic framework. The reaction gets influenced by the presence of crystal water in the salt, especially for the non-grinding process. In the non-grinding method, crystal water acts as an auxiliary solvent. Only one crystal water is present in copper nitrate Cu(NO3)2.H2O that helps to obtain HKuST-1 under non-grinding conditions [31].

During the reaction, the counteractant anion of an organic salt is used to promote the deprotonation of the carboxyl group as it acts as a Bronsted base. The anion supports coordination with the metal ion and helps in the formation of MOF. Copper acetate is used as a metal source for the synthesis of MOF. The non-girdning method has been used in the study to understand the reaction of CuX2, FeCCO2)2, (HCO2)2, and (F6acac)2) that provided HKYST.1 as a product. In the present time Zn(OAc)2 has been used by the researchers for the synthesis of Zn-MOF that helps in obtaining MOF-5. Zn(OAc)2.2H2) can be used as a metal source to prepare the coordination polymers [33]. The reaction between carboxylic acid ligand and nickel acetate tetrahydrate has been used in the study that helps to understand that without any solvent Ni-MOF (Ni(BTC)2-12H2O)can be produced by grinding for a short period.

Oxide

Oxide has been used as a metal source that focuses on ZnO in the study. Various legends have been present to react with ZnO that include DAMCO mixed legging and hzBdC, different imidazole ligands, and fumaric acid. It has been found that imidazole ligands are the most reported ligands. ZnO easily reacts with the ligands as it is a highly active amphoteric oxide. CoO and CuO are the other oxides that are hard to use in the reaction. Mechanochemical methods are used to prepare the MOFs containing mixed metals [32].

Hydride

Hydride can only be used for the preparation of MOF as a metal source in few cases. To study the reaction with H3BTC under LAG conditions YH3 can be used as a metal source. Hydrogen present in the hybrid acts as strongly based ions that capture the hydrogen present in the ligand and allow it to easily coordinate with the metal ions [34].

Spheres-Mass Ratio

In the synthesis of MOF spheres, the mass ratio is one of the important factors that has been used in the study. 2.9 and 3.5 g spheres have been used in the study to understand the synthesis mechanism. Water has been used as an auxiliary solvent and as product Zn-MOF-74 has been obtained after 3.5m intake of grinding. DMF has also been used as an auxiliary solvent, under 2.9 g of ball milling conditions that help to form an immediate phase two about 20 min and provide a product of Zn-MOF-74 [35].

3.2 Methods

Methodologies are used to complete the study systematically as it provides various tools and techniques to fulfill the objective of the study. Research approach, research philosophy, research design, and data collection method are the various methodologies used in the study. Research philosophy provides a framework that helps to complete the study efficiently, Positivism, Intervism, Paragimitms are the various types of research philosophy that are used in the study. In this study positivism research philosophy has been used to find the method that helps to know the effect of mechanochemistry in the synthesis of MOF [5]. The authentication of the study gets increased with the positivist research philosophy. Deductive and Inductive are the two types of research approaches that are used in the study. In this study Deductive research approach has been chosen as it allows to collect of the data till the end of the research [37].

Various types of research designs are used in the study to provide a framework for collecting the data. Descriptive research design has been chosen as it provides descriptive information regarding the various methods of mechanochemistry that helps to deeply analyze its efficiency on the synthesis of MOF. Two types of data collection methods are present that help to collect the data. Primary and Secondary are the two methods used for collecting the data [36]. The primary source of data collection method needs direct involvement of the participants as it includes survey, observation, and questionnaires. In this study, a secondary source has been used for collecting the data. Secondary sources of data include pdf, journal, research paper, review paper, and published articles. The authentication of the study is enhanced by using a secondary source of data in this type of study.

4. Result and Discussion

4.1 Synthesis of Metal-Organic framework in mechanochemistry

Metal-organic frameworks have unique periodic pore structures as well as excellent properties that make them widely acceptable in adsorption, catalysis, separation, sensing, and biomedical fields. Ball milling is a method used for the synthesis of metal-organic framework (MOF). The high specific surface area, high porosity, modified chemical properties, and good thermal stability are the properties of MOF that allow them to be used in optical films and drug delivery. Hydrothermal methods, ultrasonic-assisted method, microwave-assisted method, and balling milling method are the various methods used for synthesizing the MOF [39]. Ball milling is used to blend materials by grinding powders into fine particles. It is considered a cost-effective and environmentally-friendly mechanical technique that is used in various areas such as mineral processing, metallurgy, construction, and synthesis of organic compounds. The reaction time of the ball milling method is short and has large preparation amounts. In the given figure, factors that influenced the synthesis of MOF have been reviewed that include metal source type, auxiliary additives, reaction conditions, and ligand type [38].

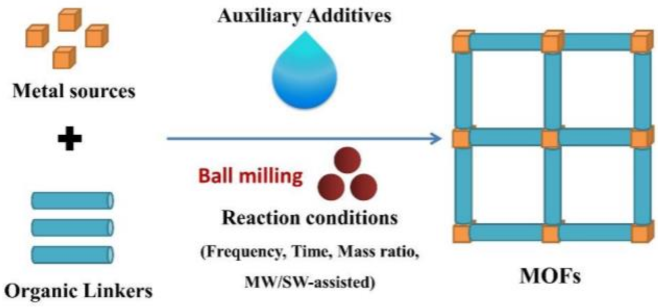

Figure 1: Scheme of the synthesis of the metal-organic framework by ball-milling

(Source: Wu et al. 2018) [48]

4.2 Effects of Auxiliary Additives

Neat Grinding (NG)

The below-given table shows the grinding process involved in the synthesis of MOFs. Two methods have been used for classifying the mechanochemical methods that are milling of reactants or grinding and another method involves the presence of additives for grinding. The activity of the reactants is increased by adding a small contribution of liquid that is good for the reaction [42]. The neat grinding method is the initial ball milling method where ball milling is directly mixed with solid raw materials to obtain the product. Copper isotonic acid Cu(INA)2 is the first synthesized MOF by the balling milling method. Cu(INA)2, Zn2(FMA)2 (BPY) are the other copper-based MOFs that have been synthesized with the help of ball milling methods. In the study, it has been found that neat grinding has been used for the reaction of 60 kinds of metal salts and organic linkers of five carboxylic acids. Powder X-ray diffraction has been used for analyzing where it has been found that crystalline products were found by 38 mixtures and 29 reactions were considered as quantitative [40]. (Cu(INA)2) and HKUST-1 are the two porous MOFs that were obtained in the study. Neat grinding doesn't require an auxiliary liquid and acts as a clean and non-polluting method. For the application in the MOFs synthesis, this method has been limited in various cases [50].

Table 1: Preparation of MOFs by ball milling

Metal source	Ligand	Auxiliary Solvent	Reaction Condition	Product
Cu(NO3)2, CuSO4	HINA; H3BTC	NG	30 Hz; 15 min	Cu(INA)2; HKUST-1
Zn(NO3)2	HINA; H2ADC; BPY;H3BTC	NG	30 Hz; 15 min	Cu(INA)2; HKUST-1
Ni(NO3)2, NiSO4	H2ADC	NG	30 Hz; 10-600 min	MIL-100(Fe)
Cu(NO3)2.H2)	H3BTC	NG,LAG	By hand; 20 min	TMU-8
Cu(OAc)2	BTC	DMF	30 Hz; 15 min	Cu(INA)2; HKUST-1
Fe(NO3)3.9H2O	INA	NG	20 Hz; 10 min	Ni(ADC)(H2O)4
Cu(OAC)2.xH2O	H3BTC	NG	30 Hz, 10-600 min	HKUST-1

4.3 Liquid Assisted Grinding (LAG)

The reaction activity gets enhanced by adding a small concentration of the liquid that makes the reaction faster and easier. Water, N, N-dimethylformamide (DMF), ethanol, and mixtures are used as auxiliary solvents in liquid-assisted grinding (LAG). The study has been done on the synthesis of Cu3(BTC)2 by taking water and ethanol mixed solvent to understand the effect of different solvent amounts. In the study, it has been found that Cu3(BTC)2 has been produced in the absence of solvent [41]. Crystal water is present in Cu(OAc)2 that is treated as an auxiliary solvent that improves the crystallinity of the product. The fluidity of the reactant is increased by adding an appropriate amount of external [49]. The crystallinity of the reaction becomes faster by increasing the amount of 50 to 400 ul. Nineteen common solvents have been studied on the effects of HKUST-1.

Hexane, toluene, cyclohexane, and dichloromethane are the weak polar liquid additives that have enhanced the reaction as compared to NG. The formation of HKUST-1 is facilitated by the aid of Protonix liquid additives. KUST-1 uses methanol as an additive that is immediately absorbed in the reaction mixture and after grinding for 5 min, maximum conversion was achieved. Conversion got slower by adding ethanol or isopropanol in the same volume in the reaction [43]. Acetonitrile, acetone is the polar aprotic liquid additive that is less efficient as compared to the protic liquids in producing KUST-1 formation. It can be concluded that the mechanochemical synthesis of HKUST-1 is highly influenced by the coordination ability of liquid additives. The auxiliary solvent is used for enhancing the rate of reaction and yield. Product types also get affected by using the various auxiliary solvent [48].

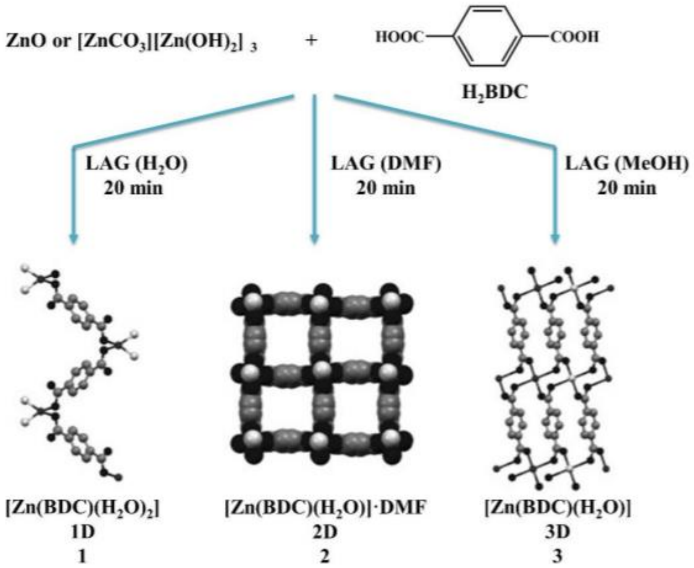

Figure 2: Synthesis of Zn metal-organic framework using liquid assisted grinding method with different auxiliary solvents (Source: Ye et al. 2020) [46]

4.4 Ion and Liquid Assisted Grinding (LAG)

Mechanochemical synthesis of MOFs can be assisted by using ions and liquid simultaneously. It has been demonstrated that MOF synthesis can be accelerated by a liquid-assisted grinding method. ZnO metal can be used in the MOF synthesis that has been demonstrated as the catalytic amount of simple salts. Template effects are used to induce the formation of the product structure. HIm, HEtlm, and LMelem are the three imidazoles that have been used in the study as shown in the given figure [46]. The synthesis of ZIF has been promoted through ammonium salt even in the absence of the liquid. An aqueous solution of tetramethylammonium hydroxide has been used as an auxiliary solvent to obtain the MIL [47].

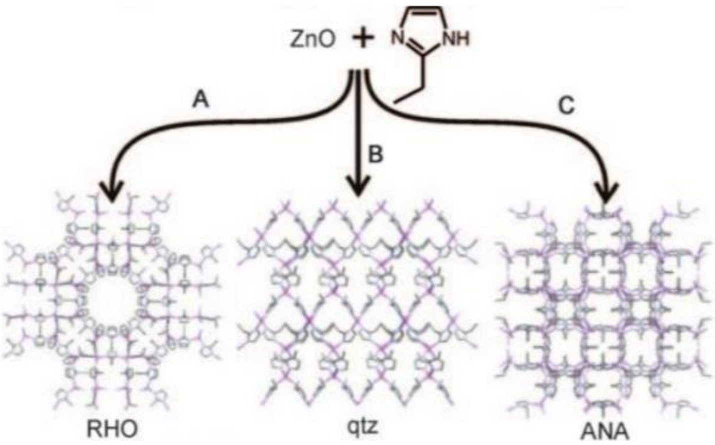

Figure 3: Overview of mechanochemical reactivity of ZnO towards ion and liquid assisted grinding, ILAG with NH4NO3 and ILAG with NH4CH3SO3.

(Source: Cao et al. 2019) [42]

4.4 Salt Assisted Grinding (SAG)

The ball milling method uses salts as a solid solvent to synthesize the MOF materials. NaCl is used as a solid solvent to improve the effectiveness of the mechanochemical synthesis pod in the micro and meso HKUST.1. Initial NaCl was pre-grind with Cu(OAc)2 and H3BTC respectively and then combined for 20 min of grinding that has been shown in the given figure. The effectiveness of the reaction increased with assisting these salts in synthesizing the MOFs as they improved the performance of iodine vapor capture [45]. The materials synthesized by the SAG method show the bumpy background features and some peak boundaries as compared to the LAG and single-crystal samples. This shows the presence of structural defects in those materials. Nacl gets trapped in the cavities during the mechanochemical synthesis that allows rearranging the structure [44].

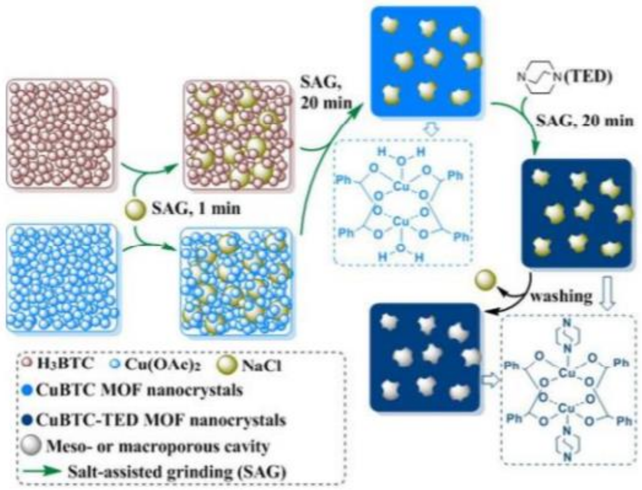

Figure 4: Scheme of salt-assisted grinding synthesis and post-synthesis of micro and macroporous HKUST.1

(Source: Qian et al. 2017) [41]

5. Conclusion

The concluded result of the study shows that mechanochemistry is the solution to avoid environmental issues that occurred with industrialization. Energy conservation plays an important role in maintaining the environmental balance. The study is centered to analyse the efficiency of mechanochemistry in maintaining the green synthesis of metal-organic frameworks. The study concluded that green-synthesis of MOFs are obtained with mechanochemistry that provides high efficiency. MOF production requires synthesis where green-synthesis is best for practicing. The present study is important to understand the concepts of MOFs and application of mechanochemistry and concluded results provide that structural characterization is required after synthesis. Characterization of MOF materials is important for the testing property. Stability is required for the processing of material and the stability could be mechanical, thermal, and chemical. Strategies methods are provided to gain stability and mechanochemistry provides the best and effective solution to gain stability. The objective of the study is fulfilled with appropriate methods and materials and also provides authentic results for the present study. Detailed information related to the green synthesis of MOFs fulfills the previous knowledge gap. A recommendation for the present study could be implemented for avoiding the present knowledge gap.

6. Recommendation

It can be recommended to used ball milling method for synthesizing MOF as it most simple and easy method that enhance the effectiveness of mechanochemsitry in maintain green synthesis of metal organic framework. Various high varieties of MOFs are present however they are limited, it is important to explore all the types of MOFs for green synthesis of metal. It is recommended to use various metal ion to increase the efficiency of the reaction that increase the synthesis of the MoF elements. It is recommended to adjust the various conditions of the ball milling reaction for decreasing the budget and it will helps in the large scale preparation of MOFs with high actual value.

Liquid can be added to improve the reaction that has insufficient activity. To solve the problem of using different auxiliary and ligand with different substituent's, it is recommended to pre-synthesize precursors that contain secondary structural units and carry out subsequent ball. It is recommended to used this study by the large scale industrial preparation of MOFs. For improving the reaction yield, it is important to understand the vairous auxiliary solvent. It is recommended to compare the various method used in the mechanochemistry to enhance the efficiency of green synthesis of MOF.

References

[1] Kong, Xiang-Jing, and Jian-Rong Li. "An Overview of Metal-Organic Frameworks for Green Chemical Engineering." *Engineering* (2021).

[2] Emam, Hossam E., Hani Nasser Abdelhamid, and Reda M. Abdelhameed. "Self-cleaned photoluminescent viscose fabric incorporated lanthanide-organic framework (Ln-MOF)." *Dyes and pigments* 159 (2018): 491-498.

[3] Ding, Meili, et al. "Carbon capture and conversion using metal-organic frameworks and MOF-based materials." *Chemical Society Reviews* 48.10 (2019): 2783-2828.

[4] Zimmerman, Julie B., et al. "Designing for a green chemistry future." *Science* 367.6476 (2020): 397-400.

[5] Zhang, Xinyan, et al. "Synthesis of MOF-derived Co@ C composites and application for efficient hydrolysis of sodium borohydride." *Applied Surface Science* 469 (2019): 764-769.

[6] Jagadeesh, Rajenahally V., et al. "MOF-derived cobalt nanoparticles catalyze a general synthesis of amines." *Science* 358.6361 (2017): 326-332.

[7] Meng, Jiashen, et al. "Generally oriented synthesis of precise carbon-confined nanostructures by low-pressure vapor super assembly and controlled pyrolysis." *Nano letters* 17.12 (2017): 7773-7781.

[8] Fan, Hongwei, et al. "MOF-in-COF molecular sieving membrane for selective hydrogen separation." *Nature Communications* 12.1 (2021): 1-10.

[9] Wei, Tz-Han, et al. "Rapid mechanochemical encapsulation of biocatalysts into robust metal-organic frameworks." *Nature communications* 10.1 (2019): 1-8.

[10] Głowniak, Sylwia, et al. "Mechanochemistry: Toward green synthesis of metal–organic frameworks." *Materials Today* (2021).

[11] Reinsch, Helge, et al. "Green synthesis of a new Al-MOF based on the aliphatic linker mesaconic acid: structure, properties and in situ crystallization studies of Al-MIL-68-Mes." *Chem. Eur. J* 24 (2018): 2173-2181.

[12] Sakamaki, Yoshie, et al. "Preparation and Applications of Metal-Organic Frameworks (MOFs): A Laboratory Activity and Demonstration for High School and/or Undergraduate Students." *Journal of chemical education* 97.4 (2020): 1109-1116.

[13] Bedia, Jorge, et al. "A review on the synthesis and characterization of metal-organic frameworks for photocatalytic water purification." *Catalysts* 9.1 (2019): 52.

[14] Howarth, Ashlee J., et al. "Best practices for the synthesis, activation, and characterization of metal-organic frameworks." *Chemistry of Materials* 29.1 (2017): 26-39.

[15] Ivanov, Vladimir, et al. "Thickness of vibrational mechanochemical solid-lubricant coating in friction pairs of transport engineering products." *IOP Conference Series. Earth and Environmental Science*. Vol. 403. No. 1. IOP Publishing, 2019.

[16] Wei, Fu-Hua, et al. "Synthesis and characterization of metal-organic frameworks fabricated by microwave-assisted ball milling for adsorptive removal of Congo red from aqueous solutions." *RSC advances* 7.73 (2017): 46520-46528.

[18] Abednatanzi, Sara, et al. "Mixed-metal metal-organic frameworks." *Chemical Society Reviews* 48.9 (2019): 2535-2565.

[20] Wang, Hsuan-Lan, et al. "Thermal stability of metal-organic frameworks and encapsulation of CuO nanocrystals for highly active catalysts." *ACS applied materials & interfaces* 10.11 (2018): 9332-9341.

[21] Yang, Dong, and Bruce C. Gates. "Catalysis by metal-organic frameworks: perspective and suggestions for future research." *ACS Catalysis* 9.3 (2019): 1779-1798.

[22] Ding, Meili, and Hai-Long Jiang. "Improving water stability of metal-organic frameworks by a general surface hydrophobic polymerization." *CCS Chemistry* 3.8 (2021): 2740-2748.

[23] Yang, Yunxia, et al. "Experimental studies of hydrocarbon separation on zeolites, activated carbons and MOFs for applications in natural gas processing." *RSC advances* 7.21 (2017): 12629-12638.

[24] Redfern, Louis R., and Omar K. Farha. "Mechanical properties of metal-organic frameworks." *Chemical science* 10.46 (2019): 10666-10679.

[25] Bellusci, M., et al. "Magnetic metal-organic framework composite by the fast and facile mechanochemical process." *Inorganic chemistry* 57.4 (2018): 1806-1814.

[26] Wang, Yang, et al. "One-pot mechanochemical synthesis to encapsulate functional guests into a metal-organic framework for proton conduction." *Chemical Communications* (2021).

[27] Liang, Jun, et al. "Cucurbituril─ Encapsulating Metal-Organic Framework via Mechanochemistry: Adsorbents with Enhanced Performance." *Angewandte Chemie* (2021).

[28] Karadeniz, Bahar, et al. "Controlling the polymorphism and topology transformation in porphyrinic zirconium metal-organic frameworks via mechanochemistry." *Journal of the American Chemical Society* 141.49 (2019): 19214-19220.

[29] Zimmerman, Julie B., et al. "Designing for a green chemistry future." *Science* 367.6476 (2020): 397-400.

[30] Howard, Joseph L., Qun Cao, and Duncan L. Browne. "Mechanochemistry as an emerging tool for molecular synthesis: what can it offer?." *Chemical science* 9.12 (2018): 3080-3094.

[31]. Xu, Jing, et al. "Validation of a deplasticizer–ball milling method for separating Cu and PVC from thin electric cables: A simulation and experimental approach." *Waste management* 82 (2018): 220-230.

[32]. Mukherjee, Nirmalya, Pintu Maity, and Brindaban C. Ranu. "Use of ball milling for the synthesis of biologically active heterocycles." *Green Synthetic Approaches for Biologically Relevant Heterocycles*. Elsevier, 2021. 167-187.

[33] Phanthong, Patchiya, et al. "Nanocellulose: Extraction and application." *Carbon Resources Conversion* 1.1 (2018): 32-43.

[34] Narayana, M. Venkat, and S. Narayana Jammalamadaka. "Tuning optical properties of graphene oxide under compressive strain using wet ball milling method." *Graphene* 5.02 (2016): 73.

[35] Liu, Z. Y., et al. "Modelling of carbon nanotube dispersion and strengthening mechanisms in Al matrix composites prepared by high energy ball milling-powder metallurgy method." *Composites Part A: Applied Science and Manufacturing* 94 (2017): 189-198.

[36]. Piras, Carmen C., Susana Fernández-Prieto, and Wim M. De Borggraeve. "Ball milling: a green technology for the preparation and functionalisation of nanocellulose derivatives." *Nanoscale Advances* 1.3 (2019): 937-947.

[37]. Tian, Yu, et al. "Polymer "Tape"-Assisted Ball-Milling Method Fabrication Few-Atomic-Layered Bismuth for Improving K+/Na+ Storage." *Energy & Environmental Materials* (2020).

[38]. Ye, Baoyun, et al. "One-step ball milling preparation of nanoscale CL-20/graphene oxide for significantly reduced particle size and sensitivity." *Nanoscale research letters* 13.1 (2018): 1-8.

[39]. Yang, Xinli, et al. "Preparation of LiNi1/3Co1/3Mn1/3O2/polytriphenylamine cathode composites with enhanced electrochemical performances towards reversible lithium storage." *Ceramics International* 45.8 (2019): 9726-9735.Protesescu, Loredana, et al. "Low-cost synthesis of highly luminescent colloidal lead halide perovskite nanocrystals by wet ball milling." *ACS applied nano materials* 1.3 (2018): 1300-1308.

[40]. Xiao, L., Zhang, Y., Wang, X., Hao, G., Liu, J., Ke, X., Chen, T. and Jiang, W., 2018. Preparation of a superfine RDX/Al composite as an energetic material by mechanical ball-milling method and the study of its thermal properties. *RSC advances*, *8*(66), pp.38047-38055.

[41]. Qian, Lingzhi, et al. "Two-step ball-milling synthesis of a Si/SiO x/C composite electrode for lithium ion batteries with excellent long-term cycling stability." *RSC advances* 7.58 (2017): 36697-36704.

[42]. Cao, Qun, et al. "A Ball-Milling-Enabled Reformatsky Reaction." *ChemSusChem* 12.12 (2019): 2554.

[43]. Kushimoto, Kizuku, Shingo Ishihara, and Junya Kano. "Development of ADEM–CFD model for analyzing dynamic and breakage behavior of aggregates in wet ball milling." *Advanced Powder Technology* 30.6 (2019): 1131-1140.

[44]. Cao, Qun, et al. "A Ball-Milling-Enabled Reformatsky Reaction." *ChemSusChem* 12.12 (2019): 2554.

[45]. Kushimoto, Kizuku, Shingo Ishihara, and Junya Kano. "Development of ADEM–CFD model for analyzing dynamic and breakage behavior of aggregates in wet ball milling." *Advanced Powder Technology* 30.6 (2019): 1131-1140.

[46]. Ye, Mengya, et al. "Effect of ball milling process on the photocatalytic performance of CdS/TiO2

composite." *Nanotechnology Reviews* 9.1 (2020): 558-567.

[47]. Sofla, M. Rahimi Kord, et al. "A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods." *Advances in Natural Sciences: Nanoscience and Nanotechnology* 7.3 (2016): 035004.

[48]. Wu, Zaoming, et al. "Effect of ball milling parameters on the refinement of tungsten powder." *Metals* 8.4 (2018): 281.

[49]. Xia, Min, et al. "Preparation of Bi2O3/Al core-shell energetic composite by two-step ball milling method and its application in solid propellant." *Materials* 12.11 (2019): 1879.

[50] Cao, Qun, et al. "A Ball-Milling-Enabled Reformatsky Reaction." *ChemSusChem* 12.12 (2019): 2554.