Adsorption 11: 503–507, 2005

Column Dynamics of Benzene Vapor Adsorption on MCM-48

WANG GEUN SHIM
Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea

DO YOUNG CHOI, SEUNG PHIL CHOI AND JAE-WOOK LEE
Deparment Chemical Engineering, Seonam University, Namwon 590-170, Korea

HEE MOON*
Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea
hmoon@chonnam.ac.kr

Abstract. Adsorption equilibrium and column dynamics of benzene vapors on various pelletized MCM-48 were examined. The adsorption equilibrium data was measured by gravimetric method. Adsorption equilibria of benzene on pelletized MCM-48 showed a type IV isotherm. In addition, the proposed hybrid isotherm equations described the adsorption data satisfactorily. The adsorbed amount greatly decreased and gradually the structural characteristics of MCM-48 were lost with increasing pelletizing pressure. It was also shown that fixed bed mathematical model with hybrid isotherm simulates the unusual behavior of adsorption breakthrough curves.

Keywords: adsorption, benzene, fixed bed, hybrid isotherm, MCM-48

1. Introduction

The emissions of solvent vapors from industrial processes have caused not only severe air pollution but also great loss of valuable chemicals. One of the most effective methods for controlling VOC is the adsorption process. Among various adsorbents used in adsorption/separation technologies, activated carbon has been widely used in industry due to easy operation, low operating cost, and efficient recovery of most VOCs (Khan and Ghoshal, 2000). On the other hand, there are well-defined porous adsorbents in the family of M41 materials, firstly reported by Mobil Co. in 1992 (Beck et al., 1992). Among them, MCM41 has a hexagonal arrangement of unidirectional pores while MCM-48 has a cubic structure modeled as a gyroid minimal surface. Many researchers have studied the synthesis and utilization of mesoporous materials because of their unique properties such as large internal surface area, uniformity of pore size, easily controlled size of pore, and high thermal stability. These mesoporous materials may be useful as supports and catalysts. However, our concern is to investigate the adsorption properties of these materials as adsorbents. Basically, in order to design the adsorption facilities, thermodynamic data on adsorption equilibria are very essential over a wide range of temperatures. Over the last ten years, a considerable number of studies have been conducted on the adsorption equilibrium characteristics of different gases and VOC vapors (Kruk et al., 2000; Zhao et al., 2001; Oh et al., 2003; Lee et al., 2004a).

In general, it has been recognized that fixed bed adsorption is an important unit operation for separation and purification in practical applications. However, the information of column dynamics of VOC is very limited in the previous studies. It is not easy to find proper information of fixed bed dynamics for gaseous vapors on mesoporous adsorbents except a report by Hartmann and Bischof (1999). Hence, in this study, MCM-48 was synthesized using conventional method to understand

*To whom correspondence should be addressed.

the adsorption equilibrium and column dynamics of the mesoporous adsorbent. For adsorption study, we measured the adsorption equilibrium of benzene on compressed MCM-48 by using a gravimetric method and also proposed a hybrid Langmuir-Sips isotherm to correlate the adsorption equilibrium data. Moreover, experimental and theoretical studies were performed in a fixed bed charged with manufactured MCM-48 to understand the unusual adsorption column dynamics.

2. Experimental

MCM-48 sample was synthesized as follows. 12.4 g of cethyltrimethylammonium bomide (CTMABr, $C_{19}H_{42}BrN$, Aldrich), 2.16 g LE-4 (polyoxyethylene lauryl ether, $C_{12}H_{25}(OCH_2CH_2)_4OH$, Aldrich) were dissolved in a Teflon bottle containing 130 g of deionized water at 333 K. This aqueous solution was added dropwise to an another aqueous solution in the Teflon bottle containing 40 g of Ludox AS-40 (Du Pont, 40 wt% colloidal silica in water), 5 g of NaOH, and 130 g of deionized water under vigorous stirring. The solution mixture was preheated in a water bath kept at 313 K and was stirred at 500 rpm for 20 min. The resultant gel was loaded to an autoclave, and the mixture was hydrothermally treated at 373 K for 78 h. The mixture was then filtered and washed with 500 mL deionized water. The washing procedure was repeated 4–5 times to assure the complete removal of bromide and other free ions. After drying at 333 K for overnight, the dried solid was then calcined in air at 873 K for 10 h.

To test the adsorption property of MCM-48, the sample was compressed using a hand-operated press. The pelletized MCM-48 diameter was 10 mm and the external pressure applied was 50 to 500 kg cm^{-2}. Subsequently, the obtained pellet was crushed and sieved to obtain pellets with a diameter of 0.1 to 0.2 mm, which were then used for adsorption equilibrium and fixed bed studies. The qualities of the pelletized MCM-48 prepared in this work were examined by the nitrogen adsorption-desorption techniques (Micrometrics ASAP 2000) and X-ray powder diffraction (Phillips PW3123).

The adsorption amount of VOC vapor was measured by a quartz spring balance, which was placed in a closed glass system (Shim et al., 2003). A total of 0.1 g of MCM-48 adsorbents was placed on the dish, which was attached to the end of quartz spring. This system was vacuumed for 15 hours at 10^{-3} Pa and 250°C to remove volatile impurities from the MCM-48 particles. Also, adsorption breakthrough curves were obtained in a fixed bed charged with pelletized MCM-48. The apparatus was constructed with stainless steel tubes. It had three major sections: (1) apparatus for preparation of vapors, (2) adsorption column in a water bath, and (3) apparatus for the analysis of gas. The experimental procedure of equilibrium and fixed bed apparatus were described in our previous reports (Shim et al., 2003; Lee et al., 2004a).

3. Results and Discussion

The physical properties of the pelletized MCM-48 are summarized in Table 1. BET surface areas and pore size distribution determined by BJH (Barret, Joyner and Halenda) method for the parent and pelletized mesoporous adsorbents were obtained by the adsorption branches of the isotherms (Barrett et al., 1951). It was clearly found that the pelletizing pressure markedly affects the pore volumes and BET surface areas. With the exception of the results of pore diameter, the pore volume and surface area decreased with the increase in pelletizing pressures, linearly. The decreased amount in the BET surface areas and the pore volumes are about 69 and 70% between the parent sample and the corresponding sample pressed at 500 kg cm^{-2}, respectively. However, the pore diameter remains unaffected for pelletizing pressures lower than 400 kg cm^{-2}, while the average value of it decreased about 3.0 nm with increasing pelletizing pressure up to 500 kg cm^{-2}.

The adsorption equilibrium data of benzene on various pelletized MCM-48 mesoporous adsorbent were obtained at 300.15 K. Figure 1(a) shows the adsorption isotherms of benzene at various pelletizing pressures. Adsorption equilibria of benzene on pelletized MCM-48 were classified as type IV according to IUPAC recommendations. To correlate experimental equilibrium

Table 1. Physical properties of pelletized MCM-48.

Adsorbent	Pressure (kg cm^{-2})	BET Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (Å)
MCM-48	50	1430.9	1.157	32.3
	100	1201.4	0.996	33.2
	200	1116.1	0.913	32.7
	300	1035.7	0.845	32.6
	400	754.6	0.628	33.3
	500	467.4	0.361	30.9

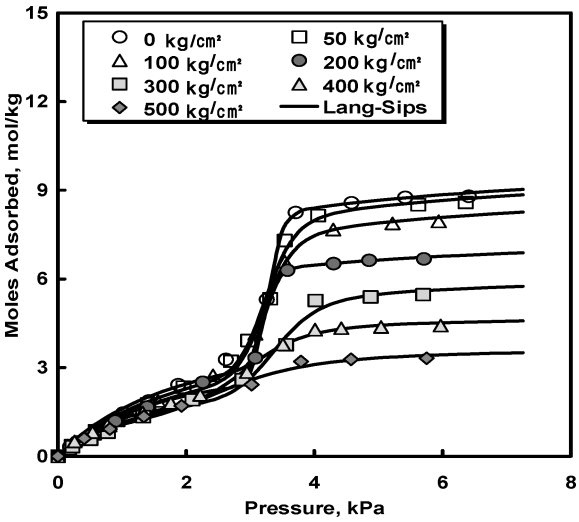

Figure 1. Adsorption isotherms of benzene on pelletized MCM-48 at 300.15 K.

data of benzene on these adsorbents, a hybrid adsorption isotherm model which described well the unusual adsorption equilibrium phenomena that has surface adsorption at low pressure and capillary condensation when high pressure were used (Lee et al., 2004a). The isotherm parameters for each adsorption were determined using a pattern search algorithm namely "Nelder-Mead simplex method" (Riggs, 1988). The comparison of fit of data by the models was based on the square of residuals (SOR), defined as follows:

$$\text{SOR} = \frac{1}{2}\sum (N_{\text{exp}} - N_{\text{cal}})^2 \qquad (1)$$

where N_{cal} and N_{exp} are the calculated and experimental amounts adsorbed, respectively. The parameters of the proposed adsorption equations as well as Sum of Residual (SOR) are listed in Table 2 (Lee et al., 2004b).

It was shown that the proposed isotherm equations satisfactorily support the experimental data. On the whole, compared with capillary condensation part, the pelletizing pressure has slight effect on the adsorption capacity in the low pressure region. The relative decreases in amounts of organic compounds are in the range of 23 to 39% between the uncompressed sample and the maximum sample pressed at 500 kg·cm^{-2}.

The performance of an adsorption-based process greatly depends upon the effectiveness of design and operating conditions. Therefore, rigorous approaches to the design and operation of the adsorption system must be adopted to ensure efficient applications. In this study, various experimental works were conducted to investigate the breakthrough patterns in terms of inlet concentrations and pelletizing pressure. The experimental conditions and simple mathematical models used in a fixed bed are shown in Table 3.

Figure 2(a) exhibits the adsorption breakthrough curves of benzene over the pelletized MCM-48 adsorbent (P-200 kg cm^{-2}) at different inlet concentrations and the total flow rate. The experimental results of benzene were collected at surface adsorption ($P = 0$–1.4 kPa), capillary condensation ($P =$ 3.2–4.4 kPa), and exterior adsorption parts ($P = 5.34$–5.37 kPa). The effect of benzene inlet partial pressure and constant feed flow rate are depicted in Fig. 2(a-1, a-2). Contrary to our expectation, the breakthrough curves are not shaper as increasing the partial pressure of benzene although adsorption equilibrium in the low pressure regions was the favorable isotherm. However in the case of capillary pressure ranges, the adsorption breakthrough curves appeared at about 10 min and then reached a plateau at the ranges of $C/C_0 = 0.6$–0.8. The length of plateau and the required time of pore filling are greatly dependent on the inlet concentrations. By increasing the inlet concentrations, the length of plateau

Table 2. Estimated isotherm parameters of benzene on MCM-48.

Isotherm model		Pelletizing pressure					
		50 kg·cm^{-2}	100 kg·cm^{-2}	200 kg·cm^{-2}	300 kg·cm^{-2}	400 kg·cm^{-2}	500 kg·cm^{-2}
Hybrid Langmuir - Sips	q_m	5.060	4.729	3.808	3.194	2.423	1.852
	b_1	0.410	0.408	0.581	0.551	1.127	1.313
	b_2	2.163×10^{-8}	3.666×10^{-8}	3.214×10^{-17}	2.721×10^{-6}	2.655×10^{-4}	1.285×10^{-2}
	n	14.947	14.594	32.700	10.431	7.446	4.303
	SOR	0.505	0.1638	0.177	0.336	0.100	0.086

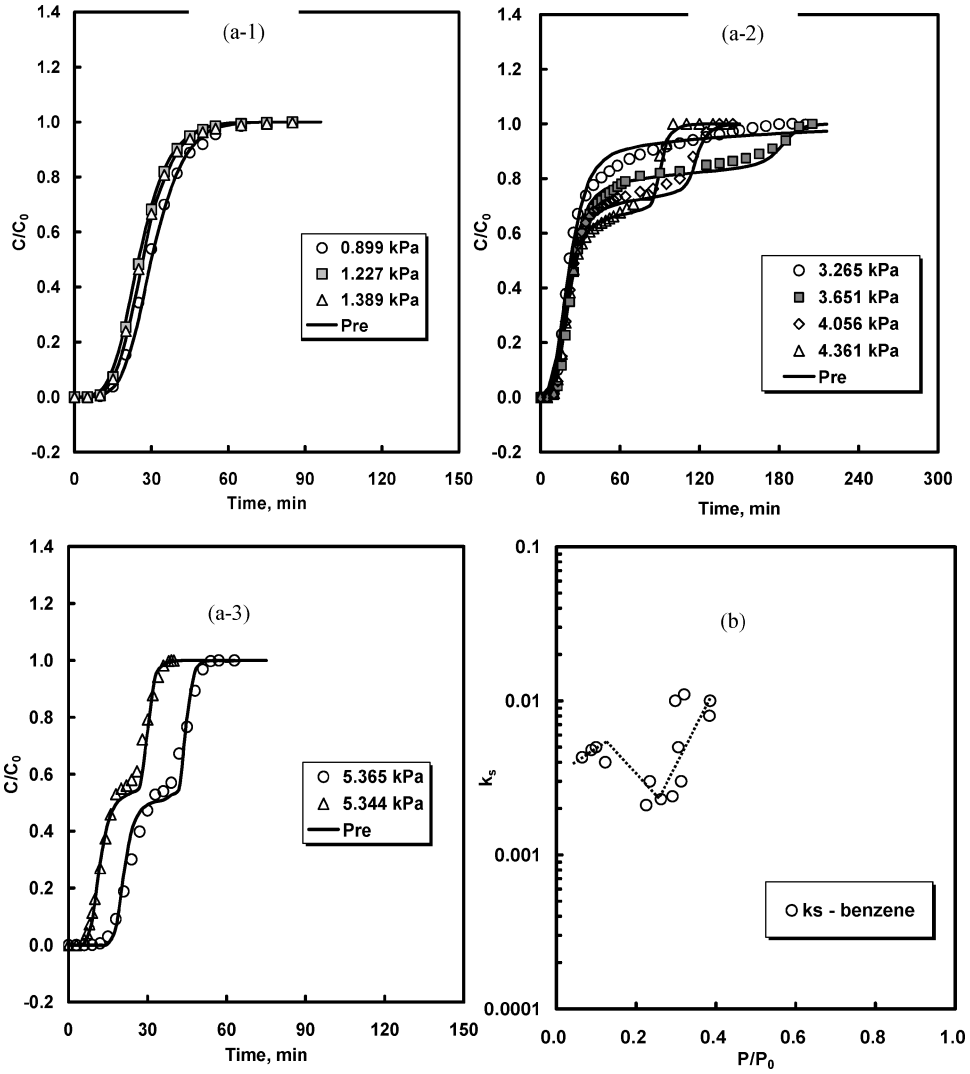

Figure 2. Comparison of experimental and theoretical breakthrough curves of benzene on MCM-48 pellet (200 kg·cm^{-2}) (a) and the variation of mass transfer coefficients with relative pressure (b).

decreases. After reaching a plateau, sharper patterns of secondary pore filling with increasing pressures were also observed. Since the flow rate is also very important factor in column design, its effect should be evaluated. Figure 2(a-3) shows the effect of total flow rate on the breakthrough profiles at constant feed concentration. The breakthrough curve appears earlier at higher flow rates. The shape of breakthrough curve is not affected by the change in total flow rates in the exterior adsorption pressure ranges since there differences are small. In Fig. 2(b), the variations in the obtained mass transfer coefficients with relative pressure on the pelletized MCM-48 adsorbents are depicted. The obtained values range initially from 4.0×10^{-3} s^{-1} to 5.0×10^{-3} s^{-1} at under $P/P_0 = 0.10$ and decrease to 2.0×10^{-3} s^{-1} at about $P/P_0 = 0.25$ before increasing to 1.0×10^{-2} s^{-1} about $P/P_0 = 0.4$. These results are identical with that of the uptake measurements by using gravimetric method (Lee et al., 2004b). It is evident that the obtained minimum values correspond to the capillary condensation pressure region in the adsorption equilibrium isotherm.

Table 3. Experimental condition and mathematical model of a fixed bed.

Experimental conditions		
Property		Unit
Length	1.40×10^{-2}–5.80×10^{-2}	m
Velocity	1.64×10^{-2}–1.31×10^{-1}	m/s
Column I.D.	1.0×10^{-2}	m
Temp	300.15	K
Mathematical models		
1. Material balance	2. LDFA model	3. Hybrid-Langmuir-Sips
$-D_L \frac{\partial^2 c}{\partial z^2} + \frac{\partial vc}{\partial z} + \frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \rho_p \frac{\partial q}{\partial t} = 0$	$\frac{\partial q}{\partial t} = k_s \cdot (q^* - q)$	$q^* = q_m \left(\frac{b_1 c}{1+b_1 c} + \frac{b_2 c^n}{1+b_2 c^n} \right)$

4. Conclusion

Experimental and theoretical studies were carried out for the adsorption of benzene on the MCM-48 adsorbents to quantitatively analyze the unusual adsorption breakthrough curves. The adsorption equilibrium data in pelletized MCM-48 were measured by gravimetric method and were well fitted with a hybrid isotherm equation. Although the surface area and pore volume markedly decrease with increasing pelletizing pressure, pore diameter still remains unaffected. It was found that inlet partial pressure and pelletizing pressure which are closely related with the adsorption isotherm shape greatly affected the adsorption breakthrough curves. The obtained mass transfer coefficients in this study show the unique feature of mesoporous media. In addition, the mathematical model employed in this study satisfactorily simulates the behavior of adsorption breakthrough curve of VOCs on MCM-48.

Acknowledgments

This work was supported by grant No (R-01-2001-00414-0(2003)) from the Korea Science & Engineering Foundation.

References

Barrett, E.P., L.G. Joyner, and P.P. Halenda, "Determination of Pore Volume and Area Distributions in Porous Substances, I. Computations from Nitrogen Isotherms," *J. Am. Chem. Soc.*, **73**, 373–380 (1951).

Beck, J.S., J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J. L. Schlenker, "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **114**, 10834–10843 (1992).

Hartmann, M. and C. Bishof, "Mechanical Stability of Mesoporous Molecular Sieve MCM-48 Studied by Adsorption of Benzene, n-Heptane, and Cyclohexane," *J. Phys. Chem. B.*, **103**, 6230–6235 (1999).

Khan, F.I. and A.K. Ghoshal, "Removal of Volatile Organic Compounds from polluted air," *J. Loss. Prevent. Proc.*, **13**(6), 527–529 (2000).

Kruk, M., M. Jaroniec, Y. Sakamoto, O. Terasaki, R. Ryoo, and C.H. Ko, "Determination of Pore Size and Pore Wall Structure of MCM-41 by Using Nitrogen Adsorption, Transmission Electron Microscopy, and X-ray Diffraction," *J. Phys. Chem. B*, **104**, 292–301 (2000).

Lee, J.W., W.G. Shim, and H. Moon, "Adsorption Equilibrium and Kinetics for Capillary Condensation of Trichloroethylene on MCM-41 and MCM-48," *Microporous and Mesoporous Mat.*, **73**, 109–119 (2004b).

Lee, J.W., W.G. Shim, M.S. Yang, and H. Moon, "Adsorption of Polar and Non-Polar Organic Compounds on MCM-48 at (303.15, 313.15, and 323.15)K," *J. of Chem. Eng. Data*, **49**, 502–509 (2004a).

Oh J.S., W.G. Shim, J.W. Lee, J.H. Kim, H. Moon, and G. Seo, "Adsorption Equilibria of Water Vapor on Mesoporous Materials," *J. of Chem. Eng. Data*, **48**, 1458–1462 (2003).

Riggs, J.B., *An Introduction to Numerical Methods for Chemical Engineers*, pp. 353–386, Texas Technological University Press, Lubbock, TX, 1988.

Shim, W.G., J.W. Lee, and H. Moon, "Equilibrium and Fixed-Bed Adsorption of n-Hexane on Activated Carbon," *Sep. Sci. Tech.*, **38**(16), 3905–3926 (2003).

Zhao, X.S. and G.Q. Lu, "Organophilicity of MCM-41 Adsorbents Studied by Adsorption and Temperature-Programmed Desorption," *Colloids and Surfaces A*, **179**, 261–269 (2001).