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The design of advanced metal-organic frameworks for carbon capture and separation

Zining Ren[1,*]

[1]Huaer Zizhu Academy, Shanghai, 200240, China

[*]15011020601@xs.hnit.edu.cn

Abstract. The greenhouse effect of fossil fuel combustion and factories is becoming more serious. And it causes various negative effects on the Earth. It would cause sea level rise, melting glaciers, and extreme climate changes. Many efforts have been put into researching stable materials to absorb greenhouse gases, especially carbon dioxide. The article introduces the design strategies of MOF (MOF) materials for efficient carbon dioxide capture and separation. The major obstacle is the design of a facile synthesis strategy for the mass production of efficient MOF materials. And the stability and the adsorbability of MOF materials is an important points. This article illustrates the reasons for the emergence of MOF materials, their development and modification, and their performance. Modification and functionalization of MOF materials will be a reliable way to improve MOF materials in the future. This paper hopes to facilitate the application of MOF-based materials in large-scale gas adsorption and stimulate the elimination of greenhouse gases.

Keywords: MOFs, Carbon Capture, Carbon Separation.

1. Introduction

Currently, the greenhouse effect has got increasing attention in nowadays' society, which has often appeared in science programs and weather reports. And the main factors of it are factory emissions and waste gases from vehicles, of which carbon dioxide is the most important of these gases. Figure 1 shows the percentage of different sources of carbon dioxide. So, with the greenhouse effect getting more and more serious. It has gradually become a focus of public concern. This text will give some solutions for these complex problems based on scientific development and economic benefits. Especially studying how to capture excess carbon dioxide [1].

The CO_2 emissions from coal combustion for electricity production occupy forty percent of the total CO_2 contributions. Figure 2 below shows the distribution of the demand for energy in the world. Considering that both methane and other climate pollutant emissions are generally being underestimated, the pollution from energy and electricity production and usage may account for an even larger share.

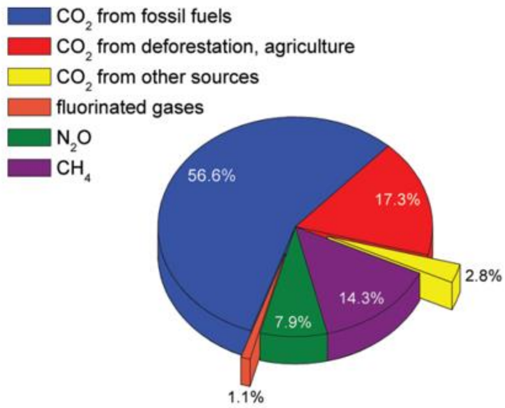

Figure 1. Different resources of CO_2 [2].

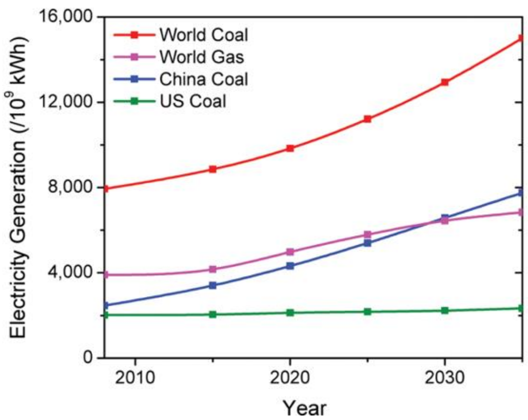

Figure 2. Worldwide distribution of electricity demand (2010-2030) [3].

If the current share of fossil fuels remains the same and energy demand doubles by 2050, the carbon emissions will be far exceeded those required to keep average global warming 2 ºC below the upper limit. Such high emissions would have catastrophic effects on the global climate. Using renewable energy is a promising way of controlling CO_2 emissions, thereby reducing energy consumption and the net carbon intensity. However, emission reductions do not mean banning the use of fossil fuels. Carbon capture and utilization, and storage (CCUS) is also an effective measure of achieving the net zero goal [3].

CCUS is a process that firstly captures carbon dioxide before it is emitted, separates it from industrial, energy use processes or the atmosphere, and then transports it to a new production process for purification and recycling or transport it to the storage site for compression and injection into the ground, and finally make it play an effective role in achieving the purpose of thorough emission reduction and resource utilization of carbon dioxide.

Capture is a process that separates carbon dioxide from the process of industrial production using pre-combustion capture, post-combustion capture, enriched oxidation capture and chemical chain capture. Transportation is carried out through tankers, ships or pipelines, which gather carbon dioxide. For example, carbon dioxide could be injected into the ground to realize the process of strengthening energy production and promoting resource extraction, such as increasing the extraction rate of oil and natural gas. The sequestering is pumping the carbon dioxide into deep geological reservoirs to achieve long-term isolation of carbon dioxide from the atmosphere. Such as land storage or marine storage.

CCUS is the most direct measure to control carbon dioxide emissions. It is considered by governments and researchers to be the most promising and effective means of reducing carbon stock

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management and important technology for reducing greenhouse gas emissions in the future. one of the paths. CCUS is a unique low-carbon and key technology that can achieve high-proportioned emission reduction while going on to use fossil sources [4]. In this paper, the typical CCUS technologies and advanced MOF materials for CCUS processes are summarized and compared, hoping to provide guidance for further related research.

2. Carbon capture technologies

The processes for CO_2 capture have three different ways, including post-combustion capture, pre-combustion capture and oxyfuel combustion. The conditions of post-combustion are using nitrogen or carbon dioxide as reactants, and the pressure is low. After combustion, the next step is separation. And carbon dioxide is separated from nitrogen, oxygen and water.

The conditions of pre-combustion need carbon dioxide and hydrogen, and the pressure is high. Its operating steps are more complex than post-combustion. The first step is conversion. Then is separation, carbon dioxide is separated, and hydrogen is formed. The final step is combustion. It needs air and produces power; its products are nitrogen, oxygen and water [5].

Besides, oxyfuel combustion needs oxygen and nitrogen as reactants, and the pressure is low. The first step is separation, which needs air, and nitrogen to be separated and form oxygen; and the last step is the combustion, which needs fuel and produces power and water. Carbon dioxide is also released in this step. The detailed steps of the three types of combustion are shown in Figure 3 below.

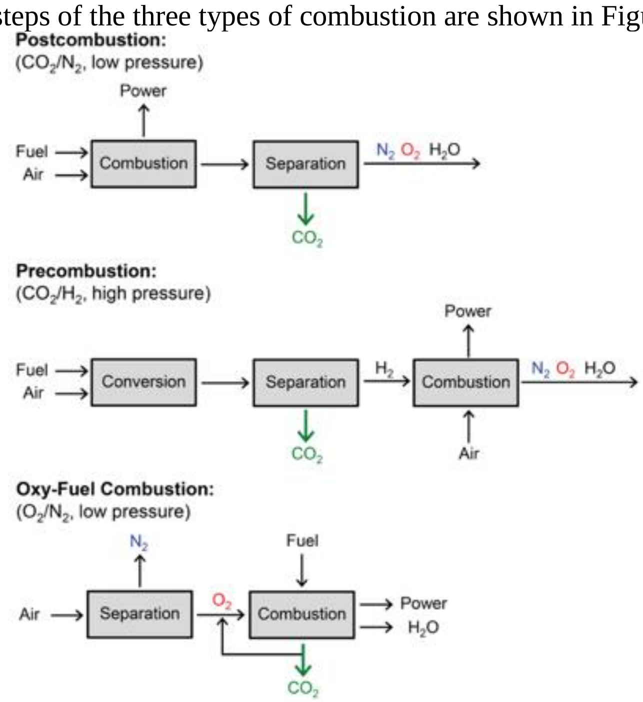

Figure 3. The scheme of the three typical CO_2 capture technologies [5].

Easier than the carbon dioxide or nitrogen separation needed for carbon dioxide capture after combustion. Once the carbon dioxide is removed from the gas mix, the H_2 is used to generate electricity, producing only H_2O as a byproduct. One another feasible way to reduce carbon dioxide emissions is oxygen-fuel combustion, where pure oxygen is used for coal or natural gas combustion. In this situation, oxygen or nitrogen is separated from air and O_2 is diluted with CO_2 before combustion to produce a flue gas of a mixture of CO_2 and H_2O, which can be used to separate effectively using existing technology.

3. MOF materials' performances in carbon capture

MOFs are often synthesized using particular modular synthesis, in which metal ions and organic ligands combine to form crystalline porous networks. A wide variety of synthetic methods have been modified in recent years to prepare these raw materials, while the conditions leading to the formation of the desired phase vary considerably. In fact, the reported synthesis processes cover different temperatures, solvent compositions, the ratio of different reagents, and concentrations of reagents. For CO_2 capture applications, materials should be more well-researched in achieving reliable performances to make the high density of packing of adsorption beds without damage to network structure. At high mechanical pressures, even slight incertitude to structural or chemical traits are possible. To a large extent, it affects the performance of the carbon capture system. Their thermal conductivity is zero. Additional bulk properties should be considered. Their thermal conductivity is an extra special property that needs to be aware of when assessing MOFs for installation within a fixed bed. This variation is important in assessing the efficiency of heating the adsorbent bed and the time of duration of the regeneration cycle of a temperature-variation and adsorption-based capture step.

3.1. Properties of MOFs for carbon capture

The weight absorption of CO_2, which leads to the amount of CO_2 adsorbed per unit mass of material, determines the mass of the MOFs required to form the adsorption bed. Volumetric capacity, which involves the density at which carbon dioxide can be stored in a material, is also an important parameter. The volume of the adsorption bed is significantly affected. These two parameters also play a unique role in ensuring the heating efficiency of the MOFs and directly affect the carbon capture performances. The lower-pressure (less than 1.2 bar) adsorption capacities for MOFs are collected at particular temperatures 293K to 313 K) [6]. Under the above conditions, the adsorption properties depend on the characteristics of the pore surface, and most high-capacity materials are those with highly functional surfaces. For post-combustion carbon dioxide capture, the flue gas pressure is from one bar and low partial pressure.

3.2. Modification of the MOF materials for carbon capture

The key point is how these modifications can solve the challenges or difficulties and what methods the researchers used for modifying the MOF materials.

Because of weak coordination bonds between metal and ligand components, the metal-organic skeleton is generally less chemically and thermally stable than zeolite and other porous inorganic solids. Many are particularly sensitive to air and moisture after stomatal discharge and need to be carefully handled under a nonvalent atmosphere if optimal performance characteristics are to be formed. In the case of MOF-5, even little exposure of the activated form of the material to air outcomes in the crystallinity of the material and rapid degradation of colitis. Using ionic liquid for MOF material modification has been a hot spot in recent research. Zhang et al. synthesized zeolite-liked MOF material, usf-ZMOF and sod-ZMOF, with the charged skeleton. The large organic cations in the skeleton were replaced by small inorganic cations by ion exchange, and the adsorption properties of CO_2 in them were studied. The experimental results show that the specific surface area of usf-ZMOF increases after Li+ ion exchange, and the adsorption capacity of CO_2 also increases, which is consistent with the results predicted by molecular simulation [7]. Furtherly, a novel adsorbent named MIL-101-ED was synthesized by grafting Ethylenediamine (ED) onto MIL-101(Cr) by solvothermal method. It was found that the CO_2 adsorption capacity has increased by 14.6%, and the CO_2/N_2 separation rate has increased by 55.6%, compared with the pristine MOF material. Also, the cycling experiment confirms the good stability of the modified MIL-101-ED [8]. Except for the above modification methods, other MOF modification methods, such as loaded carbon nanomaterials, hydrophobic group modification, amino functional group modification and other MOFs modification materials, are also widely used in the field of gas adsorption, especially CO_2 capture and separation [9].

4. Development and challenges in the MOF materials

If efficient ways of doing this through renewable energy can be developed, a potentially more promising option would be to convert a significant portion of the captured CO_2 into transport fuel. In any case, the sequestration route, however, carbon capture systems should capture CO_2 from flue gas in a productive and recyclable manner. This will be explored the emergency for new materials with reliable properties to carry out CO_2 capture is a field in pressing demand of development. Right now, the most difficult challenge.

Metal-organic skeleton materials are ideal tools for the development of next-generation carbon dioxide capture materials due to their strong adsorption capacity for waste gas, and good structural and chemical tunability. The ability to be used to select frame-pore components is predicted to allow precise control of the intimate connection of internal pore surfaces for carbon dioxide, facilitating material performance optimization for specific types of carbon dioxide capture (post-combustion capture).

Currently, the biggest challenge in achieving carbon dioxide capture at power stations is discovering more advanced materials with the right physical and chemical properties for use in real-world systems, reducing the large amount of energy required to carry out the capture step. Due to the properly low concentration of carbon dioxide (from 15 to 16%) and the amount of N2 (73 to 77%) coming from the air of coal combustion, because of high selectivity for CO2 is essential so that only pure CO_2 is captured and sequestrated [10].

Current technology involved in water amine absorber, with high selectivity to capture CO_2 from the gas mixture, but bring the energy loss of about 30% of the power plant to generate power here. The energy loss mainly comes from the need for plenty of water and heating to dissolve the amine and break the interaction between carbon dioxide and the amine functional form of the energy for the C - N key. Therefore, in terms of the economy and environmental impact of the consumption of coal, it is an emergency to research new coal consumption materials.

5. Conclusion

According to the theory of thermodynamics: higher adsorption capacity and selectivity inevitably bring greater heat of adsorption, so it is often difficult to balance high working capacity, high adsorption selectivity and low heat of adsorption, which has become a major technological challenge for porous materials to achieve high energy efficiency carbon capture. Furthermore, MOFs materials can be used in several fields, including energy storage, hydrogen storage, adsorption and separation (carbon capture, industrial gas separation, air purification, wastewater treatment and catalytic (thermal catalytic, photocatalysis, electricity), sensing, biomedicine (drug transport, hemodialysis, photodynamic therapy). And the development of European MOF materials is advanced, and there are some inevitable problems. First, there are a few kinds of industrialization. At present, there are few types of MOF materials applied in commercial applications, and the industry still lacks technical verification in batches. Most products remain in the basic research and pilot test stage. Second, the cost is high. The precursors of MOF new materials have a high cost, high energy consumption, immature energy saving and efficient preparation process, and no cost advantage in industrial production. Third, the use effect is not good. Most of the new MOF materials have low mechanical strength and poor thermal stability. Thus, more efforts will be necessary for the modification of existing MOF materials or the fabrication of new MOF materials for more efficient carbon capture.

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