Assessment of adsorption materials for carbon capturing and storage in the context of carbon neutrality

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Abstract. In order to avoid the harm caused by global warming, carbon capture and store (CCS) technology has become a global hot topic. CO$_2$ adsorption materials are an important basis for the realization of CCS. This paper explores the CO$_2$ adsorption mechanisms of the currently widespread shale reservoirs, metal-organic framework (MOF), covalent-organic framework (COF), activated carbon and evaluated the relevant factors affecting their adsorption capacity. Through the exchange of CO$_2$ and CH$_4$, shale reservoir is a natural material with great CO$_2$ adsorption and storage potential. However, due to the high implementation cost and the uncertainty of porosity, this technology is considered to be immature. MOF and COF have different chemical bonds, but they are both crystalline compounds with tunable porosity and internal surface area. They are very ideal CO$_2$ adsorption materials. However, the main disadvantage of MOF and COF lies in their instability. Moreover, activated carbon is considered to be the adsorption material with the lowest production cost among the four. The adsorption performance of activated carbon is related to its raw materials, internal surface area, pore properties and external functional groups. However, activated carbon ashes are likely to cause secondary environmental pollution. In the future, it is necessary to improve the prediction accuracy of the adsorption potential of shale reservoirs, solve the unstable characteristics of MOF and COF, and maximize the adsorption performance of activated carbon in an environmentally friendly manner. The significance of this article is to provide theoretical support for the optimization and development of physical adsorption materials in the future.

Keywords: Carbon capture and storage; CO$_2$ adsorption material; shale; MOF; activated carbon.

1. Introduction

Since the industrial revolution in the 1760s, the global climate has gradually been driven by human activities [1]. The surge in greenhouse gas emissions is the critical factor causing global warming [1]. The carbon dioxide concentration has increased from 280 to 355 ml/L from 1800 to 1994 [2]. The increase in carbon dioxide concentration has led to intensified global warming. As the records of the National Oceanic and Atmospheric Administration (NOAA) show, the current global temperature has risen by approximately 1.0 degrees Celsius compared to the average temperature in the 20th century [3]. Continued global warming has increased the annual frequency of extreme weather events from 200 to more than 400 from 1980 to 2010 [4]. In addition, the rapid changes in temperature lead to significant changes in biodiversity, causing serious ecological consequences worldwide [5]. Besides, global warming affects all aspects of human lives. For example, the increase in temperature affects the pattern of infectious diseases and further changes the interaction between pathogens and human hosts [6]. In order to avoid the possible serious consequences of global warming, governments around the world have taken many measures and reached many energy-saving and emission-reduction agreements. At the Paris COP21 in 2016, carbon neutrality was established as the common goal of the 196 participating countries [7]. In 2021, the 26th Conference of the Parties to the United Nations Convention on Climate Change (COP26) consolidated the climate consensus set out in the Paris Agreement to take more efficient measures to keep global temperature rise within 1.5 degrees Celsius higher than the pre-industrial level [7].

As one of the emission reduction methods, the technology of carbon capture and storage (CCS) through physical adsorption materials has been widely discussed and researched [8]. At present, there is still a research gap regarding the types of efficient physical carbon adsorption materials [8]. Sharma’s team reviewed the carbon dioxide adsorption performance of different types of
carbonaceous materials in a literature review published in 2021 [9]. In the same year, Ben-Mansour’s team reviewed the materials suitable for carbon dioxide capture in the exhaust gas of a typical power plant and simulated the carbon separation and adsorption process [10]. At present, most of the relevant literature reviews only evaluate a single type of carbon physical adsorption material or only emphasize the performance of carbon physical adsorption materials under a specific condition. Few literature reviews have comprehensively evaluated the mechanisms and performances of different types of carbon physical adsorption materials.

Therefore, this review will explore and compare the advantages and disadvantages of four carbon physical adsorption materials and their performance, including shale reservoirs, metal-organic framework (MOF), covalent-organic framework (COF), activated carbon materials. The paper is expected to provide theoretical support for future research on more efficient carbon physical adsorption methods.

2. Physical adsorption materials

2.1. Shale Reservoirs

As Fig. 1 shows, shale is a sedimentary rock composed of mixtures of flakes of clay minerals and fine fragments of other minerals. Thus, it has a porous structure, and its split layers thickness is usually less than 1 cm [11]. Since 2000, as a typical natural property, shale has been found to have great potential for CO$_2$ geological storage. As Nuttall’s team stated in 2005, shale was described as a continuous, low permeable and fractured carrier that can trap a large amount of natural gas, which is a suitable natural material for CO$_2$ geo-sequestration [12]. In detail, shale formations have been vigorously developed due to their rich natural gas content. Because shale formations have a higher capacity to absorb carbon dioxide than methane, scientists widely believe that the use of depleted shale reservoirs to store carbon dioxide is an important goal of CCS [13].

![Fig 1. The structure of shale](image)

The interaction of CH$_4$ and CO$_2$ with shale formation is the key mechanism of shale CCS technology [14]. Fig. 2 shows a typical CO$_2$ injection process to capture and store CO$_2$ within shale reservoir [15]. At the first stage, after the gaseous carbon dioxide undergoes its critical temperature and pressure treatment, it becomes supercritical carbon dioxide (SCCO$_2$) in liquid statue and is injected into the shale rock formation. The free CH$_4$ molecules in the reservoir will be directly driven out by the injected CO$_2$ molecules. The adsorbed CH$_4$ molecules will compete with the CO$_2$ molecules for the adsorption sites in the shale pores and organic matter structure. Since CO$_2$ is easier absorbed by shale adsorbent than CH$_4$ due to its higher ionization potential and polarizability, most CH$_4$ will be desorbed and CO$_2$ will be sequestrated [16]. The removed CH$_4$ will be collected for further human activities [14]. Therefore, this method is also called Enhancing Gas Recovery and CO$_2$ Capturing and Storing (EGR-CCS) from gas acquisition perspective [16].
The adsorption capacity of shales relates to multiple factors. Total organic carbon (TOC) and clay content positively correlate with adsorption capacity [14]. Shales with higher carbon content have the potential to become CO$_2$ reservoirs (see table 1). For example, black shale usually has a higher carbon content than gray shale and is likely to become a reservoir. The gray shale usually acts as a seal for the reservoir [12]. In addition, the richness of clay content indicates more pores and available spaces for adsorption [13]. On the other hand, temperature and wettability negatively correlate with adsorption capacity [14]. Higher temperatures reduce the adsorption capacity of CO$_2$ on shale reservoirs. The CO$_2$/CH$_4$ selectivity coefficient decreases rapidly with the increase of temperature [13]. In addition, Klewiah et al. found that the water in the shale formation is mainly adsorbed on the clay layer, which probably be the main reason for the weakening of CO$_2$ adsorption capacity under high water content [14].

**Table 1.** Summary of different types of shale and their adsorption capacity of CO$_2$.

<table>
<thead>
<tr>
<th>Shale type</th>
<th>Shale characteristic</th>
<th>Adsorption capacity (Unit: SCF per ton)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devonian gas shale</td>
<td>Black, high TOC</td>
<td>18.18 - 70.89 (Ave 84 °F, under 200 PSIA)</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.72 - 122.18 (Ave 84 °F, under 400 PSIA)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>42.67 – 161.25 (Ave 84 °F, under 600 PSIA)</td>
<td></td>
</tr>
<tr>
<td>Barnett shale</td>
<td>TOC &gt;5%; Clay content = 37.4%</td>
<td>147.4 (40 °C, 475.1 PSI)</td>
<td>[17]</td>
</tr>
<tr>
<td>Marcellus shale</td>
<td>TOC = 1.2%; Clay content = 52.0%</td>
<td>63.7 (40 °C, 263.2 PSI)</td>
<td>[17]</td>
</tr>
</tbody>
</table>

The advantages of shale reservoirs lie in their sustainability and naturalness. According to Fig 2, the CO$_2$ geo-sequestration within shales can also enhance shale gas recovery [15]. This technology indicates that the CO$_2$ generated by the shale gas-based industries can be offset during the shale gas collection stage, promoting the realization of net-zero emissions. Further, EGR-CCS technology has much less damage to the geological structure of the reservoir than other acquisition methods such as hydraulic fracturing [13]. In addition, a shale reservoir is a natural adsorbent with an outstanding self-sealing function to lock CO$_2$ inside the shale structure [15]. Most other adsorbents do not have the self-sealing feature or require human intervention to gain the sealing capacity [8, 15].

However, shale-based carbon capturing and geo-sequestration (CCGS) is not considered a mature technology. Several scholars indicate that the pore structure uncertainty will result in a significant

**Fig 2.** The mechanism of shale-based CO$_2$ adsorption [15].
variation of adsorption capacity [13]. Therefore, it is difficult to accurately estimate the potential of shale reservoirs to capture and store CO$_2$. Additionally, the pretreatment of SCCO$_2$ is costly and has potential safety hazards during operation [15].

2.2. Porous crystalline solids

2.2.1. Metal-organic framework (MOF) Material

Since the metal-organic framework (MOF) was introduced in 1995, its potential in gas adsorption, separation, storage, and catalysis has been gradually discovered [18]. As shown in Fig. 3, MOF is a type of crystalline porous material formed by the coordination of metal ions or clusters with organic linkers [19]. MOF material has four representative features: high internal surface area, high porosity, and adjustable void space [20]. The size and geometric structure of MOF are controlled by the types of metal ions or metal clusters and organic ligands [21]. Due to the porous nature, the internal surface area of the MOF material is very large. According to the data of the Cambridge Structural Database CSD as of March 2021, more than 100,000 MOFs have been recorded, and the surface area of the MOF can exceed 10,000 m$^2$/g [21]. Moreover, the pore volume of MOF exceeds 5 cm$^3$/g [21]. With high internal surface area and high pore volume, MOF is considered to have the basic conditions as a good carbon adsorption material [22].

Regarding the adsorption mechanism, according to Fig. 4, the oxygen atoms of the CO$_2$ molecule occupy the open metal site (OMS) on the Mg/DOBDC cell and then generate continuous charge exchange with the MOF to finally reach a stable adsorption state [20].

However, the magnitude of the adsorption capacity of MOF is affected by multiple factors. Some scholars pointed out that the internal surface area of MOF is positively correlated with its adsorption...
capacity, but it is not a decisive factor [20]. In contrast, the composition and structure of MOF have a higher degree of influence on its adsorption capacity [22]. Several studies have found that polar groups and amine groups are the most effective in capturing CO$_2$ [23]. In addition, the composite material constructed on the basis of MOF and mesoporous silica or graphite oxide has been found to have outstanding thermal stability and improved CO$_2$ adsorption capacity [24]. Regarding the MOF structure, some scholars pointed out that the polar structure can enhance the CO$_2$ adsorption capacity [20]. For example, the MOF containing carboxylate substituents exhibits significant CO$_2$ adsorption capacity in humid environments due to its polarity [20]. According to Table 2, the adsorption capacity of MOF-210 is equal to 2870 mg/g, which is close to the adsorption upper limit of solid materials [22].

Table 2. Summary of different types of MOF and their adsorption capacity of CO$_2$.

<table>
<thead>
<tr>
<th>MOF Type</th>
<th>Internal surface area</th>
<th>Adsorption capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-210</td>
<td>6240 -10,400 m$^2$/g</td>
<td>2870 mg/g</td>
<td>[22]</td>
</tr>
<tr>
<td>MOF-74(Zn)</td>
<td>1474 m$^2$/g</td>
<td>4.10 mmol/g</td>
<td>[27]</td>
</tr>
<tr>
<td>MOF-74(Cu)</td>
<td>1345 m$^2$/g</td>
<td>3.37 mmol/g</td>
<td>[27]</td>
</tr>
</tbody>
</table>

Besides the advantages of high internal surface area and porosity of MOF materials, the short and simple preparation process is also the reason why it has received widespread attention [25]. However, the ionic bonds and coordination bonds between metal ions and organic linkers are unstable [19]. Bosch et al. indicate that the robustness and reactivity of MOF are largely affected by the interaction between metal-organic ligands, and metal-containing clusters are easily substituted by other nucleophilic ligands such as water molecules, thereby the MOF structure may collapse in humid environment [26].

2.2.2. Covalent organic frameworks (COFs) Material

Different from MOF, covalent organic framework (COF) is a compound synthesized by covalent bonding between light elements and organic base, which was also initially introduced by Yaghi in 2005 [29]. Compared NUS-3 cell (see Fig. 5) with Mg/DOBDC cell (see Fig. 4), MOF and COF are similar in structure. COF has the same porous and crystalline properties as MOF but is relatively more stable than the latter due to the different bonding approaches [28]. Multiple voids provide space for gas adsorption, and high crystallinity means uniform pore size and firm texture [29]. Therefore, COF is also a suitable CO$_2$ capturing material as well as MOF [29]. The strong covalent bond is the key characteristic of COF, which relates to the organic linkages such as hydrogen-, boron-, carbon-, nitrogen- and oxygen- [31].

Fig 5. The structure of COF material e.g. NUS-3 [28].
COF has the same CO$_2$ adsorption mechanism as MOF [30]. Therefore, COF compounds with different adsorption properties can be produced by configuring different functional units [30]. For example, by adjusting the functional groups, the pores of the COF produced are as large as possible to adapt to the adsorption of CO$_2$ under high-pressure conditions [29]. Additionally, the CO$_2$ adsorption capacity of COF is significantly affected by different types of covalent bonds. To elaborate, imine-based and triazine-based COFs have higher adsorption capacity than boron-based COFs (see COF-102, FCTF-1-600, imine-based nitrogen-rich COF which listed in table 3) [31].

**Table 3.** Summary of different types of COF and their adsorption capacity of CO$_2$.

<table>
<thead>
<tr>
<th>COF type</th>
<th>Covalent bond type</th>
<th>Internal surface area</th>
<th>Adsorption capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-102</td>
<td>Boroxine</td>
<td>3620 m$^2$/g</td>
<td>34 cm$^3$/g (at 273K and 1 bar)</td>
<td>[32]</td>
</tr>
<tr>
<td>FCTF-1–600</td>
<td>Triazine</td>
<td>1535 m$^2$/g</td>
<td>124 cm$^3$/g</td>
<td>[32]</td>
</tr>
<tr>
<td>Imine-based nitrogen-rich COF</td>
<td>Imine</td>
<td>/</td>
<td>61.2 cm$^3$/g (at 1 atm and 273 K)</td>
<td>[33]</td>
</tr>
<tr>
<td>COF-1</td>
<td>Boroxine</td>
<td>750 m$^2$/g</td>
<td>230 mg/g (at 298 K)</td>
<td>[33]</td>
</tr>
<tr>
<td>COF-5</td>
<td>Boroxine</td>
<td>1670 m$^2$/g</td>
<td>870 mg/g (at 298 K)</td>
<td>[33]</td>
</tr>
<tr>
<td>COF-6</td>
<td>Boroxine</td>
<td>750 m$^2$/g</td>
<td>310 mg/g (at 298 K)</td>
<td>[33]</td>
</tr>
<tr>
<td>COF-103</td>
<td>Boroxine</td>
<td>3530 m$^2$/g</td>
<td>1190 mg/g (at 298 K)</td>
<td>[33]</td>
</tr>
<tr>
<td>TPE-COF-I</td>
<td>Imine</td>
<td>1535 m$^2$/g</td>
<td>73.8 mg/g (at 298 K)</td>
<td>[34]</td>
</tr>
<tr>
<td>TPE-COF-II</td>
<td>Imine</td>
<td>2168 m$^2$/g</td>
<td>118 mg/g (at 298 K)</td>
<td>[34]</td>
</tr>
</tbody>
</table>

In addition to high porosity and internal surface area, the biggest advantage of COF is the stability due to covalent bonds [28]. Compared with MOF, COF has a lower density, less hydrophobic, stronger thermal stability, and more stable frame structure [32]. However, as there is currently no convenient and suitable method to efficiently produce COF at a low cost, thereby COF still faces challenges in practical applications [29].

### 2.3. Activated carbon

Activated carbon (AC) is a form of carbon derived from high carbon content environmental wastes [35]. Normally, charcoal, lignocellulose and coal materials are used for the production of activated carbon [35]. The characteristics of activated carbon include a large internal surface area, multiple pores of different sizes, and the chemical complexity of the external area (see Fig. 6) [35]. In order to achieve a better adsorption effect of activated carbon, manufacturers usually use different chemical pathways to activate activated carbon [36]. Common chemical methods include nitric acid oxidation, KOH impregnation, heating under helium gas exposure [37].
The key to activated carbon to adsorb CO₂ is the intermolecular force. When the pore size is close to the size of the gas molecules entering, the intermolecular force reaches the strongest, thereby activated carbons with different pore sizes have different adsorption capacities for gas molecules of distinct sizes. [36].

Regarding the adsorption capacity of activated carbon to CO₂, the nature of the raw material of activated carbon will affect the adsorption strength of activated carbon [37]. According to the experimental data of Wei et al., the carbon dioxide adsorption capacity of bamboo-based activated carbon in an environment of 1 bar 298k is higher than that of any carbonaceous adsorbent, about 7.0 mmol/g [38]. Moreover, improving the surface area of activated carbon is an effective means to enhance carbon dioxide adsorption performance. For instance, ultra-microporous activated carbon is a product whose pore distribution becomes uniform and narrow after activation treatment. The ultramicroporous structure can greatly increase the internal surface area and further improve the CO₂ adsorption capacity [37]. Furthermore, several scholars believe that the pore properties are the decisive factor for the CO₂ adsorption capacity of activated carbon, and the adsorption effect reaches the best at 0.5-1.7nm [37]. For example, the CO₂ adsorption capacity of ACF-3 is 74 mg/g higher than that of ACF-4. This is mainly because the porosity of ACF-3 is closer to the optimal adsorption range [36]. Also, some experimental results indicate that the lower the temperature and the lower the temperature, the better the adsorption performance of activated carbon [37]. Based on Wickmaratane and Jaroniec’s experiment, the adsorption capacity of ACS in 25 °C is 3.50 mmol/g lower than that in 0 °C under the same pressure condition [38]. Additionally, a number of studies have shown that grafting amine functional group and hydroxyl functional group can improve the adsorption performance of activated carbon for CO₂ [39].

The advantage of activated carbon is that it has low requirements for the adsorption environment and low cost. Under normal circumstances, activated carbon does not need to add any catalyst and directly uses the microporous structure for adsorption [36]. However, as an inorganic blend of activated carbon, ash is likely to cause secondary pollution [37].

3. Conclusions

Carbon dioxide physical adsorption materials have been emphatically discussed and researched as an important technology to realize CCS. This paper focuses on four types of CO₂ adsorption materials, including shale reservoirs, MOF, COF and activated carbon. The four materials have similar adsorption mechanism related to the high porosity and internal surface area. Shale reservoirs are natural adsorption materials and have the characteristics of self-sealing. However, shale storage has an uncertain pore structure, so it is difficult to estimate its carbon adsorption potential accurately. In addition, both MOF and COF are porous crystalline polymers with adjustable pores. Neither MOF nor COF are adsorbents with high thermal and water stability. Furthermore, the CO₂ adsorption
capacity of activated carbon are affected by its raw materials, pore properties, environmental temperature and external chemical grafted functional groups. From economic perspective, activated carbon is the least costly material. Regarding future research directions, it is necessary to explore how to estimate the CCS potential of shale reservoirs accurately. In addition, it is necessary to continue to explore how to improve the thermal, water, and structural stability of MOF and COF. Moreover, the CO$_2$ adsorption potential of activated carbon needs to be fully exploited on the premise of environmental friendliness. The paper may provide a theoretical basis for the further sustainable use of shale, MOF, COF and activated carbon in the future.

References


