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Adsorption Isotherms of Polar and Nonpolar Organic Compounds on MCM-48 at (303.15, 313.15, and 323.15) K

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Adsorption equilibria of four nonpolar molecules (benzene, toluene, hexane, and cyclohexane) and two polar molecules (methanol and acetone) on mesoporous silicate MCM-48 were measured at (303.15, 313.15, and 323.15) K using a gravimetric technique. It was found that MCM-48 has a higher affinity to polar organic compounds than to nonpolar organics. A hybrid isotherm model composed of Langmuir isotherm and Sips equations was applied to fit the adsorption equilibrium data of nonpolar organics including surface adsorption and capillary condensation, while inhomogeneous Dubinin−Astakov (DA) isotherm was used to correlate those of polar organics. The proposed isotherms correlated the measured adsorption data well over the whole range at these experimental conditions.

Introduction

Volatile organic compounds (VOCs) are major air pollutants that must be controlled under increasingly stringent environmental regulations. They have been used as dissolving and cleaning agents in many industrial processes such as printing, film coating, manufacturing of magnetic tapes and electronic chips, etc.[1] Commercial technologies are available for VOC abatement such as condensation, absorption, adsorption, oxidation, and incineration. Among the adsorption and separation technologies, activated carbon adsorption is an established technology, widely used in industrial processes for the removal and recovery of VOCs from gaseous stream. However, it has been recognized that activated carbon frequently encounters problems such as combustion, pore blocking, and hygroscopicity. As a result, alternative adsorbents have received much attention.[2]

Mesoporous silicates named as M41S family were first synthesized by Mobil researchers in 1992.[3] Since then, various mesoporous materials such as MCM-41, MCM-48, MCM-50, and other species with different pore sizes and shapes were synthesized. MCM-41 has a hexagonal array of unidirectional pores, while MCM-48 has a bicontinuous cubic pore system (Figure 1). The synthesis and utilization of these materials have been investigated by many researchers because of their peculiar characteristics such as large internal surface area, uniformity of pore size, easily controlled pore size, and high thermal stability. These mesoporous materials have potential applications in adsorption, catalysis, and nonotechnology.[4,5] So far, a number of publications have dealt with the adsorption of organics on MCM-41.[6,7] However, studies on MCM-48 have been relatively limited.

Adsorption equilibrium is the most important information for modeling, simulating, and optimizing the adsorption and the catalytic hydrodechlorination processes.[8,9] This paper presents experimental and theoretical results for the adsorption equilibria of VOC on manufactured MCM-48. Adsorption equilibrium data of nonpolar and polar organic compounds on MCM-48 are reported at three different temperatures (303.15, 313.15, and 323.15 K). Four nonpolar organic compounds (benzene, toluene, *n*-hexane, and cyclohexane) and two polar organics (methanol and acetone) were chosen to compare the effect of adsorbate polarizability on adsorption amount in MCM-48. The adsorption isotherms of nonpolar organics were analyzed using a hybrid isotherm model combining the Langmuir isotherm at low pressure and the Sips isotherm at moderate pressure responsible for capillary condensation. Also, the inhomogeneous Dubinin−Astakov (DA) model was employed to correlate isotherm data of polar compounds.

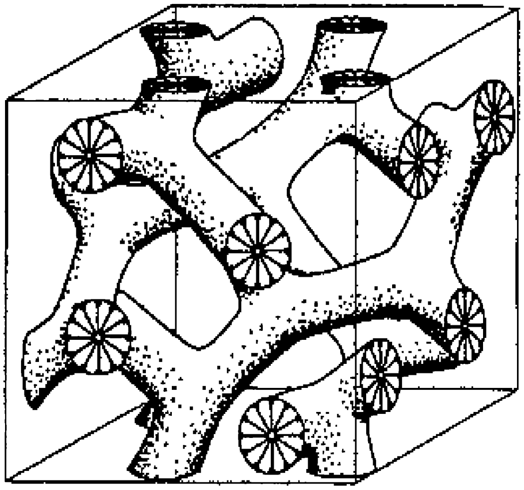

Figure 1. Cubic pore structure of MCM-48.

Table 1. Physical Properties of MCM-48

property	value
average pore diameter/Å	32
pore volume/cm^3 g^{-1}	1.08
BET surface area/m^2 g^{-1}	1 100

Isotherm Models

Hybrid Langmuir−Sips Equation. Adsorption isotherms play a key role both in the design of the adsorption-based process for the disposal of wastes containing VOCs and in modeling the catalytic oxidation process.[8,9] In the

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Table 2. Properties of Various VOCs at 303.15 K (from Ref 18)

material	benzene	toluene	hexane	cyclohexane	methanol	acetone
chemical formula	C_6H_6	C_7H_8	C_6H_{14}	C_6H_{12}	CH_4O	C_3H_6O
MW	78.11	92.13	86.17	84.16	32.04	58.08
purity/ %	99.5	99.5	95.0	99.5	99.9	99.5
density/ kg m^{-3}	0.88	0.87	0.65	0.78	0.79	0.79
vapor pressure/ kPa	15.92	4.89	24.97	16.24	35.79	38.02
molar volume/ $cm^3\ mol^{-1}$	89	107	132	109	41	74
boiling temp/ K	353.25	383.75	342.15	353.85	337.75	329.35
dipole moment/ 10^{-30} C m	0	1.334	0	1.001	5.671	9.673
surface tension/ $10^3\ N\ m^{-1}$	28.88	28.52	18.40	25.24	22.50	24.02
supply	Junsei Chemical Co., Ltd.	Junsei Chemical Co., Ltd.	Junsei Chemical Co., Ltd.	Kanto Chemical Co., Inc.	Carlo ERBA Reagents	Yakuri Pure Chemical Co., Ltd.

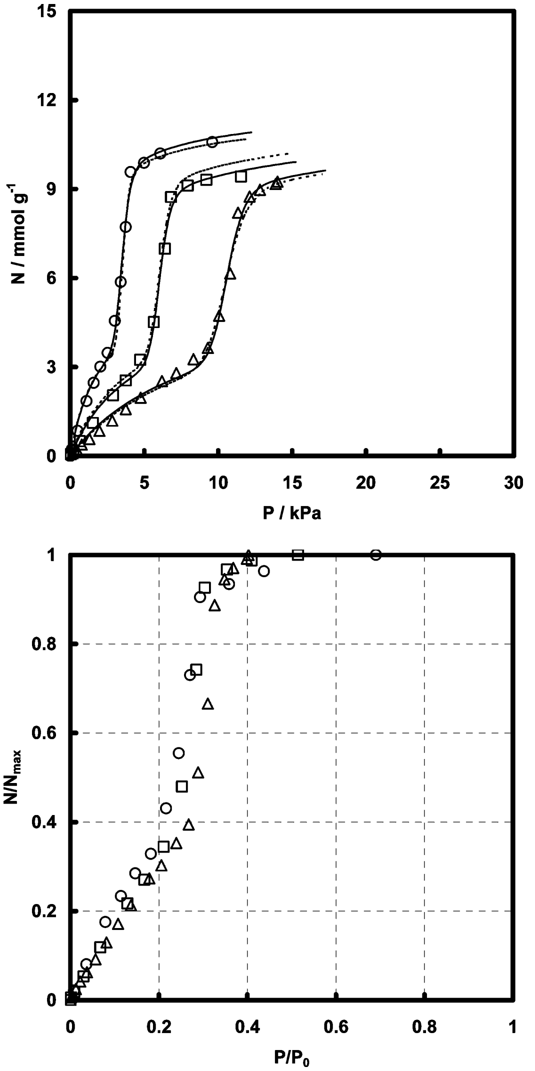

Figure 2. Adsorption isotherms of benzene vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, Langmuir–Sips isotherm (Table 6); dotted line, temperature-dependent Langmuir–Sips isotherm (Table 8).

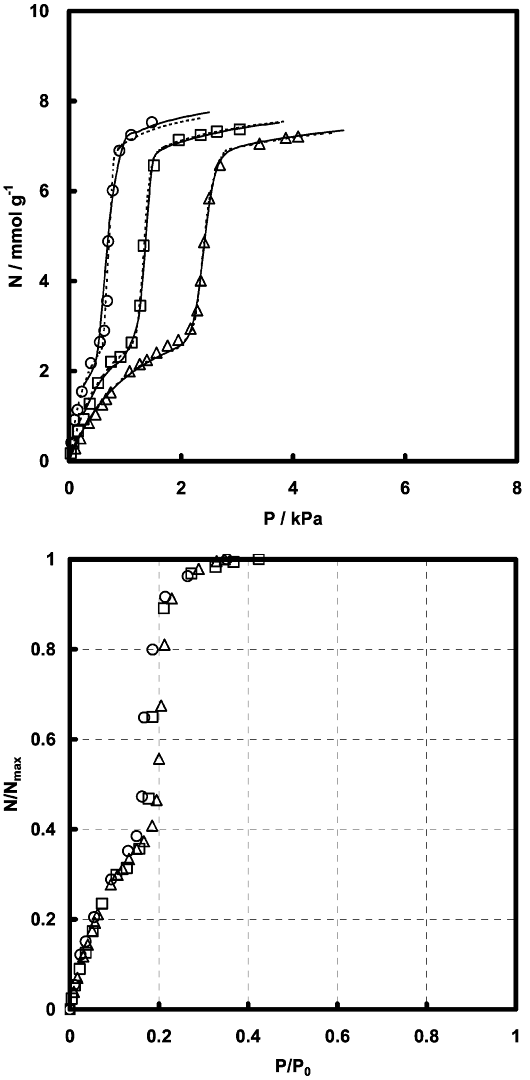

Figure 3. Adsorption isotherms of toluene vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, Langmuir–Sips isotherm (Table 6); dotted line, temperature-dependent Langmuir–Sips isotherm (Table 8).

literature, the equilibrium data with capillary condensation on mesoporous sorbent have been reported to correlate poorly with nonlinear isotherm models. Until now, many isotherms have been developed for the adsorption of condensable vapors on porous materials, and they are reviewed elsewhere.[10,11] These models are successful either at low pressures, prior to monolayer formation, or at higher pressures, corresponding to the multiplayer region in the adsorption of condensable vapors. However, none of the models gives a complete description of adsorption isotherms over a wide pressure range with a uniform set of parameters. It was found that more than one model is required because there is no universal equilibrium model that provides an accurate fit for the surface adsorption and capillary condensation on mesoporous materials, simultaneously. Thus, we have tested many hybrid isotherms to

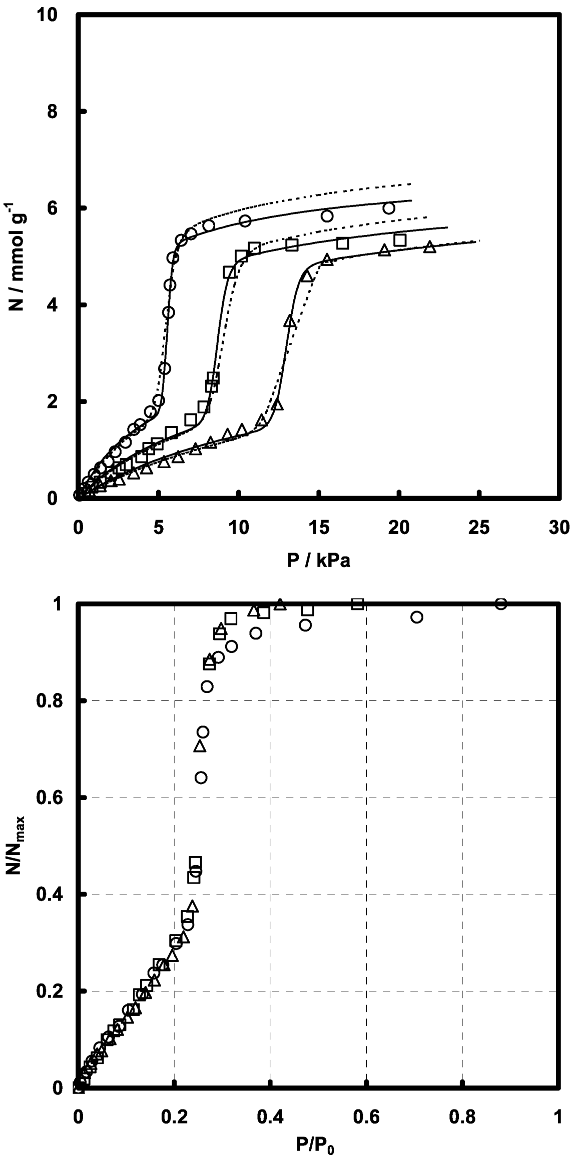

Figure 4. Adsorption isotherms of hexane vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, Langmuir−Sips isotherm (Table 6); dotted line, temperature-dependent Langmuir−Sips isotherm (Table 8).

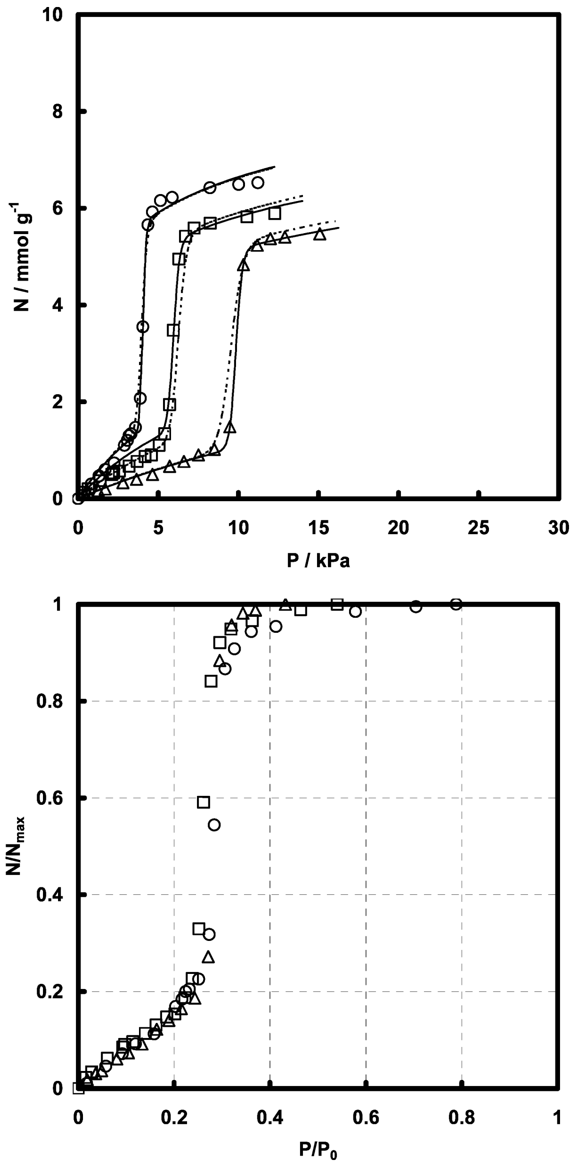

Figure 5. Adsorption isotherms of cyclohexane vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, Langmuir−Sips isotherm (Table 6); dotted line, temperature-dependent Langmuir−Sips isotherm (Table 8).

correlate equilibrium data. Two types of isotherm models successfully correlated the experimental equilibrium data of VOCs on synthesized MCM-48 mesoporous material. A hybrid isotherm of Langmuir and Sips equations with four isotherm parameters fitted the isotherm data of nonpolar organic compounds well, while the inhomogeneous DA isotherm with five isotherm parameters correlated those of polar organics successfully.[6,12] The proposed hybrid isotherm of Langmuir and Sips equations is as follows

$$N = m\left[\frac{b_1 P}{1 + b_1 P} + \frac{b_2 P^s}{1 + b_2 P^s}\right] \tag{1}$$

where N is the adsorption amount, P is the pressure, T is the temperature, and m, b_1, b_2, and s are the isotherm parameters. Almost all the adsorption processes depend on physical adsorption rather than chemisorption. Also, it has been well known that the physical adsorption from the gas phase is invariably exothermic.[8] Thus, a temperature-dependent isotherm model is basically required for the analysis of exothermic adsorption processes. To account for the heat effect, the adsorption isotherm model should be expressed as a function of temperature. Thus, four isotherm parameters (m, b_1, b_2, s) of the hybrid isotherm are given as a function of temperature as in the follow equations

$$m = m_0 \exp\left(\frac{\alpha}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \tag{2}$$

$$b_1 = b_{10} \exp\left(-\frac{\Delta H_1}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \tag{3}$$

$$b_2 = b_{20} \exp\left(-\frac{\Delta H_2}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \tag{4}$$

$$s = s_0 \exp\left(-\frac{\delta}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \tag{5}$$

where m_0, α, b_{10}, ΔH_1, b_{20}, ΔH_2, s_0, and δ are the parameters and T_m is the mean temperature. Equation 2 with isotherm parameters of eqs 2−5 is a temperature-dependent hybrid Langmuir-Sips isotherm.

Inhomogeneous DA Equation. The hybrid Langmuir−Sips isotherm model is not satisfactorily correlated with the isotherm data of polar organic compounds (methanol

Table 3. Equilibrium Data of VOCs on MCM-48 at 303.15 K

benzene		toluene		hexane		cyclohexane		methanol		acetone	
P	N	P	N	P	N	P	N	P	N	P	N
kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	KPa	mol kg^{-1}
0.112	0.232	0.041	0.409	0.093	0.066	0.250	0.067	0.190	0.724	0.101	1.229
0.502	0.849	0.109	0.913	0.372	0.199	0.820	0.301	0.311	1.177	0.224	1.647
1.103	1.853	0.151	1.134	0.622	0.331	1.311	0.468	0.390	1.358	0.392	1.893
1.590	2.471	0.230	1.543	0.991	0.497	1.705	0.602	0.733	2.083	0.600	2.188
2.044	3.012	0.392	2.173	1.392	0.630	2.252	0.736	1.012	2.355	0.873	2.286
2.530	3.475	0.552	2.645	1.874	0.762	2.892	1.104	1.490	2.717	1.280	2.434
3.014	4.556	0.631	2.897	2.308	0.961	3.083	1.204	1.850	2.989	1.874	2.631
3.410	5.869	0.680	3.558	2.941	1.160	3.191	1.305	2.483	3.441	2.540	2.827
3.761	7.722	0.705	4.881	3.460	1.425	3.300	1.338	3.480	3.894	3.475	2.926
4.080	9.575	0.781	6.015	3.872	1.524	3.584	1.472	4.464	4.347	4.524	3.319
4.991	9.884	0.904	6.896	4.491	1.790	3.891	2.074	5.513	4.709	5.091	3.516
6.093	10.193	1.110	7.243	5.020	2.022	4.045	3.550	6.442	5.071	6.173	3.663
9.612	10.579	1.481	7.526	5.392	2.684	4.360	5.654	7.461	5.615	7.412	3.909
				5.630	3.844	4.646	5.922	8.481	6.249	8.530	4.155
				5.723	4.408	5.140	6.156	9.035	6.349	9.413	4.351
				5.907	4.971	5.872	6.223	9.522	6.430	9.770	4.450
				6.422	5.336	8.233	6.424	10.321	7.064	10.304	4.647
				7.032	5.468	10.030	6.491	11.053	8.060	10.720	4.942
				8.141	5.634	11.223	6.524	11.244	12.679	11.055	5.335
				10.413	5.733			11.540	14.490	11.407	7.548
				15.525	5.833			11.933	15.396	11.761	8.728
				19.381	5.999			12.470	16.482	12.390	9.219
								13.271	17.207	13.813	9.662
								14.573	17.569	17.792	9.957
								18.381	18.565	21.591	10.006
								19.944	19.199	26.843	10.006
								20.305	19.199		

Table 4. Equilibrium Data of VOCs on MCM-48 at 313.15 K

benzene		toluene		hexane		cyclohexane		methanol		acetone	
P	N	P	N	P	N	P	N	P	N	P	N
kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}
0.041	0.058	0.031	0.173	0.401	0.099	0.365	0.134	0.144	0.453	0.140	0.344
0.204	0.174	0.082	0.394	0.852	0.232	0.634	0.201	0.332	0.906	0.241	1.082
0.664	0.502	0.164	0.661	1.374	0.331	1.385	0.368	0.743	1.721	0.402	1.352
1.522	1.120	0.263	0.929	2.064	0.530	2.114	0.502	1.125	2.083	0.493	1.696
2.897	2.046	0.372	1.275	2.553	0.630	2.213	0.535	1.761	2.626	0.749	1.942
3.753	2.548	0.521	1.732	2.991	0.696	2.581	0.569	2.411	3.079	0.950	2.041
4.732	3.243	0.750	2.204	3.968	0.862	3.183	0.669	2.963	3.351	1.118	2.114
5.662	4.517	0.921	2.314	4.407	1.027	3.691	0.770	3.517	3.532	2.747	2.581
6.393	6.988	1.122	2.629	4.925	1.127	4.192	0.870	4.164	3.622	4.934	2.950
6.829	8.726	1.272	3.448	5.810	1.359	4.583	0.903	5.102	3.804	6.992	3.221
7.942	9.112	1.334	4.786	7.022	1.624	5.062	1.104	6.517	4.256	9.301	3.516
9.208	9.305	1.515	6.566	7.842	1.889	5.415	1.338	8.009	4.619	11.262	3.737
11.556	9.421	1.963	7.132	8.313	2.320	5.722	1.941	9.481	5.071	15.071	3.958
		2.353	7.243	8.425	2.486	5.940	3.480	11.031	5.524	15.123	4.229
		2.642	7.321	9.431	4.673	6.305	4.952	13.102	6.249	19.930	4.868
		3.051	7.369	10.177	5.004	6.711	5.420	17.933	6.611	18.334	8.260
				10.986	5.170	7.247	5.587	16.445	7.154	20.903	9.146
				13.337	5.236	8.253	5.688	17.424	7.698	22.833	9.195
				16.498	5.269	10.551	5.822	18.365	8.694	24.705	9.244
				20.079	5.336	12.283	5.889	19.181	12.679		
								19.348	15.124		
								20.981	16.663		
								21.552	17.026		
								22.443	17.297		

and acetone). However, it was found that the inhomogeneous DA isotherm model was superior to the other hybrid isotherms. The inhomogeneous DA equation can be described using the following form[6,12]

$$N = W\left[\exp\left(-\frac{A}{\beta E_1}\right)^{n1} + \exp\left(-\frac{A}{\beta E_2}\right)^{n2}\right] \tag{6}$$

$$A = RT\ln\left(\frac{P_0}{P}\right) \tag{7}$$

$$\beta = \frac{V_m}{V_m^{\mathrm{ref}}} \tag{8}$$

where N is the adsorption amount, P is the pressure, P_0 is the saturation pressure, T is the temperature, R is the gas constant, and W, E_1, E_2, n_1, and n_2 are the isotherm parameters. W is the maximum adsorption amount, A is the adsorption potential, E is the characteristic energy, and n is the parameter describing the surface heterogeneity. β is the affinity coefficient (where $\beta = 1$ for reference vapor) and V_m^{ref} is the molar volume of the reference vapor. In this study, benzene was chosen as the reference vapor. As stated before, to account for the heat effect, one of isotherm parameters, W, is expressed as a function of temperature as follows

$$W = W_0\exp[-\gamma(T - T_m)] \tag{9}$$

where W_0 and γ are the isotherm parameters. Here, we assumed that the other four isotherm parameters (E_1, E_1, n_1, n_2) are independent of temperatures.

Experimental Section

Adsorbates and Adsorbent. Four nonpolar organic compounds (benzene, toluene, hexane, and cyclohexane) and two polar organics (methanol and acetone) were used

Table 5. Equilibrium Data of VOCs on MCM-48 at 323.15 K

benzene		toluene		hexane		cyclohexane		methanol		acetone	
P	N	P	N	P	N	P	N	P	N	P	N
kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}	kPa	mol kg^{-1}
0.142	0.097	0.111	0.283	0.682	0.166	0.651	0.100	0.362	0.362	0.122	0.688
0.423	0.232	0.201	0.504	1.361	0.265	1.260	0.167	0.581	0.543	0.265	0.983
0.784	0.386	0.352	0.850	2.044	0.365	1.702	0.201	1.265	1.177	0.533	1.426
1.302	0.579	0.473	1.039	2.543	0.398	2.805	0.335	2.055	1.630	2.206	2.286
1.983	0.849	0.592	1.260	3.456	0.530	3.653	0.401	3.114	1.947	3.716	2.508
2.842	1.197	0.660	1.386	4.255	0.630	4.644	0.502	4.293	2.264	5.577	2.655
3.750	1.583	0.745	1.527	5.341	0.762	5.714	0.669	5.462	2.490	7.212	2.803
4.763	1.969	1.083	2.000	6.213	0.862	6.603	0.770	6.871	2.762	9.530	2.999
6.204	2.529	1.260	2.157	7.312	1.027	7.505	0.903	8.570	3.079	11.481	3.098
7.171	2.799	1.394	2.252	8.252	1.160	8.502	1.020	10.975	3.532	13.443	3.245
8.330	3.263	1.560	2.409	9.304	1.326	9.476	1.489	13.537	3.894	16.742	3.442
9.305	3.649	1.761	2.566	10.205	1.425	10.311	4.835	16.009	4.256	19.342	3.688
10.061	4.730	1.955	2.692	11.420	1.624	11.177	5.236	18.510	4.438	24.443	3.934
10.810	6.158	2.170	2.944	12.406	1.955	12.009	5.370	19.429	4.573	26.931	5.212
11.353	8.205	2.290	3.354	13.205	3.679	12.918	5.403	20.468	4.845	27.844	6.589
12.122	8.745	2.356	4.015	14.277	4.607	15.090	5.470	20.527	4.800	29.965	7.572
12.821	8.977	2.410	4.865	15.518	4.938					31.425	7.670
13.892	9.170	2.507	5.841	19.098	4.137						
14.019	9.247	2.691	6.581	21.929	5.203						
		3.405	7.054								
		3.872	7.180								
		4.091	7.211								

as typical VOCs. The purity, the manufacturer of each adsorbate, and the chemical properties are given in Table 1. All the chemicals were used as received without further treatment. MCM-48 mesoporous adsorbent was prepared using cetyltrimethylammonium bromide (CTMABr, $C_{19}H_{42}$-BrN, Aldrich) as the template and Ludox AS-40 (Du Pont, 40 mass% colloidal silica in water) as the silicon source according to the method described in a previous report.[13,14] The template was removed by calcinations at 873 K for 10 h at a heating rate of 1 K/min in air. The resultant white powder was stored in a sealed bottle.

Characterization. The quality of the MCM-48 prepared in this study was examined by X-ray diffraction (XRD) and nitrogen adsorption techniques. XRD data were obtained on a Phillips PW3123 diffractometer equipped with a graphite monochromator and Cu Kα radiation of wavelength 0.154 nm. The XRD pattern showed the two characteristic (211) and (220) reflections in the 2θ range from 2° and 10°. Nitrogen adsorption and desorption data were measured at 77 K using a Micromeritics ASAP 2010 automatic analyzer. Prior to the adsorption measurements, the samples were outgassed at 523.15 K for 15 h in a vacuum ($P < 1 \times 10^{-3}$ Pa). Table 2 summarizes the important physical properties of MCM-48. The BET surface area was 1 100 m^2 g^{-1}, and the average pore size determined by the Barrett, Joyner, and Halenda method was 32 Å, which belongs to the typical values of MCM-48 reported by other researchers.[14]

Gravimetric Apparatus. The adsorption amounts of VOCs were measured by a quartz spring balance, which was placed in a closed glass system. An adsorbent sample 0.1 g was placed on a quartz basket attached to the end of the quartz spring. Prior to adsorption, the mesoporous sample was vacuumed to 1×10^{-3} Pa for 15 h at 523.15 K. The high vacuum system was composed of a turbomolecular pump (Edward type EXT70) and a rotary vacuum pump (Edward model RV5). Pirani and Penning vacuum gauges (Edwards Series 1000) were used for the measurement of vacuum. The pressure was measured using a Baratron absolute pressure transducer (MKS instruments type 127) with the reading accuracy of ±0.15% and a power supply read-out instrument (MKS type PDR−C-1C). VOC vapors were generated in a small tubular reservoir that was maintained at a constant temperature. During the adsorption, the adsorption cell was placed in a temperature-

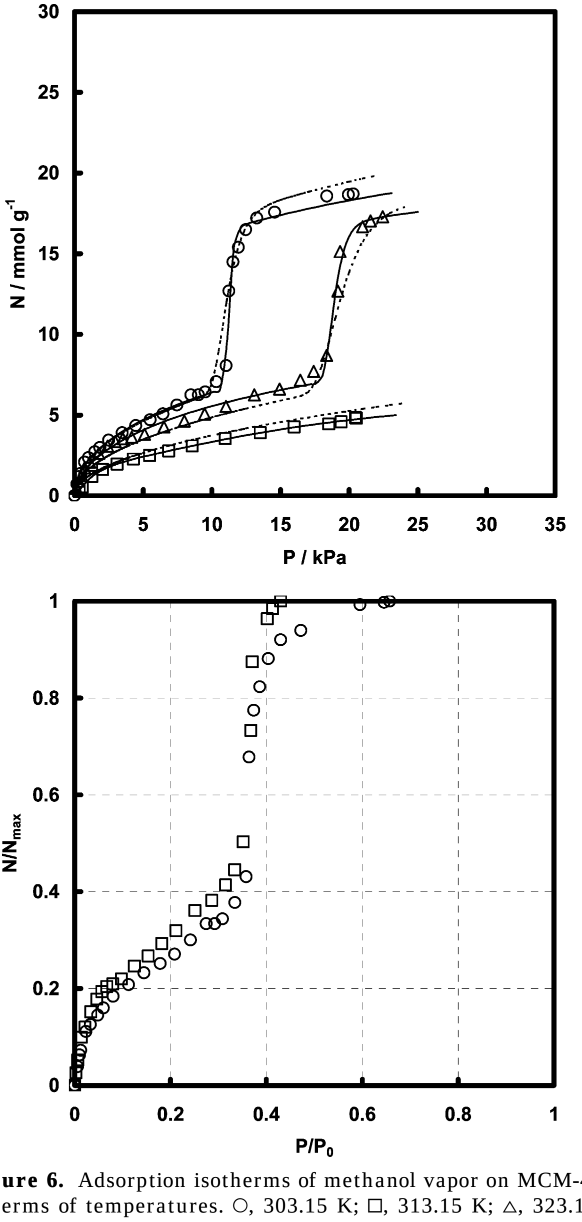

Figure 6. Adsorption isotherms of methanol vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, DA isotherm (Table 7); dotted line, temperature-dependent inhomogeneous DA isotherm (Table 9).

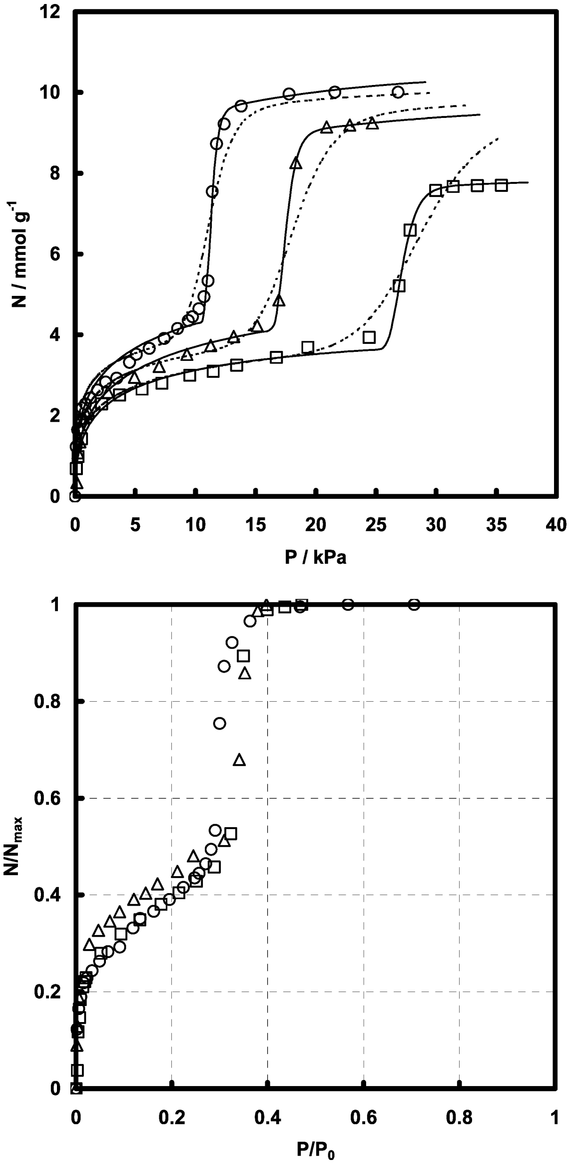

Figure 7. Adsorption isotherms of acetone vapor on MCM-48 in terms of temperatures. ○, 303.15 K; □, 313.15 K; △, 323.15; solid line, DA isotherm (Table 7); dotted line, temperature-dependent inhomogeneous DA isotherm (Table 9).

Table 6. Hybrid Langmuir−Sips Isotherm Parameters of VOCs on MCM-48 in Terms of Temperatures

materials	T/K	m/ mmol g^{-1}	b_1/kPa^{-1}	b_2/kPa^{-1}	s	SOR
benzene	303.15	5.88	4.83×10^{-1}	1.03×10^{-7}	12.8	3.51×10^{-1}
	313.15	5.61	2.15×10^{-1}	5.48×10^{-14}	17.0	2.68×10^{-1}
	323.15	5.77	1.17×10^{-1}	1.58×10^{-19}	18.3	4.02×10^{-1}
toluene	303.15	4.14	2.65×10^{0}	3.03×10^{1}	17.0	2.18×10^{-1}
	313.15	4.10	1.36×10^{0}	5.81×10^{-4}	26.2	0.58×10^{-1}
	323.15	4.05	8.62×10^{-1}	6.21×10^{-12}	29.4	0.81×10^{-1}
hexane	303.15	3.41	2.02×10^{-1}	2.66×10^{-26}	34.4	1.11×10^{-1}
	313.15	3.26	1.10×10^{-1}	4.74×10^{-26}	27.0	1.02×10^{-1}
	323.15	3.27	6.56×10^{-2}	3.84×10^{-39}	34.5	0.58×10^{-1}
cyclohexane	303.15	4.28	1.23×10^{-1}	3.00×10^{-27}	43.7	1.42×10^{-1}
	313.15	3.90	9.82×10^{-2}	4.37×10^{-26}	32.7	3.21×10^{-1}
	323.15	4.11	3.48×10^{-2}	8.63×10^{-52}	51.4	0.13×10^{-1}

controlled water bath within ±0.05 K. Adsorption isotherms were obtained by admitting successive increments of sample gas to the adsorbent sample. The adsorption equilibrium was usually attained within 0.5 to 1 h depending on the adsorbates.

Table 7. Inhomogeneous DA Isotherm Parameters of Methanol and Acetone on MCM-48 in Terms of Temperatures

materials	T/K	W/ mmol g^{-1}	E_1/J mol^{-1}	E_2/J mol^{-1}	n_1	n_2	SOR
methanol	303.15	9.81	5.76×10^{3}	1.35×10^{4}	4.91×10^{1}	1.13×10^{0}	2.05
	313.15	9.66	1.53×10^{4}	6.00×10^{3}	1.26×10^{0}	3.449×10^{1}	1.54×10^{0}
	323.15	3.00	2.58×10^{4}	1.10×10^{4}	3.24×10^{0}	2.78×10^{0}	0.17×10^{-1}
acetone	303.15	5.16	3.27×10^{3}	1.28×10^{4}	3.39×10^{1}	1.32×10^{0}	5.54×10^{-1}
	313.15	4.81	1.27×10^{4}	3.41×10^{3}	1.46×10^{0}	3.29×10^{1}	2.91×10^{-1}
	323.15	3.97	1.51×10^{4}	3.41×10^{3}	1.72×10^{0}	3.50×10^{1}	1.05×10^{-1}

Table 8. Temperature-Dependent Hybrid Langmuir−Sips Isotherm Parameters of VOCs on MCM-48

	benzene	toluene	hexane	cyclohexane
m/mmol g^{-1}	5.75	4.08	3.47	4.24
α/J mol^{-1}	5.22×10^{1}	1.59×10^{2}	3.59×10^{3}	1.91×10^{1}
b_{10}/kPa^{1-}	2.30×10^{-1}	1.45×10^{0}	9.46×10^{-2}	6.45×10^{-2}
$-\Delta H_1$/J mol^{-1}	5.59×10^{4}	4.26×10^{4}	4.08×10^{-4}	4.68×10^{4}
b_{20}/kPa^{1-}	1.89×10^{-3}	7.69×10^{-4}	1.28×10^{-18}	5.24×10^{-21}
$-\Delta H_2$/J mol^{-1}	5.04×10^{5}	1.12×10^{6}	9.27×10^{5}	8.26×10^{5}
S_0	16.3	24.8	18.7	25.5
δ/J mol^{-1}	4.94×10^{3}	3.25×10^{2}	8.60×10^{3}	1.82×10^{2}
SOR	1.70	56.99	14.18	7.69

Results and Discussion

The adsorption equilibrium data of six VOCs on MCM-48 mesoporous sorbent were obtained at (303.15, 313.15, and 323.15) K. As shown in Figures 2−7, the adsorption isotherms of benzene, toluene, hexane, cyclohexane, methanol, and acetone are unusual type IV according to the IUPAC classification. Compared to the nonpolar organics, adsorption isotherms of two polar molecules (methanol and acetone) are relatively favorable at low pressures. The four nonpolar isotherms at different temperatures may be regarded as type V rather than type IV. Similar result on the adsorption of carbon tetrachloride and nitrogen on siliceous MCM-41 was reported by Branton research group.[17] In contrast to nitrogen, the carbon tetrachloride isotherms are almost linear at $P/P_0 < 0.2$. They explained the isotherm linearity to be due to the surface heterogeneity and a compensatory entropic contribution brought about by the clustering of molecules around the most favorable sites. The mesoporous adsorbent MCM-48 used in this study has a higher affinity to polar organic compounds than to nonpolar organics. In general, the organophilicity of MCM-48 seems to be a proportional relationship with the polarizability of the adsorbed organic compounds except benzene based on the adsorption isotherms investigated in this work. This finding is similar to the results of MCM-41 reported by Zao and Branton, although the pore structures of MCM-41 and MCM-48 are different.[2,17]

A steep increase at $P/P_0 = 0.2-0.4$ for polar and nonpolar organic compounds can be seen as shown in Figures 2−7. Owing to the differences in surface tension and molecular volume of the adsorbates, the capillary condensation takes place different relative pressures for the same pore diameter. Therefore, capillary condensation for nonpolar and polar organics was observed at $P/P_0 = 0.2-0.3$ and $0.3-0.4$, respectively. Compared to the nonpolar organic compounds investigated, the adsorption isotherms of polar organics are steeper gradients at low pressure. On the other hand, we found that the capillary condensation pressure of each organic compound studied in this work is almost equal regardless of temperatures.

Table 9. Temperature-Dependent Inhomogeneous DA Isotherm Parameters of Methanol and Acetone on MCM-48

materials	W_0/mmol g^{-1}	γ/K^{-1}	E_1/J mol^{-1}	E_2/J mol^{-1}	n_1	n_2	SOR
methanol	10.70	7.18×10^{-6}	5.95×10^{3}	1.22×10^{4}	1.47×10^{1}	1.00×10^{0}	18.957
acetone	47.96	4.78×10^{-3}	1.30×10^{4}	3.34×10^{3}	1.34×10^{0}	2.25×10^{1}	3.868

The pore volume of the MCM-48 sample can be calculated from the adsorption isotherms of six organic compounds. By assuming full saturation of the pores at the relative pressure of 0.95 and using fluid density of each adsorbate, the estimated value is about 0.973, 0.840, 0.817, 0.751, 0.791, and 0.757 cm^3 g^{-1} for benzene, toluene, *n*-hexane, cyclohexane, methanol, and acetone, respectively. These values are smaller than the pore volume (1.08 cm^3 g^{-1}) estimated from the nitrogen adsorption. This difference is mainly attributed to the uncertainty of the density of the adsorbed organics.

The equilibrium data are presented in Tables 3−5. Figures 2−7 show the adsorption equilibrium isotherms of benzene, toluene, *n*-hexane, cyclohexane, methanol, and acetone at various temperatures, respectively. The two different models have been used to correlate experimental equilibrium data of four polar organic compounds (benzene, toluene, *n*-hexane, and cyclohexane) and two nonpolar organics (methanol and acetone). As shown in Figures 2−5, the solid lines are the predicted results for nonpolar organic compounds by the temperature-independent Langmuir-Sips isotherm (eq 1), and the dashed lines are those by the temperature-dependent isotherm (eqs 1 to 5), respectively. On the other hand, the adsorption data of polar organics were correlated with the temperature-independent inhomogeneous DA isotherm (eq 6) and the temperature-dependent isotherm (eqs 6 to 8) as shown in Figures 6 and 7. The temperature-independent isotherm parameters for each adsorption were determined by using a pattern search algorithm, namely, “Nelder−Mead simplex method”.[15] Also, the eight parameters (q_{m0}, α, b_{10}, ΔH_1, b_{20}, ΔH_2, s_0, and δ) of temperature-dependent hybrid Langmuir−Sip isotherm and the six parameters (W_0, γ, E_1, E_2, n_1, n_2) of temperature-dependent inhomogeneous DA isotherm were determined by using all isotherm data of each adsorbate obtained at 303.15, 313.15, and 323.15 K simultaneously. In this calculation, the Nelder−Mead simplex method was also used based on the minimizing the sum of residues, namely, the differences between experimental and estimated adsorption amount. The comparison of fit of data by the models was based on the square of residues (SOR), defined as follows

$$\mathrm{SOR} = \frac{1}{2} \sum (N_{\mathrm{exp}} - N_{\mathrm{cal}})^2 \qquad (9)$$

where N_{exp} and N_{cal} are the experimental and calculated amounts adsorbed, respectively. The SOR is an absolute value, and the magnitude is dependent on the goodness-of-fit as well as the number of experimental data.[16] The temperature-independent and temperature-dependent parameters as well as the SOR of both the hybrid Langmuir−Sips and inhomogeneous DA isotherms are listed in Tables 6 and 8. Simulated isotherms using the hybrid isotherm model and the inhomogeneous DA model are highly coincidental with the equilibrium adsorption data. Thus, we expect that the isotherm models used in this study will be widely applicable for kinetic and column dynamic studies on the adsorption and desorption of nonpolar and polar organic compounds on mesoporous materials composed of both surface adsorption and capillary condensation.

Conclusion

Adsorption equilibria of four nonpolar molecules (benzene, toluene, hexane, and cyclohexane) and two polar molecules (methanol and acetone) were classified as unusual type IV, representing surface adsorption and capillary condensation on MCM-48 mesopores. It was found that MCM-48 has a higher affinity to polar organic compounds than to nonpolar organics except benzene because of the surface heterogeneity between the mesoporous adsorbent MCM-48 and the organic adsorbate with different polarizability. The proposed hybrid isotherm model, which combined the Langmuir and the Sips equations, describes well the adsorption data of nonpolar VOCs including the surface adsorption and the capillary condensation even with a set of four parameters. On the other hand, the inhomogeneous DA isotherm successfully correlated the adsorption data of polar molecules. The experimental data and the isotherm models reported in this study might be valuable for either the design of the adsorption-based process for the disposal of wastes containing VOCs and for modeling the catalytic oxidation process using mesoporous materials.

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