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Carbon (IV) oxide adsorption efficiency of functionalized HKUST-1, IRMF-1, and UiO-66 metal organic frameworks

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Abstract

The ever-increasing consumption of fossil fuels to meet up with the global economic and industrial energy needs has led to climatic change due to uncontrollable emission of a major greenhouse gas (CO_2). As a way of mitigating the amount of CO_2 in the atmosphere, search for effective and efficient solid adsorbent has been at the front burner of current scientific research. A class of solid adsorbent known as metal organic frameworks (MOFs) have demonstrated immense potentials for CO_2 adsorption due to its porous, high thermal and chemical stability, high versatility and ease of production. Upon functionalization, the adsorption efficiency of this class of materials was found to improve tremendously. In this review, the CO_2 capture and sequestration potentials of three MOFs (UiO-66, HKUST-1, and MOF-5) and their composites were investigated in the search for economical, stable, and highly selective novel adsorbents for CO_2 adsorption.

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1. Introduction

One of the major threats to the ecosystem is the continuous emission of greenhouse gases principally due to anthropogenic activities. A major glasshouse gas constantly emitted into the atmosphere by anthropogenic procedures is CO_2. Although CO_2 has diverse applications, it is a major cause of climatic change with its attendant unpleasant socio-economic cum political implications [1–3]. In recent years, several measures like cryogenic distillation, chemical absorption, membrane separation, and amine scrubbing have been developed aimed at taming the uncontrolled discharge of this gas in the atmosphere. The aforementioned strategies are marred with challenges that ranges from consumption of high energy during production, equipment corrosion rate, large absorber volume needed, and solvent regeneration [4–6]. These challenges have led to resort to the use of reticular materials for gas adsorption because of their low capital cost, high energy efficiency, ease of scaling-up, and large separation capability [7–9].

Among the solid reticular materials used for carbon diox-

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Email address: `haslina_ahmad@upm.edu.my` (Haslina Ahmad) ide adsorption, metal organic MOFs have gained huge interest dues to their large surface area and easy modification of their surfaces. MOFs are three dimensional porous compounds derived from secondary organic linker connected together with inorganic primary building blocks. MOFs possess large pore dimensions and a great diversity of interaction areas due to limitless number of organic linkers utilized for their skeleton [10–13]. Also, the high selectivity and adsorption capacity of MOFs is attributed to their open metal sites with appropriate geometries and pore sizes [10, 14, 15]

An important reticular material widely studied is a MOF known as Hong Kong University of Science and Technology-1 (HKUST-1) or Cu_3 $(BTC)_2$. HKUST-1 is comprise up of copper nodes joined with 1, 3,5 benzenetricarboxylic acid, forming Cu dimer referred to as secondary building blocks per crystallographic unit cell [16]. The 4 carboxylate group in SBU of HKUST-1 form coordinate covalent bonds with Cu^{2+} ions to which give rise to a 3-D system that is porous Figure 1 with $[Cu_3(BTC)_2(H_2O)_3]$n as chemical formulae [17]. In hydrated form, a unit of water molecule forms a coordinate covalent bond in axial position with HKUST-1 [18, 19]. HKUST-1 has an open system that is rigid and possesses a pore size distribution that is bimodal in nature. When suitably activated, the unsaturated metal areas of the MOF known as open metal sites (OMS) can be accessed as a result of the water molecules removal from the porous material leaving free areas in capped octahedral Cu (II) ions [20, 21]. The high surface area and accessibility to the free coordination of Cu (II) metallic ions for HKUST-1 are factors responsible for its wide applications [22–25]. Research has shown that the gas absorption capability of HKUST-1 MOF is enhanced by access to the free coordination of Cu (II) metallic ions [26–28].

Also, another prominent MOF worthy of investigation is the MOF-5 material Figure 2 also known as IRMOF-1, originally synthesized by Yaghi *et al.* [9]. MOF-5 is a crucial representative of the family of MOFs. It has a 3-D structure made up of terephthalic acid and Zn_4O metal clusters [7]. Possession of controlled pore structure, open skeleton structure, high thermal stability, and pore surface area are unique features of MOF-5 that make it to be widely investigated in electrochemistry, gas storage and separation, medicine, and catalysis [24, 29–31].

Furthermore, a reticular material that has demonstrated excellent capacity to adsorb CO_2 is a zirconium (IV)-based metal organic frame work (MOF) called UiO-66. This MOF is known for high porosity, chemical and high thermal stability, high versatility and ease of synthesis [32]. UiO-66 MOF has zirconium(IV) hexanuclear clusters as inorganic component and H_2BDC (1,4-benzenedicarboxylic) as organic linkers. Twelve BDC linkers form coordinated covalent bonds with the metal atom of the cluster through one of their carboxylate groups Figure 3. The face centered cubic structure of the crystal Figure 4 [33].

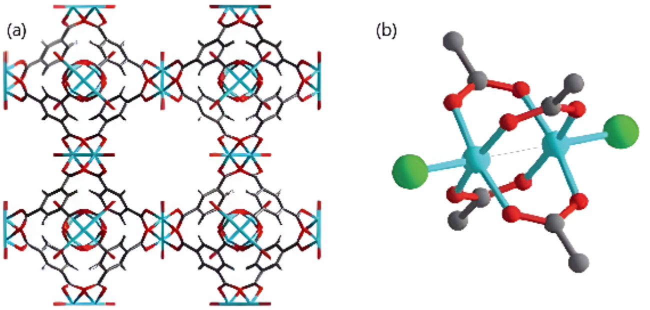

Figure 1. (a) Cubic structure of HKUST-1 and (b) the paddlewheel SBU. Light grey-H; Grey-C; cyan-Cu; and red-O [34, 35].

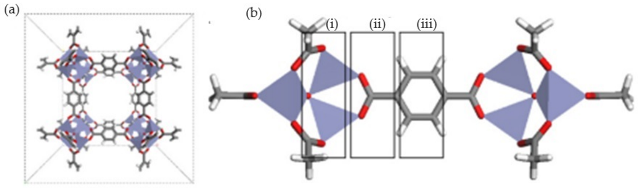

Figure 2. A typical structure of MOF-5. (a) The unit cell comprising of organic linkers and metal clusters is depicted as eight Zn_4OL_3 (L means organic linker) formula unit. (b) The position of adsorption are categorized into three different positions: (i) metal site, (ii) carboxylato site, and (iii) ring site [36].

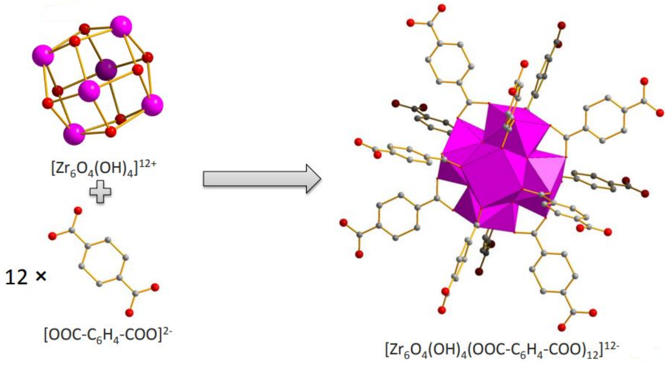

Figure 3. UiO-66 Crystal unit cell.

2. Methods of Synthesizing Metal Organic Frameworks

The MOFs production depend on some factors like time of reaction and temperature, nature of organic ligands and metal ions, solvent types, nodes size and structural features, kinetics of crystallization and the presence of counterions[37]. The classical method of synthesis is the Solvo-thermal method which requires high temperature and pressure. Other methods include; mechanochemical, electrochemical, microwave, and sono-chemical methods. These alternative methods are cheaper, faster, and produce cleaner products [38, 39]. The various MOF synthetic methods are presented as a chart in Figure 5.

2.1. Iono-Thermal and Solvo (Hydro)-Thermal Methods

In this procedure, solutions of a metal salt and a ligand are mixed in a closed vessel under autogenous pressure beyond the boiling point (usually diethyl formamide, dimethyl formamide, MeCN, EtOH, MeOH, H_2O, Me_2CO, or their mixtures) [37].

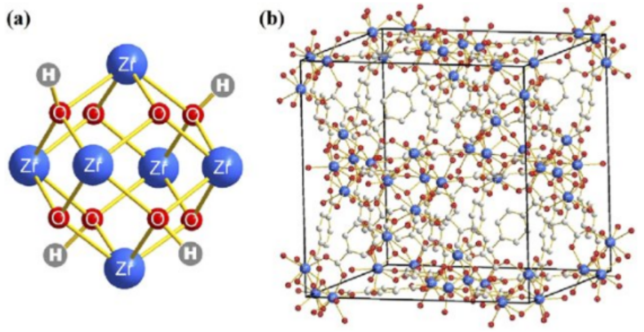

Figure 4. Crystalline structure of UiO-66: (a) Six center octahedral zirconium oxide units. (b) Face centered cubic structural units of UiO-66 (red atom: O, blue atom: Zr, and white atom: C.

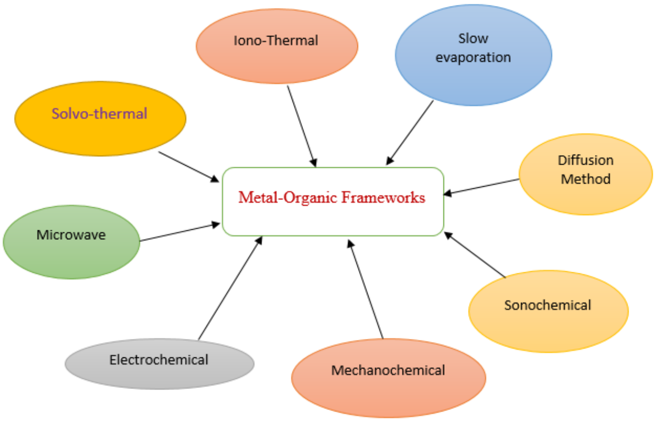

Figure 5. Methods of synthesizing Metal-Organic Frameworks.

The solvent used are usually polar and in the temperature range of 50–260°C. The reaction usually last for several hours. In the case of reactions carried out at temperature above 400°C, the Teflon lined autoclave is utilized. In instances where kinetically inert ions are used, the reaction temperature could be increased to enhance bond formation and promotes proper crystallization. Temperature has pronounced influence on crystal morphology and protracted reaction time could promote decomposition of the final products formed [37, 40, 41].

A type of Solvo-Thermal method known as the ionothermal synthesis makes utilization of ionic liquids (ILs) solvents. The use of eco-friendly ILs as solvents possess better advantages over the traditional organic solvents because they have high solubility for organic molecules, low vapor pressure, high thermal stability, and non-flammability. These features of ILs have made them outstanding reagents for the synthesis of MOFs and various classes of materials [42].

2.2. *Diffusion Methods and Slow Evaporation*

These two procedures are carried out at 25°C and requires no supply of energy. In the slow evaporation procedure, the reagents solution are mixed and allowed to evaporate slowly until crystals are formed at critical concentrations, favoring rapid crystal and nucleation growths. Sometimes, mixtures of solvents with low boiling points are added to hasten the crystal growth and nucleation [37, 43].

The diffusion method is utilized if the products formed are not soluble. Here, the reagents solutions, separated by a layer of solvents are placed on each other and diffused gradually by diving physical barriers. The crystals are produced at the interface between the layers following the diffusion of the solvent into the separate layers. In some instances, gels are deployed as diffusion and crystallization media [37, 43].

2.3. *Microwave Procedure*

This procedure is most suited for the production of crystalline MOFs such as small metal and oxide particles. Here, the solution temperature may be increased for 60 minutes or more leading to the formation of nanosized crystals. Synthesis of MOFs by microwave technique occurs at high speed and the shape and sizes of the crystals formed could be regulated. Though, this procedure cannot synthesize a crystal for single X-ray but through the adjustment of the temperature and concentration of the reaction system, nucleation occurs and crystals definite shape and size are formed [37, 43].

2.4. *Electrochemical Methods*

This method is applied in the synthesis of powdered MOFs in a commercial quantity. In this approach, the metallic ion is generated via anodic dissolution into mixtures of reactions comprising of the electrolytes and the organic ligand. The importance of this technique includes; low reaction temperature, very fast synthesis under milder conditions, and absence of anionic interferences like nitrate from metallic salt. MOFs for instance ZIF-8, HKUST-1, MIL-53(Al), NH2-MIL-53(Al), and MIL-100(Al) were produced via the electrochemical procedure [37, 43, 44].

2.5. *Mechanochemical Method*

This procedure is an option to the high pressure and temperature solvo thermal method that applies manual grinding of the reagents, instead of solvent, at 25°C to form coordination bonds. In some instances, little quantity of solvent is added to the reaction mixture in order to form, 2-D, 3-D, and 1-D coordination polymers. The method hastens reaction speed by promoting mass transfer, reduces particle size, reduces the heat of reaction, and locally melts the reagents. Its major advantages include; eco-friendliness, production of highly pure products, and high efficiency at a very short time frame. Its major drawback is found in its isolation of products that are not suitable for single crystal X ray investigations of structures [45–47].

2.6. *Sonochemistry method*

In this approach, the reaction mixture is exposed to strong vibrations obtainable from high-energy ultrasound in the range frequency of 10 MHz - 20 kHz, resulting in the creation of activation on the surface in the form of a local hot spot of a short life span having a high pressure and temperature which enhance chemical reaction and production of crystallized nuclei. It is energy efficient, eco-friendly, and unambiguous in application. The Sonochemical method of MOF synthesis has been applied in the synthesis of pure crystals of MOF-177 and MOF-5 having a size of 5–20 µm and 5–25 µm, respectively [37, 48, 49]. Table (1) presents the limitations and advantages of all the methods of synthesis of MOFs described above [50–53]

3. Characterization of Synthesized MOFs

Chemical characterization is concerned with the broad and general processes by which the structures and properties of synthesized MOFs are probed and measured. It focuses on the determination of the elemental composition, chemical constituents, and functional groups present in the compounds. Figure 6 presents the various techniques that could be used for characterizing MOFs [54–57].

Chemical Force Microscopy (CFM) is a method that could be deployed for chemical mapping of the surface of the MOF at the nanoscale by modifying the tip of atomic force microscopy to make sensitive to specific interactions. CFM makes use of chemically functionalized tip that enables an efficient chemical interaction between sample and tip. Thus, this method can be utilized to probe chemical information on the surface of the biological samples and materials at the spatial resolution of nanoscale [58]

X-ray Photoelectron Spectroscopy (XPS) could be utilized for characterizing the surface of a MOF to ascertain its surface assets as well as the composition and electronic states of the element present in the sample. In this technique, the XPS spectrum is obtained by subjecting the sample to a beam of X-ray and immediately determining the number of electrons and kinetic energy. Information obtained from XPS spectra gives the quantified composition of the outer few nanometers (< 10 nm) of a material [59].

Electron Paramagnetic Resonance (EPR) is a spectroscopic tool that could be deployed for characterization of paramagnetic complexes and detection of presence of reactive chemical intermediates. EPR is among the very few spectroscopic techniques that directly detect radicals in complex systems. It is specific for the analysis of species with unpaired electrons. The kinetic and thermodynamic stabilities of a sample could be investigated via this method too [60].

X-Ray diffraction analysis (XRD) is a nondestructive spectroscopic tool used to harness information about atomic structures because the source of electromagnetic radiation used (X rays) have wavelengths that are similar to atomic size. Information obtainable from this technique include their arrangement in each unit, spacing between the atomic plane, and the position of atoms. It is a tool that deal with the constructive interference of monochromatic X-ray and a crystal sample. Other information obtainable from this method include chemical composition, physical characteristics of the materials and crystallographic structure [61].

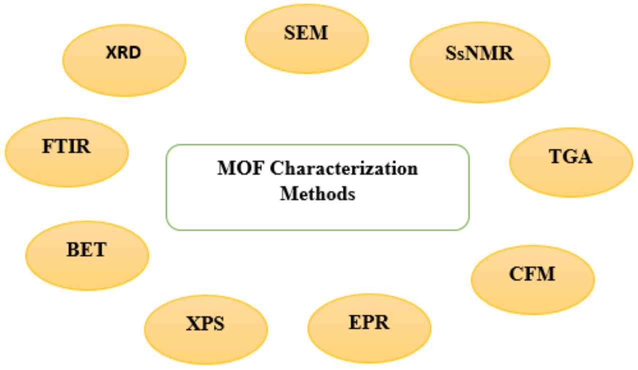

Figure 6. The advanced methods for MOFs characterization.

The Fourier Transform Infrared (FTIR) Spectrometry analyzes the chemical bonds and composition of a sample to ascertain its chemical makeup. This technique also measures covalent bonding pairs and functional groups in a sample [62].

Thermogravimetric analysis (TGA) is a tool that monitors the weight loss that occurs when a sample is heated at a constant rate. The information derived could be used to ascertain the thermal stability and volatility of a sample [62].

Scanning Electron Microscopy (SEM) is used to ascertain the morphology on the surface of the samples. Here, a magnified image of a specimen or surface is produced by a focused beam of high energy electrons instead of light. The signals obtained from electron sample interaction provides information pertaining to the chemical composition, surface morphology, crystal nature, and orientation of constituents of the specimen [62].

Brunauer-Emmett-Teller (BET) is used for analysis of a variety of solid matrices. It provides quantitative information on the specific porosity and surface area of materials. The isothermal adsorption of nitrogen at 77 K is used to implement BET measurements and the adsorption–desorption curves are used to assess the adsorption ability of the materials. BET is the main technique utilized to assess the pore volume and surface area of materials. However, the challenges of time consuming and complex experimental equipment, the requirement of large quantities of samples hamper the smooth application of BET to assess the structure of the MOF [63].

Solid State Nuclear Magnetic Resonance (SsNMR) is a spectroscopic techniques that has found immense application in the detection of dynamical effects and identification of structural parameters in materials. This technique could detect the availability of molecule or mobile substructure. A type of SsNMR known as 1-D exchange spectroscopy by sideband alternation could detect thermal motions and exchange processes in MOFs. Also, the dipolar center band which only detect the exchange (CODEX) is another type of SsNMR that could detect slow motions in milliseconds and seconds. However, the investigation of structural features of MOF itself is often done using the ^{1}H and ^{13}C NMR spectroscopy. SsNMR spectroscopy could also be used to investigate host guest interaction between the adsorbed guest species and MOF lattice which allow proper understanding of the mode of interaction [64].

Table 1. Experimental and literature density values of methyl acetate and the selected ketones at 25°C.

S/N.	Method of Synthesis	Advantage	Limitation
1	Solvothermal	-Provides versatile synthetic routes. -It allows for precise control of MOF's size and morphology.	-Low crystallinity -Transient stability of MOF-Generates large amount of solvent wastes -Requires high temperature and reaction time
2	Ionothermal	-Ionic liquids used are eco-friendly -Provides versatile synthetic routes -It allows for precise control of MOF's size and morphology	-Long operational time-Practically impossible to observe crystal growth
3	Electrochemical	-Great purity -Low reaction temperature -Absence of interference from anions of metal salts	-low output
4	Sonochemical	-Efficient -Fast -Does not require very high temperature	-limited heating depth
5	Microwave	- Efficient -Fast	-Expensive - Limited heating depth
6	Mechanochemical	-Fast -Environmentally friendly -High efficiency	-Products are amorphous - Unsuitable for single-crystal X-ray structural studies. -Difficulty in scaling up production
7	Diffusion Method	-Produces high quality MOF -Provides information about MOF microstructure	-Long synthesis cycle -Low yield -Difficult mass production
8	Slow evaporation	-Performed at room temperature -Low energy requirement	-It is specific for products that are not very soluble

4. Theoretical Chemistry Methods for Studying CO_2 Adsorption on MOFs

Theoretical Chemistry applies the concepts of classical mechanics, statistical mechanics and quantum mechanics to determine the dynamics and structure of chemical frameworks. The method of theoretical Chemistry incorporated into computer programs, referred to as Computational Chemistry has found immense applications in Chemistry [65]. Computational simulations help researchers to screen and characterize both existing and hypothetical structures of MOFs which are challenging to produce experimentally. It also assists in augmenting limited experiment studies on carbon dioxide dynamic within MOFs [66, 67]. Simulation techniques are basically made up of quantum-based calculations, Molecular Dynamics, Grand Canonical Monte Carlo Simulation, and Molecular Docking which are used predominantly to understand the relationship between the structure of porous materials and their characteristics [66, 67].

4.1. Molecular Docking Simulation

This technique is used to predict the binding interaction between one molecule known as ligand and the other known as macromolecular target (receptor). The binding affinity is usually recorded as Gibb's free energy change (ΔG). The lower the ΔG value of the ligand/target complex, the better the binding affinity, and vice versa [68, 69]. In the binding of ligands (L) to protein target (P) to form ligand –protein complex (LP), L and P constitute the reactants while LP constitutes the product. The reaction is represented by equation (1).

$$\mathrm{L} + \mathrm{p} \underset{\mathrm{K}_d}{\overset{\mathrm{K}_a}{\rightleftharpoons}} \mathrm{LP}, \tag{1}$$

where k_a and k_d are the binding and dissociation constants, respectively. These two constants are related by equation (2) at equilibrium.

$$k_a = \frac{[LP]}{[L][P]} = \frac{1}{k_d}. \tag{2}$$

[LP] in equation (2) represents the concentration of the ligand-protein complex while [L] and [P] give the concentrations of the ligand and the protein target, respectively. The reaction in equation (1) could be likened to a thermodynamic system in which L and P which constitutes the solutes undergo complex reactions and heat exchange with the solvent (i.e., water) and the buffer ions in the biological system. The standard Gibb's free energy change (ΔG^0) of the ligand –protein interaction is expressed by equation (3).

$$\Delta G^0 = -k_B \ln T(C^0 k_a) = -RT \ln(C^0 k_a), \tag{3}$$

where R = N_A x k_B, where, N_A, K_B, R, T, and C^0 are the Avogadro's constant (6.022 x 10^{23}), Boltzmann's constant (1.38 x 10^{-23} J/K), universal gas constant (R = 8.314$\mathrm{Jmol^{-1}K^{-1}}$), absolute temperature, and standard concentration of 1M for all reacting molecules, respectively. The negative value of ΔG^0 varies directly with the thermodynamic stability of the ligand –protein complex [70].

A very useful expression of $\Delta\, G^0$ in terms of chemical potential (μ) has also been provided by Statistical mechanics as shown by equation (4).

$$\Delta G^0 = \mu_{LP} - \mu_L - \mu_P$$

$$,$$

$$= -k_B T ln\left(\frac{C^0}{8\pi^2}\frac{\int e^{-(\mu_{rLP})+\left(\frac{S_{rLP}}{K_B T}\right)}dr(LP)}{(\int e^{-(\mu_{rL})+\left(\frac{S_{rL}}{K_B T}\right)}dr(L)(\int e^{-(\mu_{rP})+\left(\frac{S_{rP}}{K_B T}\right)}dr(P)}\right), \tag{4}$$

where μ_{LP}, μ_L, and μ_P are the potential energy of the complex, ligand, and protein respectively. The factors rLP, rL, and rP represent their corresponding internal coordinates (or conformations), while S_{rLP}, S_{rL}, and S_{rP} give their solvation energy values. The rotational degree of freedom of LP, L, and P are accounted for by the $8\pi^2$ factor [70].

4.2. *Quantum Chemical Calculation*

Detailed chemical and physical interactions between MOFs (adsorbent) and CO_2 (adsorbate) are simulated using the *ab initio* and density functional theory (DFT). In MOFs, CO_2 are bonded physically to its pores via van der Waals forces. These weak energy of interaction are accurately and reliably calculated through *Ab initio* methods such as the second-ordered Moller-Plesset (MP2) which has shown a measure of accuracy in describing the noncovalent interactions. The major drawback of MP2 is that it could only compute for small systems comprising of tens of atoms which may not be enough to characterize a multi-atom systems in microporous material [71, 72]

Relatively large systems could be reliably investigated using the DFT technique. The B3LYP, a DFT method possesses a high computational efficiency compared with MP2 and provides a finer approximation of electron correlation effect. Its major drawback is its poor reliability when calculating the long-range electrostatic interactions and the short-term van der Waal (vdW) potentials regarding simulation of CO_2 adsorption in MOFs [66, 73, 74].

A key factor worthy of note in a molecule is its ability to withstand both physical and chemical degradation. This unique property is influenced by energies of the frontier molecular orbitals comprising of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In the course of chemical reaction, the HOMO donates electron and the LUMO accepts electron. The energy difference (energy gap) between these orbitals computed using equation (5) determines the kinetic stability of molecules while the global electrophilicity index (ω) descriptor calculated using equation (6) influences their thermodynamic stabilities. Higher energy gap implies low chemical reactivity and excellent kinetic stability while higher ω value in a molecule implies its strong electrophilic behavior [68].

$$\Delta E(energygap) = E_{LUMO} - E_{HOMO}, \tag{5}$$

where E_{LUMO} and E_{HOMO} represents the energy of LUMO and HOMO, respectively

$$\omega = \frac{\mu^2}{2\eta}, \tag{6}$$

where η is the global chemical hardness expressed in equation (7) and μ the electronic chemical potential defined in equation (8)

$$\omega = \frac{\mu^2}{2\eta}, \tag{7}$$

$$\omega = \frac{\mu^2}{2\eta}. \tag{8}$$

4.3. *Molecular Simulation*

A more sensible and prospective technology for computing vdW interactions and predicting the gas adsorption properties within porous materials is molecular simulation forcefield and it has since been adopted as a better alternative to compute the CO_2 adsorption performance within MOFs and zeolites [75]. Molecular simulations comprises of grand canonical Monte Carlo (GCMC) and molecular dynamics (MD). Currently, molecular simulations is fast becoming a critical instrument for the exploration and investigation of adsorption capacity as well as the dynamic properties between various MOFs and CO_2 [76].

GCMC simulation is extensively employed to theoretically predict the adsorption of gas in porous materials and verification of experimental results. It allows the investigation of the thermodynamics of adsorption in rigid nanoporous material [76, 77]. GCMC mimic the adsorption of molecular fluids or mixtures within a rigid porous matrix of fixed volume (V) at specific temperatures (T) and chemical potential of the fluid (μ). In this simulation technique, arrays of configurations of the investigated system are generated in a stochastic, by random translational, rotational, and intermolecular displacements (configurations) of the molecule in accordance with each configuration's Boltzmann probability. GCMC also simulates molecular exchange between a material's pore and an external reservoir of bulk fluid, allowing direct simulation of thermodynamic equilibrium between the bulk and the adsorbate. It is worthy of note that the conditions of a Grand Canonical Monte Carlo simulation is similar to those of experimental adsorption measurements because each point of a GCMC derived adsorption isotherm is obtain via simulation at fixed μ,V, and T, and the full isotherm Nads(μ) is gotten via simulations at different values of μ, just like experimental isotherms measured as Nexcess(P), where P is the pressure of the external fluid. The macroscopic parameters obtainable from GCMC simulation include the absolute adsorption uptake (Nads) (i.e., the average number of adsorbates in the absorbent system) used in plotting adsorption isotherms. Another parameter obtainable from GCMC is the isosteric heat of adsorption [76, 78].

MD simulation is more appropriate for the investigation of structural and dynamic properties of adsorbate molecules (e.g gaseous molecules) in a wide range of materials. Aside determination of adsorption capacity, a crucial kinetic parameter worthy of investigation is the exploration of diffusion properties of the adsorbate within the adsorbent. MD simulation plays a important role in addressing this research gaps which is difficult to realize experimentally [76, 79].

5. Functionalization of MOFs with Amino Acid Based Ionic Liquids

Functionalization is a process of enhancing the gaseous adsorption capacity and selectivity of MOFs at low pressures by allowing them to form composites with other suitable chemical entities. In order to develop solvent-based technology for CO_2 separation, different kinds of absorbents have been proposed. Ionic liquids (ILs) adsorbent have drawn significant attention because they are nonvolatile, nonflammable, environmentally benign, and thermally stable. Also their chemical and physical properties are tunable, making it possible to design a specific IL for a specific CO_2 capture process. Furthermore, they have relatively high CO_2 solubility and selectivity as well as relatively low energy-demand for solvent regeneration. In addition to the aforementioned properties, a special type of IL known as amino acid based ionic liquids are relatively cheap, biocompatible and biodegradable, making them best option in the search for solvents for functionalizing MOFs [80, 81]

Owing to the large surface area of their pores, MOFs are convenient platform for designing functional adsorbents for CO_2 capture and sequestration. Hence, one of the topical challenges attracting the researchers' attention globally is functionalization of MOFs (Butova *et al.* 2016). Research has shown that functionalization of MOFs with amino acids improves their CO_2 adsorption efficiency. This is because functionalization brings about pore size adjustment, open metal site formation, and chemical modification of the porous materials [82–85]

Among the current research on CO_2 adsorption efficiency of amino acid functionalized MOFs is the work of Kinik *et al.* [84] wherein the authors studied the effect of encapsulating an amino acid based ionic liquid ([Bmim][PF6]) into ZIF-8 MOF with the aid of density functional theory (DFT) and Monte Carlo (MC) calculations. The authors concluded that the CO_2 selectivity was enhanced due to the new IL-created adsorption sites, which are occupied mostly by CO_2 molecules.

Zhao *et al.* [83] in their quest to improve the CO_2 adsorption performance of Cu-BTC, introduced l-arginine-functionalized lamellar graphene oxide into the MOF material. They found that the functionalization of Cu-BTC led to generation of new pores at the surface of the porous material and improved the CO_2 adsorption capacity of the material even at low humidity. The structural and chemical properties of the parent components and composite materials were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N_2 adsorption-desorption, thermal analysis and scanning electron microscopy (SEM). The authors further compared the CO_2 adsorption properties of the materials under different temperatures, flow rates and humidities

Lyu *et al.* [82] functionalized MOF-88 with 11 amino acids (AA) to produce a series of MOF-808-AA structures. According to the authors, the adsorption of CO_2 under flue gas conditions revealed that glycine- and DL-lysine-functionalized MOF-808 (MOF-808-Gly and -DL-Lys) have the highest uptake capacities. Enhanced CO_2 capture performance in the presence of water was observed and studied using single-component sorption isotherms, CO_2/H_2O binary isotherm, and dynamic breakthrough measurements.

Also, Cortes-Suarez *et al.* [85] in their work entitled ”Synthesis and Characterization of an SWCNT@HKUST-1 Composite:Enhancing the CO2 Adsorption Properties of HKUST-1” used single-walled carbon nanotubes (SWCNTs) as templates to grow rodlike HKUST-1 crystals. It was found that the adsorption of CO2 by HKUST-1 was enhanced by its functionalization with SWCNTs.

Abid *et al.* [86] synthesized amino-functionalized UiO-66 using 2-aminoterephthalic acid as an organic linker. The authors made use of X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and N_2 adsorption to characterized the physicochemical properties of the MOF. The CO_2 adsorption of the composite was investigated at both low and high pressure with the aid adsorption isotherms. The heat of CO_2 adsorption on amino-Zr-MOF was estimated to be 29.4 kJ/mol and the amino acid functionalized composite was found to possess better adsorption efficiency when compared to unfunctionalized UiO-66.

Koutsianos *et al.* [87] performed an assessment of the potential of post-synthetic defect exchange (PSDE) as an alternative approach to introduce amino functionalities at missing-cluster defective sites in formic acid modulated UiO-66. The researchers integrated pyridine-containing and aniline-containing monocarboxylates within defective UiO-66. The Non-defective UiO-66 were modified with linkers bearing the same amino groups (2,5-pyridinedicarboxylic acid and 2-aminoterephthalic acid) by classical post-synthetic ligand exchange (PSE). The authors found that PSDE reduces the porosity of defective UiO-66 and improves both the CO_2 uptake and the CO_2/N_2 selectivity, whereas PSE has no effect on the porosity of non-defective UiO-66 but improves the CO_2 uptake, leaving selectivity unchanged.

5.1. *Previous In silico Studies on CO2 Adsorption Capacity of UiO-66, MOF-5, and HKUST-1*

Among the recent theoretical studies on CO_2 adsorption potentials of UiO-66 is the work of Huang *et al.* [88] wherein the authors used molecular dynamics simulations to study adsorption kinetics of Zr-MOF adsorbents as well as sorbent structures optimization. The Monte Carlo method was used by the researchers to simulate the CO_2 adsorption capacity of the porous material. They found that the CO_2 uptake of UiO-66-NH_2 under room temperature and pressure reached 134mg/g-sorb. Also, the CO_2 adsorption capacity of the adsorbent under low pressure (less than 120kPa) was found to be mainly determined by the pore properties and surface modifications, while the steric hindrance had little influence. The ideal separation factor of UiO-66-NH2-50 was calculated to be 39.7, which showed the excellent CO_2/N_2 separation performance at 298K.

Ethiraj *et al.* [32] made use of DFT calculations with the hybrid B_3LYP functional to investigate the CO_2 adsorption on UiO-66-NH_2. The authors found that the interaction of the porous material with CO_2 occurs mainly around the hydroxyl and the synergistic effect of OH and NH_2 functional groups increases the binding energy up to 34.0 $kJmol^{-1}$, in agreement with the experimental results.

Arjmandi *et al.* [89] made use of Density Functional Theory (DFT) calculations techniques to study CO_2 adsorption in NH_2-, OH-, COOH-, Br- and Cl-functionalized IRMOF-1. The authors investigated the adsorption phenomenon by performing Geometry optimization, density of states (DOS), and energy analysis. The binding properties of pristine H_2BDC and X-H_2BDC as well as their complexes with CO_2 were calculated and analyzed theoretically in terms of binding energies, band structures, total density of states, and Mulliken charges. The authors found that the interaction energies were higher in COOH-H_2BDC, OH-H_2BDC and NH_2-H_2BDC complexes than in Br-H_2BDC and Cl-H_2BDC complexes.

Yang's group conducted a combined GCMC simulation on the selective CO2 adsorption efficiency of Cu-BTC on CO_2-containing gas mixtures. The simulation results revealed that the strong interactions between quadrupole moment of CO_2 and Cu^{2+} ions of the MOF could improve the CO_2 selectivity at low pressure [90].

6. Challenges and Future Prospects

The outcome of the above studies has revealed that HKUST-1, MOF-5 (IRMF-1), and Ui0-66 are promising adsorbents for CO_2 capture and sequestration owing to their high surface area, high porosity, and well-defined structures. However, the synthesis of MOFs is capital intensive owing to lack of industrial- scale manufacturing facilities, sophisticated and time-consuming batch operations with complicated separation techniques and high cost of organic solvents [91, 92].

Also, poor water stability and lattice defect are potential challenges that affects the design of effective MOFs for CO_2 adsorption. However, the former challenge could be mitigated through the use of highly charged metal ions, use of highly rigid ligands in constructing MOFs to strengthen the coordination bond connecting the metal ions nodes to the organic linkers, and the use of hydrophobic functional groups of different sizes and lengths via post synthesis modification aimed at minimizing contact between water molecules and the coordination bonds to prevent MOF hydrolysis. In addition, the challenges of lattice defect could be overcame via surface hydrophobization, buffer action of sacrificial bonds and MOF's modification with armor [93–96]

7. Conclusion

CO_2 is the major contributor of greenhouse gases that has posed serious environmental hazards to the ecosystem. Thus, the capture and sequestration (CCS) of this gas has proved to be one of the most efficient method of confronting the challenges of climate change and as such applied in industry for the sustainable economic development. The traditional commercial CO_2 adsorbents are faced with challenges of low uptake capacity, poor selectivity, high regeneration energy, slow kinetics, and short cycling life span. More efficient and effective adsorbents for CO_2 CCS include UiO-66, HKUST-1, and MOF-5 MOFs owing to their porosity, significant thermal and chemical stability. *In Vitro* and *in silico* studies has shown that the CO_2 adsorption efficiency of these MOFs improves tremendously when functionalized with amino acid based ionic liquids. Hence, the design of amino acid functionalized UiO-66, HKUST-1, and MOF-5 adsorbents for CCS would be a sustainable avenue of mitigating climate change and its attendant ecological hazards.

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