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A review on Metal-Organic Framework (MOF): Synthesis and Solid Catalyst Applications

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Abstract

Metal-organic of skeletons (MOFs) is a group compound that consists of an ion or metal group coordinated by organic ligands to make many-dimensional structured. MOFs are subclass by coordinated polymer with specialties porous structured. MOFs have a wide surface, flexible structure, and similar pore size. This MOFs many implicated in the industry for example to absorption of CO2 gas, saving energy, separation process, biomedical, sensors, and catalysts, etc. The goal of this paper is to compare the synthesis process of MOFs with some methods. Like solvothermal/hydrothermal, mechanochemical, microwave-assisted, sonochemical, electrochemical, and layer by layer synthesis. Moreover, it is to know the implementation of MOFs as a heterogeneous catalyst in the chemical industry. Based on the review paper conducted we know that MOFs synthesis with the used sonochemical method is well better than other methods. It is because the sonochemical method needs short crystallization time and eco-friendly and using energy like ultrasonic radiation (20kHz-10MHz). MOFs are can be used to fulfill like ***a*** *heterogeneous catalyst because MOFs have a wide surface, similar pore size, and has high thermal stability. MOFs application is a heterogeneous catalyst many used in the esterification process nor Transesterification and oxidation reactions.*

Keywords: MOFs, solvothermal, mechanochemical, sonochemical, solid catalyst.

I. INTRODUCTION

Metal-organic frameworks (MOFs) are porous crystalline materials consisting of metal centers or clusters with organic linkages where carboxylic acids containing N are usually used by frameworks with zinc, copper, chromium, aluminum, zirconium, and other elements (Lee et.al, 2013). Due to its large surface area, high pore volumes uniformly sized pores, flexible structure, and adjustable pore size, MOFs have widely used in CO_2 adsorption (Kitaura et. Al., 2003; Yang et. al., 2012), separation process (E. Haque et.al., 2010; E. Haque et.a al., 2011) storage processes (Zheng et. al., 2019), catalysis and others (Sony et al., 2019).

MOFs crystals can be applied as heterogeneous catalysts in various chemical reactions such as esterification and transesterification reactions (Jamil et. al., 2020), synthesis of cyclohexanone

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derivatives (Gao et al., 2020), oxygen reduction reactions (Ahmed, et. al., 2020), CO_2 cycloaddition (Jiang et. al., 2020), catalytic oxidation reactions (Fang et. al., 2020) and others. The use of MOF crystals as a catalyst can overcome the problem of heterogeneous catalysts because MOF has high porosity, high surface area, high chemical, and thermal stability, besides that MOF crystals are also easy to renew or modify (Sony et. al., 2019)

So far, MOFs are generally made by hydrothermal or solvothermal reactions using electric heaters which require reaction times varying from a few hours until several days. Other methods are used to reduce the time of synthesis reaction to obtain smaller and uniform crystals, such as with the help of microwaves, sonochemical, electrochemical, and mechanochemical methods.

In this review paper, we will describe the synthesis of MOFs which are formed from several metal compounds as inorganic connectors and various organic compounds as organic linkers. The methods reviewed for synthesizing MOFs include the solvothermal/hydrothermal method, microwave-assisted synthesis, electrochemical synthesis, sonochemical synthesis, and layer by layer synthesis. In addition to explaining the synthesis of MOFs, this paper also explains the application of MOFs as solid base catalysts in various chemical industry processes.

II. LITERATURE REVIEW

Generally, MOFs are formed from two main components, organic linkers or connecting ligands and metal ions. MOFs are made by combining organic linkers and metal ions to form crystal and porous networks. This process is referred to as modular synthesis. Various methods have been developed to obtain the best results in the synthesis process of MOFs. In general, the MOFs synthesis method is divided into conventional solvothermal methods and non-conventional methods (Sumida et. al., 2012)

II.1. Conventional Solvothermal Synthesis/ Hydrothermal

The hydrothermal synthesis technique has similarities with the solvothermal technique. The solvothermal synthesis technique uses non-aqueous solvents; otherwise, the hydrothermal synthesis technique uses a water solvent to dissolve the precursors or reactants. The use of water solvent to dissolve precursors is considered more practical besides being a common solvent which is quite abundant if we compare it to non-aqueous solvents in the solvothermal synthesis method. The principle of the hydrothermal technique is not much different from the principle of the solvothermal technique, namely heating the reactants in a closed container using a water medium where this closed system allows the pressure and temperature to increase rapidly. Hydrothermal/ solvothermal synthesis is generally defined as crystal synthesis or crystal growth at high temperatures and pressures. In conventional solvothermal synthesis, the organic linker and metal ions are mixed in a solvent and then heated using a glass bottle (for lower temperatures) or Teflon-coated autoclave or a bomb reactor (for temperatures higher than ~400 K) (Wang and Ying, 1999). The parameters that are controlled to obtain a certain structure consist of pressure, temperature, solvent composition, reagent concentration, etc. The temperature of the reaction mixture is the main parameter synthesis of MOFs. If the reaction temperature is higher than an effervescent point of the solvent, the reaction is called a solvothermal reaction and if the temperature is lower than the effervescent point of the solvent, it is called a non-isothermal reaction. The temperature of this reaction greatly determines the morphological properties of the formed crystals.

The advantages of hydrothermal/ solvothermal synthesis techniques include (1) powder formation directly from solution, (2) particle size and shape can be controlled using different starting materials and hydrothermal conditions, and (3) high reactivity of the resulting powder. While the disadvantages of this technique are (1) the solubility material must be known early, (2) the hydrothermal slurry is corrosive, and (3) the use of a high-pressure vessel will be dangerous if an accident occurs.

II.2. Non-Conventional Method

In this method, a mixture of metal salts and organic linker is ground using a mortar pestle or ball mill without using a solvent. After grinding, the mixture is slowly heated to evaporate water or other volatile molecules which are formed as a by-product. This method is also known as the mechanochemical method. In this method, the breaking of the intermolecular bonds by mechanical force occurs and is followed by a chemical transformation. This mechanochemical method is very environmentally friendly because it does not use any solvents and a higher yield product is obtained. MOF crystals with small pore sizes can be obtained in a short time of about 10-60 minutes. However, this method produces particles with irregular morphology and large sizes. In general, the raw material that is widely used comes from metal oxides when compared to metal salts. This is because the metal oxides produce only a by-product in the form of water (Sony et. al., 2019).

II.3. Microwave-Assisted Synthesis

Microwave coherence techniques have been widely applied to the rapid synthesis of nanopore materials under hydrothermal conditions and used organic synthesis. The energy used for the reaction in this method is obtained in the form of microwave radiation (MW). This technique has many advantages including a small and uniform particle size distribution, good morphological control, and a fast crystallization process. The first MOFs synthesized by this method is Cr-MIL-10 (Jhung et. al., 2005). This microwave technique method also has applied to the synthesis process of MOF which contains Fe^{3+}, Al^{3+}, Cr^{3+}, V^{3+}, Ce^{3+}.

Commercial microwave equipment already has a controllable power output equipped with temperature and pressure control devices. In the synthesis process uses the microwave technique, the sample in the form of a mixture of the substrate and the solvent is put in a Teflon vessel, tightly closed then put in the microwave unit and heated at a predetermined temperature and time. The microwave approached is applied that oscillating electric field that combined a permanent dipole molecule moment in coherence medium induces molecular rotation, results in quickly heating of liquid phase (Lee et. al., 2013).

II.4. Electrochemical Synthesis

The electrochemical synthesis of MOFs is carried out using metal ions supplied continuously through an anodic solvent instead of metal salts as the metal source. This solvent will respond with the dissolved link molecule and the conduction salt in the reaction medium. The use of the aprotic solvent in this method allows metal deposition on the cathode to be avoided, but in the process, H_2 is generated (U Mueller et. al., 2006). The electrochemical synthesis that is carried out continuously can be produce products with higher solid measure if compare to normal batch reactions.

In 2005 researchers at BASF conducted the first research on making MOFs using electrochemical methods. They developed a new synthesis procedure for the manufacture of MOFs using

1,3,5H_3BTC, 1,2,3H_3BTC, H_2BDC, H_2BDC- $(OH)_2$ as a linker, and Co, Cu, Zn, Mg as cathode materials (U Mueller et al., 2006). Schlesinger et al. (2010) researched the manufacture of HKUST-1 using the solvothermal method and the electrochemical route. The results showed that the product produced by the electrochemical pathway was of better quality due to connecting molecules fusion with and without conducting salt in the pores during crystallization.

II.5. Sonochemical Synthesis

The principle of the sonochemical method is utilizing ultrasonic waves with very high frequencies which are irradiated into a solution. When a solution is irradiated with ultrasonic waves, the solution collides between the particles that make up the solution with high pressure. Sonochemical synthesis methods through a process of homogeneous and accelerated nucleation can result in a much smaller reduction in crystallization time and particle size compared to conventional solvothermal syntheses (Gedanken A, 2004). Besides being able to shorten the crystallization time, this method is also more environmentally friendly because it uses ultrasonic radiation (20 kHz - 10 MHz) for the synthesis of MOF.

In the case of solids, micro jets are formed as a result of the cavitation process. This micro jet cleans, erodes, or activates the surface so that a dispersion of smaller agglomerated particles occurs. Chemical reactions can occur when ultrasonic radiation is applied to a homogeneous liquid. Qiu et. al (2008) was the first to perform the sonochemical synthesis of MOF $[Zn_3 (BTC)_2]$ in ethanol. The effect of reaction time on particle size is also researched in the sonochemical coherence of MOFs. A partial decomposition crystal over a long reaction time was obtained in the sonochemical synthesis of HKUST-1.

The sonochemical method has many advantages, besides the method is easier and the reaction path is faster, the sonochemical method also has the advantage of being able to break down large crystal aggregates into small crystal aggregates that can be nano-scale, faster reaction time, and more results, requiring more energy small with low reaction temperature, enable intermediate reactions, for the next reaction stage, for example, the calcination and reaction steps do not require a catalyst

II.6. Layer By Layer Synthesis

The layer by layer method is used by the manufacture of MOF flimsy. This method is based on surface chemistry in which a functional organic surface is immersed sequentially into a solution of metal ions and an organic connector. Based on research, the thickness of the film layer depends on the order through which the reactants are added. The stepwise formation kinetics in this method has been studied by use Surface Plasmon Resonance (SPR) spectroscopy. The main factors affecting the growth rate of the MOF film are the metal source and surface termination. Highly oriented growth has been observed by substrates functioning with different functional groups such as hydroxide compounds (-OH) and ester compounds (-COOH) (Sekhah et al., 2009).

Apart from this synthesis route, the MOF synthesis process can also be applied by other routes such as post-synthesis modification (when functional groups cannot be combined during MOF synthesis), chemical solution of deposition (for the manufacture of these films of MOFs), ionothermal methods (ionic liquids are used as solvents. Aiyappa et. al (2014) have reported on Fe-based MOFs made by Fe-metallogels through gel degradation. However, so far another MOF has not reported this method.

III. FINDING AND DISCUSSION

Heterogeneous catalysis is processed by the interaction of active sites in the solid surface with substrate and reagents in the gas or liquid phase. The important parameter of material catalytic activity is the wide specific area that active center located and accessibility to the active site. Because this interaction occurs in the interface between solid and fluid phases. Solid catalysts have the good catalytic capability if they have a large specific surface area.

MOF can be used as a heterogeneous catalyst because it has well-distributed pores and channels in the MOF allowing them to be selective in size and shape, such as zeolites. Although MOF has many advantages in its use as heterogeneous catalysis, this MOF catalyst also has several weaknesses. The major weaknesses of most MOF catalysts are less structural under reaction conditions and their inability to be reactivated by thermal treatment. Because some MOFs can change their structure after storage by the influence of humidity, like MOF-5. Other MOFs cannot stand contact with other reagents, especially those that can form solid metal-ligand interactions or can induce the reduction of metal ions. Like a general rule of thumb, MOFs is consisting of divalent metal cations such as Zn^{2+} or Cu^{2+} less stable than containing tri- or tetra-positive metal ions which form a stronger Columb attraction with negatively charged linkers.

The attendance of solid metal-ligand interactions in MOFs can be providing porosity permanent material and make it a possibility to remove dissolution molecules without the collapse of the structure. Based on research, MOFs have great potential to be developed as heterogeneous catalysts. in the MOF catalyst, the metal center is not completely obstructed by the organic or unsaturated ligands, that is, the labile ligands are inserted, which is a good catalyst because when the ligand is labile it is generally a solvent molecule and when it is released it leaves free coordination position on the metal.

For example, the material $[Cu_3\ (BTC)2]$ (BTC = 1,3,5-benzenetricarboxylate) HKUST-1, which the coordinated water molecules leave a coordination vacancy in Cu after thermal activation. Several other organic reactions also involve MOF nanopores as a catalyst. For example, the Knoevenagel condensation reaction is catalyzed using $[Cd(4\text{-tapa})_2(NO_3)_2]$ Hasegawa et al., 2014), (btapa= 1,3,5-benzene tricarboxylate acid tris [N-(4-pyridyl) amide]) or $[Cr_3F\ (H_2O)_2O\ (BDC)_3]$, (bdc= 1,4-benzene dicarboxylate). Jing Xu et al (2015) synthesized a new bimetallic complex Zn_4Ru_2 $(bpdc)_4.4C_2NH_8.9DMF]_n$ (H_2bpdc=4,4'-bifenildicarboxylic acid), which can absorb Ru (II) photosensitizer $[Ru\ (bpy)3]^{2+}$ and cobalamin derivative in the form of heptmethyl coordinate perchlorate (B_{12}) to form a complex B_{12}-Ru@MOF. The resulting heterogeneous catalyst can catalyze Dechlorination reactions and 1, 2 migration reactions by solid-state. For example, the catalysis of B_{12} is by using the MOF system (Jing Xu et. al., 2015).

Jamil et al (2020) researched making MOF catalysts derived from calcium and copper for biodiesel synthesis. The MOF catalyst more useful for biodiesel production because MOF has a medium surface area and more locations for catalytic applications so that biodiesel production is more stable. Copper-based MOF efficiently oxidizes alcohol as a heterogeneous catalyst, convert it is a suitable product that can promise catalyst by increased and stable biodiesel production. Coherences of calcium-based MOF with a multipurpose precursor-like carbonate are useful to processability and optimization of the transesterification process.

Jamil et al. (2006) researched the manufacture of Cu-MOF catalysts and Ca-MOF catalysts by solvothermal and hydrothermal processes. Detail characterization has been identifying the crystallographic and morphological structures catalysts being synthesized. Based on XRD analysis, it is known that Cu-MOF and Ca-MOF crystals have of each of 49.1 nm and 20.8 nm crystal sizes. SEM analysis showed a cuboid of 1.5 µm and 2 µm for Cu-MOF and Ca-MOF catalysts. The thermal stability of Cu-MOF up to 400 ° C and Ca-MOF up to 520 ° C was obtained from TGA analysis. Based on the crystallographic characterization and morphological structure, the Cu-MOF and Ca-MOF catalyst is very suitable for biodiesel synthesis. The application of Cu-MOF and Ca-MOF catalysts for biodiesel production showed biodiesel yields of 78.3% and 78%, respectively. The combination of Cu-MOF + Ca-MOF heterogeneous catalysts shows that 85% biodiesel yield is better than single combinations, so it is suitable for further enhancement. After ASTM analysis was carried out, biodiesel produced with Cu-MOF catalyst and Ca-MOF catalyst meets the standard as a fuel.

Fang et al (2020) development series on the structure of core/shell by Fe / Fe3C @ N-doped carbon hybrids which can be magnetically recycled via easy pyrolysis of a Fe-based MOF, NH2 - MIL - 88 (B) –Fe, for selective sulfur oxidation into a sulfoxide. Fe / Fe3C nanoparticles (with sizes mainly in the 20-30 nm range) are good encrusted in an N-doped porous carbon matrix, which effectively limits aggregation and growth of metal nanoparticles and promotes the wide-scale transfer of the reactants. This transition of metal-based hybrid provides a very efficient and stable catalytic performance about the oxidation of some sulfur to a suitable sulfoxide.

Besides general thermal catalysis, MOF is also widely used as a photocatalyst, including the generation of H_2 from water and the reduction of CO_2. Its use will be continuing, with an emphasis on semi-oxidation reactions, particularly water oxidation, which has not wide explore.

IV. CONCLUSION

Based on this paper, we can conclude that:

a. MOFs can synthesize use some methods i.e hydrothermal/solvothermal method, mechanochemistry method, Microwave-assisted Synthesis, electrochemical method, sonochemistry, and layer by layer synthesis.
b. The sonochemistry method has superiority if compared with another method because more eco-friendly and needs a short time in the crystallization process.
c. MOFs can apply as a heterogeneous catalyst because has a big and wide surface area, similar porous, and has high thermal stability.
d. MOFs application as a heterogeneous catalyst in the chemical industry among in biodiesel manufacturing processes, esterification and transesterification reactions, oxidation reactions, etc

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