Powder Technology 333 (2018) 377–384

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Effects of pore structure of prepared coal-based activated carbons on CH_4 enrichment from low concentration gas by IAST method

Desheng Yuan [a,b], Yuannan Zheng [a,b], Qingzhao Li [a,b,*], Baiquan Lin [b], Guiyun Zhang [b], Junfeng Liu [b]

[a] Key Laboratory of Gas and Fire Control for Coal Mines of Ministry of Education, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China
[b] School of Safety Engineering, China University of Mining and Technology, Xuzhou, Jiangsu 221116, China

ARTICLE INFO

Article history:
Received 9 January 2018
Received in revised form 21 March 2018
Accepted 18 April 2018
Available online 21 April 2018

Keywords:
Coal based activated carbon
Low concentration gas
CH_4 enrichment
Pore size distribution
IAST

ABSTRACT

In this study, low rank bituminous coals were used as raw material for the preparation of a series of coal-based activated carbons (CACs) with similar surface properties but different pore structures, and these CACs could be used to enrich methane from low concentration gas by pressure swing adsorption (PSA) method. The surface morphology of raw material changed from smooth to porous after activating reaction. In addition, the high-pressure adsorption isotherms of methane and nitrogen indicated that the adsorption performance of CACs for methane is stronger than nitrogen. The prediction results by Ideal Adsorbed Solution Theory (IAST) method also shows that prepared CACs have a high selectivity for methane and nitrogen mixture at low pressure. At higher-pressure conditions, the selectivity increases more rapidly with increasing molar fraction of methane in the gas phase. In addition, selectivity is mainly affected by micropores in the range of 0.55–0.85 nm, while mesopores and macropores have no effects on the selectivity. Present research results would provide some guidance for the preparation of excellent adsorbents and improve the efficiency of adsorption separation.

1. Introduction

As a by-product of coal production, coal-bed gas is not only an important source of coal mine safety accidents and a strong greenhouse gas with 25 times greenhouse gas effect of carbon dioxide [1], but also a variety of clean and efficient energy resource. Therefore, methane recovery from coal-bed gas is beneficial for environmental protection, energy supply and development. However, methane concentration in the coal mine gas extracted from Chinese coal seams is too low to be utilized. Generally, the average methane concentration of the drainage gas is <30% in China because of the low permeability of coal seams and some geological phenomenon, like water blocking effect [2,3]. Therefore, low concentration methane extracted from Chinese coal mine was usually discharged directly into the air, which caused serious air pollutions and greenhouse effects. Up to now, enriching methane by the pressure swing adsorption (PSA) process is an efficient method to increase the methane concentration in order to be used as a clean energy resource or raw chemical material. However, for the PSA technique, the key factor is the selection of adsorbent [4].

The extracted coal-bed gas is mainly consisting of methane, nitrogen, oxygen and a small amount of other gases. To realize the enrichment of methane from coal-bed gas, the separation of methane and nitrogen mixture would be a major issue that needs to be resolved because of the similar physicochemical properties of methane and nitrogen. Therefore, the development of suitable adsorbent for the separation of methane and nitrogen has been attracting the attention of many researchers around the world. Nowadays, activated carbons as one of the carbonaceous adsorbent has been widely studied and used in PSA field due to their well-developed pore structure, good thermal stability and low price [5] among various commercial absorbents, such as zeolite [6], carbon molecular sieve [7,8], activated carbon [9,10] and so on.

At present, research works on the separation of methane and nitrogen were mainly focus on the design of PSA process, the methane purity and the stability of adsorbents. Few studies have been done on the structure adjustment of adsorbents [9,11]. Generally, the adsorption performance of adsorbents is mainly depended on the pore structure and surface chemical properties, of which micropores are the main place for gas adsorption [11]. Based on the non-local density functional theory (NLDFT), Kluson et al. [12] demonstrated that the selectivity for methane and nitrogen mixture was a function of the pore size and adsorption pressure. Cui et al. [13] found that pores <0.31 nm would inhibit the penetration of methane and nitrogen using a slit-shape pore model because the molecular dynamic diameter of methane and nitrogen are 3.80 Å and 3.64 Å respectively.

Currently, the main raw materials for activated carbons preparation are coals [14–17] and other biomass materials including wood materials [18–21], fruit shells [22,23], agricultural wastes [24–26] and so on. Coal is widely used because of its high yield and low price. The methods of preparation activated carbons include physical activation, chemical

---

[*] Corresponding author.
E-mail address: qingzhaolee@163.com (Q. Li).

https://doi.org/10.1016/j.powtec.2018.04.045

Table 1
Proximate and vitrinite reflectance analysis of coal sample.

Proximate analysis (w/w %)				Vitrinite reflectance $R_{0,max}$(%)
FC_{ad}	V_{daf}	A_{ad}	M_{ad}	0.70
55.38	23.20	17.06	4.35	

Table 2
Carbonization and activation scheme for preparation of activated carbons.

Factor	Carbonization temperature (°C)	Carbonization time (min)	Activation temperature (°C)	Activation time (min)
Experiment no.				
T-1	400	60	800	60
T-2	500	60	800	60
T-3	600	60	800	60
T-4	500	60	800	60
T-5	500	120	800	60
T-6	500	180	800	60
T-7	500	60	700	60
T-8	500	60	800	60
T-9	500	60	900	60
T-10	500	60	800	60
T-11	500	60	800	120
T-12	500	60	800	180

activation, physical-chemical activation and many other methods. However, the pore structure of activated carbons prepared by physical activation method is poorly developed because of the poor controllability [27]. Using coal, agricultural and industrial waste materials, such as waste tires, hay, brown and bituminous coals as raw materials, Pietrzak et al. [28] prepared the activated carbons by different synthetic method. Results proved that the most effective way for preparing microporous activated carbons having high surface area (~3000 m^2/g) should follow the steps below: carbonization → activation → reaction with urea. Their XPS results had also shown that chemical activation could make nitrogen species, especially the pyrrole and pyridone groups, enriched at active carbons surfaces [29]. And also, it can make activated carbons present different physicochemical properties and relatively higher sorption capacities towards gas and liquid pollutants, such as NO_2, H_2S, methylene blue and so on [30–32]. Bahri et al. [33] prepared the activated carbons by using grape seeds with carbon dioxide activation method. Used coal as precursor and KOH as activating agent, the specific surface area of activated carbons prepared by Yao et al. [34] is only 672 m^2/g. By physical-chemical activation method, Li et al. [35] prepared the activated carbons according to the following two steps: first immersed the melon seed shells into KOH solution and then activated them by carbon dioxide. The specific surface area of activated carbons can reach to 2582 m^2/g. Moreover, many previous research works had found that high-performance activated carbons could be prepared by using KOH as activating agent. Therefore, Hütinger [36] suggests that KOH has excellent activation effect resulting from the metallic potassium generated during activation process. Metallic potassium has a good wettability to the carbon surface in a molten state and thereby reducing the tension of KOH on the carbon surface being able to react more fully with the carbon surface. Lillo-Ródenas et al. [37–39] conducted a series of experiments on the preparation of activated carbons by using anthracite as precursor adopted KOH activation method. Their results found that when the activation temperature was set above 700 °C, activation process was preferentially generated micropores and then expanded to form mesopores and macropores. Therefore, it is an effective way to prepare activated carbons by KOH activation method.

Generally, carbonization and activation process are the most significant factors influencing the pore structure of prepared activated carbons. Therefore, in this study, a series of activated carbons with similar surface properties but different pore structures were prepared through changing the carbonization temperature, carbonization time, activation temperature and activation time. Based on the high-pressure adsorption isotherms of prepared activated carbons, the prediction of adsorption separation was calculated out by IAST method. Moreover, the relationships between the pore structure, selectivity and adsorption capacity were discussed.

2. Experimental

2.1. Materials

The low rank bituminous coal samples were obtained from Binchang mining area in Shaanxi Province, China. Coal samples were firstly crushed and sieved to the particles with the size range of 250–380 μm. Then, the samples were dried at 40 °C for 24 h in the drying oven as the raw materials. The analytical pure KOH was purchased from Sinopharm Chemical Reagent Co., Ltd. in Shanghai, China. The results

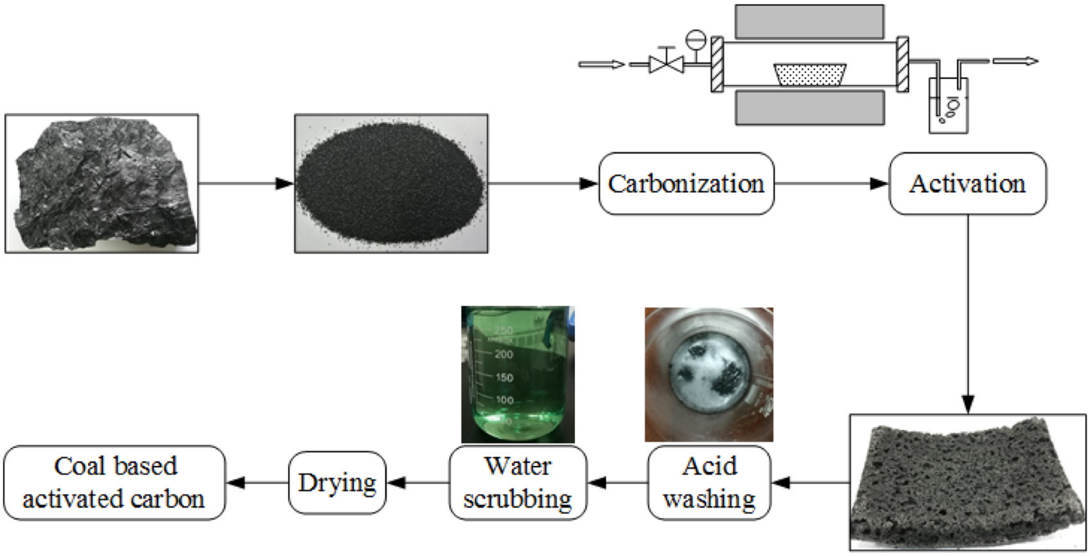

Fig. 1. The flow diagram of preparation of coal based activated carbons.