Characterization of Activated Carbon by Propane and Propylene Adsorption

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Two types of commercial activated carbons, Westvaco BAX 1100 and Chemviron LAC 30-57, were characterized by microporosity, equilibrium, and kinetic adsorption of propane and propylene. The porosity was determined by the measurement of the N_2 adsorption isotherm at 77 K. Single component equilibrium adsorption of propane and propylene on the adsorbents was measured in the temperature range (273 to 343) K and the pressure range (0.0001 to 1) bar and correlated by several well-known isotherm models. The enthalpies of adsorption were estimated by the Clausius–Clapeyron equation and its dependence on adsorption coverage. Fractional uptake experiments performed to study the single component kinetics and apparent diffusivity were evaluated.

Introduction

The development of adsorption technology for separation of hydrocarbons requires basic adsorption data (equilibrium and kinetics) in a wide range of experimental conditions. The measurements of single component adsorption over a relatively wide range of experimental conditions have different purposes. The study of adsorption equilibrium in microporous solids such as activated carbons is of the utmost importance for its use in concrete applications. Fundamental adsorption data are useful for characterizing different adsorbent surfaces and investigating the nature of their interactions with the adsorbed molecules. They are also useful for evaluating the ability of different models to correlate the data in various ranges of temperature and pressure. Reliable correlations are also essential for estimating the dependence of thermodynamic properties in the adsorption phenomena. They are extremely useful for simulating cyclic adsorption processes, such as pressure and temperature swing adsorption processes, because the process conditions vary widely during cycling.¹ The purpose of this investigation was the characterization of two types of activated carbons (BAX 1100 & LAC 30-57) by studying the porosity properties and the equilibrium and kinetic adsorption of propane and propylene.

The surface area and microporosity of both activated carbons were evaluated by nitrogen adsorption at 77 K. Equilibrium data were measured at (273, 303, and 343) K and evaluated by the Langmuir, Freundlich, Langmuir– Freundlich, Dubinin–Radushkevich, Dubinin–Astakhov, and Toth models. Kinetic measurements in this study have been done by determination of the apparent diffusivity of propane and propylene from analyzing the uptake curve.

Experimental Section

Materials. Helium (minimum purity 99.996%), propane (minimum purity 99.95%), propylene (minimum purity 99.995%), and nitrogen (minimum purity 99.999%) were supplied by Linde. The BAX 1100 activated carbon was obtained from Westvaco in the form of pellets (2 mm extru-

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Table 1. Adsorption Isotherm Models and Their
Parameters: Absolute Pressure, P; Moles Adsorbed, q;
Saturation Vapor Pressure, P ⁶ ; Adsorption Equilibrium
Constant, b; Dubinin-Astakhov Parameter, d; Toth
Parameters, k and n; Monolayer Capacity, q _m ; Limiting
Micropore Capacity, q ₀

model [ref]			fitting parameters
Langmuir [4]	$q = \frac{q_{\rm m}bP}{1+bP}$	(1)	q _m , b
Freundlich [4]	$q = bP^n$	(2)	<i>b, n</i>
Freundlich-Langmuir [4]	$q = \frac{q_{\rm m} b P^n}{1 + b P^n}$	(3)	q _m , b, n
Dubinin-Radushkevich [5]	$q = q_0 \operatorname{e}^{-\beta(\ln(P^{\mathrm{s}}/P))^2}$	(4)	q_0 , eta
Dubinin–Astakhov [5]	$q = q_0 \operatorname{e}^{-\beta(\ln(P^{\mathrm{s}}/P))^d}$	(5)	q_0, β, d
Toth [4]	$q = q_{\rm m} \left(1 + \frac{1}{kP^n}\right)^{-1/n}$	(6)	q _m , n, k

dates) and is typically used in the field of solvent recovery. The LAC 30-57 activated carbon was obtained from Chemviron Carbon as a form of pellets (3 mm extrudates) and is usually used for gas separation and purification. All adsorbents were regenerated overnight at 120 °C before being used in adsorption measurements.

Equilibrium Measurement. N₂ adsorption at 77 K is a commonly applied technique to determine various characteristics of porous materials. Total pore volume, micropore volume, surface area, and pore size distribution are derived from the N₂ (77 K) using Micrometrics ASAP 2010. This apparatus has also been used for adsorption equilibrium measurement for propane and propylene on both activated carbons at three temperatures (273, 303, and 343) K. Prior to each isotherm measurement, the adsorbents were regenerated at first in an oven overnight (120 °C for 8 h) and second in situ in a sample tube at 473 K under a vacuum of less than 10^{-4} Pa.

Kinetic Measurement. The gravimetric method was employed for the measurement of adsorption uptake using a gravimetric magnetic suspension balance built by Rubotherm GmbH. The experimental apparatus is described by Dreisbach et al.² The mass and mass change of the samples



Figure 1. N₂ adsorption isotherms at 77 K: ●, BAX; ▲, LAC.



Figure 2. N_2 loading of ACs plot versus the statistical film thickness, *a*: \bullet , BAX; \blacktriangle , LAC.

 Table 2.
 Surface Area, Pore Volume, and Pore Size of Activated Carbons

					t-plot	
	specific surface area/m²•g ⁻¹		total pore vol/	total area/	mesopore area/	mean pore
AC	BET	Langmuir	cm ³ ⋅g ⁻¹	$m^2 \cdot g^{-1}$	$m^2 \cdot g^{-1}$	diameter/Å
BAX LAC	1378 1011	2187 1443	0.734 0.501	1358 1101	208 12	32 20

located under severe atmospheric conditions can be measured with high accuracy by using a microbalance outside the measuring cell. About 0.6 g of adsorbent inside the measuring cell was heated to 473 K and kept under helium gas flow to remove any preadsorbed species until a stable weight was reached. The sample was allowed then to cool to the considered temperature while still under helium purge. An uptake experiment was initiated by replacing the helium stream by a preset mixture of diluted analysis gas in helium, and the weight of the sample was monitored continuously during the process. The total gas flow rate passing through the adsorber was kept at 300 L·h⁻¹ to neglect the external mass transfer resistance and also to dissipate any heat generated from

Table 3.	Adsorption Is	sotherm Da	ata for Prop	ylene on
BAX Act	ivated Carbor	n		-

2	273 K	3	803 K	3	343 K		
P/bar	q/mol⋅kg ⁻¹	P/bar	q/mol⋅kg ⁻¹	P/bar	q/mol⋅kg ⁻¹		
0.0001	0.1557	0.0001	0.0336	0.0002	0.0062		
0.0004	0.2830	0.0004	0.0744	0.0004	0.0126		
0.0006	0.3757	0.0006	0.1048	0.0006	0.0181		
0.0015	0.6322	0.0015	0.1993	0.0015	0.0461		
0.0039	1.0377	0.0040	0.3690	0.0042	0.1068		
0.0062	1.3042	0.0062	0.4804	0.0063	0.1460		
0.0100	1.6419	0.0100	0.6314	0.0119	0.2322		
0.0181	2.1477	0.0183	0.8726	0.0186	0.3168		
0.0266	2.5469	0.0268	1.0634	0.0263	0.3979		
0.0470	3.2421	0.0476	1.4188	0.0474	0.5776		
0.0686	3.7790	0.0683	1.6909	0.0678	0.7183		
0.1238	4.7225	0.1223	2.2181	0.1221	1.0116		
0.1773	5.3491	0.1767	2.6102	0.1766	1.2425		
0.2318	5.8614	0.2314	2.9267	0.2310	1.4376		
0.2865	6.2814	0.2853	3.1890	0.2856	1.6087		
0.3773	6.8403	0.3751	3.5472	0.3744	1.8480		
0.4697	7.3044	0.4654	3.8439	0.4639	2.0550		
0.6030	7.8748	0.6020	4.2103	0.6018	2.3222		
0.7434	8.3629	0.7435	4.5688	0.7431	2.5522		
0.8584	8.7224	0.8597	4.7703	0.8586	2.7183		
0.9736	9.0363	0.9746	4.9416	0.9734	2.8628		

 Table 4. Adsorption Isotherm Data for Propane on BAX

 Activated Carbon

273 K		3	803 K	3	343 K	
P/bar	q/mol⋅kg ⁻¹	P/bar	q/mol⋅kg ⁻¹	P/bar	q/mol⋅kg ⁻¹	
0.0001	0.1405	0.0002	0.0370	0.0003	0.0081	
0.0004	0.2539	0.0004	0.0740	0.0004	0.0111	
0.0006	0.3323	0.0006	0.1045	0.0007	0.0189	
0.0015	0.5584	0.0015	0.1939	0.0015	0.0427	
0.0039	0.9030	0.0039	0.3550	0.0041	0.1042	
0.0062	1.1339	0.0062	0.4594	0.0064	0.1455	
0.0102	1.4336	0.0105	0.6146	0.0107	0.2156	
0.0182	1.8562	0.0184	0.8274	0.0186	0.3189	
0.0261	2.1707	0.0264	0.9963	0.0270	0.4092	
0.0471	2.7786	0.0480	1.3396	0.0471	0.5826	
0.0679	3.2074	0.0682	1.5859	0.0678	0.7272	
0.1225	3.9812	0.1236	2.0798	0.1227	1.0249	
0.1779	4.5110	0.1778	2.4319	0.1784	1.2587	
0.2312	4.8978	0.2344	2.7235	0.2332	1.4495	
0.2862	5.2294	0.2869	2.9477	0.2862	1.6109	
0.3763	5.6588	0.3764	3.2609	0.3743	1.8363	
0.4686	6.0209	0.4672	3.5188	0.4621	2.0259	
0.6028	6.4560	0.6026	3.8276	0.6036	2.2746	
0.7431	6.8300	0.7439	4.0846	0.7436	2.4715	
0.8580	7.1000	0.8580	4.2592	0.8590	2.6093	
0.9735	7.3347	0.9734	4.4121	0.9734	2.7222	

adsorption and to maintain isothermal conditions. Uptake experiments were performed at 303 K and 343 K, with 2 vol % of each gas (propane and propylene) in the helium at 1 bar pressure.

The precision of the experiments was checked by carrying out multiple runs with the different adsorbent samples and repeated runs with the same samples. Accuracy was confirmed by comparison of experimental data with some experimental results in the literature.

Theory

Equilibrium Adsorption. The experimental adsorption isotherm data collected in this work were fitted by several conventional isotherm models to extend their utility. Six isotherm equations, which were used, and their fitting parameters are given in Table 1. The saturation vapor pressure, P^8 , in Dubinin–Radushkevich and Dubinin–Astakhov models was determined by Antoine's equation.

The fitting parameters of eqs 1-6 were obtained by a nonlinear regression of the experimental data, along the

 Table 5. Adsorption Isotherm Data for Propylene on

 LAC Activated Carbon

273 K		3	03 K	3	343 K	
P/bar	q/mol·kg ⁻¹	P/bar	q/mol⋅kg ⁻¹	P/bar	q/mol⋅kg ⁻¹	
0.0001	0.4209	0.0002	0.1320	0.0002	0.0227	
0.0004	0.6773	0.0004	0.2459	0.0004	0.0536	
0.0006	0.8392	0.0006	0.3305	0.0006	0.0787	
0.0015	1.2375	0.0015	0.5594	0.0015	0.1647	
0.0038	1.7599	0.0038	0.8931	0.0042	0.3300	
0.0062	2.0750	0.0062	1.1060	0.0062	0.4195	
0.0102	2.4400	0.0104	1.3824	0.0100	0.5526	
0.0194	2.9575	0.0184	1.7371	0.0189	0.7759	
0.0262	3.2136	0.0260	1.9892	0.0264	0.9176	
0.0469	3.7088	0.0472	2.4832	0.0471	1.2102	
0.0681	4.0202	0.0688	2.8321	0.0692	1.4415	
0.1223	4.4915	0.1221	3.4052	0.1223	1.8427	
0.1799	4.7868	0.1775	3.7926	0.1789	2.1505	
0.2343	4.9850	0.2324	4.0744	0.2319	2.3768	
0.2921	5.1469	0.2882	4.2989	0.2858	2.5679	
0.3773	5.3256	0.3783	4.5773	0.3778	2.8289	
0.4652	5.4645	0.4681	4.7917	0.4693	3.0362	
0.6018	5.6260	0.6017	5.0363	0.6029	3.2754	
0.7432	5.7459	0.7434	5.2421	0.7437	3.4691	
0.8580	5.8185	0.8584	5.3734	0.8580	3.6035	
0.9742	5.8797	0.9739	5.4849	0.9736	3.7124	

 Table 6. Adsorption Isotherm Data for Propane on LAC

 Activated Carbon

2	273 K 303 K		603 K	3	43 K
P/bar	q/mol·kg ⁻¹	P/bar	q/mol·kg ⁻¹	P/bar	q/mol⋅kg ⁻¹
0.0001	0.4023	0.0001	0.1367	0.0002	0.0256
0.0004	0.6635	0.0004	0.2581	0.0004	0.0558
0.0006	0.8236	0.0006	0.3393	0.0006	0.0804
0.0015	1.2176	0.0015	0.5703	0.0015	0.1661
0.0038	1.7418	0.0038	0.8968	0.0043	0.3360
0.0062	2.0605	0.0062	1.1053	0.0063	0.4215
0.0100	2.4142	0.0105	1.3782	0.0102	0.5560
0.0184	2.9026	0.0180	1.7093	0.0182	0.7540
0.0261	3.1930	0.0263	1.9756	0.0264	0.9071
0.0469	3.6670	0.0478	2.4469	0.0468	1.1905
0.0690	3.9645	0.0681	2.7474	0.0678	1.4075
0.1223	4.3770	0.1241	3.2732	0.1223	1.8095
0.1790	4.6404	0.1777	3.5836	0.1770	2.0967
0.2354	4.8197	0.2335	3.8131	0.2315	2.3188
0.2912	4.9536	0.2903	3.9908	0.2862	2.4998
0.3786	5.1140	0.3780	4.1971	0.3766	2.7347
0.4668	5.2320	0.4677	4.3563	0.4679	2.9199
0.6018	5.3576	0.6016	4.5322	0.6023	3.1279
0.7429	5.4502	0.7430	4.6684	0.7442	3.2955
0.8582	5.5020	0.8591	4.7559	0.8599	3.4049
0.9733	5.5393	0.9733	4.8230	0.9731	3.4895

mean squared error (MSE) defined by

$$MSE = \frac{\sum (q^{exp} - q^{cal})^2}{n - p}$$
(7)

where q^{exp} and q^{cal} are the experimental and calculated adsorption value, respectively; *n* is the total number of experimental data points; and *p* is the number of parameters in the model.³

Kinetics. The fractional uptake was used to investigate the adsorption kinetics of propane and propylene on the adsorbents. When the film resistance becomes negligible compared to internal diffusional resistance, and also the linear isotherm is valid, the fractional uptake will be given as follows:

$$\frac{M_{\rm t}}{M_{\rm a}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \left(\frac{D}{t^2}t\right)\right)$$
(8)

Table 7.	Fitted	Parameters	and Er	ror for	Adsorption
Isotherm	Data e	on BAX Activ	vated C	arbon	-

			Toth		
gas	<i>T</i> /K	$q_{ m m}/ m mol\cdot kg^{-1}$	10 ⁻⁴ <i>K</i> /Pa ⁻	¹ n	MSE/(mol·kg ⁻¹) ²
propane	273	29.733	181.3	0.209	0.0003
	303	18.812	2.678	0.252	0.0003
	343	10.970	0.4123	0.347	0.00006
propylene	273	49.566	17.26	0.189	0.0002
1 15	303	31.804	2.388	0.219	0.0002
	343	24.247	0.2905	0.265	0.00002
		Dubin	in–Astakh	0V	
gas	<i>T</i> /K	q_0 /mol·kg ⁻¹	β	D	$MSE/(mol \cdot kg^{-1})^2$
propane	273	9.306	0.1221	1.503	0.0003
	303	6.815	0.1043	1.623	0.0001
	343	5.462	0.08492	1.781	0.0001
propylene	273	12.326	0.1317	1.471	0.0004
	303	8.529	0.1216	1.555	0.0001
	343	7.159	0.1247	1.610	0.00001
		Dubinin	-Radushke	evich	
gas	<i>T</i> /1	K q₀/mol·kg	g^{-1} β		$MSE/(mol \cdot kg^{-1})^2$
propane	27	3 7.928	0.048	59	0.0303
	30	3 5.764	0.049	74	0.0039
	34	3 4.788	0.054	01	0.0003
propylene	27	3 10.131	0.048	16	0.0462
	30	3 6.794	0.049	64	0.0061
	34	3 5.390	0.054	4	0.0009
		Langmu	ir-Freund	llich	
gas	<i>T</i> /K	$q_{\rm m}/{ m mol}\cdot{ m kg}^{-1}$	10 ⁻³ <i>b</i> /Pa ⁻¹	n n	MSE/(mol·kg ⁻¹) ²
propane	273	13.326	3.59	1.974	0.0007
	303	8.403	1.316	1.706	0.00006
	343	6.933	0.3798	1.539	0.0004
propylene	273	17.993	3.095	1.989	0.0004
1 15	303	10.614	1.155	1.733	0.0002
	343	6.942	0.2776	1.467	0.00006
		Fi	reundlich		
gas	7	7K b/	Pa ⁻¹	n	MSE/(mol·kg ⁻¹) ²
nronono	9	72 0.1	175 9	011	0.0422
propane	2	02 0.1	475 2.	311 159	0.0433
	2	42 0.0	14303 2.	430	0.0138
propylopo	, 9	73 0.0	547 1.	907 800	0.0044
propyrene	- ~ 2	03 0.1	347 2.	367	0.0122
	3	43 0.0	0.0721 1	910	0.0341
	0			510	0.0020
			angmuir	. 1	
gas	77K	. <i>q</i> _m /mol∙kg ⁻	⁻¹ 10 ⁻⁴ <i>b</i> /F	'a ⁻¹	MSE/(mol·kg ⁻¹) ²
propane	273	7.305	1.196	5	0.1841
	303	4.819	0.657	5	0.0381
_	343	3.733	0.278	3	0.0068
propylene	273	9.128	1.026		0.2755
	303	5.509	0.572	2	0.0485
	343	3 745	() 286	5	0.0068

where M_t and M_a are the amounts adsorbed at time *t* and at infinite time, respectively.⁴ The uptake adsorption data were used for evaluation of the apparent diffusivity (D/r^2) by a nonlinear fitting of eq 8.

Results and Discussion

Microporosity and Surface Property. The adsorption isotherms of N₂ at 77 K are shown in Figure 1. Both adsorbents present an extremely narrow hysteresis loop, and their isotherm behavior shows a high micropore content. In LAC approximately 80% of the total micropores are occupied at relative pressure below 0.05 while in BAX only <50% of the total micropores will be occupied at such a relative pressure.

t-Plot. The isotherms of Figure 1 were transformed in the universal t-plot (Figure 2), taking as the standard



Figure 3. Adsorption isotherms (equilibrium loading with respect to absolute pressure) on the adsorbents: \bullet , propylene; \blacktriangle , propane. (a) BAX isotherms at 273 K: solid line, Toth fit. (b) BAX isotherms at 303 K: solid line, Dubinin–Radushkevich fit. (c) BAX isotherms at 343 K: solid line, Dubinin–Astakhov fit. (d) LAC isotherms at 343 K: solid line, Langmuir–Freundlich fit. (e) LAC isotherms at 273 K: solid line, Freundlich fit. (f) LAC isotherms at 303 K: solid line, Langmuir fit.

isotherm where the statistical average thickness was calculated by Halsey's relation.⁶ The best fits of two straight lines representing the two linear regions of the t-plot, situated at low and high relative pressure, are shown in Figure 2.

Micropore surface area and external surface area are obtained by the slope of the straight line at low and high pressure, respectively, and the intercept of the straight line at high pressure provides the total micropore volume.⁴ The specific area and the behavior of the t-plot quantitatively are given in Table 2.

The pore sizes of both adsorbents can be established by the adsorption mean diameter (4 $V_{\text{pore}}/S_{\text{BET}}$), which is given in Table 2. According to the values of the last two columns

of Table 2, BAX activated carbon has a wide pore distribution as well as a large specific surface of mesopores, and LAC activated carbon has a larger proportion of micropores than BAX.

Equilibrium Adsorption Isotherms. Adsorption isotherms of propane and propylene, measured at three temperatures (273, 303, and 343) K, are presented in Tables 3–6 and are plotted in Figure 3. The adsorption isotherm data were fitted by the Langmuir, Freundlich, Langmuir–Freundlich, Dubinin–Radushkevich, Dubinin–Astakhov, and Toth equations. The fitted parameters and error of analysis are given in Tables 7 and 8. As can be seen from these data, the isotherm data are well correlated by most models. It can be seen from Tables 3 and 4 that



Figure 4. Heat of adsorption on ACs as a function of adsorbent loading: ●, propylene; ▲, propane. (a) BAX activated carbon; (b) LAC activated carbon.



Figure 5. Sorption uptake of propane and propylene on activated carbons. Lines represent model fitting for propylene (solid line) and propane (dashed line): ■, propylene experimental; ●, propane experimental. (a) BAX activated carbon at 303 K; (b) BAX activated carbon at 343 K; (c) LAC activated carbon at 303 K; (d) LAC activated carbon at 343 K.

the Toth, Dubinin–Astakhov, and Langmuir–Freundlich equations have had the best correlating of the isotherm data.

Equilibrium loading of hydrocarbons on activated carbon relatively depends on vapor pressure. Therefore, the loading capacities of both propane and propylene with similar boiling points are comparable for every type of activated carbon. Although BAX has a higher specific area, it was expected to have more adsorption capacity. Results of equilibrium show that the degree of coverage of both gases at low pressure (depending on temperature) is higher for the LAC than for the BAX. This is due to BAX having a wider pore size distribution than LAC and to the fact that at low pressure most parts of the pores in LAC will be occupied by the gas.

Heat of Adsorption. The adsorption isotherms of propylene and propane on the adsorbents considered at three temperatures were employed for evaluating the adsorption enthalpy. For this purpose, the Clausius–Clapeyron equation was applied to the isotherm data at the three temperatures. Therefore, the isosteric heat of adsorption (ΔH) for both activated carbons was estimated by means of the linear dependency of $\ln(P)$ on 1/T at constant loading. The heat of adsorption dependency on adsorption coverage of both adsorbents is shown in Figure 4. The heats of adsorption of propylene and propane decreased with in-

Table 8.	Fitted Paramet	ers and Error	for Adsorption
Isotherm	Data on LAC A	ctivated Carb	on

			Te	oth		
gas	<i>T</i> /K	$q_{ m m}/ m mol\cdot kg$	⁻¹ 10	⁻⁴ <i>K</i> /Pa ⁻	⁻¹ n	MSE/(mol·kg ⁻¹) ²
propane	273	8.720	1	81.3	0.287	0.0013
	303	7.949		22.15	0.327	0.0015
	343	8.461		3.23	0.324	0.0003
propylene	273	7.502	1	36.5	0.322	0.0018
I IJ	303	11.789		23.1	0.272	0.0009
	343	11.309		3.124	0.287	0.0002
		Du	binin-	Astakl	10V	
gas	<i>T</i> /K	$q_0/\text{mol}\cdot \mathbf{k}$	g^{-1}	b	D	$MSE/(mol \cdot kg^{-1})^2$
propane	273	5.816	6 0	.01756	2.148	0.0003
	303	5.631	0	.02343	2.110	0.0006
	343	5.174	- 0	.0362	2.010	0.0002
propylene	273	6.310	0 0	.02092	2.058	0.0001
	303	6.935	0	.03632	1.927	0.0003
	343	6.004	0	.04426	1.918	0.0001
		Dubii	nin-R	adushk	evich	
gas	7	7K <i>q</i> ₀ /m	ol•kg [_]	1	b	$MSE/(mol \cdot kg^{-1})^2$
propane	2	73 5.	945	0.0	2368	0.0020
	3	03 5.	786	0.0	2938	0.0011
	3	43 5.	196	0.0	3698	0.0002
propylene	2	73 6.	374	0.0	2355	0.0004
1 15	3	03 6.	779	0.0	3118	0.0005
	3	43 5.	775	0.0	3707	0.0002
		Lang	muir-	-Freun	dlich	
gas	<i>T</i> /K	q _m /mol⋅kg	s^{-1} 10	⁻³ <i>b</i> /Pa ⁻	⁻¹ n	MSE/(mol·kg ⁻¹) ²
nronane	273	6 5 1 2		18.83	2 003	0.0001
propune	303	6 2 7 6		6 209	1 824	0.0002
	343	5 487		1 595	1 639	0.0002
nronvlene	273	7 203	1	19 24	2 110	0.0001
propyrene	303	7 962		5 / 96	1 915	0.0001
	343	6 335		1 524	1 680	0.0002
	010	0.000	-		1.000	0.0002
			Freu	ndlich		$ACE/(1)^2$
gas		1/K L	/Pa ·	1	1 1	MSE/(mol·kg ')~
propane		273	0.582	4.9	06	0.1344
		303	0.219	3.6	23	0.0672
		343	0.049	2.6	58	0.0171
propylen	е	273	0.558	4.7	24	0.1182
		303	0.188	3.3	41	0.0541
		343	0.045	2.5	71	0.0144
			Lang	gmuir		
gas	Τ/	K q _m /mo	l•kg ⁻¹	10^{-4}	b/Pa ⁻¹	$MSE/(mol \cdot kg^{-1})^2$
propane	27	3 5.2	22	8.0	38	0.1479
- •	30	3 4.6	77	2.7	07	0.0769
	34	3 3.6	90	0.8	95	0.0769
propylene	27	3 5.4	97	6.9	22	0.1843
1 15	30	3 5.3	35	1.9	98	0.1077
	34	3 3.9	61	0.7	887	0.0279

creasing degree of coverage. The isosteric heat of adsorption of propylene is higher than that of propane, especially at low degree of surface coverage. The dependency of the heat of adsorption on the amount of adsorbed material shows that adsorption sites are not energetically homogeneous. The higher heat of adsorption of propylene can be attributed to the interaction between adsorption sites and the π -electron cloud of the carbon-carbon double bond.

Kinetic Adsorption. The sorption uptakes of propane and propylene were studied at 303 K and 343 K for both adsorbents. The diffusion coefficient, D/r^2 , was calculated from the uptake data and is given in Table 9. Simulated curves for diffusivity are shown in Figure 5. Equation 8

 Table 9. Diffusion Time Constant Determined from

 Uptake of Gases on the Activated Carbons

sorbate	adsorbent	<i>T</i> /K	$10^{-4} (D/r^2)/s^{-1}$
propylene	BAX	303	5.67
propylene	BAX	343	13.51
propylene	LAC	303	3.38
propylene	LAC	343	5.35
propane	BAX	303	4.56
propane	BAX	343	7.39
propane	LAC	303	3.23
propane	LAC	343	5.16

has been derived for the spherical shape of an adsorbent, and for simplicity, it was used here for the pellet shape.

The data show that for both adsorbents the diffusion of propylene is slightly higher than that of propane, especially at higher temperature (343 K). The uptake rates of the gases for the BAX activated carbon are faster than those for the LAC activated carbon. This is in accordance with the wider pore size of BAX activated carbon.

Conclusions

Specific area, pore volume, pore size, loading capacity of propane and propylene, heat of adsorption, and apparent diffusivity of propane and propylene were investigated as the most important parameters of the two types of activated carbon. Both adsorbents have a high micropore content. Measurements have shown that the main difference of these adsorbents is based on the external surface area (mesopores) and pore size distribution. BAX activated carbon has a large fraction of the pore volume associated with mesopores, and LAC activated carbon has a large proportion of micropores in the pore volume. The influence of the difference in pore size of the activated carbon on the behavior of the equilibrium and kinetic adsorption of propane and propylene was checked experimentally in this work. It was seen that, at low relative pressure, the equilibrium loading was higher for LAC activated carbon than for BAX activated carbon. Furthermore, faster uptake of gases on BAX activated carbon than on LAC activated carbon was observed.

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Literature Cited

- Holland, C. E.; Al-Muhtaseb, S. A.; Ritter, J. A. Adsorption of C1-C7 Normal alkanes on BAX Activated carbon. 1. Potential theory Correlation and Adsorbent Characterization. *Ind. Eng. Chem. Res.* 2001, 40, 338-346.
- (2) Dreisbach, F.; Seif, A. R.; Lösch, H. W. Gravimetric Measurement of Adsorption Equilibria of Gas Mixture CO/H2 with a Magnetic Suspension Balance. *Chem. Eng. Technol.* **2002**, *25*, 1060–1065.
- (3) Choudary, N. V.; Kumar, P.; Bhat, T. G.; Cho, S. H.; Han, S. S.; Kim, J. N. Adsorption of Light Hydrocarbon gases on Alkene-Selective Adsorbent. *Ind. Eng. Chem. Res.* 2001, 40, 338–346.
- (4) Yang, R. T. Gas separation by adsorption processes; London Imperial College Press: 1997
- Suzuki, M. Adsorption engineering, Kodansha Ltd., Tokyo, and Elsevier Science Publishers: Amsterdam, 1990.
- (6) Halsey, G. J. Chem. Phys. 1948, 16, 931-937.

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