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Adsorption of Methane, Ethane, and Ethylene on Zeolite

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Adsorption isotherms at 283 and 303 K of methane, ethane, and ethylene on zeolite G5 have been obtained. Measurements have been made at pressures up to 1200 kPa using an automated apparatus based on the volumetric method. This study is linked to a modeling interest because of the structure simplicity of the adsorbate molecules and because of the known geometric structure of the adsorbent.

Introduction

The present study is devoted to obtaining fundamental data on the adsorption of methane, ethane, and ethylene on zeolite G5. Synthetic zeolites are characterized by a known crystallographic structure, and hydrocarbons have a simple molecular structure. Such systems can be used for statistical model lines where molecular structure is introduced into the microporous media. Other systems (activated carbon, for example) can be studied by introduction of structure and energetic defaults.

The adsorption of ethane and ethylene on synthetic zeolites has not been studied at pressures up to 1200 kPa previously. In the literature, studies have been made on zeolite 13X at pressures up to 363 and 546 kPa, respectively (Valenzula and Myers, 1989). Adsorption of methane on activated carbon has been conducted up to 13780 kPa (Valenzula and Myers, 1989).

Experimental Section

The adsorbent used in this study is zeolite G5 supplied by Ceca (Athochem). Zeolite G5 corresponds to faujasite material (FAU code assigned to that topology by the structure commission of the International Zeolite Association). Internal measurements have been conducted in our department on a Quantasorb sorption analyzer to characterize geometric structure using a conventional technique. The BET specific surface was 430 m^2/g, and the pore volume was 1.08 cm^3/g. Methane, ethane, and ethylene were obtained from Air Liquide Belgium with a minimum purity of 99.95 vol %. The impurities are O_2, H_2O,N_2, C_nH_m and CO_2. The most important one is C_nH_m ($\geq$400 ppm).

The wholly automated device is based on a volumetric method (Berlier et al., 1995). The principle of this method consists in successive expansions of the gas from a buffer tank to the adsorber. From the known volume of the tanks, the adsorbed mass can be calculated using an equation of state and knowledge of the temperature and pressure in the system before and after adsorption.

The wholly automated apparatus enables pure gas isotherms to be determined from 273 to 373 K and at pressure up to 4000 kPa. In this method, the total quantity of gas admitted into the system and the amount of gas in the vapor phase remaining after adsorption equilibrium are determined by appropriate P−T−V measurements. A schematic diagram of the apparatus is shown in Figure 1. All the components in contact with the gas are made from stainless steel. A microcomputer controlled the electrovalves (EV_1 and EV_2) and was used to acquire and store the results.

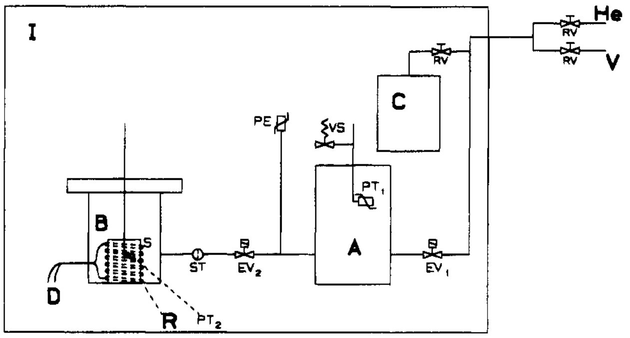

Figure 1. Experimental apparatus: (A) buffer reservoir; (B) flanged reservoir; (C) gas storage; (D) impervious passage leading to the supply of the heater wire; (EV) electromagnetic gate; (He) helium supply; (I) refrigerated air bath; (PE) electronic pressure sensor; (PT) temperature sensor; (R) heating resistance for *in situ* reconditioning; (RV) gate for manual adjustment; (S) crucible containing the adsorbent; (ST) filter; (V) vacuum pump; (VS) safety valve.

The adsorption apparatus was maintained in a refrigerated air bath (I) regulated in temperature with an accuracy of ±0.1 K. The main part of the apparatus consists in two stainless steel vessels, A (the buffer volume) and B (the adsorber), linked by the electrovalve EV_2. The use of an electrical heating system (R) allows the adsorbent sample to be regenerated *in situ*, i.e., without opening the adsorber. Pressure measurements were made by an Endress Hauser (Cerabar) absolute pressure transducer (PE) coupled to a control card. Its pressure range was from 400 to 4000 kPa, and the accuracy is about 0.1% of the programmed scale (1200 kPa in this experiment). Temperatures were measured in both volumes using 100 Ω Pt resistance thermometers (PT_1 and PT_2) with an accuracy of ±0.1 K.

In order to eliminate any trace of pollutants in the adsorbent, it was heated to 423 K for 24 h in a drying oven. Its mass was determined (about 20 g with an accuracy of ±0.1 mg), and it was introduced into the flanged reservoir (B), the so-called adsorber. The volume of B was measured for each new sample of adsorbent by expansion of helium considered as an inert gas.

The operating procedure for the determination of the pure gas isotherms was to admit the gas into the buffer volume (A), measure its temperature and pressure, then expand the gas into the adsorber (B), and finally record the equilibrium temperature and pressure. This equilibrium adsorption is attained when the pressure is constant

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Table 1. Adsorption Isotherms for Methane on Zeolite G5 at 283 and 303 K

T/K = 283				T/K = 303	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
128.25	0.7550	60.00	0.3836	67.00	0.2600
159.75	0.9016	109.50	0.6717	100.38	0.3839
192.00	1.0561	181.88	1.0375	136.38	0.5029
226.88	1.1954	256.50	1.3326	173.13	0.6360
261.00	1.3298	331.13	1.5777	211.75	0.7503
297.00	1.4476	405.00	1.7799	249.63	0.8641
333.00	1.5549	497.25	1.9927	287.13	0.9758
368.63	1.6714	587.25	2.1413	359.13	1.1456
438.75	1.8463	690.38	2.2970	428.13	1.2997
508.88	1.9863	803.63	2.4221	494.50	1.4348
578.25	2.0853	934.88	2.5399	557.50	1.5566
644.63	2.1781	1105.50	2.6899	616.75	1.6506
709.13	2.2691			670.75	1.7319
771.38	2.3417			720.25	1.8105
831.75	2.3939			764.88	1.8804
888.00	2.4551			825.25	1.9549
942.75	2.5039			891.63	2.0305
994.13	2.5531			956.50	2.0979
1063.88	2.6237			1028.50	2.1587
1147.13	2.6857				

Table 2. Adsorption Isotherms for Ethane on Zeolite G5 at 283 and 303 K

T/K = 283		T/K = 303	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
56.50	2.4146	43.50	1.7131
91.00	2.5639	72.38	2.0734
130.38	2.6724	109.50	2.2684
171.63	2.7499	156.00	2.4044
214.75	2.8068	201.00	2.4881
258.25	2.8479	246.75	2.5561
301.75	2.8859	299.63	2.6195
344.88	2.9173	347.25	2.6653
388.00	2.9455	438.00	2.7289
430.38	2.9772	527.63	2.7755
472.38	3.0031	613.13	2.8182
513.63	3.0234	694.88	2.8533
553.75	3.0409	742.50	2.8736
627.25	3.0580	816.38	2.8984
695.50	3.0862	884.63	2.9172
759.25	3.1150	947.63	2.9440
818.50	3.1423	1006.50	2.9608
873.25	3.1647	1089.38	2.9868
923.50	3.1764		
967.75	3.1924		
1024.38	3.2183		
1097.13	3.2444		

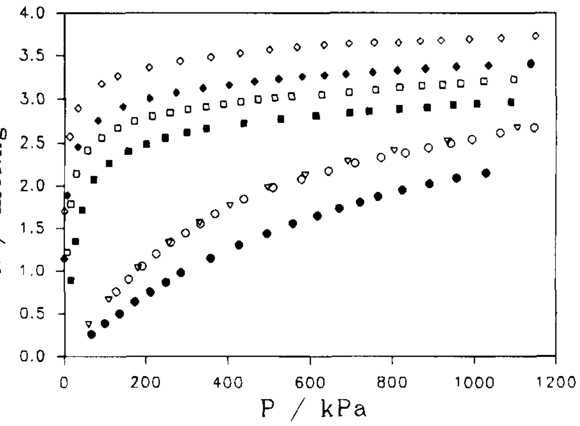

Figure 2. Adsorption of methane (○, ▽, 283 K; ●, 303 K), ethane (□, 283 K; ■, 303 K), and ethylene (◇, 283 K; ◆, 303 K).

Table 3. Adsorption Isotherms for Ethylene on Zeolite G5 at 283 and 303 K

T/K = 283		T/K = 303	
P/kPa	N/(mol·kg^{-1})	P/kPa	N/(mol·kg^{-1})
92.25	3.1799	81.63	2.7572
131.63	3.2693	142.75	2.9165
207.38	3.3675	208.38	3.0119
283.50	3.4396	274.38	3.0799
358.13	3.4875	339.25	3.1307
429.75	3.5309	403.00	3.1651
500.62	3.5737	464.13	3.2084
568.13	3.5996	523.75	3.2364
633.75	3.6321	580.38	3.2634
694.88	3.6417	634.75	3.2799
756.00	3.6529	687.25	3.2892
814.50	3.6536	751.75	3.3132
868.13	3.6725	811.75	3.3357
919.50	3.6813	881.88	3.3583
988.88	3.6987	956.50	3.3803
1066.13	3.7137	1035.63	3.3975
1150.50	3.7359	1139.88	3.4253

Table 4. Saturated Pressure (P_s) at 283 and 303 K, Critical Temperature (T_c), Critical Pressure (P_c), and Critical Volume (V_c) of Methane, Ethane, and Ethylene (Stewart et al., 1986)

gas	P_s(283 K)/kPa	P_s(303 K)/kPa	T_c/K	P_c/kPa	V_c/(m^3·kg^{-1})
methane	$283 > T_c$	$303 > T_c$	190.5	4595	0.006 17
ethane	3006	4637	305.3	4871	0.004 89
ethylene	$283 > T_c$	$303 > T_c$	282.3	5040	0.004 67

at 1.5 kPa (>0.1% of the programmed scale, i.e., 1200 kPa) for 25 min.

The knowledge of the gaseous volume, the temperature, and the pressure before and after each adsorption step gives the moles of gas before and after adsorption and finally, by difference, the adsorbed moles. The calculation of the moles in the gas phase was made using the modified Redlich–Kwong equation of state (Frère et al., 1994; Jadot, 1981; Prausnitz et al., 1986).

Results and Discussion

Adsorption isotherms for methane, ethane, and ethylene on zeolite G5 at 283 and 303 K were obtained at pressures up to 1200 kPa. The results are presented in Tables 1–3 and in Figure 2. The saturation pressures and the critical parameters (critical temperature, critical pressure, and critical volume) of these compounds are given in Table 4. Several sets of measurements were reproduced with differences of less than 3%. An example is given in Table 1 and in Figure 2 (○ and ▽). The accuracy of the pressure transducer was ±1.2 kPa, giving the maximum relative error in the pressure of 2% for the first point of the methane isotherm (Table 1). The error in the adsorbed mass is due to the accuracy of the equation of state used for the calculation of the vapor molar volumes (<±1%), the experimental error of the mass of adsorbent due to the accuracy of the balance ($\pm 5 \times 10^{-4}$%), the experimental error in the temperature (±0.05%), the experimental error on the gas volume (estimated to be less than ±1%), and the experimental error in the pressure (variable). The prime source of error is in the pressure measurement, and this results in a maximum relative error in the adsorbed mass of ±5% with a typical value of 3%. Such experimental errors are common for the volumetric method in which the adsorbed mass is not directly measured (Frère et al., 1994).

Experimental isotherms are presented in Figure 2. The curves are similar in shape and have a classic isotherm form.

Conclusion

The automated apparatus allows us to determine adsorption isotherms at pressures up to 1200 kPa. The amount of gas adsorbed on synthetic zeolites increases with an increase in carbon number and the amount of unsaturation (methane < ethane < ethylene).

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