

EQUILIBRIUM MODEL OF GAS ADSORPTION ON ZEOLITE

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Abstract

The adsorption of methane and carbon dioxide on NaY, ZSM-5 and beta have been investigated under similar conditions using volumetric adsorption apparatus. The nature of zeolite adsorbing surface is the determining factor in adsorption but the behaviors of molecules adsorb can be easily described in adsorption equilibrium where many equations based on different concept have been proposed. In order to elucidate the experimental data obtained, the adsorption data was fitted using the existing thermodynamic models. The simplest equations are Langmuir and Freundlich, each of which involves two parameters but Henry equation represents the adsorption at low coverage. Another equation that is widely used is Dubinin-Polanyi equation. Based on the model constants, considerable differences in the adsorption of CH₄ and CO₂ with these zeolites were observed.

Keywords: Zeolite, adsorption, thermodynamic model.

Introduction

Adsorption involves the enrichment of one or more components in an interfacial layer between two bulk phases, gas and solid. The adsorption mechanisms are generally governed by physical and chemical interaction that lead to physical adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption is dependent on the same intermolecular attractive and repulsive forces which are responsible for the condensation of vapors whereas chemisorption is governed by chemical bond formation between the adsorbed molecules and the surface of the solid. There is no sharp distinction between both mechanism of adsorption since various intermediate cases exist.

The adsorption measurement at constant temperature, T , may be calculated by measuring the decrease in pressure of gas or the increase in weight of solid. As it reaches equilibrium, the pressure becomes constant and the solid ceases to increase further. The amount of the gas adsorbed, x , per gram of solid then depends on p , T , the specific surface, S , and porosity of the adsorbent, and on the nature of the gas-solid system.

Adsorption equilibrium is usually characterized by the adsorption isotherm, a plot of the adsorbed phase concentration against the gas phase concentration or partial pressure at equilibrium. From a basic statistical thermodynamic principles it may be shown that for physical adsorption at sufficiently low concentrations, the isotherms should approach a simple linear form. The region of approximate linearity is known as the Henry's law region and the slope is known as the Henry's constant.

$$K(\text{dimensionless}) = \left. \frac{dq}{dc} \right|_{q \rightarrow 0} \quad (1)$$

$$K_p \left(\frac{\text{moles}}{\text{cm}^3 \text{ atm}} \right) = \left. \frac{dq}{dp} \right|_{q \rightarrow 0} \quad (2)$$

where K is Henry's constant and K_p are related by $K=(RT)K_p$.

Henry constant is in fact an equilibrium constant and, it shows the usual van Hoff temperature dependence

$$K = K_{\infty} \exp(-\Delta U_o / RT) \quad (3)$$

$$K_p = K_{p\infty} \exp(-\Delta H_o / RT) \quad (4)$$

where ΔU_o and ΔH_o represent respectively the changes in internal energy and enthalpy at very low loading. Henry constant measures the intrinsic affinity of the adsorbent for a specific adsorbate that can be used to provide quantitative comparisons of adsorption affinity [1].

At loading beyond the Henry's law region, the isotherm typically becomes curved. For microporous adsorbent, the isotherm is generally of type I form where the curve is monotonic and the isotherm approaches a saturation limit at high partial pressures. The simplest model capable of representing such behavior is Langmuir model

$$\frac{q}{q_s} = \frac{BP}{1 + BP} \quad (5)$$

where q_s represents the saturation limit and B is another adsorption equilibrium constant, related to the Henry constant by $K_p = Bq_s$. The Langmuir model is derived based on the assumptions that adsorption occurs at a fixed number of distinct sites, all sites are energetically equivalent, each site can accommodate one sorbate molecule and no interaction between sorbate molecules on adjacent sites. This is clearly a model for localized adsorption. However, even when the adsorbed molecules are mobile, the isotherm can often be approximated by the above equation. So, Langmuir model is widely used as a correlating equation even when the above assumptions are not really fulfilled.

For adsorption of polar or quadrupole molecules such as H₂O and CO₂, the accessible cations can be identified as the most favorable adsorption sites. The Henry constant is determined by sorbate-cation interaction energy and any shielding of the cations by adsorption of a strongly polar sorbate can be expected to have a major effect on the Henry constant for other guest molecules [1]. On less energetically heterogeneous surfaces, the adsorbed molecules are more mobile, jumping rapidly from one site to another site or, at high temperatures, moving freely over the surface.

Another model for gas adsorption that frequently employed is Freundlich equation. This equation is often considered to be empirical equation. It is possible to interpret this equation theoretically in terms of adsorption on an energetically heterogeneous surface. However, this model gives no limit to adsorption capacity, making the amount adsorbed go to infinity when the concentration increases. It is only applicable below the saturation concentration [2].

$$q = kC^n \quad (6)$$

Polanyi viewed adsorption system as a gradual concentration of gas molecules toward the solid surface according to potential theory, resembling the atmosphere of a planet [3]. There is a relationship between the potential field, ϵ and the volume, W above the surface for a given gas-solid system.

$$W = f(\epsilon) \quad (7)$$

$$\epsilon = \int_P^{P_o} VdP = RT \ln \frac{P_o}{P} \quad (8)$$

$$W = W_o \exp\left(-k \frac{\epsilon^2}{\beta^2}\right) \quad (9)$$

where W_o is limiting volume of the adsorbed space, which equal to micropore volume and β is the affinity coefficient characterizing the polarizability of the adsorbate. Equation (9) can be recast into the equation (10) that represent the Dubinin-Polanyi isotherm model.

$$\ln W = C - D \left(\ln \frac{P}{P_o} \right)^2 \quad (10)$$

The Langmuir, Freundlich and Dubinin-Polanyi models have been used as thermodynamic models to describe the adsorption of gas on adsorbent mostly on activated carbon and to lesser extent on zeolite. Activated carbon has hydrophobic surface properties while zeolite hydrophobic/hydrophilic properties

depending on Si/Al framework ratio. This paper presents the adsorption of gases (methane and carbon dioxide) on three types of zeolites at 300K and the adsorption data were fitted to different isotherm equations using linear regression method to obtain the model constants.

Experimental

Three different zeolites have been used to study the adsorption properties of gases on microporous material. The specific surface area and pore volume were obtained by an automatic volumetric sorption analyzer (Micromeritics, ASAP 2000) using nitrogen adsorption at 77K. Similarly, adsorption equilibrium data for methane and carbon dioxide on zeolites were also obtained by the same apparatus at temperature 300K for pressures up to 101.3 kPa. Each sample was activated at 400°C for a minimum of 2 hours before the adsorption measurement was carried out. Adsorbed amounts are expressed as volume adsorbed (cm^3) per unit mass (g) of an adsorbent.

Results And Discussion

The nitrogen isotherms (Figure 1) show profiles of microporous structures (Type 1) having relatively small external surface. It is characterized by an initial rapid increase in the amount adsorbed and a long nearly flat region at higher pressures [4]. The isotherms are also reversible and the amount adsorbed approaches the limiting value as $P/P_0 \rightarrow 1$. The effect of pore structure on the ability of the zeolite to adsorb gas can be seen from adsorption isotherm data. The size of pore window of zeolite used is large enough to allow gas molecules to diffuse ($\delta_{\text{CO}_2} = 3.3 \text{ \AA}$, $\delta_{\text{CH}_4} = 3.8 \text{ \AA}$). This paper demonstrates adsorption characteristic of zeolites using several adsorption isotherm models. Table 1 lists the physical properties of adsorbents used in this study. The adsorption isotherms of methane and carbon dioxide on NaY, ZSM-5 and zeolite beta are presented in Figure 2 and 3. Golden and Sircar [5] found out in their study that the adsorption of methane and carbon dioxide on silicalite could be best described by Langmuir model. Other researchers calculated Henry's law constant at the initial linear portion isotherms where the gas-solid system is in dilute condition.

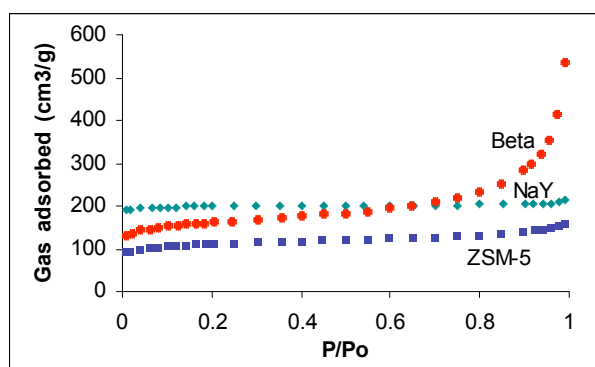


Figure 1: Nitrogen adsorption isotherms at 77K.

Table 1: Physical properties of zeolite adsorbents.

Types of zeolite	Surface area (m^2/g)		Pore volume (cm^3/g)	Average pore diameter (nm)
	Micropore	External		
NaY	809.5	10.5	0.304	1.60
ZSM-5	364.4	54.6	0.151	2.31
Zeolite beta	439.4	163.4	0.178	5.48

In order to understand the applicability of existing thermodynamic models, experimental data obtained from different types of zeolite were used to fit Langmuir, Freundlich and Dubinin –Polanyi equations by linear regression method. Langmuir model can describe well both methane and carbon dioxide adsorption on these zeolites, but Freundlich and Dubinin-Polanyi model fit at lesser degree of regression coefficient. The estimated values of the isotherm parameters for methane and carbon dioxide are presented in Table 2.

Using Langmuir model, it is possible to determine and to compare the maximum loading of gases on selected zeolite based on the assumption that monolayer adsorption occurred. Using this model, we are able to determine q_m , maximum adsorption and B , Langmuir constant. The constant ($B = e^{Q/RT} T^{-1/2}$) is temperature dependence and its value decreases rapidly with increasing temperature because Q is always positive.

However, Freundlich model is more empirical but the assumption is based on exponential shape energetic distribution on the surface of adsorbent. In this study, Freundlich equation can describe satisfactorily the adsorption of organic and non-organic molecules on three types of adsorbents. Furthermore, these isotherm data can be incorporated into adsorption modeling for process design. The experimentally-determined Freundlich coefficients may be related to some properties of adsorbates and adsorbents [6]. α coefficient is correlated to highest occupied molecular orbital (HOMO) of adsorbates and adsorbents.

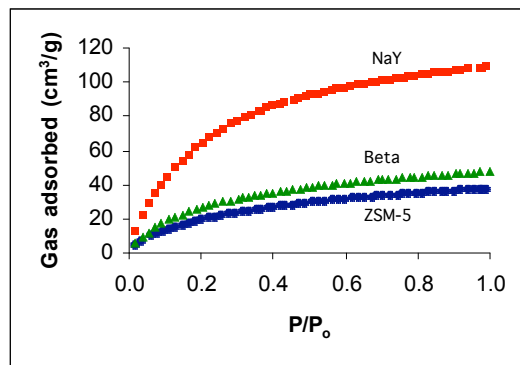
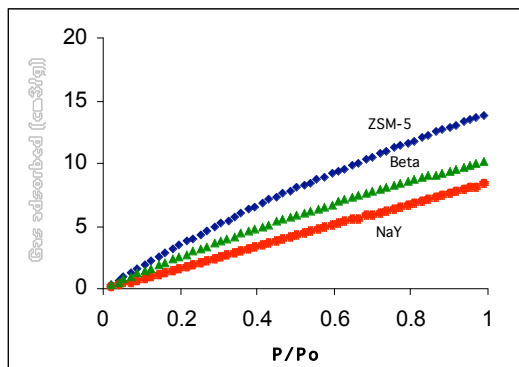


Figure 2: CH₄ adsorption isotherm at 300K.

Figure 3: CO₂ adsorption isotherm at 300K.

From these models we are able to estimate the adsorption capacity of zeolites for different type of zeolites. q_m calculated from Langmuir model shows that at monolayer coverage condition, ZSM-5 adsorbs more methane than NaY and Beta, but NaY adsorb more carbon dioxide than other zeolites. Similarly, Freundlich coefficient, k values that also determine the amount adsorb, are the highest for ZSM-5 and NaY in methane and carbon dioxide respectively.

But, based on Polanyi potential theory, the adsorption system is viewed as gradual increase in concentration of gas toward the solid surface due to potential field. Thus potential theory is uniquely powerful, and once the characteristic curve is establish at one temperature, it is possible to predict the adsorption at other temperature for the same gas-solid system. Dubinin-Polanyi constant, C also indicates that the adsorption of ZSM-5 and NaY will adsorb more methane and carbon dioxide respectively than other zeolites that have been studied.

Table 2: Model constants calculated from the fitting of CH₄ adsorption isotherm.

Type of zeolite	Langmuir		Freundlich		Dubinin-Polanyi	
	q_m	B	k	α	C	$-D$
NaY	38.91	0.20	8.59	1.03	1.66	0.29
ZSM-5	55.56	0.33	14.74	0.92	2.26	0.26
Zeolite beta	33.67	0.42	10.75	0.91	1.95	0.26

Table 3: Model constants calculated from the fitting of CO₂ adsorption isotherm.

Type of zeolite	Langmuir		Freundlich		Dubinin-Polanyi	
	q_m	k	k	α	C	$-D$
NaY	121.95	5.86	123.57	0.48	4.61	0.14
ZSM-5	37.74	6.79	53.47	0.61	3.48	0.14
Zeolite beta	49.75	6.48	52.14	0.48	3.74	0.14

Conclusion

The adsorption of methane and carbon dioxide on NaY, ZSM-5 and beta could be fitted into Langmuir Freundlich and Dubinin-Polanyi equations. The coefficients obtained shows that zeolite of different structural properties have different adsorptive characteristics. These equilibrium adsorption data are very useful and a reliable correlation can be obtained to interpolate or extrapolate data to a pressure or temperature not measured. The knowledge of adsorption equilibrium is important for the design of industrial adsorptive process.

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