



Characteristic Analysis of Activated Carbon Preparation and Gas Adsorption and Diffusion Mechanism

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Abstract In recent years, porous carbon materials have been praised as second-generation adsorbent materials because of their high specific surface area, large pore volume, high adsorption capacity, high chemical stability, low cost, and easy modification. However, the adsorption amount of the activated carbon on the gas is not particularly high, and the selectivity is also low, mainly because the gas molecules and the activated carbon are physically adsorbed, and the intermolecular force is weak. In order to enhance the force of the gas molecules and the surface of the adsorbent, it is very effective to incorporate a basic site such as an electron donor N atom into the carbon skeleton to increase the polarity of the surface. In this paper, from the process of gas diffusion, the adsorption process of activated carbon is analyzed and discussed, and relevant theoretical models are obtained.

Keywords activated carbon, adsorption, gas diffusion

1. Introduction

Coalbed methane (commonly known as coalbed methane) is an unconventional gas with coal present in coal seams. Its main components include methane, nitrogen, carbon dioxide, oxygen and a small amount of hydrogen, ammonia, nitrogen and the like. China's coalbed methane reserves are abundant. The proven CBM resources (up to 2,000 meters in depth) is about 81 trillion cubic meters, and the total amount of recoverable resources is about 10 trillion cubic meters, ranking third in the world. Effective exploitation of coalbed methane is of great significance for changing China's energy structure and protecting the ecological environment. Methane in coalbed methane is a clean and high-quality high-quality energy source, which is widely used [1]. Therefore, the full development, recycling and utilization of coalbed methane can not only save resources, turn waste into treasure, but also reduce greenhouse effect, save energy and reduce emissions, and prevent coal mining accidents. The complex coal structure is an important constraint geological condition for the exploration and development of coalbed methane in this area. Coal seams with different coal structures have different gas-bearing properties, permeability and reversibility. Therefore, it is important to identify the coal-body structure for the optimal combination of main producing layers and producing layers in multiple coal seams.

Research Status of Adsorbents

The adsorption method is an adsorption method in which a solid adsorbent is used for selective reversible adsorption of a gas in a mixed gas to separate and recover a specified gas, and is further classified into a temperature swing adsorption method (TSA) and a pressure swing adsorption method (PSA), for example, an adsorbent at a high temperature or CO₂ is adsorbed at high pressure, CO₂ is resolved after cooling or depressurization, and CO₂ is separated by periodic temperature or pressure changes. Gas solid adsorbent materials mainly include microporous and mesoporous materials carbon-based adsorbents (such as activated carbon, carbon molecular sieves), metal-framed (MOFs), molecular sieves, mesoporous silicon, etc [2].



Metal Organic Frameworks (MOFs)

In the past few decades, metal-organic frameworks have made significant advances in design synthesis and applications, mainly because of their enormous structural and chemical diversity, coupled with gas adsorption, ion exchange, molecular separation and Heterogeneous catalysis and many other fields have a good application. These porous crystalline solid materials are primarily 3D extensible network structures formed by organic bridging ligands or coordinated pillars and metal-based nodes having a uniform pore size of about 3-20 Å. A typical node includes one or more metal ions (Al^{3+} , Cr^{3+} , Cu^{2+} , Zn^{2+}) formed by bridging a specific functional group (such as a carboxyl group, a pyridyl group). At present, scientists focus on the development of industrial applications of MOFs such as gas storage, separation and catalysis, mainly because of their structural uniqueness, including structural robustness, thermal stability and chemical stability, as well as unprecedented specific surface area (up to $5000\text{m}^2\text{g}^{-1}$), high pore volume (55-90%) and low density ($0.21\text{-}1.00\text{ g cm}^{-3}$), these properties can keep the guest molecules from the pores [3]. The regular monodisperse arrangement of the micropores of such crystals is one of the most obvious differences between metal organic frameworks and gas porous materials (polymers, mesoporous silicon, carbon materials).

Molecular Sieve

Molecular sieves are a class of typical microporous adsorbent materials with high crystallinity and excellent thermal stability. It is mainly a type of crystalline aluminosilicate whose framework is formed by the mutual bonding of SiO_4 and AlO_4 tetrahedral units through common oxygen atoms. They have an open-cell structure of molecular size [4-5] so that molecules can penetrate. The negative charge generated by the AlO_4 tetrahedron instead of the SiO_4 tetrahedron can be balanced by exchange cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , etc., which are located in the pores or cavities of the entire structure. The adsorption and separation properties of molecular sieves for gases are greatly dependent on the size, charge density and distribution of these cations.

Mesoporous Silica Material

The adsorption of CO_2 by ordered mesoporous silica materials has attracted widespread attention in recent years, mainly because of their high specific surface area and the controllability of the empty net size. However, pure silica indicates that it does not provide a strong adsorption site for CO_2 molecular adsorption. Mesoporous silica materials can facilitate rapid gas diffusion compared to other porous materials such as MOFs and ZIFs. Moreover, the presence of a large amount of hydroxyl groups on the surface of the silica provides a good opportunity for the loading of the amino functional groups, primarily to increase the affinity and interaction of the silica surface and the CO_2 molecules.

2. Preparation and mechanism of porous carbon materials

Porous carbon materials are classified as ordered activated carbon-based materials and are known to be the most promising class of adsorbents because of their low cost, high specific surface area, modification of pore structure and surface functional groups and relatively easy reproducibility. According to the International Union of Pure and Applied Chemistry (IUPAC), carbon materials are classified into three categories based on pore size: microporous materials ($<2\text{ nm}$), mesoporous materials ($2\text{ nm} < d < 50\text{ nm}$) and macroporous materials ($> 50\text{ nm}$).

Ordered mesoporous carbon materials have a wide range of applications in adsorption separation, catalysis, gas storage, supercapacitors, etc., and these mesoporous or microporous carbon-based material adsorbents are much larger than other types of adsorbents in many respects. The advantages, such as the cheapness of raw materials, are unmatched by other adsorbents [4]. The wide range of sources of carbon materials makes them less costly to produce on an industrial scale. For example, these activated carbon adsorbents can be derived from coal (bituminous coal, lignite), industrial by-products (such as by-products of industrial materials, petroleum, coke) and trees, or other biomass sources (sawdust, coconut shell, olive tree [6]) The wide range of raw materials has also led to the pore size distribution of activated carbon, pore structure, active surface structure and other properties to meet their adsorption properties.



The step of preparing a carbon material from a raw material usually has two steps: carbonization and activation. Typically the stage of carbonization is the initial heating and pyrolysis of the starting materials in an inert gas atmosphere. At this stage, the precursor material releases most of the non-carbon elements such as H, O and N, leaving a rigid carbon skeleton with minimal surface functional groups. The next step is activation, mainly by physical or chemical activation, which increases the specific surface area while increasing porosity and active sites. The main method of physical activation is to partially vaporize the charcoal at a high temperature between 1100-1250 K by steam, CO₂, air or a mixture of several. During the chemical activation process, activators such as KOH, H₃PO₄, and ZnCl₂ open the microporous structure to form a developed porous structure. In general, chemical activation is lower than the temperature required for physical activation, and it is possible to produce a carbon material having a developed gap. However, the adsorption of gas on carbon materials is a physical adsorption and is a weak force, so it is highly sensitive to temperature and has low selectivity.

In recent years, research has focused on improving the force of adsorbents and adsorbates and the selectivity to gas molecules, thereby increasing the adsorption capacity of gas molecules. One method is to modify or otherwise polymerize with an amine-containing precursor by post-grafting. One method is to modify or otherwise polymerize with an amine-containing precursor by post-grafting. Another effective method is to increase the alkalinity by surface modification - the incorporation of a basic nitrogen atom into the carbon skeleton. The nitrogen element contains five valence electrons. After the nitrogen atom is incorporated into the carbon skeleton, the charge density of the carbon material can be enhanced. The difference between the radius and the carbon atom is small, which is beneficial to directly form a strong valence bond with the carbon atom. Essentially improve the internal structure of the carbon material. The latter method is relatively rich in research so far, and the basic group-nitrogen functional group on the surface of the adsorbent can not only endure the humid environment, but also improve the adsorption capacity of gas molecules.

Porous carbon adsorption mechanism

The microstructure parameters such as specific surface area, total pore volume, micropore volume, surface functional group and pore size distribution of activated carbon adsorbents affect the behavior of adsorbed gases, and the effects of these parameters on CO₂ adsorption behavior have also been reported. Generally, for activated carbon, the microporous capacity, total pore volume, and specific surface area have consistent structural values, that is, activated carbon having a large pore volume and total pore volume, and the corresponding specific surface area value is also very high. Big. Activated carbon uses different precursor materials such as shell, resin, coal, etc., and changes in surface parameters due to differences in preparation parameters (heating rate, activation temperature, atmosphere, etc.), resulting in a variety of surface functional groups, including several groups, cluster groups., vinegar type base, yoghurt base, etc [7]. Acidic functional groups tend to adsorb polar substances, while basic functional groups are more susceptible to adsorption of non-polar or weaker polar materials.

3. Diffusion Model Mechanism

Desorption and diffusion mechanism of anisole on porous carbon materials [8]. The porous carbon material was prepared by using glucose as carbon source, and the structure of the material was characterized. The desorption kinetics curve of anisole on the adsorbent was determined by gravimetric method. Based on the linear adsorption driving force model, the diffusion coefficient D_e estimation model was established. Calculate the relationship between anisole $D_e(t) - q(t)$ on the adsorbent. The influence of the pore structure of the material on the desorption rate and diffusion mechanism of anisole on the material is discussed, which provides a basis for the design and preparation of porous materials with good sustained release properties.

Diffusion Coefficient Estimation Model

It is assumed that when a spherical adsorbent adsorbs perfume molecules and suddenly puts into a large gas stream, desorption of perfume molecules occurs ($t > 0$). The fragrance molecules are desorbed from the adsorbent and can be expressed by the following linear force rate equation.



$$\frac{\partial q}{\partial t} = 15(q^* - q) \quad (1)$$

Where q is the amount of adsorption of perfume molecules per unit mass of spherical particles, $\text{g}\cdot\text{g}^{-1}$; D_e is the diffusion coefficient; R_p is the radius of the spherical particles; q^* is the adsorption phase corresponding to the concentration of the perfume molecules in the mainstream gas (The equilibrium concentration of the agent). In the experiment, an atmospheric amount of pure nitrogen was used to purge the adsorbent particles, and at this time, the concentration of the fragrance in the purge gas in contact with the adsorbent may be zero, and q^* is equivalent to zero. So the above formula can be turned into

$$\frac{\partial q}{\partial t} = -15 \frac{D_e}{R_p^2} \quad (2)$$

The above formula can be rearranged

$$D_e = \frac{-\frac{\partial q}{\partial t} R_p^2}{15q} \quad (3)$$

The above formula is also called a diffusion coefficient estimation model. In the experiment, the relationship between the adsorption amount (desorption amount) and the time $q(t)$ under constant temperature or variable temperature conditions can be determined by gravimetric method, and then the desorption kinetic curve obtained by the experiment can be fitted. The specific function expression $q(t)$ of the kinetic curve is desorbed. At this time, the desorption rate equation can be obtained by deriving the time. The experimental determination of $q(t)$ and substituting into equation (3) can estimate the diffusion coefficient D_e , and can simultaneously calculate the relationship curve of $D_e(t)$ - $q(t)$.

4. Adsorption Equilibrium Theory Model

The adsorbate molecules continuously adsorb and desorb at the interface, and when the amount of adsorption and the amount of desorption do not change over a long period of time, they are called adsorption equilibrium. Adsorption equilibrium is the most important basic information for understanding an adsorption process. When a system has multiple components, the acquisition of the adsorption equilibrium data of the pure components is the premise of understanding the whole multi-component adsorption. Obtaining this basic data, and thus the adsorption equilibrium and single-component adsorption of multiple components. Kinetics and multicomponent adsorption kinetics studies. The adsorption isotherm is a detailed description of the adsorption equilibrium. For a given solid-gas system [9]:

$$q = f(T, P, E)$$

Where q is the adsorption capacity of the adsorbate on the solid adsorbent, T and P are the absolute temperature and the gas pressure, respectively, and E is the adsorption potential between the solid adsorbent and the adsorbate gas. When T is constant, E can be considered to be unchanged. At this time, the adsorption amount (q) is only a function of pressure (P). This functional relationship is the adsorption isotherm (Adsorption isotherm). At present, researchers have proposed many different theories and models of adsorption isotherms, which can be roughly divided into three categories: Langmuir theory, Gibbs thermodynamics theory and Polanyi potential theory. The adsorption isotherm model based on Langmuir theory is used.

(1) Langmuir model

The Langmuir model was first proposed (1918) [10], based on the kinetic point of view to describe the complete theory of plane adsorption. The assumption of this model is 3 points; 1 the surface of the adsorbent is a uniform surface, and the adsorption energy of all adsorption sites is constant; 2 the adsorption of the adsorbent surface is local, that is, the adsorbed molecules or atoms are adsorbed on the surface of the adsorbent. Local position; 3 adsorbent sites can only adsorb one molecule or atom at each adsorption site. The Langmuir theory is based on the principle of dynamic equilibrium, in which the adsorption rate of the adsorbent surface is equal to the desorption rate:

$$K_a p_i \left(1 - \frac{q_i}{q_{m,i}}\right) = k_d \frac{q_i}{q_{m,i}} \quad (4)$$

Let the Langmuir model equation expression be obtained:



$$\frac{q_i}{q_{m,i}} = \frac{K_i P_i}{1 + K_i P_i} \quad (5)$$

(5) where M represents the equilibrium adsorption capacity and saturated adsorption capacity of the solid adsorbent at a certain temperature and pressure, P_i is the adsorption pressure, and K_i is the Langmuir adsorption equilibrium constant, and satisfies the Van't Hoff relationship:

$$K_i = K_{0,i} \exp\left(-\frac{\Delta H_i}{RT}\right) \quad (6)$$

(6) where $K_{0,i}$ is an infinite temperature adsorption equilibrium constant, $(-\Delta H_i)$ represents heat of adsorption, R is a molar gas constant (8.3145 J/molK), and T is an adsorption temperature.

The adsorption isotherm using Langmuir theory can help us to study the parameters such as the rate and pressure of the activated carbon material when adsorbing gas. The model is helpful for analyzing the adsorption performance of activated carbon.

5. Outlook

The preparation of activated carbon is on a laboratory scale, and various problems such as uniform activation of the burning and recovery of the sample in the actual industrial scale-up production need to be solved. In the control of the pore volume structure and specific surface parameters of activated carbon due to the differences in experimental samples, the effects obtained under different conditions are also uneven, requiring time and energy to explore.

References

- [1]. Tao Pengwan, Wang Xiaodong, Huang Jianbin, A-burning of coalbed methane in low temperature method [J]. Natural Gas Chemical, 2005, 30(4), 43-46
- [2]. Xiaohua Zhuhua Oxygenated Coalbed Methane Deoxidation LNG Process R&D Chemical Coal Chemical Industry, 2014, 42(1), 12-15
- [3]. Zhao Xuan installed Wang Tonghua, Li Lin, Liu Guan Cao Yiming. Preparation of Fe/C hybrid carbon membrane and its gas separation performance. Journal of Chemical Industry and Engineering, 2009, 60(9), 2232-2236
- [4]. Min Min, Liu Kewan, Xian Xuefu, Feng Guanyan. Preparation of Granular Activated Carbon from Anthracite Coal and Its PSA Separation of CH₄/N₂ Properties 剏 Materials Science and Engineering, 2011, 19(4), 82-87
- [5]. Yang Zhiyuan, Wang Dechao, Liu Jiaoping. Advances in Separation of Zeolite Molecular Sieves for CH₄/N₂ by Pressure Swing Adsorption [J]. Clean Coal Technology, 2015, 21, 109-113剏
- [6]. Min Min, Xian Xuefu. Coalbed methane pressure swing adsorption separation theory and technology [M]. Science Press: 2015
- [7]. Liu Chenglin, Zhu Jie, Che Changbo, Yang Hulin, Fan Mingzhu. A new round of national coalbed methane resource evaluation methods and results [J]. Natural Gas Industry, 2009, 25 (11), 130-132
- [8]. Chen Guangyin, Sun Qiang, Guo Xuqiang, Huo Yusheng, Li Jian, Liu Jian, Tang Guojun. Experimental study on continuous separation of coalbed methane by hydrate method [J]. Journal of Chemical Engineering of Universities, 2013, (4), 561-566
- [9]. Zhang Keda, Wang Peng, Dong Weiguo, Tang Nan, Li Xiaoliang. Experimental study on non-catalytic combustion and deoxidation of coalbed methane [J]. Clean Coal Technology, 2014, (4), 109-112
- [10]. Zhang Chuanquan coalbed methane liquefaction process in the raw material gas adsorption pretreatment research network. Shanghai Jiaotong University, 2008

