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Adsorption of Chlorinated Volatile Organic Compounds on MCM-48

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Adsorption equilibria of seven chlorinated volatile organic compounds on mesoporous silicate MCM-48 were obtained using a gravimetric technique. For comparison purposes, three organic sorbents (activated carbon, activated carbon fiber and nonionic polymer resin, SP850) and three inorganic sorbernts (DAY zeolite, mesoporous silicate MCM-41, and chromium-impregnated MCM-48) were used to investigate adsorption characteristics of trichloroethene chosen as a model compound of chlorinated volatile organic compounds. Mesoporous MCM-48 has a narrow pore size distribution, and capillary condensation of chlorinated volatile organic compounds can be observed at $P/P_0 = 0.2$ to 0.3. A new hybrid isotherm model for mesoporous sorbents is proposed by combination of the Langmuir isotherm at low pressure and the Sips isotherm in the multilayer region. Moreover, the surface heterogeneity of MCM-48 was evaluated in terms of an isosteric enthalpy of adsorption calculated using the proposed isotherm model.

Introduction

Volatile organic compounds (VOCs) are major air pollutants that must be controlled under increasingly stringent environmental regulations. Among them, chlorinated VOCs have been widely used in the chemical industry including the manufacture of herbicides, plastics, and solvents. Uses outside the chemical industry include solvent degreasing in the automotive and aerospace industries, dry cleaning solvents in the garment industries, and solvent cleaning in the electronic industries.[1,2] There are commercial technologies available for chlorinated VOCs abatement.[3] Among adsorption and separation technologies, activated carbon adsorption is widely used in industry because of easy operation, low operating cost, and efficient recovery of most chlorinated VOCs. However, it has been recognized that activated carbon frequently encounters problems such as combustion, pore blocking, and hygroscopicity.[4] As a result, alternative adsorbents have received attention. Hydrophobic zeolites have proven to be an advancement in controlling chlorinated VOCs.[5]

On the other hand, mesoporous silicates denoted M41S have been the subject of much interest because they were first described by Beck et al. in 1992.[6] The mesoporous silicates, M41S are classified into several members including MCM-41, MCM-48, MCM-50, and other species. MCM-41 has a hexagonal array of unidirectional pores while MCM-48 has a bicontinuous cubic pore system.[7] Their 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 size of pore, and high thermal stability. These mesoporous materials may be useful as adsorbents,[8,9] supports,[10] and catalysts.[1,11]

This study aims for the development of an energy efficient adsorption and catalytic destruction of chlorinated VOCs in MCM-48. There have been few studies on adsorption of chlorinated VOCs on MCM-48. Adsorption data are important for modeling the catalytic hydrodechlorination process, for example, studies in catalytic kinetics and catalyst deactivation. For this purpose, this paper presents experimental and theoretical results for the adsorption equilibria of chlorinated VOCs on manufactured MCM-48. To correlate isotherm data with capillary condensation in MCM-48, a new hybrid isotherm model was proposed by combination of the Langmuir isotherm at low pressure and the Sips isotherm in the multiplayer region. Also, isosteric enthalpy of adsorption was calculated using the proposed isotherm model.

Experimental Section

Adsorbents and Adsorbates. Tetrachloromethane, trichloromethane, dichloromethane, 1,2-dichloroethane, trichloroethene, tetrachloroethene, and 1,1,2-trichloro-1,2,2-trifluoroethane were used as a typical chlorinated VOCs. The chemical properties are listed in Table 1. MCM-48 sample was synthesized as follows.[12] A total of 12.4 g of cethyltrimethylammonium bromide (CTMABr, $C_{19}H_{42}BrN$, Aldrich) and 2.16 g of 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 another aqueous solution in a Teflon bottle containing 40 g of Ludox AS-40 (Du Pont, 40 mass% 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 into an autoclave, and the mixture was hydrothermally treated at 373 K for 78 h. The mixture was then filtered and washed with 500 mL of deionized water. The washing procedure was repeated 4−5 times to ensure the complete removal of the 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 at a heating rate of 1 K/min. Also, MCM-41 and Cr/MCM-48 were prepared for comparison purpose. MCM-41 was synthesized by conven-

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Table 1. Properties of Various Chlorinated VOCs

material	chemical formular	M.W.	purity (%)	density (g cm^{-3})	vapor pressure (303.15 K)	supply
tetrachloromethane	CCl_4	153.82	99.5	1.589	19.065	Junsei Chemical Co., Ltd.
trichloromethane	$CHCl_3$	119.38	99	1.484	32.345	Carloerba Reagent
dichloromethane	CH_2Cl_2	84.94	99.5	1.326	69.552	Junsei Chemical Co., Ltd.
1,2-dichloroethane	$C_2H_4Cl_2$	98.96	98	1.257	13.284	Yakuri Pure Chemical Co.
trichloroethene	C_2HCl_3	131.39	99	1.465	11.731	Kanto Chemical Co.
tetrachloroethene	C_2Cl_4	165.84	99	1.623	2.783	Junsei Chemical Co., Ltd.
1,1,2-trichloro-1,2,2-trifluoroethane	$Cl_2FCCClF_2$	187.38	99	1.564	54.168	Yakuri Pure Chemical Co.

Table 2. Physical Properties of the Various Sorbents

sorbent	manufacturer	form	BJH average pore diameter (Å)	BET surface area (m^2 g^{-1})
activated carbon	Norit, Holland	carbon pellet	32.1	1170
activated carbon fiber	Toyobo, Japan	carbon fiber	27.6	1530
DAY zeolite	Degussa, German	zeolite NaY	73.9	556
MCM-41	this work	powder	35.0	1100
MCM-48	this work	powder	32.0	993
Cr/MCM-48	this work	powder	29.0	854
SP850	Mitzubishi, Japan	polystyrene, bead	60.2	882

tional hydrothermal reaction described in the literature.[13] Cr/MCM-48 sample was manufactured by the introduction of chromium chloride during the gel-preparation stage followed by a similar treatment as applied to MCM-48.[8] The contents of chromium in Cr/MCM-48 were adjusted to be about 3 mass%. Other adsorbents were supplied as listed in Table 2 and used without further treatment. Nitrogen adsorption and desorption isotherms, BET surface areas, and Barrett, Joyner, and Halenda method for the synthesized sorbents were measured at 77 K using a Micromeritics ASAP 2000 automatic analyzer. Table 2 summarizes the important physical properties of mesoporous sorbents (MCM-41, MCM-48, and Cr/MCM-48) prepared by our laboratory and other materials supplied from companies. For the these synthesized mesoporous materials, X-ray powder diffraction data were obtained on a Phillips PW3123 diffractometer equipped with a graphite monochromator and Cu Kα radiation of wavelength 0.154 nm. XRD patterns were obtained between 2° and 50° with a scan speed of 1°/min to identify the characteristics of the mesoporous materials. The surface areas of three mesoporous sorbents were in the range of 854−1100 m^2 g^{-1}, and the average pore sizes were 29−35 Å which belong to the typical values of mesoporous materials.

Gravimetric Apparatus. The experimental apparatus made up of glass is shown in Figure 1. The vapor of chlorinated VOCs was generated in a small chamber that was maintained at a constant temperature. The adsorption amount was measured by a quartz spring balance, which was placed in a closed glass system. A total of 0.1 g of adsorbents was placed on the dish, which was attached to the end of quartz spring. Adsorbent samples were weighed with an accuracy of ±10 μg. The variation of mass was measured by a digital voltmeter that was connected to the spring sensor. Prior to adsorption, all adsorbents were vacuumed to 1 × 10^{-3} Pa for 15 h at 523.15 K except nonionic polymeric sorbent, SP850 at 423.15 K. A high vacuum system was composed of a turbomolecular pump (Edward type EXT70) and a rotary vacuum pump (Edward model RV5). A 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) allowing measurements from 0 to 133 kPa with the reading accuracy of ±0.15% and a power supply read out instrument (MKS type PDR−C-1C). During the adsorption, the adsorption cell was placed in a temperature-controlled water bath with circulator, and the temperature was maintained constant within ±0.02 K. Adsorption isotherms were obtained by admitting successive increments of sample gas to the adsorbent sample. The adsorption equilibrium was usually attained within 30−40 min. Adsorption amounts of trichloroethene on MCM-48 were measured at different temperatures of 293.15, 303.15, 308.15, 313.15, and 323.15 K.

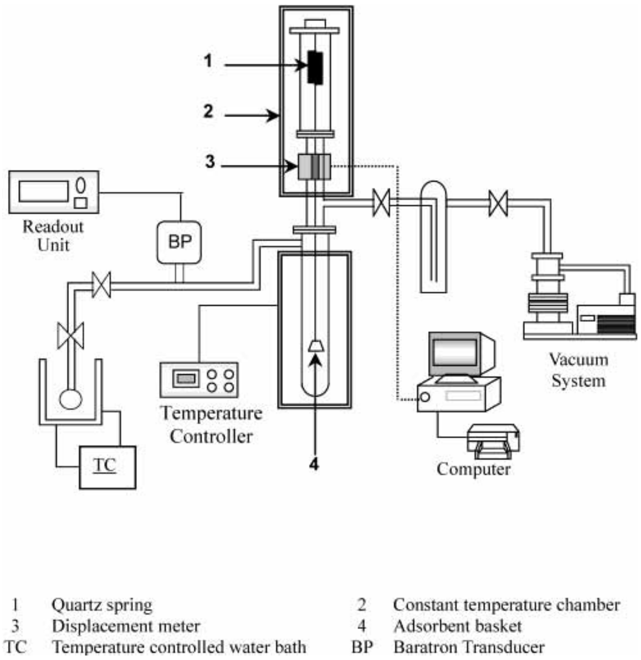

Figure 1. Schematic diagram of gravimetric apparatus.

Results and Discussion

Equilibrium Data. The isotherm data of chlorinated VOCs on organic and inorganic sorbents are presented in Tables 3−5, and many adsorption isotherms under different experimental conditions are shown in Figures 2−4. As shown in Figure 2, in general, the adsorption isotherm of chlorinated VOCs shows a Type IV according to the IUPAC classification because of the mesoporous characteristics of MCM-48. Almost linear isotherms can be observed in the low-pressure range; however, at the onset of pore filling,

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

tetrachloromethane		trichloromethane		dichloromethane		1,2-dichloroethane		trichloroethene		tetrachloroethene		1,1,2-trichloro-1,2,2-trifluoro ethane	
P	*N*	*P*	*N*	*P*	*N*	*P*	*N*	*P*	*N*	*P*	*N*	*P*	*N*
kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}
0.205	0.183	0.431	0.341	0.026	0.516	0.081	0.050	0.121	0.179	0.112	0.011	0.440	0.215
0.345	0.186	0.783	0.443	0.038	0.714	0.172	0.115	0.163	0.217	0.311	0.081	0.652	0.292
0.432	0.224	1.195	0.497	0.048	0.917	0.381	0.163	0.316	0.374	0.422	0.109	0.973	0.392
0.631	0.349	1.853	0.844	0.061	1.043	0.564	0.236	0.414	0.385	0.571	0.124	1.201	0.417
0.923	0.507	2.575	1.161	0.093	1.511	0.732	0.336	0.533	0.509	0.672	0.147	1.760	0.580
1.172	0.574	3.592	1.532	0.114	1.695	0.924	0.427	0.795	0.714	0.825	0.171	2.431	0.708
1.525	0.702	4.512	1.891	0.137	1.996	1.010	0.554	0.843	0.781	0.964	0.190	2.922	0.864
1.842	0.848	5.635	2.189	0.152	2.143	1.252	0.811	0.954	0.882	1.083	0.238	3.572	1.008
2.101	0.930	6.163	2.372	0.172	2.219	1.451	0.942	1.082	1.017	1.292	0.275	3.923	1.059
2.383	0.995	8.042	2.986	0.183	2.343	1.792	1.314	1.222	1.072	1.393	0.300	4.935	1.270
2.645	1.193	8.794	3.230	0.203	2.579	1.923	1.400	1.431	1.276	1.551	0.314	6.053	1.458
2.941	1.278	9.723	4.115	0.222	2.761	2.125	1.481	1.712	1.574	1.732	0.355	6.961	1.619
3.381	1.431	10.192	6.994	0.242	3.002	2.313	1.605	1.851	1.722	1.965	0.345	8.960	1.950
3.472	1.511	10.751	8.709	0.265	3.188	2.436	1.693	2.183	2.429	2.233	0.413	10.98	2.251
4.023	1.797	10.882	8.953	0.297	3.462	2.684	1.913	2.484	4.077	2.530	0.439	11.99	3.233
4.232	1.958	12.701	9.726	0.306	3.598	2.825	2.041	2.511	6.602	2.685	0.443	13.09	4.489
4.505	2.079	13.121	9.818	0.329	3.962	3.123	2.285	2.630	7.822	2.830	0.461	13.66	5.679
4.707	2.220	14.941	9.941	0.340	4.673	3.470	2.585	2.912	8.308			14.59	6.063
4.955	2.562	16.832	9.998	0.349	6.038	3.762	2.793	3.210	8.611			15.32	6.211
5.053	2.922	18.814	10.063	0.348	8.843	4.134	3.078	3.643	8.845			17.35	6.491
5.192	3.170	24.632	10.087	0.351	9.294	4.446	3.673	4.290	8.979			19.34	6.532
5.294	4.265			0.358	9.757	4.633	4.547	4.891	9.140			22.05	6.536
5.376	4.888			0.376	10.915	4.757	5.220					27.92	6.538
5.502	5.719			0.392	11.304	5.004	7.617					32.07	6.539
5.724	7.099			0.409	11.378	5.063	8.346						
5.843	7.197			0.454	11.590	5.232	8.996						
6.132	7.460			0.519	11.598	5.701	9.700						
6.506	7.794			0.553	11.609	5.992	10.014						
6.841	7.925			0.593	11.609	6.855	10.297						
7.172	7.978			0.664	11.609	7.566	10.382						
7.794	8.043			0.802	11.609	8.964	10.579						
8.876	8.136					9.512	10.657						
9.982	8.180												
11.291	8.258												
12.742	8.375												
14.243	8.444												
18.01	9.164												

Table 4. Equilibrium Data of Trichloroethene on Various Adsorbents at 303.15 K

activated carbon		activated carbon fiber		SP850		DAY zoelite		MCM-41		Cr/MCM-48	
P	N	P	N	P	N	P	N	P	N	P	N
kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}
0.011	0.841	0.005	1.378	0.062	0.743	0.045	0.711	0.021	0.009	0.091	0.131
0.023	1.578	0.022	2.552	0.165	1.088	0.122	1.622	0.263	0.018	0.134	0.144
0.053	2.247	0.105	3.626	0.222	1.211	0.245	1.964	0.482	0.168	0.242	0.167
0.101	2.762	0.196	4.020	0.323	1.486	0.344	2.023	0.565	0.258	0.364	0.209
0.172	3.085	0.524	4.484	0.392	1.593	0.472	2.048	0.673	0.326	0.583	0.263
0.293	3.360	0.737	4.538	0.543	1.903	0.581	2.108	0.764	0.455	0.795	0.324
0.451	3.611	0.855	4.533	0.641	2.056	0.704	2.139	0.891	0.568	1.293	0.495
0.604	3.723	1.411	4.559	0.835	2.387	0.915	2.191	1.043	0.747	1.662	0.766
0.783	3.814	1.652	4.568	1.181	2.779	1.502	2.189	1.132	0.889	2.003	1.012
1.095	3.882	2.346	4.625	1.405	2.988	1.903	2.196	1.405	1.263	2.362	1.317
1.507	3.947	3.733	4.644	2.002	3.657	2.304	2.197	1.665	1.606	2.734	1.651
1.951	3.945			2.803	4.411	2.871	2.198	1.726	1.661	3.012	1.961
2.614	3.980			3.392	4.933			1.913	1.832	3.422	2.722
3.425	3.981			3.731	5.302			2.255	2.285	3.521	2.901
3.933	3.982			4.161	5.602			2.322	2.419	3.722	3.589
				4.454	5.975			2.685	2.809	3.901	4.167
								3.012	3.316	4.162	5.096
								3.224	6.069	4.821	5.854
								3.751	8.832	5.734	6.002
								4.323	8.879	6.773	6.107
								5.072	8.939	8.261	6.233
								5.544	8.956	9.733	6.341
								5.701	8.964		

namely, capillary condensation of chlorinated VOCs can be seen as increasing pressure. The condensation pressure depends on the adsorbate, temperature, pore size, and geometry of sorbent. MCM-48 synthesized in our laboratory has a very narrow monodisperse pore size distribution obtained from Barrett, Joyner, and Halenda method. As

Table 5. Equilibrium Data of Trichloroethene on MCM-48 in Terms of Temperatures

308.15 K		313.15 K		323.15 K	
P	N	P	N	P	N
kPa	mmol g^{-1}	kPa	mmol g^{-1}	kPa	mmol g^{-1}
0.122	0.179	0.082	0.036	0.271	0.098
0.225	0.247	0.211	0.066	0.422	0.171
0.333	0.306	0.372	0.137	0.535	0.214
0.502	0.406	0.621	0.224	0.693	0.286
0.723	0.586	0.810	0.296	0.840	0.348
0.862	0.671	0.932	0.293	1.342	0.545
1.043	0.808	1.045	0.347	1.901	0.638
1.344	0.969	1.242	0.457	2.301	0.789
1.555	1.226	1.435	0.487	2.742	0.938
1.765	1.351	1.752	0.654	3.240	1.086
1.982	1.512	1.903	0.699	3.735	1.188
2.281	1.785	2.051	0.810	4.182	1.374
2.614	2.037	2.290	0.881	4.711	1.592
2.802	2.216	2.422	0.926	4.954	1.635
3.025	2.461	2.610	1.046	5.122	1.730
3.223	3.068	2.875	1.171	5.433	1.828
3.282	3.968	3.050	1.237	5.845	1.938
3.323	4.851	3.142	1.255	6.020	2.057
3.361	6.667	3.450	1.554	6.111	2.066
3.462	7.571	3.712	1.631	6.362	2.097
3.661	8.290	3.910	1.823	6.565	2.205
3.864	8.553	4.083	1.942	6.902	2.345
4.255	8.826	4.422	2.095	7.180	2.670
4.471	8.905	4.621	2.331	7.332	3.043
4.831	8.919	4.804	2.928	7.411	3.564
5.082	8.954	4.912	3.722	7.462	3.762
5.474	9.004	4.946	4.067	7.532	4.663
5.880	9.013	5.022	5.701	7.553	5.149
6.443	9.032	5.224	7.640	7.615	5.807
7.460	9.137	5.343	7.951	7.683	6.872
		5.592	8.192	7.813	7.296
		5.784	8.510	7.934	7.639
		6.055	8.641	8.261	7.918
		6.371	8.773	8.430	8.155
		7.013	8.790	8.773	8.420
		7.611	8.820	9.190	8.560
		8.312	8.840	9.882	8.600
				10.711	8.722
				11.410	8.740
				11.911	8.754

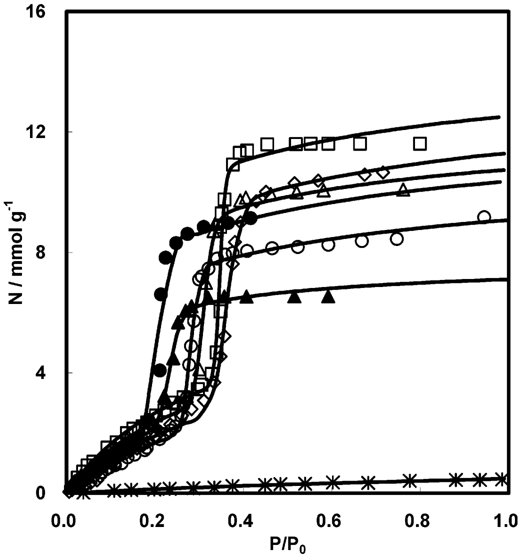

Figure 2. Adsorption isotherm of chlorinated VOCs on MCM-48 at 303.15 K. ○, Tetrachloromethane; △, trichloromethane; □, dichloromethane; ◇, 1,2-dichloroethane; ●, trichloroethene; *, tetrachloroethene; ▲, 1,1,2-trichloro-1,2,2-trifluoroethane; —, Langmuir-Sips.

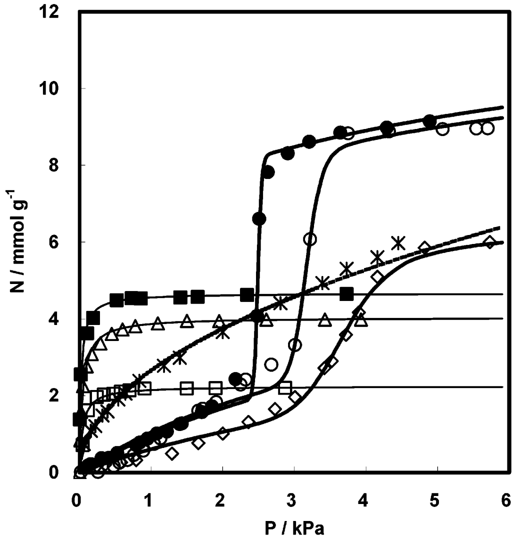

Figure 3. Adsorption isotherm of trichloroethene on various sorbents at 303.15 K. △, AC; ■, ACF; □, DAY; ○, MCM-41; ●, MCM-48; ◇, Cr/MCM-48; *, SP-850; —, Langmuir; ···,Freundlich; —, Langmuir-Sips.

shown in Figure 2, capillary condensation of chlorinated VOCs in MCM-48 can be observed at $P/P_0 = 0.2-0.3$. However, this property of tetrachloroethene was not observed because of its relatively lower vapor pressure, which is not enough to fill the mesoporous inner pore space. On the other hand, Figure 3 shows the adsorption isotherm of trichloroethene on various adsorbents for comparison purposes with MCM-48. Activated carbon and activated carbon fiber adsorb trichlorothene more effectively at low pressures, whereas the mesoporous sorbents provide the highest adsorption capacity at the highest pressures because of capillary condensation. This may result from an instantaneous filling of the inner pore space with the condensed adsorbate when a certain capillary condensation pressure is attained. The incorporation of chromium into the MCM-48 framework causes a decrease in the surface area and pore size. Because chromium species introduced in sol−gel process would be expected to react with the surface silanol groups of the walls randomly, the pores with largest population would make contact with chromium species in relatively high probability. As a result, a slight reduction in the average pore size and a significant reduction of adsorption capacity were observed when 3 mass % of chromium species are introduced as shown in Figure 3. The equilibria of activated carbon, activated carbon fiber, and DAY are favorable for trichloroethene adsorption. On the other hand, adsorption isotherms for polymer resin SP850 shows less favorable, near linear isotherms. The influence of temperatures on adsorption equilibria of trichloroethene on MCM-48 is quite sensitive as shown in Figure 4.

Adsorption Model. Adsorption isotherms play a key role in either the design of the adsorption-based process for the disposal of wastes containing chlorinated VOCs or modeling the catalytic oxidation process.[14,15] In this study, three types of isotherm models were used to correlate the experimental equilibrium data of trichloroethene on organic and inorganic sorbents. More than one model is required because there is no universal equilibrium model that provides an accurate fit for all sorbents. The equilibrium data of trichloroethene on activated carbon, activated carbon fiber, and DAY zeolite were well fitted to the Langmuir model, and those of trichloroethene on nonionic polmeric sorbent, SP850, were well correlated by the Sips isotherm. For mesoporous sorbents, however, the equilib-

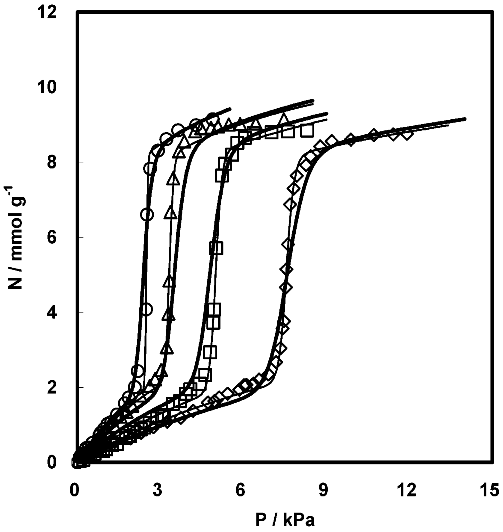

Figure 4. Adsorption isotherm of trichloroethene on MCM-48 in terms of temperatures. ○, 303.15 K; △, 308.15 K; □, 313.15 K; ◇, 323.15 K; —, Langmuir-Sips (Table 8); —, temperature-dependent Langmuir-Sips (Table 9).

rium data with capillary condensation were correlated poorly with nonlinear isotherm models reported in the literature. Until now, many isotherms have been developed for the adsorption of condensable vapors on porous materials and are reviewed elsewhere.[16,17] 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. So, we have tested many hybrid isotherms to correlate equilibrium data of trichloroethene on mesoporous materials. A hybrid isotherm of Langmuir and Sips equations with four isotherm parameters fitted the isotherm data of trichloroethene well. The proposed isotherm 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. Four parameters (m, b_1, b_2, and s) of the hybrid isotherm were determined by a nonlinear least-squares fitting routine of Nelder-Mead simplex method. The estimated isotherm parameters are listed in Table 6−8 according to the adsorption systems, respectively. As shown in Figures 2−4, a good correlation was observed.

Table 8. Hybrid Isothem Parameters of Trichloroethene on MCM-48 in Terms of Temperatures

	303.15 K	308.15 K	313.15 K	323.15 K
m/mmol g^{-1}	6.260	5.968	6.360	5.978
b_1/kPa^{-1}	1.825×10^{-1}	1.764×10^{-1}	8.592×10^{-2}	7.522×10^{-2}
b_2/kPa^{-1}	9.303×10^{-40}	3.297×10^{-25}	8.441×10^{-32}	1.993×10^{-49}
s	9.848×10^{1}	4.695×10^{1}	4.448×10^{1}	5.544×10^{1}

Isosteric Enthalpy of Adsorption. The isosteric enthalpy of adsorption (Q_{st}) can be calculated by the Clausius−Clapeyron equation:[16]

$$Q_{st} = -R\left[\frac{\partial \ln P}{\partial (1/T)}\right]_N \tag{2}$$

where P is the pressure, T is the temperature, and R is the gas constant. Adsorption isotherm model should be expressed as a function of temperature to determine the isosteric enthalpy of adsorption from adsorption isotherm. On the basis of the equilibrium data of chlorinated VOCs on MCM-48, the saturation capacity, m is almost independent of temperature. Thus, we extended three isotherm parameters (b_1, b_2, s) of the hybrid isotherm as a function of temperature as follows:

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

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

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

where b_{10}, ΔH_1, b_{20}, ΔH_2, s_0, and β are the parameters and T_m is the mean temperature. Combination eq 2 with a set of temperature-dependent isotherm model (eqs 1 and 3−5) gives the derived isosteric enthalpy of adsorption:

$$Q_{st} = \frac{\{b_1P(1 + b_1P) + b_1(-\Delta H_1)P\}(1 + b_2P^s)^2}{b_1P(1 + b_2P^s)^2 + b_2sP^s(1 + b_1P)^2} + \frac{\{b_2P^s(1 + b_2P^s) + b_2(-\Delta H_2)P^s + b_2P^s \ln Ps(-\beta)\}(1 + b_1P)^2}{b_1P(1 + b_2P^s)^2 + b_2sP^s(1 + b_1P)^2} \tag{6}$$

The isosteric enthalpy is a measure of the interaction between adsorbate molecules and adsorbent lattice atoms and may be used as a measure of the energetic heterogeneity of a solid surface. It has been recognized that surface heterogeneity may come from the energetic, structural, and geometric heterogeneity.[18] For the heterogeneous adsorp-

Table 6. Estimated Isotherm Parameters of Chlorinated VOCs on MCM-48 at 303.15 K

	tetrachloromethane	trichloromethane	dichloromethane	1,2-dichloroethane	trichloroethene	tetrachloroethene	1,1,2-trichloro-1,2,2-trifluoroethane
m/mmol g^{-1}	5.36	6.12	7.17	6.82	6.26	0.496	3.84
b_1/kPa^{-1}	1.19×10^{-1}	9.64×10^{-2}	4.25×10^{-2}	1.45×10^{-1}	1.83×10^{-1}	4.13×10^{-1}	1.06×10^{-1}
b_2/kPa^{-1}	3.25×10^{-23}	1.48×10^{-29}	5.81×10^{-80}	1.50×10^{-17}	9.30×10^{-40}	1.70×10^{-1}	1.38×10^{-21}
s	30.8	28.8	57.3	24.6	98.5	1.33	18.9

Table 7. Estimated Isotherm Parameters of Trichloroethene on Various Sorbents at 303.15 K

	AC	ACF	SP850	DAY	MCM-41	Cr/MCM-48
	Langmuir	Langmuir	Freundlich	Langmuir	Langmuir-Sips	Langmuir-Sips
m/mmol g^{-1}	4.04	4.67	2.66	2.24	5.92	3.96
b or b_1/kPa^{-1}	22.60	41.88		22.01	2.15×10^{-1}	1.82×10^{-1}
b_2/kPa^{-1}					9.34×10^{-16}	2.53×10^{-7}
s			2.02		30.0	11.7

Table 9. Temperature-Dependent Hybrid Isotherm Parameters of Trichloroethene on MCM-48

m_0	b_{10}	$-\Delta H_1$	b_{20}	$-\Delta H_2$	s_0	β
mmol g^{-1}	kPa^{-1}	kJ mol^{-1}	kPa^{-1}	kJ mol^{-1}		kJ mol^{-1}
6.14	1.12×10^{-1}	4.49×10^{4}	8.95×10^{-13}	1.23×10^{6}	1.85×10^{1}	1.24×10^{4}

tion system, the isosteric enthalpy curve varies with the surface loading. Information concerning the magnitude of the enthalpy of adsorption and its variation with coverage can provide useful information concerning the nature of the surface and the adsorbate phase. The isosteric enthalpy of adsorption was calculated from eq 6 using isotherm parameters listed in Table 9. The six isotherm parameters (b_{10}, ΔH_1, b_{20}, ΔH_2, s_0, and β) except m were determined simultaneously by using all isotherm data obtained at 303.15, 308.15, 313.15, and 323.15 K based on the Nelder-Mead simplex method by minimizing the sum of residual, namely, the differences between experimental and estimated adsorption amount. In this calculation, the value of the saturation capacity (m), 6.14 was used as an average quantity for 303.15, 308.15, 313.15, and 323.15 K listed in Table 8 because that is almost constant with respect to temperatures as shown in Figure 4. To verify the determined isotherm parameters, the predicted results are shown in Figure 4. The thin solid lines are the predicted results from the Langmuir-Sips isotherm model with four parameters listed in Table 8, and the thick solid lines are those from the temperature-dependent isotherm model with seven parameters listed in Table 9, respectively. On the other hand, the sharp variation of enthalpy of adsorption for trichloroethene with surface coverage shown in Figure 5 supports that bonding among trichloroethene molecules in the condensed phase and between adsorbed trichloroethene layer and MCM-48 surfaces play a key role in determining the desorption characteristics because the isosteric enthalpy of adsorption is considered as the isosteric enthalphy of desorption. MCM-48 surface seems to be heterogeneous because the isosteric enthalpy of adsorption changes according to the loading as shown in Figure 5. Here, the vaporization enthalpy was illustrated together for comparison. From the fact that surface heterogeneity result from the energetic, structural, and geometric heterogeneity,[19] the surface heterogeneity of trichloroethane+MCM-48 adsorption system may come from structural heterogeneity because the capillary condensation is highly sensitive to structure properties of pore size and pore distribution.

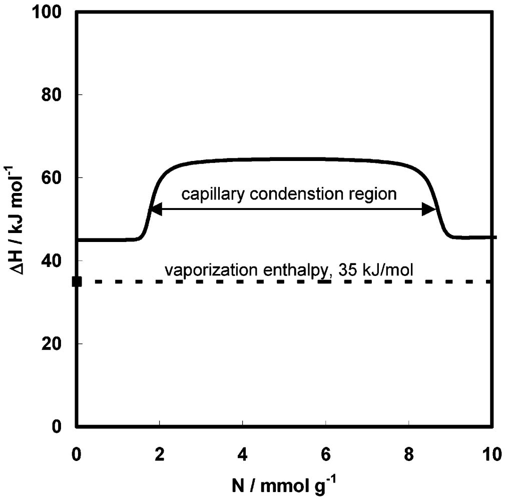

Figure 5. Isosteric enthalpy of adsorption, ΔH with respect to surface loading at 313.15 K.

Conclusion

The adsorption equilibria of chlororinated VOCs were determined gravimetrically at 303.15 K on synthesized MCM-48. Because of the narrow mesopore size distribution of MCM-48, capillary condensation can be observed at $P/P_0 = 0.2$ to 0.3 regardless of chlorinated VOCs. The equilibria of activated carbon, activated carbon fiber, and DAY are favorable for TCE adsorption, whereas those of polymer resin, SP850 shows less favorable, near linear isotherm. Generally, type IV isotherm according to the IUPAC classification can be observed in all mesoporous sorbents used in this study because of the mesopore characteristics. Surprisingly, the hybrid equation based on the Langmuir and Sips isotherms describes well the equilibrium data of trichloroethene on mesoporous sorbents such as MCM-41, MCM-48, and Cr/MCM-48. Thus, the hybrid isotherm model will be very useful for the study on adsorption kinetics and column dynamics of chlorinated VOCs in mesoporous materials. The isosteric enthalpy of adsorption varied between 45 and 65 kJ/mol with the surface loading of trichloroethene. The surface heterogeneity of trichloroethene+MCM-48 adsorption system may come from structural heterogeneity. The reported experimental data in this study might be valuable for either the design of the adsorption-based process for the disposal of wastes containing chlorinated VOCs or modeling the catalytic oxidation process using mesoporous materials.

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