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# Supercritical Adsorption Based CO<sub>2</sub> Capture from N<sub>2</sub>/CO<sub>2</sub> Mixture by Activated Carbon and Carbon Molecular Sieve

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**Abstract:** The adsorption equilibria of pure supercritical N<sub>2</sub> and CO<sub>2</sub> on the activated carbon Yigao-A and carbon molecular sieve CMS-200 were measured by the gravimetric method (IGA-001, Hiden) in the temperature region of 313.15-393.15 K and pressure region of 0-2 MPa. The adsorption kinetics of N<sub>2</sub> and of CO<sub>2</sub> on the activated carbon Yigao-A and carbon molecular sieve CMS-200 at 313.15 K in 50 kPa were tested. The Langmuir-Freundlich model was applied to analyze the adsorption isotherms. The adsorption kinetics was investigated with the Fickian model. The analysis of adsorption equilibria showed that a high temperature, low pressure is beneficial to the equilibria based selective adsorption of supercritical CO<sub>2</sub> on the activated carbon Yigao-A and carbon molecular sieve CMS-200. The investigation of adsorption kinetics exposed that the carbon molecular sieve CMS-200 is able to separate CO<sub>2</sub> from the N<sub>2</sub>/CO<sub>2</sub> mixture by its kinetic effect, and lower temperature is preferred.

**Keywords:** Supercritical Adsorption, CO<sub>2</sub> Capture, Activated Carbon, Carbon Molecular Sieve

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## 1. Introduction

As the time of technological revolution is deepening on, the CO<sub>2</sub> has become the well-known anthropogenic source of global warming, which intensifies the greenhouse effect [1]. The CO<sub>2</sub> capture has a great significance to the carbon emission control, space travel application, oil recovery, chemical industry and the other possible economic sources, so a worldwide attention in the research institutions, universities and R&Ds of pioneering enterprises are being much attracted and some advances have already been made, and an increasing rate of the technology and patents about the CO<sub>2</sub> capture could be observed in the last decade [2-4]. An urgent method of CO<sub>2</sub> capture is becoming very necessary to the anthropogenic sources of CO<sub>2</sub> emission, especially for the large scale sources like power plants since CO<sub>2</sub> concentration is still kept rising after the breakthrough of 400 ppm of CO<sub>2</sub> concentration in ambient air. Although the most available and critical method for CO<sub>2</sub> capture is the energy replacement by non-CO<sub>2</sub> emission source in the long-run, a

short-term-method of CO<sub>2</sub> capture from post treatment is very important at the present level because it doesn't affect the main part of the plant and is easy to retrofit the existing facility [5, 6].

In the history, the amine based absorption process received a wide range of application with its time efficiency although it was carrying some drawbacks like the high cost of energy, lower rate of recovery and degradation of absorbent, which is caused by SO<sub>x</sub> and NO<sub>x</sub>, and corrosion of equipment [7-10]. The membrane separation was considered the simplest, most energy efficient method of CO<sub>2</sub> capture, it is competitive to pressure swing adsorption (PSA) and cryogenic distillation in the industry. However, an efficient, high selective and permeable, tough, temperature stable, durable, non-water clogged, thin and large area packable membrane, which is applicable in the industrial scale or techno-economical design of membrane separation for CO<sub>2</sub> capture, is still on the way of the research [11-14]. The cryogenic process of CO<sub>2</sub> capture produces liquid CO<sub>2</sub>, and no separation media is required, but very high energy cost of separation and necessary requirement of operation control makes this

process only applicable for the special circumstances [15, 16]. The Biological capture by living organism in large scale use is also another potential method under the research [17-19]. Although there is no single solution for CO<sub>2</sub> emission, every method has its advantages and limitations, and an appropriate technology for CO<sub>2</sub> capture is dependent on the type of the anthropogenic source and operating conditions, an alternative various technology for CO<sub>2</sub> capture is a must have topic [20, 21]. Among a series of the art of state separation technologies including the absorption with liquids, purification by membrane, cryogenic distillation and adsorption using solids, which were developed over the past decades, and some new technologies like the enzyme based separation, calcium looping CO<sub>2</sub> capture and mixed matrix membrane, which were invented in the recent years [22], the adsorption with solids appears to be the most promising alternative strategy for CO<sub>2</sub> capture [23-25].

There are three types of adsorbents, including the inorganics, organic-inorganic hybrids and metal-organic frameworks (MOF), exist in the category of adsorption. The inorganic zeolite, especially zeolite 13X, is being widely used in the industry of CO<sub>2</sub> capture because of its higher adsorption capacity. However, it shapes the carbonates or other strong adsorption forces if the impurities like water, SO<sub>x</sub> and NO<sub>x</sub> are involved in, and it also has a shortage of pore blocking caused by the strong potential between the molecules of adsorptive and adsorbent, which lowers the rate of desorption. The organic-inorganic hybrids and metal-organic frameworks are based on the mechanism of chemical adsorption to capture CO<sub>2</sub>, which creates a great difficulty to regenerate the adsorbents, and they are with poor economic efficiency due to high cost of production and synthetic complexity, and they are not feasible to selective CO<sub>2</sub> adsorption at low partial pressure [26], and they also shows deficiency to existing of moisture. Therefore its application in large scale sources is limited. Recently, the newest type of adsorbents like "molecular basket" and "molecular cages" were synthesized and studied in the aspect of the CO<sub>2</sub> capture [27-30], and also the promising carbon based "molecular basket" sorbents with high CO<sub>2</sub> sorption capacity were also developed [31].

The pressure/vacuum swing adsorption (PSA/VSA) is much attractive and more applicable alternative method with its higher efficiency of energy and of capital cost and the smart control of operation, which is plausible to apply to the CO<sub>2</sub> capture [32, 33]. Although the adsorption method is unable to compete with the old separation technology based on absorption with amine from the aspect of productivity at the time being, it is being considered the very cost saving and energy efficient potential technology. An adsorbent with good capacity and high selectivity is a basic requisite for the adsorption process. The selectivity based on steric effect or equilibrium or kinetics is taken advantage of in the adsorption separation process [34]. Adsorption separation based on kinetic selectivity has a potential to capture CO<sub>2</sub> from N<sub>2</sub>/CO<sub>2</sub> mixture after successful separation of N<sub>2</sub>/O<sub>2</sub>, CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/N<sub>2</sub> on carbon molecular sieve CMS

[35-39]. Using an economic adsorbent also raises the process efficiency of cost and of energy for CO<sub>2</sub> capture. The carbogenic adsorbents are lightweight, elastic, heat and electric conductive (may be used in electric swing adsorption), cheap, easy-shapeable from precursors, higher specific surficial, thermal and chemical stable, durable, non-moisture sensitive, stable under the impurity, environment-protective and energy saving, it solves many difficulties of the other adsorbents possess in the process of implementation [40-44]. The activated carbon Yigao-A and carbon molecular sieve CMS-200 were adopted as the representatives of carbogenic adsorbents and they were investigated to the study of the supercritical CO<sub>2</sub> capture in this work since they would be believed that different pore size distribution and different micropore volume would effect on the adsorption properties of the adsorbents in the low partial CO<sub>2</sub> capture [45-47]. A pressure swing adsorption model simulated by E S Kikkinides and R T Yang Showed that the equilibrium selectivity dominates the kinetic selectivity in these two adsorbents, and the kinetic selectivity was not good enough in the carbon molecular sieve [48]. However, in-depth study was not undertaken both from adsorption equilibria selectivity and the kinetics selectivity on carbogenic adsorbents.

In this study, the isotherms and kinetics of N<sub>2</sub> and CO<sub>2</sub> adsorption were made on the two kinds of carbogenic adsorbents (activated carbon Yigao-A and carbon molecular sieve CMS-200), and the potentials of supercritical adsorption based CO<sub>2</sub> capture by carbogenic adsorbents were tried to evacuate from the model of adsorption equilibria and of mass transport.

## 2. Experimental

### 2.1. Experimental Process

The pure gas of N<sub>2</sub> and of CO<sub>2</sub> were selected as adsorptive, the activated carbon Yigao-A and carbon molecular sieve CMS-200 were as carbogenic adsorbents to separate CO<sub>2</sub> from the N<sub>2</sub>/CO<sub>2</sub> mixed system. The activated carbon Yigao-A was provided by Shanxi Yigao Coal-Bed-Methane Company, the carbon molecular sieve CMS-200 was from Dalian Haixin Chemical Company. The adsorbent samples were pretreated to dry at 423.15 K for at least 8 hours in vacuum by a drying oven (Type: D2F-6021, Shanghai Yiheng) and outgassed at least 6 hours to  $1 \times 10^{-4}$  Pa at 423.15 K in the reactor of an intelligent gravimetric analyzer prior to the measurement of each isotherm of adsorption equilibria. The intelligent gravimetric analyzer (IGA-001) used in the experiment was produced by Hiden Isochema Limited in the United Kingdom. The gases of N<sub>2</sub> and of CO<sub>2</sub> are from Shanghai Weichuang Industrial Gases Co., Ltd, and they are all with the purities greater than 99.99%. All adsorption isotherms were measured by the intelligent gravimetric analyzer in the pressure range of 0-2 MPa. The range of experimental temperature for each adsorption system is 313.15-393.15 K with a 20 K interval. Each temperature of

adsorption equilibria was held at constant within the change of  $\pm 0.1$  K by means of a thermostat (TF50/3/12/F, Severn Thermal Solutions).

## 2.2. Characterizations of Adsorbents

The pore size distributions (PSD) of the Activated carbon Yigao-A and carbon molecular sieve CMS-200 were characterized by CO<sub>2</sub> adsorption data at 273.15 K tested by using the intelligent gravimetric analyzer rather than N<sub>2</sub> adsorption data at 77 K as CO<sub>2</sub> molecule is sensitive to narrow micropores that are N<sub>2</sub> molecule cannot accessible to at 77 K [49]. The pore size distributions of adsorbents were calculated with the corrected Horvath and Kowazoe model for the slit shaped pore based on Matlab (The Mathworks, Inc.) codes to increase the accuracies of the characterizations [50]. CO<sub>2</sub> adsorption data on activated carbon Yigao-A and carbon molecular sieve CMS-200 at 273.15 K are represented in Figure 1. The results of PSD for the activated carbon Yigao-A and carbon molecular sieve CMS-200, which were assumed to follow a normal distribution, are depicted in Figure 2. Some parameters related to the adsorbents are shown in Table 1.

## 3. Results and Discussion

### 3.1. Supercritical N<sub>2</sub> and CO<sub>2</sub> Adsorption Study on Activated Carbon and Carbon Molecular Sieve

Although the maximum pressure of adsorption equilibria for N<sub>2</sub> and CO<sub>2</sub> is about 2 Mpa, which couldn't be neglected comparing to the saturation vapor pressure of N<sub>2</sub> and of CO<sub>2</sub>, the Gibbs excess amount was chosen to describe the amount of uptake at each experimental point since the thermodynamic stability still holds in this pressure region [51]. The pure supercritical N<sub>2</sub> gas adsorption isotherms (the critical temperature of N<sub>2</sub> is 126.1 K) measured on the activated carbon Yigao-A and carbon molecular sieve CMS-200 by the intelligent gravimetric analyzer are indicated in Figure 3 and Figure 4. The symbols represent the points acquired by the measurement, the lines represents the fitting curve of the isotherm model.

It is seen that for the supercritical N<sub>2</sub> adsorption, the higher the temperature is, the more linear the adsorption isotherm becomes in the experimental region of pressure. The pure supercritical CO<sub>2</sub> (the critical temperature of CO<sub>2</sub> is 304.4 K) adsorption isotherms measured on the activated carbon Yigao-A and carbon molecular sieve CMS-200 were also studied. The corresponding graphs are depicted in Figure 5 and Figure 6 respectively. The isotherm figures indicate that the adsorption capacity of activated carbon Yigao-A is much greater than that of the carbon molecular sieve CMS-200 at the same experimental condition. The adsorption isotherms of N<sub>2</sub> and CO<sub>2</sub>, from Figure 3, Figure 4, Figure 5 and Figure 6, appear as type I on the activated carbon Yigao-A and carbon molecular sieve CMS-200 due to the non-micropore filling mechanism of supercritical N<sub>2</sub> and CO<sub>2</sub> adsorption on the activated carbon Yigao-A and carbon molecular sieve

CMS-200, in which, the agglomerations in the pore don't liquefy in this conditions [52].

The Langmuir-Freundlich model [53] [equation-(1)] was used to fit the isotherm data.

$$\frac{q}{q_0} = \frac{(bp)^n}{1+(bp)^n} \quad (1)$$

Where  $q_0$  is the pseudo-saturation capacity at supercritical condition,  $b$  is the affinity constant and  $n$  is the heterogeneity factor; they were calculated from the isotherms by the linear regression. The values of the parameters  $q_0$ ,  $b$ ,  $n$  for the supercritical N<sub>2</sub> and CO<sub>2</sub> adsorption on each adsorbent are listed in Table 2 and Table 3 respectively.

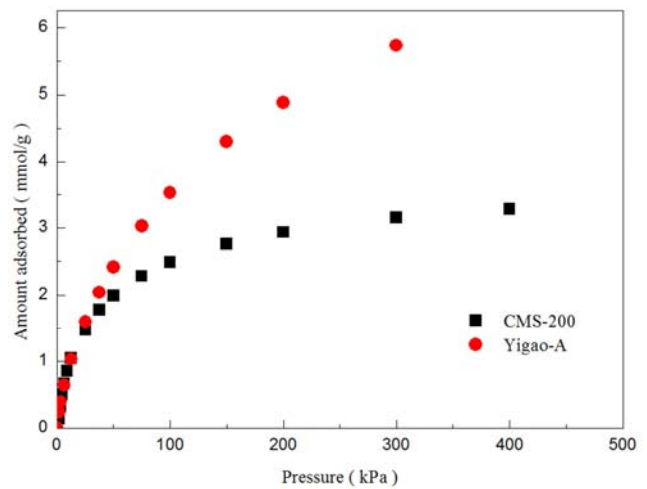


Figure 1. CO<sub>2</sub> adsorption data on activated carbon Yigao-A and carbon molecular sieve CMS-200 at 273.15 K.

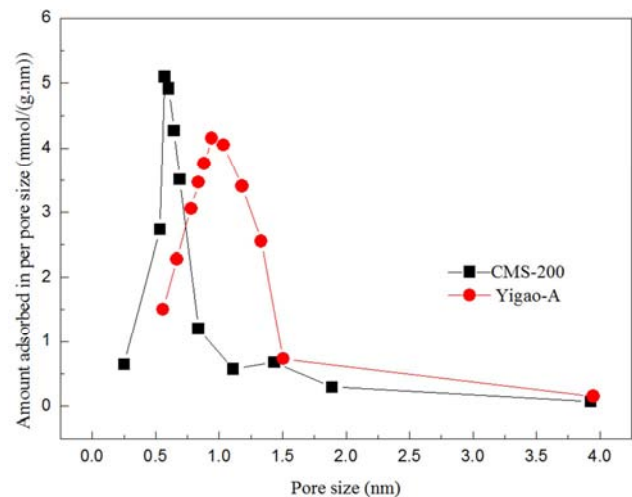


Figure 2. PSD for activated carbon Yigao-A and carbon molecular sieve CMS-200.

Table 1. Properties of adsorbents.

Adsorbent	Activated carbon Yigao-A	Carbon molecular sieve CMS-200
Complexion	Cylindrical black	Cylindrical black
Bulk density	430 g/L	650 g/L
Particle radius	2-3 mm	1.5-1.6 mm

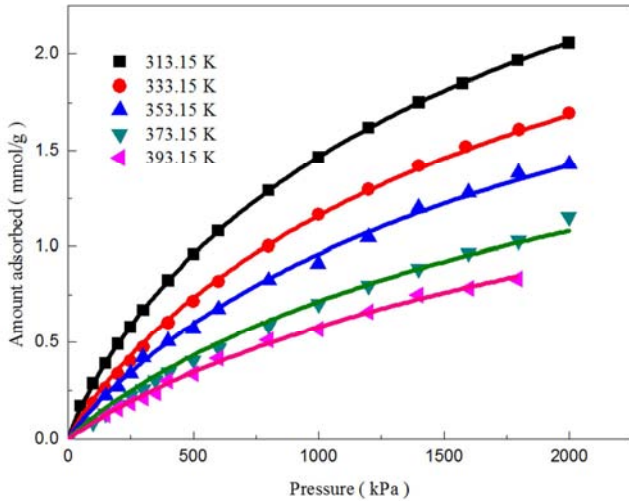


Figure 3. Supercritical N<sub>2</sub> adsorption isotherms on activated carbon Yigao-A.

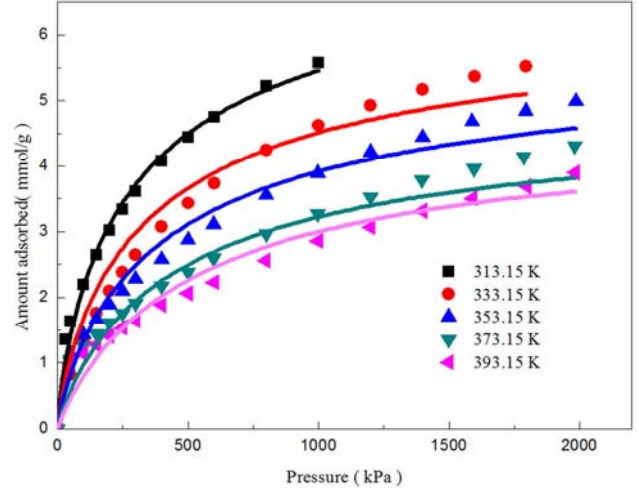


Figure 5. Supercritical CO<sub>2</sub> adsorption isotherms on activated carbon Yigao-A.

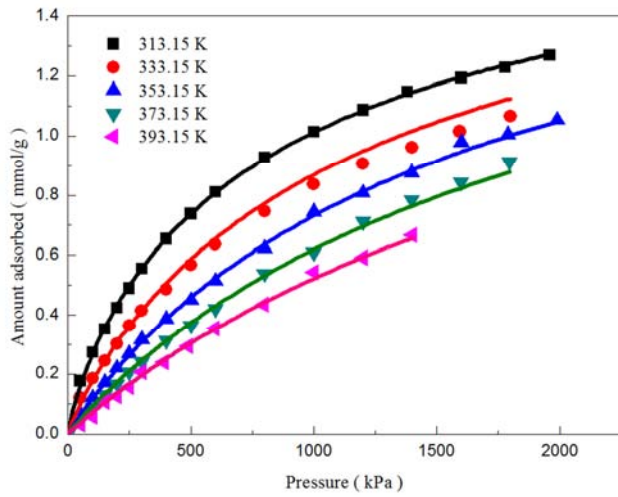


Figure 4. Supercritical N<sub>2</sub> adsorption isotherms on carbon molecular sieve CMS-200.

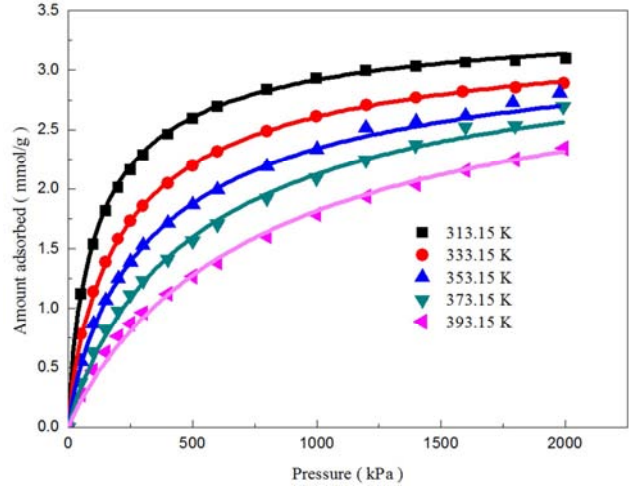


Figure 6. Supercritical CO<sub>2</sub> adsorption isotherms on carbon molecular sieve CMS-200.

Table 2. Pseudo-saturation capacity  $q_0$ , affinity constant  $b$  and heterogeneity factor  $n$  for supercritical N<sub>2</sub> adsorption.

Temperature	Parameter	$q_0$		$b$		$n$	
		Yigao-A	CMS-200	Yigao-A	CMS-200	Yigao-A	CMS-200
313.15 K		3.9367	1.9336	$5.5466 \times 10^{-5}$	$1.1535 \times 10^{-6}$	0.8840	0.9508
333.15 K		3.4246	1.9204	$4.8145 \times 10^{-5}$	$7.7094 \times 10^{-7}$	0.9150	0.9600
353.15 K		3.0768	1.9150	$4.2465 \times 10^{-5}$	$6.1058 \times 10^{-7}$	0.9210	0.9730
373.15 K		2.4790	1.9075	$3.7963 \times 10^{-5}$	$4.7349 \times 10^{-7}$	0.9350	0.9794
393.15 K		1.9652	1.8945	$3.4327 \times 10^{-5}$	$3.7680 \times 10^{-7}$	0.9500	0.9897

Table 3. Pseudo-saturation capacity  $q_0$ , Affinity constant  $b$  and heterogeneity factor  $n$  for supercritical CO<sub>2</sub> adsorption.

Temperature	Parameter	$q_0$		$b$		$n$	
		Yigao-A	CMS-200	Yigao-A	CMS-200	Yigao-A	CMS-200
313.15 K		7.7106	3.4881	$3.0498 \times 10^{-6}$	$7.5055 \times 10^{-6}$	0.7925	0.8010
333.15 K		6.5613	3.4154	$2.7469 \times 10^{-6}$	$4.1398 \times 10^{-6}$	0.8166	0.8256
353.15 K		5.8450	3.3528	$2.3343 \times 10^{-6}$	$2.6696 \times 10^{-6}$	0.8370	0.8512
373.15 K		4.8988	3.3419	$2.0866 \times 10^{-6}$	$1.8219 \times 10^{-6}$	0.8901	0.9269
393.15 K		4.6434	3.2789	$1.8865 \times 10^{-6}$	$1.2544 \times 10^{-6}$	0.9470	0.9576

### 3.2. Equilibrium Based CO<sub>2</sub> Separation Selectivity Study of Supercritical N<sub>2</sub> and CO<sub>2</sub> Adsorption

The separation selectivity based on the adsorption affinity constant is the micro appearance between the molecules of adsorbent and of adsorptive, but in the real process of adsorption, the amount adsorbed is the combined result of the affinity constant, the pore size distribution of adsorbent and the heterogeneity factor between the adsorbent and adsorptive, so it is more practical to consider the separation selectivity from the point of the amount adsorbed. CO<sub>2</sub> separation selectivity of adsorbent,  $S_e$ , was defined as equation-(2) [54, 55].

$$S_e(P, T) = \frac{n_{\text{CO}_2}(P)_T / y_{\text{CO}_2}}{n_{\text{N}_2}(P)_T / y_{\text{N}_2}} \quad (2)$$

Where, the values of the amount adsorbed  $n(P, T)$  are derived by the interpolation of adsorption isotherm after fitting the Langmuir-Freundlich equation [equation-(1)],  $y$  represents the uptake mole fraction of adsorptive at the surface of adsorbent, since the concentrations of CO<sub>2</sub> in the flue gases of most power plants is approximately 15% and it is accepted in this way in the reports[56-58],  $y(\text{CO}_2)=15\%$  and  $y(\text{N}_2)=85\%$  was also taken in this work. The corresponding results of the function  $S_e(P, T)$  for the activated carbon Yigao-A and carbon molecular sieve CMS-200 are shown in Figure 7 and Figure 8 respectively.

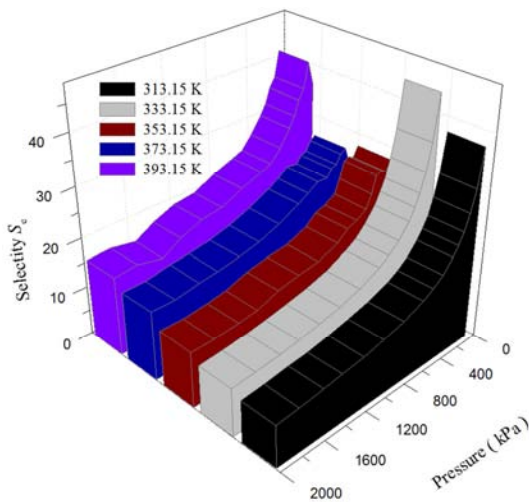


Figure 7. Plot of CO<sub>2</sub> separation selectivity  $S_e$  for activated carbon Yigao-A.

The adsorption equilibrium based CO<sub>2</sub> separation selectivity  $S_e$  of the activated carbon Yigao-A and carbon molecular sieve CMS-200 decreases with the increase of the pressure. The separation selectivity of the activated carbon Yigao-A and of the carbon molecular sieve CMS-200 is more sensitive to pressure at lower pressure range than that is in higher pressure range. In the high pressure range, the selectivity is less sensitive to the equilibrium temperature and pressure. This result of equilibrium based sensitivity with the pressure and temperature is in consistent with the report that

the bulk pressure and mole fraction are the main driving forces rather than the temperature at low pressure, and adsorption amount is relatively insensitive to pressure at high pressure in supercritical fluid mixture adsorption [59]. In all experimental range of temperature, the activated carbon Yigao-A is more sensitive to temperature than the carbon molecular sieve CMS-200 is, so the carbon molecular sieve CMS-200 proves more durable to the temperature change than the activated carbon Yigao-A does. It is shown that a lower pressure and higher temperature is preferred for these two adsorbents to apply them to the CO<sub>2</sub> capture.

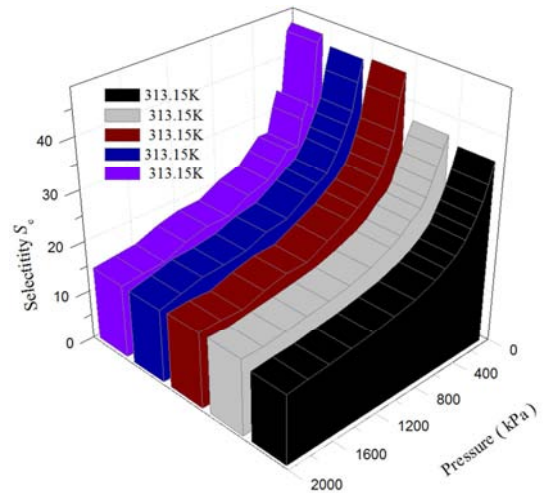


Figure 8. plot of CO<sub>2</sub> separation selectivity  $S_e$  for carbon molecular sieve CMS-200.

### 3.3. Kinetics Based CO<sub>2</sub> Separation Selectivity Study of Supercritical N<sub>2</sub> and CO<sub>2</sub> Adsorption

The ramp rate of pressure in intelligent gravimetric analyzer was kept at 20 kPa/min, the first 2.5 minutes were spent to fix the adsorption pressure at an equilibrium state in the study of kinetics. The kinetic data of supercritical N<sub>2</sub> and CO<sub>2</sub> adsorption at 313.15 K in 50 kPa on the activated carbon Yigao-A and carbon molecular sieve CMS-200 are as Figure 9,10,11 and Figure 12 respectively.

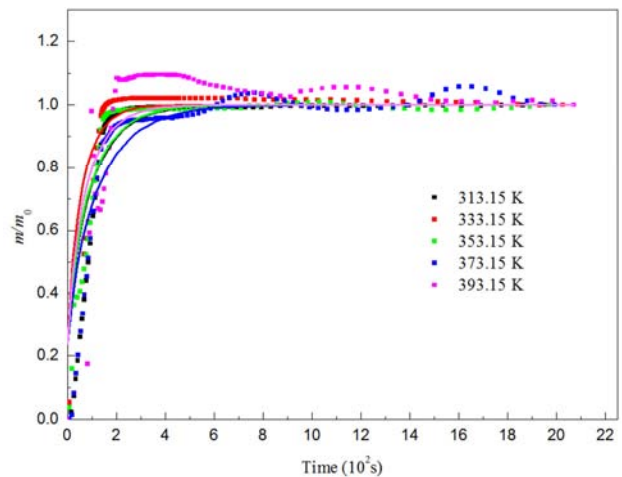


Figure 9. Kinetics of N<sub>2</sub> adsorption on activated carbon Yigao-A.

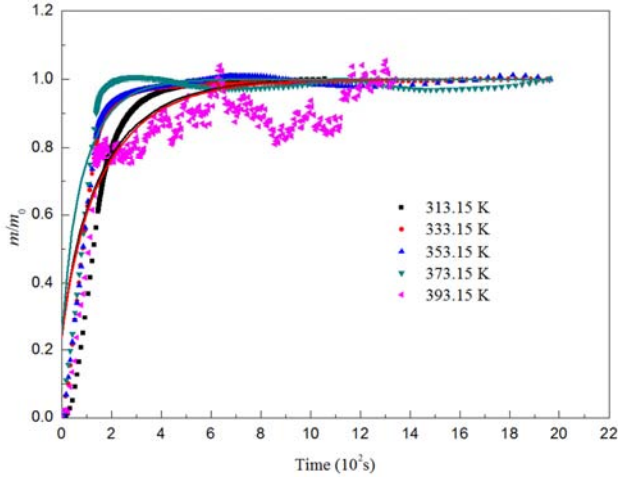


Figure 10. Kinetics of CO<sub>2</sub> adsorption on activated carbon Yigao-A.

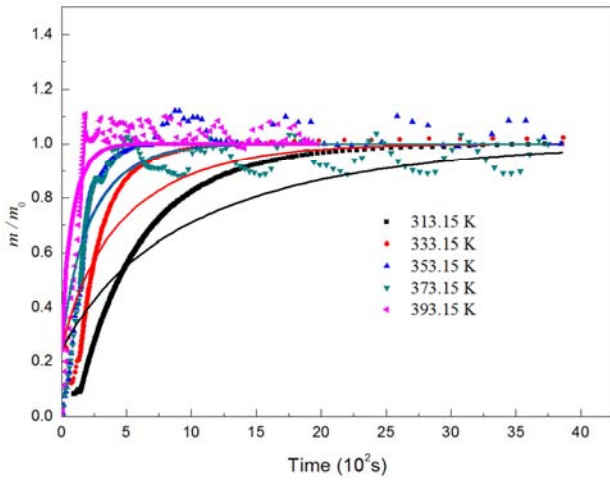


Figure 11. Kinetics of N<sub>2</sub> adsorption on carbon molecular sieve CMS-200.

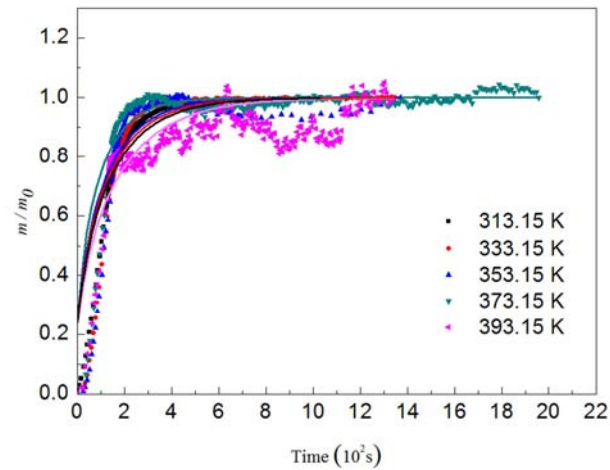


Figure 12. Kinetics of CO<sub>2</sub> adsorption on carbon molecular sieve CMS-200.

The structures of the samples are cylindrical symmetric, and the ratio of cylindrical length to the width is approximately equal 1, hence the particles of each adsorbent could be regarded as spherical in this work. The Fickian equation of mass transfer for packed spherical stack [equation-(3)] [60, 61] was applied to calculate the diffusion

coefficients  $D_c$  of N<sub>2</sub> and CO<sub>2</sub> adsorptive, where, some assumptions as following were introduced to solve the equations: 1) The bulk phase can be described by the equation of ideal gas. 2) The gravimetric balance system in the reactor of IGA-001 is isothermal. 3) Diffusion coefficients  $D_c$  of the whole particle on each temperature is considered as constant during each corresponding kinetic test [62]. Taking the initial and boundary conditions as equation-(4), -(5) and -(6) for the adsorbate, the analytical solution for equation-(3) is as equation-(7) [63,64], where,  $m$  is the amount adsorbed at the time  $t$  (mmol/g),  $m_0$  is the amount adsorbed at the equilibrium state (mmol/g),  $q(r, t)$  is the adsorbate concentration (mol/m<sup>3</sup>),  $t$  is the time of diffusion (s),  $r_c$  is the radial coordinate, The measured radius of particle of the activated carbon Yigao-A and of the carbon molecular sieve CMS-200 is  $r_c(\text{Yigao-A}) = 1.05$  mm and  $r_c(\text{CMS-200}) = 1.6$  mm,  $n$  is the natural number. The fitting of the Fickian model for N<sub>2</sub> adsorption and for CO<sub>2</sub> adsorption on the activated carbon Yigao-A and on the carbon molecular sieve CMS-200 is demonstrated in Figure 9, 10, 11 and Figure 12. The diffusion coefficient  $D_c$  (m<sup>2</sup>/s) was calculated from equation-(7) and listed in Table 4 and Table 5.

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_c \frac{\partial q}{\partial r} \right) \quad (3)$$

$$q(r, 0) = 0 \quad (4)$$

$$q(r_c, t) = q_0 \quad (5)$$

$$\left( \frac{\partial q}{\partial r} \right)_{r=0} = 0 \quad (6)$$

$$\frac{m}{m_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D_c t}{r_c^2} \right) \quad (7)$$

The mass transport of supercritical N<sub>2</sub> and CO<sub>2</sub> in the pore of the activated carbon Yigao-A and of the carbon molecular sieve CMS-200 belongs to lattice diffusion according to their order of magnitude [65] in the corresponding calculated coefficients of diffusion  $D_c$  in Table 4 and Table 5. The diffusion coefficients  $D_c$  were described by the Arrhenius equation [equation-(8)], where, the pre-exponential factor  $D_0$  for reference temperature  $T_0$  is the diffusion coefficient in micropore at zero surface coverage, and  $E_a$  is the activation energy for the localized admolecule on the surface of the adsorbent.

$$D_c = D_0 \exp \left[ -\frac{E_a}{RT} \left( \frac{T}{T_0} - 1 \right) \right] \quad (8)$$

The instantaneous CO<sub>2</sub> selectivity of the activated carbon Yigao-A and of the carbon molecular sieve CMS-200 with the time (see Figure 13 and Figure 14) were also calculated from the kinetic data. The ratio of the amount of CO<sub>2</sub> uptake to that of N<sub>2</sub> uptake at a certain time in the same condition is defined as the instantaneous CO<sub>2</sub> selectivity of the adsorbent [equation-(9)], which is the joint result of the Henry's law

constant  $k$  and diffusion coefficient  $D_c$  in the micropore. The meaning and values of parameters  $y$  ( $\text{CO}_2$ ),  $y$  ( $\text{N}_2$ ) are same as in the equation-(2).

$$S_i = \frac{n(\text{CO}_2)_{p,T,t,adsorbent} / y(\text{CO}_2)}{n(\text{N}_2)_{p,T,t,adsorbent} / y(\text{N}_2)} \quad (9)$$

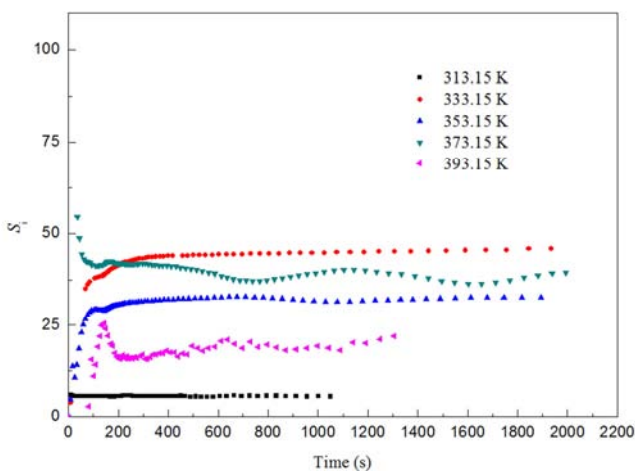
**Table 4.** Diffusion coefficients  $D_c$  calculated for activated carbon Yigao-A at 313.15 K and 50 kPa.

$T$	$D_c$ Activated carbon Yigao-A		
	$D_c(\text{N}_2)$	$D_c(\text{CO}_2)$	$D_c(\text{CO}_2)/D_c(\text{N}_2)$
313.15 K	$9.93837 \times 10^{-10}$	$5.65922 \times 10^{-10}$	0.569
333.15 K	$1.60230 \times 10^{-9}$	$5.29284 \times 10^{-10}$	0.330
353.15 K	$1.02685 \times 10^{-9}$	$1.04767 \times 10^{-9}$	1.02
373.15 K	$7.59726 \times 10^{-10}$	$1.36854 \times 10^{-9}$	1.80
393.15 K	$1.23918 \times 10^{-9}$	$5.39750 \times 10^{-10}$	0.436

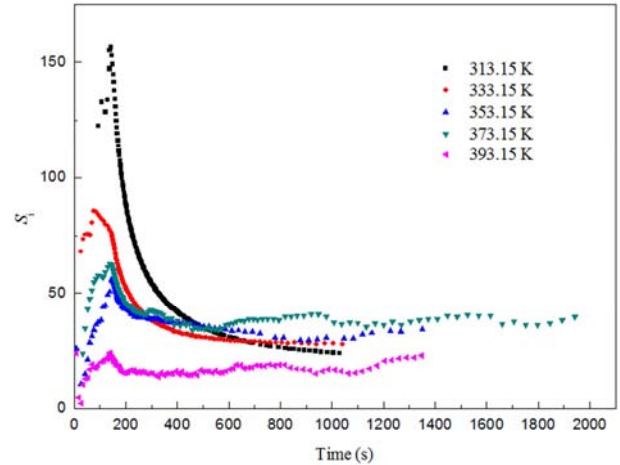
**Table 5.** Diffusion coefficients  $D_c$  calculated for carbon molecular sieve CMS-200 at 313.15 K and 50 kPa.

$T$	$D_c$ Carbon molecular sieve CMS-200		
	$D_c(\text{N}_2)$	$D_c(\text{CO}_2)$	$D_c(\text{CO}_2)/D_c(\text{N}_2)$
313.15 K	$1.98111 \times 10^{-10}$	$1.52516 \times 10^{-9}$	7.70
333.15 K	$4.37816 \times 10^{-10}$	$1.64705 \times 10^{-9}$	3.76
353.15 K	$9.30274 \times 10^{-10}$	$1.76214 \times 10^{-9}$	1.89
373.15 K	$9.10814 \times 10^{-10}$	$2.31820 \times 10^{-9}$	2.55
393.15 K	$2.62085 \times 10^{-9}$	$1.25166 \times 10^{-9}$	0.478

As it is shown in Figure 13 and Figure 14, the instantaneous  $\text{CO}_2$  selectivity over  $\text{N}_2$  on the activated carbon Yigao-A almost keep constant all over the kinetic time. However, on the carbon molecular sieve CMS-200, the curve of instantaneous  $\text{CO}_2$  selectivity is very high in the small range of kinetic time and sharply decreases with the kinetic time. This means that the carbon molecular sieve CMS-200 is much possible to separate  $\text{CO}_2$  from  $\text{N}_2/\text{CO}_2$  system by its kinetic effects than the activated carbon Yigao-A is. The instantaneous  $\text{CO}_2$  selectivity of the activated carbon Yigao-A and of the carbon molecular sieve CMS-200 are the implicit functions of the diffusion coefficients  $D_c$  of  $\text{N}_2$  and  $\text{CO}_2$  adsorptive.



**Figure 13.** Instantaneous  $\text{CO}_2$  selectivity on activated carbon Yigao-A with the time.



**Figure 14.** Instantaneous  $\text{CO}_2$  selectivity on carbon molecular sieve CMS-200 with the time.

In addition, the ratio of the diffusion coefficients  $D_c(\text{CO}_2)/D_c(\text{N}_2)$  on the carbon molecular sieve CMS-200 is greater than that on the activated carbon Yigao-A at the same external condition, and it approaches the value of the ratio of the diffusion coefficients  $D_c(\text{CO}_2)/D_c(\text{N}_2)$  on the activated carbon Yigao-A when the temperature is increased. The ratio of the diffusion coefficients  $D_c(\text{CO}_2)/D_c(\text{N}_2)$  on the activated carbon Yigao-A almost not big changes than that on the carbon molecular sieve CMS-200, this result backup the conclusion mentioned above that instantaneous  $\text{CO}_2$  selectivity decreases with the rising temperature and carbon molecular sieve CMS-200 can be applied to capture  $\text{CO}_2$  by its kinetic effect. It demands fast diffusion rate, higher  $\text{CO}_2$  selectivity and higher  $\text{CO}_2$  adsorption capacity, lower cost of energy and of facilitation, more efficient packing structure of adsorbent, excellent tolerability of adsorbent to impurities to develop an adsorption method in the  $\text{CO}_2$  capture [66, 67]. From Figure 13 and Figure 14, the instantaneous supercritical  $\text{CO}_2$  selectivities on carbon molecular sieve CMS-200 are much greater than that on activated carbon Yigao-A at a lower temperature, and there exists a sharp decrease of the instantaneous  $\text{CO}_2$  selectivity with time, so the activated carbon Yigao-A is not the ideal adsorbent to capture  $\text{CO}_2$  rather than the carbon molecular sieve CMS-200 is from the points of durability to the temperature change, diffusion coefficient of  $\text{CO}_2$ , and instantaneous  $\text{CO}_2$  selectivity on the same condition with that on the carbon molecular sieve CMS-200, this makes a feasible opportunity for carbon molecular sieve CMS-200 rather than the activated carbon Yigao-A to separate  $\text{CO}_2$  by the kinetic effect. The selection of carbon molecular sieve CMS-200 rather than activated carbon Yigao-A as an adsorbent is encouraged in the range of discussion from the equilibria and kinetic analysis of supercritical  $\text{N}_2$  and  $\text{CO}_2$  adsorption to apply to the  $\text{CO}_2$  capture in the supercritical condition. From the point of time-saving, a lower temperature greater than 313.15 K and the time smaller than the inflexion point of the curve of instantaneous  $\text{CO}_2$  selectivity is to be introduced to apply the carbon molecular sieve CMS-200 to the  $\text{CO}_2$  capture.

## 4. Conclusions

In this work, two kinds of carbogenic adsorbents, the activated carbon Yigao-A and carbon molecular sieve CMS-200 were studied to capture CO<sub>2</sub> from the N<sub>2</sub>/CO<sub>2</sub> mixed system at the supercritical conditions to help an industrial application. The equilibrium based supercritical CO<sub>2</sub> separation selectivity of the adsorbents shows that the supercritical CO<sub>2</sub> selectivity over supercritical N<sub>2</sub> is much higher at the low pressure and higher temperature, and the selectivity is much more sensitive to the pressure in low pressure region than to the temperature, and it is almost less sensitive to pressure and temperature in high pressure region, so a higher temperature and low pressure is preferred if a carbogenic adsorbent is to be utilized to capture supercritical CO<sub>2</sub> by its mechanism of adsorption equilibrium. The Fickian model of supercritical N<sub>2</sub> and CO<sub>2</sub> adsorption kinetics on the activated carbon Yigao-A and carbon molecular sieve CMS-200 shows that the carbon molecular sieve CMS-200 is able to separate CO<sub>2</sub> from the N<sub>2</sub>/CO<sub>2</sub> mixture if the kinetic time is under the proper control. Lower temperature, lower pressure and the time smaller than the inflexion point of the curve of instantaneous CO<sub>2</sub> selectivity is recommended. Since the carbogenic adsorbents has more advantages to separate supercritical CO<sub>2</sub> from a water or other impurities containing N<sub>2</sub>/CO<sub>2</sub> system, the carbon molecular sieve CMS-200 has a descent prospect to apply to the industry of supercritical CO<sub>2</sub> capture if it would be packed in the way of membrane integrated pressure/electric swing adsorption in the separators of large flue.

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