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Adsorptive removal and separation of chemicals with metal-organic frameworks: contribution of π -complexation

Nazmul Abedin Khan and Sung Hwa Jhung*

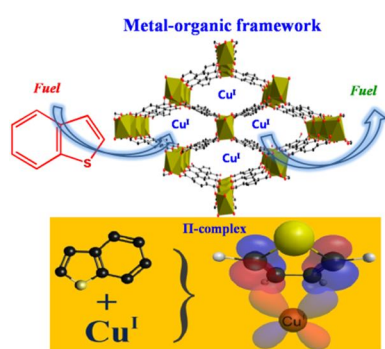
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Graphical abstract:



Highlights

- Adsorptive removal and separation of chemicals with MOFs are reviewed.
- Especially contribution of π -complexation are summarized.
- MOFs have great potential in adsorption and separation via π -complexation.
- Next possible/important research topics are suggested.

Abstract:

Efficient removal and separation of chemicals from the environment has become a vital issue from a biological and environmental point of view. Currently, adsorptive removal/separation is one of the most promising approaches for cleaning purposes. Selective adsorption/removal of various sulfur- and nitrogen-containing compounds, olefins, and π -electron-rich gases *via* π -complex formation between an adsorbent and adsorbate molecules is very competitive. Porous metal-organic framework (MOF) materials are very promising in the adsorption/separation of various liquids and gases owing to their distinct characteristics. This review summarizes the literature on the adsorptive removal/separation of various π -electron-rich compounds mainly from fuel and gases using MOF materials containing metal ions that are active for π -complexation. Details of the π -complexation, including mechanism, pros/cons, applications, and efficient ways to form the complex, are discussed systematically. For in-depth understanding, molecular orbital calculations regarding charge transfer between the π -complexing species are also explained in a separate section. From this review, readers will gain an understanding of π -complexation for adsorption and separation, especially with MOFs, to develop new insight for future research.

Keywords: Adsorption; metal-organic frameworks; review; separation; π -complexation

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1. Introduction

1.1 Adsorptive removal/separation of chemicals with metal-organic frameworks

Adsorption can be superior to other techniques for removal/separation of chemicals because of its comparatively low cost, variety of applications, simplicity of design, easy operation, low amount of harmful secondary products, and the simple regeneration of the adsorbents [1]. Since the invention of various porous materials and the huge development in adsorptive separation processes, adsorption is the key separation technique in industries. Porous materials including activated carbons [2], zeolites [1], and metal-organic frameworks (MOFs) [3-5] were studied comprehensively for the adsorption/separation of various molecules from liquids, vapors, or gases. For efficient adsorptive removal, porosity, pore architecture, and favorable adsorption sites are required [1]. In addition, some active species such as functional groups (acidic or basic), metal ions, metal oxides, metal salts, ionic liquids, and polyoxometalates are generally introduced to the porous sorbents for selective uptake of adsorbates through some common interactions such as acid-base interactions[6-9], π -complexation [10], π - π interactions [7, 11], and H-bonding [7, 12-17].

MOFs are principally composed of two key components: a metal ion or a cluster of metal ions and an organic molecule known as a linker (see Fig. 1). The organic units are usually di-, tri-, or tetradentate ligands. The attention given to MOFs is due to the huge porosity and facile tunability of their pore size/shape from the microporous to the mesoporous scale *via* alteration of the connectivity of the inorganic moiety and the organic linkers [18, 19]. As well, as shown in Fig. 2, several analogous MOFs [18] can be built from (i) the same ligand and different metal ions, (ii) identical metal ions and different ligands, and (iii) MOFs with functionality in the linkers. Furthermore, MOFs have numerous potential applications including adsorption/separation and storage [20-26]. Because of the potential applications of

MOFs in various fields, not only research on MOFs but also the number of publications (per year) related to MOFs has increased rapidly (Fig. 3). MOFs are promising solids for adsorption/separation-related applications because of the easy modification of pore surfaces, which leads to selective adsorption of specific guest molecules with particular functionalities. In addition, the central metal ions, coordinatively unsaturated sites (CUSs), and functional groups on the organic linkers were employed effectively for further interactions between the adsorbate molecules and MOF-based adsorbents; this makes MOF-type materials superior to other porous sorbents in the efficient adsorptive removal/separation of hazardous molecules [7, 10, 27, 28]. In this review, our main focus is the adsorption/separation of various compounds with π -complexing adsorbents, based mainly on MOFs. Therefore, the MOFs themselves will not be discussed in detail, since there are many outstanding review articles on MOF-type materials and their applications [29-31].

Sulfur- or nitrogen-containing organics are naturally occurring species that exist in fossil fuels such as crude oil, diesel, gasoline, jet fuel, and heating oil. Currently, around 85% of global energy originates from fossil fuels [31]. This massive combustion of fossil fuel is the key source of poisonous emissions that account for hazardous air pollution, the greenhouse effect, and global warming and an unsafe impact on living organisms [32]. Moreover, sulfur- and nitrogen-containing compounds (SCCs and NCCs, respectively) poison the catalysts of various catalytic processes in emission control systems and decrease their efficiencies in different ways. Thus, it is very important to remove SCCs and NCCs before exposing the fuel or its combustion products to the atmosphere. Recently, removal of these unsafe organic compounds from crude oils before operation has become a big challenge. For example, based on EU and US strategies, the sulfur level in fuels should not be more than 10 and 15 ppmw, respectively [33-35]. Pollutants originating from NCCs have also become alarming in recent

years. The World Health Organization (WHO) suggested a guideline to limit the exposure of NO_2 to the air. According to the WHO, yearly emissions should be limited to $40 \mu\text{g m}^{-3}$, and the exposure should not exceed $200 \mu\text{g m}^{-3}$ within any hour [36]. Vehicle-derived pollutants such as SO_2 , NO_2 , CH_4 , CO , and black carbon contribute to global warming. In addition, huge amounts of CO are produced in various oxidation processes as a byproduct and mix with other gases in the environment. Atmospheric CO is extremely poisonous to human beings as it can attach quickly to hemoglobin and hinder circulation. Currently, the carbon balance of the world is one of the most vital environmental issues; hence, reducing anthropogenic emissions of CO has become a great challenge for mankind.

1.2 Π -complex formation

So far, adsorptions in both liquid and vapor phases have been explained with a number of mechanisms/interactions. The particular mechanism for any adsorption depends on the characteristics of adsorbates and/or adsorbents. The well known mechanisms include the electrostatic interaction, acid-base interaction, H-bonding, π - π stacking/interaction, hydrophobic interactions, coordination, π -complexation and so on [7, 10].

The complexes that form *via* electronic interaction between some metal cations and π -electron clouds of chemicals are known as π -complexes for quite long time [37]. Generally, the formation of a π -complex occurs through dual-bonding of a metal atom with a π -electron cloud; both the metal and the π -electron-rich compound act as electron donor and acceptor (see Fig. 4). The σ -component of the bond forms *via* the overlap of the π -molecular orbitals (bonding) of olefins or aromatics with the vacant outermost s -orbital (bonding) of the metal. On the other hand, the π -component of the bond forms simultaneously *via* the back donation of electrons from the d atomic orbitals of the metal to the vacant π^* antibonding orbitals of the chemicals (adsorbates). The metal centers with empty outermost s -orbitals are known as π -complex-active

metals and hence are able to interact with chemicals having π -electrons. The efficiency of adsorbents and adsorbates for π -complexation generally depends on [1] (i) the number of d-orbital electrons of the metal and the capability of donation to the adsorbate, (ii) the number of π -electrons of the adsorbate and the capability of donation to the vacant s-orbital of the metal, and (iii) the emptiness of the outermost s-orbital of the metal ion. Therefore, adsorbates with high π -electron densities (for example, polyaromatic hydrocarbons) are highly favorable for π -complexation.

Π -electron-rich chemicals having little or no functionalities are generally hard to adsorb/separate efficiently since the adsorbent-adsorbate interactions such as acid-base, coordination and H-bonding are not well operative. In this review, the advantage of π -complexation in adsorbing/removing those π -electron-rich compounds (however, less active with other means) has been described specifically. Utilizing MOFs, this special binding force was successfully implemented in various applications including adsorptive removal of SCCs and NCCs, olefin/paraffin separation, and adsorptive removal of various gases such as CO from polluted air (see below). Therefore, we intend to summarize the basics and the applications (to the adsorption/separation/removal of various π -electron-rich chemicals) of π -complexing adsorbents, based mainly on MOFs. We believe that there is ample scope for utilizing these types of adsorbents, with the variation in π -complexing metal species and porous supports, to adsorb/separate/remove compounds. Moreover, this review will motivate readers to develop new materials for several important adsorption-based applications in terms of π -complexation.

2. Competitiveness of π -complexation mechanism

Π -complexation is one of the most efficient and competitive techniques to adsorb/separate π -electron-rich compounds. The important factors that categorize this

mechanism as superior to other common interactions in terms of adsorption/separation are explained briefly as follows. First, π -complexing adsorbents bind the adsorbate molecules with a moderate strength which is stronger than van der Waals interaction and quite effective in adsorption/separation-related applications. On the other hand, the π -complexing binding force is not as strong as observed in typical chemisorptions (such as acid-base and coordination). Therefore, the adsorbed molecules can be desorbed easily via mild thermal or chemical treatments which might assure the intact property of the adsorbents. Second, preferential adsorption/separation of π -electron-rich molecules is also possible based on the characteristics of adsorbates (such as hetero atoms, number of aromatic ring, and chain length of olefins). For example, the π -complexing adsorbents could adsorb various molecules in the order of NCCs > SCCs > aromatic hydrocarbons > paraffins (see below). Therefore, a number of π -complexing adsorbents have been reported as best performing materials in terms of both adsorption capacity and selectivity to adsorb/separate various π -electron-rich compounds (see below). Third, π -complexation can be obtained with various active metal centers and porous supports, ensuring the feasibility of the highest efficiency or flexibility of designing adsorbents. For example, Cu(I) or Ag(I)-based Y zeolite was reported for the first time for the π -complexation phenomenon between the metal ions and π orbitals of thiophenic rings [38]. Later, a series of π -complexing porous adsorbents with several metal ions such as Cu(I), Ag(I), Pd(II), and Ni(II) also adsorbed thiophenics [39-46]. On the other hand, various porous materials, such as carbons [39-41, 47, 48], zeolites [38, 42-46, 49-55], metal oxides [56-63], mesoporous materials [64-70], cyclodextrin [71], resin [72] and MOFs [10], could be applied as supports for active species for π -complexation. Moreover, the active metal centers could be incorporated onto the support materials facilely following a number of techniques (such as ion exchange and impregnation).

The typical drawback of π -complexation adsorbents might be harsh condition (high

temperature reduction) for the ion exchange process to introduce metal ions such as Cu(I) into zeolites. Poor regeneration of adsorbents might be another disadvantage. In most cases the regeneration of adsorbents was performed via high temperature calcination or washing with solvents. Regeneration treatments sometimes result in the change of the specific oxidation states of the metal ions via redox phenomenon (especially the disproportionation of Cu(I) (see below)). The leaching out of impregnated (loaded) metallic species might be another reason of poor reusability. Therefore, one should pay attention to select active metallic species, porous supports, and preparation procedures for effective and reusable π -complexing adsorbents.

3. Preparation of π -complexing adsorbents

Transition metal ions such as Cu(I), Ag(I), Zn(II), Pd(II), Ni(II), and Pt(II) with empty outermost *s*-orbitals (see Table 1) are active in π -complexation phenomena [1]. Several procedures were used to introduce π -complex-active metallic components into porous materials to prepare efficient π -complexing adsorbents (Scheme 1). The use of the ion exchange process to introduce metal ions into zeolites or resins was studied extensively [1, 38, 42-46, 49-55]. The electronegativity of the anions bound to the active metals is also significant in π -complexation. The more electronegative anions can pull electrons more strongly from the metal cation bound to it, resulting in a more positive charge on the metal cation. In turn, cations with higher positive charges will be better acceptors in the π -complexation mechanism [73].

For the ion exchange process, the H or NH₄ forms of zeolites are allowed to react with aqueous solutions of metal salts in order to exchange the cation of the porous solid with the desired metal ions. Thus far, Cu(I) attracted more attention as a π -complexing center within a porous support compared to other metal ions because of the abundance and low cost of copper salts as well as the possible reduction of Cu(II) into Cu(I). However, direct ion exchange with

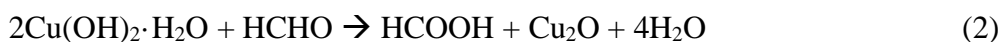
copper in the desired oxidation state (+1) may not be possible in all cases. For example, Cu(I) cannot be ion-exchanged into zeolites since cuprous salts are not soluble in water; therefore, Cu(II) ions are exchanged first and Cu(I) can be obtained through autoreduction of Cu(II) *via* high-temperature calcinations under an inert atmosphere [38]. On the other hand, metal salts with the desired oxidation states (Ag(I), Zn(II), Ni(II), Pd(II), Pt(II)) can replace the H or NH₄ ions in zeolites such as Y or ZSM-5, eliminating the need for further redox operations.

Dispersion of metal salts within the porous materials is also known for a long time. Porous supports (Al₂O₃, SiO₂, SBA-15, MCM-41, etc.) that do not have exchangeable cations on their surfaces are usually modified with π -complexing moieties through dispersion of metal salts [56-70]. In this process, aqueous solutions of metal salts are impregnated (or loaded) into the porous structure and calcined in order to obtain the proper oxidation state of the metal. Scheme 2 shows the general procedure to introduce Cu₂O (from Cu(NO₃)₂) into a porous support [74]; the Cu(NO₃)₂ salt is loaded first, followed by decomposition into CuO. Finally, high-temperature calcination at 600–700 °C results in the autoreduction of CuO to Cu₂O. The thermal reduction process aggregated the guest species, which seriously reduces the performances of the desired adsorbents [64]. Yin and co-workers showed a different way to overcome this problem by constructing a confined space for the cuprous sites in silica nanopores [64]. In their methodology, Cu(NO₃)₂-loaded SBA-15 was calcined to obtain CuO/SBA-15. Then, a layer of silica was constructed by using tetraethylorthosilicate (TEOS) and cetyltrimethylammonium bromide and allowed to coat onto CuO/SBA-15 before the thermal reduction process. Finally, after being reduced, the adsorbents coated with silica provide an excellent platform for the high degree of Cu₂O-dispersed materials. The above-mentioned two techniques are only applicable for support materials with high thermal stability (zeolites, carbons, silicas, aluminas, etc.) since thermal reduction and activation are necessary

in order to maintain the reduced oxidation state.

Nevertheless, high-temperature autoreduction of CuO yielded a mixture of CuO and Cu₂O [69]. During the preparation and operation of Cu(I)-based adsorbents, the oxidation state of Cu(I) species was unstable owing to disproportionation ($2\text{Cu(I)} \rightarrow \text{Cu(0)} + \text{Cu(II)}$) processes [49, 60, 66]. Moreover, Cu(I) can also be reduced to the metallic state by a reducing gas that is generally present in the process stream in industries [66]. More importantly, the regeneration of adsorbents, which ultimately determines the overall efficiency, becomes challenging because of the redox properties of Cu(I) species. These factors seriously hamper the effectiveness in various adsorption-based applications, since the +1 oxidation state of copper species is the precondition for π -complex formation. Thus, it is challenging to develop Cu(I)-based adsorbents that are chemically stable for redox reactions during the preparation and application processes.

Ce(III), V(III), and Fe(II) ions in Cu(I)-based adsorbents acted as redox buffers to maintain the +1 oxidation state of copper species within the adsorbents [66, 75, 76]. Jiang and co-workers reported the vapor-induced reduction of CuO to Cu₂O within the pores of SBA-15 [60]. Supported CuO was selectively reduced to Cu₂O at only 140 °C; formaldehyde/H₂O vapor was allowed to diffuse into the pores of SBA-15 and interact with the predispersed CuO (see Eqs. 1–3). The selective reduction process resulted in almost 100% Cu₂O yield without the formation of metallic copper.



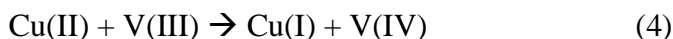
Thermally unstable porous materials (such as resins, porous polymers, coordination polymers, MOFs, organic frameworks, etc.) cannot be considered for those types of

modifications. Considering the lack of high thermal and chemical stability, modification of MOFs was performed under mild and favorable conditions to impart π -complexing sites. The most studied techniques to prepare π -complexing MOFs include: (i) synthesis of MOFs with free π -complexing central metal ions, (ii) synthesis of metal oxides/halides having the appropriate valencies within the MOF framework, (iii) synthesis of MOF/metal complex composites having the π -complexing sites, and (iv) cation exchange of functionalized linkers or grafted functional groups (of MOFs) with π -complexing metal cations. Metal halides or oxides with the desired metal valencies were synthesized within the porous structure [75, 77-80]. For example, Cu₂O nanoparticles were synthesized at low temperature after successful impregnation of synthesis precursors into a porous support [77]. CuCl was also obtained *via* room-temperature reduction of impregnated CuCl₂ with a suitable reducing agent (see below) [47, 78]. Specific functional groups introduced onto the porous frameworks may act as exchangeable centers for π -complexing cations. Porous Al₂O₃, SBA-15, or MOF-type materials were functionalized successfully to introduce -SO₃H groups into the porous framework, which ultimately led to the formation of -SO₃Ag *via* ion exchange with a Ag salt [81-83]. Very recently, composites of porous supports and Cu(I) species also showed π -complexation to remove SCCs from liquid fuels [84].

4. Adsorptive removal of sulfur- and nitrogen-containing compounds

Π -complexation was considered seriously for the adsorptive removal of SCCs from liquid fuels. Various porous materials including zeolites, metal oxides, polymers, resins, and dextrin were used successfully as π -complexing adsorbents [85-87]. Various MOFs were also applied with remarkable performances to adsorb/remove SCCs and NCCs from fuel by utilizing the huge porosity, pore dimensions, CUS, or loaded/functionalized moieties [10, 27,

35, 85, 88, 89]. Studies regarding the modification processes of MOFs to impart π -complexing metal centers were conducted for the last few years. Moreover, the competitiveness of the MOF-based adsorbents in the removal of SCCs seems very positive. Introduction of π -complexing Cu(I) sites into MOF-type materials was performed for the first time by Khan et al. [75]. CuCl₂-loaded vanadium terephthalate (MIL-47) showed remarkable adsorptive performance in the adsorption of benzothiophene (BT) from *n*-octane; the Cu(II) ions were autoreduced by the V(III) ions of MIL-47 at ambient temperature and pressure. The autoreduction of CuCl₂ was assumed to follow the following redox phenomenon (Eq. 4, Fig. 5a):



The synergy of the π -complexing Cu(I) sites and porous MIL-47 resulted in a BT adsorption capacity around 122% of the Cu(I)Y adsorbent (at that time Cu(I)Y had the highest BT adsorption capacity [46]). The high adsorption capacity was explained by the π -complexation mechanism between Cu(I) and the thiophene (Th) ring of the BT molecule. Generally, SCCs (and NCCs also) are adsorbed onto porous π -complexing adsorbents in a flat and facedown manner [10, 50, 75] (as shown in Fig. 6), which reduces the steric hindrance well and enhances the adsorption efficiency. On the other hand, the MIL-53s (Al and Cr), analogous to MIL-47, loaded with CuCl₂ did not show any favorable effects on the adsorption of BT (see Fig. 5b) [90]. Unlike V(III) of MIL-47, Al(III) and Cr(III) were not capable of reducing Cu(II) to Cu(I), which was confirmed through the X-ray photoelectron spectroscopy (XPS) studies of the metals. The central metal and its suitable redox properties were very important in various potential applications.

In separate studies, Cu₂O-loaded MIL-100(Fe) [77] and MIL-101(Cr) [91] were also investigated by the same group as π -complexing adsorbents for the adsorption of BT from *n*-

octane . The Cu(I) species was introduced in a facile manner into the porous network of MIL-100(Fe), an iron terephthalate, through single-step synthesis of Cu₂O nanoparticles under mild reaction conditions [77]. They reported a facile route to incorporate a π -complexing Cu(I) moiety without reduction of the Cu(II) species. Fig. 7a shows the XPS spectra of the copper ions in the modified adsorbent and the adsorption isotherms of the adsorbents. The maximum adsorption capacity (Q_0) increased with an increase in Cu(I) content up to a Cu/Fe (wt/wt) ratio of 0.07. The Cu₂O-loaded MIL-100(Fe) resulted in a 16% increase in the Q_0 compared to pristine MIL-100(Fe) (Fig. 7b, Table 1), even though the porosity was decreased by 9%.

Dai and co-workers reported a reusable MOF-5 (zinc-terephthalate)-based π -complexing adsorbent for the adsorption of dibenzothiophene (DBT) from *n*-octane [92]. The Cu(I)/MOF-5 composite was prepared with the addition of various amounts of CuCl through a spontaneous monolayer dispersion process. The physical mixture was activated by placing it at 400 °C under a nitrogen atmosphere. The characteristic X-ray diffraction (XRD) patterns of the composite materials confirmed the intact crystalline structures of CuCl and MOF-5 even after high-temperature treatment (Fig. 8a). Fig. 8b shows the breakthrough curves for the adsorption of DBT from *n*-octane with virgin and modified MOF-5 adsorbents. As shown in the figure, the breakthrough and saturation capacities increased with increasing CuCl amount up to certain values, which were 9.42 and 10.94 wt%, respectively (9.42 and 10.94 meaning that the adsorbed weights of S per 100 g of adsorbent were 9.42 and 10.94 g). Moreover, the Cu(I) sites were excellent in the adsorption of DBT from aromatic solvents (benzene) as well, even though the overall adsorption capacity decreased noticeably with the presence of benzene. A similar trend was observed for the adsorption of various SCCs with porous adsorbents in the presence of aromatics as co-solvent or additives [47, 90, 93].

The reusability of MOF-based π -complexing adsorbents for SCC removal might not

be investigated much since reusability information in previous reports was usually lacking, even though there are several remarkable results on reusability [6, 94, 95]. Interestingly, Cu(I)/MOF-5 was very promising in terms of reusability and the regeneration process. The authors removed the adsorbed DBT from the Cu(I)/MOF-5 adsorbents *via* simple nitrogen sweeping at 350 °C and the regenerated Cu(I)/MOF-5 showed almost identical behavior in the adsorption of DBT.

Active Cu(I) sites were also introduced to MOFs (MIL-101(Cr), MIL-100(Fe) and Cu-BTC) at low and tolerant temperature *via* vapor induced reduction of Cu(II) to Cu(I) [96]. The process allowed the selective conversion (100%) of loaded-Cu(NO₃)₂ to Cu₂O particles within the porous frameworks in the presence of methanol or ethanol vapor (mild reducing agent) at 200 °C. The vapors having higher reducing capability (formaldehyde or glycerol) led to the conversion to Cu(0) instead of Cu(I) and therefore, the reducing ability of the vapors should not be too strong. The oxidation states of copper in the modified adsorbents were analyzed by the characteristic XRD peaks of copper oxides and the XPS. Adsorption of various SCCs were investigated with the modified MOFs obtained by vapor induced reduction process; where π -complex Cu(I) sites were very efficient. For example, in the case of Th capture the Cu(I)/MIL-101(Cr) adsorbed 0.291 and 0.373 mmol S g⁻¹ at breakthrough and saturation respectively. The adsorbed amounts are remarkably higher than those with virgin MIL-101(Cr) (0.101 and 0.153 mmol S g⁻¹ at breakthrough and saturation respectively). Moreover, modified adsorbents were reusable without any loss of activity and the active Cu(I) sites were very stable even at fourth cycle.

Wang and co-workers reported a novel bimetallic MOF for the adsorption of DBT [97] under similar adsorption conditions to those reported by Dai et al. [92]. Zn/Cu-1,3,5-benzenetricarboxylate (BTC) (or zinc/copper-trimesate) was synthesized following the same

synthesis procedure for Cu-BTC but using a Zn salt to replace 35, 55, and 75 molar % Cu(II) with Zn(II). The paddle-wheel structure of Zn/Cu-BTC with axial Zn(II) and Cu(II) cations was interesting because of the existence of CUSs. DBT was adsorbed much more preferentially onto Zn/Cu-BTC than onto virgin Cu-BTC and the maximum breakthrough and saturation capacities observed for Zn/Cu-BTC were 9.93 and 11.89 wt%, respectively (9.93 and 11.89 meaning that the adsorbed weights of S per 100 g of adsorbent were 9.93 and 11.89 g, respectively). Coordinatively unsaturated Zn(II) ions have similar electronic configurations to those of Cu(I) ions ($3d^{10}4s^0$) (see Table 1), and hence, Zn(II) acted as the π -complex active species towards the π -electrons of DBT. The Zn(II) sites, active in π -complexation, in Zn/Cu-BTC showed good durability (after the fifth cycle) while the adsorption occurred even in the presence of aromatics or moisture.

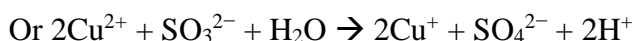
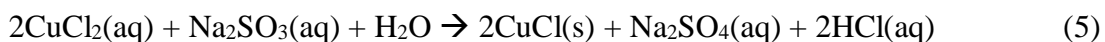
Composite of two different MOFs was also reported by Hasan et al. to adsorb BT and DBT from liquid fuel *via* π -complexation [84]. A nonporous Cu(I) MOF, $(\text{Cu}_2(\text{pyz})_2(\text{SO}_4)(\text{H}_2\text{O})_2)_n$ (pyz: pyrazine), denoted as CP, was introduced to the synthesis precursor for MIL-100(Fe). Alternatively, the formation of mesoporous MIL-100(Fe) was performed in the copresence of nonsoluble CP particles. During the synthesis the CP particles were trapped within the MIL-100(Fe) porous framework even though the cavity size of MIL-100(Fe) was smaller than a CP particle. Fig. 9 shows a scheme of the formation of the CP/MIL-100(Fe) composite and the adsorption capacities for BT of adsorbents featuring various Cu/Fe ratios. Initially, the adsorption capacity increased with an increase in CP content and the highest capacity was observed for a Cu/Fe ratio of 0.023, which gave a 12.3% higher Q_0 than virgin MIL-100(Fe) (Table 1) even with decreased porosity. The homogeneously dispersed CP particles and the Cu(I) oxidation state were confirmed through transmission electron microscopy mapping and XPS studies, respectively. The dispersed CP (Cu(I)) moieties within

mesoporous MIL-100(Fe) showed efficient π -complexation with the BT or DBT ring electrons.

Further modification of MIL-101(Cr) (chromium terephthalate) functionalized with $-\text{SO}_3\text{H}$ groups for efficient π -complex formation was reported by Huang et al. [81]. Ag(I)-immobilized $\text{AgO}_3\text{S-MIL-101(Cr)}$ was obtained *via* simple ion exchange of $-\text{SO}_3\text{H}$ moieties to yield $-\text{SO}_3\text{Ag}$ in the presence of $\text{AgNO}_3/\text{CH}_3\text{CN}$ at room temperature. Thiophene and its derivatives such as BT and DBT were adsorbed onto the $\text{AgO}_3\text{S-MIL-101(Cr)}$ adsorbent from liquid fuel (Fig. 10). Ag(I) ions form very effective interactions with the investigated SCCs through π -complexation; notably, Ag(I)-immobilized $\text{AgO}_3\text{S-MIL-101(Cr)}$ adsorbed approximately ten times more DBT than $\text{HO}_3\text{S-MIL-101(Cr)}$ did (Table 1). The regeneration of the adsorbent was performed by washing with an acetone flow under ambient conditions for two hours. There was no noticeable change in the breakthrough and saturation in DBT adsorption with the regenerated adsorbent compared to the fresh one, demonstrating the stability/durability of Ag(I) moieties as well as the efficient reusability of $\text{AgO}_3\text{S-MIL-101(Cr)}$.

Very few studies on the adsorption of NCCs with MOFs have been published compared to studies on SCC removal. Acidity/basicity, and pore functionality of adsorbents were very important since most NCCs are slightly polar (or basic) in nature and some are also capable of forming H-bonds with adsorbents [10, 15]. For example, acidic $\text{AlCl}_3/\text{MIL-100(Fe)}$ adsorbed basic quinoline preferentially owing to an acid-base interaction [98]. On the other hand, neutral indole participated in H-bond formation with $\text{HO}_3\text{S-}$, $\text{H}_2\text{N-}$, and HOOC- functionalized UiO-66 or MIL-101 adsorbents [13-15, 99, 100]. Various π -complexing adsorbents also adsorbed NCCs successfully irrespective of the chemical properties (such as polarity or acidity/basicity). Cu(I)Y adsorbed several NCCs including aniline, pyrrole, carbazole, acridine, quinoline, and indole through π -complex formation [10, 50, 101, 102]. CuCl -loaded activated carbon also adsorbed quinoline and indole from liquid fuel [103]. Similarly, Ahmed et al. reported

Cu(I)/chromium trimesate (MIL-100(Cr)) as a π -complex-active MOF-based adsorbent, which showed efficient removal of quinoline and indole from *n*-octane or mixed solvents [78]. In their study, CuCl particles were incorporated into porous MIL-100(Cr) through facile reduction of the impregnated CuCl₂ in the presence of Na₂SO₃ under mild conditions at room temperature. Na₂SO₃ was used as a mild reducing agent for the following redox process (Eq. (5)).



The adsorption isotherms are shown in Fig. 11, where the equilibrium adsorption capacity (q_e) was plotted against the equilibrium adsorbate concentration (C_e). The maximum adsorption capacities (Q_0), obtained from the Langmuir plot, of Cu(I)/MIL-100(Cr) for quinoline and indole were 457 and 171 mg g⁻¹, respectively. Compared to pristine MIL-100(Cr), the modified adsorbent produced approximately 9% and 15% increases in Q_0 , and the improvements were attributed to the selective interaction between the π -electrons of quinoline or indole and the loaded Cu(I) sites through π -complexation.

5. Adsorptive separation of olefins and other gases/vapors

Several porous adsorbents including carbons [48], zeolites

[51, 52, 104], SiO₂ [64], SBA-15 [67], and MCM-41 [66] adsorbed/separated olefins, aromatics, and gases selectively based on a π -complexation mechanism. Similar to other cases mentioned earlier, Cu(I), Ag(I), and Pd(II) were the π -complexing centers within the adsorbents for efficient and selective separation. Thus far, MOFs have been studied extensively to achieve more efficient separation of hydrocarbons from gas or liquid mixtures than those with other types of adsorbents [4, 28]. The outstanding performances were explained by the huge porosity, unsaturated metal sites, and/or various favorable interactions, which occurred owing to the

presence of beneficial functionalities on the MOF's surface [4, 28]. MOF-based separation *via* π -complexation was also studied to achieve separation of olefins from paraffins. Chang et al. prepared Cu(I)/MIL-101(Cr) adsorbents by depositing various amounts of nanosized CuCl particles onto MIL-101(Cr) *via* a “double solvent method” [80]. The stable +1 oxidation state of copper was confirmed through XRD and XPS studies. Adsorption of an ethylene/ethane (50/50) mixture was investigated at approximately 30 °C and 1 bar with the virgin and modified adsorbents. Well-dispersed Cu(I)-doped MIL-101(Cr) exhibited higher selectivity for ethylene (14.0) than for ethane whereas pristine MIL-101(Cr) resulted in negligible selectivity (1.6). The adsorption capacity for ethylene of Cu(I)/MIL-101(Cr) was 2.75 mmol g⁻¹, which is higher than that of MIL-101(Cr) (2.22 mmol g⁻¹), even though the porosity and surface area of Cu(I)/MIL-101(Cr) were reduced by half. The physical adsorption sites of MIL-101(Cr) were covered by the CuCl nanoparticles, resulting in the decrease in ethane adsorption. The high and selective uptake of ethylene was explained by the efficient π -complex formation between the Cu(I) center of the adsorbent and the C=C bond. Ag(I) in an MOF was excellent in selective ethylene uptake as reported by Zhang and co-workers [105]. In their study, HO₃S-MIL-101(Cr) was treated with AgBF₄ to exchange the sulfonic hydrogen with Ag(I). The incorporation of Ag(I) was confirmed by the silver signals in an XPS study, and inductively coupled plasma mass spectrometry (ICP-MS) revealed that approximately 51% of –SO₃H groups were transformed into –SO₃Ag. HO₃S-MIL-101(Cr) and AgO₃S-MIL-101(Cr) adsorbed 37 and 63 cm³ g⁻¹ of ethylene, respectively, from an equimolar ethane/ethylene mixture at 45 °C and 1 atm pressure. For better understanding of the role of the introduced Ag(I) ions, the authors calculated the isosteric heats of adsorption (Q_{st}) using the Clausius-Clapeyron equation at two different temperatures, 23 °C and 45 °C. As shown in Table 2, at close to zero loading, the $-Q_{st}$ value for ethylene in AgO₃S-MIL-101(Cr) is approximately six times higher than that in HO₃S-

MIL-101(Cr). The adsorption selectivities calculated for HO₃S-MIL-101(Cr) and AgO₃S-MIL-101(Cr) were 1.2 and 9.7, respectively, at 100 kPa. The remarkable selectivity was attributed to the π -complexation between the Ag(I) ions in the adsorbent and the π -electrons of ethylene molecules. Chang and co-workers also investigated the same adsorbent to separate ethylene from ethane (and propylene from propane) from equimolar mixtures [106]. The estimated adsorption selectivities of ethylene/ethane and propylene/propane were 16 (at 30 °C and 100 kPa) and 32 (at 30 °C and 1 kPa), respectively.

Some virgin MOFs containing CUSs captured ethylene molecules selectively [107]. However, in the case of AgO₃S-MIL-101(Cr) (featuring both π -complexing Ag(I) and Cr(III) CUS moieties), density functional theory (DFT) calculation study revealed that π -complexation was dominant for ethylene uptake (see section 2.6). The superiority of π -complexation in the selective uptake of olefins can be clarified using a AgSO₃-functionalized porous aromatic framework (PAF-1) [82]. The high degree of ethylene adsorption with excellent selectivity (from the ethane/ethylene mixture, see Fig. 12 and Table 1) was solely due to the π -complexation between Ag(I) and the C=C π -electrons since there is no CUS within the PAF-1 framework. Zinc-based MOF [Zn₂(bpdC)₂(bpee)·2DMF] (bpdC = 4,4'-biphenyldicarboxylate; bpee = 1,2-bipyridylethylene), also known as RPM3, was functionalized with AgNO₃ *via* the formation of a π -complex between Ag(I) and the ethylene of the bpee linker [83, 108]. The Ag(I)-functionalized RPM3 thin film was further employed to adsorb olefins (ethylene, propylene, 1-hexene) or paraffins and the adsorptions were monitored using fluorescence spectroscopy. Interestingly, the fluorescence enhancement was observed upon the introduction of olefins rather than paraffins. The Ag(I) ions in RPM3 selectively detect/bind olefins over paraffins owing to an additional π -complexation phenomenon.

CO is regarded as one of the toxic gases that exist in the atmosphere. Among the recent

CO separation and purification methods, adsorptive separation affords an eco-friendly and cost-effective option. Thus far, MOFs separated CO selectively from other gases such as CH₄, CO₂, and N₂, based on some chemical interaction in addition to physisorption within the huge porous networks [109-112]. However, it was to our surprise that separation *via* π -complexation has not been studied much. Peng et al. showed a very facile way to introduce a π -complexing moiety into the MIL-100(Fe) porous framework [79]. A divalent cuprous salt (CuCl₂) was loaded into the pores of MIL-100(Fe) *via* simple impregnation, and the loaded Cu(II) ions were reduced to Cu(I) *via* thermal treatment at 150 °C for 12 h under vacuum. The +1 oxidation state of the copper species was confirmed using XPS analysis; the characteristic peaks of CuCl were observed at 932.6 and 952.5 eV for Cu2p_{3/2} and Cu2p_{1/2}, respectively. According to the N₂ adsorption results, the Brunauer-Emmett-Teller (BET) surface area and total pore volume of the adsorbents decreased greatly (up to one third) with the incorporation of CuCl species into MIL-100(Fe). The obtained Cu(I)/MIL-100(Fe) adsorbents were allowed to adsorb CO and N₂ at 25 °C and in a pressure range of 0 to 100 kPa. From their experimentation, the uptake of CO with virgin MIL-100(Fe) increased linearly with an increase in CO pressure, whereas the modified adsorbents showed a type-I isotherm with a very high adsorption capacity at low pressure. The result suggested a strong adsorption affinity of Cu(I)/MIL-100(Fe) towards CO molecules. Moreover, irrespective of Cu(I) incorporation, the N₂ adsorption behaviors of the virgin and modified adsorbents were almost identical to each other in a pressure range of 0 to 100 kPa, indicating that the effect of Cu(I) sites on N₂ adsorption was negligible. Virgin and Cu(I)-loaded MIL-100(Fe) adsorbed 0.38 and 2.78 mmol g⁻¹ of CO, respectively, and the huge increase in adsorption capacity (see Fig. 13 and Table 1) with the modified adsorbents was ascribed to the efficient π -complex formation between Cu(I) and CO molecules. The adsorption behavior and selectivity were predicted using the dual-site Langmuir-Freundlich (DSLFF)

model for the selective uptake of CO from an equimolar CO/N₂ mixture. At 100 kPa, the selectivity for CO over N₂ was up to 169 for Cu(I)/MIL-100(Fe), whereas the selectivity of virgin MIL-100(Fe) was only 1.5. The initial $-Q_{st}$ value for virgin MIL-100(Fe) was 38 kJ mol⁻¹ and decreased sharply to approximately 5 kJ mol⁻¹ with an increase in CO loading, and was much lower than that for the modified adsorbent (see Table 2).

6. MOFs and other porous supports for π -complexation

Surface area and porosity are the most important characteristics of any adsorbent since high surface area/pore volume can accommodate more adsorbate molecules within the pore structure. The excellence of MOFs, compared to the other traditional porous adsorbents, is described in section 1.1. The high surface area, wide range of pore diameter/shape and large pore volume demonstrate the superiority of virgin MOFs for the adsorption/separation of various chemicals. Moreover, dispersion of supported species (such as π -complexing metal ions) will be high or efficient because of high porosity of MOFs. Additionally, because of central metals and CUSs, various virgin MOFs attract specific adsorbate molecules with additional forces. Adsorption/separation capability of MOFs could be improved further with numerous surface modifications. So far, the non-MOF porous supports have been modified to introduce π -complexing metal ions only *via* post synthetic (multi-steps) modification. Recently, bimetallic MOF (Zn/Cu-BTC) composed of both Zn(II) and Cu(II) showed a new way (one step) to impart π -complexing sites without further modification [97], which is an advantage of MOFs in π -complexing adsorbents. Single step synthesis of MOFs composite was also reported in co-crystallizing π -complexing nano-MOF within the mesoporous MIL-100(Fe) [84].

Similar to other porous supports, the introduction of π -complexing moieties into MOFs (*via* post synthetic modification) increases the overall adsorption capacities to a greater extent.

However, the absolute values of high adsorption capacities usually depend on the MOFs as shown in Table 3. For example, activated carbon adsorbed 112 mg g⁻¹ of BT from *n*-octane, whereas, MIL-47 adsorbed around two times of BT at the very same condition [75]. The incorporation of Cu(I) onto activated carbon and MIL-47 improved the overall adsorption capacities by 33 and 79 mg g⁻¹, respectively. The remarkable BT adsorption with Cu(I)/MIL-47 (310 mg g⁻¹) was explained by the acidity of MIL-47 (originated from the central metal ions) and the Cu(I) sites. Cu(I)/MIL-100(Cr) adsorbed much higher amounts of QUI and IND compared to Cu(I)/activated carbon mainly due to the Lewis acidity (from CUSs) and the high surface area of MIL-100(Cr). So far, virgin MOFs having different central metals (MOF-74s or CPO-27s) have shown significantly high adsorption/separation of CO [112] or ethylene [107] from other gases compared to non-MOF adsorbents. The framework type, central metal and the high surface area of the specific MOFs played the vital role for the best performances. A few MOFs shown in Table 3 are competitive to carbons and benchmark zeolites for the adsorption of CO and ethylene. With the advantage of high surface area and CUSs, the adsorption capacity increased remarkably by the introduction of Ag(I) or Cu(I) to the MOFs. Therefore, it can be anticipated that the best performing virgin MOFs such as MOF-74(Fe) (for CO adsorption) and MOF-74(Mg, Co) (for ethylene adsorption) might show more promising adsorption/separation if modified further with π -complexing moieties.

For that occasion, the modification of MOFs should be performed under moderate condition. For example, the π -complexing metal oxides or halides should be incorporated to MOFs via facile syntheses from corresponding metal salts instead of high temperature calcination procedure. The best performing virgin MOFs even with low thermal and chemical stability can be chosen to compose or co-crystallize with π -complexing metal complexes. Functional groups such as -COOH and -SO₃H were found very efficient to impart π -

complexing metal ions via cation exchange under mild condition. Depending on central metals and the length of linkers, a series of MOFs having -COOH or -SO₃H moieties in linkers can easily be synthesized. Post synthetic functionalization of linkers or CUS of MOFs also shows the possibility to impart the π -complexing sites onto MOFs beyond the stability issue. Besides, the stability of active π -complexing sites within the MOFs is also very important in terms of re-usability of the MOF-based adsorbents. The most common obstacle for re-usability of the adsorbents is leaching of loaded guest species in the stages of adsorption and re-generation. In this case adequate trapping of the π -complex active species is needed. Recently, ‘bottle-around-ship’ (BAS) and ‘ship-in-bottle’ (SIB) techniques have been promising to incorporate and as well as to trap the guest species within the porous structure of MOFs [113]. Therefore, these techniques, especially SIB, can be adopted to prepare stable π -complexing MOFs [6]. Moreover, the central metals of MOFs having CUS can also be acted as π -complexing sites [97]. The synthesis of MOFs, bimetallic MOFs or composite of MOFs having π -complex active central metal ions, might be interesting as stable π -complexing adsorbents without any post synthetic modification. Additionally, stability of MOFs (pristine or modified) in water, acid or base should also be considered for preparation and reusing of π -complexing adsorbents.

Even though the increase in adsorption capacity (for SCCs, NCCs, CO, and ethylene) does not show any clear dependence on supporting materials (MOFs vs. traditional porous materials) for π -complexing species (Table 3), MOFs are very competitive against traditional porous materials in adsorption/removal irrespective of the introduction of π -complexing species such as Cu(I) and Ag(I). As mentioned earlier, this is because of high porosity, CUSs and contribution of central metal ions of MOFs. Moreover, single step preparation of MOFs with π -complexing central metal ions is another advantage of MOFs compared with traditional materials. Further work is needed to understand the favorable contribution of MOFs in

enhanced dispersion and adequate interaction of π -complexing species.

7. Calculation/simulative studies

For in-depth understanding of π -complexation, the mechanism was explained theoretically along with experimental proofs. Thus far, various theoretical models have been employed to classify/rank the π -complexing metal centers as well as the adsorbate molecules. Yang and co-workers studied the adsorption of benzene from cyclohexane by using SiO_2 supported with various π -complexing metal chlorides [114]. Molecular orbital (MO) calculations were performed at the Hartree-Fock (HF) and DFT levels, and the heats of adsorption (negative) of benzene were in the 29.3–50.2 kJ mol^{-1} range and followed the order of $\text{Cu(I)} > \text{Pd(II)} > \text{Ag(I)} > \text{Au(III)} > \text{Pt(IV)}$, compared to 20.9–29.3 kJ mol^{-1} for cyclohexane (see Fig. 14). The low heats of adsorption of cyclohexane were due to the lack of π -electrons. Cu(I) - and Ag(I)Y zeolites adsorbed significantly high amounts of benzene and Th compared to a Na(I)Y adsorbent *via* π -complexation between Cu(I) or Ag(I) and the adsorbates [115, 116]. According to natural bond orbital (NBO) analysis, Cu(I) /adsorbate π -complexation is stronger than Ag(I) /adsorbate π -complexation, and therefore, the adsorption of benzene or Th was more prominent in the case of Cu(I)Y . The reason was the charge transfer phenomenon *via* π -complexation (see Table 4) [115]. The electron transfers between Th and Cu(I) (σ donation and $d\text{-}\pi^*$ back donation) were higher than those between Th and Ag(I) . The net charge and the overlap of electron clouds were also higher in the case of Cu(I)/Th ; hence, Cu(I)Y showed better performance in adsorptive removal of Th than Ag(I)Y . The low adsorption of benzene compared to that of Th with the adsorbents was also explained by the charge transfer mechanism, since the sharing of electrons in benzene was lower than that in Th [73, 115]. Ag(I) , Ni(II) and Zn(II) ion exchanged Y-zeolites were investigated to compare the efficiencies of

metal ions in the adsorption of Th and benzene. The adsorption capacities and theoretical energies of adsorption were in the order of $\text{Ag(I)} > \text{Ni(II)} > \text{Zn(I)}$ in the adsorption of both Th and benzene [117]. Moreover, hetero atoms such as sulfur or nitrogen (in SCCs or NCCs) also participate in the aromaticity of the rings, further enhancing π -complexation [101]. In a separate study, Yang et al. showed the effect of anions on π -complexation; Cu(I)-zeolite resulted higher (negative) adsorption energies than those of Cu(I) and Ag(I) chlorides in the adsorption of Th and its derivatives [116]. The electronegativity of anions was significant for efficient π -complexation as well as high adsorption strength; therefore, the higher electronegativities of zeolites (due to O) resulted in stronger π -complexation bonding than with metal chlorides.

Jayaraman et al. investigated π -complex-based adsorption with Cu(I)Y zeolite and tabulated the energies of adsorption for various adsorbates [101]. In their study, the effect of NCCs and polyaromatic hydrocarbons on adsorptive desulfurization was examined. According to the breakthrough experiments, the presence of trace amounts of NCCs lowers the desulfurization capacity severely, indicating preferential adsorption of NCCs over SCCs. Based on the MO calculations [101], the strengths of adsorption followed the order of $\text{NCCs} > \text{SCCs} > \text{polyaromatics} > \text{benzene}$, and the trend can be explained through factors such as additional rings, ring electrons, heteroatoms, or alkyl groups in the ring.

In the case of $\text{AgO}_3\text{S-MIL-101(Cr)}$, authors used the electronic structure to gain an understanding of the interactions between ethylene and Ag(I) and ethylene and the CUS of Cr(III) [105]. The optimizations of the $\text{C}_2\text{H}_4\text{-Ag(I)}$ and $\text{C}_2\text{H}_4\text{-Cr(III)}$ interactions were executed using the DFT method (see Fig. 15). Interestingly, the C-Ag(I) bond distances (2.19 and 2.18 Å) were shorter than the C-Cr(III) bond distances (2.54 and 2.55 Å), suggesting a stronger interaction between ethylene and Ag(I) than between ethylene and Cr(III). Therefore, π -complexation contributed dominantly in the selective uptake of ethylene molecules. Jiang and

co-workers applied DFT calculations to determine the binding energy of propylene with a Ag(I)/silica adsorbent [63]. According to the orbital-projected density of states, the hybridizations of Ag 4d electrons and C₂H₄ π -electrons govern the Ag-C₂H₄ bonding. Kim and co-workers used a computational study for an understanding of the adsorption of propylene and propane over Cu(I)- and Ag(I)-incorporated MOFs [118]. The clusters were optimized by DFT at the B3LYP and MP2 levels (see Fig. 16). The calculated binding energies of Cu(I) and propylene at the B3LYP and MP2 levels of theory were -119 and -140 kJ mol⁻¹, respectively, whereas Cu(I) and propane showed energies of only -50.4 and -58.4 kJ mol⁻¹, respectively. Propylene was adsorbed more significantly onto the metal centers of the modified MOFs because of π -complex formation. As shown in the figure, the Cu-C bond distances were shorter (2.08 and 2.14 Å) in the case of propylene than those in the case of propane (2.24 and 3.38 Å). The shorter distances (stronger interaction) for the propylene molecule were due to the presence (or overlap) of π -electrons. Prior to Ag(I)/MOFs, Cu(I)/MOFs were more efficient for the adsorption of propylene. The fundamental reason for the stronger bonding of propylene was provided by NBO analysis (see Table 4); the electron transfers resulting from both the “ σ donation” and “ π back-donation” were higher for Cu(I) than for Ag(I).

8. Concluding remarks and perspectives

In this review, we compiled the π -complexation-based adsorptions/separations of various chemicals mainly with MOF-based adsorbents. Π -complexing adsorbents were very successful in adsorbing aromatics, olefins, or some gases (even those with little or no functionalities) selectively. One of the main objectives of this review was to introduce this special interaction to the scientific community, since there is ample scope to extend the field of application through variation of the active metal ions and support materials. Hence, the ins and

outs of π -complex formation are described based on previous experimental and theoretical proofs.

MOFs recently have shown outstanding performances in various applications and sheltered various π -complex-active metals for the adsorption/separation of various liquids and gases *via* π -complexation. Thus far, zeolite and silica-type materials have been widely employed as π -complexing adsorbents for various adsorption-based applications. Considering the efficiency and competitiveness of π -complex-based applications, emerging materials including MOFs should receive more attention. The terms and conditions of π -complex formation with variations in the active metal sites and porous supports are described systematically. The facile (and low-temperature) incorporations of π -complexing metals into MOFs will motivate scientists to employ new types of porous materials (even with low thermal stability) as supports for a variety of active metals. Future research on π -complexation-based adsorption/separation is expected as follows:

(i) SCCs are widely studied adsorbates to achieve adsorption/separation *via* π -complex formation. Similarly, various aromatics and olefins can also be separated from hydrocarbon mixtures, and related studies are requisite. Only a few studies on the adsorption/removal of NCCs *via* π -complexation have been reported even though NCCs were adsorbed preferentially onto porous adsorbents. Therefore, more studies regarding π -complex-assisted removal of NCCs should be undertaken. Toxic or greenhouse gases such as CO and CO₂ are also anticipated to be trapped within the porous network through π -complex formation very efficiently. Even though the prospects seem very small, there might be ample opportunity to extend to gas-separation-based applications by employing π -complexation methodology.

(ii) Since MOFs are very fascinating as supports for π -complexing metal species, there should be adequate utilization of these types of materials. The redox properties of central metals

of some specific MOFs may be beneficial to the control of the desired oxidation state of the active metals. MOFs with specific pore sizes and shapes can be chosen depending on the size and shape of adsorbate molecules. The high surface area may also play an important role in hosting some tiny molecules *via* π -complex formation.

(iii) There are many emerging porous materials including porous aromatic frameworks, porous organic polymers, and porous carbons (derived from sacrificing various porous frameworks) that can also be considered as potential supports for π -complex-active metal species. MOF-derived carbons will possibly contain active metals (MO_x) for π -complexation.

(iv) The stability of active metal ions (in the adsorbent) is very important in terms of the reusability of the adsorbents. Most of the MOF-based research did not show explicitly the reusability of the adsorbent, which may be owing to the poor stability of the metal ions (leaching or redox phenomenon) within the framework or MOF. The overall efficiency of an adsorbent mostly depends on its reusability, and therefore, sincere attempts are needed to develop reusable adsorbents.

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Table Legends:

1. **Table 1.** Various π -complexing metal centers supported on MOFs for the adsorptions.
2. **Table 2.** Isotheric heat of adsorption (Q_{st}) values for the adsorption of gases with π -complexing MOFs-based adsorbents.
3. **Table 3.** Adsorption of various chemicals with MOFs and other porous adsorbents *via* π -complexation.
4. **Table 4.** Neutral bond orbital (NBO) analysis of π -complexation between metal ions (M) and π -electron rich adsorbates.

Scheme Legends:

1. **Scheme 1.** Modification of porous materials to impart π -complexing metal ions.
2. **Scheme 2.** Dispersion of Cu₂O within the porous support *via* one-pot thermal treatment.

Redrawn from the reference.

Figure Legends:

1. **Fig. 1.** Building principle of a typical MOF, MOF-5.
2. **Fig. 2.** Schematic presentations of analogous MOFs.
3. **Fig. 3.** Yearly published articles on MOFs. Source: Web of Science.
4. **Fig. 4.** Dewar-Chatt model of π -complex formation between metal and ethylene.
5. **Fig. 5.** XPS spectra of virgin and CuCl₂-loaded MIL-47 in copper region; (b) adsorption isotherms for BT adsorption over the virgin and CuCl₂-loaded MIL-53s and MIL-47 in *n*-octane.
6. **Fig. 6.** Π -complex formation between Cu(I) and SCCs in a flat and facedown manner.
7. **Fig. 7.** (a) XPS spectra of Cu(I)/MIL-100(Fe); (b) adsorption isotherms for BT adsorption over the MIL-100(Fe) and Cu(I)/MIL-100(Fe) at 25 °C.
8. **Fig. 8.** XRD analysis of the synthesized Cu(I)/MOF-5 adsorbents (left); breakthrough curves of DBT adsorption over virgin and Cu(I)-loaded MOF-5 adsorbents (right). The breakthrough experiments were done in aliphatic oils and at room temperature.
9. **Fig. 9.** Synthesis procedure of CP/MIL-100(Fe) composites (top); adsorbed amount of BT (from *n*-octane) at various Cu/Fe ratios (bottom). The initial BT concentration was 1000 ppm.
10. **Fig. 10.** Ag(I) immobilized HO₃S-MIL-101(Cr) and sulfur uptake values for virgin and modified adsorbents.
11. **Fig. 11.** Adsorption isotherms for (a) QUI and (b) IND over MIL-100(Cr) and Cu(I)/MIL-100(Cr).
12. **Fig. 12.** Ethylene (black) and ethane (red) adsorption isotherms at 23 °C with -SO₃Ag functionalized PAF-1. Filled: adsorption; unfilled: desorption.
13. **Fig. 13.** Amounts of adsorbed CO with virgin and Cu(I)-supported MIL-100(Fe) at 25 °C and 1 bar.

14. **Fig. 14.** Heats of adsorption for the adsorption of benzene with metal ion incorporated porous SiO_2 or Al_2O_3 . The patterns indicate the highest and lowest values of $-\text{heat of adsorption}$.

15. **Fig. 15.** C-Ag (left) and C-Cr (right) bond distances for the adsorption of ethylene molecule within $\text{AgO}_3\text{S-MIL-101}(\text{Cr})$.

16. **Fig. 16.** Optimized structures for propylene (top) and propane (bottom) interacting with Cu (left) and Ag (right). The values represent the bond distances in Å. Gray, white, blue, brown, and light blue colors represent C, H, N, Cu, and Ag, respectively

Table 1Various π -complexing metal centers supported on MOFs for the adsorptions.

Active component	Host structure, MOFs	Incorporation /condition	adsorbates	Medium, Liq./Gases	Improved uptake, %	Ref.
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-47	Auto reduction of CuCl_2 at RT	BT	Liq., RT	34.2	[75] [90]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-100(Fe)	Synthesis of Cu_2O	BT	Liq., RT	14.1	[77]
Cu(I) [Ar] $3d^{10} 4s^0$	MOF-5	Dispersion of CuCl	DBT	Liq., RT	116.6 ^a	[92]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-100(Fe)	Synthesis of copper pyrazine	BT, DBT	Liq., RT	12.3 (BT) 39.2 (DBT)	[84]
Zn(II) [Ar] $3d^{10} 4s^0$	Cu-BTC	Synthesis of dinuclear MOF (Zn/Cu-BTC)	DBT	Liq., RT	93.3 ^a	[97]
Ag(I) [Ar] $4d^{10} 5s^0$	HO_3S -MIL-101(Cr)	Immobilization of Ag	Th, BT, DBT	Liq., RT	274.8 (Th) 262.3 (BT) 1348.6 (DBT)	[81]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-101(Cr)	Vapor induced reduction of $\text{Cu}(\text{NO}_3)_2$	Th, BT, DMBT	Liq., RT	143.8 (Th) ^a	[96]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-100(Cr)	Chemical reduction of CuCl_2	Quinoline, indole	Liq., RT	8.8 (quinoline) 14.8 (indole)	[78]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-101(Cr)	Deposition of nano-sized CuCl	Ethylene	Gas, 30-50 °C	23.9	[80]
Ag(I) [Ar] $4d^{10} 5s^0$	HO_3S -MIL-101(Cr)	Immobilization of Ag	Ethylene propene	Gas, 30 °C,	424 (ethylene) 100 (propene)	[106]
Ag(I) [Ar] $4d^{10} 5s^0$	HO_3S -MIL-101(Cr)	Functionalization of Ag	Ethylene	Gas, 45 °C	70.1	[105]
Ag(I) [Ar] $4d^{10} 5s^0$	HO_3S -PAF-1	Functionalization of Ag	Ethylene	Gas, 23 °C	37.9	[82]
Cu(I) [Ar] $3d^{10} 4s^0$	MIL-100(Fe)	Thermal reduction of CuCl_2	CO	Gas, 25 °C	632	[79]

^a based on the saturation capacity from break through curve.

Table 2

Isosteric heat of adsorption (Q_{st}) values for the adsorption of gases with π -complexing MOFs-based adsorbents.

Adsorbents	Adsorbate	$-Q_{st}$, close to zero loading (kJ mol ⁻¹)	Reference
HO ₃ S-MIL-101(Cr) AgO ₃ S-MIL-101(Cr)	ethylene ethylene	10 63, 16 ^a	[105]
HO ₃ S-MIL-101(Cr) AgO ₃ S-MIL-101(Cr)	ethylene ethylene	35, 41 ^b 120, 101 ^b	[106]
PAF-1 HO ₃ S-PAF-1 AgO ₃ S-PAF-1	ethylene ethylene ethylene	14 23 106, 27 ^a	[82]
MIL-101 Cu(I)/MIL-101	ethylene ethylene	~26, ~23 ^a 40, ~27 ^a	[80]
MIL-100(Fe) Cu(I)/MIL-100(Fe)	CO CO	38 50	[79]

^a in the case of ethane

^b in the case of propylene

Table 3Adsorption of various chemicals with MOFs and other porous adsorbents *via* π -complexation.

Adsorbents	BET surface area (m ² g ⁻¹)	Adsorbates	Adsorbed amount (mg g ⁻¹)	Increased adsorption capacity (mg g ⁻¹)*	Ref.
AC	1016	QUI	64		[103]
		IND	63		
Cu(I)/AC	897	QUI	126	62	[103]
		IND	168	105	
MIL-100(Cr)	1510	QUI	420		[78]
		IND	149		
Cu(I)/MIL-100(Cr)	1310	QUI	457	37	[78]
		IND	171	22	
AC	1016	BT	112		[47]
Cu(I)/AC	898	BT	145	33	[47]
MIL-47	890	BT	231		[75]
Cu(I)/MIL-47	599	BT	310	79	[75]
AC	1170	CO	6		[119]
Cu(I)/AC	652	CO	64	58	[119]
MIL-100(Fe)	2042	CO	10		[79]
Cu(I)/MIL-100(Fe)	762	CO	78	68	[79]
5A zeolite	-	ethylene	65		[120]
Ag(I)/5A zeolite	-	ethylene	56		[121]
HO ₃ S-MIL-101 (Cr)	1570	ethylene	50		[105]
AgO ₃ S-MIL-101(Cr)	1374	ethylene	86	36	[105]
HO ₃ S-PAF-1	1087	ethylene	77		[82]
AgO ₃ S-PAF-1	783	ethylene	107	30	[82]

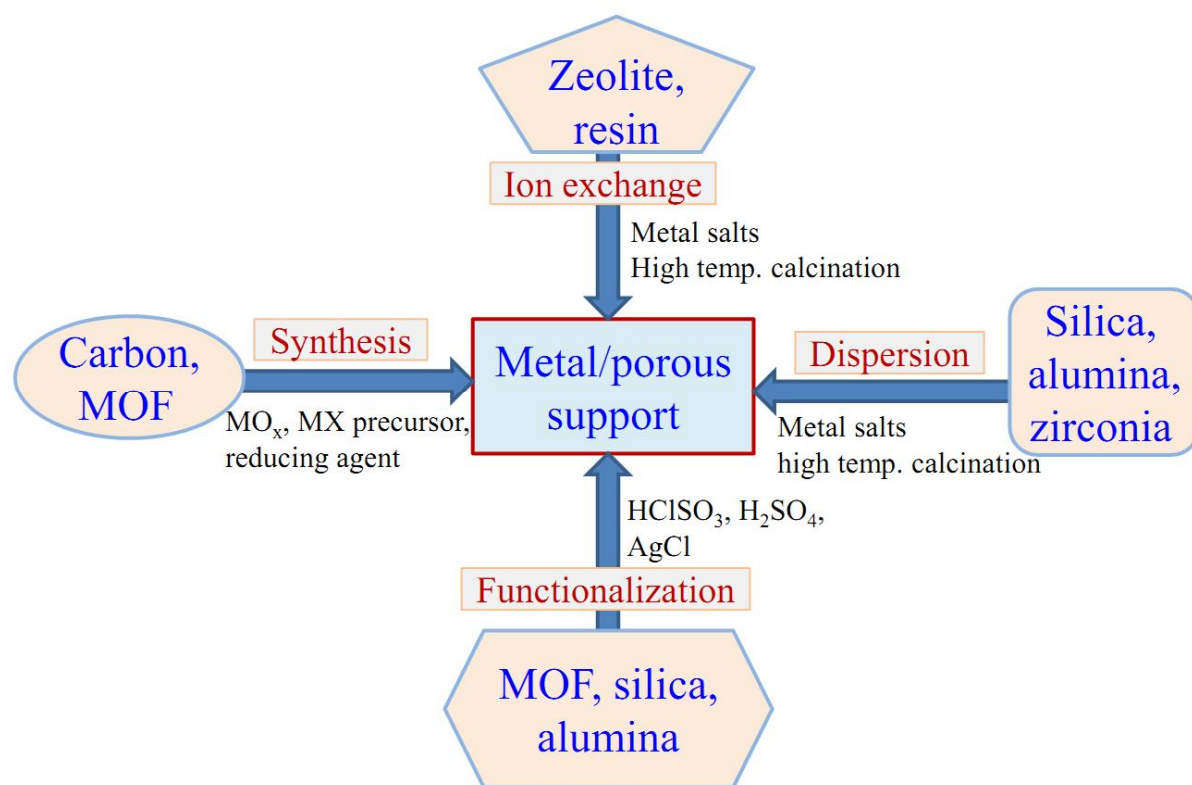
* Increased adsorption capacity by introduction of π -complexing species such as Ag(I) and Cu(I)

Table 4

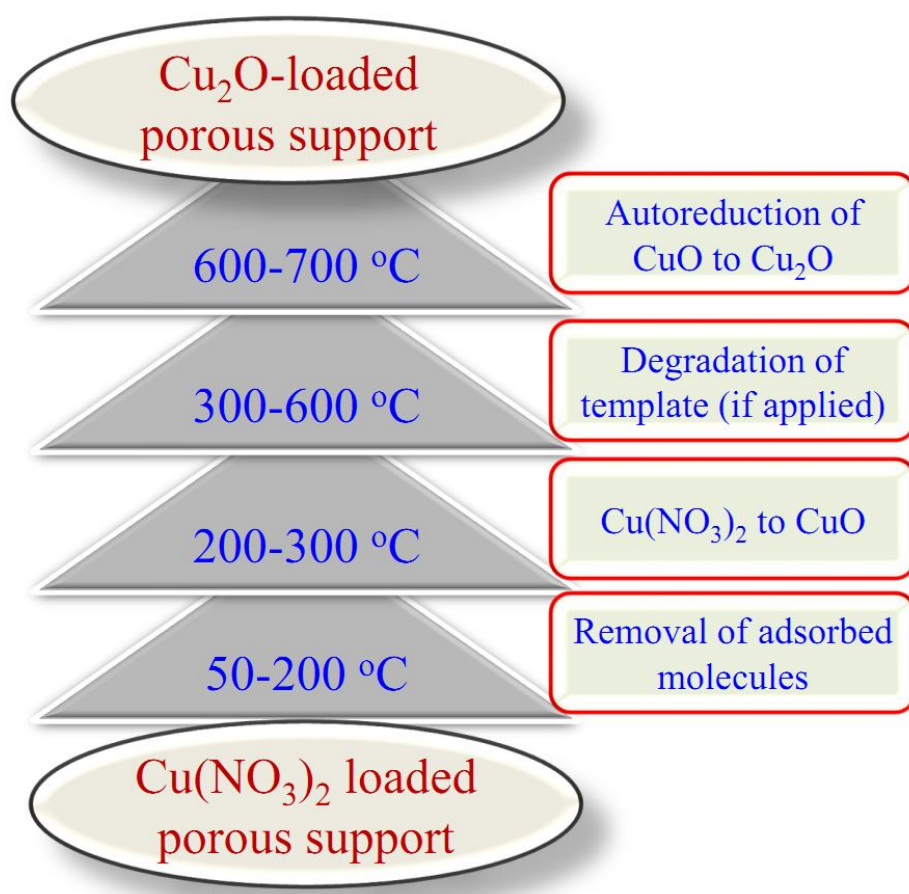
Neutral bond orbital (NBO) analysis of π -complexation between metal ions (M) and π -electron rich adsorbates.

Adsorbate	Π -complexing metal ions	C \rightarrow M (σ -donation) q_1^a	M \rightarrow C (d- π^* back donation) q_2^a	Net change $q_1+q_2^a$	Ref.
Benzene	Cu(I)	0.134	-0.013	0.122	[114]
	Ag(I)	0.003	-0.007	0.004	
Thiophene	Cu(I)	0.037	-0.022	0.015	[115]
	Ag(I)	0.022	-0.014	0.008	
Propylene	Cu(I)	0.244	-0.104	0.14	[118]
	Ag(I)	0.221	-0.089	0.132	

^a q_1 and q_2 are the amount of electron population changes in valence 's' and 'd' orbitals of the metal, respectively.



Scheme 1. Modification of porous materials to impart π -complexing metal ions.



Scheme 2. Dispersion of Cu_2O within the porous support *via* one-pot thermal treatment.

Redrawn from the reference [74].

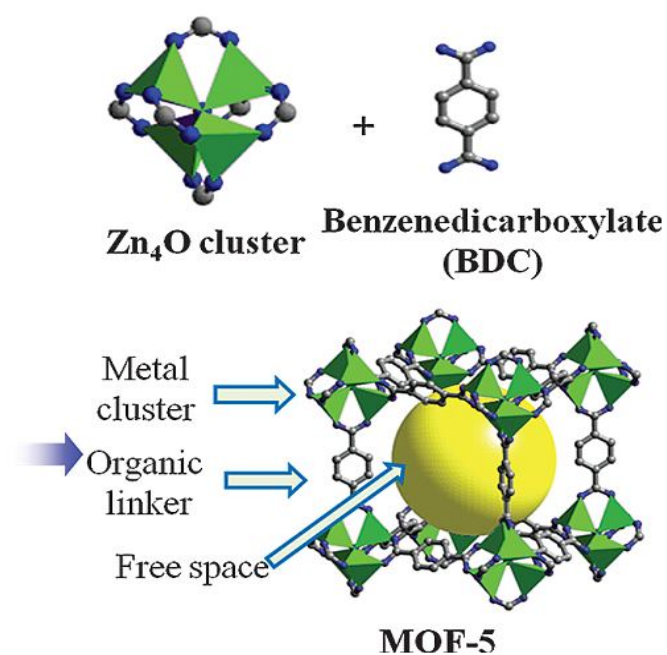


Fig. 1. Building principle of a typical MOF, MOF-5.

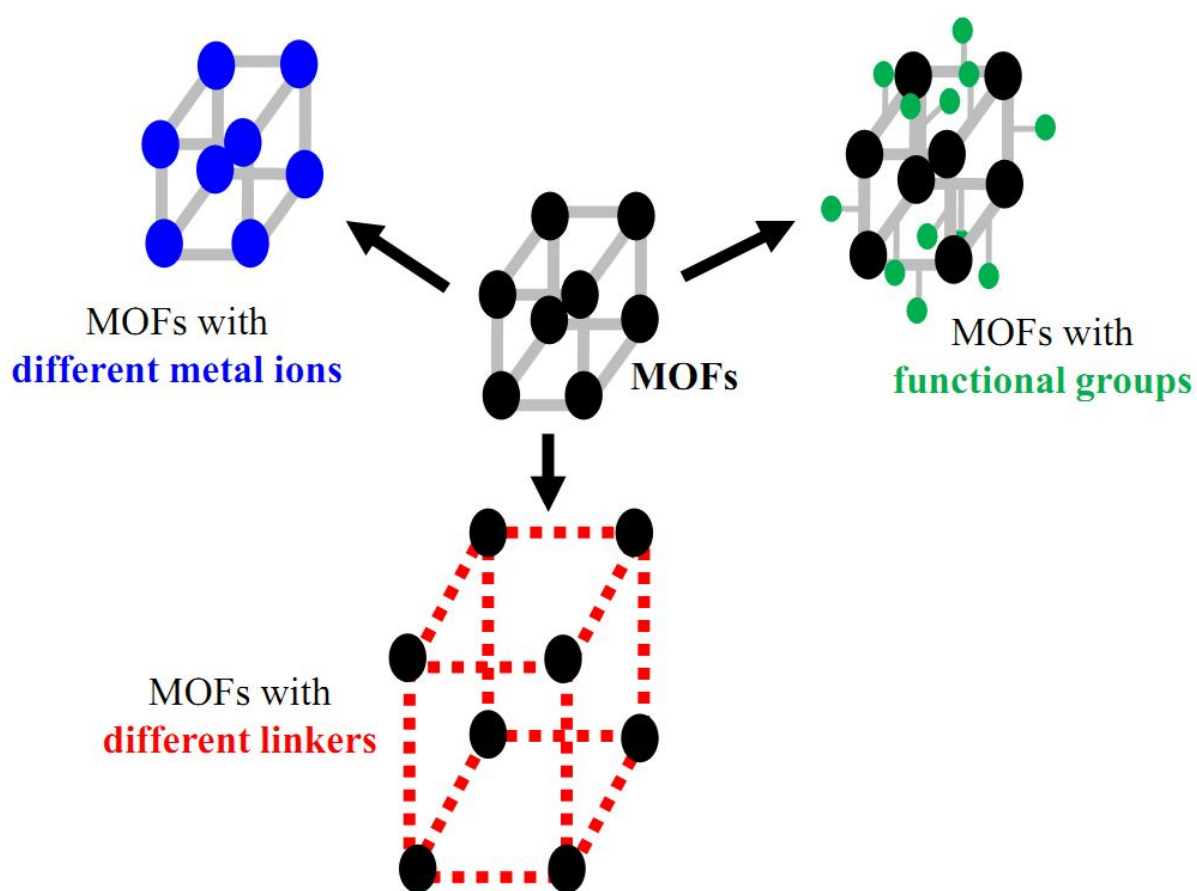


Fig. 2. Schematic presentations of analogous MOFs. Redrawn from the reference [18].

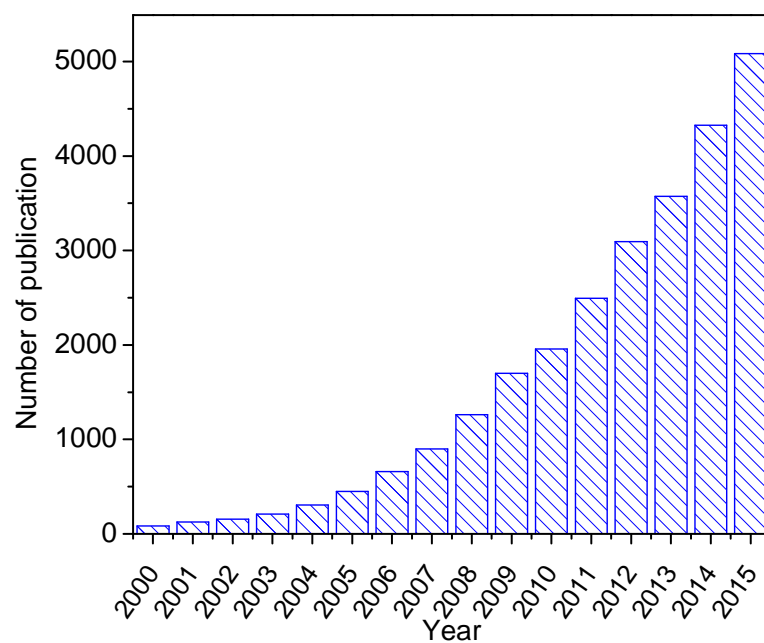


Fig. 3. Yearly published articles on MOFs. Source: Web of Science.

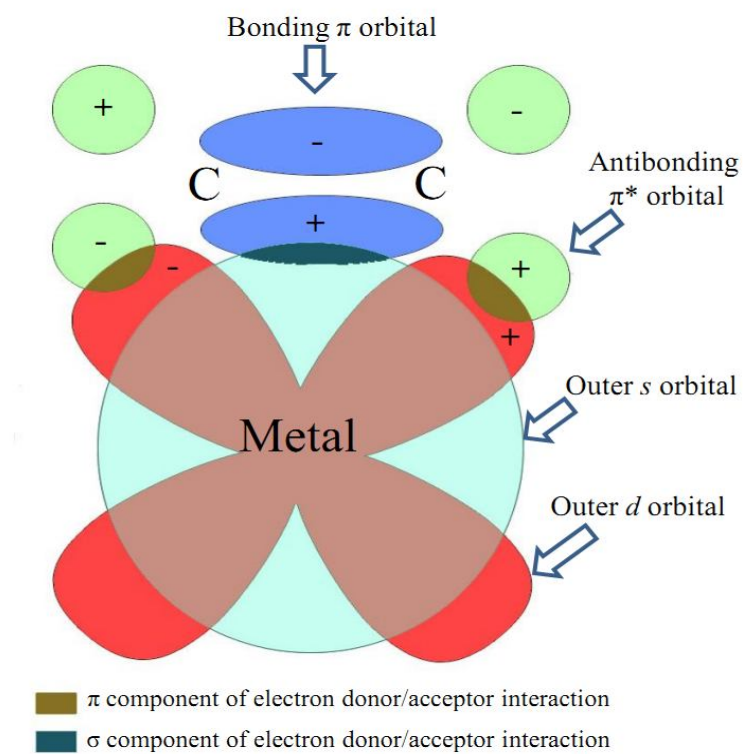


Fig. 4. Dewar-Chatt model of π -complex formation between metal and ethylene. Redrawn from the reference [37].

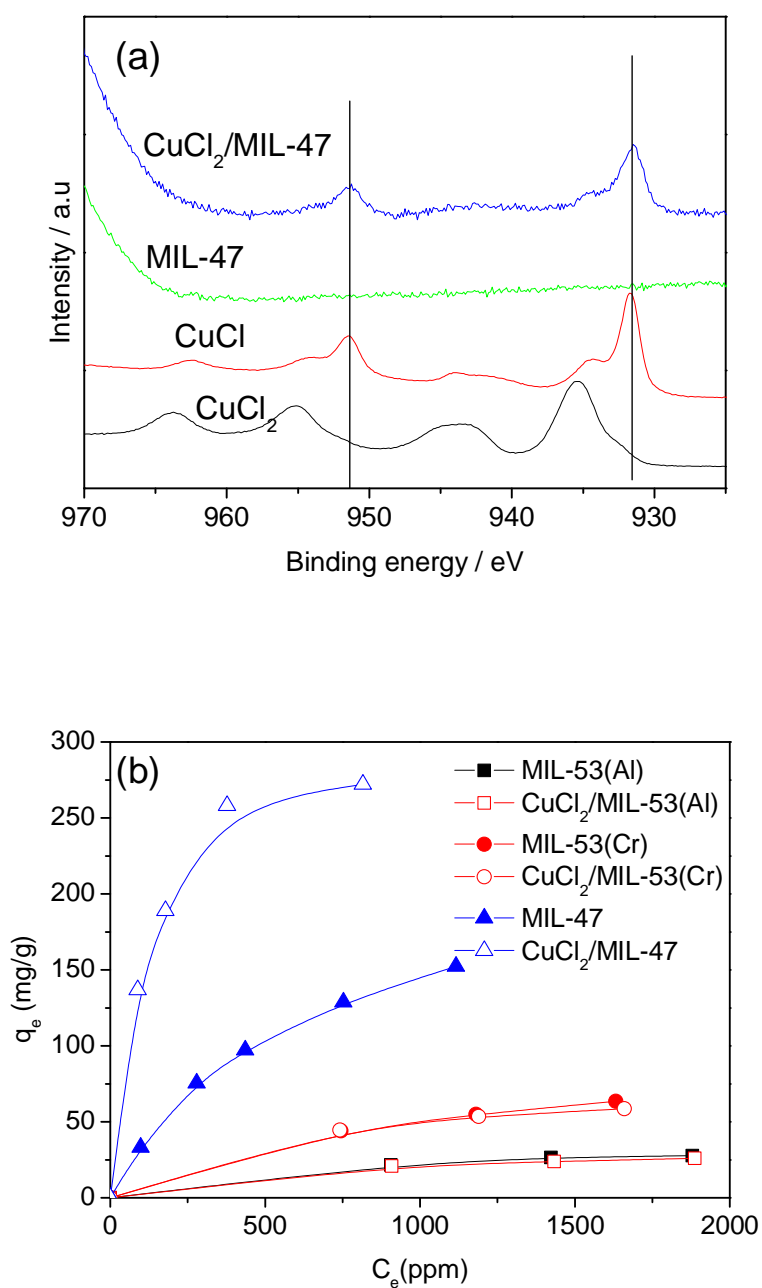


Fig. 5. XPS spectra of virgin and CuCl_2 -loaded MIL-47 in copper region; (b) adsorption isotherms for BT adsorption over the virgin and CuCl_2 -loaded MIL-53s and MIL-47 in *n*-octane. Adapted from the references [75, 90].

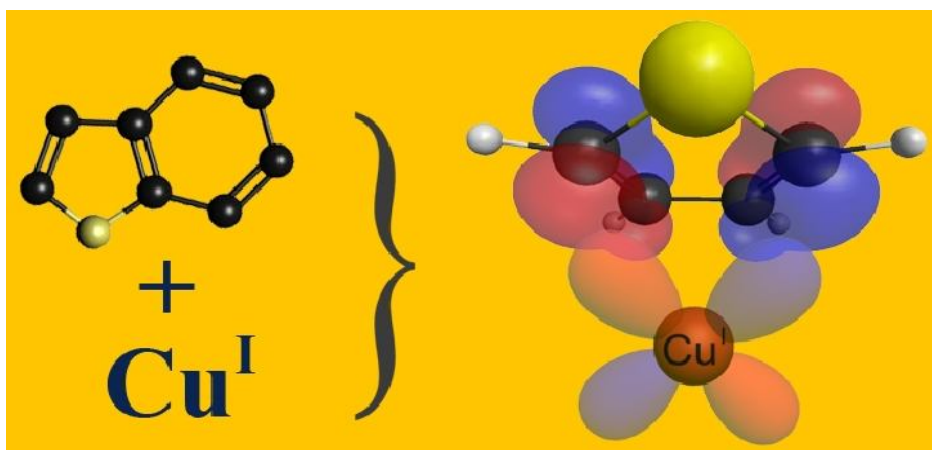


Fig. 6. Π -complex formation between Cu(I) and SCCs in a flat and facedown manner.

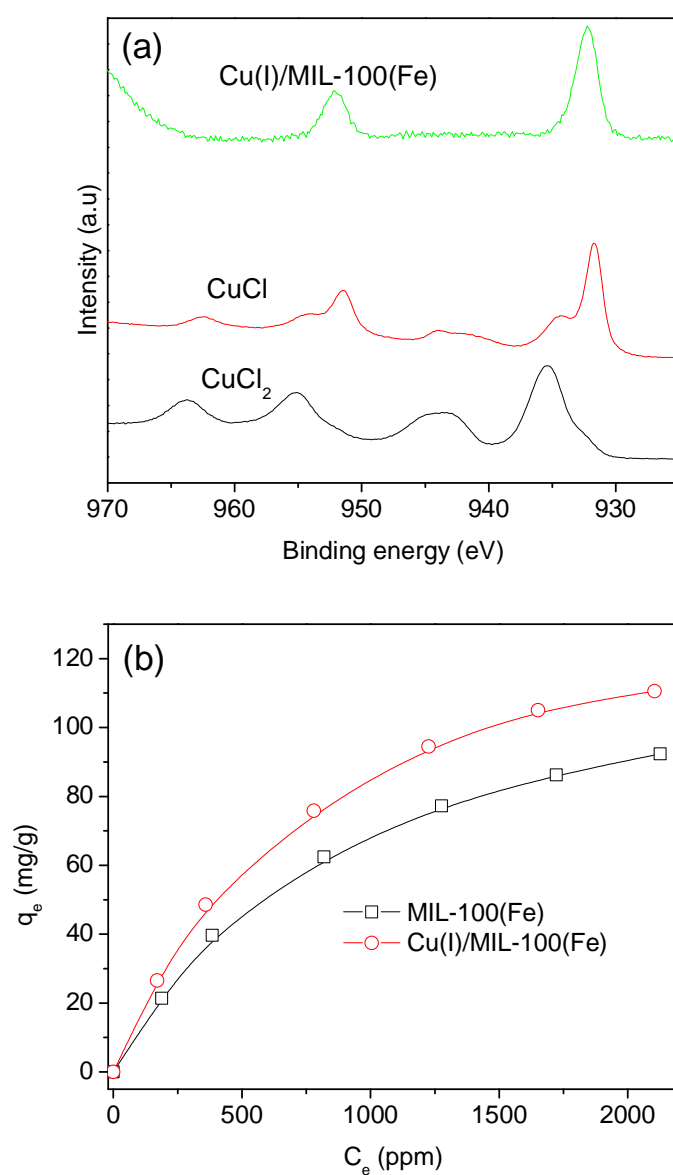


Fig. 7. (a) XPS spectra of Cu(I)/MIL-100(Fe); (b) adsorption isotherms for BT adsorption over the MIL-100(Fe) and Cu(I)/MIL-100(Fe) at 25 °C. Adapted from the reference [77].

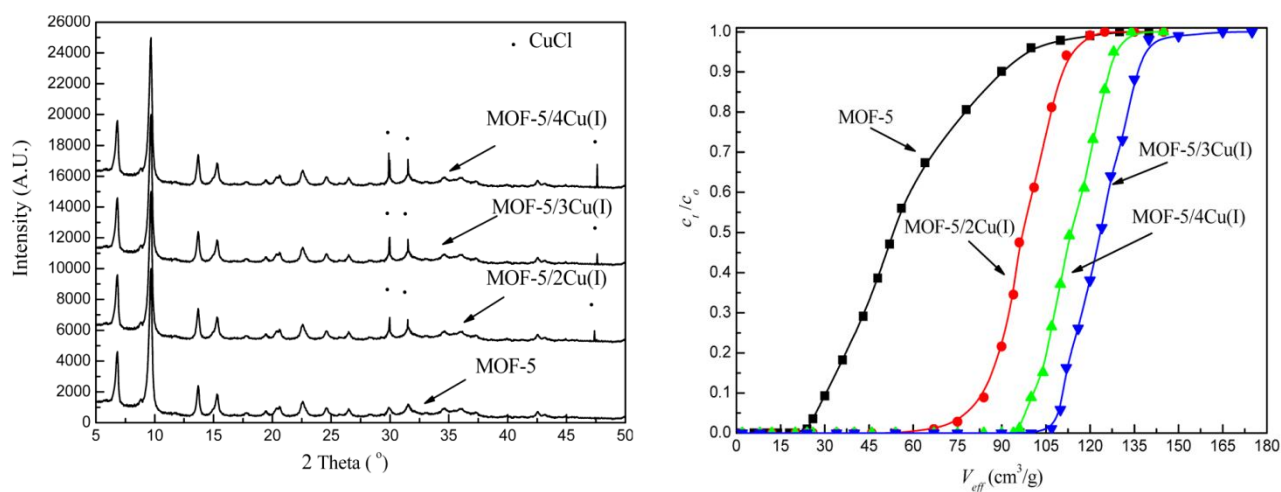


Fig. 8. XRD analysis of the synthesized Cu(I)/MOF-5 adsorbents (left); breakthrough curves of DBT adsorption over virgin and Cu(I)-loaded MOF-5 adsorbents (right). The breakthrough experiments were done in aliphatic oils and at room temperature. Reprinted with the permission from the reference [92]. Copyright © 2013 American Chemical Society.

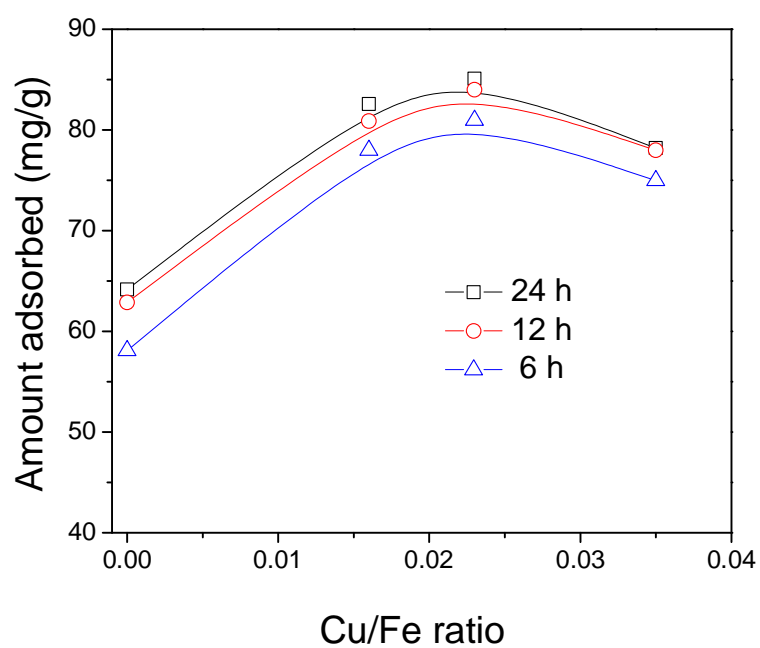
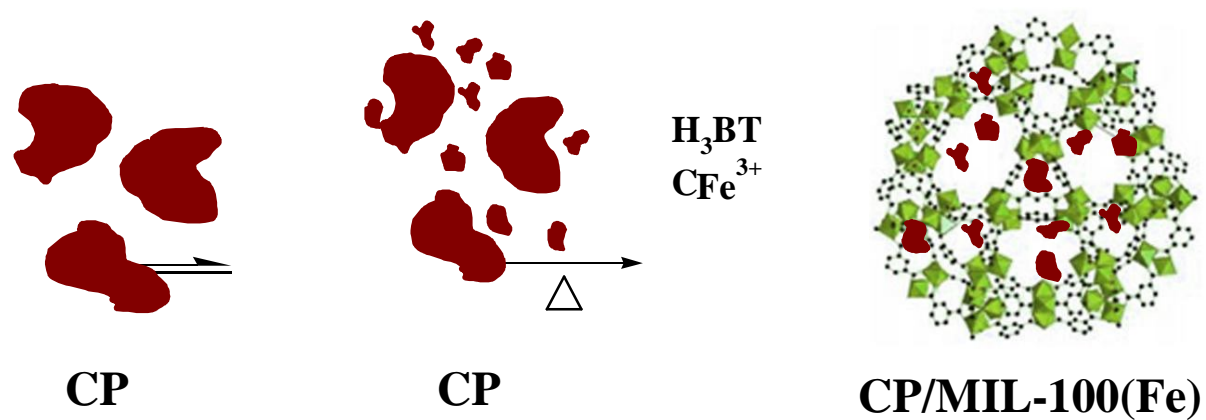


Fig. 9. Synthesis procedure of CP/MIL-100(Fe) composites (top); adsorbed amount of BT (from *n*-octane) at various Cu/Fe ratios (bottom). The initial BT concentration was 1000 ppm. Adapted from the reference [84].

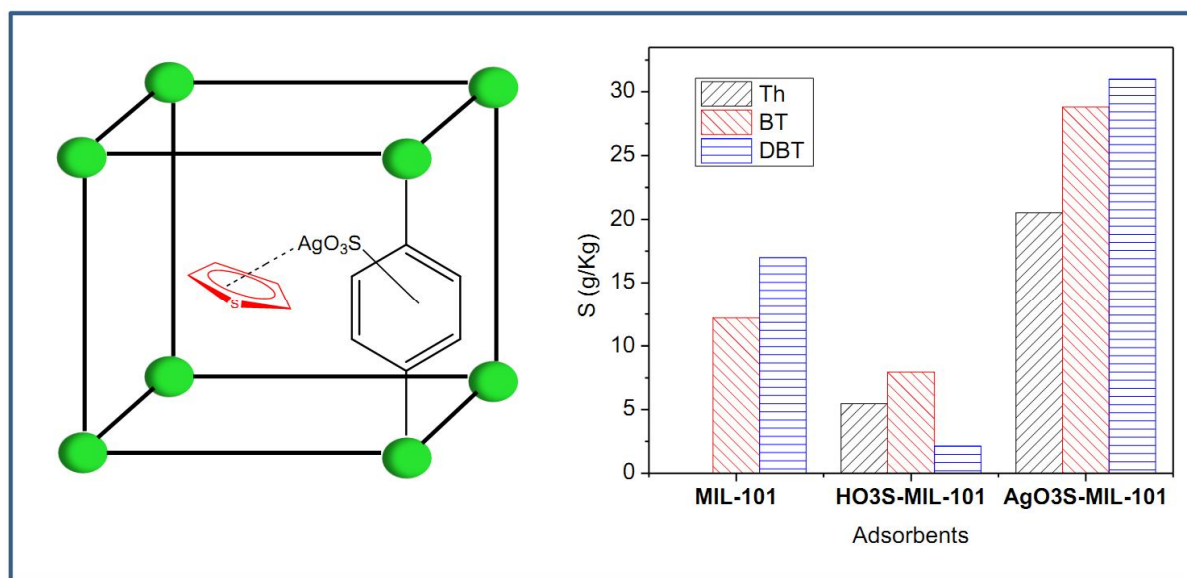


Fig. 10. Ag(I) immobilized $\text{HO}_3\text{S-MIL-101(Cr)}$ and sulfur uptake values for virgin and modified adsorbents. Adapted from the reference [81].

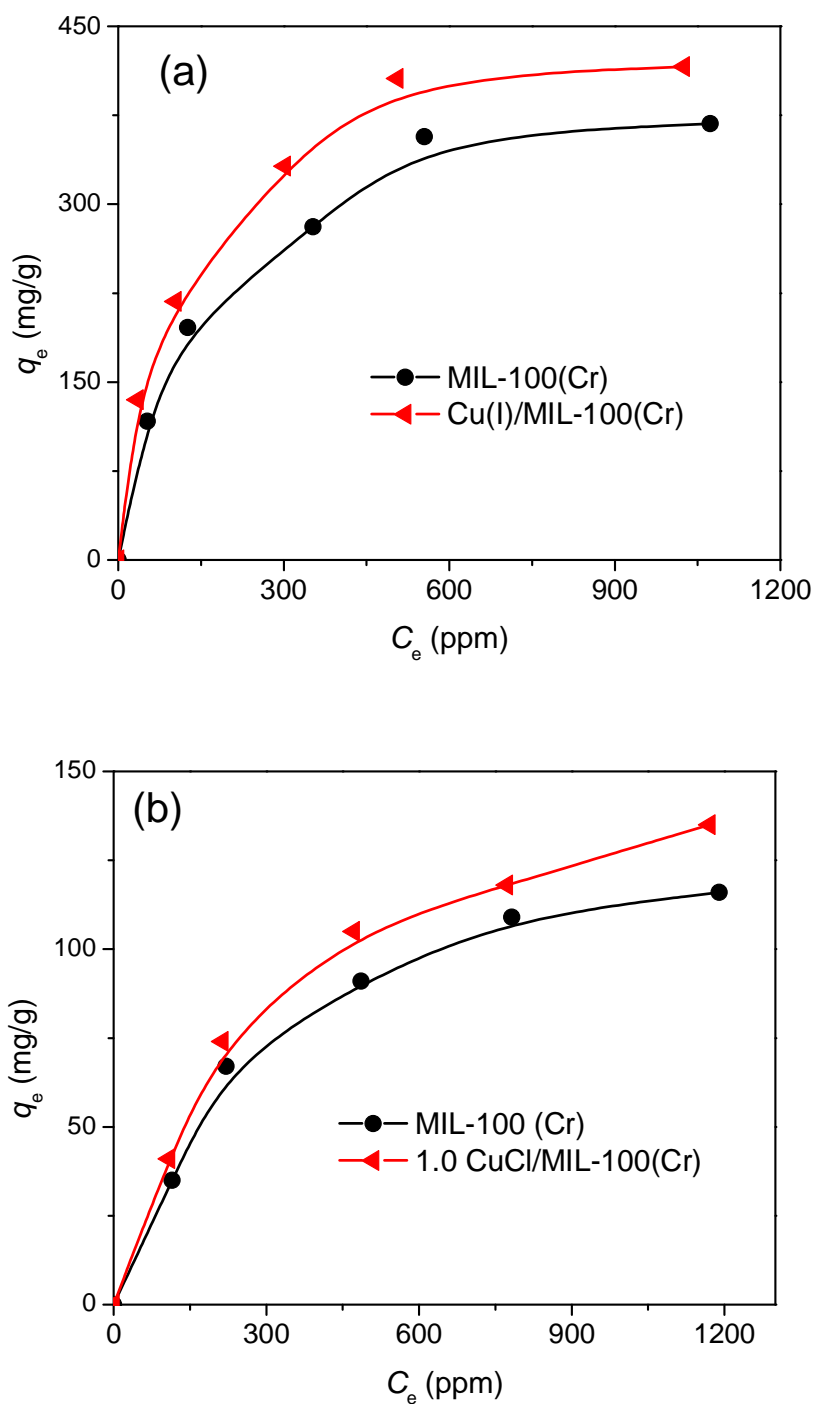


Fig. 11. Adsorption isotherms for (a) QUI and (b) IND over MIL-100(Cr) and Cu(I)/MIL-100(Cr). Adapted from the reference [78].

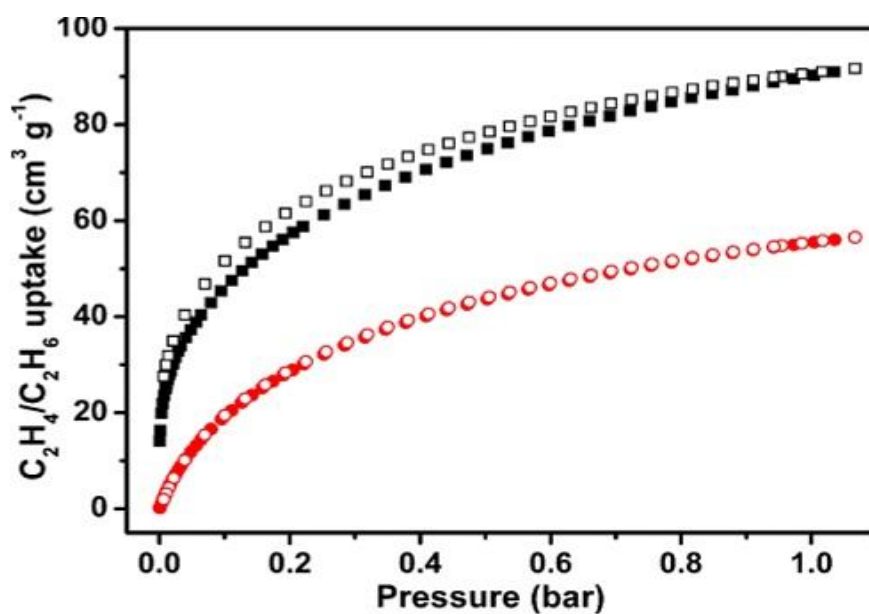


Fig. 12. Ethylene (black) and ethane (red) adsorption isotherms at 23 °C with $-SO_3Ag$ functionalized PAF-1. Filled: adsorption; unfilled: desorption. Reprinted with the permission from the reference [82]. Copyright © 2014 American Chemical Society.

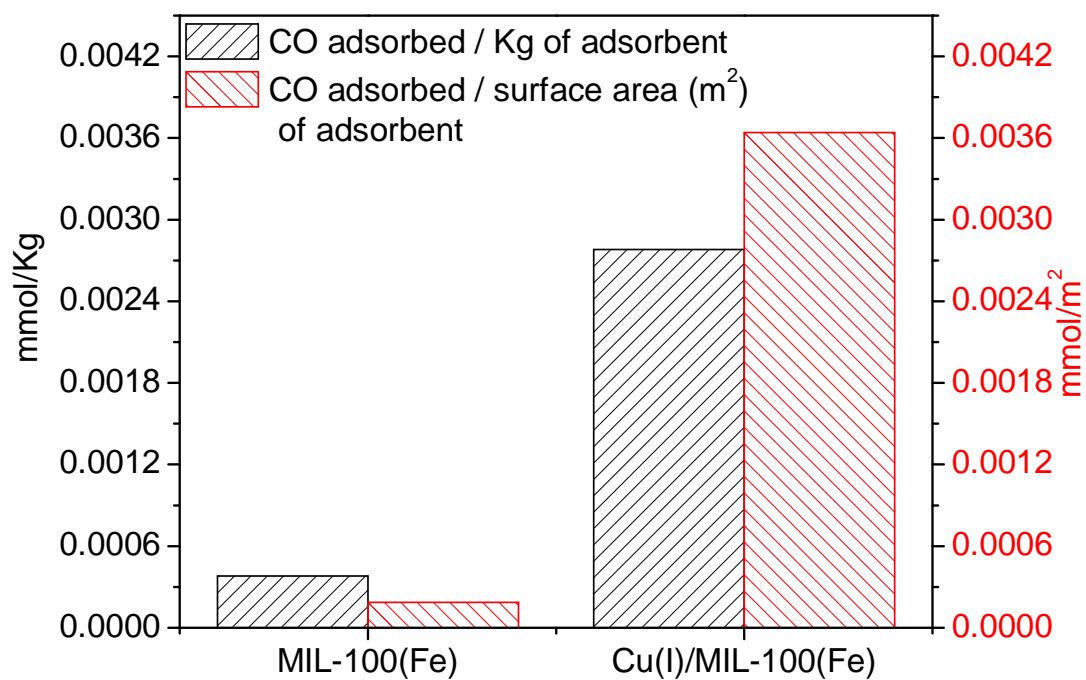


Fig. 13. Amounts of adsorbed CO with virgin and Cu(I)-supported MIL-100(Fe) at 25 °C and 1 bar. Adapted from the reference [79].

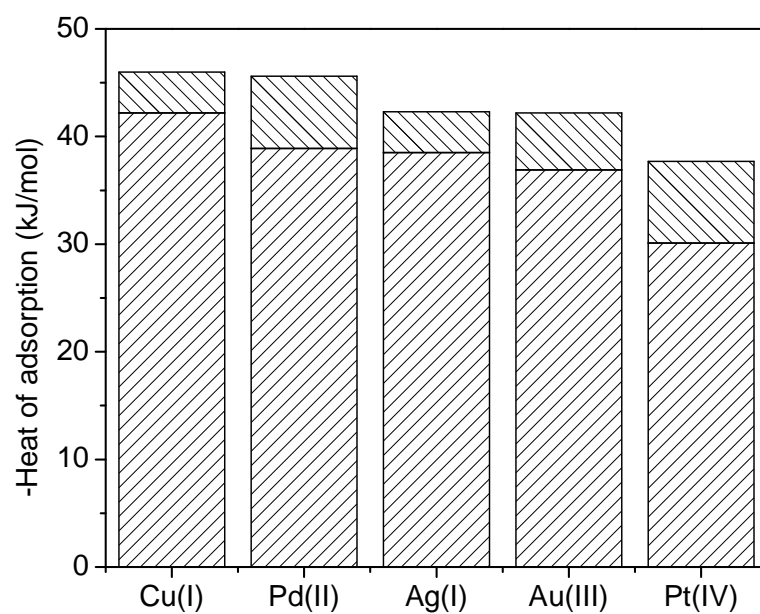


Fig. 14. Heats of adsorption for the adsorption of benzene with metal ion incorporated porous SiO_2 or Al_2O_3 . The patterns indicate the highest and lowest values of $-\text{heat of adsorption}$. Adapted from the reference [114].

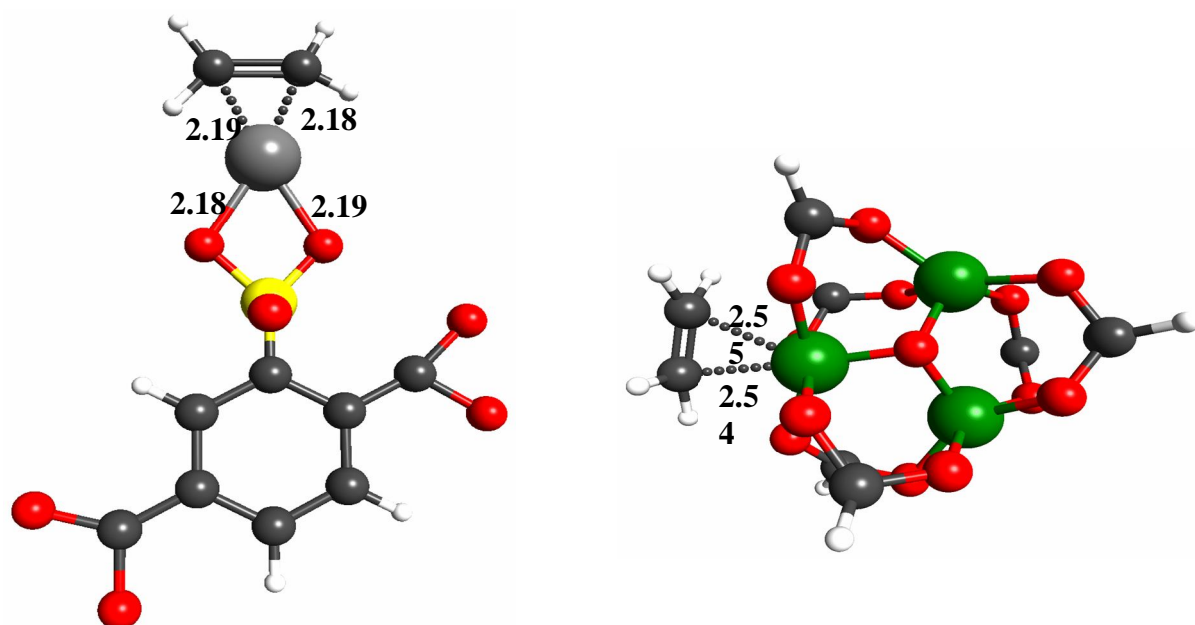


Fig. 15. C-Ag (left) and C-Cr (right) bond distances for the adsorption of ethylene molecule within $\text{AgO}_3\text{S-MIL-101}(\text{Cr})$. Redrawn from the reference [105].

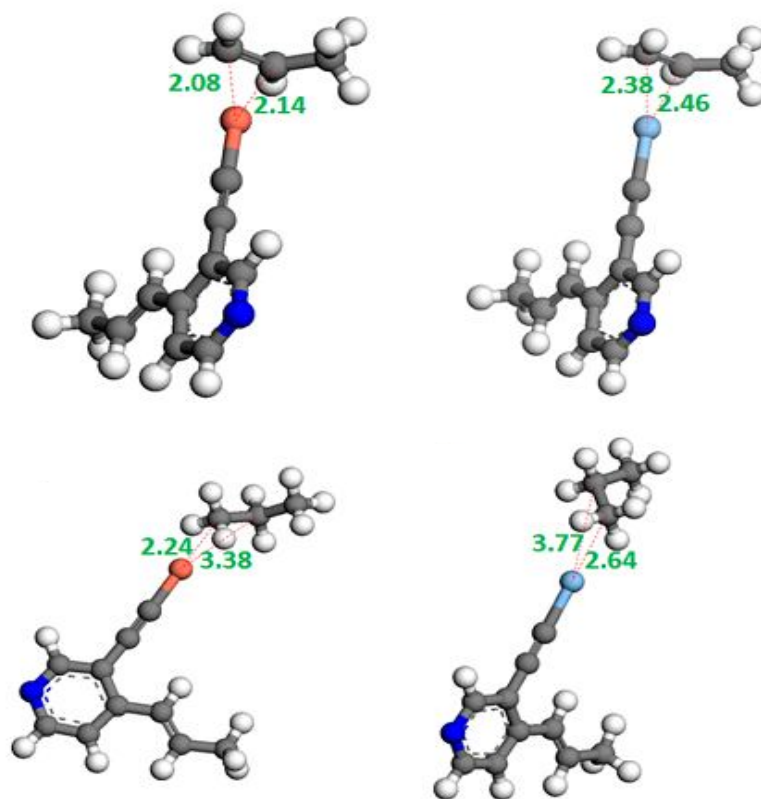


Fig. 16. Optimized structures for propylene (top) and propane (bottom) interacting with Cu (left) and Ag (right). The values represent the bond distances in Å. Gray, white, blue, brown, and light blue colors represent C, H, N, Cu, and Ag, respectively. Reprinted with the permission from the reference [118]. Copyright © 2014 American Chemical Society.