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Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on X, Y, L, and M Zeolites Using a Gas Chromatography Pulse Technique

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ABSTRACT

Sorption of methane, ethane, ethylene and carbon dioxide in NaX, NaY, HY, CeNaY, KL, HKL, NaM, and HM zeolites at 303–473 K has been investigated using a gas chromatography pulse technique. The zeolites have been compared for the heat of sorption of the sorbates at near-zero sorbate loading and also for the specific retention volume (or thermodynamic sorption equilibrium constant) of ethane, ethylene, and carbon dioxide relative to that of methane.

INTRODUCTION

Extensive efforts have recently been put forth worldwide to develop energy-efficient and commercially feasible processes for the direct conversion of methane to value added products such as ethylene (which is the keystone to the petrochemical industry), methanol, and liquid hydrocarbon fuels (1–4). Methane, ethane, ethylene, and carbon dioxide form part of the product stream in the oxidative coupling of methane (1, 5, 6). Methane, ethane, and carbon dioxide are also components of natural gas. Because the concentration of ethylene and/or ethane in these mixtures is very low (<10%), the incorporation of their separation between chemical processing steps is necessary to make any such process package commercially viable. The conventional methods of separation (for example, cryogenic methods) are not suitable in this case due to the low concentrations of C_2 hydrocarbons.

In recent years, adsorptive separation processes have gained more and more importance due to their highly selective and energy efficient operation, and zeolites form a class of adsorbents that are used in many such processes (7–9). Scanning of the adsorption literature reveals that though adsorption data for the above gases on some zeolites are available (10), the conditions used for measurement have been different, which makes the direct comparison of sorption properties extremely difficult. The present investigation was undertaken to allow for a quick and systematic comparison of the sorption properties of X, Y, L, and M zeolites for the sorption of methane, ethane, ethylene, and carbon dioxide by the gas chromatography (gc) pulse technique.

EXPERIMENTAL

Zeolites. Zeolite NaX (Si/Al = 1.3) was obtained from Laporte (UK). NaY (Si/Al = 2.4) was procured from Union Carbide (Linde Division, USA). HY was obtained by deammoniating NH_4Y (prepared by exchanging NaY repeatedly with 0.5 M ammonium nitrate solution at 353 K followed by washing and drying) at 623 K for 2 hours in a flow (10 $cm^3 \cdot min^{-1}$) of helium. CeNaY's with different Ce^{3+} exchange (46 and 72%) were prepared by repeatedly exchanging NaY with cerium nitrate solution at 353 K followed by washing and air drying at 383 K. Zeolite KL (Si/Al = 2.8) was obtained from Laporte (UK). HKL was prepared by exchanging KL with 0.1 M HCl followed by washing and drying. Commercial grade synthetic HM (Zeolon 900 H, Si/Al = 6.5) and NaM (Zeolon 900 Na, Si/Al = 5.5) were obtained from Norton Co. (USA).The zeolites were pressed binder-free and crushed to particles of 0.2–0.3 mm. Before use, the zeolites (packed in a gc column) were pretreated/calcined *in situ* at 623 K for 2 hours in a flow (10 $cm^3 \cdot min^{-1}$) of helium which was the carrier gas for the gc pulse experiments. The characterization of the zeolites is given earlier (11–15).

Gases. The hydrocarbon gases methane (obtained from Matheson, USA), ethane (obtained from Airco Industrial Gases, USA), and ethylene (obtained from L'Air Liquide, France) were of >99.9% purity. High purity carbon dioxide and helium were obtained from Indian Oxygen Ltd., Bombay. Nitrogen (Iolar, Grade II, obtained from Indian Oxygen Ltd., Bombay) was used as a nonadsorbate for dead volume corrections.

Apparatus. The gc pulse measurements were carried out using a Chemito (Thoshiniwal-Dani) gas chromatograph with a thermal conductivity detector (TCD); helium was the carrier gas. The zeolite was packed in a stainless steel column (15 cm long, 2 mm i.d.), one end of which was connected directly to the TCD, and the other end to the injection port through a 1.6-cm o.d. stainless steel tube. The sample gases were diluted with the carrier gas (He) to a concentration of 2–3 mol% and injected into the zeolite column using a gas sampling valve having a sample loop of 0.3

cm^3. A carrier gas flow rate of 10 $cm^3 \cdot min^{-1}$ (measured at STP) was used for the experiments. The pressure drop across the zeolite column was negligibly small. The chromatograms were recorded using a Spectra-Physics integrator.

RESULTS AND DISCUSSION

The heats of sorption of the different sorbates on the zeolites were calculated from the slopes of the linear plots of log V_R versus $1/T_c$ according to the equation (16)

$$\log V_R = a - \Delta H/(2.303RT_c)$$

where a is a constant, ΔH is the heat of adsorption R is the gas constant, and T_c is the column temperature. The corrected retention volume V_R was calculated from

$$V_R = (t_r - t_d)F(T_c/T_F)$$

where t_r and t_d are the retention times for the adsorbate and the nonadsorbate (N_2), respectively, F is the carrier gas flow rate, and T_F is the temperature at which F is measured.

The specific retention volume β was calculated from the chromatographic retention time data by using the equation (16)

$$\beta = t_m U_e/L = V_R/V_P$$

where t_m is the corrected retention time, U_e is the superficial gas velocity, L is the length of the column, and V_P is the volume of zeolite adsorbent.

For the determination of the heat of sorption and/or of the specific retention volume by the gc pulse method, it is essential that the data should correspond to the linear region of the adsorption isotherm (17). This was achieved by the use of a sample pulse of very low concentration (2–3%) and small volume (0.3 cm^3). Further, there was no significant change in the retention volumes of any of the sorbates on changing the carrier gas flow rate from 10 to 30 $cm^3 \cdot min^{-1}$ at the lowest temperature of study.

Representative plots of log V_R vs $1/T_c$ for the sorption of methane, ethane, ethylene, and carbon dioxide on NaY are given in Fig. 1. The heats of sorption (at near-zero coverage) of methane, ethane, ethylene, and carbon dioxide on different adsorbents are given in Table 1. The variation of specific retention volume (which is equivalent to the thermodynamic equilibrium constant) with temperature for the sorption of the sorbates in the zeolites is shown in Figs. 2 and 3.

The heat of sorption values obtained by the gc pulse method for different sorbates on NaX, NaY, HM, and KL are compared in Table 2 with those

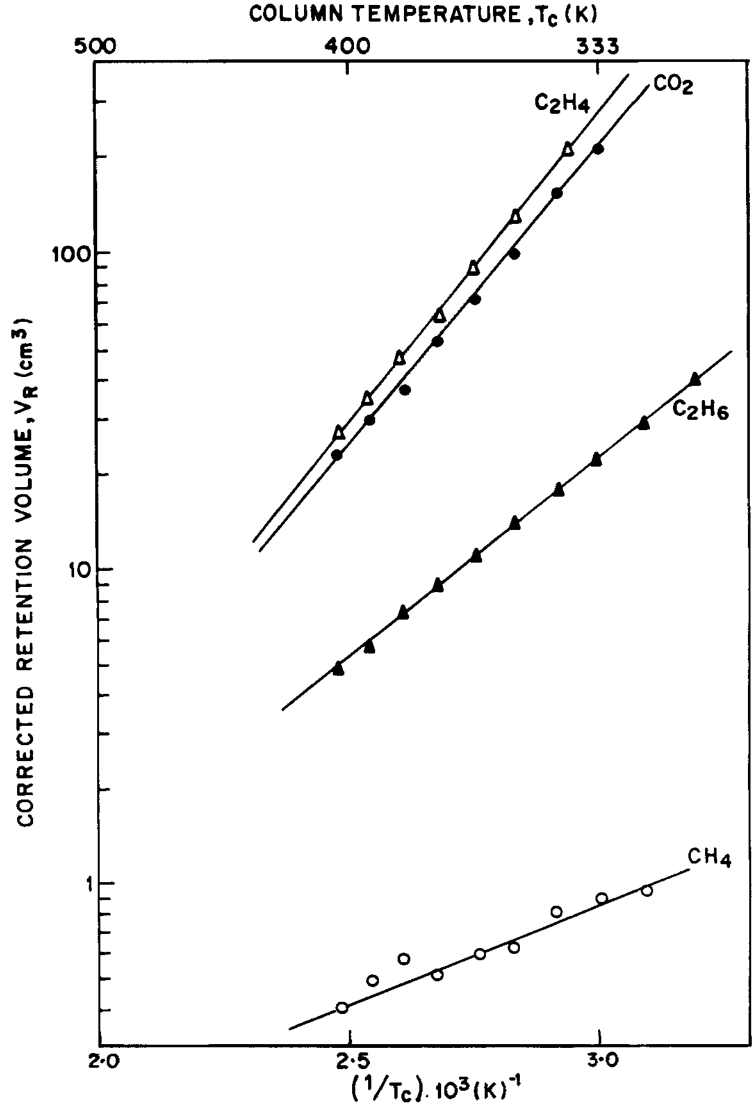

FIG. 1 Representative plots of log V_R vs $1/T_c$ for the sorption of methane, ethane, ethylene, and carbon dioxide on NaY.

TABLE 1
Heat of Sorption of Methane, Ethane, Ethylene, and Carbon Dioxide in the Zeolites

	Heat of sorption (kJ·mol^{-1})			
Zeolite	Methane	Ethane	Ethylene	CO_2
NaX	Very small	15.0	31.5	—
NaY	12.1	24.3	37.8	36.5
Ce(46)NaY	12.7	23.2	38.1	35.7
Ce(72)NaY	14.3	21.6	—	40.8
HY	14.7	20.3	32.6	27.0
KL	18.1	24.7	33.2	24.3
HKL	10.6	24.1	30.3	30.1
NaM	11.2	28.2	55.6	38.2
HM	19.3	24.9	—	44.5

reported earlier. The values of heat of sorption of ethylene in NaX, ethylene and carbon dioxide in NaY, carbon dioxide in HM, and methane and ethane in KL are quite comparable with those reported earlier, whereas the other heat of sorption values obtained by the gc pulse technique are somewhat lower. This is probably because the data obtained by the gc pulse technique corresponds to near-zero coverage of the sorbates. The heat of sorption of a sorbate in an adsorbent is a measure of the ease with which the adsorbent can be regenerated. Generally, a sorbent with a low heat of sorption is preferred because it implies greater ease of regeneration. A high heat of sorption value is attributed to strong sorbate–sorbent interactions; hence, desorption of the sorbate from the sorbent is difficult. In such cases, regeneration of the sorbent is effected by increasing the temperature (thermal swing) to a high value and/or by the application of vacuum, which increases the energy cost of the process. Further, heating the adsorbent repeatedly can affect the adsorbent life because it can cause structural degradation or fouling of the adsorbent and/or reaction of the sorbate on the adsorbent. The specific retention volume of a sorbate for a particular zeolite is a measure of sorption of the sorbate in the zeolite. Thus, it is possible to compare zeolites for the sorption of methane, ethane, ethylene, and carbon dioxide at different temperatures.

Comparison of Zeolites for Their Sorption Properties

Heat of Sorption

Among the sorbates, the heat of sorption of methane is lowest in all zeolites. In general, for all zeolites except NaX, Ce(72)NaY, and HM

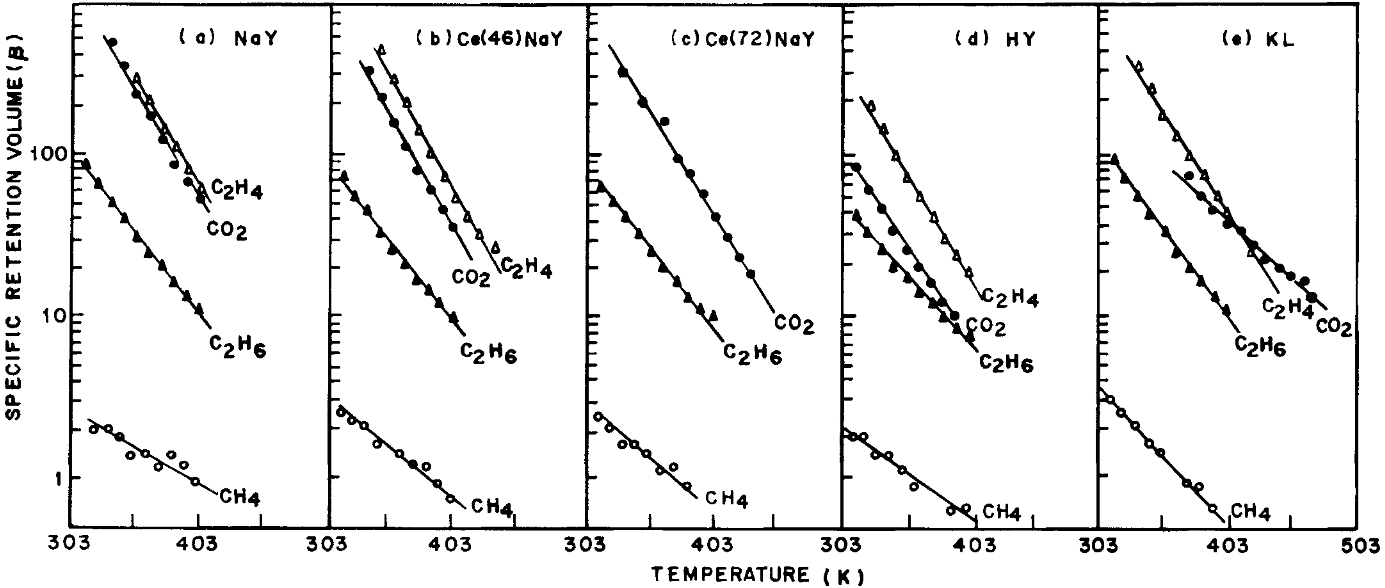

FIG. 2 Temperature dependence of specific retention volume (β) for the sorption of methane, ethane, ethylene, and carbon dioxide on NaY, Ce(46)NaY, Ce(72)NaY, HY, and KL zeolites.

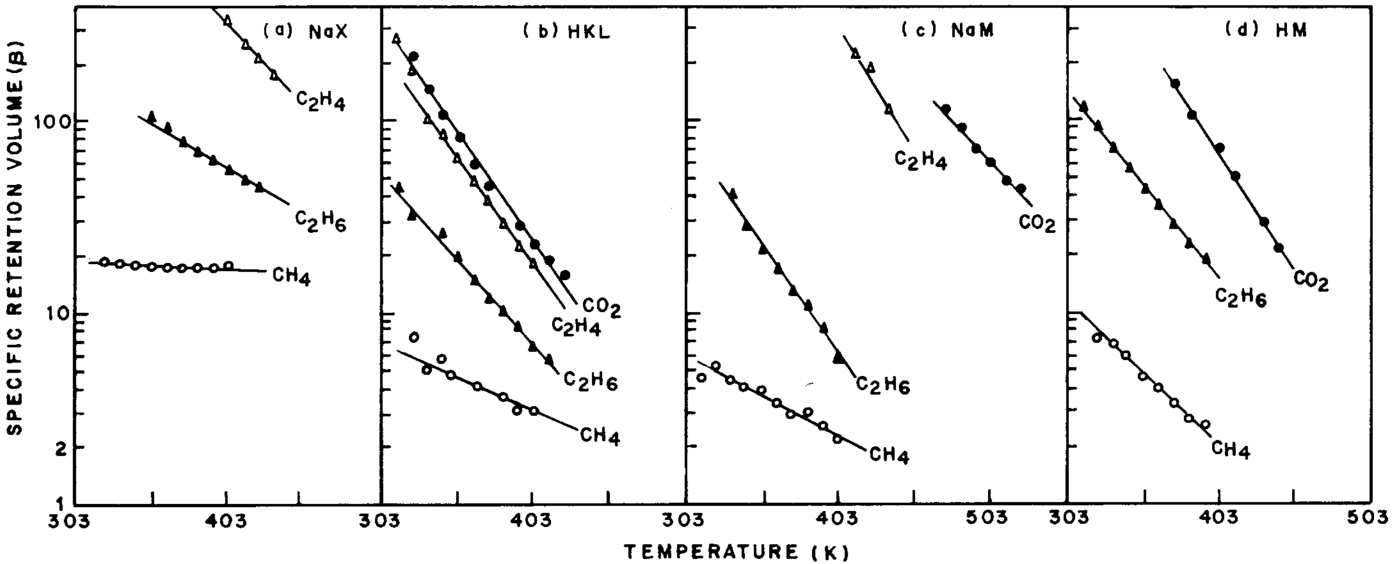

FIG. 3 Temperature dependence of specific retention volume (β) for the sorption of methane, ethane, ethylene, and carbon dioxide on NaX, HKL, NaM, and HM zeolites.

TABLE 2
Comparison of the Present and Reported Heat of Sorption Values for Various Sorbates on Different Zeolites

		Heat of sorption (kJ·mol^{-1})		
Zeolite	Sorbate	Present (by gc pulse)	Reported data	Ref.
NaX	C_2H_6	15.0	25–26	18–21
	C_2H_4	31.5	36–38.5	18–24
NaY	CH_4	12.1	16.9–18	25
	C_2H_4	37.8	31.8	26
	CO_2	36.5	31–33.5	26, 27
HM	CH_4	19.3	25.5	28
	C_2H_6	24.9	33.3	28
	CO_2	44.5	46.4	29
KL	CH_4	18.1	18.4	30
	C_2H_6	24.7	29.3	30

(Table 1), the heat of sorption of the different sorbates is in the following order: $CH_4 < C_2H_6 < CO_2 < C_2H_4$. The sorption of carbon dioxide in NaY and of ethylene in Ce(72)NaY and HM is very strong, and hence the sorbates cannot be eluted from the zeolite column at the highest temperature of this study. In the case of these zeolites, the heat of sorption of the sorbates is as follows: For NaX, $CH_4 < C_2H_6 < C_2H_4$; for Ce(72)NaY and HM, $CH_4 < C_2H_6 < CO_2$.

It is also interesting to compare zeolites for the heat of sorption of the different sorbates. The zeolites show the following orders for the heat of sorption of the different sorbates.

For the heat of sorption of methane: HM > KL > HY > Ce(72)NaY > Ce(46)NaY > NaY > NaM > HKL.

For the heat of sorption of ethane: NaM > HM > KL > NaY > HKL > Ce(46)NaY > Ce(72)NaY > HY > NaX.

For the heat of sorption of ethylene: NaM > Ce(46)NaY > NaY > KL > HY > NaX > HKL.

For the heat of sorption of carbon dioxide: HM > Ce(72)NaY > NaM > NaY > Ce(46)NaY > HKL > HY > KL.

The above comparisons reveal that the sorbate–sorbent interactions for a particular sorbate vary from zeolite to zeolite.

Specific Retention Volume

The results in Figs. 2 and 3 show that the specific retention volume for the sorbates at different temperatures varies from zeolite to zeolite. Also, for each of the zeolites, there is a large difference in the specific retention volume of the different sorbates. For the purpose of comparison, three base temperatures (323, 373, and 423 K) were chosen, and the specific retention volumes of the sorbates relative to that of methane at the different temperatures are given in Table 3. The second column in Table 3 gives the actual value of the specific retention volume for methane, and the other columns give the specific retention volume of the sorbate relative to that of methane (i.e., relative retention volume). For all the zeolites studied, the relative retention volume at 323 K is $\gg 1$, indicating that good separation of methane from the other sorbates is possible.

For all zeolites, the specific retention volume of methane and the relative retention volumes of ethane and ethylene decrease with increasing temperature. The relative retention volume of carbon dioxide also decreases with increasing temperature for all zeolites except KL, for which it increases with increasing temperature. The zeolites could be arranged in the decreasing order of retention volume for various sorbates (viz., CH_4, C_2H_6, C_2H_4, and CO_2) at two different temperatures (323 and 423 K) as follows.

For CH_4 (at 323 K): NaX > HM > HKL > NaM > KL > Ce(46)NaY > NaY $\geqslant$ Ce(72)NaY > HY.

For CH_4 (at 423 K): NaX $\gg$ HKL > NaM > HM > NaY > Ce(46)NaY > Ce(72)NaY $\geqslant$ HY > KL.

For C_2H_4 (at 323 K): NaM > NaY > Ce(46)NaY > KL > NaX > HY > HKL.

For C_2H_4 (at 423 K): NaM > KL > Ce(46)NaY > NaY > HY > NaX > HKL.

For C_2H_6 (at 323 K): NaY > KL > Ce(72)NaY > Ce(46)NaY > HY > HM > NaM > NaX > HKL.

For C_2H_6 (at 423 K): KL > Ce(72)NaY > HY > Ce(46)NaY > NaY > HM > NaX > NaM > HKL.

For CO_2 (at 323 K): NaM > NaY > Ce(46)NaY > Ce(72)NaY > HM > KL > HKL > HY.

For CO_2 (at 423 K): NaM > KL > Ce(72)NaY > NaY > Ce(46)NaY > HM > HY > HKL.

The above comparison shows a strong influence of temperature on the order of zeolites for the retention volume of the different sorbates.

The data on the relative retention volume for C_2H_6, C_2H_4, and CO_2 on the different sorbates at the two temperatures are summarized in Table 4.

TABLE 3
Comparison of Relative Specific Retention Volumes for Different Sorbates on Zeolites at Different Temperatures

Zeolite	Temperature (K)	$V_R(CH_4)$	$\frac{V_R(C_2H_6)}{V_R(CH_4)}$	$\frac{V_R(C_2H_4)}{V_R(CH_4)}$	$\frac{V_R(CO_2)}{V_R(CH_4)}$
NaX	323	18.0	7.5[a]	105[a]	—
	373	17.2	4.6	33.4[a]	—
	423	16.5[a]	2.9	13.5	—
NaY	323	2.15	29.3	270	325
	373	1.2	17.0	116	101
	423	0.8[a]	8.5[a]	42.0[a]	35.5[a]
Ce(46)NaY	323	2.3	22.6	161	260[a]
	373	1.2	14.1	113	64.6
	423	0.6[a]	9.6[a]	55.2	29.3[a]
Ce(72)NaY	323	2.1	23.8	—	190[a]
	373	1.2	13.3	—	74.2
	423	0.5[a]	11.1[a]	—	50.2
HY	323	1.55	19.3	103	36.1
	373	1.2	10.2	31.2	12.3
	423	0.45[a]	9.7[a]	18.9[a]	9.3[a]
KL	323	2.4	25.8	154	54.0[a]
	373	0.9	21.8	102	64.0
	423	0.3[a]	18.8[a]	75.6	73.0
HKL	323	6.0	7.3[a]	31.0[a]	43.0[a]
	373	5.8	1.8	6.5	8.0
	423	2.6[a]	1.7[a]	4.2[a]	6.2
NaM	323	5.0	9.6	700[a]	360[a]
	373	2.9	5.7	241[a]	255[a]
	423	1.9[a]	1.8[a]	93.9	147[a]
HM	323	8.0	11.2	—	62.5[a]
	373	3.2	10.8	—	47.5
	423	1.3[a]	6.9[a]	—	21.3

[a] Extrapolated values from the specific retention volume vs temperature plots in Figs. 2 and 3.

TABLE 4
Relative Retention Volumes on Different Sorbates

Zeolites	Temperature (K)	Order of the relative retention volume for sorbates
HY, KL, NaM	323	$C_2H_4 > CO_2 > C_2H_6$
NaY, Ce(46)NaY, KL	423	$C_2H_4 > CO_2 > C_2H_6$
HY	423	$C_2H_4 > C_2H_6 > CO_2$
NaY, Ce(46)NaY, HKL	323	$CO_2 > C_2H_4 > C_2H_6$
NaM, HKL	423	$CO_2 > C_2H_4 > C_2H_6$
Ce(72)NaY, HM	323 and 423	$CO_2 > C_2H_6$
NaX	323 and 423	$C_2H_4 > C_2H_6$

These observations reveal that the order of the relative retention volume for the sorbates is influenced by temperature for many of the zeolites.

Selection of the Adsorbent

The important factors to be considered in the selection of a suitable adsorbent for a particular adsorption separation process are the efficiency of separation (i.e., high separation factor which depends on the concentration or pressure and temperature), the sorption capacity, the ease of regeneration of the sorbent, the reactivity of the sorbates in the sorbent, the structural stability, and the cost of the adsorbent. The ideal adsorbent should possess a high separation factor, high sorption capacity, regenerate easily (i.e., should have a low heat of sorption), be inactive to all the sorbates at both the conditions of adsorption and regeneration, possess high structural stability, and be cheap. However, all these requirements are rarely met in any single adsorbent, and the selection of a suitable adsorbent is usually a compromise between the favorable and unfavorable characteristics needed to achieve the required separation effectively.

The heat of sorption at zero coverage is a measure of sorbate–sorbent interaction, and it can be taken as an indication of the ease of regeneration in terms of the energy input required. Very high heat of sorption values indicate stronger interactions, and hence a difficulty in regeneration.

The relative retention volumes (relative to methane) obtained from gc pulse data may be taken as a rough measure of the separation factor (with respect to methane). A high relative retention volume value is indicative of a high separation factor. At 303 K, all the zeolites have relative retention volumes $\gg 1$, which implies that a good separation of methane from the other sorbates is possible.

Among the zeolites, NaM, NaY, NaX, CeNaY, and KL have relative specific retention volume values (at 303 K) very much greater than unity.

However, acidic zeolites like HM, HKL, HY, and CeNaY are not suitable for use as adsorbents due to their reactivity toward ethylene and ethane.

Further detailed investigation is required to understand the exact behavior of zeolites toward the adsorptive separation of methane, ethane, ethylene, and carbon dioxide from their mixtures. However, some important clues can be obtained from preliminary screening by the gc pulse technique. This method may be used for the initial selection of a few promising adsorbents which have a greater potential for achieving a particular separation that will achieve a considerable saving in time and efforts.

CONCLUSION

From studies on the sorption properties of X, Y, M, and L zeolites for the sorption of various sorbates (viz., methane, ethane, ethylene, and carbon dioxide) by the gc pulse technique, the following conclusions can be drawn.

1. Among the sorbates, the heat of sorption of methane is the lowest and that of ethylene is the highest on all zeolites. However, when zeolites are arranged in the decreasing order of their heat of sorption for the different sorbates, the order varies from sorbate to sorbate. This reveals that sorbate–sorbent interactions for a particular sorbate vary from zeolite to zeolite.
2. The specific retention volume of methane and the relative retention volumes of ethane, ethylene, and carbon dioxide decrease with increasing temperature for all zeolites except KL. For KL, the relative retention volume of carbon dioxide shows the reverse trend. Also, the order of the relative retention volume for sorbates is influenced by temperature for most zeolites. For all the zeolites tested, the relative retention volume at 323 K is $\gg 1$, indicating that good separation of methane from the other sorbates is possible.
3. The gc pulse method provides a simple means for measuring those sorption properties useful for fast screening of a large number of adsorbents for achieving a particular separation.

NOMENCLATURE

a	constant
F	flow rate ($\text{cm}^3\cdot\text{min}^{-1}$)
ΔH	heat of sorption ($\text{kJ}\cdot\text{mol}^{-1}$)
L	length of the zeolite column (cm)
R	gas constant
T_c	temperature of zeolite column (K)
T_F	temperature at which F is measured (K)

t_r	retention time of sorbate (min)
t_d	retention time of N_2 (min)
t_m	$t_r - t_d$
U_e	superficial gas velocity (cm·min^{-1})
V_R	retention volume (cm^3)
V_P	volume of zeolite in the column (cm^3)

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