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Metal-Organic Framework Based Chromium Terephthalate (MIL-101 Cr) Growth for Carbon Dioxide Capture: A Review

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ABSTRACT

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Lowering CO₂ emissions and the concentration of greenhouse gasses become major concern to overcome the global warming issue. One method to reduce CO₂ emissions is to implement the carbon capture and storage (CCS). In addition to developing the CCS technology, the investigations on materials that have high gas separation performance and low costs are also widely executed. A new type of crystalline porous material, metal-organic framework (MOF), which consists of metal ions and organic ligands in recent years as a promising type of adsorbent has emerged. MIL-101 Cr which is comprised of trimeric chromium (III) octahedral connected to 1,4-benzenedicarboxylates, one type of MOF, has attracted a lot of attention among researchers to develop the performance of CO₂ adsorption, since this chromium terephthalate has a large pore size (29 and 34 Å) and specific surface area attaining to more than 3,000 m²/g. Thermal stability and moisture resistance of this adsorbent make this material easily modified in post-synthesis, organic functionalization, cation doping, and composite type of MOF. In this study, we review the research and development of the synthesis, functionalization, and modification for the application of CO₂ adsorption in MIL-101 Cr.

Keywords:

MIL-101, CO₂ capture, adsorption, adsorbent characteristics, metal-organic framework

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1. Introduction

World energy consumption has grown explosively, and it is expected to liven up between 2012 and 2035 to 41% [1]. The Conference on the United Nations Framework Convention on Climate Change (UNFCCC) session which delivered the Paris Agreement in December 2015 has the mission of responding to the threat of climate change seriously by preventing the increase of earth temperature below 2 °C and reducing it to 1.5 °C [2]. To achieve this ambitious objective, the obligation to decrease CO₂ emissions as early as possible is very substantial to be executed. So far, the energy sector for the industry greatly depend to the usage of fossil fuel where the emission of greenhouse

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gases is the result of fuel-oxidizer combustion [3]. Therefore, the most economical mitigation scenario is by implementing the technology of Carbon Capture and Storage (CCS) for the next few years.

The CCS technology which has been commercialized in the power sector is the chemical absorption with amine solution to separate CO₂ gas from the flue gas which is the type of Post Combustion CO₂ capture technique [4]. As for, the drawback of this method is high energy usage to heat water which serves to regenerate the solvent around 70% by weight. Thus, it has an impact on the escalation of plant operating costs. The other carbon dioxide capture methods are adsorption methods which do not require additional heating and water just like the absorption which is the viable solution to be applied. The major concern in this adsorption method is to select the appropriate adsorber which has the suitable capacity, lifetime, rapid adsorption/desorption kinetics, stable, mechanical strength and selectivity which is easy to regenerate [5].

Some adsorbents which have been synthesized and investigated for the application of CO₂ are zeolite, activated carbon, silica, metal oxide, carbon nanotubes, carbon molecular sieves, and metal-organic framework [6-8]. The characteristics of adsorber with large surface area, low density and high pore volume are the attraction for researchers to investigate as gas storage applications. This characteristic is possessed by MOF. The easy external access of nanosized cavities facilitates the incorporation of substrate in the framework. Some modifications that have been made include the functionalization of combining metal ions and doping of organic molecules or nanoparticles. MIL-101 Cr with chemical composition Cr₃(F,OH)-(H₂O)₂O[(O₂C)-C₆H₄-(CO₂)₃·nH₂O (*n* ≈ 25) is one type of MOF with Lewis acid sites that can be activated by move the guest water molecules [9, 10].

MIL-101 Cr has good stability against moisture and other chemical properties, namely by heating it at 423 K to move air under vacuum condition. Thus, it will produce two coordinatively unsaturated open metal sites (CUS) per trimeric Cr (III) octahedral cluster [11]. Another attraction is the ease of functionalized ligand during the synthesis process or various types of chemical treatment of post-synthesis in organic ligands. Compared to other MOFs such as MOF-5 and HKUST-1, MIL-101 Cr is promising adsorber for future energy and good environmental applications due to its better physicochemical properties, chemical stability and texture. This paper reviews the recent progress on the synthesis, modification or functionality of MIL-101 Cr for CO₂ adsorption applications. This paper is organized as follows. A brief description of the structure, physical properties, and MOF synthesis are in section 2. Section 3 provides an overview of surface chemistry and synthesis of MIL-101 Cr that has been done so far by various researchers. Research into the development of MIL-101 Cr and modification of MIL-101 Cr composites are presented in section 4. Finally, summaries and directions for future work are presented in section 5.

2. Metal-Organic Framework (MOF)

2.1 Structure and Physical Properties of MOF

Two major constituent components of Metal Organic Framework (MOF) also known as porous coordination polymers (PCPs) are the latest breakthrough of porous material. It comprised of secondary building units (SBUs), metal ions and organic molecule or commonly known as linker (ligands), forming into three-dimensional lattices [12]. Both of the components are attached together by covalent bond to form 3-D infinite network structures as illustrated in Figure 1. This organic ligand makes the open porous structure of MOF as it creates the distance and space of each metal.

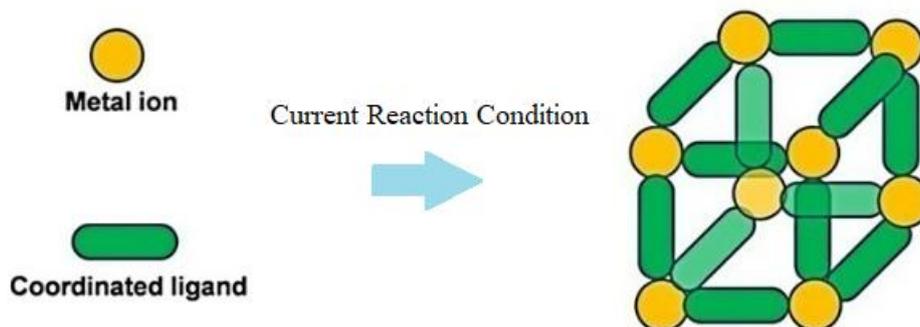


Fig. 1. Basic illustration structure of metal-organic framework [13]

A wide variety of metal ion in different coordination numbers and geometries is used such as linear, T- or Y-shaped, tetrahedral, square-planar, square-pyramidal, trigonal-bipyramidal, octahedral, trigonal-prismatic, and pentagonal-bipyramidal [14]. Whereas, for organic units/linkers are also varied, it could be electrically neutral, anionic, or cationic. Ligands with rigid backbones are often used as it is easier to predict network geometry in synthesis, and this rigid property can sustain the open-pore structure. The characteristics of MOF materials are well defined, highly porous, easily adjustable to be tuned for specific application, spatial confinement, and great geometrically and crystallographically framework structures [15]. The porosity reaching to several angstroms to nanometres by fine-tuning design makes this material has enormous potential as a media of gas sequestrate and gas storage such as carbon dioxide, methane, hydrogen, etc. Further, the giant pores of MOF can be achieved by two methods: 1) using modification of the building units (metal clusters or organic ligands) and 2) pre-constructing of precursor MOF by post-synthesis modification [16]. The ultrahigh surface area can be obtained by MOF. To date, the highest surface area of MOF was done by [17] which has succeeded doing the synthesis of MOF NU-110 without framework collapse or channel blockage which has BET surface area up to 7140 m²/g.

2.2 Synthesis of Metal-Organic Framework

There are various ways to perform MOF synthesis. Selection of MOF synthesis should be done to prevent the formation of defective metal-ligand or channel blockage. A wide variety of MOF material synthesis consist of five methods, which are namely, traditional synthesis (conventional synthesis), microwave synthesis, electrochemical synthesis, mechanochemical synthesis, and sonochemical synthesis. The summary description of each methods are illustrated in Figure 2.

The synthesis method which is often used in metal-organic framework is solvothermal synthesis. This conventional method uses polar aprotic solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethylsulfide (DMSO) and *N,N*-diethylformamide (DEF) to remove the void space of undesirable of guest molecules. The hydrothermal / solvothermal method uses an autoclave apparatus to heat MOF up to 10-48 hours. Férey, G *et al.*, [10] has investigated the synthesis of MIL-101 which is synthesized via hydrothermal method with chromium salt and H₂BDC as the metal ion and the ligand respectively. In the experiment, synthesis was performed with HF solution in an autoclave under autogenous pressure at 220^o C for 8 h. The reaction temperature, time, pH, solvent, and reagent concentration are the variables that affect the topology and MOF crystal size [18]. The variation of temperature is a factor that greatly influences the formation of MOF products. Higher temperatures will produce more dense structures and stronger morphology crystals [19]. Another important factor is the reaction times where the longer the duration of reaction, the

more degradation of MOF will be obtained. Therefore, it is important to know the equilibrium reaction in MOF synthesis to achieve the best result.

The second method of metal-organic framework is microwave-assisted synthesis. The utilization of microwave energy irradiation helps to provide energy to MOF. This energy is based on the interaction of electromagnetic waves and electrical charges [20]. Compared to solvothermal methods, this method is much faster, so it has advantages in high efficiency, phase selectivity and easy morphological control [21,22]. MIL-100 Cr was the pioneered of microwave synthesis study [23]. Similar experiments were also undertaken on MIL-101 Cr which was synthesized for 40 mins at 210^o C to adsorb benzene up to 16.5 mmol/g [24]. Other MOF experimental study on microwave-assisted synthesis, such as HKUST-1 in duration of heating for 1 h [25], MIL-53 Fe in 10 min [26], MOF-5 in 30 min [27], and IRMOF-3 in only 35 s [28] were also done to get time reduction in synthesis process.

Another rapid method of metal-organic framework synthesis which can be done faster at lower temperature is electrochemical synthesis which intends to remove anions in large-scale MOF production. Supply of anodic dissolution as a source of ionic metal is performed as a reaction agent against the solute linker molecule and the conducting salt in the reaction medium. Voltage-current density, electrolyte, temperature, and solvent are parameters in this synthesis to obtain proper MOF textural properties [29]. Shorter periods of synthesis than hydro or solvothermal methods are caused by the formation of reactive metal species in anodic dissolution. Preferably, the impurities in MOF more easily avoided and controlled with electrochemical synthesis [30]. Thus, electrochemical method was appropriate to be applied in synthesizing heterogeneous multiphase and multi-layered thin films [20].

Furthermore, MOF synthesis which does not involve solvent and utilizes ball-milling as a form of mechanical energy to break the intramolecular bonds followed by chemical transformation is the method of mechanochemical synthesis [31]. Duration of MOF particles can be obtained within 10-60 min. The use of liquid-assisted solvents in the grinding process can accelerate the reaction due to the increased mobility of the reactants in the molecule [32]. The mechanochemical synthesis method is particularly applicable to composite materials because of the homogeneity of dispersion and the mixture of different components which is a major function in this process [33].

The last method of MOF synthesis is a sonochemical reaction in which ultrasound waves can change physical and chemical reactions. Basically, the change in physical and chemical reactions does not occur because of the effects of the direct interaction between sound waves and chemical species, but because of the acoustic cavitation effect of the process, namely the generation and collapse of bubble [34]. The sonicator bar which is equipped by Pyrex reactor is used in this method with an adjustable power output without the usage of external heating, as a result it can accelerate the extreme cooling and heating rates ($>10^{10}$ K / s) which produce the fine crystallization [35]. The influencing parameters in this method are reaction time, temperature, solvent, and power level. MOF on a large scale is appropriate to be synthesized by this method, since the synthesis process does not need in long duration, efficient in energy usage, environmentally friendly, and at room temperature [35].

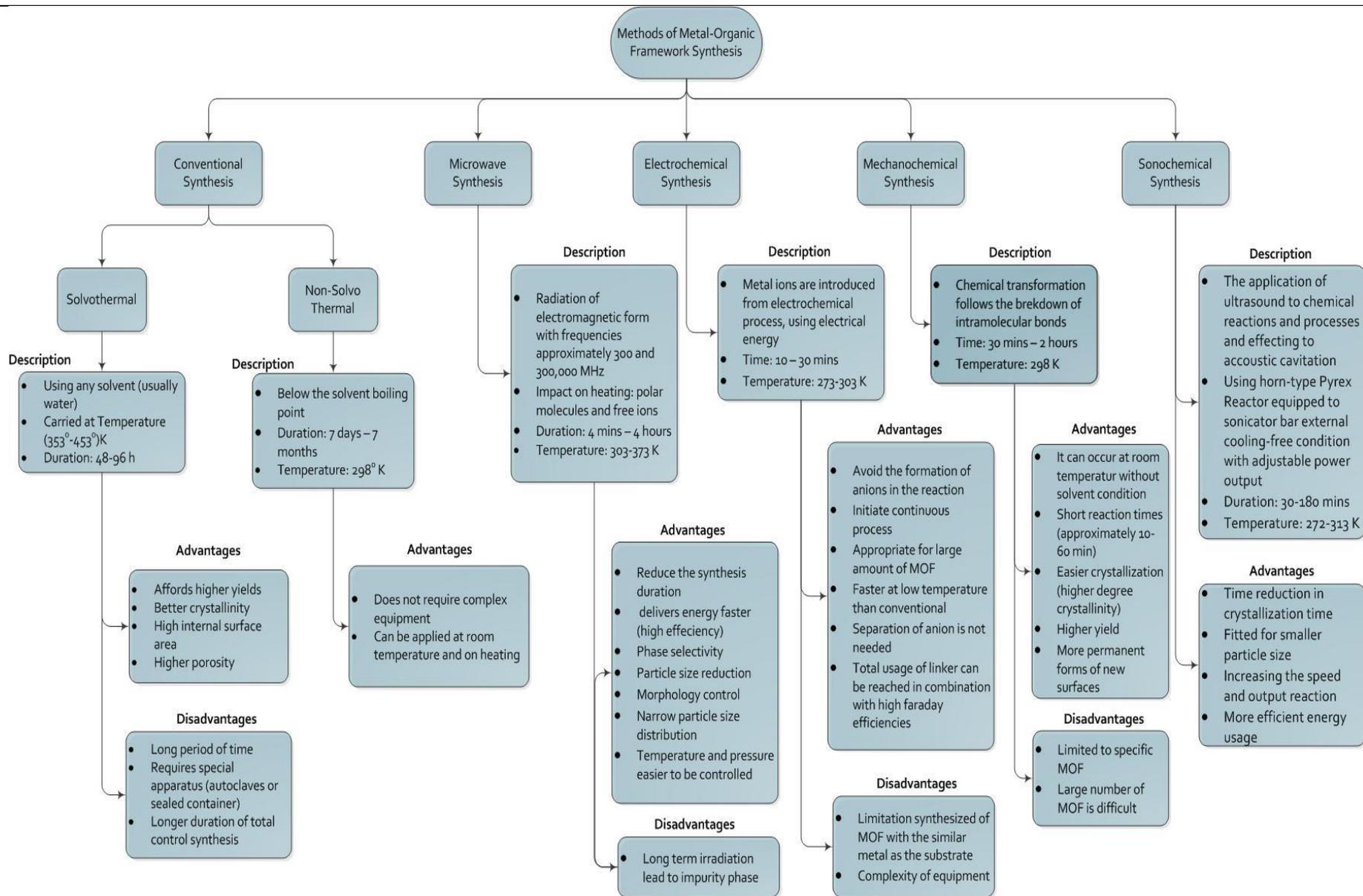


Fig. 2. Basic methods of synthesis of metal-organic framework

3. MIL-101 Cr

3.1 Surface Chemistry

Of all the MOFs materials, things that enthrall the concern of the researches in the application of MOFs material as the adsorbent are the huge pore size, large Langmuir surface, and enticing topology structure. One of the mesoporous materials of MOF which attract the most attention for research recently is MIL-101 Cr. To date, the largest Langmuir Surface area is owned by this material with the range of 4500-5500 m²/g [36].

MIL-101 Cr is a part of isostructural family of MIL-101 MOFs. Part of its group are MIL-101 Al [37,38], MIL-101 Fe, and MIL-101 Sc. In MIL-101 Cr, the cation of Cr³⁺ are connected to linker unit where the anion function is taken by 1,4-benzenedicarboxylic acid (BDC). Three chromium atoms in an octahedral surrounding with four oxygen of the bidentate dicarboxylates, one μ_3O atoms, and one oxygen atom from the terminal water or fluorine group acts as the inorganic trimers [11].

Specific surface area of MIL-101 Cr is calculated by Brunauer–Emmett–Teller (BET) method has range 3302 m²/g which has been done by [39] with a pore volume of about 1.4 cm³/g [40]. The average of ratio of two mesocages of MIL-101 is 2:1 with free internal diameters 2.9 nm and 3.4 nm and accessible windows of ~1.17 and ~1.6 nm in sequence [41,42]. The basic building of this type of MOF is illustrated in Figure 3.

Several studies have investigated the stability of MOF MIL-101 Cr, such as the resistance of this material to the steam containing nitrogen at varying temperatures and humidity up to 325 °C [43]. Furthermore, the experimental of the stability of MIL-101 Cr in deionized water at 323 K for 24 h was also carried out by [44]. In addition, the research on the stability of MIL-101 Cr was also undertaken by heating the material in the boiling temperature condition reaching to 100 °C in a closed vessel without stirring for 7 days [11]. Of all the previous numerous studies, it is found that MIL-101 Cr is the most promising MOF which can be used as an adsorbent because of its good stability.

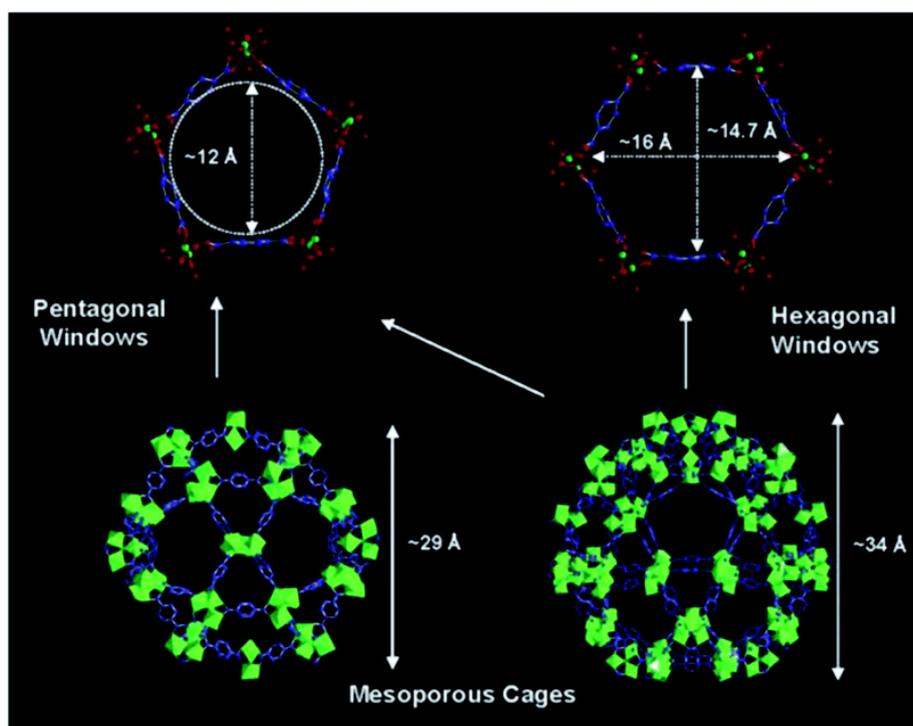


Fig. 3. Schematic representation of basic building unit and crystal structure of MIL-101 Cr [45]

3.2 Synthesis of MIL-101 Cr

The synthesis of MIL-101 Cr is being done extensively with the hydrofluoric acid free method recently. The study for the comparison of characteristics and adsorption by conventional synthesis and HF-free-synthesized method have been investigated by Liang *et al.*, [46] in 2013. The result showed that the adsorption of CO₂ relative to N₂ at pressure above 8 bar shows better performance, whereas for low pressure at temperature 25 °C, the conventional synthesis of MIL-101 Cr has higher yield. HF-free solvent is utilized recently as it still has good physicochemical properties comparing with traditional method and it supports environmentally synthesis condition.

In most cases, the traditional or conventional synthesis method is carried out by mixing Cr(NO₃)₃·9H₂O (0.400 g, 1 mmol), H₂BDC (0.166 g, 1 mmol) and HF (0.2 mL, 1 mmol) in water (4.8 mL, 265 mmol) and heated at 493 K for 8-10 hours. Then followed by some additional solvents such as water, DMF, ethanol and NH₄F [36]. This solvent is provided after a heating process to remove unreacted terephthalic acid. In addition, the additional treatment of adding tetramethylammonium hydroxide (TMAOH) which has been undertaken by Yang *et al.*, is investigated being the promotion of H₂BDC dissolution. MIL-101 has also been produced by Férey *et al.*, [42] in film form by immersing silicon wafer into MIL-101 nanoparticles in ethanol to form a film layer up to a thickness of 160 nm through dip-coating method at room temperature. The investigation of the film formation has also been conducted by Jiang *et al.*, by soaking dimethylacetamide (DMA) which was moistened with alumina plate in the reaction of Cr(NO₃)₃·9H₂O (0.400 g, 1 mmol), H₂BDC (0.166 g, 1 mmol) at 493 K for 8 hours [47]. They also escalate their investigation by immersing the alumina on MIL-101 with polyethyleneimine (PEI) with a dip-coating method to remove crack on MIL-101-PEI-n and MIL-101-NH₂-PEI-n with a thickness that can be controlled [48]. The result show that the film thickness reaching to 100-545 nm.

Another method which can be applied for MIL-101 Cr is microwave synthesis. Since the conventional synthesis takes several days to obtain material crystallization, the industrial scale is not appropriate for conventional method. Thus, it makes the microwave synthesis is the viable option. [24] investigate the effect of microwave synthesis in MIL-101 Cr. The result of his research, the faster crystallinity, giant porosity, and larger surface area are acquired compared to traditional synthesis. It is synthesized within 60 min at 483 K with the radiation 600 W. Furthermore, HF-Free synthesis has also been undertaken using this method at 473 K to produce non-aggregated nanoparticles and it has the product yield up to 37% [42][49].

Synthesis of MIL-101 Cr nanoparticles was also undertaken by dry gel conversion (DGC) method. This experiment was performed by Ahn *et al.*, [50] by grinding Cr(NO₃)₃·9H₂O with ball-milled which was then mixed with terephthalic acid and ground again for 15 minutes. The results of the mixture were placed in an autoclave stainless steel. Then, the solution of H₂O and HF are added which was then heated at 493 K for 12 hours. This type of synthesis produces BET surface area up to 4164 m²g⁻¹ with a single distilled water wash producing higher product yield up to 90%. Hereinafter, the authors also conduct the ligand functionalization by replacing terephthalic acid to 2-nitroterephthalic acid with HF-free synthesis. This method has several advantages, namely the minimum waste disposal, reaction volume that can be reduced, and high product yield. Thus, this method is appropriate to be applied in industrial scale.

The alternative approach for the synthesis of MIL-101 Cr for lowering the reaction time, temperature, and final cost has also been conducted by Pourebrahimi *et al.*, [51] The ultrasound or sonochemical synthesis is undertaken by mixing the precursors into the flask, then the ultrasonic generator (VXC 750) will be immersed in 493 K for 30 minutes. The author conducted a comparative study of three synthesis methods, namely the solvo thermal, microwave, and ultrasound synthesis.

The results found that the BET surface area from ultrasound synthesis produce a larger surface area, reaching to 2,671 m²/g. In addition, the crystallization rates increase along with the following sequence, solvothermal < microwave < ultrasound. Ultrasound and microwave synthesis procedures can be a promising synthesis in the future, specifically for smaller crystal sizes to shorten the reaction times and cost.

Over all the MOF synthesis methods, the majority of synthesis studies conducted on MIL-101 Cr recently are non-solvo thermal without the use of HF solvents. Other synthesis methods applied are dry gel conversion, microwave synthesis and sonochemical synthesis. The summary of the MIL-101 Cr synthesis method that has been done in several studies are presented in Table 1.

Table 1
 Summary of selected MIL-101 Cr synthesis method

| Synthesis Method | Solvent | Condition | Comments | Ref |
|---------------------------------------|---|-----------------------|--|---------|
| Traditional (Solvo Thermal Synthesis) | 1. H ₂ O with 1 M HF | 220 °C, 8 h | Structure analysis of MIL-101 | [10] |
| | 2. 2 ml HF, 50 ml Deionized Water | 220 °C, 8 h | Synthesis studies on adsorption of MIL-101 with GNP | [52] |
| | 3. 125 ml Deionized Water | 220 °C, 8 h | Synthesis of MIL-101 Cr incorporation with MWCNT | [53] |
| | 4. H ₂ O with TMAOH | 220 °C, 24 h | The alkaline effect towards the hydrogen storage behaviour | [36] |
| | 5. H ₂ O with CH ₃ COOH | 220 °C, 8 h | The VOC adsorption on MIL-101 | [54] |
| | 6. H ₂ O with stearic acid | 180 °C, 4 h | Size controlled of MIL-101 through monocarboxylic acid | [55] |
| | 7. H ₂ O, HF, and CTAB | 220 °C, 8 h | Synthesis of mesostructured MIL-101 cationic surfactant | [56] |
| | 8. H ₂ O, HF, and EG | 220 °C, 2 h | Synthesis of MIL-101 with Expanded Graphite (EG) | [57] |
| | 9. H ₂ O and 4-NTM | 150 °C, 24 h | Introducing 4-nitroimidazole (4-NIm) and H ₂ BDC as co-ligand | [58] |
| | 10. H ₂ O and NaOH | 220 °C, 8 h | Synthesis of MIL-101 Cr by using additives NaOH | [59] |
| | 11. H ₂ O, HF | 220 °C, 8 h | Characterization of Matrimid/PVDF into MIL-101 | [36] |
| Microwave Synthesis | 1. HF 48% | 220 °C, 1 h, 300 W | Study of adsorption and diffusion of Benzene in MIL-101 Cr | [24] |
| | 2. 50 ml H ₂ O, 0.2 ml HF | 210 °C 40 min, 1000 W | Study of MIL-101 Cr and HPW as catalyst | [24,60] |
| | 3. 3. H ₂ O and NaOH | 210 °C 1 h, 1200 W | The comparative study of microwave and conventional synthesis | [49] |
| Dry Gel Conversion | H ₂ O and HF | 220 °C for 12 h | High yield synthesis by dry gel conversion | [50] |
| Sonochemical Synthesis | H ₂ O with temperature controlled | 200 °C for 30 min | Facile Fabrication of MIL-101 Cr, the comparative of synthetic method in solvo thermal, microwave and ultrasound or sonochemical | [51] |

4. Experimental Studies of MIL-101 Cr as CO₂ Adsorption Application

CO₂ is the majority of gas greenhouses effect. Research on the development of MIL-101 Cr as solid adsorbent has been conducted extensively. Both theoretically and experimentally of CO₂ adsorption investigation in MIL-101 has been carried out by Teo *et al.*, [61] they reported that the best CO₂ capacity is 7 mol/kg at the pressure of 10 bar. It is also demonstrated by the Grand Canonical Monte Carlo (GCMC) simulation which vary the pressure from Henry's Region ($P \rightarrow 0$) to 35 bars. The more pressure, then the mole of CO₂ molecule becomes more increasingly attracted to the center of the framework. In addition, the isosteric heat of adsorption (Q_{st}) analysis is also carried out. It is found that the increment of Q_{st} value in the initial conditions of adsorption is caused by the lateral CO₂ interaction [39]. Llewellyn *et al.*, also reported that the heat of adsorption of MIL-101 is the highest of other MOF types reaching to 44 kJ/mol, and it has the same order of magnitude as zeolite as the interaction of chromium metal in CO₂.

The positive and negative effects of H₂O vapor is also reported by Xian *et al.*, who reports the presence of water vapor can reduce CO₂ adsorption capacity by 44% due to the competitive adsorption of water. In humid atmosphere condition, the adsorption rate is lower than dry atmosphere reaching to 1.37 mmol/g and 2.44 mmol /g, respectively. Furthermore, in dry atmosphere, the dynamic adsorption achieves 3.7 mmol/g [62]. Montazerolghaem *et al.*, [63] perform a comparative study of CO₂ adsorption on MIL-101 Cr in powder and pellet form. The experiment is carried out by volumetric method in three temperature variations (298.2, 310.2, and 320.2 K) and pressures up to 7.1 bar. The authors reported that the pellet form exhibit lower adsorption rate which only achieve 6.34 mmol/g at 298.2 K and 7.1 bar. They conclude that there is a 30% reduction in CO₂ adsorption capacity when MIL-101 Cr is presented in pellet form because of the reduction in surface area on the palletization process that blocked pores.

Another investigation of the humidity impact in the adsorption rate of MIL-101 has also been carried out by Liu *et al.*, [64]. The authors reported that CO₂ adsorption capacity increases marginally to 0.509 mmol/g at 10% RH. However, the decreased adsorption capacity occurs when the relative humidity reaches 10-100%. The flue gas effect, from the gas contaminants such as SO₂ and NO, is also examined by the authors. There is a reduction in adsorption capacity along with the increase in NO gas concentration, from 0 to 2000 ppm. Contradictory from the adsorption characteristics for SO₂ flue gas. There is only a very small degradation along with the increase in SO₂ concentration, namely 0.495, 0.481, 0.486, 0.478, and 0.49 mmol/g at the concentrations 0, 200, 500, 1000, and 2000 ppm respectively. Generally, MIL-101 Cr is not affected by the effects of flue gas contamination because the process that occurs is the physical adsorption process. Thus, MIL-101 Cr does not react chemically to the adsorption of the exhaust gas. In addition, due to the concentration of contaminant substances is lower than CO₂, the adsorption of CO₂ gas will always be greater. Several studies for variations in durability, stability, and comparative study of synthesized MIL-101 Cr have been summarized in Table 2.

Table 2
Various experiment techniques in MIL-101 Cr

| Research Study | Treatment | CO ₂ Uptakes | Highlight Information | Ref |
|---|--|--|--|------|
| Effect of water vapor in CO ₂ adsorption | CO ₂ -TPD is used under dry and wet condition (RH 50%). The measurement use Rubotherm magnetic suspension | 2.44 and 1.37 mmol/g in dry and wet condition respectively | The water vapor decreases the adsorption rate to 44% in RH 50% | [62] |
| Impact of flue gas contamination | The flue gas of NO and SO ₂ are varied from 0-1000 ppm | 0.495 mmol/g at 298 K | The concentration of SO ₂ has negligible effect in adsorption capacity | [64] |
| Comparative study of pellet and powder form | Using hydrothermal method by starch and sodium silicate as binder for the pellet form | 9.72 and 6.34 in powder and pellet forms respectively (298.2 K, 7.1 bar) | 30% of adsorption capacity rate decrease in the pellet form as the drop of surface area | [63] |
| Monoliths of MIL-101 Cr | Paste extrusion technique is used. Then continued by firing in a kiln for 33 h | 0.91 mmol/g at 25 ^o C, 2 bar | The monolithic pull down the adsorption rate to 36,81% | [65] |
| TSA adsorption for HKUST-1 and MIL-101 Cr | Solvothermal method, HF-free synthesis | 1.17 mmol/g at 30 °C, 48 kPa | The adsorption capacity of HKUST-1 is larger than MIL-101 Cr due to the small pores which can reinforce the adsorption field | [66] |

MIL-101 Cr is the most studied adsorbent type from MOFs which has been reported. It is caused by the large specific surface area and its greater physicochemical stability compared to other MOF [67]. Post synthesis guest encapsulation is performed on MIL-101 with the aim of increasing thermal stability and chemical stability. Escalating the micropore volume and specific surface area also attract the researchers to form a hierarchical porous structure of MIL-101 for greater CO₂ adsorption uptake. Moreover, by modifying the open metal site can increase the CO₂ adsorption capacity due to the differences in affinity of CO₂. To date, the post synthesis modification (PSM) which many scientists have done is by intermixing several chemical groups such as NH₂, OH, NO₂, and COOH as the strategy to increase the adsorption rate. Furthermore, the hybrid construction material added to MIL-101 Cr is also the solution to optimize this type of adsorbent, namely by adding some additional material, so that the MOF MIL-101 Cr composite will be formed.

Recently, MOF-based composite has been extensively researched by combining the mesoporous silica to reduce mass transfer resistance from guest molecules and to improve diffusion efficiency. Chen *et al.*, [67] for the first time constructed silica and MIL-101 Cr by hydrothermal synthesis method. A structure-directing agent is owned by MCM-41 which has good mesopore. With this merger, the type of adsorbent which is obtained is a composite MOF with smaller particle size, larger micropore volume, and larger surface area. Thus, the CO₂ adsorption rate obtained is 79% greater than the parent MIL-101 Cr. Furthermore, there is an increment in CO₂ diffusion and a reduction in

mass transfer resistance which results in a reduction in adsorption equilibrium time and an increase in the adsorption rate. Moreover, the investigations on the incorporation of carbon materials are also widely carried out in MOF modifications. Carbon material is believed to control particle size and induce MOF crystal growth to increase adsorption performance. As done by Kayal *et al.*, [68] who designs MAX-MIL, with in situ incorporation of Maxsorb-III activated carbon in the MIL-101 Cr structure. It is done to increase the gravimetric CO₂ uptakes. As so far, the large adsorption rate at MOF is only in volumetric. It is reported that MAX-MIL composite has 10% in volumetric and 15% in gravimetric better than MIL-101 Cr.

Zhou *et al.*, [69] reported the in-situ synthesis of GrO@MIL-101 for the separation of a novel composite adsorbent. MIL-101 Cr and graphene oxide are synthesized separately. The incorporation of GrO@MIL-10 is performed by adding GrO on MIL-101 Cr with a mass ratio of 1 GrO:10Cr(NO₃)₃·9H₂O with hydrothermal reaction. The combination of these two types of material is believed to increase the atomic density which can provide the dispersion forces and stronger electrostatic interactions to adsorb gas molecules at ambient pressure. From the result of the study, it is declared that the specific surface area is increased to 2,950 m²/g with pore volumes reaching to 1.42 cm³/g higher than the parent MIL-101. The authors described that the graphene layers and MOF crystal can form a new pore. CO₂ isotherms of this type of adsorbent is also measured in the variation of 298-303 K at the pressure to 25 bar. The lower the temperature, the smaller CO₂ uptakes are obtained which point out the CO₂ physisorption. About 22.4 mmol/g is adsorbed in this measurement of CO₂ adsorption, it attains 1.5 times larger than the parent.

Furthermore, the modification of MIL-101 Cr to obtain a high-quality adsorbent by accelerating the nucleation ratio and dissolution of the linker was also carried out by Zhou *et al.*, [70] by adding acetate, CH₃COO⁻, to chromium (III) terephthalate synthesis. The molar ratio modification of CH₃COOLi/Cr(NO₃)₃ and CH₃COOK/Cr(NO₃)₃ has been carried out. It is reported that the best molar ratio is 0.15: 1 which achieve the specific surface area to 3,401 m²/g and 3,398 m²/g for CH₃COOLi/Cr(NO₃)₃ and CH₃COOK/Cr(NO₃)₃ sequentially. By adding CH₃COO⁻ solution, it is confirmed that it can coordinate the terminal site which can improve the polarity and adsorption capacity of CO₂ adsorption.

The strong interaction of gases could also be enhanced by grafting the organic groups to the MOF for the existence of coordinative unsaturated metal sites. Some authors have performed amines to be grafted into MOF as done by Anbia and Hoseini [71]. The authors undertake the investigation of modifying MIL-101 Cr with pentaethylenhexamine (PEHA-MIL-101) via hydrothermal reaction by dissolving 20 g of toluene and 1 g of MIL-101 which will be refluxed for 12 hours at 373 K. Unfortunately, from the result of material characterization, the specific surface area and pore volume have reduced to 856 m²/g and 0.74 cm³/g respectively. The authors report that this degradation can occur since amine occupies the pore in MIL-101. Nevertheless, the measurement of CO₂ adsorption for PEHA-MIL-101 exhibits higher uptakes attaining to 2.67 mmol/g at 34 bar and 298 K compared to the parent MIL-101 which only achieve 2.08 mmol/g. Some amine group modification in MIL-101 are also undertaken by various researchers as this group is proven can intensify the performance of CO₂ uptakes [72-76]. Table 3 lists the result of the investigation of modification in MIL-101 Cr.

Table 3
 Summary of modification MIL-101 Cr

| Material | Specific Surface Area (m ² /g) | Total Pore Volume (cm ³ /g) | Temperature (K) | Pressure (bar) | CO ₂ Uptakes | Ref |
|--|---|--|-----------------|----------------|-------------------------------------|------|
| MIL-101 Cr with MCM-41 | 2,843.1 | 1.3 | 298 | 1 | 2.711 mmol/g | [67] |
| MIL-101 Cr with Maxsorb III | 2,670 | 1.27 | 240 | 1 | 60 cm ³ /cm ³ | [68] |
| MIL-101 (Cr, Mg) | 3,274 | 1.61 | 298 | 1 | 3.28 mmol/g | [77] |
| MIL-101 Cr with PFs | 2,174 | | 298 | 1 | 2.13 mmol/g | [78] |
| MIL-101Cr with GrO (Graphite Oxide) | 2,950 | 1.42 | 298 | 25 | 22.4 mmol/g | [69] |
| MIL-101 Cr with CH ₃ COOLi | 3,401 | 1.83 | 298 | 1 | 2.13 mmol/g | [70] |
| MIL-101 Cr with CH ₃ COOK | 2,971 | 1.62 | 298 | 1 | 1.45 mmol/g | [70] |
| MIL-101 Cr with ethylene diamine (ED) | 2,040 | | 296 | 1 | 2.7 mmol/g | [72] |
| MIL-101 Cr with diethylenetriamine (DETA) | 1,644 | | 296 | 1 | 3.6 mmol/g | [72] |
| 1% Li doped MIL-101 Cr | 2,019 | 0.96 | 220 | | 27 mmol/g | [79] |
| MIL-101 Cr with pentaethylenehexamine | 856 | 0.74 | | 32.5 | 2.67 mmol/g | [71] |
| Amine-functionalized MIL-101 Cr | 1,675 | | 289 | 25 | 14.8 mmol/g | [73] |
| PEI-300 with MIL-101 Cr | 495.23 | 0.35 | 298 | 2 | 5.7 mmol/g | [80] |
| Dual amine MIL-101 Cr | 96.4 | 0.37 | 298 | 1 | 3.6 mmol/g | [75] |
| MIL-101 Cr with 2-amino ethyl | | | 298 | 0.6 | 2.8 mmol/g | [74] |
| PEI-800 with MIL-101 Cr | 2,480 | 2.05 | | | 1.3 | [74] |
| MIL-101 Cr with graphene nanoplate | 3,032 | 1.41 | 298 | 40 | 20.62 | [46] |
| Mixed Matrix Membranes into MIL-101 Cr | | | | | 42.4 | [81] |
| MIL-101 Cr with 2-aminobenzene-1,4-dicarboxylate | 2,070 | 2.26 | 273 | 1 | 3.02 mmol/g | [82] |
| MIL-101 Cr/DETA-Ac | 1,259 | 0.76 | 298 | 1 | 2.46 mmol/g | [76] |

5. Conclusions

The primary energy source still comes from the fossil fuels. Various technical options to reduce the emission are appropriate for long term plan, whereas the CO₂ separation or capture is categorized as the mid till long term plan which is feasible to be applied. CO₂ adsorption which is one of the methods to sequester CO₂ provides the separation technique which does not spend high energy input and cost. Therefore, this method is the viable option to be implemented.

In this study, the CO₂ adsorption properties of MIL-101 Cr are reviewed. The surface chemistry and new synthesis method which has been developed are summarized. The usage of MIL-101 as an adsorber in CO₂ adsorption applications has been widely carried out. The specific surface area of MIL-101 can achieve in the range of 4,500-5,500 m²/g. The stability of this type of MOF have attracted

the concern of the researcher which has been proven through the heating experiment in boiling temperature. Most of the synthesized material is carried out by hydrothermal reaction with HF-free synthesis. However, MOF purification is still an obstacle in the synthesis step. Thus, a novel synthesis technique which results in high and effective purification should be continued. Recently, new synthesis method which have just been developed are microwave synthesis, dry gel conversion, and sonochemical synthesis which do not consume large amounts of energy and it only takes a short synthesis period. Thus, this method is appropriate for future application in industrial scale. From the results of the comparison study which have been done, the synthesis with dry gel conversion method can produce high product yield up to 90%.

A high thermal stability and good moisture resistance makes MIL-101 Cr being the promising adsorber which can be implemented in the future. There are many ways which have been done by scientists to improve this characteristic, including applying post synthesis modification (PSM) by mixing various chemical groups such as NH_2 , OH , NO_2 , and COOH^- , performing the modification of open metal site of MIL-101 structure, functionalizing the organic ligand or by involving organic/inorganic guest molecules, cation doping, doing the amine functionalized and the last but not the least is adding some material to MIL-101 to form composite adsorber types. Modifications to optimize the adsorbent MIL-101 will continue to evolve, since many industrial processes still require this technology until the adsorbent with a good capacity, lifetime, stability, and selectivity is obtained.

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